Chem. Rev. **2009,** *109,* 897–1091

Synthesis of Light-Emitting Conjugated Polymers for Applications in Electroluminescent Devices

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Received January 5, 2007

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1. Introduction

The award of the Nobel Prize for Chemistry in 2000 to Professors Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa for their discovery that "doped" polyacetylene can conduct electricity changed the way that polymers were viewed and led to major advances in plastic electronics. Among these was the discovery of electroluminescent polymers and their application in light-emitting devices. These devices are now becoming commercially available, representing the final step in the advance of organic electronics from a laboratory curiosity to a part of everyday life. It is therefore appropriate to review the synthesis of such polymers and to provide a brief introduction to their applications. In this section we present a brief description of the historical background to the review and a concise account of the basic principles of electroluminescence and of light-emitting devices.

1.1. Background and Scope of the Review

Electroluminescence (EL) in conjugated polymers was first reported in poly(*para*-phenylene vinylene) (PPV, **1**) in 1990.[1] Since then considerable effort has been devoted to developing conjugated materials as the active units in light-emitting devices (LEDs) for use in display applications. A search of the ISI Science Citation Index database during the writing

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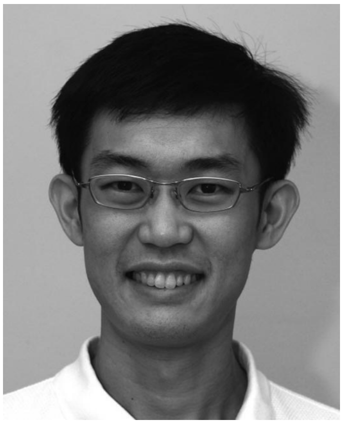
10.1021/cr000013v CCC: $71.50

Andrew Grimsdale was born in Waiouru, New Zealand, in 1963 and graduated from the University of Auckland. He received his Ph.D. there under the supervision of Professor R. C. Cambie in 1990 for work on the synthesis of analogues of biologically active drimane sesquiterpenes. He then undertook postdoctoral work on photochromic and electroactive materials with Professor A. Pelter at the University of Wales, Swansea, and with Professor Andrew Holmes at the University of Cambridge on electroluminescent polymers. From 1999 to 2005 he was project leader in charge of research into conjugated polymers in the group of Professor Klaus Müllen at the Max-Planck Institute for Polymer Research at Mainz. He rejoined the group of Professor Holmes in Melbourne in 2005 to work on materials for photovoltaic devices, before moving to Nanyang Technological University, in Singapore in November 2006. He is currently an Assistant Professor in the School of Materials Science and Engineering there, where his research interests are the synthesis of materials for optoelectronic applications and the formation of nanomaterials by self-assembly.



Khai Leok Chan was born in 1977 in Singapore. He obtained M.Sc. and Ph.D. degrees in Chemistry from University of Cambridge in 2002 and 2006 under the supervision of Professor Andrew B. Holmes. He returned to Singapore after graduation and joined DSO National Laboratories as a Member of the Technical Staff in the Advanced Materials Laboratory in 2006. He is currently a Research Scientist at the Institute of Materials Research and Engineering, under the Agency of Science, Technology and Research (A*-STAR), and his work focuses on materials and device designs for organic solar cells, thin film transistors, and light-emitting diodes.

Rainer Martin was born in Dornbirn, Austria, in 1970 and studied chemistry at the Eidgenössische Technische Hochschule (ETH) in Zürich, where he received his diploma in 1995. In the group of Prof. F. Diederich, he worked on the synthesis and physical investigation of monodisperse poly(triacetylene) oligomers and obtained his Ph.D. in 1998. In September of the same year, he moved to the Melville Laboratory for Polymer Synthesis, Cambridge U.K., for postdoctoral research with Prof. A. Holmes on electroluminescent polymers supported by a fellowship from the Swiss National Science Foundation (SNF) and a Junior Research Fellowship awarded from Churchill College. He started his professional career at F. Hoffmann-La Roche in Basel in 2000 as Head of the Laboratory in Formulation Research and switched in May 2002 to Discovery Chemistry, working as a Senior Research Scientist in the department of Medicinal Chemistry.

Pawel Jokisz was born in 1975 in Warsaw, Poland. He completed his undergraduate Chemistry degree with Prof Andrew Holmes at the University of Melbourne in 2007 and will be starting his Ph.D. studies in the area of analytical chemistry early in 2009.

of this review revealed that the original report of EL in PPV[1] has been cited over 6200 times, impressively demonstrating the large degree of scientific interest. A further sign of the high level of interest is the fact that since our last review on electroluminescent polymers was published in 1998[2] (which has itself received over 1800 citations), the number of relevant publications has at least doubled. Interestingly, there has never been a fully comprehensive review of the synthesis and applications of electroluminescent polymers. Given that the number of publications on EL in conjugated polymers will soon be so great as to make a comprehensive review unmanageably large and that much future work will probably remain confidential for commercial reasons as these materials are now entering the marketplace, it is an appropriate time to present a comprehensive overview of the subject. Since 1998 a number of comprehensive reviews on organic electroluminescence have been published.[3−14] A number of short reviews (in addition to those listed in our earlier work) have appeared covering the work of individual groups[15−21] or of individual aspects of this field,[22−30] including the physics of organic electroluminescence.[31,32] There have also been some more general reviews on the synthesis, properties, and applications of conjugated polymers,[33−36] including reviews of methods for patterning or orienting polymer films which are of potentially great importance for some device applications.[37,38]

This review is limited to polymeric organic materials. Conjugated oligomers as luminescent materials and as models

Andrew Holmes was born in 1943 and is an Australian Research Council (ARC) Federation and Inaugural Victorian Endowment for Science Knowledge Innovation (VESKI) Fellow in the School of Chemistry/Bio21 Institute at the University of Melbourne. He also holds joint appointments at CSIRO Molecular and Health Technologies and Imperial College London from where he has been seconded on leave since 2004. After undergraduate education at the University of Melbourne, he completed a Ph.D. in 1971 at University College London (supervisor Professor F. Sondheimer). He worked as a Royal Society European postdoctoral fellow at E.T.H. Zürich (Professor A. Eschenmoser) in 1971−2 and then held an academic appointment at the University of Cambridge from 1972 to 2004, where he was Professor of Organic and Polymer Chemistry and Director of the Melville Laboratory for Polymer Synthesis. His research interests are in the applications of synthesis to problems in materials science and biology, and he cofounded Cambridge Display Technology to exploit the applications of light-emitting polymers.

for conjugated polymers have recently been the subject of reviews by Martin and Diederich[39] and by van Hutten and Hadziioannou[40] and of a collection of monographs edited by Müllen and Wegner,[41] to which the reader is referred. In this review oligomers will be discussed only where they serve to illustrate a structure−property relationship, (e.g., shifts in emission spectra due to substituents), to determine a key polymer property (e.g., effective conjugation lengths), or to demonstrate a technique that may be applicable to polymers (e.g., orientation to obtain polarized emission). We have endeavored to cover comprehensively the literature up to the end of 2006 with the inclusion of a few later papers of particular importance which appeared during the final revision of the manuscript. We have concentrated on the academic literature and have not attempted to cover the patent literature, but we have cited a number of patents where these contain details of synthetic methodology not otherwise available. The study and application of electroluminescent materials is a multidisciplinary effort involving synthetic chemists, physicists, and device engineers. This review is written from a chemist′s viewpoint. Our aim is to show what types of structures have been made, how they can be made, and how their properties may be controlled by means of intelligent, rational synthetic design. We are not concerned here with details of optimization of device performance, but we shall cover aspects such as the use of charge-transporting layers and shall cite examples of where these are needed to optimize performance for individual polymers, as these factors are of relevance in designing a new polymer structure. Note also that device efficiencies will be quoted either as external quantum efficiencies (ratio of photons emitted as outcoupled light to the charge injected) expressed as a percentage or emission per unit current (cd/A) as given in the original literature. Usually these values are quoted for the maximum efficiency, which may not be the efficiency of the device at maximum brightness (quoted as cd/m^2). Readers wishing to obtain full details of device performance are directed to the primary literature−we will here cite numbers of the relative reported performance of different polymers only in order to illustrate possible ways to influence performance by means of structure.

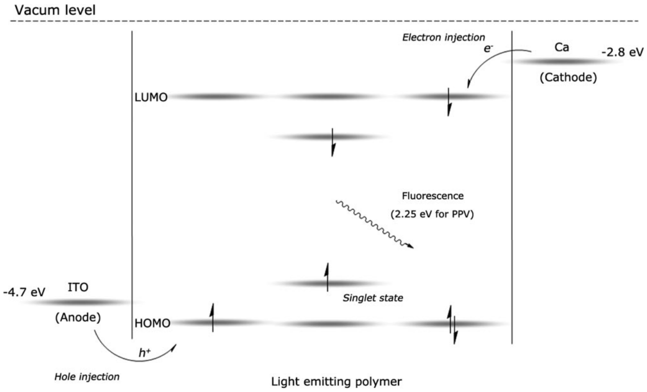


Figure 1. Illustration of electroluminescence (EL) in a conjugated polymer material. In electroluminescence, holes are injected at the ITO anode (removal of electrons from the HOMO) to give positively charged species (radical cations), and electrons at the calcium cathode are injected into the LUMO to form negatively charged species (radical anions). The charged species are drawn to the oppositely charged electrode and migrate from polymer chain to the polymer chain by a hopping process as a result of the applied electric field. When the two opposite charges combine, charge annihilation leads to singlet and triplet excited states (excitons), of which the former can emit photons through fluorescence. The work functions of the two metal electrodes are shown on the figure.

1.2. Electroluminescence and LEDs

Electroluminescence (EL) may be defined as the nonthermal generation of light upon the application of an electric field to a substrate; that is, it is the production of light by passing electricity through a material by means other than the simple incandescence seen in a standard filament light bulb. As shown in Figure 1, it results from recombination of charge carriers (holes and electrons) injected into a semiconductor in the presence of an external circuit. If these combine to give a singlet excited-state identical to that obtained in photoluminescence (PL) by excitation of an electron from the HOMO to the LUMO, then symmetry-permitted relaxation to the ground-state may occur with emission of a photon. The color of the emission obviously depends upon the size of the HOMO−LUMO energy gap, which for visible light (380−780 nm) corresponds to 1.5−3.2 eV. It should be noted that whereas chemists usually describe the energy associated with light in terms of its wavelength in nanometers (nm), physicists tend to refer to its energy in electronvolts (eV). In this review we will refer to the light emitted by the polymers using nanometers, and where we quote values from the literature in electronvolts, we will give their equivalent in nanometers. If the emitting material is oriented, e.g., by use of aligned liquid crystalline phases (the use of such phases in OLEDs has been reviewed by O'Neill and Kelly[42]), then the emitted light may be polarized, which is important in some applications, e.g. backlights for liquid crystalline displays (LCDs). The development of polarized electroluminescent devices for such applications has been reviewed by Grell and Bradley.[43]

EL has been known in inorganic materials for many years, and light-emitting devices (LEDs) using inorganic phosphors have been commercially available since the early 1960s. EL

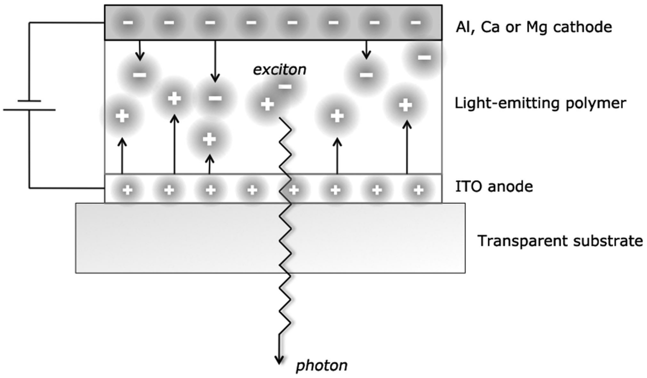


Figure 2. Schematic drawing of a single-layer EL device. Double charge injection through application of a forward bias voltage results in formation of an electron−hole pair. The singlet excited state which is formed emits a photon by radiative decay to the ground state.

was first observed in organic materials in 1963 with anthracene crystals,[44] but it was only with the development of thin films of efficient organic dye-based LEDs by Tang and VanSlyke[45] and Saito and Tsutsui[46] in the late 1980s that significant interest in organic EL devices emerged. The first commercial products using molecular organic LEDs appeared in 1997.[9] Emissive devices using polymeric emitting layers were first made by Partridge in 1974.[47,48] These used dyes incorporated into a polymeric charge-transporting matrix. The first LEDs using a conjugated polymer as emissive material were made in Cambridge in 1989 using PPV (**1**).[1] Polymer LEDs (PLEDs) have now entered the commercial marketplace, with the release by Philips of an electric shaver with a monochromatic PLED display. A fuller discussion of the history of EL and of LEDs appears in the review article by Mitschke and Bäuerle.[14]

In a typical polymer LED (Figure 2), a thin film of an emissive polymer is sandwiched between two electrodes, at least one of which is transparent. Generally, commercially available indium tin oxide (ITO) on a glass or polymer substrate is chosen as the (transparent) anode, and the cathode consists of a vacuum-deposited metal layer. However, a variety of other materials have been used as anodes or cathodes.

There are many factors that may contribute to the overall efficiency of an LED. A detailed description of the methods that have been used to optimize the efficiency of LEDs using conjugated polymers lies outside the scope of this review, but we will provide a general overview in this section.[49]

In general, the external efficiency, η_{EL}, of an OLED can be summarized by the following equation:

$$\eta_{EL} = \gamma \eta_{PL} \eta_{C} \chi_{S} \tag{1}$$

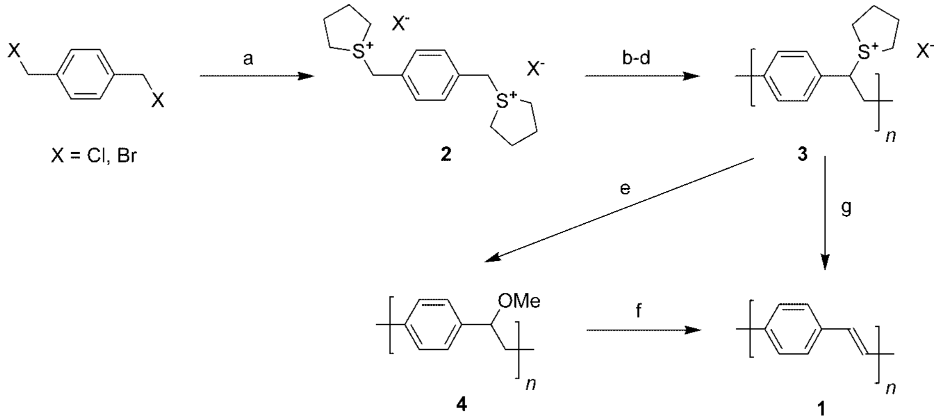
where γ relates to the charge balance in the emissive layer, η_{PL} is the photoluminescence quantum efficiency of the emitter, η_{C} is the fraction of photons coupled out of the device, and χ_{S} is the singlet fraction. If charge mobilities are not balanced, recombination can occur close to one of the electrodes where traps and defects are likely to be prevalent. Therefore, control of the charge balance γ is an important factor in improving device efficiencies.

Some further detailed discussion is also given for the specific cases of certain polymers, e.g. PPV (section 2.1) and MEH-PPV (section 2.2), as examples to illustrate the general principles. The efficiency of an LED depends greatly upon the choice of electrode materials, as the efficiency of charge injection depends upon the size of the energy barrier between the work function of the electrode and the energy level of the HOMO (for the anode) or LUMO (for the cathode). Since balanced charge injection is required (emission requires a hole and an electron to combine), the energy barriers should also be of comparable sizes. As a result, in designing a new polymer for use in an LED, care must be taken to match the HOMO and LUMO energies as closely as possible to the desired electrode materials. These problems may be partially overcome by use of charge-transporting layers (sometimes called level-matching layers) whose energy levels are intermediate between those of the electrode and emissive material. For a discussion of the factors affecting charge injection, the reader is referred to the reviews by Greenham and Friend,[50] Sheats et al.,[24,51] and Schott.[32] There are also some recent reviews on materials for hole-transport[52] and electron-transport layers[53] in LEDs.

If an LED contains more than one layer, then the question of cross solubilities arises, as the polymer layers are deposited from solution, usually by spin-coating, and so it is essential that as each layer is deposited, it does not dissolve the preceding layer. Layers are sometimes rendered insoluble by cross-linking (thermal or photochemical) of suitable substituents in order to surmount this problem. Polymers that are insoluble, e.g. PPV (**1**), are usually deposited as soluble precursor polymers, which are then thermally or irradiatively converted to the final conjugated polymer. Though precursor routes are invaluable as a means for obtaining thin films of insoluble materials, the byproducts should not corrode the electrodes or adversely dope the emissive or other layers—a factor that must be considered in synthetic design.

Electron−hole recombination of statistically generated spin states formed by double charge injection is predicted to lead to 25% of singlet states capable of spin-permitted radiative decay (fluorescence) and 75% of the relatively nonemissive and long-lived triplet states. Thus, the maximum EL efficiency obtainable would be predicted to be a quarter of the solid-state PL quantum efficiency,[54] implying a maximum theoretical external efficiency for a polymer LED of 25%.[55] The 3:1 singlet/triplet ratio has been experimentally confirmed in small molecule OLED devices.[56] However, as was first reported by Rothberg et al.,[57] the EL external efficiency for some polymer multilayer devices is apparently higher than 25% of the PL efficiency, although no research group has to our knowledge fabricated a PLED single-layer device exhibiting >25% external quantum efficiency. The value for the proportion of singlet states in conjugated polymer LEDs, and thus their maximum EL efficiency, is the subject of an ongoing debate in the physics literature, to which the reader is referred (see reviews by Köhler[58−61]), but a number of experimental[49,62−65] and theoretical[66,67] results have shown that, at least for some polymers, the potential EL efficiency of a polymer device may be up to 50% of the PL efficiency, although this is still disputed.[68] It has also been reported recently that blending cobalt−platinum nanowires with a fluorescent polymer increases the percentage of singlet excitons and thus the overall EL efficiency.[69] Maximization of the solid-state PL quantum efficiency is clearly desirable for obtaining maximal EL efficiency from conjugated polymers. It is not yet apparent how this may be done for any given structural type, except by trial and error. However, there are some general rules. For example, the presence of known fluorescence quenching functionalities such as halide or carbonyl groups on the polymer chain as impurities

Scheme 1. Sulfonium Precursor Route to PPV (1): (a) Tetrahydrothiophene, MeOH, 65 °C; (b) NaOH, MeOH/H_2O, 0 °C; (c) HCl; (d) Dialysis (water); (e) MeOH, 50 °C; (f) 220 °C, HCl(g)/Ar; (g) 180−300 °C, vacuum



(defects) formed during the reaction pathway should be avoided. As a result, the choice of synthetic pathway or reaction conditions may have a significant effect on the PL efficiency of the final polymer. The harvesting of energy from the triplet states is an increasingly important goal in research into OLEDs, as electrophosphorescent devices, i.e. LEDs utilizing emission from triplet states (phosphorescence), have potentially much higher efficiencies than those producing emission only from singlet states.[70,71] Since phosphorescence from conjugated polymers, if present, is generally very weak, the “wasted” triplet energy can be harnessed by the incorporation of phosphorescent metal complexes into the polymers or the blending of such complexes with the polymers (see section 5.3). Considerable progress has been made so that phosphorescent OLEDs are already competitive with the conventional fluorescent OLEDs.[72,73] Electrophosphorescent devices are likely to contribute strongly to the development of solid state lighting applications and to be present as the red component of all OLED/PLED displays.

As can be seen, many factors must be taken into account in designing a new polymer and its synthesis. Extensive evidence of this follows in the remainder of this review.

2. Poly(arylene vinylene)s

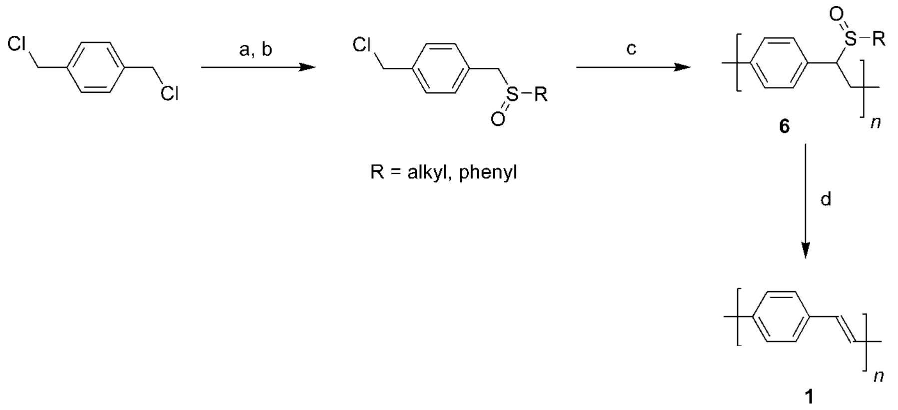
In this section we cover poly(arylene vinylene)s and related polymers such as poly(arylene ethynylene)s. Poly(arylene vinylene)s (PAVs) were the first class of conjugated polymers in which EL was demonstrated, and as a result, they form the most widely studied class of electroluminescent polymers. There are reviews on the methods for their synthesis by Scherf,[26] by Denton and Lahti,[74] and by Grigoras and Antonoaia[75] and on structure−property relationships in PAVs by Shim and Jin.[76]

2.1. Poly(*p*-phenylene vinylene) (PPV)

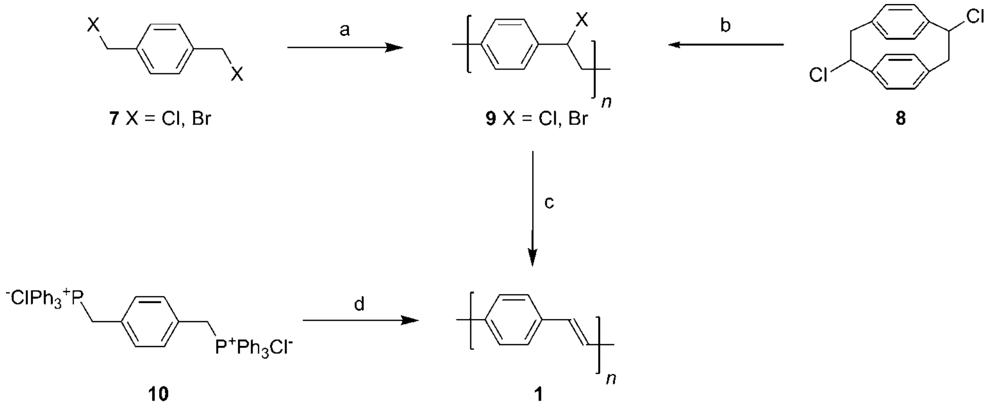
A more detailed account of the synthesis and processing of PPV than any of the other polymers is provided in this review, as the problems associated with the development of PPV and the solutions developed are illustrative of those seen for other materials. Thin films of PPV exhibit bright yellow-green fluorescence with an emission maximum at 2.25 eV (λ_{max} = 551 nm) and a secondary peak at 2.4 eV (520 nm). Extrapolation from the spectra of monodisperse phenylene vinylene oligomers suggests that the effective conjugation length for solid-state fluorescence in PPV is between 8 and 10 repeat units.[77] This correlates well with the value of 11 repeat units obtained from studies on substituted oligomers.[78] (Longer values are found in solution, which is attributed to the stronger interchain interactions in the solid state and to the existence of torsional disorder in solution.[79]) Unsubstituted PPV is insoluble, intractable, and infusible. Any synthesis that results in the preparation of PPV directly from a monomer, therefore, produces only insoluble material which cannot be further processed. This is highly undesirable, as solution processing by spin-coating is particularly useful for the production of polymer EL devices. The use of a processible poly(*p*-xylylene) precursor polymer provides a convenient way around this dilemma. The synthesis and applications of poly(*p*-xylylene)s have been reviewed by Greiner.[80] Introduced by Wessling and Zimmerman[81,82] and later modified and optimized by several groups,[83−88] the sulfonium precursor route to PPV has proven to be a versatile approach not only to PPV and its derivatives but also to a whole range of PPV-related copolymers.

Scheme 1 outlines the standard preparation of PPV (**1**),[87] using a bis-sulfonium salt monomer **2**. Although other sulfonium salts, such as those derived from dimethyl sulfide or tetrahydrothiopyran, have been used; tetrahydrothiophene is normally chosen, as it represents a satisfactory compromise between expense on the one hand and suppression of undesired side reactions (which are more prone to occur with dimethylsulfonium groups[83]) during the subsequent conversion step on the other hand. Polymerization of a methanolic solution of the monomer is induced by addition of slightly less than 1 mol equiv, e.g. 0.9 mol equiv, of aqueous hydroxide base at 0−5 °C. If 1 equiv is used, then the resulting polymer solutions become brightly colored, owing to base-induced elimination of the sulfonium groups. Studies[82,89] have shown that the presence of radical trapping agents such as oxygen can severely lower the molecular weight of the polymer, which would suggest that the polymerization proceeds *via* a radical pathway (for a discussion of the mechanism of the Wessling polymerization, which is thought to involve the transiently formed quinomethide intermediate, the reader is referred to the review by Denton and Lahti[74]), and thus the reaction must be performed under an inert atmosphere. Alternatively, the polymerization can be performed in a dispersion of aqueous droplets in mineral oil using a high-speed stirrer or homogenizer.[90] Polymer produced by this method shows similar properties to that prepared by the standard method. The molecular weight of the resulting precursor, polymer **3**, cannot be determined directly by size exclusion chromatography (SEC)

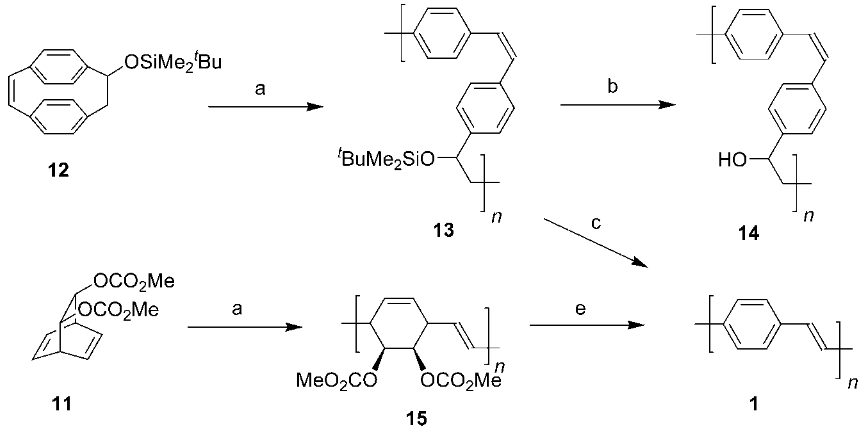
Scheme 2. Sulfinyl Precursor Route to PPV (1): (a) RSH, NaOH; (b) H_2O_2, TeO_2; (c) KO^{t}Bu; (d) 180−300 °C, vacuum



Scheme 3. Alternative Routes to PPV (1): (a) 500−700 °C, 0.01 mbar; (b) 580 °C, 10 Pa; (c) 200 °C, vacuum; (d) CH_3CN, 5.5 V



Scheme 4. ROMP Routes to PPV (1): (a) [Mo(=NAr)(=CHCMe$_2$Ph){OCMe(CF$_3$)$_2$}]; (b) Bu$_4$NF; (c) HCl(g), 190 °C; (d) 105 °C; (e) 280 °C

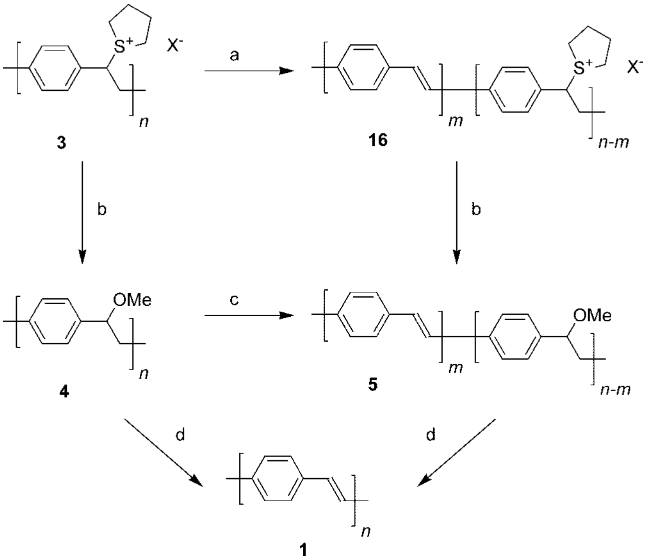


due to the polyelectrolyte nature of the polymer, but treatment with refluxing methanol affords a neutral polymer **4**, which on analysis by SEC shows a number-average molecular mass of *ca.* 100,000 g/mol, corresponding to about 750 repeating units, with a polydispersity of 5.7.[91] Prasad and co-workers have prepared PPV by performing the polymerization inside reverse micelles.[92] They were able to control the conjugation length by varying the micelle size, so that the PL maximum could be tuned between 493 and 505 nm.

Although the purified, mainly aqueous, polymer solutions can be used directly, there are considerable advantages to isolating the polymer and redissolving it in methanol. Such solutions can be safely stored at −20 °C for several months. Solutions of the polyelectrolyte **3** in water,[83] methanol,[87] or cyclohexanone[93] are highly viscous even at a concentration of only 1% (w/w) of polymer, which facilitates their processing by spin-coating; however, using methanolic rather than aqueous solutions produces thin films of higher quality.[87] Alternatively, the precursor polymer **3** has been cast with a precision doctor-blade machine which can coat areas of about 25 cm^2.[82,93]

The sulfonium precursor polymer **3** is typically converted into PPV (**1**) by heating thin films at 220−250 °C for 12 h under vacuum (10^{-6} mbar).[1,87] The luminescence efficiency of PPV produced by this method seems to be strongly dependent upon the conversion conditions. A detailed study on the mechanism of the elimination reaction found that the mechanism was complex and that reducing the heating rate and/or converting under a reducing atmosphere gave PPV with higher PL efficiencies.[94] Friend and co-workers reported that the PL efficiency of PPV converted on ITO substrates was optimal at a conversion temperature of 205 °C.[95] The

Scheme 5. Synthesis of Partially Conjugated PPV Copolymers: (a) Bu_4NOH, MeOH; (b) MeOH, 50 °C; (c) 300 °C, vacuum; (d) 220 °C, HCl(g)/Ar



EL efficiency of single-layer devices increased with increasing conversion temperature, while that of double-layer devices using an electron-transporting layer decreased. A Korean group has reported that conversion at 230 °C for 5 min under nitrogen gave optimal EL efficiency in single-layer LEDs.[96] Using the bromide instead of the chloride salt enables the conversion to occur at temperatures as low as 100 °C.[88,97] Replacing the chloride with a dodecylphenylsulfonate counterion also lowers the conversion temperature, so that complete conversion occurs rapidly at 115 °C.[98,99] The properties of PPV prepared by elimination of sulfonium precursor polymers are found to depend upon the leaving group with an increase in intrachain order and a decrease in interchain order with increasing size of the leaving group.[100,101] The neutral precursor polymer **4** can be converted to PPV by simultaneous heat and acid treatment. Halliday et al.[102,103] reported that treatment of the precursor polymer **4** with base, followed by methanolysis, gave partially conjugated material **5** (Scheme 5). Subsequent conversion to the fully conjugated polymer produced PPV which was more highly ordered than standard PPV[101] and which showed a red-shift in the absorption maximum.[104] The properties of this material have been found to depend strongly on the experimental conditions applied, and oligomeric material may be responsible for the observed properties. Furthermore, the process is not easily amenable to EL device fabrication, as the conversion step tends to cause corrosion of the electrodes. A similar partially converted precursor polymer can be obtained by long-term storage of **3** in methanol at 0−5 °C. PPV prepared from this precursor is also reported to be more highly ordered than standard PPV.[105]

It has been found that traces of oxygen in the conversion atmosphere cause reduction in EL in the final PPV film due to the formation of carbonyl group defects,[106−108] which can be suppressed by performing the elimination reaction in an atmosphere of nitrogen and hydrogen.[106,107] PPV prepared under these conditions was found to have higher PL and EL quantum yields.[94,109] Schwoerer and co-workers[110−112] have found that the conversion temperature can be lowered to 160° by performing the conversion under an argon atmosphere. This enables LEDs to be fabricated on flexible polymer foil substrates. It has been reported[113,114] that the elimination of the sulfonium groups from the precursor polymer can be performed even at room temperature by use of protic acids followed by dedoping of the resulting polymer with aqueous sodium hydroxide. However, this method is unlikely to prove suitable for the production of PPV films for LED devices, owing to the problems involved in obtaining complete dedoping (acids are not compatible with most electrode materials) and also to the nucleophilic displacement of a proportion of the sulfonium groups by water, which will give rise to a reduced degree of conjugation in the resulting polymers. A study on the fluorescence of doped PPV films[115] showed that doping with lithium or sulfuric acid gave red and blue-shifts, respectively, in the photoluminesence spectra but that the material properties of the films were adversely affected, making such polymer films unsuitable for use in electroluminescent devices. Elimination can also be induced by irradiation with UV light,[116−118] laser light,[119,120] or microwaves.[121] Irradiation of PPV films with light leads to cross-linking and a consequent decrease in the luminescence of the film, which can be used as a means of patterning PPV films.[122] Films of PPV prepared from Langmuir−Blodgett (LB) films of precursor polymer **3**[123] also show electroluminescence despite the fact that the PPV is contaminated by surfactant residues.[124−129] Langmuir−Blodgett or self-assembled films of the sulfonium precursor **3** with dodecylphenylsulfonate counterions can be converted at temperatures as low as 80 °C.[130−132] The fluorescence of PPV prepared from self-assembled films of the precursor and sulfonated polystyrene is reported to be blue-shifted with respect to the case of standard PPV, indicating a shorter conjugation length.[133] Ordered LB films of PPV have been shown to emit circularly polarized PL.[134]

Other methods have also been exploited to prepare PPV for use in LEDs. A modified Wessling synthesis using a sulfinyl (or sulfonyl) precursor **6** has been reported by Vanderzande and co-workers (Scheme 2)[135−142] which produces PPV with lower defect levels.[143] A disadvantage of this method is that the monomer synthesis is more complicated though the initial low yield has since been greatly improved.[144] This synthesis has been shown to proceed via a radical mechanism.[145] The same group has recently reported that a dithiocarbamate precursor is easier to make, but the quality of the materials produced is not as good as that from the sulfinyl route.[146] Galvin and co-workers have described a modified Wessling route to PPV using an organic soluble xanthate precursor polymer which gives better quality PPV films and higher device efficiencies than the standard route.[147,148]

PPV films have also been prepared by chemical vapor deposition of 1,4-bis(halomethyl)benzene **7**[149−151] or bis-halocyclophane **8**[152] to give α-halo-precursor polymer film **9**, which is converted to PPV at 200 °C under vacuum (Scheme 3). LEDs made from the chloro precursor show rather low (0.002%) EL efficiency,[149,150] but films made from the bromo precursor have properties comparable to those of standard PPV.[153] Use of the bromomethyl monomer **7** (X = Br) also leads to the formation of more ethanediyl defects and thus a blue-shift in the PL of the resulting PPV.[154] The use of UV light enables the conversion of the precursor to be performed at room temperature.[155] PPV films can be grown selectively by CVD in patterns on surfaces treated with iron or other group VIII metal salts.[156] PPV can also be produced electrochemically.[157] Electropolymerization of a xylylene bisphosphonium salt **10** gives films of PPV (**1**) whose absorption and emisssion spectra are blue-shifted with respect to those of materials produced by other methods, indicating that the electropolymerized material has a shorter conjugation length, probably due to incomplete elimination of phosphonium groups. A device fabricated using electropolymerized PPV emitted green (λ_{max} 530 nm) light.[158] It is reported that LEDs using electropolymerized PPV show lower EL efficiencies than those using standard PPV.[159]

A synthetically elegant approach to the preparation of PPV is the ring-opening metathesis polymerization (ROMP) of a bicyclo[2.2.2]octadiene monomer **11**[160] or of a silyloxy cyclophene **12**,[161] followed by thermal elimination of the resulting precursor polymers **13**−**15** (Scheme 4). A related approach using ROMP on a cyclophanediene has been used to prepare PPV derivatives with alternating *cis/trans* microstructure.[162]

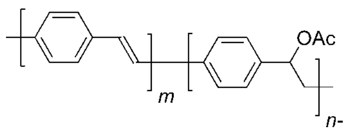
As mentioned in the introduction, it has been clearly demonstrated that choosing the correct electrode combination is crucial to the efficient operation of polymer LEDs. In the case of PPV, the best early results (0.1%) with regard to device efficiency (photons emitted vs electrons injected) were achieved with indium tin oxide (ITO) as the hole-injecting electrode and calcium, a low work-function metal, as the cathode.[163,164] However, a problem with converting the sulfonium precursor to PPV on ITO is that it leads to doping with indium chloride, which reduces the PL efficiency.[165] It might be expected that this decrease in PL efficiency would also lower the EL efficiency, but Morgado et al. have reported that indium-doped PPV, prepared by doping the precursor polymer **3** with indium(III) chloride before conversion, showed a lower PL quantum efficiency but an increased EL efficiency.[166] Other materials such as tin oxide have been explored in place of ITO as anode but without improvement in device performance.[1,167] Use of a *p*-doped silicon anode offers the possibility of integrating PLEDs with microelectronic circuitry on a silicon chip.[168] As a result of its reactivity (especially its moisture-sensitivity), calcium is not particularly suitable for use in commercial devices, although it can be encapsulated in aluminum. In order to construct devices which can be used outside a glovebox, less reactive metals such as aluminum are preferred. The efficiency of the first PPV LEDs using ITO and Al electrodes was only 0.01%, owing to poor electron injection.[164] Introduction of a thin interfacial layer of aluminum oxide[169] or a lithium-doped polyarylene[170] between the PPV and Al layers is reported to lead to a marked improvement in device efficiency due to charge carrier confinement. A double-layer cathode with a low work-function strontium layer sandwiched between air-stable indium and the PPV layer has also been found to give improved electron injection.[171] It is reported that the emission spectrum from PPV varies with different metal cathodes, with the intensity of the peak at 550 nm being greater with lower work function metals.[172] A similar increase in the relative intensity of the 550 nm emission peak has been observed upon increase of either the thickness of the PPV layer or the drive voltage in an ITO/PPV/Al device,[173] or by increasing the temperature of the PPV conversion.[174] The addition of an electron-transport layer between the PPV and the cathode has been found to considerably improve both the power efficiency and the stability of devices.[54,164,165,175−191] Use of a hole-transporting layer on the other hand causes a decrease in efficiency, indicating that the main limiting factor in PPV-based LEDs is electron injection and transport.[174,192] Incorporating a phenylene-based polyacid between two layers of PPV has been reported to increase the EL efficiency 250 times.[193] Heterostructure LEDs made from self-assembled multilayers of PPV and polyanions such as sulfonated polyaniline have been constructed; charge recombination at the interface is presumed to cause emission of bright yellow-green light with low drive voltages.[194−202] The emission can be blue-shifted by increasing the thickness of the nonconjugated polyanion layers.[203] Polarized emission has been obtained from a stretched PPV film, with emission parallel to the stretching direction being 8 times stronger than that perpendicular to it.[204] Rubbing alignment of films of the precursor polymer **3** prior to conversion gives even better anisotropy (12 times stronger emission parallel to the rubbing direction).[205,206] Micropatterning of PPV films has been achieved by patterning films of the precursor polymer **3** with a scanning tunnelling microscope (STM) tip prior to conversion.[207,208] The areas affected by the STM show no emission, possibly due to oxidation of the precursor. Patterning of PPV has also been achieved by a microlithographic process,[209] by holographic lithography,[210] by micromolding of the precursor film,[211,212] and by screen or inkjet printing.[212]

Improved efficiencies in PPV devices can also be achieved by the deliberate introduction of disorder into the polymer main-chain, thus interfering with polymer chain packing. Son et al.[213] have synthesized amorphous PPV by using a modified Wessling synthesis with a xanthate group. The resulting PPV is claimed to have a mixture of *cis*- and *trans*-vinylene units which reduces conjugation and interferes with packing. Efficiencies of up to 0.22% for single-layer devices with aluminum−aluminum cathodes and 2% for double-layer devices using a dispersion of a diaryloxadiazole in poly(methyl methacrylate) as electron-transporting layer were obtained. Subsequent work with solution-processible PPVs and a well-defined *cis/trans* microstructure has not substantiated this observation as general.[162]

A simple modification of the PPV synthesis gives access to PPV-derived blue light-emitting polymers with a high concentration of a fluorescent chromophore yet at the same time having only a short conjugation length. The objective is achieved by partial conversion of precursor homopolymer **3** or **4** to produce statistical copolymers **16** and **5** with regions of saturated and unsaturated units (Scheme 5).[214,215] Conversion of **3** to **16** can be achieved either thermally or by treatment with base as mentioned above. Studies on the elimination of PPV precursor polymer **2** have shown that the degree of elimination can be influenced by careful control of conversion conditions.[216,217] Incompletely converted PPV is reported to be unstable with devices showing poorer stability, although higher initial efficiency.[218] Heeger and co-workers have studied thermal partial conversion and found that conversion at 160 °C for 2 h gave the copolymer **16** with the best stability and emission efficiency.[219] As indicated before, polymer **3** undergoes substitution with methanol at 50 °C to give polymer **4**, another precursor polymer to PPV. Complete conversion of polymer **4** to PPV (**1**) can only be achieved by simultaneous heat and acid treatment. Thermal treatment alone results in partial conversion to copolymer **5** with intermittent regions of saturated and unsaturated units. This copolymer can also be obtained by leaving a solution of polymer **3** in methanol at ambient temperature for several days and then thermally converting the resulting copolymer in which the sulfonium groups have been partially displaced by methanol.[220] The UV−vis spectrum of copolymer **5** prepared in this way indicates that the polymer contains conjugated sequences mainly comprising stilbene and distyrylbenzene units.

Films of copolymer **5** so formed are thermally stable against further elimination, requiring combined heat and acid to be converted to PPV (**1**). When incorporated in an EL device using aluminum and ITO as electrodes, copolymer **5** shows a broad emission spectrum and the emitted light appears blue-green to the eye. The EL maximum is distinctly blue-shifted (2.44 eV, $\lambda_{max} = 508$ nm) compared with that of PPV (2.25 eV, $\lambda_{max} = 551$ nm),[215,221] indicating that the EL emission of **5** is closer to that reported for distyrylbenzene (2.6 eV, $\lambda_{max} = 475$ nm).[222] The device efficiency is twice that of PPV in the same device configuration, which correlates well with the fluorescence yields of the two polymers.[214] A similar tuning of the conjugation length of PPV prepared by the Vanderzande sulfinyl precursor route can be achieved by partial oxidation of the sulfinyl groups to sulfones, followed by selective elimination of the former.[223,224] CVD copolymerization of a bis-chloromethylbenzene with an unsubstituted cyclophane enables the controlled introduction of unsubstituted ethanediyl units into the resulting PPV chloro precursor, so that the PL maximum of the final PPV can be tuned between 470 and 525 nm. LEDs using this material show blue ($\lambda_{max} = 420$ nm) emission.[225] Copolymers of PPV and poly(vinyl alcohol) (PVA) have been prepared by spin coating a mixture of the precursor **4** and PVA, followed by thermal conversion. Partial displacement of the sulfonium groups in **4** by the hydroxyl groups of the PVA gives rise to cross-linked materials with short conjugation lengths. By increasing the ratio of PVA used, the PL emission maximum may be shifted from green ($\lambda_{max} = 550$ nm) to blue ($\lambda_{max} = 485$ nm).[226] Partial (<5%) displacement of sulfonium groups in **3** with fluorescent dyes by nucleophilic substitution or ion-exchange followed by thermal elimination has been used to prepare polymers which are claimed to show fluorescent efficiencies higher than those for PPV and whose emission color can be tuned by varying the fluorescent dye chosen.[227]

The copolymer **17** prepared by partial (up to 30%) displacement of the sulfonium groups by acetate followed by thermal elimination of the remaining sulfides has been used to make highly efficient LEDs.[228,229] The use of a PEDOT/PSS conducting layer between the ITO and these PPV layers gives devices with particularly high efficiency, brightness, and operating stability, and significantly longer lifetimes (>7000 h).[228] These lifetimes, however, are still well short of those needed for commercially viable devices, and as a result, PPV is no longer being actively examined as a suitable emissive material for such applications.



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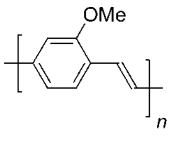
2.2. Alkoxy-, Thioalkyl-, and Alkylamino-Substituted PPVs

Substitution of PPV (**1**) with alkoxy groups has two effects. First, the band gap is reduced, leading to a marked red-shift in emission. Thus, while PPV shows yellow-green PL with maxima at 2.25 eV ($\lambda_{max} = 551$ nm) and 2.4 eV ($\lambda_{max} = 520$ nm),[1] the monomethoxy derivative **18** emits in the yellow with a single maximum at 550 nm,[230,231] and the 2,5-dimethoxy polymer **19** shows orange-red emission with maxima at 2.06 eV ($\lambda_{max} = 603$ nm) and 1.91 eV ($\lambda_{max} = 650$ nm).[232] Second, poly(2,5-dialkoxy-1,4-phenylene vinylene)s (RO-PPVs) with at least one long, solubilizing alkoxy side-chain, e.g. poly[2-methoxy-5-(2-ethylhexyl)-1,4-phenylene vinylene] (MEH-PPV, **20**), dissolve in organic solvents, such as chloroform, toluene, or tetrahydrofuran.[233-241] Branched side-chains, as in MEH-PPV, generally enhance solubility more than linear ones with the same number of carbon atoms. In addition, the fluorescence efficiency of polymers bearing longer side-chains is increased by several orders of magnitude compared with that of the dimethoxy polymer **19**. Longer alkyl chains also lower the glass transition temperature of the polymers.[242]



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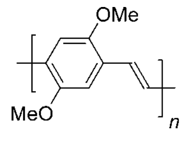

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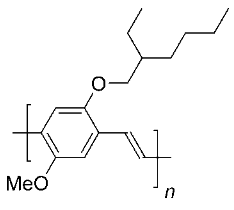

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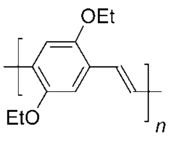

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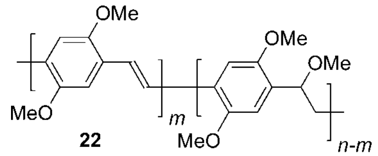
The first LEDs using such soluble PPV derivatives were fabricated independently by researchers at Sumitomo[233,234] and at Santa Barbara.[235,236,238,240,243] They have become the most widely studied group of electroluminescent conjugated polymers. Such soluble polymers no longer require thermal treatment during device fabrication, which is the drawback of the PPV precursor route. As the sulfonium precursor polymer **2** can be processed from methanolic solutions and like PPV (**1**) does not dissolve or swell in chloroform, whereas most of the substituted PPVs used in EL devices can be processed from chloroform, one can design multilayer devices consisting of sandwich structures with layers of different polymers, *viz.* PPV and substituted PPVs.[244,245]

Mono- and dialkoxy-substituted PPVs can be prepared by a sulfonium precursor route as described for the synthesis of PPV (**1**).[87,232,240,246-250] Delmotte et al.[251] have studied the synthesis of poly(2,5-diethoxy-1,4-phenylene vinylene) (**21**) by the sulfonium precursor route and found that partial elimination of the sulfonium groups occurred when >1 equiv of base was used. This elimination was found to be selective for short conjugated fragments, yielding only tetraethoxystilbene units even when up to 35% of leaving groups had been eliminated. They explained this as being due to an E_2 mechanism where the formation of tetraethoxy stilbene units represents the highest gain in resonance energy at each step. These units gave blue emission centered at an emission maximum of 415 nm.

There has been much interest in controlling the conjugation length of alkoxy-PPVs, both in order to achieve the entire color spectrum in LEDs and because the presence of nonconjugated segments on the backbone of dialkoxy-PPV derivatives is reported to increase their EL efficiency.[252] A fairly straightforward method for the preparation of 2,5-



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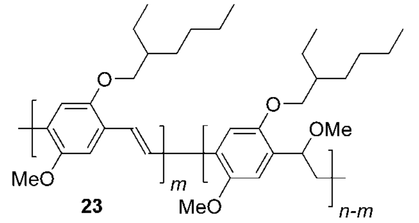

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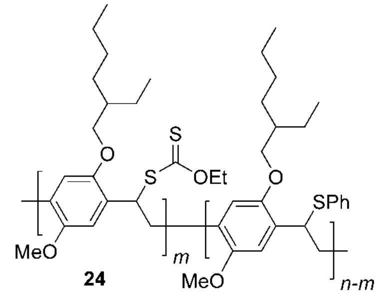

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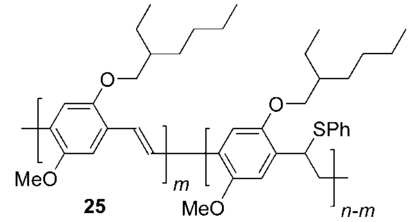

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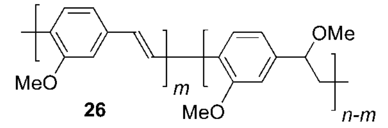

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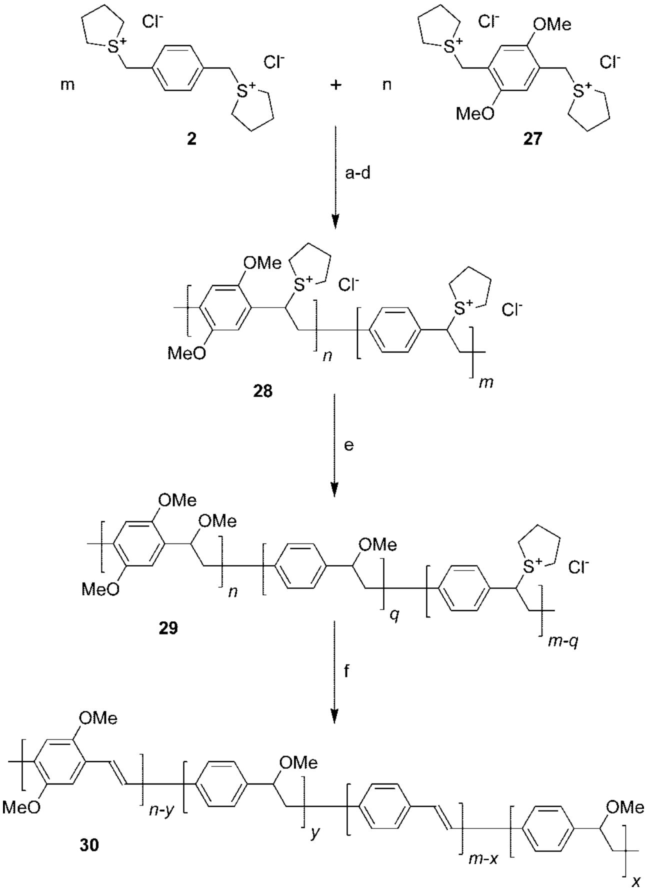
dimethoxy substituted PPV **19** with varying degrees of conjugation was presented by Ramakrishnan and coworkers[253,254] using a process already developed by Cambridge Display Technology.[228] Sulfonium polyelectrolyte precursor polymers prepared *via* the standard Wessling route were subjected to competitive nucleophilic substitution using varying ratios of methanol and NaOAc in acetic acid. The acetate groups underwent selective thermal elimination upon heating to 250 °C, affording partially conjugated statistical copolymers **22** showing colors from light yellow to deep red. [We use the extended wavy line connection (as in structure **22**) to represent a statistical copolymer.] As the degree of conjugation decreased, the PL and EL efficiencies increased.[255] This approach was readily adopted to prepare MEH-PPV precursors **23** but failed in the case of unsubstituted PPV (**1**).[256] Similar control of conjugation length has also been obtained by means of the precursor polymers **24**, in which the xanthate groups could be selectively eliminated.[257] A similar approach developed by Hwang et al.[258] is to replace some of the sulfonium groups with thermally stable thiophenoxy groups prior to thermolysis. The PL maximum of the resulting copolymers **25** has been tuned between 507 and 585 nm.

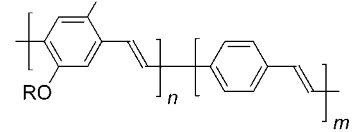
A similar control of the conjugation length of the methoxy-PPV **18** prepared by the Wessling method has been obtained by performing dialysis of the sulfonium precursor with methanol−water (9:1) for varying lengths of time. Thermal conversion gave precursor polymers **26** with varying degrees of nonconjugation. Longer dialysis times produced greater degrees of nonconjugation with a concomitant blue-shift in emission. A double-layer device in which a layer of more-conjugated **26** was deposited upon a layer of less-conjugated **26** showed an unusual emission spectrum with peaks at 560 and 590 nm, and an increase in efficiency over single-layer devices. The peak at 590 nm did not correspond to the emission maximum of either layer and was attributed to a new optical interaction at the interface between the layers. If the order of the layers was reversed, these effects were not observed.[259−261]

Scheme 6. Synthesis of PPV/Dialkoxy-PPV Copolymers: (a) NaOH, MeOH/H$_2$O, 0 °C; (b) HCl; (c) Dialysis (Water); (d) MeOH; (e) 220−300 °C, vacuum; (f) 220 °C, HCl(g)/Ar



The sulfonium groups in the precursors to alkoxy-PPVs prepared by the Wessling route are more labile toward nucleophilic substitution than those in the PPV precursor **2**, as is shown by the tendency for gelation in the preparation of dimethoxy-PPV **19**, due to displacement of sulfonium groups by water.[232] This has been used to good advantage by the Cambridge group to produce copolymers of PPV and dialkoxy PPV chemically tuned to possess improved properties for EL and for patterned waveguides. This is exemplified by the preparation of copolymers incorporating phenylene vinylene (**1**) and dimethoxyphenylenevinylene **10** repeat units (Scheme 6), although other copolymers have also been investigated.[163,262,263] Statistical copolymerization of the sulfonium monomers **2** and **27** affords a statistical copolymer **28**, whose composition is simply controlled by using different feed ratios of the two monomers. The copolymerization solvent mixture permits selective substitution of the tetrahydrothiophene groups by methanol, as this occurs at a faster rate at those benzylic carbons which are attached to the more activated dimethoxyphenylene rings. The resulting copolymer **29** has two leaving groups with methoxy groups being adjacent to all dimethoxyphenylene and a small amount of phenylene units, and sulfonium groups adjacent to most of the phenylene units

During subsequent heat treatment (220 °C for 2 h at 10^{-5} mbar) of spin-coated thin films (thickness *ca.* 100 nm) of polymer **29**, the sulfonium groups are completely eliminated whereas the methoxy groups mainly remain, to give homogeneous, dense, and uniform films of copolymer **30** which are stable toward further heating. NMR spectra confirm the presence of methoxy leaving groups after thermal conversion, while the IR spectra show a decrease of a diagnostic band for the benzylic methoxy groups. The longest-wavelength absorption band of polymer **30** exhibits a distinct blue-shift with respect to that of polymer **29** which increases as the content of dimethoxyphenylene units in the copolymer rises, showing that the polymer backbone consists of a statistical assembly of discrete conjugated segments separated by saturated units. The EL efficiency of polymer **30** varies with the composition of the copolymer and has its peak with a copolymer obtained from a feed ratio of $m/n = 9:1$. The maximum efficiency measured in this case was 0.3%, which was 30 times higher than that of PPV (**1**) (0.01%) in the same device configuration (Al−Al_2O_3/polymer/Al).[221,262] As both PPV and **30** are insoluble in chloroform, it is possible to make multilayer devices, containing these polymers and also soluble PPV derivatives, with a wide variation in the thicknesses and order of the layers. Such devices allow the color and brightness of the emitted light to be controlled, which clearly emphasizes the scope which copolymers offer as organic light-emitting materials.[245] In fact, the basis of this invention lies at the heart of all commercial solution-processible light-emitting polymer technology. When the thermal treatment of copolymer **29** is carried out in the presence of hydrogen chloride, the fully converted polymer **31** is obtained. Polymer **31** can also be prepared by thermal elimination of the sulfonium precursor copolymer **29** obtained from Wessling copolymerization under the standard conditions.[264−266] The efficiency of LEDs using an emitting layer of **31** is increased 10-fold by use of a PPV hole-transporting and a polyquinoline electron-transporting layer.[267] A similar copolymer **32** is soluble in organic solvents due to the longer dodecyl chains. The emission maximum of these copolymers can be tuned between the maxima of the homopolymers at 515 and 590 nm, simply by altering the composition.[268]

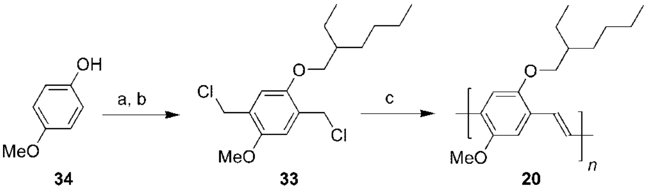


31 R = Me

32 R = $C_{12}H_{25}$

The Cambridge group also used this behavior advantageously in a patterning process for copolymer films. Conversion of thin films of copolymer **29** at 220 °C under vacuum produces tetrahydrothiophene and hydrogen chloride as byproduct, which normally escape quickly. In principle, HCl can promote further conversion of polymer **30** to **31**, if the acid stays long enough within the copolymer film. It does so in thick copolymer films, or in thin films when the byproducts are deliberately trapped. This can be used to produce two colors within a single film, by depositing an aluminum mask onto the precursor copolymer surface according to a predefined lithographic pattern. The aluminum cap provides a physical barrier to the HCl, which causes the formation of more conjugated polymers. After etch-removal of the metal mask, the polymer that was underneath it shows a deeper orange appearance to the eye than the uncovered material and a striking difference in refractive index.[269,270] In an EL device with ITO and Ca contacts, such a two-color-patterned copolymer shows emission from the regions containing the partially conjugated polymer **30**.[262,263] This observation is consistent with the fact that the partially conjugated material **30** has a higher quantum efficiency for EL than the fully conjugated polymer **31**, and it demonstrates the ability to produce passive emissive elements by a negative lithography process. The same patterning procedure can also be applied to the design of waveguides.[262,270]

Scheme 7. Synthesis of MEH-PPV (20): (a) 3-(Bromomethyl)heptane, KOH, EtOH, reflux; (b) HCHO, concentrated HCl, dioxane; (c) KO^{t}Bu, THF

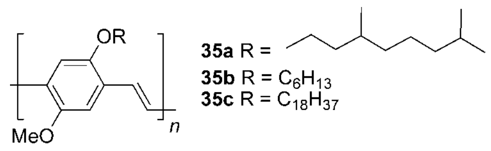


The Vanderzande sulfinyl precursor method has also been used to make alkoxy-PPVs.[139,223,271,272] The synthesis of the monomers is complicated compared with those for other routes but has recently been greatly improved.[273,274]

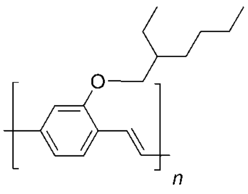
MEH-PPV was first synthesized by Wudl using the Wessling sulfonium precursor route,[240] and as shown above, the Wessling and Vanderzande routes may be used to make a variety of mono- or dialkoxy-substituted PPV derivatives (RO-PPVs). However, in most cases an alternative method first developed by Gilch[275] is preferred, involving polymerization of 1,4-bis-halomethylated benzene derivatives which are susceptible to base-promoted 1,6-elimination, with a large excess of base, usually KO^{t}Bu.[233,234,238−240,243,276] This approach for MEH-PPV was first disclosed in the patent literature.[241]

This shortens the preparation of the conjugated polymer by two steps compared with the Wessling route and consequently usually increases the yield. Scheme 7 shows the synthesis of the most studied dialkoxy-PPV−MEH-PPV (**20**).[240,243] The bis-chloromethyl monomer **33** is synthesized in good yield by alkylation of 4-methoxyphenol **34** with 2-ethylhexyl bromide, followed by chloromethylation.[240] Polymerization of the monomer **33** with a 10-fold excess of potassium *tert*-butoxide in tetrahydrofuran (THF) gives the bright red-orange MEH-PPV (**20**), which is purified by several reprecipitations from methanol. A problem with this reaction is the formation of insoluble gels of high molecular weight polymer (gelation), but this can be overcome by use of DMF as solvent.[277] Benzyl halides can be used as chain terminating agents, either to control the molecular mass (*vide infra*) or to introduce terminal functional groups.[278]

Electroluminescent RO-PPVs other than MEH-PPV have been similarly prepared.[233,239,240,272,279−284] The polymerization has also been performed under phase-transfer catalysis conditions,[285] reportedly giving better molecular masses and lower polydispersities than the standard method.[286] Polymerization of a mixture of monomers gives statistical copolymers whose properties are determined by the ratio of monomers.[268,281] Molar masses of soluble RO-PPVs, obtained by polymerization of bis-chloromethyl compounds with KO^{t}Bu, are comparable with the same polymers prepared by the sulfonium precursor route. Interestingly, comparison of OC$_1$C$_{10}$-PPV (**35a**) (where C$_{10}$ is 3,7-dimethyloctyl) made by the Gilch and Vanderzande methods showed that the former had higher PL and EL efficiencies though the latter was obtained in better yield and had fewer structural defects.[272] If <1 equiv of base is used, a soluble α-chloro precursor polymer is obtained which can be thermally converted to the conjugated polymer—a method known as the chloro precursor route.[239,276,287,288] The alkoxy substituents strongly promote the loss of HCl from the precursors, so that they usually contain a proportion of conjugated segments. Bulky secondary alkyl substituents tend to promote this elimination less, due to the greater steric constraints on the polymer backbone rotation necessary for elimination.[288] MEH-PPV made by the chloro precursor route is insoluble, possibly owing to its high molar mass, making it suitable for use in multilayer devices.[287,289] Burn compared the properties of poly[2-(2-ethylhexyl)-1,4-phenylene vinylene] (**36**) made from chloro- and from *S*-methyl and O-ethyl xanthate precursors, and they found that the chloro precursor route gave the material with the highest PL efficiency when converted on quartz but the lowest efficiency when converted on ITO, due to reaction of the liberated HCl with the ITO. was also lower than that for the material made from the xanthate precursors.[291] [290,291] As a result, the EL efficiency was also lower than that for the material made from the xanthate precursors.[291]



35a R =
35b R = C_6H_{13}
35c R = $C_{18}H_{37}$



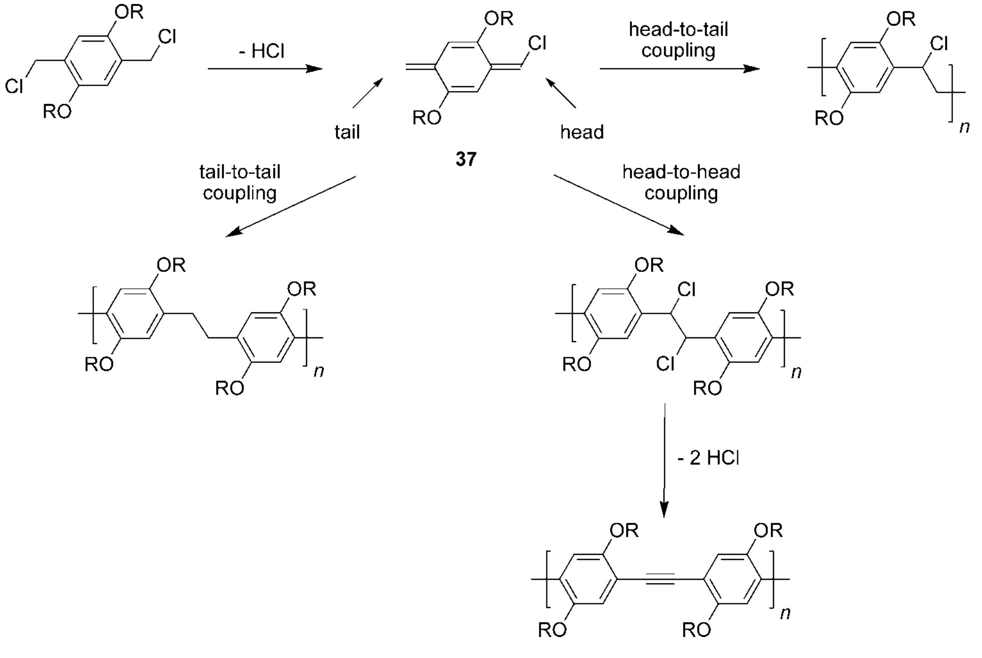
36

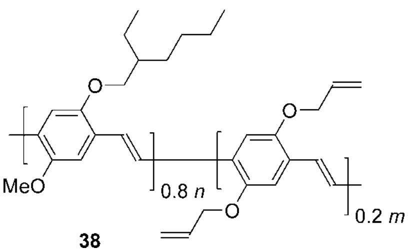
The mechanism of the Gilch reaction has been the subject of some debate. An anionic mechanism has been proposed,[292] supported by such evidence as the ability to control the molecular mass of MEH-PPV by addition of either polyethylene glycol, which enhances anionic polymerization by assisting in the dissociation of ion pairs,[293] or a benzyl bromide chain-stopper[294−296] or 4-methoxyphenol, which can act as an anionic initiator.[297] More recent studies by Vanderzande[298,299] and by Rehahn[300] indicate that the primary mechanism is a radical pathway, with anionic pathways giving only low molecular mass materials. Since the Gilch reaction proceeds via a quinodimethane intermediate **37** as in the Wessling polymerization, which is now generally accepted to proceed by a radical mechanism, it would seem most probable that the Gilch reaction is also a radical process.

Despite the wide application of the Gilch dehydrohalogenation polymerization for the synthesis of PAVs, it is only recently that defect structures generated during the polymerization process have been systematically investigated.[301−303] Studies on the ^{13}C-labeled polymer OC$_1$C$_{10}$-PPV (**35a**) using a combination of 1D- and 2D-NMR techniques identified the formation of tolane ($C\equiv C$) and bisbenzyl ($ArCH_2CH_2Ar$) moieties in amounts of 1.5−2.2% as the major source of defects through nonregioregular coupling of the presumed quinodimethane intermediate **37** (Scheme 8). It was recently reported that low molecular weight fractions of MEH-PPV from Gilch polymerization show blue-shifted PL due to the presence of *cis*-vinylene groups.[304] To explain their absence in the higher mass fractions, it was suggested that these defects hinder chain growth.

MEH-PPV emits orange-red light with a maximum in the yellow at $\lambda_{max} = 590$ nm and a long tail into the red. As with PPV, electron injection into MEH-PPV is poorer than hole injection, so that use of a low work-function cathode such as calcium is required to get high efficiency. Efficiencies

Scheme 8. Formation of Defects during Gilch Synthesis





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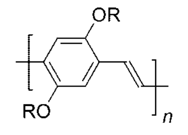
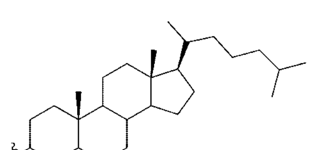


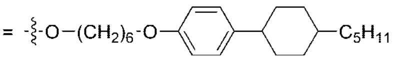
39 R = alkyl

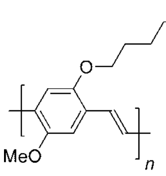
39a R = 2-ethylhexyl
39b R = 2-cholestanyl
39c R = 3,7-dimethyloctyl
39d R = C_6H_{13}
39e R = C_3H_7
39f R = C_7H_{15}
39g R = $C_{10}H_{21}$
39h R = C_9H_{19}
39j R = C_8H_{17}
39k R = $C_{12}H_{25}$



2-cholestanyl

39i R =





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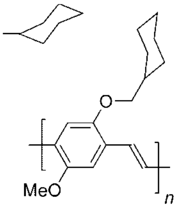

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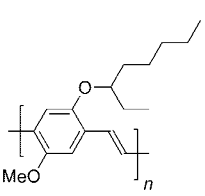

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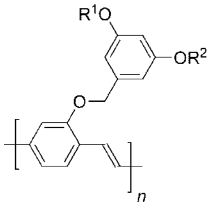
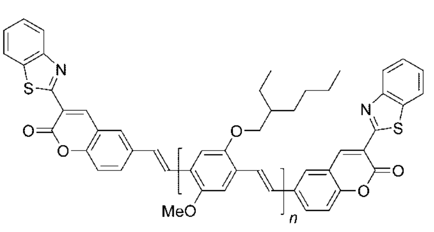


43 R^1 = 2-ethylhexyl, R^2 = 3,7-dimethyloctyl

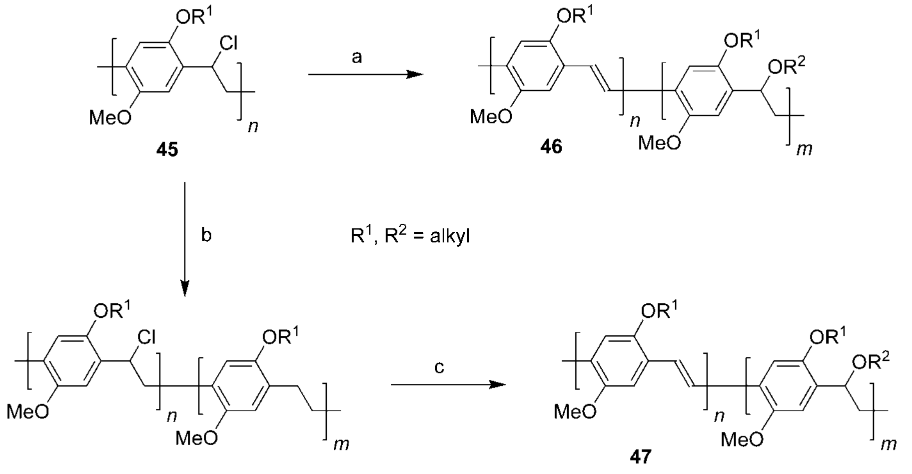


44

of 1% were obtained from devices using calcium cathodes, but the efficiency of devices using aluminum was over 2 orders of magnitude lower.[235,305] Insertion of a thin hole-blocking layer of a poly(methyl methacrylate) (PMMA) LB film is described as giving up to a 4-fold increase in quantum efficiency with aluminum cathodes,[306−308] while insertion of a barium(II) fluoride layer between the MEH-PPV and the aluminum cathode has been found to boost the efficiency by 2 orders of magnitude.[309] A combination of ultrathin layers of electron transporting aluminum tris(8-hydroxyquinolate) (Alq_3) and lithium fluoride gives even better results (2.5% efficiency).[310] Composite electrodes containing a thin layer of calcium or barium between the polymer and aluminum also enhance device performance,[311,312] as does the introduction of an electron-injecting layer.[176,186,187,287,289,313−322] The use of polyaniline (PANI) or composite ITO/PANI or PANI−camphorsulfonic acid (CSA) electrodes is reported to reduce the driving voltage and to increase the quantum efficiency and lifetimes of devices based on MEH-PPV as emissive layer by over 30%.[323−331] Similar effects have also been reported from use of ITO coated with a PEDOT:PSS[332] or polythiophene[311] layer, or with self-assembled layers of a silazane[333] or polyelectrolyte multilayers[334] as anode. MacDiarmid and co-workers have shown that introduction of ionic dopants by treatment of the MEH-PPV layer with iodine leads to a drop in turn-on voltage and a 10-fold increase in efficiency.[335−339] The use of a doped emeraldine base polyaniline (EB-PANi)[337−339] or poly(styrene sulfonic acid)[340] layer has similar effects. Devices have been constructed using doped silicon as anode, thus opening the possibility of integrating polymer LEDs with silicon-chip technology.[168,341−343] A thin layer of silicon dioxide on the surface of the anode has been found necessary for light emission. Other anodes such as polypyrrole[344] or diamond-coated silicon[345] have also been tried but did not show any improvement of efficiency. Flexible devices have been produced with MEH-PPV as emissive layer in which instead of ITO-coated glass a flexible anode such as a poly(ethylene terephthalate) film coated with polyaniline is used.[237,346,347] Similarly, an "inverted" polymer LED with layers of a transparent polyaniline electrode and MEH-PPV wrapped around a cylindrical metal cathode has been constructed.[348] Gel-processing of a blend of MEH-PPV in polyethylene leads to oriented films which show anisotropies of 60:1 in their PL emission spectra, with the preferred direction of emission being parallel to the draw axis.[349,350] Such oriented emission might be useful as backlighting for a liquid-crystal display. Devices have also been constructed using LB films of MEH-PPV but were of low efficiency.[351] The use of a polymeric electron-transport layer was found to boost the efficiency by 1 order of magnitude.[352]

Studies on MEH-PPV (**20**) have shown that the processing conditions can have major effects on its PL and EL properties. Schwartz and co-workers have shown that in some solvents MEH-PPV **20** forms aggregates in solution which remain in the film after deposition, leading to a drop in PL efficiency and the appearance of a second band at 635 nm in the PL spectrum, producing an overall red-shift in the emission.[353,354] Conversely, the films with high aggregate content show higher EL efficiency due to better interchain charge transport.[354] They were able to exploit this to make devices in which a layer of polymer **20** deposited from THF, in which aggregation is low, was sandwiched between two layers deposited from chlorobenzene, in which **20** aggregates strongly. The stronger interchain interactions in the aggregated layers improved the EL efficiency by enhancing the transport of charges to the emissive middle layer.[355] Yang has shown that this aggregation can also be controlled by changing the concentration or varying the spinning rate at which the solutions are spin-coated.[356,357] Higher concentrations or lower spinning rates lead to more aggregation and subsequently higher EL efficiency.[356] A similar red-shift in the PL and EL of polymer **20** is also observed if the film is annealed before deposition of an aluminum cathode.[358] Annealing at high temperature after deposition on the other hand causes complete suppression of the aggregate emission band. A systematic study of the effects of heat treating films of polymer **20** has shown that the appearance and disappearance of supramolecular order is temperature-dependent.[359] The aggregate emission band is also reported to decrease in intensity at higher electric fields.[360] Emission from aggregates has also been reduced and the EL efficiency enhanced by heating MEH-PPV with AIBN to produce a

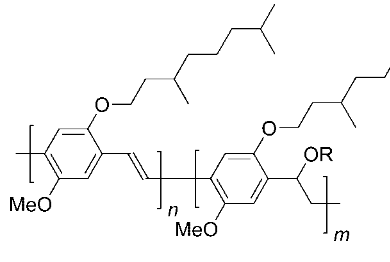
Scheme 9. Modification of Conjugation Length in RO-PPVs Made by the Chloro Precursor Route: (a) ROH, reflux; (b) Bu_3SnH; (c) 165 °C, vacuum



nanoporous film.[361] Cross-linking has also been used to enhance the EL efficiency of MEH-PPV. MEH-PPV containing 3% cross-links is still soluble but shows red-shifted emission with improved EL efficiency, presumably due to enhanced chain aggregation.[362] The copolymer **38** by contrast loses PL and EL efficiency upon photoinduced cross-linking, but blending **38** with MEH-PPV and then cross-linking leads to emission with enhanced efficiency.[363]

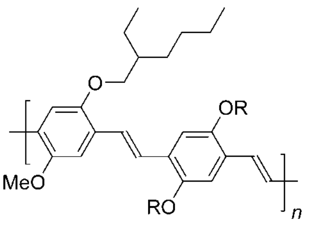
The size of the substituents can have a dramatic effect on the luminescence efficiency. Efficiencies of 2.1% have been reported by industrial groups for single-layer devices using RO-PPVs.[364] Studies on RO-PPVs **39** with different sized *n*-alkyl chains have shown that, after initially rising with increasing length of the alkoxy group, EL efficiency passes through a maximum and decreases again with even longer side-chains.[234] These effects are presumably due to the bulkier groups reducing nonradiative decay pathways due to better exciton confinement. Similarly, the solid-state PL[365] and EL[366] efficiency of MEH-PPV (**20**) is increased by copolymerization with other monomers bearing bulkier alkoxy side-chains; for example, polymer **40** with a bulkier side-chain than MEH-PPV shows six times greater EL efficiency.[367] The structurally very similar polymer **41** not only shows a higher luminance efficiency but also produces devices that fail at higher potential. Additionally, its luminance maximum ($\lambda_{max} = 567$ nm) is also slightly blue-shifted with respect to MEH-PPV.[368] A similar blue-shift with increase in EL efficiency is observed in copolymers with polyhedral oligomeric silsesquioxane (POSS) units on the side-chains.[369,370] Blending these with MEH-PPV red-shifts the EL and further increases its efficiency.[370] By contrast, polymer **42** ($\lambda_{max} = 566$, 602 nm) exhibits lower PL and EL efficiency than MEH-PPV, as does polymer **39a** with two 2-ethylhexyl substituents ($\lambda_{max} = 583$, 626 nm).[371] The very large substituents in the bis-cholestanyloxy-substituted polymer **39b**,[279,371,372] moreover, seem to overpower and "dilute" the semiconducting properties of the conjugated polymer, thus reducing the efficiency, though the solid-state PL efficiency is very high (53%). They also cause a blue-shift in the emission maximum to 563 nm.[371] PPVs **43** bearing first-generation dendrons produce green-yellow EL ($\lambda_{max} = 540-546$ nm) with moderate efficiency (0.37−0.40 cd/A).[373,374] The emission from the corresponding polymers with second generation dendrons is slightly blue-shifted ($\lambda_{max} = 531-535$ nm) and less efficient (0.13−0.22 cd/A). Blue-shifted emission ($\lambda_{max} = 560$ nm) has also been obtained from MEH-PPV **44** end-capped with blue emitting coumarin units;[278,375] no emission is observed from the coumarins, suggesting the effect is due to disruption of the chain packing. The EL efficiency of the polymer $OC_{10}C_{10}$-PPV (**39c**) with two bulky branched alkyl substituents is lower than that for the polymer OC_1C_{10}-PPV (**35a**) with only one such substituent, because the better hole mobility of **39c** causes greater quenching of the fluorescence to occur at the cathode.[376] This may also explain the similar difference in efficiencies between **20** and **39a**. The efficiency of LEDs using LB films of **35b** with hexyloxy chains[377] is higher than that from devices using the analogous polymer **35c** using octadecloxy side-chains[378] due to the greater order in the films of the former. As with MEH-PPV (**20**), efficiencies of LEDs using other RO-PPVs have been increased by the use of an electron-transporting/hole-blocking layer,[379−382] while use of a thin layer of sulfonated polyaniline as a hole-transport layer produces a decrease in driving voltage with an increase in luminance.[383]

The conjugation length of RO-PPVs made by the chloro precursor route may be controlled by treatment of the precursor **45** with methanol (Scheme 9). These displace a proportion of the chloro substituents to give α-methoxy substituents, which are resistant to thermal elimination. Thermal conversion of these modified polymers thus gives copolymers **46** with a mixture of conjugated and nonconjugated units. The luminance maximum for the copolymers varies from 590 nm ($m < 15\%$) to 560 nm ($m > 30\%$). Copolymers **46** with 10−20% of nonconjugated segments have been found to have increased EL efficiencies compared with fully conjugated RO-PPVs.[241] The OC_1C_{10}-PPV copolymer **46a**, in which the chloroprecursor was treated with 2-dimethylaminoethanol, shows much higher efficiencies than the α-methoxy copolymer **46b**, with indium (1.1% vs 0.16%) or gold (0.25% vs 0.01%) cathodes after an initial "burn-in" period.[384,385]

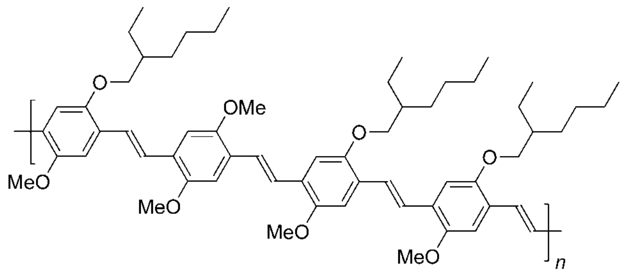


46a R = Me
46b R = $C_2H_4NMe_2$
46c R = $C_2H_4NMe_3^+$

Quaternization of the amines with methyl iodide to give **46c** raises the efficiencies for indium and gold cathodes to values (1.3% and 1.1%, respectively) which are equal to that of a device with a calcium cathode (1.2%).[384,385] Photoprocessed, micropatterned LEDs have been constructed using copolymer **46c** with 5% nonconjugated segments.[386] The photoprocessing was found to increase the effective conjugation length concomitant with a drop in PL and EL quantum efficiencies. An alternative method for controlling the conjugation length of ROPPVs developed by Burn is to treat the chloro precursor **45** with tributyltinhydride to replace some of the chloro substituents with hydrogens (Scheme 9).[387] The proportion of saturated ethanediyl units in the resulting copolymers **47** after thermal elimination of the remaining chloro substituents corresponds closely to the number of equivalents of the hydride used. In a reverse procedure, treatment of the dihexyloxypolymer **39d** with *N*-halosuccinimdes to reintroduce a proportion (up to 30%) of α-halogens has also been shown to blue-shift the PL by interrupting conjugation and to increase fluorescence efficiency, as the bulky halogen atoms reduce interchain interactions.[388]



48a R = Me
48b R = C_8H_{17}



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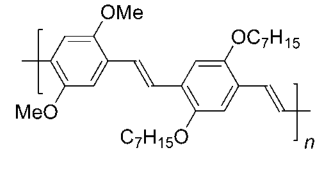
Other routes have also been used to make RO-PPVs. Hörhold and co-workers have prepared MEH-PPV (**20**) by the Horner coupling of a bis-aldehyde and a bis-phosphonate.[389−391] The PL and EL properties of this material are reported to match those of the standard material from the Gilch route, but the solubility is better due to its lower molar mass. This method can also be used to make alternating copolymers.[390,391] The copolymers **48a** and **49** with dimethoxy-phenylene units show similar properties to those of MEH-PPV **20**, but the copolymer **48b** with dioctyloxy-phenylene moieties shows much more long wavelength emission, possibly due to greater aggregation.[391]



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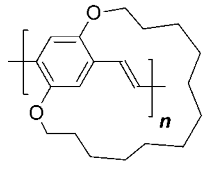

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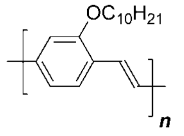

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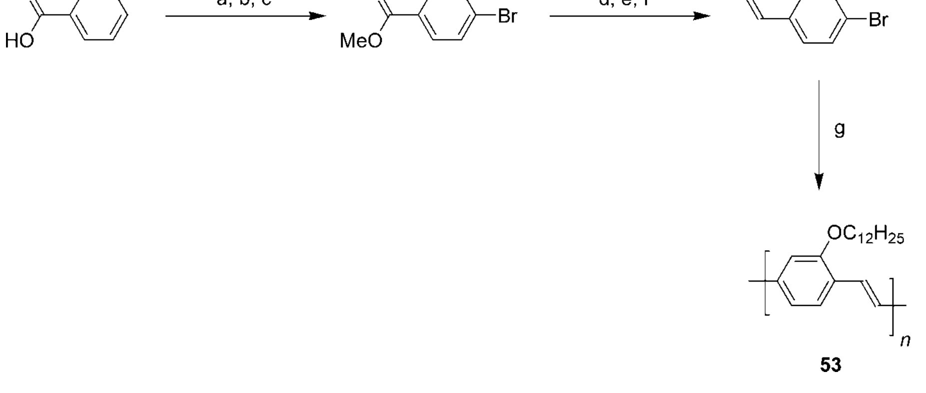
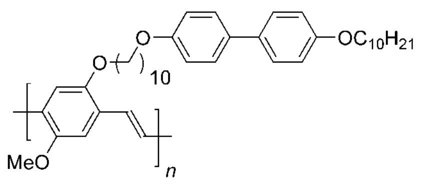
The copolymer **50** shows orange (λ_{max} = 585 nm) EL emission in forward, reverse, and alternating current (ac) modes.[392] Dimethoxy-PPV (**19**) has been made by vapor deposition polymerization of a bischloromethyl monomer, and thermal elimination of the resulting chloro precursor polymer.[393] Low molecular mass polymers can be prepared by Stille coupling of dialkoxyaryl dihalides or ditriflates with bis-stannylethene.[394,395] The cyclophane-substituted PPV **51** prepared by Stille coupling shows yellow-green EL (λ_{max} = 563 nm).[396] Cross metathesis of 2,5-dialkoxy-1,4-divinylbenzenes produces oligomeric **39e−g**.[397−399] Cathodic electropolymerization of 2,5-bis(dibromomethyl)decyloxybenzene has been used to make the decyloxy-PPV **52**.[400] Lahti and co-workers have used Heck coupling of a 4-vinylbromobenzene AB monomer to make regioregular (head-to-tail) poly(2-dodecyloxyphenylene vinylene) (**53**) (Scheme 10), which shows strong yellow PL and EL (λ_{max} = 542 and 540 nm, respectively).[401] So far there has been no comparative study on regiorandom vs regioregular dodecyloxy-PPV **53**, but it is known that regioregularity in other conjugated polymers, e.g. poly(3-alkylthiophene)s (see section 3.6 below), can lead to better electrical and optical properties.

Scheme 10. Synthesis of Regioregular Poly(2-dodecyloxyphenylene vinylene) (53): (a) Br_2, HOAc; (b) MeOH, H^+; (c) $C_{12}H_{25}Br$, K_2CO_3; (d) $LiAlH_4$; (e) PCC; (f) Ph_3PCH_2Br, BuLi; (g) $Pd(OAc)_2$, P(*o*-tolyl)$_3$, DMF





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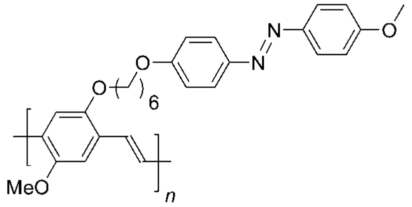

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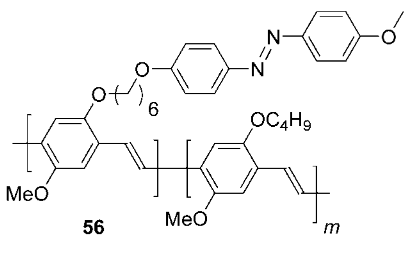

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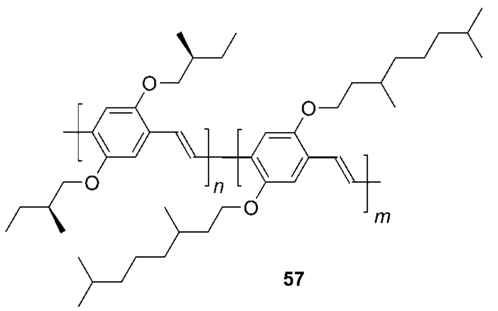

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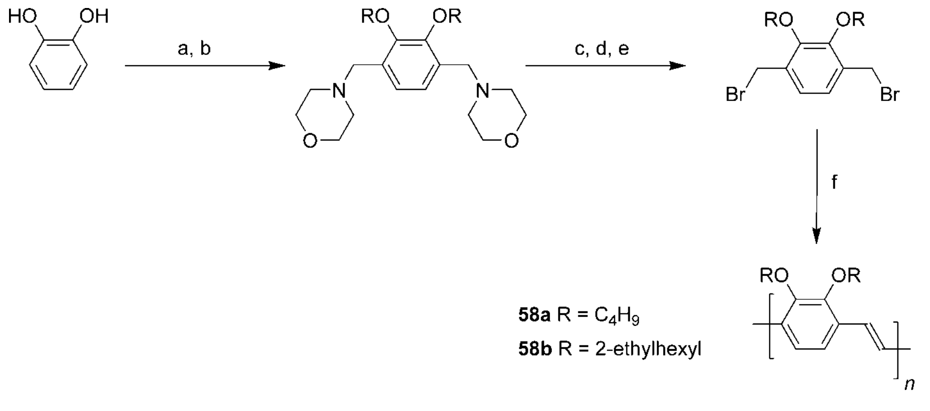
Yoshino and co-workers[402] have reported that poly[(2,5-dinonyloxy-1,4-phenylene) vinylene] (**39h**) forms a nematic liquid crystalline phase upon melting. Cooling of the melted material to room temperature gives an oriented film with a lower energy gap (2.08 eV, 597 nm) than for an unoriented film (2.21 eV, 562 nm) formed by spin-casting of a chloroform solution of the polymer. Rubbing of a film of this material is reported to induce molecular orientation, giving rise to polarized electroluminescence.[403] Attempts have also been made with varying success to induce liquid-crystallinity (and thus potentially polarized emission) in RO-PPVs by attaching side-chains bearing mesogenic groups. Thus, the polymer **54** forms a smectic liquid crystalline phase and shows green-yellow PL (λ_{max} = 550 nm).[404] The EL is bias-dependent with broad yellow (λ_{max} = 600 nm) emission in forward bias but blue (λ_{max} = 400 nm) emission from the mesogen in reverse bias. A similar liquid crystalline polymer **39i** made by Heck coupling[405] shows only weak EL (λ_{max} = *ca.* 560 nm) and unpolarized PL.[406] The polymer **55** and copolymer **56** with azobenzene mesogens in the side-chains have been reported to show yellow-green PL (λ_{max} = 550 nm), but there is no published data on liquid crystalline properties or polarized emission.[407,408] Introduction of chiral substituents can lead to circularly polarized luminescence. Meijer and co-workers have produced circularly polarized EL from devices using the copolymer **57**.[409] The best results were obtained for a copolymer with an *m*:*n* ratio of 8:1.

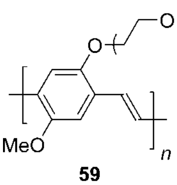
Holmes and co-workers have developed synthetic routes toward 2,3-dialkoxy-substituted PPVs **58**.[410−416] Their more recent improved route[412,415] is shown in Scheme 11. By comparison with the classical 2,5-substituted PPV derivatives, this substitution pattern results in a notable blue-shift in the emission maximum accompanied by an increase in the solid-state PL efficiency. As a result, the dibutoxy-PPV **58a** shows green emission (λ_{max} = 530 nm) with a PL efficiency of 40%[410,416,417] (*cf.* 15−20% for MEH-PPV[235,418]). The efficiencies of single-layer devices (λ_{max} = 520 nm) using **58a** were up to six times higher than those for similar devices using PPV.[417,419] Efficiencies were even higher for the double-layer devices ITO/PPV/**58a**/Ca. The EL efficiency can also be boosted up to 200 times by use of electron-transporting layers.[420] Increasing the steric constraints by using branched chains as in **58b** leads to a further blue-shift in the emission (λ_{max} = 513 nm), accompanied by a drop in PL efficiency to 28%.[413−415] LEDs using polymer **58b** (λ_{max} = 505 nm) show only slightly higher efficiency than PPV devices.[413−415]

Polymers have been prepared with one methoxy tris(ethoxy) (**59**) (λ_{max} = 601 nm) or two methoxy mono-, bis-, and trisethoxy- side-chains (**60**) [λ_{max} = 640 nm].[421−425] The disubstituted polymers with short side-chains (**60a,b**) are best made by the Wessling route,[425] but the Gilch route has been found to be superior for those with longer side-chains—**59** and **60c**.[422−425] These polymers show very low EL efficiency in LEDs due to their low (<10%) solid-state PL efficiencies, but their good ion-transporting properties make them suitable materials for use in light-emitting electrochemical cells (LECs—see section 6.3 below). The PL efficiencies can be improved by copolymerization with monomer units having higher PL efficiencies, e.g. phenylenes with alkylsilyl side-chains (see section 2.3 below). Polymers **61**[411] and **62**[426] with crown ether units can be prepared by the same route as

Scheme 11. Synthesis of Poly(2,3-alkoxy-1,4-phenylene vinylene)s: (a) HCHO, Morpholine; (b) RBr, K_2CO_3; (c) Ac_2O, NaOAc; (d) K_2CO_3, MeOH−THF−H_2O; (e) CBr_4, PPh_3, THF; (f) KO^{t}Bu, THF



for 2,3-dialkoxy-PPVs above (Scheme 11), by using a suitable oligo(ethylene oxide) bis-tosylate as alkylating agent. They show green-yellow emission ($\lambda_{max} = 553$ and 534 nm, respectively), but their PL efficiencies are low. The solubility of polymer **61** is too low to be useful in fabrication of an LED, but devices have been made with polymer **62** using an Alq_3 electron-transport layer with low (0.04%) efficiency.[426] The luminescence efficiency of polymer **61** has been improved by copolymerization with alkylsilyl- (see section 2.3 below) or 2,3-dialkyloxyphenylenes.[411,427,428] Thus, the copolymers **63** show solid-state PL efficiencies of 38% (**63a**) and 52% (**63b**), respectively (*cf.* 9% for homopolymer **61**). As might be expected given their good ion-transporting properties, these copolymers give better performance in LECs (see section 6.3 below) than in LEDs.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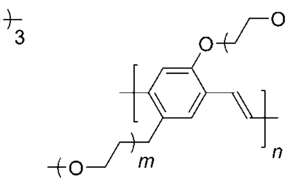
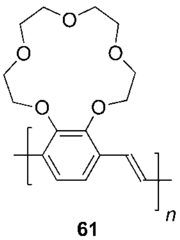

60a $m = 1$
60b $m = 2$
60c $m = 3$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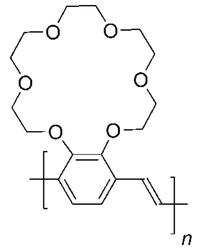
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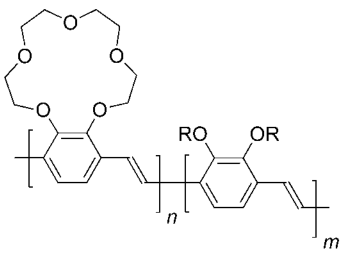
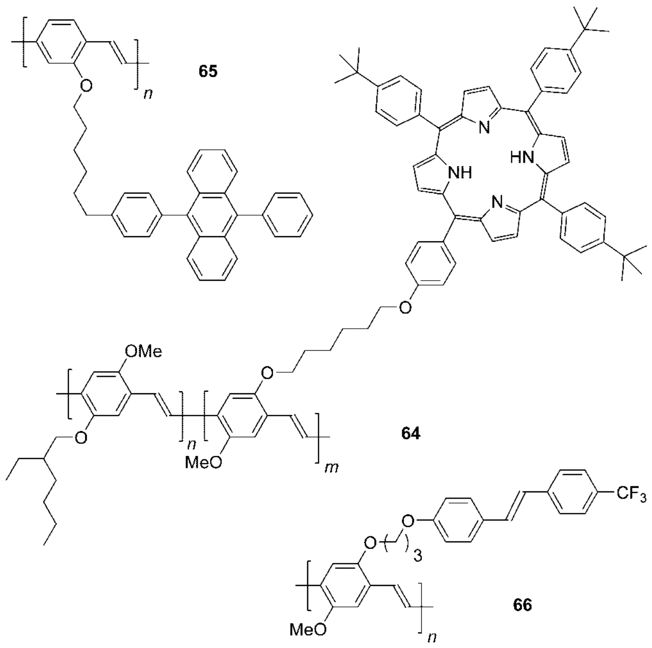

63a R = C_4H_9
63b R = C_8H_{17}

As shown above, ROPPVs can be efficient green, yellow, or red-orange emitting materials, but as yet, no pure red emitting ROPPV has been reported. The problem with most red fluorescent polymers is that there is considerable energy emission in the far-infrared region. Such materials are therefore very energy-inefficient in the emission of red visible light. This problem is nicely circumvented with red electrophosphorescent emitters. An attempt has been made to produce a pure red emitting material by attaching red emitting porphyrin units in the side-chains. Porphyrins are interesting candidates for red light emission, as they exhibit good stability toward light, heat, and oxygen, despite their high tendency toward $\pi-\pi$ aggregate formation with concomitant quenching of fluorescence. Copolymers of type **64** with 5 mol % and 8 mol % porphyrin loading made by the Gilch route showed emission predominantly from the porphyrin units at $\lambda_{max} = 659$ and 725 nm, respectively. However, the PL efficiencies for both copolymers were under 4%, possibly due to aggregation, making them unsuitable for use in efficient LEDs.[429] Attachment of ruthenium(II) bipyridyl complexes onto the side-chains of a PPV leads to emission from the substituents with a broad EL spectrum (500−800 nm).[430] Broad (400−700 nm) emission has also been obtained from the polymer **65** with a pendant diphenylanthracene chromophore due to emission occurring from both the substituent and the main-chain, making this a candidate for a white-light-emitting LED.[261,431] By contrast, no emission is seen from the side-chain in polymer **66**, with energy transfer occurring from the stilbene to the main-chain to produce only yellow EL.[432]

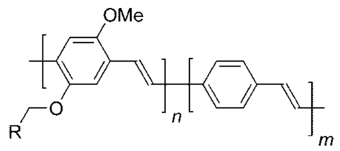

65

64

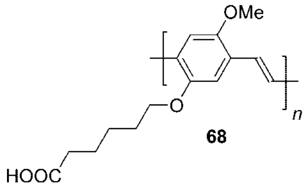
66

Using ω-substituted alkyl side-chains allows one to tune the emission color by other means. Davidov and coworkers[433] have made copolymers **67a** and **67b** with polar side-chains by the Wessling route. The emission maximum of copolymer **67a** can be tuned between 520 and 580 nm by varying the n:m ratio. Self-assembled multilayer films of **67a** with sulfonated polystyrene and poly(ethylene imine)[203,433] show a blue-shift in emission compared with spin-cast films of **67a**, with PL maxima at 540 nm (*cf.* 580 nm) for the homopolymer (n:m = 1:0) and 500 nm (*cf.* 535 nm) for the 20% copolymer (n:m = 2:8). The emission from the acidic polymer **67b** is pH dependent and can be tuned between $\lambda_{max} = 550$ nm (pH 2) and $\lambda_{max} = 520$ nm (pH 12).[433] The very similar polymer **68** shows orange emission ($\lambda_{max} = 580$ nm), and its sodium salt is water soluble.[434] Water solubility can also be obtained by attaching quaternary ammonium salts as in the copolymers **69a**[435] or **69b**,[436] both of which show green PL ($\lambda_{max} = 510$ and 519 nm, respectively) in aqueous solution. Charge-transporting groups can also be attached *via* alkyl tethers. The hole-transporting triarylamine groups in **70** enhance its EL efficiency markedly over MEH-PPV, presumably by making hole injection more favorable.[437] The effects of electron-transporting groups attached to PAVs *via* alkyl tethers are discussed in section 2.5 below.

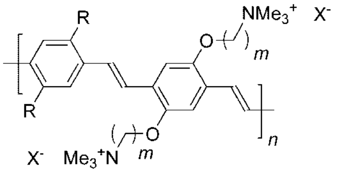
Aryloxy substituents can also be used as solubilizing groups.[438] The phenoxy- and diphenoxy-PPVs **71** and **72a** show solid-state PL maxima at $\lambda_{max} = 522$ and 589 nm, respectively. The red-shift between the solution and solid-state emission maxima is much more pronounced for the diaryloxylated **72a** ($\Delta\lambda_{max} = 68$ nm) than for the monosubstituted **71** ($\Delta\lambda_{max} = 27$ nm). Alkyl substitution of the lateral phenyl rings as in structure **72b** produces a slight blue-shift in emission ($\lambda_{max} = 577$ nm), while the larger biphenyl



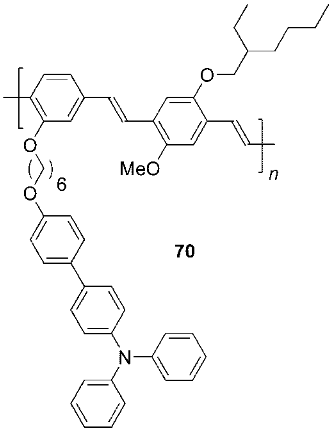
67a R = CH_2OH
67b R = COOH



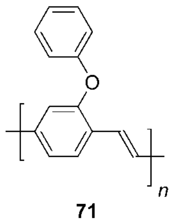
68



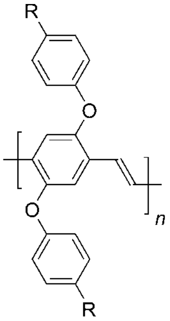
69a R = H, *m* = 2, X = Tf^-
69b R = $O(CH_2CH_2)_2H$, *m* = 4, X = I^-



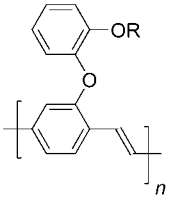
70



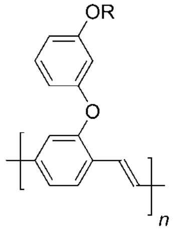
71



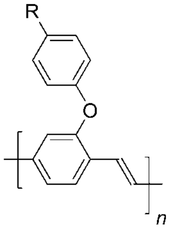
72a R = H
72b R = ^{t}Bu
72c R = Ph



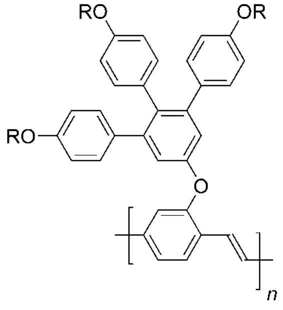
73 R = 3,7-dimethyloctyl



74 R = 3,7-dimethyloctyl



75a R = 3,7-dimethyloctyloxy
75b R = $SiMe_2C_{12}H_{25}$

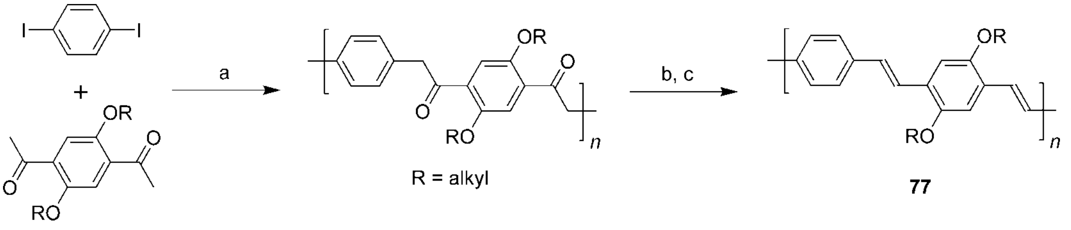


76 R = 2-ethylhexyl

groups in **72c** cause a significant red-shift (λ_{max} = 626 nm), probably due to $\pi-\pi$ interactions. The position of the substituents also has a marked effect on the emission color. Thus, polymers **73**−**75a** with *o*-, *m*-, and *p*-substituted phenoxy side-chains display EL maxima at 541, 560, and 568 nm, respectively.[439,440] This red-shift can be explained by a reduction in steric interactions between the alkoxy group and the main chain leading to a more planar chain conformation and thus an increase in conjugation. However, the *m*-substituted **74** possessed the highest PL efficiency (54% *cf.* 40−43% for **73** and **75a**). Replacing the alkoxy with a silyl group in **75b** produces a slight blue-shift in the emission maximum to 540 nm.[441] The polymer **76** shows blue-green PL (λ_{max} = 476 nm), due to the very bulky dendron-like side-chains causing twisting of the polymer backbone.[442]

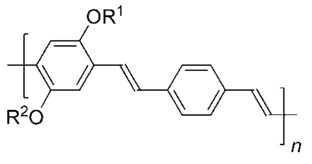
Alternating RO-PPV/PPV copolymers **77** have been made by several research groups by Wittig or Horner coupling of a terephthaldehyde with a bis-phosphonium salt or bis-phosphonate.[443−450] These polymers typically show green emission (λ_{max} = 530−550 nm), but bulky dendritic side-chains induce a marked blue-shift to produce blue-green PL (λ_{max} = 480 and 471 nm for the G1 **77b** and G2-dendronized **77c** polymers, respectively).[451] This is presumably a result of twisting in the polymer backbone as a result of the steric bulk of the dendritic substituent. It has been shown that high polydispersity in such polymers lowers their EL efficiency.[450] End-capping with styryl groups produces a polymer which can be thermally cross-linked to permit solution processing of other layers on top of it.[452] The Horner route is reported to give material with better resolved spectra.[447] An alternative route to such copolymers is the Heck coupling of dihalobenzenes with divinylbenzenes.[453,454] Heck coupling of a dibromodistyrylbenzene with divinylbenzene produces a green emitting polymer **78a** (λ_{max} = 548 nm) with alkoxy groups on every fourth repeat unit.[455] Polymers with *cis*-double bonds have recently been prepared by a Suzuki-coupling method, but their optical properties have not been reported.[456] The polymers **77b**−**c** with Fréchet-type dendritic side-chains show liquid crystalline behavior[454] giving rise to polarized PL.[457] Polarized emission has also been obtained by deposi-

Scheme 12. Synthesis of RO-PPV-PPV Copolymers 77 via Polyketones: (a) $Pd_2(dba)_3$ or $Pd(OAc)_2$, PR_3, NaO^tBu, THF; (b) $LiAlH_4$; (c) H^+



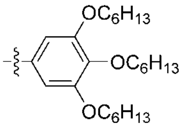
R = alkyl

77

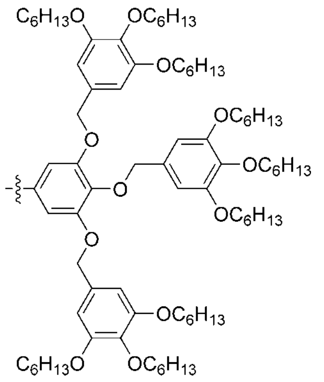


77a R^1, R^2 = alkyl
77d R^1, R^2 = $C_{12}H_{25}$
77e R^1 = Me, R^2 = 2-ethylhexyl
77f R^1, R^2 = C_8H_{17}

77b R^1, R^2 =

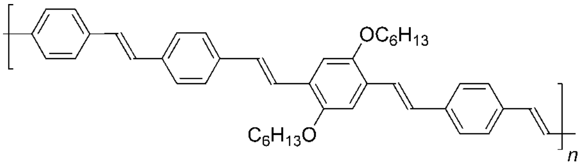


77c R^1, R^2 =

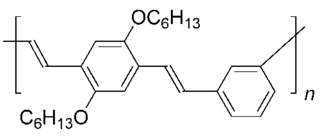


tion of polymers **77b** and **77d** on rubbing-aligned poly(tetrafluoroethylene) substrates.[458] The PL efficiency of polymer **77b** with first generation dendritic side-chains is higher than that of **77a** due to the bulkier side-chains suppressing aggregation of the polymer chains.[459] A novel route to copolymers of type **77a** developed by Wu and co-workers uses the palladium-catalyzed coupling of diiodobenzene with diacetylbenzenes to give polyketones which are then converted to the conjugated polymers by reduction and subsequent dehydration (Scheme 12).[460]

The Wittig and Horner routes have also been used to make copolymers **79**[234,445,446,448,461−469] and **80**[448,470,471] incorporating *meta-* and *ortho*-linked phenylene units. In the case of the butyloxy-copolymer **79a**,[464] Wittig coupling was found to give a product with 65% *cis*-double bonds, which could be isomerized with iodine to give 91% *trans*-linkages, while the Horner route gave a material with 88% *trans*-bonds. The PL emission spectra and efficiencies of these materials were almost identical, but the Wittig-prepared material showed higher PL intensity and a slightly broader EL spectrum. By contrast, the hexyloxy polymer **79b** made by the Horner route displayed red-shifted (λ_{max} = 530 nm cf. 507 nm) solid-state PL compared with the corresponding product from the Wittig process.[471] Iodine residues lower EL efficiency in the isomerized Wittig-made material. Comparison of the octyloxy-copolymer **77c** made by Wittig and Horner routes under a variety of conditions revealed that the Horner method consistently produced a polymer with higher molecular weight and a higher proportion of *trans*-bonds.[461,462,466,472] The *meta-* and *ortho*-phenylene units in such polymers cause a blue-shift in the emission, the former by interrupting the conjugation, and the latter because of steric interactions between the adjacent substituents twisting the polymer chain. For example, the MEH-PPV-*alt*-PPV copolymers **79d** and **80a** show PL maxima at 550, 490, and 500 nm, respectively.[448] The octyloxy-copolymer **79c** has been used to make efficient (up to 1% efficiency) green (λ_{max} = 504 nm) LEDs.[444−446,473,474] The Sumitomo group has made copolymers **81** containing varying proportions of *para-* and *meta*-linkages.[444−446] The highest efficiency was achieved using copolymers with 25% of *meta*-linkages ($m = n$). Regular polymers **82** with the *meta*-linkages in every fourth unit have been made and produce yellow-orange EL (λ_{max} = 566 nm).[475] Incorporation of 2,3-dialkoxybenzene units in the copolymer **83**, made by the Horner route, produces a marked blue-shift in the emission so that blue EL (λ_{max} = 456 nm) is obtained.[476] The alkoxy groups can also be on the *meta*-phenylenes as in **84a** (λ_{max} = 489 nm) or **84b** (λ_{max} = 509, 543 nm).[477] Polymers such as **85** with two side-chains on the *meta*-phenylenes show blue-green EL (λ_{max} = 496, 520 nm).[468,478−480] Polymers **85** with alternating *meta*-linkages have been made by the Wittig method and show blue EL (λ_{max} = 463, 475 nm) with a marked increase in efficiency after the *cis*-bonds are isomerized to *trans*.



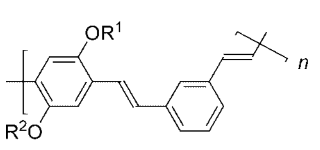
78a



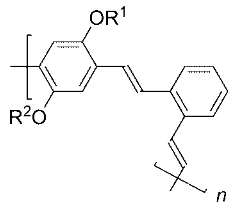
78b

Heck coupling has also been used to make alternating copolymers with dialkoxyphenylene vinylene and other phenylene vinylene units. Swager and co-workers have made the triptycene-containing copolymers **87** by coupling of diiodobenzenes with divinyltriptycenes.[481] As expected, the fluorescence of the 2,3-dialkoxy-copolymer **87a** (λ_{max} = 484 nm) is blue-shifted compared with that of the 2,5-dialkoxy copolymer **87b** (λ_{max} = 512 nm). The copolymer **88** with *ortho*-phenylene units has been made by Heck coupling of 1,2-didodecyloxy-4,5-diiodobenzene with 2,5-didodecyloxy-1,4-divinylbenzene.[470] The substituents on the *ortho*-phenylene units cause a red-shift in the emission (λ_{max} = 542 nm) and a halving of the solid-state PL efficiency (39%), compared with the copolymer **80b** made by the Horner route.

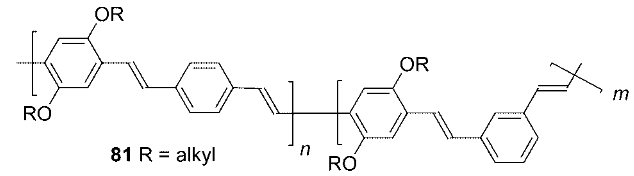
There have been only a few reports on PPV derivatives bearing thioalkyl substituents. Depending on the oxidation state, sulfur can serve either as an electron donating or accepting group, which might allow fine-tuning of the optical properties. Shim and co-workers have prepared the polymers **89**−**90** by the Wessling route,[482,483] while a Chinese group have prepared **89** and **91** by Heck coupling.[484] The emission of the MEH-PPV analogue **89** is blue-shifted compared with that of MEH-PPV (**20**) so that the EL is green (λ_{max} = 530 nm)[482] or yellow (λ_{max} = 556 nm).[485] The difference in reported emission color suggests that the Heck method produces more conjugated material. This shift may be explained by the poorer electron donating capability of the thioalkyl as compared to the alkoxy group. The alkylthio polymers **90a** and **91** also show green EL (λ_{max} = 525 and 545 nm, respectively), while the emission of the hexylsulfinyl polymer **90b** displays a slight bathochromic shift to yellow (λ_{max} = 550 nm), owing to the internal donor−acceptor system formed by the methoxy-sulfinyl substituents.[483] The



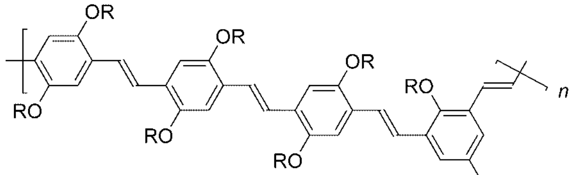
79 R^1, R^2 = alkyl
79a R^1, R^2 = C_4H_9
79b R^1, R^2 = C_6H_{13}
79c R^1, R^2 = C_8H_{17}
79d R^1 = 2-ethylhexyl, R^2 = Me



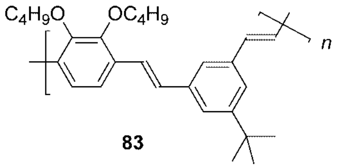
80 R^1, R^2 = alkyl
80a R^1 = 2-ethylhexyl, R^2 = Me
80b R^1, R^2 = $C_{12}H_{25}$



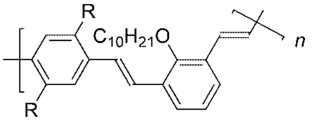
81 R = alkyl



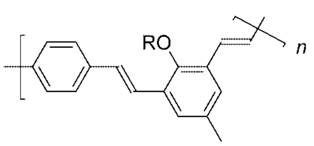
82 R = alkyl



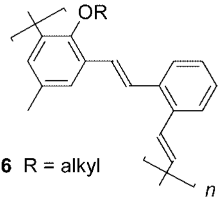
83



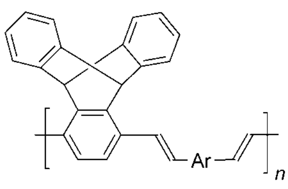
84a R = H
84b R = $OC_{10}H_{21}$



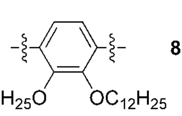
85 R = alkyl



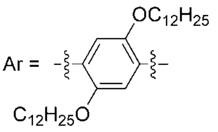
86 R = alkyl

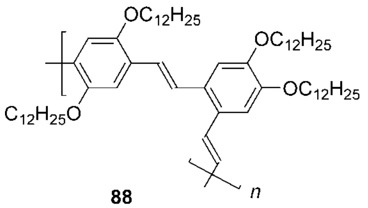


87a Ar =

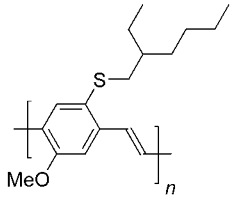


87b Ar =

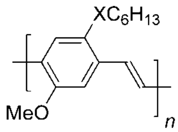




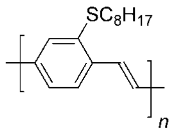
88



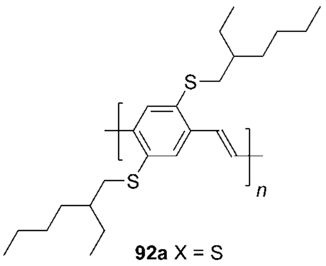
89



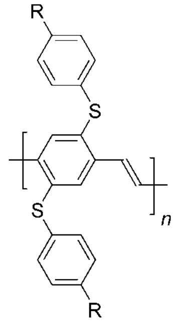
90a X = S
90b X = SO



91



92a X = S
92b X = SO



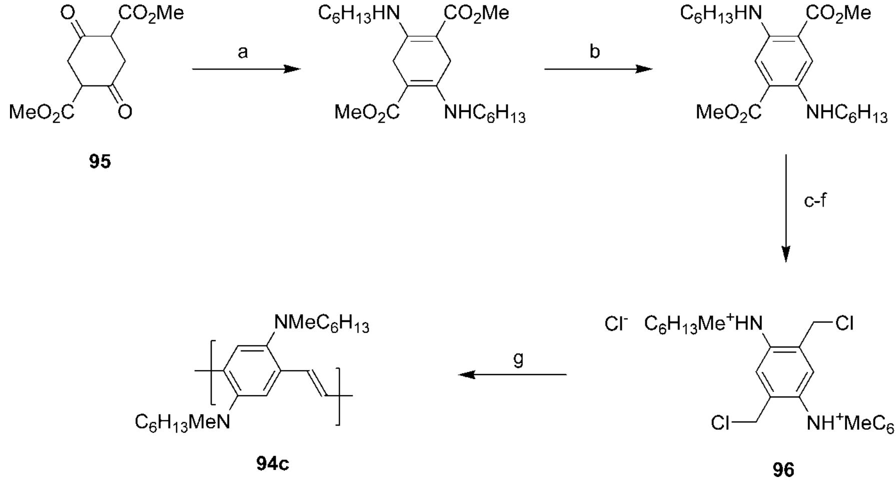
93a R = H
93b R = ${}^tBu$

efficiency of devices using thio-substituted polymer **89** made by either route is much higher than that of a corresponding MEH-PPV device.[482,484] The bis-thioalkyl **92a** and bis-sulfinyl **92b** polymers are reported to have been made by the Gilch method.[485] The Scherf group has prepared the thiophenoxy polymers **93a,b** by the Gilch route.[438] Their solid-state emissions (λ_{max} = 582 and 534 nm) are slightly blue-shifted with respect to those of their aryloxy analogues **78a** (λ_{max} = 589 nm) and **78b** (λ_{max} = 577 nm), though their solution spectra are almost identical, indicating that sulfur produces weaker interchain interactions than oxygen.

Alkylamino-substituted PPVs have received very little attention. Stenger-Smith and co-workers have prepared bis(*N*-methyl-*N*-alkylamino)-PPVs **94a–c** by the Gilch route.[486–488] The solubility of polymers **94a,b** with propyl and butyl substituents is too low to make films suitable for use in LEDs, but the hexylamino polymer **94c** exhibits good solubility in solvents such as xylene.[488] The synthesis of **94c** (Scheme 13) starts from a cyclohexanedione **95**. Enamine formation with *n*-hexylamine followed by aromatization with bromine leads to the monomeric dihydrochloride **96**. Under Gilch dehydrohalogenation conditions, the monomer is not only polymerized but also deprotonated to the free amine. LEDs using **94c** show green emission (λ_{max} = 564 nm) with moderate (0.3%) efficiency. Recently, Schwartz and co-workers[489] have shown that though **94c** appears to be fully dissolved after stirring in xylene for 2 days, this is in fact a suspension of microparticles, and that heating or prolonged stirring at room temperature is required to obtain a true solution. Films cast from these solutions show smoother morphologies and better LED performance. Heating a solution of **94c** also leads to aggregation of the polymer chains, which consistently reduces device efficiency. In dilute solutions, partial protonation causes chain twisting and a blue-shift in emission, while, in concentrated solutions, protonation produces a red-shift.[490] Deposition from acidic solutions also produces a red-shift in the emission of the resulting films. These results illustrate how much has still to be learnt about the processes of polymer dissolutio, and how minor changes in processing can affect the performance of conjugated polymers in LEDs.

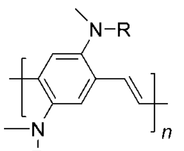
The copolymers **97**[491] and **98**[492] with bis(diphenylamino)phenylene units have respectively been made by Wittig and Horner polycondensation routes. They show yellow-green (λ_{max} = 556 nm) and blue-green EL (λ_{max} = 483 nm) respectively with low (<3 V) turn-on voltages.

Scheme 13. Synthesis of Bis(*N*-methyl-*N*-hexylamino)-PPV (94c): (a) $NH_2C_6H_{13}$, reflux; (b) Br_2, $CHCl_3$; (c) MeI, NaH, THF; (d) DIBAL; (e) dry HCl; (f) $SOCl_2$; (g) KO^{t}Bu, THF

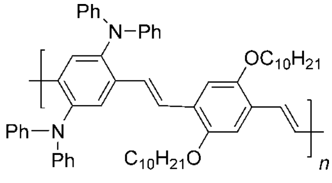


2.3. Alkyl- and Silyl-Substituted PPVs

Unlike the case of alkoxy substituents, introduction of alkyl substituents does not produce a red-shift in the emission compared with PPV. Thus, dimethyl-PPV **99**, which has been prepared both by the sulfinyl precursor route[139] and by vapor deposition polymerization,[393] shows green emission with an EL maximum at 507 nm and a secondary peak at 534 nm.[139] So far, only a few syntheses of poly(dialkylphenylene vinylene)s have been performed. A synthesis of diheptyl-PPV **100** by the Wessling route[493,494] was low-yielding both in preparation of the monomer and in the polymerization step due to the instability of the monomer caused by steric hindrance between the alkyl and sulfonium groups. The polymer did not dissolve well in organic solvents, possibly due to cross-linking.



94a R = C_3H_7
94b R = C_4H_9
94c R = C_6H_{13}



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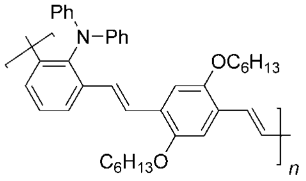
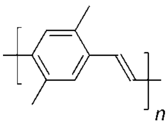


98

Gilch and chloro precursor route syntheses have proved more successful, but again there have been problems with the synthesis of the monomers. A group at Philips have prepared the methyl-dodecyl-PPV **101** by the chloroprecursor route (Scheme 14) but reported that the preparation of the bis-chloromethyl monomer **102** by chloromethylation of 4-dodecyltoluene proceeded in only 15% yield.[495] The polymerization of the bischloromethyl benzene derivative **102** with KO^{t}Bu proceeded in high yield to give the soluble α-chloro precursor polymer **103**, which could be converted into the conjugated polymer **101** by thermal elimination in refluxing cyclohexanone (155 °C). Addition of methanol to the thermal elimination mixture gave rise to stable, partially conjugated polymers **104**, in which the degree of nonconjugation could be controlled by the amount of methanol added. These polymers were found to be more soluble than fully conjugated **101** and showed a blue-shift in the electroluminesence peak emission from 532 to 516 nm. Increasing the nonconjugated ethylene linkages from 5% to 45% raised the photoluminescence efficiency from 47% to 63%. Surprisingly, this was accompanied by a drop in electroluminescence efficiency from 0.21% to 0.07%, which was attributed to the nonconjugated segments impeding intra- and interchain charge transport.[252,495]

Other dialkyl-substituted PPV derivatives have been prepared by this route and used to make green LEDs.[496] Copolymers **105**, whose PL maxima could be tuned between 505 and 523 nm, were obtained with varying degrees of elimination by Gilch polymerization.[497] The materials with lower chlorine content, and thus a higher degree of conjugation, showed lower solubility and PL efficiency than their less conjugated counterparts. The butyl-ethylhexyl-PPV (BuEH-PPV) **106** has also been made by the Gilch route and found to have a high (62%) solid-state PL efficiency.[371] The EL efficiency is only 0.1% in single-layer devices but rises to 3.2% with the use of a PVK hole-transporting layer. The luminance shows two maxima at 524 and 554 nm, with the former more intense in the PL, and the latter more intense in the EL spectrum.



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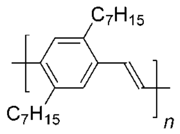

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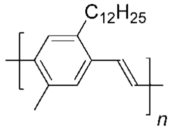

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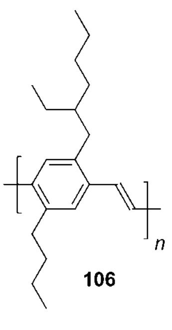

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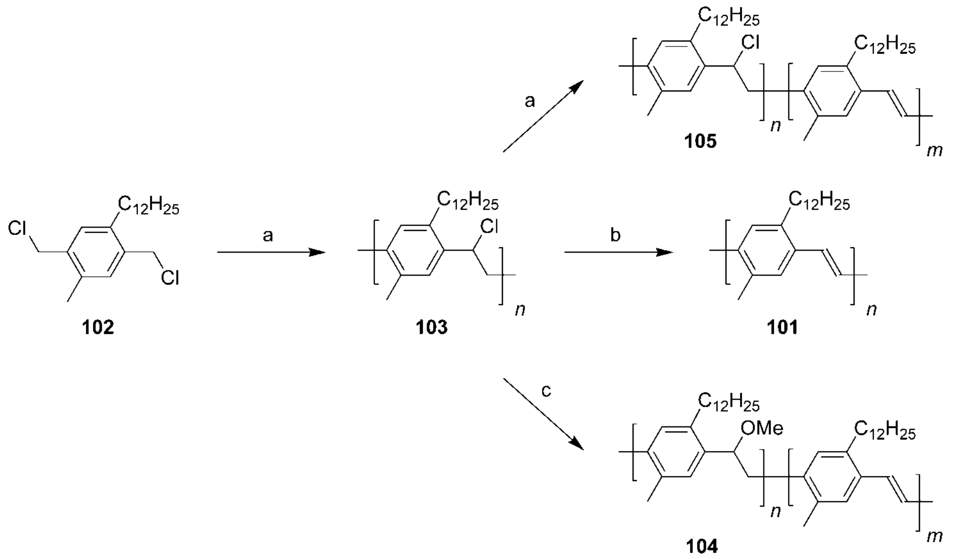
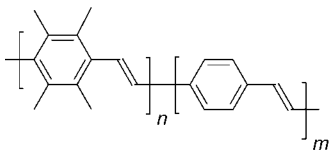
Scheme 14. Synthesis of 2-Dodecyl-5-methyl-PPV (101): (a) KO^{t}Bu, THF; (b) Refluxing Cyclohexanone; (c) MeOH, Reflux



Thorn-Csányi and co-workers[397,498,499] have prepared poly(2,5-diheptyl-1,4-phenylene vinylene) **100** by metathesis polycondensation of 2,5-diheptyl-1,4-divinylbenzene in the presence of a molybdenum catalyst. The material was of low molecular mass (*ca.* 3500 Da), indicating a length of 10−12 phenylene vinylene units, with a very narrow polydispersity. The fluorescence spectrum showed an emission maximum at 500 nm. Stille coupling of bis-stannylethene and dialkyl aryl dihalides or ditriflates has also been used to prepare low number average molar mass (*ca.* 8500) dialkyl-PPV derivatives,[394,500] as has McMurry coupling of dialkylterephthaldehydes.[501]



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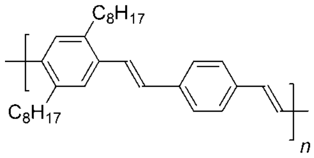
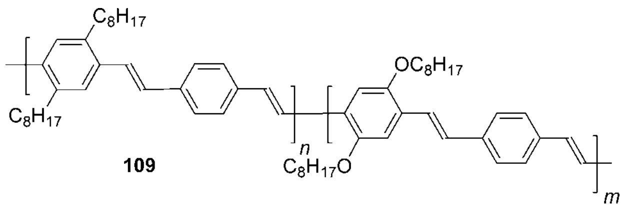


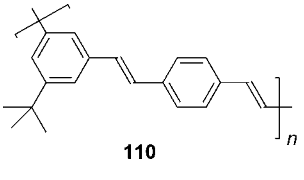
108

A copolymer **107** derived from phenylene vinylene and tetramethyl phenylene vinylene units has been made by the Wessling route.[502] The emission is slightly blue-shifted with respect to the case of PPV (**1**), and the EL efficiency is more than 10 times higher due to partial disruption of the conjugation caused by the sterically induced twisting of the tetramethylphenyl units. The Sumitomo group has made the alternating copolymer **108** by Wittig condensation of a dialkylaryl-bis-phosphonium salt with terephthaldehyde.[445] The emission is blue-green (λ_{max} = 496 nm), and the PL intensity is higher than that for the corresponding alkoxy-PPV copolymer **77f**, though the EL efficiency was found to be lower. Random copolymers **109** containing alkyl- and alkoxy-phenylene moieties were also made by the Wittig route. The PL intensity was highest for the copolymer with 90% alkyl units, but the EL efficiency was found to be optimal for a 1:1 copolymer.



109

The methods that have been used to control the conjugation length in ROPPVs can also be applied to the alkyl-substituted polymers. Thus, the conjugation length of **106** has been varied by partial removal of halides from the chloro precursor using tributyltin hydride.[503] A blue-green emitting (λ_{max} = 475 nm) copolymer **110** containing a *meta*-phenylene linkage has been made by the Wittig method.[504] As with the corresponding alkoxy polymers discussed in section 2.2 above, isomerization of the *cis*-alkenes to the *trans*-forms can be achieved with iodine.



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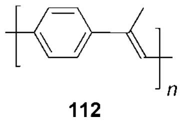
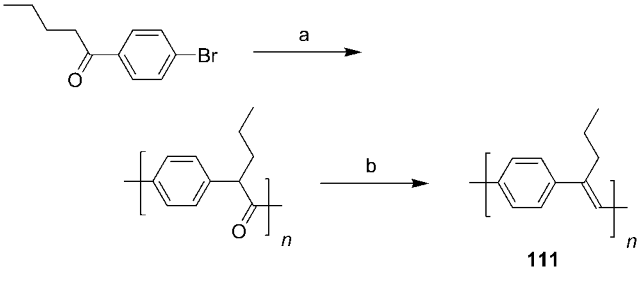
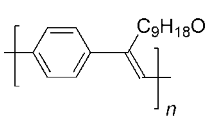


112

Polymer **111** (M_n 10100 Da) with propyl groups on the vinylene moiety has been prepared by Wu and co-workers

Scheme 15. Synthesis of Poly(phenylene 1-propylvinylene) (111): (a) $Pd_2(dba)_3$, BINAP, NaO^{t}Bu, THF; (b) $LiAlH_4$; (c) H^+





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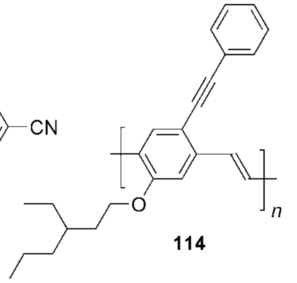

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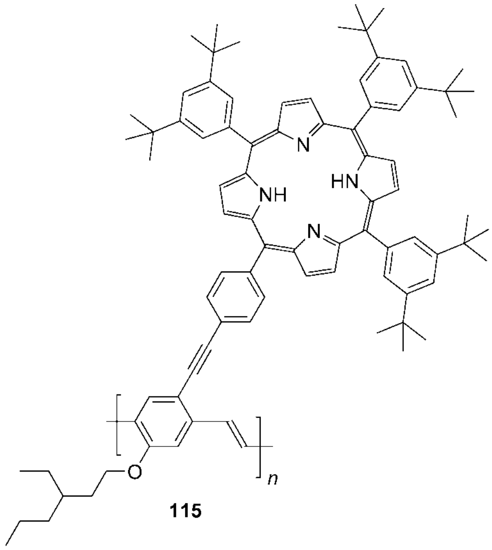
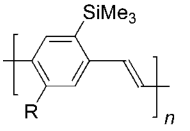


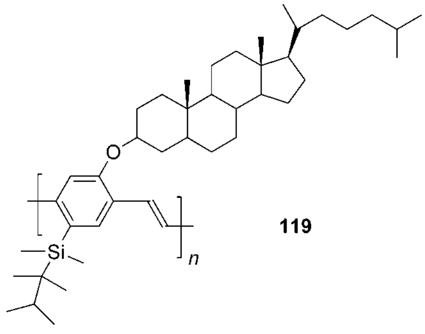
115

via a soluble polyketone precursor (Scheme 15).[505] Similar polyketones have been made with other alkyl groups, but the polymerizations were much less satisfactory. The methyl-substituted polymer **112** has also been made by the sulfinyl precursor route.[506] The emission from polymers **111** and **112** is blue (λ_{max} = 420 nm). Another polymer **113** with a mesogenic group attached to the vinylene via an alkyl chain was made by Heck coupling of a terminal alkene with *p*-dibromobenzene[507] and showed green emission (λ_{max} = 540 nm). This material exhibited liquid crystalline behavior, and polarized PL has been obtained from a film deposited on a rubbing-aligned Teflon substrate.

There are two reports of PPVs with alkyne side-chains. The properties of the polymer **114** with a phenylacetylene side-chain vary greatly depending upon the precursor method used to prepare it.[508] The chloro- and *S*-methylxanthate precursor routes gave materials with PL maxima at 680 and 665 nm and solid-state PL efficiencies of 11% and 14%, respectively, while an *O*-ethylxanthate precursor produced a polymer with strongly blue-shifted emission (λ_{max} = 580 nm) and with a much lower efficiency (2%). Lo and Burn have prepared polymer **115**, where the porphyrin unit is attached to the PPV main-chain by a rigid phenylacetylene linker.[509] PL studies indicated that the red emission (λ_{max} = 604, 653 nm) originated from the porphyrin chromophore. The EL device performance was rather poor.



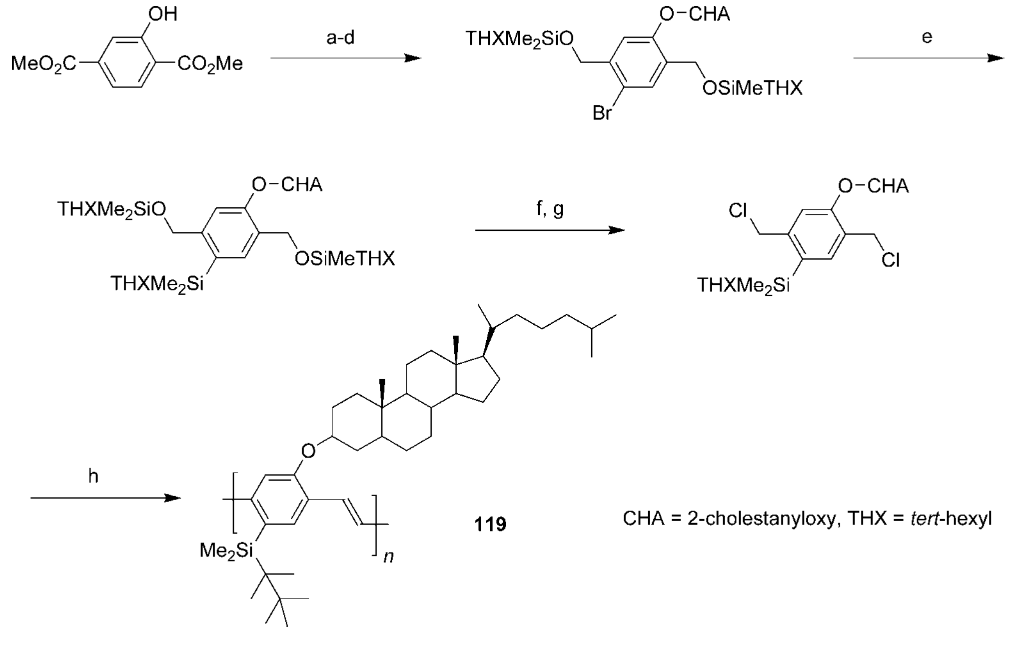
116 R = H
117 R = OMe
118 R = SiMe$_3$



119

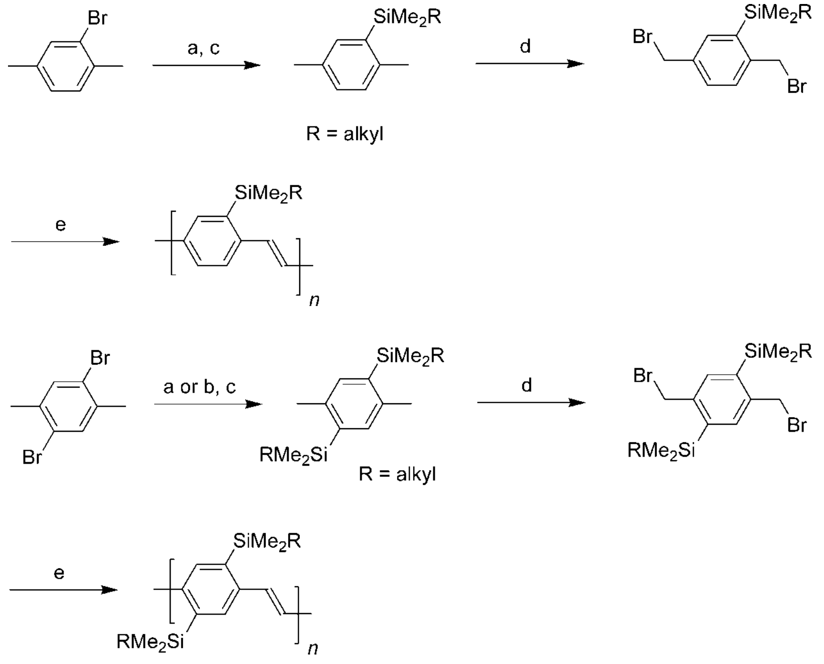
Like alkyl-PPVs, PPVs bearing silyl substituents show green emission and recently have attracted much interest, as they may exhibit PL efficiencies exceeding 60% in the solid-state.[510−512] The trimethylsilyl (TMS-PPV) **116**,[513,514] methoxy-trimethylsilyl **117**,[515] and bis-trimethylsilyl (BTMS-PPV) **118**[516,517] polymers show only limited solubility and so are best prepared by the Wessling route. TMS-PPV (**116**) shows green (λ_{max} = 540 nm) EL.[514] BTMS-PPV (**118**) has been made from both a sulfonium and a thiophenoxy precursor. The PL emission of this latter material is slightly blue-shifted (λ_{max} = 505 versus 518 nm), but the film quality

Scheme 16. Synthesis of Cholestanyloxy-silyl-PPV 119: (a) CHA-OH, DEAD, PPh$_3$; (b) LiAlH$_4$; (c) Br$_2$; (d) THXSiMe$_2$Cl; (e) ^{t}BuLi; (f) Bu$_4$NF; (g) SOCl$_2$; (h) KO^{t}Bu, THF

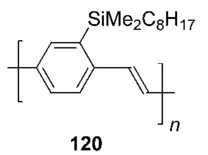


CHA = 2-cholestanyloxy, THX = *tert*-hexyl

Scheme 17. Standard Gilch Synthesis of Monosilyl-Substituted and Bis-silyl-substituted PPVs: (a) Mg, THF; (b) Na, THF; (c) RMe$_2$SiCl; (d) NBS; (e) KO^{t}Bu, THF



after solution processing is much higher and it has been used to make green LEDs (λ_{max} = 545 nm).[516] The emission of the methoxy-trimethylsilyl polymer **117** shows a bathochromic shift into the yellow (λ_{max} = 560 nm) due to the electron-donating character of the methoxy group.[515] Other polymers **119**−**121** with longer alkyl substituents on the silicon show good solubility and so are accessible by the Gilch route.[413,428,510,512,517−523] The PL and EL emission of polymer **119** is green (λ_{max} = 515 nm) despite the presence of the alkoxy group, indicating that the electronic effects of the silyl group are dominant in this polymer.[524] The polymers **120**−**121** also show green luminescence (λ_{max} = 510−525 nm) and have been used to make green emitting devices with efficiencies better than those for PPV (**1**).[510,511,517,520,524−526] The efficiency of devices using poly(dimethyloctylsilyl-1,4-phenylene vinylene) (DMOS-PPV, **120**) increases from 0.5% to 2% upon insertion of an electron-transporting layer with aluminum cathodes.[512] Addition of a hole-transporting layer of PEDOT/PSS increased the efficiency of devices using polymer **121c** nearly 8-fold, while use of calcium instead of aluminum cathodes produced only a minor improvement in efficiency, suggesting that electron injection is not the limiting factor for efficiency in this polymer.[517] The bis-(dimethyloctylsilyl)-PPV **121b** (BDMOS-PPV) shows a thermotropic liquid crystalline phase upon heating, giving polarized PL emission.[526]



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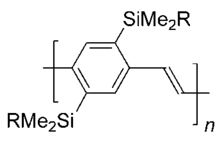
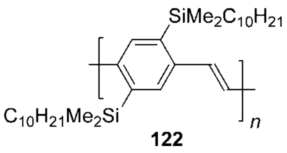


121a R = C$_4$H$_9$
121b R = C$_8$H$_{17}$
121c R = C$_{10}$H$_{21}$
121d R = C$_{12}$H$_{25}$
121e R = C$_{18}$H$_{37}$



122

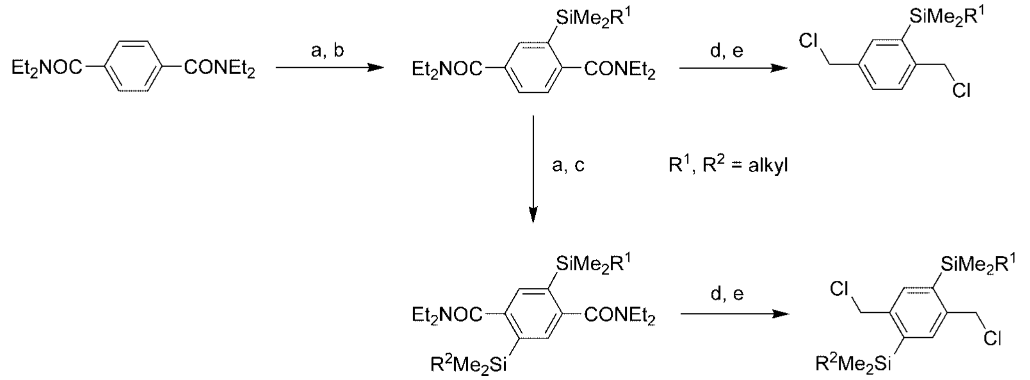
The key step in the synthesis of alkylsilyl-PPVs is the introduction of the alkylsilyl group. The first synthesis of an alkylsilyl-PPV, that of the cholestanyloxy-dimethylhexylsilyl-PPV **119** by Wudl and co-workers,[518] used an unusual transfer reaction to introduce the silyl substituent onto the aromatic ring (Scheme 16).

Subsequent syntheses of mono- or bis-alkylsilylated PPVs introduced the alkylsilyl substituents by alkylsilylation of aryl organometallic reagents (Scheme 17).[510,517,520] Most commonly, a Grignard reagent is used, but it has been reported that this can lead to incomplete silylation when making the dialkylsilyl compounds,[517] and so arylsodiums have been used instead for making these compounds.[428] Care must also be taken during the bromination of the side-chains, as use of excess brominating agent can lead to bromodesilylation of some of the silyl groups.[517]

The most recent synthesis developed by Holmes and co-workers involves directed metalation of tetra-*N*-ethylphthalamide at −100 °C followed by silylation to cleanly introduce one or two silyl groups in high yields (Scheme 18).[413,523] This route also permits the synthesis of unsymmetrically substituted monomers, which allows the preparation of polymers such as **122**, which would be difficult to synthesize by the more classical routes.[523] The use of two side-chains of different lengths has proved beneficial for the EL efficiency of dialkoxy-PPVs (see section 2.2 above), and it will be interesting to see if this also applies to bis(trialkylsilyl)-PPVs.

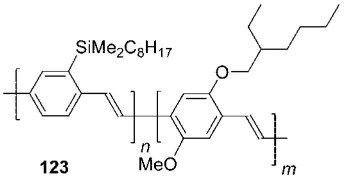
Devices emitting green light fabricated from both DMOS-PPV (**120**)[510,519,525] and BDMOS-PPV (**121b**)[526] suffer from rather high turn-on voltages of about 15 V. Interestingly, single-layer devices made from the bis(dimethylbutylsilyl)-PPV **121a** show significantly reduced turn-on voltages of about 6 V, with visible green light observable at about 7.5 V.[520] One way to reduce turn-on voltages of silyl-containing PPVs in electroluminescent devices is the incorporation of more electron rich building blocks. The statistical copolymers **123**, containing DMOS- and MEH-PPV units in varying relative ratios, have been synthesized by Gilch copolymer-

Scheme 18. Synthesis of Silyl-PPV Monomers by the Method of Holmes: (a) ^{t}BuLi, THF, −100 °C; (b) R_1Me_2SiCl; (c) R_2Me_2SiCl; (d) BH_3, THF; (e) CH_2=CHCOCl

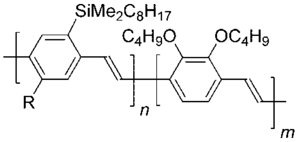


ization.[422] It is also claimed that block copolymers of DMOS-PPV and MEH-PPV can be prepared by adding the monomers sequentially to a Gilch polymerization.[485] Increasing the relative percentage of MEH-PPV in the copolymers results indeed in a significant decrease of turn-on voltages (down to 6 V) but is also accompanied by a reduction of efficiency. Furthermore, lowering of the relative amount of DMOS-PPV units in the polymer chain results also in a bathochromic shift of the photoluminescence maxima, so that the optical properties of the copolymer increasingly resemble those of MEH-PPV (**20**). Similar reductions in turn-on voltage have been observed for copolymers **124**−**125** with 2,3-dibutoxy-PPV units.[412,414,415] These show green emission (λ_{max} = 548 and 544 nm, respectively) with respectable PL efficiencies of 48% and 28%. By using PEDOT charge-transporting layers, the turn-on voltages could be reduced to only 2−4 V. Incorporation of silyl-PV units has been used to raise the PL and EL efficiencies of PPVs **59**−**61** with ethylene oxide and crown ether units which have very low efficiencies (see section 2.2 above). Thus, the DMOS-PPV copolymers **126**−**127** show yellow emission (λ_{max} = 590−598 nm) similar to those of the homopolymers **50**−**60** (λ_{max} = 601 and 640 nm), but with much higher solid-state PL (19% and 14%, *cf.* 0.6% and 8.8%) efficiencies and about 5 times higher EL efficiencies.[424] The BDMOS-PPV copolymer **128** also shows higher PL efficiency (17%) and yellow EL (λ_{max} = 590 nm) with a turn-on voltage of 5 V.[519,527,528] By contrast, the crown-ether-PPV copolymers **129**−**130** show green luminescence (λ_{max} = 555 and 549 nm, respectively), again with much better PL efficiencies (48% and 28%) than those for the homopolymer **61** (9%). Somewhat unusually, the EL efficiency was higher with an aluminum (1.4%) than with a calcium (0.7%) cathode for **123**.[427,428] The copolymers **124**−**128** show even better performance in LECs (see section 6.3 below).

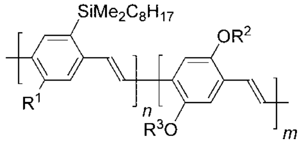
Shim and co-workers have prepared the alternating copolymers **131**−**133** of BTMS-PPV with PPV, having *para*-, *meta*-, and *ortho*-phenylene linkages, by Wittig polycondensation. These display blue-green emission, with the *meta*-**132** and *ortho*-PPV **133** copolymers showing blue-shifted emission (λ_{max} = 440 and 470 nm, respectively) compared with the *para*-linked copolymer **131** (λ_{max} = 485 nm).[448,529] Huang and co-workers have made a copolymer **134** with the silyl substituent on the *meta*-phenylene unit by the Wittig method. It shows blue-green emission in solution (λ_{max} = 452, 479 nm) and, slightly red-shifted, in the solid state (λ_{max} = 479, 502 nm).[530] Green EL (λ_{max} = 515 nm) has also been obtained from the trialkylgermanyl-PPVs **135** made by the Wessling route.[531,532]



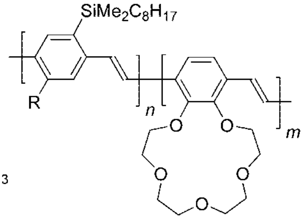
123



124 R = H
125 R = C_8H_{17}



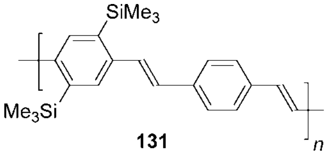
126 R^1 = H, R^2 = Me, R^3 = $(CH_2CH_2O)_3CH_3$
127 R^1 = H, R^2, R^3 = $(CH_2CH_2O)_3CH_3$
128 R^1 = C_8H_{17}, R^2, R^3 = $(CH_2CH_2O)_3CH_3$



129 R = H
130 R = C_8H_{17}

2.4. Aryl-Substituted PPVs

A variety of methods have been used to make PPV derivatives with aryl substituents on the aromatic ring. For example, poly(2-phenylphenylene vinylene) (PPPV, **136**) was first made in low molar mass by means of Heck coupling of 2,5-dibromobiphenyl with ethene.[533,534]



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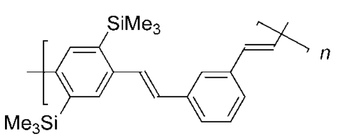

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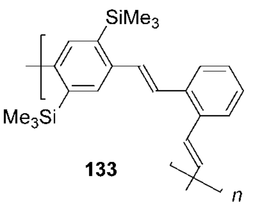

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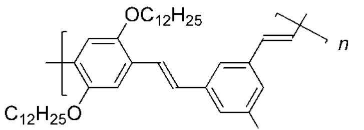

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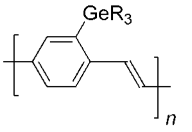
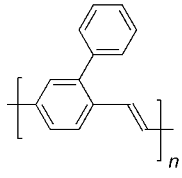


135a R = Me
135b R = C_2H_5

Higher molecular mass materials and better yields can be obtained by the Wessling sulfonium,[535] Gilch,[536] and chloro precursor[537,538] routes. Other methods that have been used to make aryl-substituted PPVs are the Horner[539] and Wittig[540] reactions. Hsieh and co-workers at Kodak[537,538,541−544] have made a systematic study of the preparation and properties of PPVs bearing phenyl groups on the aromatic ring. The key steps in the monomer syntheses (Scheme 19) are Suzuki coupling of a (di)bromoterephthalate **137** with phenylboronic acid for 2- or 2,5-disubstituted PPVs, and a Diels−Alder addition of an alkyne **138** to 3,4-diphenylcyclopentadienone **139** for 2,3-di-, tri-, and tetrasubstituted PPVs.[538] They found that polymers with one (**136**) or two (**140−141**) phenyl substituents could be made by the chloro precursor route, but the triphenyl-PPV **142a** had to be made by the xanthate precursor route due to the insolubility of the chloro precursor.[538,541,544,545] By contrast, the 2,3-diphenyl-5-biphenyl polymer **142b** can be prepared via a soluble chloro precursor.[541,542] The tetraphenyl-PPV **143** could not be synthesized, as the tetraphenyl terephthalate intermediate **144** (R_1, R_2 = Ph) could not be reduced during the attempted preparation of the monomer.[542] The 5-alkyl-2,3-diphenyl **145** and 6-alkyl-2,3,5-triaryl **146** polymers were made by a modified Gilch synthesis in which *para-tert*-butylbenzyl chloride was used as an end-capping/initiating reagent.[543,544,546]



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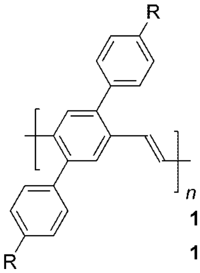
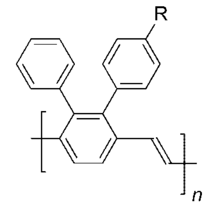


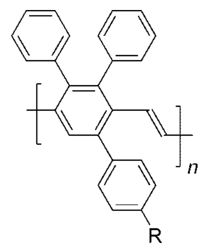
140a R = H

140b R = 2-ethylhexyloxy



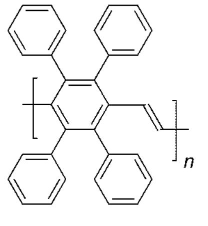
141a R = H

141b R = 3,7-dimethylocytloxy



142a R = H

142b R = C_6H_5



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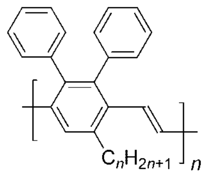
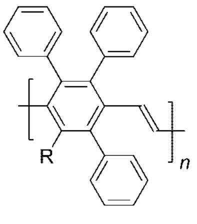
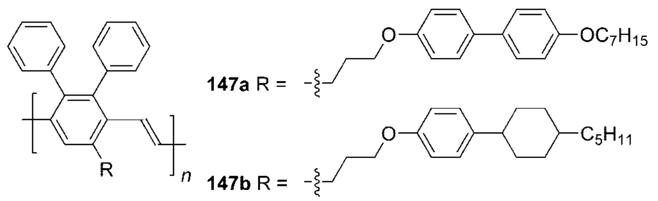


145

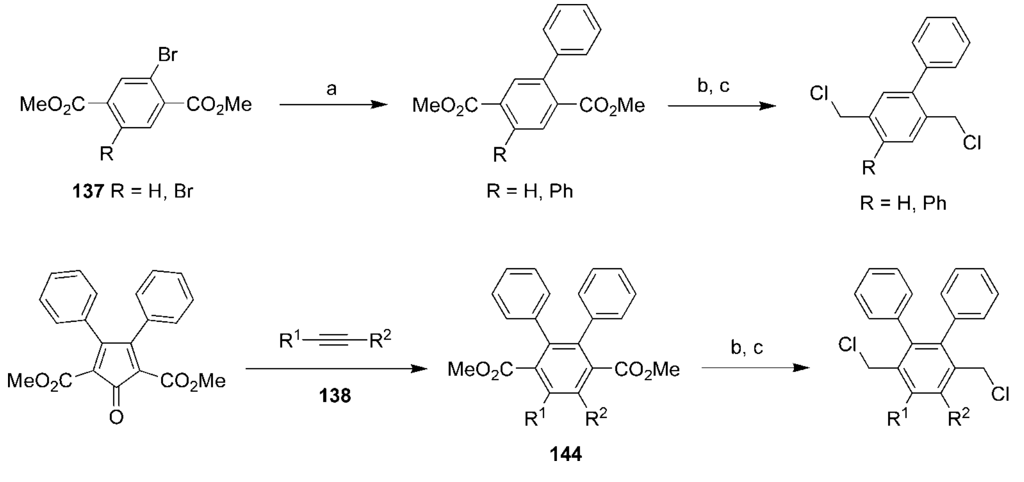


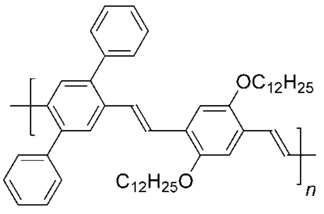
146 R = alkyl



PPPV (**136**) is reported to show broad green (λ_{max} = 550 nm) EL.[547] The introduction of an *ortho* second phenyl ring in **141a** produces a marked blue-shift moving the emission maximum to 500 nm.[537,541,545] Introduction of a second ring para to the first has a lesser effect so that the emission maximum for **140b** is between 526 and 562 nm.[548] As for PPV, electron injection is limiting for these materials, as shown by the large increase in EL efficiency in going from an aluminum to a magnesium cathode[537] or on using an Alq_3 electron-transporting layer.[545,549] The extra aryl substituent in **142b** produces no further blue-shift in emission,[541] but the alkyl-substituted **145** has an emission maximum at 490 nm, which makes it the most blue-shifted of all fully conjugated PPVs yet reported,[543] with a very high solid-state PL efficiency of 65%. Copolymers of **145** with MEH-PPV show EL ranging from green to orange (λ_{max} = 530−560 nm) with increasing MEH-PPV content.[550] Attachment of mesogenic groups at the 5-position in **147** induces liquid-crystallinity, and these materials show polarized blue-green emission when deposited on rubbing-aligned substrates.[551] An alternating copolymer **148** has been prepared by the Horner method, whose emission (λ_{max} = 553 nm) is more efficient than that of the corresponding RO-PPV homopolymer **39**.[552]

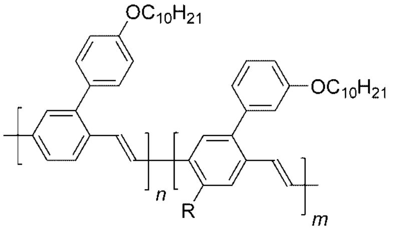
Scheme 19. Synthesis of Monomers for PPVs with Phenyl Substituents: (a) $PhB(OH)_2$ or $PhSnBu_3$, $Pd(PPh_3)_4$; (b) $LiAlH_4$; (c) $SOCl_2$



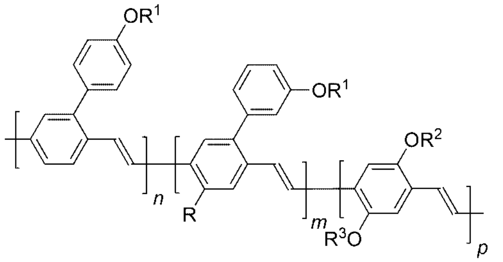


148

The solubility of PPPV can be improved by attaching solubilizing groups to the phenyl side-chains. The Covion group has prepared a 1:1 copolymer **149a** with 4- and 3-dodecyloxyphenyl substituents by the Gilch route which shows green emission (λ_{max} = 515 nm).[284] Incorporation of RO-PPV units gave copolymers **150a** whose emission color could be tuned from green to orange (λ_{max} = 567 nm) by increasing the amount of the RO-PPV from 0% to 10%.[284,553] Subsequently, a study[302,554] of the correlation between the extent of defects in the polymer produced during the Gilch polymerization (see Scheme 12 above) and the monomer structures was conducted which found that the 2-phenyl monomers produced much higher defect levels (6% versus 2%) than the dialkoxy-PPV monomers, with a concomitant drop in device lifetime. The study also revealed that the defect level could be lowered by incorporation of a monomer with both aryl and methoxy substituents, as in **149b**. As a result, polymer **149b** (*m* = *n*) shows a longer operational lifetime than **150a** (*n* = 4%). The emission is slightly red-shifted by the methoxy group so that **149b** displays an EL maximum between 548 and 575 nm depending upon the *m*:*n* ratio.[554] However, a disadvantage of this monomer is that it promotes gelation. These copolymers are the best performing PAVs yet produced and are the active layers in the first commercial PLED displays such as the Philips shaver and "magic mirror" mobile telephone. Recently, it was reported that highly efficient LEDs can be made using these polymers with Al cathodes by inserting a poly(ethylene oxide) buffer layer into the devices.[555] The efficiency and durability of devices using the similar copolymer **150b** has been enhanced by using an ROPPV as a hole-transporting layer.[556]



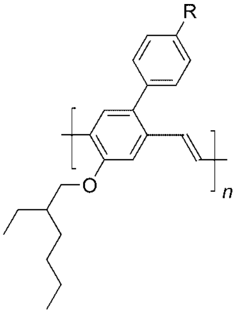
149a R = H
149b R = OMe



150a R^1, R^2, R^3 = $C_{10}H_{21}$
150b R^1, R^2 = 3,7-dimethyloctyl, R^3 = Me, *m* = 0, *n* = *p*

Polymers **151a,b** with a branched alkoxy substituent have been prepared by the bromo precursor route.[557] The alkoxy groups caused a slight bathochromic shift in the emission compared with PPPV (λ_{max} = 560 nm). The electron accepting sulfonyl group in **151b** causes a slight blue-shift in emission (λ_{max} = 550 nm) with no improvement in the EL efficiency.[557] The biphenyl-substituted polymer **151c** has been made by the Gilch route and is reported to show green emission (λ_{max} = 552 nm).[548] (Polymers with electron accepting aryloxadiazole side-chains are discussed in section 2.5 below.) By contrast, the alkoxy substituent in **141b** improves solubility without red-shifting the emission (λ_{max} = 504 nm).[558] Copolymers **152a** with 10% MEH-PPV units display red-shifted emission (λ_{max} = 548 nm) with much higher EL efficiency (6.14 cd/A *cf.* 0.69 cd/A). Copolymerization with dimethoxyphenylene vinylene units to give **152b** produces a smaller red-shift (λ_{max} = 540 nm) and efficiency gain (3.39 cd/A). Interestingly, the maximum emission intensity from **152b** (16,910 cd/m^2) is very much higher than that from **152a** (1936 cd/m^2). Andersson and co-workers have prepared the 2,5-dialkoxyphenyl-PPV **153a** by the Gilch route.[559,560] This polymer shows green PL (λ_{max} = 489, 524 nm) with a modest PL efficiency (28%). The EL efficiencies are 0.21% for a single-layer device and 0.63% for a double-layer device with a PVK hole-transporting layer. Copolymers **153b** with MEH-PPV units show red-shifted emission (λ_{max} = 542−551 nm) with higher emission efficiencies. The PL efficiency is maximal (36%) with 20 mol % MEH-PPV units, while the single-layer (0.68%) and double-layer (1.15%) EL efficiencies are optimal for 30% and 40% MEH-PPV, respectively.[559,560] A study of the effects of the polymerization temperature on the properties of **153a** found that polymerization at 0 °C led to polymer of lower molecular mass but with fewer defects. The PL efficiency was also higher (60%), but the EL efficiency was lower than that for material made at higher temperature.[561,562] Similar effects were seen for the methoxy-substituted polymer **153c**, which displayed red-shifted EL (λ_{max} = 529, 561 nm) with slightly higher efficiency than that for **153a**.[563] A combination of a red-shift and an efficiency increase upon methoxylation is also seen in the emission of the polymers **154a** and **154b** (λ_{max} = 515 at 0.81 cd/A and 545 nm at 1.75 cd/A, respectively).[564,565] A 1:1 copolymer **154c** displayed even greater efficiency (2.68 cd/A) with an intermediate emission color (λ_{max} = 541 nm).

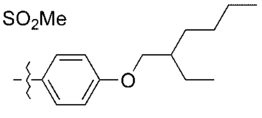
The efficiency has been further improved to 5 cd/A by use of an Alq$_3$ buffer layer.[566] The effects of the substitution patterns on the formation of defects during the Gilch polymerization are also illustrated by the isomeric dialkoxyphenyl-substituted PPVs **155**−**157**.[567] Here the presence of a bulky *ortho*-phenyl group in **155** reduces the amount of defects by an order of magnitude (0.36% *cf.* 3.79% for **156** and 3.72% for **157**). These polymers produced blue-green PL and blue-green to green EL with EL emission maxima at 496 nm (efficiency 0.37%), 488 nm (0.66%), and 525 nm (0.25%), respectively. That the efficiency of the 2,4-dialkoxysubstituted polymer **156** is higher than that of the corresponding 3,4-disubstituted isomer **155** despite its higher defect level was attributed to a change in the geometry of **155** in the excited state. Interestingly, polymer **155** showed the largest red-shift in PL when going from solution to thin film, but the EL spectrum of polymer **157** was markedly red-shifted compared with its solid-state PL spectrum, which was attributed to aggregation. Polymers **158** and **159a** with silyl solubilizing substituents on the phenyl side-group also show green emission (λ_{max} = 524−529 nm).[568−570] Copolymers

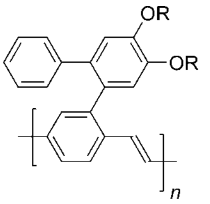


151a R = H

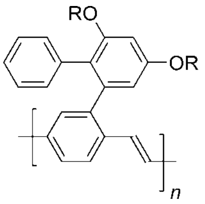
151b R = SO_2Me

151c R =

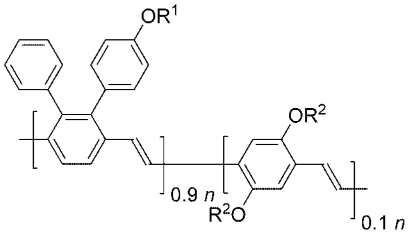




155 R = 2-ethylhexyl

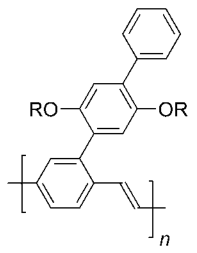


156 R = 2-ethylhexyl

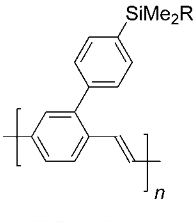


152a R^1, R^2 = 2-ethylhexyl

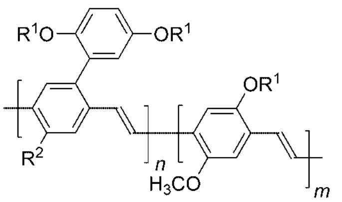
152b R^1 = 2-ethylhexyl, R^2 = Me



157 R = 2-ethylhexyl



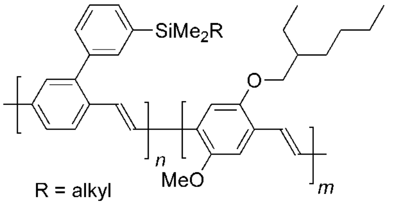
158 R = alkyl



153a R^1 = 2-ethylhexyl, R^2 = H, *m* = 0%

153b R^1 = 2-ethylhexyl, R^2 = H, *m* = 20-40%

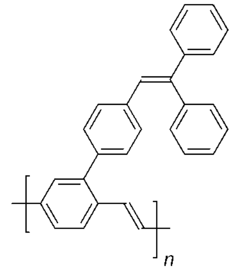
153c R^1 = 2-ethylhexyl, R^2 = Me, *m* = 0%



R = alkyl

159a *m* = 0%

159b *m* = 30-70%



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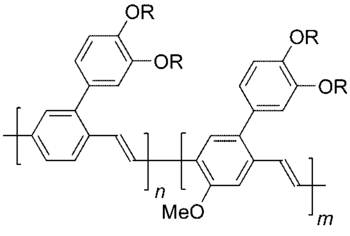
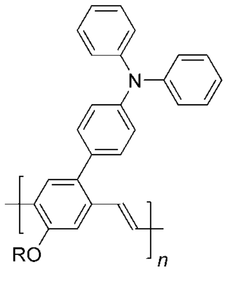


154a *m* = 0%

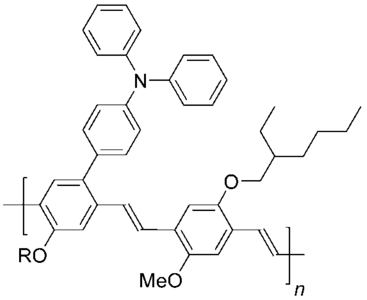
154b *m* = 0%

154c *m* = *n*

R = 3,7-dimethyloctyl



161 R = 2-ethylhexyl

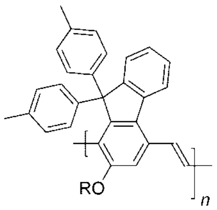


162

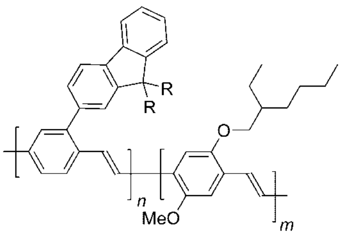
159b with 30−70 mol % of MEH-phenylene vinylene units all displayed orange-red EL (λ_{max} = 590 nm).[569] By contrast, polymer **160** with a phenylstilbene side-chain emits in the yellow (λ_{max} = 548 nm),[571] as do polymer **161** (λ_{max} = 537 nm) and copolymer **162** (λ_{max} = 552 nm), with hole-transporting triphenylamine side-chains.[572,573] The PL quantum efficiencies of the homo- and copolymers are very similar in solution (37% vs 42%), but copolymer **162** is a much more efficient emitter in the solid state (11% vs 31%). The EL efficiency of copolymer **162** is reportedly twice that of MEH-PPV.[572]

Other aryl substituents have also been attached to a PPV backbone. Poly(1,4-fluorenylene vinylene) **163** is reported to produce green EL (λ_{max} = 515 nm) with only modest efficiency (0.13 cd/A).[574] The polymers **164a,b** with a dialkylfluorenyl substituent made by the Gilch route exhibit green EL (λ_{max} = 520 nm).[575−577] Copolymers **164c** with MEH-PPV show red-shifted EL (λ_{max} = 561−585 nm) with the highest EL efficiency from the copolymer with 7.5% MEH-PPV content (λ_{max} = 561 nm).[576] The adjacent phenyl substituent in **165a** blue-shifts the emission (λ_{max} = 500 nm).[558] Copolymers with MEH-PPV **165b** and dimethoxy-PPV **165c** display red-shifted EL (λ_{max} = 528 and 520 nm, respectively) with higher maximum efficiencies (1.91 cd/A and 0.45 cd/A *cf.* 0.23 cd/A) and emission intensities (1990 cd/m^2 and 6100 cd/m^2 vs 438 cd/m^2) than the homopolymer. Copolymer **166** with a diaryl-PPV had an even greater maximum brightness (14,070 cd/m^2) but a maximum efficiency of only 1.51 cd/A. It is reported that the emission from the alkoxy-substituted polymer **167** (λ_{max} = 526−552 nm) is blue-shifted compared with that of structurally very similar **151c**.[548]

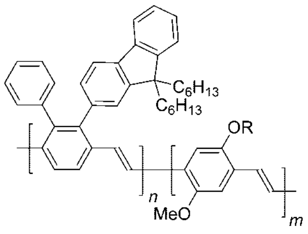
Polymer **168** with a spirobifluorene substituent displays green-yellow EL (λ_{max} = 515, 560 nm), indicating that the bulkier substituents on the fluorene do not induce greater twisting of the backbone.[578,579] Polymer **169a** with a diphenylanthracene side-group has been made by both the Wessling[261,580] and Gilch[581] routes and shows green PL (λ_{max} = 500, 550 nm). The alkyloxy substituent in **169b** causes a red-shift in the emission band, which is also broadened.[581] The EL efficiency of **169b** is reported to be 10 times higher than that of PPV (**1**). The bulky dendrimer-like side-chains



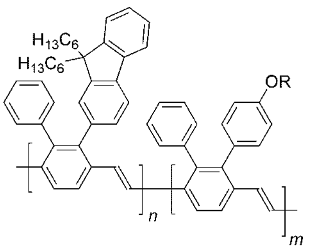
163 R = 2-ethylhexyl



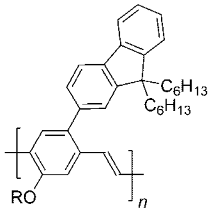
164a R = C_6H_{13}, *m* = 0%
164b R = C_8H_{17}, *m* = 0%
164c R = C_6H_{13}, *m* > 0%



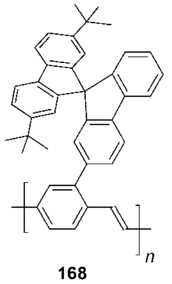
165a *m* = 0%
165b R = 2-ethylhexyl, *m* = 10%
165c R = Me, *m* = 10%



166 R = 3,7-dimethyloctyl



167 R = 2-ethylhexyl



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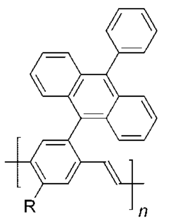
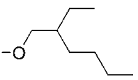
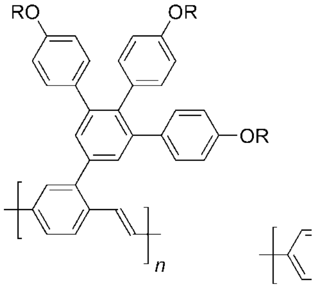
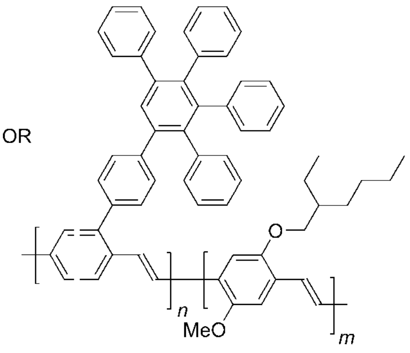


169a R = H
169b R =

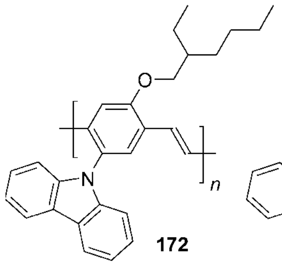




170 R = 2-ethylhexyl



171a *m* = 0%
171b *m* > 0%



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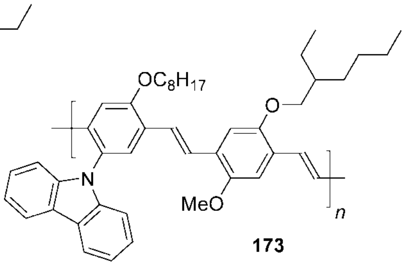

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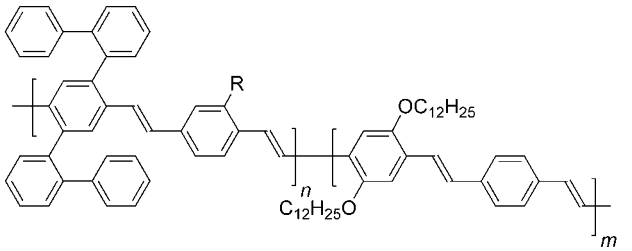


174a R = H, *m* = 0%
174b R = $OC_{12}H_{25}$, *m* = 0%
174c R = $OC_{12}H_{25}$, *m* = *n*

in polymer **170** induce twisting of the polymer chain so that the PL is blue-green (λ_{max} = 476 nm).[442] As the branching point in polymer **171a** is further away from the backbone, the twisting-induced blue-shift in the emission is smaller (λ_{max} = 502 nm).[582] The emission maxima of copolymers **171b** with MEH-PPV have been tuned between 530 and 574 nm by varying the molar ratios of the two monomers in a Gilch synthesis. The highest PL and EL efficiencies were observed for the copolymer with 25% of MEH-phenylene vinylene units (λ_{max} = 547 nm).

The only examples of heteroaryl-substituted PPVs apart from the oxadiazole-substituted polymers discussed in section 2.5 below are polymers **172** and **173** with a hole-transporting carbazole side-chain. Homopolymers **172** show green emission with a maximum at 540 nm and a secondary peak at 510 nm,[583−585] while the alternating copolymer **173** made by the Wittig route is a red emitter (λ_{max} = 609 nm).[586]

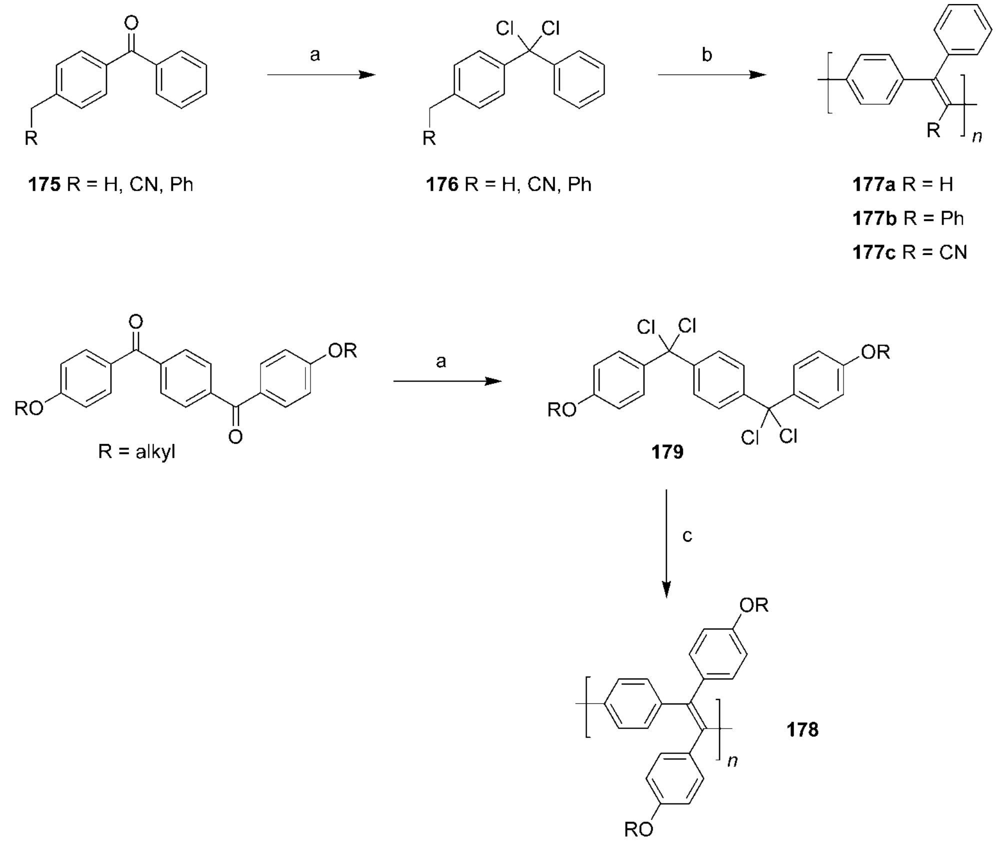
Peng and co-workers have made polymers **174** with 2,5-bis(2-biphenyl)-PPV units by the Horner reaction.[587,588] These polymers show high solid-state PL efficiencies (61−82%). The highest PL efficiency was seen for **174a**, but this also shows a very low molecular weight corresponding to a degree of polymerization of only six, making it more of an oligomer than a polymer. Not surprisingly, it also shows the lowest wavelength emission maximum (λ_{max} = 504 nm). Copolymers **174b,c** have much higher molar masses and show PL maxima at 520 and 522 nm, with efficiencies of 61% and 77%, respectively.

PPV derivatives with aryl substituents on the vinylene moiety have been prepared by the acid-catalyzed polycondensation of bis(diazobenzyl)arylenes,[589] which only gives low molar mass materials, but are best made by a dehydrochlorination method (Scheme 20) developed by Hörhold and co-workers[590−593] and subsequently used by the Hsieh group,[594,595] to produce a variety of polyphenyl PPV derivatives (M_n 7000−20000 Da). A substituted benzophenone **175** is converted to a bis-aryldichloromethane **176**, which undergoes polydehydrochlorination in pyridine. The use of appropriate starting materials allows derivatives bearing one (**177a**) or two (**177b**) aryl substituents, or an aryl and a cyano substituent (**177c**) on the vinylene moiety to be synthesized. Derivatives **178** with alkoxyaryl substituents on the vinylene moiety are best prepared by reductive dechlorinative coupling of bis(aryldichloromethyl)benzenes **179** with chromium(II) acetate (Scheme 20).[591,593,596,597]

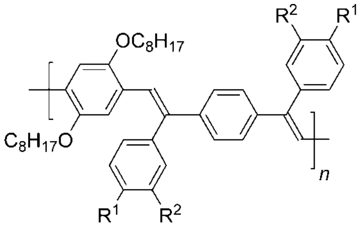
The absorption and fluorescence spectra of these polymers generally show a blue-shift compared with PPV, due to the bulkiness of the aryl substituents which twist the conjugated backbone out of plane, so that their PL emission maxima are between 512 and 530 nm.[598,599] Alternating copolymers **180**−**181** have been prepared by the Horner reactions of bis(alkoxybenzoyl)benzenes with aryl bis-phosphonates.

The emission from the polymer **180a** is green (λ_{max} = 515 nm), but the emission from the others is blue-shifted by the bulkier side-groups and the *meta*-linkage to produce blue

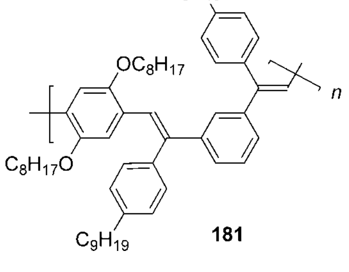
Scheme 20. Hörhold Routes to PPVs with Phenyl-vinylene Units: (a) PCl_5; (b) Pyridine, 150−180 °C; (c) $Cr_2(OAc)_4$



PL (λ_{max} = 480 and 490 nm, respectively).[600] The polymer **182** with *meta*-phenylene units has been prepared by McMurry coupling of 1,3-dibenzoylbenzene and found to show blue PL (λ_{max} = 487 nm).[601] Polymer **183** containing phenylene 1-phenylvinylene units has been prepared by aromatization of a random styrene-cyclohexadiene copolymer **184** (Scheme 21).[602] The conjugated segments must be quite short, however, as the PL maximum occurs at 460 nm. The authors report that the polymer shows a strong tendency to alternation.



180a R^1 = C_9H_{19}, R^2 = H
180b R^1, R^2 = OMe



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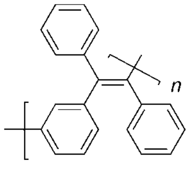

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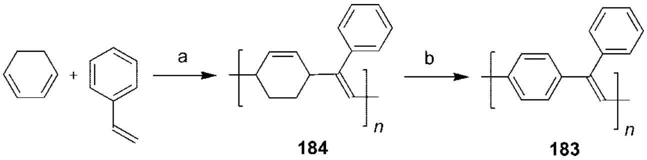
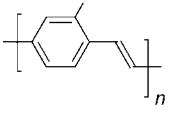
Scheme 21. Preparation of a Quasi-poly(phenylene phenylvinylene): (a) BuLi, cyclohexane; (b) Chloranil



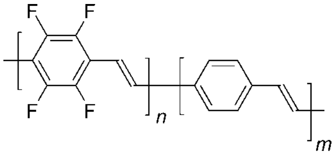
2.5. PPVs with Electron-Withdrawing Substituents

PPV derivatives with electron-withdrawing substituents such as halogen atoms on the benzene ring are of considerable interest, as they might facilitate electron injection, influence electronic properties, promote triplet formation, as well as possibly stabilize the conjugated backbone against oxidation or other unwanted degradative events. It is expected and has been confirmed by calculation[603−605] that a cyano substituent (and presumably other electron withdrawing groups) on the ring or vinylene moiety should lower the HOMO and LUMO energies and increase the electron affinity of the polymer, thus improving the efficiency of electron injection and the potential efficiency of an LED using such a polymer.

A number of halogen-substituted PPVs have been prepared. Fluoro-PPV **185a** has been prepared independently

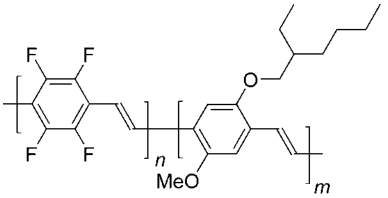


185a R = H
185b R = F
185c R = OC_6H_{13}



186a *m* = 0%
186b *m* > 0%

by groups in Korea[261,606,607] and in America[608] using the Wessling route. Its emission spectrum is similar to that of PPV (λ_{max} = 560 nm), but its EL efficiency with an aluminum cathode is 10 times higher than that for PPV due to its better electron-accepting properties.[606−608] The difluoro-PPV **185b** and alkoxy-fluoro-PPV **185c** were also made by the Wessling route[608] and show yellow EL (λ_{max} = 610 and 630 nm, respectively). By contrast, the tetrafluoro-PPV (PTFV, **186a**) made by the bromo-precursor route shows blue-green emission (λ_{max} = 485 nm), presumably because of the steric bulk of the fluorines causing twisting of the backbone.[609] Copolymers with PPV (**186b**) have been prepared by the Wessling route.[610] An increase in PTFV content leads to a blue-shift in the emission maximum of up to 60 nm (for 60% PTFV). The threshold voltages for EL are higher than those for PPV, however, and the luminescence is weak, making these materials unsuitable for use in LEDs. Similar copolymers with MEH-phenylene vinylene (**187**)[611,612] also show lower efficiencies than those observed for MEH-PPV **20**.



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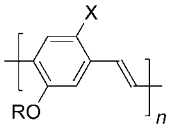
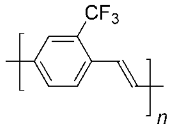


188a X = Cl
188b X = Br



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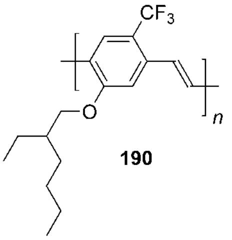
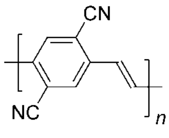


190

The chloro and bromo polymers **188a** and **188b** have also been made by a Wessling-type precursor route.[613] Molar masses were initially only 15−20,000 Da, but rigorous purification of the monomers and optimization of the polymerization conditions produced material with molar masses of up to 250,000 Da. Holmes and co-workers have also prepared the alkoxy-bromo-PPV **188b**[614] with molar masses of over 100,000 Da by means of a bromo precursor route. Like their fluoro analogue **185c**, these asymmetric halogen-substituted “push−pull” systems display red emission (λ_{max} = 618 and 626 nm),[613] which is even more red-shifted compared with that of the parent PPV than in the case of MEH-PPV (λ_{max} = 590 nm). The Holmes group has also prepared trifluoromethyl substituted PPV derivatives **189** and **190** by means of the bromo precursor route.[615−617] They show yellow PL (λ_{max} = 520 and 540 nm, respectively) but have very low (<10%) PL efficiencies. CV measurements revealed that these polymers have high electron affinities,[617] and as a result, their EL efficiencies in bilayer devices, with PPV as hole-injecting layer, are equal with aluminum and calcium cathodes.[615−617] Their EL efficiencies are only 0.01% (comparable to that of a PPV single-layer device with an aluminum cathode), however, due to the polymers' low PL efficiencies, so that they show more promise as electron-transporting than emissive materials.

Other PPVs with electron-withdrawing groups on the aryl ring have also been made. For example, dicyano-PPV **191** has been made by the Wessling route but is reported to show only very weak PL.[618] The Gilch method has been used to make the random copolymer with MEH-phenylene vinylene units **192a**.[619] Similar random **192b**[620] and alternating **193**[621] copolymers have been made by the Wittig method. These copolymers all show similar EL spectra to MEH-PPV, but due to better charge injection, their EL efficiencies are higher. A copolymer **194** with RO-phenylene vinylene and phenylene vinylene units has also been made by the Wittig method and shows orange-red EL (λ_{max} = 610 nm).[622] This emission is markedly red-shifted compared with that from the corresponding copolymer **78a** without cyano substituents (λ_{max} = 548 nm).[455] A PPV with 2,3-dicarboxylate groups **195a** (R = Me, ^{t}Bu) has been made by ROMP and shows blue-green (λ_{max} = 489 nm) emission.[623] The disodium salt **195b** (λ_{max} = 501 nm) is water-soluble. Unlike carbonyl groups on the main-chain (see section 2.1 above), these carboxylate groups do not quench the luminescence.



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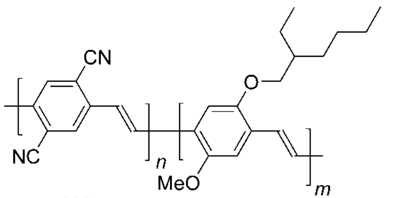
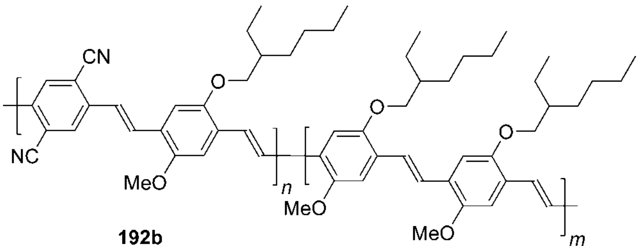
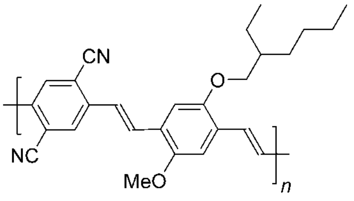


192a



192b



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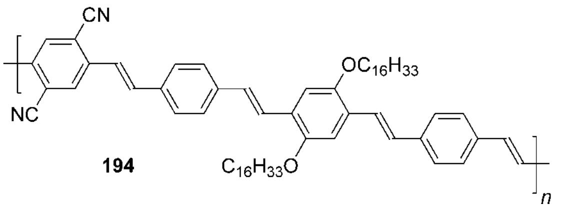

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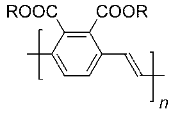
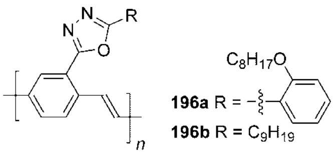
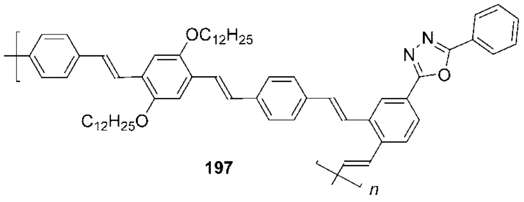
Oxadiazoles are an important class of compounds that have been used as electron transporting materials in LEDs,[2,53] and so there has been considerable interest in seeing if substitution of PPVs with such groups would improve their electron accepting properties. The oxadiazole-substituted PPVs **196a**[624] and **196b**[625] were made by the Gilch route. The oxadiazole rings were prepared by condensation of 2,5-dimethylbenzoic acid with the appropriate carboxyhydrazide. They both show yellow solid-state PL emission (λ_{max} = 569 and 583 nm, respectively) and better electron affinities than PPV. The EL emission from **196a** is slightly red-shifted (λ_{max} = 583 nm) compared with the PL. Copolymers such as **197**



195a R = alkyl
195b R = Na



196a R =
196b R = C_9H_{19}



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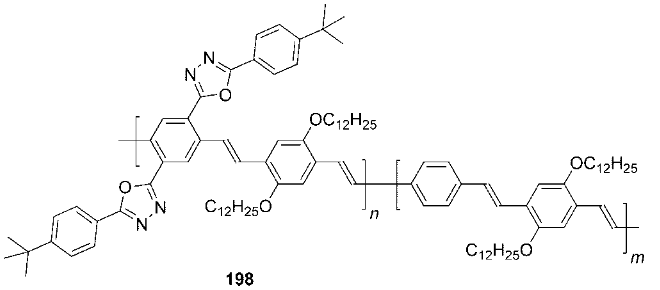

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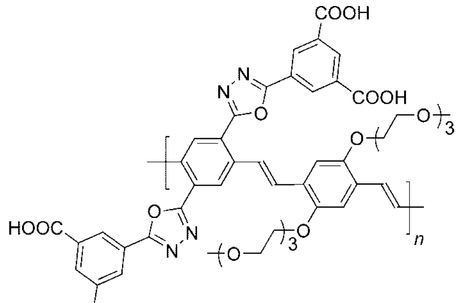

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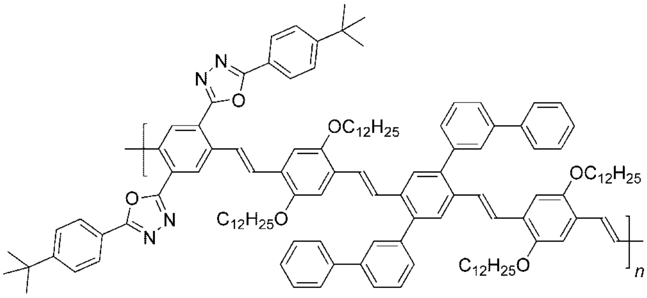

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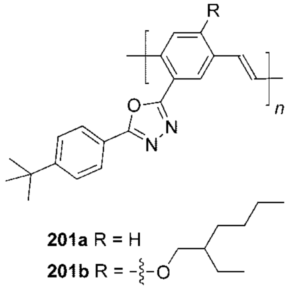
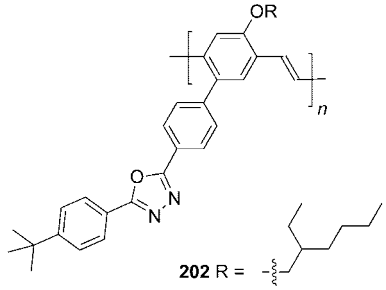


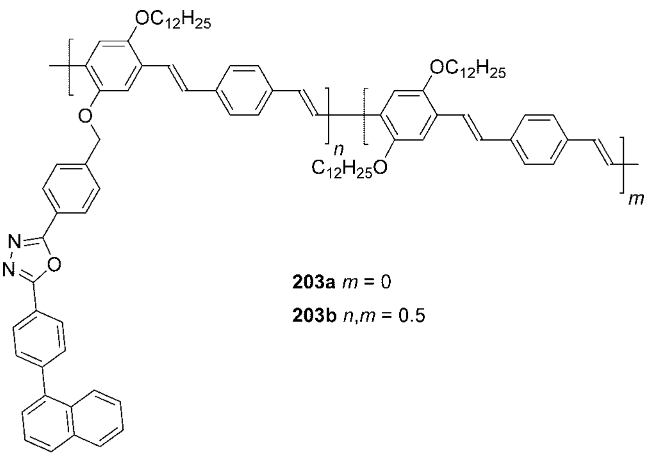
201a R = H
201b R = -O



202 R =

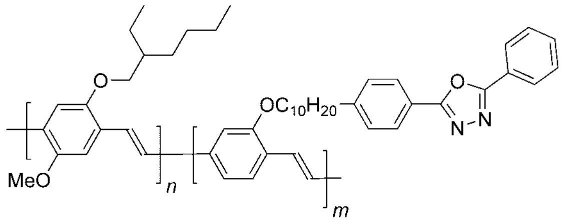
with oxadiazole substituents on *ortho*-phenylene units (prepared starting from a 3,4-dimethylbenzoate) have been made by the Wittig method.[626] These show yellow emission (λ_{max} = 544 nm for **197**) with a red-shift in emission and a strong decrease in efficiency in the solid state attributed to aggregation. Similar effects have been seen when oxadiazoles are attached to other arylene vinylene polymers.[627] Copolymers **198** have been made by Heck coupling and show red solid-state PL (λ_{max} = 640 nm).[588,628] Decreasing the oxadiazole content from every second (m = 0) to every fourth unit (m = 0.5) halves the efficiency for devices using aluminum cathodes, but the efficiency of devices using calcium cathodes is unchanged, though the turn-on voltage increases. The EL efficiency of single-layer devices using the copolymer with m = 0 is 20 times higher for aluminum and 7 times higher for calcium cathodes than for copolymers with no oxadiazole units (m = 1). Attempts to further improve the electron affinity, by attachment of electron-withdrawing groups to the oxadiazole[629,630] or by using branched side-chains containing more than one oxadiazole ring,[631] produced materials with very low PL efficiencies due to charge-transfer processes becoming favorable. Such compounds may, however, be useful as electron-transporting materials. The free carboxylic acid groups in **199** provide water solubility. A shift in the PL maximum from 555 nm in DMSO to 593 nm in aqueous base is observed.[629] The low PL efficiencies of such materials can be overcome by copolymerization with substituted PPV segments having high PL efficiencies. Thus, Peng and coworkers[588] have made copolymer **200** by Heck coupling, in which the oxadiazoles boost the electron affinity while the 2,5-bis(2-biphenyl)-PPV units provide high PL efficiency. As a result, the copolymer has a solid-state PL efficiency of 38% with a PL maximum at 585 nm, but the EL efficiency has not yet been reported.

Aryloxadiazole substituents have also been attached to PPVs. A Korean group has made polymers **201a,b** by the Gilch route.[583,632] During the monomer synthesis, the aryloxadiazole substituents were attached by Suzuki coupling of a bromo-oxadiazole with a substituted phenylboronic acid. Both polymers show green EL (λ_{max} = 529 and 536 nm, respectively) with EL efficiencies with aluminum electrodes 16 and 56 times better than those for PPV (**1**). Thermal aging of polymer **201b** is reported to lead to a slight red-shift in the EL emission maximum to 541 nm with a slight increase in efficiency.[632] Polymer **202** with a diaryloxadiazole side-chain is reported to have an EL efficiency 1 order of magnitude better than that of MEH-PPV.[585] Diaryloxadiazoles have also been attached via alkoxy linkers. A group at Bell Laboratories made the copolymers **203** by Heck coupling.[212,633] They show orange-red EL (λ_{max} = 580 nm) with higher efficiencies than those for PPV. For polymer **203b** the efficiency is only 2−3 times higher, but for polymer **203a** the efficiency is 10 times higher than that for PPV with aluminum cathodes, though it is only 2 times higher with calcium electrodes. The polymer **204a** and its copolymers with MEH-PPV **204b** have been made by the Gilch route.[634] The homopolymer **204a** shows a PL maximum at 549 nm, while the emission maximum of the copolymers can be tuned between 567 and 578 nm by varying the feed ratio of the comonomers. The EL efficiency of **204a** is twice that of



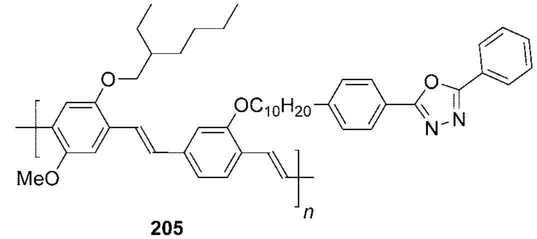
203a $m = 0$

203b $n,m = 0.5$



204a $n = 0$

204b $n = 0.24\text{-}0.75$



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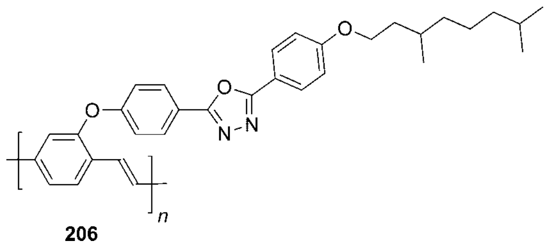
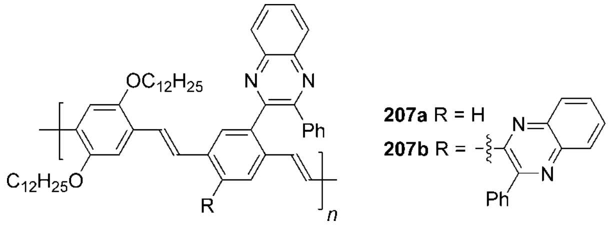


206

MEH-PPV **20** using calcium and 20 times higher using aluminum cathodes. The copolymers **204b** can show even higher efficiencies, with the optimal efficiencies being 9 times higher than those for MEH-PPV with calcium cathodes for a copolymer with $n = 0.37$ and 38 times higher than those for MEH-PPV with aluminum electrodes for $n = 0.75$. The alternating copolymer **205** displays EL very similar to that of MEH-PPV ($\lambda_{max} = 586$ nm), but with an efficiency 50 times higher.[635] The most remarkable enhancement in EL efficiency is seen for the polymer **206** prepared by a Korean group.[636] An efficiency of 21.1 cd/A was obtained at a luminance of 5930 cd/m^2 with aluminum cathodes, which was attributed to highly efficient electron injection and transport being induced by the oxadiazole units, with matching efficient hole transport along the PPV chain.

Another heterocyclic electron-accepting group that has been attached as a side-chain to a PPV is quinoxaline. The copolymer **207a** displays green PL in solution ($\lambda_{max} = 504$ nm) but yellow emission from thin films ($\lambda_{max} = 563$ nm). The second quinoxaline substituent in **207b** produces a marked blue-shift in both the solution and solid-state PL ($\lambda_{max} = 404$ and 470 nm, respectively). However, the EL efficiency of **207a** ($\lambda_{max} = 550$ nm) was low (0.004%).[637]

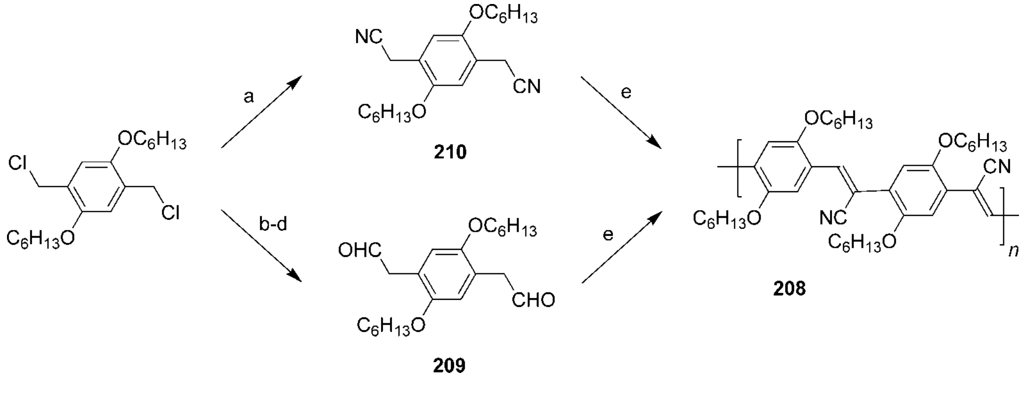


207a R = H

207b R =

Improvements in EL efficiency have also been obtained by placing the electron-withdrawing substituents on the vinylene moiety, as was first shown with CN-PPV **208**, in which the cyano substituent on the ethylene linkage serves to lower both the HOMO and LUMO energy levels. This polymer was prepared by Knoevenagel condensation between the appropriate dialdehyde **209** and diacetonitrile **210** (Scheme 22).[638,639] The HOMO−LUMO gap of CN-PPV **208** (2.1 eV, $\lambda = 590$ nm) is determined by the combined effects of the alkoxy substituents, which also serve to promote processibility in the fully conjugated form, and the cyano substituents, which increase the electron affinity of the polymer compared with that of PPV. Two-layer electroluminescent devices with PPV as hole-transporting layer operated with up to 4% efficiency,[640,641] but the lifetimes of these devices were relatively short. Salaneck and coworkers[642] have shown that the lifetimes of ITO/**208**/Ca devices can be optimized by depositing the cathode under high vacuum with a partial pressure of oxygen of 10^{-6} mbar.

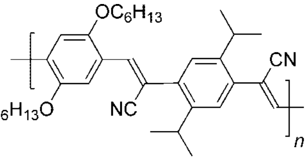
Scheme 22. Synthesis of CN-PPV by Knoevenagel Polycondensation: (a) NaCN; (b) NaOAc; (c) KOH; EtOH; (d) PCC; (e) ^{t}BuOK, Bu$_4$NOH, ^{t}BuOH, THF, 50 °C



This effect appears to be due to the formation of an oxide layer at the polymer−metal interface, which prevents doping of the polymer with calcium ions. A device has been constructed with polymer **208** as emissive layer upon a silicon substrate,[643−646] thus opening the possibility of constructing LEDs which can be operated directly from a silicon chip.

The Knoevenagel route is extremely flexible and lends itself to considerable variation, enabling synthesis of many other α-cyano PPV derivatives.[252,573,647−650] Some of these show similarly high emission efficiencies in double-layer devices with PPV[644,646,651] or other hole-injecting layers.[649,652] Blue-shifts to give green emission (λ_{max} = 510 nm) have been achieved by use of bulky isopropyl substituents as in **211**, while the incorporation of *meta*-linkages as in polymer **212** produces blue fluorescence.

Other methods have also been used to make PPVs with cyano substituents on the vinylene moiety. The copolymer **213** was made by Heck coupling of a bis(α-cyanostyryl)-benzene **214** made by a Knoevenagel condensation with a divinyl benzene.[653] It shows red (λ_{max} = 590 nm) EL with an efficiency of 0.062% in a double-layer device with PPV as a hole-transporting layer. Whereas the above polymers have an alternating structure, polymer **215** has a random structure and has been made by treating the bis-chloromethyl monomer of MEH-PPV **33** with cyanide followed by oxidation of the resulting precursor polymer **216** (Scheme 23).[654] The degree of conjugation can be tuned between 34% and 95% by varying the amount of oxidant used. The PL is orange-red (λ_{max} = 560−580 nm). Cyanostilbene units have themselves been used as electron-accepting substituents in polymer **217**, whose orange-red EL (λ_{max} = 583 nm) is reportedly 20 times more efficient than that of MEH-PPV.[655]



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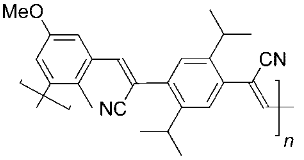

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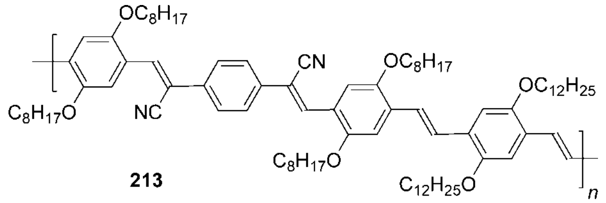

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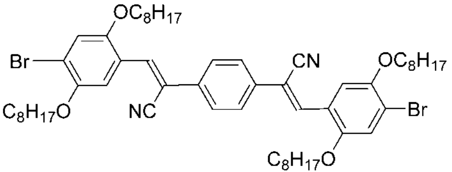

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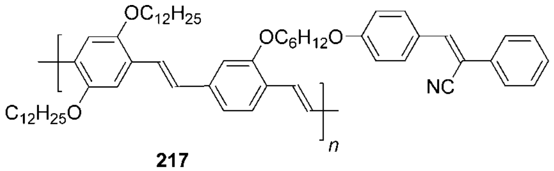

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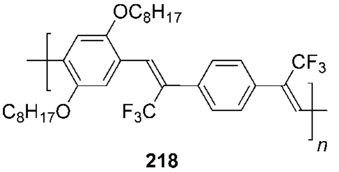

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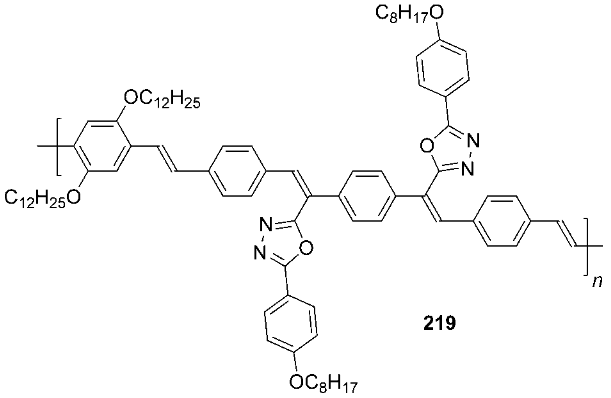

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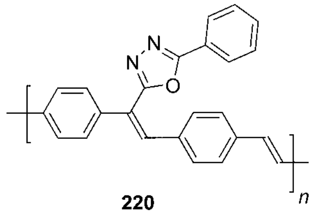

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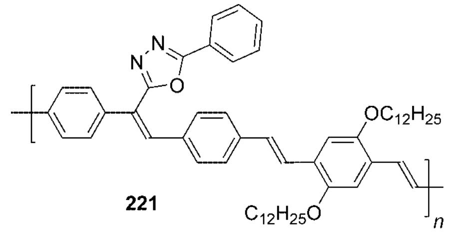

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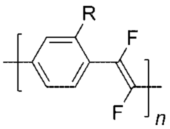
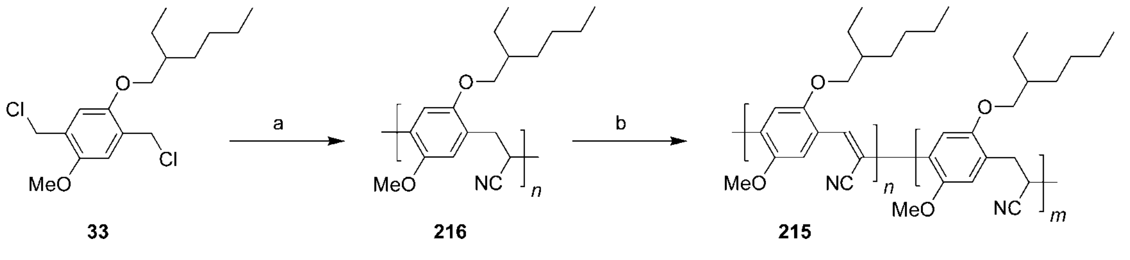


222a R = SiMe$_2$C$_8$H$_{17}$
222b R = H

Another electron-withdrawing substituent that can be attached to the vinylene moiety of PPVs by a polyconden-

Scheme 23. Preparation of a Nonalternating CN-PPV: (a) NaCN, Dioxan-Water, Reflux; (b) DDQ



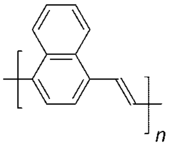
sation is trifluoromethyl. Lux et al. prepared the polymer **218** by Horner condensation of a bis-phosphonate with 1,4-bis(trifluoroacetyl)benzene.[656]

This polymer emits in the orange-red (λ_{max} = 590 nm) and shows strong electron affinity according to CV measurements. When used as an electron-transporting layer with PPV, the efficiency of the PPV emission increased from 0.002% to 0.4% with aluminum cathodes. The copolymer **219** with oxadiazole units on the vinylene moieties has been made by Heck coupling.[657] It exhibits yellow emission (λ_{max} = 565 nm), and the improvement in its electron accepting properties due to the oxadiazole units is shown by the similarity in efficiency for LEDs using aluminum (0.34%) and calcium (0.43%) cathodes. The brightness is higher and the turn-on voltage is lower for the latter. The related polymers **220** and **221** are reported to display blue-green (λ_{max} = 470, 503 nm) and green (λ_{max} = 517 nm) fluorescence, respectively.[658] The polymers **222** with fluorines on both of the vinylene carbons are made by a modified Gilch procedure using 1,4-bis(bromofluoromethyl)benzenes, in which the bromines are preferentially eliminated. These polymers are soluble in DMF and *o*-dichlorobenzene. The emission of the silyl-polymer **222a** (λ_{max} = 540 nm) is blue-shifted compared to that of the unsubstituted **222b** (λ_{max} = 565 nm), presumably due to steric interactions between the silyl and fluorine substituents, and its EL efficiency is about 6 times higher (2.7 cd/A vs 0.47 cd/A).[659]

2.6. Other Poly(arylene vinylene)s

Poly(arylene vinylene)s containing fused polycyclic arylenes cannot always be synthesized by the Wessling or related routes, as the quinodimethane intermediates do not always polymerize. For example, poly(1,4-naphthalene vinylene) (**223**) can be made by the Wessling method,[660,661] whereas poly(9,10-anthacene vinylene) (**224**) cannot be prepared in this way.[662] A study by Garay et al. found that the polymerizability of an arylene bis-sulfonium salt was determined by the enthalpy of formation of the quinodimethane intermediate, thus making it possible to predict if a given polymer is accessible by the Wessling route.[663]

The emission color of poly(naphthalene vinylene)s, like that of PPVs, depends upon the substitution pattern. Poly(1,4-naphthylene vinylene) ($P\bar{1}$,4-NV, **223**), which is prepared by the Wessling route,[660,661] shows yellow-orange EL (λ_{max} = 605 nm).[664,665] By contrast, poly(2,6-naphthalene vinylene) (P-2,6-NV, **225**) made by the sulfonium[666] or sulfinyl precursor routes,[139,667,668] shows green (λ_{max} = 518 nm) EL. The yield and molecular mass of **225** made by the Wessling route is reported to be lower than those for **223** prepared in the same way.



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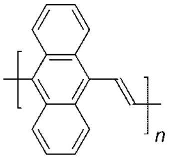

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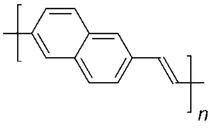

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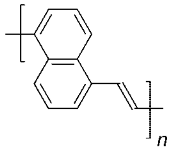

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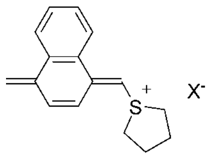
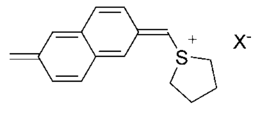
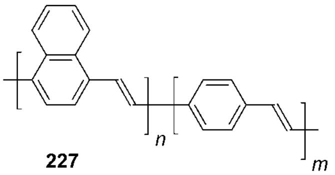


223a



225a

This has been rationalized as being due to the relative stability of the quinodimethane intermediates **225a**, in which all aromaticity is lost, and **223a**, in which aromaticity is retained in the unsubstituted ring.[666] Poly(1,5-naphthylene vinylene) ($P\bar{1}$,5-NV, **226**) has been obtained by the Gilch route as an insoluble powder, which shows blue PL (λ_{max} = 480 nm).[669] Copolymers of phenylene vinylene units with 1,4-naphthalene vinylene units (**227**) and 2,6-naphthalene vinylene units (**228**) have been prepared by the Wessling route.[670−673] As with the homopolymers, the yield and molecular masses for the 1,4-naphthalene copolymers **227** are greater than those for their 2,6-naphthalene containing analogues **228**. The yield is also reported to be greater for copolymers **227** with higher proportions of naphthalene units. The color of the copolymers' PL and EL emission is tunable between the colors of the homopolymers by controlling the ratio of comonomers; for example, copolymer **227** with 50% naphthalene units shows an EL maximum at 580 nm.[672] Ternary copolymers **229** with tetrafluorophenyl units have also been made by the Wessling route, but in low yield and molecular mass.[672] The PL maximum of the copolymer **229** with 50% naphthalene and 10% tetrafluorophenyl units is at about 550 nm. Self-assembled multilayers of the copolymers **229** and nonconjugated insulating polymers have been prepared and found to display much greater stability and emission efficiency.[674] The EL emission color of the self-assembled layers was red-shifted with respect to that for spin-coated films of **227**.[671,673] The PL emission color could also be tuned for assemblies of copolymer **227** by altering the thickness of the nonconjugated spacer layers.[203]



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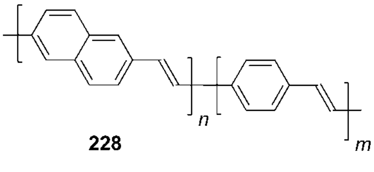

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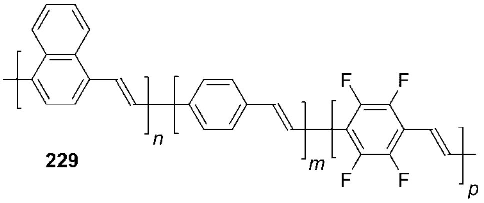
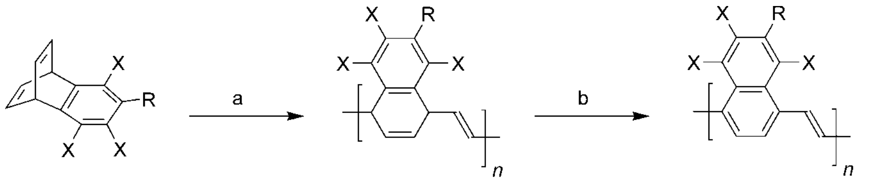


229

The above polymers and copolymers are insoluble, as they lack solubilizing groups. Grubbs and co-workers have prepared soluble alkylated PNV derivatives **230a−c** by oxidation of a precursor obtained by ROMP polymerization

Scheme 24. Synthesis of Soluble PNVs by ROMP: (a) $\mathrm{Mo({=}CHCPhMe_2)({=}NC_6H_3Me_2)[OCMe(CF_3)_2]_2}$; (b) DDQ



231 R = alkyl, X = H, F, Cl

232 R = alkyl, X = H, F, Cl

230a R = alkyl, X = H
230b R = alkyl, X = F
230c R = alkyl, X = Cl

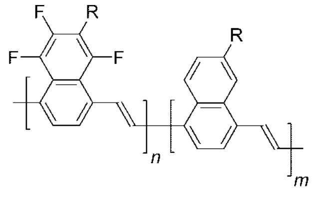
of alkyl benzobarrelenes **231**, followed by oxidation of the resulting precursor polymers **232** with DDQ (Scheme 24).[675−678]

The halogenated polymers **230b−c** show slightly red-shifted PL ($\lambda_{\max}$ = 568, 579 nm) compared with the unhalogenated **230a** ($\lambda_{\max}$ = 551, 561 nm). The EL of polymer **230a** is red-shifted with respect to the PL to give red-orange light ($\lambda_{\max}$ = 620 nm).[675] Since ROMP is a living process, it is possible to use it to prepare block copolymer **233**, which shows PL emission very similar to that of **230a** ($\lambda_{\max}$ = 568, 577 nm).[677,678] Other soluble PNVs have also been made by ROMP.[679] Substitution with alkoxy groups leads to a blue-shift in the emission, due to steric interactions between the substituents causing out-of-plane twisting of the polymer backbone. Thus, polymers **234a,b** show solid-state PL emission maxima at 534 and 549 nm, respectively, with the rather low efficiencies of 15% and 7%, respectively. A block copolymer **235** with a disubstituted phenylene vinylene unit shows emission from both the phenylene vinylene ($\lambda_{\max}$ = 492 nm) and naphthalene vinylene ($\lambda_{\max}$ = 581 nm) segments with a slightly higher efficiency of 18%. The alternating copolymer **236** with dialkoxy-1,5-naphthalene groups has been made by Heck coupling.[680] It shows blue PL in solution ($\lambda_{\max}$ = 466 nm), which is significantly red-shifted in the solid state ($\lambda_{\max}$ = 542 nm). The cyano-PNV **237** made by Knoevenagel condensation shows green EL in a single-layer device ($\lambda_{\max}$ = 500 nm).[681,682] Two-layer devices with PPV show emission from both layers, while a two-layer device using a copper phthalocyanine hole-transporting layer shows a slightly red-shifted EL maximum ($\lambda_{\max}$ = 527 nm).[683] Varying the substitution patterns as in the copolymers **238−239** containing alternating 2,6- and 1,5-naphthalene units produces only minor changes in the PL spectra ($\lambda_{\max}$ = 499 and 506 nm, respectively), but only **238** exhibits EL ($\lambda_{\max}$ = 513 nm).[683]

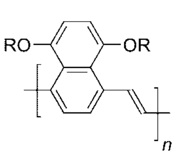
A number of soluble PNV-PPV copolymers have been prepared. Copolymers **240** of 1,5-naphthalene vinylene and MEH-phenylene vinylene units made by the Gilch route, containing less than 50 mol % of PNV are soluble in organic solvents, in which they show green-yellow PL ($\lambda_{\max}$ = 537−551 nm).[669] Yellow EL ($\lambda_{\max}$ = 586 nm) has been obtained from the 1:1 copolymer. The 2,6-NV-PV copolymers **241a,b** made by Horner polycondensation show blue PL ($\lambda_{\max}$ = 480 and 470 nm, respectively). The *meta*-phenylene unit in **242** induces a blue-shift in the emission ($\lambda_{\max}$ = 435 nm).[600] The 1,6-NV copolymer **243a** has also been made by the Horner route.[491] It shows green EL ($\lambda_{\max}$ = 542 nm) with a low (<3 V) turn-on voltage. The similar copolymer **243b** was prepared by Heck coupling.[680,684] It shows blue-green PL in solution ($\lambda_{\max}$ = 499 nm) which is slightly red-shifted ($\lambda_{\max}$ = 515 nm) in the solid state. The solid-state PL efficiency is 33%, which is more than double that of the similar PNV **237**.

The polymer **244a** with alternating MEH-PV and 1,4-NV units was made by Wittig polycondensation.[443] The PL is green in solution ($\lambda_{\max}$ = 542 nm), with a marked red-shift into the yellow in the solid state ($\lambda_{\max}$ = 565, 606 nm). Even more red-shifted emission ($\lambda_{\max}$ = 590 nm) is seen from copolymer **244b**.[685] The 1,5-NV-PV alternating copolymers **245**, by contrast, are blue-green emitters ($\lambda_{\max}$ = 486−491 nm).[685] A series of 2,6-NV-PV copolymers **246a−c** with cyano substituents on the vinylene have been made by Knoevenagel polycondensation.[5] Copolymer **246a** with unsubstituted phenylene units shows a PL maximum at 555 nm. This is blue-shifted by alkyl substitution in **246b** ($\lambda_{\max}$ = 530 nm) and red-shifted by alkoxy substitution in **246c** ($\lambda_{\max}$ = 595 nm).

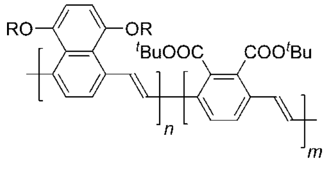
The alternating copolymers **247−249** containing dialkylfluorene units are also organic solvent soluble. The 1,4-naphthalene copolymer **247** shows more red-shifted EL ($\lambda_{\max}$ = 523 nm) than the 2,6-naphthalene analogue **248** ($\lambda_{\max}$ = 484 nm).[686] The PL from the 1,2-naphthalene derivative **249** is strongly blue-shifted ($\lambda_{\max}$ = 465 nm) due to the steric



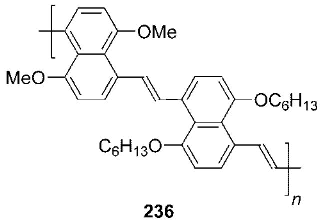
233 R = alkyl



234a R = 2-ethylhexyl
234b R = C_8H_{17}



235 R = 2-ethylhexyl



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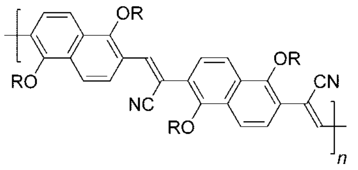
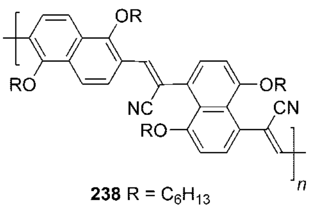
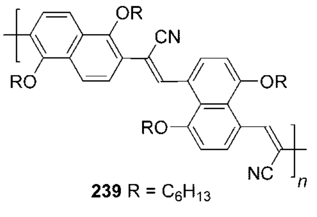


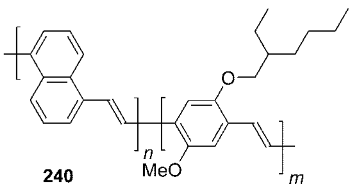
237 R = C_6H_{13}



238 R = C_6H_{13}



239 R = C_6H_{13}



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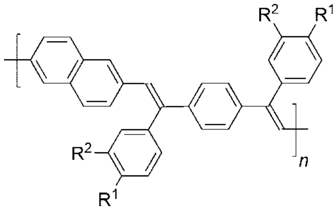
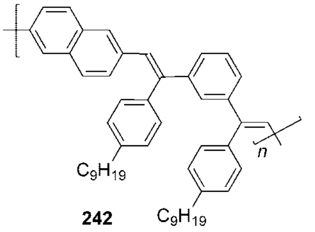


241a $R^1 = C_9H_{19}$, $R^2 = H$
241b R^1, $R^2 = OMe$



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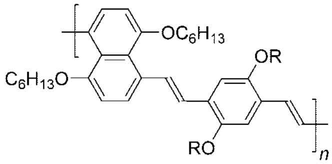
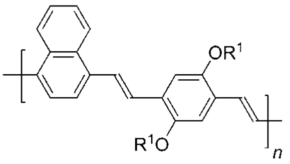
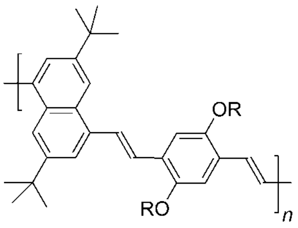


243a $R = NPh_2$
243b $R = OC_{12}H_{25}$

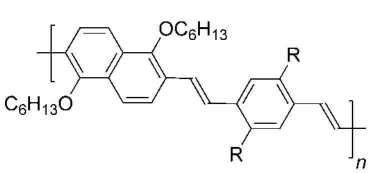


244a R^1 = 2-ethylhexyl, R^2 = Me
244b R^1, $R^2 = C_6H_{13}$

interactions between the *ortho*-substituents twisting the polymer backbone. The 1,4-naphthalene carbazole copolymer **250** produces yellow EL ($\lambda_{max} = 553$ nm), whereas the 2,6-naphthalene analogue **251** produces white EL with a maximum at 496 nm, a long tail into the red, and an excimer band at 730 nm.[687]

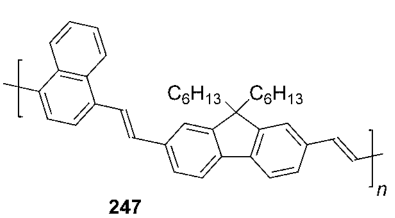


245 $R = C_6H_{13}, C_{10}H_{21}, C_{14}H_{29}$

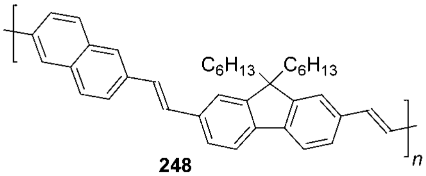


246a R = H
246b $R = C_6H_{13}$
246c $R = OC_6H_{13}$

As mentioned above, poly(9,10-anthracene vinylene) (**224**) cannot be made by the Wessling route. A series of oligomers have been prepared, from which it was estimated that the band gap of **224** should be 2.15 eV.[662] A soluble derivative **252** has been made by a route analogous to that used for soluble PNVs above, involving the ROMP of a dibenzobarrellene, followed by dehydrogenation of the resulting precursor polymer **253**.[688] The PL of **252** is red-orange (λ_{max} = 580 nm), with a band gap of 2.4 eV measured by cyclic voltammetry. An alternating copolymer with MEH-PV units **254** has been made by the Wittig[443] and Horner[689] routes and shows red-orange (λ_{max} = 600 nm) EL.[689]



247



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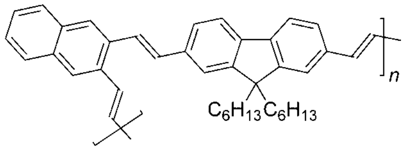

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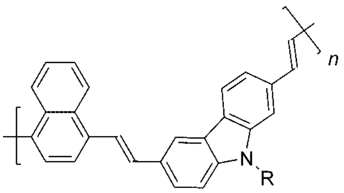

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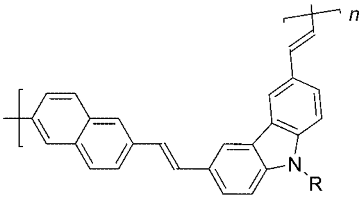
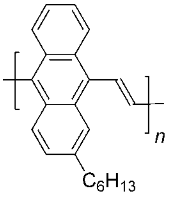


251

Poly(3,6-phenanthrylene vinylene) (**255**), whose emission is slightly blue-shifted (λ_{max} = 515 nm) with respect to PPV, has been prepared by oxidative photocyclization of an α-siloxy PPV precursor polymer **13**.[161,690] An alternating copolymer **256** made by Heck coupling of a 2,7-diodotetraalkoxyphenanthrene with a divinylbenzene displays green emission (λ_{max} = 499 nm) in solution.[691]



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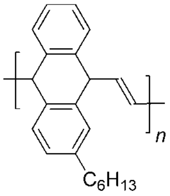

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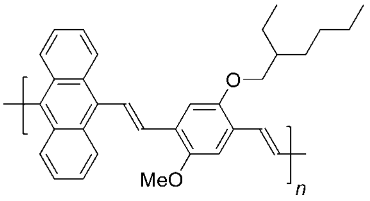
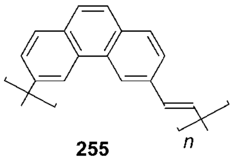


254

PPV (**1**) may be thought of as an alternating copolymer of phenylene and ethene units. Since polyphenylenes are blue emitters (see section 3 below), increasing the amount of phenylene content might be expected to produce a blue-shift in the emission of a PPV derivative. Accordingly, there has been some interest in the synthesis of poly(oligophenylene vinylene)s. Poly(4,4-biphenylene vinylene) (**257**) has been prepared by the sulfinyl precursor route and found to show green-blue PL and EL (λ_{max} = 467, 497 nm).[139,667,668]



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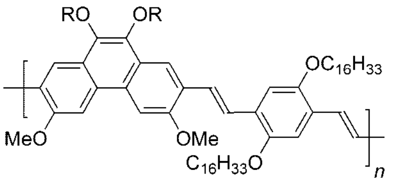
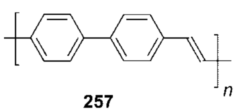


256 R = 2-ethylhexyl



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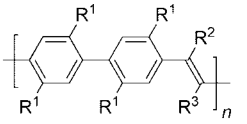
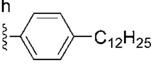


259a R^1 = alkyl, R^2, R^3 = H

259b R^1 = H, R^2, R^3 = alkyl

259c R^1, R^3 = H, R^2 = Ph

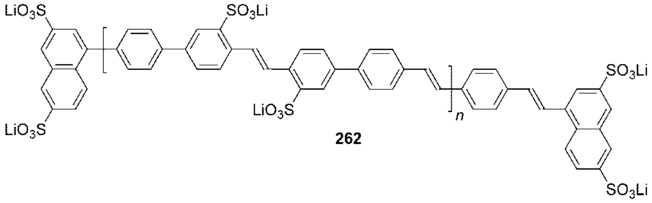
259d R^1 = H, R^2, R^3 = Ph

259e R^1 = H, R^2, R^3 = 

259f R^1 = H, R^2, R^3 = Ph

This polymer is insoluble, but a variety of soluble substituted derivatives can be prepared by a wide range of synthetic methods (Scheme 25). Nickel(0) coupling of dibromostilbenes **258** has been used by several groups to make polymers with substituents on either the aryl or the vinylene moieties.[601,692−698] Blue emission is obtained from polymers with alkyl substituents on the ring, as in **259a** (λ_{max} = 418−426 nm), or the vinylene, as in **259b** (λ_{max} = 443−460 nm),[692−694] and also from polymer **259c** (λ_{max} = 460 nm), with one phenyl group on the vinylene.[698] By contrast, polymers with two phenyl substituents on the vinylene, as in **259d−e**, reportedly show green emission (λ_{max} = 512−527 nm).[601,692−694,697] A study[601] on the emissive properties of the diphenyl derivative **259d** containing various ratios of *cis* and *trans* double bonds found that a 1:1 *cis*/*trans* ratio gave the highest solid-state PL efficiency (41%, λ_{max} = 515 nm). Other ratios not only gave lower efficiencies but also showed a slight red-shift in emission (λ_{max} = 523 nm). The polymer **259d** has also been prepared by McMurry coupling of dibenzoylbiphenyl **260** (Scheme 25).[699−701] The material made by this route has been found to have a 1:1 ratio of *cis* and *trans* double bonds.[601] Green emitting LEDs have been made using it. Multilayer devices with PPV and PVK were found to give much higher efficiencies.[702] A novel route to biphenylene vinylene polymers used by Sengupta et al.[703] is the Heck coupling of bis-diazonium salts with vinyltriethoxysilane. The polymers **261a,b** made by this method show blue PL (λ_{max} = 465 and 430 nm, respectively).

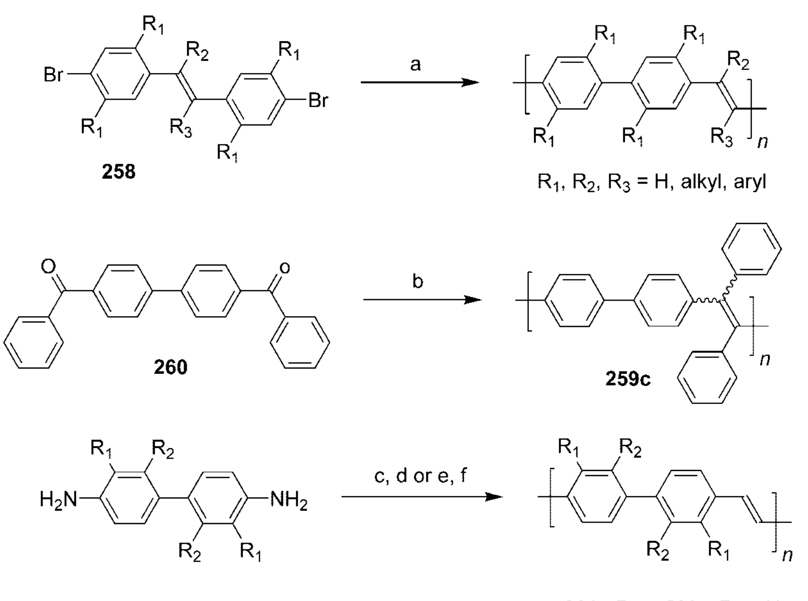
The sulfonate groups in **262** can bind to cyclodextrins to form a soluble polyrotaxane, which shows better LED performance than the uncomplexed polymer.[704]



262

Increasing the bulkiness of the aryl substituents as in **263** causes a major blue-shift in emission (λ_{max} = 353 nm) due to increased out-of-plane twisting of the polymer chain.[697] Similar but smaller blue-shifts are produced by the extra bulk of the pentafluorophenyl substituents in **259f** (λ_{max} = 505 nm), and the *meta*-linkages in **264** (λ_{max} = 495 nm),[601] and **265** (λ_{max} = 493 nm).[705] The polymer **266a** made by nickel(0) coupling of a dibromostilbene with a fluorene

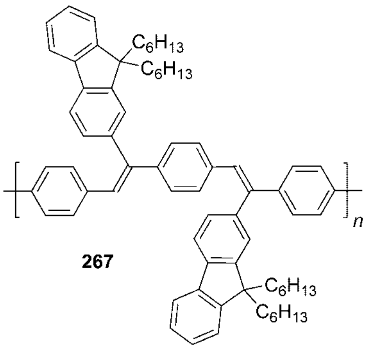
Scheme 25. Routes to Substituted Poly(biphenylene vinylene)s: (a) Ni(0); (b) $TiCl_3$, $LiAlH_4$; (c) $NaNO_2$, HCl, $NaBF_4$; (d) $CH_2{=}CHSi(OEt_3)$, $Pd(OAc)_2$, EtOH, 80 °C; (e) $NaNO_2$; HCl, morpholine; (f) $CH_2{=}CHSi(OEt)_3$, $Pd(OAc)_2$, EtOH, 70% $HClO_4$, 80 °C



261a R_1 = OMe, R_2 = H

261b R_1 = H, R_2 = CO_2Me

substituent on the vinylene moiety shows blue EL (λ_{max} = 465 nm).[695,696] The EL efficiency is enhanced nearly 7-fold by blending with PVK, which also produces a small red-shift in the emission (λ_{max} = 470 nm). The copolymer with fluorene **266b** shows almost identical emission (λ_{max} = 468 nm) to **266a**.[706] Blue emission has also been obtained from the copolymers **267** (λ_{max} = 480 nm) and **268** (λ_{max} = 473 nm).[707]



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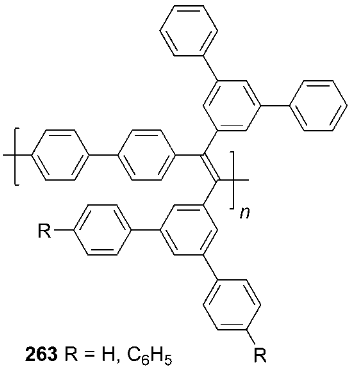
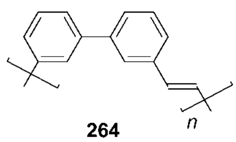


263 R = H, C_6H_5



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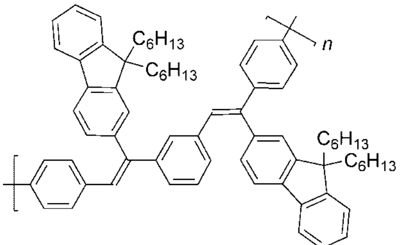

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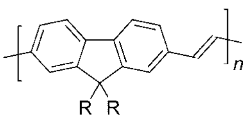
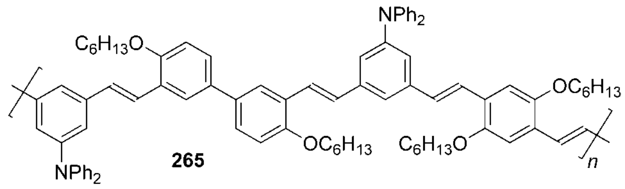


269a R = C_8H_{17}

269b R = C_6H_{13}



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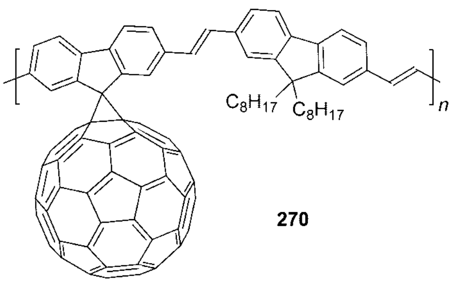

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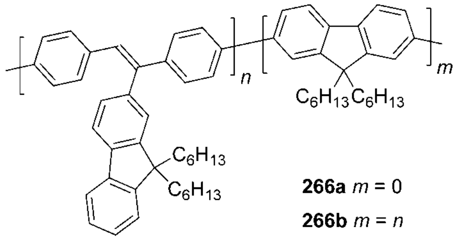
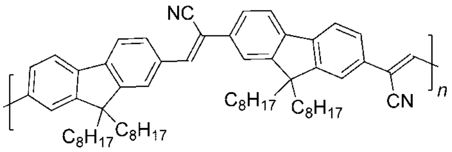


266a *m* = 0

266b *m* = *n*



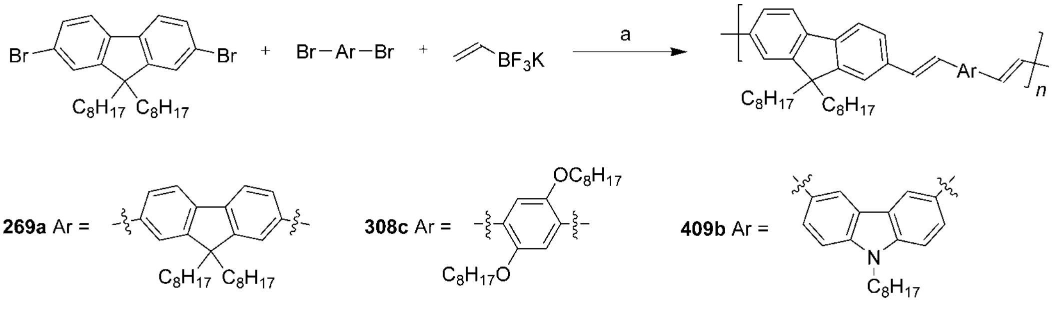
271

Poly(9,9-dioctyl-2,7-fluorenyl vinylene) (PFV, **269a**) has been made by the Gilch route,[708] by cross metathesis polymerization of a divinylfluorene,[709] by Heck coupling,[710] by Horner coupling,[711] and by a new cascade Suzuki−Heck process (Scheme 26).[712] The Horner route is reported to give the most defect-free material. The *all-trans* polymer shows blue-green PL emission very similar to that of **257** (λ_{max} = 465, 497 nm).

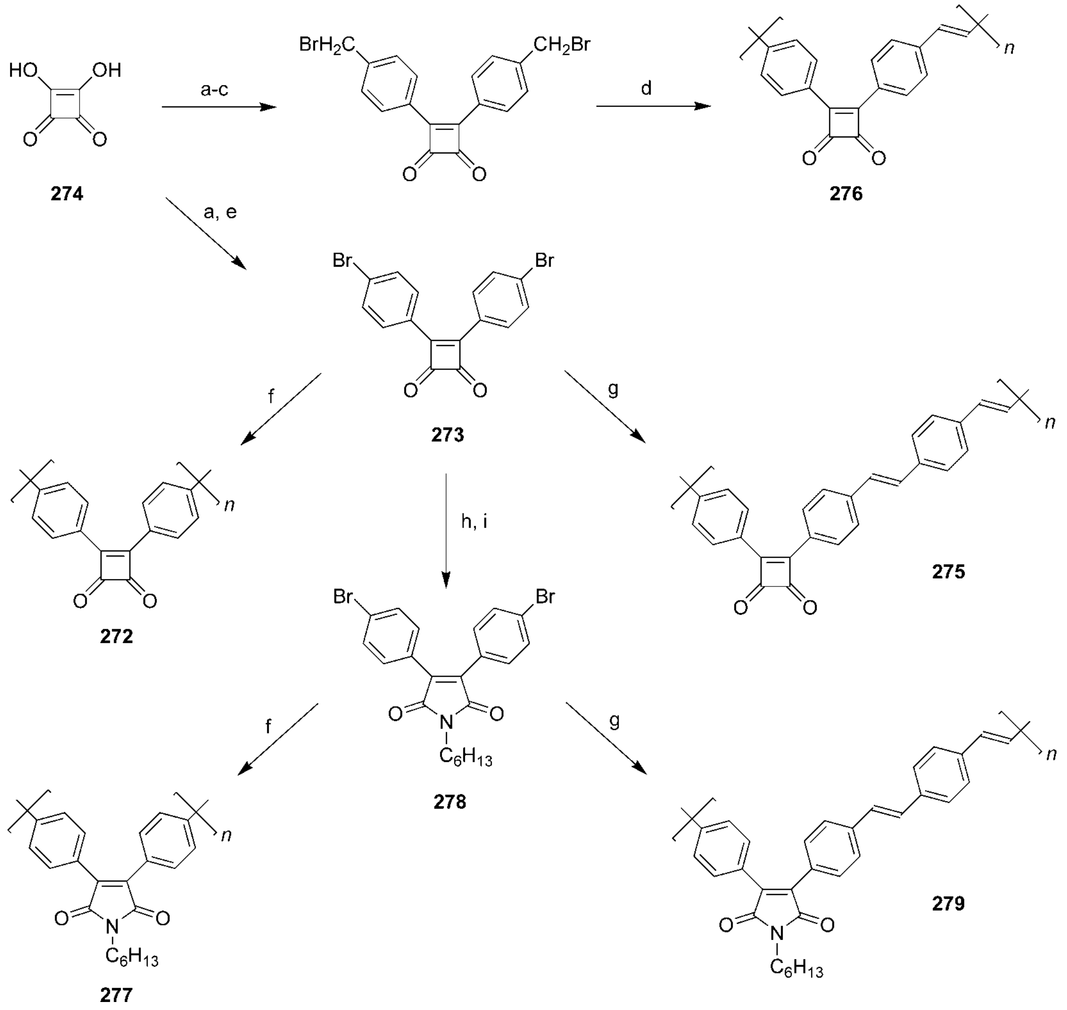
Broad EL emission extending into the red around 700 nm has been reported for the dihexylfluorene polymer **269b** made by the Heck route.[713] A copolymer **270** with C60 substituents made by the Horner route produces blue EL (λ_{max} = 450 nm).[714] Since C60 is a good quencher of emission, it may be difficult to interpret this result. The cyano-substituted polymer **271** is green emitting (λ_{max} = 530 nm).[715]

Poly(biphenylene vinylene)s with the double bond locked into the *cis*-configuration have been made. Polymer **272**, with the vinylene incorporated into a cyclobutenedione ring, was made by nickel(0) coupling of the dibromo monomer **273** derived from squaric acid (**274**) (Scheme 27).[716,717] It shows blue PL (λ_{max} = 471 nm). The alternating copolymer with PPV **275** made by Heck coupling of **273** with divinylbenzene exhibits green PL (λ_{max} = 522 nm).[717] The copolymer **276** with alternating *cis*- and *trans*-double bonds, made by the Gilch route, shows an exceptionally large red-shift in the

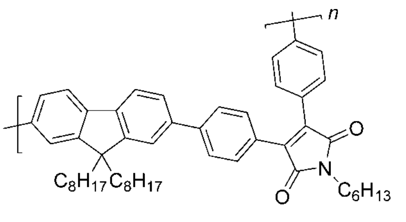
Scheme 26. Cascade Suzuki−Heck Route to Fluorenylene Vinylene Polymers: (a) Pd(PPh$_3$)$_4$, K$_2$CO$_3$



Scheme 27. Synthesis of Polymers with Diarylcyclobutenedione and Diarylmaleimide Units: (a) $SOCl_2$; (b) Toluene, $AlCl_3$; (c) NBS, CCl_4; (d) KO^{t}Bu, 18-crown-6, Toluene; (e) $BrC_6H_4B(OH)_2$, $Pd(PPh_3)_4$; (f) $NiCl_2$, Zn, PPh_3, DMF; (g) 1,4-Divinylbenzene, $Pd(OAc)_2$, P(*o*-tolyl)$_3$, DMF; (h) mCPBA; (i) $C_6H_{13}NH_2$



PL spectrum in going from blue-green emission in solution (λ_{max} = 472 nm) to orange emission in the solid state (λ_{max} = 574 nm).[718] By contrast, the poly(diarylmaleimide) **277** made via Baeyer–Villiger oxidation of **273** to **278** (Scheme 27) shows green-yellow PL (λ_{max} = 539 nm).[719] Heck coupling of the monomer **278** with divinylbenzene gives copolymer **279**, which shows orange emission (λ_{max} = 570 nm) in benzene solution.[720] Suzuki polycondensation of **278** with a fluorene bis-boronic acid produces the yellow-orange emitting (λ_{max} = 560 nm) copolymer **280**.[721]



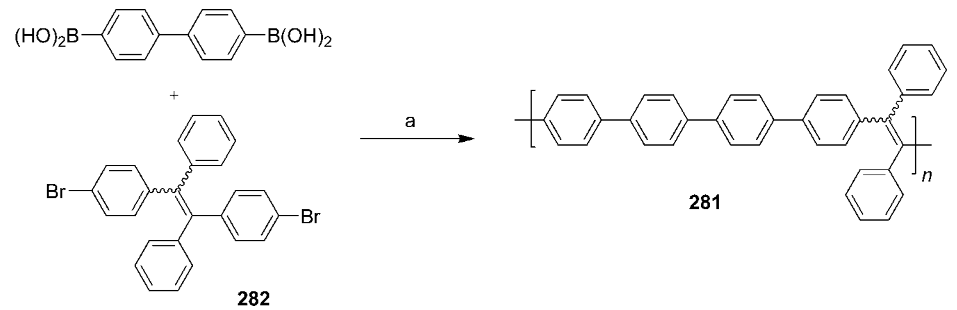
280

Other poly(oligoarylene vinylene)s are made by Suzuki coupling of oligoarylene and stilbene units as exemplified by the synthesis of poly(tetraphenylene diphenylvinylene) (**281**) (Scheme 28).[601] By varying the ratio of *cis*- and *trans*-dibromostilbene **282** used, the ratio of *cis*- to *trans*-vinylene units can be controlled. Increasing the *cis*-vinylene content from 32% to 62% has been found to increase the molecular mass of the polymer, with a concomitant red-shift in the emission from λ_{max} = 517 to 533 nm. The highest solid-state PL efficiency (53%) was obtained from the polymer with 48% *cis*-vinylene content (λ_{max} = 520 nm), consistent with the results obtained for the diphenylene vinylene polymers **259** above.

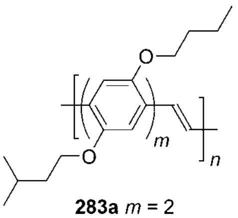
Polymers **283a–c** have been prepared by Neher and co-workers.[722,723] As expected, the emission blue-shifts with increasing phenylene content from λ_{max} = 480 nm for **283a** to λ_{max} = 446 nm for **283c**. This shift is accompanied by an increase in the solid-state PL efficiency from 9% to 49%, though the efficiencies in solution decrease slightly from 56% to 49%. A copolymer **284** with a 4:1 ratio of terphenyl to pentaphenyl units shows emission from the terphenylene units (λ_{max} = 480 nm), but with a much higher solid-state efficiency (40%).

Similarly, a statistical copolymer **285** (Chart 1) with a mixture of ter- (m = 3), penta- (m = 5), and heptaphenylene (m = 7) units with an average of five phenylenes per vinylene shows a PL spectrum similar to that of the pentaphenylene homopolymer **283c** (λ_{max} = 448 nm), but with a much higher PL efficiency (69%). The EL spectra of these polymers are slightly red-shifted compared with the solid-state PL spectra. The highest EL efficiency (4%) was obtained from a triple-layer device using the polymer **284** with hole and electron

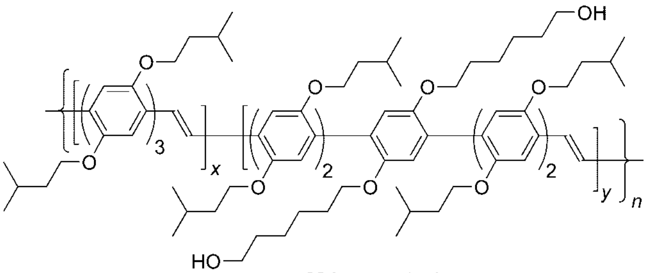
Scheme 28. Synthesis of Poly(tetraphenylene diphenylvinylene): (a) Pd(0), Base, THF



transporting layers and a calcium cathode. Incorporation of ethanediyl units in the polymer **286** (*m*/*n* = 4:1) produces a small (<5 nm) blue-shift in the emission but a major increase in both solid-state PL (45% cf. 9%) and EL efficiency (1.4% cf. 0.4% for triple-layer devices).[722,723] Bulky alkyl substituents on the vinylene moiety in polymer **287** induce a marked blue-shift in the PL emisssion (λ_{max} = *ca.* 400 nm), due to increased out-of-plane twisting of the backbone to minimize steric interactions.[724] By contrast, phenyl groups on the vinylene, as in the polymer **288**,[725] or the fluorenyl substituents in the polymer **289**[707,726] do not produce such marked twisting of the backbone, as the PL and EL emission of such polymers is blue or blue-green (λ_{max} = 450−466 nm).[725−728] The use of *meta*-linkages in polymer **290**[707] or **291**[729] does produce a blue-shift in emission (λ_{max} = 454 and 463 nm, respectively), due to reduced conjugation. Polymers **292** with >95% *cis*-vinylene units have been prepared, but the emission was found to occur from the residual (1−5%) units with *trans*-vinylene moieties (λ_{max} = 447 and 490 nm, respectively), illustrating the tendency for emission in conjugated polymers to occur from the lowest energy site available.[729] Other aryl units can readily be incorporated by the Suzuki methodology; e.g. the bis-anthracene units in polymer **293**.[729] Due to low solubility, the material obtained is oligomeric (n = 5) with blue PL emission (λ_{max} = 458 nm).

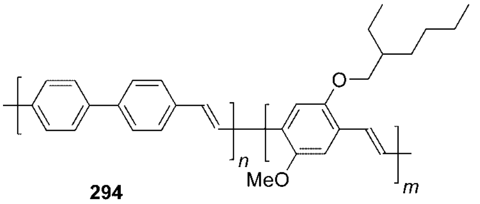


283a $m = 2$
283b $m = 3$
283c $m = 5$



284 $x : y = 4 : 1$

Copolymers with a mixture of oligoarylene vinylene and phenylene vinylene units can be prepared in several ways. A random copolymer **294** containing biphenylene vinylene and MEH-phenylene vinylene units, made by the Gilch route, shows emission peaks in the blue (λ_{max} = 464, 495 nm) and orange (λ_{max} = 590 nm) corresponding to the two homopolymers, while an alternating copolymer **295a** made by the Horner route shows yellow-green (λ_{max} = 550 nm) emission.[730] Other soluble copolymers of biphenylene vinylene with RO-PPVs **295b**−**c** show green EL (λ_{max} = 511−516 nm).[731] In alternating copolymer **296** made by the Wittig route, the bulky phenyl substituents cause a hyperchromic shift in the emission so that the EL is blue (λ_{max} = 450 nm).[732] The Wittig method has been used to make the twisted biphenylene copolymers **297**, whose PL emission can be varied from green to blue by altering the proportions of the comonomers.[733]



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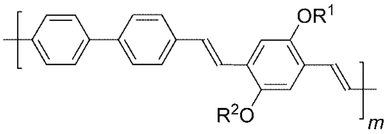
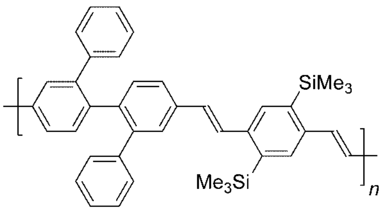


295a R^1 = Me, R^2 = 2-ethylhexyl
295b R^1, R^2 = C_6H_{13}
295c R^1, R^2 = $(CH_2CH_2O)_2CH_2CH_3$



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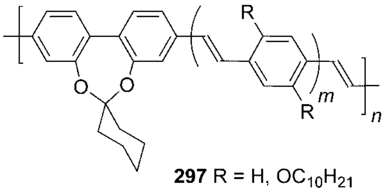
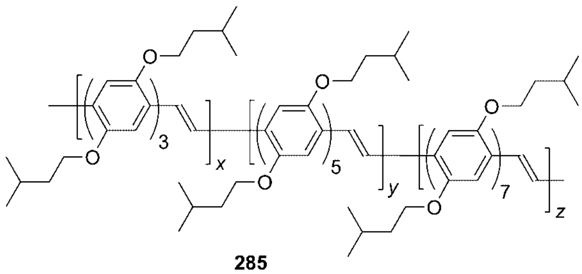


297 R = H, $OC_{10}H_{21}$

Copolymer **298** with malonate substituents on the vinylene units has been made by Endo and co-workers using a three-component one-pot palladium-catalyzed coupling method (Scheme 29).[734] It shows blue-green EL (λ_{max} = 475 nm).

Chart 1



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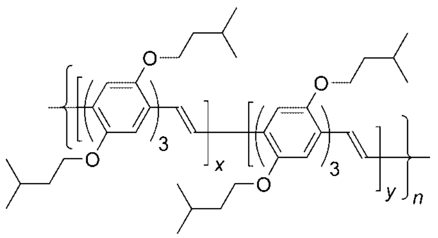
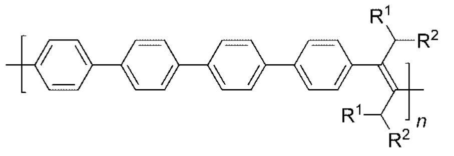
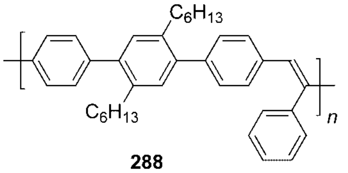


286 $x : y = 4 : 1$



287 $R^1 = R^2 = C_4H_9, C_6H_{13}$



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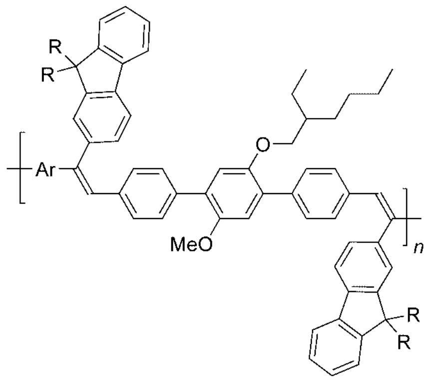
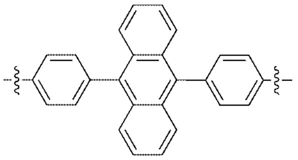
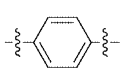




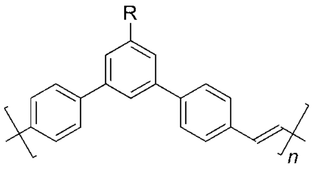
289a Ar =

$R = C_6H_{13}$

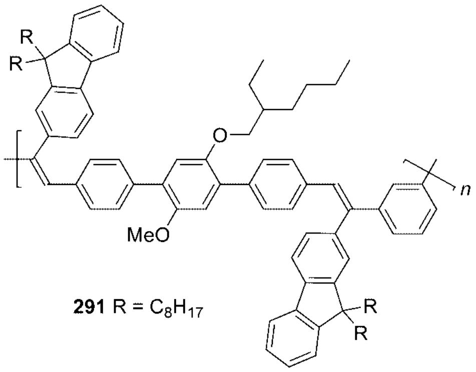


289b Ar =

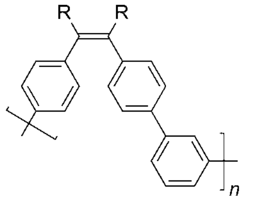
$R = C_8H_{17}$



290 R = alkyl

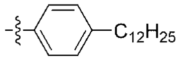


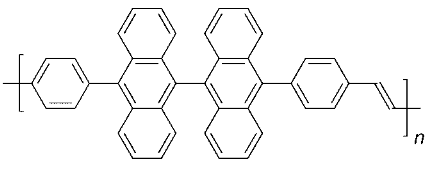
291 $R = C_8H_{17}$



292a $R = C_{11}H_{23}$

292b R =



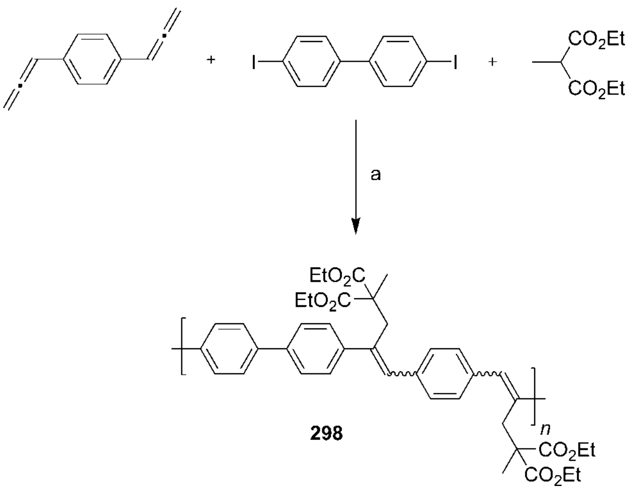


293

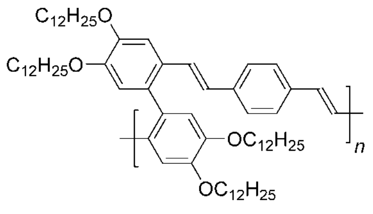
Copolymer **299** with *ortho*-substituted biphenyls has been made by Horner coupling and shows blue PL ($\lambda_{max} = 452$, 477 nm) with a high (76%) solid-state quantum efficiency.[735] Copolymers such as **300a**−**c** with *meta*-biphenylene units have also been made by this method.[736,737] Polymer **300a** with unsubstituted biphenyl units produces blue-green EL ($\lambda_{max} = 484$ nm), which is only slightly red-shifted by the *ortho*-alkoxy units in **300b** ($\lambda_{max} = 492$ nm) or the *para*-alkoxy groups in **300c** ($\lambda_{max} = 511$ nm). Whereas the PL efficiencies are greatest for **300c** (42%) and smallest for **300a** (26%), the EL efficiencies follow the reverse order (0.0082% vs 0.17%).

Random copolymers **301a** of 2,7-fluorenyl vinylene with phenylene vinylene units ($m = 9-41\%$) made by the Gilch method produce blue-green EL ($\lambda_{max} = 472-475$ nm),[738] while the corresponding copolymers with MEH-phenylene

Scheme 29. Three Component Synthesis of Substituted Biphenylene Vinylene−Phenylene Vinylene Alternating Copolymer 298: (a) Pd(OAc)$_2$, P(*o*-tolyl)$_3$, Dioxan, 80 °C



vinylene units **301b** ($m = 5-50\%$) display yellow or orange EL ($\lambda_{max} = 574-592$ nm) with an optimal EL efficiency at 10% MEH-PPV units.[739]



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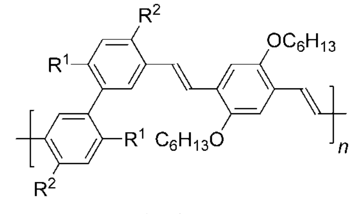
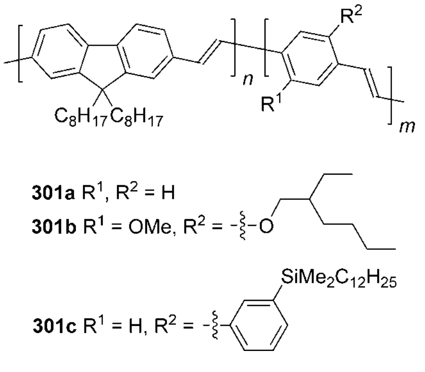
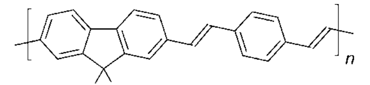


300a R^1, R^2 = H
300b R^1 = OC_6H_{13}, R^2 = H
300c R^1 = H, R^2 = OC_6H_{13}

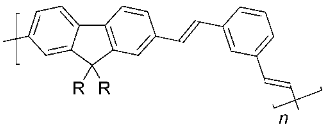


301a R^1, R^2 = H
301b R^1 = OMe, R^2 = -O
301c R^1 = H, R^2 =

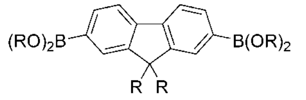
Copolymers of 2,7-fluorenyl vinylene with an arylphenylene vinylene **301c** containing more than 30% of the comonomer show green emission similar to that of the PPV homopolymers **159a**.[570] The highest EL efficiency (3.13 cd/A) was observed for the copolymer with 31% of phenylene units. The alternating dialkylfluorenylene vinylene−phenylene vinylene copolymers **302a** and **303a** have been made both by Wittig[740] and by Heck coupling.[710,741] A Suzuki polycondensation of a fluorene bisboronate **304** with the dibromide **305** has been used to make the copolymer **302b**.[742] The *meta*-linkage in **303a** causes a blue-shift in its EL emission ($\lambda_{max} = 426$ nm) compared with that of **302a** ($\lambda_{max} = 482$ nm).[740]



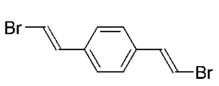
302a R = C_6H_{13}
302b R = 2-ethylhexyl
302c R = C_4H_9



303a R = C_6H_{13}
303b R = H



304 R = 2-ethylhexyl



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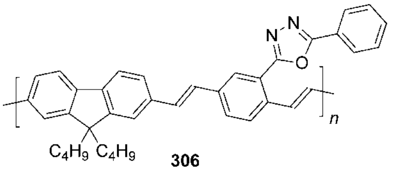

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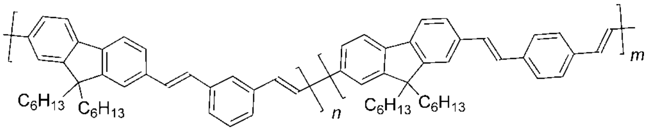
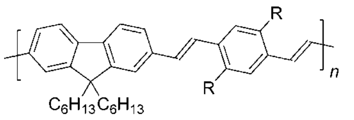


307

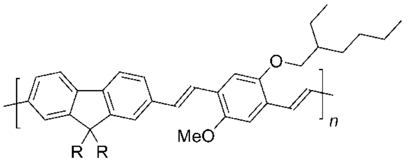
The oxadiazole units in **306** cause a marked red-shift in the solid-state emission compared with **302c** ($\lambda_{max} = 493$ nm *cf.* 473 nm) accompanied by a marked drop in the PL efficiency (14% vs 24%).[627] The monoalkylfluorenylene vinylene copolymer **303b** (made by the Wittig method) shows green ($\lambda_{max} = 560$ nm) EL due to formation of aggregates, but blue emission ($\lambda_{max} = 420$ nm) can be obtained by dilution with PVK to break up the aggregates.[743] A copolymer **307** containing a mixture of *para*- and *meta*-phenylene vinylene units, prepared by Heck coupling, shows PL emission from the former ($\lambda_{max} = 475$ nm).[741,744,745] The highest PL efficiency was obtained with 70% *meta*-linkages ($n/m = 7{:}3$). Substitution of alkoxy groups onto the phenylene unit leads to a red-shift in the PL emission of the polymers **308a**[710] ($\lambda_{max} = 495$ nm) and **309a**[746] ($\lambda_{max} = 540$ nm), which were made by the Wittig route. The copolymer **308b** with trimethylsilyl units, synthesized by the same method, shows blue-green PL ($\lambda_{max} = 495$ nm) with a much higher solid-state PL efficiency (81%) than for **309a** (26%). The EL ($\lambda_{max} = 500$ nm) efficiency of single-layer devices using **308b** with aluminum cathodes is reported to be 32 times higher than that for MEH-PPV devices with the same configuration.[746] Copolymer **308c** has been made by a cascade Suzuki−Heck process (Scheme 26),[712] while **308d**

(λ_{max} = 464 nm) has been made by Heck coupling.[747] The green emitting (λ_{max} = 507 nm) copolymer **310** with a 2,3-dialkoxyphenylene unit was made by Suzuki coupling of a fluorene bis-boronate with a dibromodistyrylbenzene.[416]

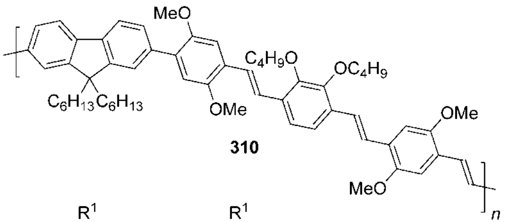
Hadziioannou and co-workers obtained the blue emitting (λ_{max} = 440 nm) copolymer **311a** in low (4500 Da) molar mass by Heck coupling of 1,4-divinylbenzene with substituted terphenyls.[748−751] The alkoxy-substituted polymer **311b** prepared by the same method shows a much higher molecular weight (39 kDa), and the emission is red-shifted to give blue-green (λ_{max} = 490 nm) EL.[750,751] The EL efficiencies are higher for **311a** than **311b** (0.02% cf. 0.009% with Al cathodes).[752] This method has since been used to make other blue emitting terphenylene vinylene copolymers.[753,754] Similar copolymers are also accessible by Wittig coupling, e.g. the green emitting (λ_{max} = 508 nm) copolymer **312a** and the yellow (λ_{max} = 555 nm) emitting **312b** containing an anthracene unit.[755] The Wittig method has also been used to make the blue emitting (λ_{max} = 430 nm) copolymer **313**.[756] Suzuki coupling of a dibromodistryrylbenzene with benzene bisboronate has been used to make the green-yellow emitting copolymer **311c** (λ_{max} = 524 nm).[455]



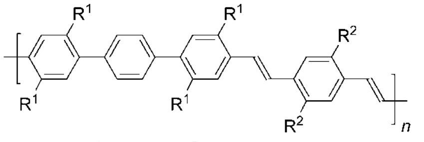
308a R = OC_6H_{13}
308b R = $SiMe_3$
308c R = Me



309a R = C_6H_{13}
309b R = C_8H_{17}

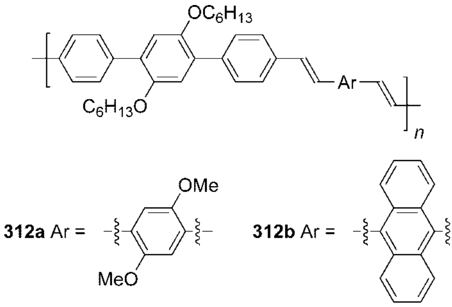


310

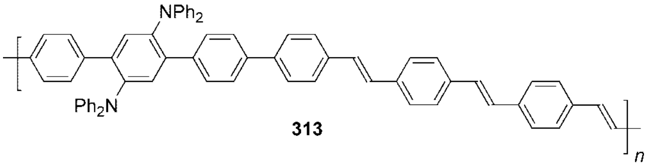


311a $R^1 = C_8H_{17}$, R^2 = H
311b $R^1 = OC_8H_{17}$, R^2 = H
311c R^1 = H, $R^2 = OC_6H_{13}$

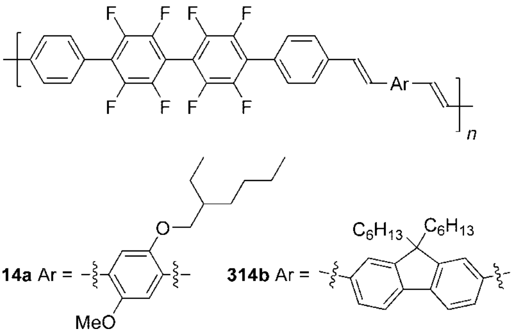
Some efforts have been made to improve injection of charge, especially of electrons, into poly(oligoarylene vinylene)s. Copolymers **314** with octafluorotetraphenylene units have been prepared by Horner coupling.[757] The copolymer with MEH-PV units **314a** shows blue-green EL (λ_{max} = 490 nm), while the fluorenyl copolymer **314b** shows blue EL (λ_{max} = 465 nm), but with a high (22 V) turn-on voltage. This suggests that the fluorine substituents do not improve charge injection into the polymer, despite their high electronegativity.



312a Ar = **312b** Ar =

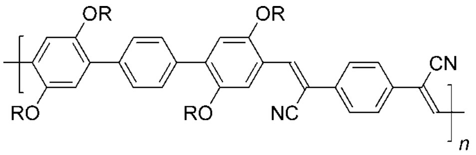


313

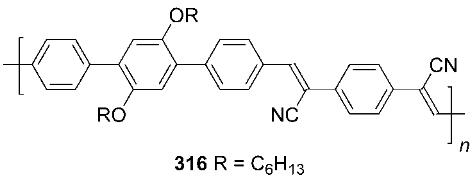


314a Ar = **314b** Ar =

Attachment of cyano groups onto the vinylene moieties has proved more successful. Poly(terphenylene vinylene)s **315** and **316** with alkoxy side-chains made respectively by Knoevenagel polycondensation[750] and by Suzuki coupling[758] show orange EL (λ_{max} = 570 and 590 nm, respectively). The EL efficiency of **315** is only slightly higher (0.023% *cf.* 0.02%) than that for the corresponding polymer **311b** without the cyano substituents.[750,752] The polymers **317a,b** have also been made by Suzuki coupling of a cyanostilbene with a benzene bis-boronate, but unlike the previous polymers, they show blue-green PL and EL (λ_{max} = 498 and 489 nm, respectively).[759−761] The dicyano-substituted polymer **317c** by contrast emits in the yellow (λ_{max} = 561 nm).[762] The tetraphenylene copolymers **318** have slightly blue-shifted emission (λ_{max} = 474−476 nm).[760,763] Advincula and co-workers have prepared the copolymers **319a−c** by the Knoevenagel route.[764] As expected, the emission from the *meta*-linked **319b** (λ_{max} = 468 nm) and *ortho*-linked **319c** (λ_{max} = 561 nm) polymers is markedly blue-shifted compared with that of the *para*-linked **319a** (λ_{max} = 547 nm) due to the reduced conjugation. The LED efficiencies of **319b** (0.73

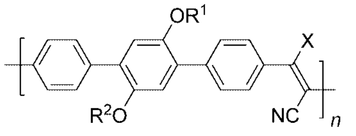


315 R = C_8H_{17}

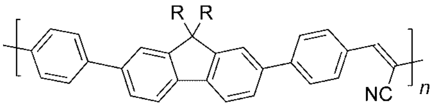


316 R = C_6H_{13}

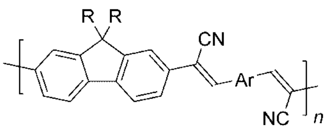
cd/A) and **319c** (0.12 cd/A) are considerably lower than those for **319a** (2.7 cd/A). The copolymer **319d** with electron-accepting cyano substituents on the vinylene and hole-accepting arylamine units on the phenylene has also been made by the Knoevenagel route.[491] It shows red EL (λ_{max} = 668 nm), with a very low (<3 V) turn-on voltage. The cyano-substituted copolymer **320a** has been made by Heck coupling and exhibits orange EL (λ_{max} = 599 nm).[765] Substitution of the central benzene with alkoxy groups (**320b**) increases the EL efficiency (from 0.07 to 0.21 lm/W) markedly but has little effect on the EL color, while replacing that benzene with a biphenyl (**320c**) blue-shifts the EL (λ_{max} = 557, 585 nm) while reducing the EL efficiency dramatically.

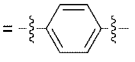


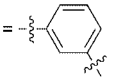
317a R^1 = 2-ethylhexyl, R^2 = Me, X = H
317b R^1, R^2 = C_6H_{13}, X = H
317c R^1, R^2 = C_6H_{13}, X = CN

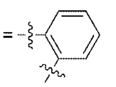


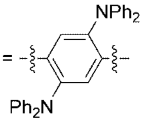
318 R = 2-ethylhexyl

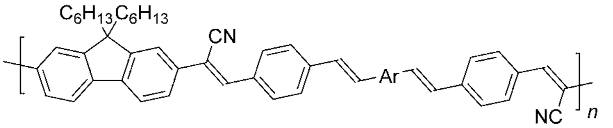


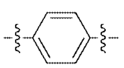
319a R = C_8H_{17}, Ar =


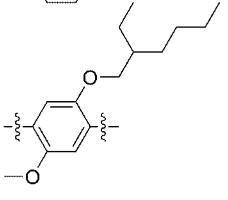
319b R = C_8H_{17}, Ar =


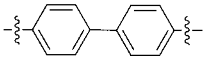
319c R = C_8H_{17}, Ar =


319d R = C_6H_{13}, Ar =


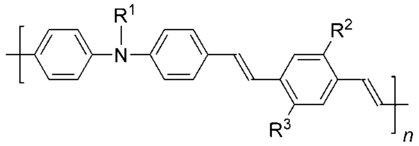


320a Ar =


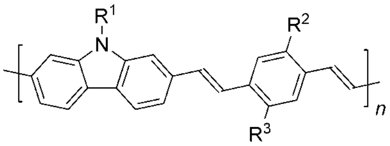
320b Ar =


320c Ar =


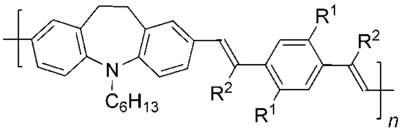
Whereas cyano groups can be expected to enhance the electron affinity of polymers, triphenylamines (TPAs) are hole-transporting units. Interestingly, unlike ether bridges, nitrogen bridges between aryl groups do not seem to totally interrupt the conjugation. As a result, polymers **321** with TPA groups in the main-chain, which are most commonly made by Wittig polycouplings, often produce emission only slightly blue-shifted from that of the corresponding polymers without the nitrogen bridges.[441,766,767] Thus, the EL from polymer **321a** is green (λ_{max} = 494 nm), while **321b,c** both show yellow-green emission (λ_{max} = *ca.* 550 nm). If the nitrogen bridge is part of a cycle, then the size of the ring affects the degree of conjugation. Thus, the emission from the carbazole copolymer **322a** (λ_{max} = 514 nm) is slightly red-shifted compared with that from the structurally similar copolymers **323a,b** (λ_{max} = 494−498 nm), which reflects the relative planarity of the two rings.[768,769] Cyano substitution in **323c** produces a marked red-shift in the EL (λ_{max} = 559 nm). Even though the nitrogen bridges do not appear to block through conjugation, the EL properties of nitrogen-bridged polymers will be discussed in more detail alongside those of materials with nonconjugative linkers (section 4.4 below).



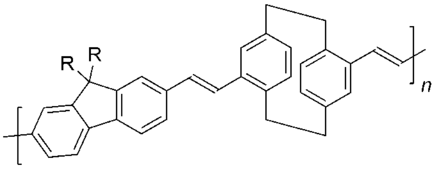
321a R^1 = Ph, R^2, R^3 = OC_8H_{17}
321b R^1 = C_6H_{13}, R^2, R^3 = H
321c R^1 = C_6H_{13}, R^2 = OMe, R^3 = 2-ethylhexyloxy
321d R^1 = Ph, R^2, R^3 = H



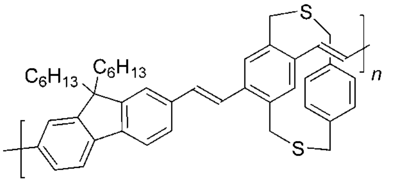
322a R^1 = 2-ethylhexyl, R^2, R^3 = OC_6H_{13}
322b R^1 = 2-ethylhexyl, R^2 = 2-ethylhexyloxy, R^3 = OMe
322c R^1 = 2-ethylhexyl, R^2, R^3 = $SiMe_3$



323a R^1, R^2 = H
323b R^1 = OC_6H_{13}, R^2 = H
323c R^1 = OC_6H_{13}, R^2 = CN

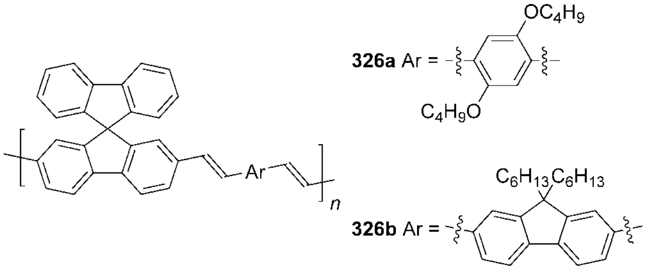


324 R = alkyl



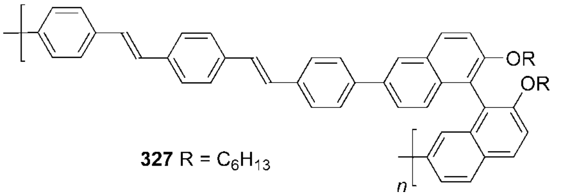
325

Comparison of the EL maxima of the cyclophane-containing copolymers **324**[770] (λ_{max} = 490 nm) and **325** (λ_{max} = 476 nm)[747] with those for **302a** (λ_{max} = 475 nm) and **307d** (λ_{max} = 464 nm) suggests that the cyclophane units in **324** do not significantly interrupt the conjugation of the polymer chain. By contrast, the emission maxima of the spirobifluorene-containing copolymers **326a**[771,772] (λ_{max} = 474 nm) and **326b**[772] (λ_{max} = 446 nm) are markedly blue-shifted compared with those of **307a** (λ_{max} = 495 nm) and **302a**, suggesting that the spiro-linkage does affect through conjugation. The EL emission from **326a** is red-shifted (λ_{max} = 516 nm) and broadened, probably due to the formation of excimers.



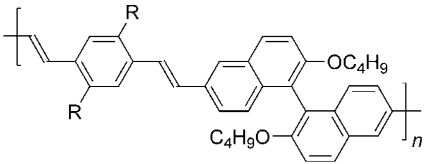
326a Ar =

326b Ar =

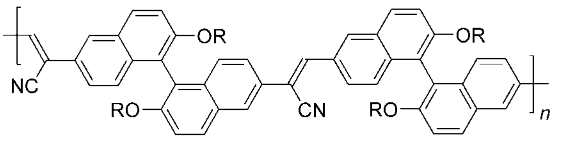


327 R = C_6H_{13}

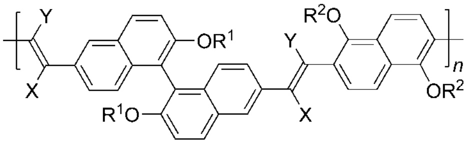
Poly(arylene vinylene)s incorporating chiral binaphthyl units might be expected to show circularly polarized emission. A copolymer **327** has been made in both racemic and chiral forms by Suzuki coupling.[773−775] It shows efficient blue fluorescence (λ_{max} = 468 nm). The polmer **328a** prepared by the Horner method shows blue PL in solution (λ_{max} = 447, 462, 500 nm), but green emission in the solid state (λ_{max} = 525 nm).[776,777] The EL is described as blue-green in color (λ_{max} = *ca.* 525 nm). Substitution of the phenylene units with cyano groups in polymer **328b** leads to a red-shift in the emission (λ_{max} = 600 nm) and an increase in the EL efficiency (0.056% cf. 0.016%). A smaller red-shift (λ_{max} = 555 nm) is seen for the polymer **328c** with alkyoxy substituents, but the EL efficiency is slightly higher (0.06%). Binaphthylene vinylene polymers **329**−**330** with cyano substituents have been made by the Knoevenagel method.[778,779] The strong steric repulsions between the binaphthyl units reduce the effective conjugation length of these materials so that they show blue-green (λ_{max} = 475−496 nm) PL. The polymer **331** made by Suzuki coupling has even greater steric crowding about the inter-naphthyl bond and so produces blue PL (λ_{max} = 457 nm).[760] Circularly polarized PL has been seen from optically active polymers.



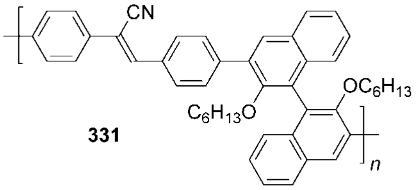
328a R = H
328b R = CN
328c R = 2-ethylhexyloxy



329 R = $C_{12}H_{25}$



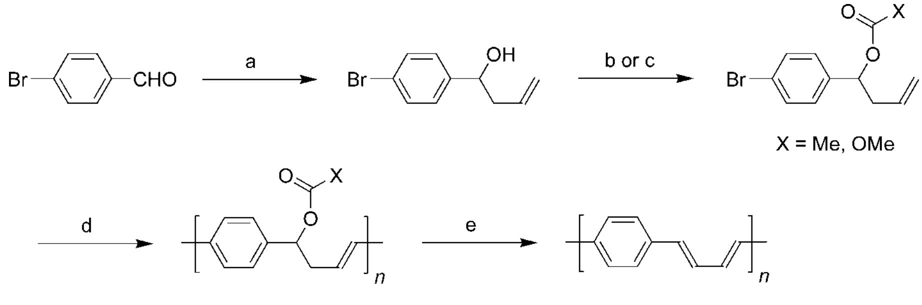
330a $R^1 = C_{12}H_{25}$, $R^2 = C_6H_{13}$, X = CN, Y = H
330b $R^1 = C_{12}H_{25}$, $R^2 = C_6H_{13}$, X = H, Y = CN



331

If increasing the phenylene content of PPV (**1**) leads to a blue-shift in the emission spectrum, it is logical to expect that increasing the vinylene content will produce a red-shift. This is borne out by the small number of polymers with extended double-bond systems so far produced. Poly(phenylene 1,3-butadiene-1,4-ylene) (PPB, **332**) has been made by a precursor method involving Heck polymerization of an AB monomer (Scheme 30).[780] The PL emission is slightly red-shifted with respect to PPV (λ_{max} = 530−560 nm). The conversion temperature for the acetoxy precursor **333a** is higher (350 °C) than that for the carbonate precursor **333b** (250 °C). MEH-PPB **334**, the butadienylene analogue of MEH-PPV (**20**), has been made by Horner polycondensation and shows red emission (λ_{max} = 604 nm).[390] The polymer **335** with a diphenyl-substituted butadienyl unit has also been made by the Horner method, but there is no report on its fluoresence, though the wavelength of highest absorption is red-shifted compared with that of **334**.[390] The polymer **336**

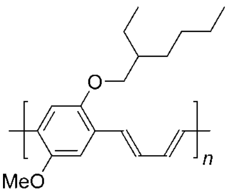
Scheme 30. Precursor Route to Poly(phenylene butadienylene) (332): (a) CH_2=$CHCH_2MgBr$, THF; (b) Ac_2O; (c) $ClCO_2Me$; (d) $Pd(OAc)_2$, Et_3N, PPh_3; (e) 250−350 °C



333a X = Me
333b X = OMe

332

made by nickel(0) coupling of a dibromo-substituted tetrabutylarene shows very weak green PL (λ_{max} = 542 nm).[781]



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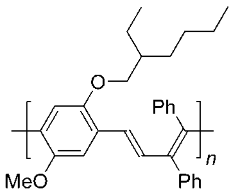

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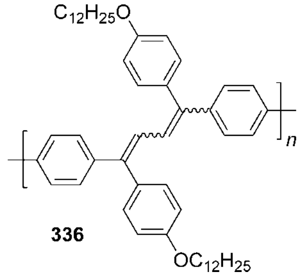


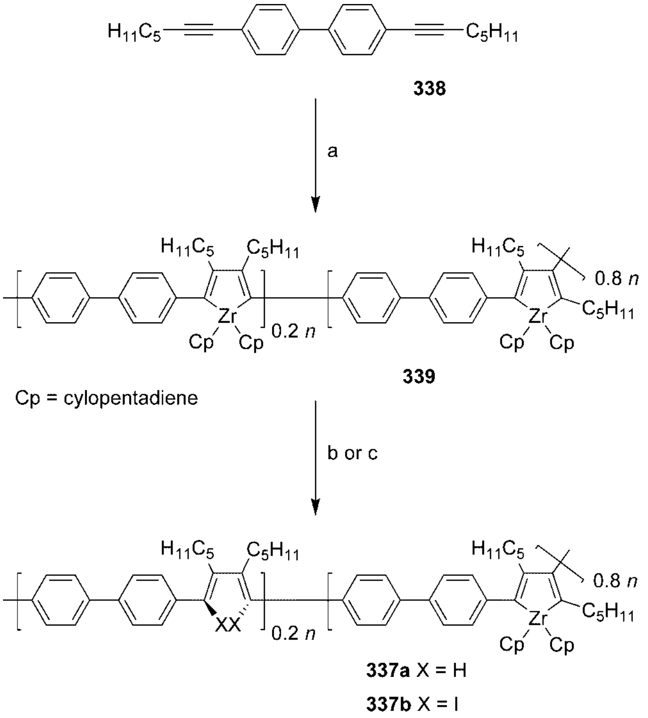
336

An unusual route to poly(biphenylene butadienylene)s **337** developed by Tilley and co-workers (Scheme 31) proceeds *via* zirconocene addition to a diphenyldiyne **338** to give the precursor polymer **339**.[782] The addition of the zirconium is not regiospecific, giving a 4:1 mixture of isomeric zirconocycles in the polymer chain. Treatment of **336** with acid gives **334a**, while treatment with iodine gives the iodo-substituted polymer **334b**. Both show blue emission (λ_{max} = 428 and 432 nm), but with low (<5%) PL efficiencies. A similar approach, which avoids the problem of regioisomers, uses Hagihara−Sonogashira coupling of a diyne and an aryl dibromide, followed by addition of zirconocene to make zirconocene precursors (Scheme 32), *e.g.* **340**.[783,784] The resulting final polymer **341** shows blue PL (λ_{max} = 470 nm) with only 4.3% efficiency. Other similar polymers with other aryl units show even lower efficiencies. In a variation of this method (Scheme 33), compound **342** is zirconylated to give **343**. Reaction of **343** with ethyl *cis*-iodoacrylate, followed by nickel(0) coupling, gives polymer **344**, which shows blue-green PL (λ_{max} = 488 nm).[785] Oligomers **345** containing tropone units have been made by Wittig chemistry.[786] They display yellow PL (λ_{max} = 560 nm).

2.7. Poly(heteroarylene vinylene)s

Poly(arylene vinylene)s with a wide range of heterocyclic groups in the main-chain have been prepared. As heteroatoms such as nitrogen or sulfur have higher electronegativities than carbon, incorporation of heterocycles offers a potential way to increase the electron affinity of π-conjugated polymers. Also, the lower symmetry and the lower resonance energy of most heterocycles compared with those of benzene offer new opportunities and challenges for modification of polymer structures and properties.

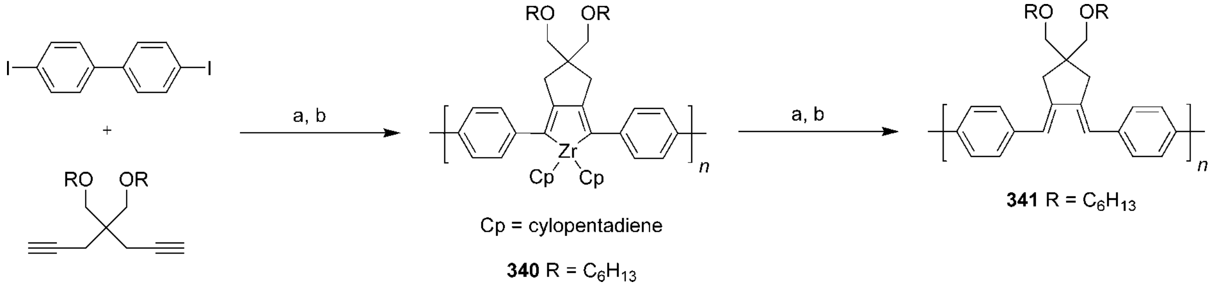
Scheme 31. Zirconocene Route to Biphenylene Butadienylene Polymers: (a) Cp_2ZrCl_2, *n*-BuLi, THF; (b) HCl; (c) I_2



The most widely studied poly(heteroarylene vinylene)s have been derivatives of poly(2,5-pyridinylene vinylene) (PPyV, **346a**). PPyV was first prepared by Swager and co-workers by the Stille coupling of 2,5-dibromopyridine (**347a**) and 1,2-bis(tributylstannyl)ethylene (**348**) (Scheme 34),[787,788] as an orange powder of low (5500 Da) molecular mass which was soluble in acidic solvents and in *m*-cresol due to the basicity of the nitrogen atoms. Higher molecular mass material can be made by precursor routes. The polymer **346a** was also prepared[789] by chloro, sulfonium, and methoxy precursor routes, with the chloro precursor route proving the best route for obtaining high-quality thin films, but the PL efficiency of such material was only 2%. The highest molecular mass PPyV was made by the sulfinyl precursor route, with molecular masses of up to 730 kDa being obtained.[790] This material also shows higher PL solid-state efficiency (14%) than that of the PpyV made by other precursor routes. Alkylation and protonation of **346a** gives the *N*-alkylated (**349**) and *N*-protonated (**350a**) derivatives, respectively (Scheme 34), which are soluble in chloroform, though **349** is unstable in the presence of nucleophiles.[788,791,792] The substituted polymers **346b,c** are made by Stille coupling of 3-alkyl-2,5-dibromopyridines (**347b**, Scheme 34).[792,793] The butyl-substituted polymer **346c** is soluble in conventional organic solvents.

PPyV **346a** shows red PL in the solid state (λ_{max} = 610 nm),[789,791] which is considerably bathochromically shifted compared with the emission in solution (λ_{max} = 485 nm),[793] suggesting the presence of strong polymer interchain interactions in the solid state. Orange-red EL (λ_{max} = 585 nm) has been obtained from PPyV films spun from formic acid.[794,795] With PPV as a hole-transporting layer the efficiency increased from 0.0065% to 0.08%. The C-alkylated polymers **346b,c** exhibit a red-shift in their solid-state emission (λ_{max} = 630 nm) compared with PPyV.[793] The emission of **346c** in solution shows a marked red-shift in going from dilute (λ_{max} = 485 nm) to concentrated solution (λ_{max} = 630 nm).[793] Similar effects are seen on dispersing **346c** in PMMA, confirming that there are strong interactions between polymer chains giving rise to the red emission.[793] Orange-red emission has been obtained from LEDs using polymer **346c**.[793] The device efficiency was increased from 0.02% to 0.05% by use of a PPV hole-transporting layer. By contrast, the *N*-alkylation in polymer **349** causes a blue-shift in emission (λ_{max} = 540 nm) and the PL spectrum is almost identical in both solution and the solid state.[793] The protonated polymer

Scheme 32. Improved Zirconocene Route to Biphenylene Butadienylene Polymers: (a) Pd(PPh$_3$)$_4$, CuI, ^{i}Pr$_2$NH, THF; (b) Cp$_2$ZrCl$_2$, *n*-BuLi, THF; (c) HCl

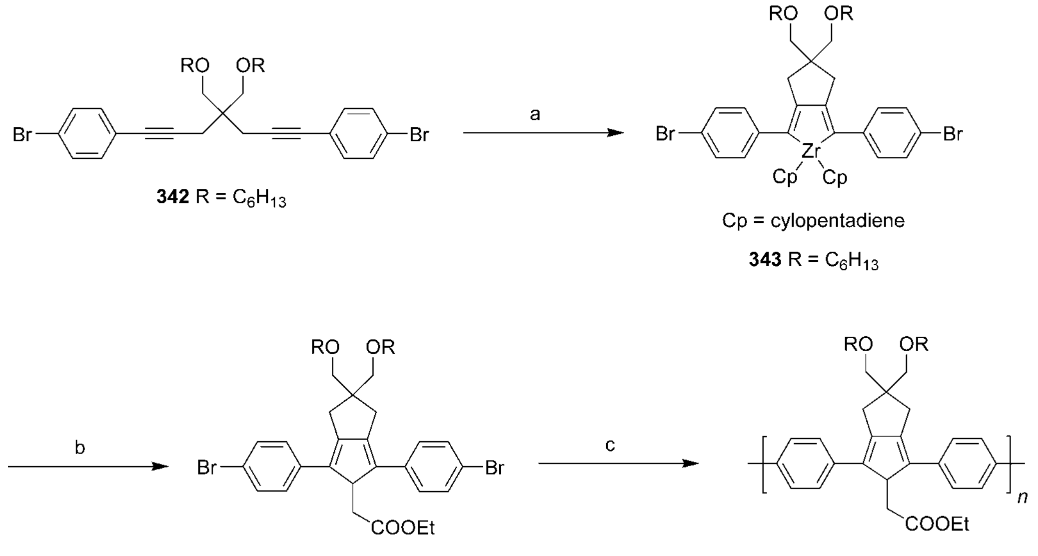


Cp = cylopentadiene

340 R = C_6H_{13}

341 R = C_6H_{13}

Scheme 33. Zirconocene Route to Biphenylene Cyclopentadienylene Polymer 344: (a) Cp$_2$ZrCl$_2$, *n*-BuLi, THF; (b) *cis*-ICH=CHCO$_2$C$_2$H$_5$; (c) Ni(COD)$_2$, 2,2-Bipyridine, Toluene, DMF



342 R = C_6H_{13}

Cp = cylopentadiene

343 R = C_6H_{13}

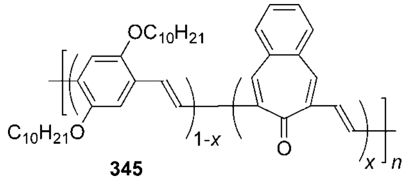
344 R = C_6H_{13}

(PHPyV, **350a**) also shows a blue-shift in PL emission in both solution (λ_{max} = 550 nm) and solid-state (λ_{max} = 535, 570 nm).[793] Self-assembled layers of **350a** and sulfonated polyaniline (SPAn) have been used in LEDs.[796−798] Devices containing monolayers show yellow EL (λ_{max} = 630 nm), while multilayer-based devices displayed greenish-yellow, emission (λ_{max} = 610 nm). The butyl-substituted derivative **346c** and its protonated form **350b** have been used to make multilayer films with poly(sodium 4-styrene sulfonate) (PSS). Their EL emission is blue-shifted by 20 nm with respect to the bulk polymer films, but lifetimes and emission qualities are markedly inferior.[792,793]

Owing to the lower symmetry of the pyridine ring, PPyV (**346a**) can exist in three regioisomeric forms: head-to-head (HH, **351**), head-to-tail (HT, **352**), and random (R). Swager and co-workers[787] have prepared the regioregular polymers **351**−**352** (Scheme 35). The key step in the synthesis of the head-to-head polymer **351** is the preparation of compound **353** by Stille coupling of **348** with an excess of **347a**. This is then coupled with more **348** to give the HH polymer **351**. For the preparation of the head-to-tail polymer **352**, tributylvinyltin was regioselectively coupled to the 2-position of **347a** to give the monoadduct **354**, which was used as the AB monomer for formation of polymer **352** in a Heck polycoupling. The three isomers show different UV−vis absorption, and PL and EL emission spectra, with EL emission maxima at λ_{max} = 575 nm (R), 584 nm (**352**), and 605 nm (**351**), respectively.[799] The bathochromic shift of the emission maxima of the regioregular isomers indicates a longer effective conjugation length in these isomers compared with the regiorandom material. A device fabricated in the configuration Al/**351**/ITO and driven by alternating current exhibited a turn-on voltage of 5 V for forward bias and 15 V for reverse bias with more intense emission being obtained from the forward bias mode. However, no alteration in the EL spectrum was observed.[800]

Copolymers **355**−**357** with alternating 2,5-pyridinylene vinylene and phenylene vinylene units have been made by Swager and co-workers by Heck coupling.[801] Both copolymers **355** and **356a** exhibit a solid-state PL maximum at 2.1 eV (λ_{max} = 590 nm), while copolymer **357** with a cyclophane unit shows two solid-state PL maxima at 2.05 and 2.25 eV (λ_{max} = 551 and 605 nm, respectively).[802]

Interestingly, all these materials show marked red-shifts in emission in going from solution to the solid state. That this is due to the formation of aggregates has been demonstrated by the marked blue-shift in emission upon dilution of polymer **357** in PMMA.[803] Single-layer LEDs using **355** and **357** show low efficiency. Bilayer devices using PVK show better efficiencies, but this is accompanied for **355** by a blue-shift in the emission maximum to 2.5 eV (λ_{max} = 496



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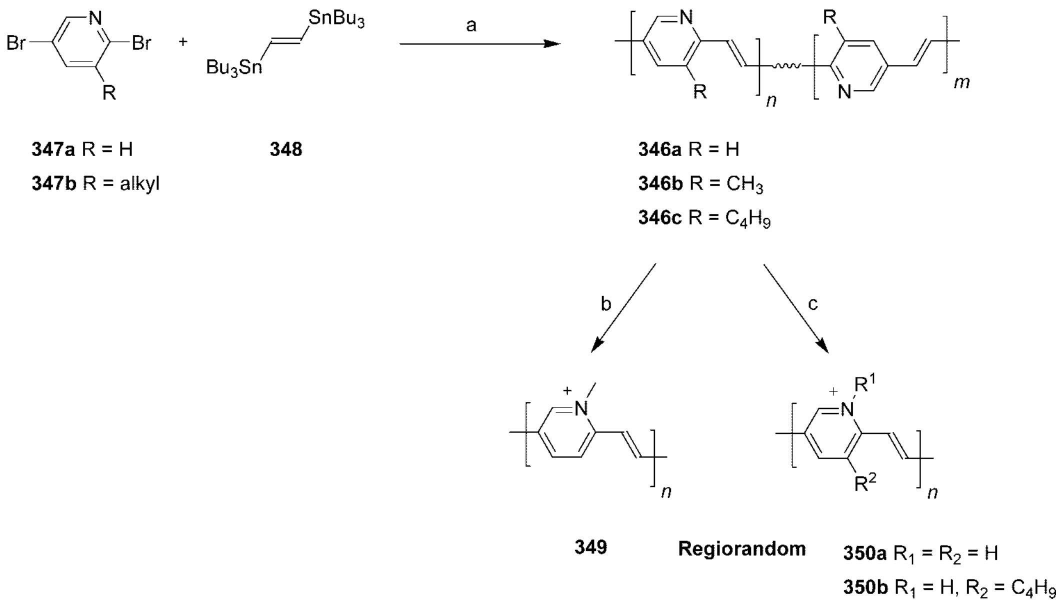
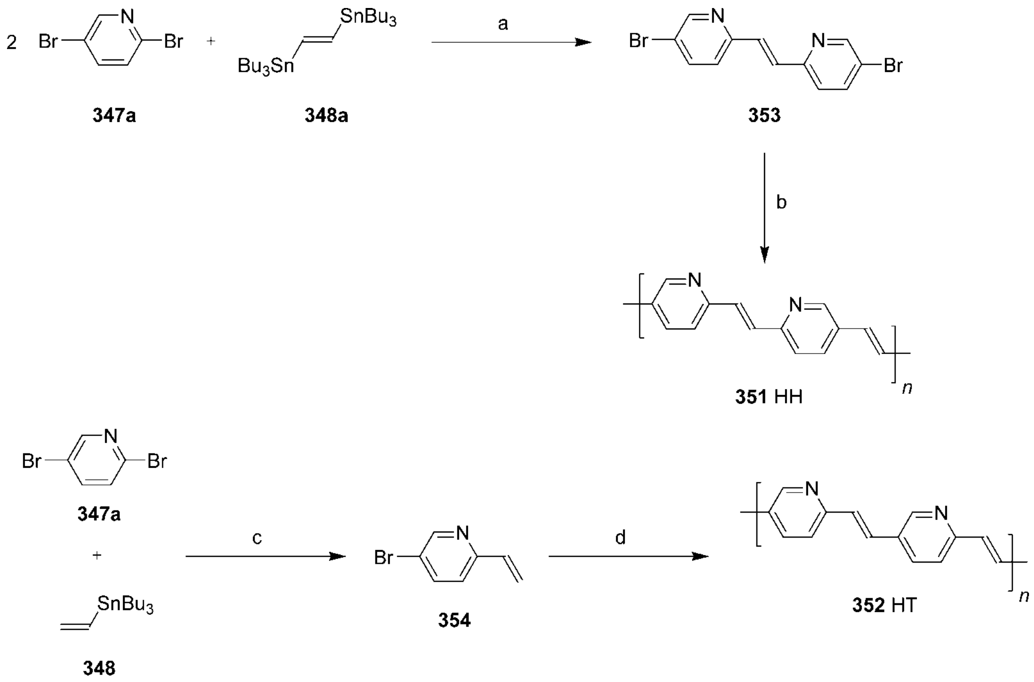
Scheme 34. Synthesis of Regiorandom PPyV 346 and Derivatives: (a) Pd(PPh_3)$_4$; (b) MeOTf; (c) H^+

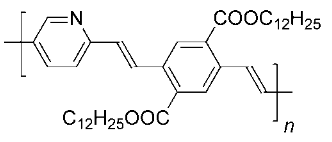


Scheme 35. Synthesis of Regioregular PPyV: (a) Pd(PPh_3)$_4$; (b) 348, Pd(PPh_3)$_4$; (c) $PdCl_2(AsPh_3)_2$, THF, 60 °C; (d) $PdCl_2(PPh_3)_2$, NMP, Et_3N, 120 °C



nm) due to formation of an excited-state complex (exciplex) between PVK and **355**.[802−805] Similar exciplex emission has been seen in the PL from bilayers of polymers **356a** and **356b** with PVK.[805] Copolymer **356b** produces red EL (λ_{max} = 650 nm).[800,806]

Copolymers **358** containing between 1% and 10% of 2,6-pyridinylene vinylene units have been prepared by the Wessling route.[807,808] The EL emission spectrum for the copolymer containing 1 mol % of pyridinylene units shows



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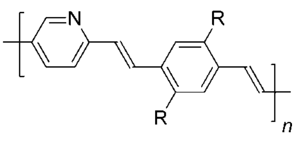
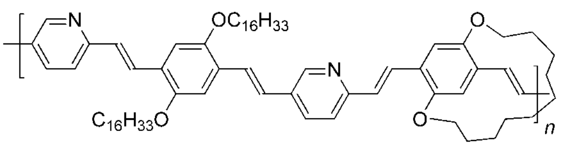


356a R = $C_{12}H_{25}$
356b R = $OC_{16}H_{33}$



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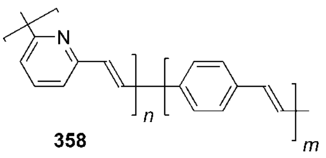

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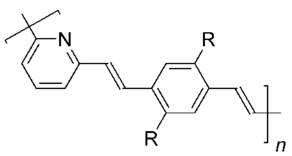
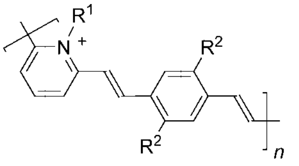


359a R = H
359b R = $OC_{12}H_{25}$
359c R = OC_8H_{17}
359d R = OC_7H_{15}

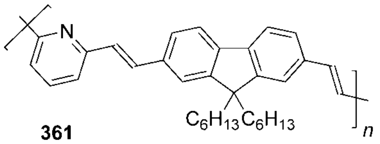
a primary green emission at around 530 nm and a secondary red emission at around 600 nm at an applied potential of 12 V. At higher applied voltages, the intensity and width of the secondary emission increase markedly to produce a distinct red-shift in the overall emission, thus giving voltage-controlled variable emission.

A similar red-shift and broadening in the emission spectra with increasing applied voltage were also observed for the copolymer with 10 mol % of pyridinylene units. Comparison of EL intensity against applied voltage for the green and for the red emission bands showed that the latter had a higher threshold (turn-on) voltage. The 10 mol % copolymer has been used as the active layer in a microfabricated polymer LED pixel array.[809] Protonation of polymer **355** produces a broadening of the PL and EL spectra with an overall increase in the amount of red emission and enables self-assembled multilayers with SPAn to be made.[203] Alternating copolymers of 2,6-pyridinylene vinylene and other arylene vinylene units have been made by the Wittig method. The copolymer with PPV **359a** produces blue PL (λ_{max} = 431, 476 nm), which is slightly red-shifted upon protonation to form **360** (λ_{max} = 492 nm).[810,811] Substitution with alkoxy units also produces a red-shift in emission, which is greater for the dodecyloxy copolymer **359b** (λ_{max} = 505 nm) than for the octyloxy copolymer **359c** (λ_{max} = 495 nm).[810,811] Even stronger red-shifts are seen for the *N*-ethylated polymer **360b** (λ_{max} = 590 nm)[810,811] and the heptyloxy copolymer **359d** (λ_{max} = 572 nm).[812] The copolymer **361** with dihexylfluorenyl vinylene units shows mainly blue PL (λ_{max} = 440, 470 nm) with a broad weak band in the green (λ_{max} = 540 nm) when deposited from chlorobenzene, but predominantly emission from the latter band when deposited from formic acid, which suggests a greater formation of aggregates in the latter solvent.[744] The EL emission is green (λ_{max} = 540 nm).



360a R^1, R^2 = H

360b R^1 = C_2H_5, R^2 = OC_8H_{17}



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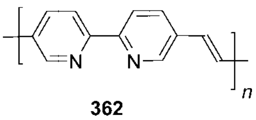

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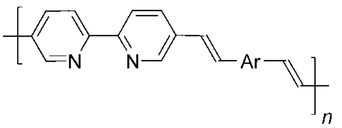
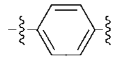
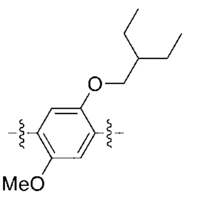
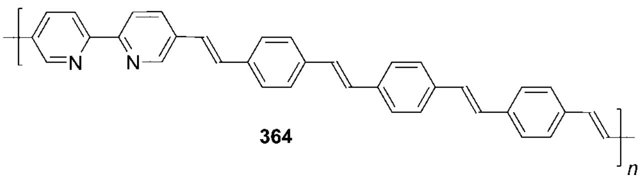


363a Ar =



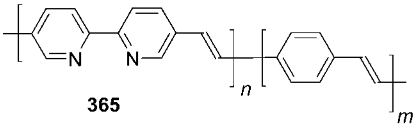
363b Ar =





364

Poly(2,2′-bipyridinylene vinylene) **362** has been made by the Gilch route.[813] It is soluble only in acidic solvents and shows green-yellow PL (λ_{max} = 566 nm). Alternating copolymers such as **363**−**364** and a random copolymer **365** with phenylene vinylene units have been made by Wittig coupling.[813,814] Copolymer **363b** is soluble in standard solvents and shows red emission (λ_{max} = 610 nm), which can be red-shifted up to 80 nm by protonation with formic acid.[813] Copolymer **363a** shows orange-red PL (λ_{max} = 580 nm) and EL (λ_{max} = 585 nm).[814] Protonation with gaseous HCl enables the PL emission to be reversibly red-shifted up to 90 nm depending on the concentration of HCl. The PL of **364** (λ_{max} = 578 nm) and **365** (λ_{max} = 582 nm) also show similar red-shifts (λ_{max} = 627 and 635 nm, respectively) upon protonation. Red-shifted EL has been obtained by protonation of films of **363a** with formic acid (λ_{max} = 615 nm) or HCl (λ_{max} = 640 nm). A poly(pyridinylene butadienylene) **366**, made by the zirconocene precursor route used to make **341** (Scheme 32), shows green PL (λ_{max} = 548 nm).[784]



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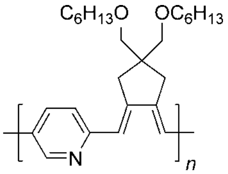

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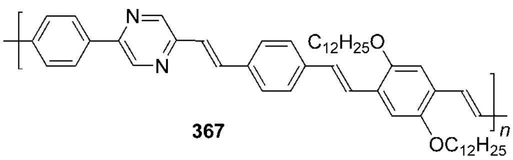

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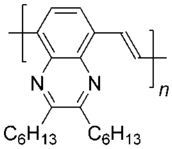

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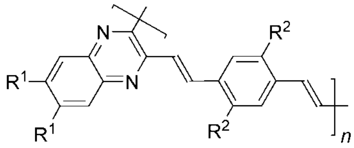
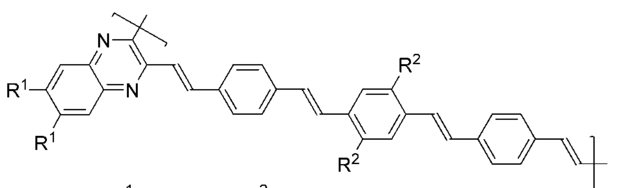


369a R^1 = $OC_{12}H_{25}$, R^2 = H

369b R^1 = H, R^2 = OC_6H_{13}



370a R^1 = $OC_{12}H_{25}$, R^2 = H

370b R^1 = $OC_{12}H_{25}$, R^2 = Br

370c R^1 = H, R^2 = $OC_{12}H_{25}$

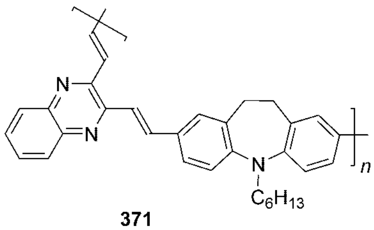
Heterocycles containing more than one nitrogen atom are even better electron acceptors than pyridine, and there are a few examples of polymers with such units which have been made as electron transporting and emissive materials. The pyrazine vinylene copolymer **367** has been made by Heck coupling.[653] It displays orange EL (λ_{max} = 550 nm), with slightly higher efficiency (0.012%) in single-layer LEDs with aluminum cathodes than seen for PPV in devices of the same configuration (0.01%). The efficiency is no higher with calcium cathodes, indicating that electron injection is not the limiting factor for the EL efficiency. Use of a PPV hole-injecting layer produces a modest increase in efficiency (0.015%).

Quinoxalines have also been incorporated into PPVs in order to enhance their charge-accepting abilities. The poly(quinoxaline vinylene) **368** has been made by Heck coupling.[815] The EL is yellow-green (λ_{max} = 550 nm). The copolymer **369a** undergoes a remarkable red-shift in emission from blue-green PL in solution (λ_{max} = 492 nm) to red PL and EL in the solid state (λ_{max} = 628 nm) due to aggregation of the polymer chains.[816] Increasing the proportion of phenylene vinylene units as in **370a,b** produces a slight blue-shift in the emission (EL λ_{max} = 612−614 nm). By contrast, the copolymers **369b** and **370c** display only modest red-shifts between their solution (λ_{max} = 518 and 561 nm, respectively) and solid-state (λ_{max} = 556 and 568 nm, respectively) emission maxima, and the emission of **371** is essentially the same in both solution and the solid state (λ_{max} = 554 nm).[817] The diphenylquinoxaline copolymers **372a** and **373** also display only slight red-shifts between their solution PL (λ_{max} = 519 and 536 nm, respectively) and EL emissions (λ_{max} = 535 and 543 nm, respectively),[637] whereas the EL from the copolymer **372b** contains extra shoulders in the red (600−700 nm) not seen in the solid-state PL spectrum.[713] The EL efficiencies of **372a** (0.06%) and **373** (0.01%) are considerably higher than those for the copolymer **207a** with quinoxaline side-chains.[637] The copolymer **374** made by Heck coupling produces EL in the near-infrared (λ_{max} = 715 nm), which is attributed to the donor−acceptor nature of the polymer.[806]

Triaryltriazoles have been used as electron-accepting layers in OLEDs,[53] so that there has been some interest in incorporating such units into PAVs to improve their EL efficiencies. The triazole-containing copolymers **375a,b** (Chart 2) show blue-green (2.5 eV, λ_{max} = 496 nm)[187,818] and green (λ_{max} = 526 nm)[819] emission, respectively. The PL (33%) and single-layer EL efficiencies (0.021% with Al cathode) of **375a** are modest, but it has proved to be a useful electron-transporting material in PPV and MEH-PPV-based devices, producing major (up to 60-fold) increases in efficiency.[187,818] The copolymer **376** with a TPA unit also produces green EL (λ_{max} = 522 nm).[820] Copolymer **377** made by Heck coupling displays green-yellow EL (λ_{max} = 538 nm), with rather low efficiency (0.024 cd/A).[455,821] Increasing the phenylene content as in polymers **378** and **379**, made by Horner and Suzuki coupling, respectively, blue-shifts the emission (λ_{max} = 525 and 504 nm, respectively) and lowers the EL eficiency, which is attributed to greater torsion of the polymer chain reducing the through conjugation.

As has been mentioned in section 2.5, aryloxadiazoles are particularly good electron accepting units, and a number of poly(arylene vinylene)s incorporating them in the main-chain have been prepared. The di(4-bromostyryl)oxadiazole **380** has been incorporated as a comonomer in the synthesis of substituted PPPs (see section 3.2) and polyfluorenes (see section 3.4) by Suzuki polycondensation. It is reported that PL emission occurs from the styryloxadiazole units due to energy transfer, but there is as yet no report of the EL.[822]

Monoaryloxadiazole vinylene copolymers **381**−**383** have been prepared by Heck coupling.[823,824] Whereas **381** and **382** display yellow-green PL (λ_{max} = 515 and 558 nm, respectively), **383** is a blue emitter (λ_{max} = 443 nm). The EL from **381** undergoes an irreversible blue-shift, due to changes in the polymer conformation, as the applied potential is increased from 9 to 16 V with the maximum moving from 558 to 527 nm. The diaryloxadiazole polymer **384** (Chart 3) shows blue-green EL (λ_{max} = 483 nm) when made by the Wessling route. Synthesis by the Horner method produces material with a slightly red-shifted emission maximum (λ_{max} = 509 nm).[825,826] The alternating copolymer **386** made by the Wittig route displays blue PL in solution (λ_{max} = 440 nm) but green PL in the solid-state (λ_{max} = 502 nm).[827] Single-layer LEDs using **386** were unstable, but more durable blue EL (λ_{max} = 470 nm) was obtained from a double-layer device using an oxadiazole charge transport layer. Shim and co-workers have prepared the copolymers **387a** and **388** by Wittig coupling and **389** by Heck coupling.[828] The *para*-linked polymer **387a** shows green PL and EL (λ_{max} = 510 nm), while the *meta*-linked polymer **388** shows a marked blue-shift in the PL (λ_{max} = 470 nm) and produces only very weak blue EL despite the more electron rich phenyl rings, owing to the oxyalkyl side-chains next to the oxadiazole units. The *ortho*-linkages in **389** produce only a small blue-shift in the PL and EL (λ_{max} = 500 nm). The copolymers **387b,c** made by Wittig polycondensation show yellow EL (λ_{max} = 560 nm),[829,830] with an efficiency for **387b** of 0.08% in a single-layer device with an Al cathode.[829] Copolymer **390** with a diaryldioxadizole is a blue-green emitter (λ_{max} = 483 nm).[824] By contrast, copolymer **391a** with a higher ROPPV content, made by Heck coupling, shows yellow EL



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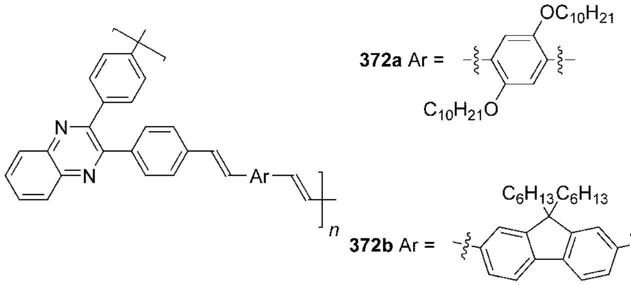

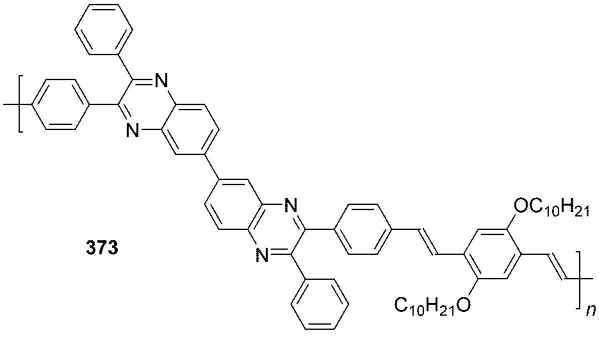

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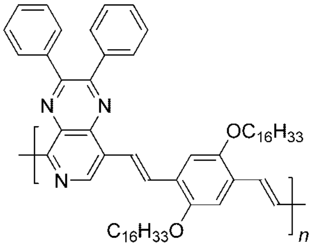

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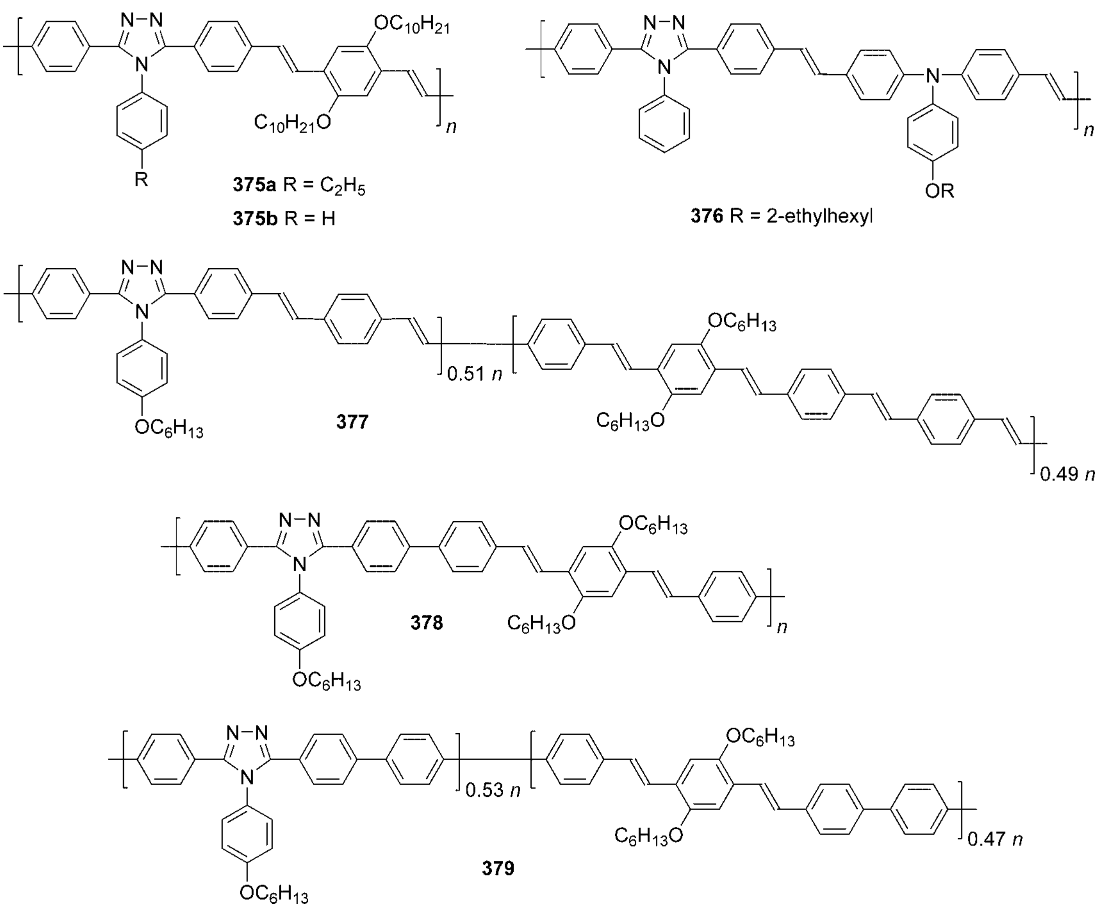
Chart 2



375a R = C_2H_5

375b R = H

376 R = 2-ethylhexyl

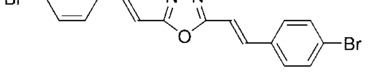
377

378

379

(λ_{max} = 560 nm) with an efficiency of 0.15% in the same device configuration as **387b** and a low turn-on voltage (6 V).[829,831]

Attaching further oxadiazoles as side-chains in **392** (Chart 4) causes a red-shift in the EL (λ_{max} = 600 nm), accompanied by a drop in EL efficiency (0.07%) and an increase in turn-on voltage to 10 V,[832] while reducing the number of alkoxy groups in **391b** produces a slight blue-shift in the EL maximum to 549 nm.[626] Increasing the number of oxadiazole units as in **393**[833] or **394**[455] also blue-shifts the EL (λ_{max} = 541 and 530 nm, respectively). The copolymer **395** with a 2,6-pyridyl ring has an EL maximum at 555 nm despite the *meta*-linkage, which is presumably due to aggregation in the solid state, as the solution PL is blue-green (λ_{max} = 492 nm).[834]



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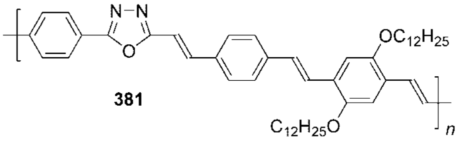

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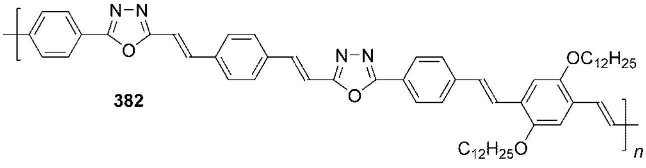

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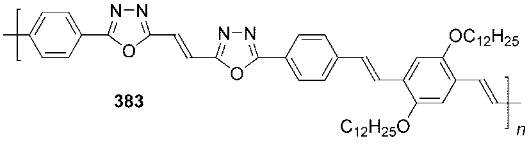
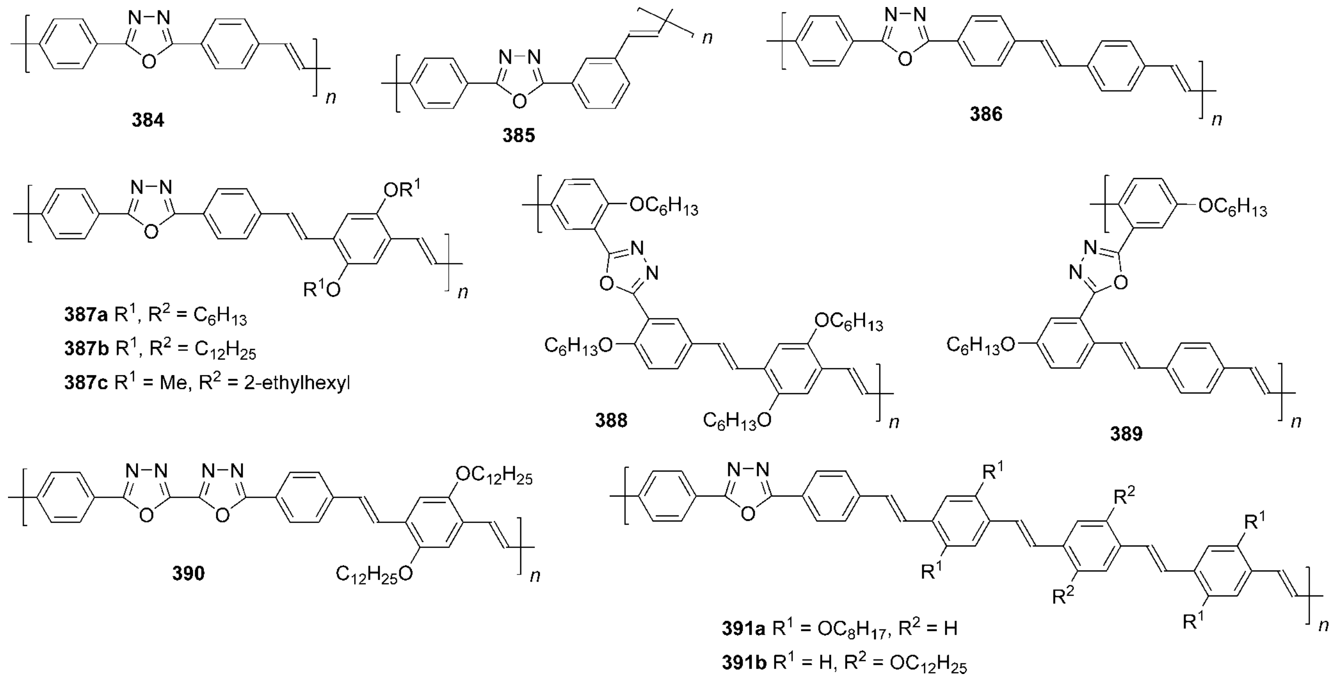


383

Polyarylene vinylenes have been made incorporating both oxadiazoles and hole-transporting TPA units. Copolymer **396** produces blue-green emission in the solid-state (λ_{max} = 473 nm).[835] The copolymer **397a** (Chart 5) is reported to exhibit an EL efficiency 15 times higher than the copolymer **321d** lacking the oxadiazole units.[836] The EL of both polymers is green with a maximum at *ca*. 550 nm. A comparison of polymers **397b**, **398**, and **399** with different electron-accepting units showed that the oxadiazole copolymer **397b** had the highest EL efficiency.[837] The emission of this polymer was also slightly blue-shifted (λ_{max} = 535 nm) compared with those of the other two (λ_{max} = 555–560 nm). Stable single-layer devices (λ_{max} = 502 nm) have been made using the copolymers **400** with 3,6-carbazole units. Double-layer devices of **400a** with PBD show blue-shifted EL (λ_{max} = 475 nm).[827] The EL efficiency of **400b** (λ_{max} = 495 nm) is reported to be 36 times higher than that for PPV in the same device configuration.[529,838] Incorporation of *meta*-linkages in **401** produces a blue-shift in the EL (λ_{max} = 450 nm) and an 18-fold drop in EL efficiency.[529,838] Polymer **402** with thiadiazole units has been made by the Wessling route and shows blue-green EL (λ_{max} = 485 nm) with a low (4 V) turn-on voltage.[839]

Other polycylic nitrogen-containing heterocycles have also been incorporated into PAVs. Poly(2,6-quinoline vinylene)

Chart 3



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387a R^1, R^2 = C_6H_{13}

387b R^1, R^2 = $C_{12}H_{25}$

387c R^1 = Me, R^2 = 2-ethylhexyl

388

389

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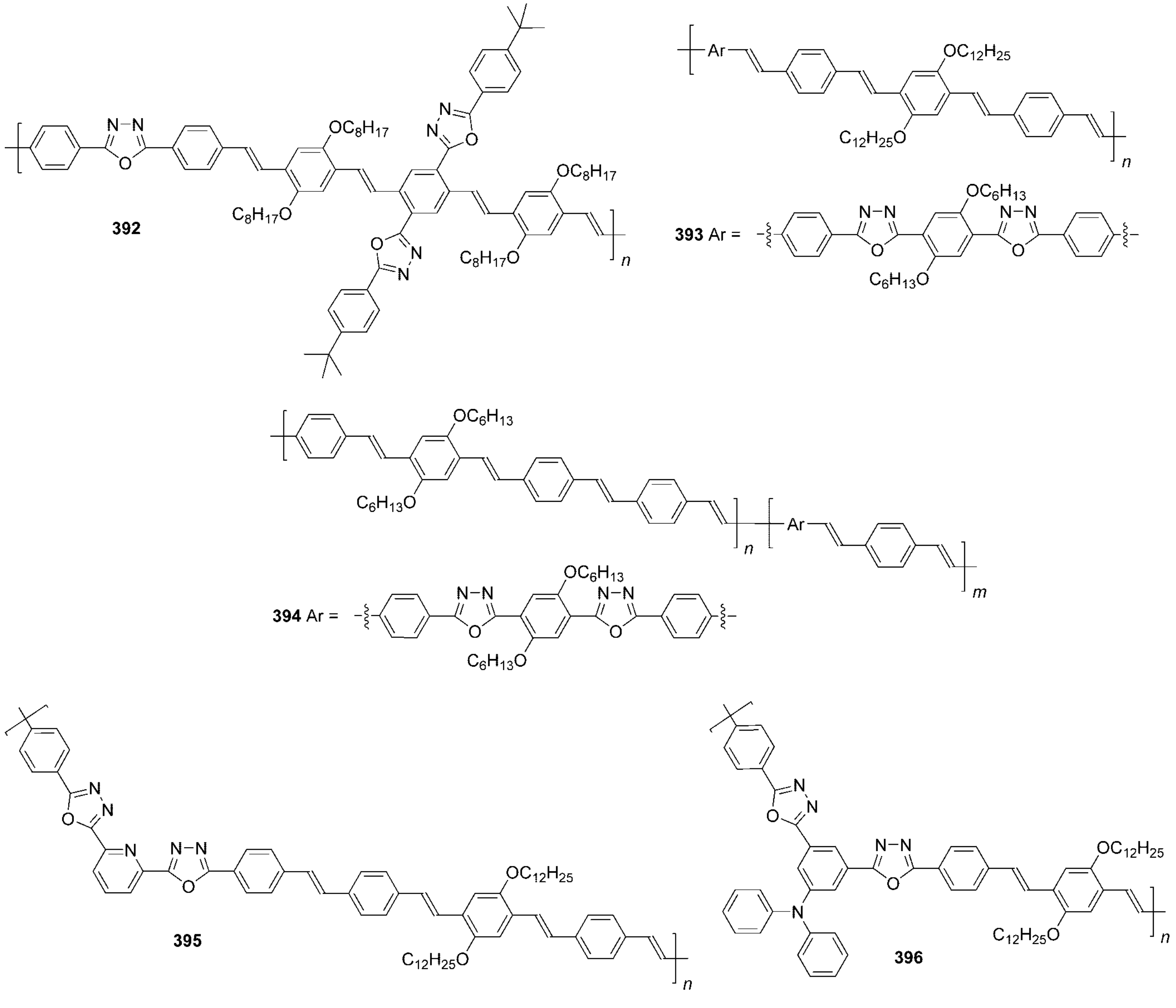
391a R^1 = OC_8H_{17}, R^2 = H

391b R^1 = H, R^2 = $OC_{12}H_{25}$

Chart 4



392

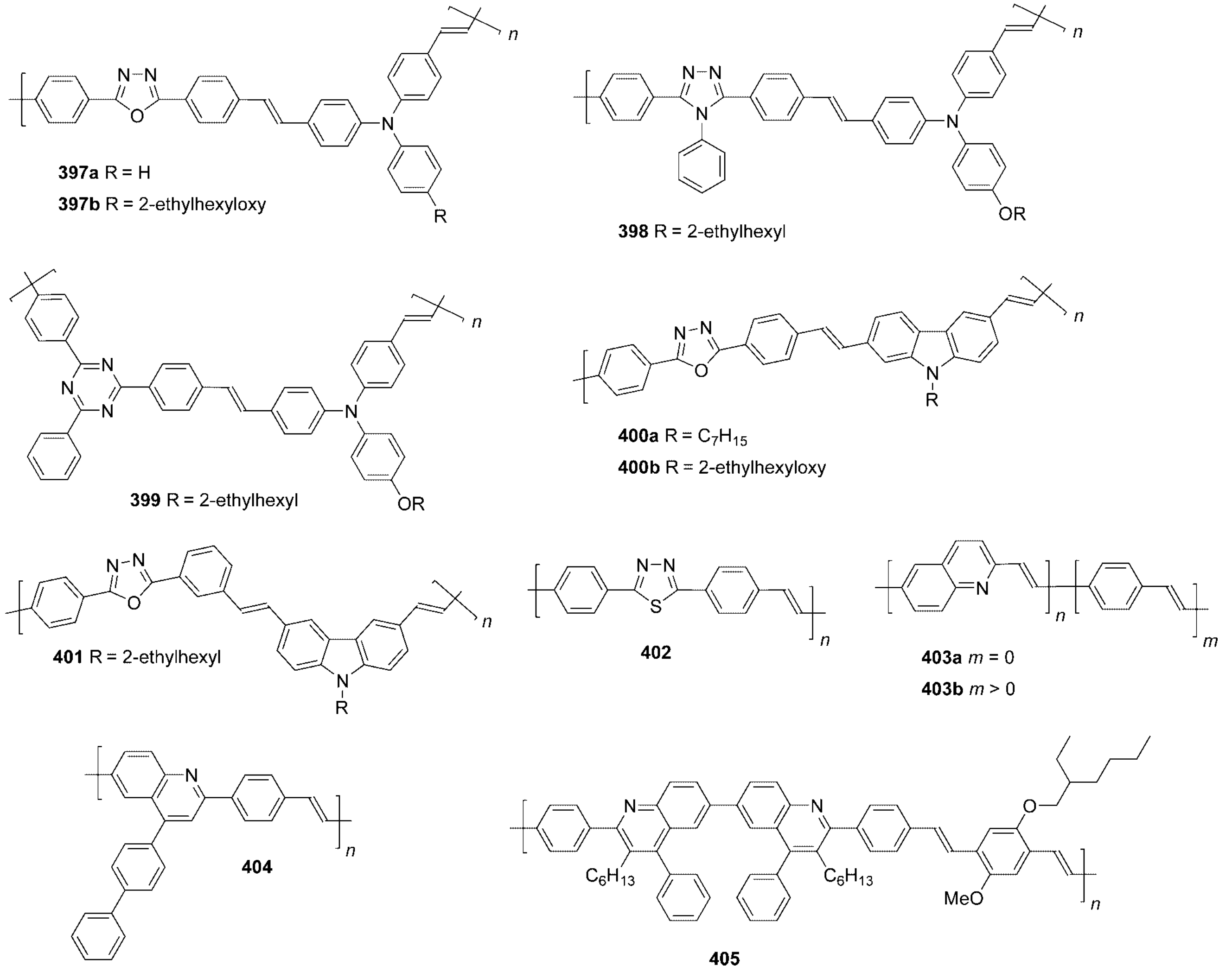
393 Ar =

394 Ar =

395

396

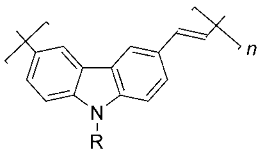
Chart 5



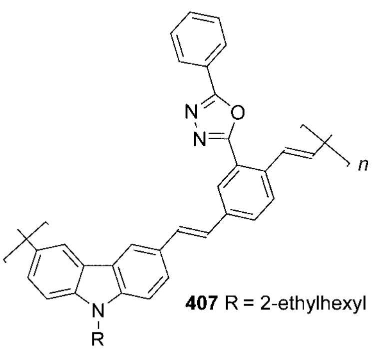
403a has been made by a xanthate precursor route and shows yellow-green EL ($\lambda_{max} = 530$ nm).[840] A copolymer with PPV **403b** made by a mixed-precursor route emits blue EL (λ_{max} = 425, 445 nm) but on blending with PPV yellow-green EL (λ_{max} = 530 nm) is obtained with much higher efficiency.[841] Polymer **404** made by Friedländer polycondensation shows blue PL in solution ($\lambda_{max} = 449$ nm), but the emission is red-shifted into the green (λ_{max} = 494, 540 nm) in the solid state, which is attributed to excimer emission.[842] The EL is even more red-shifted ($\lambda_{max} = 572$ nm). Blending with PVK suppresses the excimer formation to give blue EL ($\lambda_{max} = 446$ nm). A bis-quinoline copolymer **405** made by Wittig coupling shows greenish-yellow EL ($\lambda_{max} = 550$ nm).[843]

Carbazoles are well-known for their hole-accepting properties, and a number of PAVs containing them have been prepared. Poly(3,6-*N*-2-ethylhexylcarbazolyl vinylene) (PCzV) (**406**) prepared by Stille coupling of 3,6-dibromocarbazole with bis(tributylstannyl)ethylene[844] or by Horner polycondensation[845] shows green EL ($\lambda_{max} = 510$ nm). Copolymers **322** and **407**−**409** with other arylene vinylene units have been prepared by the Wittig method.[627] Copolymer **322a** shows green EL ($\lambda_{max} = 512$ nm) with a low (3.7 V) turn-on voltage.[846] Copolymer **322b** with MEH-PV units shows high solid-state PL ($\lambda_{max} = 520$ nm) efficiency (59%) while copolymer **322c** with silyl-PV units shows an even higher PL efficiency (64%) and blue-green EL ($\lambda_{max} = 480$ nm).[746] By contrast, the solid-state PL efficiency of the oxadiazole-substituted polymer **407** ($\lambda_{max} = 521$ nm) is very low (4%).[627] The *N*-aryl copolymers **408a,b** with PPV and MEH-PPV produce blue-green ($\lambda_{max} = 520$ nm) and green EL (λ_{max} = 507 nm), respectively.[847] The copolymer **409a** with fluorenyl vinylene units shows blue PL ($\lambda_{max} = 480$ nm), but the EL spectrum is broad, giving white emission (λ_{max} = 480, 530 nm).[848] This is probably due to excimer emission as a blend of **409a** with PVK produces blue EL ($\lambda_{max} = 460$ nm). Copolymer **409b** has been made by a cascade Suzuki−Heck process (Scheme 26).[712]

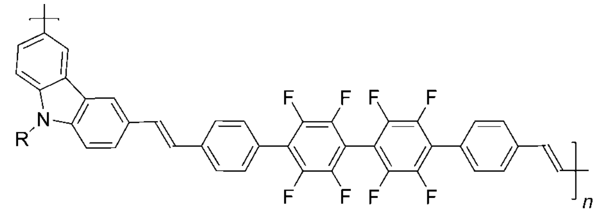
Copolymer **410** with an octafluorotetraphenylene unit has been made by the Horner method and shows blue-green EL ($\lambda_{max} = 467$ nm), but with a relatively high (12 V) onset voltage.[757] Oxidative copolymerization of carbazoles and stilbene with iron(III) chloride produces polymers **411a,b** which show blue PL (λ_{max} = 451 and 470 nm, respectively).[849] The PL efficiency in toluene for **411b** (18%) is much lower than that for **411a** (68%), but the measurements are very solvent dependent. In the above copolymers, the carbazoles were linked through the 3- and 6- positions and so the conjugation is through the nitrogen bridge. Recently, routes to polymers based on 2,7-carbazoles in which the conjugation is along the benzene−benzene bond have been developed (see section 3.7 below), and the 2,7-carbazole vinylene copolymers **412** have been made.[850] The ROPPV copolymer **412a** shows green PL ($\lambda_{max} = 508$ nm) in solution



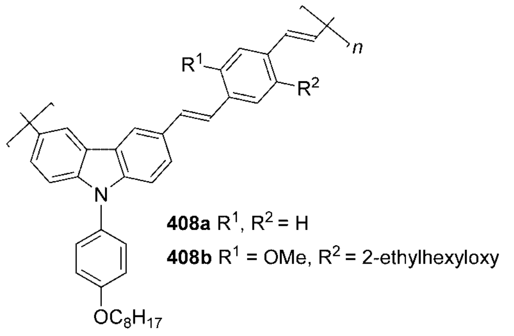
406 R = 2-ethylhexyl



407 R = 2-ethylhexyl

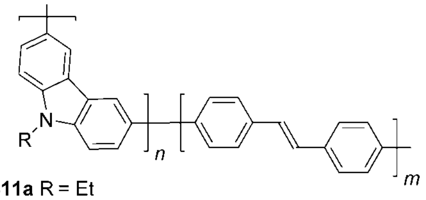


410 R = 2-ethylhexyl



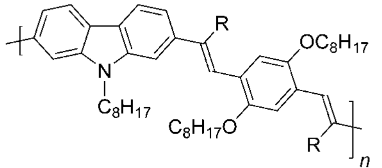
408a R^1, R^2 = H

408b R^1 = OMe, R^2 = 2-ethylhexyloxy



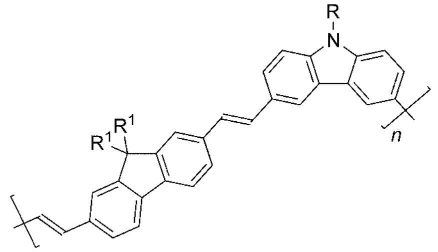
411a R = Et

411b R = C_7H_{15}



412a R = H

412b R = CN



409a R^1 = C_6H_{13}, R^2 = 2-ethylhexyl

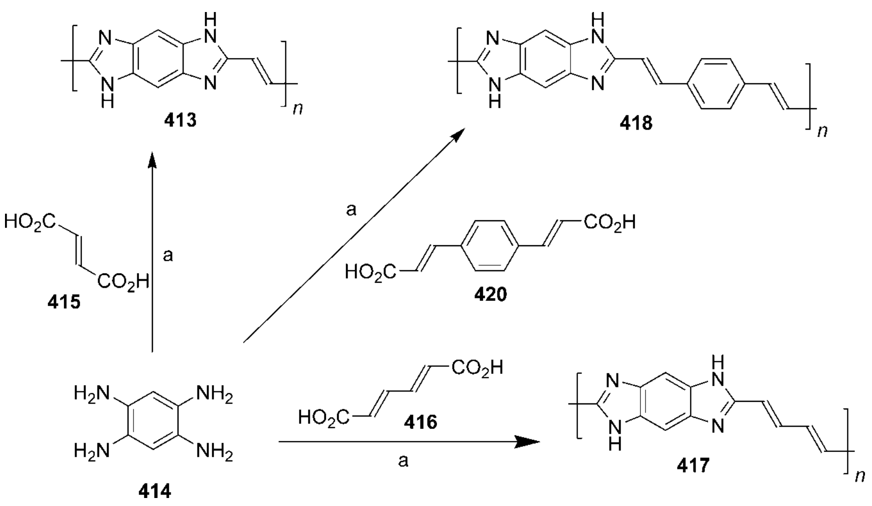
409b R^1 = C_8H_{17}, R^2 = 2-ethylhexyl

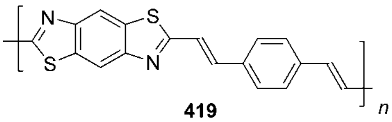
but is nonemissive in the solid state. The cyano-PPV copolymer **412b**, however, produces red EL (λ_{max} = 640 nm) with moderate efficiency (0.17 cd/A).

Jenekhe and Osaheni[851] have obtained orange (λ_{max} = 620 nm) emission from a device using poly(benzo-bis-imidazole vinylene) (**413**) prepared by condensation of 1,2,4,5-benzenetetramine (**414**) and fumaric acid (**415**) (Scheme 36). Condensation of **414** with muconic acid (**416**) produced a butadienylene polymer **417**, whose EL emission was slightly red-shifted (λ_{max} = 652 nm) compared to that of **413**. They also obtained red (λ_{max} = 640 nm) EL from the heteroarylene vinylene phenylene vinylene alternating copolymers **418**−**419** prepared by condensation of 1,4-benzene bisacrylic acid (**420**) with **414** or 2,5-diaminobenzene-1,4-dithiol (**421**).[851−853] The polymer **418** has also been made by a precursor route.[854]

Sulfur-containing heterocycles have been less studied as units in PAVs. Poly(thienylene vinylene) (**422**) is reported to show only very weak red EL.[855] It is difficult to prepare by precursor routes. The alternating copolymer **423a** made by the Wittig method shows bright red EL (λ_{max} = 620 nm).[855,856] Copolymer **423b** made by Horner polycondensation also shows red EL (λ_{max} = 620 nm) with a low (<4 V) onset voltage.[491] Copolymer **424** with a mesogen side-chain displays yellow-green PL.[857] It also shows liquid crystalline behavior, which means that polarized emission is possible. The bithiophene vinylene polymer **425** has been prepared by oxidative coupling of a bis-thienylethene monomer with iron(III) chloride.[858] This polymer exhibits red EL (λ_{max} = 610 nm), as do the copolymers **426a,b** (λ_{max}

Scheme 36. Synthesis of Benzobisimidazole Vinylene Containing Polymers: (a) Polyphosphoric Acid, P_2O_5, 120 °C





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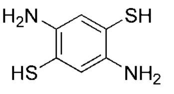

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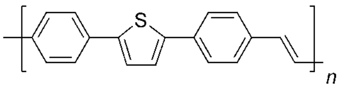

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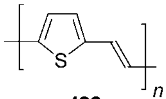

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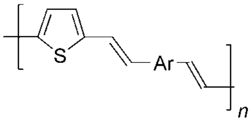
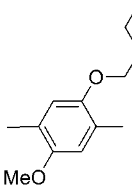
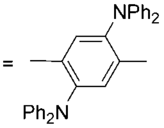
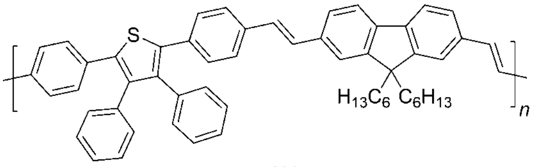




423a Ar =



423b Ar =



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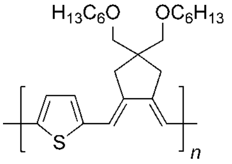

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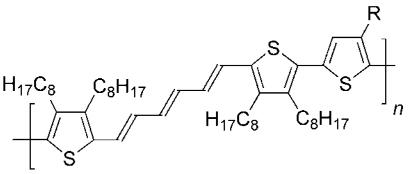
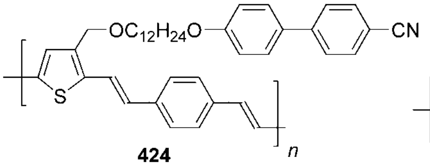


431a R = H
431b R = C_8H_{17}



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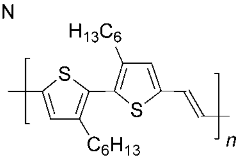

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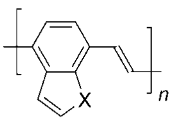
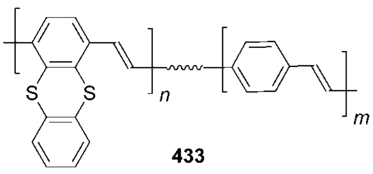


432a X = S
432b X = O



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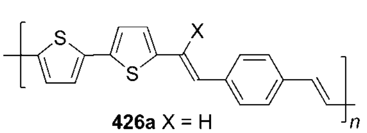
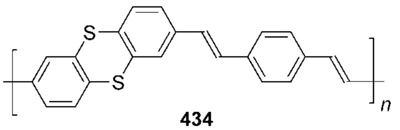


426a X = H
426b X = CN



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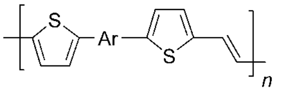
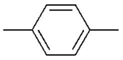
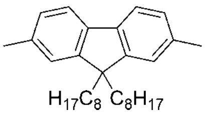
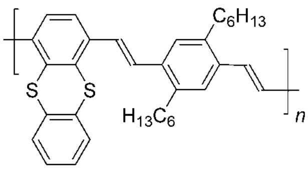




427a Ar =



427b Ar =

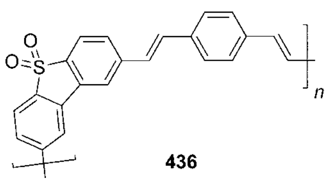


435

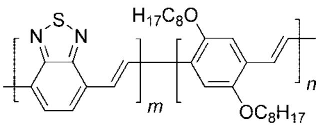
= 614 and 655 nm, respectively) with PPV.[859] The phenylene−thiophene copolymer **427a** is a blue emitter with λ_{max} = 458 nm.[860] Polymer **428** with the inverse ratio of phenylenes to thiophenes is by contrast a green emitter (λ_{max} = 533 nm) and has green EL (λ_{max} = 560 nm),[861] while the fluorenyl copolymer **427b** is a yellow emitter (λ_{max} = 595 nm).[862,863] Copolymer **429** made by Heck coupling is a blue emitter (λ_{max} = 445 nm).[713]

The thienylene butadienylene polymer **430** has been made by the zirconocene precursor route (Scheme 32) and shows yellow PL (λ_{max} = 569 nm).[784] The terthienyl hexatrienylene polymers **431a,b** were made by Moreau and co-workers[864] using Stille coupling of a bis-stannylthiophene with a dithienylhexatriene made by the Horner reaction. The PL from the polymer **431b** with the additional octyl substituent is blue-shifted (λ_{max} = 620 nm), compared with that from **431a** (λ_{max} = 636 nm), probably due to steric interactions between the octyl side-chains causing greater out-of-plane torsion of the polymer main-chain.

Poly(benzothienylene vinylene) (**432a**) has been made by the Wessling route and shows yellow PL (λ_{max} = 570 nm), as does the benzofuran analogue **432b** (λ_{max} = 582 nm).[618] Polymers **433**−**435** with thianthrene units have been prepared by Friedrich and co-workers, and their EL properties have been studied.[865,866] The statistical copolymer **433** with phenylene vinylene units, prepared by the Wessling route, shows green PL (λ_{max} = 547 nm) and EL (λ_{max} = 562 nm). The 2,6-thianthrene alternating copolymer **434** made by the Wittig route produces white EL (λ_{max} = 532 nm) with a broad emission spectrum, while the 1,4-thianthrene copolymer **435** shows green PL (λ_{max} = 513 nm), but no EL was observed from single-layer devices. Double-layer devices with Alq_3 showed green emission (λ_{max} = 545, 575 nm) with some emission from both layers.

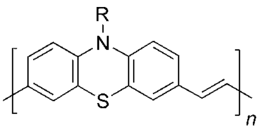


436

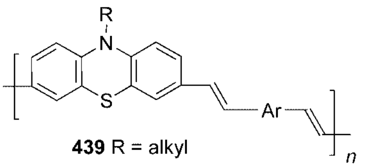


437

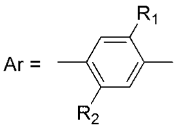
A copolymer of PPV **436** containing electron-accepting dibenzothiophene-5,5-dioxide units is blue-green emitting (λ_{max} = 457 nm), but the EL is weak.[867] Benzodithiazole copolymers **437** containing 0.5−50 mol % of the heterocycle were made by Stille coupling.[868] The EL red-shifts with increasing thiazole content, with the emission maximum being tunable from 519 to 724 nm. The highest EL efficiency is 0.31% for the 1% copolymer (λ_{max} = 663 nm). Phenothiazinylene vinylene homopolymer **438** has been made by the Horner route and produces yellow EL (λ_{max} = 570 nm).[845]



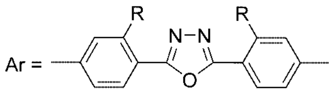
438 R = 2-ethylhexyl



439 R = alkyl

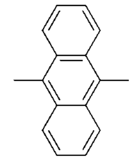


439a R_1, R_2 =H
439b R_1, R_2 = OC_6H_{13}
439c R_1 = 2-ethylhexyloxy, R_2 = Me

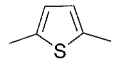


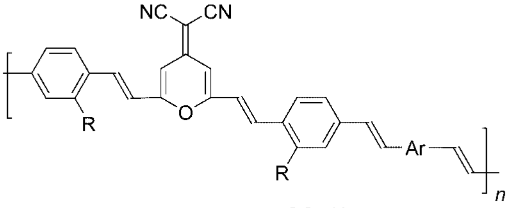
439d R = H
439e R = OC_8H_{17}

439f Ar =

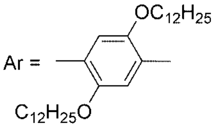


439g Ar =

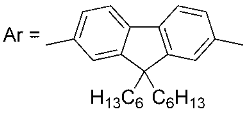


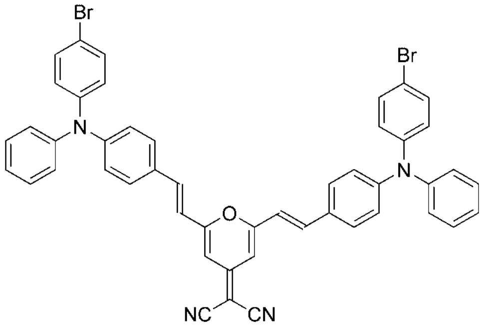


440a R = H, Ar =



440b R = H
440c R = OC_6H_{13}
440d R = $OC_{12}H_{25}$

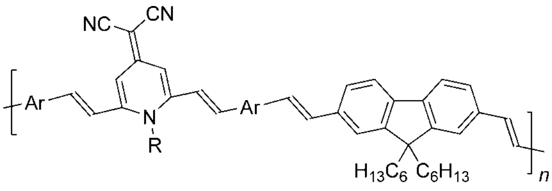




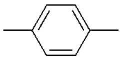
441

Copolymerization with 3,6-carbazole is reported to red-shift the emission. The phenothiazine copolymers **439a−c** made by the Wittig route also produce yellow EL (λ_{max} = 552−560 nm), reportedly with better efficiencies than those for the similar copolymer **323a**.[869,870] By introducing an oxadiazole unit in **439d,e**, yellow EL (λ_{max} = 566 nm) with an efficiency of 1% has been obtained.[870,871] Red emission (λ_{max} = 650−658 nm) has been obtained by incorporating an anthracene unit as in **439f**[872] or a thiophene as in **439g**.[873]

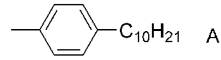
Red emission can also be obtained by incorporating pyranylidene vinylene units as in the copolymers **440**.[874,875] Both **440a** and **440b** have an EL emission maximum at 653 nm, while the ortho-alkoxy units in **440c,d** slightly blue-shift the emission (λ_{max} = 636 nm). The emission in all cases comes from the distyrylpyran units. Incorporation of 0.5−10% of **441** into a polyfluorene produces yellow to red emission (λ_{max} = 557−634 nm).[876] The highest efficiency of 0.54 cd/A was obtained for the copolymer containing 2% of **441** (λ_{max} = 608 nm). The copolymers **442** containing a similar chromophore exhibit orange-red EL with emission maxima ranging from 570 nm for **442a** to 598 nm for **442c**.[877] The fluorescence of a copolymer incorporating a photochromic dithienylethene unit is blue (λ_{max} = 450 nm) in the ring-opened form **443a** and red (λ_{max} = 673 nm) in the ring-closed form **443b** produced by irradiation of **443a** with UV light.[878] In theory, this might provide a way to produce an LED whose emission could be switched between the two colors, but as the ring-opening reaction is induced by visible light, it is probable that self-absorption by **443b** would make the emission color unstable.



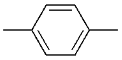
442a R = C_6H_{13} Ar =



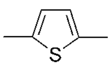
442b R =

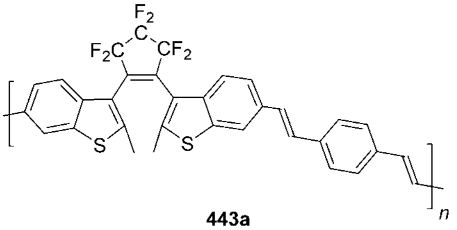


Ar =

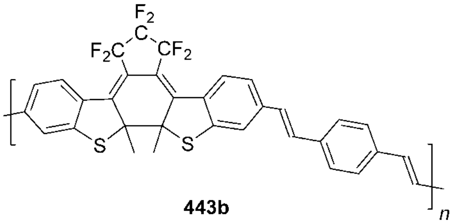


442c R = C_6H_{13} Ar =

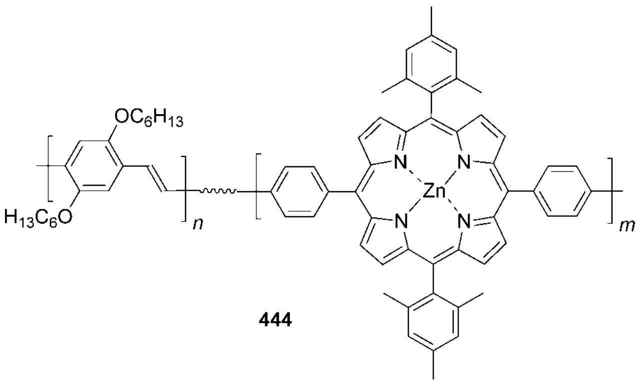




443a

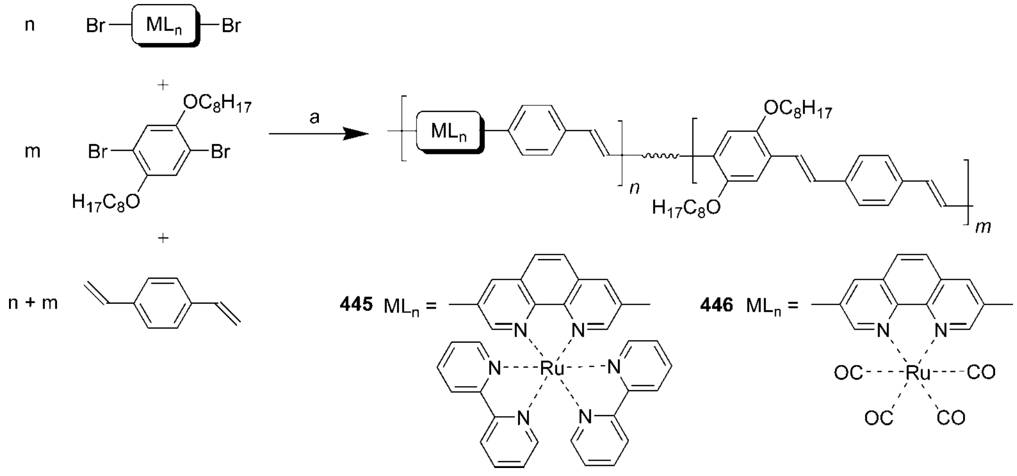


443b



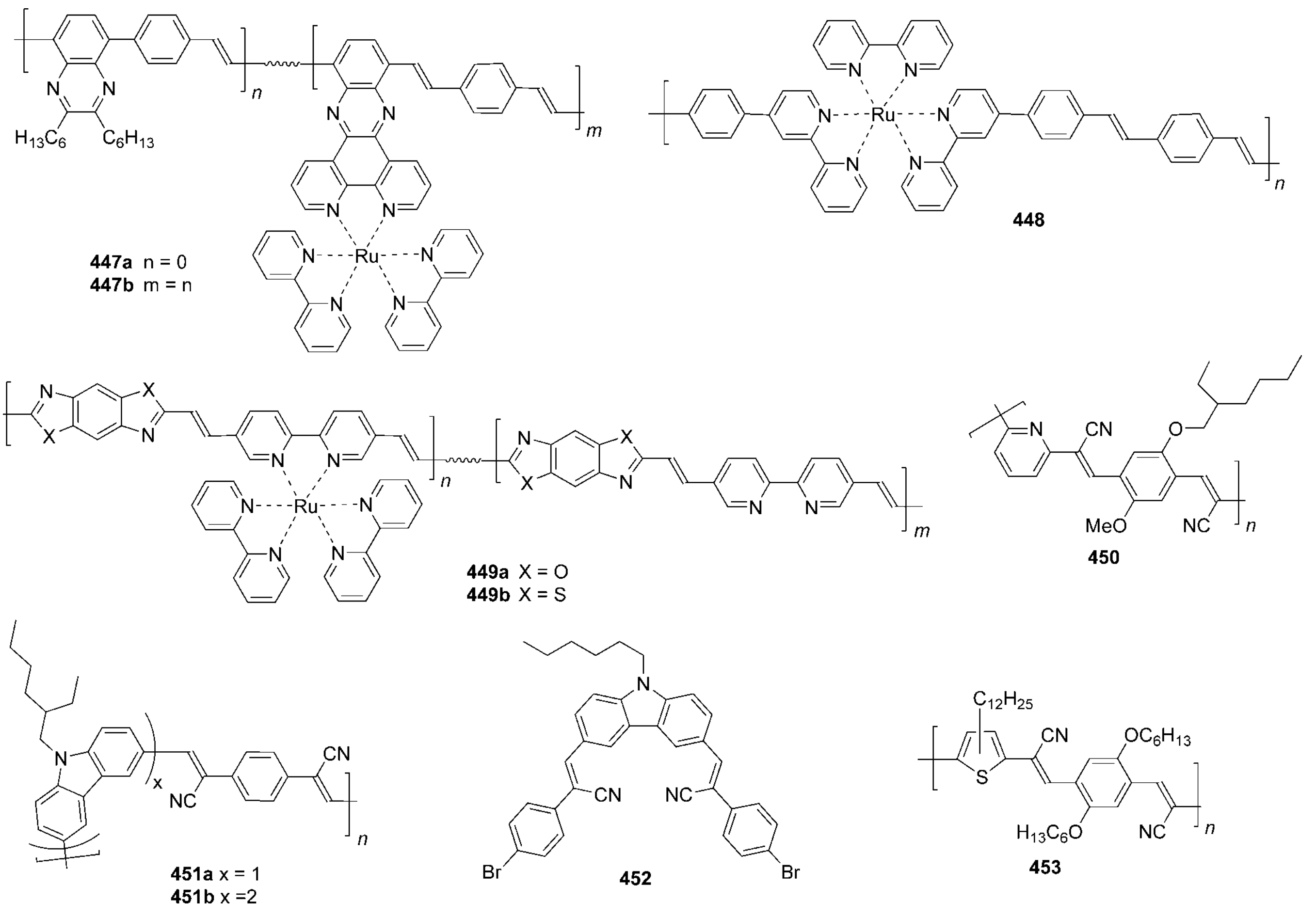
444

Scheme 37. Synthesis of PPVs Incorporating Organometallic Complexes: (a) $Pd(OAc)_2$, $P(o\text{-tolyl})_3$, Bu_3N, DMF, 100 °C



Organometallic dyes have also been incorporated as units in PAVs. A PPV copolymer **444** containing metalloporphyrin units in the chain ($m = 1-2\%$) has been made by the Gilch route.[879] It shows PL emission from both the PPV (green) and the porphyrin (red) units. Electroluminescent copolymers containing rubidium(II) or rhenium(I) moieties have been made by Heck coupling (Scheme 37).[880] At high concentrations of the metal complex ($m > 0.5$), only red emission from the organometallic complexes is observed, but at lower levels of metal content, orange ($\lambda_{max} = 570-600$ nm) emission from the ROPPV units is also seen. The highest EL efficiencies were seen for the complexes **445** ($\lambda_{max} =$ 710 nm, 0.17%) and **446** ($\lambda_{max} = 700$ nm, 0.21%). Higher luminances and slightly lower onset voltages were obtained by use of oxadiazole-substituted bipyridyl moieties instead of phenanthroline units in the polymer chain, but at the cost of lower efficiencies (maximum 0.01%). Similar polymers **447** (Chart 6) have also been made by Heck coupling.[815] The homopolymer **447a** shows red EL ($\lambda_{max} = 650$ nm), while the copolymer **447b** shows EL emission from both units ($\lambda_{max} = 550$ and 630 nm, respectively). Red EL (λ_{max} = 725, 770 nm) has also been obtained from polymer **448**, in which the metal forms part of the main-chain.[430] The emission clearly comes from the metal complexes. (For similar polymers with a nonemissive metal center, see section 4.4 below.) Copolymers **449a,b** were made by condensation

Chart 6



447a n = 0
447b m = n

448

449a X = O
449b X = S

450

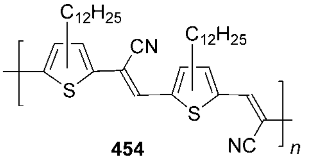
451a x = 1
451b x =2

452

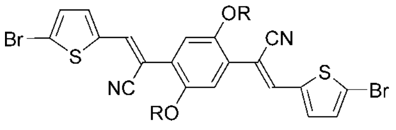
453

of bipyridyl dicarboxylic acid with the appropriate aromatic diamine (*cf.* Scheme 36) followed by treatment of the resulting polymer with a ruthenium(II) complex. They both show red EL (λ_{max} = 700 and 702 nm, respectively).

Heteroarylene vinylene polymers bearing cyano substituents on the vinylene moieties in order to improve their electron accepting properties can be made by Knoevenagel condensation. Only very weak emission is obtained from single-layer LEDs containing the 2,6-pyridinylene vinylene copolymer **450**, due to poor hole injection.[881] This can be overcome by blending **450** with hole-transporting PVK to give bright orange-red emission (λ_{max} = 580 nm), though the onset voltage is still high (20 V). A lower driving voltage has been observed for a LEC-containing (see section 6.3 below) polymer **450**. Use of a PPV hole-transporting layer also improves efficiency, but the emission is voltage dependent, with red emission from **450** being seen at a potential of 19 V and green PPV emission being obtained at 21 V. The polymer **451a** with a carbazolyl group shows green (λ_{max} = 510 nm) EL.[882] The use of a polypyrrole hole-transporting layer enhances the EL efficiency significantly.[883] The biscarbazole copolymer **451b** also shows green EL (λ_{max} = 558 nm).[884,885] The dibromo compound **452** has been incorporated into blue emitting polyfluorenes (see section 3.4).[886] White EL has been seen from the resulting copolymers, as emission occurs from both the fluorenes and the incorporated chromophore.

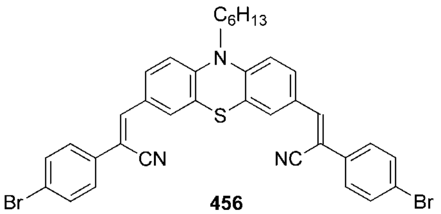


454

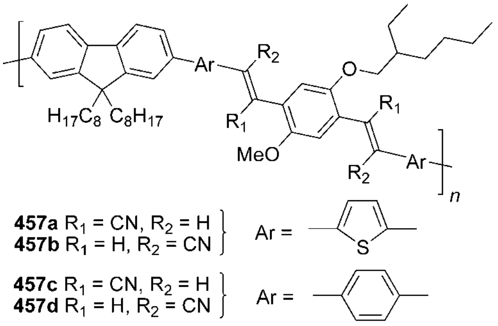


455 R = 2-ethylhexyl

Incorporation of thiophenes into PPVs reduces the band gap by raising the HOMO level. Replacement of one of the phenylene units in CN-PPV **208** to give the copolymer **453** reduces the band gap from 2.1 eV (λ_{max} = 590 nm) to 1.75 eV (λ_{max} = 740 nm), and so **453** emits in the near-infrared. The device ITO/PPV/**453**/Al was the first organic polymer based infrared-emitting LED.[887] Replacement of both aryl rings with thienyl groups in **454** results in a further reduction of the band gap to 1.56 eV (λ_{max} = 800 nm).[647,888] Like compound **452**, dibromo-oligomer **455** has been incorporated into polyfluorenes in order to tune the emission color.[889,890] As the amount of **455** increases from 1 mol % to 15 mol %, the emission changes from green (λ_{max} = 540 nm) to red (λ_{max} = 630 nm). Similarly, incorporation of 10−50% of **456** into a polyfluorene shifts the EL maximum from 572 to 614 nm.[891] The alternating copolymers **457a,b** produce red emission with maxima at 602 and 674 nm, respectively.[892] The EL efficiency (0.73 cd/A) is much higher when the cyanos are α- to the phenylene, as in **457b**, than when they are next to the thiophene, as in **457a** (0.04 cd/A). The EL efficiency of the thienyl copolymer **457a** is also higher than that for the corresponding phenylene copolymer **457c** (λ_{max} = 525 nm, 0.2 cd/A), but the reverse is true for **457b** and **457d** (λ_{max} = 555 nm, 0.36 cd/A). A similar red-shift in EL emission with a drop in efficiency is seen upon replacement of a phenylene with a thienyl unit for polymers **458a** (λ_{max} = 537 nm, 0.19 cd/A) and **458b** (λ_{max} = 627 nm, 0.05 cd/A).[763]

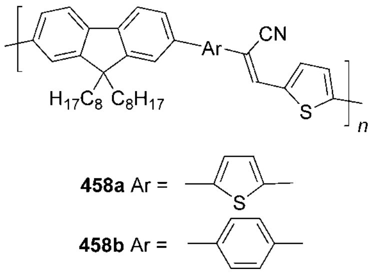


456



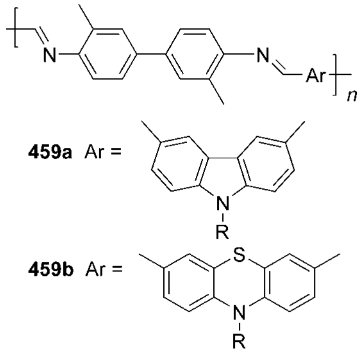
457a R_1 = CN, R_2 = H
457b R_1 = H, R_2 = CN

457c R_1 = CN, R_2 = H
457d R_1 = H, R_2 = CN



458a Ar =

458b Ar =



459a Ar =

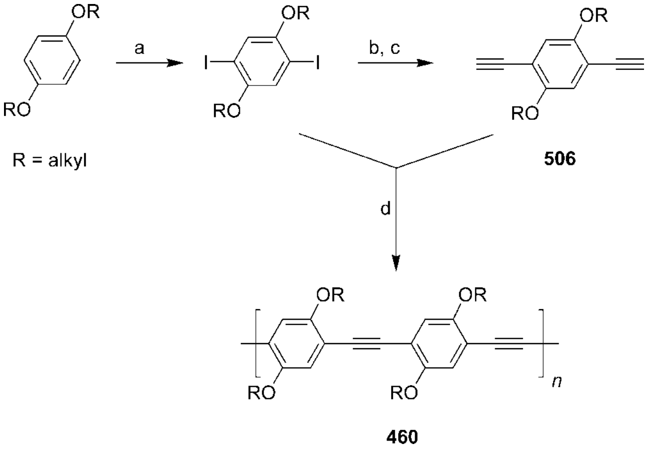
459b Ar =

Polyazomethines made by polycondensation of aryldialdehydes with aryldiamines are isoelectronic with PAVs. So far, the only such polymers from which EL has been reported are copolymers of dimethylbenzidine with phenothiazine **459a** and carbazole **459b** units, which show yellow-green (λ_{max} = 568 nm) and yellow-orange (λ_{max} = 581 nm) emission, respectively.[893]

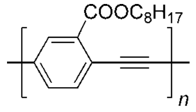
2.8. Poly(arylene ethynylene)s

Poly(arylene ethynylene)s (PAEs) can be viewed as the dehydro analogues of PAVs, in which the ethyne groups impart an additional rigidity to the polymer structure. They reportedly show better photostability than PAVs.[894] Their synthesis and properties, including their high PL efficiencies in solution, have been the subject of reviews by Giesa[895] and Bunz.[896] There are two general methods for the

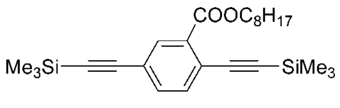
Scheme 38. Synthesis of RO-PPEs by Hagihara−Sonogashira Coupling: (a) I_2, KIO_3, H_2SO_4, HOAc; (b) $HCCSiMe_3$, CuI, $PdCl_2(PPh_3)_2$, Diisopropylamine; (c) KOH, MeOH; (d) CuI, $PdCl_2(PPh_3)_2$, Diisopropylamine



preparation of PAEs. The most widely used method is the Hagihara−Sonogashira coupling of diethynylarylenes and dihaloarylenes, illustrated in Scheme 38 for the synthesis of poly(phenylene ethynylene)s (PPEs, **460**) containing solubilizing alkoxy substituents. This method permits the synthesis of alternating copolymers as well as homopolymers and random copolymers, and it has been used to make a large number of soluble PPEs.[897−906] It has even been performed in a combinatorial manner in order to rapidly screen new materials.[907] The main defects in the polymers prepared by this route are diynes, which undergo photoinduced cross-linking in the solid-state over time, reducing the solubility. Heitz and co-workers have made a defect-free PPE **461** with carboxylic ester side-chains, by using the silyl-protected diyne **462**, in a one-pot deprotection−polymerization process.[908]



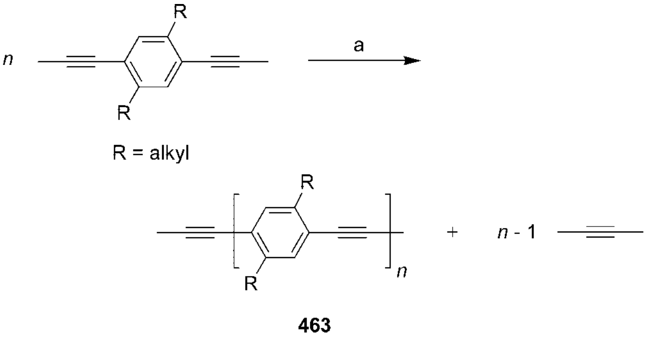
461



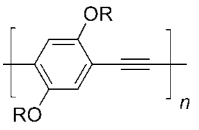
462

The other route to PAEs is the transition-metal-catalyzed metathesis of diynes, which is illustrated for the synthesis of PPEs **463** with alkyl substituents (Scheme 39).[909,910] To make alkoxy-substituted PPEs with this catalyst system, the 4-chlorophenol must be replaced with 4-trifluoromethylphenol. The metathesis polymerization of alkynes has been developed by Bunz and co-workers to make a range of PAEs.[911−916] For a more comprehensive discussion of the scope and limitations of this and the Hagihara−Sonogashira method, the reader is referred to the review by Bunz.[896]

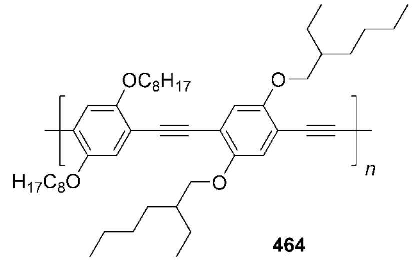
Scheme 39. Synthesis of PPEs by Alkyne Metathesis: (a) $Mo(CO)_6$, 4-Chlorophenol, *o*-Dichlorobenzene, Reflux



The substituent and other effects on the behavior of PPEs closely match those seen for PPVs and so will not be discussed exhaustively here. The effective conjugation length for a dihexyloxy-PPE (**460a**) has been estimated to be about 9 units, which is comparable with the values in PPVs.[917] The first LEDs using poly(2,5-dialkoxy-1,4-phenylene ethynylene)s (RO-PPEs, **460**) as emitters, made by Shinar[898,918,919] and Wrighton,[920] showed emission maxima at around 1.95 eV ($\lambda_{max} = 600$ nm) with rather poor efficiency. Unlike PPV derivatives, the EL spectra of the PPE derivatives were red-shifted by 20 nm with respect to the PL spectra. They also showed an appreciable long-wavelength tail. These effects were ascribed to increased radiative decay from the longer conjugated segments during EL. As the polydispersities of the PPE derivatives were higher than those for the corresponding PPV derivatives, there was an increased concentration of shorter conjugation segments leading to a larger Stokes shift between absorption and emission spectra and to weakly resolved vibronic structure in the EL and PL spectra. These LEDs also showed unusual symmetric current−voltage and luminescence−voltage curves for forward vs reverse biases.[921] Better EL performance has since been achieved by Weder and co-workers using higher molecular mass materials made by an improved synthetic



460a R = OC_6H_{13}
460b R = OC_8H_{17}



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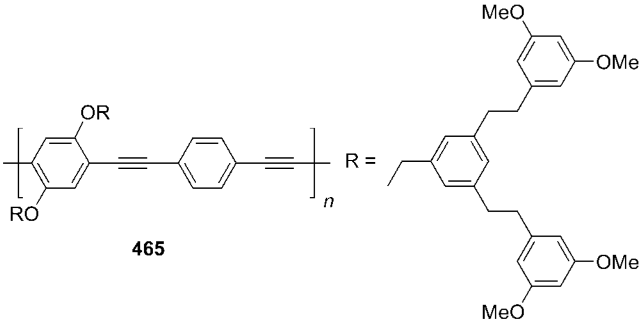

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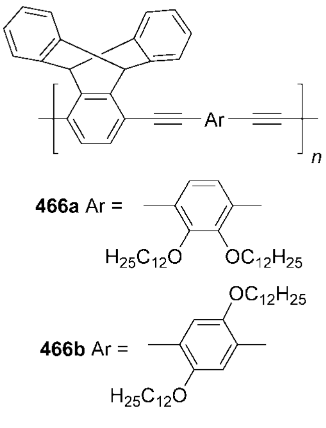
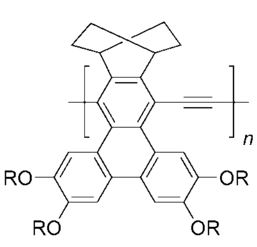


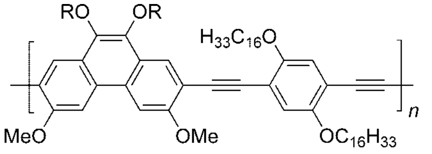
466a Ar =

466b Ar =

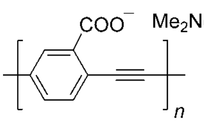


467 R = alkyl

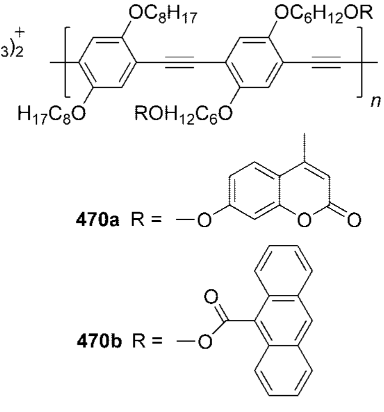
protocol.[922,923] Their polymers **460b** and **464** showed green-yellow EL (λ_{max} = 535 nm) with a modest efficiency of 0.07% and with rather high (16−19 V) onset voltages. The onset voltages were lowered to under 10 V, by blending **460b** with a hole-transporting polymer.[924] This also increased the maximum luminance from 4 cd m^{-2} to 147 cd m^{-2}. A further increase in luminance was achieved by use of an electron-transporting layer. There is a significant red-shift between the EL (λ_{max} = 535 nm) and PL (λ_{max} = 478 nm) for both polymers **460b** and **464**. This is even more marked for polymer **461**, which shows blue PL in solution (λ_{max} = 426, 468 nm), green PL in the solid state (λ_{max} = 516 nm), and green-yellow EL (λ_{max} = 557 nm).[908] These large red-shifts suggest that there are significant interactions between polymer chains. For alkyl-substituted PPEs, Bunz and co-workers have presented strong evidence that aggregate formation is the cause of these bathochromic shifts,[925] while Swager and co-workers have shown that such aggregates can produce strong emission from excimers.[926] Further support for this hypothesis is provided by the blue solid-state PL from polymers, *e.g.* **465** (λ_{max} = 454 nm), bearing bulky dendron substituents that efficiently suppress interchain interactions.[905,927] Similarly, some PAEs containing large iptycene[481,928−931] or cyclophane units[932,933] display blue PL in the solid state with high quantum efficiencies, although blue-green or green emission is seen from other PPEs with cyclophane units.[747,934,935] The PL of the polymer **466a** with 2,3-dialkoxyphenylene units is blue-shifted (λ_{max} = 424 nm) compared to that of its 2,5-dialkoxyphenylene counterpart **466b** (λ_{max} = 460 nm),[481] which mirrors the behavior of the corresponding RO-PPV derivatives **87a,b** (see section 2.2 above).

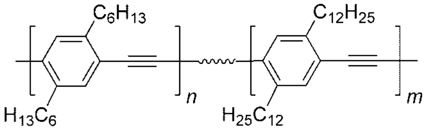


468 R = 2-ethylhexyl

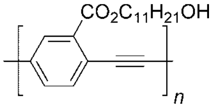


469





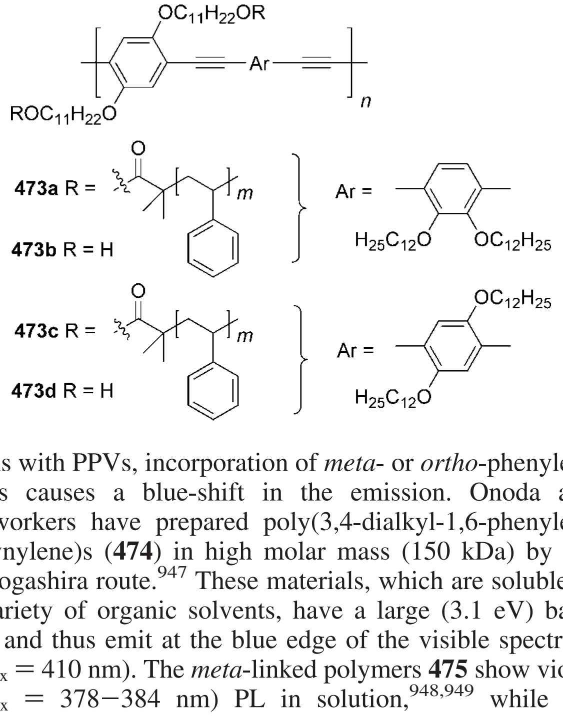
471



472

Polymers with triphenylene, e.g. **467** (λ_{max} = 480 nm),[936] or phenanthrene, e.g. **468** (λ_{max} = 455 nm),[691] units also show blue-shifted emission. Blue-green EL (λ_{max} = 500 nm) has been obtained from the polymer salt **469**.[937] Attachment of electron-withdrawing groups to PPEs causes little change in the emissive properties,[906] but the coumarin and anthracene dyes attached to polymers **470a,b** cause a marked increase in PL efficiency due to energy transfer from the chromophore to the conjugated polymer backbone.[904]

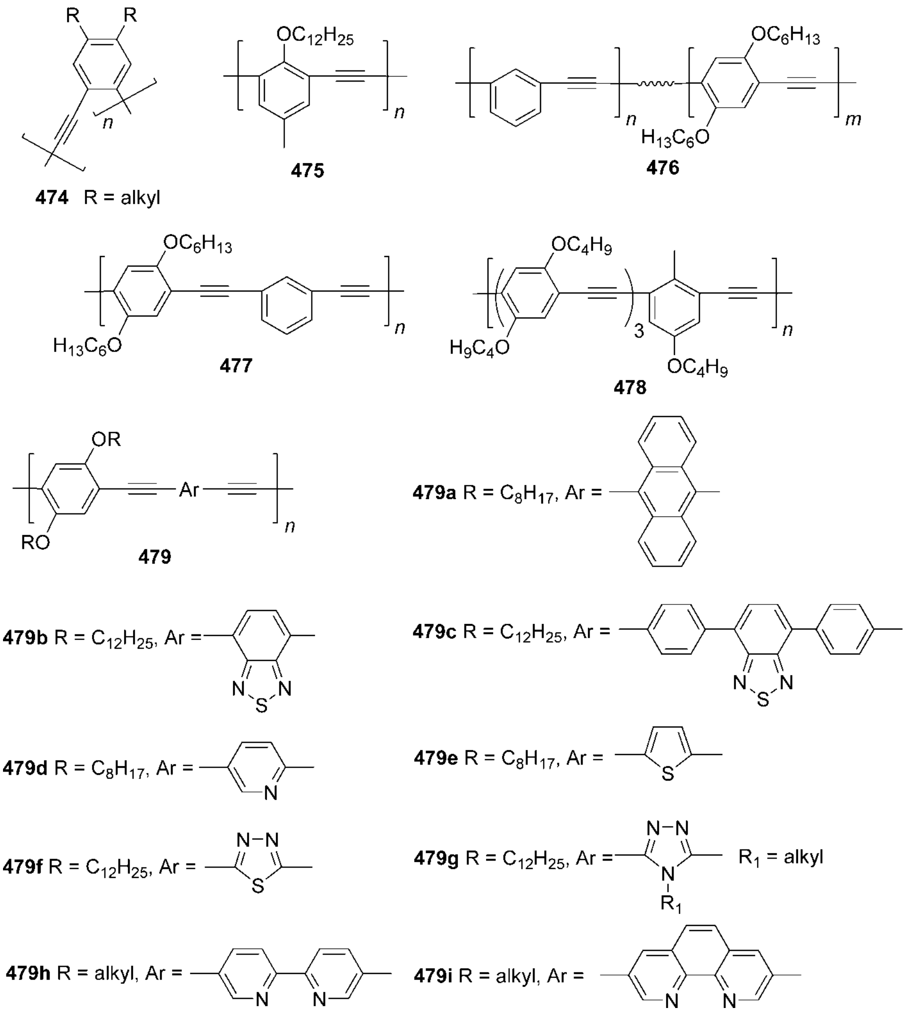
Although the EL performance of PPEs is generally inferior to that of PPVs, they show promise as emitters of polarized light, owing to their rigid rod structure. Weder, Smith, and co-workers have found that blends of **460b** and other RO-PPEs with high molecular mass polyethylene can form highly oriented films through uniaxial stretching[938,939] or melt-processing.[940] Films treated in such ways show polarized emission with high anisotropies, making them promising materials for use as backlights in liquid crystalline displays (LCDs).[938,939,941−943] Polarized EL has also been obtained from rubbing-aligned films of polymers **471**[944] and **472**.[945] Another way to incorporate PPEs within a nonemissive polymer matrix is to attach polystyrene chains as side-groups as in **473a,b**.[946] The emission from **473a** (λ_{max} = 456 nm) and **473b** (λ_{max} = 476 nm) is blue-shifted compared with those of copolymers **473c** (λ_{max} = 472 nm) and **473d** (λ_{max} = 498 nm) without the polystyrene chains. EL efficiencies of over 1% have been obtained by blending a hole-transporting material with **473a,b**.



As with PPVs, incorporation of *meta*- or *ortho*-phenylene units causes a blue-shift in the emission. Onoda and co-workers have prepared poly(3,4-dialkyl-1,6-phenylene ethynylene)s (**474**) in high molar mass (150 kDa) by the Sonogashira route.[947] These materials, which are soluble in a variety of organic solvents, have a large (3.1 eV) band gap and thus emit at the blue edge of the visible spectrum (λ_{max} = 410 nm). The *meta*-linked polymers **475** show violet (λ_{max} = 378−384 nm) PL in solution,[948,949] while the copolymers **476** (Chart 7) show blue emission in solution, which can be fine-tuned from λ_{max} = 475 to 440 nm by increasing the proportion of *meta*-linkages. However, such a blue-shift is accompanied by a drop in PL intensity.[950] The alternating copolymer **477** also emits blue PL in solution, but the solid-state PL and EL is green (λ_{max} = 545 nm).[951] The EL emission maximum for the copolymer **478** is voltage tunable from 577 nm at 12 V to 547 nm at 17 V.[952]

The emission color of PPEs can be tuned by copolymerization with other arylene building blocks. Thus, red EL is obtained from copolymers with anthracene **479a** (λ_{max} = 590 nm)[953,954] or benzothiadiazole units **479b** (λ_{max} = 620 nm),[955] while yellow PL is seen from the diphenylbenzothiadiazole copolymer **479c** (λ_{max} = 559 nm).[956] A polymer with both cyclophane and benzodithiazole units produces orange PL (λ_{max} = 565 nm).[957] By contrast, the EL from copolymer

Chart 7



474 R = alkyl

475

476

477

478

479

479a R = C_8H_{17}, Ar =

479b R = $C_{12}H_{25}$, Ar =

479c R = $C_{12}H_{25}$, Ar =

479d R = C_8H_{17}, Ar =

479e R = C_8H_{17}, Ar =

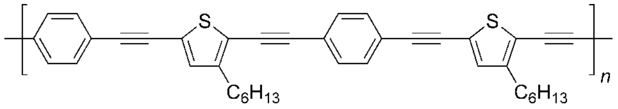
479f R = $C_{12}H_{25}$, Ar =

479g R = $C_{12}H_{25}$, Ar = R$_1$ = alkyl

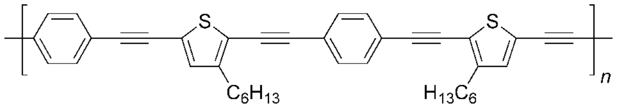
479h R = alkyl, Ar =

479i R = alkyl, Ar =

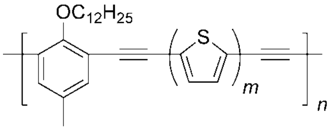
479d containing pyridine units is blue-green (λ_{max} = 480 nm),[953,954] while green EL is seen from the thiophene copolymer **479e** (λ_{max} = 530 nm).[954] Alkyl substituents on the thiophene ring produce a slight red-shift in the PL.[958] Nitro-groups on the thiophene strongly red-shift the solution PL spectrum, but the PL in the solid-state is quenched due to the close packing of the polymer chains.[959] Such packing also leads to marked red-shifts in the solid-state PL (λ_{max} = 520−560 nm *cf.* 448−478 nm) of copolymers **479f,g** containing thiadiazole and triazole units. The EL emission from **479d** is more intense than that from the homopolymer **460b**, but that from **479e** is less intense, which may be due to its lower PL efficiency (25% in solution vs 50%[960]). Li and Pang have studied the effects of regioregularity on the PL properties of copolymers with alternating phenylene ethynylene and 3-alkylthiophene ethynylene units.[961] The emission of the regioregular head-to-tail polymer **480** is blue-shifted (λ_{max} = 525 nm) compared with regiorandom material (λ_{max} = 530 nm), possibly owing to the greater rigidity of the former polymer, and the solid-state PL efficiency is over twice as high. The head-to-head polymer **481** has red-shifted emission (λ_{max} = 534 nm) with a PL efficiency 6 times higher than that of the regiorandom polymer. The copolymers **482** show a red-shift in their emission in chloroform solution as the number of thiophene rings inceases from one (λ_{max} = 410 nm) to three (λ_{max} = 485 nm) accompanied by a drop in PL efficiency from 33% down to 9%.[948] The bipyridyl copolymers **479h** show blue PL in solution (λ_{max} = 450 nm) with high efficiency (71−78%).[962,963] Interestingly, the similar copolymers **479i** show similar emission (λ_{max} = 452−460 nm), but with lower efficiencies (55−59%).[964]



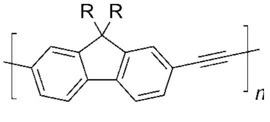
480



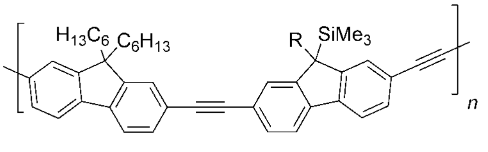
481



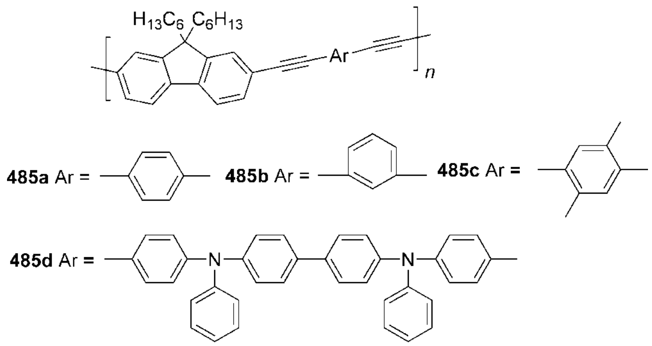
482 m = 1-3

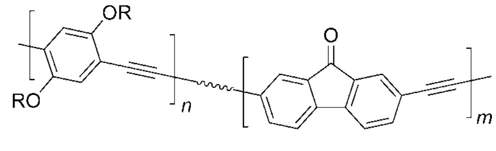


483a R = C_6H_{13}
483b R = 2-ethylhexyl

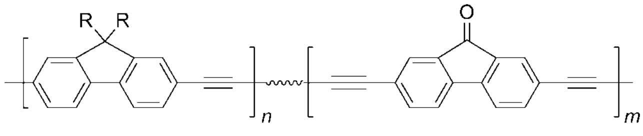


484a R = H
484b R = $SiMe_3$

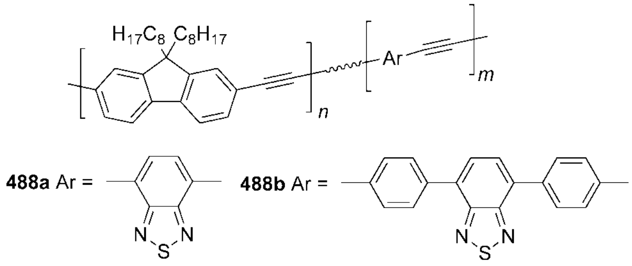


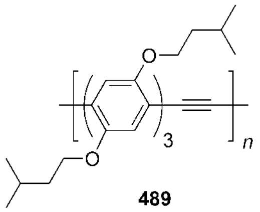


486 R = alkyl

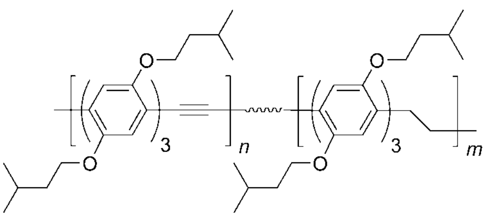


487 R = alkyl





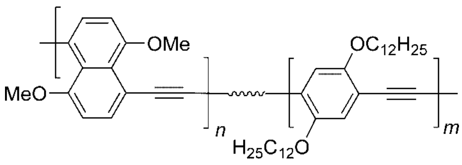
489



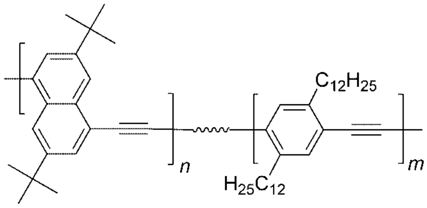
490 $n : m = 4 : 1$

As with PAVs, incorporation of oligophenylenes into PAEs leads to blue-shifted emission. The properties of the poly(fluorenylene ethynylene) (PFE) **483a** containing dihexylfluorene units depend upon the synthetic method used. Material prepared by Sonogashira–Hagihara coupling shows blue PL ($\lambda_{max} = 475$ nm) but green EL ($\lambda_{max} = 550$ nm).[965] Blending with PVK leads to blue PL and EL ($\lambda_{max} = 425$ nm), suggesting that emission is solely from the PVK.[965] The same polymer when made by alkyne metathesis shows blue-shifted solid-state PL ($\lambda_{max} = 428$ nm).[913] Similarly, the PFE **483b** with ethylhexyl substituents shows solid-state emission which is green ($\lambda_{max} = 530$ nm) if made by the Sonogashira–Hagihara method[966] and blue ($\lambda_{max} = 431$ nm) if made by the metathesis method.[913] Bunz and co-workers have made other alkyl-substituted PFEs by alkyne metathesis,[913,915] all of which show blue solid-state PL ($\lambda_{max} = 428–434$ nm).[913] This difference in behavior is probably due to the presence of defects in the polymer chains of the materials made by the polycoupling route. The alternating copolymers **484**–**485** have been prepared by that route. Copolymers **484a,b** both show broad emission spectra ($\lambda_{max} = 490$, 540 nm) and produce blue-white EL.[967] Somewhat unexpectedly, the PL emission from the polymer **485a** with *para*-phenylene is blue-shifted ($\lambda_{max} = 472$ nm) compared with that of the *meta*-phenylene containing **485b** ($\lambda_{max} = 490$ nm).[968] The EL from **485b** is green ($\lambda_{max} = 560$ nm). The methyl substituents in **485c** produce a small red-shift in emission ($\lambda_{max} = 478$ nm).[747] Green EL ($\lambda_{max} = 510$ nm) has also been obtained from copolymer **485d** containing triarylamine hole-transporting units in the polymer main-chain.[966] The random copolymers **486** and **487** containing fluorenone units, which have been made by metathesis polymerization, show blue PL ($\lambda_{max} = 425$, 450 nm) in solution, but in the solid-state, energy transfer leads to emission only from the fluorenone units ($\lambda_{max} = 522–544$ nm).[916] The emission maximum can be tuned in the benzodithiazole copolymers **488a** between 614 and 640 nm and between 598 and 701 nm for the dithienylbenzodithiazole copolymers **488b** by varying the amount of comonomer from 1% to 50%.[969] The poly(terphenylene ethynylene) **489** shows a remarkable red-shift between the blue solid-state PL ($\lambda_{max} = 452$ nm) and the red EL ($\lambda_{max} = 650$ nm).[723] Incorporation of ethanediyl units in **490** produces a small blue-shift in the PL ($\lambda_{max} = 445$ nm) and a slight increase in the PL efficiency (33% *cf.* 25%). Other terphenylene ethynylenes also show blue PL.[753,970]

Only weak luminescence is observed from poly(naphthalene ethynylene)s (PNEs). Thus, polymer **491a** made by the Hagihara route shows blue PL in solution ($\lambda_{max} = 450$ nm) with low efficiency (14%), but no emission in the solid state, probably due to quenching of emission by aggregate formation.[680,684] Copolymer **491b** produces blue PL both in solution ($\lambda_{max} = 445$ nm) and in the solid state ($\lambda_{max} = 445$ nm). Unusually, the efficiency is greater in the solid state than in solution (28% *cf.* 26%). Similarly, the PNE homopolymer **492a** made by metathesis[912] shows only weak solid-state PL, but films of the copolymers **492b** show strong luminescence, which can be tuned from $\lambda_{max} = 446$ nm to



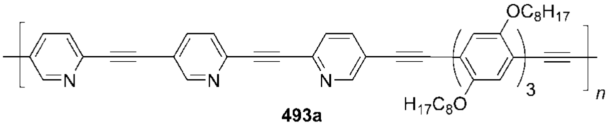
491a $m = 0$
491b $m > 0$



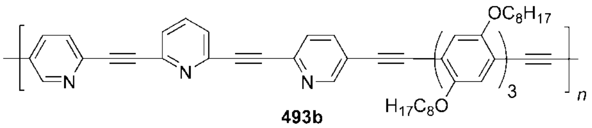
492a $m = 0$
492b $m > 0$

λ_{max} = 422 nm, by increasing the naphthalene content from 16% (m:n = 5:1) to 67% (m:n = 1:2).[911] The EL emission is also blue-shifted by enhancing the naphthalene content, with an accompanying drop in luminance from 100 cd m^{-2} for m:n = 2:1 (λ_{max} = 472 nm) to 20 cd m^{-2} for m:n = 1:1 (λ_{max} = 428 nm).[914] Optically active PAEs containing chiral binaphthyl units have been made which might display polarized emission, but as yet there is no report of their luminescence properties.[971]

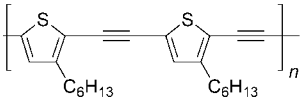
A variety of poly(heteroarylene ethynylene)s have been made by the Sonogashira–Hagihara coupling route. Copolymers **493a,b** with alternating blocks of phenylene ethynylene and pyridinylene ethynylene display blue emission (λ_{max} = 477 and 481 nm, respectively).[972] In the case of poly(thienylene ethynylene), the head-to-tail **494** and head-to-head **495** polymers show identical yellow solid-state PL emission (λ_{max} = 575 nm), with the emission intensity of **494** being 10 times higher than that for **495**.[973] The terthienyl ethynylene polymer **496** shows orange PL (λ_{max} = 569, 614 nm).[974] Incorporation of phenylene units in **497a** produces a blue-shift in the PL (λ_{max} = 551 nm), while the anthracenes in copolymer **497b** lead to bathochromically shifted emission (λ_{max} = 644, 704 nm). The emission spectra of the sexithienyl copolymers **497c** (λ_{max} = 569, 626 nm) and **497d** (λ_{max} = 525, 725 nm) are only slightly red-shifted compared to those of their terthienyl counterparts. Copolymer **498** with alternating thiophene and carbazole units shows blue PL (λ_{max} = 450, 480 nm) in solution but yellow PL and EL (λ_{max} = 580 nm) in the solid state.[975]



493a



493b



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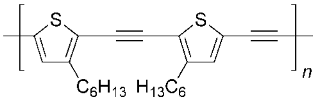

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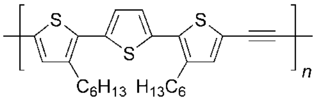

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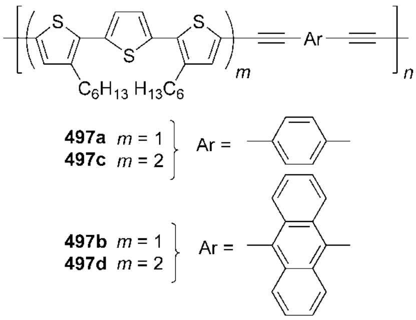
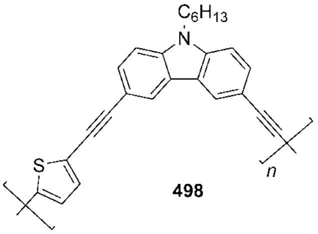
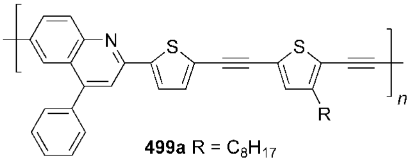


497a m = 1
497c m = 2 } Ar =

497b m = 1
497d m = 2 } Ar =

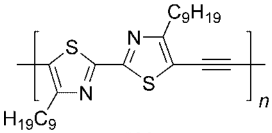


498

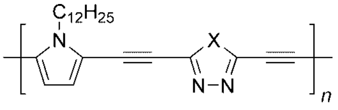


499a R = C$_8$H$_{17}$
499b R = C$_{12}$H$_{25}$

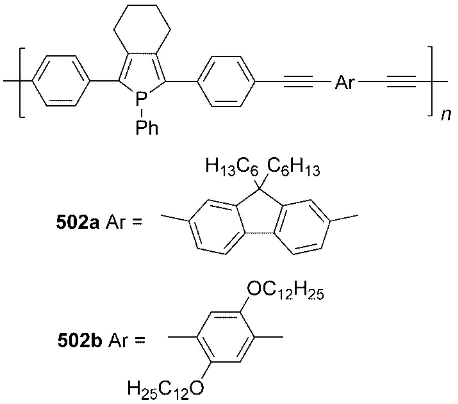
The quinoline containing copolymers **499a,b** also show a marked red-shift in going from solution (λ_{max} = 470 and 508 nm, respectively) to the solid state (λ_{max} = 560 and 605 nm, respectively), with no drop in the PL quantum yield in the solid state (69% and 48%, respectively, in solution and 64% and 46%, respectively, in the solid state). The emission of quinoline- and quinoxaline-containing PPEs is reported to be strongly quenched by protonation or the presence of some metal ions, suggesting such materials may be more useful in sensors than in LEDs.[976,977] The poly(bithiazole ethynylene) **500** emits bright red PL (λ_{max} = 600 nm).[978,979] Copolymers **501a** and **501b** show large red-shifts between their solution (λ_{max} = 499 and 415 nm, respectively) and solid-state (λ_{max} = 587 and 526 nm, respectively) PL emission spectra due to the efficient stacking of the polymer chains.[959] The EL spectrum is broader than the PL spectrum and slightly red-shifted (λ_{max} = *ca.* 640 nm).



500



501a X = S
501b X = NC$_{12}$H$_{25}$

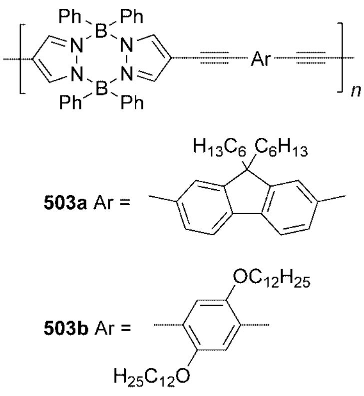


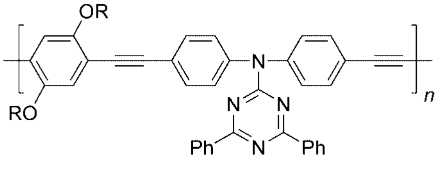
502a Ar =

502b Ar =

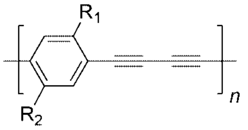
Blue or blue-green emission is seen from phosphole-containing polymers with fluorene **502a** (λ_{max} = 435 nm) or phenylene units **502b** (λ_{max} = 487–490 nm).[980] The corresponding copolymers containing pyrazabole units **503a,b** have somewhat blue-shifted emission (λ_{max} = 406 and 430 nm, respectively), suggesting interruption of conjugation by the heterocycle.[981] In contrast, the nitrogen bridge in **504** does not interrupt the conjugation, as the solid-state emission is green (λ_{max} = 509 nm).[982] The effect of the triazine unit is to lower the LUMO energy and thus improve electron injection into the polymer.

Soluble poly(phenylene butadiynylene)s (**505**) have been prepared by the oxidative coupling of diethynylbenzenes **506**.[983,984] Their PL is blue or blue-green (λ_{max} = 435–489

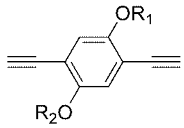




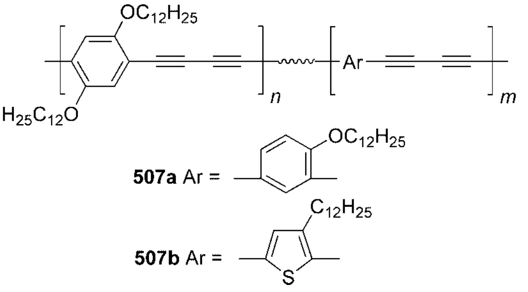
504 R = $C_{12}H_{25}$



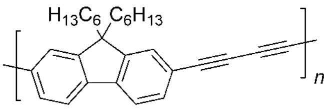
505 R_1, R_2 = alkyl, alkoxy
505a R_1, R_2 = $OC_{12}H_{25}$
505b R_1, R_2 = $OC_{10}H_{21}$
505c R_1 = $OC_{10}H_{21}$, R_2 = OMe
505d R_1 = C_8H_{17}, R_2 = Me



506 R_1,R_2 = alkyl, alkoxy



nm) in solution and blue-green or yellow (λ_{max} = 484−546 nm) in the solid state depending upon the substituents. They display liquid crystalline behavior, so that polarized emission has been obtained from films oriented by rubbing-alignment.[985] The EL from polymers **505b** is blue-green (λ_{max} = 510 nm) while that from **505c,d** is red with maxima at 600 and 630 nm, respectively.[986] The incorporation of up to 67 mol % *meta*-phenylene units in the copolymers **507a** leads to a slight red-shift and an increase in PL intensity, but greater *meta*-phenylene content causes a marked blue-shift in emisssion and a decrease in intensity so that the all-*meta* polymer (n = 0) shows blue emission (λ_{max} = 416 nm) with only 5% of the intensity of the all-*para* polymer **505a**.[987] The copolymer with 33 mol % *meta* units produces blue-green EL (λ_{max} = 500 nm).[988] The thienyl copolymer **507b** produces red-shifted emission (λ_{max} = 518 nm) with only half the PL intensity compared to that of polymer **505a**.[987] Poly(9,9-dihexylfluorenyl butadiynylene) (**508**) shows blue PL (λ_{max} = 440 nm).[988,989] The EL spectrum is broader than the PL spectrum, producing bluish-white emission. Incorporation of 33 mol % of *meta*-phenylene units has little effect on the emission spectrum. By contrast, the emission of the thiophene-*meta*-phenylene copolymer **509a** is blue-shifted compared with the case of the homopolymer **509b** (λ_{max} = 610 nm vs 640 nm).[988] A copolymer **510** containing both ethynylene and butadiynylene units is blue-green emitting (λ_{max} = 497 nm).[990] Oxidative coupling of a bis-butadiynylbenzene gives the poly(phenylene octatetraynylene) **511**, which shows green (λ_{max} = 510 nm) emission in chloroform solution with PL intensity lower than that for the corresponding butadiynylene polymer **505a**.[991]



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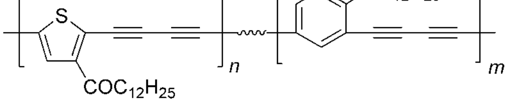
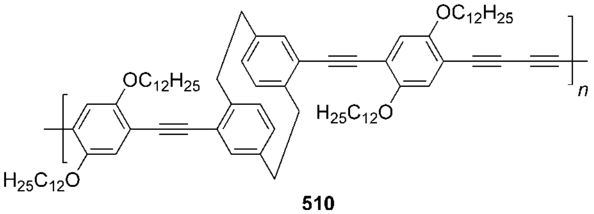


509a m = 0.33
509b m = 0



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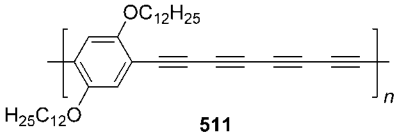

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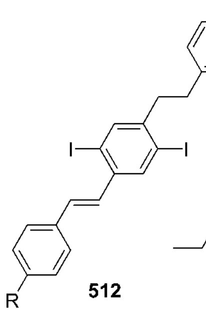

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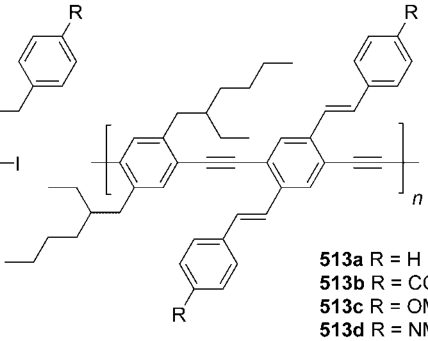
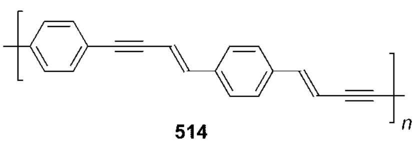


513a R = H
513b R = CO_2Me
513c R = OMe
513d R = NMe_2

Polymers containing both double and triple bonds can be prepared by various methods. The Bunz group have prepared a series of diiododistyrylbenzenes **512** by Horner coupling and then coupled them with a dialkyldiethynylbenzene to produce the cross-conjugated copolymers **513**.[992] Their PL in solution is blue or blue-green (λ_{max} = 442−496 nm) except for that of **513d** (λ_{max} = 530 nm). The solid-state PL is red-shifted into the green (λ_{max} = 504−550 nm). Electrochemical measurements suggest these should be much better charge acceptors than the dialkyl-PPEs **460**, but as yet there is no report on their EL efficiency.

Several routes have been used to make other PPE-PPV hybrids with both single and double bonds in the main-chain. The insoluble polymer **514** was made by the thermally induced retro-Diels−Alder elimination of cyclopentadiene from the precursor polymer **515**, which was itself made by the palladium(0)-catalyzed coupling of norbornadiene, *p*-

diiodobenzene, and *p*-bis(trimethylsilylethynyl)benzene.[993] The emission from **514** is blue-green ($\lambda_{\max}$ = 494 nm).



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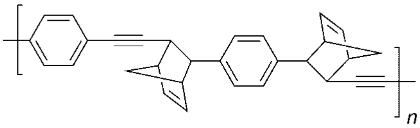

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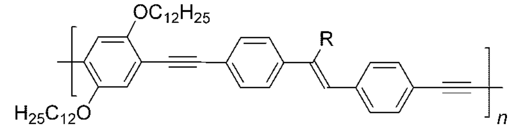
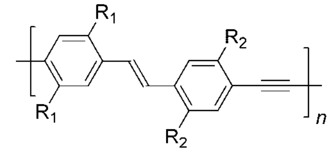
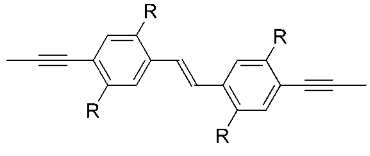


516 R = H, CN

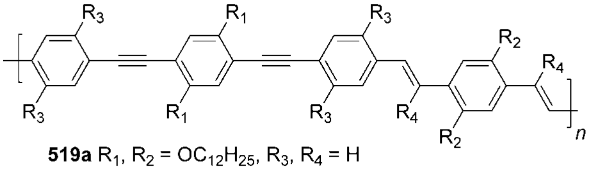


517a $R_1 = R_2$ = alkyl
517b $R_1 = OC_{18}H_{37}$, R_2 = H
517c $R_1 = OC_{18}H_{37}$, $R_2 = OC_8H_{17}$

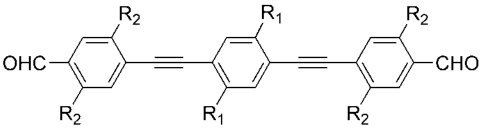
Polymers **516** containing phenylene vinylene and phenylene ethynylene units have been prepared by Sonogashira−Hagihara coupling of 4,4′-dibromostilbenes with 1,4-bis-ethynylbenzenes (**506**).[994] These polymers show a broad EL emission between 500 and 700 nm, with unusual symmetrical current−voltage and luminance−voltage behavior.[995] The alternating copolymers **517a** have been made by the metathesis of diethynylstilbenes **518**.[915] They show blue-green solid-state emission ($\lambda_{\max}$ = 460−490 nm). The alkoxy-substituted copolymers **517b,c** have been made by Egbe and co-workers by Sonogashira−Hagihara coupling of dibromostilbenes with diethynylstilbenes.[996] These show yellow-green solid-state PL ($\lambda_{\max}$ = 547 and 578 nm, respectively). Yellow EL ($\lambda_{\max}$ = 554 nm) has been obtained from **517c**, but with low efficiency.



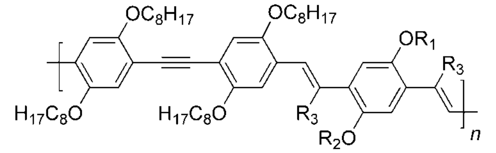
518 R = alkyl



519a R_1, $R_2 = OC_{12}H_{25}$, R_3, R_4 = H
519b R_1, $R_2 = OC_8H_{17}$, R_3, R_4 = H
519c $R_1 = OC_{18}H_{37}$, $R_2 = OC_8H_{17}$, R_3,R_4 = H
519d $R_1 = OC_8H_{17}$, $R_2 = OC_8H_{37}$, R_3, R_4 = H
519e R_1 = 2-ethylhexyloxy, $R_2 = OC_8H_{17}$, R_3, R_4 = H
519f $R_1 = OC_{17}H_{35}$, $R_2 = OC_7H_{15}$, R_3, R_4 = H
519g R_1 = 2-ethylhexyl, $R_2 = OC_8H_{17}$, R_3, R_4 = H
519h $R_1 = OC_{18}H_{37}$, R_2, $R_3 = OC_8H_{17}$, R_4 = H
519i R_1, R_2, $R_3 = OC_8H_{17}$, R_4 = H
519j $R_1 = OC_{12}H_{25}$, $R_2 = OC_8H_{17}$, R_3 = H, R_4 =CN
519k $R_1 = OC_{12}H_{25}$, $R_2 = OC_8H_{17}$, R_3, R_4 = H



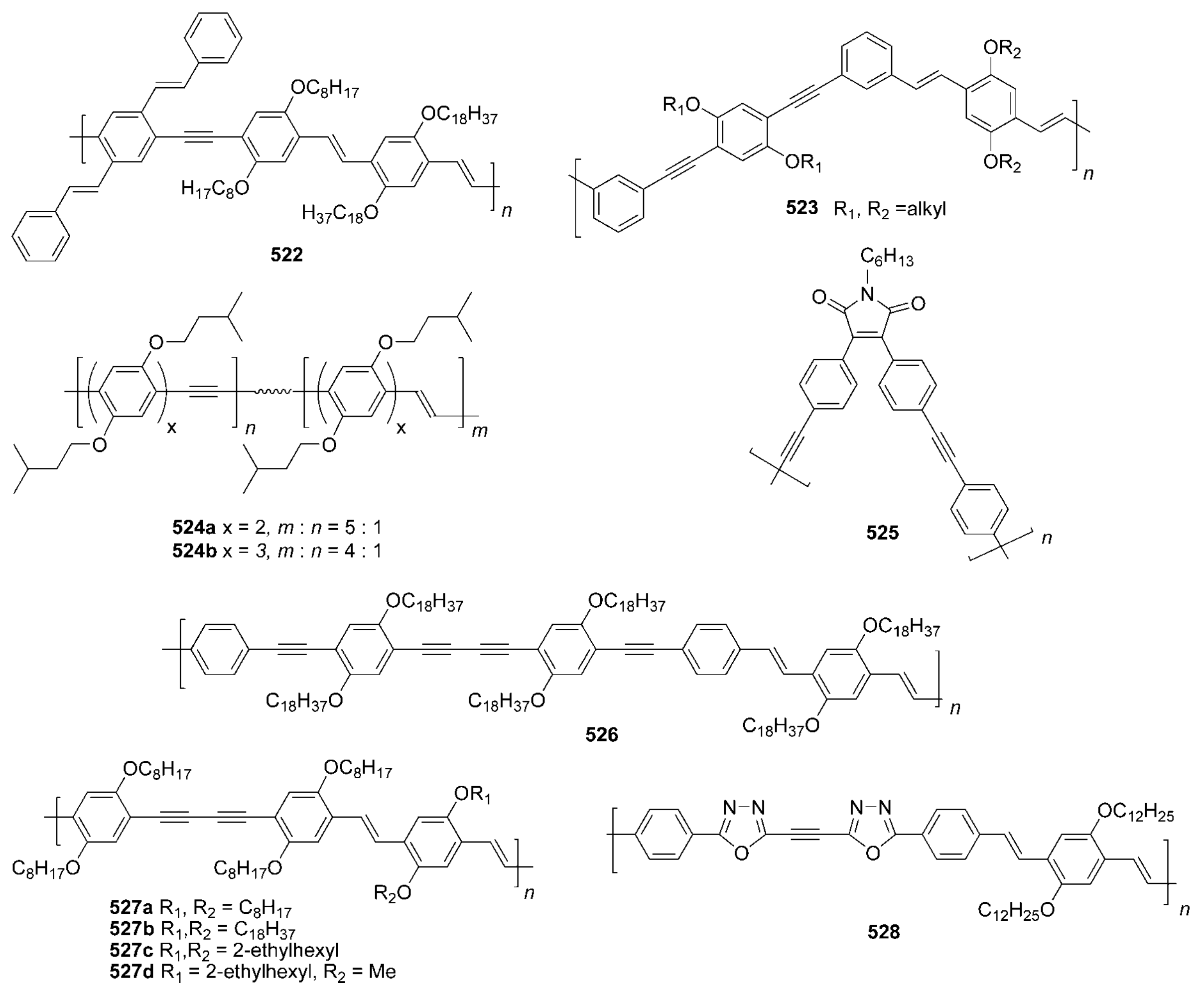
520 R_1 = alkyl or alkoxy, R_2 = H or alkoxy



521a R_1,$R_2 = C_{18}H_{37}$, R_3 = H
521b R_1,R_2 = 2-ethylhexyl, R_3 = H
521c R_1, $R_2 = C_8H_{17}$, R_3 = CN
521d R_1, $R_2 = C_8H_{17}$, R_3 = H

The same group have also made a series of copolymers **519** by Horner coupling of a benzene bis-phosphonate with dialdehydes **520**.[997−999] All polymers show blue-green ($\lambda_{\max}$ = *ca.* 490 nm) PL in solution. The substituent sizes and positions were found to markedly affect the solid-state properties. When the alkoxy chains are the same length as those in **519a,b**, the solid-state PL is only slightly red-shifted ($\lambda_{\max}$ = 508−509 nm) compared with that from solution, with PL efficiencies of 34−44%, but in **519c**, where they are of very dissimilar lengths, the solid-state emission is highly red-shifted ($\lambda_{\max}$ = 602 nm) compared with the case in solution, and the PL efficiency is only 19%, presumably due to stronger interchain interactions.[997,998] The polymer **519d** with the positions of the alkyl substituents reversed displays a much smaller red-shift in the solid state ($\lambda_{\max}$ = 510 nm) and a larger PL efficiency (29%) than **519c**.[998] The branched substituents in **519e** enhance the solid-state PL ($\lambda_{\max}$ = 512 nm) efficiency to 44%. The EL emission from polymers such as **519c** ($\lambda_{\max}$ = 608 nm, 1.79 cd/A) with an odd number of atoms in the side-chain is red-shifted and more efficient compared with those of polymers such as **519e** ($\lambda_{\max}$ = 539 nm, 0.67 cd/A) with an even number of atoms in the side-chain.[1000] The EL from **519c** is dependent upon the solvent used to process the film, with films cast from chloroform producing more red-shifted emission ($\lambda_{\max}$ = 643 nm) than those cast from chlorobenzene cited above. By contrast, casting films of **519e** from chloroform does not red-shift the emission but the EL efficiency is increased to 0.99 cd/A. Films of **519c** cast from aromatic solvents display voltage-dependent EL emission, with the emission maximum irreversibly shifting from the red to the green ($\lambda_{\max}$ = 559 nm) as the voltage increases. This effect is attributed to changes in the conformation of the polymer backbone brought about by local heating. Alkyl-substituted polymers such as **519f** show only a very small (3−4 nm) blue-shift in their PL emission compared with their all-alkoxy analogues.[999] Introducing further alkoxy groups as in **519g,h** only slightly red-shifts the emission.[998] Again, the polymer **519h** with dissimilar alkyl chain lengths has much higher solid-state PL efficiency than the all-octyloxy polymer **519i** (54% vs 29%). The EL spectra of these polymers generally match the solid-state PL spectra, with the highest efficiency being reported for **519e** ($\lambda_{\max}$ = 521 nm, 4.0 cd/A, 0.95%)[1001] and **519h** ($\lambda_{\max}$ = 551 nm, 4.4 cd/A, 0.98%).[1002] Reducing the amount of triple bonds in such hybrid copolymers enhances the EL efficiency so that copolymers **521a**,**b** ($\lambda_{\max}$ = 551−552 nm) have efficiencies of 2.15% and 1.82%,

Chart 8



respectively.[1003] The vinylene side-chains in **522** (Chart 8) red-shift the EL (λ_{max} = 602 nm) but reduce the efficiency to 0.15%. Introducing cyano groups as in **519j** and **521c** red-shifts the EL (λ_{max} = 582 and 612 nm, respectively) but reduces the efficiency (0.23 and 0.07 cd/A, respectively) compared with the case of the analogous polymers **519k** (λ_{max} = 510 nm, 2.05 cd/A) and **521d** (λ_{max} = 559 nm, 0.3 cd/A) without cyano groups.[1002,1004] The *meta*-linkages in **523** blue-shift the EL (λ_{max} = 501, 529 nm).[1005] Random copolymers **524a,b** have been made by Suzuki coupling of benzene bis-boronic acids with a mixture of 4,4′-dibromostilbenes and bis(4-bromophenyl)acetylenes.[723] Their solid-state emission is blue-green (λ_{max} = 476 and 478 nm, respectively) with quantum efficiencies of 35% and 40%, respectively. The copolymer **525**, in which the double bond is fixed in the *cis* conformation due to the maleimide ring, has been made by Sonogashira−Hagihara coupling of diethynylbenzene and the bis-bromide **278**.[720] In solution it shows green emission (λ_{max} = 530 nm). The PL from copolymer **526** containing both a butadiyne and a vinylene unit is at most only slightly red-shifted (λ_{max} = 529 nm) compared with that of the polymer **519b** (λ_{max} = 524 nm).[1006] The EL spectra of the copolymers **527** (λ_{max} = 552−557 nm) also closely match those of the analogous polymers **521**, but the efficiencies are lower (best value is 1.25 cd/A for **527c**) in identical LED configurations, despite the diyne-containing polymers **527** having better electron affinities (lower LUMO energies) than their yne-containing analogues **521**.[1007] As their HOMO energies are also lower, this may reflect poorer hole-injection in the devices.

The only strongly luminescent PPV-PPE hybrid polymer containing a heterocycle yet reported is **528**, which shows blue PL emission (λ_{max} = 453 nm, 43%) in THF solution and blue-green emission (λ_{max} = 510 nm) in the solid-state.[824] Replacement of some of the phenylene units in **519** or **521** reportedly leads to almost total quenching of the solid-state luminescence, so that such materials are more promising as materials for solar cells than LEDs.[1008]

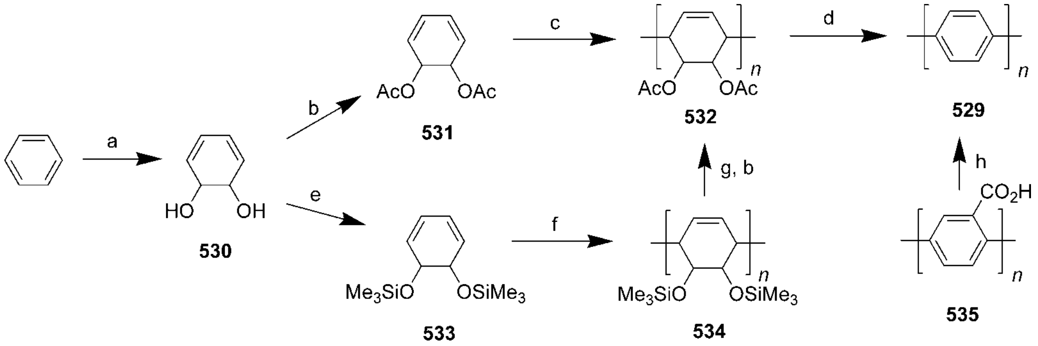
3. Polyarylenes and Polyheteroarylenes

This section covers the extensive work that has been done into synthesis of polyarylenes, particularly polyphenylenes, and polyheteroarylenes, especially polythiophenes, for use in LEDs. The former have been of particular interest as potential blue emitters. The synthesis of polyphenylenes has been the subject of a monograph by Scherf.[26]

3.1. Poly(*para*-phenylene) (PPP)

The main interest behind the use of poly(*para*-phenylene) (PPP) (**529**) as an electroluminescent material stems from the fact that it is a blue light emitter (λ_{max} = 459 nm), as shown by Leising and co-workers.[1009−1011] Like PPV, unsubstituted PPP is insoluble, but films of oligomeric (up to 9−10 rings) polyphenylenes can be prepared by vacuum

Scheme 40. Precursor Routes to Poly(*para*-phenylene): (a) *Pseudomonas putida*; (b) Ac_2O, Pyridine; (c) Azo(bisisobutyronitrile), 70 °C; (d) 310−340 °C, Ar; (e) Me_3SiCl, DMAP, Pyridine; (f) Bis[(η^3-allyl)(trifluoroacetato)nickel(II)]; (g) TBAF, MeOH; (h) Cu(II)

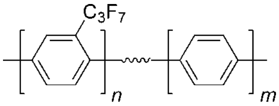


deposition[1012−1015] or by a precursor method.[1016] The effective conjugation length for PPP has been estimated from studying the emission from films of oligomers made by the precursor route to be about 10 units. However, this may be an underestimate, as other studies suggest that the effective conjugation length of PPP should be nearer 20.[26] The major problem with these predictions is that there is no optical data available for structurally well-defined PPP with ≥15 repeat units. The EL efficiency of such films increases with increasing chain-length to a maximum of 0.028% for the decamer. Insertion of a PVK charge-transporting layer improves the efficiency of devices using vaccum deposited films 10-fold, but at low voltages there is considerable emission (λ_{max} = 550 nm) from an excimer between PVK and PPP.[1015] As the voltage increases, this emission decreases as the recombination zone shifts into the bulk of the PPP layer, thus giving voltage-tunable EL. Well defined films of a hexaphenyl oligomer (**529**, n = 6, sexiphenyl) have been used in blue emitting devices, with an emission maximum at 425 nm.[1017−1024] Comparison of the EL spectra of sexiphenyl films with the orientation of the oligomers variously parallel or perpendicular to the substrate shows that the latter gives brighter emission with a narrower spectrum.[1025] Polarized emission has been reported from oriented films of sexiphenyl.[1026,1027] Leising et al. have made red and green emitting devices using thin films of sexiphenyl covered with appropriate dyes to convert its blue emission.[1021,1028−1033] White emission is obtainable by appropriate color mixing.[1033]

As with PPV, films of PPP have to be prepared via precursor routes which have been reviewed by Gin and Conticello.[1034] A study of the PL efficiency of PPP thin films of varying chain-length concluded that for highly ordered PPP films a chain-length of 25−30 units was optimal.[1035] The route usually used to prepare films of PPP for application in LEDs (Scheme 40) starts with a microbial oxidation of benzene to cyclohexadienediol **530**. Radical-initiated polymerization of the diacetate **531** gives the precursor polymer **532**. However, the material is not regioregular, as it contains about 15% of 1,2-linkages.[1036,1037] A number of other diesters of **530** have been polymerized by the same method (again with 10−15% of 1,2-linkages in the polymer) and thermally converted to PPP, with the highest molecular weights being obtained with dimethyl carbonate and dipivaloyl esters.[1038] Copolymers with blue-shifted PL spectra can be prepared by copolymerization of **532** and vinylbiphenyl or *N*-vinylcarbazole.[1039,1040] Totally regioregular PPP has been prepared by Grubbs and co-workers by a stereoregular nickel(0)-catalyzed polymerization of a cyclohexadienediol disilylether **533**, followed by conversion of the resulting polymer **534** to **529** via the acetoxy precursor **532** (Scheme 40).[1041−1044] However, to assist processing, they used an acid catalyst in the final step, which badly contaminated their product, making it unsuitable for use in LEDs. A third precursor route used to make films of PPP for LEDs involves decarboxylation of the polyacid **535** with copper oxide.[1016] PPP films can also be prepared by electropolymerization of benzene under either reductive or oxidative conditions, but the EL properties have been found to be highly dependent on the polymerization conditions.[1045] Oriented films of PPP have been prepared by a friction deposition method and found to show highly polarized fluorescence.[1046]

3.2. Substituted PPPs

A soluble PPP derivative **536** has been obtained by perfluoropropylation of PPP and used to construct a device whose emission color was found to shift from green to blue with increasing applied voltage.[1047] More generally, PPP derivatives **537** with solubilizing side-chains are prepared by transition metal catalyzed couplings (there is a short review on routes to substituted PPPs by Schlüter and Wegner[1048]). The main methods used are Suzuki polycondensation of aryl (bis)boronic acids with aryl halides and coupling of substituted dihalobenzenes **538** with nickel(0) (Yamamoto polycondensation) (Scheme 41).



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The Suzuki method can involve homocoupling of a bromoarylboronic acid **539** or coupling of a phenyl bisboronic acid **540** with a dihalobenzene **538**. The latter procedure allows the preparation of alternating copolymers **541**, but there can be experimental difficulties, as exactly equimolar amounts of **538** and **540** are required to obtain high molecular weight materials. In particular, boronic acids are hygroscopic and often difficult to purify. For a fuller description of the scope and problems of Suzuki polycondensation, the reader is referred to the review by Schlüter.[1049] The Suzuki method has been optimized by Wegner[1050−1054] and others.[1055−1057] The Yamamoto method has the advantage of experimental simplicity but is limited to homopolymers and random copolymers and requires stoichiometric amounts of often expensive nickel(0) reagents. For a more

Scheme 41. Suzuki and Yamamoto Routes to Soluble PPPs: (a) BuLi; (b) $B(OMe)_3$; (c) H^+; (d) $Ni(COD)_2$, Bipyridine, Toluene, DMF; (e) $Pd(PPh_3)_4$, Na_2CO_3, Toluene

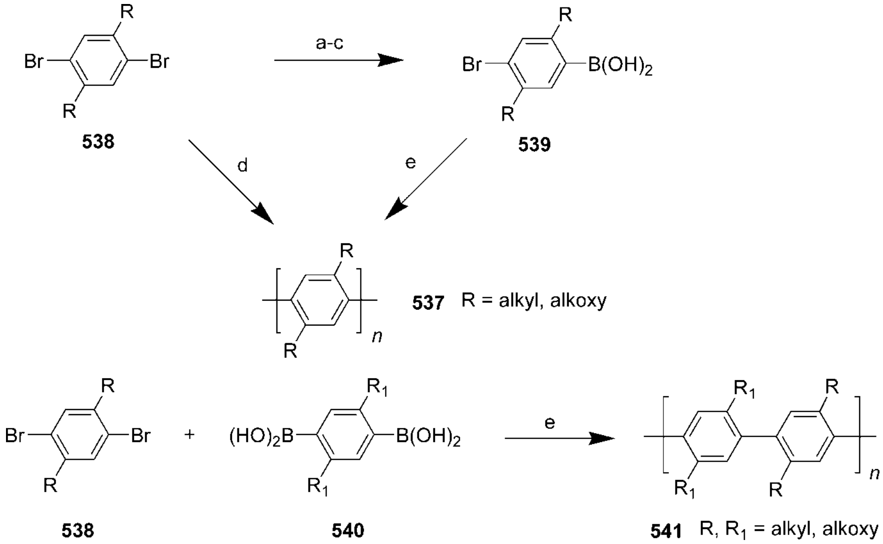
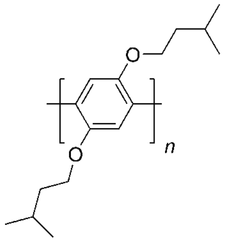


Chart 9



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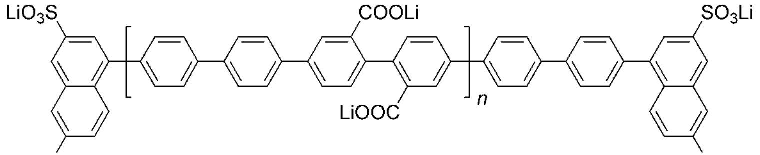

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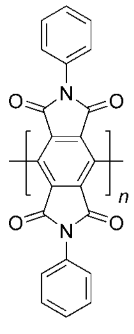
comprehensive discussion, the reader should consult the reviews by Yamamoto.[1058,1059] As well as dihalides, the coupling can be performed on hydroquinone bis-triflates[1060−1062] or bis-mesylates.[1060,1063] The Suzuki method has been reported to give higher degrees of polymerization than other methods.[1064] Poly(dialkoxyphenylene)s have also been made by oxidative coupling of 1,4-dialkoxybenzenes with iron(III) chloride.[1065]

Soluble PPP derivatives made by these routes with a variety of solubilizing side-chains have been used by various groups to make blue emitting LEDs.[722,1066−1082] Efficiencies of up to 3% have been reported using calcium cathodes, and ones of up to 0.8% have been reported using other, more air-stable metal cathodes. Sulfanato-substituted derivatives are reported to give higher efficiencies than dialkoxy-substituted derivatives.[1072] Use of sulfonate or other ionic substituents also gives solubility in polar solvents including water.[1083−1086] Use of a PANI anode or blending of the PPP derivative with a hole-transporting material lowers the operating voltage.[1069,1070] Polarized EL emission has been obtained from a device using a soluble PPP derivative **542** (Chart 9) deposited as a Langmuir−Blodgett (LB) film.[722,1071] The emission is mainly yellow due to the formation of aggregates, with the emission parallel to the dipping direction (λ_{max} = 536 nm) slightly red-shifted compared to the perpendicular emission (λ_{max} = 524 nm). Polarized emission has also been obtained by rubbing-alignment of a dialkoxy-PPP film[1087] and from polymers with mesogenic[405,406,1088] or chiral side-chains.[1089−1091] Complexation of a PPP **543** bearing carboxylate substituents with cyclodextrin gives a fluorescent polyrotaxane which shows a PL maximum at 410 nm compared to 430 nm for the uncomplexed chain.[1092] An LED has been constructed using this complex.[704]

A major drawback of these materials is that steric interactions between the alkyl or alkoxy substituents lead to an increased phenylene−phenylene torsion, with a resulting blue-shift in absorption and emission, so that the emission is in regions of the spectrum where the eye is not very sensitive. From a study on oligomers, the effective conjugation length for such polymers has been determined to be 11 phenyl rings for absorption and 7 rings for emission.[1093] An exception is the bis-imide **544**, which shows green PL (λ_{max} = 553 nm), which is similar to that of the monomer, which presumably indicates that the π-systems of the repeat units are orthogonal.[1094] A soluble poly(*meta*-phenylene) **545** made by Reynolds which has an even shorter conjugation length emits mainly in the ultraviolet (λ_{max} = 346 nm),[1095] as do poly(terphenyls) with *meta*-linkages, e.g. **546** (λ_{max} = 400 nm).[1096] The *meta*-linked polymers **547**, however, show blue-green PL (λ_{max} = 445−532 nm), as the emission comes from the substituents.[1097]

One way to red-shift the emission is to make copolymers with only partial substitution. Fu prepared copolymers **548** by Grignard coupling.[1098] As the amount of unsubstituted phenylene spacer increased from $x = 0$ to $x = 2$, the PL emission maximum moved from 415 to 450 nm, and a secondary peak around 490 nm appeared. Copolymers **549** with alternating substituted and unsubstituted phenylenes have also been made by Stille[394,500] or Suzuki coupling.[1064,1099,1100] These copolymers show violet to blue (λ_{max} = 370−425 nm) fluorescence. The emission from the dialkoxy-substituted polymers was red-shifted by *ca.* 50 nm compared with those of their dialkyl analogues.[394,500,1081,1099]



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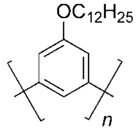

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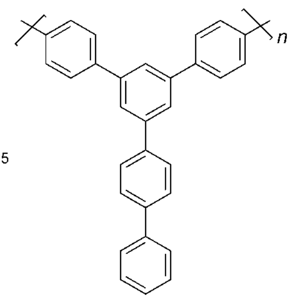

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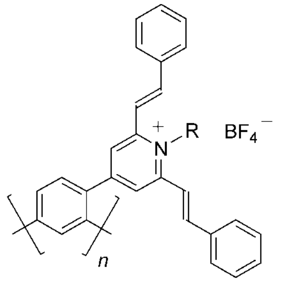
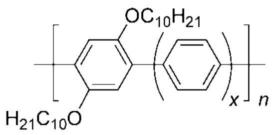
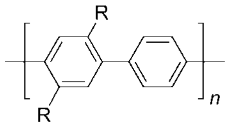


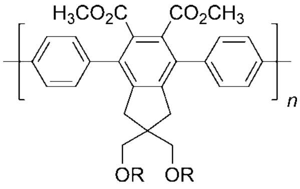
547 R = alkyl, phenyl



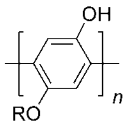
548 x = 0-2



549 R = alkyl, alkoxy



550 R = C_6H_{13}



551 R = alkyl

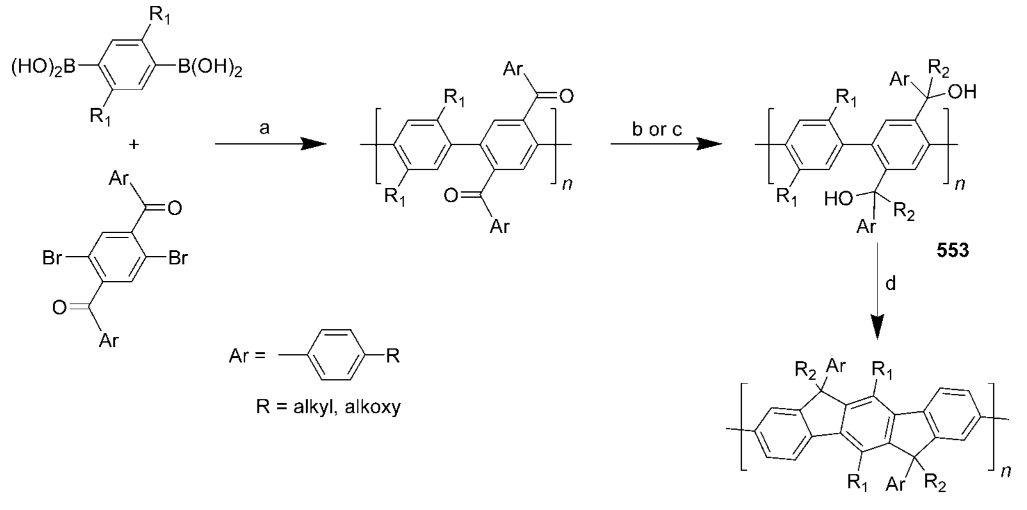
These copolymers also show less red-shifted emission due to aggregates than the corresponding homopolymers.[1081] The polymer **550** made *via* the zirconcene **343** (Scheme 33) shows a PL maximum at 378 nm.[785] It is reported that the emission from substituted PPPs may be red-shifted to give blue (λ_{max} = 446 nm) emission by blending them with PVK.[1101] Incorporating 5−30% of 2,6-distyrylpyridine units into the polymer backbone also produces blue solid-state PL (λ_{max} = 436 nm).[1102] White emission is reported from an exciplex of a dialkoxy-PPP and PVK.[1077] The hydroxy-substituted polymer **551** (λ_{max} = 401 nm) shows a marked red-shift in its PL in the presence of metal ions (λ_{max} = 474 nm).[1103]

3.3. Ladder-type PPPs

In order to overcome the problem of phenylene−phenylene torsion in substituted PPPs, Scherf and Müllen prepared a ladder-type polyphenylene (LPPP, **552a**, Scheme 42),[1104−1107] in which the phenylene rings are kept planar to each other (ladder polymers have been reviewed by Scherf[1108]). The key step is the polymer analogous Friedel−Crafts ring-closing reaction on the precursor polymer **553**. Planarization of the PPP backbone in ladder polymers and copolymers is found to lead to better vibrational resolution in both absorption and emission spectra and to a much smaller Stokes shift,[1017] but contrary to expectation, it has been found that increased planarization of the aromatic π-system leads to a decrease and not an increase in the effective conjugation length for absorption in PPP derivatives.[1109] The effective conjugation length in LPPPs has been estimated to be about 11 phenyl rings by extrapolation from the properties of small ladder-type oligophenylenes.[26] Comparison of the properties of a ladder-type undecaphenylene with those of Me-LPPP (**552b**), however, shows that it is slightly larger than 11 phenyl rings.[1110]

Blue emission (λ_{max} = 450−460 nm) has been observed from LPPP films but was found[1111] to be unstable due to the appearance of a yellow emission band. The emission of yellow (λ_{max} = 600 nm) light in the solid state was originally attributed to aggregation[1018,1111−1113] but more recently has been shown to arise from an emissive defect.[1114,1115] A double-layer device using PPV as a hole-transporting layer and a LPPP as an emissive layer produced yellow light (0.6% efficiency).[1116] Modification of LPPP **552a** by substituting a methyl group at the methine bridge gives Me-LPPP

Scheme 42. Synthesis of Ladder-Type PPPs: (a) Pd(PPh$_3$)$_4$, K$_2$CO$_3$, Toluene−Water; (b) LiAlH$_4$; (c) R$_2$Li, THF; (d) BF$_3$-Et$_2$O



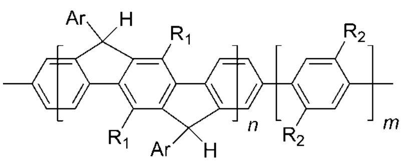
552a R_1 = alkyl, alkoxy; R_2 = H
552b R_1 = alkyl, alkoxy; R_2 = Me
552c R_1 = alkyl, alkoxy; R_2 = Ph

(**552b**),[1117] which exhibits stable blue-green (λ_{max} = 461, 491 nm) emission with reported EL efficiencies of up to 4%.[1019,1022,1118,1119] Recently, nanospheres of Me-LPPP have been used as the emissive components in PLEDs.[1120] Statistical copolymers called "stepladder" copolymers **554** contain oligo-LPPP units connected via twisted phenylene spacers. They form stable films which remain blue emitting even after annealing.[1111] Emission from the "stepladder" copolymers **554** is reported to be blue-shifted with respect to PPP due to out-of plane twisting of the phenylene rings.[1113,1121] Blue emitting LEDs with efficiencies of nearly 1% have been made using these materials.[1122] Pure blue emission (0.1% efficiency) can also be obtained by diluting LPPP **552a** (1−10 wt %) in a PVK hole-transporting polymer matrix.[1116,1123] The phenyl-substituted polymer Ph-LPPP (**552c**) shows bright yellow electrophosphorescence (i.e., triplet emission) (λ_{max} = 600 nm), whose strength depends upon the palladium content of the polymer.[1124] It is proposed that this emission arises from palladium complexes which are formed by a reaction between phenyllithium and residues of the palladium complex from the Suzuki polycondensation, and incorporated into the polymer backbone. The absence of such emission from Me-LPPP is because methyllithium does not react with the palladium catalyst in this way. If instead of a benzene bis-boronate, a fluorene bis-boronate is used in the above synthesis, then polymers **555** can be made in which the number of bridges formed during the polymer analogous ring-closure step is halved and thus there is less chance of an emissive defect being formed by incomplete ring closure.[1125] These materials are reported to produce blue-green EL (λ_{max} = 460 nm) with greater stability than that of LPPP. A chiral LPPP containing cyclophane units has been prepared.[1089,1126]

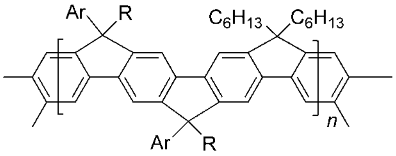
A novel ladder polymer **556** with two sp^3 bridging atoms has been made by samarium(II) iodide coupling of a poly(diacylphenylene) precursor. This polymer shows strong blue-green fluorescence in solution (λ_{max} = 459 nm) and in the solid-state (λ_{max} = 482 nm).[1127] The polymer **557** with two sp^2 bridging atoms prepared by treatment of a poly(diacylphenylene) with boron sulfide[1128,1129] also shows blue-green emission (λ_{max} = 478 nm) with some long wavelength emission in the solid state attributed to aggregates. The EL efficiency is reported to be low (<0.1%).[1130]

3.4. Poly(9,9-dialkylfluorene)s and Related Polymers

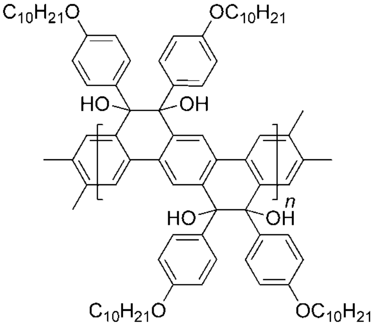
Polymers intermediate in structure between PPP and LPPP have been looked at as blue emitting materials, with the aim of achieving a balance between the excellent photophysical properties of LPPP (small Stokes shift and well resolved vibronic structure in the emission spectrum) and synthetic accessibility. In particular, poly(9,9-dialkylfluorene)s (PDAFs, **558**), the simplest and most synthetically accessible of such polymers, have attracted considerable interest in recent years due to their large PL quantum efficiencies and excellent chemical and thermal stability, as evidenced by a number of recent reviews.[1131−1133] The first report of blue EL from PDAFs was by Yoshino and co-workers, who made low-efficiency blue emitting (λ_{max} = 470 nm) devices[1134−1136] using poly(9,9-dihexylfluorene) (**558a**). The more recent interest in PDAFs began when Bradley and co-workers[1137] used poly(9,9-dioctylfluorene) (**558b**) to make a blue (λ_{max} = 436 nm) LED with high efficiency, being obtained when a hole-transporting layer was used. Polymer **558a** used by Yoshino was obtained by oxidative coupling of the monomer with iron(III) chloride.[1138,1139] However, this material was of rather poor quality, with low molecular weight and high levels of structural defects. Subsequent syntheses of PDAFs have, therefore, generally used Suzuki polycondensations[1140,1141] or Yamamoto Ni(0) couplings of dibromo monomers.[1142,1143] A group at Dow[1144−1149] has developed a particularly efficient Suzuki cross-coupling route leading to high molecular weight PDAFs. It is reported that the EL efficiency of **558b** is optimal at a molecular weight of 105 kDa.[1150] Circularly polarized PL and EL emission has been obtained from polymers, e.g. **558c**, bearing chiral side-chains.[1151−1154] Polarized emission has also been obtained from aligned films of **558b** or **558c**[944,1143,1155−1161] and of oligomers of **558c**.[1162] Polymers **558d**[1142] and **559**[1163] with ethylene oxide side-chains have been prepared by Ni(0) coupling, as emissive materials for blue emitting LEDs and LECs (section 6.3).



554 R_1, R_2 = alkyl, alkoxy



555 R = H or Me



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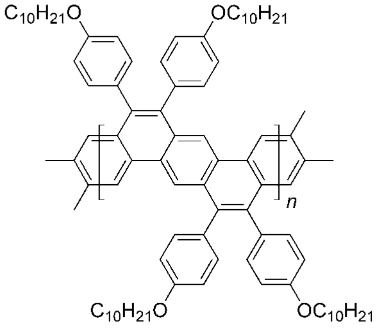
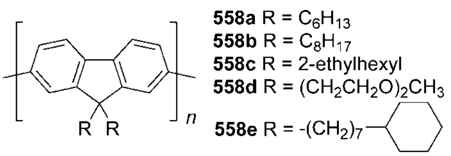
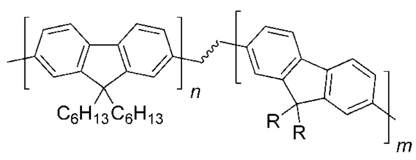


557

The emission from PDAFs is blue-violet with a primary emission maximum at about 425 nm and a secondary peak at about 445 nm. Well-defined oligomers of **558a** have been prepared, and as a result the effective conjugation length for PADFs has been determined to be about 12 units (24 phenyl

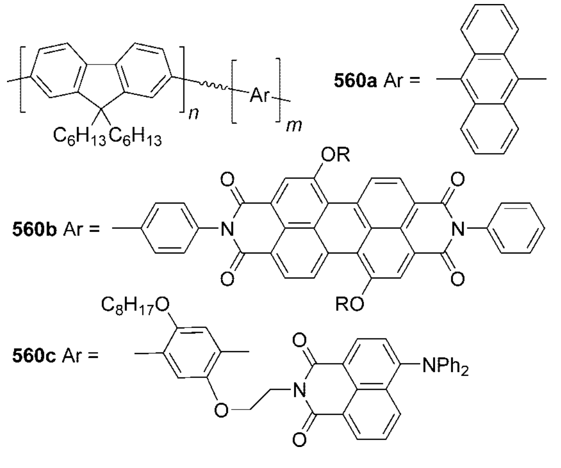




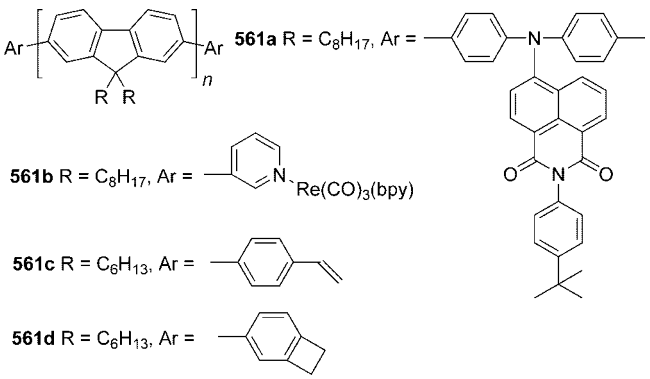
559 R = $C_6H_{12}O(C_2H_4O)_3CH_3$

rings) for absorption and 6 units for emission,[1164−1166] indicating that the geometries of the ground and excited states are different. As with LPPP, the blue emission from PDAFs is unstable, with the appearance of a strong emission band in the yellow region of the spectrum after annealing or upon running an EL device.[1167,1168] Longer side-chains are reported to enhance the formation of this emission band upon annealing.[1169] Initially, this long wavelength emission band was believed to be due to emission from excimers, but more recently, it has been shown that it is due to emission from fluorenone defect sites, produced by oxidation during synthesis and/or processing of the polymers, which act as charge and/or energy traps.[1133,1170−1178] The appearance of the long wavelength emission band after annealing or during operation of devices is now attributed to formation of further defect sites by oxidation coupled with increased interchain interactions (aggregation), leading to enhanced charge and exciton migration to the defect sites.

Considerable effort has gone into developing stable blue emission from PDAFs. Attempts have been made to remove the defects by purification of the polymer or monomer. Fractionation of the polymer to remove low molecular mass material has been reported to reduce long wavelength emission.[1179] Presumably, a fluorenone unit lowers the solubility of a growing chain, and so the defect is disproportionately found in the low mass fraction. Meijer and co-workers showed that purification of a dialkylfluorene monomer so as to remove traces of monoalkylfluorenes, which are implicated in the formation of fluorenone defects, leads to much more stable blue emission.[1180] The presence of bromine end-groups is reported to enhance the formation of green emission,[1181] and the introduction of triphenylamine end-groups (*vide infra*) is reported to stabilize the emission.[1182]

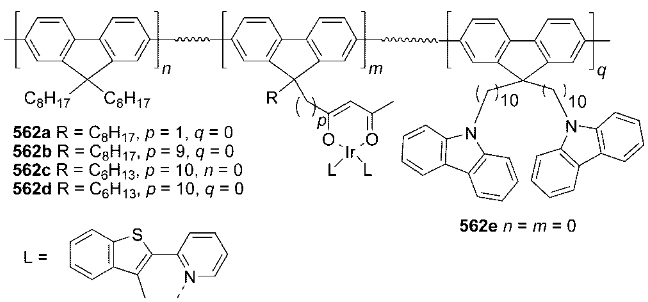


Introduction of comonomers has also been used to stabilize the emission. Miller and co-workers at IBM have prepared copolymers **560a** of dihexylfluorene with anthracene which show stable blue emission (λ_{max} = 455 nm) even after prolonged annealing.[1166,1183] As the ratio of anthracene (15 mol %) to fluorene (85 mol %) units was too low to produce significant steric repulsion between the polymer chains, they attributed the absence of long-wavelength emission to trapping of the exciton at the anthracene sites and subsequent emission therefrom.[1184] Similar copolymers with dioctylfluorene are reported to show an EL maximum at 435 nm.[1185] Incorporation of 2,6-distyrylpyridine units is also reported to stabilize the solid-state blue PL of polyfluorenes.[1102] Similar exciton trapping was also obtained by copolymerization with cyanostilbene or perylene units, which resulted in emission in the solid state coming solely from these lower energy chromophores.[1184,1186] Such exciton trapping has been exploited by Müllen and co-workers, who prepared copolymers of dialkylfluorenes and perylene-based dyes, e.g. **560b**.[1187−1189] Efficient Förster energy transfer and/or exciton trapping led to the emission coming only from the dye units, thus enabling tuning of the emission across the whole visible range. Efficient green EL has also been achieved from the copolymers **560c** containing 1−4% of naphthalimide dyes.[1190] At very low concentrations of dye (0.2%), the emission from **560c** is blue but the efficiency is 3.54% (6.85 cd/A), which is much higher than that from **558a**.[1191] Similar results have been obtained from polymers in which the comonomer is a 3,6-carbazole with the naphthalimide attached to the ring nitrogen.[1192] Wang and co-workers have obtained highly efficient (up to 7.4 cd/A) green EL (λ_{max} = 545 nm) from copolymers **561a** end-capped with naphthalimide dyes.[1193] This approach can also be extended to triplet-emitting (phosphorescent) chromophores; for example, **561b** end-capped with a rhenium complex shows green EL (λ_{max} = 516 nm) from the end-groups.[1194]

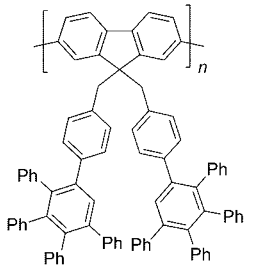


Copolymers **562** with phosphorescent iridium complexes attached via suitably functionalized side-chains have been prepared.[1195,1196] Dexter energy transfer causes the emission to come from the complex so producing red EL (λ_{max} = 620 nm) with efficiencies of up to 2%. Due to triplet back transfer, the efficiencies were lower for polymers **562a** with short alkyl tethers than those for polymers (**562b**) with long tethers. The carbazole units in **562c** increase the EL efficiency considerably compared with that of the corresponding copolymers **562d** without them.[1195]

Most effort has gone into suppressing aggregation of the polymer chains. Polymer **558e** with cyclohexyl groups at the ends of the alkyl substituents reportedly displays no green EL emission.[1197] When the cyclohexyls are attached via



562a R = C_8H_{17}, p = 1, q = 0
562b R = C_8H_{17}, p = 9, q = 0
562c R = C_6H_{13}, p = 10, n = 0
562d R = C_6H_{13}, p = 10, q = 0
562e n = m = 0



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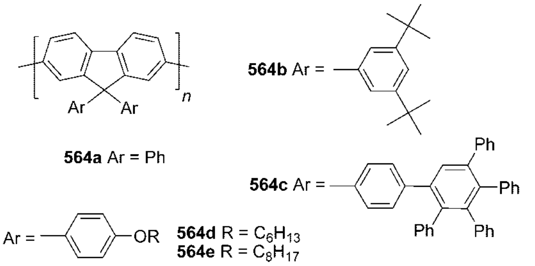
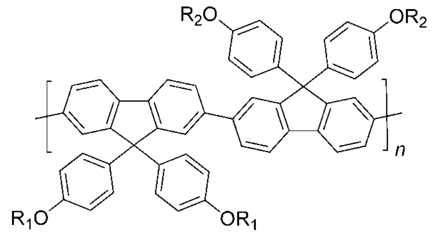


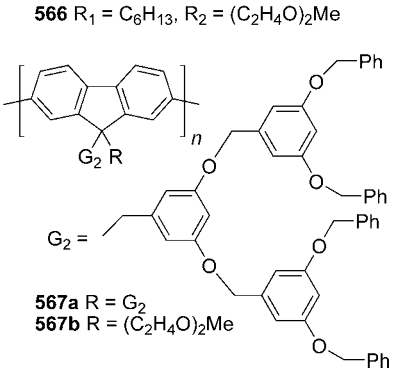
564a Ar = Ph
564b Ar =
564c Ar =
564d R = C_6H_{13}
564e R = C_8H_{17}

shorter spacers, however, green EL is seen. Polyfluorenes end-capped with vinyl groups **561c**[1198,1199] can be thermally cross-linked to produce insoluble materials which show stable blue emission. By contrast, no suppression of the long wavelength emission is seen upon cross-linking similar polymers **561d** end-capped with cyclobutene groups.[1200] Possibly, oxidation occurs at the higher temperature required for cross-linking in this case. In order to suppress aggregation without losing solubility, bulky substituents can be attached. The IBM group have shown that end-capping PDAFs with Fréchet-type dendrons of generation four produced stable blue emission.[1201] The Müllen group have shown that polymer **563** with first generation polyphenylene dendrons on the side-chains gives stable blue emission with device characteristics (turn-on voltage, emission efficiency, and brightness) comparable to those for the PDAFs **558a**−**c**.[1202] Interestingly, the bulky side-chains produce no blue-shift in absorption or emission, indicating that there is no increased steric repulsion between adjacent fluorene units. As the benzyl linkages in **563** are susceptible to photo-oxidation, potentially more stable poly(9,9-diarylfluorene)s **564a**−**c** were prepared (Scheme 43). As aryl groups, unlike alkyl groups, generally cannot be directly substituted onto the 9-position of fluorenes by nucleophilic substitution, the monomers were prepared by addition of aryllithium reagents to the biphenyl-2-carboxylic acid methyl ester **565**, followed by ring closure. The diphenylfluorene polymer **564a** was insoluble, but materials **564b** with di-*tert*-butylphenyl and **564c** with first generation dendron side-chains were processable from toluene. A convergent route to the monomer of **564c** has also been developed enabling preparation of a range of dendronized fluorenes.[1203] Stable blue emission has been obtained from both **564b** and **564c**.[1188,1204] Originally, this was interpreted as meaning that phenyl substituents at the 9-position are sufficiently bulky to achieve effective suppression of aggregation, but it is now thought that the stability arises from the suppression of defect formation. Stable blue EL has also been obtained from polymers **564d,e**,[1205,1206] whose monomers are made by condensation of phenol with dibromofluorenone (*cf.* Scheme 44 below) followed by alkylation. More recently, a similar cyclization route for the synthesis of dialkyl analogues was also reported to give defect-free PDAFs, e.g. **558b**, with very stable blue emission.[1207]

The EL efficiency of copolymer **566** (0.26%) is more than twice that of **564e** (0.1%).[1206] There is evidence that the extremely bulky dendrimer groups in **564c** not only slow down migration to defect sites[1208] but also increase the triplet lifetime,[1209] which is likely to lower EL efficiency. The use of the less bulky aryl groups thus seems preferable for obtaining high efficiency. That aryl substituents reduce chain interactions has been confirmed by atomic force microscopy experiments, which showed that, whereas the chains of PDAFs stack to form ordered fibrillar structures, aryl-substituted polymers form amorphous films with no evidence for ordered aggregates of chains.[1210] The IBM group has also managed to obtain stable blue EL emission from polymers with Fréchet-type dendrons as side-chains, but polymers, e.g. **567a**, with second generation or larger dendrimers are required to achieve effective suppression of aggregation due to their lack of shape persistence.[1211] As the dendronized monomers are less reactive, obtaining high molar mass materials usually requires making alternating or random copolymers with dialkylfluorenes.[1211,1212] Pure blue PL has also been reported from the polymer **567b** with a single second generation dendrimer side-chain.[1213] Attachment of polyhedral silsesquioxane units as side-chains has also been used successfully to suppress the green emission,[1214−1216] as has cross-linking the polymer chains by siloxane bridges.[1217]



566 R_1 = C_6H_{13}, R_2 = $(C_2H_4O)_2Me$



567a R = G_2
567b R = $(C_2H_4O)_2Me$

An alternative method to minimize long wavelength emission is to use spiro-substitution at the fluorene 9-position. Thus, it is reported that polymers **568a**−**c** (Chart 10) with spiro-cyclohexyl groups display less green emission than standard PDAFs.[1218,1219] Spirobifluorenes have been investigated by Salbeck and co-workers[364] and found to be

Scheme 43. Synthesis of Poly(9,9-diarylfluorene)s: (a) KOH, Ph_2O, 180 °C; (b) MeOH, H^+; (c) ArLi, THF, −78 °C; (d) H^+; (e) $Ni(COD)_2$, Bipyridyl, COD, Toluene−DMF, 80 °C

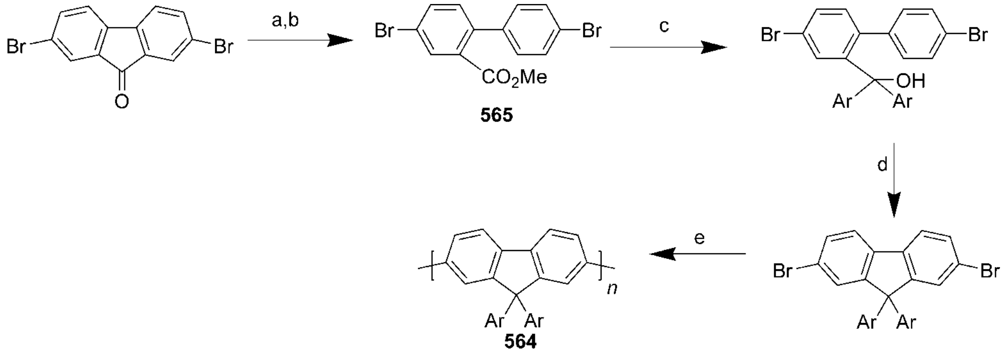
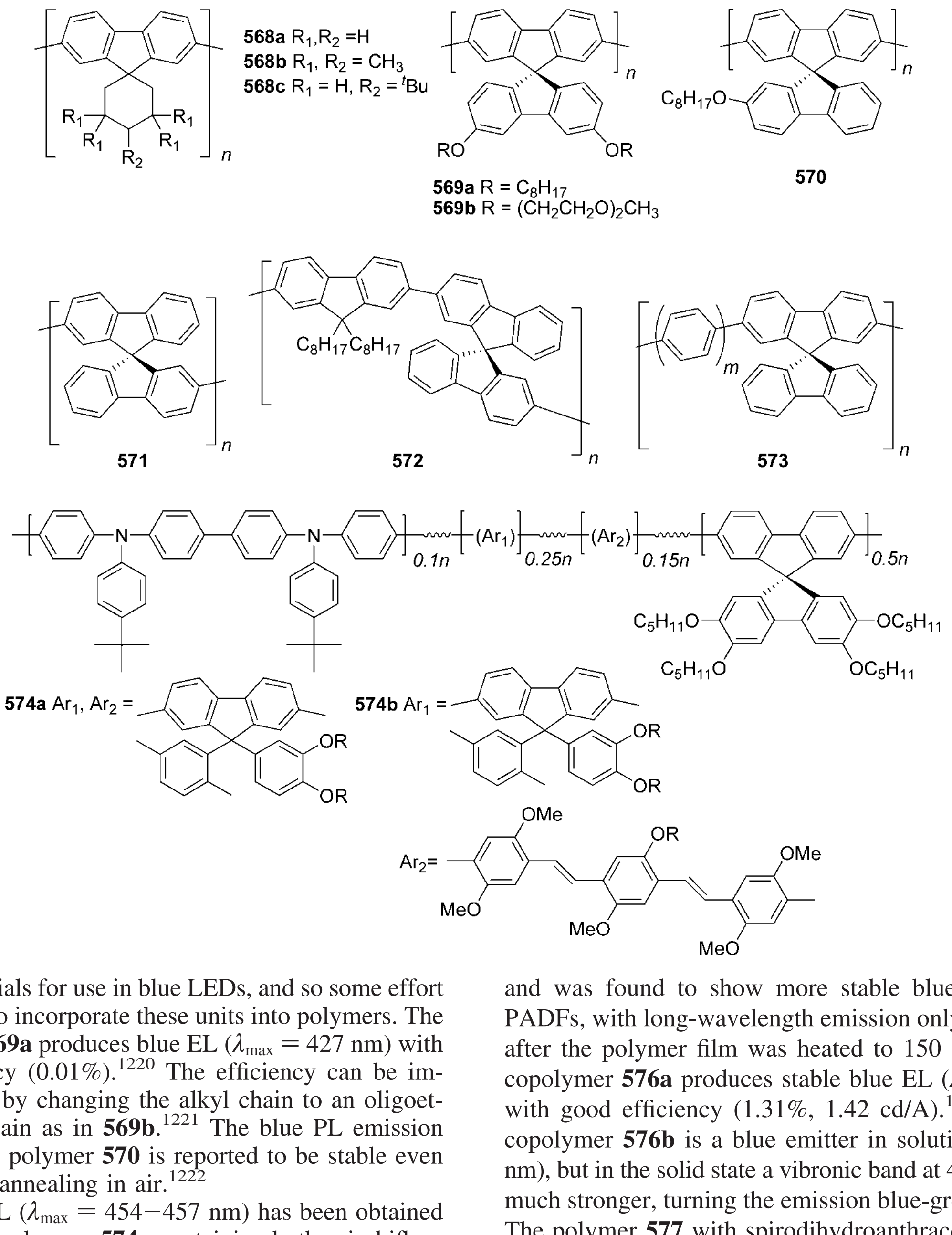
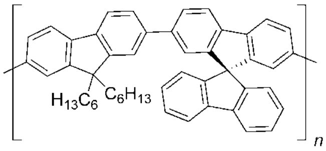


Chart 10



promising materials for use in blue LEDs, and so some effort has been made to incorporate these units into polymers. The homopolymer **569a** produces blue EL (λ_{max} = 427 nm) with modest efficiency (0.01%).[1220] The efficiency can be improved to 0.6% by changing the alkyl chain to an oligoethylene oxide chain as in **569b**.[1221] The blue PL emission from the similar polymer **570** is reported to be stable even after prolonged annealing in air.[1222]

Stable blue EL (λ_{max} = 454−457 nm) has been obtained from random copolymers **574a** containing both spirobifluorene and diarylfluorene units with high efficiency (2.9−3.0 cd/A). Incorporating a distyryl benzene unit in **574b** produces efficient green EL (λ_{max} = 507 nm, 7.0 cd/A). An alternating copolymer **575** has been prepared by Huang and co-workers and was found to show more stable blue emission than PADFs, with long-wavelength emission only being detected after the polymer film was heated to 150 °C.[1223,1224] The copolymer **576a** produces stable blue EL (λ_{max} = 455 nm) with good efficiency (1.31%, 1.42 cd/A).[1225] The similar copolymer **576b** is a blue emitter in solution (λ_{max} = 467 nm), but in the solid state a vibronic band at 497 nm becomes much stronger, turning the emission blue-green in color.[1226] The polymer **577** with spirodihydroanthracene units shows blue EL (λ_{max} = 420 nm, 0.2%, 0.19 cd/A).[1227] Similar emission (λ_{max} = 426 nm) is reported from the similar polymer **578**, but with significantly higher efficiency (1.33%, 0.82 cd/A).[1228]



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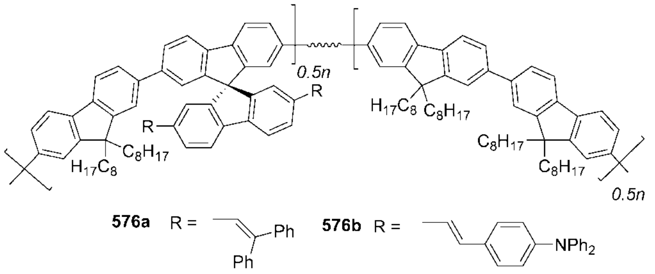
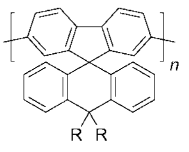
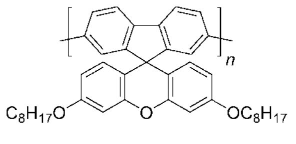


576a R = **576b** R =



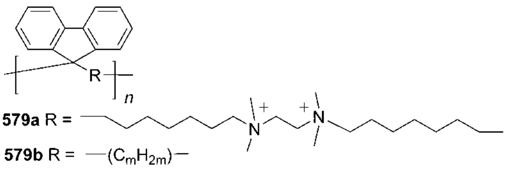
577 R = 2-ethylhexyl



578

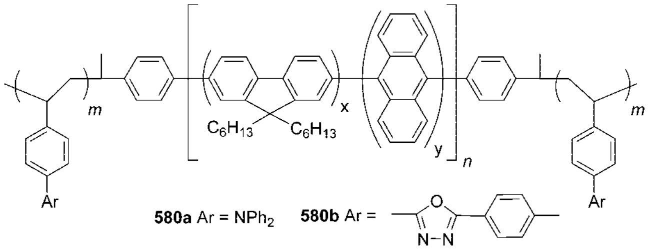
The emission from polymer **571**[1229] and its copolymer with fluorene **572**[1230] is slightly blue-shifted (λ_{max} = 417 nm) due to the shorter conjugation length. Blue EL (λ_{max} = *ca.* 425 nm) emission has been obtained from poly(spirobifluorene oligophenylene) copolymers **573** (*m* = 0−2).[1231]

Advincula et al. have reported that the fluorene-containing polyionene **579a** undergoes oxidative cross-linking with iron(III) chloride to give an insoluble violet-blue emitting material (λ_{max} = *ca.* 410 nm).[1232] Similar insoluble blue emitting cross-linked materials are obtained by oxidation of the polymers **579b**,[1233] which have been used to make blue emitting LEDs.[1234]

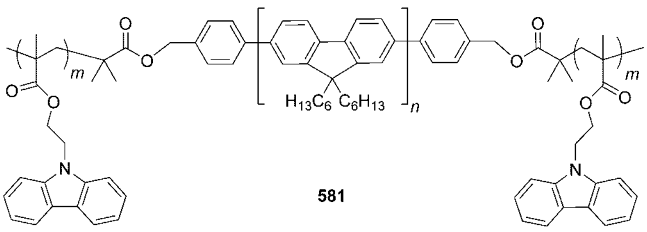


579a R =

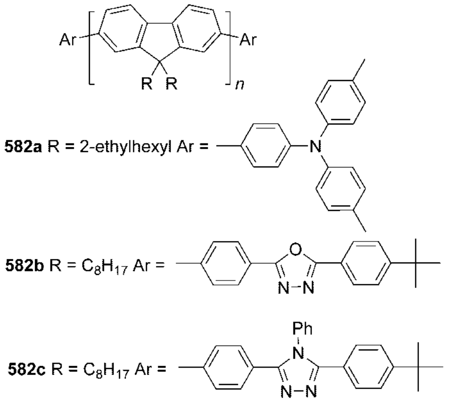
579b R = —(C_mH_{2m})—



580a Ar = NPh_2 **580b** Ar =



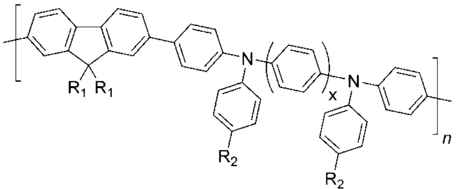
581



582a R = 2-ethylhexyl Ar =

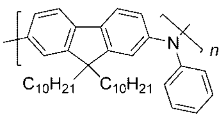
582b R = C_8H_{17} Ar =

582c R = C_8H_{17} Ar =



$R_1 = C_6H_{13}$, $R_2 = C_4H_9$

583a x = 1
583b x = 2

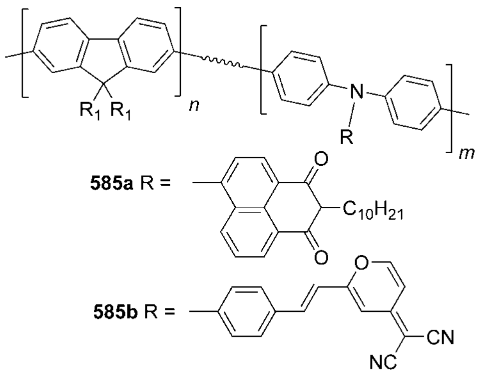


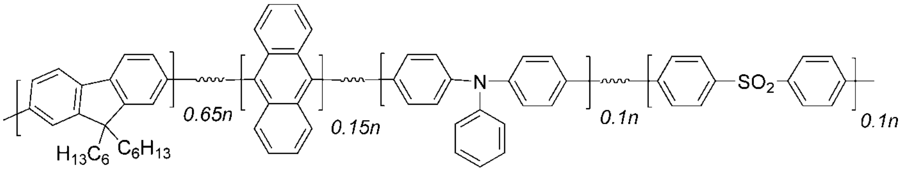
584

A second problem with PDAFs is that their relatively low lying HOMO and high lying LUMO orbitals hinder charge injection. There is a good match between the LUMO energy and the work function of the cathode when calcium is used (a composite LiF/Ca/Al cathode is reported to give better electron injection than a simple calcium cathode[1235]), but there usually remains a large gap between the HOMO and ITO energy levels. As a result, hole-injecting layers are applied in PDAF devices in order to obtain good efficiency.[1137,1236−1238] The use of charge transporting layers also reduces green emission, suggesting that this is in part produced by interactions between the electrodes and the polymers.[1173,1239] Another approach is to incorporate charge-transporting groups into the polymer, either as end-groups, as units in the polymer chain, or as side-chains. The IBM group[1240] has reported that triblock polymers with anthracene−dialkylfluorene copolymer emissive blocks between hole-transporting triphenylamine (**580a**) or electron-transporting oxadiazole (**580b**) units showed higher emission efficiencies than the anthracene−PDAF copolymer **560a** alone with calcium and aluminum cathodes, respectively. The best results were found for double-layer devices of **580b** with a hole-transporting layer and a calcium cathode. Similar triblock copolymers **581** with hole-transporting carbazole substituents are also reported to show superior device performance to the homopolymer **558a**.[1241] The IBM group reported that triple-layer devices using cross-linked **561b** with a cross-linked triphenylamine hole-transporting layer and an oxadiazole electron transporting layer are more efficient than single- or double-layer devices.[1242]

Scherf, Neher, and co-workers have obtained polarized emission with improved efficiencies from liquid crystalline polyfluorenes, e.g. **582a**, end-capped with triarylamine units and oriented on an aligned polyimide substrate.[1243] The EL efficiency of PDAFs has been enhanced nearly four times by use of a series of three cross-linked hole-transporting layers of varying work function.[1244] The Dow group has prepared alternating copolymers of dialkylfluorene with hole-transporting triphenylamines.[1146−1149,1236] These polymers are blue emitters, e.g. **583a**[1245] (λ_{max} = 486 nm) and **583b**[1146]

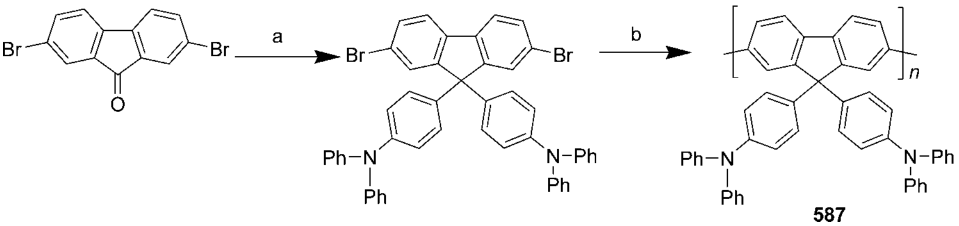
Chart 11





586

Scheme 44. Synthesis of Poly[9,9-bis(triphenylamine)fluorene]: (a) Ph_3N, $MeSO_3H$, 140 °C; (b) $Ni(COD)_2$, Bipyridyl, COD, Toluene−DMF, 80 °C

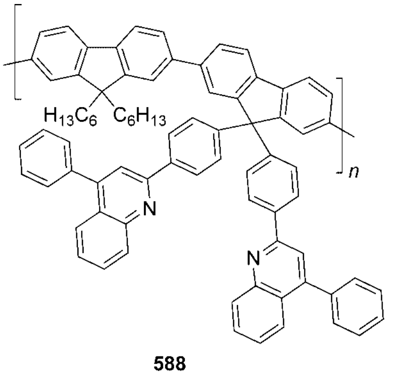


587

(λ_{max} = 481 nm), as is the nitrogen-bridged polymer **584** (λ_{max} = 420 nm) made by Ullmann coupling of a diiodofluorene with a bis-aminophenylfluorene.[1246] It would appear, however, that these materials are primarily intended to be used as hole-transporting rather than emissive materials. Copolymers **585a** (Chart 11) with naphthalimide dyes on the TPA unit emit white EL, due to simultaneous blue emission from the backbone and red emission from the dyes.[1247,1248] Red EL (λ_{max} = 620 nm) has been obtained from similar copolymers **585b** with other dye units.[1249]

The IBM group have investigated the incorporation of charge-transporting groups into the copolymer **560a**.[1166] Introduction of hole-transporting triphenylamine units produced a slight red-shift in the EL spectrum, while electron-accepting diphenylsulfone units caused a small blue-shift in the emission, in both cases with a decrease in the EL efficiency. However, copolymer **586** with 10% of both types of charge-transporting groups incorporated showed stable blue EL (λ_{max} = 460 nm) with nearly twice the efficiency of **560a**. Müllen and co-workers have prepared polymer **587** (Scheme 44), in which the triphenylamine units attached at the 9-position not only act as hole-transporting units but also prevent aggregation of the polymer chains.[1250] The triphenylamine substituents are introduced by Friedel−Crafts alkylation of triphenylamine with 9-fluorenyl cations produced from dibromofluorenone under the reaction conditions. Polymer **587** shows stable blue EL (λ_{max} = 428 nm), but the overall EL efficiency is lower than that for PDAFs despite the better hole-accepting properties, probably because of the lower PL efficiency of **587** (22%, *cf.* 55% for **560b**[1137]).

Similar emission with moderate efficiency (0.69 cd/A) is seen from the quinoline-substituted copolymer **588**.[1251] Polymer **562e** with carbazoles attached via alkyl chains is reported to show much higher EL efficiency (0.74%, 1.28 cd/A vs 0.05%, 0.049 cd/A) than **558b**.[1195] Copolymers bearing Fréchet-type dendrons with hole-transporting car-



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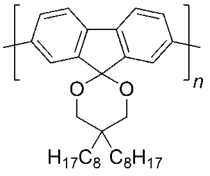

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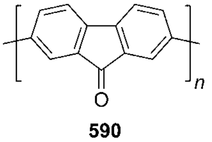

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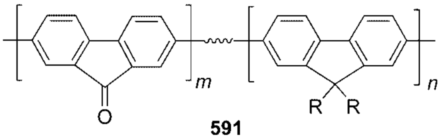
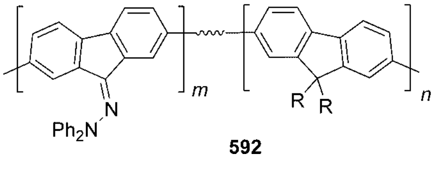
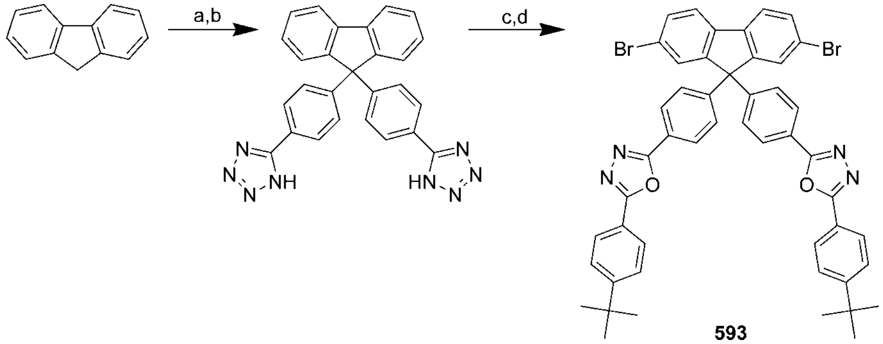


591



592

Scheme 45. Synthesis of a Fluorene with Two Oxadiazole Substituents: (a) 4-Fluorobenzonitrile, K_2CO_3; (b) NaN_3; (c) 4-*tert*-Butylbenzoyl Chloride; (d) Br_2, $PhI(OCOCF_3)_2$

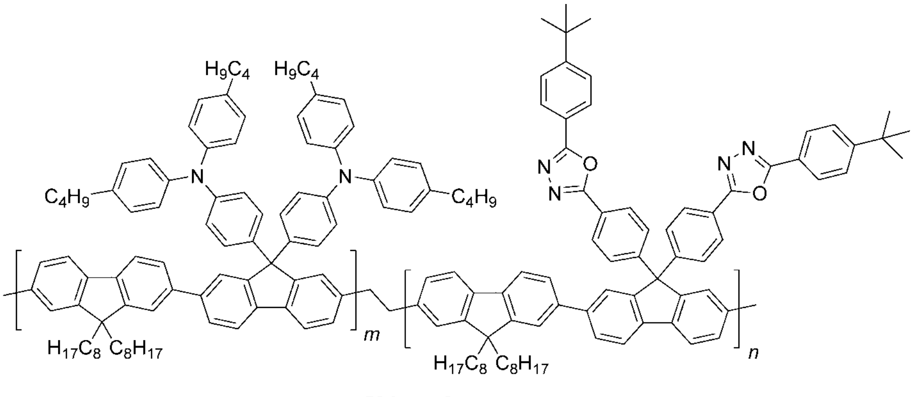


bazole groups on their periphery have recently been prepared, but there is as yet no report on their EL properties.[1252]

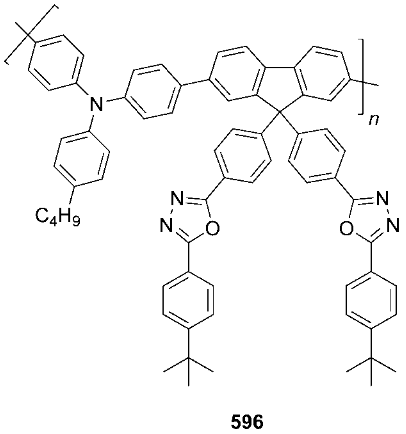
Müllen and co-workers have prepared a blue emitting (λ_{max} = 450 nm) polyketal **589**, films of which can be converted by exposure to dichloroacetic acid vapor to the orange emitting (λ_{max} = 580 nm) polyfluorenone **590**, which shows useful electron-transporting properties, though the acidic residues from the conversion are a potential source of problems for light-emitting device applications.[1253,1254] Jenekhe and co-workers reported that single-layer LEDs with aluminum cathodes based on copolymers **591** containing fluorenone units produced green EL (λ_{max} = 535 nm), with the optimal efficiency of 0.19% being obtained for the copolymer with 3 mol % of fluorenone.[1255] By contrast, Pei et al. have more recently reported yellow EL from **591** with an emission maximum varying from 540 to 579 nm as the amount of fluorenone increased from 0.1 to 25%, and efficiencies of over 1% for copolymers with over 10% of fluorenone in similar devices using Ba/Al cathodes.[1256] It should be noted that the same group also reported green emission (λ_{max} = 535 nm) from a sample of the homopolymer **558a** and that their polymers were of consistently lower molar mass than those used in the earlier study. This suggests that their polymers may have contained significantly higher levels of fluorenone than they reported. Similar copolymers **592** with a 9-hydrazone containing unit also show green EL which red-shifts (λ_{max} goes from 522 to 531 nm) and loses efficiency (from 0.51 cd/A down to 0.16 cd/A) as the amount of hydrazone increases from 1 to 3 mol %.[1257]

Recently, Shu, Jen, and co-workers[1258] prepared a fluorene **593** with two electron-accepting oxadiazole substituents by nucleophilic substitution of 4-fluorobenzonitrile with fluorenyl anion and subsequent conversion of the nitriles to oxadiazoles via tetrazole intermediates (Scheme 45). The alternating copolymer with dioctylfluorene **594** (Chart 12) showed better color stability and higher efficiency in a single-

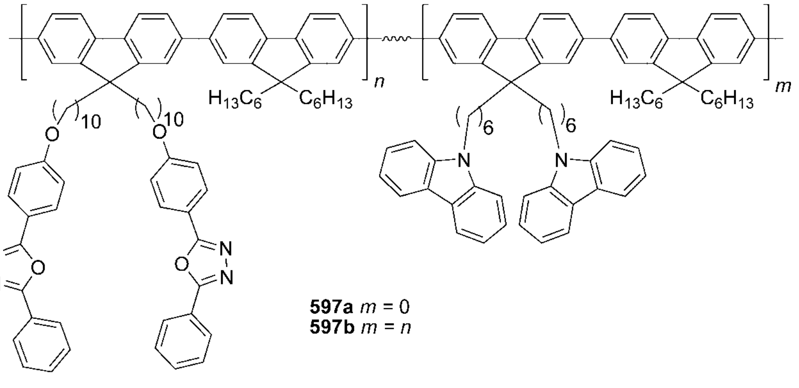
Chart 12



594 *m* = 0
595 *m* = *n*

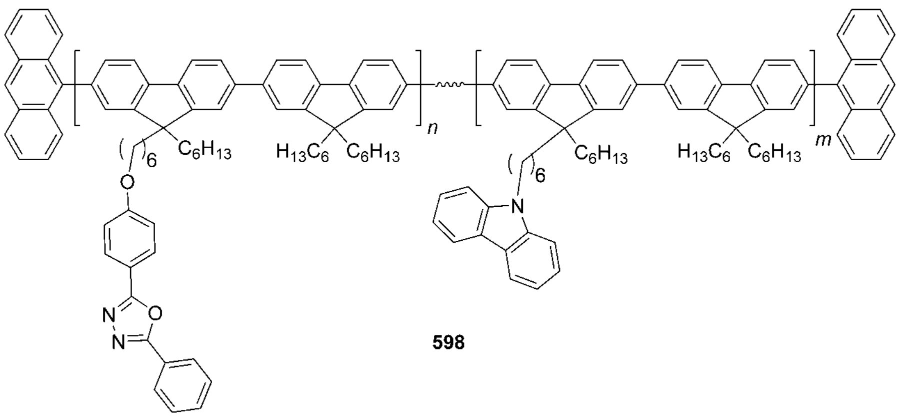


596

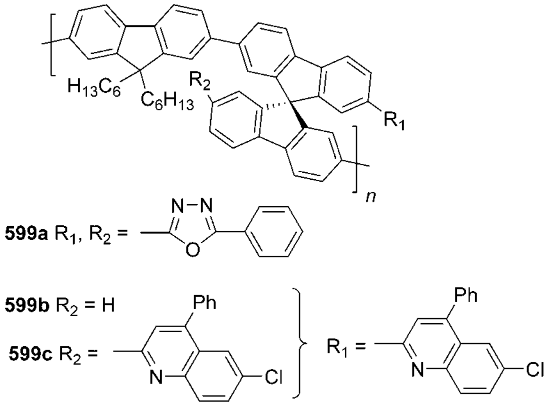


597a *m* = 0
597b *m* = *n*

Chart 13



598

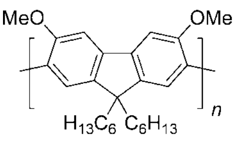


layer device (0.52%) than poly(dioctylfluorene) (**560b**) (0.2%) due to its improved charge accepting ability. Copolymer **595** (*m*:*n* = 1:1) with both hole- and electron-accepting substituents displayed even better efficiency (1.21%).[1259] Blending **595** with **576b** has been found to suppress the vibronic emission band from the latter at 497 nm, so producing pure blue EL (λ_{max} = 461−468 nm) with good efficiencies (up to 3.88 cd/A).[1226]

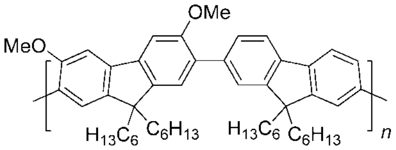
Efficient (2.07 cd/A), stable blue (λ_{max} = 460 nm) EL is reported from copolymer **596** with oxadiazole side-chains and triarylamines in the main chain.[1260] Oxadiazoles have also been attached to polyfluorenes via alkyl side-chains, e.g. **597a**, which produces blue EL with good efficiency (λ_{max} = 424 nm, 1.13 cd/A).[1261] Copolymer **597b** bearing hole-transporting carbazole units displays even higher efficiency (1.28 cd/A). Even better results have been obtained from copolymers **598** (2.13 cd/A for *n*:*m* = 1:9) with shorter alkyl linkers.[1262] Copolymers bearing Fréchet-type dendrons with diaryloxadiazole groups on their periphery show poorer EL efficiency with increasing generation number.[1263] Unlike in the previously quoted examples, copolymerization with units bearing carbazole groups lowers the device efficiency. Copolymers **582b,c** end-capped with electron-transporting groups have been prepared by a Taiwanese group.[1264] The triazole-end-capped polymer **582c** showed much higher efficiency than the oxadiazole-end-capped polymer **582b** (1.67 cd/A vs 0.56 cd/A).

Electron-transporting groups have been incorporated into the fluorene-spirobifluorene copolymers **599** (Chart 13).[1265] The emission of the oxadiazole-containing polymer **599a** (λ_{max} = 452 nm) is slightly red-shifted compared with that from the quinoline-containing copolymers **599b** (λ_{max} = 439 nm) and **599c** (λ_{max} = 429 nm). The EL efficiencies were similar for all three polymers (0.17−0.21 cd/A).

A final approach to manipulating the charge accepting properties of polyfluorenes is to introduce substituents onto the fluorene units. Thus, the methoxy groups in **600** and **601** raise the polymers' HOMO energy levels by about 0.2 eV, improving their hole-accepting abilities.[1266] The solid-state PL maxima are at 430 and 434 nm, suggesting that the methoxy groups do not cause any marked out-of-plane twisting of the polymer backbones.

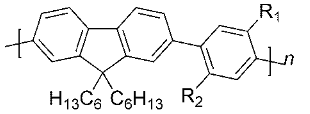


600

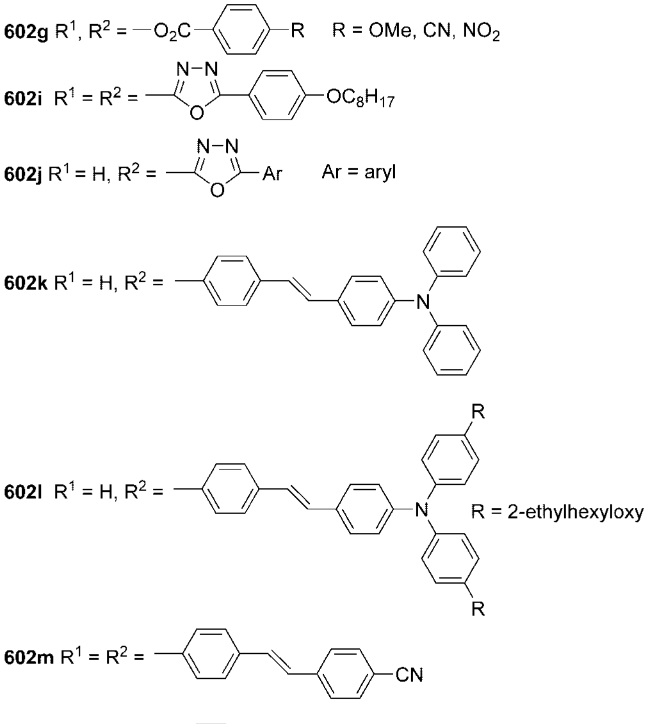


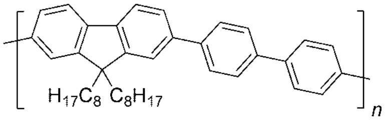
601

As would be expected, alternating copolymers of PDAF and PPP such as **602a** have been found to be blue emitting (λ_{max} = 420 nm).[710,1267−1272] The biphenylene copolymer **603** shows violet-blue emission,[1268,1270] as does a copolymer with cyclophane.[1273,1274] Substitution of the phenylene ring with alkyl groups in **602b** produces a marked blue-shift in the PL emission (λ_{max} = 404 nm),[1271,1274] whereas the alkoxy substitution in **602c** reportedly has no effect on the PL and EL maxima (λ_{max} = 420 nm).[1275,1276] Attachment of polyhedral oligosilsesquioxide groups as side-chains on a copolymer of PADF and a dialkoxyphenylene reportedly enhances the efficiency of the EL emission (λ_{max} = 415 nm).[1277] Quaternization of the amino side-chains on the copolymer **602d** is reported to give solubility in water,[1278,1279] as do the carboxylates in **602e**.[1280] The quaternized **602d** has been used as an electron-transporting layer in LEDs, as its water and alcohol solubility enables it to be deposited from polar solvents in which the underlying emissive layer is not soluble.[1281] The carboxylate substituents on the phenylene in **602f** produce a red-shift in the PL (λ_{max} = 443 nm) together with a drop in PL efficiency (20%, cf. 78% for **602a**).[1271] Copolymers **602g** with benzoate substituents on the phenylene undergo a large red-shift in their solid-state emission upon annealing, with λ_{max} going from 442−447 nm to 550−555 nm.[1282]



602a $R^1 = C_6H_{13}$ or C_8H_{17}, R^2 = H
602b $R^1 = R^2 = C_6H_{13}$
602c $R^1 = C_6H_{13}$, $R^2 = OC_{10}H_{21}$
602d $R^1 = R^2 = OC_2H_4NMe_2$
602e $R^1 = R^2 = CO_2Na$
602f $R^1 = C_6H_{13}$, $R^2 = CO_2C_2H_5$
602h $R^1 = C_6H_{13}$, R^2 = CN

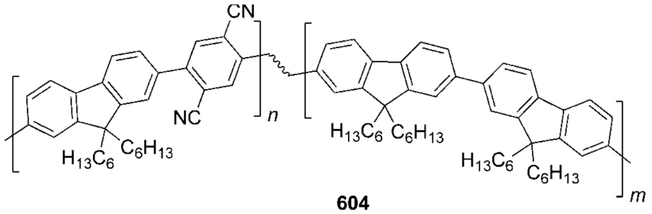




603

Jen and co-workers have prepared copolymers **602h** (λ_{max} = 447 nm) and **604** (λ_{max} = 477 nm) with electron-accepting dicyanobenzene units by Suzuki polycondensation.[1283] The alternating copolymer **602h** shows only marginally higher EL efficiency than the PADF homopolymer **558a**, but the other copolymer **604** with only 25 mol % of dicyanobenzene units ($m = n$) shows an EL efficiency over 10 times higher (0.50% vs 0.044%) in double-layer devices with PEDOT and calcium cathodes. Copolymers **602i** with two oxadiazole units produce blue EL (λ_{max} = 452 nm), whereas copolymers **602j** with one oxadiazole produce violet-blue emission (λ_{max} = 406−431 nm).[1284] The LUMO energy level in **602j** can be tuned from −2.64 to −2.84 eV by altering the aryl substituent.

Copolymers **602k,l** with a styryl substituent produce blue-green emission (λ_{max} = 472 and 492 nm, respectively),[1285] while copolymers **602m,n** with two styryl substituents produce blue-green (λ_{max} = 468 nm) and green (λ_{max} = 506 nm) EL, respectively.[1286]



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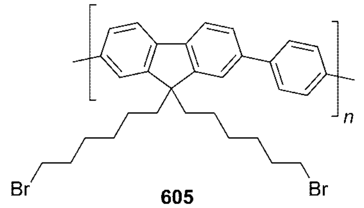

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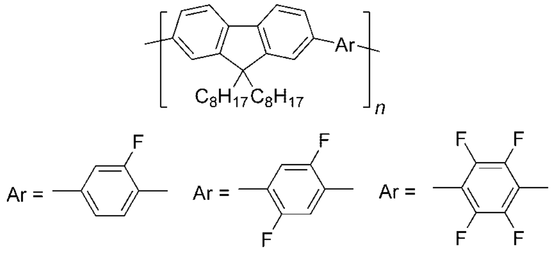
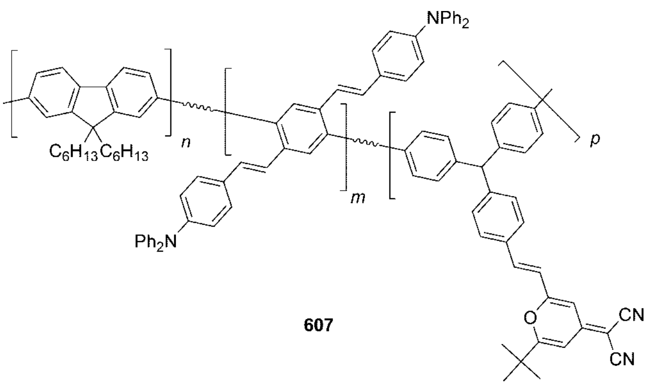


606a **606b** **606c**

Copolymer **605** with ω-bromoalkyl groups has better hole-accepting properties and so has a lower turn-on voltage than **602a**.[1287] Copolymers **606a−c** have been prepared by the Suzuki route.[1288,1289] The steric hindrance induced by fluorine substituents produces a blue-shift in the PL emission due to increased steric repulsion, so that the PL maxima in solution shift from λ_{max} = 400 nm for **606a** to λ_{max} = 382 nm for **606c**. Copolymer **606b** is reported to display better EL performance than either **558a** or **602a**.[1290] Copolymer **607** containing red emitting dye units produces white EL with modest efficiency (0.1 cd/A).[1291] Red emission (λ_{max} = 612 nm) is seen from copolymer **608** bearing phosphorescent metal complexes on the side-chains.[1292] The highly phenylated copolymers **609a,b** are made by a Diels−Alder route (Scheme 46). They show violet-blue (λ_{max} = 404 nm) and blue (λ_{max} = 436 nm) EL, respectively.

As the amount of *meta*-linkages in the copolymers **610** increases, the emission maximum blue-shifts from 409 nm (m = 0) to 385 nm (n = 0).[1293] The *meta* linkages are reported to reduce the rate at which fluorenone defects form upon annealing the polymers and the rate of energy transfer to defect sites, by disrupting chain packing and, more significantly, by reducing exciton mobility owing to decreased conjugation. Copolymer **611** with *meta*-phenylenes shows violet PL (λ_{max} = 397 nm) which is red-shifted (λ_{max} = 412 nm) and has its efficiency sharply increased by complexation with ruthenium(II).[1294] The similar copolymers



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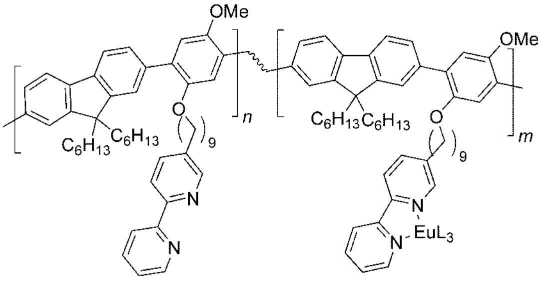


608 L = ligand

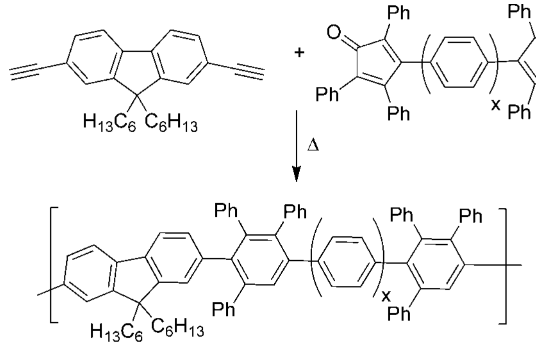
612 with europium complexes exhibit red PL ($\lambda_{\max} = 612$ nm) from the metal complexes.[1295]

Jen and co-workers have prepared copolymers **613** of dihexylfluorene and binaphthyl which show EL maxima at 420 or 446 nm in double-layer devices depending upon the device structure.[1296,1297] Copolymers of dioctylfluorene with tetracene and pentacene are reported to show green ($\lambda_{\max}$ 520 nm) and red ($\lambda_{\max}$ 623 nm) EL, respectively, due to energy transfer, but the lifetimes of the devices are short due to the rapid photo-oxidation of the acene units.[1185] An industrial group has reported obtaining efficient red, green, and blue emission from fluorene-arylene-based alternating copolymers prepared by Suzuki polycondensation, but without publishing their structures.[1298,1299]

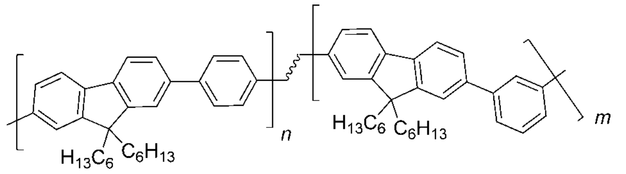
Incorportion of dibenzothiophene units into the copolymers **614** is reported to improve the color purity of the EL, as long wavelength emission is suppressed.[1300] Other fluorene-heterocycle copolymers are discussed in section 3.8.

Poly(9,10-dihydrophenanthrene)s **615**, which are analogous to polyfluorenes, but with two sp^3 bridging atoms instead of one, have been prepared by Yamamoto and co-workers.[1301] The PL emission from **615** ($\lambda_{\max} = 431$ nm) and the alternating copolymer **616** with dioctylfluorene ($\lambda_{\max} = 428$ nm) is similar to that from polyfluorenes. The alternating ethynylene copolymer **617** has slightly red-shifted PL ($\lambda_{\max} = 440$ nm).

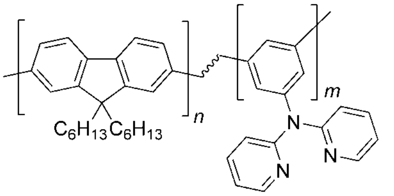
Scheme 46. Diels−Alder Synthesis of Highly Phenylated Fluorene Copolymers



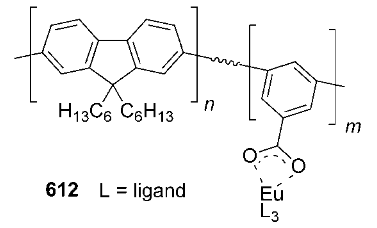
609a x = 1 **609b** x = 2



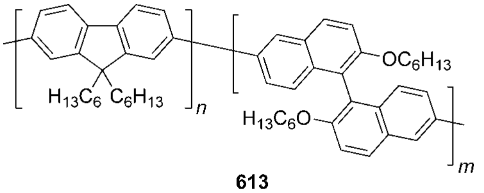
610



611



612 L = ligand



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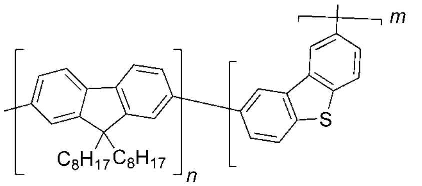

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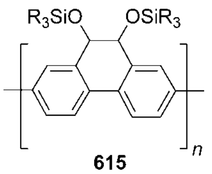

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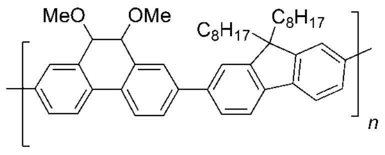
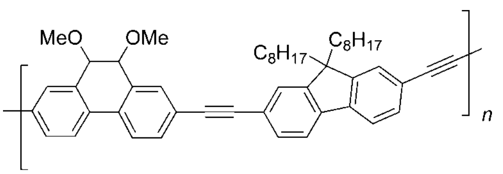


616

Poly(4,9-dioctyl-4,5,9,10-tetrahydropyrene) **618**, which has two sp^3 bridging atoms per monomer unit, has been synthesized by Müllen and co-workers[1302] through Yamamoto coupling of the dibromo-monomer and has been used to make a blue emitting ($\lambda_{\max} = 457$ nm) device.[1303] When longer bridges are used, the biphenyl units become twisted, reducing the conjugation so that copolymers such as **619** are violet emitters ($\lambda_{\max} = 395$ nm).[1304,1305] Introduction of 30−40 mol % of such units into fluorene copolymers **620a−d** has been shown to suppress the long wavelength emission seen for the fluorene homopolymers.[1306] The best EL efficiency (0.24 cd/A) was seen for **620a**, which is, however, significantly below that of **558a** (0.51 cd/A[1307]).



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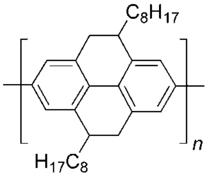
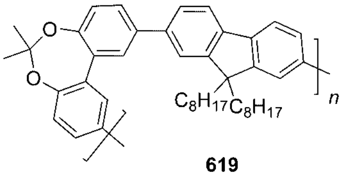


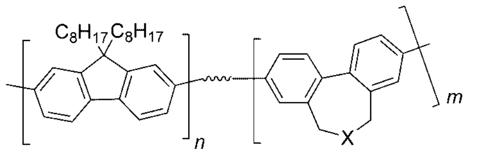
618

These effects are attributed to disruption of the chain packing, which not only hinders exciton migration to emissive defects but also charge transport.

Poly(tetraalkylindenofluorene)s (PIFs, **621a**), which are intermediate in structure between PADFs and LPPP, have been prepared by the Müllen group and found to show PL maxima in solution around 430 nm,[1308] making them attractive candidates for use in blue LEDs. Unfortunately, they suffer from similar problems to poly(dialkylfluorene)s in that their EL emission rapidly turns green,[1309] which is now attributed to formation of emissive ketone defects.[1310] As with PDAFs, copolymerization with anthracene gives materials which show stable blue EL (λ_{max} = 445 nm), probably due to exciton confinement on the anthracene.[1311] The stability of the blue emission from PIFs is greatly enhanced by replacing the alkyl substituents with aryl groups, as in **621b**.[1203,1312] Polymer **622**, with spiro linkages at both bridging atoms, shows stable blue PL and EL (λ_{max} = 445 nm).[1313]

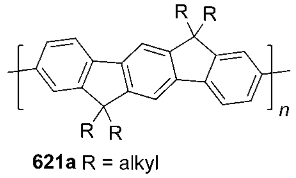


619

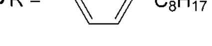


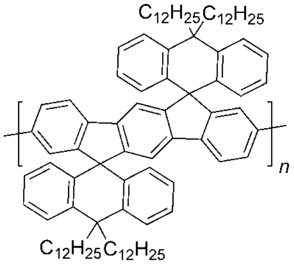
620a X = O, **620b** X = S, **620c** X = SO_2, **620d** X = NR

The gap between PIFs and LPPPs has been bridged by the Müllen group, who prepared the poly(ladder-type tetraphenylene) **623**[1307] and the poly(ladder-type pentaphenylene) **624a**.[1314] These both produce pure blue PL emission (λ_{max} = 441 nm) with a very small Stokes shift analogous to that seen for LPPP, but whereas **624a** exhibited blue EL, the emission from devices using **623** is dominated by a green emission band at 510 nm, the origin of which is as yet unknown. It does not appear to be due to oxidative degradation, as heating of **624a** in air produces a band at 575 nm, which is attributed to formation of a ketone at the central bridging atom. Polymer **624a** also shows a small polaron absorption, suggesting it could be a good candidate for laser applications. The *all*-aryl polymer **624b** displays remarkably stable blue EL.[1315]

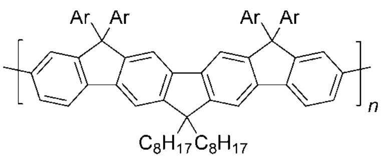


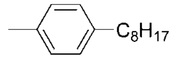
621a R = alkyl

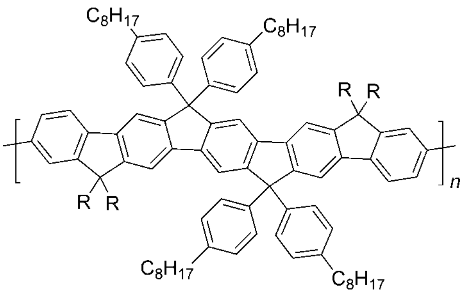
621b R =




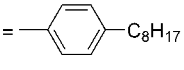
622



623 Ar =




624a R = C_8H_{17}

624b R =


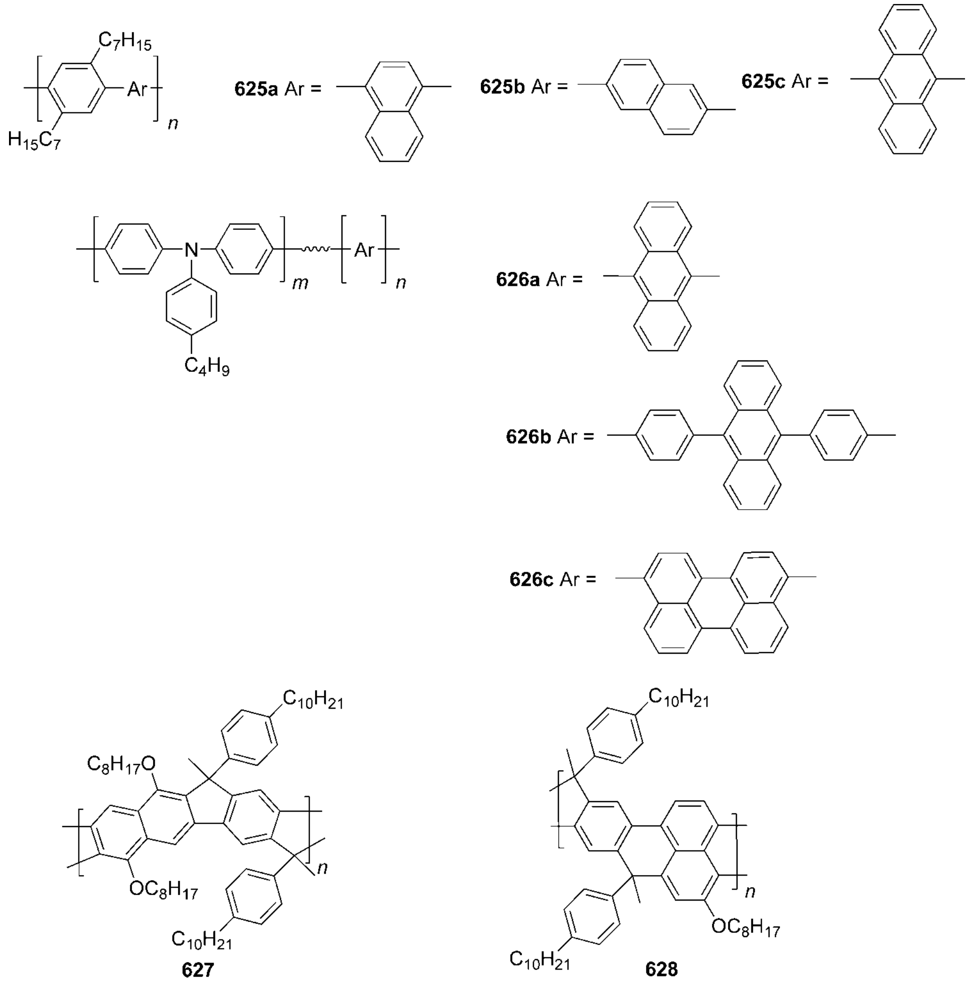
3.5. Other Polyarylenes

Luminescence from polymers of larger arylenes has been little studied. Shen and co-workers[1316] have obtained blue-green electroluminescence (λ_{max} = 485 nm) from an insoluble ill-defined polynaphthalene deposited as a thin film by plasma polymerization of naphthalene. Polymer samples deposited under different conditions showed different PL spectra. Soluble dialkylphenylene−naphthalene alternating copolymers **625a** and **625b** (Chart 14) have been prepared by Suzuki cross-coupling and show violet-blue emission (λ_{max} = *ca.* 375 nm).[1100] The analogous copolymer **625c** with anthracene units showed emission maxima at 415 and 437 nm with a much smaller Stokes shift.[1100] Oxidative copolymerization of anthracene and dialkoxybenzenes gives ill-defined blue emitting copolymers (λ_{max} = 468 nm).[1317,1318] Copolymers **626a** and **626b** containing anthracene and TPA units are green emitting (λ_{max} = 506−514 nm), while the corresponding perylene copolymer **626c** is a yellow emitter (λ_{max} = 559 nm).[1319] This difference is probably due to twisting of the backbone in **626a** and **626b** to reduce interactions between the anthracene units.

Scherf and co-workers have prepared the naphthalene−phenylene ladder-type copolymers **627**−**629**.[1320] The 2,6-naphthalene-based polymer **627** shows blue PL (λ_{max} = 458 nm), but the 1,5-naphthalene copolymers **628** and **629** are blue-green emitters (λ_{max} = 485 and 508 nm, respectively). The anthracene−phenylene ladder copolymer **630** is also a blue-green emitter (λ_{max} = 498 nm).[1321]

The polyphenanthrenes **631a,b** (λ_{max} = 524 and 530 nm, respectively) and phenanthrene−phenylene copolymer **632**

Chart 14



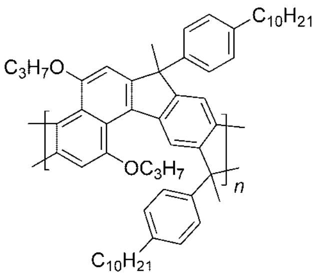
(λ_{max} = 378, 390 nm) have been prepared by oxidative cyclization of phenyl-substituted PPV derivatives **633** and **634** with iron(III) chloride.[597] It is interesting to note the different regiochemistry of the aryl couplings in **633** and **634**. Green (λ_{max} = 524 nm) emission has been reported from a device using a blend of the diphenoxy derivative **631a** in PVK or polycarbonate.[598] The related polymer **635** with a bridged phenthrene monomer is a blue-violet emitter (λ_{max} = 400 nm), indicating a short conjugation length, probably due to large torsion angles between adjacent units.[1322] Poly(anthracene-2,6-diyl) (**636**) and its alternating copolymer with PPP **637** has been prepared by a precursor route and found to show yellow-green fluorescence (emission data not given).[1323]

Binaphthyl units are chiral, and incorporation of such units into polymers offers a potential route to getting circularly polarized emission. The synthesis and properties of binaphthyl containing oligomers and polymers has been reviewed by Pu.[775,1324] The only report of electroluminescence is for the poly(binaphthyl) **638** prepared by Suzuki polycondensation.[1325] This polymer shows blue PL (λ_{max} = 390, 408 nm) with a broad secondary peak at 500−560 nm assigned to an excimer, while the EL emission is blue-green (λ_{max} = 554 nm).[1326] The alternating copolymer **639** with dihexyloxyphenylene units shows blue PL in both solution (λ_{max} = 417 nm) and the solid state (λ_{max} = 404 nm).[1327] Slightly blue-shifted emission (λ_{max} = 386, 401 nm) is seen for a binaphthyl-phenylene copolymer with Fréchet-type dendrons attached to the binapthyl units.[1328]

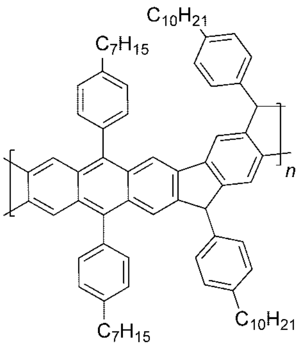
3.6. Polythiophenes

Unquestionably, the class of polyheteroarylenes most widely investigated for luminescence purposes have been polythiophenes (PTs). As well as a general review of luminescent PTs by Wudl and coauthors,[1329] there are reviews of the synthesis and chemistry of PTs by McCullough,[1330] and on the control of their properties by modifying the substituents by Leclerc[1331] and by Hutchinson.[1332] In addition, two Swedish groups have published reviews of their work on the synthesis and applications of these polymers.[1333,1334]

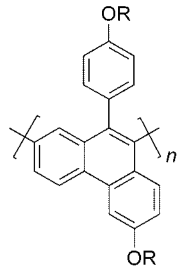
A vapor-deposited film of insoluble unsubstituted polythiophene **640** has been reported to be electroluminescent, but no spectral details were provided.[1335] Soluble oligothiophenes have been studied as emitters in LEDs, and the values for their emission maxima provide a useful basis for comparison with those for the soluble polymers so as to estimate their degree of conjugation and also illustrate some of the substituent effects to be expected in those materials. The use of oligothiophenes in electronic devices has been reviewed.[1336,1337] A study of octyl-substituted oligomers **641** (*n* = 0−6) (Chart 15) found that the effective conjugation length was at about 20 thiophene rings (*n* = 2).[1338] The conjugation length in poly(3-alkyl thiothenes) is very dependent on the nature of the substitutents. For example, ring fusion at the 3,4-positions can deliver a conjugation length of 96.[1339] There are many examples of theoretical predictions



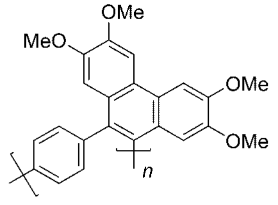
629



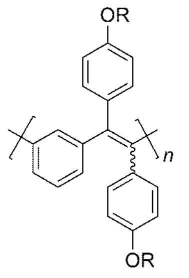
630



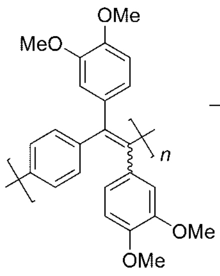
631a R = Me, **631b** R = Ph



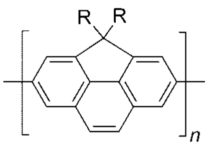
632



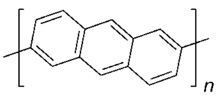
633a R = Me, **633b** R =Ph



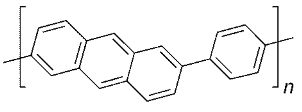
634



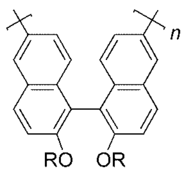
635 R = 2-ethylhexyl



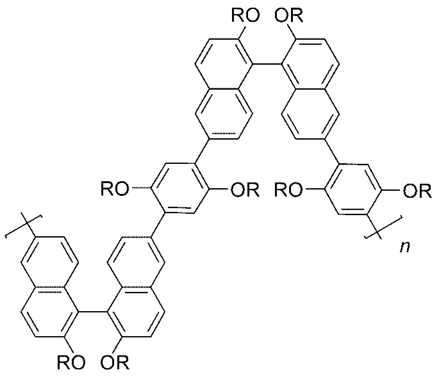
636



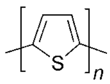
637



638 R = C_6H_{13}



639 R = C_6H_{13}



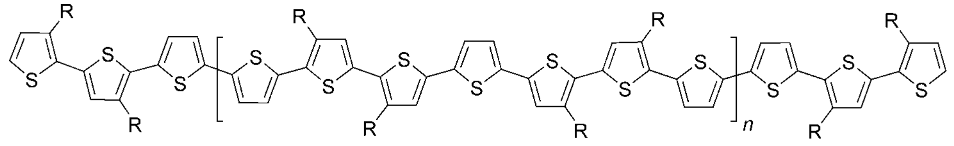
640

and experimental estimates of conjugation length in polythiothenes.[1340,1341]

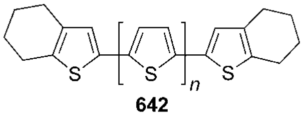
As expected, studies of end-capped oligothiophenes **642** (n = 1−3)[1342] and **643** (n = 1−4)[1343] have shown a correlation between the wavelength of maximum luminescence and the inverse number of thiophene rings, although most studies provide too few data points for a good correlation.[1341] Similarly, the emission maximum for the distyryloligothiophenes **644** shifts with increasing number of thiophene rings from green (λ_{max} = 508 nm) for $n = 1$ to yellow (λ_{max} = 574 nm) for $n = 3$, respectively. A red-shift was observed upon substitution of the aryl rings as in **644b** due to electronic effects, while substitution of the thiophene rings as in **645** gave a blue-shift due to a decrease in effective conjugation caused by the increased torsion angle between the thienyl rings induced by steric repulsion between the alkyl chains.[1344] Green emission has been obtained from devices using a Langmuir−Blodgett (LB) film of quinquethiophene **646a** as emissive layer.[1345−1347] Uchiyama et al.[1348] reported that dimethylsexithiophene **646b** displays electroluminescence with the emission maximum at 2.1 eV (λ_{max} = 600 nm) and that using other dimethyloligothiophenes with higher band-gaps as charge confinement layers gave increases in device efficiency of up to 3 orders of magnitude.[1349] Horowitz and co-workers[1350,1351] have shown that two-layer devices using sexithiophene **646c** and dialkylsexithiophenes are more efficient than monolayer devices by 2 orders of magnitude. Taliani and co-workers have achieved polarized EL emisssion by controlling the morphology of vacuum-sublimed films of **646c**.[1352,1353] Garnier and co-workers have reported that **646c** gives much better LED performance when dispersed in a hole-transporting matrix.[1354]

Soluble poly(3-alkylthiophene)s (P3AT)s such as poly(3-hexylthiophene) (P3HT, **647a**) are readily prepared by polymerization of the corresponding 3-alkylthiophene monomers either electrochemically or by oxidation with iron(III) chloride.[1355] Electropolymerization leads to defects due to coupling at the 4-position, while iron(III) chloride oxidation produces regioselective coupling only at the 2- and 5-positions. Coupling of 2,5-bis(trimethylsilyl)thiophenes is reported to give high molecular mass polymers with a high degree of conjugation.[1356,1357] Nickel-catalyzed coupling of 2,5-dihalothiophenes with thiophene Grignard reagents[1358,1359] or palladium-catalyzed coupling of thienyl mercuric chlorides[1360,1361] also affords defect-free P3ATs. Electroluminescence in P3ATs with varying alkyl chain lengths has been reported by several groups.[1136,1362−1371] Typically, the emission maxima was at about 1.9 eV (640 nm), and the emission intensity was found to increase with elongation of the side-chain due to enhanced confinement of charge carriers on the main-chain and longer interchain distances. It should be noted that the solid-state emission from P3ATs is usually significantly red-shifted compared with that in solution, which suggests there are strong interactions between the polymer chains in the solid state, as do the typically low solid-state PL quantum efficiencies for these materials.[1332,1334] LB films of P3HT (**647a**) and poly(3-hexadecylthiophene) (**647b**) have been used as emissive layers in LEDs.[1372−1377] Poly(3-octylthiophene) (P3OT, **647c**) has also been used as a hole-transporting layer in LEDs.[1371,1378] Use of a charge carrier confinement layer[1363,1379] or doping with fluorescent dye materials[1380−1382] also markedly increases device efficiency.

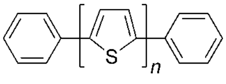
Chart 15



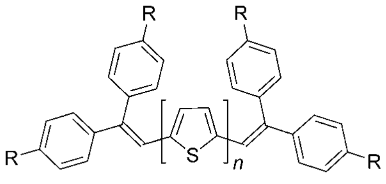
641 R = C_8H_{17}



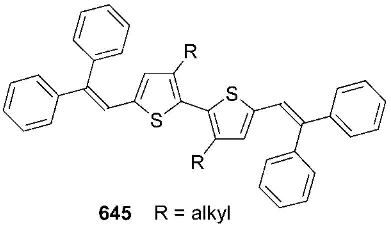
642



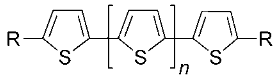
643



644a R = H
644b R = CH_3

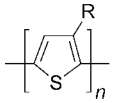


645 R = alkyl

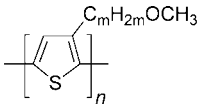


646a *n* = 3, R = H
646b *n* = 4, R = CH_3
646c *n* = 4, R = H

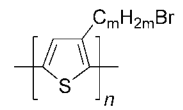
Polymers with substituted alkyl side-chains have also been studied. The emission from the *ω*-methoxyalkyl polymers **648** is similar to that of the corresponding P3ATs.[1383−1385] Oriented LB films of **648** produce polarized EL.[1386−1388] A slight blue-shift in the EL compared to the PL spectra of these films has been attributed to interactions between the polymer and the aluminum cathode, leading to a slight decrease in the effective conjugation length.[1389] The PL of poly[3-(*ω*-bromoalkyl)thiophene]s **649** is green (λ_{max} = 550−575 nm) in solution[1390,1391] but red-orange (λ_{max} = 670−680 nm) in the solid state.[1391] The spectral properties of the polyesters **650** depend upon the size of the ester alkyl group.[1392] The emission is bathochromically shifted for longer alkyl groups, so that the ethyl ester **650a** has emission maxima at 602 and 636 nm, while the nonyl ester **650b** has an emission maximum at 738 nm. Polymers **651a,b** with urethane side-chains are reported to show orange EL (λ_{max} = 590 nm)[1393,1394] with higher efficiency for **651a** in devices under reverse bias.[1393] The EL efficiency of **651a** is enhanced up to 5-fold by addition of complexes of ruthenium or europium.[1395] The similar polymer **651c** has been used to make a layer-by-layer self-assembled film with a europium complex, which also shows orange-red EL (λ_{max} = 590 nm).[1396,1397] Polymer **652a** with an electron-accepting benzotriazole group attached to the side-chain shows orange-red EL (λ_{max} = 580 nm) with an efficiency seven-times that of P3OT (**647c**).[1398] Substitution with chlorine in **652b** to increase the electron-accepting properties of the substituent produced a slight red-shift in the emission (λ_{max} = 588 nm), but the EL efficiency was less than half that of **652a**. Polymers, e.g. **653**, with liquid-crystalline mesogens in the side-chain produce polarized PL.[1088,1399] The perfluoroalkyl substituents in **647d** make this material soluble in supercritical carbon dioxide.[1400]



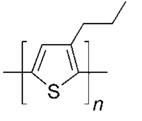
647a R = C_6H_{13}
647b R = $C_{16}H_{33}$
647c R = C_8H_{17}
647d R = C_8F_{17}
647e R = $C_{12}H_{25}$
647f R = alkoxy
647g R = $C_{10}H_{21}$



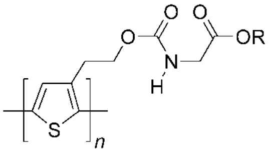
648a m = 5
648b m = 6
648c m = 10



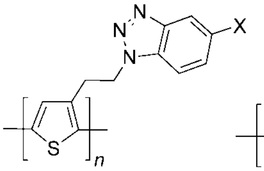
649 m = 4,6,10,12



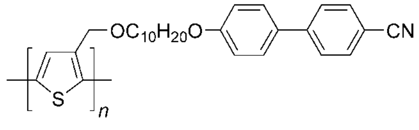
650a R = C_2H_5
650b R = C_9H_{19}



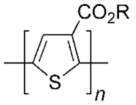
651a R = C_3H_7
651b R = C_4H_9
651c R = H



652a X = H
652b X = Cl



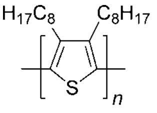
653



654a R = C_6H_{13}
654b R = C_8H_{17}

Polymers **654a** and **654b** have been obtained by coupling of 2,5-dibromothiophene-3-carboxylates using copper or nickel(0).[1401] Their PL emission maxima vary from 555 to 570 nm in solution and from 595 to 630 nm in the solid state depending upon their method of preparation. The EL maxima for **654a** and **654b** are observed at 600 and 615 nm, respectively.[1402−1404]

It has been found that the color of the emission from PTs can be tuned by controlling the nature and regularity of the side-chains on the polymers. Hadziiannou and co-workers[1405,1406] studied the alkylated polymers **655**−**658** and found that there was a correlation between their emission maximum and the inverse number of thiophene units between two consecutive head-to-head (2,2′-coupled) dyads. Thus, polymer **655** showed an emission maximum at 2.7 eV (λ_{max} = 460 nm) while polymer **658** had an emission maximum at 2.25 eV (λ_{max} = 550 nm). Similarly, Holdcroft and co-workers[1407,1408] reported that the emission maximum for P3HT (**647a**) was blue-shifted with increasing amounts of head-to-head dyads. Yamamoto and co-workers[1409] reported that polymer **659** of a 3,4-crown-ether-substituted thiophene showed an emission maximum in the blue at 2.7 eV (λ_{max} = 470 nm) while the emission maximum of the alternating copolymer with



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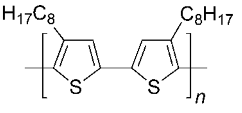

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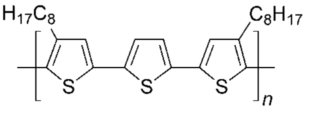

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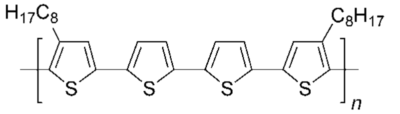

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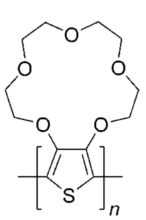
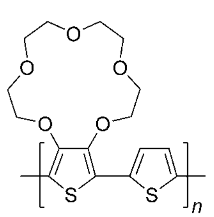
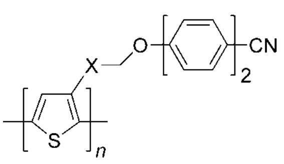


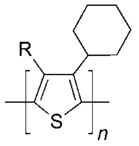
659



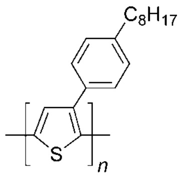
660



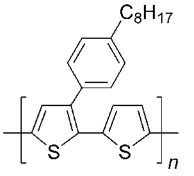
661 X = CH$_2$, O



662a R = H
662b R = CH$_3$



663



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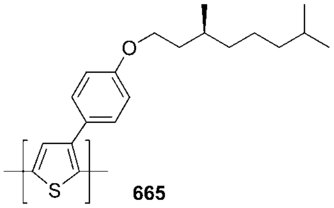

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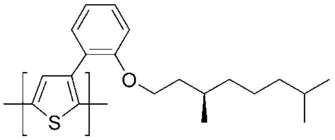
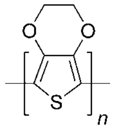


666

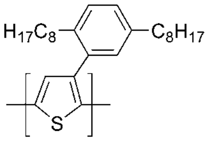


667

thiophene **660** was in the yellow at 2.25 eV ($\lambda_{max} = 550$ nm). Polymers, e.g. **661**, with bulky oligophenylene side-chains are also claimed to be blue emitting.[1410] Copolymers of such materials with alkylthiophenes, however, are orange emitting.[1411] Inganäs and co-workers found that the incorporation of a bulky cyclohexyl side-chain in **662a** produced a blue-shift such that the emission was green ($\lambda_{max} = 555$ nm).[563,1412−1414] Introduction of a 4-methyl group to give **662b** produced blue emission ($\lambda_{max} = 460$ nm).[563,1413,1414] These effects can be attributed to the bulky substituents causing the conjugated backbone to be twisted out of plane and thus reducing the effective conjugation length. By contrast, the 4-octylphenyl-substituted polymers **663** and **664** emitted in the red ($\lambda_{max} = 670$ and 620 nm, respectively).[563,1413,1414] The emission from polymers **665** and **666** is green in solution ($\lambda_{max} = 534$ and 525 nm, respectively) but red in the solid state ($\lambda_{max} = 607$ and 600 nm).[1415] The slight blue-shift in the emission from **666** compared with **665** may reflect greater steric interaction between the alkoxy substituents and the main chain.

Both modification of the polymer structure and improvements in device design have led to considerable advances in the control of the color of LEDs using polythiophenes as the active materials. Insertion of a poly(methyl methacrylate) (PMMA) layer between an emissive P3HT (**647a**) layer and the cathode significantly changes the device characteristics and performance due to accumulation of charge carriers at the interface.[1416] Bilayer devices containing polymer **663** and a diaryl oxadiazole layer emit white light[1417] or blue light with the emission maximum in the near-ultraviolet ($\lambda_{max} = 397$ nm),[1418] depending on the exact device structure. Polarized emission has been obtained from a device using a stretched film of polymer **663** on polyethylene as emissive layer.[1419] Polarized emission can also be obtained from rubbing aligned P3ATs, with the best results being reported using polymer **647e**.[1087] Circularly polarized emission has been obtained from polymers with chiral side-chains.[1420] Deposition of polymer **661** in pores of a film of electrically conducting PEDOT (**667**) gives access to miniature LEDs with diameters in the micro- or nanometer range.[1421−1423]

PTs with substituents at the 3-position produced by polymerization of monomers with iron(III) chloride or by Grignard coupling reactions are regiorandom, with a preponderance of head-to-tail (2,5′) coupling, varying from 52% to 80% according to the method used.[1359,1424,1425] Better control of material properties requires the ability to synthesize polymers with high regioregularity. Coupling of alkyloligothiophenes by iron(III) chloride or Grignard coupling methods gives regioregular copolymers.[1405,1426,1427] Andersson and co-workers[563,1428] have shown that high molecular weight (M_n 23000 Da), regioregular (94% head-to-tail) polymer **663** can be readily obtained from polymerization of the 3-arylthiophene monomer with iron(III) chloride, by careful control of the oxidation conditions due to preferential stabilization of the cationic charge in the intermediates at the 2-position by the aryl group (which restricts this method to thiophenes with a substituent capable of such stabilization). This material has been found to exist in two forms.[1429] Spin-casting gives a metastable state with a band gap of 1.85 eV ($\lambda_{max} = 670$ nm) which emits orange-red light. Upon heating or exposure of the film to chloroform vapor, an irreversible transformation of the film to a stable low band gap (1.55 eV, $\lambda_{max} = 800$ nm) form occurs to produce a material which emits in the infrared. The change is due to an increase in the ordering of the polymer chains which has been confirmed by X-ray diffraction studies.[1430] The same method has been used to make other highly regioregular P3ATs.[1431−1433] High regioregularity has also been obtained by vanadium-catalyzed oxidative polymerization of a 3-arylthiophene.[1434] These polymers often show higher solid-state photoluminescence quantum efficiencies than their 3-alkyl analogues. For example, the PL quantum efficiency of 2,5-dioctylphenyl-substituted polymer **668** in solution is only a third higher than that for P3OT (37% versus 27%) but is six times higher in the solid state (24% versus 4%).[1334,1435,1436] This is attributed to the regioregularity and the bulky substituents keeping the polymer chains separated, thus reducing the efficiency of nonradiative decay pathways. High crystallinity as well as good separation of the polymer chains is required to get high PL quantum yields, as shown by the low (4%) solid-state PL efficiency for copolymer **669**. The photoluminescence efficiency of blue emitting polymers such as **662b** is reported to be much lower than that of P3OT due to more efficient nonradiative decay pathways.[1334,1436] The emission of copolymers **670** shows a marked blue-shift from the red ($\lambda_{max} = 660$ nm) into the yellow ($\lambda_{max} = 570$ nm) region of the visible spectrum, as the proportion of 3-arylthiophene increases, with a concurrent increase in the EL efficiency.[1437] Polymers **671** and **672** bearing ethylene oxide side-chains have been used to make red emitting (λ_{max} 615 nm) LECs and surface LEDs.[1438−1440]



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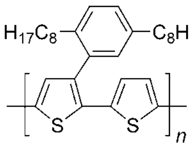

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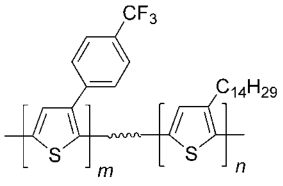

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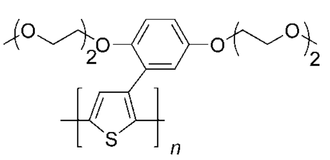

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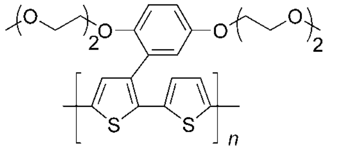
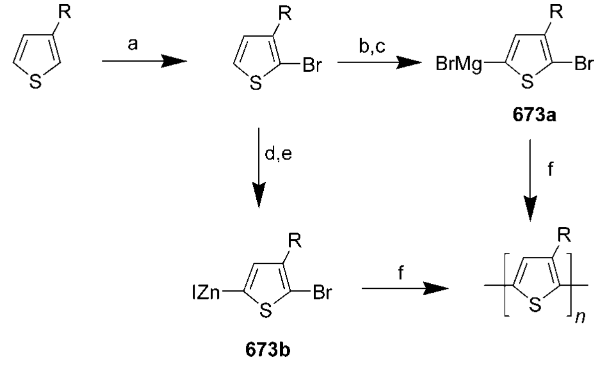


672

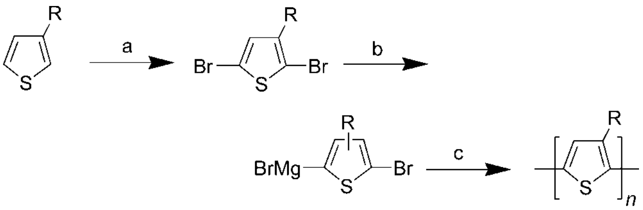
In recent years, a number of routes to highly regioregular polythiophenes have been developed by several research groups. Bäuerle and co-workers[1441−1445] have developed a solid-supported method for preparing defect-free regioregular head-to-tail coupled oligomers up to the dodecamer by Suzuki coupling, but this method is unlikely to prove suitable for preparation of polymers. Routes for the synthesis of regioregular (head-to-tail) P3AT s were first developed by the groups of McCullough[1446−1449] and Rieke[1450,1451] utilizing nickel-catalyzed coupling of 2-halo-5-metallothiophenes **673a** and **673b** (Scheme 47). In order to obtain high molecular weight polymers, extremely pure monomers are required.

It has been proposed that the high regioregularity and low polydispersity of P3ATs made by the McCullough (and probably the Rieke) method proceed via a regioselective intramolecular transfer of the nickel catalyst to the end of the growing chain so that each polymer chain arises from just one catalyst molecule.[1452] McCullough and co-workers[1453] have subsequently developed a modification of their original route involving Grignard metathesis (Scheme 48) which enables the large scale synthesis of regioregular polymers. This method involves formation of two isomeric Grignard monomers but still gives >95% head-to-tail (HT) coupling, which has been shown to be due to a combination of kinetic and thermodynamic effects.[1454] This method has been shown to be quasi-"living" in nature.[1455]

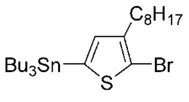
Scheme 47. McCullough and Rieke Routes to Regioregular P3ATs: (a) Br_2, HOAc; (b) LiN^iPr_2, −40 °C; (c) $MgBr_2 \cdot Et_2O$, −40 °C; (d) I_2, HNO_3, CH_2Cl_2; (e) Rieke Zinc; (f) $Ni(dppe)Cl_2$ or $Ni(dppp)Cl_2$



Scheme 48. Grignard Metathesis Route to Regioregular P3ATs: (a) Br_2, HOAc; (b) MeMgBr, THF; (c) $Ni(dppp)Cl_2$

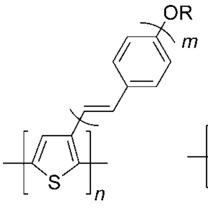


Moreau and co-workers made regioregular (>95% HT) P3OT (**647c**) by Stille coupling of a thienyltin compound **674**.[1456] Lemaire and co-workers have recently reported that palladium-catalyzed Heck type coupling of 2-iodo-3-alkylthiophenes gives regioregular oligomers.[1457,1458] All these methods leave a halide terminal substituent on the polymer, which permits end-capping of the polymer, thus opening a route toward block copolymers.[1459−1462] Most recently, an efficient Suzuki coupling route to regioregular P3ATs has been reported.[1463] Regioregularity, by controlling the amount of head-to-head dyads, influences the color of emission, and it has been reported that regioregular P3HT (**647a**) shows a longer effective conjugation length than that for the corresponding regiorandom material.[1464] Interestingly, the McCullough group has reported that devices using regioregular P3HT showed higher EL efficiencies than those using regiorandom material, probably due to less crystalline regions in the polymer.[1465] However, comparison of regioregular and random P3ATs prepared by Holmes and co-workers showed no significant differences in their emission spectra or EL efficiencies.[418,1466]

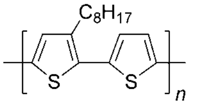


674

The properties of regioregular random copolymers can be tuned by varying the length of the alkyl side-chains and the relative ratios of the organometallic monomers.[1448,1467] Polymers and copolymers with functionalized alkyl side-chains can be prepared by these routes,[1468] as can poly(3-alkoxythiophene)s (**647f**).[1469−1472] A regioregular polymer with chiral side-chains has been made by the Rieke route, but it is not reported if the EL ($\lambda_{max} = 697$ nm) is circularly polarized, as would be expected for a chiral polymer.[1473] Polymers bearing styryl, e.g. **675a**, or oligo(phenylene vinylene), e.g. **675b**, substituents have been made by the Grignard metathasis route for use in photovoltaic devices.[1474] Their PL emission comes from the thiophene backbone (λ_{max} = *ca.* 540−560 nm) rather than the side-chains due to efficient energy transfer. Regioregular PTs with functionalized side-chains have also been prepared by Stille coupling.[1475,1476] Holmes and co-workers have prepared copolymers with side-chains containing terminal azide groups which have enabled cross-linking of the deposited films to produce insoluble materials for application in multilayer devices.[1477] The cross-linking produces a blue-shift in luminescence and an increase in luminescence efficiency.[1478] Holdcroft and Lowe have made similar cross-linkable copolymers with methacrylate groups on the side-chains for potential photolithographic applications.[1479] By combining the thermochromism of PTs with this cross-linking, they were able to tune the band gap of the polymers.[1480]



675a $m = 1$
675b $m = 2$



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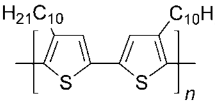
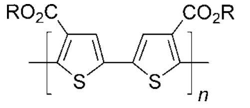
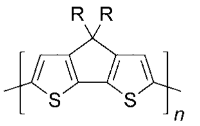


677

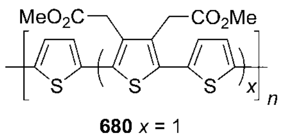
The properties of substituted poly(bithiophene)s are also affected by their degree of regioregularity. For example, copolymer **676** can be made in regiorandom[1481] or regioregular[1456,1482,1483] form by organometallic coupling methods and shows yellow PL and EL (λ_{max} = 570 nm).[1482,1484] Compared with the regiorandom form, the absorption of the regioregular form is reported to be red-shifted, indicating a longer effective conjugation length.[1483] Regioregular polymer **677** shows green emission (λ_{max} = 540 nm), and the PL quantum efficiency is reported to vary from 6.5% to 10% depending on the method of preparation.[1485,1486] The EL maximum can be tuned over a 50 nm range by altering the thickness of the emitting layer and the refractive index of the transparent electrode.[1487] Increasing the length of the alkyl chains is reported to cause a blue-shift in the absorption and a drop in the conductivity due to increased out of plane torsion of the thiophene rings.[1488] The regioregular poly(bithiophene bis-carboxylate)s **678a** and **678b** display red-orange EL (λ_{max} = 590 and 600 nm, respectively). Their EL efficiencies were observed to be four times lower than those for the regiorandom polymers **654a** and **654b**, however, probably due to poorer charge transport along the conjugated backbone because of the greater out-of-plane torsion induced by the head-to-head interactions between the substituents.[1489,1490] Polymers **679**, in which the bithiophene units are linked by a methine bridge, have been made by Ni(0)-coupling of the dibromo monomer and display red PL (λ_{max} = 639 nm).[1491] The poly(terthiophene) **680**[1492,1493] and poly(quinquethiophene) **681** both produce red EL (λ_{max} = 600 nm), but the efficiency of the latter (0.13%) is a hundred times better.[1493]



678a R = C_6H_{13}
678b R = C_8H_{17}



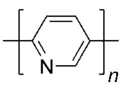
679 R = 2-ethylhexyl



680 $x = 1$
681 $x = 2$

3.7. Other Polyheteroarylenes

Heterocycles with sp^2-hybridized nitrogen atoms tend to be good electron acceptors, and so their polymers have been studied as both emissive and electron-transporting materials. Poly(2,5-pyridine) (PPy, **682**) is isoelectronic with PPP, but due to the basicity of the nitrogens, it can be processed from acidic solvents. Regiorandom PPy is prepared by coupling of 2,5-dibromopyridine with Ni(0) reagents. Yamamoto and co-workers[1494] reported they obtained the highest molecular mass PPy by using nickel(0) bis(cyclooctadiene) and 2,2′-bipyridyl, but other groups[1495−1498] have reported better results using a reagent generated *in situ* by the reduction of nickel(II) chloride with zinc in the presence of triphenylphosphine.[1499] The PL from the PPy prepared by the Yamamoto group was blue (λ_{max} = 440 nm) in solution but yellow-green (λ_{max} = 550 nm) in the solid-state.[1494] Other groups have reported a PL emission maximum from thin films of PPy at 530 nm,[1495,1497,1498] while the EL is reported to be blue-green (λ_{max} = 497 nm).[1495,1496,1500] Regioregular (>95% head to-tail) PPy and poly(6-hexyl-2,5-pyridine) (**683**) have been made by a Grignard coupling method similar to the McCullough route to regioregular P3ATs (see Scheme 47 above).[1501] It is reported that PPy single-layer devices with ITO and Au electrodes show higher efficiency and luminescence and are more stable during operation when run in reverse bias (i.e., with ITO as cathode).[803,805] Double-layer devices with PVK hole-transporting layers show better performance than single-layer devices.[803,805] PPy has also been used as an electron transporting layer in devices using PPV (**1**) and MEH-PPV (**20**), where it enhances the EL efficiency by a factor of up to 60.[186,190] A double-layer device using PPy and sexiphenyl shows emission which is voltage tunable from blue through white to green.[1502] A double-layer device with an emissive dendrimer gives 10-fold better emission than a single-layer device, with the emission coming from either layer depending on their thicknesses.[1503] The emission of PPy is reported to be pH dependent, with a small blue-shift accompanied by an increase in PL intensity occurring with increasing acidity.



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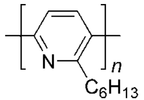

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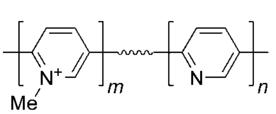

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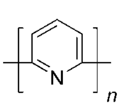

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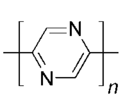
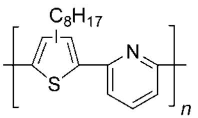


686

Methylation of the nitrogen causes an even greater increase in PL intensity with a 6-fold increase reported for the 25% methylated PPy polymer **684** (*n*:*m* = 3:1).[1504] Ring alkylation seems to have little effect on the PL properties of PPy.[1494] The PL spectrum of poly(2,6-pyridine) **685** is blue-shifted compared with that of the 2,5-analogue **682**, due to the interruption of the conjugation by the *meta*-linkages, so that the emission is violet (λ_{max} = 410 nm) in solution and blue (λ_{max} = 465 nm) in the solid state.[1498] Poly(2,5-pyrazine) (**686**) is soluble only in strong acids, where its emission maximum is at 477 nm.

The pyridine−thiophene **687**[1505] and bithiophene copolymers **688a**−**c**[1506] have been made by Stille coupling. Blue-green EL (λ_{max} = 500 nm) has been obtained from **687**, while



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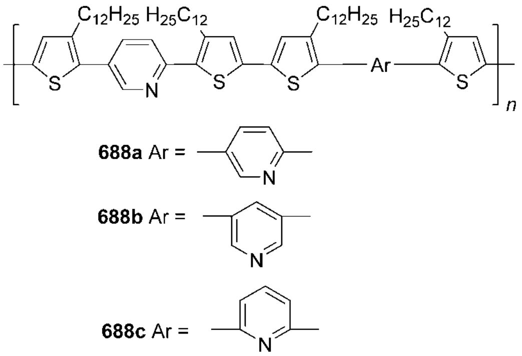
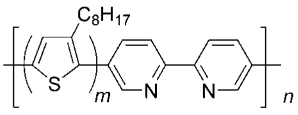
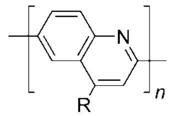




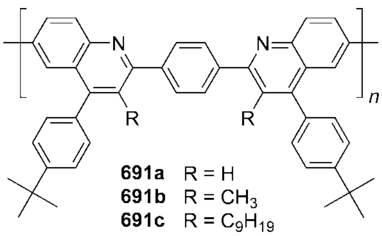
689 $m = 4, 6$

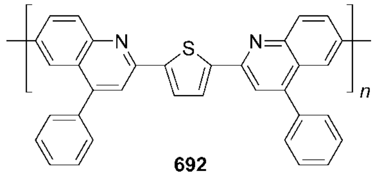
the solid-state emission of the bithiophene copolymers **688a** is green ($\lambda_{max} = 540$ nm) with only slight blue-shifts upon introduction of the *meta*-linked 2,6-pyridine ($\lambda_{max} = 534$ nm) and 3,5-pyridine ($\lambda_{max} = 528$ nm) units. Copolymers **689** were also made by Stille coupling of bis-stannyl(oligothiophene)s with dibromobipyridine and are reported to show EL, but no details have been published.[1507]

Jenekhe and co-workers have prepared a number of polyquinoline based polymers **690**−**694** for use in LEDs, by means of polycondensation reactions between (di)amines and (di)ketones.[1508−1517] These polymers show only very weak EL from single-layer devices due to poor hole injection, but double-layer devices using PVK or a blend of a triarylamine in polystyrene as a hole transporting layer gave efficient (up to 1%) emission.[1518] The alkyl **690a** and aryl **690b** homopolymers respectively show yellow ($\lambda_{max} = 552$ nm) and orange ($\lambda_{max} =$ *ca.* 590 nm) EL emission, while the emission from the copolymers could be tuned from blue to red. The phenyl copolymer **691a** emits in the yellow ($\lambda_{max} = 554$ nm), but introduction of methyl groups yielding polymer **691b** shifts the emission into the blue ($\lambda_{max} = 426$ nm). Larger alkyl substituents induce a further blue-shift in the emission so that the emission maximum is at 410 nm for **691c**. The thiophene unit in **692** produces a major red-shift to give red emission ($\lambda_{max} = 622$ nm), while interruption of the conjugation with a bis-phenylene methane unit in **693a** leads to green ($\lambda_{max} = 534$ nm) emission. Similar emission ($\lambda_{max} = 530$ nm) is seen from the bithiophene copolymer **694a**. This is due to the twisting induced by the alkyl groups on the thiophenes, as similar copolymers **694b,c** without these substituents show more red-shifted EL ($\lambda_{max} = 550$−600 nm).[1519] The silicon-linked materials **693b**−**d** show blue ($\lambda_{max} = 420$ nm) or blue-green ($\lambda_{max} = 471$ nm, 500 nm) emission.[1516] The vinylene **693e** and ethynylene copolymers **693f** show yellow emission with maxima between 550 and 580 nm. Some of these materials have also been examined in double-layer devices with PPV.[1520] Here, they can act not only as electron-transporting materials but also as emitters. They proved to be good electron-transporting materials and raised the efficiencies of LEDs using aluminum cathodes by up to 2 orders of magnitude compared with those of the PPV single-layer devices. By altering the relative thickness of the layers in these devices, the emission color could be tuned from red-orange to green. In some cases, the emission color was also voltage-tunable.



690a R = alkyl
690b R = Ph





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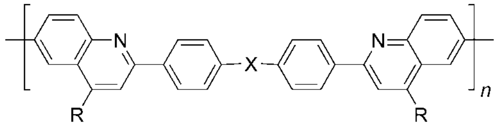
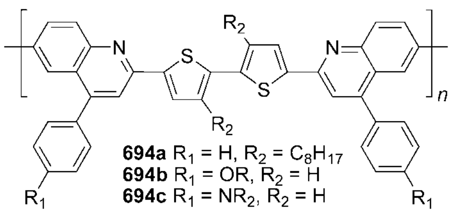
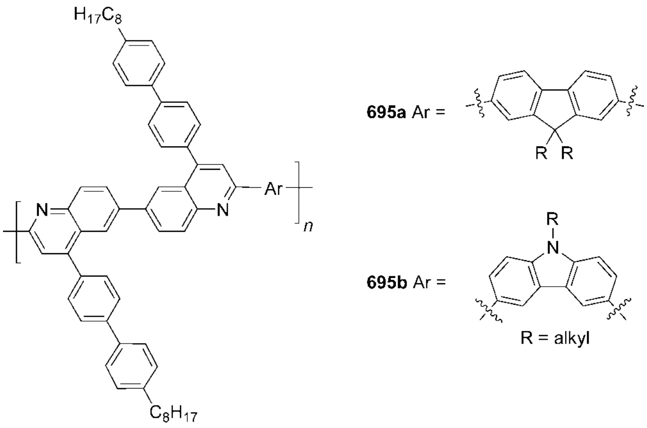
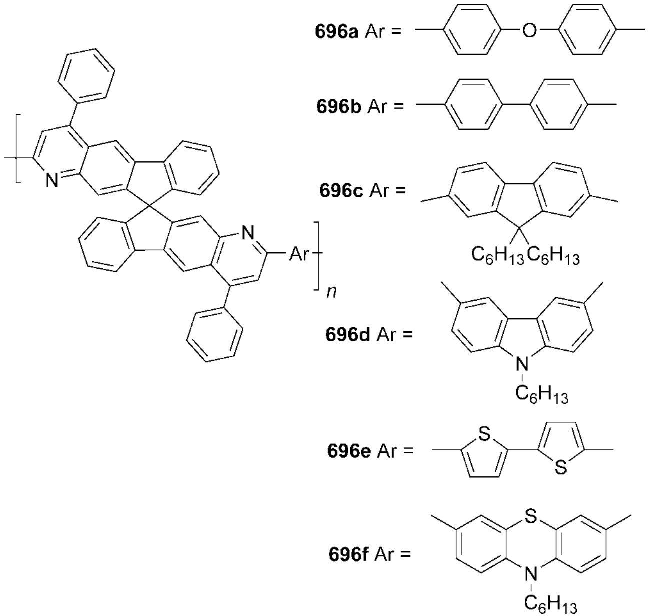


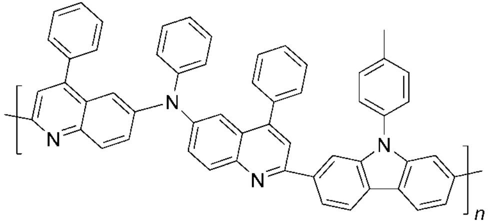
693a R = Ph, X = CH_2,
693b R = C_6H_{13}, X = $SiPh_2$
693c R = Ph, X = $SiPh_2$
693d R = Ph, X = $SiMeC_8H_{17}$
693e R = Ph, X = —=—
693f R = Ph, X = —≡—





Similar copolymers **695a,b** have been made by Hong and co-workers.[1521] The fluorene copolymer **695a** shows green ($\lambda_{max} = 530$ nm) EL, while the carbazole copolymer **695b** exhibits yellow ($\lambda_{max} = 574$ nm) emission with a much lower turn-on voltage. Copolymers of quinolines with spirobifluorene and spiro-linked quinolines such as **696** have been prepared.[1522−1524] Their emission ranges from blue (**696a,b**, $\lambda_{max} = 435$ nm) through green (**696c,d**, $\lambda_{max} = 500$−510 nm) to yellow-green (**696e,f**, $\lambda_{max} = 540$−550 nm). Yellow EL ($\lambda_{max} = 570$ nm) has been obtained from the nitrogen-bridged polymer **697**, which is 30 nm red-shifted compared with the PL emission.[1525]





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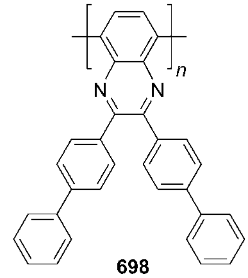

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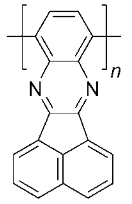

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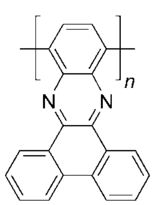
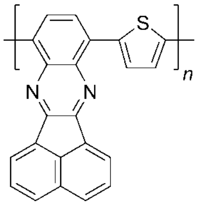
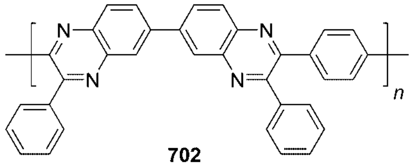


700



701

The poly(diarylquinoxaline)s **698** have been prepared by nickel(0)-catalyzed coupling of dihalides and show blue-green (λ_{max} = 490 nm) emission.[1526,1527] Use of polymeric hole transporting layers increases emission efficiency by up to 2 orders of magnitude.[1528] The emission can be red-shifted to λ_{max} = 565 nm by addition of a diaryldiamine to the emitting layer to create an exciplex.[1527,1529] A double-layer device containing layers of PPV and the polyquinoxaline **698** shows emission from both layers in a ratio of 3:1, which is independent of the applied field.[1530] The fused structures **699** and **700** show green emission (λ_{max} = 560 and 574 nm, respectively), while **701**, a copolymer of **700** with thiophene, emits in the yellow (λ_{max} = 600 nm).[1531] The poly(phenyl quinoxaline) **702** showed no EL emission in a single-layer device due to poor hole-injection, but broad red (λ_{max} = 650 nm) emission was obtained from a double-layer device using a PVK hole-transporting layer.[812,1532] Blue EL (λ_{max} = 434−448 nm) has been obtained from copolymers **703** containing an oxygen linkage.[1533] Poly(phenylquinoxaline)s are also good electron-transporting materials for LEDs.[1534−1536]



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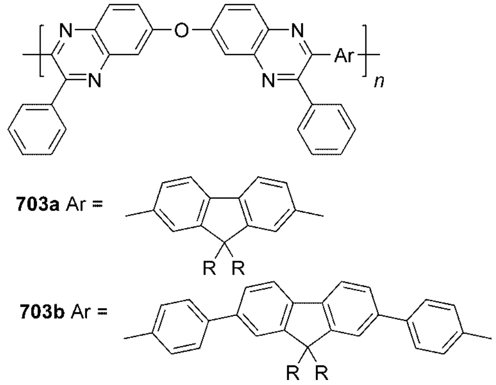
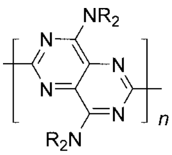
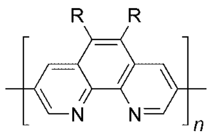


The poly(pyrimidopyrimidine)s **704a** show blue-green PL with an emission at 469 nm and secondary peaks at 501, 540 and 590 nm in solution.[1537,1538] Due to aggregation, yellow emission with a maximum at 552 nm is seen in the solid state for the octyl polymer **704a**, but the hexyl **704b** and decyl **704c** polymers are blue-green emitters (λ_{max} = 472 nm).[1539] The EL turn-on voltages are very high (>18 V) but can be lowered a little by blending with **558b**.



704a R = C_8H_{17}
704b R = C_6H_{13}
704c R = $C_{10}H_{21}$

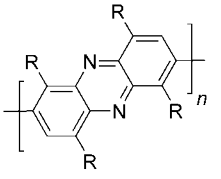


705a R = H
705b R = alkoxy

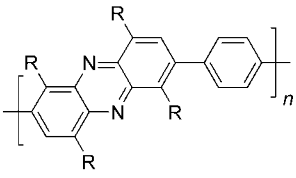
Polyphenanthroline **705a** shows green excimer-like emission (λ_{max} = 540 nm),[1540,1541] which is slightly red-shifted by introduction of alkoxy groups in **705b**.[1542] Yellow-green PL (λ_{max} = 537 nm) is observed for the polyphenazine **706**.[1543] Copolymers of **706** with PPP (**707**) and PPV (**708**) show slightly blue-shifted PL with emission maxima at 487 and 516 nm, respectively.

In addition to the six-membered heterocycles described above, five-membered nitrogen heterocycles have also been investigated. The polypyrroles **709** and **710** are both reported to show blue PL in solution (λ_{max} = 423 nm).[431,1544] The isomeric polybenzopyrroles **711** and **712** are green emitters (λ_{max} = 505 and 490 nm, respectively).[1545] Copolymerization with phenylene produces a marked blue-shift in the PL (λ_{max} = 414−424 nm) while the butadiynylene copolymer **713** emits at 483 nm.

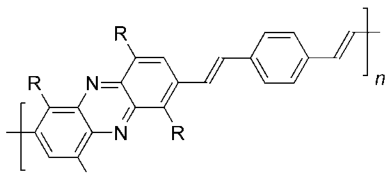
Polybenzimidazoles **714** show solvent-dependent emission.[1546] For substituted polymers **714b,c** the PL maximum is at 490 nm in nonacidic solvents and around 410 nm in



706 R = C_6H_{13}

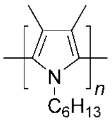


707 R = C_6H_{13}

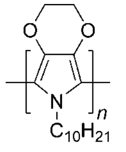


708 R = C_6H_{13}

acidic solvents, while for the unsubstituted **714a** polymer the maximum is at 440 nm in nonacidic solvents. Red luminescence has been seen from the N-substituted dithienopyrroles **715**.[1547] The emission maximum is around 615 nm for *n*-alkyl substituents and slightly blue-shifted for branched alkyl and aryl substituents.



709



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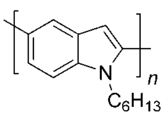

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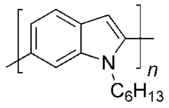

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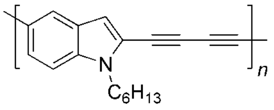

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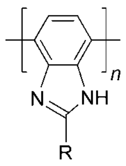
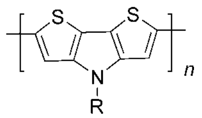
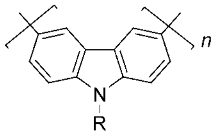


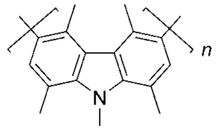
714a R = H
714b R = alkyl
714c R = Ph



715 R = alkyl, aryl



716 R = alkyl



717

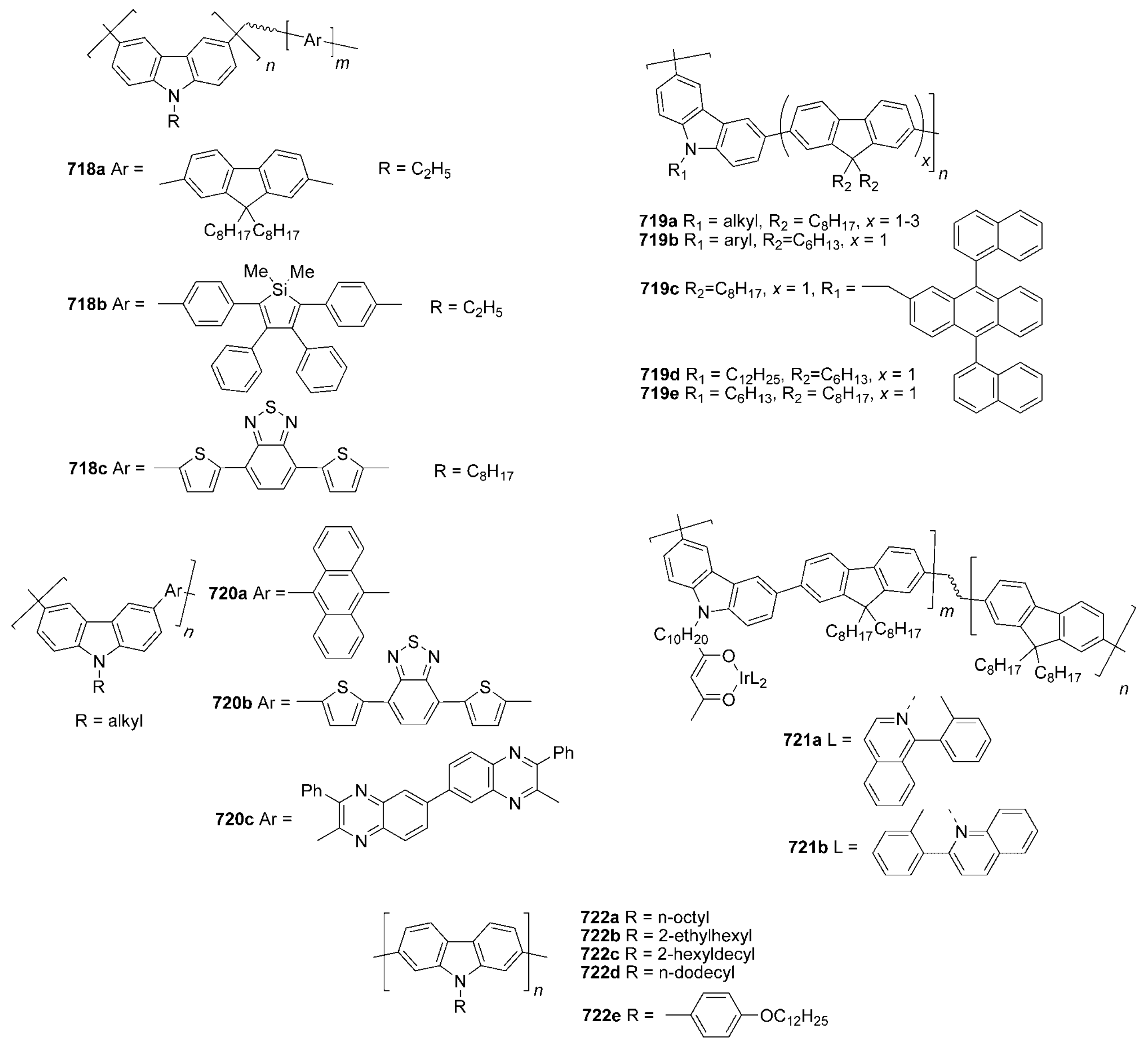
Carbazole-based polymers are of wide interest as materials for electronic devices.[1548,1549] Poly(*N*-alkyl-3,6-carbazole)s (**716**) have been synthesized by electropolymerization of *N*-alkylcarbazoles or condensation of dibromocarbazoles with nickel(0).[1550−1552] They produce blue-green EL (λ_{max} = 470 nm), suggesting there is still good conjugation through the nitrogens. Polymer **716** exhibits a large red-shift (to 490 nm), owing to aggregation and excimer emission.[1550] By contrast, the substituents on the ring in **717** induce twisting of the polymer chain to produce blue-violet PL (λ_{max} = 415 nm).[1553] The PL emission from the random copolymers **718a** (Chart 16) of *N*-alkyl-3,6-carbazoles and dioctylfluorene is very similar to that of the fluorene homopolymer **558b**, but with less long wavelength emission after annealing, which has been attributed to the carbazole units inducing greater disorder in the polymer backbone, and so minimizing exciton migration.[1554] Blue EL (λ_{max} = *ca.* 440 nm) is also seen from alternating copolymers **719a,b** of 3,6-carbazoles and (oligo)fluorenes.[1555−1558] The blue emission reported from **719c** bearing dinaphthylanthracene units on the carbazole moieties comes from the substituents.[1559] Alternating copolymers of 3,6-carbazoles with other arylenes and heteroarylenes have also been prepared by Suzuki polycoupling.[1560,1561] These have emission maxima ranging from 420 nm for **720a** to 723 nm for **720b**, but their EL efficiencies were all low (<0.3%). The copolymer **720c** has been made by a polycondensation and displays blue-green EL (λ_{max} = 484 nm) with modest efficiency (0.35%, 0.7 cd/A).[1562] Ill-defined blue emitting copolymers of 3,6-carbazole and pyridine have been prepared by oxidative polymerization of *N*-alkylcarbazole and pyridine *N*-oxide followed by reduction of the *N*-oxide.[1563] The EL emission from copolymers **718b** with tetraphenylsilole red-shifts from green (λ_{max} = 526 nm) to yellow-green (λ_{max} = 557 nm) with increasing silole content.[1564] The optimal efficiency (0.77%) was observed from the 20% copolymer (λ_{max} = 539 nm). There is still considerable potential for exploitation of nitrogen heterocycles either in emissive polymers or in their precursors. Attachment of emissive metal complexes in copolymers **721a,b** leads to red emission (λ_{max} = 610 and 580 nm, respectively) from the complexes.[1565]

Poly(*N*-alkyl-2,7-carbazole)s (**722**)[1566] are harder to prepare than the 3,6-polymers **716**, as the 2,7-halocarbazole monomers **723** needed for the Suzuki or Yamamoto polycondensations cannot be obtained by halogenation of carbazole and so must be totally synthesized by ring-closure of nitrobiphenyls, as illustrated in Scheme 49.[1566,1567]

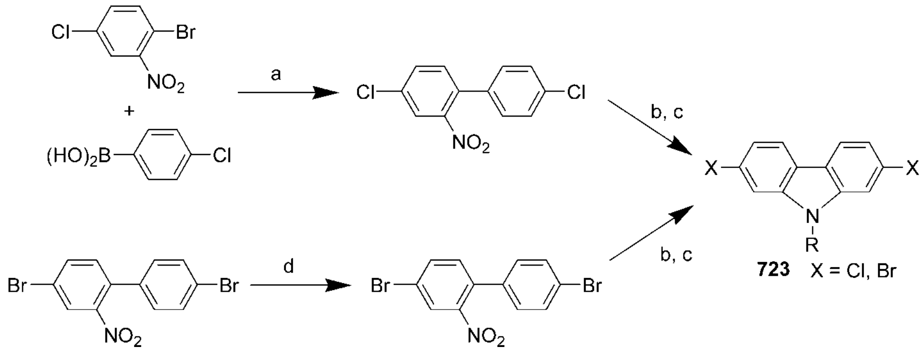
Due to the lower number of alkyl chains per monomer unit, these polymers are less soluble than the corresponding PDAFs, and so their molecular masses are lower, so that long branched alkyl substituents are needed to obtain good solubility and reasonable molar masses.[1568] Polymers **722a** show blue PL in both solution (λ_{max} = 417 nm) and as a thin film (λ_{max} = 437, 453 nm). The PL quantum efficiency is reported to be higher for *N*-aryl, e.g. **722e**, than *N*-alkyl polymers such as **722a**.[1569] Unlike the structurally very similar PDAFs **558** (see section 3.4), the polymers **722** show no long-wavelength emission in the solid-state.[1566] Blue emitting LEDs have been prepared from **722a,b**, with the highest efficiencies coming when a hole-transporting compound was blended with the emissive polymer and use of an oxadiazole-based electron transporting layer.[1570] Copolymers with aromatic units such as dioctylfluorene (**724a**),[1566] phenylenes (e.g., **724b**),[1571] binaphthyl (**724c**),[1571] and pyridines (**724d−g**)[1572,1573] also show stable blue PL in the solid state (λ_{max} = 423−463 nm), while the copolymers with bithiophene **724h**[1566] and quinoxaline (**724i**)[1572] show green PL (λ_{max} = 500−504 nm) both in solution and as thin films. Red emission (λ_{max} = 671 nm) has been obtained from a copolymer with a quinquethiophene *S*,*S*-dioxide (**724j**).[1572]

A problem with 2,7-carbazoles is that they are electrochemically unstable due to facile oxidation at the electron-rich 3- and 6-positions.[1568] The stability can be enhanced by full (**725**) or partial (**726**) substitution of these positions with methyl groups, but this results in a blue-shift in the emission (λ_{max} = 396−403 nm) due to increased torsion between adjacent carbazole units.[1574] As with phenylenes, this can be overcome by bridging adjacent units together to make ladder or stepladder-type polymers. Ladder-polymers based upon carbazole−phenylene copolymers (**727**)[1575] and

Chart 16



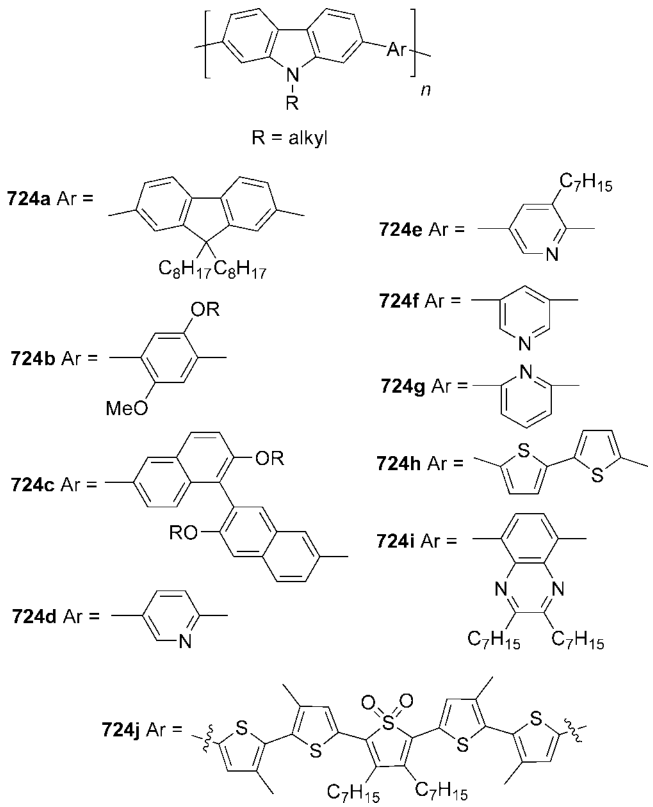
Scheme 49. Synthesis of *N*-Alkyl-2,7-dihalocarbazoles: (a) Pd(PPh$_3$)$_4$, K$_2$CO$_3$, Benzene, Water, Reflux; (b) P(OEt)$_3$, Reflux; (c) RBr, K$_2$CO$_3$, DMF, 80 °C; (d) HNO$_3$



carbazole homopolymers (**728**−**729**)[1576] have been prepared, which all show blue-green PL with emission maxima at about 470 nm.

Blue EL has been obtained from a random stepladder copolymer **730** (λ_{max} = 447 nm)[1577] and a nitrogen-bridged poly(ladder-type tetraphenylene) **731** (λ_{max} = 445 nm).[1307] The latter is much more stable toward oxidative degradation than the corresponding carbon-bridged polytetraphenylene **623**.

Both poly(4,4′-dialkyl-2,2′-bithiazole)s such as **732a** and poly(4-alkylthiazole)s **733** show yellow PL in solution, which for **732a** is red-shifted about 80 nm in the solid-state. The



R = alkyl

724a Ar =

724b Ar =

724c Ar =

724d Ar =

724e Ar =

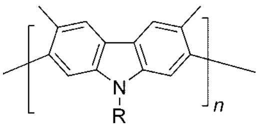
724f Ar =

724g Ar =

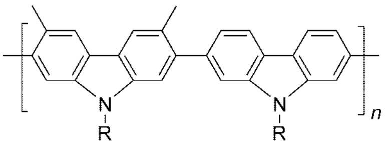
724h Ar =

724i Ar =

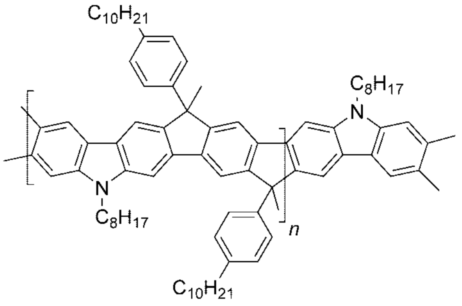
724j Ar =



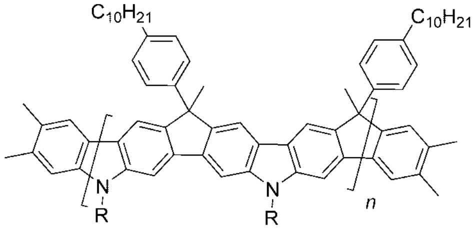
725



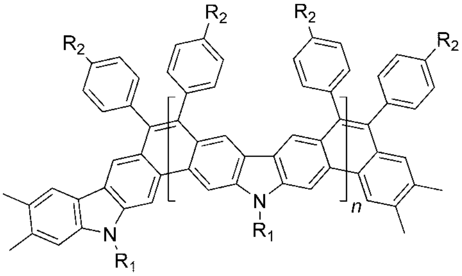
726



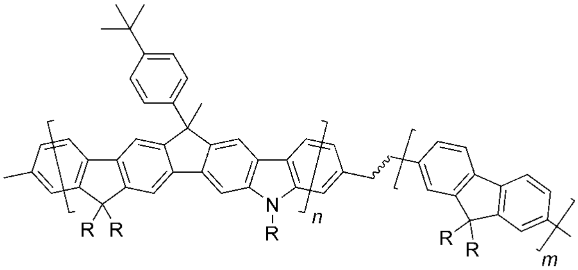
727



728 R = 2-ethylhexyl



729 R_1 = 2-ethylhexyl, R_2 = $C_{10}H_{21}$



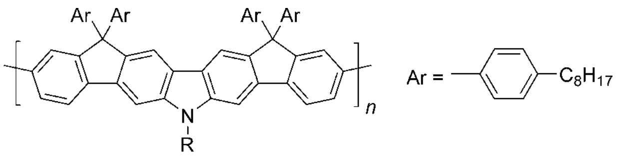
730 R = 2-ethylhexyl

dimethyl polymer **732a** shows weak red (λ_{max} = 680 nm) excimer-like EL emission from a multilayer device.[1541,1578] By contrast, the aryl-substituted polymer **732b** emits green PL (λ_{max} = 511 nm) and a copolymer with *meta*-phenylene **734** is blue emitting (λ_{max} = 452 nm) as a result of the interruption of the conjugation.[978,979,1579]

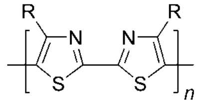
The thiophene–oxadiazole copolymers **735** have been made by polycondensation of the corresponding thiophene-2,5-dicarboxylic acids with hydrazine followed by acid-catalyzed ring-closure.[1580] The parent polymer **735a** shows blue PL in the solid state (λ_{max} = 453 nm). Substitution with methoxy groups (**735b**) produces a red-shift in the emission (λ_{max} = 476 nm) and a marked drop in the PL efficiency from 46% to 18%. Longer alkoxy groups produce a further red-shift (λ_{max} = 496 nm for **735c**) and drop in PL efficiency (7% for **735c**). Blue PL is also reported from the thiophene–triazine copolymers **736** (λ_{max} = 449–479 nm), while the thiophene–thiadiazole copolymer **737** is a green emitter (λ_{max} = 535 nm).[1581] The copolymer **738** containing electron-rich thiophene and pyrrole and electron-deficient benzothiadiazole units produces EL in the near-infrared (λ_{max} = 800 nm).[1582] Copolymer **739**[1583] also with a donor–acceptor structure produces red PL (λ_{max} = 628 nm), while the alternating copolymer **740**[851] has been used as an electron-transporting layer to boost the efficiency of PPV and MEH-PPV-based LEDs.[1584] The polyphenothiazines **741** produce blue-green EL (λ_{max} = 480 nm), as do their copolymers with dialkylfluorenes (λ_{max} = 480–490 nm).[1585,1586]

Siloles have recently become of interest as units for conjugated oligomers and polymers because their low LUMO energy levels make them potential electron accepting or transporting units.[1587,1588] Although silole-based oligomers and polymers are primarily of interest as charge-accepting or -transporting materials, there are some reports on their use as emitters. For a recent review on the synthesis and uses of silole-containing polymers, see ref 1589.

The silicon-bridged analogue of polyfluorene, poly(2,7-dibenzosilole) (**742**), has recently been synthesized by the Holmes group.[1590] The PL and EL are very similar to those of the polyfluorenes **558**, but since the silicon cannot be oxidized to a ketone, the emission is much more stable with no green emission band appearing even after prolonged heating in air. The analogous 3,6-dibenzosilole polymer **743** is an ultraviolet emitter (λ_{max} = 355 nm), as the silicon bridges interrupt the through conjugation.[1591] A copolymer of **558b** with 10 mol % of 3,6-dibenzosilole produces blue EL (λ_{max} = 420 nm) with high efficiency (3.34%, 2.02 cd/A).[1592] A silabifluorene copolymer **744** displays blue PL in solution (λ_{max} = 423 nm), with an additional solid state emission band in the blue-green (λ_{max} = 495 nm) attributed

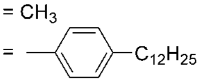


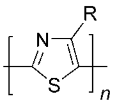
731 R = 2-ethylhexyl



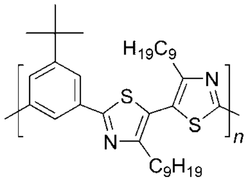
732a R = CH_3

732b R =

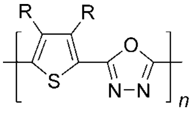




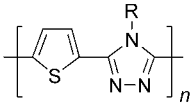
733 R = alkyl



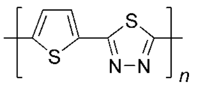
734



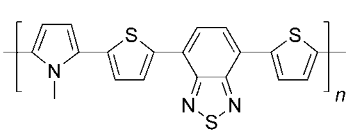
735a R = H
735b R = OCH_3
735c R = $OC_{12}H_{25}$



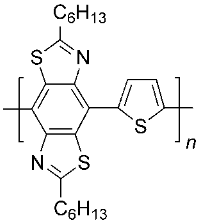
736 R = alkyl



737



738



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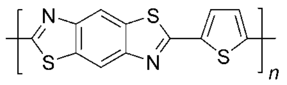
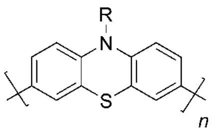
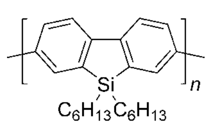


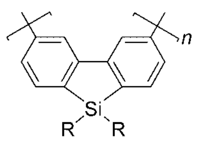
740



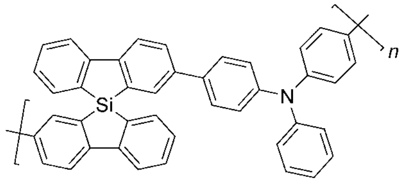
741a R = C_6H_{13}
741b R = 2-ethylhexyl



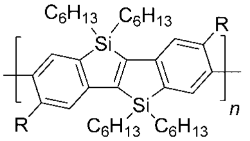
742



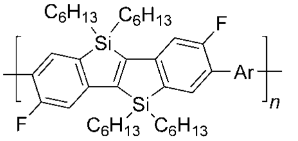
743



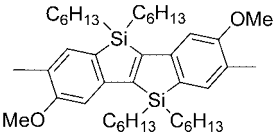
744



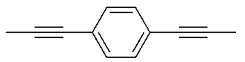
745a R = OCH_3
745b R = F



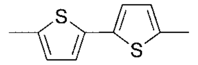
746a Ar =



746b Ar =



746c Ar =

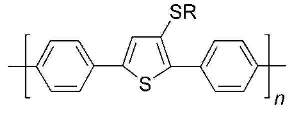


to aggregation.[1593] Blue EL has been obtained from **744**, but in very low efficiency (0.03%), suggesting it has more promise as a hole-transporting material. Polymers **745a,b** based on silicon-bridged stilbenes display blue-green PL ($\lambda_{\max}$ = 476 and 454 nm, respectively).[1594] The quantum efficiency of the fluoro polymer **745b** is distinctly higher than that of the methoxy polymer **745a** (63% *cf.* 36%). An alternating copolymer **746a** displays intermediate properties ($\lambda_{\max}$ = 467 nm, 51%). Copolymer **746b** with PPE is a green emitter ($\lambda_{\max}$ = 506 nm) while the bithiophene copolymer **746c** produces yellow-green PL ($\lambda_{\max}$ = 547 nm), but with very low efficiency (2.5%).

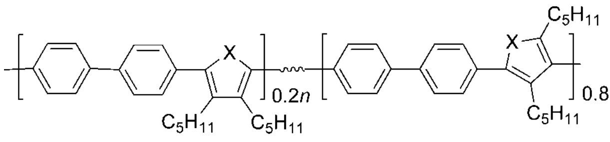
3.8. Polyarylene/Heteroarylene Copolymers

Generally, copolymers containing arylene and heteroarylene units show properties intermediate between those of the corresponding homopolymers, thus enabling the optical and electrical properties to be altered through control of their composition. An excellent example of how the optical properties can be tuned is provided by arylene–thiophene copolymers. Introduction of thiophene units into polyarylenes usually produces a red-shift in the PL and EL emission, and the wavelength of the maximum emission can thus be tailored by varying the ratios of phenylene to thiophene units and by the type and degree of substitution. The biphenylene–thiophene polymers **747** prepared by Ni(0) coupling of the dichloromonomers show blue-green emission ($\lambda_{\max}$ = 485 nm).[1595] Copolymer **748a**, made by treatment of the zirconocene precursor polymer **339** with sulfuryl chloride, emits blue ($\lambda_{\max}$ = 426 nm) PL.[782] The corresponding phosphole copolymer **748b** is made by reacting **339** with phenyldichlorophosphine and shows blue-green PL ($\lambda_{\max}$ = 470 nm).[782]

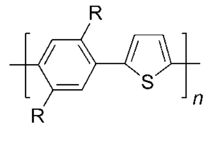
The alternating copolymers **749**, which can be prepared in low molecular mass by Stille coupling of dialkyl or dialkoxybenzenedihalides or ditriflates with bis-stannylthiophene,[394,500,1596] or in higher molecular masses by Suzuki coupling,[1064,1100,1597] also show blue-green emission. The emission from the dialkoxy polymers **749a** ($\lambda_{\max}$ = 520–530



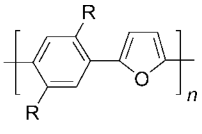
747 R = alkyl



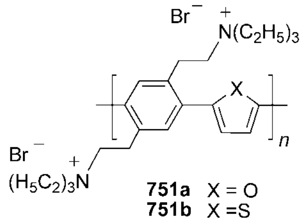
748a X = S
748b X = PPh



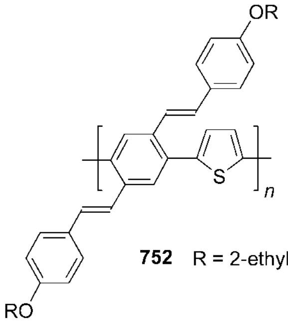
749a R = alkyl
749b R = alkoxy
749c R = C_5H_{11}
749d R = C_7H_{15}
749e R = CO_2– C_7H_{15}
749f R = OC_8H_{17}



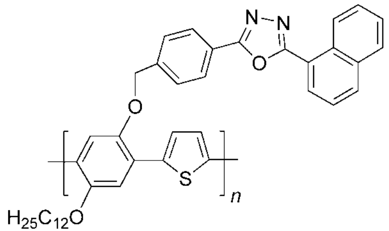
750 R = alkyl



751a X = O
751b X =S



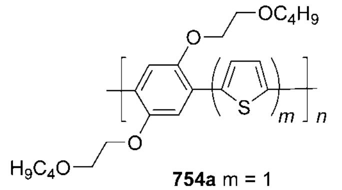
752 R = 2-ethylhexyl



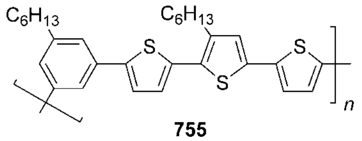
753

nm) is red-shifted with respect to the case of the dialkyl analogues **749b** (λ_{max} = *ca.* 475 nm). The EL maximum of the polymer **749c** is reported to be 445 nm,[1598] whereas bright turquoise EL (λ_{max} = 500 nm) has been obtained from a device using **749d**.[1599] Green PL (λ_{max} = 532 nm) is seen from polymer **749e** with a chiral carboxylate substituent.[1600] Replacement of the thiophene heterocycle with a furan moiety to give **750** leads to a red-shift in emission (λ_{max} = 490 nm) and an increase in EL intensity, but the furan ring is highly susceptible to photooxidation, leading to rapid loss of luminescence.[1598] A similar red-shift is seen in the PL emission from the water-soluble copolymers **751a** compared with **751b**.[1099] Yellow EL (λ_{max} = 558 nm) has been obtained from **751b**.[1601] Green EL emission (λ_{max} = 520 nm) has been obtained from the styryl-substituted polymer **752**.[1602] The oxadiazole-substituted copolymer **753** is reported to show up to 9 times better EL efficency than the dioctyloxy polymer **749e**.[212,1603]

Copolymers **754a−c** bearing ethylene-oxide side-chains illustrate nicely how the emission properties can be tuned by increasing the thiophene content. The PL emission maximum shows a red-shift from 520 nm for the thienyl **754a** to 543 nm for the bithienyl **754b** copolymer, while the PL quantum efficiency in solution drops from 87% to 42%. Going to the terthienyl copolymer **754c** produces only a small further bathochromic shift (λ_{max} = 547 nm) while the PL efficiency remains constant (42%).[1604] Polarized emission has been obtained from an oriented film of the thienyl copolymer **754a**.[1605] The *meta*-phenylene copolymer **755** shows green-yellow PL (λ_{max} = 550 nm),[729] while the similar polymer **756** shows orange EL (λ_{max} = 584 nm); in some cases, the **meta** linkages do not appear to produce a major reduction in the effective conjugation length.[1606] The use of an aluminum tris(8-hydroxyquinolate) (Alq_3) electron-transporting layer boosts the EL efficiency of devices using **756** by 3 orders of magnitude.[1606] The ortho-biphenylene linkages in **757** blue-shift the PL (λ_{max} = 475 nm),[1607] as do the 2,3-thiophene linkages in **758** (λ_{max} = 454 nm).[1597]



754a m = 1
754b m = 2
754c m = 3



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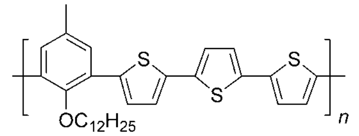

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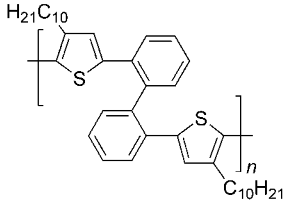

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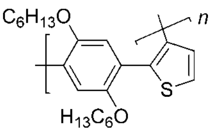

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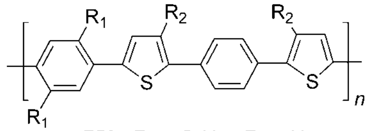
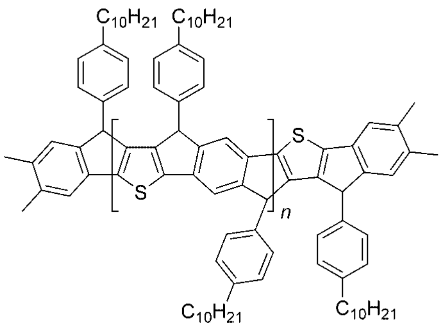


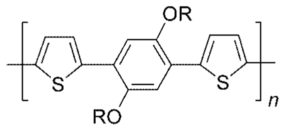
759a $R_1 = C_8H_{17}$, R_2 = H
759b R_1, R_2 = H
759c R_1 = H, R_2 = Br
759d R_1 = H, R_2 = Cl,
759e R_1 = H, R_2 = CN
759f R_1 = H, R_2 = OMe

The regioregular copolymer **759a** made by Grignard coupling shows green EL (λ_{max} = 517 nm).[1608] The copolymers **759b−f** have been made by Stille coupling.[1609] The polymer with unsubstituted thiophene rings (**759b**) shows blue PL (λ_{max} = 467 nm). Halogenation (**759c,d**) produces a small red-shift (λ_{max} = 484 and 492 nm, respectively), while the cyano (**759e**) and methoxy (**759f**) substituted polymers show a marked bathochromic shift in their emission (λ_{max} = 532 and 540 nm, respectively). Similar emission is seen from thioalkyl-substituted copolymers.[1610] The ladder-type phenylene−thiophene copolymer **760** shows orange PL (λ_{max} = 536 nm).[1611] The substituted dialkoxyphenylene−bithiophene copolymers **761** are readily made by oxidation of the dithienylbenzene monomers.[1612,1613] Their fluorescence is described as green, but more spectral details have not been reported.

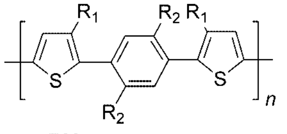
The phenylene−dialkylbithiophene polymers **762a** have also been prepared by oxidative coupling of monomers.[1614] Their solid-state PL emission shows a noticeable red-shift (λ_{max} goes from 512 to 529 nm) with longer alkyl substituents. By contrast, the bathochromic shift in solution is only 2 nm (492 to 494 nm). Copolymer **762b** with methyl substituents on the phenylene is a blue emitter (λ_{max} = 480 nm).[747] An even greater blue-shift (λ_{max} = 454 nm) is obtained by incorporating the phenylene into a cyclophane. Introduction of various-sized solubilizing side-chains on both



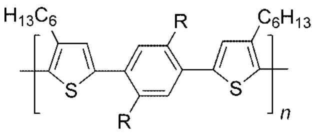
760



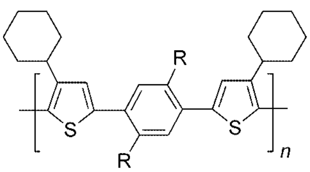
761 R = alkyl



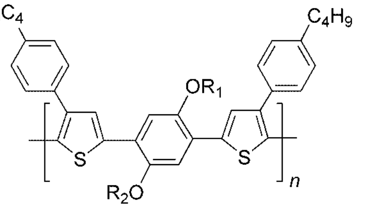
762a R_1 = alkyl, R_2 = H
762b R_1 = alkyl, R_2 = Me



763a R = H
763b R = Me
763c R = $OC_{10}H_{21}$



764a R = $OC_{10}H_{21}$
764b R = Me

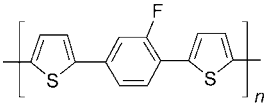


765 R_1, R_2 = alkyl

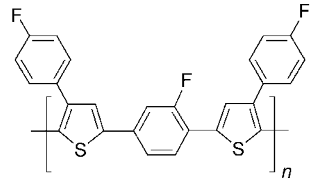
thienyl and phenyl rings has been used to tune the emission color, as shown by polymers **763** and **764** made by coupling of the monomers with iron(III) chloride.[1615−1618] The hexylthienyl polymer **763a** with unsubstituted phenyl ring shows green PL (λ_{max} = 524 nm) with 20% quantum efficiency. Introduction of a methyl substituent in **763b** causes a hypsochromic shift producing blue emission (λ_{max} = 477 nm) and a concomitant drop in the PL efficiency to 10%. Introduction of decyloxy substituents in **763c**, on the other hand, causes a red-shift (λ_{max} = 505 nm) and an increase of the PL efficiency to 29%. The bulkier cyclohexyl groups in polymers **764a,b** cause a blue-shift in the emission and a drop in PL efficiency so that the decyloxy derivative **764a** shows blue-green (λ_{max} = 505 nm) emission with a PL efficiency of only 16%, and the dimethyl derivative **764b** has a PL emission maximum at 466 nm, with a PL efficiency of merely 6%. These materials have been used to make blue, blue-green, and green emitting LEDs whose relative efficiencies mirror the PL efficiencies of the emitting polymers. The EL emission maxima of polymers **765** were determined to be between 532 and 538 nm, which demonstrates that aryl groups on the thienyl rings produce less of a blue-shift than alkyl or alkoxy side-chains.[1619,1620]

Similar trends have been observed with the fluoro-substituted polymers **766**−**768**.[1621] For instance, polymer **766** is blue-green emitting (λ_{max} = 490 nm), and aryl substitution in **767** produces a red-shift to give green emission (λ_{max} = 548 nm). Introduction of substituents on the central ring can also have a profound influence on the emission properties. Thus, the symmetrically substituted polymer **768a** has an emission maximum at 542 nm, whereas the unsymmetrically substituted **768b** was found to have its emission maximum at 563 nm. This is in contrast to the case of polymers **765**, where the substitution pattern has little effect on the emission maximum.

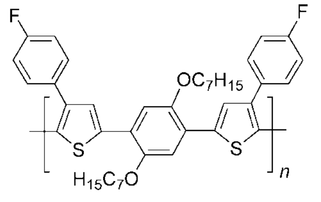
Only a few copolymers of polycylic aromatic compounds and thiophenes have been reported. The naphthalene−thiophene copolymers **769** and **770** have been made by Suzuki coupling.[1622] Full spectral details have not been published, but the PL spectra show emission maxima in the blue-green (λ_{max} = *ca.* 490 nm). The anthracene−bithiophene copolymer **771** made by coupling of a dibromo-monomer with nickel(0) also emits in the blue-green (λ_{max} = 477 nm).[1618]



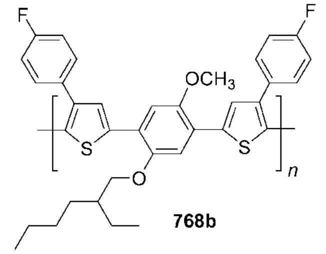
766



767

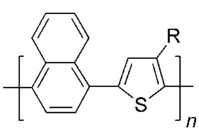


768a

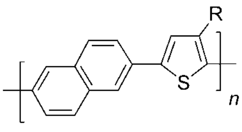


768b

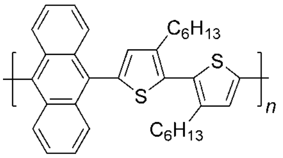
Similar substituent effects are seen with fluorene−thiophene copolymers. The alternating copolymers **772a**−**c** with one to three thiophenes have been made by Suzuki or Stille coupling.[862,863,1149,1267,1623,1624] The thiophene copolymer **772a** shows blue-green EL (λ_{max} = 480 nm), while **772b** and **772c** are yellow-green emitters (λ_{max} = 543 and 567 nm, respectively).[1268,1270] Attaching POSS units to some of the side-chains in **772b** is reported to increase the EL efficiency more than 2-fold.[1277] Methyl substitutents on the thiophene ring cause a small blue-shift due to steric interactions, so that **773** is blue emitting (λ_{max} = 468 nm). The ethylenedioxythienyl (EDOT) copolymer **774a** shows blue-green PL (λ_{max} = 494 nm) in solution but yellow EL (λ_{max} = 530 nm) with a band at 580 nm which is attributed to excimer emission.[1268,1270,1625] It is reported that for random copolymers of EDOT and fluorene the PL red-shifts and its efficiency decreases with increasing EDOT content.[1626] Random copolymers of fluorene and thiophene or EDOT show EL emission whose emission maximum can be tuned between 490 nm and 562 nm by varying the thiophene content.[1627] The bis-EDOT copolymer **774b** shows green PL and EL (λ_{max} = 536 nm).[1268,1270] The copolymers **775**−**777** with decylated thiophene rings have been prepared by Huang and co-workers by Suzuki coupling.[1628,1629] The bithiophene copolymer **777a** was also synthesized with higher molecular mass by iron(III) chloride oxidation of the monomer. Curiously, the other bithiophene copolymer **776** could not be prepared by iron(III) oxidative coupling. The monodecylthiophene copolymer **775a** emits blue-green light (λ_{max} = 492 nm), with a relatively high quantum yield (65% in solution). Introduction of the second decyl group in **775b**



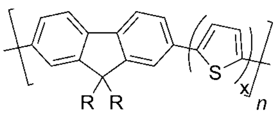
769 R = alkyl



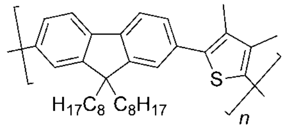
770 R = alkyl



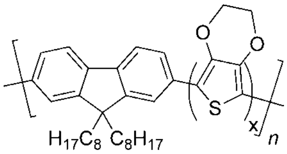
771



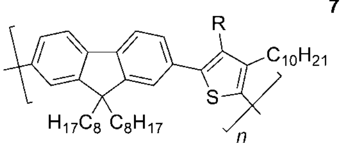
R = alkyl
772a x = 1
772b x = 2
772c x = 3



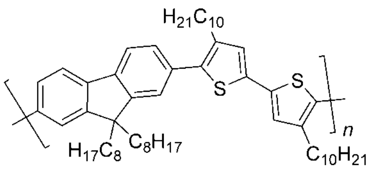
773



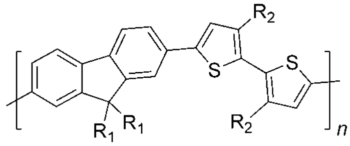
774a x =1
774b x = 2



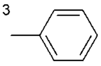
775a R = H
775b R = $C_{10}H_{21}$



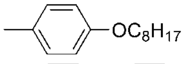
776



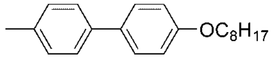
777a $R_1 = C_8H_{17}$, $R_2 = C_{10}H_{21}$
777b $R_1 = R_2 = C_6H_{13}$
777c $R_1 = C_6H_{13}$, R_2 =



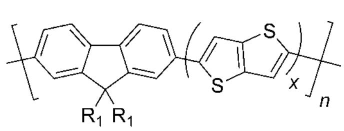
777d $R_1 = C_6H_{13}$, R_2 =



777e $R_1 = C_6H_{13}$, R_2 =

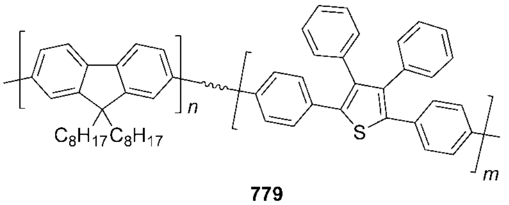


causes a hypsochromic shift in the emission (λ_{max} = 458 nm) and a significant drop in PL efficiency to 39%. The bithienyl copolymers **776** and **777a** show blue-green emission (λ_{max} = 490 and 493 nm) with similar PL efficiencies of 31% and 28%, respectively. The relative EL efficiencies reflect those for PL.[1630] The dihexylbithienyl polymer **777b**, made by Ni(0)-coupling of the dibromo monomer, has been used to make an efficient (0.6%) green emitting LED (λ_{max} = 493 nm) using a PVK hole-transporting layer.[1618,1631] The aryl-substituted copolymers **777c**−**e** are green emitters (λ_{max} = 516−528 nm) with only moderate efficiencies (0.04−0.29%, 0.11−0.94 cd/A).[1623] The efficiency of **777d** is enhanced by blending it with PVK (0.46%, 1.03 cd/A).

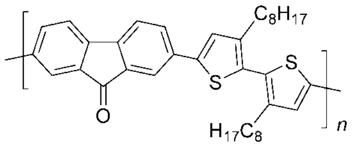


778a *x* = 1
778b *x* = 2

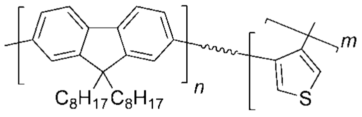
Green EL is also seen from the fused bithiophene copolymer **778a** (λ_{max} = 513 nm).[1632,1633] The PL from copolymer **778b** is reported not to be red-shifted compared with **778a**.[1624] Blue EL (λ_{max} = 419 nm) has been obtained from copolymers **779** containing 50% of tetraphenylthiophene units.[1634] Copolymers with lower thiophene content produced blue-green EL with maxima at 427 and 528 nm. Red emission is seen from films of the fluorenone−bithiophene copolymer **780**.[1635] Aligned films of **772a** and **772b** produce polarized EL emission.[1157,1158] Introduction of 3,4-thiophene units has been used to interrupt the conjugation in polyfluorenes so that the emission from the resulting copolymers **781**



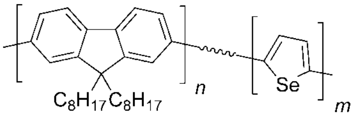
779



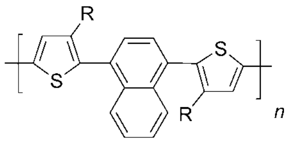
780



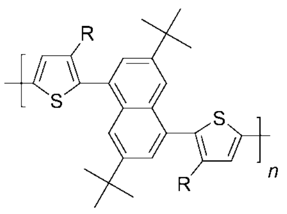
781



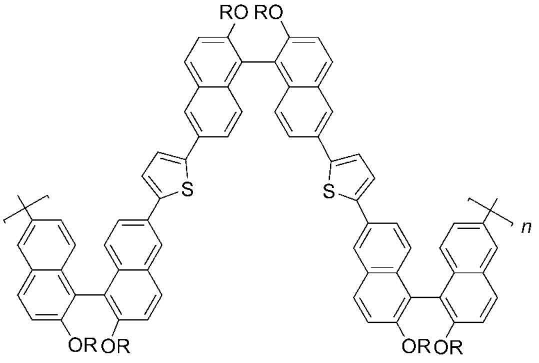
782



783 R = C_8H_{17}



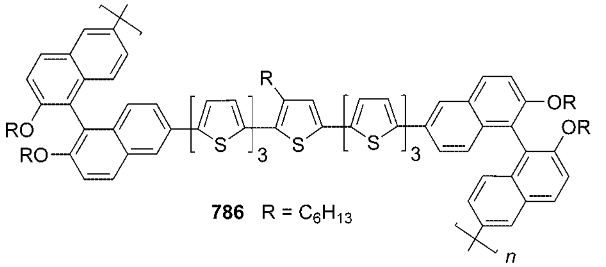
784 R = C_4H_9, C_8H_{17}, $C_{12}H_{25}$



785 R = C_6H_{13}

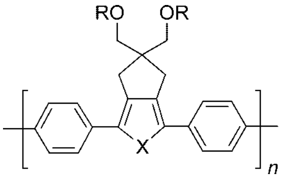
is blue-shifted compared with that from **558**.[1636] The EL emission maximum of the random copolymers with selenophane **782** can be tuned between 464 and 536 nm by varying the amount of the heterocycle between 1 and 50 mol %.[1637] The highest efficiency (0.5%) is seen for the 5% copolymer.

Copolymers **783** and **784** of dialkylbithiophene with 1,4- and 1,5-naphthalene, respectively, are blue-green emitters (λ_{max} = 474−486 nm).[685] Pu and co-workers have synthesized a series of binaphthyl−oligothiophene coplymers in which the binaphthyl units interrupt the linear conjugation of the backbone, so that the emission can be tuned from blue for **785** (λ_{max} = 421, 446 nm) to yellow-orange (λ_{max} = 545, 583 nm) for **786**.[1638]

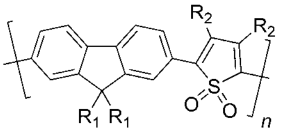


786 R = C_6H_{13}

Another way to tune the emission is to alter the oxidation level of the thienyl sulfur. Thus, the emission of the biphenylene−thiophene polymer **787a** is blue (λ_{max} = 472 nm), while the polymers **787b** and **787c** with oxidized sulfur atoms emit in the green (λ_{max} = 562 and 558 nm, respectively).[785] Similarly, the emission from the fluorene−thiophene-*S*,*S*-dioxide copolymer **788a** is significantly red-shifted (λ_{max} = 604 nm) compared with that of the corresponding thiophene copolymer **772a** (λ_{max} = 474 nm).[1269,1272,1639] An orange emitting LED has been made using **788a**.[1639] The alkyl groups on the thiophene in **788b** blue-shift its emission (λ_{max} = 550 nm).[1640,1641]

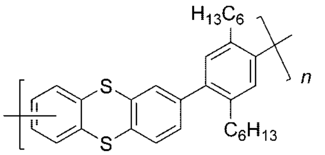


787a X = S
787b X = SO
787c X = SO_2

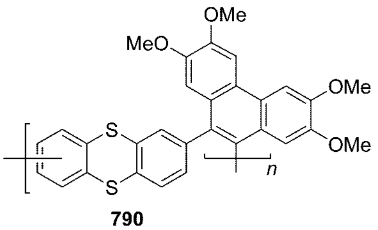


788a R_1 = 2-ethylhexyl, R_2 = H
788b R_1 = C_8H_{17}, R_2 = C_6H_{13}

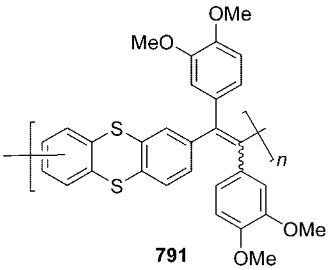
The alternating thianthrene−phenylene copolymer **789** obtained by Suzuki coupling of a phenylene bis-boronic acid with dibromothianthrene (an inseparable 1:1 mixture of 2,6- and 2,7-dibromo isomers was used) shows green PL (λ_{max} = 520 nm), but the EL is blue-green (λ_{max} = 486 nm).[865,866] The thianthrene−phenanthrene copolymer **790**, obtained by oxidation of the green emitting (λ_{max} = 516 nm) poly(thianthrene vinylene) **791** with iron(III) chloride, shows blue-green PL (λ_{max} = 494 nm).[597]



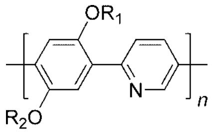
789



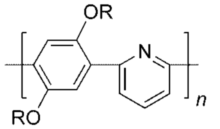
790



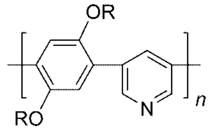
791



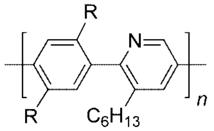
792a R_1,R_2 = alkyl
792b R_1 = H, R_2 = alkyl



793 R = alkyl

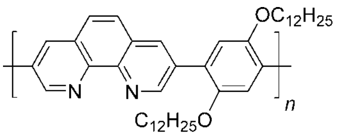


794 R = alkyl



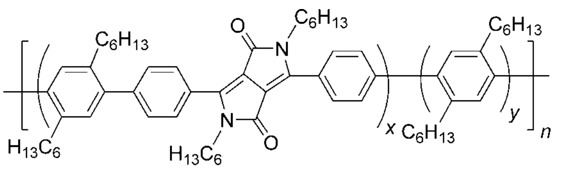
795 R = H, OMe
Regiorandom

Copolymers of arylenes with nitrogen-based hetrocycles have been studied not only as emitting but also as electron-transporting materials. Blue emitting alternating copolymers of PPP and PPy have been made by Suzuki coupling. The emission maxima for the regioisomeric 2,5-**792a**, 2,6-**793**, and 3,5-pyridine **794** copolymers are at 445, 428, and 435 nm, respectively.[1625,1642−1645] The EL from polymer **792a** can be significantly red-shifted from the blue into the orange (λ_{max} = 579 nm) by electrochemical doping[1646] or protonation.[1647] The emission from the hydroxyphenylene copolymer **792b**, in which the hydroxyl group can hydrogen bond to the pyridine nitrogen, is very slightly red-shifted (λ_{max} = 451 nm) compared with that from **792a**. The alkylated copolymers **795** also show PL maxima around 440 nm. Used as electron-transport layers in MEH-PPV-based LEDs, they caused a 10-fold increase in EL efficiency.[1648]

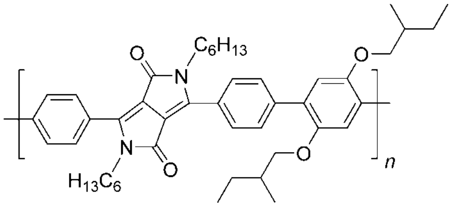


796

The phenanthroline copolymer **796** is a blue emitter (λ_{max} = 445 nm), which can be complexed with a variety of metals to obtain materials displaying green (λ_{max} = 536 nm, Zn complex), orange (λ_{max} = 604 nm, Ir complex) or red (λ_{max} = 600 nm, Eu complex) EL.[1649] Copolymer **797** containing dioxopyrrolopyrrole units shows green PL (λ_{max} = 544 nm) but orange EL (λ_{max} = 627 nm).[1650] A related copolymer **798** displays voltage-dependent emission, with the emission maximum shifting from 646 nm at 15 V to 631 nm at 20 V.[1651] Blue PL (λ_{max} = 483 nm) and green PL (λ_{max} = 512 nm) have been observed respectively from the pyrazole copolymers **799**[1652] and **800**.[1653]



797



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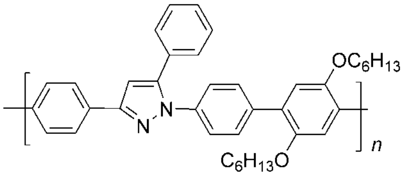

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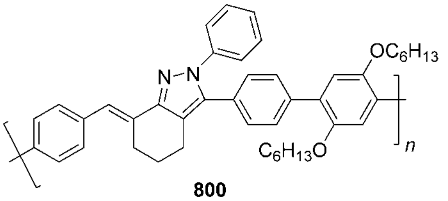
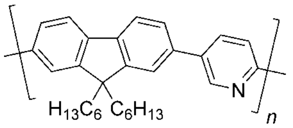


800



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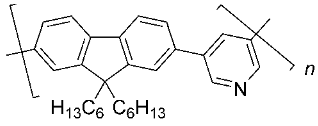

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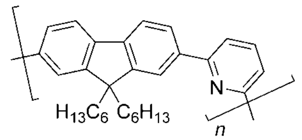

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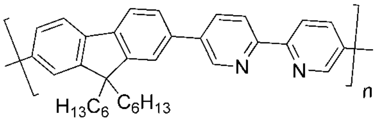

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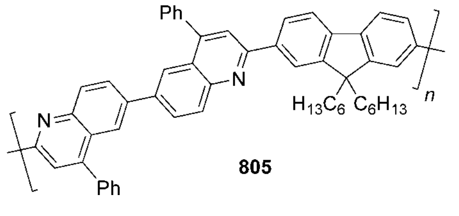

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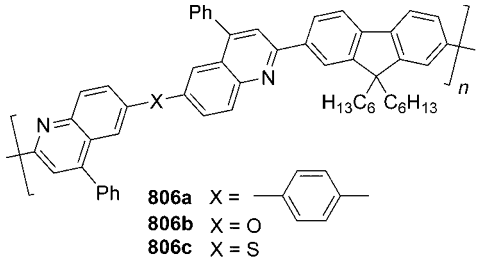
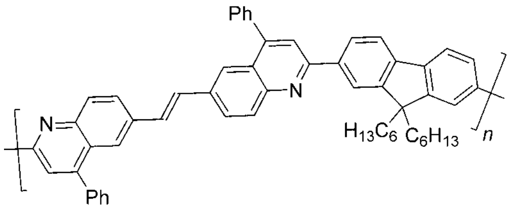
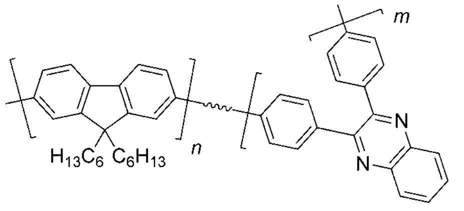


806a X =
806b X = O
806c X = S



807



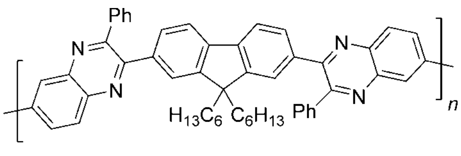
808

Fluorene−pyridine copolymers have been made by various groups.[1625,1654−1657] The PL of the alternating copolymers **801−803** are at 430, 420, and 407 nm, respectively.[1656,1657] The fluorene−bipyridine copolymer **804** undergoes complexation with rhenium to introduce an emissive metal complex into the main chain. Due to energy transfer, the PL emission comes from the complex (λ_{max} = 520 nm).[1658] The polyquinoline−fluorene copolymer **805** prepared by a polycondensation reaction of a diacetylfluorene with a 3,3′-bisbenzoyl-4,4′-diaminobiphenyl displays blue PL in solution (λ_{max} = 434 nm) and blue-green PL in the solid state (λ_{max} = 446, 480 nm). However, the EL was found to be green (λ_{max} = 544 nm) due to excimer formation.[1659] Similar aggregation produces a green emission band at 500 nm from the phenyl copolymer **806a**, but blue EL (λ_{max} = 438 nm) can be obtained by diluting it in PVK.[1660] Interruption of the conjugation in the backbone via an ether linkage as in polymer **806b** produces a blue-shift in both PL (λ_{max} = 414 nm) and EL (λ_{max} = 480 nm) emission.[1659] Replacement of an ether with a thioether **806c** induces a red-shift in emission (λ_{max} = 434 nm), while introduction of a vinylene linker in **807** results in green emission (λ_{max} = 496, 534 nm). Blending of **805** and **807** with PVK leads to suppression of the longer wavelength excimer emission to produce blue PL (λ_{max} = 440 and 450 nm, respectively). Polymers **805** and **806b** when used as electron-transporting layers in devices with fluorene vinylene copolymers as emitters cause a greater than 10-fold improvement in their EL efficiency.[1661]

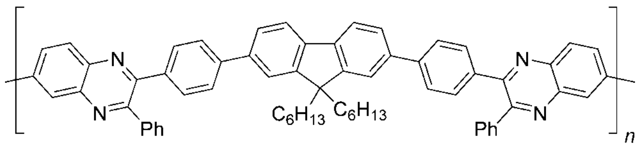
Blue EL (λ_{max} = 429−439 nm) is produced by the fluorene−quinoxaline random copolymers **808**, with optimal efficiency (1.03%) obtained from the copolymer with 5 mol % of quinoxaline.[1662] Blue PL has also been observed for the alternating copolymers **809** (λ_{max} = 447 nm) and **810** (λ_{max} = 468 nm).[1663]

Fluorescent fluorene−pyrazoline copolymers have been made. Copolymers **811** and **812** are green emitters (λ_{max} = 512 nm).[1664] Red EL has been obtained from the diketopyrrolopyrrole copolymers **813a** (λ_{max} = 602 nm), which is only slightly blue-shifted by incorporation of a *meta*-linkage in **813b** (λ_{max} = 593 nm).[1665]

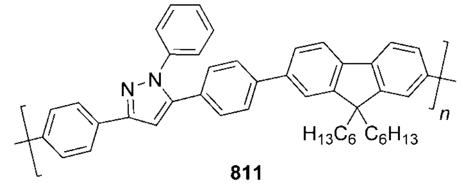
Copolymers **814** of fluorene with both pyridine and thiophene have been made by Suzuki coupling.[1666] Copoly-



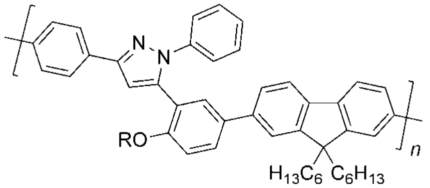
809



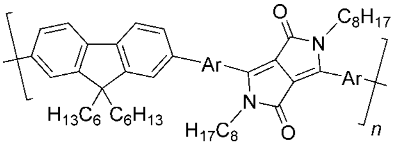
810



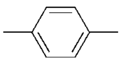
811



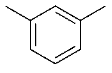
812 R = C_6H_{13}, $C_{12}H_{25}$

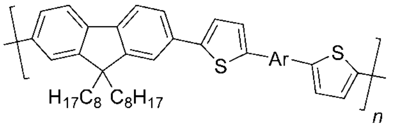


813a Ar =

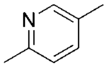


813b Ar =

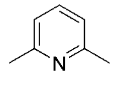




814a Ar =



814b Ar =



mer **814a** with a 2,5-pyridine ring allowing through conjugation is an orange emitter (λ_{max} = 580 nm), while the 2,6-pyridine unit in **814b** reduces the conjugation so that this polymer displays blue-green EL (λ_{max} = 493 nm).

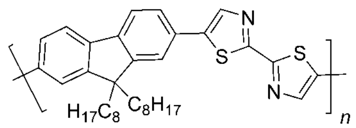
The fluorene–bithiazole copolymer **815** (Chart 17) produces green EL (λ_{max} = 515 nm).[1667] Green emission (λ_{max} = 545 nm) has also been obtained from the fluorene–benzothiadiazole alternating copolymer **816**, with very high efficiencies (up to 3.8%) and brightnesses (up to 25,000 cd/m^2) reported for devices using fluorene–triarylamine copolymers as hole-transporting layers.[1668–1671] Similar efficiencies have also been obtained from fluorene–benzodithiazole random copolymers, while a remarkable 6.0% (18.5 cd/A) efficiency has been reported for copolymer **817a**.[1672,1673] Devices using **816** with flexible plastic anodes are reported to show better performance than those with ITO on glass anodes.[1674–1676] Aligned films of **816** produce polarized EL emission.[1157,1158] The emission from copolymers **818a** is tunable between λ_{max} = 529 nm and λ_{max} = 543 nm by increasing *m* from 0.5 to 15 mol %. The EL efficiency, however, decreases from 3.2% to 1.8%.[1677] Quaternizing the amines (**818b**) red-shifts the emission (λ_{max} = 537–581 nm), lowers the efficiency (maximal at 1.0% for the 1 mol % copolymer), and provides water and methanol solubility.[1677,1678] The inverted solubility of the quaternized copolymer **818b** has been made use of to construct an inverted LED in which an electron-transport layer of **818b** is spin-cast from methanol upon an aluminum cathode, the MEH-PPV emissive layer is spin-cast on top of the layer of **818b** from toluene (in which **818b** is insoluble), and finally a gold anode is vacuum-deposited on top of the MEH-PPV layer.[1679] The device efficiency is reported to be 2.71% (1.6 cd/A). The oxetane units in copolymer **817b** by contrast enable it to be cross-linked to give an insoluble green emitting film (λ_{max} = 538 nm).[1680]

Copolymers **819** containing very small amounts (0.03 mol %) of benzodithiazole show white EL as one gets a combination of blue emission from the fluorene (**819a**) or fluorene–phenylene (**819b**) segments and orange emission from the heterocycles.[1681] Efficiencies of up to 9 cd/A have been obtained from white-light-emitting devices using **819a**. White EL has also been obtained from copolymers **820** (Chart 18) with 0.005–0.05 mol % of benzodithiazole and 0.1–0.5 mol % of iridium, with efficiencies of up to 6.1 cd/A.[1682] The purest white emission was seen from polymers with 0.2 mol % of iridium and 0.01–0.03 mol % of benzodithiazole. Benzodithiazoles have been incorporated into the green-yellow (λ_{max} = 547–548 nm) emitting copolymers **821** as electron-transporting units.[1633] The EL efficiency is lower for copolymer **821a** (0.64 cd/A) with triarylamine hole-transporting units than for **821b** without them (1.35 cd/A).

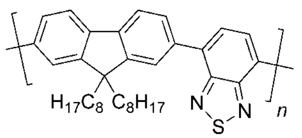
The emission from these polymers can be significantly red-shifted by incorporating thiophene units so as to obtain the orange emitting **822** (λ_{max} = 590 nm)[1667] and the red emitting (λ_{max} = 613–672 nm) copolymers **823a**[1683–1686] and **824** (Chart 19).[1678] The EL emission maximum of the red emitting copolymers **825** is tunable between 633 and 656 nm by increasing the amount of the dithienylbenzothiadiazole component from 1 mol % (**825a**) to 15 mol % (**825c**).[1687] Red EL (λ_{max} = 650 nm) has also been obtained from the cross-linkable copolymer **826**.[1688] Cross-linking the polymer made no significant difference to the EL efficiency (slight enhancement from 1.0 to 1.1 cd/A) while improving the stability of the polymer layer. The hexylthienyl copolymers **823b** have a maximum efficiency of 2.54% (1.45 cd/A) for the 10 mol % copolymer (λ_{max} = 638 nm).[1685]

Replacing sulfur with selenium also leads to red-shifted emission. Thus, the EL emission maximum from copolymers **827a**[1689,1690] and **827b**[1691] (Chart 20) of fluorene with benzoselenodiazole (*m* = 2–50 mol %) varies from 573 to 609 nm with increasing heterocyclic content. The highest efficiency (1.0%) is obtained from the 15 mol % copolymers. Orange EL (λ_{max} = 563 nm) with an efficiency of 5.53 cd/A has been obtained from the fluorene copolymer **828** incorporating 5 mol % of the heterocycle.[1692] Deep-red emission is obtained from both the diselenophanylbenzothiadiazole **829a** (λ_{max} = 671–713 nm, *m* = 1–50 mol %) and

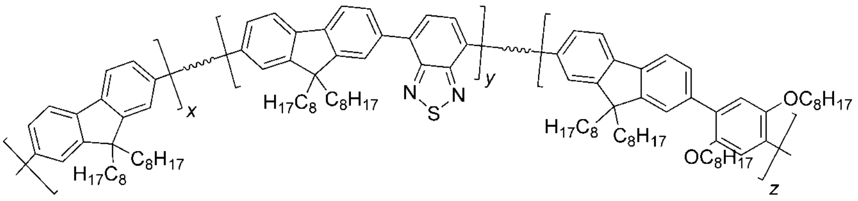
Chart 17



815

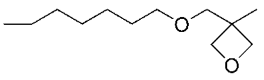


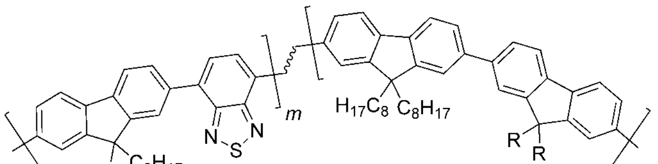
816



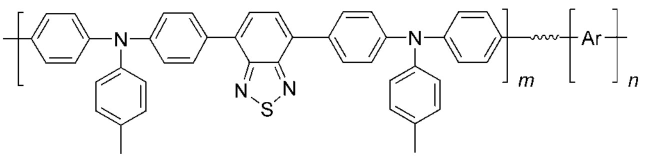
817a $x = 0.5n$, $y = 0.25n$, $z = 0.25n$, R = C_8H_{17}

817b x = 0, R =

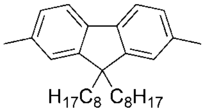




818a R = $C_6H_{12}NMe_2$
818b R = $C_3H_6N^+Me_2EtBr^-$



819a Ar =



819b Ar =

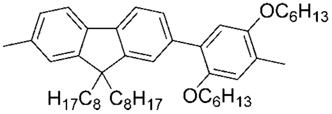
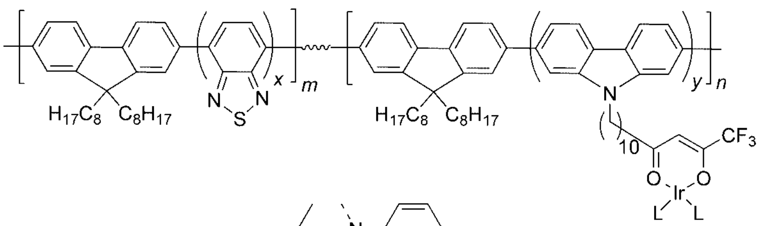
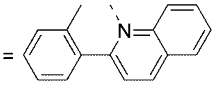
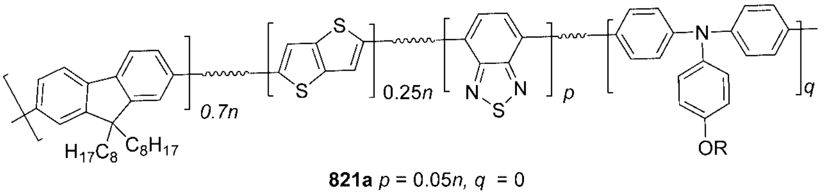


Chart 18



820 L =

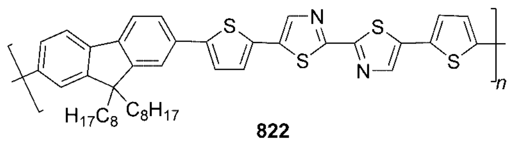




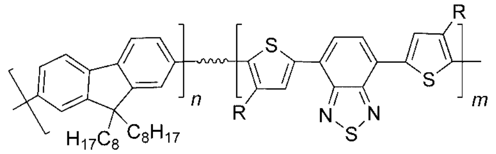
821a $p = 0.05n$, $q = 0$
821b $p = q = 0.025n$

diselenophanylbenzoselenodiazole **829b** (λ_{max} = 734−790 nm, m = 1−50 mol %) copolymers.[1693] The random copolymers **830** with 1−30 mol % of heterocycle emit in the deep red and/or near-infrared (λ_{max} = 734−780 nm).[1694] The highest EL efficiency of 0.6% was obtained for the 5% copolymer (λ_{max} = 734 nm). The most red-shifted EL emission yet reported comes from the alternating copolymer **831** (λ_{max} = 970 nm).[1695,1696]

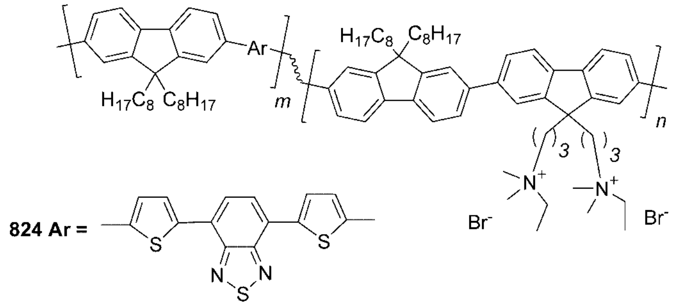
Chart 19



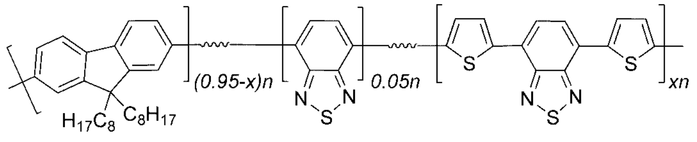
822



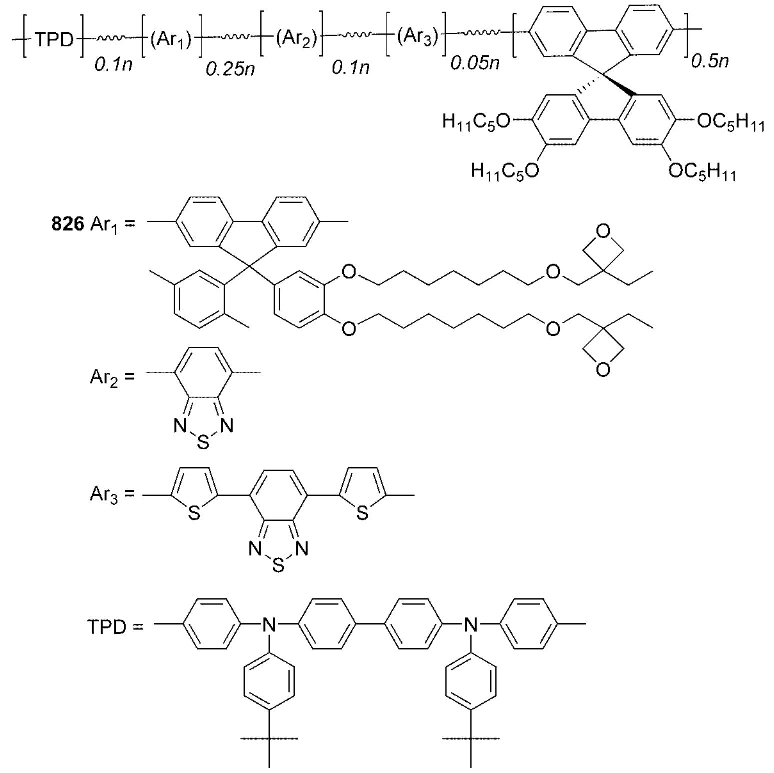
823a R =H
823b R = C_6H_{13}



824 Ar =



825a x = 0.01, **825b** x = 0.1, **825c** x = 0.15



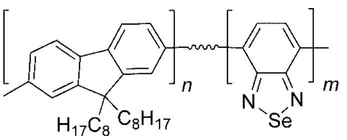
826

Copolymers **832** of fluorene with diphenylthiazolothiazole show similar EL spectra to those of the fluorene homopolymer **558b** (λ_{max} = 445−450 nm), but the EL efficiency of polymers with 25% or more of the heterocycle is much higher than that for **558b**.[1697]

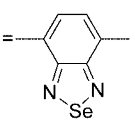
Jenekhe and co-workers have prepared a range of heteroarylene/arylene copolymers including **833**−**835** by condensations of 1,2,4,5-benzenetetraamine, 2,5-diaminobenzene-1,4-dithiol, and 2,5,-diamino-1,4-dihydroxybenzene with aryl diacids.[851,852,1698−1702] The EL emission maxima of these polymers range from green (λ_{max} = 500 nm, **833c**) to yellow (λ_{max} = 578 nm, **834a**).[851] Condensations with a mixture of arylene and aliphatic diacids gave copolymers **835** containing isolated conjugated segments separated by flexible alkyl spacers, whose PL quantum efficiencies (6−12%) were up to 7 times greater than those for the equivalent fully conjugated polymers and whose emission color could be tuned from blue to red by altering the relative ratios of the diacids.[1700] These materials have also been used as electron-transporting layers to boost the efficiency of LEDs with PPV or MEH-PPV as emissive layer.[1584] The best results were obtained using **833a**, which enhanced the EL efficiency of

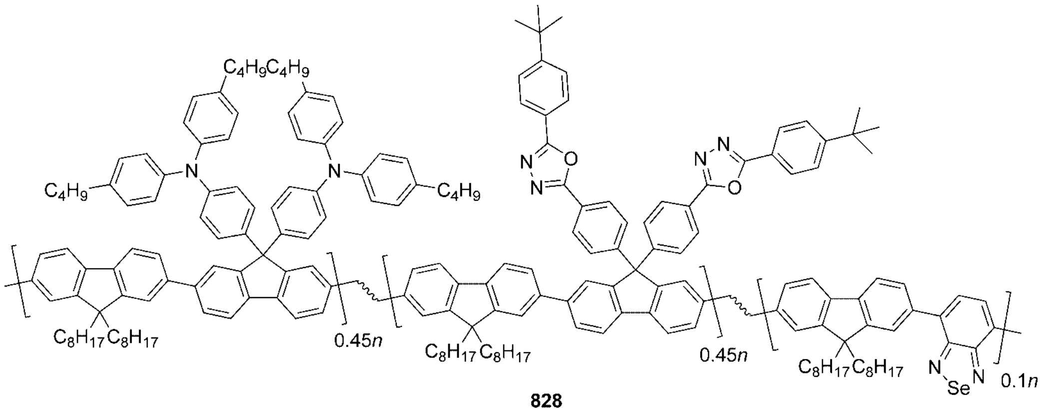
Chart 20

827a

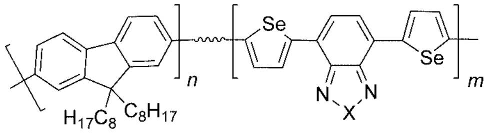


827b Ar =

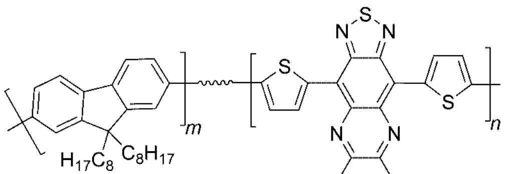




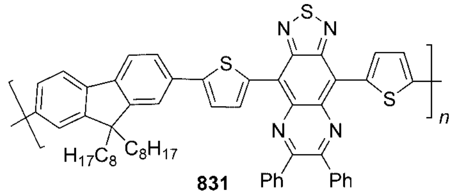
828



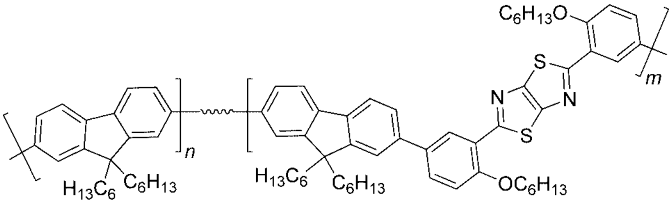
829a X = S
829b X = Se



830

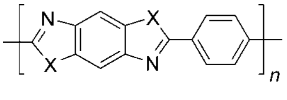


831

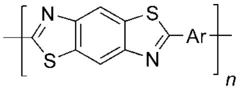


832

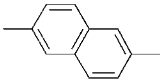
PPV by 2 orders of magnitude and of MEH-PPV by 1 order of magnitude, in devices using aluminum cathodes. The copolymers **834b** and **834c** show green emission (λ_{max} = 543 nm) in which keto–enol tautomerism (for **834c**) gives rise to a large Stokes shift.[1701,1702] Polarized emission has been obtained from oriented films of **833c**. The ladder polymer **836** prepared by condensation of 1,2,4,5-tetraaminobenzene and 1,4,5,8-naphthalene tetracarboxylic acid[1703] emits in the near-infrared (λ_{max} = 740 nm).[851]



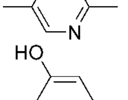
833a X = S
833b X = NH
833c X = O



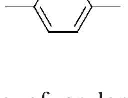
834a Ar =



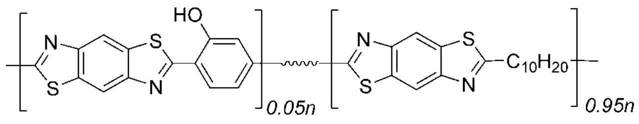
834b Ar =



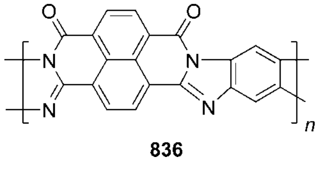
834c Ar =



One of the most widely studied classes of arylene–heteroarylene copolymers are arylene–oxadiazoles, in which the electron deficiency of the oxadiazole units is used to improve the electron-accepting/hole-blocking properties of the polymers. The syntheses and applications of polymers containing aryloxadiazoles have been reviewed by Schulz and Brehmer.[1704] The general method of preparation of aryl oxadiazoles is by condensation of aryl acylhydrazides with aryl carboxylic acids or acylhalides, followed by dehydrative ring closure. An example is the preparation of the polymers **837** (Scheme 50) by Janietz et al.[1705] These polymers emit in the blue, with solvent-dependent PL maxima between 425 and 450 nm in solution and at 475 nm in the solid state. The emission from a double-layer device with PPV as hole-transporting layer is tunable from blue (λ_{max} = 480 nm) to green (λ_{max} = 525 nm) by reducing the thickness of the polyoxadiazole layer.

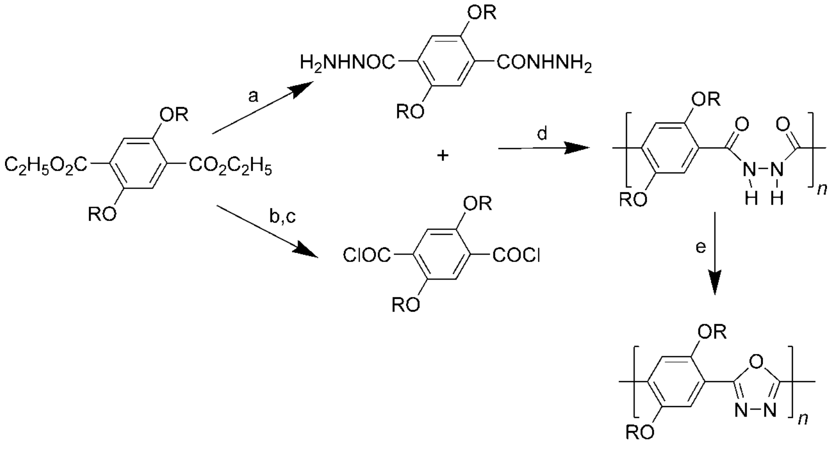


835



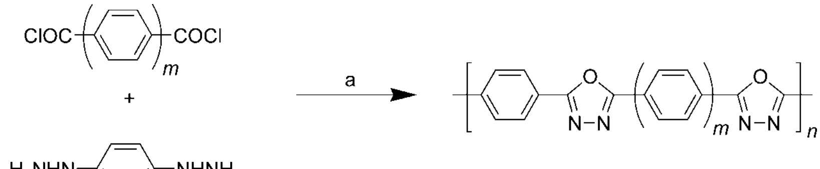
836

Scheme 50. Synthesis of Poly(phenylene oxadiazole)s: (a) $NH_2NH_2 \cdot H_2O$; (b) KOH; (c) $SOCl_2$; (d) *o*-Dichlorobenzene, Pyridine, Δ; (e) $POCl_3$, Δ



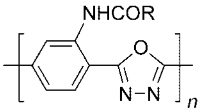
837 R = alkyl

Scheme 51. Preparation of Phenylene–Oxadiazole Polymers by Vapor-Deposition Polymerization: (a) 300 °C, 0.001 Pa

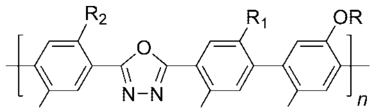


839

Blue emission has also been reported for the alkylamido-substituted polymers **838**.[1706] A chemical vapor deposition route to make films of the polymers **839** (Scheme 51) has been developed by Tsutsui et al.[1707] The emission was reportedly red (λ_{max} = 610 nm), but on incorporation of a hole-transporting aromatic amine into the polymer layer, blue emission was observed. This approach has been extended using other monomers to give polymers that emit in blue and green.[1708,1709]



838 R = alkyl



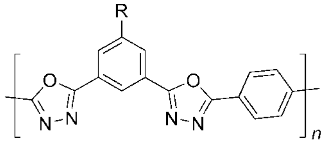
R = 2-ethylhexyl

840a R_1, R_2 = H

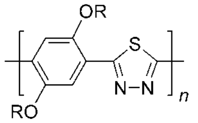
840b R_1 = 2-ethylhexyloxy, R_2= alkyl

Terphenyl oxadiazole copolymers such as **840a**[1710] and **840b**[1711] have also been prepared by Suzuki coupling of diphenyloxadiazoles with benzene bis-boronic acids. The emission of these polymers is blue-shifted (λ_{max} = 444 nm and *ca.* 410 nm, respectively) compared to that of the phenyl copolymers **837**. A single-layer device using **840a** shows blue emission with low efficiency due to poor hole injection. When used as an electron-transporting layer in devices with MEH-PPV as emissive layer and aluminum cathodes, copolymer **840a** boosted the EL efficiency 26-fold over that of the corresponding single-layer devices.[1710] Polymers with the conjugation interrupted by *meta*-linkages as in **841**[181,617] reportedly show intense violet-blue emission (λ_{max} = 420 nm). The thiadiazole polymers **842** are reported to display blue-green (λ_{max} = 457 nm) PL in solution and green emission (λ_{max} = 514–530 nm) in the solid state.[1712]

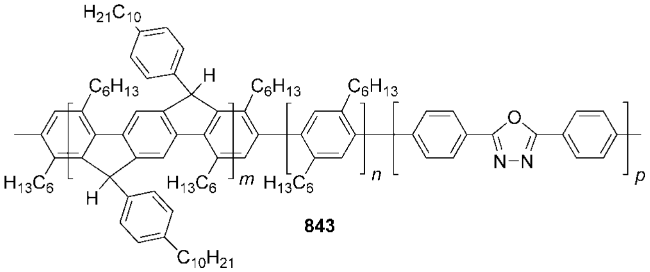
Copolymer **843** containing dialkyl PPP, ladder-type PPP, and electron-transporting diaryloxadiazole segments has been prepared by Stern et al.[1713] It emits blue light (λ_{max} = 410, 480 nm) with an efficiency of 0.4% when aluminum cathodes were used.[1714] This is twice the efficiency obtained for similar devices using copolymers **556** without the oxadiazole units. The incorporation of more than 20 mol % of diphenyloxadiazole units in the random copolymers **844a** is reported to blue-shift the emission slightly and to lower the EL efficiency compared with that of **558b**.[1715] A similar blue-shift is observed in the solid-state PL of the copolymers **844b** containing both oxadiazole and triarylamine charge-transporting groups, but there is as yet no report on the EL properties.[835]



841 R = H, ^tBu

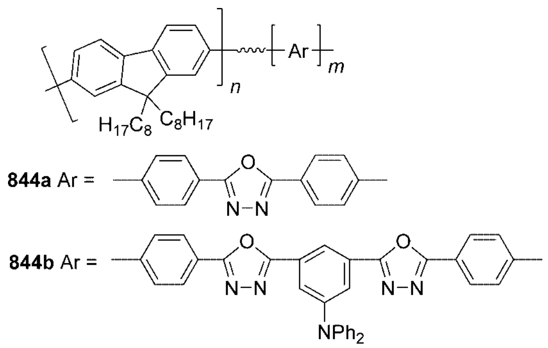


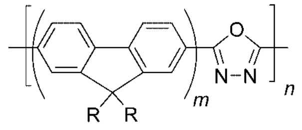
842 R = alkyl

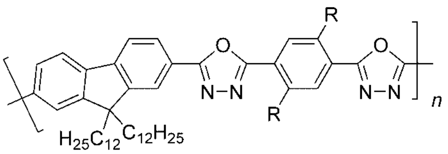


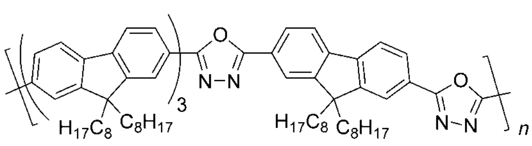
843

Emission from the fluorene–oxadiazole alternating copolymer **845a** is dependent upon its preparation method.[1716] High molar mass material made in a one-step process has a maximum at 432 nm, with a secondary band at 459 nm, attributed to aggregates, while a lower mass material made by isolating the intermediate polyhydrazide and then dehydrating shows opposite intensities for these bands. This


844a Ar =
844b Ar =


845a R = $C_{12}H_{25}$, *m* = 1
845b R = C_8H_{17}, *m* = 1
845c R = C_8H_{17}, *m* = 3
845d R = C_8H_{17}, *m* = 4


846a R = H
846b R = 2-ethylhexyloxy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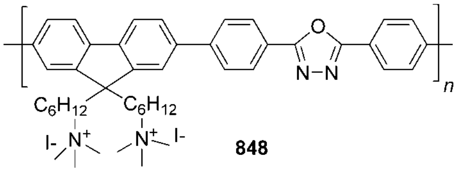
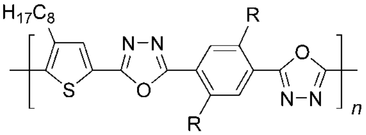
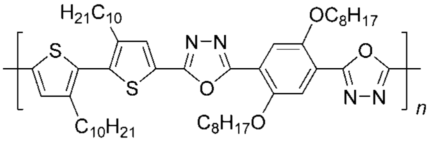

848


849a R = H
849b R = OC_8H_{17}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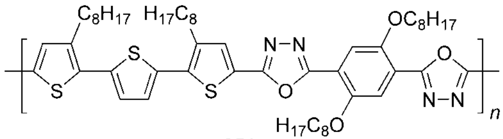
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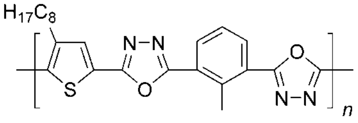
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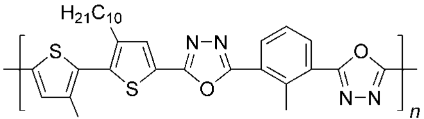
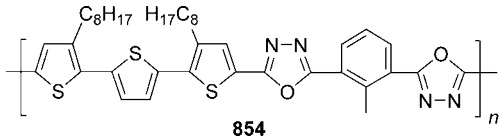
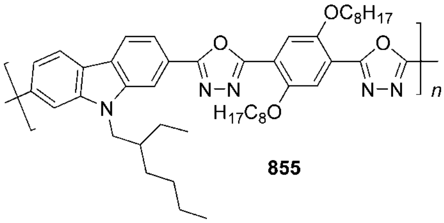

853


854

variance is not seen for the phenylene copolymers **846**.[1716] Blue EL (λ_{max} = 430 nm) with 0.1% efficiency has been obtained from **846b** in a device with a PVK hole-transporting layer. Ding et al. have made the copolymer **845b** by a variant of the above synthetic route using a fluorene bis-tetrazole instead of a bis-hydrazide, and the oligofluorene–oxadiazole copolymers **845c,d** and **847** have been made by Suzuki coupling of bis-fluorenyloxadiazoles with oligofluorene bis-boronates.[1717] Polymers **845b–d** and **847** all produced blue EL with spectra similar to that of the fluorene homopolymer **558b**, but the devices displayed much better stability, with no green emission appearing even after several hours of operation.[1718] Efficiencies of up to 1.0 cd/A have been obtained from devices using films of **845d** with suitable hole-transporting layers.[1719] The water and methanol-soluble copolymer **848** has been used as an electron-transporting layer in LEDs.[1720]

Huang and co-workers have prepared a series of aryl oxadiazole copolymers containing thiophene units. The emission color could be tuned by varying the thiophene content and/or the substitution pattern. Thus, **849a,b** are blue (λ_{max} = 486 and 489 nm, respectively) emitters, while **850** and **851** show green (λ_{max} = 530 nm) and orange (λ_{max} = 579 nm) emission, respectively.[1721−1724] Incorporation of a *meta*-phenylene unit causes a blue-shift in emission so that the PL emission maxima for the polymers **852–854** are at 462, 498 (secondary peak at 526), and 568 nm, respectively.[1722,1725] They have also prepared polymers **855**[1726] and **856**[1727] incorporating both hole-transporting carbazole and electron-transporting oxadiazole groups. These polymers show blue PL (λ_{max} = 448 and 430 nm, respectively) in solution and green-blue (λ_{max} = 475 and 485 nm, respectively) emission in the solid state and have good electron-transporting properties.

Some other heterocycles have also been used as monomers in arylene–heteroarylene copolymers. The copolymers **857** show green EL emission from the thienosilole units, with a maximum at *ca*. 520 nm for the 5 mol % copolymer and at *ca*. 550 nm for the 10 mol % copolymer.[1728] This difference is attributed to greater interchain interactions in the latter. The behavior of the copolymers **858a** (Chart 21) is more complex, with blue PL from the fluorenes being seen in solution for copolymers with up to 20 mol % silole, with silole emission at 571 nm visible also for the 5–20 mol % copolymers, and purely silole emission being seen at 587 nm for the 50 mol % copolymer. The energy transfer to the siloles is more efficient in the solid state with silole emission dominant from the 10 mol % copolymer. The EL is white from the 1% copolymer, with silole emission being seen for all the others.[1729] Similar PL properties are seen for the



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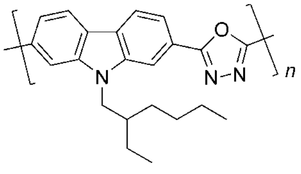

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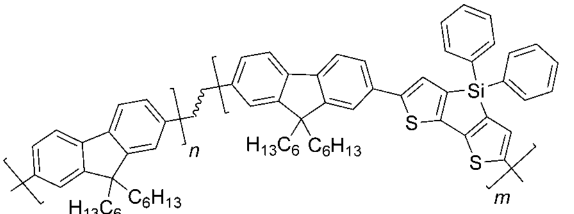


857

random and alternating copolymers ($m = 5-50$ mol %) of fluorene with tetraphenylsilole **858b**, but all show green EL ($\lambda_{max} = 524$ nm) from the silole.[1730] The poly(diphenyl germole) **859** was made by transmetalation of the zirconocene **343**, followed by polycoupling with nickel(0), and shows green PL ($\lambda_{max} = 500$ nm).[1731] The dibenzophosphole copolymers **860** are blue emitters ($\lambda_{max} = 413-433$ nm) with high quantum efficiencies in solution.[1732]

The first conjugated polymers containing a phosphorescent unit in the chain for which EL has been reported were the fluorene copolymers **861a,b**, which were made by Holmes and co-workers by adding red or green emitting iridium complexes with monobrominated aryl ligands into a Suzuki polycondensation.[1733] The EL is entirely from the iridium complex for short fluorene chains, but with longer chains a small amount of emission from the polyfluorenes is seen. This approach has since been adopted by other groups who reported copolymers of fluorene with triplet emitters such as red emitting platinum salen complexes (**862a**, $\lambda_{max} = 640$ nm),[1734] porphyrins (**862b**, $\lambda_{max} = 684$ nm),[1735,1736] and green emitting zinc-salen chromophores (**863a**, $\lambda_{max} = 534$ nm) (Chart 22).[1737] Green EL has also been obtained from phenylene (**863b**, $\lambda_{max} = 548$ nm) and carbazole-based (**863c**, $\lambda_{max} = 541$ nm) copolymers incorporating zinc-salen chromophores,[1737] while the carbazole-fluorene-based copolymer **864** produces orange EL ($\lambda_{max} = 577$ nm),[1738] as does the phenylene-based copolymer **865** ($\lambda_{max} = 580$ nm).[1739] Efficient red EL has recently been reported from copolymers **861c** ($\lambda_{max} = 630$ nm) and **861d** ($\lambda_{max} = 590$ nm).[1740] The highest efficiency reported for a neat polymer is 5.4 cd/A (4.1%) obtained from **864**,[1738] but efficiencies of up to 6 cd/A are claimed for blends of **862a** with the fluorene homopolymer **558c**.[1734]

4. Other Luminescent Polymers

This section covers the remaining classes of conjugated polymers used in light-emitting applications. These include polyacetylenes, dendrimers, and hyperbranched polymers. Also included are polymers in which the conjugated chromophores are isolated, either by being attached as a side-chain or by being separated by nonconjugated segments on the backbone. Polymers with isolated (main-chain or side-chain) oligoarylene or oligo(arylene vinylene) chromophores have been reviewed by Segura and Martín.[28] Also included are block copolymers, including rod-coil copolymers, where a nonconjugated coil is attached to a conjugated emitting rod, and also copolymers with two conjugatively linked emissive blocks.

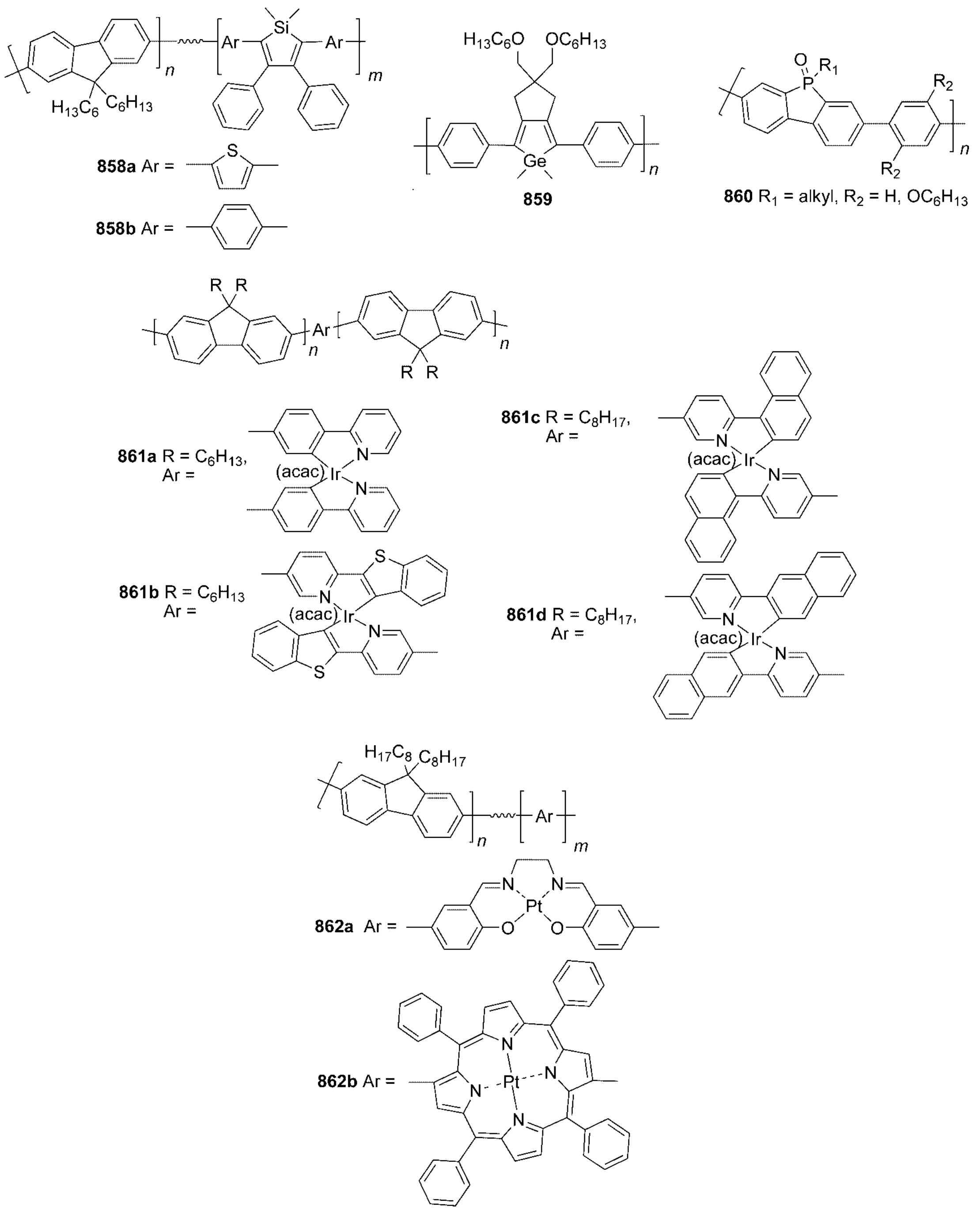
4.1. Polyacetylenes

Polyacetylene itself is not luminescent, but a range of luminescent polymers have been prepared by transition-metal-catalyzed polymerization of aryl and alkylacetylenes, most notably by the group of Tang.[1741−1743] The first such material reported was the poly(diphenylacetylene) **866** with one solubilizing perfluoroalkyl group per two monomer units synthesized (Scheme 52) by Yoshino and co-workers and used to make an LED which showed green emission ($\lambda_{max} = 530$ nm).[1744] The parent polymer **867** is virtually insoluble in common organic solvents also shows green PL ($\lambda_{max} = 520$ nm).[1745] Green emission has also been obtained from other poly(diarylacetylene)s, e.g. **868a**−**c**.[1746−1752] Bulky or long alkyl substituents are reported to increase the luminescence intensity.[1748] Polymer **868d** bearing a hole-transporting carbazole substituent, shows green PL and EL ($\lambda_{max} = 540$ nm), with much better efficiencies and brightnesses than those for **868c**.[1745,1753] A bilayer device with Alq_3 shows voltage tunable emission as the recombination zone moves into the Alq_3 layer with increasing voltage.[1753]

Blue PL is reported from the poly(anthrylacetylene)s **869** ($\lambda_{max} = 470$ nm)[1754] and the acid-substituted polymer **870** ($\lambda_{max} = 462$ nm).[1755] The polymer **871a** with fluorene side-groups is reportedly nonemissive, whereas the terfluorene-substituted polymer **871b** is a blue emitter ($\lambda_{max} = 430$ nm).[1756] The poly(phenylacetylene) **872a** has been variously reported as showing green[1747] or blue[1757] EL emission. Halogen-substituted polymers e.g. **872b** show blue-green EL ($\lambda_{max} = 500$ nm) while poly(1-alkyl-2-arylacetylene)s such as **872c** emit in the blue ($\lambda_{max} = 470$ nm).[1746,1749−1751,1758] Longer alkyl chains produce more intense EL.[1751] Addition of the fullerene C_{60} to the reaction mixture is reported to increase the rate of polymerization of 1-phenyl-1-alkynes, and the resulting materials show stronger PL.[1759,1760] Stretching of a film of **872c** is reported to cause polarization of the PL parallel to the stretching direction.[1751] The Tang group have prepared a wide range of polymers bearing alkyl chains ω-functionalized with chromophoric groups such as biphenyl, fluorene, carbazole, or naphthalene[1741,1742,1761−1763] The emission is generally blue with high PL, but only moderate EL efficiencies, e.g. 0.85%, were reported for polymer **873** ($\lambda_{max} = 460$ nm).[1741,1764,1765] Longer alkyl chains reduce the EL efficiency in such polymers.[1741] By contrast, the emission from the silole-containing polymers **874** and **875** is blue-green or green ($\lambda_{max} = 496$ and 512 nm, respectively).[1741,1766−1768]

Polymer **876** with no linker displays red EL ($\lambda_{max} = 664$ nm).[1766,1767] Attachment of mesogenic groups in the side-chains induces liquid crystallinity and thus the potential to produce polarized emission.[1741,1742,1762,1763,1769] Polymer **877a** with an ethynyl substituent shows green emission ($\lambda_{max} = 521$ nm), while the arylethynyl-substituted polymers **877b** and **877c** show violet ($\lambda_{max} = 368$ nm) and blue ($\lambda_{max} = 405$ nm) EL, respectively.[1757] Polymer **878a** with a bulky *ortho*-substituent shows orange-red EL ($\lambda_{max} = 600$ nm),[1750]

Chart 21



while weak red emission ($\lambda_{max} = 680$ nm) has been reported for **878b**. A blend of **878b** with **868c** shows strong red emission, which is attributed to energy or charge transfer from **868c** to **878b**.[1751] Similarly, blending **872b** with **868c** leads to strong green emission from the latter due to energy transfer.[1770] The poly(pyridiniumacetylene) **879** shows red PL ($\lambda_{max} = 710$ nm), whose intensity decreases with increasing temperature.[1771]

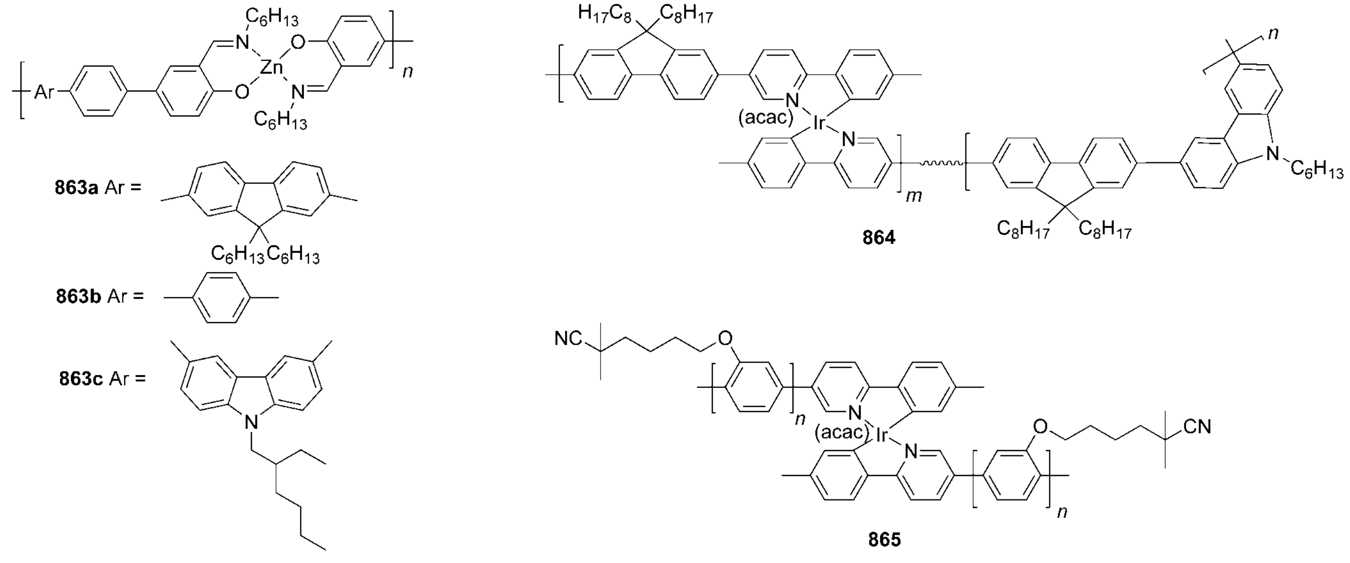
Tang and co-workers[1769,1772−1777] have also prepared a range of violet or blue emitting poly(1-alkylacetylene)s, e.g. **880a,b**, which show more efficient PL than the poly(arylacetylene)s discussed above. Longer alkyl chains generally produce higher PL intensity. Polymer **881** is water soluble with a PL maximum at 510 nm.[1778]

4.2. Dendrimers and Hyperbranched Polymers

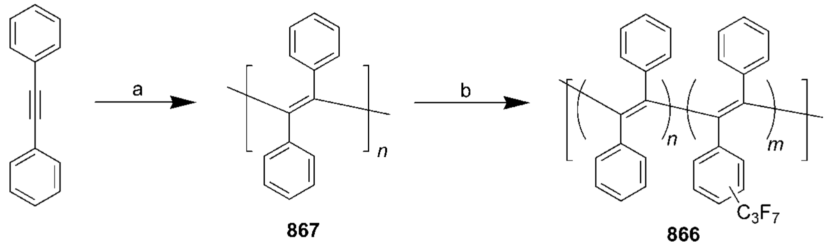
Hyperbranched polymers have been little studied as emissive materials for LEDs. The hyperbranched polymer **882** with a stilbene chromophore shows a broad PL spectrum ($\lambda_{max} = 508$ nm).[1779] Polymer **883** with a distyrylbenzene chromophore displays blue PL ($\lambda_{max} = 433$ nm) in solution and blue-green emission ($\lambda_{max} = 479$ nm) in the solid-state.[1780]

A blue emitting ($\lambda_{max} = 446$ nm) 1,3,5-hyperbranched PPV **884** can be made by a Wittig or a Gilch route (Scheme 53), with the latter giving higher molecular mass material.[1781] A 1,3,4-branched PPV **885** has been made by Heck coupling and displays green PL whose emission maximum moves from 524 to 550 nm with increasing molar mass.[1782]

Chart 22

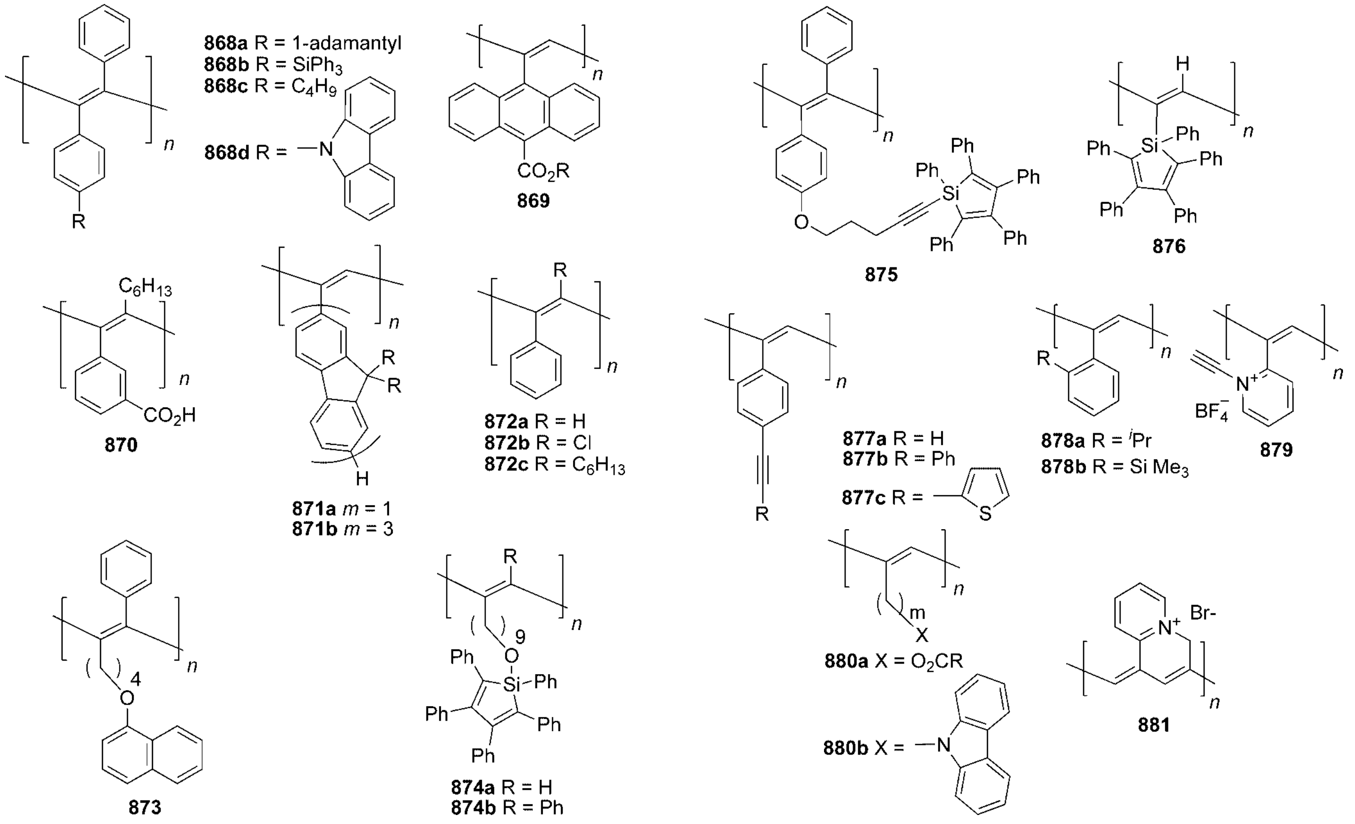


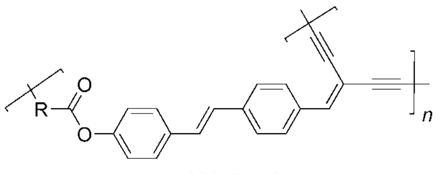
Scheme 52. Synthesis of a Soluble Poly(diphenylacetylene) Copolymer: (a) $TaCl_5$, $Sn(C_4H_9)_4$, Toluene, 80 °C; (b) $(C_3F_7CO_2)_2$, Cl_2FCCF_2Cl, 40 °C



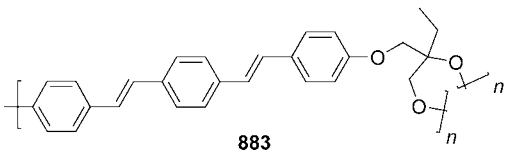
Introduction of triphenylamine units into such a structure reportedly leads to broad EL emission between 430 and 740 nm.[1597]

The hyperbranched RO-PPVs **886** (Chart 23) made by the Wittig method show blue-green PL (λ_{max} = 492−501 nm depending upon R).[1783,1784] Green EL (λ_{max} = 540 nm) has





882 R = C_8H_{16}



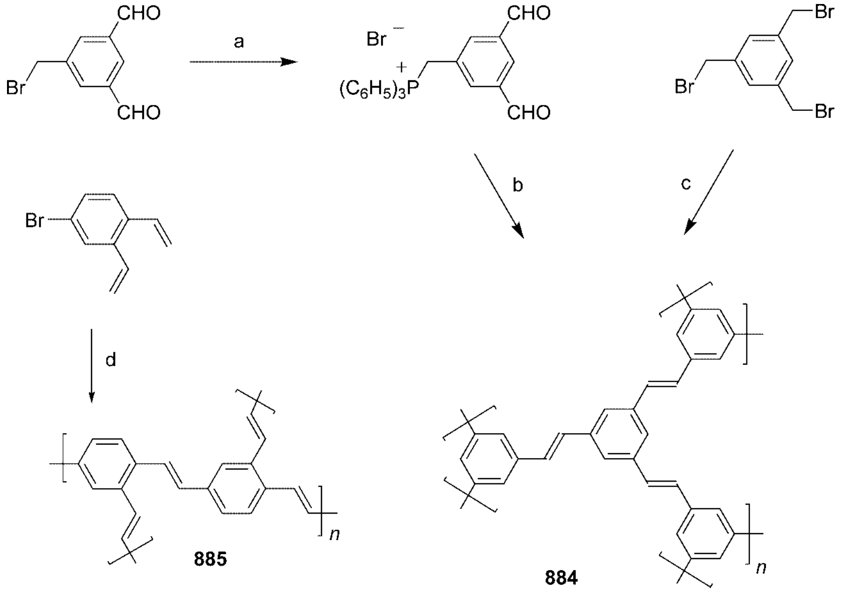
883

been obtained from **886** end-capped with dimethylaminobenzene units.[1785] Orange-red EL (λ_{max} = 595 nm) has been reported from the hyperbranched PPyV **887** made by Heck coupling.[1786] The linear analogue had slightly blue-shifted PL (λ_{max} = 589 nm), suggesting the conjugation in the hyperbranched system was slightly more extensive.

Sonogashira−Hagihara coupling of 3-hexyl-2,5-diiodothiophene with 1,4-diethynylbenzene and 1,3,5-tri- and 1,2,4,5-tetraethynylbenzene gives hyperbranched poly(arylene ethynylene)s **888** and **889**, respectively, which show blue PL in solution (λ_{max} = 457 nm).[1787]

Tang and co-workers have made hyperbranched polyarylenes **890** by the cocyclotrimerization of arylene diynes

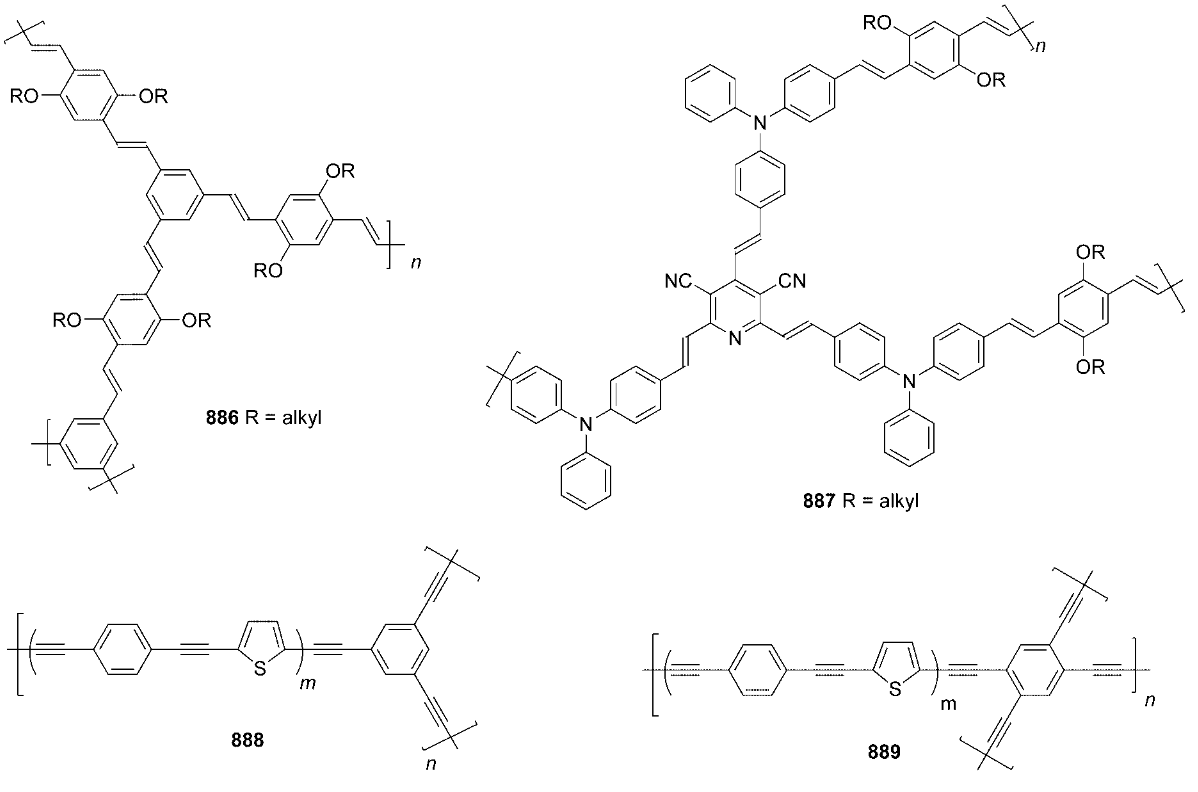
Scheme 53. Synthesis of Hyperbranched PPVs: (a) PPh_3; (b) C_2H_5OK; (c) ^{t}BuOK, THF; (d) $Pd(OAc)_2$



885

884

Chart 23



886 R = alkyl

887 R = alkyl

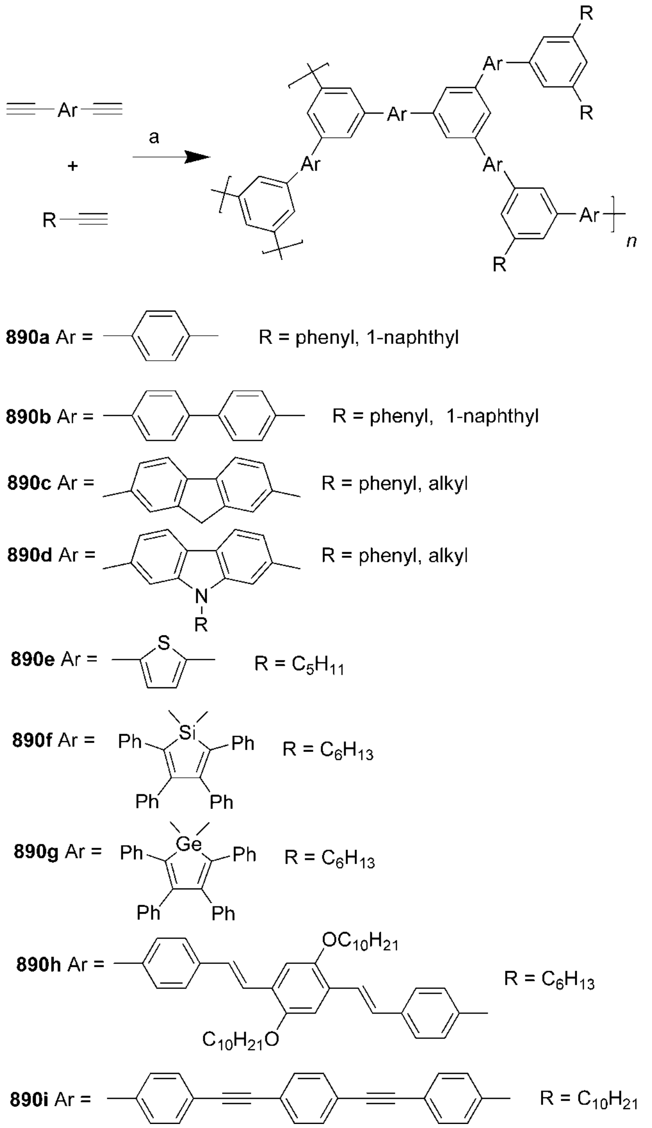
888

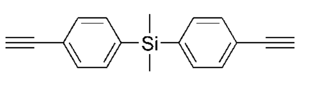
889

and aryl- or alkyl-acetylenes (Scheme 54).[1742,1766,1767,1788−1793] The phenylene **890a** and biphenylene-based **890b** materials show violet-blue PL (λ_{max} = *ca.* 400 nm), as do the carbazolyl- and fluorenyl-based polymers **890c,d** (λ_{max} = 408, 416 nm), while polymers **890e−g** containing thiophene, silole, and germole units emit in the blue-green (λ_{max} = 486−504 nm). Polymer **890h** with arylene vinylene units is also a blue-green emitter (λ_{max} = 479−493 nm),[1764] while the analogous polymers such as **890i** with arylene ethynylene units emit in the violet (λ_{max} = 399 nm).[1794,1795] Other units that have been polycyclotrimerized are the silane **891**[1796] and the triphenylamine **892**.[1797] These produce violet and blue emitting hyperbranched materials. Oxidative coupling of **891** with copper(I) produces a blue emitting hyperbranched polymer containing diarylbutadiyne units.[1798]

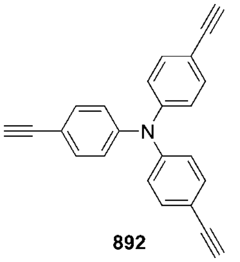
Hyperbranched polyarylenes can also be made by Suzuki polycondensations. Thus, copolymerization of the bromofluorene boronic acid **893** and the dibromobenzene boronic acid **894** produces polymers whose PL emission maximum can be varied between 425 and 444 nm by altering the ratio of the two comonomers.[1799] Blue or blue-green EL has been obtained from these materials (λ_{max} = 420−482 nm) with efficiencies of up to 2.46%.[1800] The polymers **895−896** were also prepared by Suzuki polycondensation of a fluorene bisboronate with the appropriate tetrabromides.[1801,1802] Blue EL has been obtained from **895d** and **896** (λ_{max} = 415 and 426 nm, respectively). Blue emitting hyperbranched fluorene−carbazole copolymers have been prepared by the same method.[1558,1803] Hyperbranched fluorene−oxadiazole copolymers **897** made by Suzuki polycondensation also produce blue EL (λ_{max} = 423 nm).[1804] Insertion of a PVK hole-transporting layer increases the EL efficiency to 1−1.5% with a red-shift in emission (λ_{max} = 446 nm).

Scheme 54. Synthesis of Hyperbranched Polyarylenes by Cyclotrimerization: (a) $TaCl_5$, Ph_4Sn, Toluene





891



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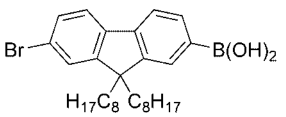

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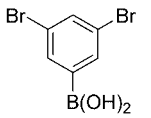

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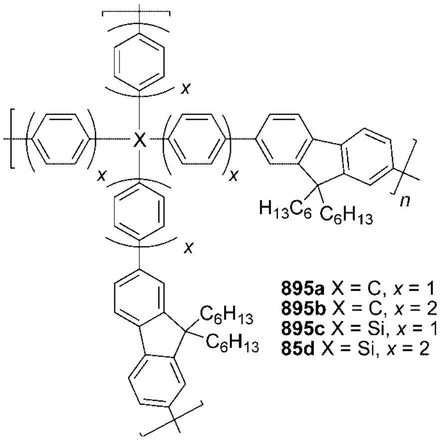
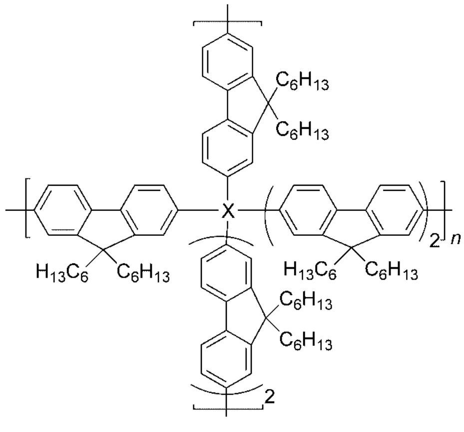
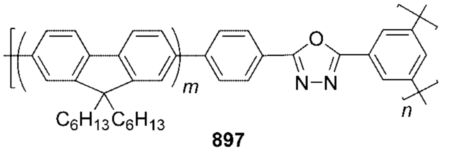


895a X = C, *x* = 1
895b X = C, *x* = 2
895c X = Si, *x* = 1
85d X = Si, *x* = 2

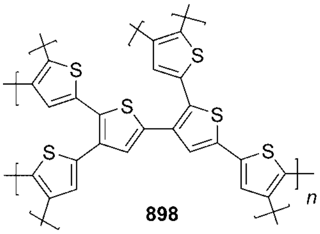


896 X = C, Si

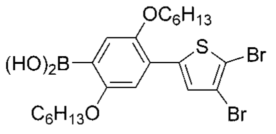


897

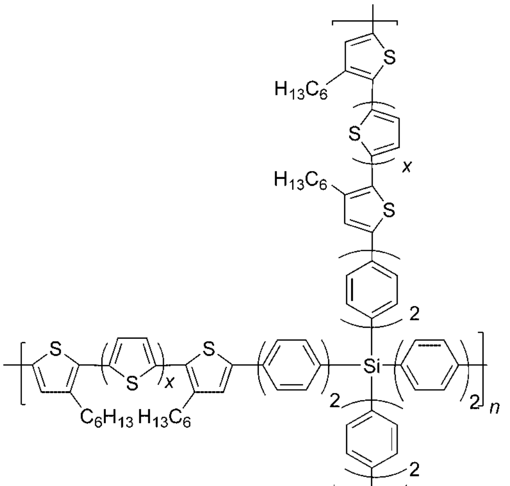
Hyperbranched polythiophenes **898** showing green PL (λ_{max} = 533 nm) have been made by nickel(II)-catalyzed coupling of 4,3-dibromothiophene-5-magnesium bromide.[1805] Suzuki coupling of the dibromothiophene benzeneboronic acid **899** yields a hyperbranched phenylene−thiophene copolymer which is a blue-green emitter (λ_{max} = 482 nm).[1597] The hyperbranched copolymers **900** were made by nickel(II)-mediated coupling of an oligothienyl bis-magnesium bromide with tetrabromosilane.[1802] The bithienyl polymer **900a** produces green EL (λ_{max} = 530 nm), while the terthienyl polymer **900b** is a red emitter (λ_{max} = 538 nm). Hyperbranched soluble polythiothenes have also been prepared by Stille coupling.[1806]



898

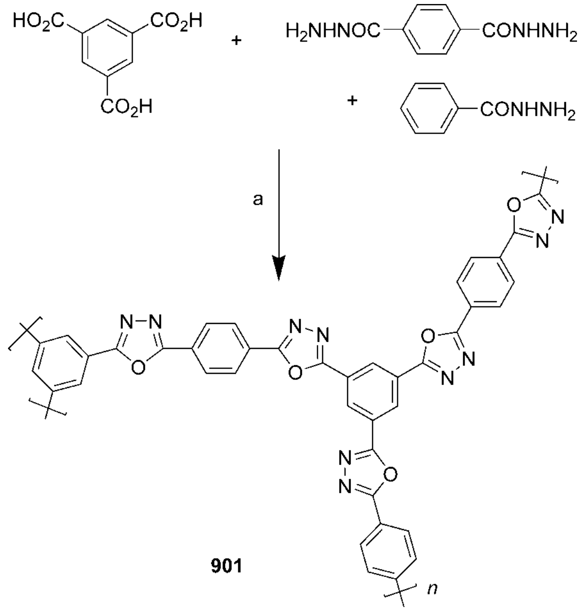


899



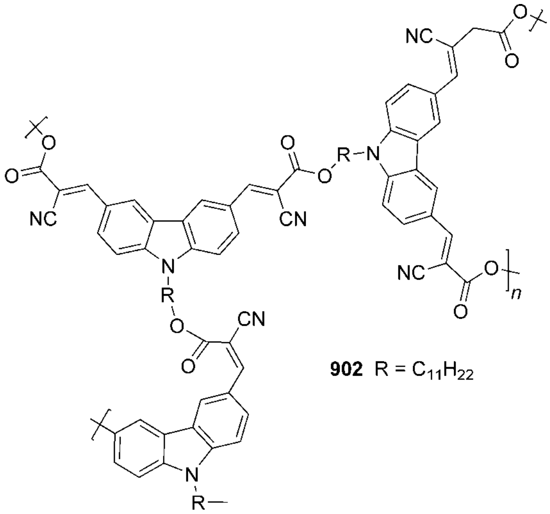
900a x = 0
900b x = 1

Scheme 55. Synthesis of a Starburst Oxadiazole Polymer: (a) P_2O_5, CH_3SO_3H, 100 °C

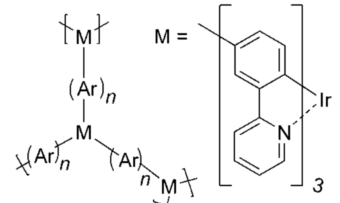


901

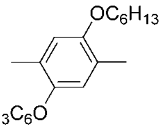
Oxadiazole-containing hyperbranched polymers have been investigated as charge-transport materials. A radialene polyoxadiazole might be expected to be more efficient in its electron transfer processes than a linear molecule due to the enhanced charge migration opportunities (analogous to the movement in a "catherine wheel") and show improved solubility due its dendrimer-like structure. Thus, Holmes and co-workers have synthesized the starburst polymer **901** (Scheme 55) which was processable in trifluoroacetic acid. The band gap was determined to be 3.3 eV, and the material showed blue fluorescence in solution. A double-layer device ITO/PPV/**901**/Ca gave PPV emission with 0.1% efficiency.[617,1807] A number of oxadiazole-containing dendrimers have also been prepared for use as electron-transporting materials.[1808,1809] A hyperbranched polycarbazole **902** has been prepared by condensation of *N*-11-hydroxyundecanylcarbazole-3,6-bisaldehyde with ethyl cyanoacetate, as an electron-transporting material for use in multilayer LEDs.[1810] It shows blue (λ_{max} = 480 nm) PL and has been used as the emissive layer in a blue emitting (λ_{max} = 480 nm) double-layer device with poly(*N*-alkylcarbazolyl butadiyne) as the hole-transporting layer.[1811,1812] Hyperbranched phosphorescent polymers **903** have been made which show green EL (λ_{max} = 520−530 nm) arising from the iridium complexes.[1739]



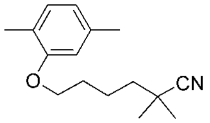
902 R = $C_{11}H_{22}$



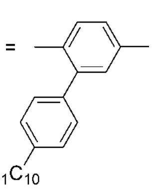
903



903a Ar =



903b Ar =

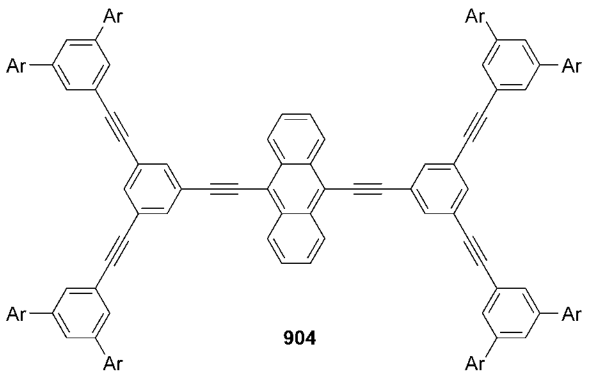


903c Ar =

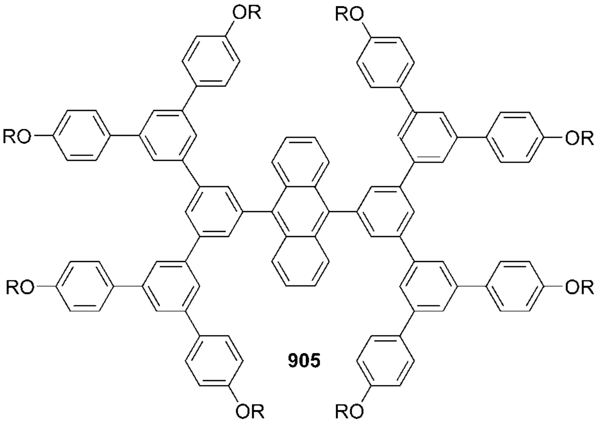
Dendrimers containing fluorescent chromophores have not been extensively investigated as materials for use in LEDs.

Their well-defined sizes and shapes have, however, made them especially suitable materials for studying the fundamental photophysics of luminescent materials. The chromophores may be incorporated as core units or as substituents on the periphery, or especially for arylene vinylene or arylene ethynylene dendrimers, the branching units (dendrons) themselves may be luminescent. Dendrimers are prepared either by attachment of the preformed dendrons to a core (convergent approach) or by building the dendrons stepwise from the core (divergent approach).

The first reported electroluminescent dendrimers **904** were made by Moore and co-workers using Sonogashira−Hagihara coupling of the dendrons to an anthracene core and showed broad weak red (λ_{max} = *ca.* 550 nm) emission with magnesium cathodes.[1813] No emission was seen with aluminum cathodes, which suggests that electron injection was poor. By contrast, the anthracene-cored dendrimer **905** is a blue emitter (λ_{max} = 442 nm). Efficiencies of up to 1.05% have been obtained from LEDs using a PVK hole-transport layer and barium/aluminum cathodes.[1814]



904



905

Burn and co-workers have obtained more efficient EL emission from phenylene vinylene dendrimers containing red (λ_{max} = 660 nm) **906a** (Chart 24), yellow-green (λ_{max} = 550 nm) **907**, and blue emitting (λ_{max} = 480 nm) **908** cores.[1815−1817] Dendrons with an aldehyde substituent were prepared by iterative Heck coupling and then condensed with pyrrole to give **908** and with aryldiphosphonates to give **907** and **908**. As described in section 3.7 above, double-layer devices with PPy gave better EL.[1503] The PL and EL efficiencies for **908** have been found to be dependent on the dendrimer generation, with the highest efficiencies being seen for the second generation dendrimer.[1818,1819] It is reported that the EL efficiency of asymmetric dendrimers such as **909** (λ_{max} = 395, 417 nm) is higher than that of their symmetrical analogues.[1820] The emission color of **908** rapidly changes from blue to white by an undetermined process which is not thermally induced, with the higher generation materials showing greater stability.

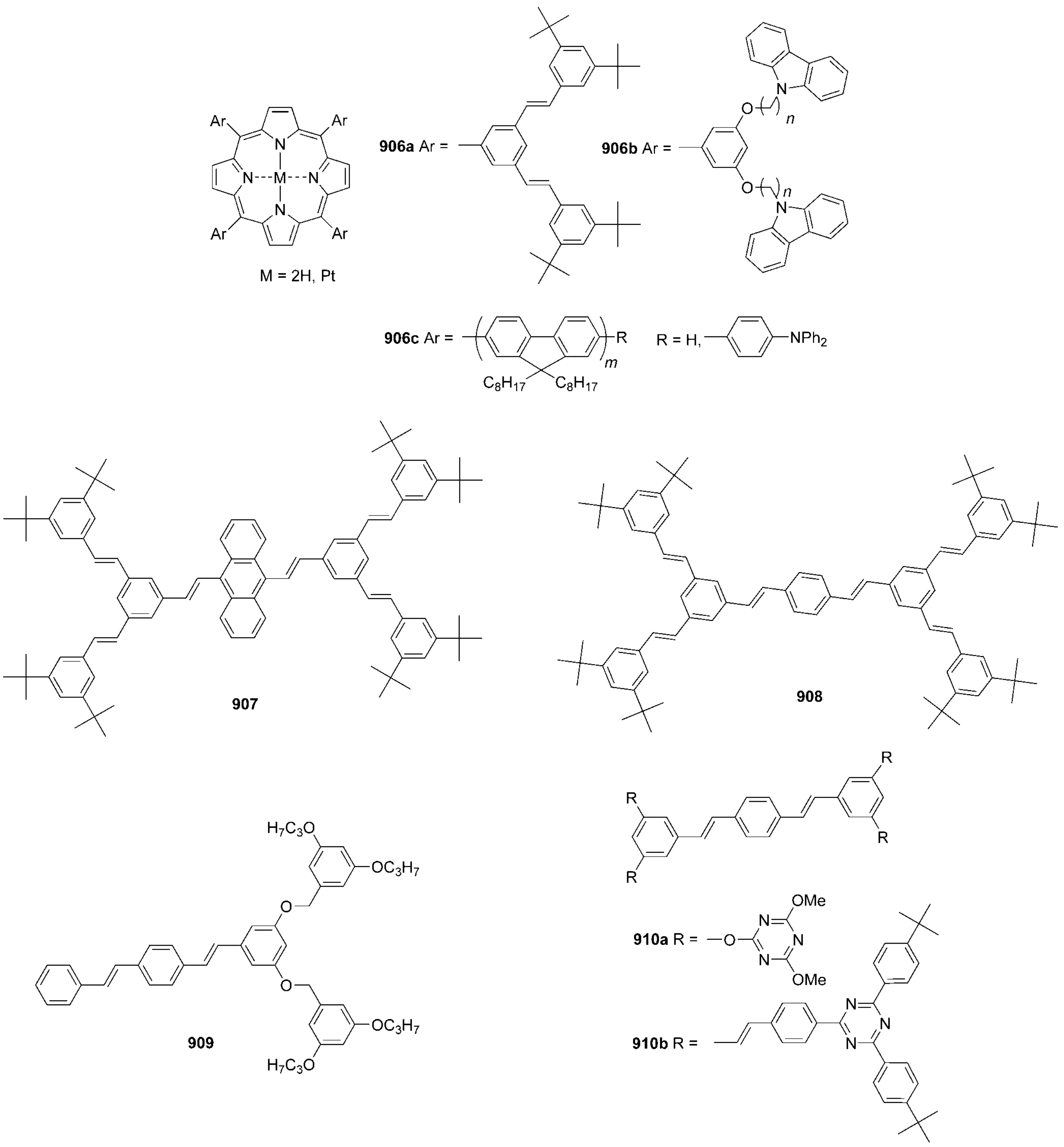
Similarly, the dendrimer **910a** with electron-transporting triazine substituents initially shows blue PL (λ_{max} = 462 nm) and blue-green EL (λ_{max} = 506 nm), but the emission color changes to white over time.[1821] By contrast, similar dendrimers **910b** show stable blue-green EL (λ_{max} = 470 nm),[1822] as do dendrimers such as **911** (Chart 25) with a triphenylamine core (λ_{max} = *ca.* 490−530 nm depending upon generation).[1823−1825] The emission maximum blue-shifts and the EL efficiency increases with increasing generation. Red EL (λ_{max} = 580−618 nm) has been obtained by attaching dyes at the periphery as in **911b,c**, with efficiencies of up to 6.14 cd/A.[1826] A Spanish group have prepared dendrimers **912a−c** with a variety of substituents on the periphery by Horner or Heck coupling methods.[1827] Symmetrically substituted first generation dendrimers such as **912a** showed blue-violet (λ_{max} = 396−425 nm) emission in solution, except for the tris(dimethylamino) dendrimer **912b**, which showed blue PL (λ_{max} = 460 nm). Unsymmetrically substituted dendrimers, e.g. **912c**, with a mixture of electron-donating and electron-withdrawing substituents, showed more red-shifted emission (λ_{max} = 428−505 nm). The behavior of the second generation dendrimers resembled that of the first generation materials. Green PL has been obtained from dendrimers, e.g. **912d**, bearing phenothiazine units.[1828] Blue PL has been observed from dendrimers **913** with chiral binaphthyl units in the core[1829] and from **914** with polyene cores.[1830]

Müllen and co-workers have obtained red EL from polyphenylene dendrimers such as **915** and **916** (Chart 26) with perylene-based dyes as cores.[1831−1833] The dendrons, which are built up from the ethynyl-substituted core by iterative Diels−Alder addition of functionalized tetraarylcyclopentadienones, act as steric shields, preventing interaction of the cores, thus making these materials of interest for photophysicists, as they contain totally isolated chromophores. They have also made dendrimers with perylene dyes attached to the periphery.[1833] Due to their possessing discrete numbers of chromophores in well-defined spatial orientation to each other, these materials have been the focus of photophysical studies involving single-molecular spectroscopy techniques to investigate the interactions between the chromophores, but they have not been studied as emissive materials for devices.[1834]

Burn, Samuel, and co-workers have prepared efficient LEDs using polyphenylene dendrimers containing phosphorescent cores which emit in the red, e.g. **917** (λ_{max} = 634, 693 nm, 5.7% efficiency),[1835−1837] green, e.g. **918** (λ_{max} = 518 nm, 16% efficiency),[1837−1845] or blue, e.g. **919** (λ_{max} = 460 nm, 10.4% efficiency).[1846] The highest efficiencies were obtained by blending the dendrimers with carbazole-based host materials. Green EL with an efficiency of up to 16.6% (57.9 cd/A) has been reported for the phosphorescent dendrimer **920** with carbazole-based dendrons.[1847]

Blue EL (λ_{max} = 401, 421 nm) has been obtained with 1% efficiency from the bifluorene-cored dendrimer **921a**.[1843,1848] Replacement of one of the fluorenes with a thiophene as in **921b** leads to only a small red-shift in the PL in solution (λ_{max} = 415 nm) but a marked red-shift in the solid state resulting in blue-green emission (λ_{max} = 477 nm) due to intermolecular interactions. Blending **921a** and **921b** together partially suppresses these interactions, and LEDs using the

Chart 24

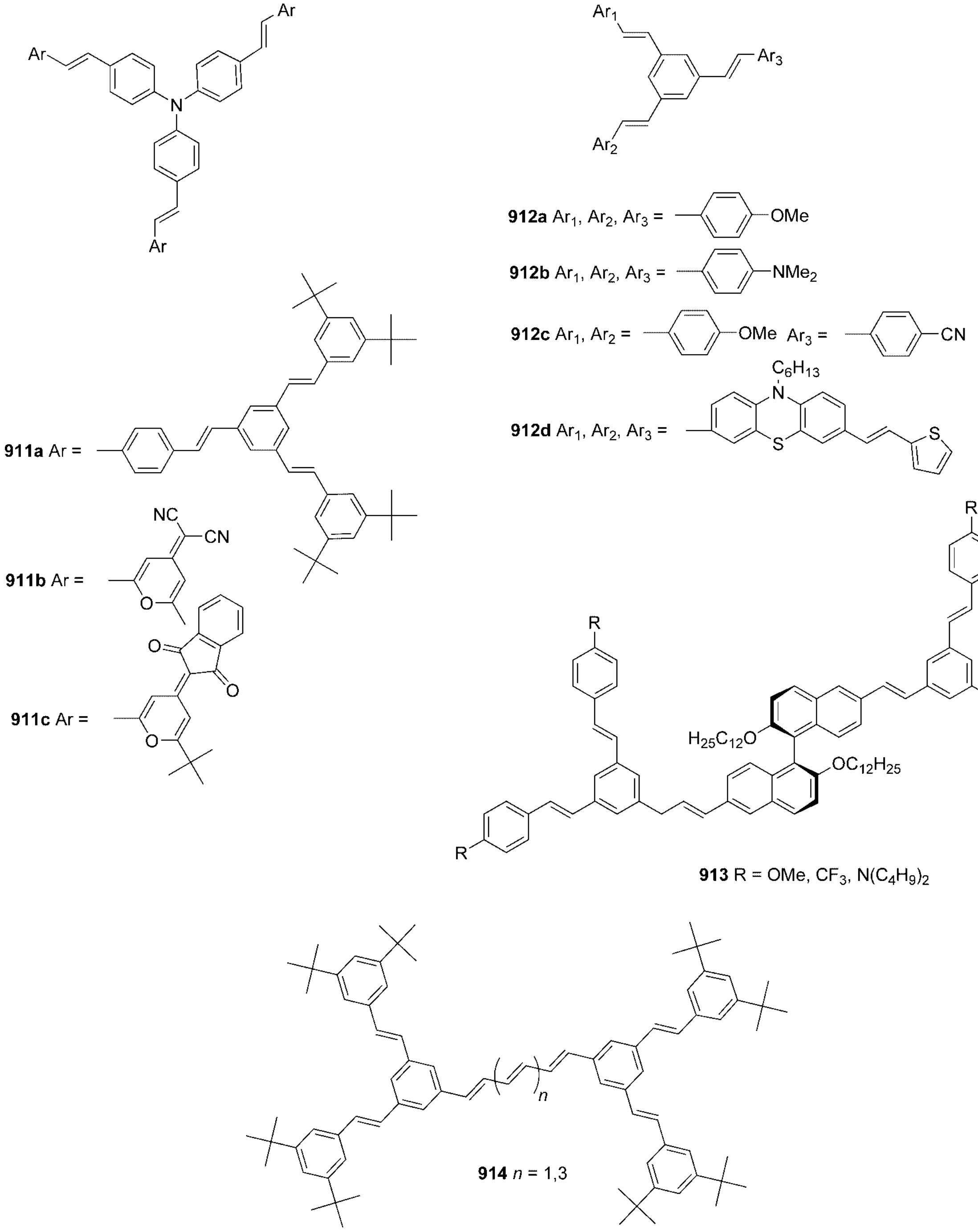


blends display markedly higher power efficiency in devices than does pure **921a** (Chart 27).

It is possible to introduce different functionalities into each layer of a dendrimer. Thus, the Müllen group has prepared a second generation dendrimer **922** with blue emitting chromophores on the periphery, green-yellow emitting chromophores on an inner layer and a red emitter at the core. Due to efficient energy transfer, excitation of any of the chromophores produces PL emission only from the core (λ_{max} = 708 nm).[1849] Red EL has been obtained from a blend with PVK.[1833] The Fréchet group has prepared dendrimers with dye chromophores at the core and charge-transporting moieties at the periphery, which show bright PL and EL due to efficient energy transfer between the periphery and the core. The emission colors are blue (λ_{max} = 480 nm) for the coumarin **923a** and green (λ_{max} = 550 nm) for the quinquethienyl **923b** chromphore (Chart 28).[1850]

In a similar approach, Jenekhe and co-workers prepared green emitting (λ_{max} = 520−534 nm) dendrimers such as **924** (Chart 29) with quinoline units on the periphery.[1851] The highest EL efficiency (0.01%) was obtained for the second generation dendrimer. The efficiency was greatly enhanced by blending with PVK (0.23%). When used as an electron-transporting layer, this dendrimer enhanced the EL efficiency of an MEH-PPV-based LED to 5.0%. Red EL

Chart 25



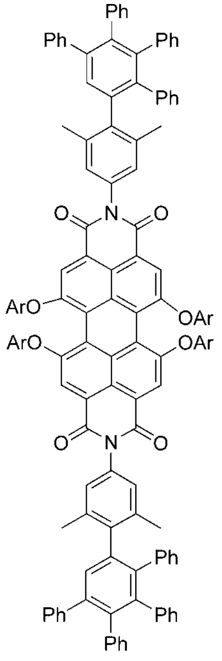
(λ_{max} = 660 nm) has been obtained from dendrimers **906b** with platinum porphyrin cores and carbazoles on the periphery.[1852]

Green EL (λ_{max} = 519 nm) has been obtained from azomethine dendrimers such as **925−926**, but it is reported they function better as hole-transporting materials.[1853,1854] Peng and co-workers have made a range of PPE-based dendrimers such as **927** by Heck coupling.[1855−1858] They show blue or blue-green PL (λ_{max} = *ca.* 450 nm) with high quantum efficiencies. Blue-green EL emission (λ_{max} = *ca.* 500 nm) has been obtained from truxene-based dendrimers **928** made by a cyclotrimerization method.[1859,1860]

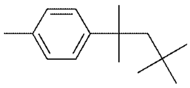
A class of molecules related to dendrimers, but distinct in that the arms are not branched, are star-polymers in which a number of linear polymer arms radiate from a central core, for example, compounds **929** (Chart 30) with three arylene vinylene branches radiating from a benzene core.[1861] The PL from compound **929a** with PPV chains is blue in solution (λ_{max} = 423 nm) and blue-green from the thin film (λ_{max} = 474 nm). The substituted PPV chains in **929b** result in green and blue-green solid-state emission (λ_{max} = 524 and 508 nm, respectively). EL has been obtained from **929b** (λ_{max} = 533 nm) and **929c** (λ_{max} = 520−580 nm).

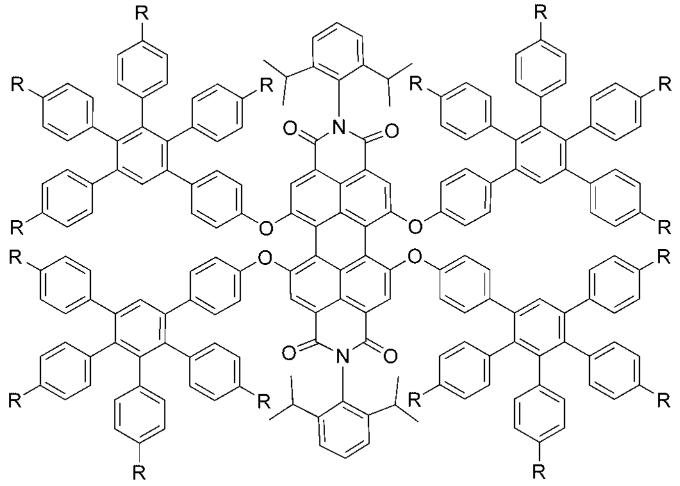
Branched oligophenylenes have been made by Suzuki or Grignard coupling reactions. The emission (λ_{max} = 420−440 nm) from the three-branched materials, e.g. **930**, is blue-shifted compared with that (λ_{max} = 490−496 nm) from the corresponding four-branched compounds, e.g. **931**, with the same number of phenylene rings in each branch.[1862]

Chart 26

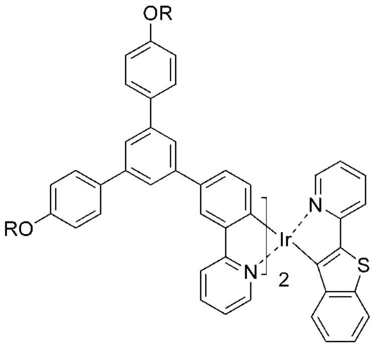


915 Ar =

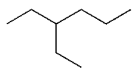


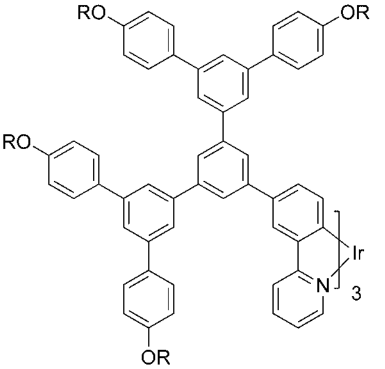


916 R = alkyl

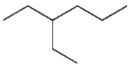


917 R =





918 R =

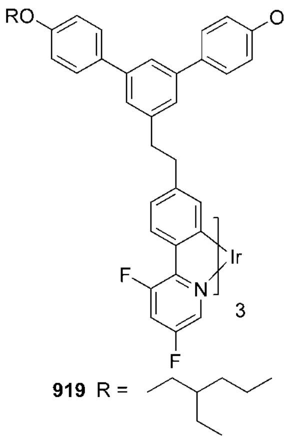


A number of blue emitting molecules have been prepared with oligofluorene chains attached to tetrarylmethane,[1863] tetraarylsilane,[1863] or truxene[1864,1865] cores. By contrast, the emission from the porphyrin-cored starburst material **906c** is red ($\lambda_{max} = 662$ nm).[1866] Blue EL has been obtained from compounds **932a,b** in which oligofluorenes and pyrenes radiate from the corners of a cubic polysilsesquioxane core.[1867,1868] The emission from the molecules **933** with oligothiophenes attached to a truxene core changes from violet-blue ($\lambda_{max} =$ *ca.* 370 nm) to blue-green ($\lambda_{max} =$ *ca.* 480 nm) as the number of thiophenes increases from one to four.[1869] Oxidative coupling of the monothienyl-substituted compound produces a blue-green emitting hyperbranched material ($\lambda_{max} = 491$ nm).

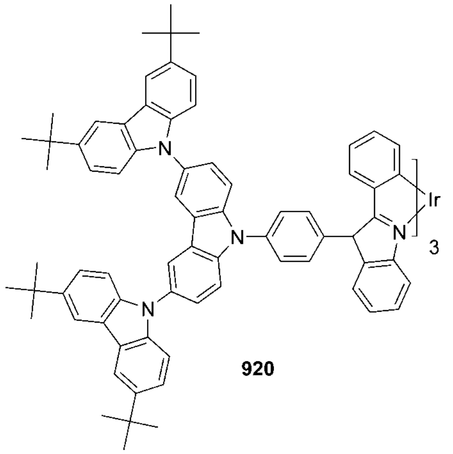
4.3. Polymers with Luminescent Side-Chains

Polymers can be prepared in which luminescent moieties are pendant to the polymer chain. Although these are not strictly conjugated polymers, the supermolecular organization of the polymer backbone can allow pendant electroactive substituents to interact sufficiently to allow the polymer to behave as a semiconductor. The pendant polymers may be prepared either by polymerization of monomers containing the chromophore or by attaching chromophore units to an existing polymer chain. This approach has the advantage of producing polymers where the chromophore is well defined and also enables the utilization of the considerable body of expertise developed in classical polymer synthesis to control the physical properties of the polymer. As the chromophores used are usually of fairly short conjugation length, this method is particularly attractive for the synthesis of blue emitting polymers.

In the simplest case, the chromophore is a polycyclic aromatic or heteroaromatic moiety. For example, poly(*N*-vinylcarbazole) (PVK, **934a**) in addition to being useful as a hole-transporting layer in LEDs, has also been used as an emissive layer. Kido et al.[1870] obtained bright violet-blue ($\lambda_{max} = 410$ nm) emission from a trilayer device using PVK as the emissive material and a 1,2,4-triazole compound



919



920

and Alq$_3$ as electron-transport layers. A single-layer PVK device is reported to give slightly red-shifted (λ_{max} = 426 nm) emission, which may reflect differences in internal absorption within the devices.[1871] Exciton emission at 618 nm has also been observed and was removed by blending with anthracene.[1872] The EL efficiency of PVK is reported to be increased by up to 3 orders of magnitude by doping with an ammonium salt.[1873] Substituted PVKs have also been studied. Sulfonation of PVK is reported to lowered the PL efficiency, without changing the emission spectrum markedly.[1874] Halogenated PVKs show more complex spectra, with the monohalopolymers **934b** and the dibromopolymer **934c** showing a second broad emission maximum around 550 nm, and the dichloropolymer **934d** displaying a broad emission spectrum with almost white emission.[1872,1875] These effects are attributed to excimer formation. This illustrates a potential problem with these types of polymers; the difference between the alkyl backbone and the conjugated side groups may lead to aggregation of the latter.

Gaudiana and co-workers[1876,1877] have constructed devices with the blue-green (λ_{max} = 500 nm) emitting polysiloxanes **935a**,**b** and yellow-green (λ_{max} = 521 and 535 nm, respectively) emitting poly(methyl methacrylate)s (PMMAs) **936a**,**b**. Efficiencies of 0.01% were obtained with ITO and Al electrodes. Addition of an oxadiazole compound as an electron-transporting layer increased the efficiency to 0.1%. Compounds **935b** and **936b** containing carbazole moieties illustrate how easily emissive and charge-transporting units can be combined in a single polymer.

The polymethacrylate **937**, as well as showing blue (λ_{max} = 405 nm) electroluminescence, possessed hole-transporting properties due to the triarylamine groups, and a device ITO/**937**/**935a**/Al gave blue-green light from **935a** with an efficiency of 0.2%.[1878] Polystyrenes with similar diarylaminobiphenyl substituents have been used as hole-transporting materials in OLEDs.[1879] Coumarins are well-known blue-green emitting laser dyes, and electroluminescent PMMAs **938** bearing them have been reported. A group at Thomson-CSF have obtained green (λ_{max} = 524−536 nm) emission from polymethacrylates and polystyrenes bearing naphthalimide chromophores, e.g. **939**.[1880−1883] Similar polymers **940** bearing anthracene chromophores are blue (λ_{max} = 460 nm) emitting.[1880] Green EL (λ_{max} = 521 nm) has been reported from the polystyrene **941**.[1879] Copolymer **942** formed by Williamson ether condensation of 9-chloromethylanthracene and poly(styrene-*co*-*p*-acetoxystyrene) gives red emission (λ_{max} = 590 nm).[1884] Poly(*p*-vinylpyridine) **943** forms gels in pyridine which show very unusual PL behavior, with the emission color depending on the excitation wavelength. Thus, excitation at 395, 455, and 557 nm produces blue (λ_{max} = 477 nm), green (λ_{max} = 527 nm), and red (λ_{max} = 585 nm) PL emission, respectively.[1885,1886] Partial protonation gives a soluble polycation which forms self-assembled layers with PSS. These show blue PL (λ_{max} = 425 nm) and very weak green EL (λ_{max} = 550 nm).[1887] These materials illustrate the range of colors available from polymers with such simple chromophores, but their relatively low efficiencies make them unsuitable for commercial applications.

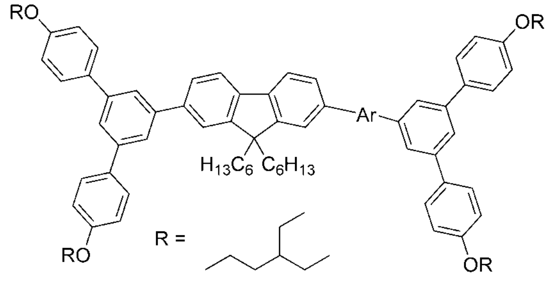
More commonly, the chromophore is an oligoarylene or oligo(arylene vinylene). Heck coupling of a brominated polystyrene copolymer with 4-vinyl-*trans*-stilbene gives a polymer **944a** with distyrylbenzene side-chains which shows blue (λ_{max} = 460 nm) emission.[1888,1889] Polymers **944b** with longer side-chains have been made by the same method and also used to make blue emitting LEDs.[1890] Similar polymers **945** and **946** have been prepared by radical polymerization of the monomers.[1891,1892] Similarly, coupling of *p*-chloromethylstilbene with poly(*p*-acetoxystyrene) and poly(*p*-acetoxystyrene-*co*-styrene) gives polymers **947a**,**b** with emission maxima at 450 nm.[1893−1895]

A cyanostilbene-substituted polyurethane **948** shows green EL (λ_{max} = 540 nm).[1896,1897] Replacement of the cyano with a coumarin substituent as in polymer **949** produced a considerable bathochromic shift to give orange-red emission (λ_{max} = 630 nm).[1896] The solid state PL from the copolymers **950** is dependent upon the amount of the emissive chromophore attached.[1898] Thus, copolymers with 2, 8, and 49 wt % of chromophore display blue, blue-green, and yellow emission (λ_{max} = 455, 476, and 528 nm, respectively), which is due to the increasing amount of aggregation of the emissive side-chains.

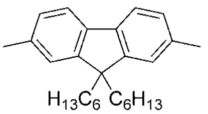
Polystyrenes **951** with diphenylanthracene chromophores made by controlled radical polymerization show blue PL (λ_{max} = *ca*. 425, 440 nm).[1899] The emission from the copolymers **951a** is reported to be stronger than that from homopolymer **951b**. Khanna and co-workers[1900,1901] have prepared polymers with terthiophene **952** and terphenylene **953** units pendant to a polyethylene chain, which show strong blue-green luminescence. Attachment of oligothiophenes to a polymethacrylate chain gave polymers **954** which could be oxidatively cross-linked to give insoluble materials containing quater- and sexithiophene chromophores.[1902,1903]

As already mentioned, a significant advantage of this type of polymer is that it is easy to make by simple copolymerization of monomers with charge transport and emissive

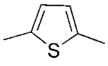
Chart 27

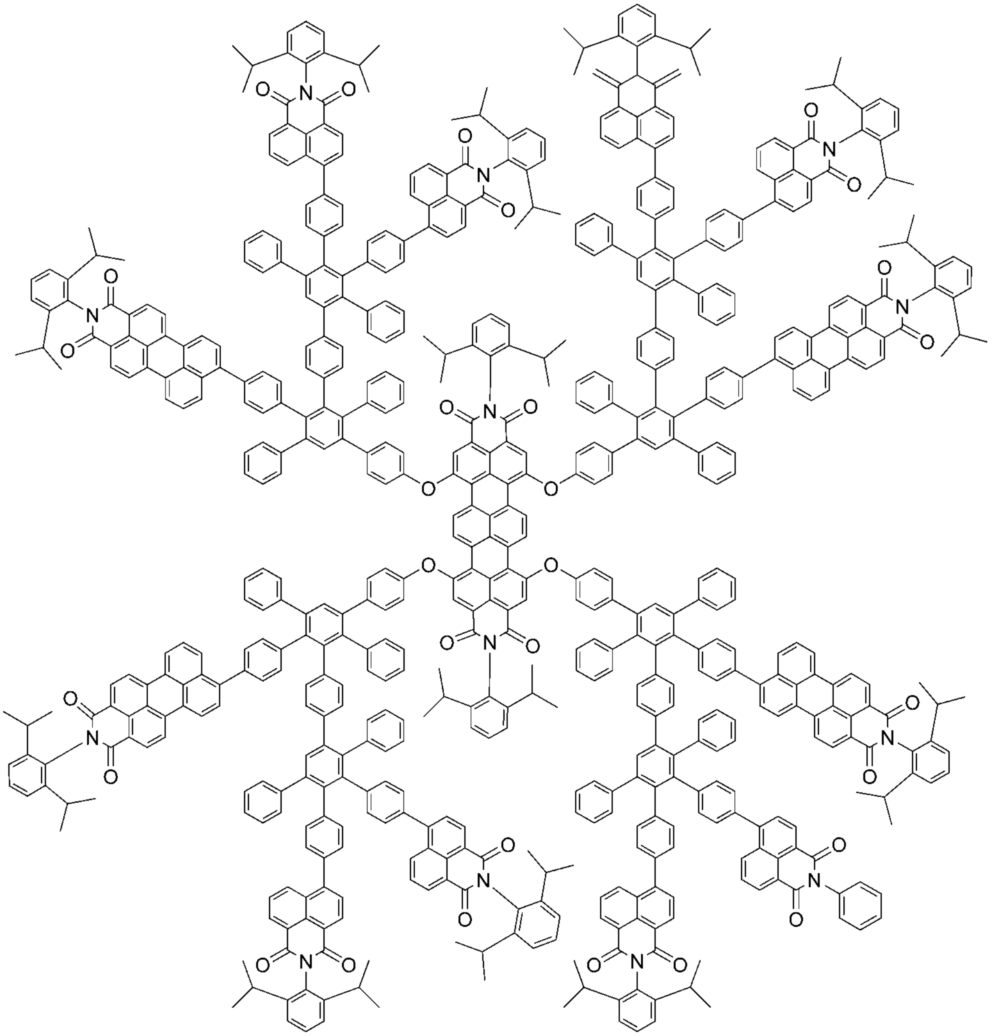


921a Ar =



921b Ar =

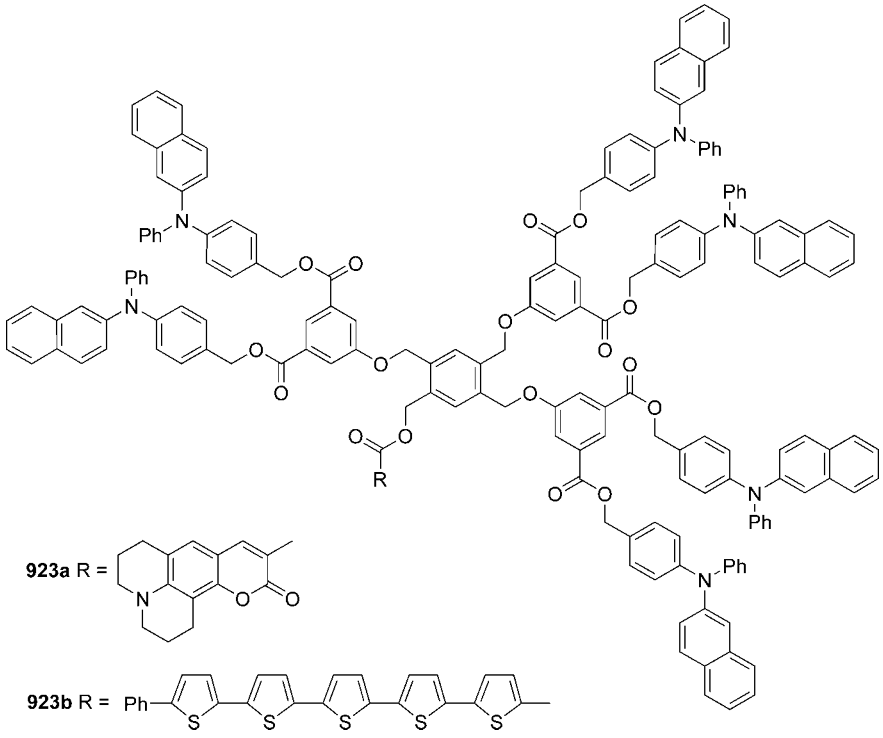




922

substituents, polymers containing both emissive and charge transporting moieties. Importantly, the charge transporting units do not affect the optical properties of the emissive units. Thus, the Cambridge group prepared polymethacrylate copolymers **955a** bearing diaryloxadiazole charge transport and distyrylbenzene emissive units as side-chains.[180,617,1807,1904] Bilayer devices with **955a** as the emissive material and PPV as a hole-transport layer showed blue emission ($\lambda_{max} = 457$ nm) (with a tail in the yellow-green region due to emission from PPV) but with a very low efficiency of 0.037%. The analogous polymer **955b** with no electron-transporting side-chains gave only short-lived nonuniform emission due to poor charge mobility. Blending polymer **955b** with polymers **956a,b** bearing diaryloxadiazole side-chains improved the electron transport, so that a bilayer device with PPV showed uniform green emission with a spectrum resembling that of

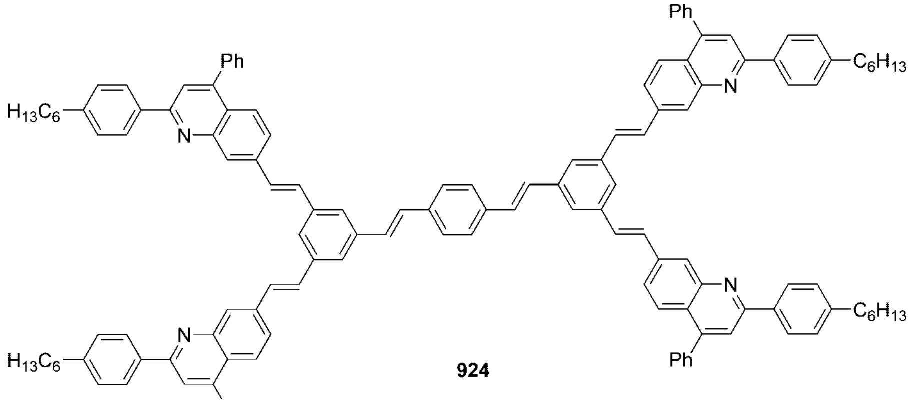
Chart 28



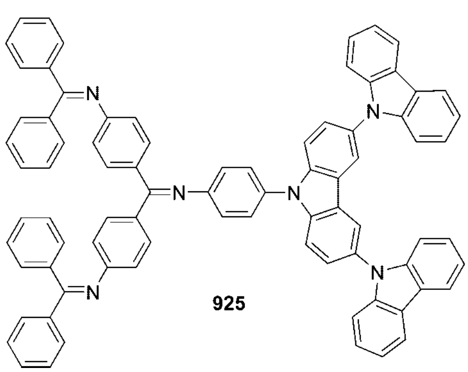
923a R =

923b R =

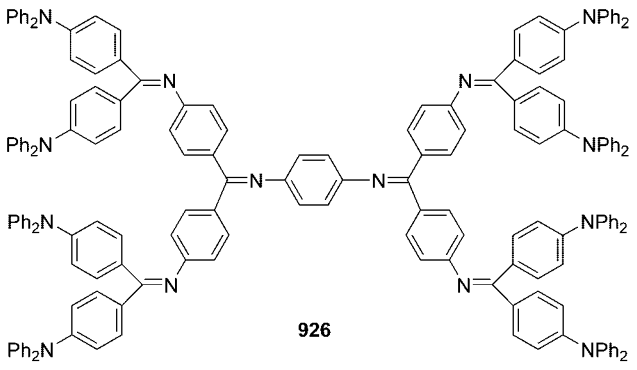
Chart 29



924



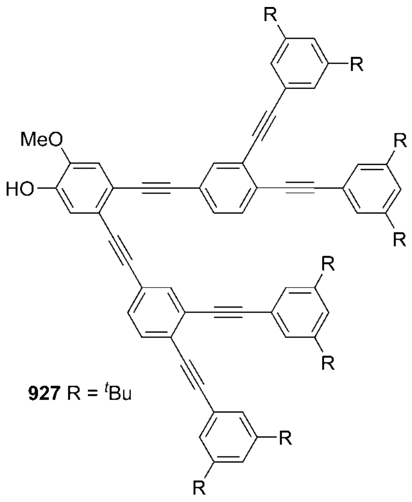
925



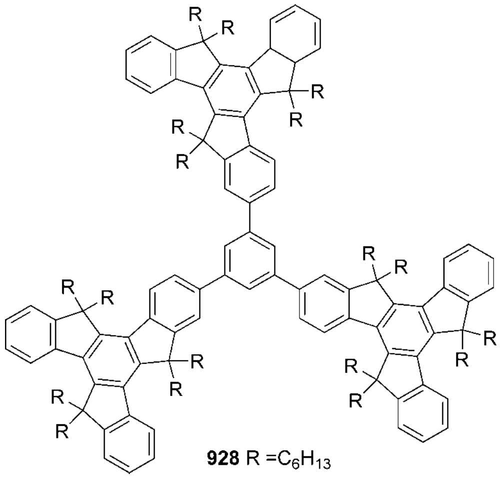
926

PPV, but with marked enhancement of the higher energy peak at 505 nm.

Polymers **955**−**956** are not very stable, degrading on storage, upon photoexcitation, and during device operation. A more stable material has been obtained by cross-linking a polymer **957** containing cinnamoyl groups.[617,1905] Polymethacrylate **956c** in which the diaryloxadiazole units act as both emissive and electron transporting units shows blue PL (λ_{max} = 450 nm), but the EL (λ_{max} = 450, 530 nm) contains an extra emission band at 530 nm which is attributed to aggregation of the chromophores.[1906] The emission maximum of the copolymers **958** red-shifts slightly from 440 to 446 nm as the amount of chromophore increases from 0.5 to 8 mol %.[1907] The highest EL intensity was observed from the 1% copolymer (**958**; m = 1 mol %) but was still too low for viable applications.



927 R = ^{t}Bu



928 R = C_6H_{13}

Lee et al.[1908] have prepared polymethacrylates **959** with carbazole hole-transporting and phenylene vinylene emissive units. Blue-green (λ_{max} = 475 nm) emission was obtained from **959a**. Cyano-substitution of the vinylene units in an attempt to improve the electron affinity caused a red-shift in emission so that the monocyano polymer **959b** produces yellow-green (λ_{max} = 532 nm) emission. The dicyano-substituted polymer **959c** displays yellow PL (λ_{max} = 526 nm) but orange-red EL (λ_{max} = 603 nm), presumably due to excimer formation. The cyano-substituted polymers **959b,c** also show lower quantum efficiencies and higher turn-on voltages than **959a**, which indicates that the charge injection has not been improved compared with the case of **959a**. Similar EL properties have been observed for copolymers **960a** with a mixture of carbazole and emissive substituents[1909] and for blends of PVK with the homopolymer **960b**,[1910] indicating that such copolymers have many of the advantages of blends without the problem of phase separation. In both cases, optimal efficiency was obtained with 0.5 mo% of coumarin units. Bright red EL (λ_{max} = *ca.* 700 nm) with an efficiency of up to 0.67% has been reported from polymers **961** with hole-transporting triphenylamine and red emitting dyes as side-chains on polystyrene.[1911] These efficiencies, while still below those required for commercial applications, do suggest that if sufficiently highly efficient chromophores are chosen, polymers with fluorescent side-chains might be suitable materials for making such devices. One problem may be the insulating backbones which will reduce the conduction of charge.

Both hole and electron transporting units can be incorporated on the same polymer. Bright blue-green (λ_{max} = *ca.* 500 nm) emission has been obtained from polymers **962** and **963** combining emissive naphthalimide and charge transporting carbazole and oxadiazole units.[1912,1913] This approach is not confined to random copolymers but has also been extended to block copolymers.

A triblock copolymer **964** with charge-transporting blocks flanking an emissive block has been made by living radical polymerization of, successively, *N*-vinylcarbazole, a pyrenylalkyl vinyl ether, and 2-chloroethyl vinyl ether, followed by Williamson ether condensation of the chloroethyl units with a hydroxy-substituted diaryloxadiazole. The PL maxima are at 375 and 400 nm, and the EL maximum is at 430 nm. However, the EL efficiency is reported to be low with a high turn-on voltage for a single-layer device suggesting poor charge injection and/or transport.[1914] This might reflect phase separation between the blocks, in which case alteration of the block ratios might produce higher performance. The possibility of controlling phase separation and thus device performance by such means makes this approach worthy of further investigation.

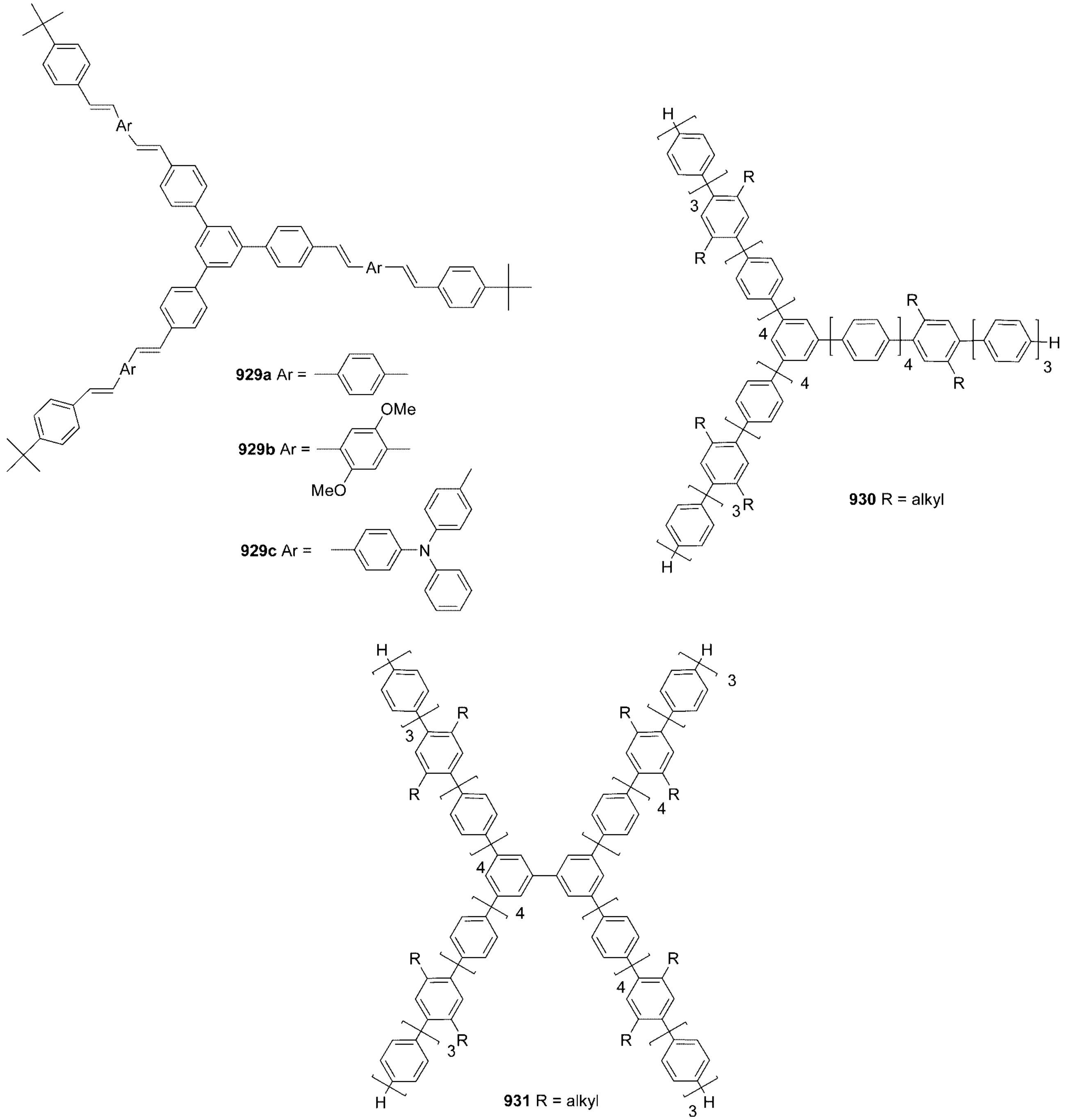
Polymer **965** (Chart 31) bearing electron accepting quinoline units is made by acetylation of polystyrene followed by Friedländer condensation to form the quinoline units.[1915] The PL in solution is pH-dependent, with blue (λ_{max} = 425 nm) emission being obtained from a solution in dichloromethane, while a solution in formic acid displayed green PL (λ_{max} = 509 nm). The solid-state emission is blue (λ_{max} = 435 nm). This material further illustrates the range of synthetic procedures and methods for controlling emission color available, but it is unlikely that its EL efficiency if measured will be any better than that for the polymers discussed already in this section.

Polarized emission can be obtained from polymers with chromophores in the side-chains. Photopolymerization of the reactive mesogen **966** on top of a photoalignment layer gives rise to a green emitting polymer which displays polarized EL with a dichroic ratio of 13:1 for emission parallel/emission perpendicular to the alignment direction.[1916]

Ring opening metathesis polymerization (ROMP) offers a way to make polymers bearing functional side-chains with exceptional control of the molecular weight. Schrock and co-workers[1917] have used ROMP of a norbornene monomer **967** with a distyrylbenzene chromophore attached to produce polymer **968** (Scheme 56), which shows blue EL (λ_{max} = 475 nm) with 0.3% efficiency and a turn-on voltage of 12 V with a calcium cathode. An efficiency of 0.55% was obtained from a blend of **968** and an oxadiazole electron transport material though the turn-on voltage was relatively high at 17 V. Double-layer devices of the configuration ITO/PPV/**968**/Ca showed 0.21% efficiency and a turn-on voltage of 15 V. The lower efficiency appears to be due to absorption of emitted light by the PPV layer, which is supported by the fact that the emitted light is green-blue instead of blue.

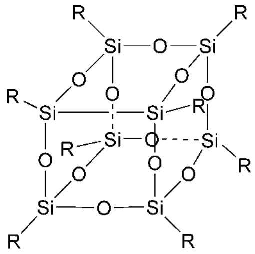
A similar blue emitting (λ_{max} = 410−420 nm) polymer **969** has been made by this method by Ogawa and co-workers.[1918] Using a 1:1 mixture of norbornenes with emissive and charge transporting units gives blue emitting (λ_{max} = 450 nm) statistical copolymers **970**.[1919] The Schrock group have sulfonated the polynorbornene backbone of polymers similar to **968** and **970** with sulfur trioxide to obtain polyanionic species which were used to form self-assembled multilayers, which were tested in single- and double-layer

Chart 30

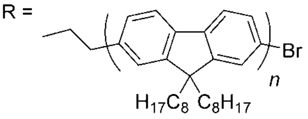


LEDs.[1920] The best EL performance was obtained from a blue-white emitting single-layer device using the sulfonated polymer **971** (Chart 32), but the external EL efficiency was still miserably low (5.4 × 10^{-4} %). The anthracene-susbtituted polynorbornenes **972a,b** display blue-green solid-state PL (λ_{max} = 450 and 470 nm, respectively), but single-layer LEDs produce white EL with an additional red emission band in the red assigned to aggregates.[1921] Blue-green emission was obtained from double-layer devices with an electron-transporting layer. This difference is attributed to the emission occurring at the interface between the layers where the aggregate concentration is low. The corresponding polymers with benzene or naphthalene substituents are violet emitters. Blue-violet EL (λ_{max} = 410 nm) has been reported from polynorbornene **973** with fluorene−carbazole emissive units.[1922] While these polymers are very well defined and their synthesis is elegant, their EL efficiencies are low, probably due to the large amount of insulating material in the backbones.

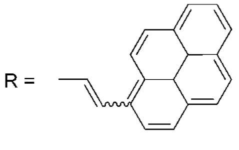
Recently, there has been considerable interest in using phosphorescent metal complexes as emissive side-chains. Thus, PVK copolymers **974a,b** and **975** bearing iridium complexes have been prepared, which respectively produce efficient red (λ_{max} = 620 nm, 5.5% efficiency), green (λ_{max} = 520 nm, 9%), and blue (λ_{max} = 475 nm, 3.5%) EL.[1923] A blend of **974a** and **975** (10:1) emitted white EL with 4.5% efficiency. Efficient green emission has also been obtained from polymers bearing tris(phenylpyridyl)iridium complexes, e.g. **976** (λ_{max} = 512 nm, 4.4%).[1924] Slightly red-shifted PL (λ_{max} = 550−9 nm) is seen in polymers **977**, in which the tether is conjugated with the complex.[1925] Highly efficient LEDs have been made from copolymers **978a** (λ_{max} = 512

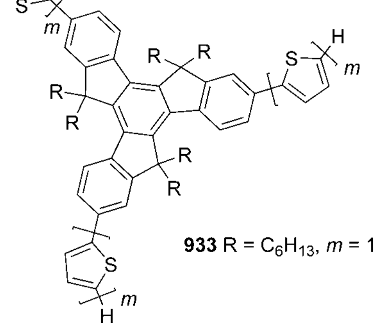


932a R =

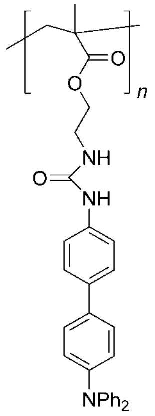


932b R =

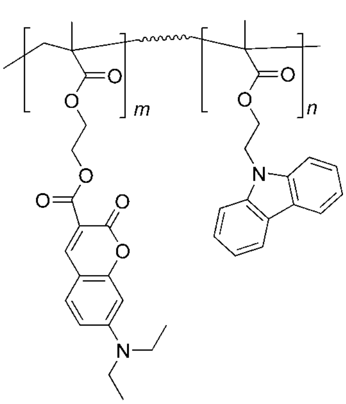




933 R = C_6H_{13}, *m* = 1-4



937



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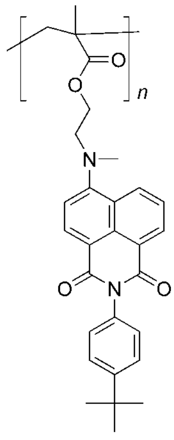

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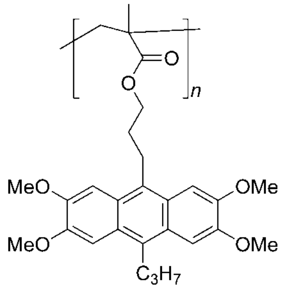
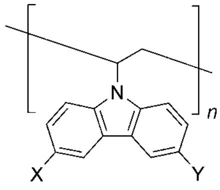
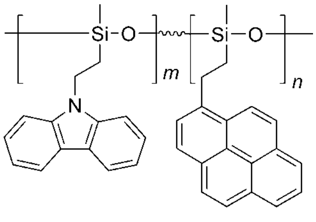


940

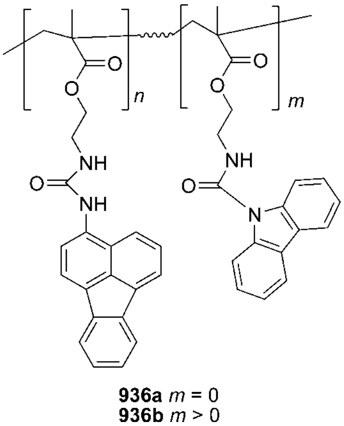
nm) bearing both hole- and electron-transporting units.[1926] The optimal EL efficiency from **978a** was 10.0% with 8 mol % iridium attached, which was slightly lower than that from a blend of **978b** with 8 mol % of untethered iridium complex. Increasing the amount of iridium complex in **978a** to 13 mol % reduced the EL efficiency to 7.3% due to self-quenching. Doping **978b** with a red emitting porphyrin produced white EL with an efficiency of 4.9%. Near-white EL with efficiencies of up to 4.6% has been obtained from copolymers **978c** with a platinum complex attached.[1927] The much higher efficiencies obtainable by using phosphorescent emitters make these polymers the only side-chain chromophore polymers yet reported which would be useful in applications, provided that their stabilities, which have not been reported, are adequate. ROMP has been used to prepare polynorbornenes bearing green or yellow emitting iridium complexes.[1928] Reducing the iridium complex content blue-shifts the emission; for example, the maximum for **979** changes from 550 to 534 nm as *m/n* changes from 0:1 to 20:1. ROMP has also been used to make polynorbornenes and polycyclooctenes **980** bearing ytterbium complexes which emit in the infrared (λ_{max} = 971 nm).[1929] Near-infrared EL (λ_{max} = 790 nm) has also been obtained from polystyrenes **981** bearing ruthenium complexes.[1930] Emissive polymers have also been prepared by attaching yellow emitting iridium complexes (λ_{max} = 540−560 nm) to the ends of polystyrene or poly(ethylene oxide) chains, but as yet there is no report on EL from such materials.[1931] It is likely that the emissive elements will aggregate which could reduce emission efficiency, and with their probably lower concentration of iridium than the side-chain polymers, they are likely to show poorer emission intensities.



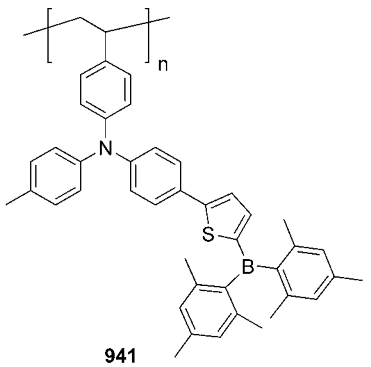
934a X, Y = H
934b X = Br, Cl, Y = H
934c X, Y = Br
934d X, Y = Cl



935a *m* = 0
935b *m* > 0



936a *m* = 0
936b *m* > 0



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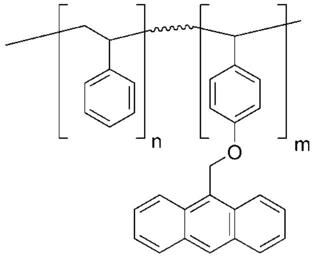

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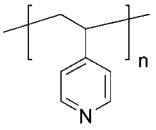

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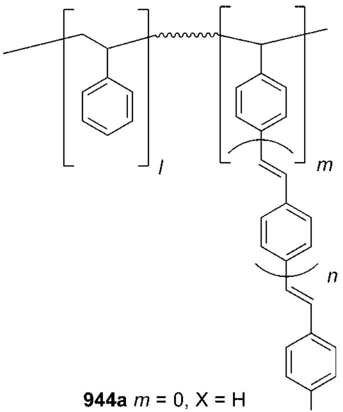
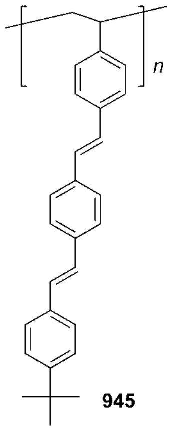


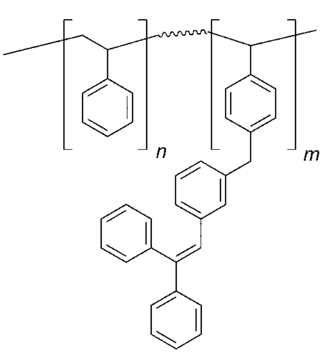
944a *m* = 0, X = H
944b *m* = 0-2, X = Br



945

4.4. Alternating Copolymers with Isolated Conjugated Groups

Alternating copolymers with well-defined chromophores separated by nonluminescent spacer units potentially combine the optical advantages of molecular lumophores (high quantum efficiencies and narrow, well resolved emission spectra) with the processibility of polymers. Such materials have particular potential as a way of obtaining blue light-emitting polymers. As a result, a considerable number of such polymers containing a wide range of chermophores have been prepared by various methods, although to date none of them has shown anywhere near sufficiently high efficiency and stability to make commercially viable devices.



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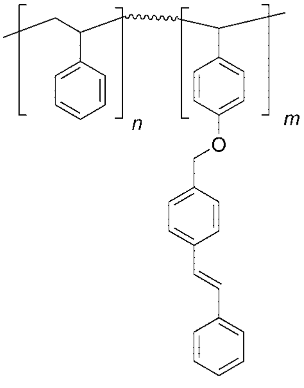
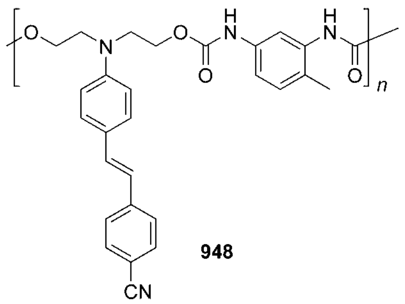
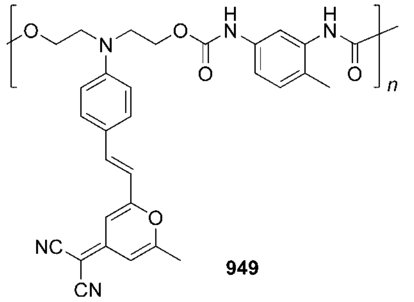


947a x = 0 **947b** x = 2



948



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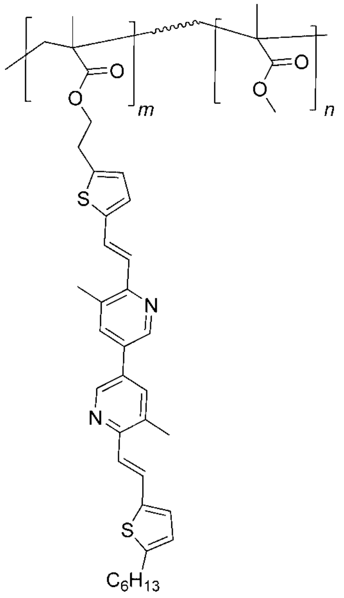
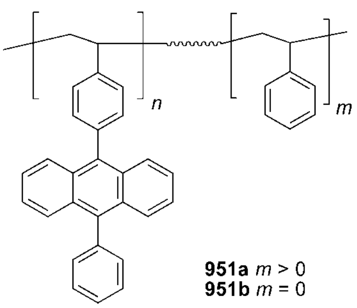


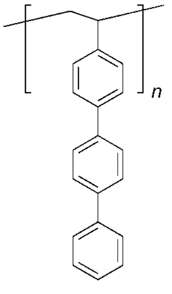
950

Two general synthetic approaches exist. Either the chromophore is prepared as part of the polymerization step, or a substituted chromophore is polycondensed with a suitable linking agent. The first approach is well exemplified by the synthesis of polyethers, e.g. **982a−d**, with distyrylbenzene segments separated by flexible alkyl chains, by a Wittig polycondensation method (Scheme 57) first developed by Karasz and co-workers[1932,1933] and subsequently applied by other groups.[231,444−446,1934−1945] A disadvantage of this method is that a high proportion of the double bonds formed have *cis*-geometry, and to get *all-trans* configuration, the polymers must be treated with iodine, which leads to a loss of material during the subsequent purification step.

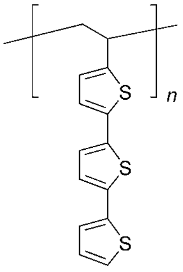
It has been shown that *all-trans* **982a** can be prepared directly by Heck coupling of a diiodobenzene **983** with a divinyl compound **984** (Scheme 58),[1946] and this method has



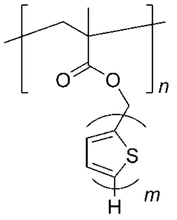
951a $m > 0$
951b $m = 0$



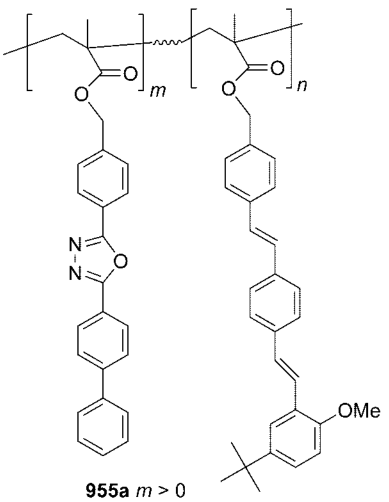
952



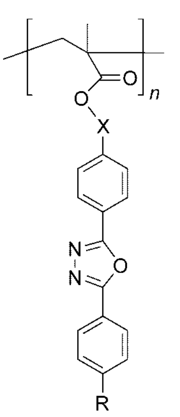
953



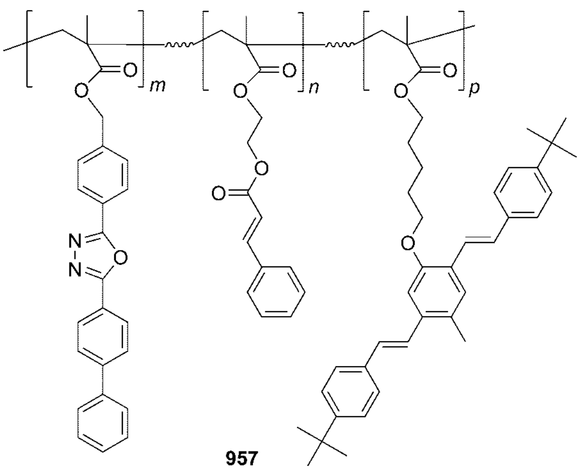
954 $m = 1,2$



955a $m > 0$
955b $m = 0$



956a X = CH_2, R = Ph
956b X = CH_2, R = ^{t}Bu
956c X = NH, R = NMe_2



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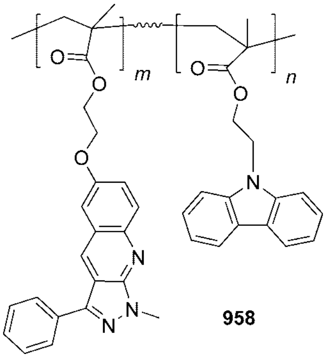
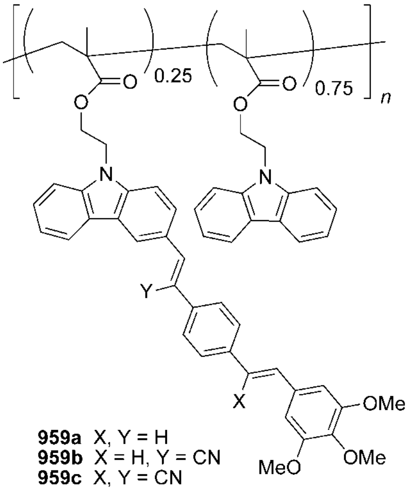


958

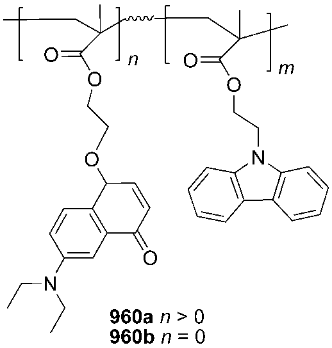
since been used to make other similar polymers.[1947,1948] The second approach of condensing a suitable chromophore with a linking agent offers an alternative route to an *all-trans* material. For example, condensation of *all-trans* bis(4-hydroxystyryl)benzene with polyethylene glycol dimesylate gives *all-trans* polymer **985** ($x = ca.$ 20).[1949]

The mechanical and optical properties of these polymers are dependent on the length of the alkyl spacer. Longer spacers produce a drop in the T_g of **982a**, so that for $x = 12$ it is about 50 °C. The T_g can also be lowered by blending with plasticizers, which is accompanied by a blue-shift in the PL.[1950] Longer alkyl spacers also improve the EL efficiency due to phase separation, leading to increased confinement of the exciton on the conjugated segments. The efficiency of single-layer devices reaches a peak of 0.03% for $x = 10$ and then starts to drop again for longer spacers, as the T_g drops too close to the operating temperature of the devices.[1951] Similarly, polymer **985** with a long ethylene glycol spacer ($x = 20$) shows only short-lived blue EL,[1949] whereas material with a shorter spacer ($x = 3$ or 6) shows stable emission ($\lambda_{max} = 466$ nm).[1952,1953] The use of an Alq_3 electron-transport layer enhances the EL efficiency from 0.1 to 0.5 cd/A.[1953] The emission color can be controlled by varying the substitution patterns. Polymers **982a** with unsubstituted central rings display blue ($\lambda_{max} = 465$ nm) emission.[1954,1955] Polymers **982b** and **982c**, with alkoxy and cyano substituents, produce green emission ($\lambda_{max} = 515$ and 558 nm, respectively),[1936,1938−1940] while the silyl-substituted polymers **982d** show blue-green emission ($\lambda_{max} = ca.$ 495 nm).[231,1934,1935] By contrast, alkyl substituents as in polymer **982e** ($\lambda_{max} = ca.$ 450 nm) produce a slight blue-shift in the emission. In a slight variation of the Wittig methodology, the fluoro-substituted polymers **986** (Chart 33) with alkylidene or ethylene glycol spacers were made by a Horner polycondensation.[1956] The PL maxima in solution are at 463−465 nm for **986a** and at 426 nm for **986b**. The solid-state PL is red-shifted for the former to $\lambda_{max} = 487-501$ nm, indicating some degree of π-stacking. The emission color can also be tuned by varying the effective conjugation length of the chromophore. Thus, the stilbene-containing polymers **987** with a significantly less extended conjugated system than that for **982** show violet−blue emission ($\lambda_{max} = 380-400$ nm, 1%) in $CHCl_3$ and a broad solid state emission (420−520 nm),[1957] while 1 wt % of **988** doped in PVK exhibits blue-green emission ($\lambda_{max} = 497$ nm) with modest EL efficiency.[1958]

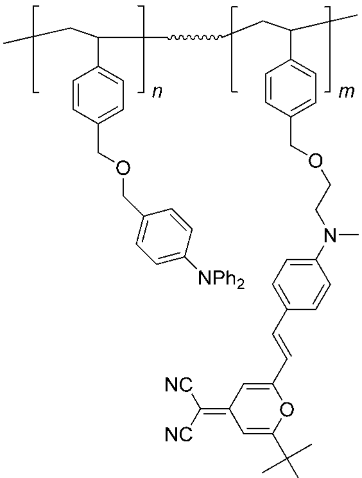
Hay and Klavetter[1959] have prepared copolymers of type **989** by using variable amounts of a flexible chain dialdehyde or diphosphylidene in a Wittig polycondensation. The PL varies from blue ($\lambda_{max} = 460$ nm) to yellow-green ($\lambda_{max} = 550$ nm) with decreasing flexible linker content. Thus, the emission color can be readily tuned by varying the comonomer feed ratio. This method has also been used by a group at Sumitomo to make copolymers **990a** (Chart 34).[444−446] The emission spectra of the homopolymers **77f** and **990b** are very similar ($\lambda_{max} = 534$ and 528 nm, respectively), as are their EL efficiencies, but the fluorescence intensity of polymer **990b** with isolated chromophores is over 13 times



959a X, Y = H
959b X = H, Y = CN
959c X, Y = CN



960a *n* > 0
960b *n* = 0



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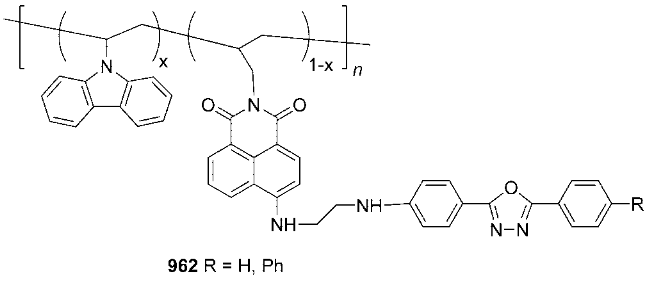
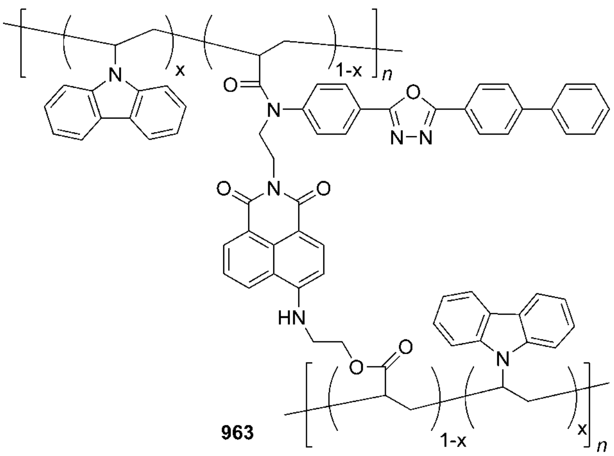


962 R = H, Ph



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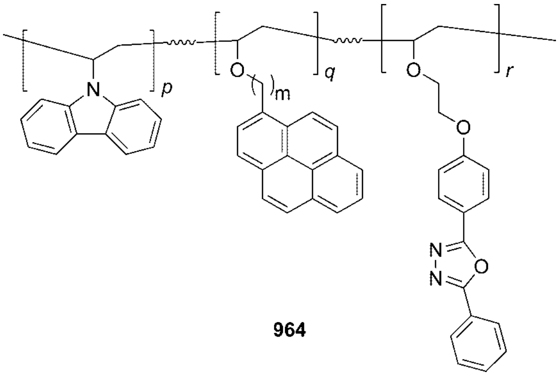


964

higher than that of **77f**, presumably due to exciton confinement hindering nonradiative decay. As the content of spacer in the copolymer decreases, the relative PL intensity also declines, but the EL efficiency initially increases until it reaches a maximum for the 50 mol % copolymer (*m* = *n*). Another way to alter the effective conjugation length is to incorporate *meta*-linkages. Thus, copolymers **991** show violet PL ($\lambda_{\max}$ = 399−416 nm).[1960] However, their EL emission is blue ($\lambda_{\max}$ = 471−489 nm). Copolymer **992** displays emission only from the alkoxy-PPV units due to energy transfer from the larger to the smaller band gap chromophores.[1961]

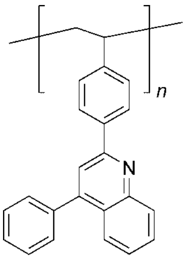
Other arylene vinylene chromophores can be incorporated by the above methods, as demonstrated by polymers **993a** (PL, film; $\lambda_{\max}$ = 447 nm),[710] **993b** (PL, film; $\lambda_{\max}$ = 480 nm),[1962] **993c** (PL, film; $\lambda_{\max}$ = 470 nm, 32%),[1963] **994** (PL, film; $\lambda_{\max}$ = 496 nm),[1964] **995** (PL, film; $\lambda_{\max}$ = 493 nm),[1943] and **996** (PL, film; $\lambda_{\max}$ = 511 nm).[1948]

Copolymers **997a,** prepared by condensation of 9,10-bis(4-acetoxystyryl)anthracene with 1,*ω*-dibromoalkanes polymers, show yellow PL ($\lambda_{\max}$ = 580 nm) in solution with, depending upon the chain-length, a slight red- ($x = 7$) or blue-shift ($x = 12$) in the solid-state spectrum.[1965] This variance presumably reflects differences in the degree of polymer interchain interactions due to variable degrees of phase separation. The PL maximum of the methoxy-substituted polymers **997b** shows a slight hypsochromic shift with increasing chain-length from $x = 4$ ($\lambda_{\max}$ = 583 nm) to $x = 12$ ($\lambda_{\max}$ = 578 nm).[689] The EL maximum for the latter is at 574 nm.

Polymers such as **998** have been made with crown ether units as spacers.[1941,1942] Spacers, such as the ethylene oxide units in polymers **985**, make these materials suitable for use in LECS (see section 6.3).

Aryl or alkyl−aryl ether spacer groups have also been used. The use of an arylene spacer unit in polymers such as **999a** (PL, film; $\lambda_{\max}$ = 413 nm) or **999b** (PL, film; $\lambda_{\max}$ = 533 nm), made by the Wittig method, leads to higher T_g values than those for the corresponding polymers containing a polyalkyl spacer.[1966] Emissive poly(aryl ether)s such as **1000a** or **1000b** (PL, film; $\lambda_{\max}$ = 462−465 nm) can be

Chart 31



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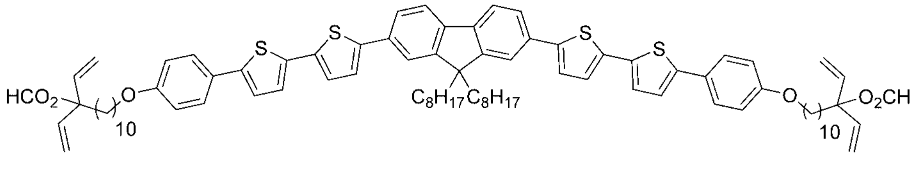


966

prepared by polycoupling of emissive bisphenols with aryldifluorides.[1967]

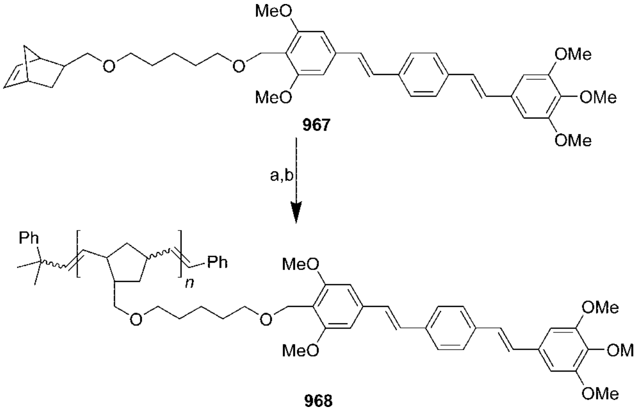
The above methods have also been used to make a considerable number of polymers showing green or blue fluorescence, which contain arylene vinylene chromophores with a variety of other nonconjugated linkages. These materials generally behave much like the polyethers described above, and with a few exceptions, they will not be further discussed in detail. Materials with ester,[1888,1968−1975] amide,[1972,1974,1976−1978] imide,[1979] carbonate,[1980] or urethane[1981−1983] linkages are usually made by the condensation of a chromophore with a linker group. Polymers with alkane,[628,1984] stannane,[1985] or sil(ox)ane[749,751,1986−2006] linking groups, however, are generally made by the Wittig, Heck, or Horner routes. For a review on the synthesis and uses of polymers with alternating organosilicon and conjugated units, see ref 2007. Other synthetic methods have also been used to make polymers with isolated arylene vinylene chromophores. Polymers **1001a,b** with adamantyl spacer groups are made by Suzuki coupling of the bisboronic acid **1002** with the appropriate bis(*p*-bromostyryl)arylene.[1984] They show blue ($\lambda_{\max}$ = 470 nm) and green ($\lambda_{\max}$ = 516 nm) EL.

A new route to silyl linked polymers with arylene vinylene chromophores developed by Luh and co-workers[1992,1996,2001,2008] uses the polyhydrosilylation of diethynylarenes (Scheme 59). The polymers are blue or blue-green emitters ($\lambda_{\max}$ = 420−496 nm). A blend of polymer **1003** with PVK shows voltage-dependent emission tunable from $\lambda_{\max}$ = 516 nm at 18 V to $\lambda_{\max}$ = 496 nm at 26 V.[1996,2001] These rather high operating voltages may reflect poor charge transport in these systems. The related polymer **1004** displays a broad EL spectrum with a maximum at 520 nm.[2009]

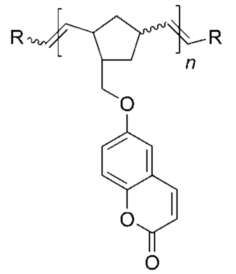
Copolymers **1005**, in which the chromophores are linked via the pyridinium nitrogens, are prepared by polycondensation of the bis(pyrenium salt) **1006** with diamines (Scheme 60).[2010] These materials show violet-blue PL in solution ($\lambda_{\max}$ = 409−416 nm) and blue PL in the solid state ($\lambda_{\max}$ = 454−471 nm). The similar polymers **1007** (Chart 35) show an even bigger red-shift between the solution ($\lambda_{\max}$ = 408 nm) and the solid-state ($\lambda_{\max}$ = 516−523 nm) PL.

Silane **1008** shows two EL emission bands—one in the blue ($\lambda_{\max}$ = 420 nm) and one in the yellow ($\lambda_{\max}$ = *ca.* 580 nm) region—possibly due to exciton formation, and at operating voltages above 12 V, the emission becomes nearly white.[1990,1991,1995,1999] White EL has been seen from copolymer **1009** at higher operating voltages due to the appearance of an extra band in the red part of the spectrum which was attributed to charge transfer complexes since it was not seen in the PL spectrum.[2011]

Scheme 56. Synthesis of a Polynorbornene with Chromphore Side-Chains by ROMP: (a) $Mo(=CHMe_2Ph)(=NAr)(^tBuO)_2$; (b) PhCHO



The emission color of silane **1010** is molecular weight dependent. Synthesis by the Horner method produced higher molar mass material than that which was obtained by the Wittig method. Interestingly, both materials showed blue PL in solution with an emission maximum at $\lambda_{\max}$ = 442 nm, with a strong shoulder at 418 nm for the lower molar mass material. Their solid-state PL spectra, however, were quite



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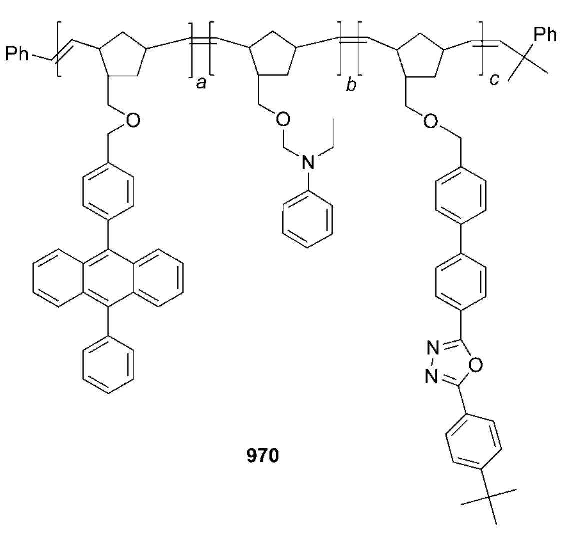

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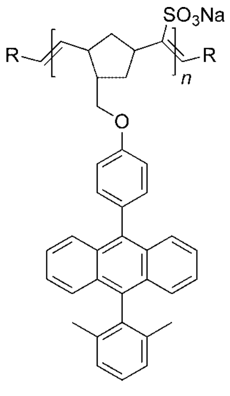
Chart 32



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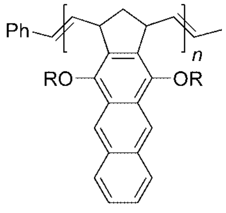
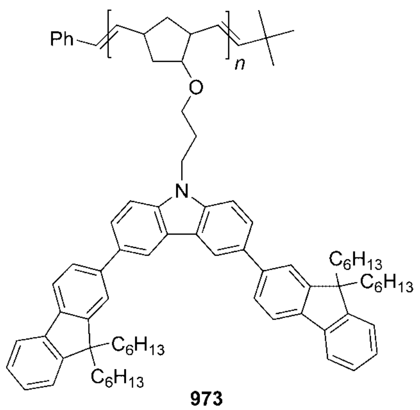


972a R = CH_3
972b R = 2-ethylhexyl



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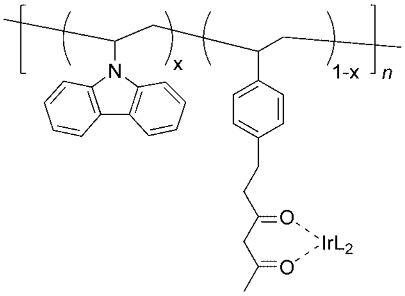
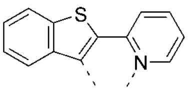
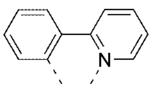
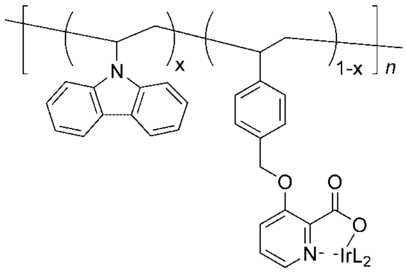


974a L =

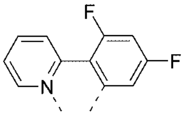


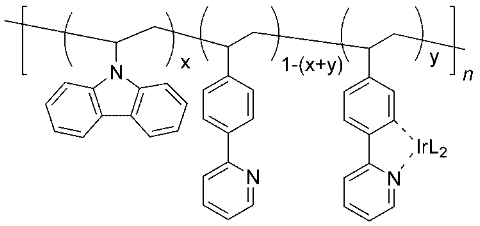
974b L =



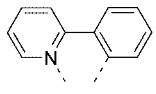


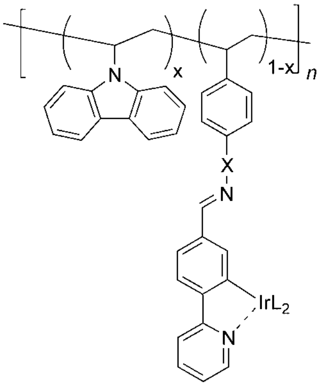
975 L =



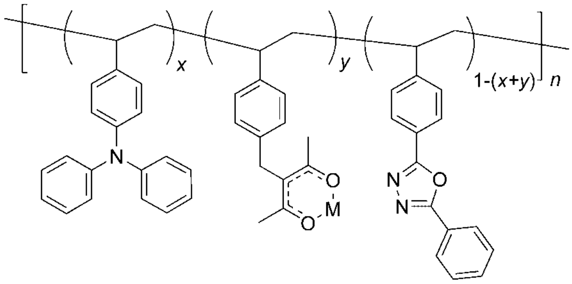


976 L =



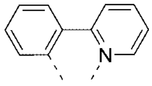


977 X = CH_2, $CH_2NC_4H_8$



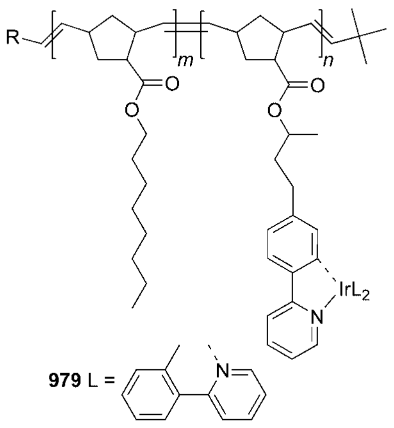
978a $y > 0$ M = IrL_2
978b $y = 0$
978c $y > 0$, M = PtL

L =



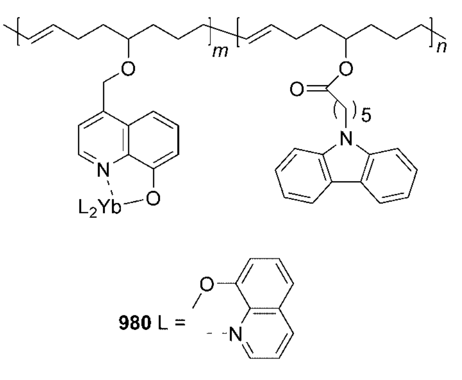
different with maxima at $\lambda_{max} = 524$ nm and $\lambda_{max} = 479$ nm for the higher and lower mass materials, respectively.[1997] This difference has been explained as being due to the longer molecular chains allowing more highly ordered molecular alignment in the solid state, resulting in stronger intra- and interchain interactions.

Polarized emission ($\lambda_{max} = 460$ nm) has been obtained from films of the liquid crystalline polyester **1011** (Chart

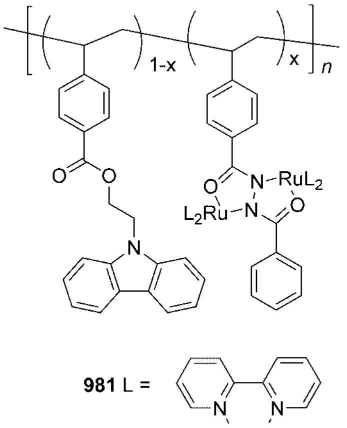


979

Statistical copolymer



980



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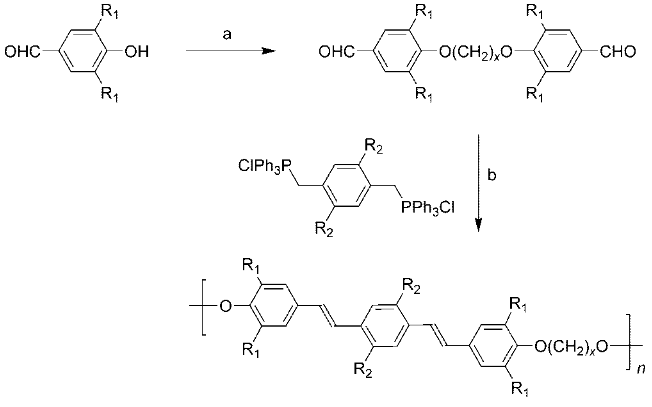
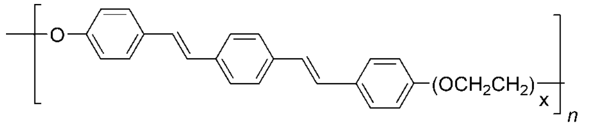
Scheme 57. Wittig Route to Copolymers with Isolated Chromophores: (a) $Br(CH_2)_xBr$, K_2CO_3; (b) KO^{t}Bu, DMF



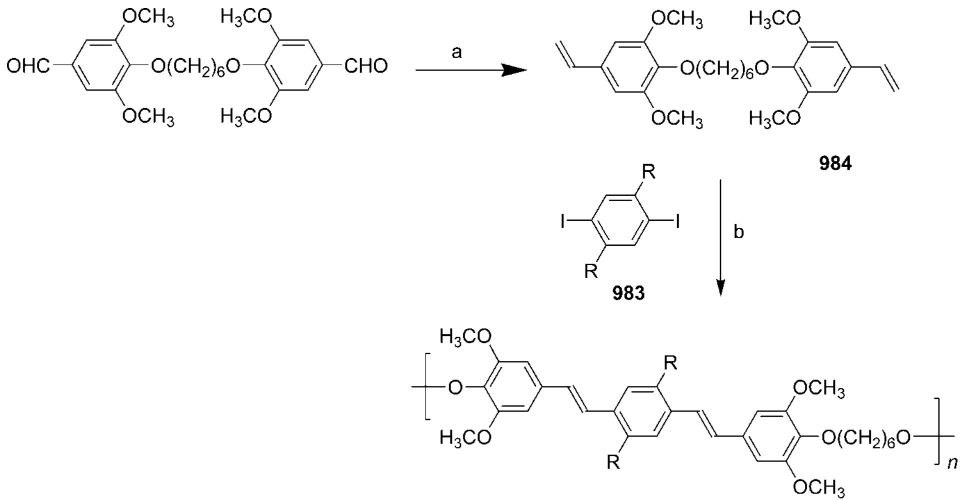
982a R_1 = OMe, R_2 = H, x = 6
982b R_1 = R_2 = OMe
982c R_1 = OMe, R_2 = CN
982d R_1 = H, R_2 = $SiMe_3$



985

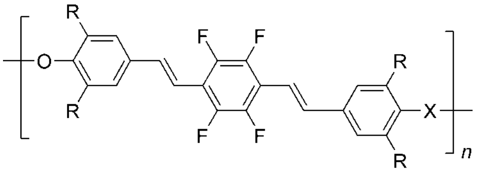
36) deposited on rubbing-aligned polyimide.[1971,1975,2012−2015] Polyimides, e.g. **1012**, prepared by polycondensation of 2,5-bis(4-aminostyryl)pyrazine with alicyclic or aromatic tetracarboxylic dianhydrides, show weak orange-red EL (λ_{max} = 550−565 nm).[2016] Since the emission from distyrylpyrazines is green or blue,[2017] this emission must come from an excimer, suggesting that phase separation leading to stacking of the π-systems is occurring. The pyrazine-containing copolymer **1013** with cyclotriphosphazene linkers, made by Heck coupling, shows yellow solid-state PL (λ_{max} = 545 nm).[2018] Red emission (λ_{max} = 613 nm) has been obtained from copolymers **1014** containing emissive metal complexes.[2019] Laser-deposited films of the bisacrylate **1015** can be photocross-linked to give an insoluble film which shows green EL (λ_{max} = *ca.* 530 nm).[2020] Polymer **1016**, made by Heck coupling, is interesting in that the spacer group is itself fluorescent (blue-violet), but owing to energy transfer the PL emission comes solely from the arylene vinylene moieties

Scheme 58. Heck Route to Polymers with Isolated Chromophores: (a) CH_3PPh_3Br, BuLi; (b) $Pd(OAc)_2$, P(*o*-tolyl)$_3$, $(C_2H_5)_3N$, DMF

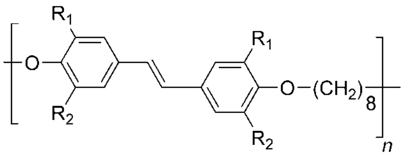


982a R = H
982e R = alkyl

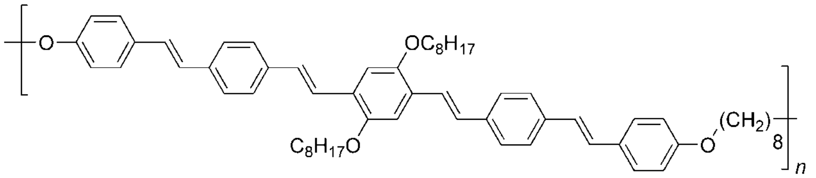
Chart 33



986a R = OMe, X = O$(CH_2)_x$
986a R = Me, X =$(OCH_2CH_2)_x$



987 R_1, R_2 = H, OMe



988

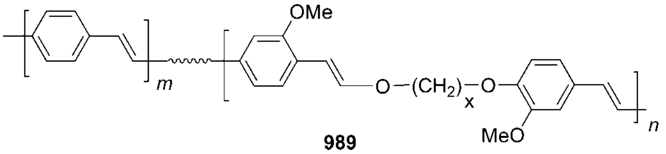


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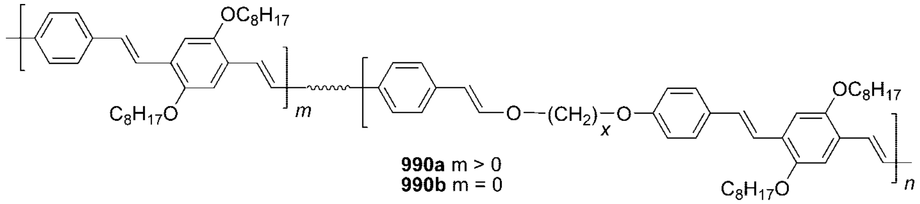
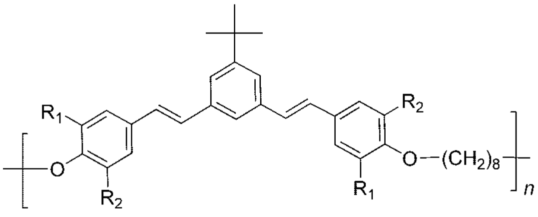
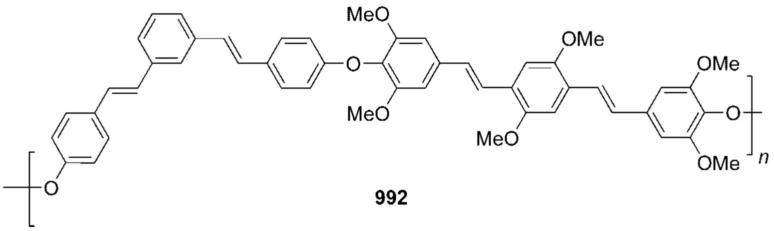
Chart 34



990a m > 0
990b m = 0



991 R_1, R_2 = H, alkyl, alkoxy

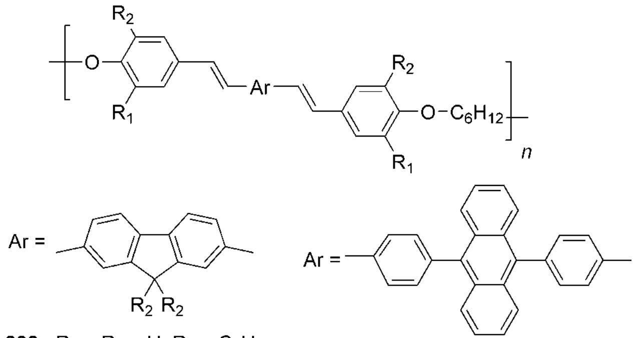


992

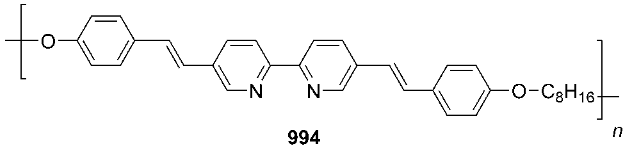
(λ_{max} = 440 nm).[2021] The EL maximum is red-shifted by about 30 nm compared with the PL.

The color of emission can sometimes be tuned by varying the spacer. For example, polymers **1017a** and **1017b**, with ether and sulfide links, have been made by the Wittig method.[2022] The EL emission from **1017a** is blue-shifted (λ_{max} = 505 nm) compared with that from **1017b** (λ_{max} = 525 nm). Reduction of the carbonyl linkage in polymer **1017c**, made by Horner polycoupling, to alcohol **1017d**, produces a blue-shift in the PL emission from λ_{max} = 486 nm to λ_{max} = 447 nm.[2023] The EL from **1017c** and **1017d** is described as being green and blue, respectively.

One problem with polymers having nonconjugated units in the backbone is that these units can hinder charge transport so that the operating voltage for devices using them is frequently higher than that for fully conjugated materials. One way to overcome this is to incorporate charge transporting units into either or both of the emissive and spacer units. Copolymers **1018a−c** have been made by the Wittig method.[2024] They all show blue-green EL (λ_{max} = 480−509 nm) and are also suitable materials to be used as electron transporting layers. The EL properties of **1018a** vary with the length of the spacer. With long spacers (x = 8, 10), only blue-green EL is seen, but with a short spacer (x = 3), the emission becomes voltage dependent.[2025] Up to 15 V, the emission is blue-green, but at 25 V, it becomes nearly white due to the appearance of a band at λ_{max} = 586 nm, which is attributed to an exciplex. In double-layer devices using **1018a** (x = 8) with an underlying PPV, the EL spectrum is dependent upon the thickness of the emissive layer.[2026] With thinner films of **1018a**, some emission occurs from the PPV which has been attributed to interfacial energy transfer. Polymers with oxadiazoles in the spacers units, e.g. **1000b**, have been made by various routes.[1967,2027−2032] Polymers **1019a,b** have been made by the Horner route.[2027] Their PL emission (λ_{max} = 459 and 466 nm, respectively) is very slightly blue-shifted compared with those of the corresponding polymers **1019c,d** (λ_{max} = 466 and 469 nm, respectively) without the oxadiazole units, but their PL efficiencies are significantly higher (40% and 37% for **1019a,b**, vs 29% and 23% for **1019c,d**, respectively) and their electron affinities as measured by cyclic voltammetry are higher. Other electron-accepting units such as cyano-substituted oligophenyls[1967,2031] or triazoles[821,2032,2033] have also been incorporated into



993a $R_1 = R_2 = H, R_2 = C_6H_{13}$
993b $R_1 = R_2 =$ OMe, $R_2 = C_2H_5$
993c R_1 = OMe, R_2 = H



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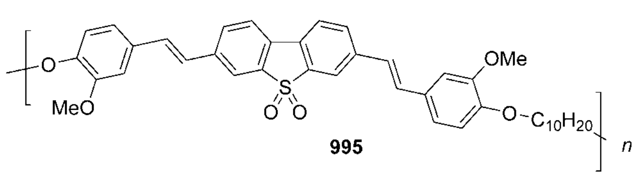

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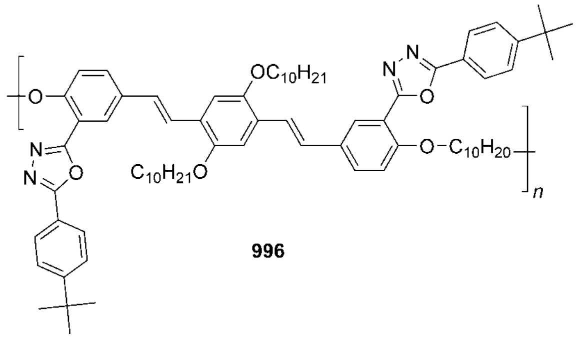

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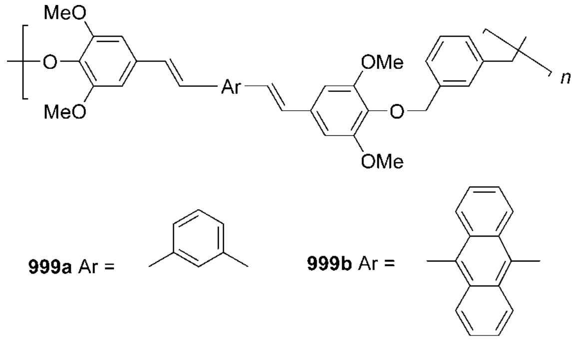
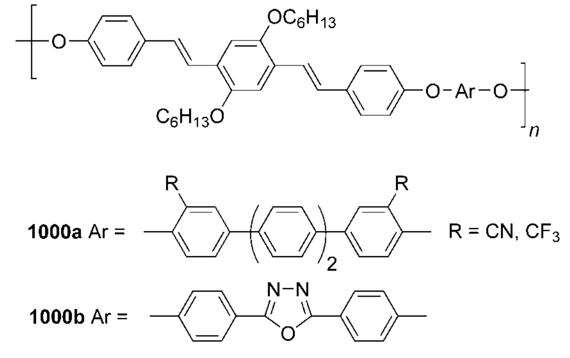
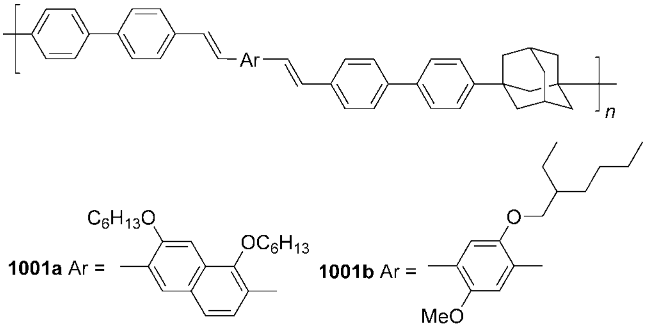
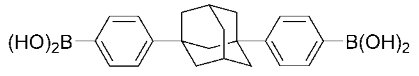




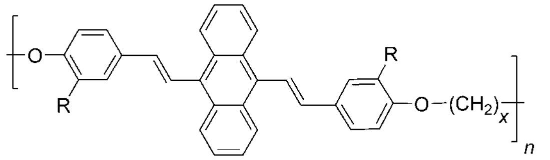




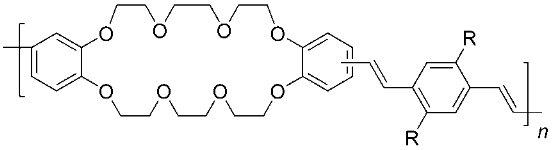
1002

spacer units. Polymers **1020a–d** containing octafluorobiphenyl units show blue to blue-green EL ($\lambda_{max} = 458-494$ nm), but with very low efficiency, due to the electrons becoming trapped on the fluorinated segments.[2034–2036]

Several similar polymers have been prepared combining arylene vinylene moieties with hole-transporting arylamines incorporated into either or both spacer and emitter units.[428,441,766,767,1961,2023,2037–2055] For example, Tsutsui and co-workers have made polymer **1021** (Chart 37) with triarylamine hole-transporting units in the spacer whose emission is blue-green ($\lambda_{max} = 488$ nm),[2038] whereas a similar polymer **1022a** with the triarylamine in the chromophore is a green ($\lambda_{max} = 520$ nm) emitter.[2039] This further demonstrates, how as already mentioned in section 2.6 above, unlike the oxygen bridges in **982**, the nitrogen bridges in TPA units appear not to block conjugation, so that the chromophore in **1022a** is much longer and thus red-shifted in emission, compared with that in **1021**. Copolymer **1022b** with a bisstyrylanthracene chromophore gave red ($\lambda_{max} = 600$ nm) emission with very similar EL characteristics to those of the molecular bisstyrylanthracene chromophore.[2040,2056,2057] One effect of the triarylamine units is to lower the onset voltages for these polymers; for example, polymer **321a** shows green EL with an onset voltage of only 2.6 V, compared with 17 and 11 V for **1022a,b**, respectively.[2023] Another effect is to lower the PL efficiency due to charge transfer occurring between the chromophore and the triarylamine.[2049] A more extended TPA unit improves the charge transport as shown by polymers **321a**[2023] and **1023**.[2043] Both show green EL, but the efficiencies of single-layer devices with calcium cathodes are only 0.02% and 0.11%, respectively. Oxidative copolymerization of triphenylamine and stilbene with iron(III) chloride gives copolymer **1024**, which shows blue PL ($\lambda_{max} = 413$ nm).[2058]

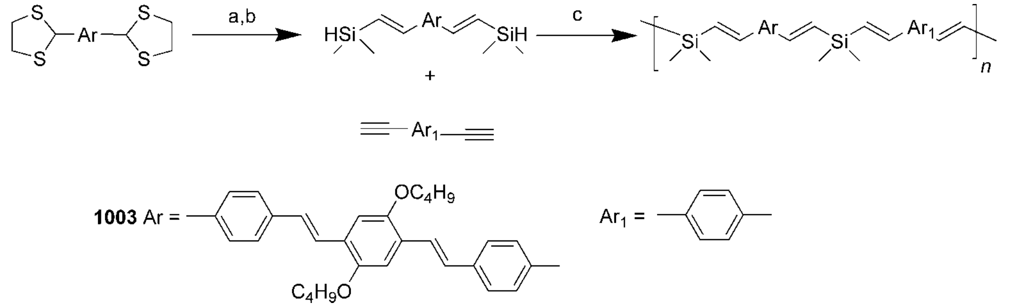


997a R = H
997b R = OMe

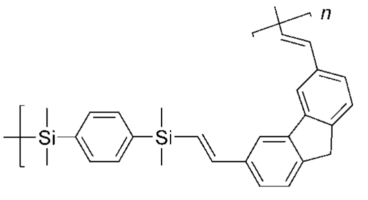


998a R = H
998b R = OMe

Scheme 59. Arylene Vinylene/Silylene Copolymers by Hydrosilylation: (a) $(^{i}PrO)Me_2SiCH_2MgCl$, $NiCl_2(PPh_3)_2$; (b) $LiAlH_4$; (c) $RhCl(PPh_3)_3$



Lu et al. have prepared polymer **1025** (Chart 38), containing both electron- and hole-transporting units, by condensation of difluoride **1026** with a bishydroxy chromophore.[2059] It showed poor performance in a single-layer LED, but a double-layer device with an oxadiazole hole blocking layer gave bright blue emission (λ_{max} = 465 nm). Blue EL (λ_{max} = 460 nm) has also been obtained from the unusual polymer **1027**, which has oxadiazole units in both the main- and the side-chains.[2060] Polymer **1028**, containing an electron-accepting diphenylsulfone unit, has been made by the Wittig route.[2061] This polymer produces blue EL (λ_{max} = 470 nm) with an onset voltage of 14 V.



1004

Polymers with oligo-CN-PPV units can be prepared by Knoevenagel polycondensations.[666,1940,1993,1995,2062−2066] The red emitting polymer **1029** (λ_{max} = 613 nm), however, was made by Heck coupling of a distyrylbenzene to a cyclotriphosphazene with two stryene units attached.[2018] The cyano substituents tend to produce a red-shift in the emission; for example, the PL maximum for polymer **1030** is at λ_{max} = 512 nm,[666] compared to λ_{max} = 470 nm for **981a**. The EL maximum is at 518 nm, with an efficiency of 0.05 cd/A.[666] Similarly, the polymer **1031a**[2067] has an emission maximum at λ_{max} = 560 nm compared with λ_{max} = 530 nm for **1031b**.[2041] In the case of the green (λ_{max} = 505 nm) emitting polyurethane **1032a**, the red-shift in the emission is so large that **1032b** emits in the yellow region of the visible spectrum (λ_{max} = 590 nm).[1981] Blends of these polymers show emission at intermediate wavelengths.

Scheme 60. Synthesis of Poly(pyridinium salt)s with Arylene Vinylene Chromophores: (a) $BF_3 \cdot Et_2O$; (b) NH_2-X-NH_2

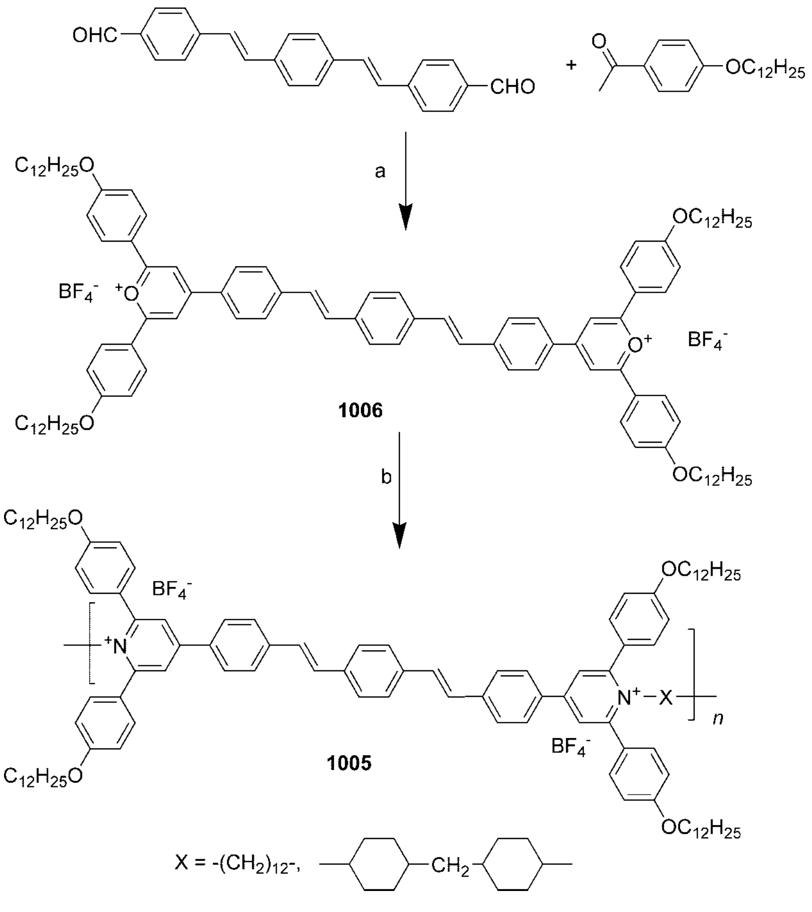
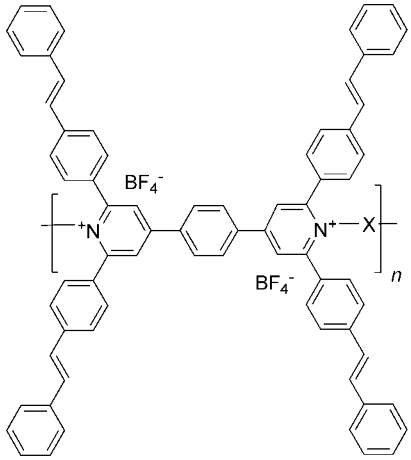
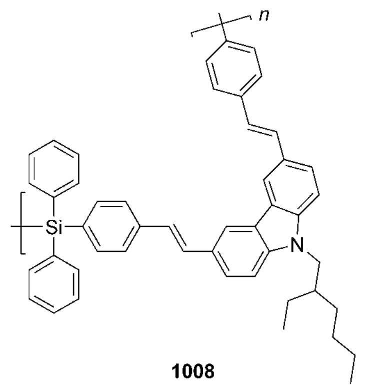


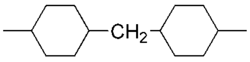
Chart 35

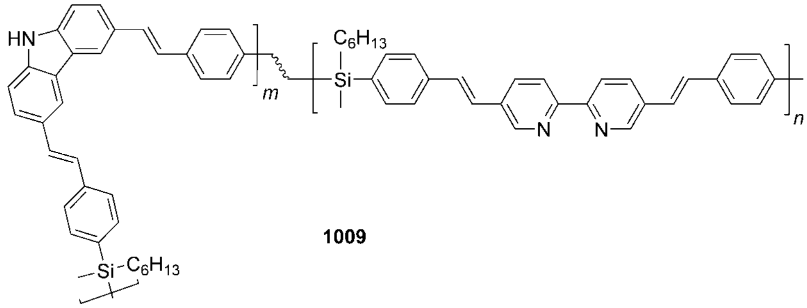




1008

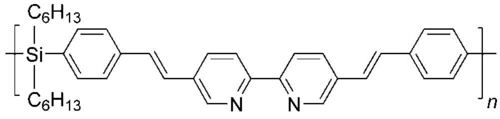
1007 X = -C$_{12}$H$_{24}$-,





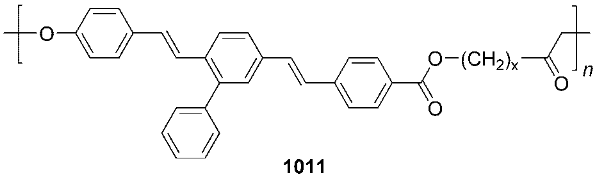
1009

Other arylene units can be incorporated by this method, e.g. polymer **1033** containing carbazole units which shows green emission (λ_{max} = 510 nm).[2068] The incorporation of the cyano substituents on the vinylene moieties is intended to improve the EL efficiency by facilitating electron injection. Polymer **1030** has been used as an electron-transporting layer in a bilayer device with PPV and increased the EL efficiency by a factor of 25.[2063] Introduction of cyano groups lowers the turn-on voltage in these polymers. For instance, silyl-linked polymers such as **1034** have a turn-on voltage of 7 V compared with 9−12 V for the corresponding polymers without the nitrile groups.[1993,1995] Polymers **1035** and **1036** were designed to have high EL efficiency by incorporating both hole-tranporting triarylamine and electron-accepting cyano groups.[2065] They show orange emission (λ_{max} = 590−600 nm) with efficiencies in single-layer devices with Al cathodes an order of magnitude higher than those for MEH-PPV (**20**). Although this is still well below what is needed for commercial applications and the lifetimes are not reported, this suggests such materials might with further improvements produce commercially viable devices. Polymer **1037** with trifluoromethyl substituents on the vinylenes has

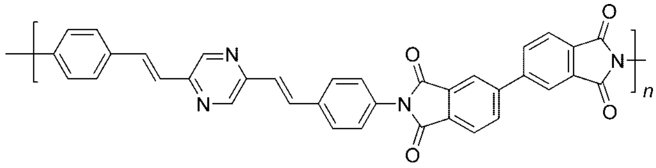


1010

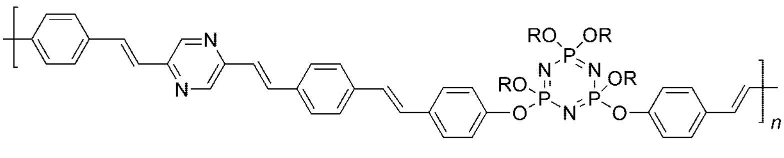
Chart 36



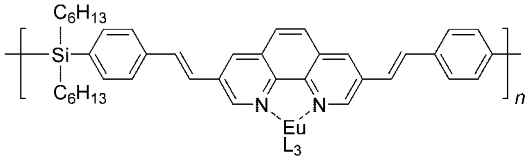
1011



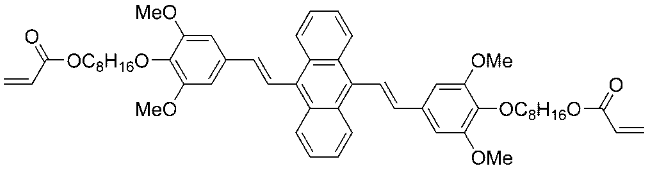
1012



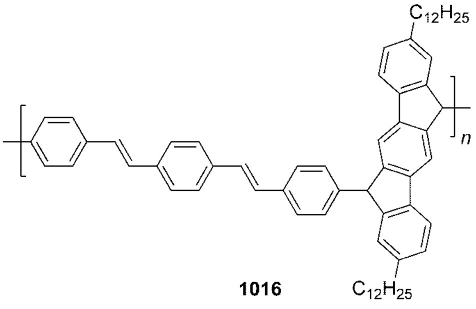
1013



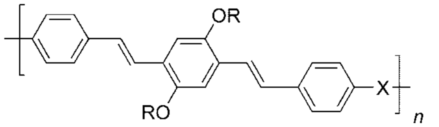
1014 L =



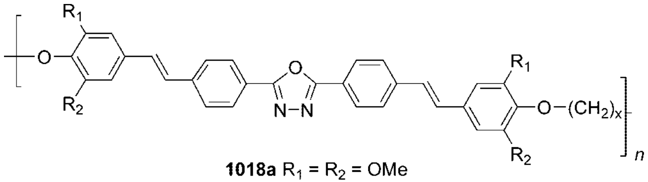
1015



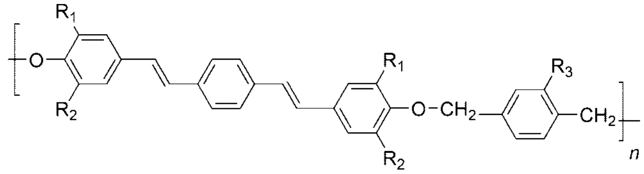
1016



1017a R = C_6H_{13}, X = O
1017b R = C_6H_{13}, X = S
1017c R = C_8H_{17}, X = CO
1017d R = C_8H_{17}, X = CHOH

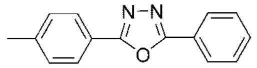


1018a $R_1 = R_2$ = OMe
1018b $R_1 = R_2$ = Me
1018c R_1 = OEt, R_2 = H

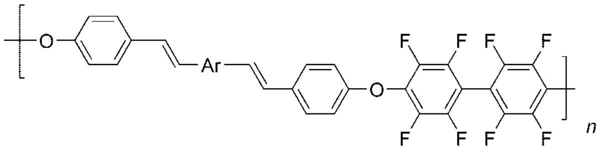


1019a R_1 = OEt, R_2 = H
1019b $R_1 = R_2$ = OMe

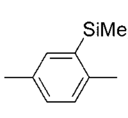
R_3 =



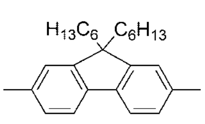
1019c R_1 = OEt, $R_2 = R_3$ = H
1019d $R_1 = R_2$ = OMe, R_3 = H



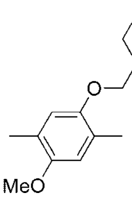
1020a Ar =



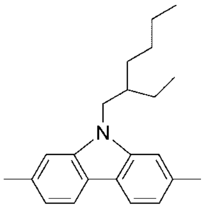
1020c Ar =



1020b Ar =



1020d Ar =



been prepared by Horner polycondensation and shows blue PL (λ_{max} = 480 nm).[656]

A novel polymerization method developed by Chujo and co-workers[2069−2071] is the hydroboration of arylene diynes with mesitylborane to give the arylenevinylene polymers **1038a−f**. The phenylene and biphenylene polymers **1038a** show blue PL with λ_{max} at 440 nm. The emission is slightly bathochromically shifted for the fluorene **1038b** (λ_{max} = 455 nm) and anthracene **1038c** polymers (λ_{max} = 462 nm). Blue-green emission is seen for the thienyl **1038d** (λ_{max} = 488 nm) and furyl **1038e** polymers (λ_{max} = 495 nm), while the pyridyl polymer **1038f** displays three PL maxima at 416, 495, and 593 nm in a wide emission band. Polymers **1039** with a transition metal complex in the main-chain show blue-green PL (λ_{max} = 481−498 nm). Hydroboration of oligothiophene dinitriles gives the cyclodiborazane copolymers **1040a−d**.[2072] As expected, the PL emission bathochromically shifts with increasing length of the chromophore from **1040a** to **1040d** both in solution (λ_{max} = 450 and 536 nm, respectively) and in the solid state (λ_{max} = 536 and 632 nm, respectively).

The PPE copolymer **1041** is made by Heck coupling of a linked bis-aryliodide with a diethynylbenzene.[906] It shows emission maxima at λ_{max} = 450 and 480 nm in solution, with a long tail into the yellow region. Copolymer **1042** with a chiral diimide linker group produces yellow EL (λ_{max} = 568 nm).[2073] The linker groups help suppress interchain interactions which are known to reduce the efficiency of PPE-based LEDs (see section 2.8 above). Copolymer **1043** produces blue EL (λ_{max} = 445 nm).[2074] Incorporation of a biphenyl unit in **1044** produces a blue-shift (λ_{max} = 413 nm), while emission from the butadiyne copolymer **1045** is slightly red-shifted (λ_{max} = 455 nm). Copolymer **1046** made by lithiation of an aryl diyne followed by treatment with dimethoxymesitylborane shows blue PL (λ_{max} = 456 nm).[2075]

Polymers with isolated oligoarylene chromophores have been developed for use in blue emitting LEDs. Both synthetic approaches described for the arylene vinylene polymers above are also applicable here. For example, the chromophores in the tetra- and hexaphenylene polyethers **1047a** (λ_{max} = 396 nm) and **1047b** (λ_{max} = 429 nm) are prepared by Yamamoto and Suzuki coupling as shown in Scheme 61. A device containing a blend of **1047** and PVK and using an aluminum cathode produced violet-blue emission (λ_{max} = 395 nm) with only 0.05% efficiency.[2076] Similar polymers **1048** have also been made by the Suzuki route.[2077] By contrast, other blue emitting oligophenylene polyethers, e.g. **1049−1051** have been prepared by condensation of the oligophenylene diacetates with alkyldibromides.[1965,2078−2080] Polarized emission has been obtained from a stretching-aligned film of the pentaphenylene polyether **1049**.[2081] Violet emission has been seen from similar polyethers and polyesters **1052** and **1053** with *meta*-linked oligoarylenes.[2082]

Copolymers such as **1054** and **1055** with electron-transporting units in the linking group have been made by Hay and co-workers.[2083] All display violet PL (λ_{max} = 394−396 nm), except for **1055**, which shows blue emission (λ_{max} = 442 nm). Blue (λ_{max} = 442 nm) emission has also been obtained from the polyester **1056** made by condensation of a trifluorene diacid and a diol.[2084] Other blue emitting polyesters with oligoarylene emissive units have also been prepared by this method.[2085]

Yoshino and co-workers have prepared blue emitting polymers containing oligophenylenes with bisilanylene

Chart 37

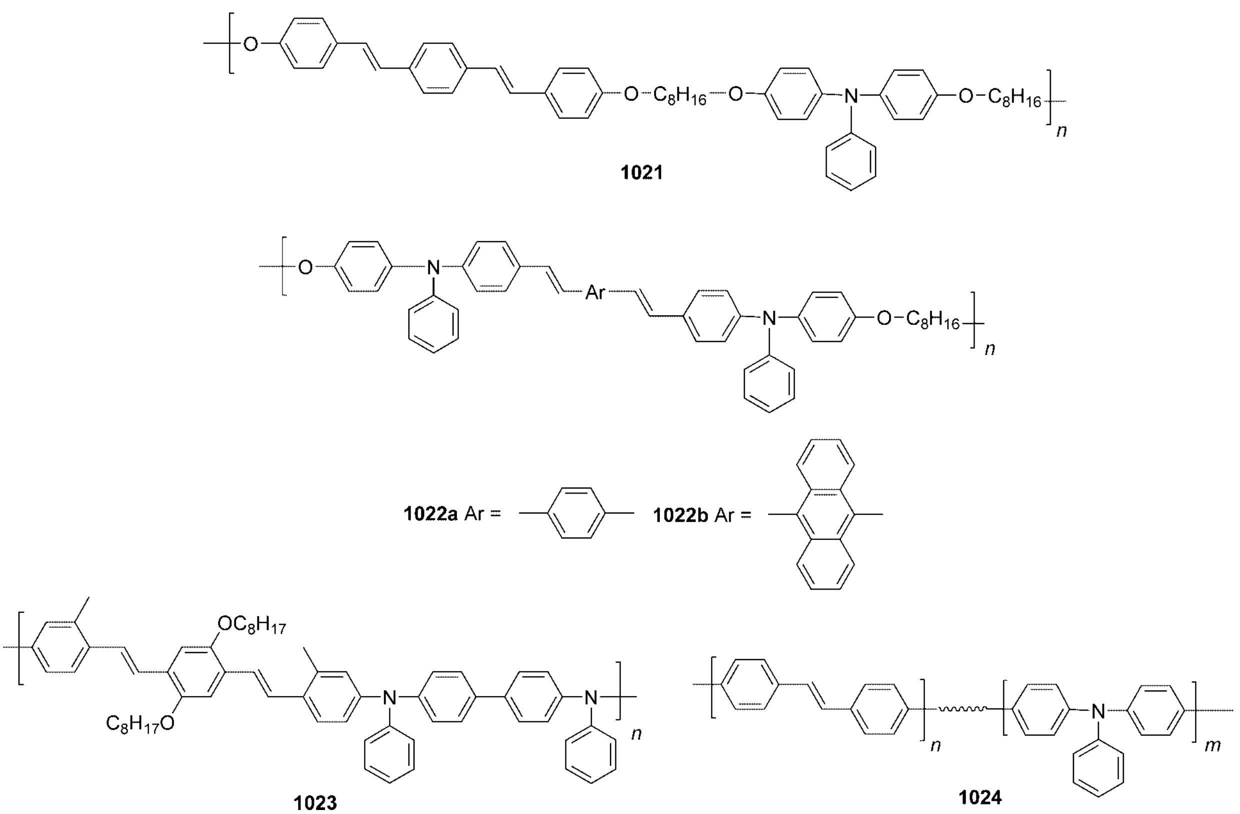
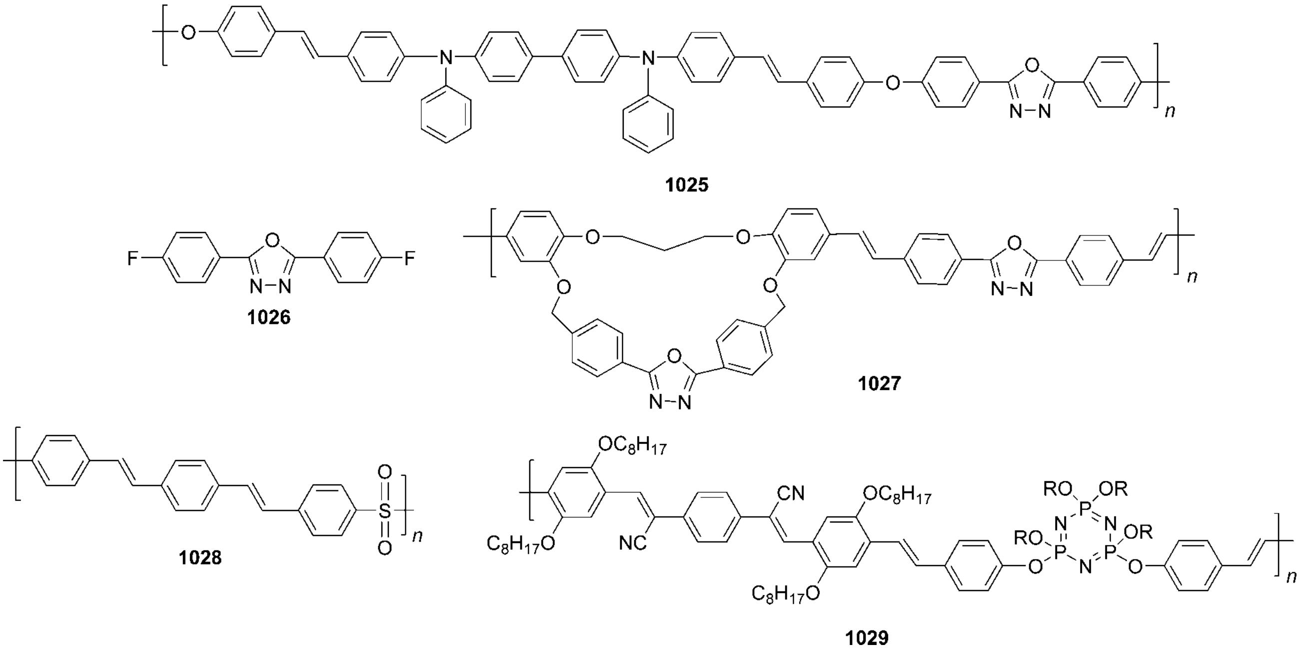
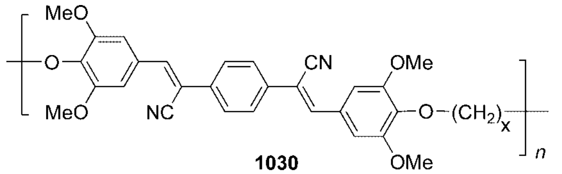


Chart 38

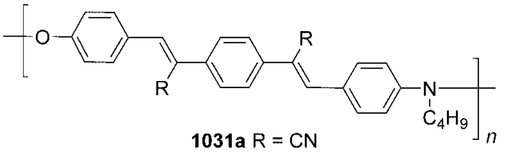


spacers **1057**.[2086,2087] Polymers with oligophenylene units separated by fluorenylidene linkages, e.g. **1058**, have been made by Suzuki coupling, but no details regarding their fluorescence properties have yet been published.[2088,2089] In the polymers **1057a–d** the emissive units are orthogonal to the polymer backbone. The triarylamine-substituted polymers **1059a,b** show red-shifted EL emission (λ_{max} = 450 and 442 nm, respectively) compared with the polymers **1059c,d** without these groups (λ_{max} = 401 and 419 nm, respectively), but with much higher efficiency (up to 2 cd/A).[2090]

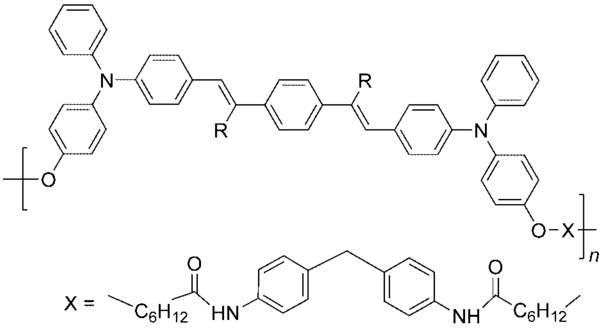
Xia and Advincula have prepared the copolymers **1060** by alkylation of diphenylindenofluorene **1061** with *n*-butyllithium and 1,ω-dibromalkanes.[2091] Their solid-state PL emission is violet-blue (λ_{max} = 375–377, 395–398 nm) with an extra band at λ_{max} = 495 for the polymer with the shortest spacer group (m = 4), which is attributed to excimer emission. The PL efficiency in solution was found to increase with longer spacer group length from 44% (m = 4) to 58% (m = 8), presumably due to a reduction in interaction between the chromophores. The PPP–TPA copolymer **1062** shows blue PL (λ_{max} = 461 nm) but red EL (λ_{max} = 618



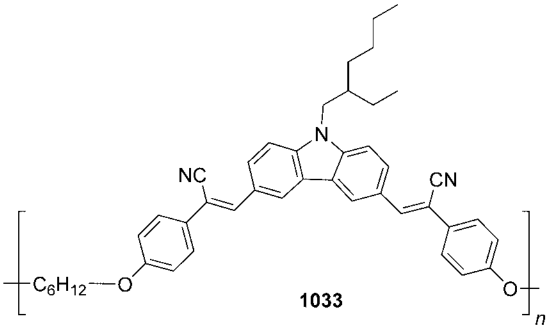
1030



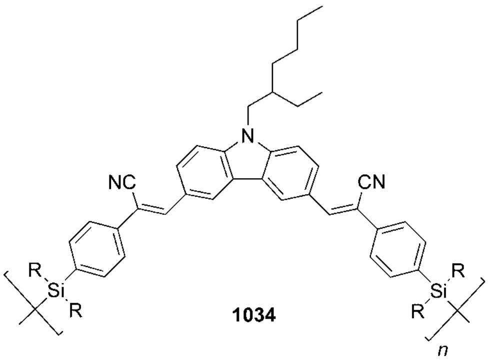
1031a R = CN
1031b R = H



1032a R = H
1032b R = CN

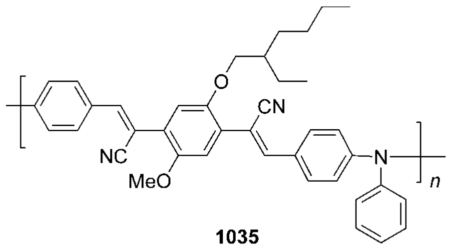


1033

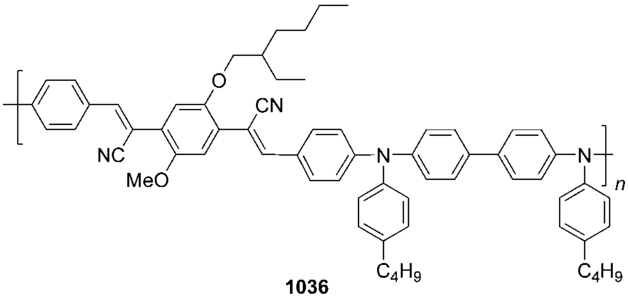


1034

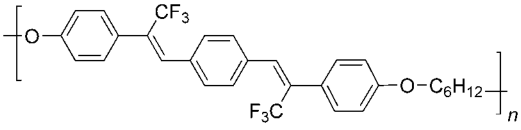
nm).[2092] The cause of this extraordinary bathochromic shift may be excimer formation. Near-white EL has been obtained from films of emeraldine-base polyaniline **1063**. The emission spectrum is broad (380−750 nm), and the intensity increases with increasing applied voltage. The emission seems to come from the reduced units with phenyl rings linked by amine groups rather than from the quinonoid units.[2093] Near-white EL has also been seen from copolymer **1064**.[2094]



1035



1036



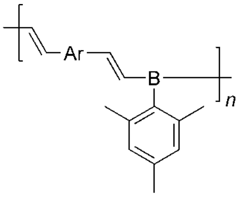
1037

Blue fluorescence has been reported from polyesters **1065** (λ_{max} = 420 nm) and **1066** (λ_{max} = 478 nm) containing bi- and terthiophene chromophores made by polycondensations with terephthaloyl dichloride.[2095] Polymer **1067** made by condensation with succinoyl dichloride shows yellow EL (λ_{max} = 595 nm).[2096]

Hadziioannou and co-workers have prepared (Scheme 62) oligothiophene−dibutylsilanylene copolymers **1068**−**1069**,[2097−2101] whose emission maxima could be tuned between blue (λ_{max} = 415 nm) for **1069a** and red (λ_{max} = 612 nm) for **1069b** by altering the number of thiophene and silanylene units. The red-shift produced by increasing the number of silane units is minor, and the emission color is mainly controlled by the number of thiophene units.[1406] Similar polymers containing 3−7 thiophene units, whose emission maxima ranged from 550 to 640 nm, have been made by Yoshino and co-workers.[2087] Silylene copolymers with other chromophores, e.g. **1070a**−**c**, have been made by a similar route.[2102] Their emission ranges from violet-blue (λ_{max} = 404 nm) for **1070a** to blue (λ_{max} = 474 nm) for **1070c**. The copolymer **1071** produces green EL (λ_{max} = 511 nm) despite having the same chromophore as **1070c**, suggesting that alkyl and silyl spacers may interact in different ways with the chromophore.[861]

Copolymer **1072** (Chart 39) is made by condensation of the linked bis(aminophenol) **1073** with a substituted terephthalic acid (*cf.* Scheme 36).[2103] Both single-layer devices and double-layer devices using PVK as a hole-transporting layer show blue-white EL with emission maxima around 2.6 eV (480 nm) and 2.2. eV (565 nm), with an efficiency of 0.86% for the double-layer devices.[2104] Copolymers **1074** with naphthalimide chromophores, which are made by a polycondensation route, are reported to show green PL and EL (λ_{max} = *ca.* 530 nm).[2105] Similar copolymers such as **1075** with thionaphthalimide chromophores are reported to show strong fluorescence, but no spectral details have been published yet.[2106]

Parker et al. have reported[2107] the construction of an efficient (2.5%) blue LED (λ_{max} = 450 nm) utilizing copolymer **1076a** with a quinoline chromophore. Such an efficiency if combined with good lifetimes would be good



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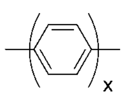
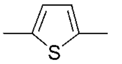

x = 1,2

1038d Ar =


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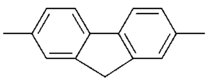

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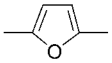
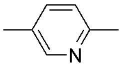
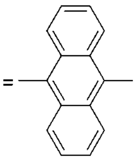
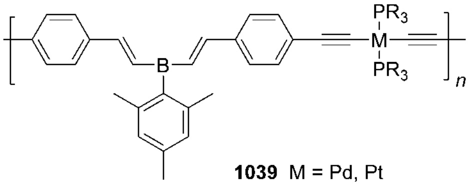
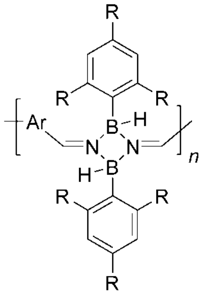


1038f Ar =


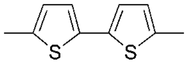
1038c Ar =


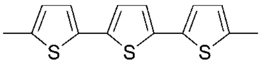


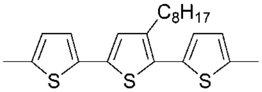
1039 M = Pd, Pt

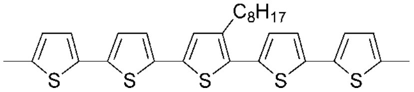


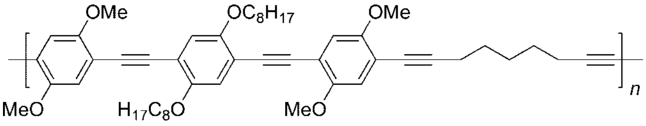
R = Me, ^{i}Pr

1040a Ar =


1040b Ar =


1040c Ar =


1040d Ar =




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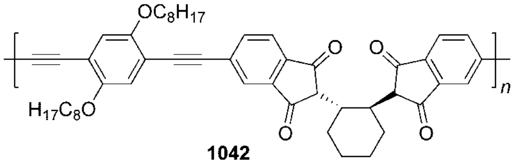

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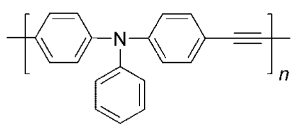

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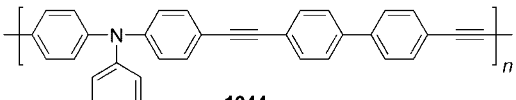
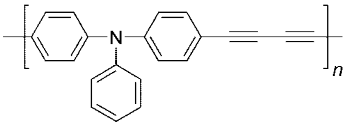


1044



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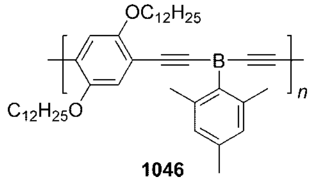
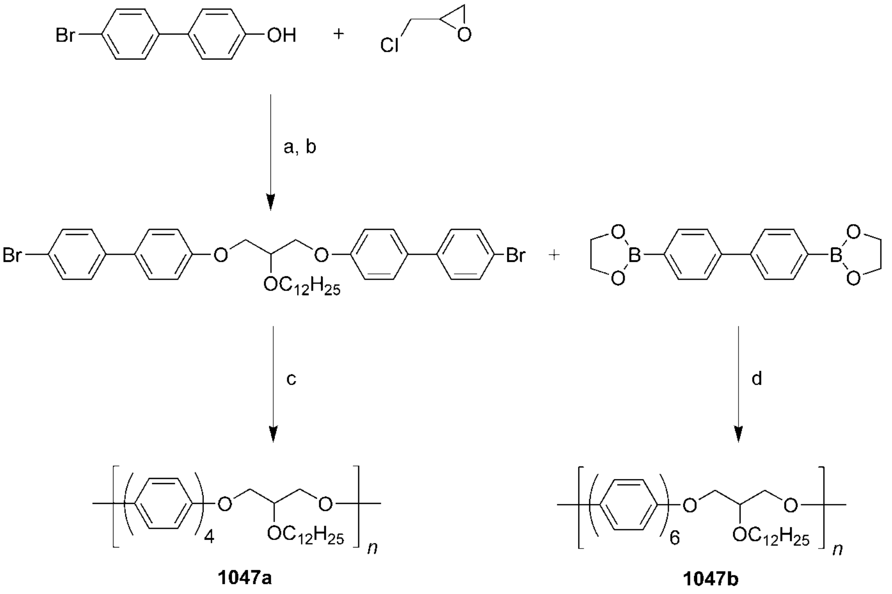


1046

enough for commercial applications. A similar polymer **1076b** with tetraphenyldiaminobiphenyl (TPD) hole-transporting units, made by condensation of a bisarylfluoride with a dihydroxy-TPD, shows green PL (λ_{max} = 547 nm). The EL maximum varies between 530 and 570 nm depending upon the device structure.[2108] The corresponding polymer **1077a** with the TPD units attached directly to the chromophore is made by a polycondensation of a diacetyl-TPD and a dibenzoylbiphenyldiamine and also displays bright green PL (λ_{max} = 550 nm) and EL (λ_{max} = 515−550 nm, again depending upon device structure).[2109] Green-yellow PL (λ_{max} = 528 nm) and EL (λ_{max} = 523 nm) have also been obtained from polymer **1077b** with a bis(trifluoromethyl)methane linker.[2110] Polymer **1078** (Chart 40) shows a broad PL emission spectrum with maxima at λ_{max} = 440, 500, and 536 nm. The efficiency of the EL is reported to be comparable with that of MEH-PPV (**20**), but spectral details are not given.[2110] Copolymers with benzoisoquinoline, e.g. **1079**, and benzophthalazine, e.g. **1080**, units show green emission (λ_{max} = 540−560 nm and 505−530 nm, respectively).[2111] It is reported that the carbazole−fluorene copolymer **1081** with silyl groups interrupting the conjugation exhibits blue (λ_{max} = 441 nm) PL in the solid-state with a much higher fluorescence efficiency than that of the fully conjugated alternating copolymer **719d** (52% vs 8%).[1558]

A number of polymers with isolated chromophores containing electron-transporting aryloxadiazole units have been synthesized by condensation of aryldiacylhydrazides with suitable diacids or diacylhalides, followed by dehydrative ring-closure. Pei et al.[313,2112] have reported blue (λ_{max} = 445−475 nm) emission from a device using the oxadiazole-containing copolymer **1082**. They obtained an efficiency of 0.1% with polyaniline and polymer **1083a** as hole- and electron-transport layers, respectively, and Ca as cathode material. The blue emitting (λ_{max} = 430 nm) copolymers **1084** are reported to display liquid crystalline behavior, offering the prospect of obtaining polarized emission.[2113] Copolymers with the conjugation interrupted by silane groups generally show violet or blue emission, as exemplified by polymers **1085**[1906] (λ_{max} = 405 nm) and **1086**[1707] (λ_{max} = 450 nm). However, copolymer **1087** shows blue (λ_{max} = 445 nm) PL, but green (λ_{max} = 540 nm) EL, possibly due to excimer formation.[1906] Similar polymers prepared by the

Scheme 61. Synthesis of Oligo(arylene) poly(ether)s: (a) NaOH, dioxan; (b) n-$C_{12}H_{25}Cl$, NaOH (aq), THF, 48 h, Δ; (c) $Ni(COD)_2$, 2,2′-bipyridyl, DMF, 65 °C; (d) $Pd(P(Ph)_3)_4$, $NaHCO_3$, THF, Δ



Holmes group, where the conjugation is disrupted by bis(trifluoromethyl)methane units, e.g. **1083b**,[179,617,1807] also show intense blue ($\lambda_{max} = 420$ nm) fluorescence. Copolymer **1088** shows violet ($\lambda_{max} = 362$ nm) PL but blue EL ($\lambda_{max} = 420$ nm).[1906]

Copolymers with a bent bis(terphenyl)oxadiazole chromophore and a variety of linking groups have been prepared, which show violet or blue emission, for example polymer **1089** ($\lambda_{max} = 420$ nm) (Chart 41).[2083] Similar copolymers with a linear bis(biphenyl)oxadiazole chromophore, e.g. **1090**, show more red-shifted emission ($\lambda_{max} = 451-478$ nm).[2083] Violet emission is also seen from copolymers, such as **1091**, containing both phenylquinoxaline and aryloxadiazole units.[2114] These, like the other violet emitting copolymers described above, are more suitable for use as charge-transporting than as emissive layers. Other copolymers are potentially useful as emitters, e.g. the copolymer **1092** containing hole-transporting carbazole, which produces blue EL ($\lambda_{max} = 450$ nm).[2115]

The polyimides **1093** and **1094** containing electron-rich furan rings have been prepared by a soluble precursor route and show blue PL ($\lambda_{max} = 418$ and 436 nm, respectively).[2116,2117] Replacing the linker in **1093** with bisphthalimide linking groups to give polymers **1095a,b** causes a red-shift in the emission ($\lambda_{max} = 480$ and 460, nm respectively).[2118]

Polyethers **1096** (Chart 42) with quinoxaline chromophores made by condensation of the dihydroxy chromophores with alkyl dihalides show blue PL ($\lambda_{max} = 442$ nm).[2119] Polyethers **1097** with isoindole chromophores are prepared by condensation of *o*-difluorobenzoyldi- or tetraphenylbenzenes with bis-phenols, followed by formation of the indole rings by condensation of the resulting precursor polymers with *p*-toluidine in a polymer analogous reaction. The emission is blue with maxima at $\lambda_{max} = 468$ nm for the tetraphenylindole polymer **1097a** and $\lambda_{max} = 486$ nm for the diphenylindole polymers **1097b**.[2120] Blue emission ($\lambda_{max} = 421-430$ nm) has also been seen from polymers **1098a,b** containing both emissive and charge-accepting units.[2121]

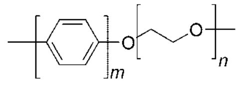
Copolymers containing a mixture of different chromophore units can be prepared. Thus, copolymerization of a mixture of 9,10-bis(4-acetoxystyryl)anthracene and other aryl bisacetates with alkyl dibromides produces copolymers **1099a−c** (Chart 43), which show yellow PL ($\lambda_{max} = 538-550$ nm) in solution due to efficient Förster energy transfer from the other chromophores to the distyrylanthracene chromophores. The solid-state PL behavior is more complex and depends on the relative compositions, length of spacer units, and excitation wavelength. In some cases, effects such as red-shifting and changes in spectral shape have been observed.[2122]

A copolymer **1100** (Chart 44) prepared by Suzuki polycondensation displays orange-red EL ($\lambda_{max} =$ *ca.* 600 nm) from the dye chromophore due to energy transfer from the polyfluorene segments.[2123] Irradiation of **1100** in the presence of gaseous trialkylsilanes leads to bleaching of the dye units so that blue-green emission from the fluorenes appears. This is a possible method to produce photopatterned multicolor emission from polymer films.

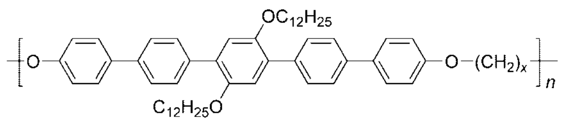
All of the above polymers are covalently linked materials. It is also possible to make a luminescent supramolecular polymer in which the monomer units are held together by noncovalent bonds. The first such materials reported were the luminescent polymers **1101** (Scheme 63) formed by self-assembly of the emissive units through metal complexation between the terpyridine ligands at each end of the chromophore and zinc ions.[2124] Their PL maxima range from 450 nm for **1101a** to 567 nm for **1101c**. Polymers **1101a** and **1101b** have been used to make blue ($\lambda_{max} = 450$ nm) and green ($\lambda_{max} = 572$ nm) emitting LEDs, respectively, which display only moderate EL efficiencies.

Schenning, Meijer, and co-workers have found that hydrogen-bonded assemblies of oligofluorenes **1102** ($n = 1-7$) display blue PL ($\lambda_{max} =$ *ca.* 410−420 nm) in the solid-state, and they state that they are promising candidates for LED applications, though as yet their EL properties have not been reported.[2125]

Two-component luminescent supramolecular polymers are also known. A Taiwanese group have reported that hydrogen-bonded networks of bispyridyl compounds such as **1103−1104** bonded with polyacids such as **1105** are luminescent, with emission colors ranging from blue ($\lambda_{max} = 396$ nm) for **1103a/1105** to red ($\lambda_{max} = 642$ nm) for **1104a/1105**.[2126] Due to the poor film quality of the networks, EL



1048 m = 3-6



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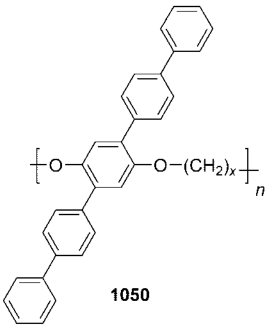

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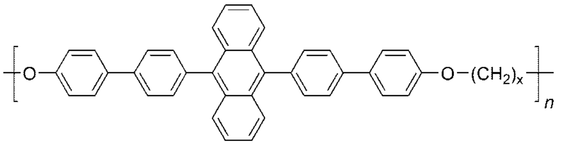

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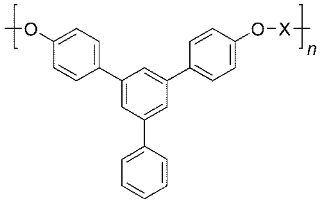

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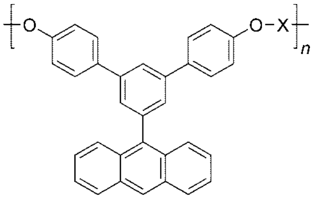

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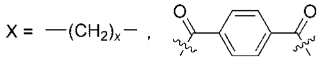

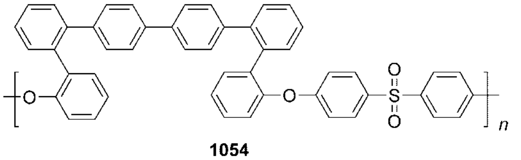

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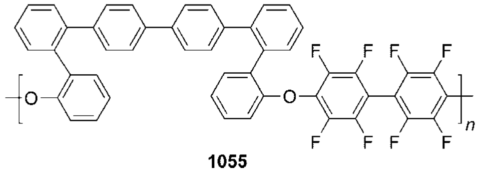
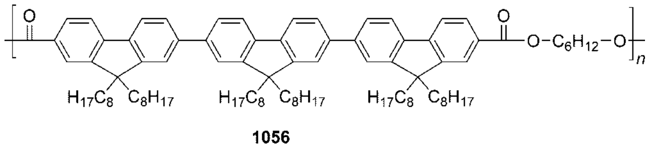


1055

devices were constructed using blends of **1103c** in PVK and of **1103c** complexed with the molecular acid **1106** in PVK. It was found that the complex produced green EL (λ_{max} = 510 nm) with narrower emission and higher brightness than uncomplexed **1103c** in PVK. It remains to be seen whether such supramolecular polymers will display markedly better EL performances than the covalently linked materials.



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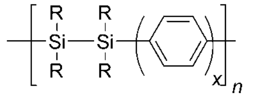
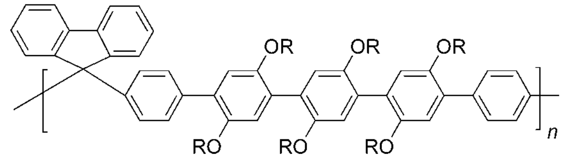
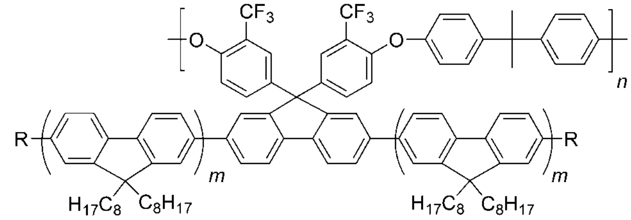


1057 x = 3,4



1058 R = alkyl



1059a m = 1, R = NPh$_2$
1059b m = 2, R = NPh$_2$
1059c m = 1, R = H
1059d m = 2, R = H

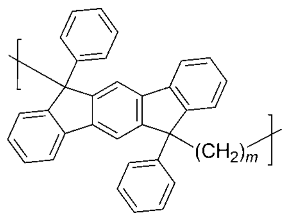
Despite the massive amount of work involving a huge range of structures and synthetic methods described above, polymers with isolated main chain chromophores still do not appear to offer any real prospect of commercial utility, with only one report of a high efficiency (>1%) device using them. Incorporation of phosphorescent moieties into such systems has apparently not been investigated, despite offering the best chance for obtaining acceptable EL efficiencies.

4.5. Block Copolymers

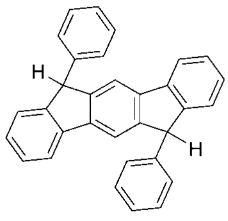
To date, most luminescent block copolymers reported have been rod−coil copolymers with luminescent rods. There exist two approaches to the synthesis of block copolymers: first, the "grafting from" approach, where one component is used as a macroinitiator for the preparation of the other, and second, the "grafting onto" method, where the second component is covalently attached to a suitably end-functionalized first component. The first approach was used by François and co-workers to prepare block copolymers of polystyrene (PS) with PPP **1107** and poly(3-hexylthiophene) **1108** (Scheme 64).[2127−2132]

The PS−PPP copolymer **1107** exhibits different optical properties from those of PPP (**529**), and the blue EL emission width is much narrower than the PL emission.[2133,2134] A similar but smaller narrowing of the EL as compared with the PL emission width is seen for the red emitting PS−P3HT copolymer **1108**.[2134] Doping of the copolymer **1108** with iron(III) ions increases the efficiencies of LEDs by a power of magnitude, accompanied by a drop in turn-on voltage and a slight blue-shift in the emission maximum.[2135] The synthesis of **1107** has recently been restudied by Advincula and co-workers.[2136]

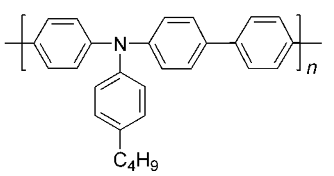
Bazan et al. have prepared the block copolymer **1109** containing PPV and poly[bis(trifluoromethyl)norbornadiene] units by means of living ROMP of siloxycyclophane **12** and 1,2-bis(trifluoromethyl)norbornadiene **1110** (Scheme 65).[2137] Polymerization of **12** requires a *cis*-specific highly reactive bis(hexafluoro-*tert*-butoxy)molybdenum initiator,[161] while



1060 m =4,5,6,8



1061



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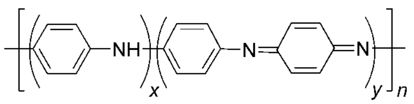

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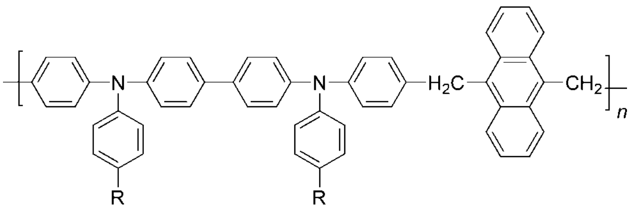

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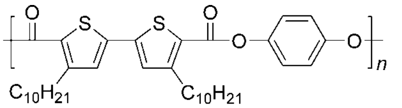
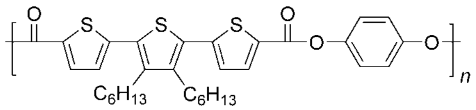


1065



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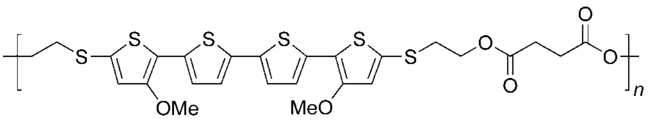
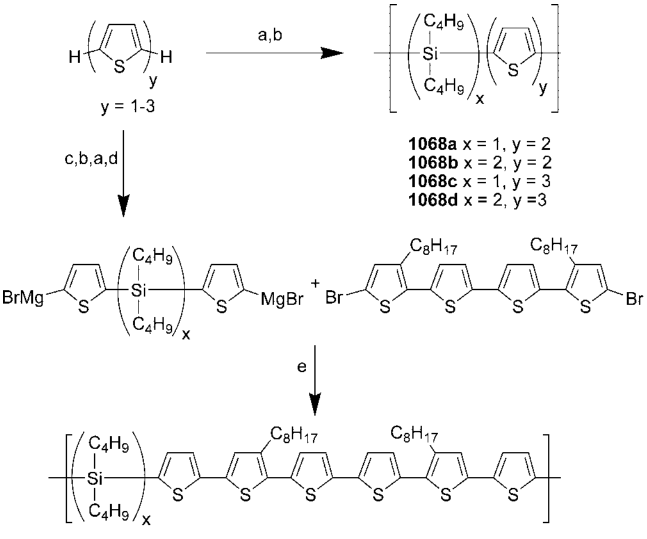


1067

Scheme 62. Synthesis of Poly(silyanylene thiophene)s: (a) 2 mol equiv of *n*-BuLi, Cl[Si(C_4H_9)$_2$]$_y$Cl; (b and c) *n*-BuLi, TMEDA; (d) 2 mol equiv of $MgBr_2 \cdot Et_2O$; (e) $NiCl_2$(dppp)$_2$



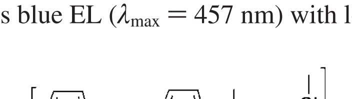
1069a x = 1, **1069b** x = 2

polymerization of the norbornadiene derivative is optimal with a less reactive *trans*-specific bis(*tert*-butoxy)molybdenum complex, so that a ligand exchange step is required. The final copolymers **1109** ($n = 10, 20, m = 50-200$) have very low (<1.1) polydispersities, and the PPV segments are of >95% *trans* configuration. Copolymers with *m* up to 200 are soluble in organic solvents. Preliminary results suggest that the bis(trifluoromethyl)norbornadiene units retard photodegradation of the PPV units.

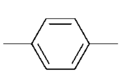
Block copolymers **1111** of PPV and norbornene can also be prepared by this route without the need for ligand exchange,[161] and they undergo oxidative cyclization to give poly(phenanthrylene vinylene)/poly(norbornene) copolymers **1112**.[690] It has been found that the PL quantum yield for these polymers increases, and the rate of photodegradation of the PPV units decreases with increasing poly(norbornene) block length.[2138] The final conversion step can be performed by photolithographic methods, thus enabling patterned films of **1109** to be made.[2139]

Hadziioannou and co-workers have developed methods for the preparation of PPV-PS copolymers **1113** by end-capping a PPV block with a TEMPO unit, which can then act as an initiator for a living radical polymerization of styrene (Scheme 66).[2140] A similar macroinitiator made by end-capping with a nitroxide radical has been used to make a PPV-poly(butyl acrylate) copolymer.[2141] These polymers form unusual honeycomb-like structures in the solid state.[2142]

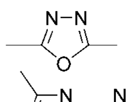
Zhang et al. have found that copolymerization of a dialkoxy bis(sulfonium) salt and acrylamide gives block copolymers **1114** (Chart 45).[2143] As the amount of acrylamide per gram of sulfonium salt increases from 0 to 20 g, the emission maximum is shifted from $\lambda_{max} = 550$ to 509 nm, and the material becomes water soluble. Reaction of a *p*-(bis-chloromethyl)benzene or *p*-(chloromethyl)benzenesulfinyl PPV monomer with a PEO-monomethyl ether under basic conditions gives copolymer **1115** with a short PPV block.[2144,2145] Similarly, addition of styrene to the Gilch polymerization of a 4,4′-bis-halomethyl biphenyl produces copolymer **1116**.[2146] (It should be noted that the published structure is almost certainly incorrect, as it would involve anionic or radical attack upon the more substituted carbon.) This produces blue EL ($\lambda_{max} = 457$ nm) with low efficiency.



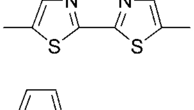
1070a Ar =

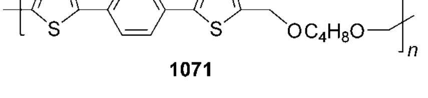


1070b Ar =



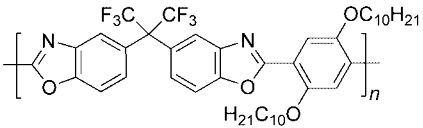
1070c Ar =





1071

Chart 39



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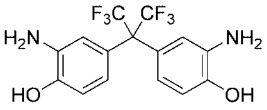

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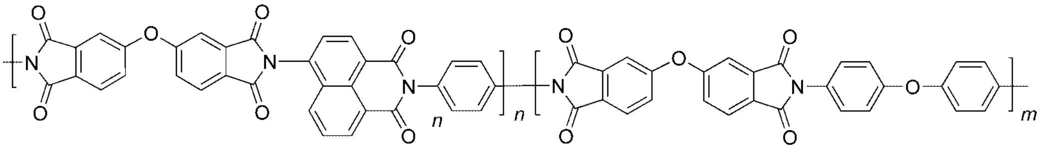

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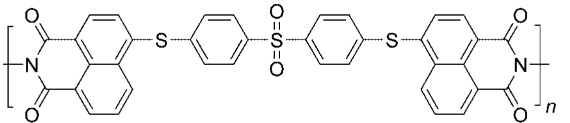

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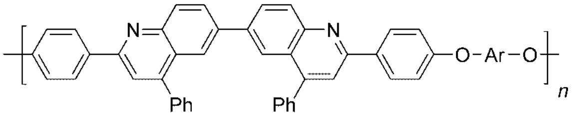
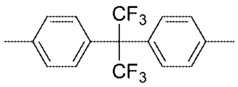
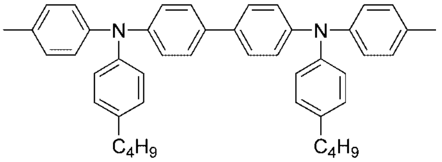
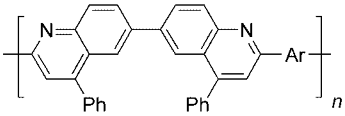


1076a Ar =

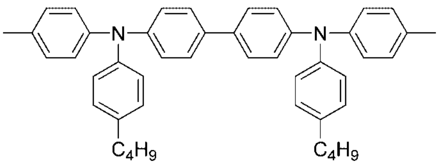


1076b Ar =





1077a Ar =



1077b Ar =

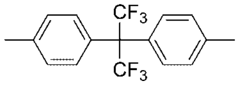
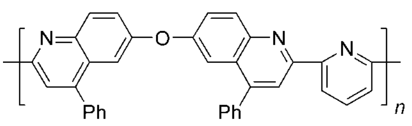


Chart 40



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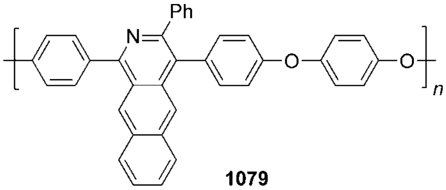

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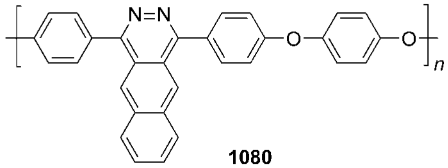
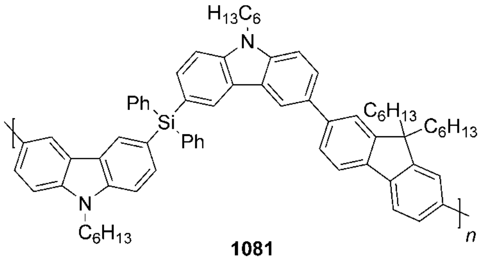


1080



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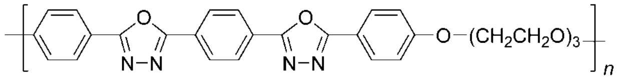

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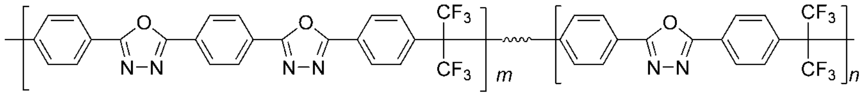
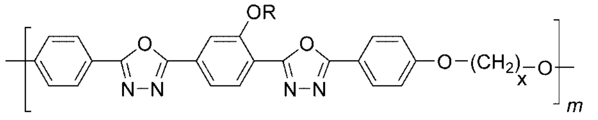
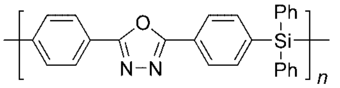


1083a m = 0
1083b m > 0

A suitably functionalized fluorene trimer was used as a macroinitiator to prepare violet-blue emitting copolymers such as **1117**.[2147−2149] Similarly, an end-capped polyfluorene was used as a macroinitiator for the radical polymerization of a carbazole-substituted methacrylate to produce the blue emitting block copolymers **581**.[1241] Copolymers **580**[1240] are



1084 R = C_5H_{11} or C_8H_{17}, x = 6 or 12



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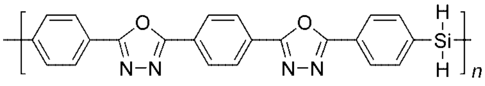

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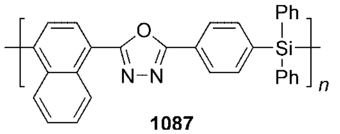

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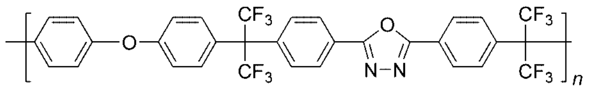
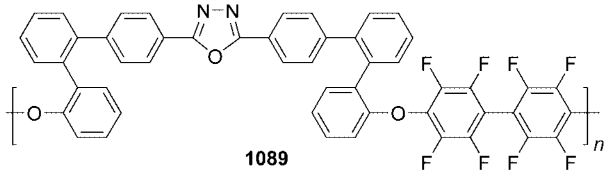


1088

probably also produced by such a method, though their synthesis has not yet been published.

Müllen and co-workers have used the alternative "grafting onto" approach to make a number of rod−coil copolymers, by making end-capped conjugated rods and attaching nonconjugated coils. By addition of first ethyl 4-bromobenzoate and then phenylacetylene to a Sonogashira−Hagihara polycoupling of a *p*-iodophenylacetylene, they were able to make an ester end-capped PPE. Hydrolysis, followed by esterification with PEO gave the PPE−PEO copolymer **1118** (Chart 46).[2150] In an analogous procedure, addition of first bromobenzene and then 4-formylbenzeneboronic acid to the Suzuki polycoupling of a 4-bromobenzeneboronic acid gave a PPP end-capped with an aldehyde functionality, to which PS or PEO chains were added, producing copolymers **1119** and **1120**.[2151] This methodology was also used to make the PDAF−PEO copolymer **1121**.[2152] Addition of end-capping reagents to a Yamamoto polymerization of a dibromofluorene enables doubly end-capped polyfluorenes to be made, and this has been used to make triblock copolymers e.g. **1122** and **1123**.[2153] The optical properties of the PPP copolymers do not differ from those of the homopolymer, but the PADF copolymers show slight differences in their solid-state PL spectra compared with those of the homopolymer which

Chart 41



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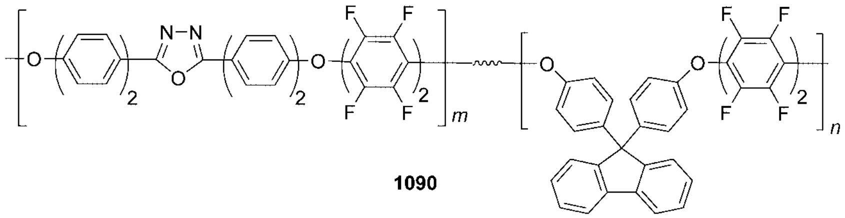
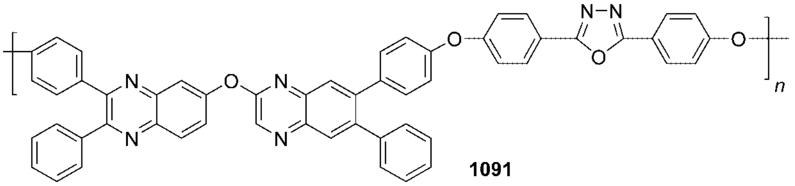


1090



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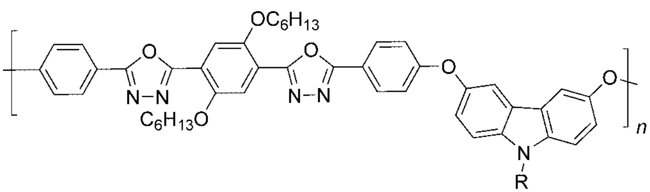
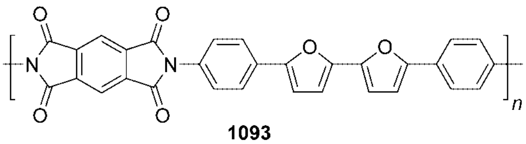


1092 R = 2-ethylhexyl



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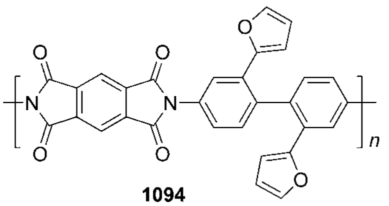
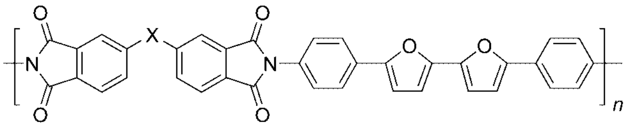
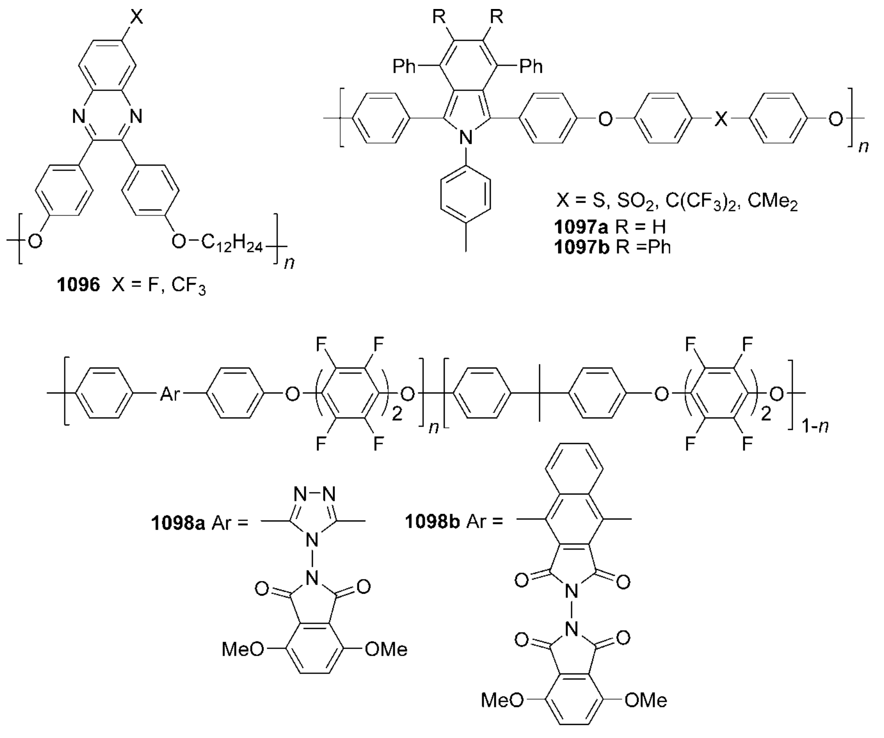


1094



1095a X = O
1095b X = $C(CF_3)_2$

Chart 42



1096 X = F, CF$_3$

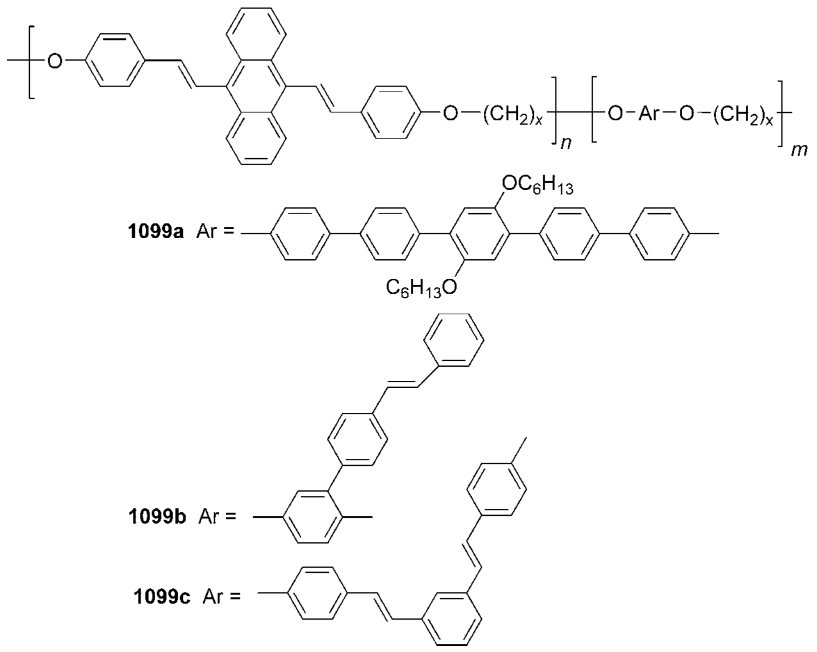
1097a R = H

1097b R = Ph

1098a Ar =

1098b Ar =

Chart 43

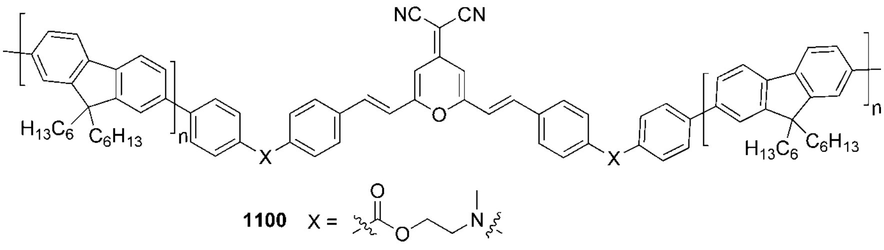


1099a Ar =

1099b Ar =

1099c Ar =

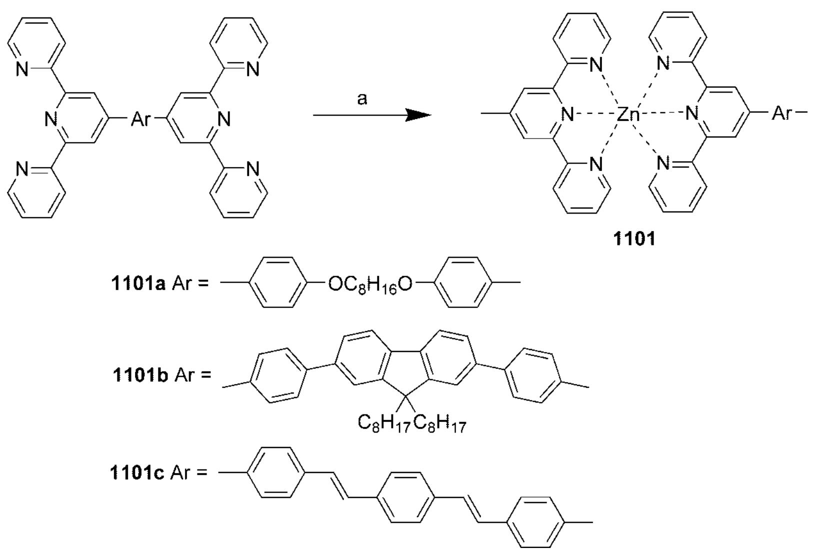
Chart 44

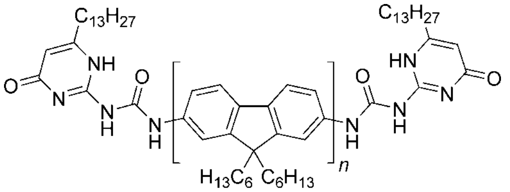


1100 X =

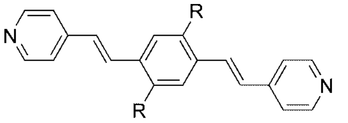
suggest that there is a higher degree of order in the films. Studies of the morphology of some of these rod−coil copolymers have shown that they form extended one-dimensional fibrillar structures due to π-stacking of the

Scheme 63. Self-Assembled EL Polymers Formed by Metal Complexation: (a) $Zn(OAc)_2$, KPF_6

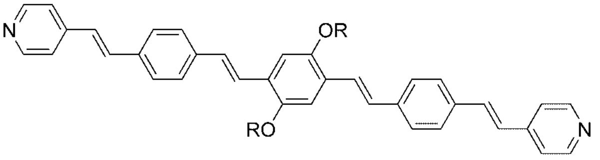




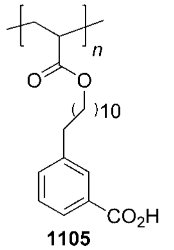
1102



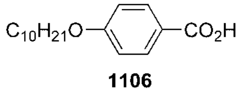
1103a R = H
1103b R = OMe
1103c R = OC_8H_{17}



1104a R = C_8H_{17}
1104b R = $C_{12}H_{25}$



1105



1106

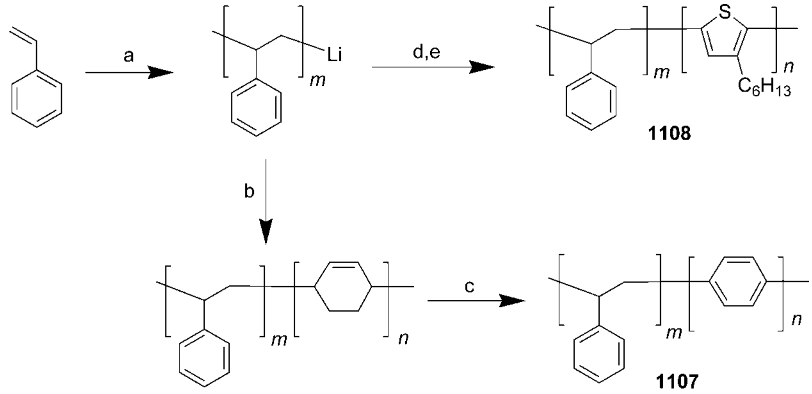
rods.[2154−2157] The stacking of the chains is dependent upon the ratio between the conjugated and nonconjugated blocks.[2153] However, no study of the effects of the coils on the luminescence properties of these polymers has yet been reported.

It has been reported that terfluorene−polystyrene copolymers such as **1117** show no evidence for ketone formation even after annealing in air.[2147−2149] The corresponding copolymers with methacrylates, by contrast, do undergo oxidation upon annealing.[2148] The "grafting onto" method has also been used to make PPV-based rod−coil copolymers, by coupling coils to well-defined oligomers of PPV made by methodologies using Wittig and/or Heck coupling. Examples are the copolymers with polyethylene oxide **1124**,[2158] polyisoprene **1125**,[2159] and the triblock **1126**,[2160] which shows emission from both the PPV (λ_{max} = 465 nm) and the triphenylamine (λ_{max} = 368 nm) segments, with evidence for energy transfer between these two nonconjugatively linked blocks.

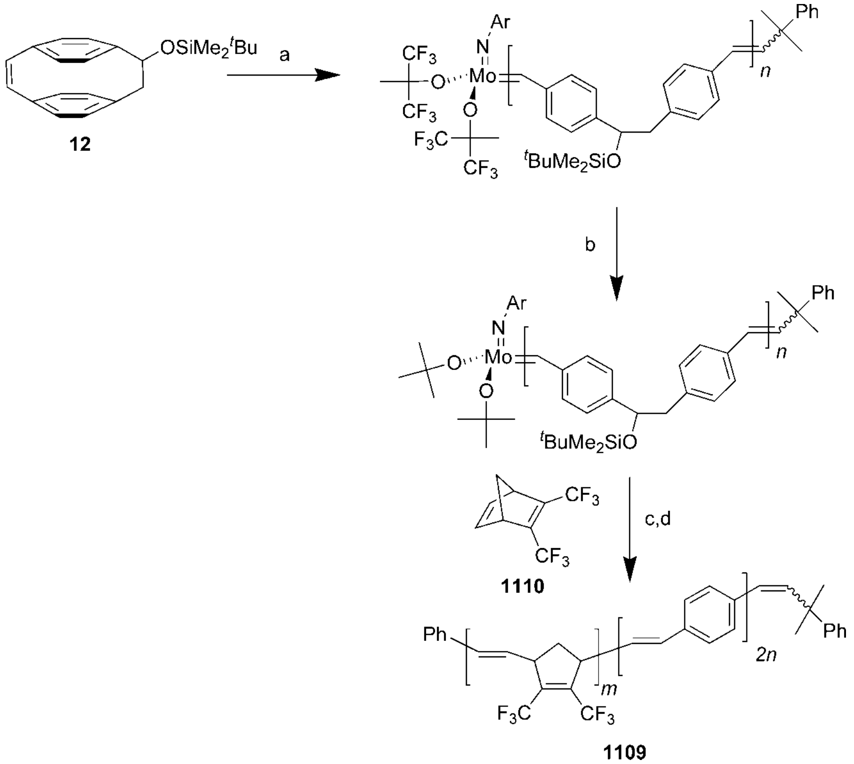
Jenekhe and Chen have prepared copolymers **1127** and **1128** (Chart 47) by a reverse "grafting-onto" procedure in which a PS coil was end-capped with one or two acetophenone units, which were then used to make polyquinoline rods by a Friedländer polycondensation.[2161,2162] The PL from the triblock copolymers **1128** is blue (λ_{max} = 460 nm) in solution but orange (λ_{max} = 598−608 nm) in the solid-state, due to excimer emission from aggregates.[2163] The luminescence behavior of the diblock copolymers **1127** is more complex. In solution, a minor component of the emission comes from isolated chromophores (λ_{max} = 455−460 nm), but the major component is from the aggregates and is concentration dependent. As the concentration increases, the emission maximum blue-shifts from λ_{max} = 582 nm to λ_{max} = 515−520 nm. The solid-state emission depends upon the morphology. Depending upon the relative lengths of the two blocks, the copolymers can form spherical (λ_{max} = 454−460 nm), lamellar (λ_{max} = 576 nm), or cylindrical (λ_{max} = 594 nm) aggregates.[2161,2163]

There also exist syntheses of rod−coil copolymers which do not fit neatly into either of the above categories. Miller and co-workers have prepared coil−rod−coil triblock copolymers in a one-pot method by using end-capping agents in the Yamamoto polymerization of dibromodihexylfluorene, which also act as initiators for the formation of the coils by living radical polymerization of styrene to produce **1129** or ring-opening polymerization of caprolactone to give **1130**. This method can be thought of as a combination of the two approaches. The copolymer with PMMA **1131**, however, had to be made in a stepwise "grafting onto" procedure, as the initiator for the atom transfer radical polymerization (ATRP) of methyl methacrylate was not stable under Yamamoto reaction conditions.[2164] The coil−rod−coil polymer **1132** has been prepared by end-capping two PS coils with terthiophene units and then linking them together with more thiophene units as shown in Scheme 67.[2165] The PL maximum is at

Scheme 64. Synthesis of Polystyrene−Polyarylene Block Copolymers: (a) *sec*-BuLi; (b) Cyclohexa-1,3-diene; (c) Chloranil, 120−150 °C; (d) 2,5-Dibromo-3-hexylthiophene; (e) 3-Hexylthiophene, FeCl$_3$



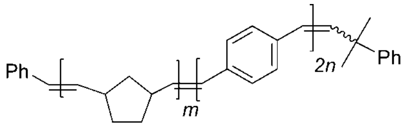
Scheme 65. ROMP Synthesis of a PPV−Polynorbornadiene Copolymer: (a) [Mo(=NAr)(=CHCMe$_2$Ph){OCMe(CF$_3$)$_2$}]; (b) 2 mol equiv of LiO^{t}Bu; (c) PhCHO; (d) Pyridine·HF



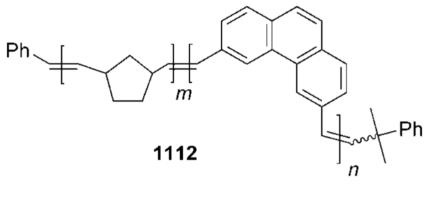
2.18 eV (λ_{max} = 570 nm), with secondary peaks at 2.05 eV (λ_{max} = 605 nm) and 1.87 eV (λ_{max} = 664 nm).

There are two reports in the literature of a synthesis of block copolymers with all conjugated blocks. Oxidation of mixtures of 3-octylthiophene and *N*-ethyl- or *N*-octylcarbazole with iron(III) chloride gives block copolymers **1133**, in which the polythiophene blocks are separated by carbazole dimers.[1550] The average length of the thiophene blocks could be varied from m = 6 to m = 100, by controlling the ratio of the two monomers. With increasing thiophene content, the EL maxima were red-shifted from λ_{max} = 602 nm (m = 6) to λ_{max} = 650 nm (m = 100). The EL efficiency of the copolymer with long thiophene blocks (m = 100) was equal to that of the thiophene homopolymer **647c**, while the copolymers with shorter thiophene blocks (m = 6, 30) showed efficiencies an order of magnitude higher than those of the homopolymer, but this is still quite low (<0.1%).

Polymers **1134** and **1135** were prepared by Suzuki polycondensation of a fluorene monoboronic acid in the presence of the bromo-substituted oligo-PV units **1136** and **1137**.[2166] From the molecular masses of the polymers, the total number of fluorene units in **1134** and **1135** is about 18. The PL in solution comes from the fluorene blocks (λ_{max} =

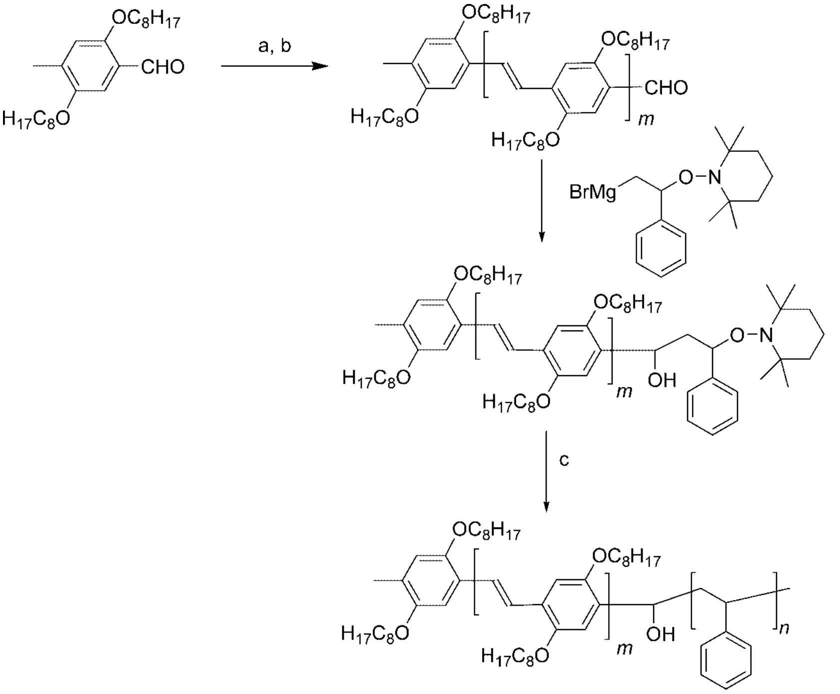


1111



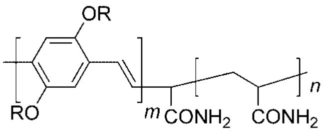
1112

Scheme 66. PPV-PS Copolymers Using PPV-Macroinitiator: (a) PhNH$_2$; (b) KO^{t}Bu, DMF; (c) Styrene, Δ

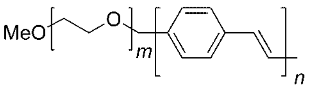


1113

Chart 45



1114



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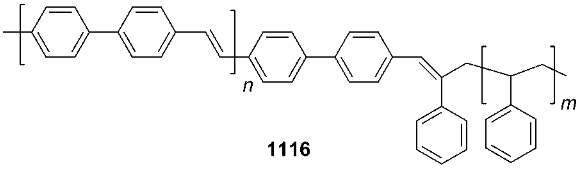

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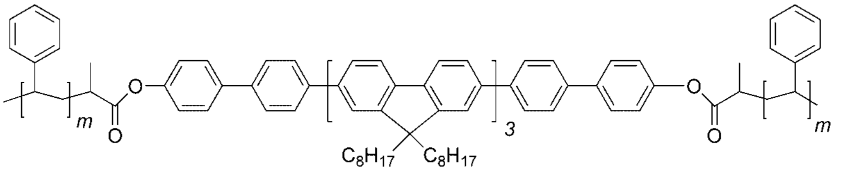


1117

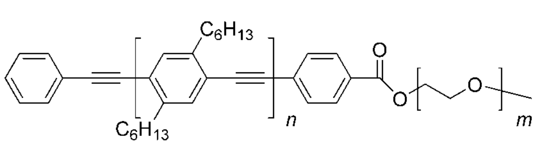
425 nm), but in the solid state, energy transfer to the arylene vinylene units produces emission only from them (λ_{max} = *ca.* 490 nm and *ca.* 525 nm, respectively). As the polymers are surely contaminated with the fluorene homopolymer, inter- as well as intrachain energy transfer must be occurring. These polymers are claimed to be promising candidates for polymer lasers (see section 6.5 below).

While block copolymers represent challenging synthetic targets and can display fascinating phase behavior, which from a purely academic interest justifies the extra effort required for their synthesis, it is not clear that they possess any particular merit as emitting materials. They seem to possess more potential as materials in photovoltaic applications where control of phase separation is a major issue.

5. Blends and Combinations of Polymers with Other Materials

One approach to tuning the properties of a luminescent polymer for use in LEDs and other devices is to blend it with another material, either another luminescent polymer, a nonluminescent polymer (acting as a matrix or charge transporting material), or a molecular substance (luminescent or otherwise). The properties may be enhanced or modified by blending in a number of ways. First, the other components may act as an energy or charge transporting material to boost the overall luminescence efficiency. Second, one effect of diluting the polymer with another material is to separate the polymer chains, thus reducing interchain interactions and producing a higher degree of excited-state confinement which

Chart 46



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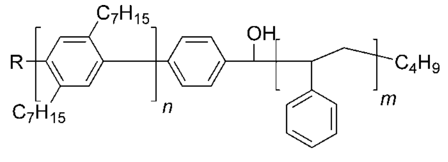
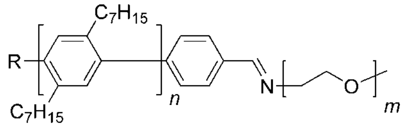
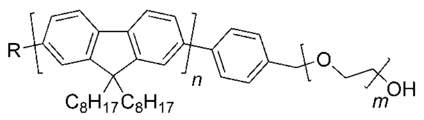


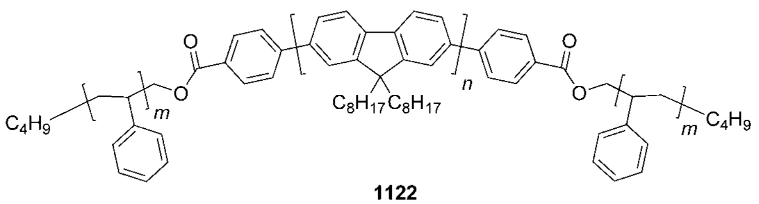
1119 R = H, Ph



1120 R = H, Ph



1121 R = H, Ph



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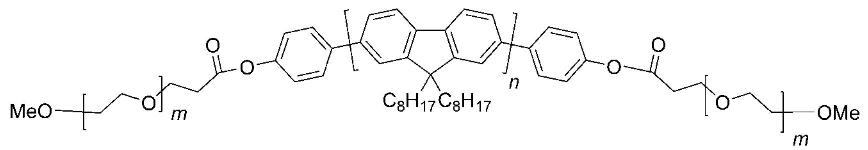


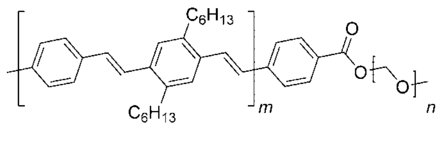
1123

can increase the luminescence efficiency and by suppressing excimer formation prevent red-shifts in the emission. Alternatively, the two materials may form an exciplex to create a new emission band. Third, by combining materials with different emission maxima, new colors may be produced, and it may even be possible to obtain white emission. There is a recent short review on methods for obtaining white EL from organic LEDs by Chen and Chang.[27] It should be noted that when two luminescent materials are mixed, whether only one or both show emission depends upon whether energy transfer can occur, which in turn depends upon the overlap between the emission of the larger band gap component and the absorption of the other, and upon the distance between the two components. Controlling the degree of energy transfer by altering the blend composition or dilution with other materials can thus profoundly affect the emission color. An obvious problem with blends is that of phase separation over time, especially under the effect of an electric field, which can lead to device stability problems.

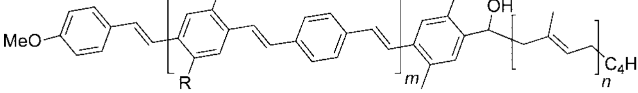
5.1. Blends of Luminescent Polymers

Blending two luminescent polymers together can produce emission whose maximum is intermediate between those for the two components, and with higher efficiency than either. This was first demonstrated by Yu et al.,[2167] who found that blending red emitting MEH-PPV (**20**) and poly(3-hexylthiophene) (P3HT, **647a**) gave an initial increase in LED efficiency with increasing P3HT content up to a maximum of 1.7% (calcium cathode with 1 wt % of P3HT), which is twice the efficiency of an identical device made from pure MEH-PPV and 3 orders of magnitude higher than that for pure P3HT. The emission maximum ($\lambda_{\max} = 650$ nm) was intermediate between those of the two polymers. Salaneck and co-workers have found that a blend of the blue-green (2.6 eV, $\lambda_{\max} = 479$ nm) emitting phenylene–thiophene copolymer (**749d**) and violet-blue emitting (3.2, 2.8 eV, $\lambda_{\max} = 389$, 443 nm) polyphenylene (**1138**) emits blue light (2.7 eV, $\lambda_{\max} = 460$ nm) with an optimal efficiency of 1.9% (10 wt % of **749d**).[2168−2170]

Jenekhe and co-workers found that a blend of the polyquinoline copolymers **692** and **1139a** also showed EL emission intermediate in color between that of the two components, with an optimal EL efficiency of 0.11% for a blend containing 0.1 wt % of **1139a** (*cf.* the EL efficiencies for **692** and **1139a** are only 0.03% and 0.004%, respectively).[2171,2172] A blend of **1139a** with copolymer **690b**, by contrast, displayed EL emission only from **1139a**, with a small increase in EL efficiency, while blends of copolymer **691a** with copolymers **690b** or **1139b** showed emission from **691a** without any improvement in efficiency. A blend of polyfluorene **558a** and the blue emitting copolymer **1140a** ($\lambda_{\max} = 445$ nm) shows EL emission from the latter with an efficiency of up to 1% in a single-layer device, which is 2



1124 *m* = 4,6



1125 R = C_8H_{17}, OC_8H_{17} , *m* = 1-6

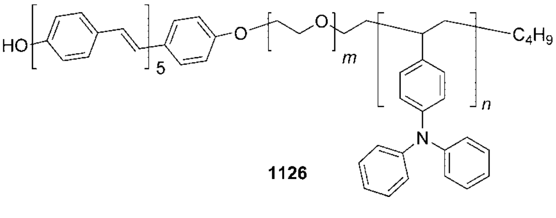


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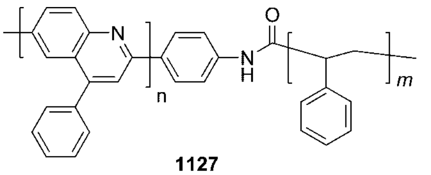
Chart 47



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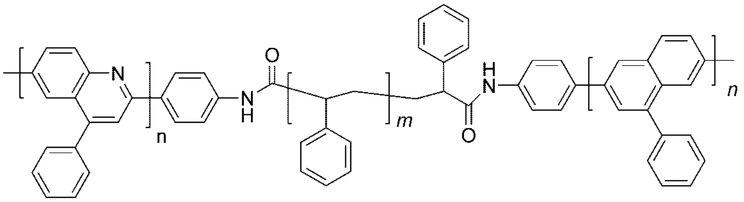
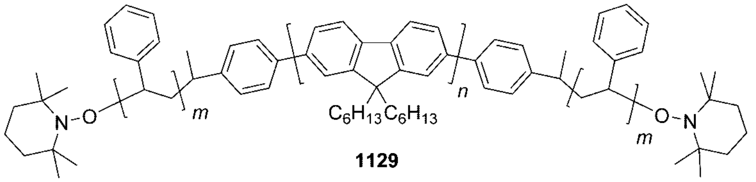


1128



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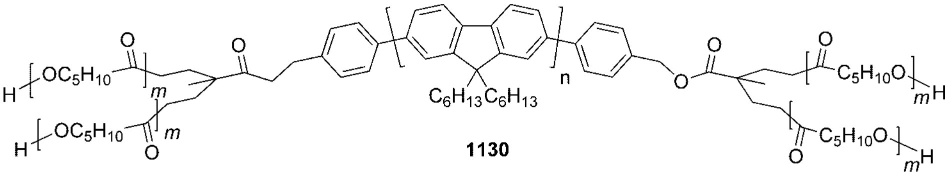

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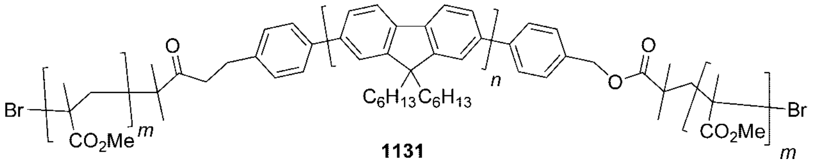


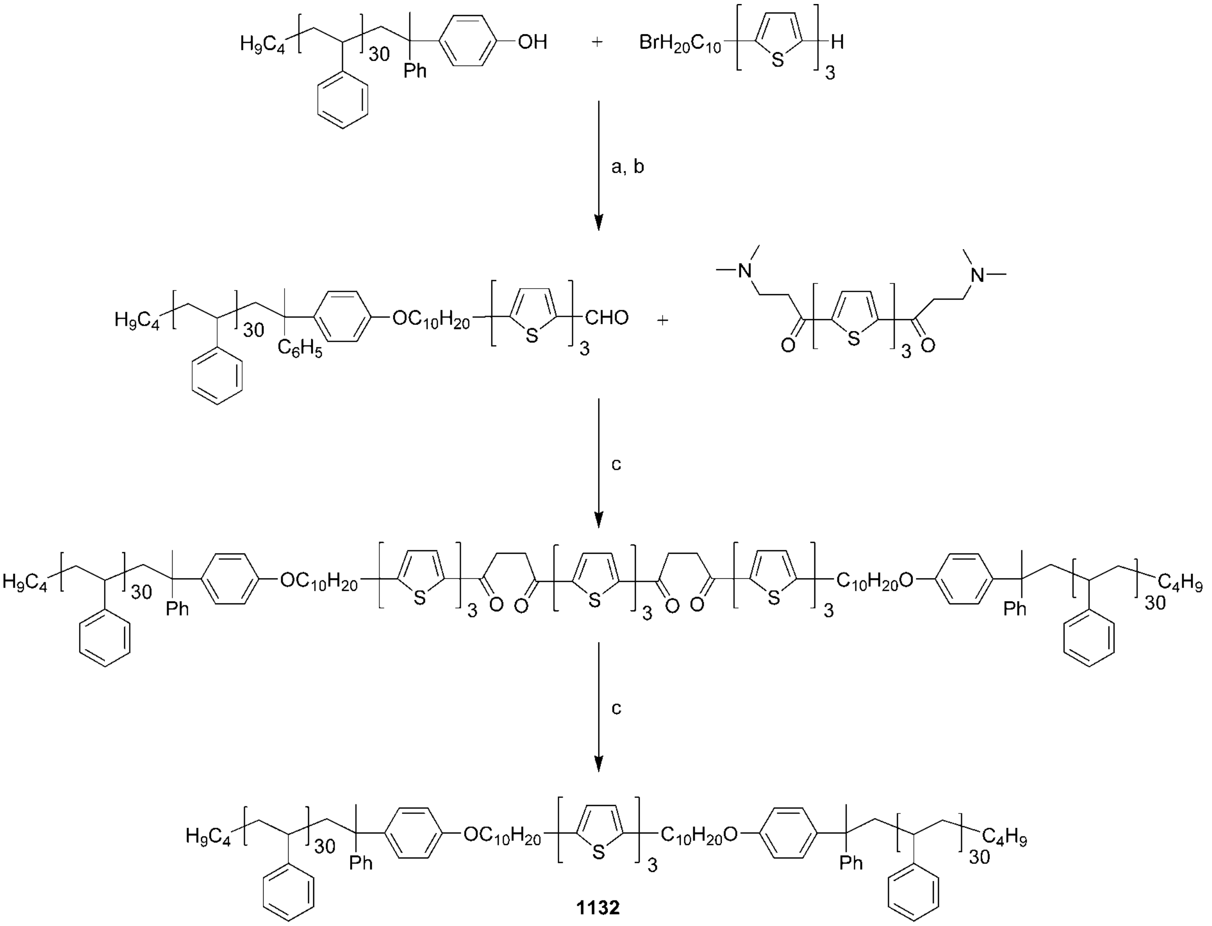
1131

orders of magnitude higher than that for **558a** alone.[2173,2174] The turn-on voltage for blends of **1141** with **833a** decreases from 14 to 4 V as the content of **833a** increases, while the EL maximum red-shifts from 542 to 600 nm.[2175] This was attributed to the rigid backbone of **833a** causing the coil-like **1141** to adopt a more planar extended chain configuration, enhancing charge delocalization.

In the preceding cases, the two polymers have fairly similar luminescence maxima; when polymers with very different emission colors are mixed, then usually the emission comes largely from the one with the smaller band gap, with the other material acting to enhance the emission efficiency by charge or energy transfer. For example, the Yoshino group have found that mixtures of poly(2,5-alkoxyphenylene vinylene)s (**39j,k**) and poly(9,9-dihexylfluorene) (**558a**) show emission only from **39**, except at high concentrations of the PADF.[2176] Blending **558b** with **39i** enhances the EL efficiency of the latter 6-fold, but with a slight blue-shift in the emission spectrum.[2177] Shim et al.[2178−2181] found that blends of MEH-PPV (**20**) and the blue emitting copolymer **982d** ($x = 3$) showed emission largely from the MEH-PPV. The emission maximum was blue-shifted by 20−40 nm from that of MEH-PPV. The optimal efficiency for a blend **982d/20** = 15:1 with an Al cathode, was nearly 500 times greater than that for a similar device made from MEH-PPV alone. As blending of MEH-PPV with insulating polymers, e.g. polystyrene, gave a less than 10-fold increase in the emission efficiency, dilution effects clearly play only a minor part in the observed enhancement. The enhancement was therefore attributed to the charge-transport properties of copolymer **981d**, leading to confinement of charge on the MEH-PPV. Similar enhancements of the EL efficiency of MEH-PPV and other red-orange emitting alkoxy-PPVs have been reported by blending them with other green or blue emitting polymers **649**,[2182] **1142**,[2183] **385**,[2184] **389**,[2184] **1143**,[2185] **1020a−c**,[2036] **1144a**,[2186] and **694a**.[2187] In the last case, the emission is voltage-tunable between red ($\lambda_{max} = 585$ nm) and green ($\lambda_{max} = 530$ nm).

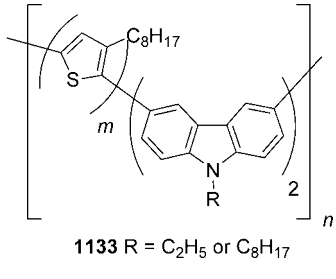
Emission from a blend of **694a** and **647c** is not voltage-dependent but does show an improvement in efficiency. MEH-PPV (**20**) has also been used as the larger band gap component in blends with red emitting copolymers. Thus, a 1:2 blend of MEH-PPV **20** with **719b** produces efficient red EL ($\lambda_{max} = 633$ nm, 3.8%).[1687] The emission from blends of MEH-PPV **20** and **720b** (R = C_8H_{17}) varies depending upon the composition, with the emission maximum ranging between 585 and 718 nm.[2188] The highest efficiency of 3.8% was obtained for a 240:1 ratio of **20/720b** ($\lambda_{max} = 680$ nm). A mixture of the fluorenylene vinylene−phenylene vinylene copolymers **302a** and **303a** shows emission only from the former ($\lambda_{max} = 480$ nm), but the emission spectrum is narrower with less vibronic structure and the efficiency is ten times higher than that for pure **302a**.[2189,2190] Blending **303a** with PVK suppresses yellow excimer emission ($\lambda_{max} = 540$ nm) to give pure blue emission ($\lambda_{max} = 425$ nm).[2190] Similarly, a mixture of polymers **1144b** and **1145** shows

Scheme 67. Synthesis of PS−Oligo(thiophene)−PS Triblock Copolymer: (a) NaH, THF, DMF; (b) $POCl_3$, PhNMeCHO; (c) NaCN, DMF; (d) Lawesson's Reagent

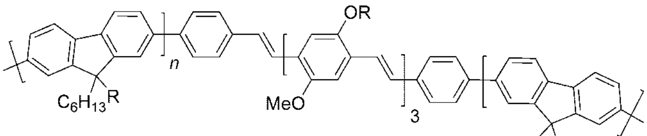


emission only from the former (λ_{max} = 460 nm) with the highest luminance from a 17:83 mixture. Addition of an Alq_3 electron transporting layer improves efficiency, but for mixtures with lower **1145** content, some emission comes from the Alq_3.[2191] A mixture of the arylene ethynylene copolymers **479d** and **479e** shows EL emission from the latter (λ_{max} = 530 nm).[954]

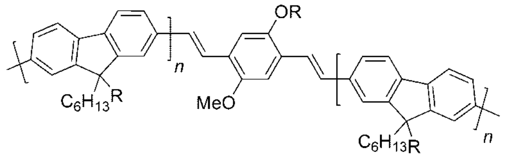
Polyfluorenes have been used as hosts for green emitting polymers. Thus, blends of **558b** with copolymers **772c**, **788a**, and **816** display EL from the copolymers with enhanced efficiencies.[2192−2194] The EL efficiency of blends of **558b** and **816** depends upon the composition, with the highest efficiency coming from a 19:1 blend.[2195] A blend of the fluorene copolymer **582a** with the fluorene vinylene copolymer **309b** produces green EL (λ_{max} = 505 nm), with a highest efficiency of 12.6 cd/A for the 3:7 blend.[2196] The efficiency of EL from blends of the copolymers **1140b** and **816** has been found to vary depending upon the solvent used to deposit them.[2197,2198] This has been shown to be due to differences in the film morphology with vertically phase-separated blends in which the top of the emissive layer is rich in **816** and the bottom is rich in **1140b** showing much better efficiencies than films in which the components are laterally separated. The emission efficiency and stability of blue emitting polyfluorenes and fluorene copolymers can be



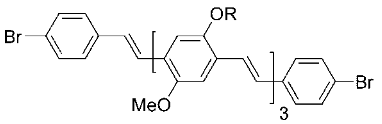
1133 R = C_2H_5 or C_8H_{17}



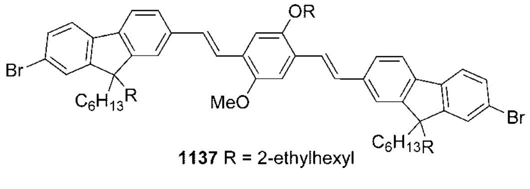
1134 R = 2-ethylhexyl



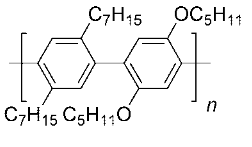
1135 R = 2-ethylhexyl



1136 R = 2-ethylhexyl



1137 R = 2-ethylhexyl



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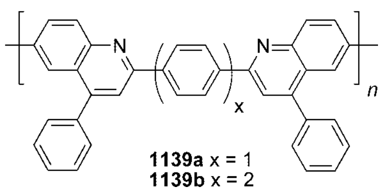
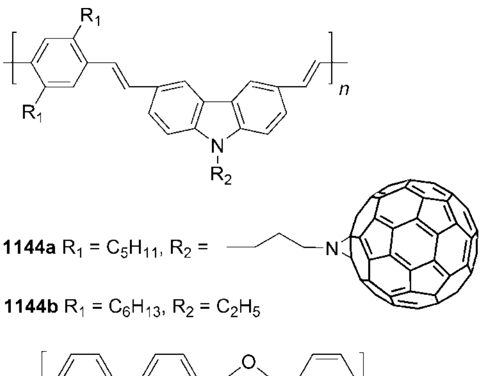
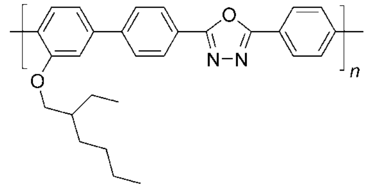


1139a x = 1
1139b x = 2

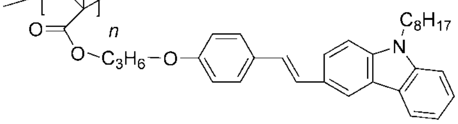


1144a $R_1 = C_5H_{11}$, R_2 =

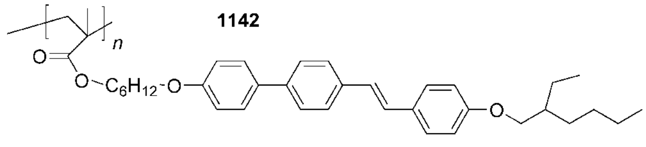
1144b $R_1 = C_6H_{13}$, $R_2 = C_2H_5$



1145



1142

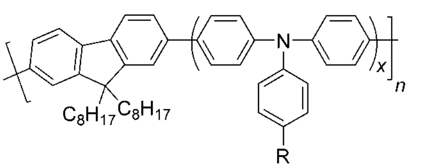


1143

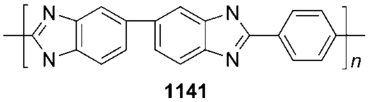
enhanced by blending them with violet emitting polymers. Thus, blends of polyfluorenes **558** with **1146** produce stable blue EL with none of the green emission usually seen from these polymers.[1305] A 1:4 blend of polydialkylfluorene-co-dibenzothiophene (1−50%) with the EHO-PPP **1147a** displays blue EL (λ_{max} = 435 nm) with four times higher efficiency (1.8%) than that for the pure copolymer.[2199]

In some cases, the emission comes from both polymers in the mixture. For example, blends of MeLPPP (**552b**) with the P3AT **647g** produce emission from both polymers to give an overall emission color of yellow.[2200] The emission maximum for the component of the emission from **647g** red-shifts from λ_{max} = 550 nm to λ_{max} = 580 nm, which is the emission maximum value for **647g** in solution, as the amount of **647g** increases from 0.5% to 2%. The EL efficiency is highest (4.2%) for a blend with 1 mol % of **647g**. Similarly, blends of copolymers **307** and **361** show EL (λ_{max} = 475 and 540 nm, respectively) from both, with the relative intensities of their emission dependent upon the composition of the mixture, indicating that there is no energy transfer between them.[744] By contrast, blends of **307** with PVK show emission from **307** with a 5-fold increase in the EL efficiency to 0.1%, while blends of **361** and PVK show blue EL whose emission maximum (λ_{max} = 440 nm) corresponds to the PL emission maximum of nonaggregated **359** (see section 2.7 above).

Sometimes the emission from a blend may come from both or either component depending upon composition or voltage. Thus, blends of **982a** and the green emitting **75b** with PVK and an oxadiazole added to improve charge transport show emission from both components for low concentrations of **982a**, but they show emission only from **75b** with a much enhanced efficiency at higher concentrations of **982a**.[2201] The emission color from mixtures of the blue emitting copolymer **982a** (*x* = 8) and the green emitting copolymer **1148** (Chart 48) can be tuned between the emission maxima of the two components (λ_{max} = 465 and 535 nm, respectively) by altering the composition of the blend. The highest efficiency was obtained for a blend containing 15 mol % of **1148** which gave green (λ_{max} = 510 nm) emission. Addition of hole-transporting PVK (**934a**) and an electron-transporting oxadiazole compound to the mixture gave lower turn-on voltage due to better charge injection, while addition of a red emitting laser dye led to red emission through energy transfer. Near-white EL was also obtained by blending the red, green, and blue emitting components together with the PVK and oxadiazole in a different proportion in which energy transfer between them was minimized.[2202] Epstein and co-workers have obtained bias and voltage variable emission from blends of a red emitting (λ_{max} = 610 nm) PPyV copolymer **357** with other emitting polymers. A blend with the green emitting (λ_{max} = 545 nm) copolymer **1149** (Chart 49) showed red emission under positive bias and green emission under negative bias.[2203−2205] Blends of **357** with the polyacetylenes **868c** and **872c** also showed red emission under positive bias, but under reverse bias the emission was tunable from red to green by increasing the applied voltage.[2206] Blends of copolymers **78b** and **1149** show interesting luminescence behavior.[2207] As the amount of **1149** increases, the PL undergoes a bathochromic shift from λ_{max} = 509 nm to λ_{max} = 514, 530 nm (*cf.* λ_{max} = 517, 530 nm for **1149**). Single-layer LEDs show blue-green EL



1140a *x* = 2, R = Me **1140b** *x* = 1, R = C_4H_9



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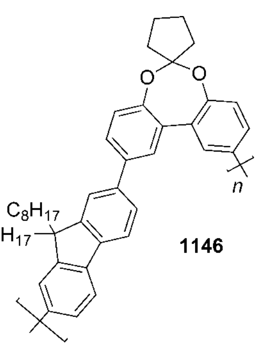

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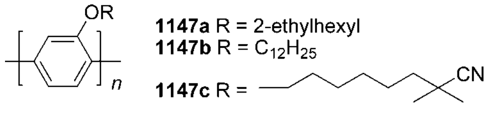
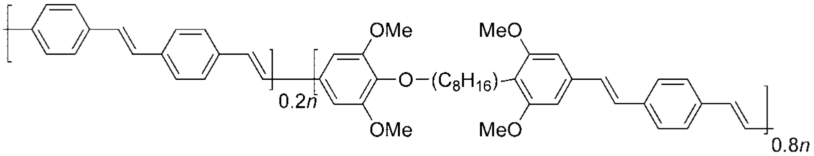


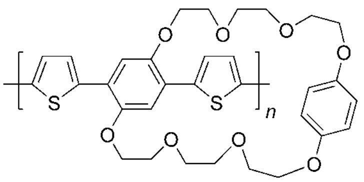
1147a R = 2-ethylhexyl
1147b R = $C_{12}H_{25}$
1147c R =

Chart 48

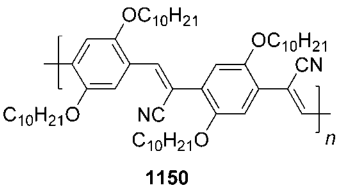


1148

Chart 49



1149



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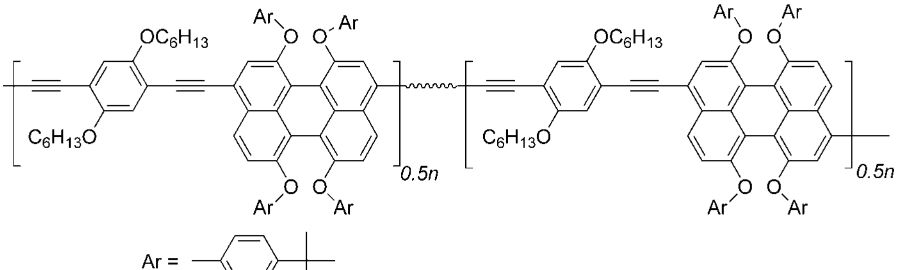
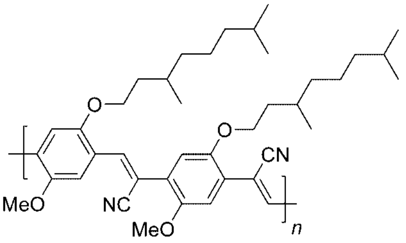


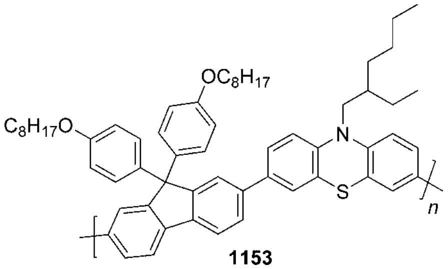
1151

(λ_{max} = 494−505 nm) intermediate between the EL of the components (λ_{max} = 454 and 513, 539 nm, respectively), while double-layer devices with a PEDOT hole-transporting layer show EL only from **1149**.

If the components of the blend have complementary emission colors, white emission can be obtained. Near-white EL has been observed from blends of copolymer **982a** (x = 10) and the red-orange emitting polymers **39j** and **1150**.[2208] Blends of MeLPPP (**552b**) and red emitting PPDB (**1151**) show predominant emission from the latter even at concentrations of only 0.2 wt % PPDB. The emission is orange at 0.2 wt % PPDB with an EL efficiency of 1.6% (*cf.* 1% for MeLPPP and 0.01% for PPDB) but drops rapidly at higher PPDB concentrations. The PL efficiency is optimal (41% *cf.* 30% for MeLPPP and 11% for PPDB) with 0.7 wt % PPDB and again drops as the concentration increases.[1033,2209−2211] A blend with 0.05 wt % PPDB shows high (0.8%) efficiency white EL emission due to emission from both polymers.[1023,1033,2211] Blending the polymers with PMMA leads to separation of the emissive polymer chains and less efficient energy transfer so that 0.08 wt % of PPDB is required for obtaining white emission, but the EL efficiency is increased to 1.2%. White emission has also been observed from blends of polyfluorenes with green and orange emitting PPV derivatives. Thus, a blend of **575** with 0.5 wt % MEH-PPV produces white EL with 1.3% efficiency (3.4 cd/A).[1225,2212] White EL is also seen from blends of **558c** (95 wt %), the green emitting **121b** (4 wt %), and either MEH-PPV or the CN-PPV **1152** as the red emitting component (1 wt %).[2212] An efficiency of 6% has recently been reported for a device using a blend of **558c** and MEH-PPV (2 wt %).[2213] White EL has also been obtained from blends of siloxane-end-capped **558b** with the yellow emitting PAV **150a**.[2214] A blend of 9 wt % of **828** in **558b** produces voltage-stable white EL with an efficiency of 1.64% (4.08 cd/A).[1692] A blend of the fluorene-phenathiazine copolymer **1153** and MEH-PPV is also reported to produce white EL.[2215]

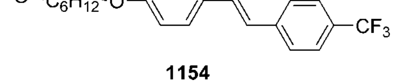


1152

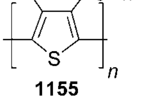


1153

Sometimes, the two polymers may form an exciplex leading to new emission bands. For example, a mixture of MEH-PPV and the blue emitting (λ_{max} = 420 nm) side-chain polymer **1154** shows an exciplex band at 800 nm. For a 1:10 blend, the PL is largely from the MEH-PPV and is red (λ_{max} = 580 nm), but the EL is nearly white with maxima at λ_{max} = 400, 580, and 800 nm.[2216] A similar exciplex emission has been observed from a bilayer device ITO/PVK/**1147b**/Ca/Ag in which the second layer was deposited from toluene (in which PVK is soluble) so that a partial mixing occurred



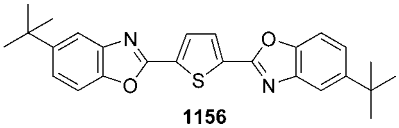
1154



1155

at the interface. The resulting emission was white due to formation of a red emitting exciplex between the two polymers; by contrast, the device showed blue emission if the second layer was deposited in hexane in which PVK is insoluble.[1077,2208]

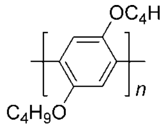
Blends of more than two emissive polymers have also been used. Inganäs and co-workers have found that the light emission from blends of the polythiophenes **662**−**664** could be tuned from red to green by controlling the applied voltage.[1413,2217−2219] The emissive color range could be controlled by varying the proportions in the blend or by adding nonluminescent polymers.[2220] A blend of polymers **662a**, **664**, and **1155** in poly(methyl methacrylate) (PMMA) emits white light.[2221] The PMMA acts as an insulating matrix, which reduces the degree of exciton transfer between the polymers. The EL efficiency of a green emitting (λ_{max} = 530 nm) blend of **558b** and **816** (95:5) can be increased from 1.0% to 1.3%, and the onset voltage can be reduced from 3.7 to 2.7 V, by incorporation of the hole-transporting polymer **582a**.[2222] This is despite a reduction in the PL efficiency of the mixture from 64% to 44%.



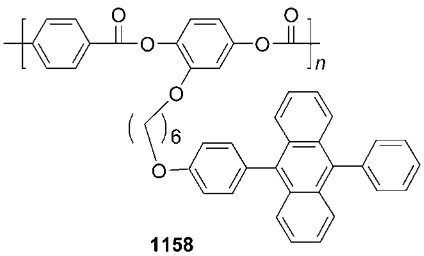
1156

PVK (**934a**) is a luminescent material but is usually added to blends so as to improve the injection and transporting of holes. In some cases, the blends show emission from both the PVK and the other polymer. Heeger, Rieke, and co-workers[2223] have constructed a device using a blend of PVK and regioregular P3HT (**647a**). The emission is a mixture of blue light from the PVK and red light from the polythiophene. The best efficiency of 0.2%, representing a 4-fold increase over PVK and an increase of 2 orders of magnitude over the polythiophene alone, was reported for a blend containing 2 wt % of P3HT. White EL has been obtained from a blend of PVK, P3HT (0.039 wt %), and charge-transporting TPA (2.2 wt %) and molecule **1156** (3.0 wt %),[2224] and from a blend of PVK with **823b**.[2214] Wang and co-workers have studied the emission from devices using poly(3-octylthiophene) (P3OT, **647c**) doped with varying amounts of PVK as emissive layer and found optimal efficiency from an equimolar mixture.[2225−2227] In this case, the emission was almost entirely from the P3OT.

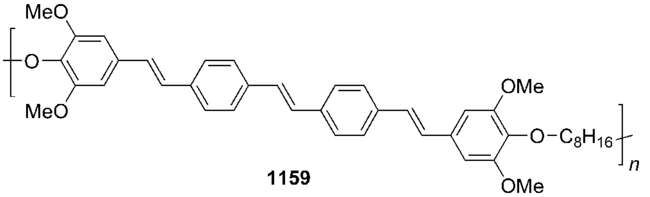
In other cases, the emission is intermediate between that of PVK and the other polymer. Blue emission has been obtained from blends of PVK and the polyphenylene **1157**.[2228] The emission maximum is at 448 nm, which is intermediate between the emission maxima of PVK (λ_{max} = 418 nm) and **1157** (λ_{max} = 460 nm). A blend of **1157** and PBD in PVK, however, showed violet-blue (λ_{max} = 424 nm) emission, but with an efficiency 100 times greater than that for pure **1157**.[1075] Blue (λ_{max} = 430−450 nm) emission has also been obtained from a blend of PVK and the luminous side-chain polymer **1158** (λ_{max} = 460 nm).[2229] A blend of the polymer **982a** (x = 6) with PVK also shows blue EL with an emission maximum (λ_{max} = 450 nm) intermediate between that of **982a** (λ_{max} = 465 nm) and PVK. The EL efficiency is much higher than that for the pure polymer and increases with increasing PVK content.[2230]



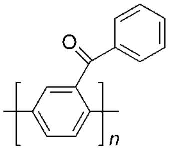
1157



1158

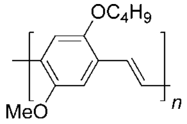


1159

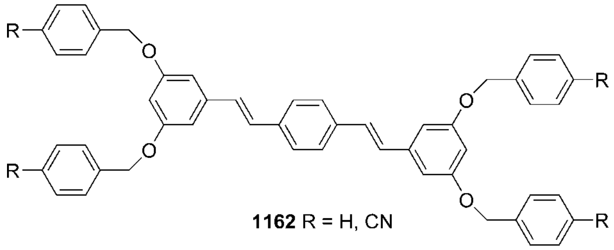


1160

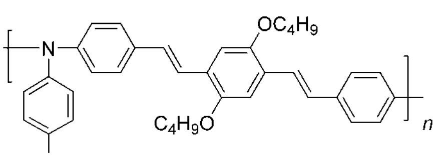
Emission from an exciplex at 476 nm becomes the dominant feature in the EL spectra of blends of the green emitting copolymer **1159** (λ_{max} = 515 nm) and PVK for blends containing 3 wt % or more of **1159**.[1871] The luminance from this blend can be enhanced 5-fold by use of a thin (15 nm) hole-transporting layer of PPV.[2231] If a thicker (60 nm) layer of PPV is used, the emission comes from the PPV instead, suggesting the recombination zone in these devices is close to the anode. Blending of poly(2-phenylphenylene vinylene) (PPPV, **136**) with high-molecular weight PVK is reported to improve the film-forming capability of the PPPV.[536] A blue-shift of the electroluminescence with respect to that of PPPV was observed. By contrast, blending the polyphenylene **1160** with PVK produces a red-shift in the EL from λ_{max} = 433 nm[1074] to λ_{max} = 446 nm.[1101]



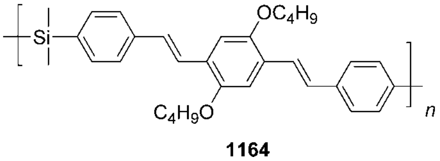
1161



1162 R = H, CN

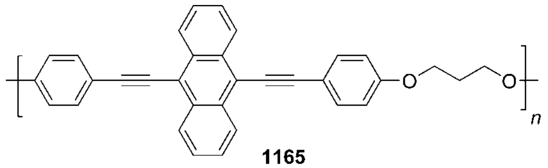


1163

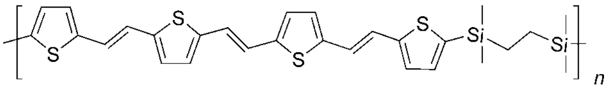


1164

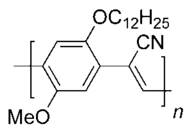
There are also several examples of blends with PVK merely acting as a hole-transporting matrix, e.g. with the PPV **1161**,[2232] the dendrimers **1162**,[2233] and the polymer **1163** with interrupted conjugation.[2234] Blending the silyl-interrupted PPV copolymer **1164** with PVK leads to an increase in PL quantum efficiency from 6% to 24%, but to only a small increase in EL efficiency in a one-layer device. Addition of a PBD hole-blocking layer leads to a dramatic 60-fold increase to 3.2% efficiency due to much improved charge carrier confinement.[1989] A blend of PVK with MEH-PPV (**20**) and copolymer **307** (19:1:1) produces white EL due to emission from both **20** and **307**.[2235] Another reason for blending emissive polymers with PVK may be to alter the EL behavior by suppressing aggregation. For example, blending the regioregular PPyV derivative **339** with PVK leads to a change in the EL color from red to green.[2236] In the case of the polymers **1165** and **1166**, blending with PVK is required to obtain EL emission, as, due to aggregation, their solid-state PL is weak and no EL can be detected. The PL maxima for the blends (λ_{max} = 498 and 442 nm) are similar to their solution maxima (λ_{max} = 493 and 405 nm) (cf. λ_{max} = 530 and 570 nm for films), and their EL maxima can be tuned between 493 and 580 nm for **1165** and from 520 to 580 nm for **1166**, respectively, by increasing the PVK content. The emission color changes from blue-green to white and then to red with increasing PVK content. The emission at 580 nm may come from an exciplex.[2237] For a blend of **1167** with PVK, the emission color changes from blue (λ_{max} = 420 nm) at 5 V to orange (λ_{max} = 520 nm) at 9 V, but with a drop in efficiency.[2238]



1165



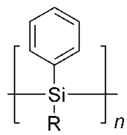
1166



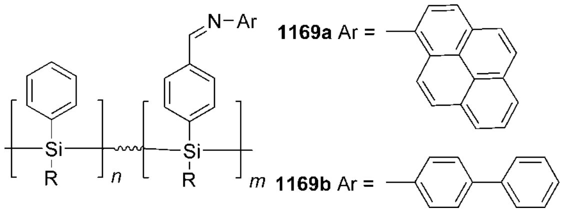
1167

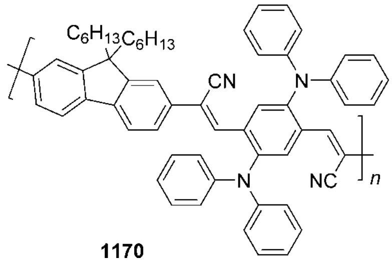
Blending the PPP derivative **542** with the ultraviolet (λ_{max} = 354 nm) emitting polysilane **1168a** leads to a 50-fold increase in the EL efficiency and the suppression of an aggregate emission band around 530 nm, so as to give pure blue emission (λ_{max} = 430−440 nm).[1081] Similar effects are seen with white emitting substituted polysilanes **1169a,b**. Blending the polymer **283b** with polysilane **1168b** leads to a 25-fold increase in EL efficiency. Use of a PBD electron-transporting layer leads to a further 4-fold increase in efficiency.[2239]

Recently, it has been demonstrated that the emission from blends of polymers can be tuned by chemical or photochemical means.[2240] A mixture of MEH-PPV (**20**, 0.5 wt %) and polyfluorene **558c** produces EL only from the lower band gap **20**. Irradiation of the blend with UV light in the presence of hydrazine leads to a reduction in the emission from the MEH-PPV, due to reduction of the vinylene bonds by the hydrazine, and also produces a new band in the EL spectrum at 475 nm, which is attributed to a new emissive species produced by reaction of the base with ketone defect sites in the polyfluorene. In this way, the emission color can be tuned from red to yellow. Patterned emission can be obtained by irradiating through a shadow mask.[2241,2242] This method can be extended to three-component systems. Thus, a blend of blue emitting **558b** (80 wt%), green emitting **309b** (15 wt %), and red emitting **1170** (5 wt %) produced red EL before treatment. Irradiation for 10 s changed the EL to green, and blue EL was obtained after 60 s.[2243] A similar method for tuning the emission color of blends utilizes the addition of thiols to the double bonds in poly(arylene vinylene).[2244] Irradiation of blends of **560b** with **20** or with **309b** in the presence of gaseous propanethiol changed the EL to blue from orange-red and green, respectively. A ternary blend of **560b** (93 wt %), **309b** (5 wt %), and **20** (2 wt %) could thus be used for red (untreated), green (5 s irradiation), or blue (20 s irradiation) LEDs. An obvious disadavantage of these methods is the toxicity of the reagents used, which has recently been overcome by the use of silanes as the photoreactive reagents.[2245]



1168a R = Me
1168b R = biphenyl



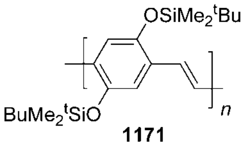


1170

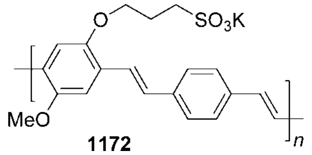
While blends of luminescent polymers clearly offer an effective method for enhancing the efficiency and/or tuning the color of emission, the issue of phase separation is likely to determine the utility or otherwise of such blends, and it remains unclear whether this will prove an insuperable obstacle to their use.

5.2. Blends of Luminescent and Nonluminescent Polymers

Blends with nonluminescent polymers have also been used in LEDs. Such a blend might be needed to improve the film-forming properties of the emissive material; for example, PPV oligomers in a polystyrene matrix have been used to make a blue emitting (λ_{max} = 480 nm) LED.[2246] More commonly, the polymer is acting as a matrix, leading to improvement of efficiency by dilution effects. In some cases, such dilution is needed to see EL at all. For example, no EL is seen from the pure disilyloxy-PPV **1171**, but a blend with polystyrene shows weak blue (λ_{max} = 480 nm) emission.[2247] More generally, the effect is to improve the efficiency and/or the electrical properties of the device. Thus, a blend of PPV (**1**) with poly(*N*-vinylpyrrolidinone) (PVP) shows higher PL and EL intensities and a lower onset voltage than PPV alone.[2248] A composite PPV–Nafion film shows only one PL maximum at λ_{max} = 510 nm (*cf.* λ_{max} = 520, 551 nm for unblended PPV), suggesting that the PPV chains are less ordered, but the EL has not yet been reported.[2249] Mixing PPV sulfonium precursor **3** with a lyotropic liquid crystalline mesophase leads after conversion to a composite with oriented isolated PPV chains which shows blue EL (λ_{max} = 450 nm), with a small amount of emission from the matrix.[2250,2251] A small blue-shift in the PL emission of the water soluble PPV-dicarboxylate **195b** has been observed upon blending with such a matrix.[2252] Blending MEH-PPV (**20**) with poly(methyl methacrylate) (PMMA) reportedly lowers the onset voltage for EL from 5.5 to 2.5 V.[2253] Such blends show nanophase separation which affects the EL efficiency. The highest efficiency, which is marginally higher than that for pure MEH-PPV, is reported to come from blends with 75 wt % of **20** in which the emissive polymer forms a continuous network surrounding isolated domains of PMMA.[2254] Ternary blends of MEH-PPV and polyfluorene **558b** in PMMA display voltage variable EL, whose color changes from yellow to green as the applied potential increases from 8 to 12 V.[2255,2256] The EL efficiency of **20** with aluminum cathodes is greatly enhanced (up to 2.6 cd/A) by blending with electrolytes such as poly(ethylene glycol)[2257] or poly(sodium styrene sulfonate).[2258] Blending the blue emitting (λ_{max} = 480 nm) polyanionic PAV **1172** with an ionic conducting polyurethane has been found to enhance the EL efficiency and lower the turn-on voltage.[2259] Unlike most PLEDs, the devices using the blends work almost equally well under both forward and reverse biases.



1171



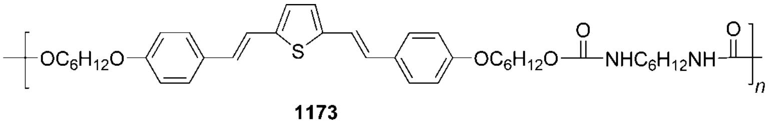
1172

Bässler et al.[2260,2261] have found that blending PPPV (**136**) with polystyrene caused an increase in quantum efficiency for the EL emission (λ_{max} = 560 nm) of 2 orders of magnitude (to 0.1%) over PPPV alone. Blending of regioregular (HT) PPyV (**349**) with nylon-6,6 has been found to increase the current density for a given applied potential (above the threshold voltage). A slight red-shift in the EL maximum from λ_{max} = 585 nm to λ_{max} = 600 nm was observed.[800] Red emitting devices have been made using films of **1170** embedded in a cross-linked poly(perfluoroaryl ether).[2262] As mentioned in section 2.8 above, highly polarized emission has been observed from aligned films of blends of dialkoxy-PPEs such as **452b** with high molar mass polyethylene.[938,939,941,943] Polarized emission has also been achieved by aligning blends of the polyfluorene **558b** with polyethylene.[2263] A composite film of poly(3-alkylthiophene)s **647** and nitrile butadiene rubber (NBR) prepared by electropolymerization of 3-alkylthiophenes onto an ITO glass electrode precoated with a thin film of NBR has been used as an emissive layer in LEDs.[2264] LEDs have been constructed using LB films of P3HT in a variety of polymer matrices, with the best results coming from use of a cross-linkable linoleic acid matrix.[2265] Blending the polythiophene **648a** with PMMA is reported to improve the film quality. Two-layer devices with Alq_3 show voltage tunable emission with green Alq_3 emission at 15 V and red emission from **648a** at 30 V.[2266] The PL efficiency of blends of the blue-green emitting (λ_{max} = 460 nm) polyurethane **1173** (Chart 50) in PMMA is reported to be higher for low concentrations of **1173** due to dilution effects.[1982] Blends of the poly(azomethines) **1174a,b** with 50 mol % of a sulfonated polystyrene produce white EL.[2267]

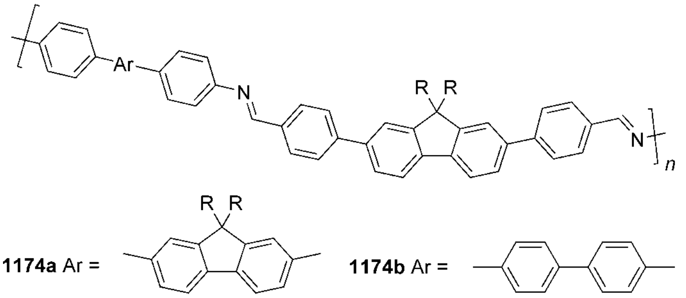
The optical stability of conjugated polymers can also be enhanced by blending with nonemissive polymers. Blending MEH-PPV (**20**) with the viologen-containing polymer **1175** not only lowers the turn-on voltage and increases the EL efficiency but also improves the photostability.[2268] Similarly, blending the polyfluorene **560b** with polystyrene or the quinoline-substituted polymer **1176** not only increases the EL efficiency but also suppresses the appearance of the green emission band seen from pure PDAFs (see section 3.4 above).[2269]

As was the case for blends of two or more luminescent polymers discussed in the previous section, blending emissive polymers with nonemissive polymers can enhance the emission performance, but to date this approach does seem likely to produce any dramatic advances in device efficiencies or lifetimes.

Chart 50

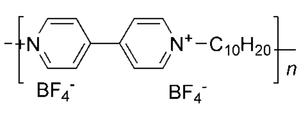


1173

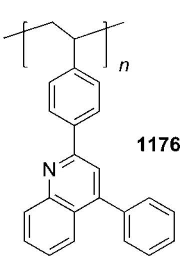


1174a Ar =

1174b Ar =

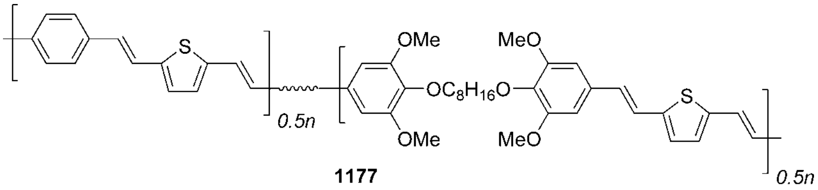


1175

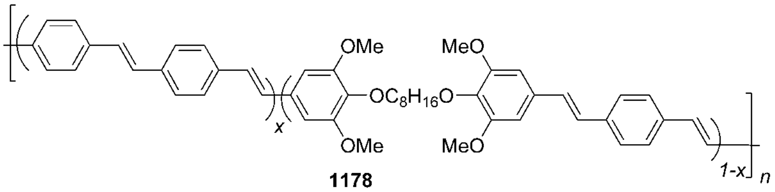


1176

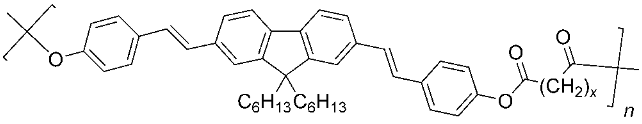
Chart 51



1177



1178



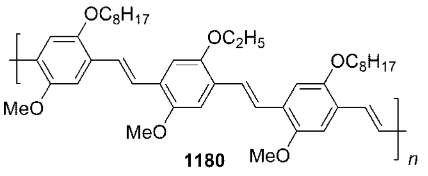
1179a *x* =3 **1179b** *x* = 8

5.3. Blends with Nonpolymeric Materials

Devices can be constructed using blends of conjugated polymers and nonpolymeric dyes. This was first demonstrated by Partridge,[47] who obtained blue emission from blends of blue emitting dyes in PVK. Due to poor electron injection, cesium cathodes had to be used in order to see EL emission. By adding electron-accepting cyanobenzenes, he was able to obtain emission using calcium or barium cathodes.[48] Other more efficient devices have since been made using PVK and a variety of dyes with emission colors covering the whole visible spectrum. In all cases, energy transfer occurs from polymer to dye, causing emission from the latter, and efficiencies are improved by use of electron-transporting layers.[2270−2273] Tada and Onoda have developed a technique for doping PVK with dyes whereby red, green, and blue emitting LEDs can be constructed on the same substrate.[2274] A layer by layer self-assembled film of PPV (**1**) and a red emitting cyanine dye show emission from the latter due to energy transfer. Addition of a yellow emitting (λ_{max} = 575 nm) dye to the PAVs **172a** or **202** results in EL emission largely from the dopant.[2275] The emission is voltage dependent due to charge trapping, which affects the relative formation of excitons on host and guest. Addition of a red emitting coumarin dye to the polymer **939** with green emitting naphthalimide substituents produces red emission (λ_{max} = 602 nm) with EL efficiencies of up to 2.2% (*cf.* 0.9% for **939**).[1881−1883] Energy transfer leading to emission from the dye has also been seen for a blend of a red emitting dye (λ_{max} = 645 nm) and the yellow emitting copolymer **1177** (Chart 51). When the same dye was blended with the blue ($x = 0$) and green ($x = 0.2$) emitting copolymers **1178**, the emission color was found to be tunable between blue-green (λ_{max} = 510 nm) and red-orange (λ_{max} = 640 nm) by increasing the amount of dye. At concentrations of dye below 0.02%, the energy transfer is incomplete, thus permitting emission from the polymer.[2276] Addition of PVK and PBD as charge-transporting components improved the EL efficiency. It is reported that a ternary blend of the copolymers **302a** and **1179a** with a red emitting dye produces more efficient red EL than a binary blend of the dye with either polymer.[2277] A blend of the blue emitting polyfluorene **595** with both a green and a red emitting dye has been used to obtain white EL with 0.82% efficiency.[2278] Similarly, doping PVK with a blue-green and an orange emitting dye produces white EL with 1.3 cd/A efficiency.[2279]

Emissive metal complexes have also been used as dopants. A 5:1 blend of the RO-PPV copolymer **1180** (λ_{max} = 560 nm) and a blue emitting (λ_{max} = 465 nm) gallium dye shows voltage-dependent EL.[2280] At 18 V, yellow-green (λ_{max} = 540 nm) emission from **1180** is observed, while, at 24 V, green EL (λ_{max} = 500 nm), possibly from an exciplex, is seen, and at 28 V, the emission is from the dye. Blends with lower proportions of **1180** show emission only from the dye. Yoshino and co-workers[2274,2281,2282] have shown that a device containing as emitting layer a mixture of an ROPPV **39j** and Alq_3 produces a voltage-dependent variable emission of orange to green light. A two-layer device gave emission from the polymer layer, with weak emission from the dye layer seen only at low voltage. Blends of PVK or a blue emitting PPP derivative **1147c** with red emitting europium complexes (λ_{max} = *ca.* 600 nm) can also show efficient red emission.[2283−2285] The efficiency of the energy transfer depends upon the ligands on the metal. Near-infrared (NIR) emission has been obtained by blending conjugated polymers with NIR-emitting lanthanide dyes. A blend of MEH-PPV with an NIR-emitting ytterbium porphyrin complex (λ_{max} = 977 nm) produced emission mainly from the dye.[2286] A blend of the PPP **1181** with the same dye also showed NIR emission plus some weak emission from the triplet state of the dye (λ_{max} = 600−700 nm), while blends of **1181** with a holmium (λ_{max} = 1197 nm) and a europium porphyrin complex (λ_{max} = 1560 nm) gave emission only from the latter.[2287−2290] The fluorene copolymer **816** has been mixed with a neodynium complex containing a lissamine dye substituent on the ligand.[2291] The EL contains emission from both the dye (λ_{max} = 580 nm) and the metal (λ_{max} = 890 nm).

Blending polymers with phosphorescent dyes offers a way to harvest the polymers' triplet excited states for emissive purposes, and this has become an approach of increasing research interest. The first examples of this approach used porphyrins as the phosphors. Efficient (up to 3.5%) red (λ_{max} = 650−656 nm) emission has been obtained from blends of poly(dioctylfluorene) (**558b**) with platinum(II) por-



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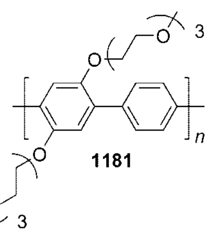
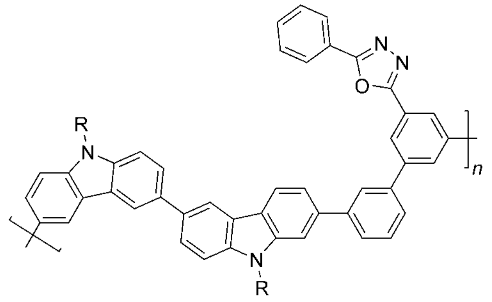


1181

phyrins.[2292−2297] The highest efficiency was obtained from a blend containing 4 wt % of porphyrin. Similar results have been obtained from other blue emitting polymers as hosts such as LPPPs,[2298] polythiophene **1155**,[2299] or PVK.[2300,2301] EL in the NIR has been obtained from blends of an ethyne-bridged porphyrin dimer (λ_{max} = 720 nm) and trimer (λ_{max} = 820 nm) in PVK.[2302] The EL efficiency of blends of PVK with red phosphorescent porphyrins (λ_{max} = 647 nm) has been found to be significantly lower than that from blends with green emitting iridium(III) complexes (λ_{max} = 510−517 nm) (0.6% vs 1.9%, respectively), which is due to the better spectral overlap in the latter case.[2300−2302] There have now been many reports of highly efficient LEDs utilizing green emitting iridium complexes in blue emitting hosts such as PVK (maximum efficiency 18.8%, 67 cd/A),[2300,2303−2310] PPPs **1147a,c**,[2311] polythiophene **1155**,[2299,2312] polyfluorenes,[2313] poly(spirobifluorene)s,[2314] poly(3,6-carbazoles) (**716**),[2315] and carbazole copolymers such as **1182**[2315] and from a ternary blend with both PVK and a fluorene copolymer.[2316] High efficiency red EL has been reported from blends of other iridium(III) complexes (λ_{max} = 605−624 nm) in PVK (maximum efficiency 13.9%, 16.9 cd/A),[2303,2305,2310,2317−2321] **558b** (10.4%, 9.4 cd/A),[2317,2322,2323] **595** (7.9%), **602d** (1.5%),[2324] and a star-polymer **1183** (7.9%).[2317] The efficiency of the emission can be increased by blending both a green and a red emitting complex together in PVK.[2303] Red emission has also been obtained from blends of osmium complexes (λ_{max} = 628−662 nm) with PVK (efficiency up to 6.5 cd/A),[2325] the polyfluorenes **595** (2.1% efficiency),[2326] and **596** (9.3%),[1260] or with the violet emitting polymer (λ_{max} = 395 nm) poly(vinylnaphthalene) (**1184**) (2.2%).[2327]



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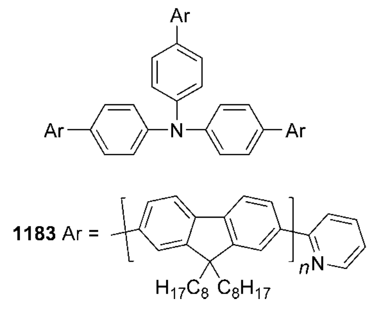

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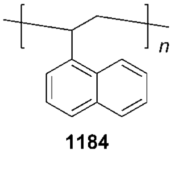


1184

Other emission colors have also been obtained from blends of iridium(III) complexes and PVK. Thus, yellow emission (λ_{max} = 565 nm) has been obtained with 2% efficiency,[2303] while blue emission has been obtained with efficiencies of up to 18.2 cd/A.[2310,2320,2328,2329] Adding a down-conversion phosphor layer to a device with such a blend as emissive layer produces white emission.[2330] Blue emission has also been obtained from a blend of an iridium complex in the polysilane **743**.[2331] Near-infrared EL (λ_{max} = 720 nm, 0.25% efficiency) has recently been reported from a blend of PVK with an iridium complex.[2332] Blending a mixture of blue, yellow, and red emitting complexes in PVK produces white EL with 2.1% efficiency.[2303] White EL has also been achieved by adding red and green or blue emitting complexes to polyfluorene **558b** (maximum efficiency 9.4 cd/A),[2333] a fluorene-carbazole copolymer **719e**,[2334] PVK (5.0% efficiency),[2320] or a mixture of PVK and **558b** (12.11 cd/A).[2335] Other ways to obtain white emission are blending a yellow-orange emitter with **558c** (2.8%, 4.57 cd/A)[2336] or adding a red emitter to a mixture of the end-capped polyfluorene **582b** and the fluorene−fluorenone copolymer **591** (21 cd/A).[2337] Phosphorescent and fluorescent dopants can be combined. Thus, a blend of PVK with both a green emitting (λ_{max} = 520 nm) rhenium complex and a red emitting dye produces emission from the latter with an efficiency of 0.42 cd/A, which is considerably higher than that for a blend of just PVK and the dye.[2338,2339] White EL has been obtained with high efficiency (6.12%, 132 cd/A) from a blend of a blue fluorescent dye and an orange phosphorescent osmium complex in PVK.[2340] The extremely high efficiencies obtained from these devices make blends of phosphorescent complexes in charge-transporting polymers one of the promising classes of materials for commercial LEDs. The key issues will be lifetimes and device stability due to the potential problem of phase separation.

Energy transfer can also occur from the dye to the polymer. Blending P3ATs with fluorescent dyes has been found to enhance the EL intensity by a factor of up to 70 with an increase in efficiency of up to 500-fold.[1380−1382,2282,2341−2343] The enhancement in EL efficiency is greater for polymers with longer alkyl chains. With an oxadiazole dye as dopant, the emission color changed from red-orange to white with increasing voltage. Use of a photochromic dye enabled the PL intensity to be altered by switching the photochrome between its two forms. Rubbing alignment of a film of P3AT blended with dye leads to polarized emission.[1087] Doping MEH-PPV with rubrene is reported to increase the EL efficiency by a factor of 10.[2344] Blends of dyes with oriented films of PPEs, e.g. **464**, or MEH-PPV (**20**) can show polarized emission from the polymer[943,2345] or unpolarized emission from the dyes indicating that the dye molecules are randomly oriented.[2346]

Blending with charge-transporting materials can also be used to improve EL efficiency. Thus, the EL efficiency of MEH-PPV (**20**) can be improved by 2 orders of magnitude by blending with an electron-transporting oxadiazole compound.[2347] The degree of improvement in efficiency and color stability from annealed blends of **20** with oxadiazoles is reported to be greatest at higher concentrations of dopant.[2348] Blending of the silyl-PPV **116** with an oxadiazole electron-transporting material has been found to improve the efficiency of devices by a factor of over 18.[372] The emission efficiencies of **558b** and **1147a** have been enhanced to 1.5% by blending with an electron-accepting silole compound.[2349]

Incorporation of 1 wt % of triarylamine hole-transporting molecules into Me-LPPP (**552b**) boosts the EL efficiency due to better charge transport.[2350] Blending polyfluorenes e.g. **558b** with triarylamines not only improves the EL efficiency but also suppresses the long wavelength emission from defects.[2351] Improved EL efficiency has also been observed by blending spirobifluorene-based polymers with hole-transporting materials.[2352] When triarylamines are blended with fluorene−dicyanophenylene copolymers such as **604**, emissive exciplexes are formed with emission maxima between 550 and 600 nm, depending on the composition of the copolymer.[2353] A cross-linked blend of **1145** with a cross-linkable triarylamine has been used as a hole-transporting layer in LEDs using **816** as emitter.[2354] The efficiencies are reported to be significantly higher than those when PEDOT was used.

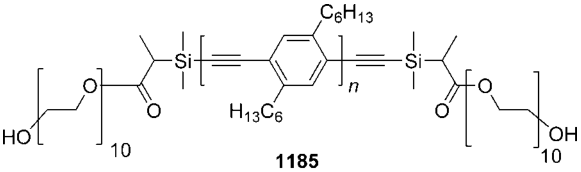
Blending the PPV copolymer **74c** with multiwalled nanotubes leads to a slight blue-shift in the PL and an increase in the PL intensity due to suppression of aggregation as the polymer chains wrap themselves around the nanotubes.[466] The blend shows yellow EL (λ_{max} = 560 nm) with greater stability in air than pure **74c**.[2355] This composite material has also been used as an electron-transporting layer in MEH-PPV-based LEDs.[2356] Single-walled nanotubes are reported to enhance the EL efficiency of MEH-PPV by improving charge transport.[2357] Multiwalled nanotubes similarly enhance the EL performance of **833c**.[2358] A composite of an oxadiazole and single-walled nanotubes has been used to enhance the EL efficiency of PVK.[2359] It is interesting to note that nanotubes improve charge mobility in conjugated polymers without affecting their luminescence, unlike C_{60}, which quenches luminescence due to its excellent electron-accepting properties.[2282] Despite this quenching behavior, EL has been obtained from nanoseparated blends of MEH-PPV and C_{60}.[2360,2361] Considerable improvements have also been obtained in the luminance of MEH−PPV and other conjugated polymers by blending them with surfactants. The EL efficiencies with aluminum cathodes are reported to be as high as those obtained for the unblended polymers with calcium electrodes.[2362,2363]

From the above results, it can be seen that blends of emissive and charge-transporting small molecules with emissive polymers offer extremely good prospects for future development of commercially viable devices, provided that problems of phase separation can be avoided.

5.4. Composites with Inorganic Materials

Blending of conjugated polymers with inorganic substances to form composite materials has also been found to have positive effects on luminescence properties. PPV has been encapsulated within zeolites by introducing the monomer **2** and then polymerizing it *in situ*.[2364] The optical properties are reported to match those of the pure polymer, but the EL was weak. Composites of PPV with porous silicon show lower turn-on voltages than PPV.[2365,2366] Dielectric nanocrystals are reported to broaden the emission spectra of PPV and the PPP **1147a**, but whereas the spectrum of PPV is blue-shifted, the latter shows a red-shift.[2367] The fluorescence of composites of polyquinolines **690b** and porous silica is reported to depend upon the pore size, with the emission maximum occurring at 490 nm in small pores and at 545 nm in large ones.[2368] Similarly, the emission from a PPE rod−coil copolymer **1185** varies from 420 to 500 nm with increasing pore size. Composites of MEH−PPV with nanoparticles of silica or titanium dioxide show EL efficiencies up to 1 order of magnitude better than those for the pure polymer due to better charge injection and transport.[2369−2371] For the composites with rutile-type TiO_2, the efficiency was found to increase with increasing nanoparticle size.[2372] A MEH−PPV/layered organosilicate nanocomposite material shows an EL efficiency with an Al cathode 2 orders of magnitude better than that for pure MEH−PPV.[2373]

Composites of PPV and silicate gel glasses can be prepared from mixtures of PPV precursor **3** and silicon alkoxides in methanol by a sol−gel process.[2374,2375] The UV−vis absorption and PL emission spectra of these materials are blue-shifted with respect to those of PPV, indicating a shorter conjugation length. Devices have been constructed using these materials with emission maxima around 510 nm.[2374] Similar composites have been prepared with copolymers of PPV and poly(1,4-naphthalene vinylene) (**223**)[2376] and with polyquinoline (**690b**).[2377] MEH−PPV end-capped with a phosphonium group, after being made by the Wittig method, and the polythiophene **1186** have also been used to make composites with silica by a sol−gel method.[2378] The optical properties of the MEH−PPV composite and of a composite of **1186** with 11 mol % of hydroxyl side-chains are similar to those of the pristine polymers, but that from the composite of **1186** bearing 22 mol % of hydroxyl groups was markedly blue-shifted, indicating a decrease in conjugation length.



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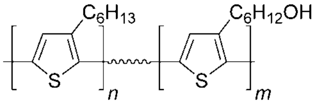


1186

Composites have also been made with emissive semiconductor nanoparticles. A composite of PPV and CdSe nanoparticles shows white EL from the latter.[2379] A composite of PVK with ZnS-based nanocrystals shows emission from both components (λ_{max} = 430 and 610 nm, respectively).[2380] Near-infrared emission (λ_{max} = 1000−1600 nm) has been obtained from composites of MEH−PPV with InAs/ZnSe[2381,2382] or PbS,[2383] and of Me-LPPP with HgTe.[2384] As mentioned in the Introduction, addition of ferromagnetic cobalt−platinum nanowires is reported to enhance the proportion of singlet excitons generated in MEH-PPV, thus increasing the EL efficiency, especially in the presence of a magnetic field and in blends of PVK with an iridium phosphor, where the electrophosphoresence is reduced by the presence of an external magnetic field.[69] Doping polyfluorene **558b** with lithium bromide is reported to enhance the EL efficiency,[2385] while a nanocomposite of **558b** with tin(IV) sulfide is reported to display much more stable blue EL than **558b**.[2386] End-capping the fluorene−thiophene copolymer **772a** with thiols and then binding gold nanoparticles to the end-groups, is reported to increase the EL efficiency from 0.21 to 1.99 cd/A.[2387] Blending the polymer with the nanoparticles, by contrast, only enhanced the efficiency to 0.53 cd/A.

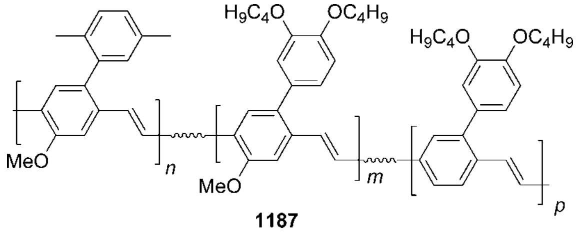
Composites of organic polymers with inorganic materials are liable to suffer even more from problems with phase separation than are all-organic blends. As a result, while some promising results have been obtained, this approach is unlikely to prove fruitful for developing commercially viable devices.

6. Other Types of EL Devices Using Conjugated Polymers

The prospects for the development of conjugated polymer-based LEDs as commercially viable display devices depend not only on development of new materials but also on the development of new device designs. In the previous sections we have generally been describing the use of conjugated polymers in standard LEDs containing only one emissive layer. However, devices can also be made using multiple emissive layers. There also exist a number of other types of light-emitting devices in which conjugated polymers can be used. In this section we briefly discuss their use in such devices.

6.1. Devices with Multiple Emissive Layers

The most obvious way to obtain multicolor emission from a multilayer device is to address each emissive material separately. Thus, a Chinese group have constructed multilayer devices containing blue (PDAF, **558a**), green (aryl-PPV, **151a**), and red (MEH-PPV, **20**) emitting layers with the structure ITO/PEDOT/**558a**/Ba/Al/**151a**/Ba/Al/**20**/Ba/Al.[2388] Emission can be obtained from each of the emissive layers separately by applying a potential to the appropriate metal injection layers. Other groups have adopted approaches in which charge blocking layers are inserted between emissive layers so as to control the site of recombination. Yoshino and co-workers[2389−2393] have made multilayer devices using PDAF **558a** and red emitting materials, e.g. the polythiophene **647e**, separated by an electron-blocking layer, e.g. PVK. The electron blocking layer causes confinement of the electrons within the layer nearest the cathode, so that the devices emit either red or blue light depending on the bias. Green emission can be obtained by using a layer of PPV in place of the red emitting layer.[2392] With alternating current, emission from both materials is observed. They have since demonstrated the generality of this approach by constructing multilayer devices using PPV (**1**), a polythiophene **647e**, and a dialkoxy PPV derivative **39h** as emissive layers with PVK (**934a**) as charge-blocking layer.[2394] A Chinese group has made devices with emissive layers of PPV and Alq$_3$ doped with a coumarin dye, and they investigated the effect of inserting a LB film of a blend of a triarylamine and copper phthalocyanine as a charge-blocking layer.[2395] With no blocking layer, emission is from both layers ($\lambda_{max} = 513$, 591 nm), while, with a thick charge-blocking layer, only the Alq$_3$ layer emits ($\lambda_{max} = 591$ nm). A thin blocking layer leads to voltage dependent emission, with emission being seen from the Alq$_3$ layer alone at <7 V and from both layers at higher potentials. Recently, Zyung and co-workers have constructed similar devices ITO/AlO$_x$/**118b**/AlO$_x$/**20**/AlO$_x$/Al using aluminum oxide as charge confinement layers.[2396] Emission from both polymer layers was seen, whereas, in a double-layer device without the AlO$_x$ layers, only emission from the MEH-PPV (**20**) layer occurred, with one tenth of the efficiency. Identical emission was obtained from a device with the emissive layers in the opposite order, with a lower operating voltage. Voltage tunable red, green, or blue EL has also been obtained from multilayer devices using **558c**, **146**, and **20** as the emissive layers without intervening layers.[2397] Jenekhe and co-workers[2398] have made bilayer devices using PPV and polyheterocycles. The emission color of bilayer devices using **833a** and PPV could be tuned from green to orange by varying the relative thickness of the two layers. In some devices, the color becomes voltage tunable from yellow-orange to green.[1520] An unusual example of variable emission from a bilayer device is seen in devices using PPV (**1**) and the copolymer **450**. When the cathode is potassium, green PPV emission is seen, while, with aluminum, red emission from **450** occurs. Thus, by depositing patterns of potassium followed by aluminum as the cathode, patterned emission can be obtained.[2399] Another way that has been used to obtain patterned emission was to cross-link the red emitting polymer **35** with an electron beam. The noncross-linked material was then removed by washing with solvent, and a layer of yellow emitting **1187** was deposited on top of it. Red EL was seen from the double-layered areas and yellow EL from where there was only one emissive layer.[2400]



1187

Bolognesi et al. have constructed devices with oriented emissive layers of PPV and **648b** with the two emissive layers oriented perpendicular to each other.[2401] The emission is voltage dependent, with only emission from **648b** being seen at 7 V, with the onset for PPV emission at 8 V, and approximately equal intensity of emission from both polymers being achieved at 11−12 V. As the emission from both layers is polarized, the emission color can be switched from red to green simply by rotating the axis of a polarizer. White EL has been seen from double-layer devices with a cross-linked red emitting ROPPV covered by a blue emitting poly(diayloxadiazole).[2402] White EL has also been obtained by using a layer of polyfluorene **558b** blended with MEH-PPV (**20**), plus a layer of either **558b** or of **558b** blended with a green emitting fluorene copolymer.[2403]

Multilayer devices using sexiphenyl and conjugated polymer emissive layers have been made which show voltage-dependent emission.[2205,2404,2405] A bilayer device ITO/sexiphenyl/PPy(**682**)/Al shows blue emission from the sexiphenyl ($\lambda_{max} = 425$, 450 nm) at 17 V; as the voltage increases, an emission peak at 565 nm from the PPy layer gains intensity so that the emission color changes to white and then green. Incorporation of a PVK hole-transporting layer increases the EL efficiency and shifts the green emission maximum to 605 nm. At operating potentials above 27 V, an irreversible change in the EL spectrum occurs to give greenish-white emission ($\lambda_{max} = 605$ nm). A trilayer device ITO/**357**/sexiphenyl/**682**/Al also shows blue emission from sexiphenyl at low voltages. As the potential increases, new peaks at $\lambda_{max} = 530$ and $\lambda_{max} = 700$ nm appear, giving white emission, which changes to greenish-white at higher voltages. For a bilayer ITO/**357**/sexiphenyl/Al device, emisssion maxima at 425, 450, and 605 nm are seen at all voltages, but the first two decrease and the third increases in intensity as the potential rises.

The emission from a multilayer device may come from an exciplex at the interface between the layers. A bilayer device using PVK and **357** shows an exciplex emission at 2.38 eV ($\lambda_{max} = 520$ nm) with an EL efficiency 2 to 3 orders of magnitude higher than that for a **357** single-layer device.[2205,2406] Similarly, a bilayer device using P3HT (**647c**) and a green emitting fluorene copolymer produces efficient red emission ($\lambda_{max} = 612$ nm, 1.3 cd/A) from an exciplex formed at the interface.[2407] The same emissive exciplex was seen from a blend of the two polymers, but the emission was less efficient (0.9 cd/A). Doping the polyfluorene layer with a red emitting fluorene copolymer red-shifted the emission maximum to 628 nm but halved the efficiency to 0.6 cd/A. Doping the green emitter with MEH-PPV (**20**) did not affect the emission spectrum but reduced the efficiency even more to 0.43 cd/A. Adding a third layer of blue emitting **558b** led to white EL with emission coming from the exciplex and both the green and blue emitting polymers.

Multilayer devices using PPV and Alq_3 are reported[2408−2410] to show emission from both polymer and dye, with the relative intensities dependent on the thicknesses of the layers. Similar effects are seen in double-layer devices using MEH-PPV and Alq_3.[318] Bilayer devices using Alq_3 and the PPV copolymer **424** show voltage variable emission, with green Alq_3 emission dominating at 8 V and red ($\lambda_{max} = 616$ nm) emission from **424** at 18 V.[855,856] Combinations of organic polymers and inorganic phosphors can also be used. Depending on the relative thicknesses of the layers, the emission may be from both layers or only from the nanocrystals.[2411−2413] Devices have been constructed[2414] in which layers of cadmium selenide nanocrystals were deposited onto either ITO or ITO/PPV layers to give LEDs of structure ITO/CdSe/PPV/Mg:Ag and ITO/PPV/CdSe/Al. At low voltages, red to yellow EL from the cadmium selenide (color varies with nanocrystal size) occurs, but at higher voltage, green emission from PPV predominates. Bilayer devices using PPV and ZnS doped with manganese show EL from both layers (mainly from the ZnS) under forward bias but only from the ZnS under reverse bias. By contrast, a bilayer device using LPPP **552a** shows emission mainly from the former.[2415] Hybrid devices using CdS:Mn/ZnS core−shell nanocrystals with PPV and PVK layers, respectively, produce green EL from the PPV and orange ($\lambda_{max} = 585$ nm) EL from the nanocrystals.[2416]

While some impressive results have been obtained from these multilayer systems, their greater complexity compared with the standard LED designs is liable to make them less attractive due to higher costs.

An interesting new concept is the hybrid LED, where a blue InGaN LED is used to stimulate PL from layers of red-orange emitting RO-PPVs encapsulated between two glass plates. By controlling the polymer thickness, the color of the overall emission can be tuned and even white light is obtainable. The lifetimes of these devices are reported to be comparable with those of inorganic LEDs.[2417,2418] Provided the energy losses within the organic layer are not too high, this may prove a commercially viable way to tune emission colors of LEDs.

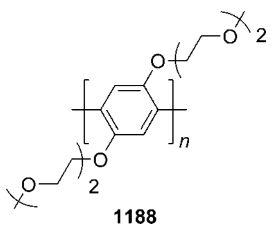
6.2. Symmetrically Configured Alternating Current Light-Emitting Devices

Another potential advance in device design has been the development by Epstein and co-workers[800,2419−2429] of symmetrically configured alternating current light-emitting (SCALE) devices, which have the typical structure electrode/“insulating” polymer/emissive polymer/“insulating” polymer/electrode. The emissive layers used to date have included polypyridine (**682**) (blue), MEH-PPV (**20**), and the PPV/PPyV copolymers **357** and **356b** (red). The “insulating” polymers used have been emeraldine base polyaniline (PANI), sulfonated polyaniline (SPAN), and P3HT (**647a**). Use of P3HT with **357** as emissive layer gave a device in which the color of emission varied between forward ($\lambda_{max} = 590$ nm) and reverse ($\lambda_{max} = 635$ nm) bias modes, probably due to charge recombination occurring at different interfaces in the two modes, while with PANI the EL spectra were essentially identical in both modes with a maximum at $\lambda_{max} = 635$ nm. Similarly, when a device ITO/PANI/**357**/SPAN/Al is run under forward bias, red emission from inside the bulk of the emissive layer is seen, but under reverse bias, green emission is produced due to the recombination occurring at the interface between **357** and the SPAN where protonation of the former by the latter takes place.[2406] As with standard LEDs, transparent ITO on glass is used as one of the electrodes while air-stable metals such as Al, Cu, or Au have been used as the other electrode, since, unlike in standard LEDs, the two electrodes do not need to have dissimilar work-functions. Turn-on voltages are reported to be lower than those for the corresponding ITO/polymer/metal devices.

There does not appear to have been any recent work done on these types of devices, suggesting that they are unlikely to feature in future commercial development of emissive devices.

6.3. Light-Emitting Electrochemical Cells

A new type of luminescent device which has attracted a lot of interest are polymer based light-emitting electrochemical cells (LECs). In these devices, the luminescent material is mixed with an electrolyte.[2430] They show some marked differences in their behavior from LEDs, for example nonrectifying current voltage characteristics and emission with similarly low threshold voltages under both forward and reverse bias, which are nearly independent of the film thicknesses. Their efficiencies are also relatively insensitive to the work function of the electrodes. As first developed by Heeger and co-workers,[329,1142,2431−2438] they consisted of a conjugated polymer blended with poly(ethylene oxide) (PEO), a well-known charge-transporting polymer, and lithium triflate (LiOTf), sandwiched between ITO and aluminum electrodes. They were able to obtain red-orange, green, and blue emission by using MEH-PPV (**20**), PPV (**1**), and a soluble PPP derivative **1188**, respectively. A surface configuration with interdigitated electrodes was also developed.[2438,2439] They determined that the devices operated by production of *p*- and *n*-doped layers at the anode and cathode, respectively, which extend toward the center of the layer to form an internal *p*−*n* junction where recombination and emission occur. When a surface configuration was used, the junction could be directly observed. Santos et al. have studied the properties of blends of **20** with PEO and LiOTf in various proportions and reported that the blends showed clear phase distinctions, but with uniform structures.[2440] Friend and co-workers have shown that when MEH-PPV was mixed with ions at concentrations much lower than those found in a LEC, the resulting devices showed behavior intermediate between those of a LEC and a standard LED, i.e. low threshold voltages, but with rectifying behavior still being seen.[2441] LEC-like behavior has been observed for blends of MEH-PPV and tetrabutylammonium tosylate, but the concentration of the latter was not reported.[2426−2428] Doping with ITO particles results in multiple *p*−*n* junctions being formed between the ITO particles, so leading to EL being produced across the whole of the polymer film in the form of thousands of individual emissive dots.[2442] For a fuller discussion of the operating principles of LECs and their differences from LEDs, readers are referred to the review by Neher et al.[2443]

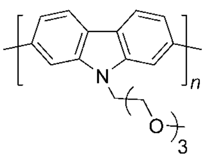


1188

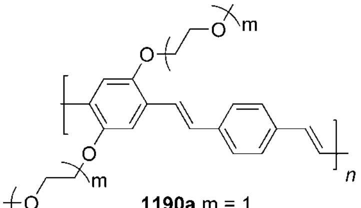
The efficiencies of LECs are sometimes much higher than the optimal values for LEDs using the same emissive polymer. For example, the efficiency of a LEC using BCHA-PPV (**39b**) is 2.8%, compared with a best value of 1.0% in a double-layer LED using a PVK hole-transporting layer.[371] For BuEH-PPV (**106**), by contrast, the efficiency of 3% for a LEC is slightly lower than the best value for a double-layer LED (3.2%), but it is much better than the efficiency of a single-layer device (0.1%). The onset voltages for LECs are also sometimes much lower than those for the corresponding LEDs. For example, a blend of polymer **450** in PVK has an onset voltage of 20 V in an LED (see section 2.7 above), but equally efficient emission has been obtained from a LEC containing **450** with a turn-on voltage of 3 V.[423] Variations on the basic LEC structure using MEH-PPV have been reported. The ITO anode can be replaced by transparent gold,[2444] and three layer devices have been made using a layer of MEH-PPV sandwiched between hole- and electron-transporting polyelectrolyte layers which are reported to have higher EL efficiency than the single-layer devices.[2445]

A two-color LEC using PPV and MEH-PPV has been made in which the emission color can be varied from red to green by altering the applied voltage.[2446] White emission has been obtained from a blend of the oligoethylene oxide-substituted polyfluorene **558d** and PEO.[2447] Use of appropriate color filters gives red, green, or blue emission. Without the PEO, the emission from **558c** is initially blue but rapidly turns blue-green due to formation of yellow emitting aggregates.[1142] The emission of the similar copolymer **559** also changes rapidly from blue to blue-green.[1163] A phosphorescent LEC has been made by blending a red emitting iridium complex with **558d** and lithium triflate.[2448] The EL efficiency is reportedly six times that of the corresponding LED without the lithium salt. Highly efficient blue emission has also been obtained from LECs using Me-LPPP (**552b**), but the emission rapidly turns green.[2449,2450] A blend of **552b** and MEH-PPV (**20**) shows emission voltage tunable between orange and yellow-green.[2449] Higher EL efficiency and intensity has been obtained for a PPV LEC by incorporation of a hole-blocking layer of poly(lithium 4-styrene sulfonate) in PEO.[2451] A blend of the *n*-dopable blue-green (λ_{max} = 530 nm) emitting polyquinoxaline **702** (Ar = *p*-tolyl) and the *p*-dopable blue (λ_{max} = 440 nm) emitting polycarbazole **1189** shows orange-yellow (λ_{max} = 590 nm) emission in a LEC.[2452] The individual polymers show poor performance in LECs, but the blend shows good efficiency. The color change has been attributed to an interpolymer radiative recombination process which offers a new way to tune the emission color of conjugated polymers.

The PEO can be omitted when the polymer carries ethylene oxide or crown ether substituents. A variety of PPV derivatives with PEO or crown ether substitutents have been made and used in LEDs and LECs (see section 2.2 above). Generally, they show much lower onset voltages and higher EL efficiencies in LECs than in LEDs. The homopolymers **59**−**60** and **62** show red-orange emission,[422,424,2453] while the alternating copolymers **1190** show yellow-green emission (λ_{max} = 552 nm).[449,2454] A LEC using a blend of homopolymer **60b** and copolymer **1190b** displays bias dependent emission, with the copolymer emitting under forward bias and the homopolymer under reverse bias.[2455] The SiPPV copolymers **126**−**128** show similar emission spectra with much higher EL and PL quantum efficiencies than those of the homopolymers **59**−**60**.[423,424,519,527,528] The copolymer **124** with 2,3-dibutoxy-PV units shows yellow EL (λ_{max} = *ca.* 600 nm) with an efficiency higher than that for the homopolymer of either comonomer in LECs made using LiOTf, both with and without PEO.[2456] The addition of PEO gave better emission efficiencies, especially for devices with thicker emitting layers. The crown-ether-substituted PPV copolymer **129** has been used to make a green emitting (λ_{max} = 515 nm) LEC.[427,428] The addition of PEO was found to markedly increase the EL efficiency and response time of the device, as the crown ether units lowered the ion mobility. Red-orange emitting LECs have also been made using polythiophenes **671**−**672** with ethylene oxide substituents.[1439] Green EL (λ_{max} = 520 nm) has been obtained from a LEC using the water-soluble PPV **1191** with sulfonate groups on the side-chain.[2457] Neher and co-workers have obtained blue emission from an LEC using sulfonated PPP **1192** as the emissive polyelectrolyte.[1072] A one-component blue emitting LEC has been made using the polycation **1193**.[2458,2459] Polymers containing arylene vinylene chromophores linked by ethylene oxide, e.g. **984**, or crown ether spacers, e.g. **998**, have also been used to make blue or blue-green emitting LECs.[1941,1942,2460−2462] Efficiencies of up to 3.7 cd/A have been reported.[1942] Blue-green LECs have also been constructed using a hyperbranched phenylene vinylene **886** (R = Me).[1784] Conversely, it has been found that the lithium salts can be omitted from blends of PEO with polyrotaxanes formed by complexation of polymers, e.g. **543**, with cyclodextrin.[2463] These blends produce much more efficient EL than the pure polyrotaxanes.

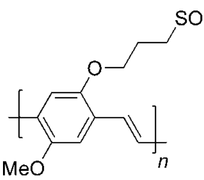


1189



1190a m = 1
1190b m = 2

A new type of LEC has been developed that uses a frozen *p*−*n* junction. The *p*−*n* junction is first produced at a temperature well above the intended operating voltage, and then the device is run at a lower temperature where the junction is frozen due to the lower ion mobilities. These devices retain most of the advantages of the normal dynamic junction LECs, e.g. low threshold voltages and high EL



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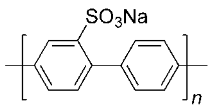

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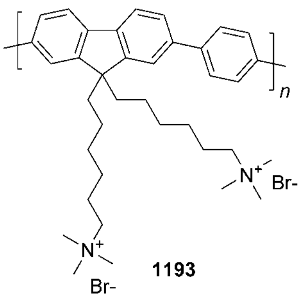


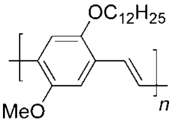
1193

efficiency, but do not show their normal drawbacks of low response times and overdoping. Their electrical properties are similar to those of LEDs with rectifying behavior and emission only in forward bias. The frozen junctions were first demonstrated using MEH-PPV-based LECs, where the junction was only stable at temperatures below 200 K.[2464−2467] Subsequently, it was found that in LECs using BuEH-PPV (**106**) or BCHA-PPV (**39b**) the junction could be formed at 60−80 °C and then frozen at room temperature.[2468] By using ionic liquids as the electrolytes, such junctions have recently been produced at similar temperatures in LECs using MEH-PPV also.[2469] Briefly heating MEH-PPV-based frozen-junction PLECs above the T_g of the polymer is reported to enhance the device efficiency by converting the frozen *p*−*n* junction to a *p*−*i*−*n* junction.[2470]

While LECs continue to be investigated, it would appear that the problems of their short shelf life and operating lifetimes will inhibit commercial development for the foreseeable future.

6.4. Electrogenerated Chemiluminescence Cells

Electrogenerated chemiluminescence (ECL) involves the generation of light-emitting species by electron transfer in solution between radical ions formed by electron transfer reactions with electrodes.[2471] An ECL cell is thus essentially an electrolytic cell. Bard and co-workers recorded an early example of the observation of ECL using the polymer **951b**.[2472] Later examples have been reported using MEH-PPV (**20**),[2473] P3HT (**647a**),[2474] or MDOPPV (**1194**)[2474] as films cast on the working electrode. ECL has also been observed from **1194** in solution and as a blend with PEO.[2475] Other examples in solution have also been reported.[2476,2477] The ECL spectra generally closely match the PL spectra. These devices bear an obvious similarity in their working processes to the LECs described in the previous section. For a fuller discussion of organic ECL cells and their similarities and differences to LECs, see the review of organic electroluminescence by Mitschke and Bäuerle.[14] Yang and co-workers have fabricated LEDs with polymer solutions or gels sandwiched between the electrodes, from which the emission is generated by ECL.[2478] A gel of MEH-PPV shows red-orange emission, whose emission maximum ($\lambda_{max} = 575$ nm) lies between the emission maxima for MEH-PPV in solution and the solid state ($\lambda_{max} = 560$ and 592 nm, respectively).[2479] Blue ECL ($\lambda_{max} = 430$, 450, 482 nm) has been observed from a solution of poly[9,9-bis-(3,6-dioxaheptyl)fluorene-2,7-diyl] sandwiched between two transparent electrodes.[2480] The problems with encapsulating such devices mean these are likely to remain merely objects of scientific curiosity.



1194

6.5. Polymer Microcavities and Lasers

One aim of new device designs is to enhance the emission intensity and/or purity. One method for achieving this is to use a microcavity structure in which the electroluminescent material is sandwiched between two planar, highly reflecting mirrors. When the polymer film thickness is of the order of the wavelength of the emitted light, the device acts as a resonator for a standing electromagnetic wave which produces a marked narrowing in the emission spectrum.[722,812,2481−2485] A microcavity device has been constructed using ladder-type PPP (**552a**) in which the emission color can be tuned from red to blue by altering the thickness of the polymer layer.[2486] A prototype pixelated three-color display using microcavity devices has been made.[2487]

The ultimate enhancement of emission is amplified stimulated emission leading to lasing. Lasing from conjugated polymers was first observed by Moses in 1992 from a solution of MEH-PPV (**20**).[2488] The first observation of lasing from conjugated polymers in the solid state was from a blend of MEH-PPV and titania nanoparticles in polystyrene in 1996.[2489] Soon afterward, a microcavity device using PPV was reported to show optically pumped lasing behavior.[2490] Similar optically pumped superradiance and lasing phenomena were shortly thereafter reported from films of other conjugated polymers.[2491−2493] As a result, there has been considerable recent interest in attempting to develop optically and electrically pumped polymer lasers. To date, only optically pumped lasing has been observed for conjugated polymers, but it is hoped to eventually obtain electrically pumped polymer laser diodes. A discussion of the methods used to obtain lasing from conjugated polymers and of the prospects for obtaining electrically pumped polymer lasers lies outside the scope of this review, and so the reader is referred to the reviews by Lemmer,[2494] Tessler,[2495] and McGehee and Heeger.[2496] There are also short accounts by the groups of Heeger[2497,2498] and Friend[2499] of their contributions to this field. Lasing has been seen from many of the classes of conjugated polymers discussed in this review, with emission colors covering the whole spectral range. The great majority of the work so far published has been on PPV[2490,2500−2503] and its derivatives,[391,2489,2491,2498,2504−2521] including polymers with interrupted conjugation,[1949,2004,2493,2522−2526] and the block copolymers of PPV and polyfluorene **1134** and **1135**.[2166,2527] Other materials from which lasing has been observed are a substituted PPP **1147c**,[2489,2505] polyfluorenes,[2489,2505,2521,2528−2532] poly(diphenylacetylene)s,[2508,2513,2533] polythiophenes,[2534] and Me-LPPP (**552b**).[1031,1033,2535−2538] Materials that seem to be regarded as having particular promise are BuEH-PPV (**106**)[2504,2509,2511] and Me-LPPP (**552b**).[1031,2535] The latter has been used to make a flexible optically pumped polymer laser.[2536,2537] Lasing has also been investigated in blends; for example, a blend of **301a** and the interrupted conjugated polymer **1179b** is reported to have a low threshold for stimulated emission.[2539] Lasing has been seen from blends of PMMA with PPV (**1**)[2540] and PPPV (**136**).[2541] Blends of conjugated polymers with inorganic nanoparticles have also been investigated, as the nanoparticles may act as scattering centers[2489,2509] or to lower the refractive index.[2499] One possible future development may be the use of hybrid systems combining inorganic lasers with organic polymer layers similar to the hybrid LEDs described in section 6.1 above.

6.6. Integrated Polymer Devices and Other Devices

Polymer LEDs can be combined with other devices to form integrated optoelectronic devices. For example, they can be coupled with photovoltaic devices to make optocouplers.[2542,2543] Integrated devices in which a polymer-based FET drives a polymer LED have been made,[2544−2546] which represent a major step toward the development of all-polymer integerated circuits. It may also be possible to combine LEDs with other devices using luminescent polymers, e.g. so-called "plastic retinas" in which MEH-PPV has been used with PANi to make polymer grid triodes for image enhancement.[2547]

7. Limitations and Future Prospects of Electroluminescent Conjugated Polymers

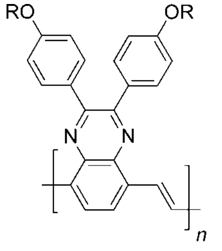
The three main factors (other than cost) which will determine the commercial utility of polymer LEDs as light sources are that they display satisfactory efficiencies (which determine brightness for a given current), threshold (turn-on) voltages (which affect power consumption), and lifetimes (over 10,000 h is necessary for most commercial applications). The first two of these criteria had already been met at the time we wrote our last review,[2] with reported efficiencies of over 4%, and threshold voltages of 5 V or below having been obtained, enabling devices to be run from low-power sources such as batteries, and the first reports of satisfactory device lifetimes appeared soon after.[1299,2548−2552] Since then, there have been major advances in PLED lifetimes, so that, as mentioned in the introduction, they are now entering the commercial marketplace.

The one significant obstacle remaining to the more widespread use of polymer LEDs to date is that their reported lifetimes still remain lower than those of the best inorganic or small-molecule organic devices. For commercial reasons, most of the device lifetime work is unpublished, but values of over 100,000 h even for blue emitters have been claimed for some time on company Web sites or in press releases—we have not cited these, as the numbers are rapidly changing and are not subject to independent verification, but the most recent numbers we could find that have been presented in a public scientific forum are given in section 7.4 below. If the rate of increase in verified lifetimes achieved in recent years continues, there is every reason to believe that polymer devices will soon be available with lifetimes comparable to those of the best LEDs currently on the market, in which case, their intrinsic advantage of lower production costs should earn them a significant market share.

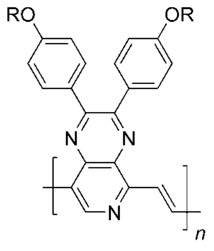
In this section we will briefly discuss photoxidation of conjugated polymers, and polymer−electrode interactions, which are the two main causes of polymer degradation leading to device breakdown, and how these may be controlled. For a more comprehensive account of the mechanisms of polymer LED breakdown, and of methods for extending their lifetimes, see the review by Sheats and Roitman.[2553] We also mention some new methods for fabrication of polymer LEDs.

7.1. Photo-oxidation of Conjugated Polymers

Photo-oxidation of conjugated polymers by water and oxygen has been proposed as being the major cause of breakdown in polymer LEDs. The resulting oxygenated groups such as carbonyls then act as traps hindering charge migration and enhancing nonradiative decay pathways.[2554] There is a review of the photo-oxidative degradation of conjugated polymers by Cumpston and Jensen.[2555] It is generally established that conjugated polymers are susceptible to degradation in the presence of oxygen. For example, the alkoxy-PPV **35** is reported to be 1000 times more stable under an inert atmosphere than in air.[2556] Some structure−stability correlations have been reported. Thus, poly(phenylene ethynylene)s (PPEs) are more stable toward photo-oxidation than poly(phenylene vinylene)s (PPVs), and among PPVs, those with *meta*-linkages are less stable than those with *para*-linkages.[894] PPVs with phenyl[2557,2558] or trifluoromethyl[656] groups on the vinylene moieties are less susceptible to photodegradation than other PPVs, probably because the electron-withdrawing susbstituents make the double bond less attractive to attack by electrophilic oxygen. The aryl-substituted PPV **157** is also reported to be less susceptible to photo-oxidation than PPV.[559] For the copolymers **158**, the rate of degradation increases as the amount of MEH-PV units increases. The effects of substituents can vary considerably from one polymer structure to another, however, which complicates the making of hard and fast structure−stability correlations. For example, it is reported that, in polymers **1195**, aryl substituents stablize the polymers toward photo-oxidation, while, in the very similar polymers **1196**, they have a destabilizing effect.[2559]



1195 R = 2-ethylhexyl



1196 R = 2-ethylhexyl

The mechanisms of the photodegradation of conjugated polymers have been established in some cases. Studies on PPV have shown it is oxidized by oxygen in the presence of light to produce fluorescence quenching carbonyl defects.[107,2560−2562] Singlet oxygen has been shown to cleave the vinylene groups in MEH-PPV (**20**) and bischolestanyloxy PPV (**43**) to give ester or aldehyde groups.[2563−2566] A study on the stability of MEH-PPV under various conditions found that irradiation or heating in air led to formation of carbonyl groups, while irradiation under an inert atmosphere did not.[2567] Irradiation with X-rays under high-vacuum led to a loss of PL intensity and solubility, which was attributed to cross-linking of the vinylene units. It has been suggested that differences in the behavior of PPV and MEH-PPV during photo-oxidation may indicate that different degradation processes are occurring.[231,2568] It has been shown that the photo-oxidation of films of **35** on a transparent substrate is not limited by oxygen diffusion, as it always occurs most strongly on the side of the film that is irradiated, suggesting that in LED structures the side of the emissive layer nearer the transparent electrode (usually the anode) is the most vulnerable.[2569] Photo-oxidation has been used to pattern a film of the ROPPV **1180**, as the oxidized areas show little or no PL or EL.[2570,2571] There is evidence that attack of the side-chains and backbones of P3ATs leads to chain scission and introduction of carbonyl defects.[2572−2577] Again, the photo-oxidation behavior differs from that of PPV derivatives, suggesting a different mechanism is involved.[2571] It has been suggested that photo-oxidation of alkoxy-substituted PPP derivatives proceeds via formation of phenoxide radicals which isomerize to quinones, followed by ring cleavage.[1079] This would suggest that alkyl-substituted polymers should be more resistant to oxidation, and polydialkylfluorenes do appear to be more photostable than alkoxy-PPPs. It has been reported that their photo-oxidation in air results in formation of fluorenones,[2578] and it is now generally accepted that this oxidation also occurs during operation of LEDs, leading to the appearance of a new emissive band in the yellow region of the spectrum (see section 3.4 above). As shown in sections 3.3 and 3.4 above, bridged-phenylene-based polymers with available hydrogens at the bridging atom give the least stable blue EL while the diaryl-substituted analogues seem to be the most stable.

One problem with photo-oxidation studies on conjugated polymers is that as they are usually performed in the absence of an electric field, they do not fully reflect what happens inside LEDs. An exception to this is the report by Barbara and co-workers that the fluorescence modulation traces of isolated chains of MEH-PPV in an LED-like structure differ in the presence and absence of an electric field.[2579] This was interpreted as being due to the polymer luminescence being quenched by formation of a charge transfer complex with oxygen which was reversed by the electric field reducing the polymer. Evidence has also been presented that degradation of PPV inside LEDs requires both electric stress and exposure to air.[2580] Studies of PPV-based LEDs[2581−2583] have shown that exposure to air produced a drop in efficiency and an increase in threshold voltage accompanied by degradation of the polymer and electrodes. The degradation was much lower when the devices were run under an inert atmosphere,[2582] suggesting that protection from aerial oxidation may be a significant factor in improving the lifetime and efficiency of devices. Analysis has shown that the dark spots which appear causing device breakdown have a high oxygen content.[2584] Scott and co-workers have shown that degradation of the polymer is one of the primary processes involved in the breakdown of dialkoxy-PPV-based LEDs.[2585−2590] It has been found that ITO acts as a reservoir of oxygen for photo-oxidation in MEH-PPV LEDs and its replacement or coating with polyaniline reduces the photodegradation.[2589] Other studies on degradation of red, green, and blue emitting polymers in OLEDs have confirmed that degradation occurs at the ITO−polymer interface, and they found that gold or pentacene layers on top of the ITO suppress it.[2591] A study of LEDs using the polythiophenes **654a,b** found evidence for oxidation of the polymer and degradation of the electrode with metal ion diffusion into the polymer, which acts to quench the luminescence.[2592] Surface configured LEDs using **672** showed reversible quenching of EL in the presence of air, indicating that oxidative degradation is not the only process for quenching of luminescence by oxygen.[2593] In this case, formation of a charge transfer complex may be involved. It is interesting that a study on PPV films showed that while water interacts reversibly with PPV to disrupt the conjugation, as shown by changes in the absorption spectrum, no such changes were seen upon exposure to oxygen, which strongly suggests that oxygen is only a problem in the presence of light and that water may be an equally important cause of luminescence degradation.[2170,2594] The effects of photo-oxidation on the behavior of PLEDs has been reviewed by Tada and Onoda.[2595]

Other mechanisms have also been demonstrated to be involved in the breakdown of polymer LEDs. As no evidence for formation of carbonyl groups has been found in degraded encapsulated devices using ROPPVs, oxidation has been ruled out as the cause of their breakdown, and instead cross-linking of the polymers has been proposed as an alternatve mechanism.[2549,2550] There is evidence that electrochemical degradation of the ITO anode[2596,2597] or the metal cathode[2598] induced by the strong electrical field inside the devices may occur in PLEDs.

Improvements in device design or encapsulation offer potential methods for improving their lifetimes, but there is also scope for innovative synthetic chemistry to assist. For example, the Wessling PPV precursor polymer contains large amounts of chloride and oxygen due to side reactions, which are reported to be considerably reduced by using the Vanderzande sulfinyl precursor route, though there is as yet no report on the relative lifetimes of devices using these precursors.[2582] Better synthetic methodology to reduce the amount of such impurities or of photosusceptible defects, such as for example in the recent work by Holmes and co-workers to produce dialkylfluorenes by a route that excludes the formation of oxidizable monoalkylfluorene impurities,[1207] or the reduction of the susceptibility of the polymer toward photo-oxidation should lead to improved lifetimes. As an example of the latter approach, as mentioned above, it has been shown that PPV derivatives with electron-withdrawing trifluoromethyl groups on the vinylene moiety are more resistant to photo-oxidation,[656] and so the introduction of electron-withdrawing groups onto oxidation-susceptible parts of other conjugated polymers might be worthy of investigation.

7.2. Polymer−Electrode Interactions

As the efficiency of charge injection into the emissive polymer at the electrodes is the major determinant of the overall efficiency of polymer LEDs, an understanding of the processes occurring at the polymer−electrode interface during construction and operation of the devices is thus vital to optimizing device performance. Also, chemical interaction between the electrodes and the polymer may lead to polymer degradation, lowering device lifetimes. Much of the work on studying these interfaces has been done by Salaneck and co-workers, and the reader is referred to the reviews on this subject by them.[25,2599−2601]

The effect of the choice of metal cathode material on device efficiency does not depend solely upon its work function. A recent study on the efficiency of polyfluorene-based LEDs using a variety of cathodes showed that the chemical properties of the cathode were also relevant, as some metals can dope the polymer with luminescence-quenching ions.[2602,2603] The method of deposition of the metal is also clearly important, as it has been shown that the deposition of aluminum on PPV using electron beam methodology leads to degradation of the polymer by low energy electrons.[2604] Silver electrodes have been deposited onto PPV by chemical means, but the resulting LEDs had poorer performance than those using conventionally deposited silver cathodes.[2605] Vacuum deposition, which is the normal method for cathode fabrication, can lead to implantation of metal ions into the polymer, but by controlling the deposition conditions, in particular the partial pressure of oxygen present, it is possible to incorporate a metal oxide layer between the bulk of the metal and the polymer. Aluminum reacts with conjugated polymers, forming covalent linkages which disrupt the conjugation,[2606,2607] so formation of an oxide layer may improve performance. Calcium, by contrast, interacts with conjugated polymers ionically by doping them with calcium ions. Salaneck and co-workers have reported that deposition of calcium in the presence of a low partial pressure of oxygen—so-called “dirty calcium”—leads to longer lifetimes in LEDs using CN-PPV (**208**).[642] Conversely, LEDs using a dialkoxy-PPV and calcium[2608] or magnesium[2609] cathodes showed best results when the cathode was deposited under ultrahigh vacuum to avoid oxide formation. Calcium doping has been implicated in the formation of the green emission band in polyfluorenes, and the use of a buffer layer between the emissive layer and the cathode has been shown to suppress this in LEDs.[1173]

The effect of the anode material has been less directly investigated. ITO remains the standard anode material despite reports that different samples may show different work functions and lead to variable performance in devices.[2610,2611] The variance in device performance does not depend solely on the work function, and so it must reflect as yet unstudied differences in the interaction with the polymer layers. The effect on the EL and PL of superimposed polymers, of treating ITO by various methods has been investigated, with the best results in terms of luminescence efficiency and device lifetimes being obtained by treatment with oxygen plasma.[2612,2613] Conversion of PPV precursor into PPV on ITO has been shown to lead to doping of the PPV with indium chloride, which also affects the ITO work function. Insertion of an interfacial layer between the ITO and the polymer layer makes the barrier to charge injection independent of the ITO work function.[2614] Migration of indium into the polymer layer has been detected in aged PLEDs and may be implicated in device breakdown.[2615] As a result, tin oxide[2616] and fluorinated tin oxide[2617] have been proposed as alternative electrode materials. It has been reported that polyimide layers hinder indium migration and enhance the lifetimes of devices using MEH-PPV.[2618] An ITO electrode chemically modified with an oligophenylene has been reported to produce much improved performance and lifetimes in bilayer LEDs using PPP and Alq_3.[2619] Better performance has been obtained from polyfluorene-based devices using flexible polymer substrates in place of ITO on glass.[1675] The use of PEDOT/PSS layers to improve charge injection and avoid problems due to the roughness of ITO has become near universal in devices recently, but it is reported that the luminescence of PPV is partially quenched due to formation of defects at the interface with PEDOT.[2620] No such quenching is seen with poly(spirobifluorene)s.

So far, work on optimizing device performance by controlling polymer−electrode interfaces has looked at the electrode material and its deposition methods. As our knowledge and understanding of these interactions improves, however, it should become possible to design polymers so as to give optimal interactions with a given electrode material.

7.3. New LED Fabrication Methods

In the devices described so far, the active polymer layers have been deposited by spin-coating or vacuum deposition. Other techniques for depositing conjugated polymer films for use in light-emitting devices by hybrid inkjet printing,[2621−2626] bar-coating,[2627] electrophoretic deposition of nanoparticles,[2628] microcontact printing,[2629] screen printing,[2630−2632] electrophoretic deposition from suspension,[2633] and the use of liquid buffer layers to permit sequential deposition of multiple polymer layers without disturbance of previously deposited layers[2634] have been described, and the inkjet printing method is now being extensively developed in industry.[2635,2636] These can be combined with the more traditional methods for making devices. For example, a red, green, and blue emitting patterned array has been made by deposition of red (PPV doped with dye) and green (PPV) emitting materials by hybrid inkjet printing on a thin film transistor array, followed by spin coating of the blue emitting polyfluorene layer.[2637] The development of new techniques for processing conjugated polymers may require new synthetic efforts to develop new materials or to improve known materials so as to optimize their performance, since as has been shown above, the behavior of a given material is often dependent upon how it is processed. New ways to organize conjugated polymers so as to maximize their transport properties or to obtain polarized emission are being sought. For example, Swager and Zhu have shown that PAVs and PAEs dissolved in nematic liquid crystals form highly ordered structures which might offer a new way to obtain highly ordered films of such polymers.[2638] One promising area for future research is into construction of nanosized LEDs, as it has been shown that diminuation in LED size can improve device efficiency and lifetime.[2639] Already it has been shown that nanopatterning of ITO by electron beam lithography enables LEDs to be made with emission coming from regions of approximately 170 nm in diameter.[2640] Whether advances in nanotechnology will enable even smaller devices to be made and integrated with other nanosized electronic devices promises to be one of the most interesting and potentially exciting areas in LED research in the near future.

7.4. Commercial Materials and Device Lifetimes

Excellent progress has been made in device efficiencies and lifetimes, as reported by Fyfe (Cambridge Display Technology/Sumation).[2641] If these numbers can be obtained reliably and reproducibly from mass-produced devices, then P-OLEDs can indeed expect a major increase in market share in the near future.

Table 1 shows efficiency for RGB and white P-OLED in cd/A measured at a luminance of 1000 cd/m^2; RGB efficiency data is obtained from spin-coated test devices using common HIL, interlayer, and cathode. Data is reproduced courtesy of Sumation.

Table 2 shows LT_{50} measured from an initial luminance of 1000 cd/m^2 (h); RGB lifetime data is obtained from spin-coated test devices using common HIL, interlayer, and cathode under constant current driving with no initial burn in. Data is reproduced courtesy of Sumation.

8. Conclusion

One of the key aspects in the ongoing improvement in the performance of luminescent polymers has been the identification of the chemical species (defects) involved in limiting device performance, and the development of new structures and/or synthetic methods to minimize their formation.

Of the classes of polymers we have covered, the earliest class developed—poly(arylene vinylene)s—has been the first to become commercially viable, where the chemical defects in PPV derivatives made by the Gilch route were identified, and the insights gained from this were used to design new materials with much lower defect levels. It is no coincidence that the very first commercial PLED device used a material developed from this work. Advances in understanding the mechanism of the Gilch and other routes to PPVs will no doubt continue to lead to improvements in the performance of these polymers, but they are unlikely to become useful as blue emitters. The major advance in the related poly(arylene ethynylene)s has been the development of metathesis polymerization, but these materials seem unlikely to be featured in commercial PLEDs, owing to the problem of severe aggregation in the solid state, which lowers luminescence efficiencies.

Phenylene-based polymers, especially polyfluorenes, appear to be the best candidates for blue emission and, as copolymers, constituents of all other emissive layers. A key factor here was the identification of fluorenone units as the source of the green emission, and the subsequent investigations to prepare polymers that cannot be readily oxidized to form such defects. Other polyarylenes, such as polythiophenes, may not be commercialized as emissive materials. However, the remarkable work by several groups to develop methods for the synthesis of highly regioregular polythiophenes is expected to show promise in field effect transistors and photovoltaic devices.

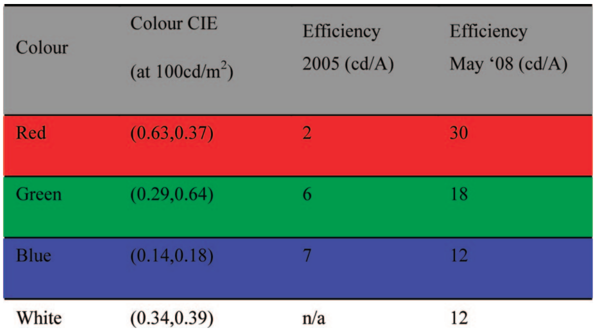
The other classes of materials covered have generated much interesting work but have so far not produced many commercially interesting materials; however, phosphorescent dendrimers and polymers are likely exceptions.

Blends of, or covalently linked, emissive polymers with phosphorescent dyes have produced the most efficient solution processible materials for devices yet and will play a significant role in commercial PLEDs. All red emissive materials can be expected to incorporate a phosphorescent component, as these emit significantly less emission in the infrared region of the spectrum.

The development of new fabrication techniques and new device structures will continue to provide new challenges for innovative polymer synthesis to create new materials with suitable properties. In addition, there still exists considerable scope for development of new and improved techniques for synthesis, purification, characterization, and processing of conjugated polymers. The most significant breakthroughs are likely to emerge in the areas of materials selection and purification. The development of nanostructured materials is another highly exciting research topic that may well lead to advances in EL devices.

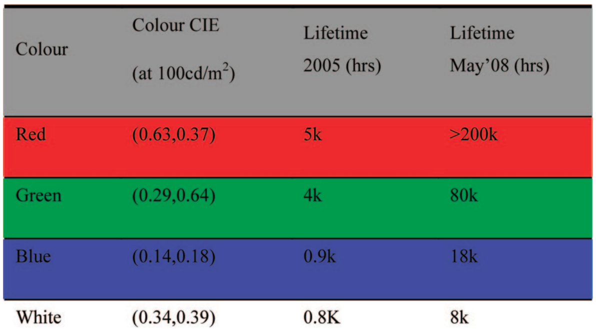
A wide range of conjugated polymers and copolymers possessing electroluminescent properties suitable for use in LEDs and related devices have been made by a variety of synthetic methods. Efficient emission across the entire visible spectrum and even into the near-ultraviolet and near-infrared has been obtained. Although improvements in device stability and lifetime will continue to be made, the published results demonstrate that polymer LEDs are now commercially viable and may soon be fully competitive with inorganic or molecular organic electroluminescent materials for display applications. Niche applications for alphanumeric displays have already been established, and the first commercial full color virtual reality headset is now available. It is apparent that rapid progress in white lighting will make these devices the components of choice for low energy solid state lighting.[2642] In every sense of the term, luminescent polymers have a bright future ahead of them.

Table 1. P-OLED Efficiency Data



Colour	Colour CIE (at 100cd/m^2)	Efficiency 2005 (cd/A)	Efficiency May '08 (cd/A)
Red	(0.63,0.37)	2	30
Green	(0.29,0.64)	6	18
Blue	(0.14,0.18)	7	12
White	(0.34,0.39)	n/a	12

Table 2. P-OLED Lifetime Data



Colour	Colour CIE (at 100cd/m^2)	Lifetime 2005 (hrs)	Lifetime May'08 (hrs)
Red	(0.63,0.37)	5k	>200k
Green	(0.29,0.64)	4k	80k
Blue	(0.14,0.18)	0.9k	18k
White	(0.34,0.39)	0.8K	8k

9. List of Abbreviations Used

AIBN	azobis(isobutyronitrile)
Alq$_3$	aluminum tris(8-hydroxyquinolate)
^{t}Bu	tertiary butyl
CSA	camphorsulfonic acid
CVD	chemical vapor deposition
DMF	*N*,*N*-dimethylformamide
ECL	electrochemiluminescence
EL	electroluminescence
Et	ethyl
HOMO	highest occupied molecular orbital
ITO	indium tin oxide
LB	Langmuir−Blodgett
LCD	liquid crystal display
LED	light-emitting device (diode)
LUMO	lowest unoccupied molecular orbital
LPPP	ladder-type polyphenylene
Me	methyl
MEH-PPV	poly[2-methoxy-5-(2-ethylhexyl)-1,4-phenylenevinylene]
NIR	near infrared
NMR	nuclear magnetic resonance
OLED	organic LED
PANI	polyaniline
PAV	poly(arylene vinylene)
PEDOT	poly(3,4-ethylenedioxythiophene)
P3AT	poly(3-alkylthiophene)

PDAF	poly(dialkylfluorene)
Ph	phenyl
PL	photoluminescence
PLED	polymer LED
PMMA	poly(methyl methacrylate)
PNE	poly(naphthalene ethynylene)
PNV	poly(naphthalene vinylene)
POSS	polyhedral oligomeric silsesquioxide
PPB	poly(phenylene butadienylene)
PPP	poly(para-phenylene)
PPPV	poly(phenylphenylene vinylene)
PPV	poly(phenylene vinylene)
PPy	polypyridine
PPyV	poly(pyridinylene vinylene)
PSS	poly(sodium 4-styrenesulfonate)
PVA	poly(vinyl alcohol)
PVK	poly(*N*-vinylcarbazole)
RGB	red, green, blue
ROMP	ring opening metathesis polymerization
ROPPV	poly(2,5-dialkoxy-1,4-phenylene vinylene)
SPAn	sulfonated polyaniline
STM	scanning tunneling microscope
THF	tetrahydrofuran
TPA	triphenylamine

10. Acknowledgments

We thank the Australian Research Council, the Commonwealth Scientific and Industrial Research Organisation (Australia), the Victorian Endownment for Science, Knowledge and Innovation, International Science Linkage Project CG 100059 (DIISR, Australia), and the U.K. Engineering and Physical Sciences Research Council for generous financial support. We thank Drs. David Fyfe and Scott Brown (CDT) for supplying the data in ref 2641 and OSRAM/Ingo Maurer for permission to reproduce the images of the PLED solid state lighting (see ref 2642 and cover).

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CR000013V