The electroluminescence of organic materials

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This article provides a review about electroluminescence from organic materials and deals in detail with organic light-emitting diodes (OLEDs), light-emitting electrochemical cells (LECs) and electrogenerated chemiluminescence (ECL) reflecting different electrooptical applications of conjugated materials. It is written from an organic chemist's point of view and pays particular attention to the development of organic materials involved in corresponding devices. In recent years a substantial amount of both academic and industrial research has been directed to organic electroluminescence in an effort to improve the processability and tunability of organic materials and the longevity of OLEDs and LECs. On the eve of the commercialization of organic electroluminescence this review provides an overview of lifetimes and efficiencies attained and reflects materials and device concepts developed over the last decade. In this context electrogenerated chemiluminescence is discussed with respect to its importance as a versatile tool to simulate the fundamental electrochemical processes in OLEDs.

A. Organic light-emitting diodes (OLEDs)

### 1. Historical evolution of light-emitting diodes—function and characteristics of OLEDs

In contrast to photoluminescence, the light emission from an active material as a consequence of optical absorption and relaxation by radiative decay of an excited state, electroluminescence (EL) is a non-thermal generation of light resulting from the application of an electric field to a substrate.[1] In the latter case, excitation is accomplished by recombination of charge carriers of contrary sign (electron and hole) injected into an inorganic or organic semiconductor in the presence of an external circuit.

This phenomenon was first discovered for inorganic materials in 1936, when Destriau *et al.* observed high field electroluminescence from a ZnS phosphor powder dispersed in an isolator and sandwiched between two electrodes.[2] In the early 1960s, General Electric introduced commercially available light-emitting devices (LED) based on the inorganic semiconductor GaAsP.[3] Since the energy of the emitted photons and therefore the colour of the diode is determined by the energy gap of the semiconducting material in the active region of the LED, early LEDs only emitted red. The development of further materials granted access to colours other than red and made orange, yellow and green, as well as infrared accessible.[4] Materials that were generally used for inorganic LEDs are compounds of elements from groups III and V of the periodic table such as GaAs, GaP, AlGaAs, InGaP, GaAsP, GaAsInP, and more recently AlInGaP. Blue LEDs, however, were difficult to obtain since semiconductors with large energy gaps are required. Nevertheless, blue diodes based on SiC, ZnSe, or GaN were developed, but exhibited distinctly lower efficiencies in comparison to other diodes.[4]

Research is currently focused on the development of new highly efficient materials and technologies similar to the technology utilized to fabricate silicon integrated circuits. However, since materials used to fabricate LEDs are more complex than elemental silicon and are more difficult to produce and to process, the evolution of an analogous technology is still far behind technologies evolved for silicon. As a consequence, automation, cost reduction, size of crystals grown, defect densities and volumes of devices produced need to be further improved.[4] The development of new device structures and in particular the emergence of metal-organic vapor-phase epitaxy (MOVPE) as a crystal growth technique allowed continuous improvement of the device efficiencies. In the late 1990s, inorganic LEDs typically possess luminous efficencies—a measure for the efficiency with which electrical power is converted into light by the device—beyond 10 lm W^{-1} and are expected to be significantly improved within the next decade. For comparison, the performance of an incandescent bulb is typically in the range of 15 lm W^{-1}.[4]

Electroluminescence from organic crystals was first observed for anthracene in 1963.[5] Since the efficiencies and lifetimes of resulting devices were significantly lower than those obtained for inorganic systems at the same time, research activities were focused on the inorganic materials. In the late 1980s, Tang and VanSlyke,[6] as well as Saito and Tsutsui *et al.*[7] revived the research on electroluminescence of organic compounds, developing a new generation of light-emitting diodes with organic fluorescent dyes.

Another fundamental work concerning the evolution of organic light-emitting diodes (OLEDs) was published by Friend *et al.* in 1990.[8] They overcame the drawback of expensive and technologically inconvenient vapor deposition of fluorescent dyes and inorganic semiconductors by using a highly fluorescent conjugated polymer—poly(*p*-phenylene-vinylene) (PPV) **1**—as the active material in a single-layer OLED.
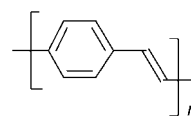
PPV **1**

Although PPV itself is insoluble and difficult to process, Friend *et al.* found a way to build up PPV-OLEDs *via* the thermoconversion of a processable precursor polymer. Their greatest merit however was that they indicated for the first time the possibility of producing large area displays by simple coating techniques. The PPV diode embodies the prototype of a single-layer OLED and is typically composed of a thin film of the active organic material (30–500 nm) which is sandwiched between two electrodes (Fig. 1).

Since one of the electrodes needs to be semitransparent in order to observe light emission from the organic layer, usually
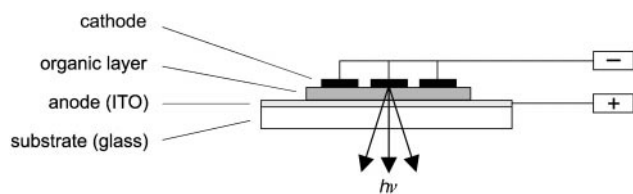
Fig. 1 Schematic configuration of a single-layer OLED.

an indium tin oxide (ITO)-coated glass substrate is used as the anode. Electropositive metals with low work functions such as Al, Ca, Mg, or In are used as cathodes in order to guarantee efficient electron injection.

If an external voltage is applied at the two electrodes, charge carriers, *i.e.* holes, at the anode and electrons at the cathode are injected into the organic layer beyond a specific threshold voltage depending on the organic material applied. In the presence of an electric field the charge carriers move through the active layer and are non-radiatively discharged when they reach the oppositely charged electrode. However, if a hole and an electron encounter one another while drifting through the organic layer, excited singlet and triplet states, so-called excitons, are formed. The singlet state may relax by emission of radiation (fluorescence). [A more detailed explanation of the basics of EL generation from organic materials is provided in ref. 9(*a*).] The *internal EL quantum efficiency* η_{int} of an OLED (the ratio of the number of photons emitted per electrons injected) can be calculated from the measured *external EL quantum efficiency* η_{ext} using eqn. (1).[9a,10] Due to refraction all photons emitted cannot be perceived by an external observer. External efficencies η_{ext} are accordingly diminished by the factor of $2n^2$ (n = refractive index of the organic layer) with respect to η_{int}.

$$\eta_{int} = 2n^2\eta_{ext} \qquad (1)$$

Power efficiencies η_{pow}, the ratio of output light power to input electric power, can be determined from η_{ext} using the known values of the applied voltage U and the average energy of the emitted photons E_p [eqn. (2)].

$$\eta_{pow} = \eta_{ext}E_pU^{-1} \qquad (2)$$

Luminous efficiencies η_{lum} are determined by multiplication of η_{pow} by the eye sensitivity curve S as defined by the Commission Internationale de L'Eclairage (CIE). This function pays regard to the fact that the human eye possesses distinct sensitivities with respect to different colours [eqn. (3)].

$$\eta_{lum} = \eta_{pow}S \qquad (3)$$

Finally, the *brightness* of an OLED (given in cd m^{-2}) is also used by several authors to estimate the efficiency of their device. For comparison, the brightness of a conventional laptop display reaches values of approximately 100 cd m^{-2}.

Since most common organic semiconductors are intrinsic *p*-type conductors and therefore are better suited to transport positive charges, electrons and holes usually recombine in the immediate vicinity of the cathode. As a consequence, the lifetimes and efficiencies of the corresponding diodes are limited. A lot of work was done in the 1990s to overcome this problem and to shift the recombination zone towards the centre of the organic layer.[9] Solutions were found by changing device structures and introducing multilayer OLEDs in which electron and hole transport are performed in different materials and layers. Another approach was the synthesis of oligomers and polymers with higher electron affinity in order to guarantee balanced charge injection.

The basic works mentioned above have stimulated huge industrial and university research interest all over the world

which will be partly reviewed in the following chapters. Main targets were the improvement of device characteristics such as lifetime and efficiency, and the development of new materials for electrooptical applications.[9] Physicists and material scientists are typically engaged in the preparation of several more complex device structures involving multiple emissive or transport layers, the employment of flexible and transparent electrodes, the optimization of device manufacture techniques, and the development of models in order to obtain an insight into the basic processes of charge generation, transport and recombination. Synthetic chemists are focusing their activities on the synthesis of a great variety of polymeric, oligomeric, and low molecular weight materials with different colour emissions, electron affinities, ionization potentials, and fluorescence efficiencies. In consideration of the size of the global market for electronic displays, it is not surprising that research is not only done in universities but also in companies in an effort to capture a share of this market. Due to some promising features, in particular organic displays are considered to gain more and more importance.

Besides the possibility of producing large area displays, organic materials offer further advantages in comparison to their inorganic counterparts.[9] First of all, they are much cheaper to produce and they can be processed even as very thin films in the range of 100 nm thickness. This renders possible the construction of flexible displays which could be used for instance to create roll-up TV screens in the future. OLEDs can be operated with low DC voltages and use significantly less power than comparable inorganic LEDs or backlit liquid crystal displays (LCDs). Another advance is their capability to be illuminated uniformly over a large area and the possibility of making complex character patterns by simple lithographic processes. This guarantees fabrication by standard printing or roll-to-roll manufacturing techniques. The greatest advantage of organic materials, however, is the tunability of their emissive colour, which can be adjusted by structural modifications. Even highly efficient blue and white LEDs, rarely attainable by use of inorganic materials, have successfully been constructed. Recently, OLEDs emitting polarized light have also been developed and investigated.[9b,c] Finally, expensive and inconvenient inorganic semiconductor technology can be replaced by simple coating or vapor deposition techniques.

2. Low molecular weight, oligomeric, and polymeric materials for OLEDs

The basic requirements for organic electroluminescent materials are the capability to undergo charge transfer to an electrode, the ability to transport charge and to fluoresce efficiently. A variety of organic materials have been investigated as active components in order to optimize device performance.[9] With respect to their molecular structure they can be distinguished and classified into one of the following four groups: while scientists in Europe and North America usually preferred *conjugated polymers* as electroluminescent materials, research and development in Japan was initially focused on *low molecular weight materials* such as metal chelates, simple oxadiazole compounds and triarylamines. *Conjugated oligomers* with precise chain length and defined electrical and optical qualities are used all over the world as valuable alternatives. The most recent class of materials comprises *main chain polymers with isolated chromophores* and *side chain polymers with linked chromophores*. They represent the attempt to combine the processability of polymers with the rigorously defined structure of oligomers in order to gain access to different advantages of previously developed materials.

2.1. Conjugated polymers in OLEDs. Conjugated polymers are organic semiconductors with delocalized π-molecular orbitals along the polymeric chain. Different types of

conjugated polymers such as polyacteylene (PA), poly(*p*-phenylene) (PPP), poly(*p*-phenylenevinylene) (PPV), polyaniline (PAni), polypyrrole (PPy) and polythiophene (PT) have been developed and intensively investigated. Their chemistry and physics have been reviewed in some excellent articles and book publications.[11]

As previously stated, the first conjugated polymer used for fabrication of an OLED was PPV.[8] With the device configuration ITO/PPV/Al substantial charge injection was observed just below 14 V. Emitting in the yellow–green part of the electromagnetic spectrum, an external quantum efficiency of 0.05% was attained. As a consequence of a deeper understanding of the operation of this device, its characteristics have been considerably optimized in the last decade and its luminous efficiency was greatly improved up to 2 lm W^{-1} at the beginning of 1999.[9d,12] The incorporation of PPV into OLEDs is typically performed *via* a soluble precursor polymer that is spincast into thin films and converted to PPV by thermal treatment. Since the quality of the resulting PPV films strongly depends on the individual processing steps of the precursor route, the complete sequence has been carefully elaborated and revised.[9] In particular the influence of the conversion temperature on film properties has been intensively studied.[13]

PPV-films have also been generated by other procedures such as layer-by-layer processes taking advantage of self-assembling,[14] or Langmuir–Blodgett techniques[15] in order to increase molecular order and consequently the efficiency of the corresponding devices. Chemical vapor deposition (CVD) in combination with ROMP (ring opening metathesis polymerization) of suitable cyclophane precursors has been suggested as a potential alternative to the conventional sulfonium-route of PPV synthesis.[16]

The introduction of substituents into the PPV skeleton on one hand allows the modification of the electronic properties (*e.g.* band gap, electron affinity, and ionization potential) and on the other hand enables the generation of PPVs that are soluble in organic solvents. In 1991, Heeger and Braun reported a red–orange emitting OLED based on the unsymmetrically substituted soluble PPV derivative poly[2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylenevinylene] (MEH-PPV **2**) in a simple single-layer device configuration (ITO/MEH-PPV/Ca) with an external quantum yield of 1%.[17]

MEH-PPV **2**   **3**
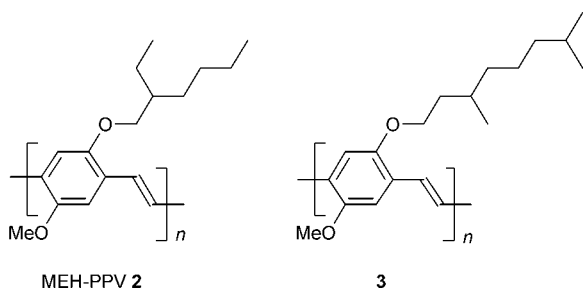
A variety of PPV derivatives containing long alkyl[18] and alkoxy[18a,b,19] chains, cholestanyloxy[18a,20] and oligoethenyloxy[21] substituents have been synthesized by polycondensation, Wittig-, or Heck-type reactions. PPV derivatives with at least one long solubilizing alkoxy side chain are soluble in organic solvents such as chloroform or THF providing sufficient processability with respect to electrooptical applications.[9a] In comparison to PPV, their emission maximum is typically bathochromically shifted. Furthermore, long side chains separate the polymeric chains from each other and hence impede the formation of non-emissive relaxation sites. This effect seems to be advantageous with regard to the fluorescence and electroluminescence efficiencies of corresponding polymers.

Up to now, the highest external quantum efficiency that has been obtained for a single-layer OLED reached a value of 2.1%.[19a] This OLED, developed at Philips in 1996, was based on dialkoxy-substituted PPV derivative **3** and revealed a brightness of 100 cd m^{-2} with a luminous efficiency of 3 lm W^{-1} at an operation voltage of 2.8 V. These values were approximately repeated for a flexible version based on an ITO-coated poly(ethylene terephthalate) PET anode which was designed in the laboratories of Hoechst.[19a] The incorporation of a polyaniline (PAni) layer between ITO and MEH-PPV (ITO/PAni/MEH-PPV/Ca) strongly increases the efficiency of the corresponding device enabling external quantum efficiencies up to 2–2.5% and luminous efficiencies of 3–4.5 lm W^{-1}.[22] This effect can be attributed to a more efficient hole injection due to advantageous morphological changes at the anode surface. PAni smoothens the rough ITO surface, provides an efficient electrical contact and enables significantly reduced operating potentials.[23] Since a polymeric anode should prevent oxygen diffusion into the electroluminescent layer, the brightness and lifetime of the corresponding diodes are increased. Analogous improvements of device performances have been reported for OLEDs which contain poly(3,4-ethylenedioxythiophene) (PEDOT) instead of PAni.[9d,23a–d,24,25]

The introduction of silyl substituents, as realized for PPV derivative **4**, gave an increase in solubility and a widening of the band gap with respect to PPV, enabling the emission of green light.[21a,26]

4
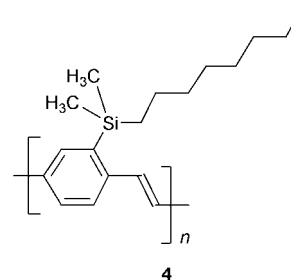
An orange colour became accessible by use of copolymers with unsubstituted phenylene and statistically distributed alkoxy-substituted phenylene segments.[27] Other successful approaches to tune the band gap were the introduction of oligo(*p*-phenylene) moieties[28] as well as the incorporation of *m*-phenylene segments.[29] The ease of the tunability of the band gap and the electronic properties of organic materials in general are not only important with respect to the resulting emission wavelength, but also on account to device engineering. A highly efficient performance crucially depends on appropriate energy level alignment at the layer interfaces. Besides the use of copolymers, the variation of the temperature in the final step of the PPV synthesis is a versatile tool to control the band gap.[27] Incomplete elimination leads to polymers with a statistically interrupted conjugation due to remaining sp^3-hybridized carbon atoms. The shortening of the effective conjugation length was reported to shift the emissive colour hypsochromically and to improve fluorescence qualities.[27a,b,30] This effect was interpreted as a diminished ability of excitons to diffuse to non-emissive relaxation sites.

Introduction of phenyl substituents at different positions of the PPV skeleton has also proved to be effective in order to increase the solubility of polymers. Phenyl groups have been attached at the vinylene bridge[9e,31] as well as at the phenylene moieties[9e,23b,32] of PPV. The most important example, poly(2,3-diphenyl-*p*-phenylenevinylene) **5**,[32a–d] exhibits EL in a single-layer configuration (ITO/**5**/Al) with an external quantum efficiency of 0.04%[32a,b] similar to values obtained for simple PPV-diodes.[8]

5 **6**
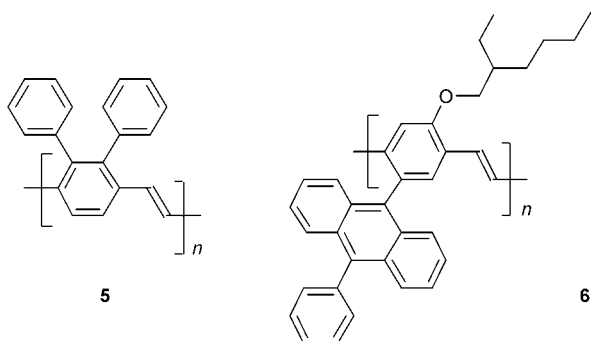
Besides improved processability, phenyl substitution seems also to enable enhanced photostability[31a,33] and higher photoluminescence efficiencies.[32c] The latter effect was assigned to the steric demand of the phenyl groups which prevents self-quenching processes *via* exciplexes or polaron pairs, induced by closely packed emissive segments.[34] Consequently, power efficiencies of single-layer OLEDs up to 16.1 lm W^{-1} at 100 cd m^{-2} and a maximum brightness of more than $10\,000 \text{ cd m}^{-2}$ at low voltage were reported for alkoxyphenyl-substituted PPV derivatives.[9d,23b] For a related system, external quantum efficiencies up to 0.3% were observed.[32e]

Pendent phenylanthryl substituents have proven to increase the EL efficiency of single-layer devices based on polymer **6** by a factor of 10 in comparison to LEDs based on PPV.[35] This improvement was interpreted with both increased interchain distance and an intrachain electronic energy transfer between the main chain and the pendants. The latter effect was expected to slow down the decay of the excited state.

As noted previously, organic compounds in general and conjugated polymers in particular tend to have low electron affinities rendering electron injection more difficult than hole injection. One strategy to overcome this problem is the use of metals with lower work functions for the cathodes. Indeed, the replacement of aluminium contacts by calcium electrodes in a conventional PPV-diode typically increases the efficiency of analoguous devices by a factor of 10.[17,36] However, calcium is highly susceptible to atmospheric degradation. Therefore, it seems to be more advantageous to alternatively improve the electron affinity of the inserted polymer. This concept was first used by Friend and Holmes *et al.* in 1993.[37] They attached electron withdrawing cyano groups to the vinylene bonds of an dihexyloxy-substituted PPV, which was synthesized by a Knoevenagel condensation polymerization of suitable monomers. A bright red fluorescent material was obtained (CN-PPV **7**). Internal efficiencies of 0.2% were reported for a single-layer configuration Al/CN-PPV/metal, independent of the type of cathode material (Al or Ca).
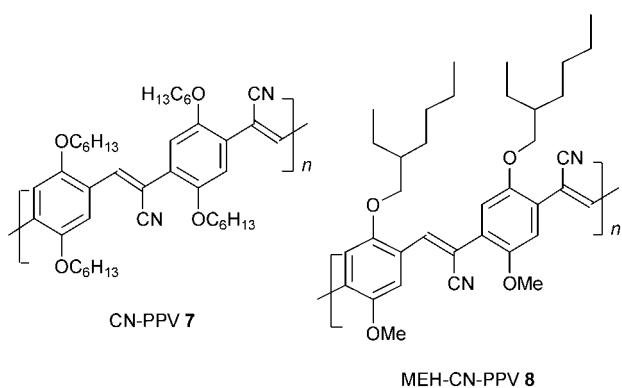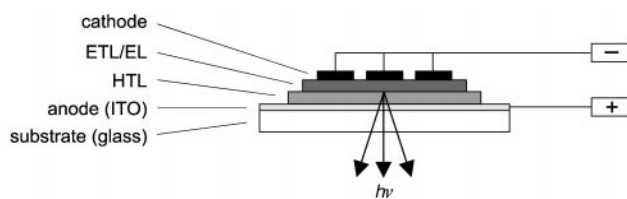
transporting/emitting layer are successively deposited onto an ITO anode (Fig. 2). This configuration allows better control of electron and hole injection rates by creating barriers for the charge transport at the heterojunction between two semiconducting layers.

Two-layer OLEDs comprising ITO/PPV/CN-PPV/metal (metal = Ca/Al) revealed internal efficiencies up to 4% indicating the possibility of fabricating highly efficient OLEDs with air-stable electrodes such as aluminium.[37] Interestingly, emission was only found to occur from the lower-gap polymer, which is in this case CN-PPV **7**.

The Knoevenagel synthesis of CN-PPVs tolerates a wide range of monomer units and a variety of CN-PPV derivatives with long alkyl and/or alkoxy groups[27a,38] and thienyl analogues[39] have been reported. A representative example, MEH-CN-PPV **8**, was found to be highly efficient in a two-layer configuration with PPV (ITO/PPV/MEH-CN-PPV/Al).[40] Red light with a brightness of 1000 cd m^{-2} at an operation voltage of 6 V and a luminous efficiency of 2.5 lm W^{-1} has been observed. Device lifetimes of a few thousand hours and internal quantum efficiencies exceeding 10%, which correspond to external values up to 2.5%, have been reported for this type of two-layer device. These levels of brightness and efficiency are target values for low-level backlighting and for computer monitors, respectively.

Stimulated by these excellent results several attempts have been successfully carried out to introduce other electron-withdrawing groups such as trifluoromethyl,[41] halide,[42] and trifluoromethanesulfonyl[43] substituents at both vinylene and phenylene moieties. However, without exception their photo- and electroluminescence efficiencies were found to be uncompetitive with CN-PPV derivatives.

As previously stated, the fabrication of blue inorganic LEDs is difficult and expensive. Polymer OLEDs emitting in the blue region are therefore an attractive target for research. Blue emission from the active luminescent material requires a HOMO–LUMO energy gap of approximately 2.7–3.0 eV.[9f] In 1992, Leising *et al.* for the first time reported on blue electroluminescence from OLEDs containing poly(*p*-phenylene) (PPP) **9**.[44] They observed external quantum efficiencies for simple single-layer devices (ITO/PPP/Al) of 0.05%. Like PPV, PPP is also insoluble and infusible and has to be incorporated into an electrooptical device *via* a soluble precursor polymer.[45]

CN-PPV **7**

MEH-CN-PPV **8**

In order to provide balanced charge injection and to improve device efficiency significantly, two-layer OLEDs were constructed in which a hole transporting and an electron
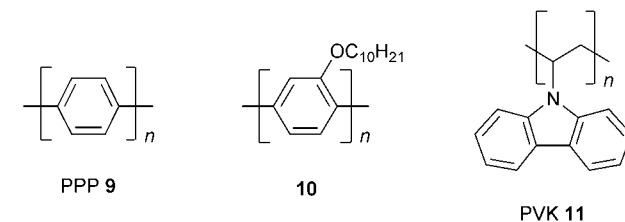

PPP **9**   **10**   PVK **11**

In an effort to improve processability, PPP derivatives bearing solubilizing alkyl, aryl, alkoxy, or perfluoroalkyl side chains have been synthesized by transition metal-catalyzed polymerization of appropriate monomers and have been utilized as active organic materials in OLEDs.[9,11,28,46–48]

Since due to their steric demands substituents affect the torsion angle of consecutive rings, the band gaps E_g of PPP derivatives crucially depend on the substitution pattern. In a theoretical study Brédas *et al.* found a hyperlinear increase of the band gap with increasing torsion angles.[49] Empirically determined values cover the whole range between $E_g = 2.8$ and $E_g = 3.5$ eV enabling stepwise adjustment of the emissive colour.

Although PPP and its derivatives reveal extraordinarily high thermal and oxidative stabilities, corresponding single-layer OLEDs exhibit only low EL efficiencies. Higher efficiencies have been achieved by preparing polymer blends or by virtue of two-layer OLED-configurations. External efficiencies up to 3% were determined for an ITO/PVK/**10**/Ca OLED, with an alkoxy PPP derivative **10** as the active luminescent material.[47] Poly(*N*-vinylcarbazole) (PVK) **11** was used to enhance hole injection and to serve as an electron blocking layer.

Internal quantum efficiencies up to 4% in the blue region have been achieved in triple-layer devices based on copolymer **12** (ITO/PVK/**12**/PBD/Ca). Balanced charge injection of both electrons and holes, was accomplished by incorporating 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD /→ chapter 2.3.3.) and PVK **11**, respectively, into the device.[28a]


12
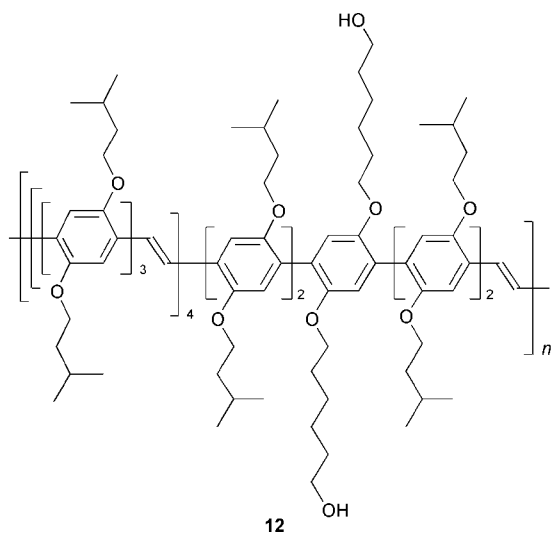
The external quantum efficiency was measured to be close to 2% for blends of poly(2,5-diheptyl-2′,5′-dipentyloxybiphenylene) **13** and a poly(*p*-phenylenethienylene) copolymer **14**.[48] Maximum performance was found with a loading of 10% of polymer **14** in polymer **13**. The extraordinarily high efficiency of a mixture of both polymers exceeds the values obtained for single layer devices based on each polymer alone by more than one order of magnitude and was attributed to exciton confinement as a result of trapping effects.

13   **14**
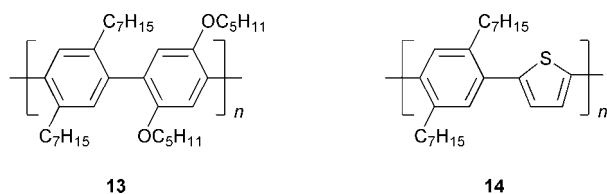
As previously mentioned, the introduction of substituents on the PPP skeleton leads to increased distortion of adjacent rings. This effect causes a blue-shift of emission but is, unfortunately, often accompanied by a reduction of the fluorescence quantum yield.[9a] In order to overcome this problem, Scherf and Müllen *et al.* developed ladder-type PPP derivatives **15–17** with a rigid planarized polymeric backbone.[50] Processability of these compounds is achieved by attachment of solubilizing substituents at the methylene bridges.
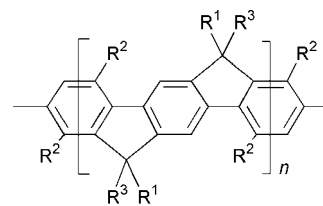
15 R^1 = H, R^2 = C_6H_{13}, R^3 = *p*-*t*BuC_6H_4 (**a**), *p*-$C_{10}H_{21}C_6H_4$ (**b**)
16 R^1 = CH_3, R^2 = C_6H_{13}, R^3 = *p*-*t*BuC_6H_4 (**a**), *p*-$C_{10}H_{21}C_6H_4$ (**b**)
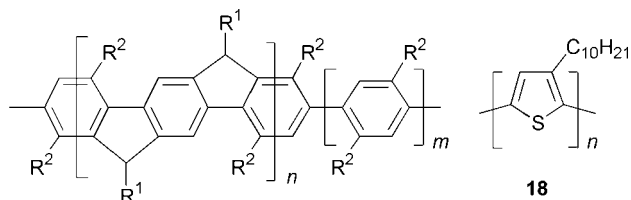

17 R^1 = *p*-$C_{10}H_{21}C_6H_4$, R^2 = C_6H_{13} **18**

Films of derivatives **15** were found to reveal unstable blue electroluminescence. As operation time increases a yellow component is emitted that can be assigned to a morphological reorganization and to excimer formation in the solid state.[51] Different solutions were found to avoid aggregate emission and to separate adjacent polymeric chains. Successful approaches were the incorporation of **15** into a PVK matrix,[52] the attachment of a methyl group at the bridging carbon atom in **16**,[53] and the statistical interruption of planarized segments by oligophenylene spacers as realized for copolymer **17**.[50a,51a,54] Taking advantage of these concepts stable blue electroluminescence with external quantum efficiencies up to 4% became accessible.[50b,53a,54,55]

The best performance yet reported for PPP-based diodes with an external efficiency beyond 4% was achieved with a blend of ladder-type polymer **16b** and small amounts of poly(3-decylthiophene) **18** in a single-layer configuration (ITO/**16b:18**/Al).[56] Depending on the selected ratio of polymers, the emissive colour can gradually be shifted from blue to yellow. External quantum efficiencies up to 1.6% have been reported for a similar blend system based on a ladder-type polymer **16** and a red-emitting poly(aryleneethyinylene) **19**.[50b,57] The emissive colour of corresponding devices can be adjusted from blue to red–orange with an increasing amount of guest polymer **19**. At a specific concentration (0.05% **19**), both polymers reveal electroluminescence resulting in white light emission.[50b,57a,58]

With a structure between PPP and ladder-type PPP derivatives, polyfluorenes have aroused interest as components of OLEDs because of their exceptionally high solution and solid-state fluorescence quantum yields as well as their thermal and chemical stability.[59] Poly(9,9-dihexylfluorene) **20a** has been used as a blue emitter in multicolour devices.[60] The dioctyl analogue **20b** has been employed in a highly efficient green-emitting OLED with luminous efficiencies up to 8.2 lm W^{-1} (ITO/PEDOT:PSS/**20b**/Ca/Al).[25] An additional hole transport/injection layer consisting of poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate) (PSS) was introduced to increase the longevity of that device. Very recently, Cambridge Display Technology measured an even higher luminous efficiency of more than 20 lm W^{-1} for an analogous OLED, which is the highest value reported for any organic light-emitting device so far.[9d] Moreover, poly(9,9-dialkylfluorene)s have been shown to exhibit polarized electroluminescence in aligned devices.[9b,61]

Designed as a polyelectrolyte for light-emitting electrochemical cells (LECs / → section B), a polyfluorene **20c** bearing 3,6-dioxaheptyl side groups was reported by Pei and Yang in 1996. In an ITO/**20c**/Ca configuration, single-layer LEDs
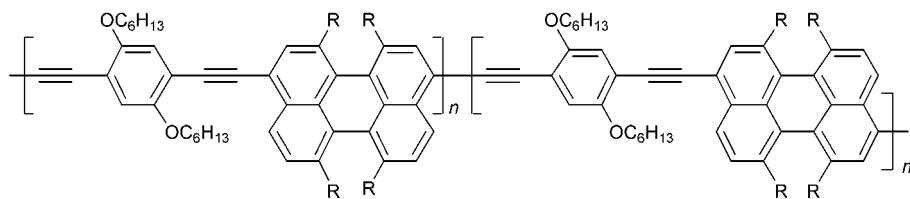
19 R = p-tBuC$_6$H$_4$O
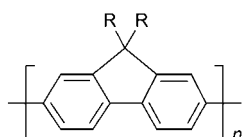
20 R = C$_6$H$_{13}$ (**a**), C$_8$H$_{17}$ (**b**), (CH$_2$CH$_2$O)$_2$CH$_3$ (**c**)

showed external quantum efficiencies of 0.3%.[62] Hewlett Packard attained higher efficiencies (1.3%) for OLEDs based on oligomeric 9,9-dialkylfluorenes ($n \approx 5$–12) **21**. The strained four-membered cyclobutene end-caps undergo thermal opening, followed by cycloaddition delivering a complex, three dimensional polymer network formation.[63]
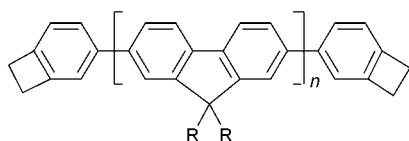

21
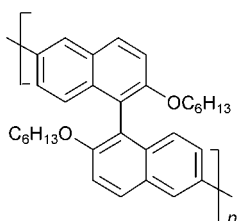
22

Similar to ladder-type PPP derivatives **15**, polyfluorene films were also reported to reveal excimer formation upon annealing. In order to overcome aggregate emission and to gain band gap control by structural modification, random copolymers derived from poly(alkylfluorene)s and anthracene[59a,b] as well as combinations of poly(alkylfluorene) and PPV **1** segments[64] have been synthesized. Furthermore, deep blue emission ($\eta_{ext} = 0.60\%$) was demonstrated for a copolymer comprising fluorene and alkoxy substituted p-phenylene units.[65] Cross-linkable polymers based on poly(9,9-dihexylfluorene) were obtained by attachment of styryl groups in terminal positions. Thermoconversion to insoluble materials enabled multilayering of polymers in OLEDs, allowed the supramolecular ordering to be controlled and, hence, led to suppression of troublesome excimer aggregation. Taking advantage of this approach blue multi-layer OLEDs with external quantum efficiencies of more than 1% were demonstrated.[66] Owing to its twisted nonplanar backbone, even higher external quantum efficiencies ($\eta_{ext} = 2\%$) and an excellent luminous efficiency (4.9 lm W^{-1}) were attained for poly[6,6'-(2,2'-dihexyloxy)-1,1'-binaphthyl] **22** in a two-layer configuration that used a fluorinated copper phthalocyanine as the electron transporting layer.[67]

On account of their good solubility and chemical stability poly(3-alkylthiophene)s (PATs) have attracted considerable interest. Their syntheses are usually performed either by electrooxidative or oxidative polymerization or by transition metal-catalyzed coupling reactions of suitable monomers.[11a] Both sequences tolerate a wide range of substitution patterns. The properties of polythiophene derivatives (PTs) in general can easily be altered by structural modification which allows the control of the torsion of the main chain and thus the adjustment of the effective conjugation length. PATs and other PT derivatives are attractive electroluminescent materials due to their ease of tunability.[68–74] Although simple PATs **23** usually exhibit red emission,[68,69] all other colours from blue to near infrared have been realized in OLED applications. Alkyl side chain substitution by incorporation of ether, ester or urethane functions in **24** was found to cause a colour change to yellow and orange emission.[70] With the increasing steric demand of the substituents in β-positions (**25**) emission is shifted stepwise to green and blue.[71] Two-layer OLEDs based on **25b** (ITO/25b/PBD/Ca:Al) revealed blue electroluminescence with an maximum external quantum yield of 0.6%.[71a] Again, the incorporation of aryl substitutents, as for PTs **26** and **27**, granted improved processability due to higher solubility.[68,71]
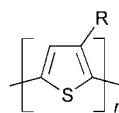
23 R = C$_6$H$_{13}$ (**a**), C$_8$H$_{17}$ (**b**), C$_{12}$H$_{25}$ (**c**), C$_{18}$H$_{37}$ (**d**), C$_{22}$H$_{45}$ (**e**)
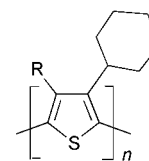
24 R = CO$_2$C$_6$H$_{13}$ (**a**), CO$_2$C$_8$H$_{17}$ (**b**), C$_{10}$H$_{20}$OMe (**c**), C$_2$H$_4$CO$_2$NHCH$_2$CO$_2$C$_4$H$_9$ (**d**)

25 R = H (**a**), CH$_3$ (**b**)
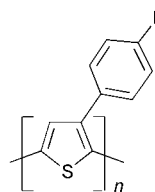
26 R = H (**a**), C$_8$H$_{17}$ (**b**)
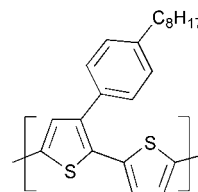
27
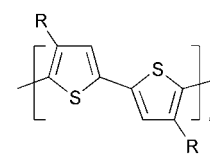
28 R = C$_6$H$_{13}$ (**a**), C$_8$H$_{17}$ (**b**), C$_{10}$H$_{21}$ (**c**)

Although PTs tend to exhibit fluorescence intensities smaller than PPVs and PPP derivatives they have frequently been used as active layers in electrooptical applications.[68–74] Enhanced efficiencies have been achieved with increasing molecular order by virtue of regioregularity,[72] in polymeric blends,[56,69a,71b,73] and in multilayer structures.[60a,69b] Regioregular PATs synthesized by the McCullough[75] or Rieke[76] method were found to show distinctly higher quantum efficiencies than corresponding regiorandom PATs. External quantum efficiencies up to 0.5% have been reported for regioregular poly(4,4'-dialkyl-2,2'-bithiophene)s **28** in a single-layer configuration (ITO/28/Ca:Al).[72a]

Polarized luminescence was observed for OLEDs based on

Langmuir–Blodgett films of PATs.[74] A blend of MEH-PPV **2** and poly(3-hexylthiophene) **23a** was used in a red-emitting single-layer OLED. With external quantum efficiencies up to 1.7%, its performance was reported to be significantly improved in comparison to devices deriving from only one of the materials.[73]

Due to its extraordinarily low oxidation potential the thienyl analogue of PPV, poly(2,5-thienylenevinylene) (PTV) **29**, has been used as a promoter of hole injection.[77] In a trilayer structure with **30** as the hole transport emitter and PBD as the electron transport layer the external efficiency was found to be doubled to 0.3% upon insertion of a PTV layer.[77a]

PTV **29**

30
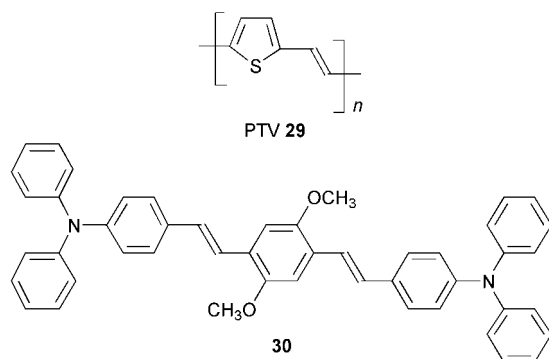
Conjugated polymers based on electron-deficient heterocyclic units, in particular systems containing electron-withdrawing imine nitrogen atoms (C=N), have attracted considerable interest as electron-transporting layers in the fabrication of multilayer devices. As previously indicated, polyheterocycles with high electron affinities enable the construction of highly efficient OLEDs, even with air-stable electrodes.

Like PPV, its nitrogen derivative poly(pyridinevinylene) (PPyV) **31** is neither soluble nor fusible and needs to be synthesized by a precursor route similar to that developed for PPV.[78,79a] Due to the lower symmetry of the pyridine ring three regioisomeric, statistically distributed relative orientations of adjacent pyridine moieties can be obtained (head-head/tail-tail/head-tail).
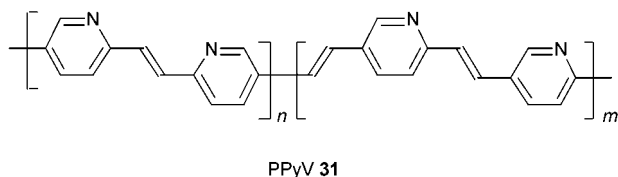

PPyV **31**

PPyV **31** has been used as an electron transporting material in several multilayer devices.[79] Although single-layer devices (ITO/PPyV/Al) are reported to show only barely visible emission,[79a] PPyV was found to lower the threshold voltage and to increase the efficiency of PPV diodes, in which it is introduced as electron-transporting layer (ITO/PPV/PPyV/Al).[79b] According to PPV/CN-PPV diodes previously mentioned, emission was found to occur from the lower-band gap polymer PPyV **31** exclusively.

Similar pyridine-based polymers with high electron affinities have been synthesized as block copolymers with both PPyV and PPV moieties.[79c,80]

Polyquinoxalines (PQxs) combine advantageous features such as high electron affinity, good thermal stability, and good processability with sufficiently low refractive indices. On account to their chemical structure PQxs that have been utilized as electron transporting materials in OLEDs can be devided into two groups: poly(quinoxaline-2,6-diyl)s[81] and poly(quinoxaline-5,8-diyl)s.[82] The most frequently used compound, poly[2,2′-(p-phenylene)-6,6′-bis(3-phenylquinoxaline)]

(PPQ) **32**,[81] belongs to the first class. Taking advantage of their facile synthetic access, several 5,8-derivatives **33** have been synthesized and investigated in OLEDs.[82] In both classes, sufficient processability was guaranteed by phenyl or alkyl substitution, respectively.

32 PPQ

33 R = C$_7$H$_{15}$ (**a**), Ph (**b**)
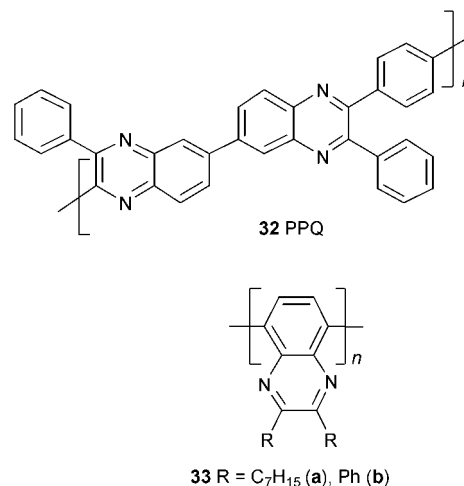
Both types of PQxs have been proven to significantly increase efficiencies of multilayer devices.[81,82] Improvements of external efficiencies by one order of magnitude upon introduction of a PQx layer have been reported.[81a] In addition to their obvious capability to transport electrons, PQxs are also expected to gain increasing importance due to their remarkably low refractive indices. Since the output efficiency of an LED is closely related to the refractive index of the emitting layer (→ chapter 1), low refraction values are advantageous with respect to highly efficient electroluminescence. PQxs are therefore considered to improve external quantum efficiencies of EL devices in the near future up to ∼20%.[82a]

Polyquinolines and copolymers containing quinoline and thienylene segments have been suggested as electron transport emitters for EL devices.[83] Polymer **34** revealed bright yellow emission in a two-layer device with a triphenylamine derivative as the hole transport material.[83a] The quantum efficiency and the luminance of this device were 1% and 280 cd m^{-2}, respectively. In an effort to combine both electron and hole transport abilities in a single layer, electron-affinitive biquinoline segments were also introduced into the conjugated backbone of an alkoxy-substituted PPV derivative.[84]


34
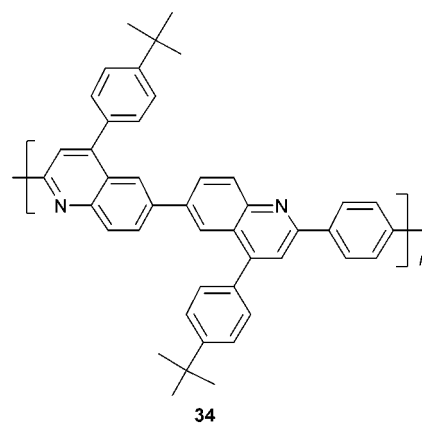
Due to the electron-withdrawing character of the 1,3,4-oxadiazole ring, certain low molecular weight aromatic 1,3,4-oxadiazole derivatives have been used in OLEDs to facilitate injection and transport of electrons (→ chapter 2.3.3.). However, usually their applicability has been limited by crystallization and aggregation effects. Several aromatic

polymeric analogues have been developed in order to overcome this problem. However, poly(1,3,4-oxadiazole)s lack sufficient solubility and hence processability. One approach to increase solubility was the introduction of flexible ether, perfluoralkyl, or diphenylsilyl linkers. This concept will be reviewed in chapter 2.1.2.4. Fully conjugated polymeric 1,3,4-oxadiazoles have been designed as copolymers with thiophene, carbazole, or p-phenylene units bearing solubilizing alkoxy or alkyl side chains.[85–87] In a single-layer configuration (ITO/35/Ca), copolymer **35** revealed moderate blue electroluminescene.[86a] With the length of the oligothiophene segments increasing, the emissive colour could be tuned from blue to green and orange.[86b]

In order to mediate balanced charge injection, oxadiazole

2.2. Conjugated oligomers in OLEDs. Main chain conjugated polymers inevitably contain random dispersed defects leading to a statistical distribution of lumophore lengths.[11] In contrast, well-defined conjugated oligomers allow strict control of the effective conjugation length. Initially, they have been synthesized as model compounds in order to gain more insight into the structural and electronic peculiarities of the corresponding polymers.[11b,c,90] However, on account of their controllable and rigorously defined structure, conjugated oligomers have also been used as novel materials and potential alternative in electrooptical applications.
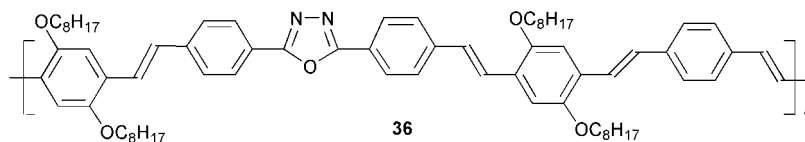
Thin-film optoelectronic devices such as OLEDs require the deposition of one or more semiconductor layers onto a suitable substrate. Like the corresponding polymers, conjugated
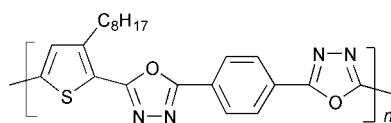
35
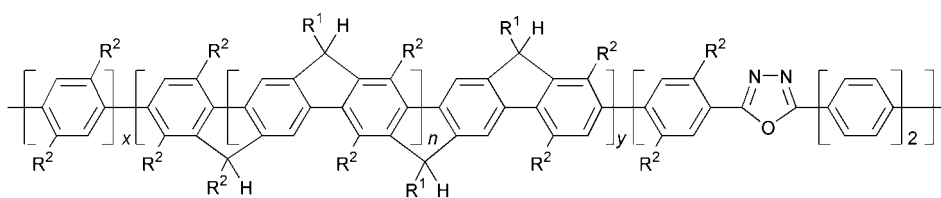
37 R^1 = p-C$_{10}$H$_{21}$C$_6$H$_4$, R^2 = C$_6$H$_{13}$; x = 0.42, y = 0.40, z = 0.18

36
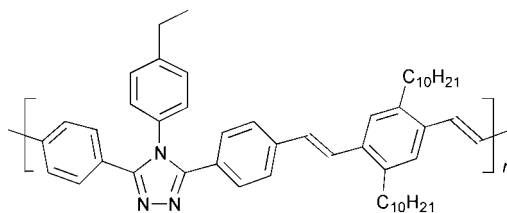
38

moieties have been integrated into p-type conjugated polymers like PPV, alkoxy substituted PPVs, and ladder-type poly(p-phenylene)s either as main chain segments[87] or as pendant groups.[88] Single-layer devices of polymer **36** with bipolar carrier transport abilities revealed good operating stabilities and external quantum efficiencies up to 0.15% with air-stable aluminium electrodes (ITO/36/Al).[87a]

Blue electroluminescence with an internal quantum efficiency of 0.5% has been observed for ladder-type polymer **37** with PBD segments in the polymeric chain (ITO/37/Al).[87b] In a multilayer structure, however, the insertion of an additional PPV hole transport layer was found to increase the efficiency to 1.2%.

Fully conjugated polymers containing triazole units have been suggested as electron transporting/hole blocking layers in elelectroluminescent devices. In a two-layer configuration with PPV (ITO/PPV/38/Al), copolymer **38** produced an external quantum efficiency of 0.08% at a luminance of 150 cd m^{-2}, a significant improvement in comparison to analogously prepared PPV single-layer devices.[29a,89]

oligomers can be deposited from solution or, since they are molecular materials, by sublimation. The method of choice depends mainly on the molecular weight and solubility of the material. Many small molecular semiconductors are rather rigid and planar molecules which are generally insoluble in many organic solvents. Therefore, they need to be incorporated into electroluminescent devices by sublimation techniques. Solution processing demands sufficient solubility which is typically ensured by introduction of solubilizing side chains. Pursuing this concept, a wide range of oligo(p-phenylenevinylene)s (OPVs) with alkyl[91–93] or alkoxy[94–97,98a–c] substituents has been synthesized. They have been incorporated into OLEDs as spincast films,[92,93] in polymeric blends,[94a,98a] and via the Langmuir–Blodgett technique.[98b] Like their unsubstituted analogues,[98d,99] substituted OPVs have occasionally also been vacuum deposited as thin films.[94b,95,98c] Although electroluminescence from oligomeric p-phenylenevinylenes has been studied with less intensity in comparison to the corresponding polymers, several highly efficient devices have been reported.[92–99] Hadziioannou et al. fabricated a single-

layer OLED with an external quantum yield of 0.15% based on vacuum deposited films of oligomer **39a** (ITO/**39a**/Ca).[95a] In order to provide balanced charge injection and to increase electron affinity, cyano-substituted derivatives have been synthesized and utilized in multilayer configurations with air-stable aluminium electrodes.[91a,95b,97] For a two-layer device (ITO/**39a**/**39b**/Al) efficiencies up to 0.1% have been attained. This corresponds to an increase of more than one order of magnitude compared with single-layer diodes based on **39a**.[95b]

39 R = H (**a**), CN (**b**)
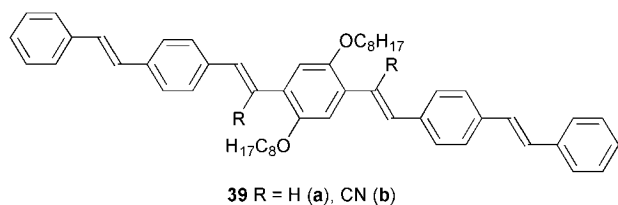
For single-layer devices based on alkyl-substituted oligo(*p*-phenylenevinylene)s **40** (ITO/**40**/Ca/Ag) even higher efficiencies up to 1.36% have been attained.[92] Owing to its ability to confine electrons in the emitting layer, the insertion of an additional PVK layer was found to enhance the stability of the device significantly.

40 *n* = 2 (**a**), 4 (**b**)
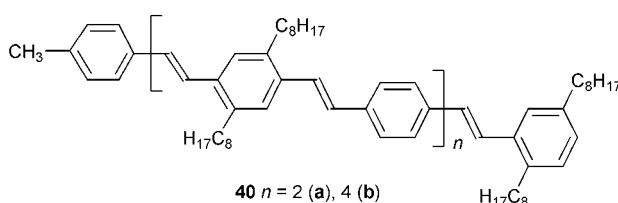
Haarer *et al.* investigated the electroluminescent behaviour of a homologous series of alkoxy-substituted *p*-phenylenevinylene oligomers in devices based on evaporated films[94b] as well as blend systems[94a] formed by spin-coating of oligomers in a polystyrene (PS) matrix. By variation of conjugation length, emission wavelengths could be controlled within a wide spectral range. Interpretation of the external quantum efficiency as a function of chain length, however, remained complex due to intermolecular interactions and aggregation phenomena. In blend systems the concentration of oligomers in the polystyrene matrix was also found to influence the device performance significantly.

Efficiencies up to 0.1% have been reported for single- and multilayer devices of vacuum deposited random oligo(*p*-phenylene)s and oligo(*p*-phenylenevinylene)s.[99] The morphology of the films, whether highly ordered or polycrystalline, was found to depend crucially on the substrate temperature during evaporation. Again, emission wavelengths within the whole visible range were obtained by controlling the composition of the oligomer layers.

Oligo(*p*-phenylene)s have been used as blue emitters in electroluminescent devices.[58,100–103] The most frequently used oligomer is sexi(*p*-phenylene) **41a**.[58,100–102]

41 R = H (**a**), *t*Bu (**b**)
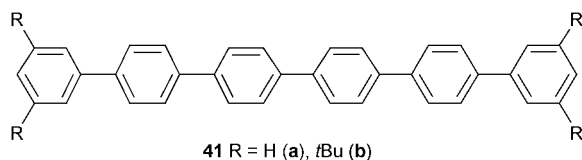
Single-layer devices based on oligomer **41a** (ITO/**41a**/Al) emit blue light with a brightness of about 500 cd m^{-2}.[100a] The maximum external quantum yield is increased from 1 to 2% by the careful deposition of aluminium.[100b] Lowering the deposition rate results in lower onset voltages for the corresponding diodes as a consequence of the reduced extent of the interface
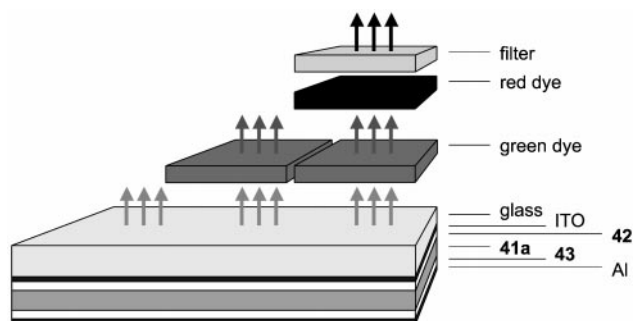
Fig. 3 Schematic configuration of a red–green–blue OLED developed by Leising *et al.* (redrawn from ref. 102*a*).

region. Two additional layers of an oligoazomethine derivative **42** and diaminooctafluorobiphenyl **43** enable effective hole and electron injection and shift the recombination zone towards the sexi(*p*-phenylene) layer in the centre of the device. Multilayer configurations have also shown improved performance and attain external quantum efficiencies up to 2% (ITO/**42**/**41a**/**43**/Al).[100c]

42

43

44
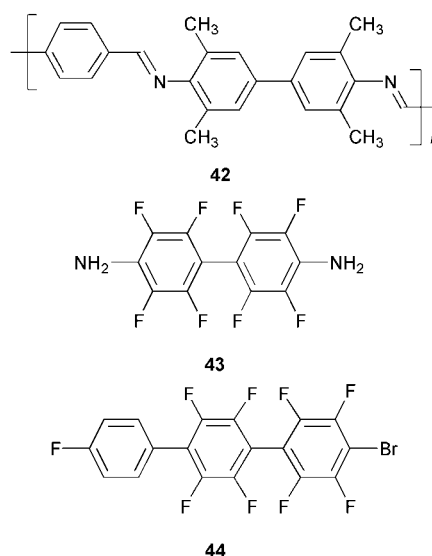
For two-layer diodes including a different fluorinated oligo(*p*-phenylene) **44** as electron transport material (ITO/**41a**/**44**/Al), even higher efficiencies of approximately 3.4% have been reported.[100d]

Since their light emission can be efficiently converted into any other colour by external or internal colour conversion techniques, blue emitting OLEDs are of crucial importance for polychromatic display applications. Leising *et al.* developed an efficient red–green–blue electroluminescent device based on sexi(*p*-phenylene) **41a**, suitable matrix dye layers, and a dielectric filter (Fig. 3).[58,102] Blue light is used to excite a highly fluorescent green coumarin dye (Coumarin 102) located in an external conversion layer. Repeating the process, green light can be used to generate red light *via* a second conversion layer containing a red fluorescent dye (Lumogen F300). Based on a blue sexi(*p*-phenylene) OLED with a power efficiency of 0.5 lm W^{-1}, green and red emission have been observed with efficiencies of 3.5 and 1.3 lm W^{-1}, respectively.[58]

Yanagi *et al.* investigated the electroluminescence of epitaxially oriented films of sexi(*p*-phenylene) **41a** with either the molecular axis lying or standing next to the substrate surface.[101] Compared to a cell containing upright molecules, the cell which contained flat lying molecules revealed spectral narrowing and a higher light intensity at remarkably low driving voltages. Its distinct electroluminescent behaviour was

interpreted with respect to an anisotropic distribution of the polarized emission light as well as the efficiency of carrier transport due to ordered molecular arrays in different orientation modes.

Molecular organic EL devices often suffer from recrystallization of the amorphous films during operation or storage, leading to rapid degradation of device performance.[11d] In order to overcome this problem, amorphous molecular materials have attracted much attention because of their morphological stability, excellent processability, transparency, the absence of grain boundaries, and their isotropic properties. Non-polymeric organic glasses **45** with high glass transition temperatures based on oligo(p-phenylene)s containing rigid spiro-linkages were synthesized by Salbeck *et al.*[103] Tetramethyl- and tetrakis(trimethylsilyl)-substituted derivatives of tetramer **45a** were presented by Tour *et al.* before.[104] Single-layer devices of spiro-hexamer **45b** (ITO/**45b**/Al:Mg) revealed bright blue electroluminescence.[103a] Unfortunately, a rather high turn-on voltage of 9 V was necessary to observe light emission. In order to reduce the threshold voltage, an electron transporting layer (Alq$_3$) was introduced into a two-layer configuration (ITO/**45b**/Alq$_3$/Al:Mg) exhibiting brightnesses up to 900 cd m^{-2}. However, since the emission zone had partially been shifted towards the Alq$_3$ layer, a colour change towards green occurred.
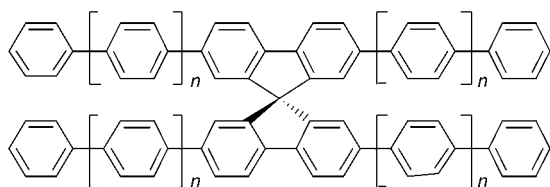
45 R = H, *n* = 0 (**a**), 1 (**b**), 2 (**c**), 3 (**d**)

Molecular solid films of spiro-type compounds have also been reported to reveal spectral narrowing without exhibiting any concentration quenching effects.[103b,c] On account of their remarkably high solid-state photoluminescence quantum yields, spiro-linked oligo(p-phenylene)s have therefore been suggested as attractive candidates for molecular solid-state lasers.

The first reported single-layer thin-film oligothiophene OLEDs, demonstrated by Umbach *et al.*, are based on vacuum deposited films of cyclohexene end-capped oligothiophenes **46**.[105a]

At relatively low voltages (starting at about 2.5 V), these devices (ITO/ECnT/Al) emitted light in the yellow–orange range of the visible spectrum. However, taking internal reflection and absorption, geometric effects, and internal energy conversion processes into account, their quantum efficiencies were rather low—an estimated 10^{-2} to 10^{-3}%. This was attributed to unfavourable energy level alignment, interface reactions, disadvantageous film morphology, and the electrochemical properties of the molecules. Oligothiophenes are intrinsically electron-rich compounds exhibiting low electron affinity. Carrier mobility is therefore ill-balanced and charge transport is mainly performed by holes shifting the recombination zone unfavourably close to the cathode. In spite of device optimization by variation of the cathode metal, operation temperature, and the layer thicknesses, external efficiencies of single-layer diodes based on EC6T **46b** remained consequently relatively low at 10^{-3}%.[105b,c]
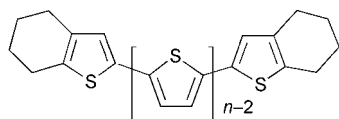
ECnT **46** *n* = 5 (**a**), 6 (**b**), 7 (**c**)

With respect to an improvement of the electron transport capability of oligothiophenes, the incorporation of electronegative oxygen and nitrogen atoms should enable more balanced charge carrier injection.[106] Accordingly, the insertion of an additional layer of the more electron-deficient oligoheterocycle **47** into a two-layer configuration with air-stable silver electrodes (ITO/**46b**/**47**/Ag) gave an improvement of the external quantum efficiency by more than one order of magnitude (0.05%).[107]
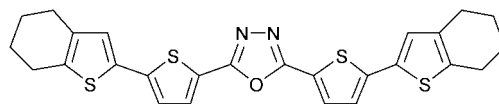
47

The green light of this device exclusively originates from thiophene/oxadiazole oligomer **47**. Since EC6T **46b** would be preferred as a recombination centre on account of its smaller band gap, the recombination zone thus cannot be located at the interface between the organic layers and must lie within the oxadiazole layer. However, compared to end-capped sexithiophene EC6T **46b**, the electron transporting qualities of the thiophene/1,3,4-oxadiazole oligomer **47** are obviously improved, and the hole transport in these devices is, therefore, still partially performed by oligoheterocycle **47**.

Besides sublimed molecular film devices, composite OLEDs based on polymeric matrices embody an alternative approach to introduce oligothiophenes as hole transport emitters into EL devices. However, this concept demands sufficient solubility and hence processability of the oligomeric material, which is typically accomplished by alkyl or aryl substitution. Following this approach, Bäuerle and Meerholz *et al.* synthesized phenyl-substituted and spiro-fluorenyl-bridged oligothiophenes **48** and **49**, respectively, and demonstrated their application in composite OLEDs.[108]
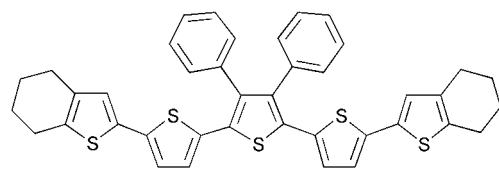
48
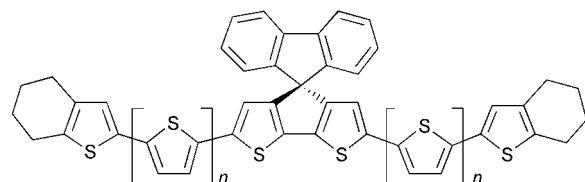
49 *n* = 0 (**a**), 1 (**b**)

Single-layer devices were fabricated by blending TPD, an oligothiophene and polystyrene as polymeric matrix. In order to improve the injection of negative charge carriers in a two-layer configuration, TPD was replaced with an electron transporting oxadiazole (PBD) and an additional hole transporting layer was introduced that consisted of an cross-linkable TPD derivative (→ chapter 2.4.2.). These devices yielded brightnesses of more than 5000 cd m^{-2} under continuous operation. The colour of the diodes could easily be adjusted by choice of the molecular dopant applied.

Taking advantage of its extraordinarily high solid-state quantum efficiency (37%) thiophene/thienyl *S,S*-dioxide oligomer **50** was recently used as an electron transport emitter in composite light-emitting diodes.[109] Two-layer devices in a ITO/PEDOT/**20b**:**50**/Ca/Al configuration exhibited maximum lumi-

nances of $200\ \text{cd m}^{-2}$ and (estimated) internal quantum efficiencies up to 5.8%. Furthermore, owing to the high electron affinity of **50** a substantial improvement of both the turn-on and operating voltage in comparison to conventional polythiophene based OLEDs was demonstrated.

50
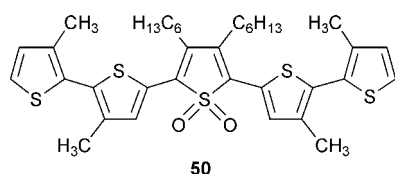
In contrast to blending in composite OLEDs, sublimation techniques have occasionally been reported to yield highly ordered films of conjugated oligomers. Films of sexithiophene **51** containing molecules standing upright on the substrate surface revealed partially polarized electroluminescence (ITO/**51**/Al) with an estimated external quantum yield of 10^{-3}%.[110]

51
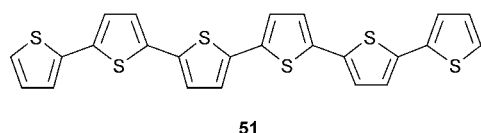
Several authors have reported significantly increased EL efficiencies in multilayer configurations based on different oligothiophenes.[111–113] These approaches derived benefit from the introduction of an additional quaterthiophene-layer in sexithiophene-based diodes close to the cathode to block holes and enhance the recombination at the organic heterojunction[111,112] or the insertion of bulky side chain substituted sexithiophene-layers to hamper aggregation and thus the formation of non-emissive relaxation sites.[113]

Renouncing their luminescent properties, oligothiophenes have also been used as charge transport and electron blocking layers in OLEDs.[114–116] Hosokawa *et al.* reported a highly efficient multilayer device (ITO/**51**/**41b**/Alq$_3$/Mg:Ag) with bright green emission beyond $2000\ \text{cd m}^{-2}$ using Alq$_3$ as the electron transporting and emitting layer.[114a] Sexithiophene **51** was used to provide efficient hole transport. Furthermore, alkylated oligo(*p*-phenylene) **41b** was inserted to confine electrons within the Alq$_3$ layer.

Amorphous materials containing oligothiophene moieties such as compounds **52** have proven to form morphologically

52 *n* = 1 (**a**), 2 (**b**), 3 (**c**), 4 (**d**)

53 R = H; *n* = 1 (**a**), 2 (**b**), 3 (**c**)

R = CH$_3$; *n* = 1 (**d**), 2 (**e**), 3 (**f**)

54 R = H (**a**), *t*BuPh$_2$Si (**b**), 2-thienyl (**c**)

stable hole injecting layers.[115] A double layer EL device containing oligothiophene **52c** and Alq$_3$ (ITO/**52c**/Alq$_3$/Mg:Ag) exhibited a maximum luminance of $\sim 13\,000\ \text{cd m}^{-2}$ at a driving voltage of 18 V, an external quantum efficiency of 0.9% and a luminous efficiency of $1.1\ \text{lm W}^{-1}$ at a luminance of $300\ \text{cd m}^{-2}$.[115a] Similar characteristics have been attained by Kawate *et al.* for oligothiophenes **53** in a two-layer configuration containing Alq$_3$ as an electron transport layer (ITO/**53**/Alq$_3$/Mg:In). Typical luminous efficiencies were 0.2–$0.4\ \text{lm W}^{-1}$ with maximum luminances of more than $1000\ \text{cd m}^{-2}$.[116]

Thienyl-substituted siloles **54** have been synthesized by Tamao *et al.* as electron transporting materials and as potential alternatives to Alq$_3$ in electrooptical applications. However, with a maximum value of $0.16\ \text{lm W}^{-1}$ at $100\ \text{cd m}^{-2}$ luminous efficiencies of corresponding devices (ITO/TPD/**54b**/Mg:Ag) remained low.[117]
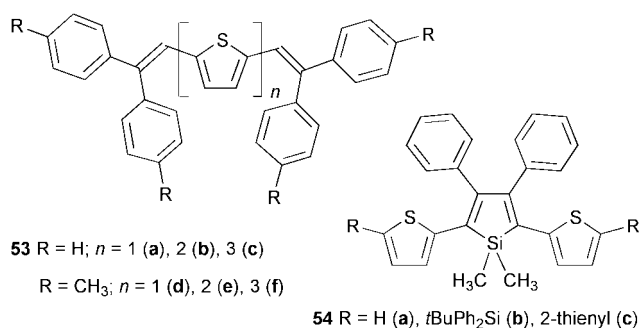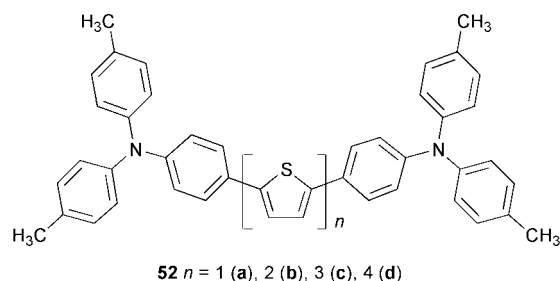
2.3. Low molecular weight materials in OLEDs. Since the basic principles of electroluminescence are essentially the same, no matter which type of organic material is used, the choice of materials is usually determined by the method of fabrication preferred. As previously mentioned, conjugated polymers are processed from solution by coating techniques. Due to their low molecular weight, small organic semiconductors can also be vaccum deposited as thin films. This preparation technique to build up electroluminescent devices was first utilized by Tang and VanSlyke at Kodak in their basic work on OLEDs in 1987.[6] Their device contained two layers of different carrier transport properties (ITO/**56**/Alq$_3$/Mg:Ag). Alq$_3$ **55a** is used for electron transport and at the same time as an emitting layer, but is unable to carry holes. In contrast, bis(triarylamine) **56** was inserted to provide efficient hole transfer. Therefore, recombination was largely confined to a region near the interface between both organic materials. As a consequence, high external quantum efficiencies (1%), remarkable luminous efficiencies ($1.5\ \text{lm W}^{-1}$) and brightnesses ($> 1000\ \text{cd m}^{-2}$) were achievable at an operating voltage below 10 V.

55 R = H (**a**, Alq$_3$), CH$_3$ (**b**)

56
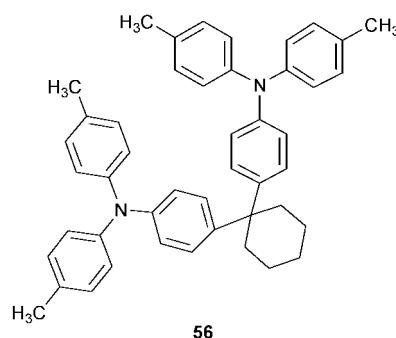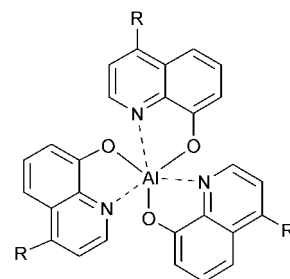
The approach to separate and distribute distinct functions such as fluorescence, electron and hole transport on different materials requires the fabrication of multilayer devices. In contrast to the development of polymer-based OLEDs, the concept of designing materials with only one or two specific

functions was realized at an early stage in OLED history. On account to their function in electroluminescent devices, low molecular weight materials can therefore be classified into five groups: electron transport emitters, dopant emitters, electron transport and hole blocking materials, hole transport materials, and finally, electron and hole transport emitters.

2.3.1. Electron transport emitters. Metal chelates and in particular Alq$_3$ **55a** are the most prevalent electron transport emitters in organic EL devices.[9] Thin films of Alq$_3$ exhibit green photoluminescence with a quantum efficiency around 32%.[118] Interesting features include its propensity to form morphologically stable thin films upon vacuum deposition and its high electron mobility. Since the first report of electroluminescence from Alq$_3$ in 1987[6] it has been extensively used as an active material in OLEDs. Diodes based on Alq$_3$ belong to the most efficient EL devices exhibiting excellent values of luminous efficiencies, brightnesses, and external quantum efficiencies.[29b,119,120] In order to tune the emission wavelength and the energetic position of the frontier orbitals, many derivatives of Alq$_3$ have been synthesized and studied as organic light-emitting materials.[9g,9h,121]

Kido *et al.* used the methyl derivative **55b** as an electron transport and host material in a highly efficient dye-doped multilayer OLED (ITO/CuPc/NPD/**55b**:**57**/**55b**/LiF/Al).[119] In order to reduce the driving voltage, copper phthalocyanine (CuPc) **58** and LiF were used as hole and electron injecting layers, respectively. Triarylamine NPD **59** was inserted to provide efficient hole transport. This multilayer device revealed green emission from coumarin **57** exhibiting a maximum luminance of more than 140 000 cd m^{-2} and an external quantum efficiency of 7.1%, a value close to the theoretical limit. Due to spin statistics only a quarter of all excitons belong to the singlet manifold from which fluorescence may occur.[122] The upper limit for the internal quantum efficiency is therefore 25%. Owing to refraction in the device this value is typically further diminished to a maximum of about 5% external quantum efficiency. Since the device fabricated by Kido *et al.* already exceeded this maximal value, the authors assumed that triplet–triplet annihilation which forms additional singlet excited molecules may be responsible for its extraordinarily high efficiency. Similar characteristics with brightnesses greater than 200 000 cd m^{-2}, luminous efficiencies above 8 lm W^{-1} and lifetimes exceeding 10 000 h have been attained at IBM for rubrene doped devices (ITO/CuPc/NPD/NPD:rubrene/Alq$_3$/Ca and ITO/CuPc/NPD/Alq$_3$:rubrene/Alq$_3$/Ca, respectively).[123]
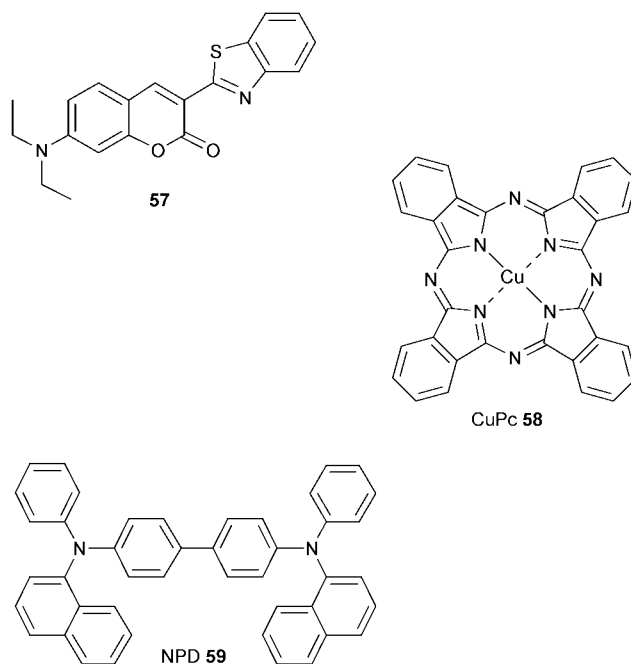
Recent efforts have been directed towards an improvement of device efficiency enabled by phosphorescent emission from triplet states.[122a,124] Baldo *et al.* demonstrated peak external and internal quantum efficiencies of 4 and 23%, respectively, from Alq$_3$-based OLEDs doped with the phosphorescent dye 2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphine platinum(II).[124a] Although efficiencies of OLEDs have been significantly improved during the 1990s, this concept might allow a further distinct improvement of device characteristics in the near term.

Designed for high-resolution full-colour displays, Forrest and Burrows *et al.* developed an independently controlled three-colour device which was constructed with a vertically stacked pixel architecture (Fig. 4).[125] The 12-layer device consisted of sequentially stacked layers of metal oxide, organic and metal thin films deposited either by thermal evaporation or by radio-frequency sputtering. This device allowed independent tuning of colour, grey scale, and light intensity. Alq$_3$ **55a**, metal chelate **60**, and porphyrin **61** were utilized as green, blue, and red emitters, respectively. Efficient charge carrier transport was provided by NPD **59**, perylene **62** (holes), and Alq$_3$ (electrons). Total external quantum efficiencies of green, blue, and red light were determined to $\eta_{ext} = 0.26$, 0.96, and 0.11%, respectively.
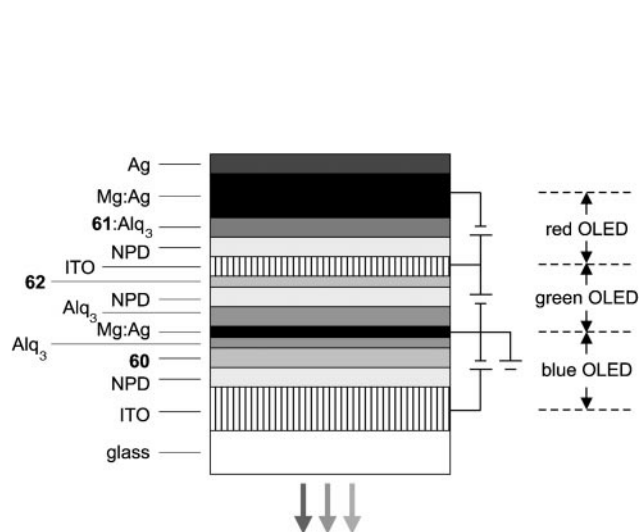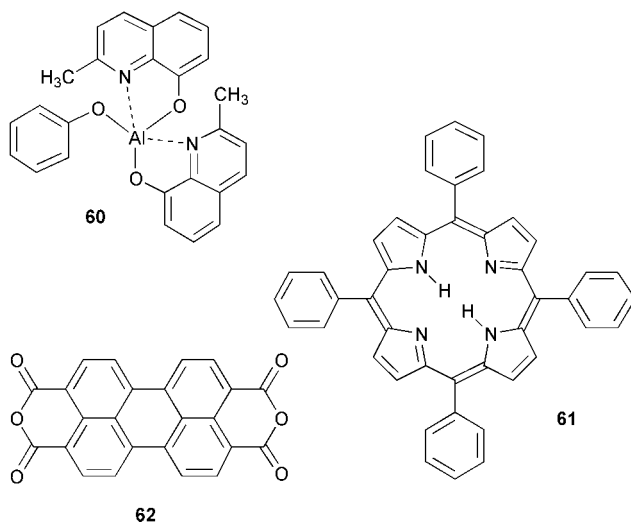

CuPc **58**

NPD **59**

Fig. 4 Schematic configuration of a red–green–blue OLED developed by Forrest and Burrows *et al.* (redrawn from ref. 125a).


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62

Recently, Schmidt *et al.* demonstrated a combinatorial approach to ascertain the ideal layer thickness of ITO/TPD/

Alq$_3$/Al two-layer devices.[126] They prepared a matrix of 49 OLEDs with linear and orthogonal gradients and confirmed the existence of an optimum Alq$_3$ layer thickness. Moreover, since the authors successfully extended their concept to investigate the influence of an additional electron transport material, this approach provides a fast and efficient method to evaluate ideal device parameters even in complex multilayer configurations.

Along with Alq$_3$ and its derivatives, other metal chelates,[127–129] lanthanide,[130–132] and boron[133] complexes have been used as electron transport emitters in OLEDs. They form stable vacuum deposited thin films and exhibit good charge transport mobilities as well as high solid-state luminescent yields.

Zinc complex 63 revealed a yellow luminance of 16 200 cd m^{-2} in a standard device configuration (ITO/TPD/63/Mg:In).[127] By far the most noteworthy electron transport emitter besides Alq$_3$ is beryllium complex 64, which achieved a brightness of 19 000 cd m^{-2} and a luminous efficiency of 3.5 lm W^{-1} in a two-layer device (ITO/TPD/64/Mg:In).[128a]

63

64

65 M = Tb, Eu, Dy, Gd

R^1 = CH$_3$, phenyl, 2-thienyl

R^2 = CH$_3$, CF$_3$, phenyl
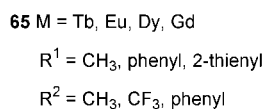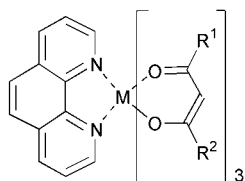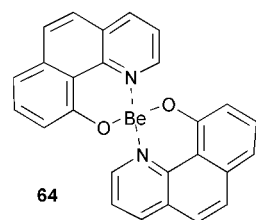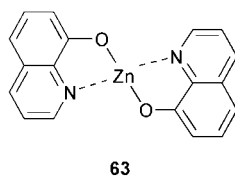
Lanthanide complexes of the general structure 65 have been used as luminescent dopants[130] and electron transport emitters[131] in EL devices with external quantum efficiencies up to 1%.[131a] Spectral narrowing and luminescence enhancement were reported for Fabry–Pérot microcavity multilayer structures based on europium and terbium complexes.[132]

Rare-earth chelates have attracted interest since they are expected to provide a possible way to circumvent the theoretical upper limit of 25% of the internal quantum efficiency. This could be accomplished via energy transfer from the triplet state of the ligand to the singlet state of the emitting lanthanide cation. So far, however, devices based on rare-earth chelates have not demonstrated very good performance characteristics, but they could prove to be the best choice on a long-term basis.

2.3.2. Dopant emitters. Highly efficient organic fluorescent dyes, in particular in the solid-state, tend to suffer from various degrees of quenching which typically causes broadening of emission bands and bathochromic shifts. This drawback can be overcome by doping or dispersing fluorescent dyes as guests in a host matrix which typically serves as a hole and/or electron transport material. Following this concept, self-quenching can be minimized and emission from the guest molecule can be obtained by energy transfer. However, there are several criteria for dopants that need to be fulfilled in order to guarantee highly efficient electroluminescene. First of all, they should be evaporable and exhibit high fluorescence quantum yields. Efficient energy transfer demands coordinated energy levels of the host and the guest. Finally, narrow emission bands of dopants are favourable to maintain chromatic purity.

Saito and Tsutsui et al.[7] reported on electroluminescence of small fluorescent dyes in a three-layer device using TPD and a perylenedicarboximide or PBD as hole and electron transport

materials, respectively. Anthracene, coronene, perylene, benzoxazole 66, pentaphenylcyclopentadiene 67, and tetraphenylbutadiene 68 among others were used as emitters. The best device based on butadiene 68 (ITO/TPD/68/PBD/Mg:Ag) revealed blue emission with a luminance of 700 cd m^{-2}.[7a]

66

67

68
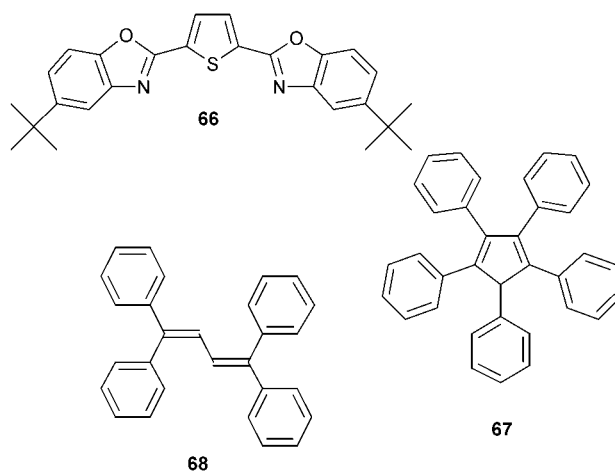
At Kodak, Tang and VanSlyke significantly improved the efficiency of their original ITO/56/Alq$_3$/Mg:Ag device to an external quantum efficiency of 2.5% by doping the Alq$_3$ layer with small amounts (typically 0.5–1%) of highly fluorescent coumarin 57 and 4-dicyanomethylene-4H-pyran (DCM) derivatives 69.[134] Higher concentrations were found to affect the device performance unfavourably, as various quenching mechanisms became prevalent. Emission colours could be tuned from blue–green to orange–red by a suitable choice of dopants as well as by changing their concentrations.

69a

69b
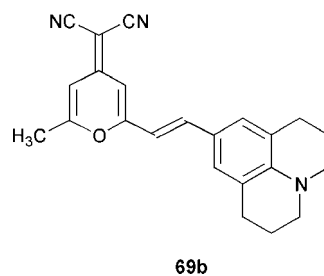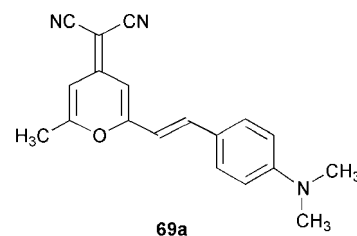
Doping Alq$_3$, TPD, or PVK with highly fluorescent dyes increases the photoluminescence quantum yields and the morphological stabilities of composite materials, resulting in devices with enhanced electroluminescence quantum efficiencies and prolonged lifetimes. Condensed aromatics,[81b,128b,135] porphyrins,[136] benzoxazoles,[137] stilbenes,[98c,138] derivatives of quinacridone,[135a,139] coumarin,[119,129a,140] and DCM,[98a,124a,140a,141] as well as squarylium cyanine dyes[142] have been used as dopants with different electron and hole transporting materials.

By far the most frequently used dopant is rubrene 70.[123,128c,135a,138a,141a,143] In comparison to the undoped system improved stability and a doubling of the luminous efficiency to 2.35 lm W^{-1} have been achieved by doping 5 wt% rubrene into the TPD layer of a simple two-layer device (ITO/

TPD:**70**/Alq$_3$/Mg:Ag).[143a,b] This effect has been interpreted as a rubrene-mediated improvement of hole and electron injection due to a better energy level alignment at both the ITO/TPD and the Alq$_3$/TPD interface.
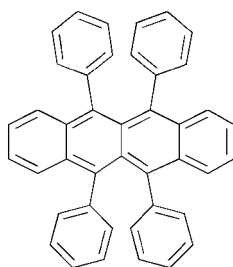
70
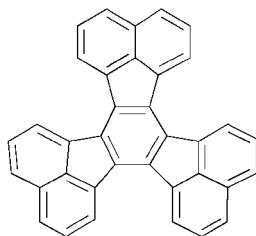
71
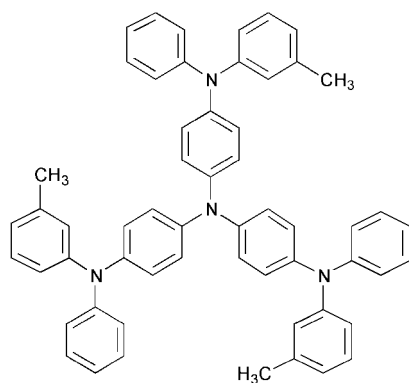
72

TDK reported on a passive matrix display based on a rubrene **70** and coumarin **57** doped OLED (ITO/PT/TPD/TPD:**70**/Alq$_3$:**57**/Mg:Ag/Al) with two emitting layers exhibiting an estimated lifetime of 50 000 h at 300 cd m^{-2}.[143c] The use of two dopants provides wide-range emission from green to red and enables the construction of a three-colour OLED display *via* an external colour filter. With a high luminous efficiency beyond 2 lm W^{-1} and an extremely long lifetime, device characteristics are already sufficient for practical applications.

Even higher efficiencies of 3.2 lm W^{-1} at 100 cd m^{-2} and a strong green emission up to 33 500 cd m^{-2} have been achieved at Sanyo for a decacyclene **71** doped multilayer device containing the triarylamine **72** as hole transport layer (ITO/**72**/TPD:**71**/**64**/Mg:In).[128b] In comparison to an undoped system the significant lifetime improvement was explained by the stable molecular structure, high fluorescent yield, and suitable HOMO level of the dopant. A colour switch to yellow accompanied by an increase of both maximum luminance to 61 000 cd m^{-2} and luminous efficiency to 9.8 lm W^{-1} was attained by replacing decacyclene **71** with rubrene.[128d] Pioneer reported on devices made with quinacridone **73a** doped Alq$_3$ as green emissive layer and recorded similar high luminous efficiencies of 10 lm W^{-1} at a luminance of 100 cd m^{-2}.[9d,139a] Even highly efficient blue OLEDs with external quantum efficiencies of 2.4% and luminous efficiencies up to 6 lm W^{-1} have been reported for molecular doped devices based on distyrylarylene **74**.[138b,c]
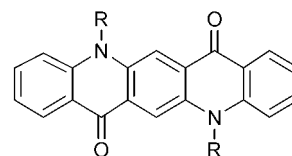
73 R = H (**a**), 3-methylbutyl (**b**)
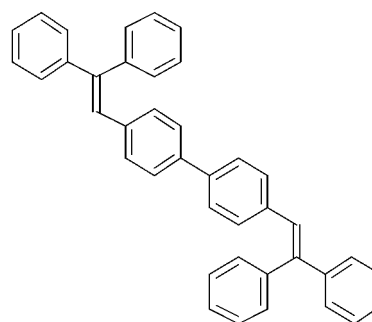
74

2.3.3. Electron transport and hole blocking materials.

Although oxadiazoles have occasionally been used as blue emitters, their use in OLEDs was typically determined by their electron transport and hole blocking qualities. Oxadiazoles fulfil major requirements for electrooptical applications. They form uniform vacuum sublimed thin films, reveal high electron affinity and mobility, and exhibit large ionization potentials for efficient hole blocking.[9i,144]

The most important low molecular weight oxadiazole compound is 2-biphenyl-4-yl-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole **75** (PBD), first utilized by Tsutsui *et al.*[145] in vapor deposited organic dye devices as early as 1989. Due to its extremely low hole affinity PBD has been widely used as an electron transporting and hole blocking layer in OLEDs. It has been introduced into electroluminescent devices either by sublimation[71b–d,137] or by spin-coating as a dispersion in several standard polymers (PMMA, PS *etc.*[26a,46a,120a,130a,135b,140b,146]) or electroluminescent polymers.[147] In particular, blend systems PBD/polymer have been reported to exhibit high performances. External quantum efficiencies larger than 1% have
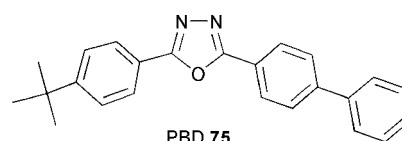
PBD **75**
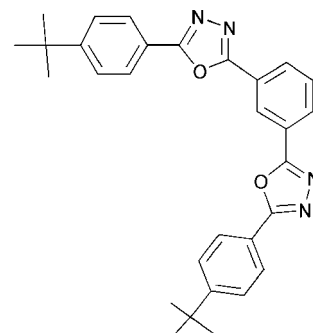
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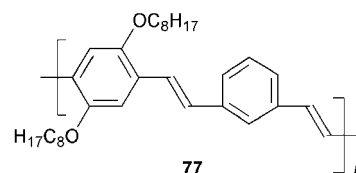
77

been reported for multilayer OLEDs based on phenyl and alkoxy substituted PPVs even with air-stable aluminium cathodes.[146a,b,147a]

Since PBD is a crystalline material, vapor deposited LEDs based on PBD films often lack stability and lifetime because PBD, especially at higher temperatures, tends to recrystallize. Blending of PBD in an inert polymer matrix was found to inhibit crystallization to a large extent. However, this embedding technique could not always warrant morphological stability. To obtain amorphous films and to overcome the problem of recrystallization and grain boundaries, many attempts have been carried out to synthesize low molecular weight compounds with higher glass transition temperatures. A dimeric oxadiazole **76** exhibits a smaller tendency to crystallize spontaneously.[29c,116,120b,131b,148] Exhibiting the same electron transport qualities, vacuum sublimation of oxadiazole **76** gave uniform glassy films with higher softening temperatures than that of PBD. A three-layer OLED (ITO/PVK/**77**/**76**/Mg:Ag) containing poly(phenylenevinylene) **77** as emitter, PVK as hole transporter and oxadiazole **76** as electron transporting material, gave an external quantum efficiency of 1% corresponding to a luminous efficiency of 6 lm W^{-1}.[29a,c]

In an attempt to synthesize amorphous materials which form stable glasses, a variety of spiro[103b] and branched[140c,149] derivatives of PBD as well as a starburst-dendrimer[150] **78–80** have been synthesized and suggested as electron transport and hole blocking materials for electrooptical applications. The improvement in device characteristics ($\eta_{ext}=1\%$) of a PPV-LED using an additional layer of branched oxadiazole **78** is comparable to the results obtained with systems in which PBD is immobilized in a polystyrene matrix.[140c,149a] A considerable increase in external quantum efficiency was also attained by use of dendrimer **80** as an electron transporting and hole blocking layer in a PPV-LED.[150]

Triazoles are another interesting class of electron deficient thermostable materials similar to oxadiazoles. The use of 1,2,4-triazoles as electron transporting and hole blocking material was first demonstrated by Kido et al.[151] The most representative derivative is 3-(1,1'-biphenyl-4-yl)-5-(4-tert-butylphenyl)-4-phenyl-4H-1,2,4-triazole **81a**, which is not only a good electron transporter but also a better hole blocker than PBD.[151] Since most organic materials are efficient hole transport materials, the employment of hole blocking triazoles as

electron transport layers in OLEDs[98c,132a,135c,152] enables exciton confinement at the organic interfaces. This material is therefore advantageous with respect to a high efficient performance of the corresponding devices.
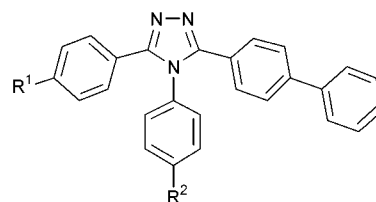
81 R^1 = tBu, R^2 = H (**a**); R^1 = N(CH$_3$)$_2$, R^2 = C$_2$H$_5$ (**b**)

Taking advantage of the hole blocking qualities of triazole **81a**, Hörhold et al. fabricated a highly efficient three-layer device (ITO/TPD/**81a**:**30**/**81a**/Ca/Al) with a luminous efficiency of 3 lm W^{-1}, a maximum brightness of about 5500 cd m^{-2} and a luminance of 500 cd m^{-2} at moderate voltages (7 V).[98c] Green emission was found to exclusively occur from a diphenylamino-terminated oligo(p-phenylenevinylene) **30** that had been doped into the triazole host layer.

Occasionally, triazoles have also been used as blue emitters. Kido et al. reported on a simple two-layer device (ITO/TPD/**81b**/Mg:Ag) based on TPD as hole transport material and a dimethylamino-functionalized triazole **81b** as electron transport emitter.[152a] The maximum brightness of 1200 cd m^{-2} achieved at 14 V is one of the highest luminances reported for pure blue light emitting organic EL devices.

In spite of the prevalence of Alq$_3$, oxadiazoles, and triazoles, several other materials have been suggested as electron transporting and hole blocking materials for EL devices.[153–158] Low molecular weight materials containing electron deficient 1,3,5-triazine units have been synthesized by Schmidt et al.[9i,153] In order to obtain amorphous materials with high glass transition temperatures ether linkages as well as spiro-cores have been utilized as structural motifs. An additional layer of the triazine derivative **82** located close to the cathode was found to increase the efficiency of various Alq$_3$ diodes.[153] The improvements of device characteristics were attributed to the hole blocking capability of the triazine compounds.

Low molecular weight phenylquinoxalines such as com-

78

80

79

O

82

(CH₃)₃C ... (CH₃)₃ ... C(CH₃)₃ ... C(CH₃)₃

F₃C C CF₃

H/CF₃ CF₃/H

CF₃/H

H/CF₃

CF₃/H

H/CF₃

84

83
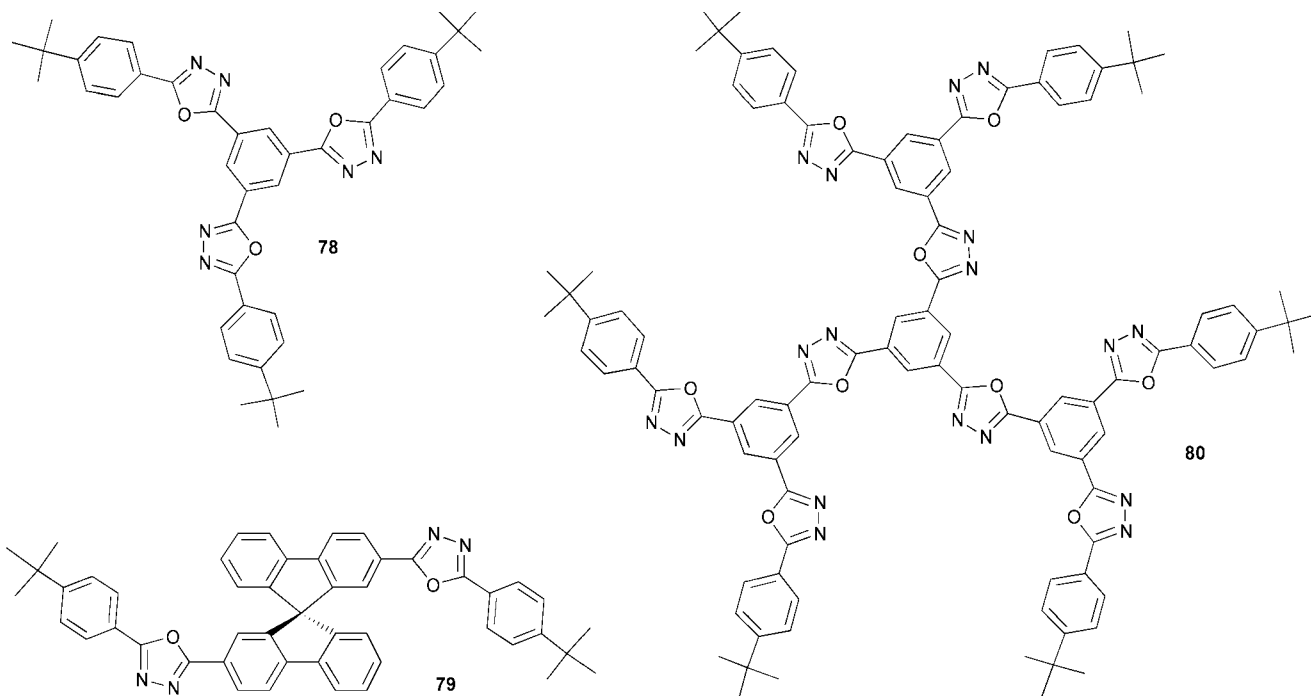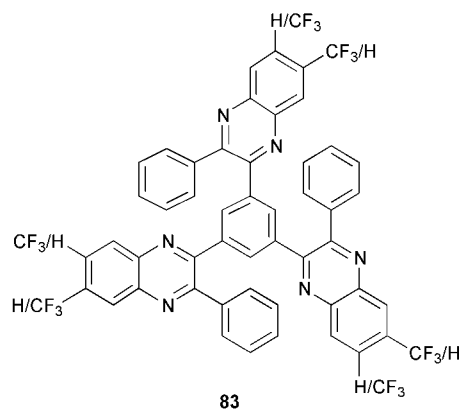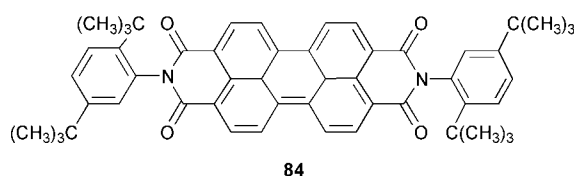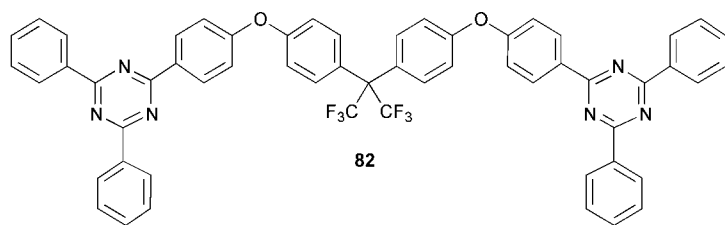
pound **83** inserted as a electron transporting and hole blocking layer in simple PPV diodes (ITO/PPV/**83**/Ag) proved to increase device characteristics significantly.[150a] The improvement of the external quantum efficiency up to 0.11% was interpreted with a shift of the recombination zone towards the PPV/quinoxaline interface. In order to ascertain morphological stability spiro-structures have been proposed.[126] Exciplex electroluminescence with an external quantum efficiency of 0.65% and a maximum brightness of 600 cd m^{-2} has recently been observed from bilayer devices composed of TPD and quinoxaline derivatives.[154] The applicability of simple low molecular weight quinoxalines and triazines as electron transporting materials has also been tested by Strukelj et al. However, the lifetime of the corresponding devices was found to be affected by recrystallization processes.[155a]

Several naphthalene-[156] and perylenedicarboximides[7,135d,157] have been used as electron transporting materials in EL devices. However, these compounds typically do not exhibit hole blocking qualities. For some applications this property was found to be advantageous. Ohmori et al. reported a two-colour OLED (ITO/**84**/TPD/**20a**/Al) that shows either blue or red emission, depending on the polarity of the electric field applied.[60b,c] In the forward direction with ITO working as the anode and Al as the cathode, only blue emission from the polyfluorene layer can be observed. In the case of a negative bias, holes are injected from aluminium to polyfluorene **20a** and electrons from ITO to perylene **84**. The central TPD layer provides hole transport and blocks electrons efficiently confining excitons to the adjacent perylene layer. As a consequence, a colour change occurs and red light originating from the perylene layer is emitted.

2.3.4. Hole transport materials. Numerous materials have been developed as hole transport layers in organic EL devices.[9f,g] Initially conceived as hole transport materials in xerography, triarylamine derivatives have gained importance due to their ability to be vacuum deposited and their high hole drift mobilities. *N,N'*-Diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) **85a** and *N,N'*-bis(1-naphthyl)-*N,N'*-diphenyl-1,1'-biphenyl-4,4'-diamine (NPD) **59** are the most prevalent derivatives, which have been widely used as hole transport layers in OLEDs.[9]

However, the propensity of simple triarylamines to crystallize on aging is thought to be one of the main reasons of degradation in organic EL devices. Vacuum deposited TPD,

R¹ ... R² ... R²

N ... N

R² ... R² ... R¹
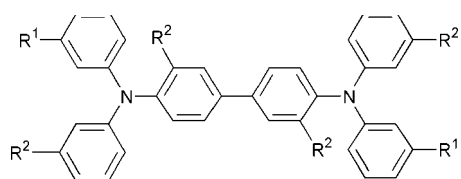
85 R¹ = CH₃, R² = H (**a**, TPD); R¹ = R² = CH₃ (**b**)

for instance, was found to crystallize at ambient temperature after a few hours.[9g] Similar to PBD, several approaches have been used to overcome this problem. One successful strategy was the insertion of TPD into polymer matrices like PMMA, PS, polysulfone, polycarbonate, *etc.*[108,122b,140b,159] However, blending was found to be occasionally affected by phase separation which limits the durability of the corresponding devices. Morphological stability can forcibly be obtained when TPD moieties are covalently attached as side groups to a polymer backbone or integrated in the backbone itself. This concept will be further elucidated in the following chapter ($\rightarrow$ 2.4.). Another approach to prevent crystallization induced degradation was the design of amorphous materials with high glass transition temperatures that enable the preparation of high quality and morphologically stable films. Besides simple molecular modifications by virtue of bridging, anellation, and substitution at the TPD scaffold,[160] different structural patterns have been examined to provide the required properties. Salbeck et al. synthesized spiro-linked structures **86** similar to TPD and found significantly enhanced glass transition temperatures indicating increased morphological stability.[103a] Other successful approaches to obtain thermostable amorphous films have been carried out by Shirota et al.[120c,143d,149b,161] and Tanaka et al.,[149c,162] who reported on novel hole transporting "starburst" shaped molecules (e.g. **72**, **89**) and linear oligomeric triphenylamines (e.g. **88**), respectively. Oligomeric triphenylamines have also been presented by Yakushchenko et al.[152b] Finally, Schmidt et al. suggested similar compounds containing a central 1,3,5-triaminobenzene core (e.g. **87**) as amorphous hole transport and electron blocking materials for EL devices.[160a,163]

The most widely used amorphous hole transport material is triarylamine **72** which has been incorporated in highly efficient multilayer devices with significant durability.[120c,128b–d,129a,149b,161a] Charge injection was found to be facilitated when a layer of amine **72** was inserted close to the anode. Due to its high hole-carrier drift moblity, significantly reduced threshold voltages became accessible.[164] Starburst triarylamine layers have therefore been suggested as hole injecting buffer layers in EL devices. Suppressing the formation of leak currents, the reliability of a simple TPD/Alq₃ device (ITO/TPD/Alq₃/Mg:Ag) was improved by incorporation of an additional layer of amine **89** close to the anode.[149b] This enabled a distinct enhancement of both lifetime and efficiency ($\eta_{lum} = 2.5$ lm W^{-1}).

2.3.5. Electron and hole transport emitters. Several attempts have been carried out to combine all essential functions of charge transport and fluorescence in a single molecule.[165] The most successful approach, based on a molecular structure with both electron transporting oxadiazole units and hole transporting triphenylamine groups, has been reported by Adachi et al.[165a] A series of different electron and hole transport emitters was applied in various single- and multilayer configurations.

86 R = H (**a**), OCH$_3$ (**b**)

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87

89
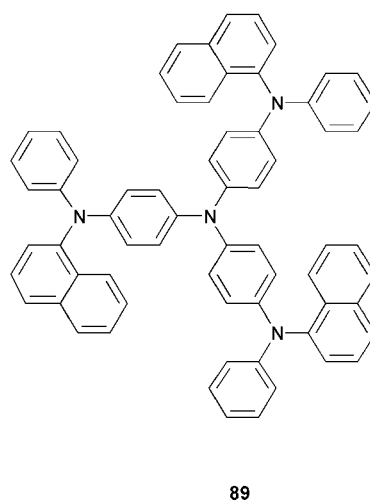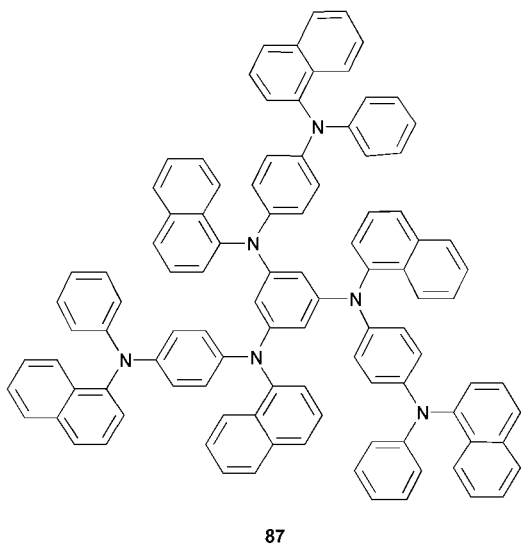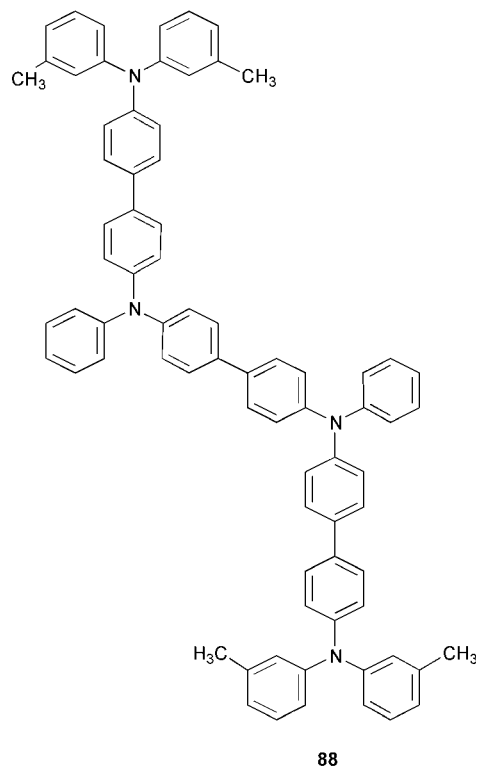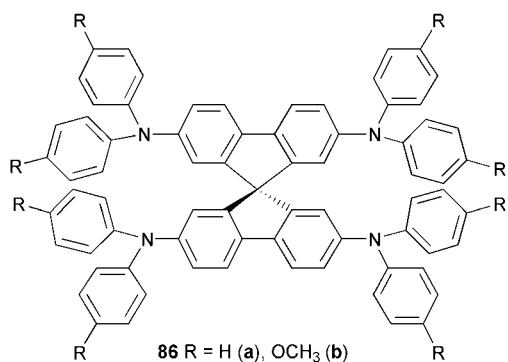
The most efficient device was based on compound **90**, with Alq$_3$ as electron injecting layer, starburst oxadiazole **91** as electron transporting material, and a hole transporting TPD derivative **85b** (ITO/**85b**/**90**/**91**/Alq$_3$/Mg:Ag). This device exhibited blue–green electroluminescence with an external quantum efficiency of 4%, a luminous efficiency of 3.75 lm W^{-1}, and a maximum luminance exceeding 19 000 cd m^{-2}. However, durabilities were found to be quite inferior. The time for the luminance to decay to half of the initial brightness was below 1 h.

2.4. Main chain polymers with isolated chromophores and side chain polymers with linked chromophores in OLEDs. Taking advantage of both the processability of polymers and the defined optical and electrical properties of low molecular weight materials, a new class of materials for EL devices has been developed. In order to overcome several drawbacks of established compounds, defined charge transporting and/or emissive chromophores have been incorporated as conjugated main chain segments into a polymeric backbone or have alternatively been attached as pendant groups to a non-

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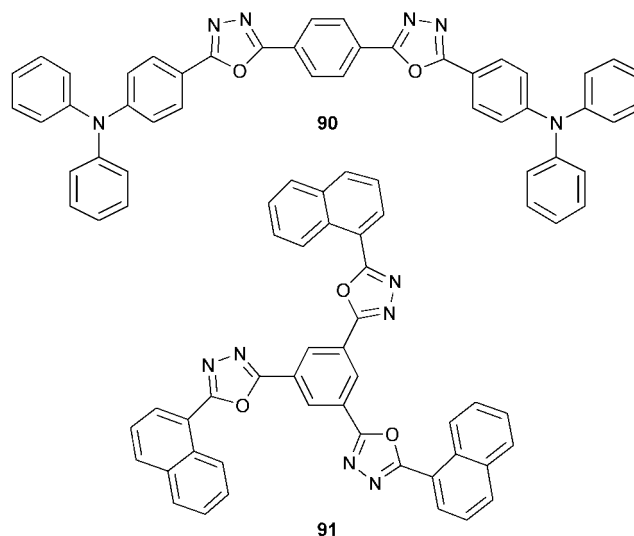
conjugated polymer. This approach ensures control of the conjugation length as well as emissive colour while diminishing the probability of non-emissive relaxation due to π-stack formation. With respect to low molecular weight oxadiazoles and triarylamines, recrystallization processes can be suppressed and the covalent attachment to a polymeric network impedes phase separation, which was found to be the main disadvantage of blend systems. Finally, the polymeric nature yields amorphous films and warrants morphological stability.

2.4.1. Main chain polymers with isolated chromophores. The introduction of non-conjugated segments into polymer backbones results in π-electron confinement in the conjugated part. By choice of appropriate chromophores and spacers, the conjugation length and hence emissive colour of a multiblock copolymer can be effectively tailored. Ether,[120a,145,148a,166–175,176a,177a] ester,[176b,178–180] amide,[176b,181] hexafluoropropylidene,[26a,148a,168–170,177,182] and silane[176c,183–188] groups have been used as spacers in polymers comprising different chromophoric units including hole transporting triarylamines and electron transporting oxadiazoles.

Blue and green electroluminescence have been reported for several block copolymers containing oligo(p-phenylenevinylene) segments.[120a,166] Taking advantage of energy transfer processes in corresponding polymer blends significant improvements of efficiencies of polymer based EL devices have been obtained.[166a,b,183a] A blend of a partially conjugated Si-containing PPV copolymer **92a** and PVK was found to exhibit bright blue electroluminescence with an internal quantum efficiency of 3.2% in a two-layer configuration with PBD (ITO/**92a**:PVK/PBD/Al).[183a] Blue superradiant emission accompanied by spectral narrowing has been observed in thin films of a related polymer **92b**.[183b]
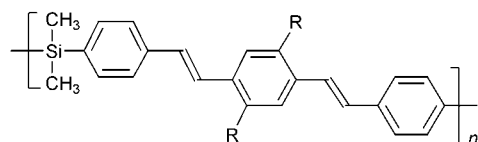
92 R = OC$_4$H$_9$ (**a**), C$_8$H$_{17}$ (**b**)
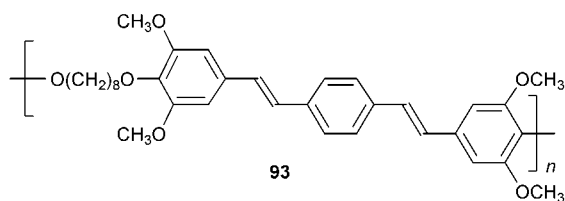
93

The improvement of quantum efficiencies of simple polymer OLEDs of PPV-related alternating block copolymer **93** in comparison to PPV by more than one order of magnitude has been attributed to morphological differences between the two polymers.[166c] Compound **93** can provide greater excitonic confinement by virtue of a phase-segregated morphology.

Blue electroluminescence has also been reported for block copolymers containing oligo(p-phenylene)s as chromophoric units in the main chain.[167,184] Polymers with unsubstituted quater- and sexiphenylene segments have been synthesized and applied in EL devices.[167] A two-layer OLED based on a blend of **94** and PVK exhibited an external quantum efficiency of 0.05% in a simple single-layer configuration (ITO/**94**:PVK/Al).

Hadziioannou et al.[185] and Yoshino et al.[186] reported on a series of poly(disilanyleneoligothienylene)s **95**. The electroluminescence of single-layer devices (ITO/**95**/Mg:In) was found to be gradually shifted from green to red with increasing length of the oligothienylene unit comprising three to seven thiophene rings.[186] The tunability of the emissive colour as a function of
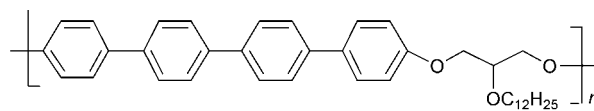
94
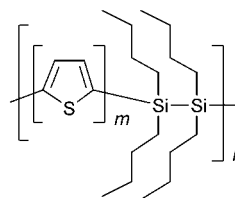
95 *m* = 3 (**a**), 4 (**b**), 5 (**c**), 6 (**d**), 7 (**e**)

chain length has been confirmed in several further publications on thiophene-based block copolymers containing silane,[187] polyester,[156a,178] or polyamide[181] spacers.

Intense blue and green emission has been reported for conjugated/non-conjugated copolymers containing terthiophene, distyrylterthiophene, distyrylnaphthalene, distyrylanthracene or distyrylcarbazole units.[176]

As previously stated, fully conjugated aromatic poly(1,3,4-oxadiazole)s are often lacking in sufficient solubility and hence processability. To increase solubility without losing thermal stability, block copolymers containing flexible ether,[148a,168,174,177a] perfluoroalkyl,[148a,168,26a,177] or diphenylsilyl[188] linkers have been developed and incorporated as electron transporting and hole blocking layers in EL devices.[85a] Applying polymer **96** with PPV as emitter and hole transport layer in a two-layer OLED (ITO/PPV/**96**/Ca), the external quantum efficiency could be increased by one order of magnitude up to 0.2%.[148a,168] Similar improvements could be achieved by insertion of polymers **97a**[177b] or **97b**[26a] as electron transport layers into OLEDs based on PPV derivatives. However, **97a** was found to increase the operating voltage considerably and **97b** exhibited lower hole blocking capability in comparison to PBD blend systems. Occasionally, oxadiazole containing copolymers have also been used as emitters in EL devices.[177a,188a] Bright blue emission with an external quantum efficiency of 0.1% has been reported for a two-layer diode based on polymers **97a** and **98** (ITO/PAni/**98**/**97a**/Ca).[177a]
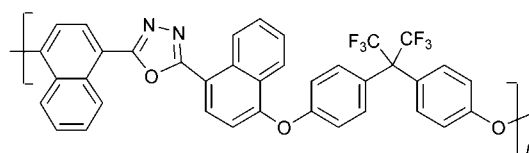
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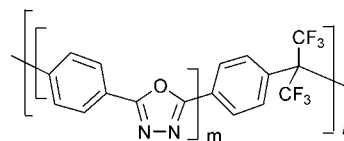
97 *m* = 1 (**a**), 2 (**b**)
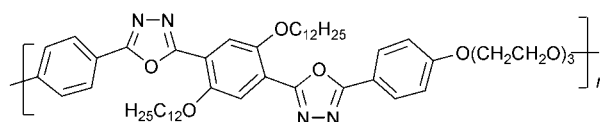
98

There are several other electron-deficient heterocycles which have been incorporated into conjugated/non-conjugated block copolymers. Besides main chain oxadiazoles, Strukelj et al.

synthesized various main chain poly(triazole ether)s to test their applicability as electron transporting and hole blocking layers in two-layer OLEDs with PPV as hole transporter and emitter.[155] Although the internal quantum efficiency was found to be somewhat diminished, the introduction of **99** turned out to be advantageous in terms of enhanced stability, high current carrying capability, and low onset voltage.

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100

101

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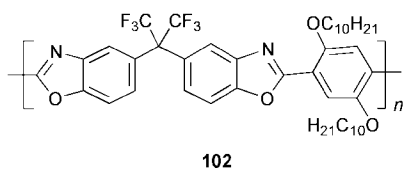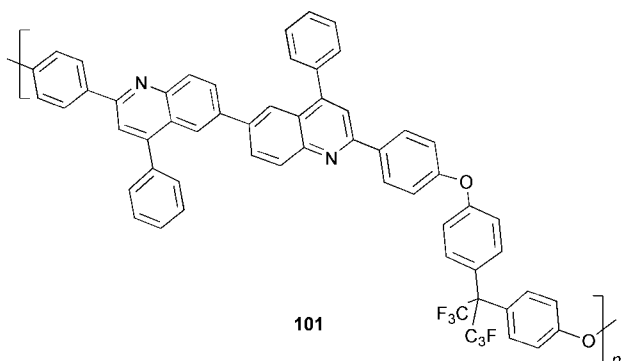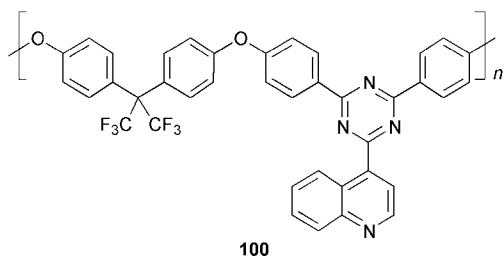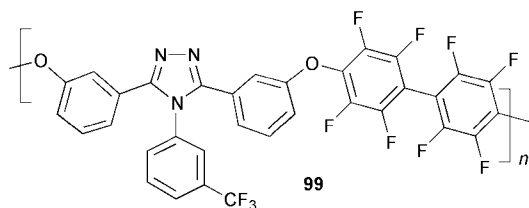
Polymeric triazines,[169] benzoxazoles,[182] quinoxalines,[9i] and quinolines[170] have also been suggested as electron transporting layers for EL devices. Triazine block copolymer **100** was found to improve the efficiency of PPV diodes due to an increase of light intensity and a decrease of current density.[169] Taking advantage of their emissive qualities, polyquinoline **101**[170] and polybenzoxazole **102**[182] have been used as blue electron transport emitters in multilayer configurations with PVK. Both compounds revealed bright blue electroluminescence with internal quantum efficiencies of 4 and 0.86%, respectively.

In order to overcome recrystallization induced degradation of TPD devices, several main chain polymers with isolated TPD units and carbonate[179] (*e.g.* **103a** and **103b**) or ether[9e,171a] spacers (*e.g.* **103c**) have been synthesized and successfully incorporated as morphologically stable hole transport layers in EL devices. OLEDs based on thick hole transport layers composed of **103b** and tris(4-bromophenyl)aminium hexachloroantimonate as a dopant showed greatly enhanced device stabilities, particularly to pinhole problems, without exhibiting the high cell resistance of conventional undoped devices with the same thicknesses of the organic layers.[179a]
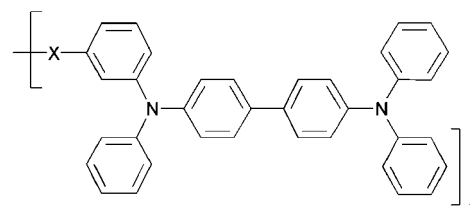
103 X = OCOO (**a**), OCO(OCH₂CH₂)₂OCOO (**b**), O (**c**)

Polycarbonate-based triphenylamines have also been used as hole transport emitters. Copolymer **104** showed bright blue electroluminescence with a luminance of 130 cd m^{-2} in a two-layer diode with PBD (ITO/**104**/PBD/Mg:Ag).[180] An analogous approach based on polyurethanes and polyethers containing chromophores with both charge transporting and emissive capability was presented by Tsutsui *et al.*[189] Recently, copolymers containing both hole transporting triarylamine and light-emitting oligo(*p*-phenylenevinylene) moieties were demonstrated.[190] Single-layer devices in the conventional ITO/organic/Al configuration revealed high luminous efficiencies (up to 3.0 lm W^{-1}) at low turn-on voltages (1.5 V).[190a]

Bipolar light-emitting polyethers containing both hole and electron injecting/transporting segments have been synthesized for single-layer applications.[172,173,175] However, polymer **105** revealed much better electron transporting properties despite the presence of hole transporting triphenylamine moieties.[172] This remained unaltered when the ether linkages were removed.[191] In order to guarantee balanced charge injection in both cases an additional copper phthalocyanine or PVK layer was necessary to improve device performance. The similar system **106**, presented by Kido *et al.*, based on TPD and oxadiazole segments, exhibited moderate luminance in a single-layer configuration (ITO/**106**/Mg:Ag).[173] However, the maximum brightness could be significantly improved upon doping with coumarin **57**.

In a similar approach, copolymers **107** containing MEH-CN-PPV and triphenylamine moieties with triad properties of efficient photoluminescence, good hole injection and high electron affinity revealed bright luminances up to 2100 cd m^{-2} and maximum external quantum efficiencies of 0.1% in a single-layer device (ITO/**107a**/Al).[192]

2.4.2. Side chain polymers with linked chromophores. The concept of attaching chromophoric groups to or as the side chain of a non-conjugated polymer was found to be of great advantage for the transformation of crystalline electroluminescent materials to amorphous derivatives. Advantageous aspects of this approach are the availability of a great variety of functionalized amorphous polymers suitable for grafting reactions and the high loading capacity without segregation of fluorophores. Since electrooptical properties can be tuned by modification of the molecular structure and by copolymerization, tailor-made materials for EL devices are accessible by means of this approach.

Following this strategy, polyethylenes,[193] polynorbornenes,[194a,195a] polymethacrylates,[148a,194b,195b,c,196a] polystyrenes,[194c–f,197a,198] polysiloxanes,[196a] polyesters,[196b] and polyethers[197b,199] with different side chain chromophores have been synthesized and applied in OLEDs. A large variety of fluorophores including oligo(*p*-phenylenevinylene)s,[194] oligo(*p*-phenylene)s,[197] oligothiophenes,[193] condensed aromatics,[171,196] as well as hole transporting triphenylamines,[195,198,199] and electron transporting/hole blocking oxadiazoles[140d,148a,155,194g,200] have been attached as pendant groups.

Blue electroluminescence with an external quantum efficiency up to 0.55% was reported for blends of polynorbornene **108** and PBD in a simple single-layer configuration (ITO/**108**:PBD/Ca).[194a] Methoxy substitution at the phenylene
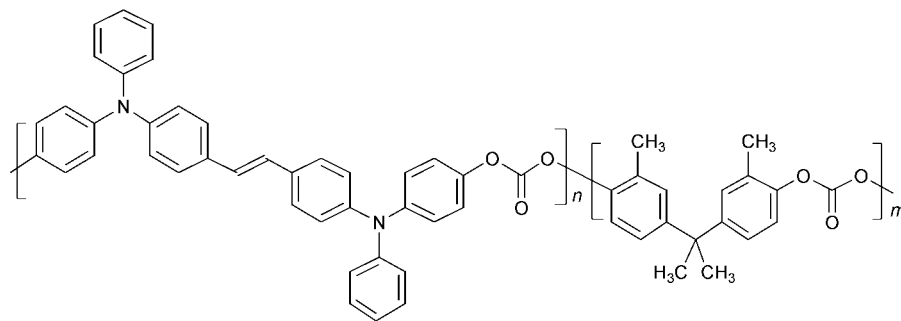
104
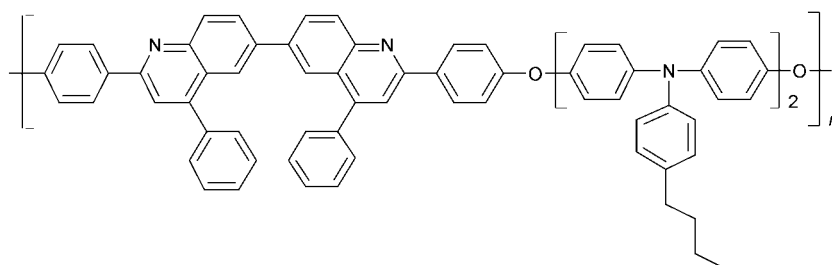
105

106
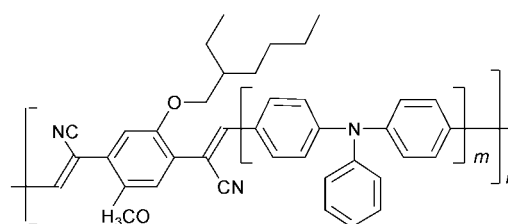
107 *m* = 1 (**a**). 2 (**b**)

groups was found to be necessary in order to provide sufficient processability.

108

109 R = CF₃ (**a**), *t*Bu (**b**)

110
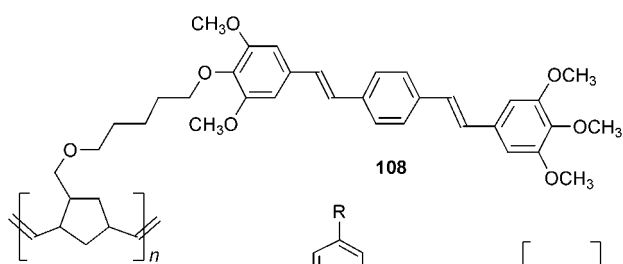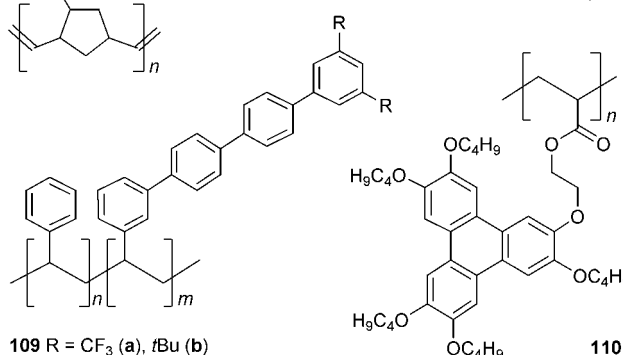
Polystyrenes **109** with quaterphenylene segments in the side chain were utilized as electron transporting material.[197a] The key step to realization of processable materials here is *meta* substitution on the phenylene ring of the polystyrene moieties which avoids crystallization of the phenylene segments.

Although the first examples of organic LEDs were demonstrated with anthracene single crystals,[5] the employment of multinuclear arenes in OLEDs is usually limited by exciplex formation and their tendency to crystallize. However, these problems can be mitigated and occasionally overcome by the side chain approach.[171,196] Polyacrylate **110** with pendant triphenylene segments was used as an efficient hole transport-

ing material in a two-layer configuration with Alq₃ (ITO/**110**/Alq₃/Al).[171a] In order to obtain triphenylene networks as insoluble hole transport layers for solution-processed multilayer devices, analogous monomers with two or even three laterally attached acrylate moieties were lately demonstrated.[171b]

Side group polymers with laterally fixed charge transport units have proven to provide a homogeneous, amorphous morphology essential to device stability. Side chain oxadiazoles have been tested as electron transporting/hole blocking layer in polymeric LEDs.[140d,148a,155,194g,200] Significant improvements of efficiencies by several orders of magnitude and reduced turn-on voltages were reported upon insertion of polyoxadiazoles **111–113**[148a,200a–c] into PPV devices. However, some of these devices were found to reveal low stability due to photoexcitation, being subject to degradation in particular under operating conditions.[155a,194g]

In an effort to simplify device fabrication and restrict all functions to a single layer, a series of copolymers containing both charge transport and emissive chromophores on pendent side chains has been synthesized.[194g,200a,d,e] In a single-layer configuration, copolymer **114** exhibited blue electroluminescence.[200a] However, the incorporation of an additional hole transporting PPV-layer was found to increase efficiency. Internal quantum efficiencies up to 0.1% were reported for single-layer devices of a poly(methacrylate) copolymer **115** bearing a blue emitting distyrylbenzene, an electron transporting oxadiazole moiety and a UV-sensitive cross-linkable unit.[200e]

Hole transport polymers yielding amorphous and morphologically stable films have been obtained by introducing carbazole, TPD or similar arylene amine segments as pendant groups.[195,198,199] By far the most important polymeric hole transport material is poly(*N*-vinylcarbazole) (PVK) **11**, which has extensively been used in multilayer structures,[29c,31b,]
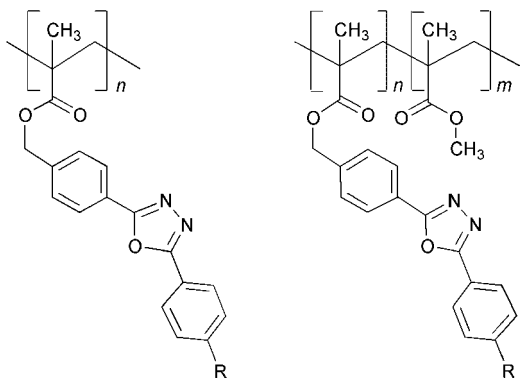
111 R = H (**a**), Ph (**b**), *t*Bu (**c**)   **112** R = CF$_3$ (**a**), NO$_2$ (**b**)
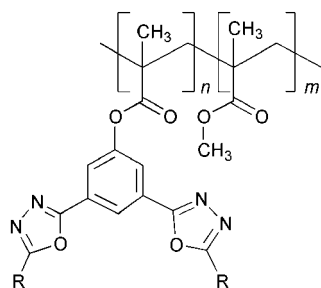
113 R = *p*-*t*Bu-phenyl (**a**), 1-naphthyl (**b**)

[68a,154,170,182] in polymeric blends,[46a,166d,183a] and as a host polymer for low molecular weight doping.[129b,130a,b,137,138c,140b–d]

Peyghambarian *et al.* synthesized TPD-modified polystyrene
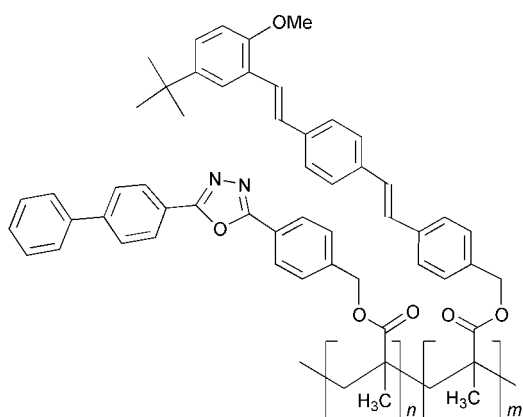
114
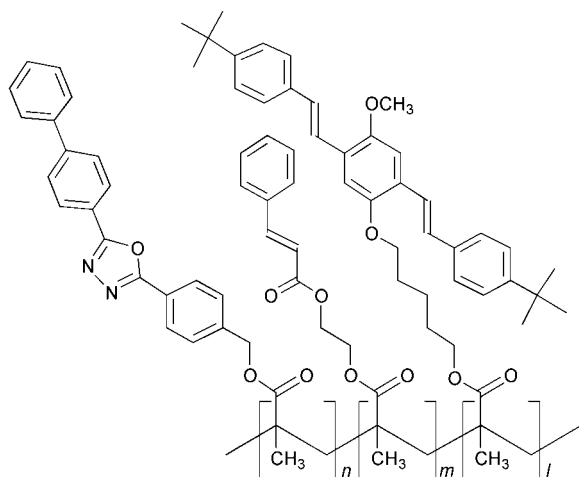
115

116a and various fluoro- or methoxy-substituted derivatives (*e.g.* **116b**).[198] The efficiency of two-layer devices with Alq$_3$ in which **116a** was used as hole transporting material was found to increase with higher electron-withdrawing character of the substituents. This effect was interpreted as being due to a better energy level alignment at the organic heterojunction and a better balance of hole and electron charges in the diode. Device stability, however, was reported to follow the opposite trend. An optimized device consisting of a fluorinated derivative **116b** as the hole transport layer, quinacridone doped Alq$_3$ as the emission layer, and a LiF/Al cathode resulted in a maximum luminous efficiency of 20 lm W^{-1} corresponding to an external quantum efficiency of 4.5%.[198a]
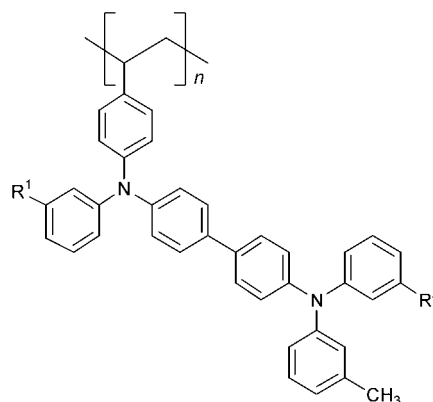
116 R^1 = CH$_3$, R^2 = H (**a**); R^1 = R^2 = F (**b**)

Recently, Nuyken and Meerholz *et al.* presented cross-linkable hole transport materials based on monomers **117**.[199] The oxetane functionalities can be photoreacted in the bulk material after spin-coating to form a durable covalent polyether network yielding insoluble films suitable for the following preparation steps. In a comparative study cross-linked hole transport layers revealed higher maximum currents and hence significantly improved device stabilities. A two-layer configuration with a blend of PBD and perylene as dopants, and poly(α-methylstyrene) as host matrix exhibited blue electroluminescence with a brightness of more than 2000 cd m^{-2} under continuous operation.

In a similar manner, robust, pinhole-free, and adherent thin films with covalently cross-linked, glassy structures of controllable thickness were formed by siloxane condensation of trichlorosilane-functionalized triarylamine **118** in the presence of moisture. Using this approach, high performance LEDs with minimal leakage currents and brightnesses up to 1700 cd m^{-2} were demonstrated.[201]

3. Towards applications and commerzialization—trends, stability, and optimization of OLEDs

As a consequence of a deeper understanding of device physics and the fundamental processes of charge injection, transport and recombination,[9j–l,11d,161b,190b,202] the efficiency and reliability of OLEDs have been improved significantly during the last decade. The performance of OLEDs in the late 1990s meets many of the targets necessary for applications in displays. Top values of efficiency reported for polymer and sublimed molecular film diodes already exceed a luminous efficiency of 10 lm W^{-1} at a luminance of 100 cd m^{-2} required as target brightness for display applications. On the basis that efficiency is inherently limited to 25% due to the singlet–triplet ratio, these values are close to the theoretical limit. Probably the most critical performance characteristic for OLEDs is that of device lifetime, both under storage and operation. For most applications, operating lifetimes in excess of 10 000 hours and minimum storage times of five years are required. Although
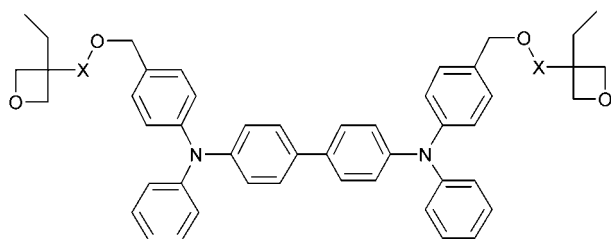
117 X = CH_2 (**a**), (CH_2)_6OCH_2 (**b**)
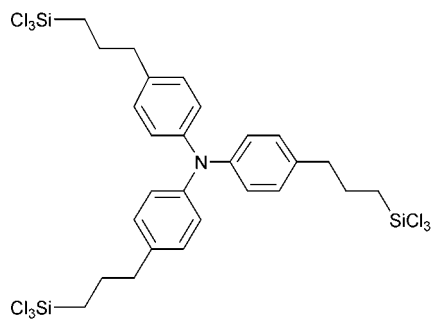
118

stabilities of OLEDs are less well documented than efficiencies, several long-term stable devices based on conjugated polymers,[29b,203,204] low molecular weight materials,[205] and molecular doped systems[123,128b,c,138b,c,139a,143a–c,144a,204,206] have been reported in the literature.

As previously stated, the best results with an estimated lifetime over 50 000 hours have been attained for sublimed molecular films doped with fluorescent dyes.[143c] Blue OLEDs based on a multilayer structure and distyrylarylene **74** as dopant emitter exhibiting a half lifetime of 20 000 hours at an initial luminance of 100 cd m^{-2} have been reported by Hosokawa et al.[138b] By virtue of an external colour conversion technique, Idemitsu Kosan fabricated a red–green–blue multicolour display based on this device and succeeded in micropatterning of devices by a photolithographic method.[138b] Similar longevities sufficient for commercial applications have also been reported for rubrene[123,206] and quinacridone[139a,c,144a,204a] doped systems.

Detailed studies concerning long-term stability of polymer OLEDs at Philips[203a] and UNIAX[203b] demonstrated that alkoxy PPV based OLEDs already meet lifetime requirements for commercial products. Operation at conventional display brightnesses beyond 10 000 hours has routinely been achieved with little loss of luminance under constant current drive. However, the most problematic ageing process was found to be the gradual rise in drive voltage required to maintain constant current. This is considered to be due to a reduced carrier mobility in the polymer and has been associated with irreversible chemical changes.

Degradation and failure mechanisms of polymer[9a,33,59a,166e,207,208] and vapor deposited[209] OLEDs have been intensely studied with respect to device optimization. These investigations revealed that the performance of OLEDs, both for lifetime and efficiency, is decisively determined by solid state morphology. Layer-wise topographic analyses of OLEDs have been carried out using scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), and scanning tunneling microscopy (STM) as spectroscopic methods.[166e,209a,210] The images that were obtained from the different surfaces revealed the characteristic morphology of the interfaces between the active organics and the electrodes. While ITO showed a granular structure, aluminium in particular exhibited a rough surface containing defect areas with large metallic protrusions into the polymer

film. Silver forms large clusters with chinks and hollows in their surface that allow water and oxygen to penetrate an EL cell. The surface roughness and maximum height variations of the different layers in a single-layer polymer based OLED can locally sum up to variations in the distance between the two electrodes approximately equal to the average polymer film thickness, thereby significantly influencing the device performance.[210a] Therefore, the organic thin film uniformity, its thickness, and its homogeneity (whether crystalline or amorphous) have a strong impact on the EL intensity and durability of OLEDs. In polymer-based diodes morphological changes leading to a higher degree of crystallinity caused by elevated temperatures during device operation are thought to be the main reason for the initial rapid decay of luminance.[207a] The film morphology of low molecular weight materials and the degradation tendency of their devices is influenced by the evaporation conditions during device manufacture (in particular the rate of deposition and the process vacuum).[210b,211] As previously stated, morphological changes provoked by the crystallization of low molecular weight materials are thought to be the main cause for device failure. Although this problem has partially been overcome with the evolution of a large variety of stable amorphous glasses, water and/or oxygen induced chemical reactions are still problematic. Alq_3 was reported to undergo a ligand exchange reaction with water which readily adsorbs at the surface of Alq_3 films.[209b,c] Furthermore, humidity seems to induce the growth of crystalline Alq_3 structures in originally amorphous films and results in cathode delamination and hence the formation of nonemissive spots.[209d] Reversible interactions of water and oxygen with conjugated polymers have been reported under certain conditions.[212] However, there is clear evidence for a chemical modification of the active organic layer under conventional device operation. Both classes of materials, polymers and low molecular weight organics, were found to be susceptible towards water and/or oxygen-activated photodegradation.[9a,33,207b–d,209e] Studies on the photodegradation of luminescent polymers clearly revealed photoinduced defect creation due to photooxidation in the presence of atmospheric oxygen.[59a,207b,208] Besides the possibility that ambient oxygen may diffuse through the cathodic contact into the active organic layer of an OLED, the ITO anode is also thought to act as an oxygen source. In any case oxidation of conjugated backbones leads to the formation of aromatic carbonyl groups which are known to quench fluorescence significantly.[9a,207e–h] Furthermore, the concomitant chain scission results in reduced carrier mobility and a hypsochromic shift of the EL spectrum. In order to attain long-term stability, devices must therefore be encapsulated against ingress of water and oxygen. Although encapsulation has already been realized for devices made on glass, this problem is still unsolved for flexible substrates. For polyfluorenes, photoinduced aggregate formation and loss of luminous intensity by exciton transfer and relaxation through excimers was also reported.[59a]

Another phenomenon of OLED degradation is related to the deterioration of diode performance through formation of "black spots" which have been identified with local electrical short-circuits.[207e,f,i,j,209a,d,f] Their occurrence was found to be accompanied by morphological changes that lead to delamination of the semiconductor film from the metal surface.[204b,207i,209a,d] SEM images of these areas showed catastrophic local failure due to thermal runaway combined with increased charge injection and mobility with temperature increasing.[207e] However, such local shorts do not lead to immediate breakdown of the whole device. These shorts can heal themselves to a certain extent because the metal cathode cannot sustain the high local current density and melts. The molten metal pulls away from the centre of the short, preventing further current flow.[207e,k] Nevertheless, each shorting event reduces the active area, and hence the luminous output, of the device. The origin

of these short-circuits has not unequivocally been identified. However, the presence of pinholes in the cathode metal and the roughness of its surface, elevated temperatures, contamination and inhomogeneity (for example, nanocrystallinity) in the organic layer itself and ingress of water and/or oxygen seem to favour this phenomenon.[9d,207e,209a] It has also been suggested that preexisting particles or imperfections on ITO may be involved in this process.[209f] Several attempts have therefore been undertaken to assure a better contact at the anodic interface but also to prevent photo-oxidative degradation of polymers induced by oxygen diffusion from ITO into the active organic medium. As previously mentioned, successful approaches were the incorporation of polyaniline (PAni)[22,23] or poly(3,4-ethylenedioxythiophene) (PEDOT)[9d,23a–d,24] layers. Thin films of these polymers smoothen the rough ITO surface, guarantee an efficient electrical contact, and enable significantly reduced operating potentials. The insertion of a copper phthalocyanine **58** buffer/injection layer close to the anode was also found to be advantageous with respect to device characteristics and in particular device durability.[119,123,138c,143b,213] This effect has been attributed to a more balanced charge distribution in the device and an improved contact between ITO and an adjacent hole transport layer.[123,143b,213a] As a consequence of the enhanced stability, voltage increase during device operation in a constant current mode could be completely suppressed.[213b] The buffer character of CuPc interlayers is particularly advantageous in Alq$_3$-based diodes, where an impeded hole injection into the HTL is reasonable with respect to a diminished hole injection into the Alq$_3$ layer that otherwise would lead to rapid degradation.[209g]

Long-term wearout of OLEDs associated with the decrease of quantum efficiency and luminance along with an increase in voltage, while the device is stressed under constant current, has been attributed to impurities in the emissive zone, introduced either during device fabrication or produced by electrochemical reactions.[207l,209f,h] Impurity-induced failure mechanisms may include exciton quenching, charge trapping or catalysis of degradative reactions. At Hewlett Packard, quinacridone-doped Alq$_3$-devices revealed increased lifetimes, by a factor of 10^4, together with a much slower voltage increase when the dopant (of 98% nominal purity) was subjected to train sublimation before being introduced into the device.[209f] However, the loss of light output was occasionally reported to be reversible.[209h] Observation of partial recovery of the luminance of coumarin-doped (ITO/PVK:**57**/Alq$_3$/Mg/Ag) devices led to the assumption that ionic impurities might build up an internal field during device operation. When a forward bias is applied, the ionic impurities are expected to diffuse towards the electrodes, cations towards the metal layer and anions towards the ITO layer. Consequently, an internal electric field is formed and the effective electric field for carrier injection is reduced. Thus, the current density and luminance decrease even under a constant bias voltage. It was suggested that an internal electric field may also arise from permanent and induced electric dipoles. When the forward bias is released the internal electric field decreases with time and the initial luminance may be attained anew by re-setting the external field. The employment of neat materials is therefore essential with regard to device stability to reduce ionic diffusion and depress the formation of internal electric fields. However, impurities formed during device operation (*e.g.* by photooxidation) still may generate an opposing internal field. This was recently affirmed for polymer OLEDs based on an alkoxy-substituted PPV derivative.[214] Nevertheless, the development of the internal field is less pronounced in vacuum than in an ambient atmosphere and can be completely suppressed under inert conditions. Although photoinduced degradation can be overcome by encapsulation intrinsic irreversible modifications in the chemical structure of the organic materials during operation can also affect device lifetime. The ultimate

degradation of polymer-based OLEDs seems to come from a bulk degradation that was attributed to the passage of electrons through the polymer film.[207a] The injection of holes to Alq$_3$ leads to formation of unstable cationic species and hence degradation products which are regarded to be efficient fluorescence quenchers.[209g] This observation also explains the dramatically increased LED stabilities (and efficiencies) reported for OLEDs containing a mixed emitting layer of hole (*e.g.* NPD) and electron (Alq$_3$) transporting molecules, placed between pure hole and electron transport layers.[209g,215] As NPD and Alq$_3$ molecules are in close contact in the mixed layer, the direct recombination of holes and Alq$_3$ anions to produce excited states of Alq$_3$ directly will be a dominant recombination process. Following this approach, the injection of holes into the Alq$_3$ layer—detrimental to device stability—can significantly be repressed. This argument might also be the explanation for the previously mentioned remarkable longevity of Alq$_3$-based OLEDs containing doped hole transport layers (HTLs). Since molecular dopants like rubrene form hole traps and therefore reduce the hole mobility in the organic layers, the transport of holes to the HTL-Alq$_3$ interface is distinctly slowed down and, hence, the unfavourable injection of holes into the Alq$_3$ layer is suppressed.[209g]

Interactions of the organics with the electrodes[216–220] have also been suggested to bear a share of long-term reduction of quantum efficiency. Using quantum-chemical calculations as a theoretical tool and photoelectron spectroscopy as experimental probe, Salaneck and Brédas *et al.* investigated the chemical structure of interfaces in EL devices.[48a,216] Alkali metals such as sodium, which would be ideal candidates for EL applications due to their extremely low work function, were reported to dope polymers instead of forming a suitable metal/polymer heterojunction.[48a,216a,b] Calcium was found to form an oxide at the metal/polymer interface giving good electron injection and hence, improved performance.[48a,216a–c,219a] As a result of two contrary directed effects, advantageous oxide formation and degradation in the presence of oxygen, simple PPV-diodes revealed best performance at a specific oxygen background pressure during device fabrication. This is in sharp contrast to results obtained for magnesium, where best performance was obtained under oxygen-free UHV conditions.[216d] Aluminium was found to form covalent bonds to vinylene carbons and to the cyano groups of PPV and CN-PPV, respectively.[216a,e,219b] In comparative studies, the impact of different metal electrodes on the performance of simple TPD/Alq$_3$[221] as well as PPV[217] diodes has been investigated. Aluminium and indium exhibited a significant decrease of electroluminescence in the bathochromic area of PPV emission, indicating a covalent interaction that leads to a shortening of the effective conjugation length. Consequently, this effect was even emphasized with decreasing layer thickness. Studies on polythiophenes revealed aluminium attack at the α-carbon atoms.[216a] Covalent bonds interrupt π-conjugation, lead to modifications in the electronic structure of polymeric semiconductors and have therefore to be taken into consideration with regard to device optimization.

Thin buffer layers of metal oxides close to the cathode have proven to reduce the driving voltage and to increase both device efficiency and durability.[110,148a,219c,222] These improvements have been attributed to the hole-blocking quality of metal oxides[148a,222a] and the removal of interface gap states induced by defects and chemical bonds between the cathode metal and the organic semiconductor, which trap carriers and non-radiatively quench singlet excitons.[110,222b] Furthermore, since the recombination zone is removed from the immediate vicinity to the cathode, a metal oxide buffer will act as a protecting layer[219c] against metal-induced fluorescence quenching.[218,219c] Similar improvements of device characteristics have been observed upon insertion of a thin LiF or MgF$_2$ layer at the

cathodic interface in a conventional multilayer structure based on Alq[3] as electron transport emitter.[223]

Interfacial chemistry leading to a partial destruction of conjugated chains has also been traced at the anode interface.[216f] In PPV-based OLEDs different oxidized carbon species have been identified in the interface region between ITO and PPV. Besides the already mentioned introduction of CuPc, PAni, or PEDOT layers several other concepts have been investigated in order to overcome degradation of semiconductors at the ITO interface and to improve long term stability of EL devices. Successful approaches were the dispersion of surfactant-like additives[224] into the active organic medium and the introduction of ultrathin self-assembled monolayers[23e,225] close to the anode. Morphological analyses of thin films of low molecular weight materials on ITO by scanning electron microscopy (SEM) showed a better wettability and hence improved morphological stabilities of interfaces in the presence of a monomolecular interlayer.[226] Accordingly, remarkably reduced threshold voltages and increased durabilities were observed for PPP-based OLEDs when the anode was chemically derivatized by attachment of terminal carboxylated oligophenylenes.[225a] Finally, a proper preparation of the anode turned out to be advantageous to efficient and durable device performance. Smooth high-quality ITO films have been obtained by pulsed laser deposition (PLD).[227] Besides ultrasonic cleaning of commercially available ITO in organic solvents, plasma treatment[24a,25,223a,228] and hydrogen peroxide processing followed by Ar or Ne-ion sputtering[23f] have been suggested as cleaning procedures to remove impurities from the ITO surface and proved to guarantee enhanced performances of polymer-based OLEDs. Distinct cleaning methods were found to affect the O/In and In/Sn ratios as well as the concentration of C-containing contaminants and hence the work function of the anode to strongly different extents (from 4.0 to 4.8 eV).[229] Occasionally, indium contamination of organic layers originating from the ITO anode has been found to contribute to a reduction in device brightness.[230] For PPV diodes prepared via the precursor route, InCl[3] crystals at the ITO/PPV interface, formed by reaction of ITO with hydrogen chloride that had been eliminated during the thermal conversion to PPV, were found to quench fluorescence significantly.[231] In order to overcome this problem, fluorine-doped tin oxide (FTO) has been suggested as a potential alternative,[231a,b] though its devices suffer from a higher leakage current.[231a] Other materials that have been used as an anode in OLEDs include semi-transparent thin films of gold[7b,231c,d,232] and titanium nitride.[233]

The disclosure of the main degradation paths of OLEDs and the solutions that have been suggested to enhance durability and to overcome failure have dramatically improved device characteristics over the last decade. The evolution of multi-colour OLEDs has been another step towards high-end applications such as large-area full-colour displays. As previously mentioned, RGB (red–green–blue) devices have been fabricated by combination of independent monochrome diodes in a vertically stacked multilayer structure.[60b,125,234] Though a stacked configuration enables higher resolution in multicolour flat panel displays, different coloured pixels have also been arranged laterally.[235,236a,b]

Another strategy that has successfully been carried out in an effort to build up multicolour OLEDs derived benefit from the voltage dependence of the emission colour in various devices.[80a,83b,157a,237,238] Multicolour structures of that type typically possess two or more emitters in multilayer configurations or blend systems which emit different colours simultaneously. Since their ratio of emitted light is voltage dependent, a colour switch occurs with varying the applied voltage. However, such OLEDs have very limited control of the brightness at a desired colour. This problem can be overcome in bipolar/alternating current light-emitting devices where the colour is controlled by the polarity of the applied field and the brightness is adjustable by the magnitude of the driving voltage.[60,80a,141b,238a,239] Though these devices typically exhibit only two different colours their extension to full-colour emission in a stacked multilayer structure has been demonstrated by Ohmori et al.[60b] Dichromatic, polarity dependant light emission has also been reported for symmetrically configured, alternating current, light-emitting (SCALE) devices (electrode/PAni/polymer blend/PAni/electrode).[80a,240] The employment of alternating current and insulating polyaniline (emeraldine base) layers in this kind of device was found to be advantageous with respect to diminished impurity/ion migration and significantly reduced threshold voltages, respectively.

As previously stated, RGB devices have also been fabricated by an external colour conversion technique based on highly efficient blue or UV-LEDs and thin films of fluorescent dyes.[58,102,138b,241] This concept leads to displays with laterally arranged different coloured pixels. If necessary, the emission light obtained can be subsequently spectrally purified by additional layers of non-absorbing interference filters.

Finally, the application of red, blue, or green absorption filters on spectrally broad, white OLEDs is another approach towards full-colour displays.[143c] However, this technique requires the development of highly efficient white OLEDs as a prerequisite. Several approaches to obtain white light emission have been reported in the literature. Owing to the fact that spectrally broad electroluminescence is typically the result of two or more emitters, best results with respect to performance and chromaticity have been obtained with devices based on polymer blends,[57a,58,194b] polymer/low molecular weight host–guest systems,[71b–d,138d] and doped low molecular weight multilayer configurations.[120d,135c,143c,213a,242] Occasionally, white emission has also been reported for a single polymeric emitter.[195a,b] As previously mentioned, white single-layer OLEDs of polymer blends of polymers **16** and **19** were found to exhibit external quantum efficiencies up to 1.2%.[57a,58] Although the fabrication of multilayer diodes involves greater expense, the hue of the emitted light can be fine-tuned more effectively by the content and kinds of dopants as well as by controlling the thickness of its layers. Following this approach, Strukelj et al. fabricated a multilayer device (ITO/TPD/**119**/ Alq[3]/Alq[3]:**69a**/Alq[3]/Li:Al) with a luminance intensity and an external quantum efficiency as high as 4000 cd m^{-2} and >0.5%, respectively.[120d] The white light of this diode is composed of a green/blue part emitted by oxazole **119** and the red fluorescence of DCM dye **69a**.

Pursuing the same concept, similar characteristics with a luminous efficiency of 0.5 lm W^{-1} at 100 cd m^{-2} and a maximum luminance of 3000 cd m^{-2} have been reported by

119

120

121
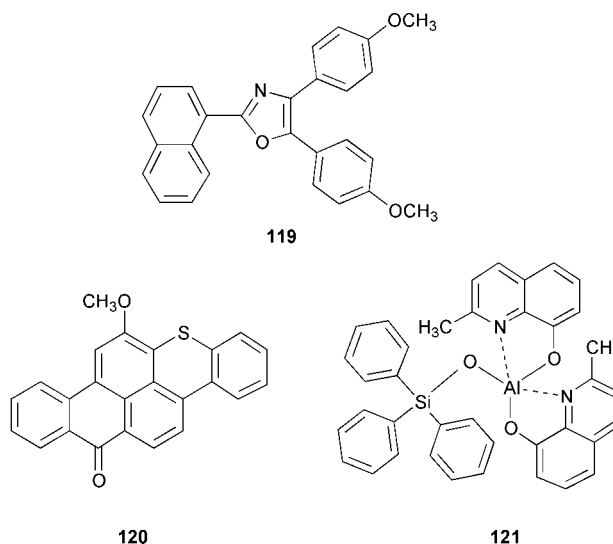
Sato et al. (ITO/CuPc **58**/NPD:**120**/**121**/Alq$_3$/Mg:Ag).[213a] An orange-emitting benzothioxanthene **120** and a blue aluminium chelate **121** were utilized to attain pure white emission. And recently, even higher brightnesses (up to 11 800 cd m^{-2}) were reported for doped low molecular weight multilayer devices based on rubrene **70** and spiro oligo(p-phenylene)s (e.g. **45a**) as yellow and blue emitters, respectively.[242a]

Inorganic/organic hybrid structures have also been suggested as a source for white electroluminescence.[243,244] UNIAX developed a white LED based on a commercially available InGaN LED that served as the blue component and short wavelength pump source for a thin layer of an orange fluorescent alkoxy-substituted PPV derivative.[243]

Especially designed as backlights for conventional liquid crystal displays (LCDs), OLEDs with highly aligned emitters have been developed. As a consequence of molecular orientation these devices emit linearly polarized light. Several methods have been used to achieve orientation of organic materials including mechanical alignment, Langmuir–Blodgett deposition, liquid-crystalline self-organization and substrate-induced alignment.[9b,c] In this context, especially poly(9,9-dialkylfluorene)s[9b,61] and liquid-crystalline low molecular weight compounds bearing long alkoxy side groups[9b,245] have attracted considerable interest. Moreover, circularly polarized emission has been observed from conjugated polymers bearing chiral side groups.[9b]

Although it will still take a couple of years of development before competitive high-end applications such as flat television screens will reach market maturity, commercialization of organic electroluminescence has already begun. The first commercial high-resolution organic light-emitting display was introduced by Pioneer in a car stereo in 1997.[9m] Based on low molecular weight materials this monochrome display exhibited a high external efficiency (more than 4%) and a device lifetime that exceeded 10 000 hours of continuous operation. Furthermore, it boasted a better contrast ratio than comparable liquid crystal displays and had a low power consumption of only 0.5 W. A similar system has been devoloped by TDK and is planned to be commercialized in late 1999.[9m] Although all commercially available organic displays up to now are based on low molecular weight materials, polymer based systems will be available in the near future. Preferring spin-coating rather than sublimation techniques, Philips has announced the setting up of a pilot line for polymer displays.[9d] Their first commercial product is expected to reach the market at the end of this year—a device for backlighting liquid crystal displays (LCDs) and for displaying logos. UNIAX has recently demonstrated a passive-matrix high-resolution display, which is planned to be used in cellular telephones.[9m]

The construction of organic light-emitting displays required the development of appropriate methods for patterning and addressing. Well-defined microscalar-patterned OLEDs have been fabricated by different photolithographic processes,[63,138b,143c,237,246] by etching,[138b,235,247] by ink-jet printing,[216,247] and by shadow mask patterning.[235,248] Thereby, the bottom ITO electrode is easily patterned using standard photolithography and wet etching, while the cathode and sublimable low molecular weight materials are typically defined by deposition through a shadow mask. Since conjugated polymers are deposited from solution, ink-jet printing can be used to achieve direct patterning and to avoid etching of organic films as an indirect alternative. The elaboration of these concepts and the introduction of different coloured pixels by lithographic as well as printing techniques led to full-colour graphic displays (for computer monitors and for video displays). Idemitsu Kosan, NEC and Pioneer demonstrated prototypes of full-colour five-inch-diagonal displays based on low molecular weight materials.[9d,138b,235] Cambridge Display Technology and Seiko-Epson recently presented a black and white television screen on electroluminescent polymers and

announced a full-colour version for late 1999.[9d] Unlike LCD panels, these screens have no restriction on viewing angles or blurring of fast action shots.

Besides displays, illumination devices and light-emitting signs are other applications for OLEDs.[9m] The possibility of producing flat large-area devices is particularly advantageous in those cases where space is limited—inside cars or aircraft, for example. Creating the potential for roll-up or conformable displays on curved surfaces, flexible devices represent another interesting feature of organic electroluminescence. Flexible OLEDs have been fabricated with both low molecular weight[249] as well as polymeric materials.[11d,19a,250] The rigid ITO-coated glass substrate of a conventional device has been replaced by polyaniline or ITO-coated polyesters, in particular poly(ethylene terephthalate) PET. Forrest et al. demonstrated a transparent flexible device with an external quantum efficiency of 0.24% based on Alq$_3$ and TPD that could be bent over a 7 mm radius of curvature without failure.[249] Even higher efficiencies of 1% have been reported by Heeger et al. for a mechanically robust device based on a MEH-PPV **2** coated polyaniline electrode.[250a,c]

Finally, conjugated polymers[9a,32f,81c,251] and several low molecular weight materials[103c,125b,252] have also been suggested as active media for thin-film solid-state lasers. This interest was initiated by the demonstration of spectral narrowing for organic semiconductors that had been incorporated into microcavity resonator structures.[9a,132a,b,139b,251a–c,253] Photopumped lasing and light amplification by stimulated emission have been reported for different geometric structures. In microcavities a semiconductor is sandwiched between highly reflecting mirrors. Planar waveguides formed from the refractive index mismatch at the organic/air and organic/substrate interfaces of a thin film are another structure. However, there is still uncertainty if conjugated materials will have the capability to sustain the high current densities required for electrically pumped laser diodes.

In conclusion, OLEDs have greatly been improved with respect to reliability, efficiency and tunability. Their performance is now comparable to, and in some cases even better than, that of commercially available light-emitting devices based on inorganic semiconductors. Moreover, they can produce polarized light and any colour in the visible region, including white—something that is still difficult to achieve with inorganic materials. Materials scientists have designed and synthesized a great variety of appropriate materials over the last couple of years. Only a few of them have been investigated thoroughly. Possibly, the best materials are still unknown or the potential of already available materials has not been recognized. Currently, two concepts compete for prevalence in the field of organic electroluminescence. Devices of both conjugated polymers and low molecular weight materials have been reported to exhibit excellent performances. Up to now, the most promising materials are polyfluorenes, polyquinoxalines and poly(p-phenylenevinylene)s on one hand and multicomponent systems comprising metal chelates (Alq$_3$), highly fluorescent dopant emitters (rubrene, coumarins, quinacridone), triarylamines (TPD, NPD) and simple oxadiazole compounds (PBD) on the other hand. The highest luminous efficiency reported for a poly(9,9-dialkylfluorene)-based OLED exceeded a value of 20 lm W^{-1} and is hence already competitive with commercially available inorganic LEDs. On the contrary, the highest external quantum efficiency beyond 7% has been attained for a coumarin-doped sublimed molecular film device that used an Alq$_3$ derivative as electron and NPD as hole transporting material. Though the "small-molecule" approach has a tentative advantage in brightness (with values surpassing 140 000 cd m^{-2}) and demonstrated lifetime (exceeding 50 000 h of continuous operation), the current development and improvements of diodes based on both types of materials are extremely fast. The polymer

approach seems to be less sensitive to higher temperatures and holds out the promise of much lower fabrication costs. Whilst the production of sublimed molecular film devices typically requires vapor deposition, conjugated polymers offer the possibility to manufacture large area displays by simple roll-to-roll coating techniques. However, the two concepts seem not to exclude one another, since combinations of both approaches have already been demonstrated. For the near term, it appears that both technologies with their specific advantages and drawbacks will coexist. Although efficiency and durability of devices based on any type of organic material still can and need to be further improved with respect to high-end applications, these obstacles will soon be overcome if the current rate of progress continues.

B. Light-emitting electrochemical cells (LECs)

Combining the electrochemical and electroluminescent properties of conjugated polymers with the ionic conductivity of polymer electrolytes, light-emitting electrochemical cells (LECs) offer a new approach to light-emitting devices.[203a,243a,254] Early LECs, first presented by Heeger *et al.* in 1995, contained a blend of a semiconducting polymer (PPV **1**, MEH-PPV **2** or PPP derivative **122**) admixed with a polyelectrolyte, typically the complex of poly(ethylene oxide) (PEO) and lithium trifluoromethanesulfonate (triflate), in a sandwich configuration between ITO and aluminium electrodes.[255]

Unlike conventional OLEDs, these devices exhibit some unique features, in particular antisymmetric current voltage characteristics (no rectification) and light emission with similarly low threshold voltages under forward as well as under reversed bias. Moreover, the onset voltage was found to be almost independent of the film thicknesses. LECs exibited significantly improved electroluminescence efficiencies compared with analogous, conventional OLEDs and proved to be fairly insensitive to the electrode work-function. The external quantum efficiencies obtained in these initial experiments were 0.4 and 1% for green-emitting PPV and MEH-PPV LECs, respectively. Even 2% photons per electron injected were attained for a blue LEC based on PPP derivative **122**.[255]

These unusual properties were explained by an electrochemical two-step process, which is schematically depicted in Fig. 5. The semiconducting polymer and the polyelectrolyte form an intimate blend with a phase-separated bicontinuous network morphology in which both ionic and electronic charge-carriers are mobile (Fig. 5a). When a sufficiently high voltage is applied across the layer, the conjugated polymer is oxidized at the anode and reduced at the cathode. Maintaining charge neutrality, the *p*-type and *n*-type doped layers, formed during this initial step, are stabilized by provision of counterions that are available in the ion-conducting phase (Fig. 5b). Under the influence of the applied field these regions extend towards the centre of the layer, forming an electrochemically induced *p-n* junction, where the *p*-type carriers (holes) and *n*-type carriers (electrons) meet and recombine under emission of photons (Fig. 5c). Higher quantum efficiencies of LECs in comparison to analogous OLEDs have been attributed to a balanced electron and hole injection as well as the favourable location of the emissive layer in the centre of the organic medium. However, though LECs exhibited sufficient storage reliability,[255a] stress lifetimes of LECs, which are currently up to about 100 hours, are rather short.[254a] It was presumed that ions do undergo charge transfer reactions at the interfaces, forming reactive species, but experimental evidence in support of this suspicion is still missing.
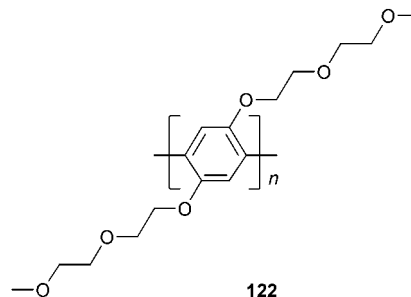
Several types of polymers and different device concepts have been explored. LEC devices have been fabricated either from blends of conjugated polymers and PEO,[18a,255,256] from single components such as luminescent polymers substituted with oligo(ethylene oxide) side chains,[21a,b,62,257] or even solid polyelectrolytes possessing both luminescent and ionic moieties.[19b,258]

Recently, blue LECs based on a blend of ladder-type poly(*p*-phenylene) **16**, PEO and lithium triflate have been fabricated, that yielded external quantum efficiencies of 0.3% and luminance values of 250 cd m^{-2} at operating voltages of 10 V. In comparison to an OLED fabricated in a similar single-layer configuration and with the same thickness, a significant decrease of the voltage from 12 V required for the onset of electroluminescence to 2.2–2.7 V has been observed.[256a]

Significantly increased external quantum efficiencies up to 2.5% and improved lifetimes have been reported for LECs based on MEH-PPV **2**, PEO and lithium triflate after addition

122
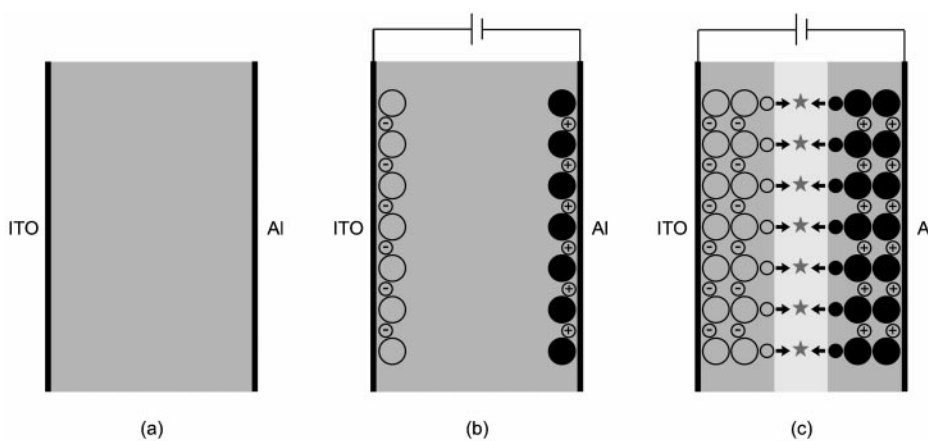
Fig. 5 Schematic diagram of the electrochemical processes in a solid-state light-emitting electrochemical cell comprising oxidized molecules (large open circles), reduced molecules (large close circles), anions (circled minus), cations (circled plus), holes (small open circles), electrons (small closed circles) and photons (stars) (redrawn from ref. 255*b*).

of octyl cyanoacetate.[256b] Similarly prepared LECs based on an alkyl-substituted PPV derivative **123** revealed an even higher external quantum efficiency of 3%.[18a] Bifunctional surfactant-like additives like octyl cyanoacetate have proven to ameliorate the device performance of LECs with respect to higher brightness, faster turn-on response and lower threshold voltages. These improvements have been interpreted with an increased surface area of the interpenetrating polymer networks. Moreover, additives seem to have a stabilizing effect with respect to the network morphology preventing large scale phase segregation caused by self-heating during continuous operation.

123

A straightforward approach to avoid phase separation is the fabrication of single component LECs in which an appropriate polymer provides charge as well as ion transport.[21a,b,62,257] As previously stated, polyfluorenes have aroused considerable interest due to their extraordinary high solid-state fluorescence quantum efficiency. Pei *et al.* synthesized a polyfluorene **20c** bearing 3,6-dioxaheptyl side groups which can dissolve lithium salts and serve as an ionic conductor.[62,257a] Solid-state LECs based on polymer **20c** and lithium triflate exhibited bright blue electroluminescence with a power efficiency of 12 lm W^{-1} and an external quantum efficiency of 4% at low operating voltages (3.1 V). When additional PEO was blended into the emissive layer, phase separation between polymer **20c** and PEO occurred and the emissive colour was shifted to white.[257a] Efficient white LECs of this type with a brightness of 400 cd m^{-2} and external quantum efficiencies up to 2.4% have been demonstrated and utilized to fabricate RGB multicolour devices by application of external RGB colour filters.

Voltage controlled two-colour LECs have been constructed with a polymer bilayer structure (PPV **1** and MEH-PPV **2**) sandwiched between two electrodes.[256c] When biased at one polarity, the voltage induced *p-n* junction was solely located inside the PPV layer resulting in green light emission. By changing the polarity of the applied electrical field the emissive zone is shifted to the MEH-PPV layer and orange electroluminescence could be observed.

The ultimate approach to impede phase separation is the employment of solid polyelectrolytes. They combine both luminescent and ionic properties in a single polymer and can be manufactured into LECs without any additives. Pursuing this concept, Neher *et al.* reported on blue LECs based on sulfonated poly(*p*-phenylene) **124** with a low onset voltage and external quantum efficiencies up to 0.8%.[258]

124

Polymer LECs have typically been studied in a dynamic-junction mode in which the *p-n* junction forms and decays with the external bias. Recent results have demonstrated that polymer LECs can be operated such that the *p-n* junction is created in a first step at an elevated temperature (where ion mobility is high), whereas at the lower operating temperature (where ion mobility is negligible) the junction is frozen.[259]

Using an ion transport polymer with a high glass transition temperature like **123**, frozen-junction LECs can be operated at or even well above room temperature. LECs operated in the frozen-junction mode retain all the advantages of LECs operating in the dynamic-junction mode, including balanced charge carrier injection, high EL efficiency, and low operating voltage. Moreover, the principal drawbacks of conventional LECs—slow response speed and overdoping—are overcome by freeze-out of ionic mobility. LECs in the frozen-junction mode reveal electrical and optical characteristics similar to polymeric OLEDs, including rectifying current–voltage dependence, light emission in forward bias only, and fast response. The external EL efficiency and luminous efficiency of a LEC based on polymer **123** operated in the frozen-junction mode were reported to attain values as high as 2.4% and 5.6 lm W^{-1}, respectively.[259a] These values rank among the best for EL devices with green emission. The freeze-out of ionic motion allows these LECs to be driven to high bias voltages well beyond the electrochemical stability window of the luminescent polymer resulting in maximum brightnesses above 20 000 cd m^{-2}.

In conclusion, the electrochemical generation of a dynamic or frozen *p-n* junction in blends of luminescent conjugated polymers with solid electrolytes lead to a new type of EL devices. Polymer LECs offer significant advantages over conventional polymer OLEDs, such as low operating voltage and high EL efficiency enabled by balanced charge injection. The performance of LECs has already been significantly improved through a combination of material blending and chemical derivatization. However, the reliability of such devices, in particular in continuous operation mode, has scarcely been quantified and seems to be—at least at present—uncompetitive with conventional polymeric OLEDs.

C. Electrogenerated chemiluminescence (ECL)

Electrogenerated chemiluminescence (ECL) is defined as the generation of light-emitting species by homogeneous electron transfer between radical ions in solution which themselves are formed by heterogeneous electron transfer in electrode reactions.[260] An ECL cell is essentially an electrolytic cell consisting of two electrodes placed in a dielectric housing and filled with a liquid composition comprising an electroluminescent species (activator), a solvent, and a supporting electrolyte. The mechanism of ECL can be described in the following simplified way:

$$M + e^- \rightarrow M^{\cdot -}$$
$$M \rightarrow M^{\cdot +} + e^-$$

$$M^{\cdot +} + M^{\cdot -} \rightarrow {}^1M^* + M \qquad M^{\cdot +} + M^{\cdot -} \rightarrow {}^3M^* + M$$
$${}^1M^* \rightarrow M + h\nu \qquad {}^3M^* + {}^3M^* \rightarrow {}^1M^* + M$$
$${}^1M \rightarrow M^* + h\nu$$

SINGLET-ROUTE   TRIPLET-ROUTE

After the initial steps, the formation of anion and cation radicals in successive electrochemical pulses, electronically excited fluorescent states can be reached by recombination of cation and anion radicals *via* a singlet or a triplet route. The excited singlet state can be formed directly by electron transfer (singlet-route) or *via* a non-emissive triplet intermediate and a subsequent triplet–triplet annihilation (triplet route). Direct emission from the triplet manifold (phosphorescence) enabled by the heavy-atom effect has only occasionally been observed for transition metal complexes.[261] In particular, condensed polyaromatics have been reported to reveal excimer emission.[262] The intermediate formation of excimers has been

attributed to alternative electron transfer and triplet–triplet annihilation reactions:

$$M^{\cdot +} + M^{\cdot -} \rightarrow {}^1(M_2)^* \rightarrow 2\,M + h\nu_E$$
$$2\,{}^3M^* \rightarrow {}^1(M_2)^* \rightarrow 2\,M + h\nu_E$$

Anion and cation radicals do not have to necessarily originate from the same neutral species. Electrogenerated chemiluminescence has been observed for both uniform as well as mixed systems.[260] In the presence of two fluorophores, emission from both species has occasionally been reported.[263] If a fluorescent species can solely be oxidized or reduced to form a stable radical ion, the addition of a suited electron donor or acceptor can provide ECL in a mixed system. Suitable donor or acceptor molecules should fulfil several criteria for their successful application. Their lowest energy excited state should be energetically inaccessible, they should be inefficient fluorescence quenchers and they typically yield radicals which are stable within the time-scale of the experiment at easily attainable potentials. The most commonly used additives are N,N,N′,N′-tetramethyl-p-phenylenediamine (TMPD), peroxodisulfate ($S_2O_8^{2-}$), and oxalate ($C_2O_4^{2-}$).[260] TMPD is a suitable donor molecule and can be reversibly oxidized to its cation radical. In contrast, peroxodisulfate and oxalate are irreversibly reduced or oxidized, respectively, to form the oxidizing $SO_4^{\cdot -}$ and reducing $CO_2^{\cdot -}$ ions. These radical ions are sufficiently stable within the ECL time frame and can be used in electron transfer reactions to produce electrochemiluminescence.

The aprotic organic solvents and electrolytes used in ECL compositions must be electrochemically inert over a wide range to comprise both oxidation as well as reduction potentials of the electroluminescent species. Suitable solvents have a considerable dipole moment, a pronounced capacity for solvating ions, as well as a permittivity high enough for the supporting electrolyte to undergo complete dissociation. However, the solvent must not prevent the association of heteropolar ion radicals, which preceeds an electron transfer event. For these reasons, the most commonly utilized solvents are DMF and acetonitrile.

A variety of materials, in particular transition metal complexes,[260a,264] conjugated polymers,[265] condensed poly-aromatics,[135e,260,264a,266] and other low molecular weight materials,[267] have been investigated as active components in ECL experiments. Electrochemiluminescent compounds need to satisfy several basic prerequisites. First of all, reversible one-electron electrochemistry is necessary which should occur in a convenient potential range for the solvent system used. The radical ions must be stable for the duration of the ECL experiment with rate constants of side reactions sufficiently small on the ECL timescale. Finally, the kinetics of the reactions involved must be sufficiently rapid to keep the rate of photon production detectable. Many substances were found to reveal inherently weak or no ECL for a number of reasons, even if they possess high photoluminescence quantum yields. Inactivity can result from a relatively short lifetime of the reduced or oxidized species in solution. The annihilation reaction may favour the formation of ground-state products, even if excited-state generation is energy sufficient, or competes with a more efficient irreversible decay. Moreover, breakdown products and impurities may interfere with the electrode processes, or act as quenchers for excited molecules.

The most prevalent ECL systems are based on ruthenium, osmium, palladium, or platinum complexes.[260a,264] Most investigations have centred on $Ru(bpy)_3^{2+}$ **125** or its derivatives due to the exceptionally high stability of the corresponding reduced and oxidized species enabling annihilation efficiencies close to 100%.[264b] Accordingly, high efficiency

ECL with values up to 24% have been reported for ruthenium chelates **126**.[264c]
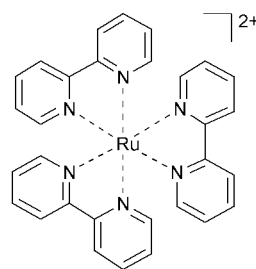
125
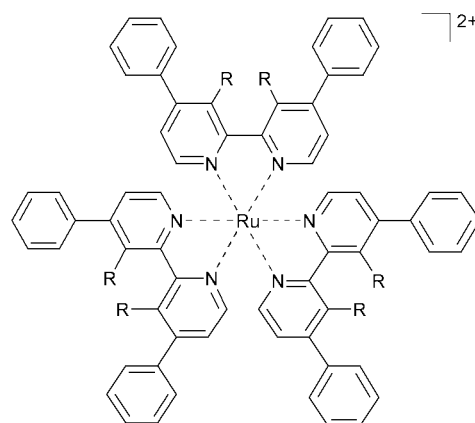
126 R = H (**a**), R—R = (**b**)

This extraordinarily good performance has prompted the employment of ruthenium complexes in solid-state devices.[129c,268] External quantum efficiencies up to 1% and luminance levels as high as 1000 cd m^{-2} at low voltages were realized with thin film devices of **125** and some of its derivatives.[268a] Devices based on sequentially absorbed layers of a $Ru(bpy)_3^{2+}$-based polyester and poly(acrylic acid) exhibited even higher external quantum efficiencies up to 3%, however, at a lower maximum light output level of 40–50 cd m^{-2}.[268b,c]

The electrochemiluminescence of ruthenium complexes has been extended to a powerful analytical technique exhibiting both high sensitivity and selectivity.[260] For example, the oxalate concentration in blood und urine has been determined by the ECL intensity of the $Ru(bpy)_3^{2+}/C_2O_4^{2-}$ system.[269] The immobilization of the ECL active complex at the electrode by incorporation into a Nafion polymer has led to the development of ECL sensors.[270] Following this approach, several biologically relevant, redox-active substances have been detected to trace levels.

The ECL experiment has also proven to provide helpful information with respect to the fundamental electrochemical processes in corresponding solid-state light-emitting devices. Besides the identification of the active fluorophores, ECL investigations deliver valuable hints with respect to the relative stability of the radical ions involved, the efficiency of an electroluminescent system, and the probability of different reaction pathways. The system Alq₃ **55a**/TPD **85a** (Alq$_3^{\cdot -}$/TPD$^{\cdot +}$) was found to produce emission spectra from the Alq₃ singlet-state which were nearly identical to those seen from OLEDs based upon these molecules.[267a] Moreover, simulating molecularly doped EL devices based on quinacridone derivative **73b**, the ECL reactions in the systems **73b**$^{\cdot -}$/**73b**$^{\cdot +}$, Alq$_3^{\cdot -}$/**73b**$^{\cdot +}$ and **73b**$^{\cdot -}$/TPD$^{\bullet +}$ have been investigated. All experiments resulted in the same emission indicating the exclusive formation of only one emissive singlet state (^{1}**73b***). These

observations are in accordance with results obtained for analogous OLEDs doped with quinacridone **73b**.

A large variety of condensed polyaromatics[135e,260,264a,266] and low molecular weight materials[267] used as dopants in OLEDs have also been subjected to ECL experiments. One of the best materials is rubrene **70** whose transformation efficiency reaches approximately 9%.[260b] Other efficient compounds are 9,10-diphenylanthracene and further phenylated acenes,[260,264a,266a–c] perylene and its derivatives,[260,266d,e] N-methyl-acridone,[260b] trans-stilbene derivatives,[260] and tetraphenyl-furan[260b] exhibiting strong ECL combined with high stabilities of their ion radicals. ECL cells containing multi-component activators have also been described.[260,266f] This approach enables the employment of materials with only one type of radical ion of sufficient stability. Examples of such compositions include binary systems like thianthrene **127** and 2,5-diphenyl-1,3,4-oxadiazole **128** which provide efficient ECL due to the stability of their radical cations and anions, respectively.[260a]

127   **128**

129
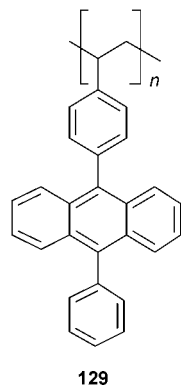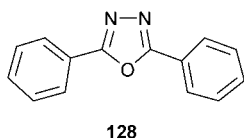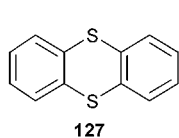
Finally, electrogenerated chemiluminescence has also been observed from thin films of redox-active luminescent polymers such as poly[9-phenyl-10-(4-vinylphenyl)anthracene] **129**,[265a] MEH-PPV **2**,[265b] poly(3-hexylthiophene) **23a**,[265c] and poly-fluorene **20c**[265d] deposited on the working electrode and immersed in a liquid electrolyte. In a modified approach, a strong oxidant or reductant was added, which can undergo an electron transfer reaction with MEH-PPV **2** to generate light.[265b] As previously stated, the redox-active additives (e.g. $SO_4^{\cdot-}$) were formed in situ by irreversible electrochemical reactions. In this case, the ECL efficiency, defined as the ratio of the integrated emission intensity and the number of electron transfer reactions in the forward electrolysis, was 0.4%.

Since charge carriers are generated by electron transfer reactions at the electrodes and electrolytes establish an appropriate voltage drop and provide counterions, the fundamental electrochemical processes of polymer-based ECL are very similar to those identified for light-emitting electrochemical cells (LECs).[254a] In the ECL experiment, however, charge transfer always occurs at the same electrode. Light is generated by stepping the potential, or by driving redox reactions simultaneously with two redox species. Furthermore, ions are not mixed directly into the layer but supplied by the liquid electrolyte. Even though the differences between the two concepts seem to be minor, polymer-based ECL appears to be uncompetitive with LECs in respect of brightness and stress lifetime.

In conclusion, a variety of redox-active substances have successfully been used as electroluminescent materials in ECL

experiments. Besides other applications, ECL has been elaborated to an analytical technique in biophysics. In particular, $Ru(bpy)_3^{2+}$ **125** has proven to detect a range of selected compounds in aqueous media with notable sensitivity. With regard to the application of electroluminescent materials in OLEDs, electrogenerated chemiluminescence provides a versatile tool to obtain valuable information concerning radical ion stability and electroluminescence intensity without involving great experimental expense.

This article reviewed the electroluminescence from organic materials and dealt in detail with organic light-emitting diodes (OLEDs), light-emitting electrochemical cells (LECs) and electrogenerated chemiluminescence (ECL) reflecting different electrooptical applications of conjugated materials. Different materials and device concepts that have been designed in recent years to enhance reliability and efficiency of electrooptical devices were presented. Particular attention was paid to current efforts to improve the processability and tunability of organic materials. In this context, electrogenerated chemiluminescence was discussed with respect to its importance as a versatile tool to simulate the fundamental electrochemical processes in OLEDs. On the eve of commercialization of organic electro-luminescence recent developments concerning the disclosure of the main degradation processes, the employment of polymeric anodes, white light emission, multicolour displays, and polarized electroluminescence were reflected.

Acknowledgements

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