

Functionalized oligoarylenes as building blocks for new organic materials

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Some of the current directions in research on new organic materials based on functionalized oligoarylenes are reviewed. Particular emphasis is placed upon the use of chemical synthesis for the incorporation of suitable functionalized oligoarylenes into more complex molecular and polymeric systems. Selected examples of applications of these materials in different fields such as light-emitting diodes, photovoltaic devices, nonlinear optics, two-photon dyes, molecular switches or ligands will be presented.

1 Introduction

During the last decade, an explosive growth of activity in the field of polymeric and molecular materials in electronic and optoelectronic devices has occurred. Hundreds of groups around the world are engaged in the research and development of new organic light emitting diodes (OLEDs), solid-state lasers, photoconductive and photovoltaic devices, nonlinear optics materials or field-effect transistors.¹ One important milestone in the development of these fields was the discovery in Cambridge of electroluminescence in conjugated polymers.² Conjugated polymers are a class of semiconductors that combine the optical and electronic properties of semiconductors with the processing advantages and mechanical properties of polymers.³ The simplicity of manufacture, arising from the fact that many organic polymers are processable either as the final materials or as a precursor, thus allowing the fabrication of large-area thin films, and the possibility of tuning the material's optical and electronic properties by using the enormous versatility of organic chemistry have allowed the realization of different applications of practical relevance⁴ from what a decade ago was no more than wishful thinking on the part of a few researchers. One characteristic of main-chain conjugated polymers is that they inevitably contain randomly distributed defects, *i.e.* non-conjugated segments, which lead to a statistical distribution of conjugated lengths. Thus, shortly after the publication of the first practical applications of conjugated polymers, the study of monodisperse conjugated oligomers^{5,6} started as a way to develop structure–property relationships to rationalize the properties of the parent polydisperse polymeric materials. With this aim, conjugated oligomers have been used as model compounds to (i) study the solid-state structure of polymers⁷ in order to be able to tune the molecular structure for given macroscopic electrooptical properties,⁸ (ii) apply a quantum-chemical approach to optical phenomena,⁹ (iii) explain the electrochemical behavior,¹⁰ and (iv) investigate the photophysical properties of conjugated polymers.¹¹ However, in recent years, the study of well-defined monodisperse oligomers has advanced into a strong field in its own right,¹² given that they also exhibit interesting optoelec-

tronic properties.⁵ All of the above explains the huge amount of work that has been devoted to the development of new synthetic strategies towards the synthesis of conjugated oligomeric materials with precise length and constitution. All this work has been recently summarized in comprehensive review articles covering from the recent progress in the synthesis and characterization of monodisperse π -conjugated oligomers,^{5,12,13} to the study of the synthetic principles for band-gap control in π -conjugated systems¹⁴ and the construction of nanoarchitectures.^{15,16} Less studied has been the chemical functionalization of conjugated oligomeric materials in order to incorporate them into more complex molecular and polymeric systems. Thus, the purpose of this feature article is to complement the above cited literature with the study of new synthetic methodologies that allow the incorporation of appropriately functionalized oligoarylenes into more complex molecular and polymeric systems with applications in materials science.

2 Oligoarylenes as building blocks for the synthesis of materials for LEDs

As stated above, the study of well-defined monodisperse oligomers as new materials that exhibit interesting optoelectronic properties has been the subject of intense study. In this section we will concentrate on the study of different macro-molecular systems, namely polymers and dendrimers that incorporate conjugated oligoarylenes in their structures rather than in the study of luminescent conjugated oligoarylenes which have already been extensively studied.⁵

Although the use of low molecular weight oligomers allows strict control of the effective conjugation length and therefore of the emitting properties, molecular organic EL devices often suffer from recrystallization of the amorphous films during operation or storage, leading to a rapid degradation of device performances.³ In order to combine control of the conjugation length with processability properties of polymeric materials,¹⁷ syntheses of different partially conjugated polymers have been carried out.

2.1 Non-conjugated polymers incorporating oligoarylenes either as side chains or as a part of the main chain

In partially conjugated polymers, chromophores can either be attached as side groups to a non-conjugated polymer backbone or integrated in the backbone itself. Materials of this type can be seen as long chains of separated small dye molecules connected by spacer units. Different luminescent fragments as well as hole-transport and electron-transport materials have been incorporated as substituents in polymeric systems,¹⁸ but because of the possibility of tuning the wavelength of emission as well as the electron affinity and ionization potential by

means of synthetic strategies, conjugated oligomers present special interest from a chemist's point of view.

There are various ways in which the great number of non-conjugated polymeric materials containing isolated fragments of conjugated oligomers can be classified, either by studying the different spacers used or by the nature of the arylene building block of the conjugated oligoarylenes. Thus, we will study how differently functionalized conjugated oligoarylenes containing the same arylene building blocks have been incorporated in polymeric systems by using a variety of linkers.

Some of the most extensively studied oligoarylenes are those containing the phenylenevinylene moiety. Strategies towards the stepwise synthesis of oligo(phenylenevinylene)s have been recently reviewed^{12,13a} and have made it possible to obtain a great number of appropriately functionalized oligo(phenylenevinylene)s to be incorporated in a variety of systems.

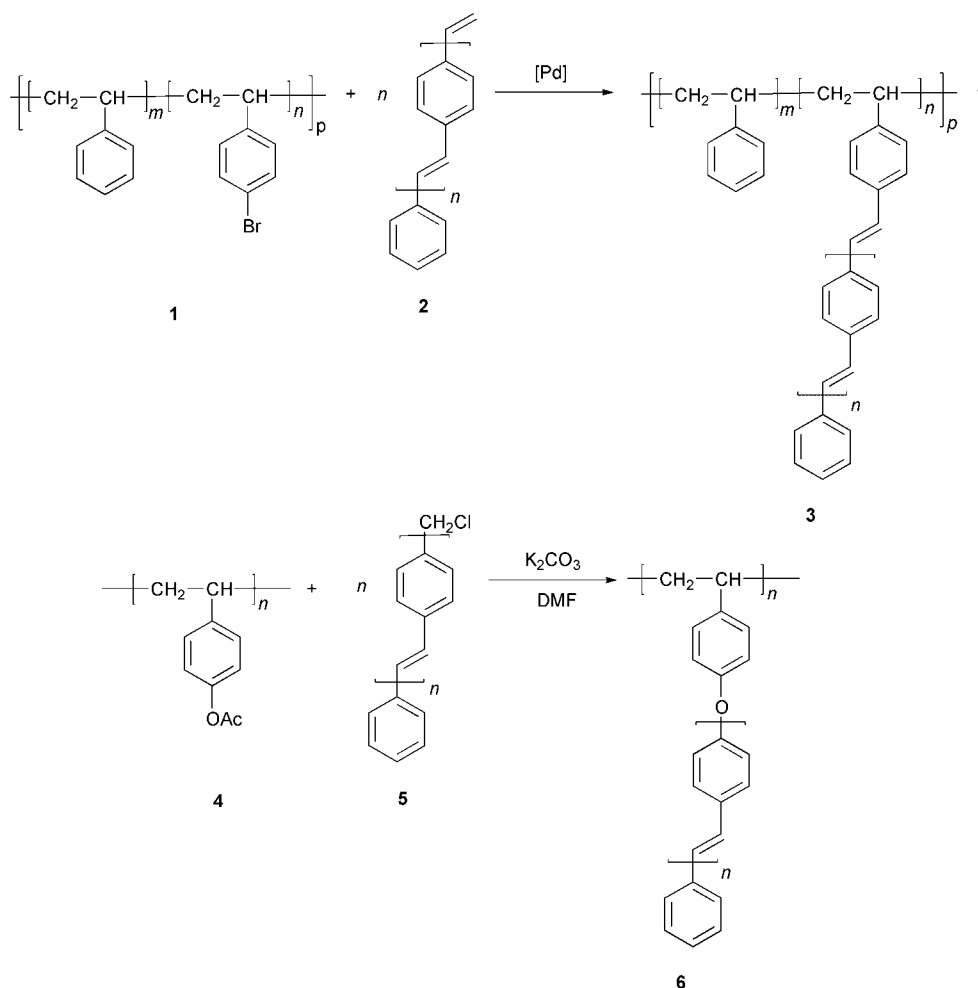
Monofunctionalized oligo(phenylenevinylene)s can be incorporated as side-chains in polymeric systems while difunctionalized analogues can be introduced as a part of the main chain in the so called 'segmented' polymers. In Scheme 1 are depicted two examples of oligo(phenylenevinylene)s incorporated in polymeric systems as side chains. The first strategy, developed by Greiner and coworkers,¹⁹ leads to polymers with well-defined conjugated structures in the side chains (**3**) by grafting vinyl-substituted oligo(arylenevinylene)s (**2**) on to partially brominated polystyrene (**1**) using the palladium catalyzed Heck²⁰ coupling reaction. Efficient organic light emitting devices (OLEDs) could be manufactured from spin coated solutions of **3** and other polymers prepared by using the same synthetic procedure.²¹ As an alternative to the above presented strategy, Karasz and coworkers prepared polystyrene deriva-

tives containing oligoarylenes (**6**) by using the Williamson condensation of a precursor poly(*p*-acetoxystyrene) **4** and chloromethyl substituted oligo(phenylenevinylene)s (**5**).²² The polymers are soluble with good film-forming ability and emit blue light when used as the active layer of an LED.

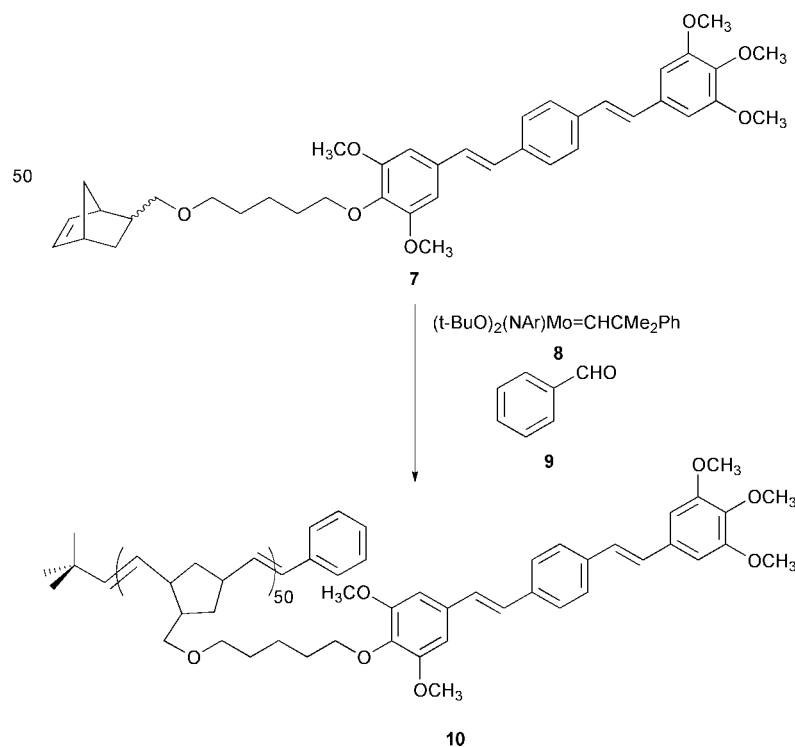
A completely different approach for the preparation of polymers containing oligo(phenylenevinylene)s is depicted in Scheme 2. A norbornene monomer (**7**) containing a phenylenevinylene oligomer unit as a side chain was polymerized by using a ring-opening metathesis polymerization method to yield a blue-light emitting electroluminescent polymer (**10**). Mo(NAr)(CHCMe₂Ph)(O-*t*-Bu)₂ (**8**) was used as the initiator. Electroluminescent quantum yields of up to 0.55% were obtained in LED devices with single layers of **10** using ITO as the anode and Ca as the cathode.²³

Other researchers have chosen the central ring of the oligo(arylenevinylene) moieties to link them to the non conjugated polymer chains. Thus, Holmes and coworkers have incorporated distyrylbenzene units to a poly(methacrylate) (**13**) by polymerizing styrene monomers endowed with oligo(phenylenevinylene)s as substituents (**12**) under standard radical conditions (Scheme 3). Together with the oligo(phenylenevinylene), other monomers (**11**) containing charge-transport moieties can be introduced. The composition of the polymer can be varied by simply changing the ratio of the starting monomers, so as to adjust the charge-transporting capability, the extent of crosslinking and even the wavelength of emission.²⁴

The number of polymers in which difunctionalized oligo(arylenevinylene)s have been introduced as a part of the main chain in non-conjugated polymeric systems is so big that an



Scheme 1



Scheme 2

exhaustive overview of these materials would not be practical. In Scheme 4 are depicted some representative examples of these conjugated–non-conjugated block copolymers in which the oligo(arylenevinylene) system has been incorporated through an ether linkage.

Derivatives **16** were obtained by Wittig condensation polymerization between the bis(triphenylphosphonium) salt **14** and dialdehyde **15**. Thus, the conjugated oligomer skeleton was formed after the polymerization reaction.²⁵ Similarly, derivatives **19** were obtained either by Wittig–Horner condensation polymerization of dialdehyde **17** and the bis(phosphonate) **18**²⁶ or by Heck-coupling between the 1,4-diiodo-substituted central core of the oligomer **21** and the moiety containing the flexible spacer **20**.²⁷ A major improvement in the use of the Heck methodology is that it directly produces polymers with fixed *trans* double bonds, which are critical to maximizing the efficiency of luminescence and wavelength output in OLEDs.

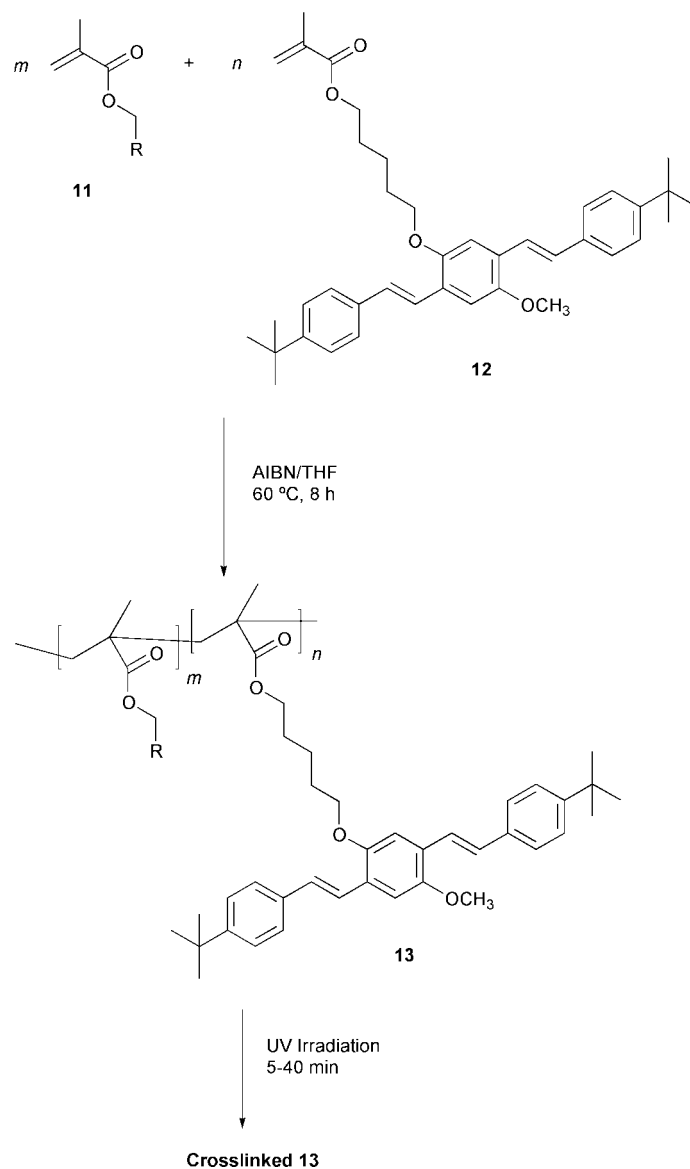
Alternatively, polymer **24** was obtained by reaction of the α,ω -dihydroxy-functionalized oligomer **22** with an oligoethylene glycol bis(mesylate) **23** (Scheme 5). In this case the functionalized conjugated oligomer skeleton was synthesized first and then reacted with an appropriately functionalized spacer to yield the block copolymer.²⁸ α,ω -Dihydroxy-functionalized oligo(arylenevinylene)s **22** have also been reacted with aliphatic diacid dichlorides (**25**) to yield the corresponding linear aryl-aliphatic polyesters **26** showing good solubility in organic solvents at ambient temperatures which enables film processing by standard techniques like spin coating.²⁹ These polyesters are amorphous and, above the glass transition temperature, anisotropic melts are formed which typically represent a smectic A phase. The optical properties related to absorption and emission spectra of these polyesters duplicate the optical properties of other conjugated-oligomer containing segmented polymers. Deposition and annealing of these light-emitting liquid crystalline polymers on rubbed polyimide results in preferential orientation of chromophores, which yields UV-dichroism and polarized photo- and electroluminescence.²⁹

Other interesting types of oligo(arylenevinylene)-containing polymeric systems are those containing Si-spacers. Wittig

reaction between the Si-containing-bis(triphenylphosphonium) salt **27** and terephthalaldehyde **28** yielded the corresponding polymeric system **29** which was subsequently isomerized to the all-*trans* configuration by refluxing for 4 h in toluene in the presence of a catalytic amount of iodine (Scheme 6).³⁰ Similarly to the above mentioned polymers, this class of silicon-containing poly(*p*-phenylenevinylene) derivatives are highly soluble in common organic solvents. Derivatives of **29** with different substituents on the central benzene ring have been synthesized and their photophysical properties have been studied. Multilayer LEDs based on these polymers have been made exhibiting efficient blue emission.³¹ Furthermore, Hadziioannou and coworkers observed lasing in the super-radiant regime in optically pumped films of the parent dioctyl-substituted **29** which paves the way for the possible development of solid-state electrically-pumped polymer lasers.³²

A particular case of these ‘segmented polymers’ are those in which tertiary amino groups are incorporated as part of the polymer chain. Some representative examples (**30–32**) of this class of compounds are depicted in Fig. 1. Jen and coworkers reported the synthesis of polymers **30** by Wittig–Horner condensation polymerization, similarly to that depicted for **17** and **18** in Scheme 4, in which the ether linkage was replaced by a tertiary amine.³³ Similarly, derivatives **31** and **32** could be also obtained by Wittig–Horner reaction of suitable substrates.³⁴ This type of compound combine the features of high luminescence efficiency and low oxidation potential for efficient hole injection in electroluminescent devices. In fact, it has been observed that these polymers also show potential as hole transporting materials by virtue of their low oxidation potentials.

It is important to point out that the amino groups do not interrupt the extended conjugation along the main chain as is the case for the above silylene, ether or ester linked analogues. As Hörhold has recently pointed out, the aromatic amino groups are able to stabilize and localize positive charges which are formed in photogeneration or hole injection processes.³⁵ Thus, incorporation of the electron-rich amino groups in the backbone does not interrupt the main-chain conjugation but has the effect of making the electron transfer reversible and



Scheme 3

stabilizes the π -cationic stages. Therefore, amino-PPVs are strong photoconductors and can be good candidates for use as electroluminescent and photorefractive materials.³⁵

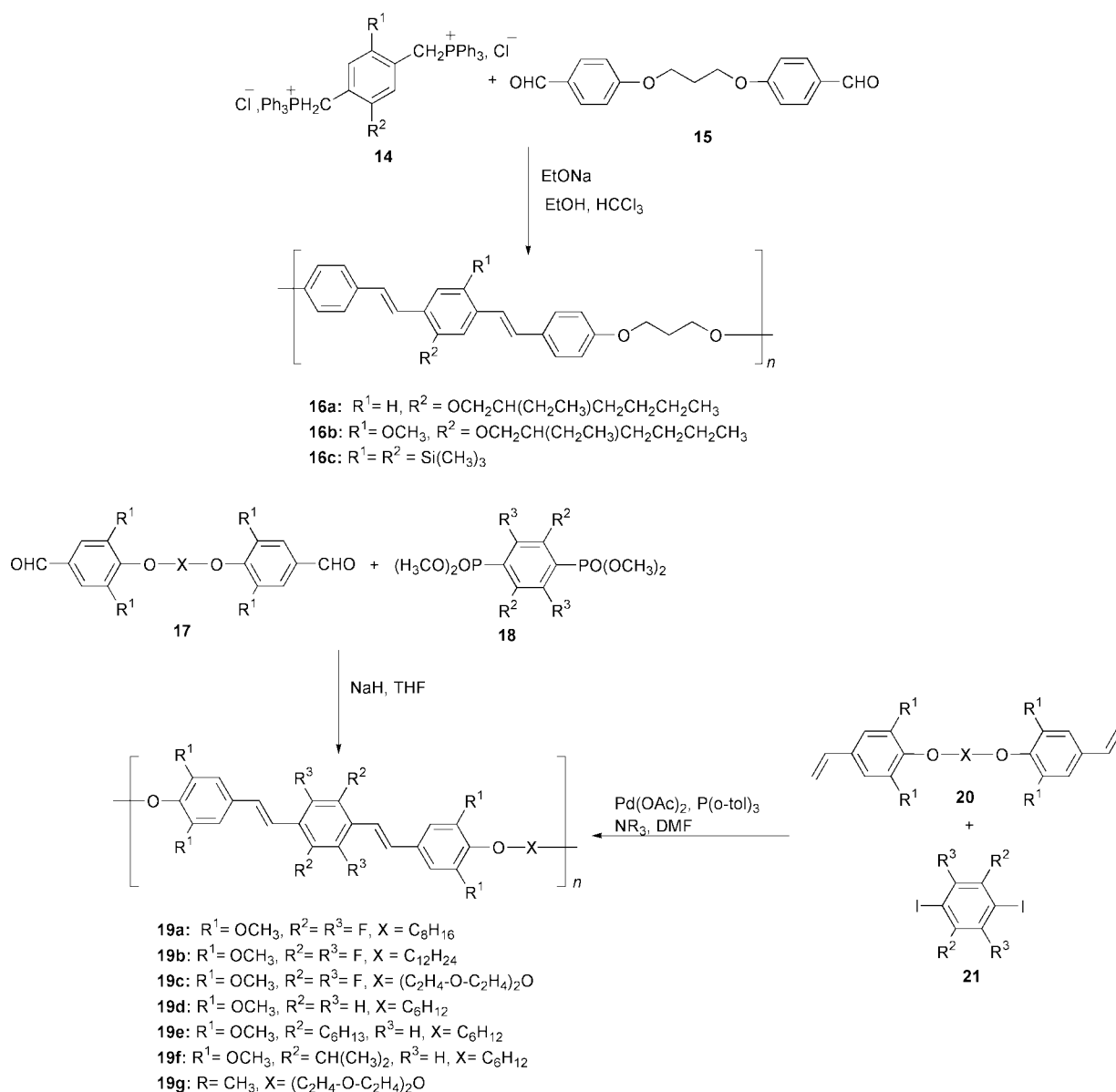
We have recently introduced the use of binaphthyl derivatives in the search for chiral polymers with isolated conjugated oligo(phenylenevinylene)s in their skeleton.³⁶ Binaphthyl derivatives are optically active materials, their chirality being derived from the restricted rotation of the two naphthalene rings. The angle between the rings ranges from 60 to 120° and therefore, conjugation between the two naphthalene units is minimal.³⁷ Thus, the conjugated system in polymers containing binaphthyl units is confined to the region between the two binaphthyl units (Fig. 2).

The synthesis of the polymers (**33**) was carried out by Knoevenagel condensation polymerization between bis(cyano-methyl)binaphthyl derivatives and naphthalenedicarbaldehyde. The emission color of these polymers can be tuned by introducing differently functionalized oligoarylenes between the binaphthyl units and they exhibit circularly polarized luminescence. The polymers exhibit a relatively good electron acceptor ability due to the presence of the cyanovinylene moieties on the conjugated system. As materials exhibiting high electron affinity are of special interest for the manufacture of LEDs given that they can be used in combination with air

stable electrodes, these materials are promising candidates for use in the fabrication of LEDs emitting circularly polarized light. Recent developments in the functionalization of binaphthyl units³⁸ allow the incorporation of this versatile building block in polymeric systems³⁹ not only through Knoevenagel condensation polymerizations but also *via* Suzuki cross coupling⁴⁰ or Wittig olefination reactions.

There are two 'classical' modifications that have been carried out in conjugated polymers^{17,18} in order to tune properties like color of the emission, electronic affinity or ionization potential: i) replacement of the vinylene linkage between the phenylene units in poly(phenylenevinylene) by an acetylenic triple bond like in poly(phenyleneethynylene) or suppression of the vinylene linkage like in poly(*p*-phenylene) and ii) substitution of the phenylene unit by other arylene building blocks like in polythiophene, poly(thienylenevinylene), poly(pyridine), poly(naphthylenevinylene) and others.

By combining this last approach with the different spacers outlined along this section, a great number of polymers have been synthesized containing different oligoarylene units either as side chains or as part of the main chain. In order to avoid repetition given that the main synthetic pathways towards the incorporation of these oligomers to polymeric systems are similar to that already reviewed for the oligo(phenylenevinylene-



Scheme 4

lene) units, we will briefly present a selection of the most significant polymeric systems containing other oligoarylenes.

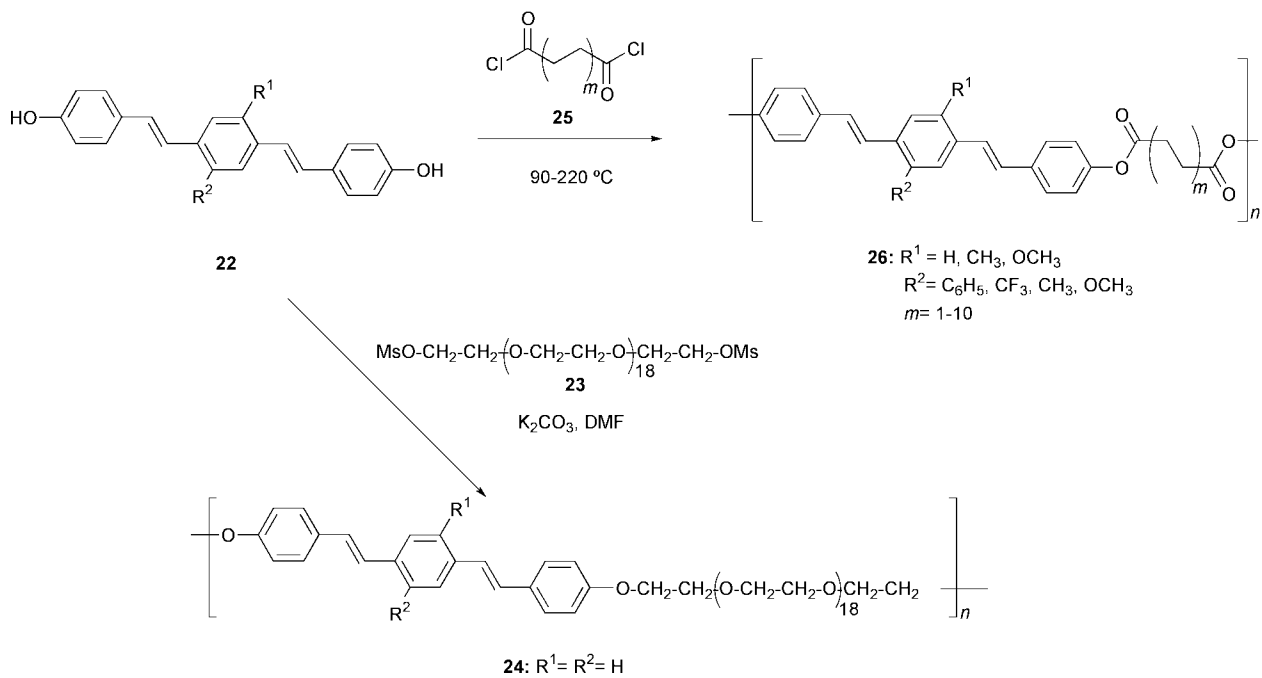
In Fig. 3 are depicted some representative examples of polymers containing isolated oligophenylenes (**34**,⁴¹ **35**,⁴² **36**,⁴³ **37**,⁴⁴ **38**⁴⁵) and oligo(phenyleneethynylene)s (**39**)⁴⁶ in their structures. Special attention is deserved by polyethers containing oligophenylenes **35** and **37** which have been found to combine solubility and film-forming properties with liquid crystalline behavior at temperatures where the polymers are thermally stable. Furthermore, these polymers exhibit blue-light emission, a photophysical property that, when combined with orientation at the molecular level, is a very promising concept for new optical materials.

On the other hand, the incorporation of different heterocycles into the structure of conjugated oligoarylenes allows not only the tuning of the emission color of these materials but also the enhancement of their donor or acceptor character.⁴⁷ Probably the most extensively studied oligoarylenes are those containing thiophene units⁴⁸ and, consequently, different polymers with isolated thiophene-based oligomers have been synthesized and studied (Fig. 4). As in the case of the parent oligophenylene derivatives, oligothiophenes have been incorporated in polymeric systems both as side chains (**40**)⁴⁹ or as part of the main chain using silicon atoms as spacers (**41**),⁵⁰

amide groups (**42**),⁵¹ ester groups⁵² (**43**)⁵³ or binaphthyl moieties (**44**).⁴⁰

By simply changing the length of the oligothiophene chromophore in a homologous series of polymers such as **44**, it is possible to tune the emission color from yellow-green (**44**, $n=1$) to dark red (**44**, $n=7$). Furthermore, some of these polymers have been used to understand electrical conduction in conjugated polymers. Miller and coworkers have studied how oligothiophenes form molecular stacks in solution.^{52c} In order to confirm the hypothesis that π -stacks are important in polymer conductivity, oligothiophene moieties were incorporated into polyesters.⁵⁴ As the polymers are not fully conjugated they cannot conduct *via* polarons or bipolarons; however they exhibit good conductivity and their EPR and optical spectra are quite similar to those of oxidized polythiophenes thus suggesting the importance of interchain electron transport.

In addition to the use of the 'electron excessive' thiophene moiety, other polymeric systems containing conjugated oligomers with different electron-deficient and electron-rich heterocyclic units have been studied. In this respect, incorporation of furan and pyrrole moieties usually led to more electron-rich systems, indicated by the easier oxidation and the reduction at more negative potentials than in the parent oligothiophene



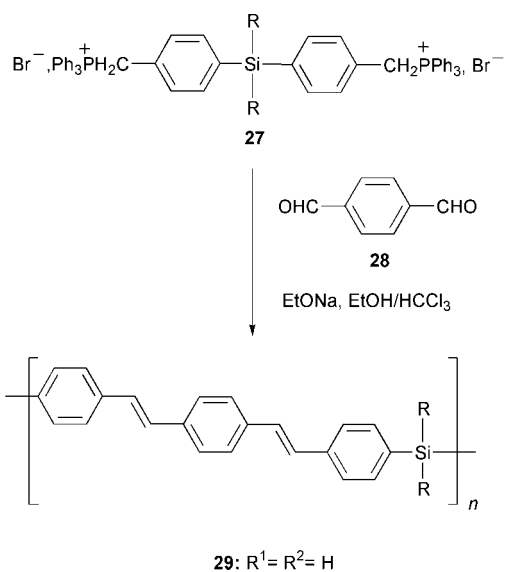
Scheme 5

derivatives. On the other hand, incorporation of electron-poor aromatic moieties such as pyridine or fluorenones resulted in electron-deficient conjugated oligomers that could be applied as electron-transporting materials in electrooptical devices.^{47,55} In Fig. 5 are depicted representative examples of alternating copolymers containing isolated oligomers with electron-rich furan (**45**)⁵⁶ and electron-deficient oxadiazole units (**46**,⁵⁷ **47**,⁵⁸ **48**)⁵⁹.

Polyimide **45** containing furan moieties is insoluble in common organic solvents, thermally stable up to 370 °C and emits intense blue luminescence with a double peak maximum at 419 and 436 nm. Systems containing the oxadiazole unit deserve special interest. Several small organic molecules containing the oxadiazole unit have been successfully used as electron-injection material to improve the balance of charge injections and to increase the photon/electron quantum efficiency in LEDs. Therefore, certain efforts have been made to prepare processable and thermally stable oxadiazole-containing polymers. Polymer **46** has been successfully used in the fabrication of OLEDs in double layer devices

together with PPV and using aluminium and ITO contacts. Polymer **47** has been efficiently used as the electron injection layer to improve the quantum efficiency of polymer LEDs based on dialkoxy derivatives of PPV.⁵⁸

Finally, Pei and Yang have demonstrated that by proper modification of the chemical structure, 1,3,4-oxadiazole-containing polymers can be used not only as electron-transport layers but also as luminescent materials. Thus, they have reported bright blue-light emission from polymer LEDs based on the oxadiazole-containing polymer **48**.⁵⁹ We will shortly mention the synthetic route used to synthesize this polymer given that it is somewhat different to that previously discussed



Scheme 6

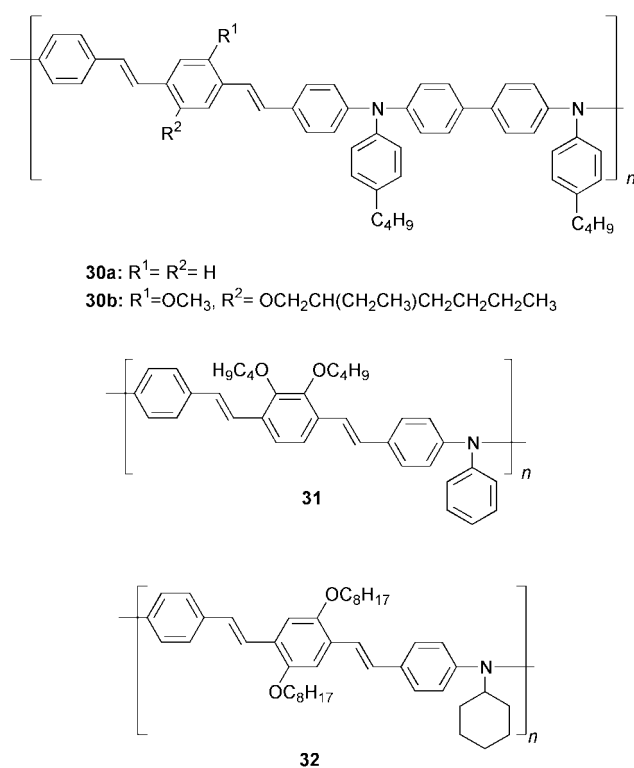


Fig. 1 'Segmented polymers' with tertiary amino groups as part of the main chain.

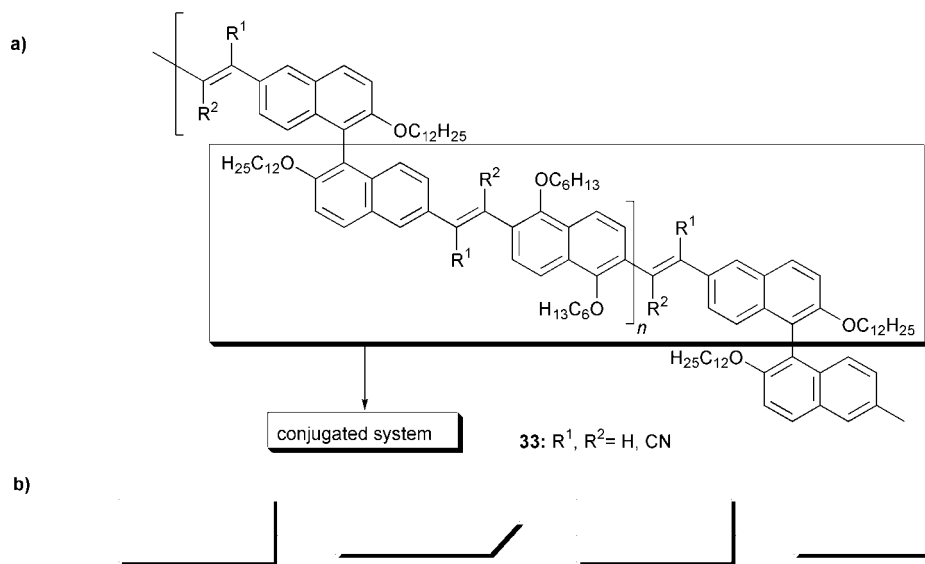


Fig. 2 Structure of binaphthyl containing conjugated–non-conjugated block copolymers showing the conjugated region.

for related oligophenylene-containing derivatives. In the synthesis of **48**, the formation of the oxadiazole system takes

place as the last step of the synthetic route once the polymeric skeleton is formed (Scheme 7). Condensation of the dihydra-

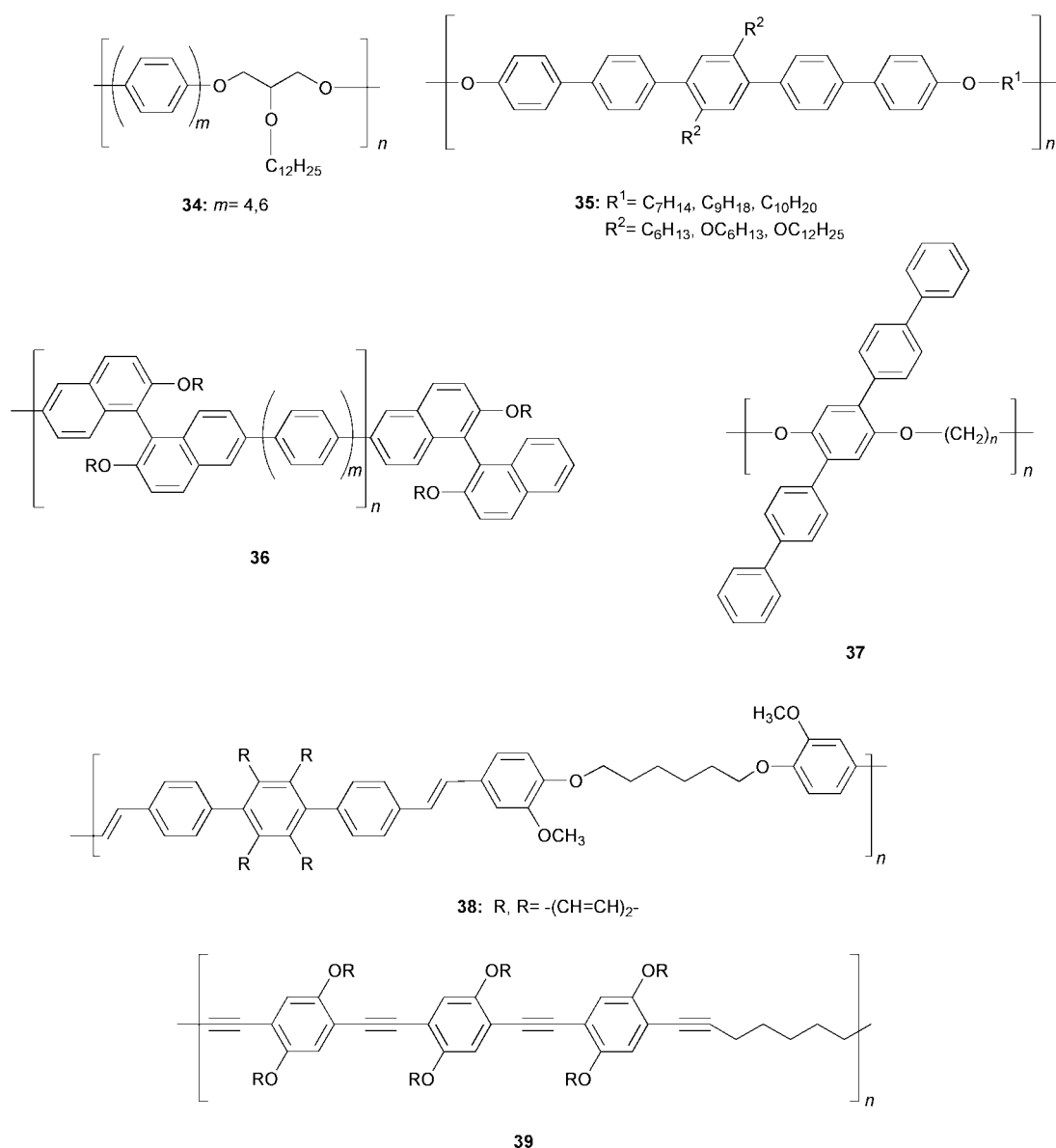


Fig. 3 Representative examples of polymers containing isolated oligophenylenes and oligo(phenyleneethynylene)s.

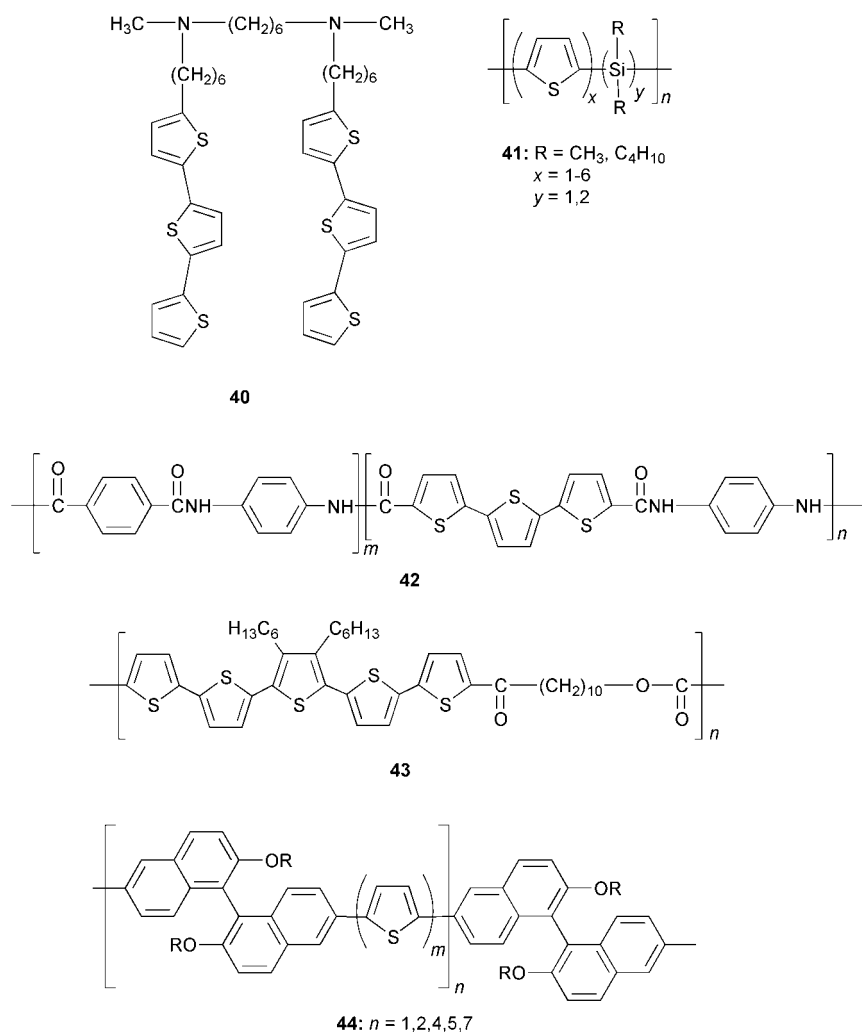


Fig. 4 Selected examples of polymers containing isolated thiophene-based oligomers.

zide **50** and 1,2-bis[2-(4-(chloroformyl)phenoxy)ethoxy]ethane **51** quantitatively yielded the poly(hydrazide) **52**. Cyclodehydration of **52** was carried out in phosphorus oxychloride to prepare the 1,3,4-oxadiazole-containing polymer **48**.^{59a}

To conclude this section dedicated to the study of non-conjugated polymers incorporating oligoarylenes as a part of their structures, we will review a different group of polymeric materials, the so-called end-functionalized polymers or rod-coil block copolymers.⁶⁰ In this type of polymer the physical properties of conjugated oligoarylenes are tuned by linking polymer chains to one or both ends of a well defined oligoarylene segment. The use of a rigid π -conjugated block linked to a non-conjugated flexible block represents a new class of self-assembling materials which offer the ability to achieve one-, two- or three-dimensional confinements of the conjugated domains. Synthetic strategies toward rod-coil block copolymers involve either polymerization using a macroinitiator ("grafting from" or "polymerization from" process) or condensation of two preformed blocks ("grafting onto" process).

A monofunctionalized block may be used as macroinitiator to start a "grafting from" process as described by Zhong and François.⁶¹ They used living polystyrene (**53**) as their macroinitiator. After treatment with cyclohexadiene (**54**) a polystyrene-*block*-poly(cyclohexa-1,3-diene) (**55**) was formed and subsequently aromatized with *p*-chloranil to yield the corresponding oligophenylene attached to a polystyrene chain (**56**, Scheme 8a). Although the aromatization was not complete and several cyclohexene rings remain between oligophenylene moieties, they discovered unique non-equilibrium honeycomb

morphologies in which monodisperse pores were arranged in hexagonal array. Very recently, Müllen and coworkers have succeeded in synthesizing structurally perfect rigid poly(fluorene-2,7-ylene) into rod-coil block copolymers by using α -(phenyl)- ω -(hydroxymethylphenyl)-poly(fluorene-2,7-ylene) (**57**) as macroinitiator (Scheme 8b).⁶² By treatment of **57** with an appropriate amount of ethylene oxide (**58**), the corresponding rod-coil block copolymer **59** together with a small amount of poly(ethylene oxide) homopolymer was obtained. Subsequent purification was carried out by repeated washing with methanol. The absorption and fluorescence measurements of **59** reveal an influence of the coil blocks on the optoelectronic properties of the rods.

The second method of preparing a block copolymer is by coupling two appropriately functionalized polymers or oligomers. Evidently, this approach requires a quantitative end-functionalization of the oligo- or polyarylene moiety. Thus, as an alternative to obtain analogues to the above block copolymer **56** (Scheme 8) fully aromatized, Müllen and coworkers prepared perfectly end-functionalized oligo(2,5-dihexyl-*p*-phenylenes) (**60**) with 7–10 repeat units. Further reaction of **60** with either polystyrene (**53**) or poly(ethylene oxide) **62** yielded the corresponding luminescent rod-coil block copolymers (**61**, **63**, Scheme 9).⁶³

As previously stated, the scope of these strategies is not limited to oligo(phenylene)s. Thus, functionalized oligo(phenylenevinylene)s,^{64,65} oligo(phenyleneethynylene)s^{66,67} and oligo(thiophene)s⁶⁸ have also been incorporated in rod-coil block copolymers.

Yu and coworkers have recently reported the synthesis of

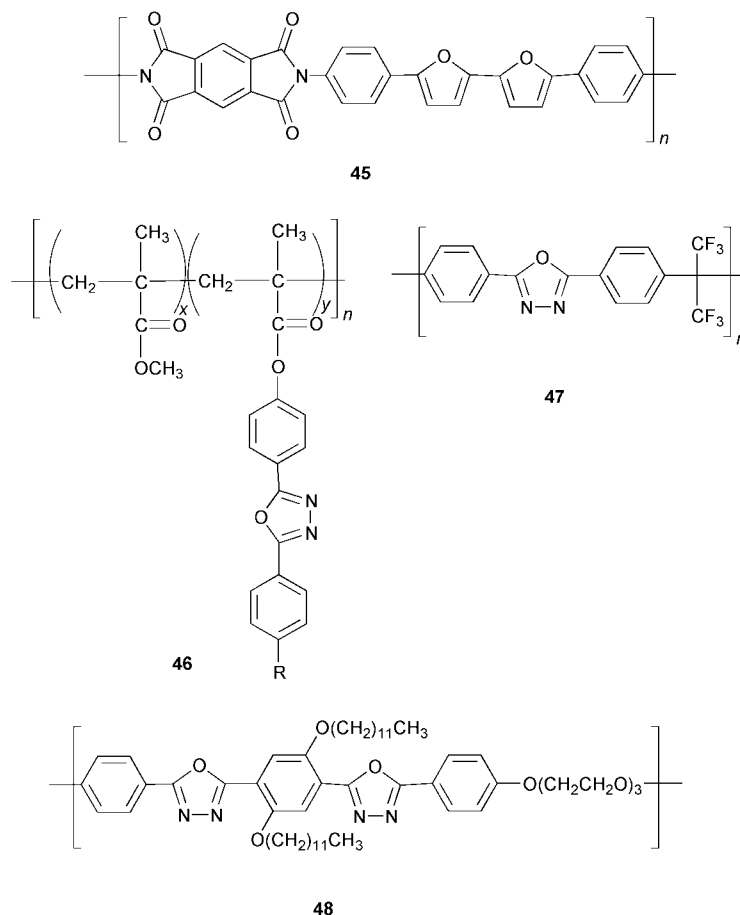


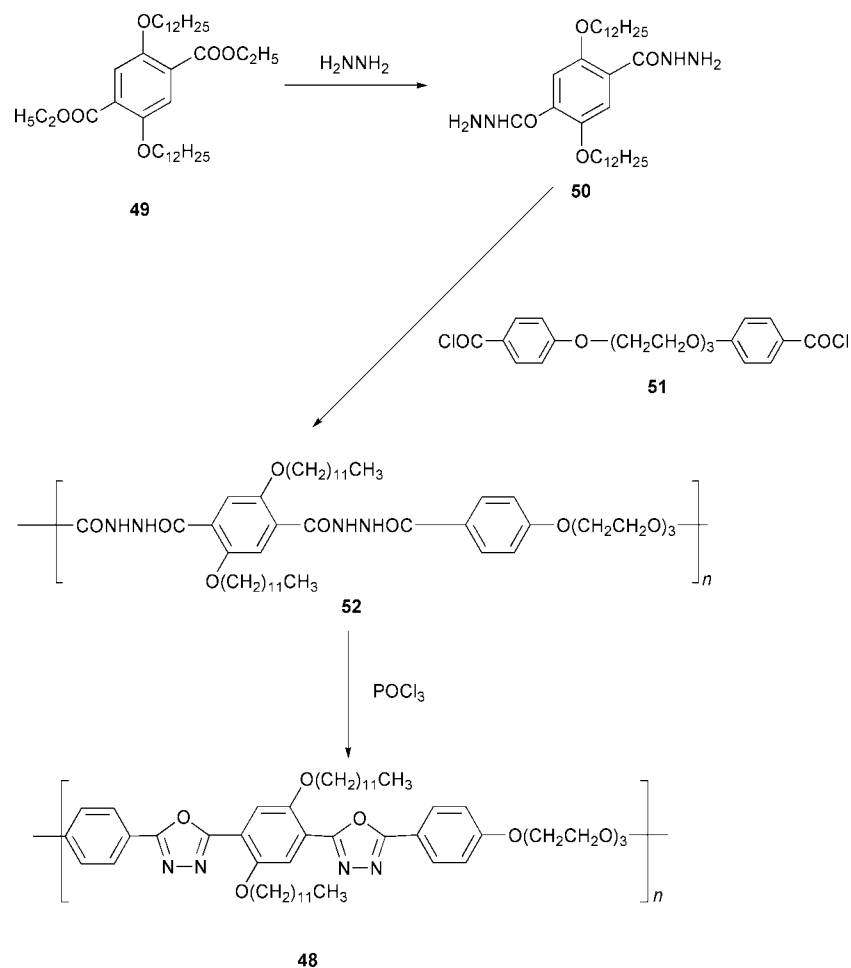
Fig. 5 Alternating copolymers containing isolated oligomers with electron-rich furan and electron-deficient oxadiazole units.

rod-coil block copolymers containing oligo(phenylenevinylene)s linked to either polyisoprene (PI, **66**)^{64b} or poly(ethylene glycol) (PEG, **70**).^{64a} The first one (**66**) was obtained by reaction of a living anionic polyisoprene derivative (**65**) with oligo(phenylenevinylene)s endowed with an aldehyde group (**64**, Scheme 10a). Four copolymers that have the same oligo(phenylenevinylene) block but different lengths of the PI block were synthesized. Alternating strips of oligo(phenylenevinylene) and PI-rich domains were observed, the domain sizes of the strips suggesting that these macrostructures could be bilayer lamellar phases. As Yu and coworkers point out,^{64b} the self-assembled domains bring these conjugated oligomer derivatives into order and hence offer the opportunity to study the intrinsic physical properties of conjugated polymers. On the other hand, it could be observed that as the conjugation length increases, the solubility of the conjugated block decreases dramatically, thus limiting the size of the conjugated block to be used in the coupling reaction. In order to solve this problem, Yu and coworkers modified the above presented synthetic strategy by first coupling the coil block (in this case a polyethylene glycol derivative) with a difunctionalized oligo(phenylenevinylene) (**67**) followed by coupling of the functionalized rod-coil polymer formed (**68**) with another monofunctionalized oligo(phenylenevinylene) (**69**) to yield a much longer conjugated block in the final block copolymer (**70**, Scheme 10b).^{64a} The large differences in structure and solubility between the two blocks are expected to facilitate the phase separation even when the molecular weight of the copolymer is low.

Other interesting rod-coil block copolymers recently synthesized are depicted in Fig. 6. Hempenius *et al.* employed a polystyrene with a phenolic terminus that was modified by an α -terthiophene unit, followed by a coupling reaction to yield a well-defined triblock copolymer of poly(styrene-*block*-oli-

gothiophene-*block*-styrene), with the oligothiophene moiety containing eleven thiophene units (**71**). In this polymer, electrochemical doping was hampered by the polystyrene segments, while chemical doping afforded small nanoscopic charged aggregates that were soluble in organic solvents.⁶⁸ Müllen and coworkers synthesized the rod-coil poly(*p*-phenyleneethynylene-*block*-ethylene oxide) **72** by reacting the terminal carboxy group of an oligo(*p*-phenyleneethynylene) with the hydroxy end-group of poly(ethylene oxide).⁶⁶ More recently, the syntheses of diblock poly(*p*-phenyleneethynylene-*block*-isoprene) **73** and triblock poly(isoprene-*block*-*p*-phenyleneethynylene-*block*-isoprene) **74** have been reported by Godt and coworkers by using polyisoprene with hydroxy end-groups.⁶⁷ Oligo(*p*-phenyleneethynylene) containing materials are specially interesting given that they present a favorable rigid-rod structure which strongly tends to spontaneously assemble into stable, structurally well-defined nanostructures. This, together with the special attention that poly(phenyleneethynylene) homopolymers have attracted in the area of optical and electronic devices make these materials interesting targets for more in-depth studies.

In recent years, the group of Stupp has reported on different supramolecular materials formed by molecules with triblock architecture that self-organized into discrete mushroom-shaped nanostructures.⁶⁹ They have prepared self-organized films formed by triblock molecules containing phenylenevinylene segments.^{65a} The nanostructured materials obtained contain thousands of molecular layers organized with polar ordering and give rise to strong photoluminescence. More recently, they have incorporated into these supramolecular materials triphenylamine moieties which, as previously stated, are of interest as hole transport layers in light emitting devices. Living anionic polymerization starting from *n*-butyllithium and triphenylamine (TPA) derivative **76** followed by quenching of the



Scheme 7

reaction with ethylene oxide as gas afforded an oligomer of TPA (**77**). Polymerization of ethylene oxide yielded the diblock copolymer **78**. Reaction of **78** with difunctionalized oligo(phenylenevinylene) **79** yielded a triblock copolymer endowed with an aldehyde functionality which was further reacted with a second oligo(phenylenevinylene) derivative (**80**) through a Wittig–Horner reaction. Final deprotection of the terminal *tert*-butyldimethylsilyl (TBDMS) group led to the triblock-copolymer **81** endowed with terminal hydroxy polar groups (Scheme 11).^{65b} Electron diffraction (ED) on films of **81** indicates that this material contains crystalline domains with rod segments oriented perpendicular to the plane of the film, being both ethylene oxide segments and TPA segments contained in amorphous domains. The emission of **81** when excited with light at 302 nm shows substantial emission from oligo(phenylenevinylene) segments and additional experiments suggest that energy transfer occurs between the coil-like TPA and rod-like PPV segments of these polymers. This work paves the way for the use of a broad range of functional chemistries to design nanostructured organic materials.

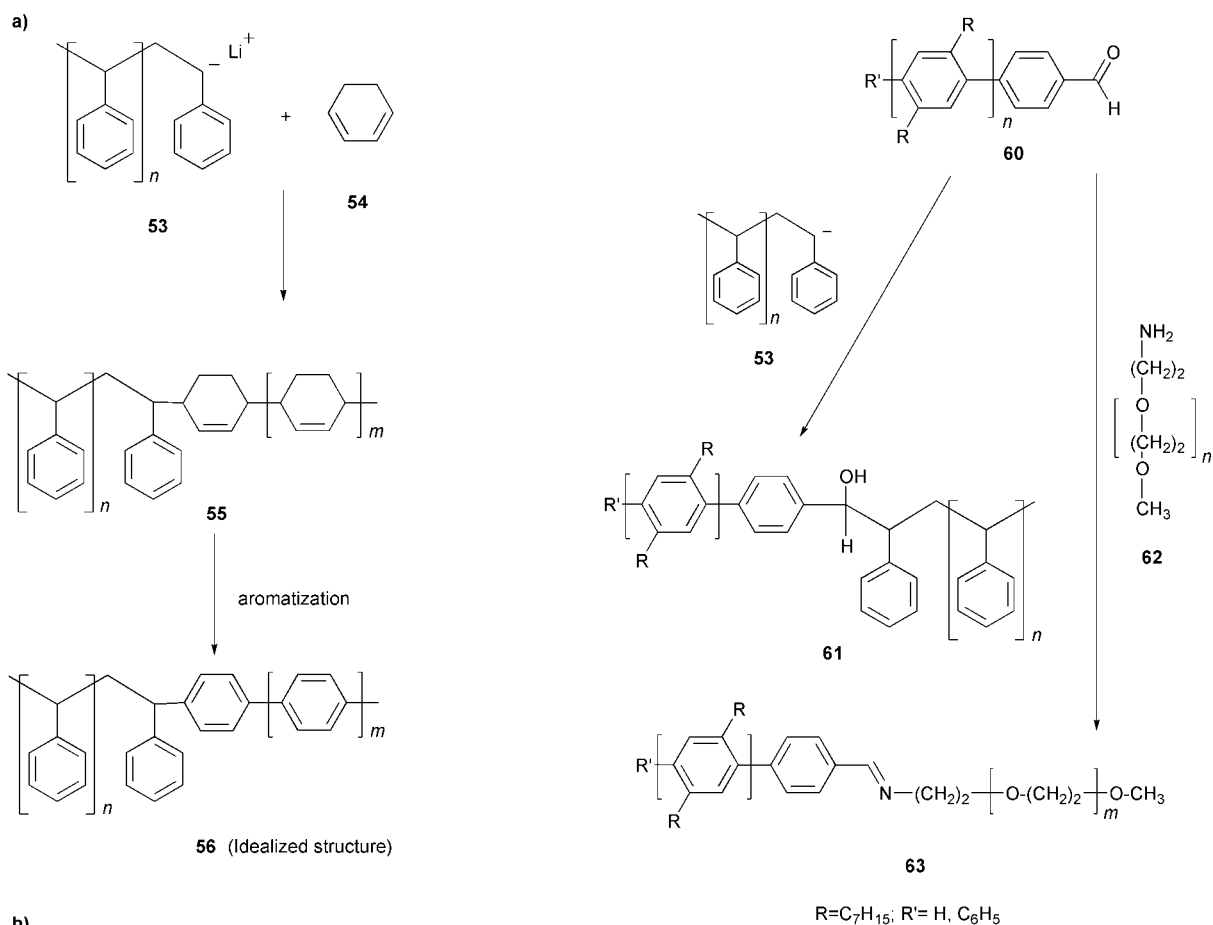
2.2 Oligoarylene-containing molecular materials for LEDs

Some interesting charge-transport materials with applications in LEDs have been synthesized by functionalizing oligoarylenes. As we have already seen, different oligoarylenes have been reported to function as emitting materials in organic LEDs; however, in general, their performances are poor probably because oligoarylenes with well-defined structures are crystalline in nature and therefore they form polycrystalline films by vacuum deposition or spin coating. It has been observed, for example, that the fluorescence quantum efficiencies of polycrystalline films of oligothiophenes are significantly

reduced as compared with those of the corresponding solutions and it has been suggested that the fluorescence quantum efficiency may not be significantly reduced in the amorphous film state.⁷⁰ In this sense is remarkable the work of Shirota and coworkers who have developed synthetic strategies toward the preparation of efficient luminescent amorphous materials derived, among others, from functionalized oligoarylenes.⁷⁰

One interesting example is a family of oligothiophenes end-capped with bis(dimesitylboryl) functional groups (**82**, Fig. 7) which readily form stable amorphous glasses with high glass transition temperatures (T_g s).⁷¹ It is thought that glass formation is due to the incorporation of the nonplanar dimesitylboryl groups. The color of the emission can be tuned by choosing an oligothiophene derivative of appropriate length. Moreover, the incorporation of the dimesitylboryl moiety provides electron-accepting properties (half-wave reduction potential of trimesitylboryl moiety: -1.94 V vs. SCE)⁷² and therefore may be used as electron-transport amorphous molecular materials.⁷³

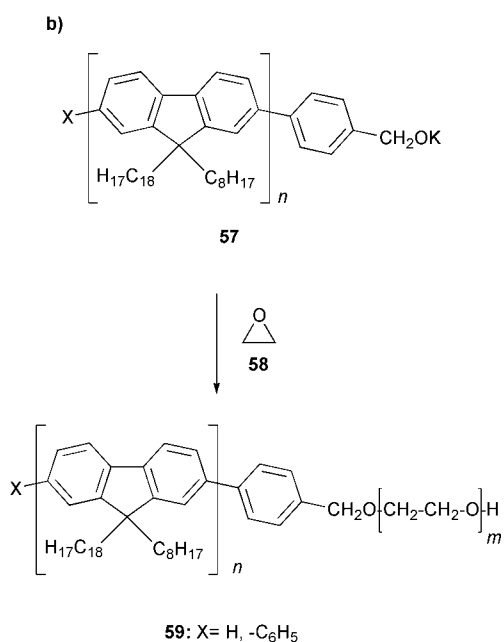
Other important series of molecular amorphous materials derived from oligothiophenes are **83a–d** (Fig. 7) which consist of oligothiophenes of different lengths ($n=1–4$) end-capped with the triphenylamine donor group.⁷⁴ These compounds readily form stable amorphous glasses with T_g s of 86, 90, 93 and 98 °C respectively when the melt samples are cooled. While the HOMO levels of these compounds are more or less the same, the HOMO–LUMO gap progressively decreases with increasing conjugation length of the oligothiophene moiety and therefore the emission color is blue, yellowish green, yellow and green for $n=1, 2, 3$ and 4 respectively. In contrast to the above mentioned dimesitylboryl derivatives, these systems present hole-transporting properties and can be efficiently used as the



Scheme 9

with dendritic chains **84** with the purpose of hindering aggregation of the oligomeric system thus making easier the manipulation of the molecular wires.⁷⁷ The synthetic procedure used involved the synthesis of the corresponding oligo(thienylenevinylene) end-functionalized with two aldehyde functional groups followed by Wittig–Horner olefination reactions with Fréchet-type dendrons⁷⁸ functionalized with phosphonate groups. Electrochemical studies performed on these systems confirm the expected absence of dimerization of radical cations formed upon oxidation as a consequence of the decrease in the inter-chain interactions.

In 1999, Freeman *et al.* described the luminescent properties of multi-component single layer OLEDs containing molecularly designed, oligothiophene-containing dendrimers **85**.⁷⁹ Highly efficient Förster energy transfer from the donors on the surface to the emitters at the dendrimer core was demonstrated through luminescence studies, both in solution and in the solid state. This strategy can be used to incorporate many other donor/emitter pairs which will allow the fine tuning of the emitting properties of materials. Moreover, as Freeman *et al.* point out, the physical separation of dyes by the sheer steric bulk of the surrounding dendrimer should allow several different conjugated oligoarylenes-containing dendrimers to be mixed within a single layer, thus affording a readily accessed and very simple color tunable system.⁷⁹



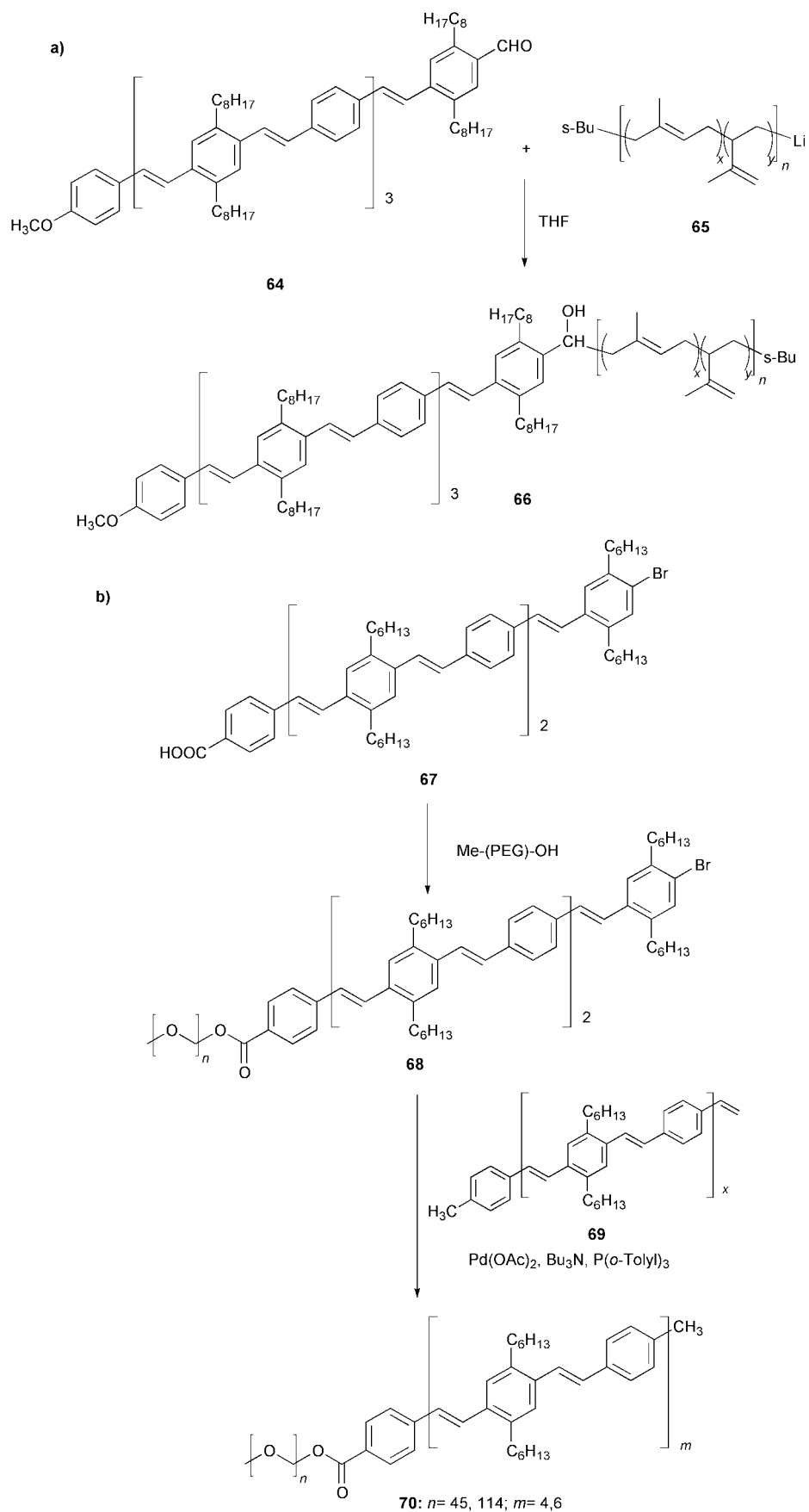
Scheme 8

emitting layer in two-layer LEDs together with different electron transport layers.⁷⁵

The next type of compounds lie in the frontier between molecular and polymeric materials. They are conjugated oligomeric systems in dendritic molecules which are very interesting given that they may allow supramolecular control of interchain interaction in order to develop at will either compact materials with high electron mobility or, in contrast, single molecular wires. In Fig. 8 and 9 are depicted two representative examples of systems containing oligoarylenes in a dendritic environment. Thus, in 1998 Roncali and coworkers synthesized *n*-oligo(thienylenevinylene)s (*n*TVs)⁷⁶ end-capped

3 Photoinduced electron and/or energy transfer in oligoarylene-containing dyads and triads

Photoexcited electron transfer between donor and acceptor molecular semiconductors provides a method of efficient charge generation following photoabsorption, which can be exploited in photovoltaic diodes.⁸⁰ The main advantages of using organic semiconductors in these devices are the



Scheme 10

possibility of depositing large area films from solutions at low cost and the possibility of selecting systems with a variety of energy gaps and chemical modifications in order to make more

efficient the use of the solar spectrum.^{81,82} On the other hand, the photogeneration of charge carriers in conjugated polymers has proved to be of interest for applications in photoreceptors,

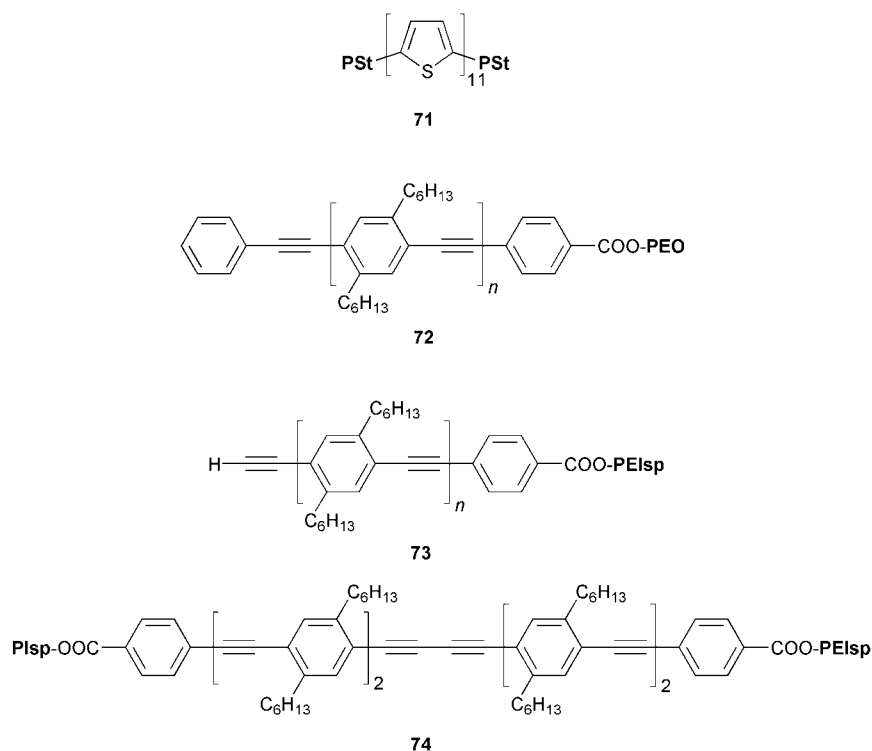
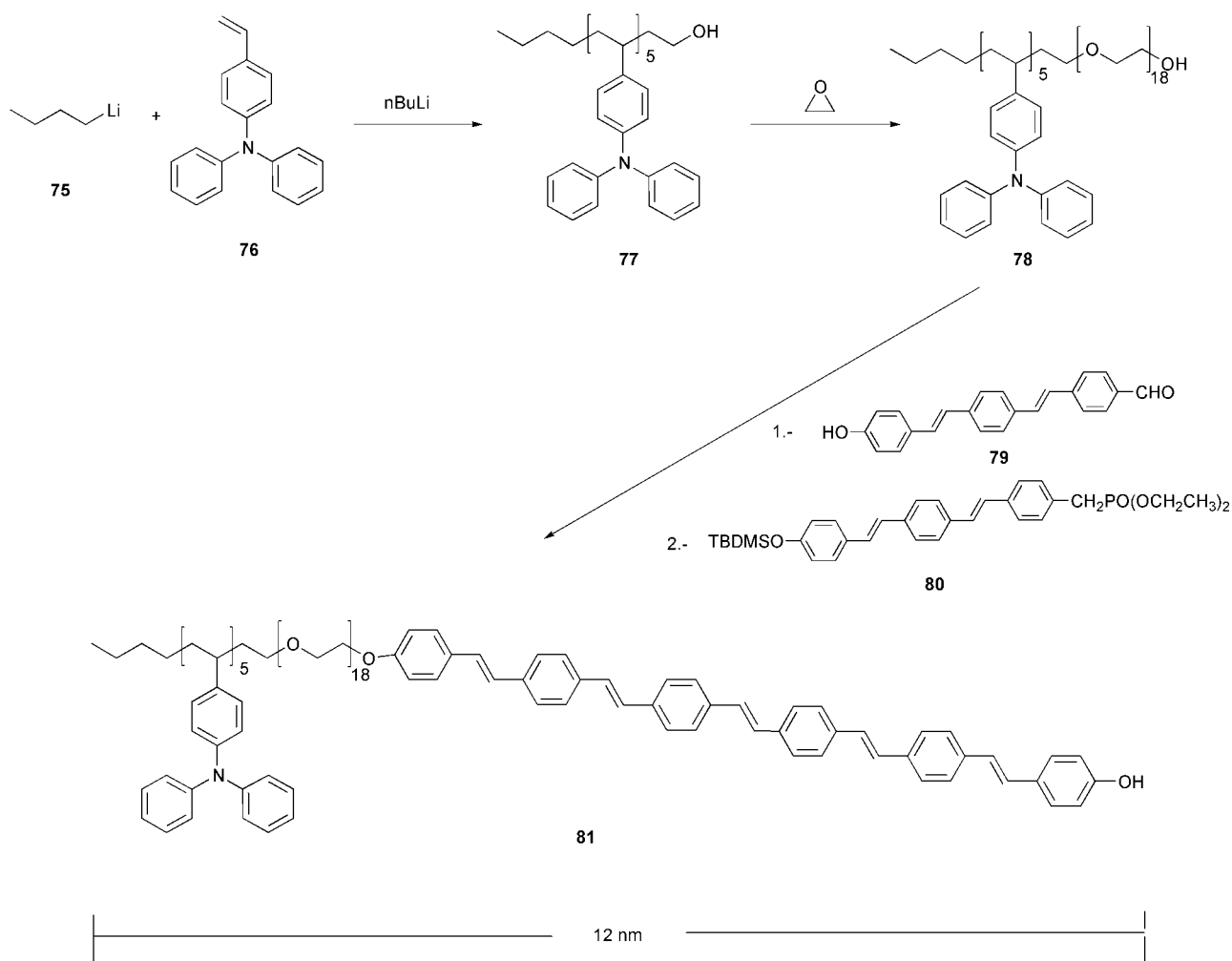


Fig. 6 Selected examples of rod-coil block copolymers.

photodiodes and solar cells.^{3,83} The first simple photovoltaic devices fabricated from single-layer, thin films of polymers

were inefficient in the conversion of photons to electrical current.⁸⁴ Although the devices had broad absorption bands in



Scheme 11

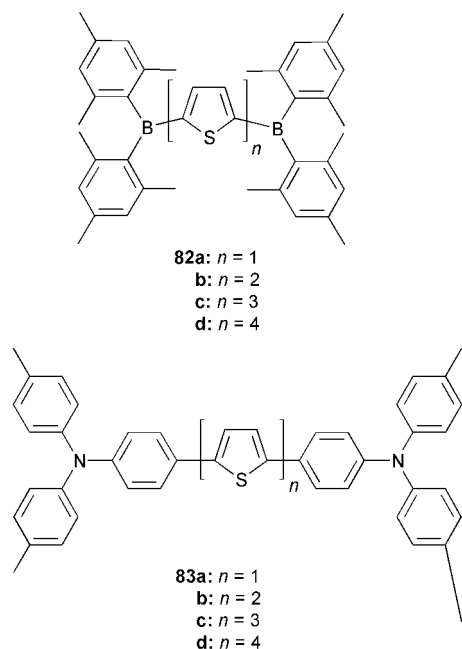


Fig. 7 Oligoarylene-containing molecular materials for LEDs.

the visible region, separation and collection of the generated electron-hole pairs (excitons) were poor. It was subsequently recognized that enhanced charge separation occurs at an interface between two materials with disparate electron affinities, allowing for transport of the carriers in separate

materials with a low probability of recombination. Materials introduced into the polymer to create heterojunctions for improved device performance have included small organic molecules,⁸⁵ polymers^{80,83} inorganic nanocrystals⁸⁶ and fullerene C_{60} .^{87,88} The fullerene C_{60} provides a useful high electron affinity semiconductor and, in mixed composites together with conjugated polymers, ultrafast photoinduced electron transfer can occur with high quantum efficiency. However, the tendency of C_{60} to phase-separate and crystallize limits its solubility in conjugated polymers. As uniformity and high quality of conjugated polymer- C_{60} thin films are essential for optoelectronic device applications, soluble functionalized C_{60} derivatives have been synthesized in an attempt to suppress the phase separation once these derivatives are blended with the conjugated polymers.⁸⁹ As an alternative to these procedures, other research groups have focused their efforts on the synthesis of molecular dyads⁹⁰ and triads⁹¹ bearing conjugated oligomer moieties covalently linked to the electron acceptor C_{60} fullerene. As noted above, well-structured oligomers allow the possibility of mimicking the basic structural and electronic properties of the related polymers and, therefore, different examples of conjugated oligoarylene- C_{60} dyads have been recently reported.

We have developed a synthetic route towards the preparation of end-functionalized oligo(2,6-naphthylenevinylene)s. In Scheme 12 is depicted how, by reaction of the bis(triphenylphosphonium) salt derivative **88** with functionalized naphthalene **87**, the corresponding trimeric system **89** end-functionalized with bromine groups could be obtained. Treatment of **89** with copper cyanide in dimethylformamide led to a mixture of the corresponding monocyano (**90**) and dicyano (**92**) derivatives

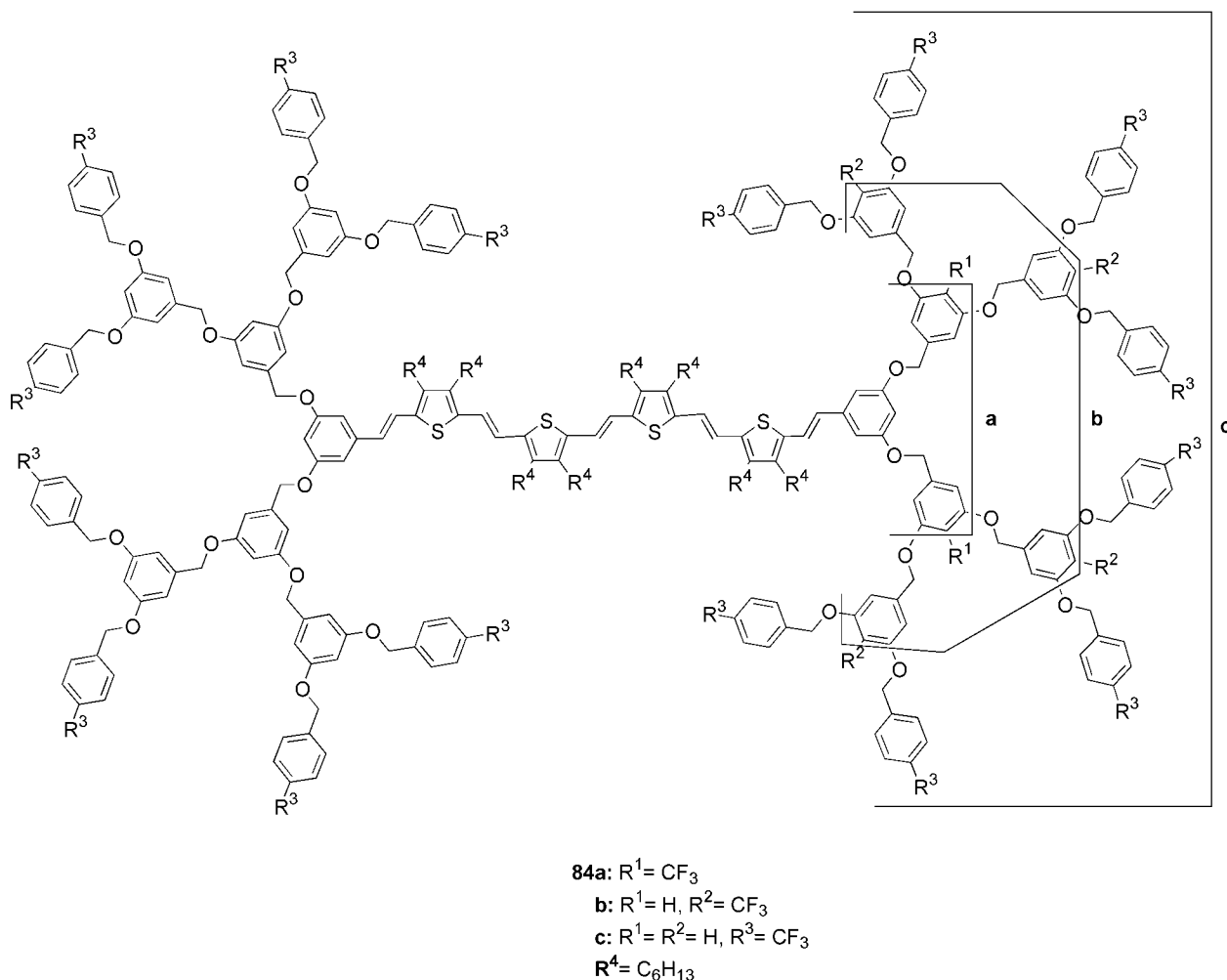
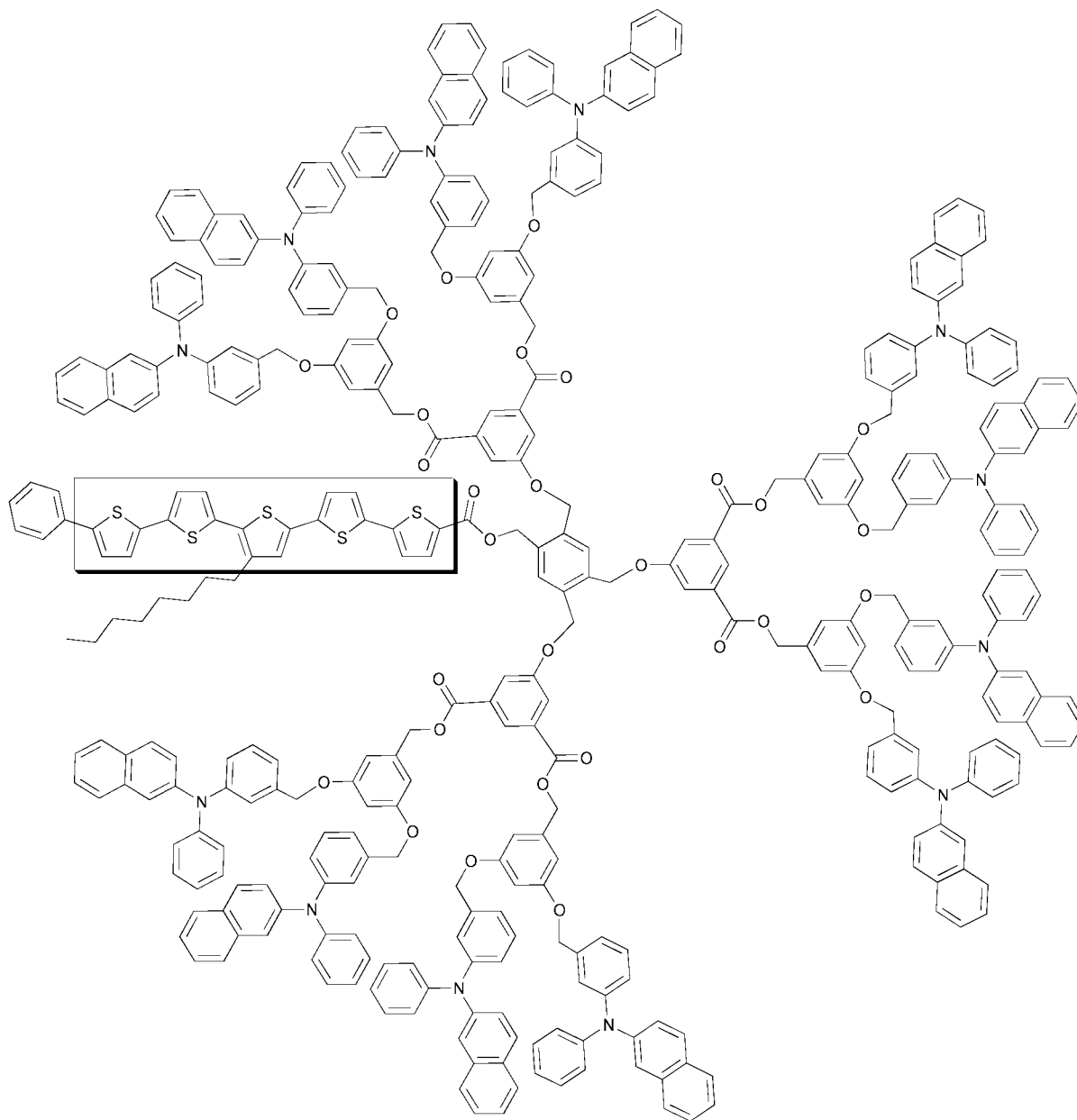


Fig. 8 *n*-Oligo(thienylenevinylene)s end-capped with dendritic chains.



85

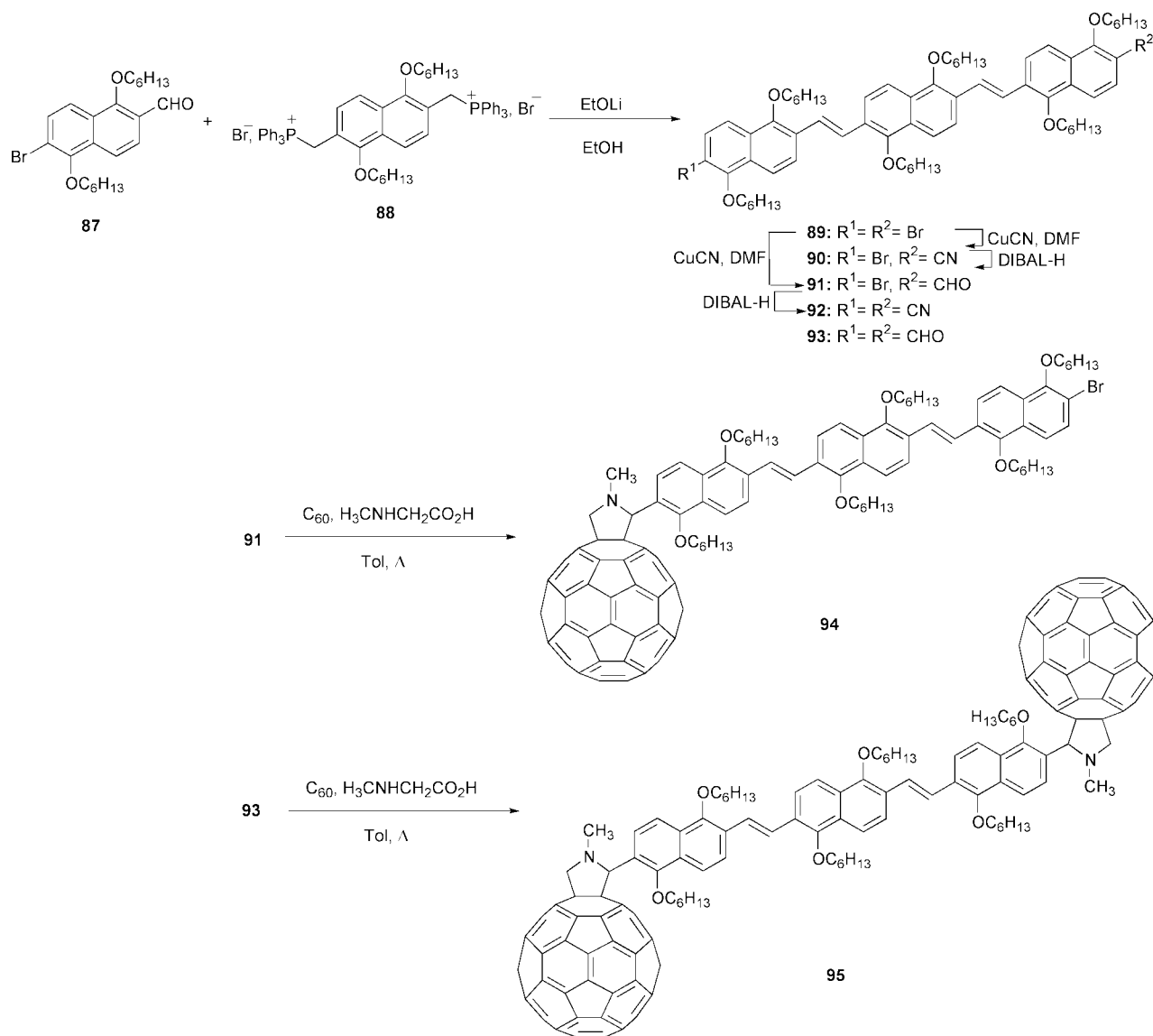
Fig. 9 Oligothiophene-containing dendrimer used as multicomponent luminescent material for OLEDs.

that can be easily separated. Further reduction of the nitrile groups with DIBAL-H gave the trimeric systems functionalized with one (**91**) or two (**93**) aldehyde groups.⁹² Among the suitable procedures for the functionalization of fullerenes, the 1,3-dipolar cycloaddition of azomethine ylides to C_{60} emerged as an important methodology for the production of stable fullerene derivatives.⁹³ We have adapted this synthetic approach for the preparation of dyad **94**⁹⁴ and triad **95**.⁹¹ Interestingly, the presence of the long alkoxy chains in the naphthylenevinylene units provides enhanced solubility of these systems in common organic solvents thus allowing appropriate spectroscopic and electrochemical characterization. This fact is specially noteworthy for triad **95** given that unsubstituted fullerene dimers are highly insoluble materials.⁹⁵ The redox properties of these systems were studied by cyclic voltammetry showing amphoteric redox behavior due to the oxidation of the conjugated oligomer and the reduction of the fullerene moiety. Relative to the strong emission of the oligomer references, in the C_{60} containing materials the trimer emission is nearly quenched. Photophysical studies on

dyad **94** show competition between electron and energy transfer in this system.

By following similar synthetic methodologies, the synthesis of other dyads (**96**,^{90e} **97**,^{90c} **98**^{90f}) and triads (**99**)^{91b} have been reported (Fig. 10). A decrease in the fluorescence quantum yields, similar to that observed for **94** and **95**, is observed for oligothiophenes covalently attached to a C_{60} moiety **96** which means that an efficient fluorescence quenching of the oligothiophene by the fullerene chromophore takes place. Interestingly, Yamashiro *et al.* observed that intramolecular singlet-singlet energy transfer occurs on the picosecond time scale and markedly depends on the chain length of the oligothiophene moiety, in other words, the distance between the two chromophores.^{90e} Similar efficient energy transfer could be also observed in triad **99** containing also an oligothiophene moiety.^{91b}

Nierengarten and coworkers incorporated dyad **97** in a photovoltaic device by spin casting the dyad on a glass substrate coated with indium tin oxide (ITO) followed by vacuum evaporation of an aluminium electrode on the films.



Scheme 12

Under the light the device shows clear photovoltaic behavior with an open circuit voltage of *ca.* 0.2 V and short-circuit current density of 10 $\mu\text{A cm}^{-2}$ corresponding to a collecting efficiency of 1%.^{90c} More recently, photoinduced energy transfer has been also observed in the fullerene derivative **98** which is similar to **97** although the fullerene moiety is now linked to two oligo(phenylenevinylene) moieties.^{90f} The results obtained from the photophysical studies suggest the possibility of building up more complex arrays where a large number of oligo(phenylenevinylene) fragments allow an even more pronounced excitation selectivity with an antenna effect.

A different approach for the synthesis of light harvesting systems containing fullerene and conjugated oligomer systems has been developed by Effenberger and coworkers. Instead of the above mentioned 1,3-dipolar cycloaddition of azomethine ylides to C₆₀, they used a Diels–Alder reaction between C₆₀ and a conjugated oligomer endowed with a thiophene 5,5-dioxide moiety (**100**).^{90a,b} An *o*-quinodimethane type⁹⁶ reactive diene (**102**) is formed upon heating the thiophene 5,5-dioxide moiety through extrusion of SO₂ and reacts with the C₆₀ moiety through a [4+2] cycloaddition to yield the corresponding dyad **103a** (Scheme 13). Furthermore, by using this synthetic strategy they have also synthesized what the authors call a trichromophoric “supermolecule” **103b** which contains an anthracene donor linked to the fullerene acceptor through a conjugated oligothiophene bridge (Scheme 13). This is an

interesting variation on the above presented structures. In this system the anthracene unit acts as antenna and transfers the energy of absorbed light *via* the oligothiophene π -bridge to the fullerene acceptor. There is a new role for the oligoarylene moiety in these systems: they are acting as “molecular wires”.^{90a,b} The photoinduced electron transfer studies in dyad **103a** and triad **103b** show that both molecules exhibit long-lived charge-separated states at *T* = 5 K thus indicating that the dyad is sufficient for allowing photoinduced charge-transfer in these molecules.

In an attempt to enhance electron or charge-transfer, Echegoyen and coworkers have synthesized the new donor (D)–acceptor (A) systems **104** in which different oligo(thiophenevinylene) moieties act as spacers between a fullerene acceptor moiety and a dialkylaniline donor fragment (Fig. 11).^{90d} Cyclic voltammetry analysis of **104** shows four quasi-reversible reduction waves with cathodic peak potentials at –1.052, –1.594, –2.208, and –2.428 V vs. Fc/Fc⁺ and two irreversible reductions at –2.704 and –2.883 V. In addition, two quasi-reversible oxidation processes occur with anodic peak potentials at 0.140 and 0.364 V. The first three successive and nearly equally spaced reductions and the fifth reductions are C₆₀ based while the fourth and sixth reductions are centered on the conjugated donor part. Although no information about possible charge-transfer interactions between the donor and acceptor parts of the molecule has been reported, good

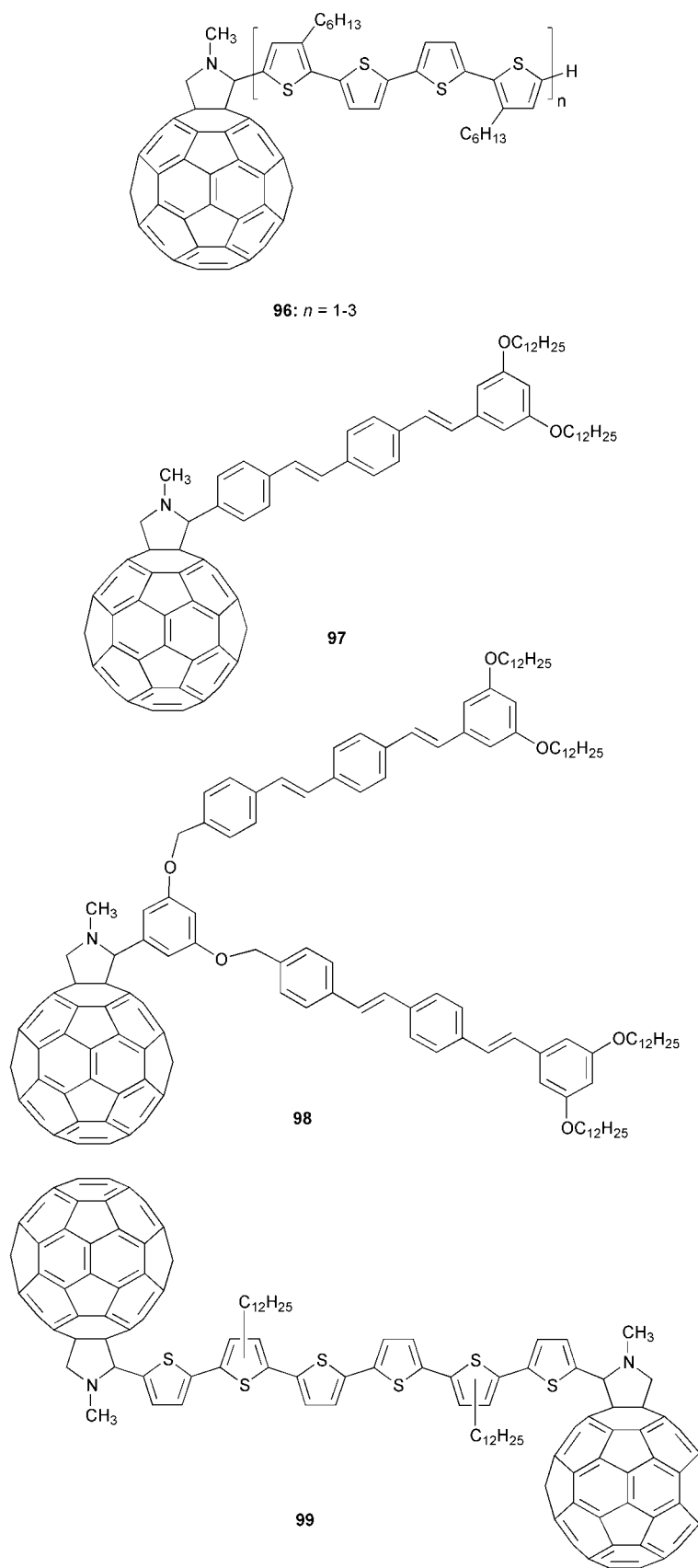


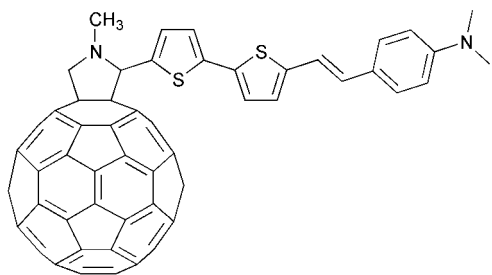
Fig. 10 Molecular dyads and triads bearing conjugated oligomers covalently linked to the electron acceptor C₆₀ fullerene.

intramolecular electron or charge-transfer can be anticipated for **104**, because of the strong donor ability of the dialkylaniline moiety and the low aromatic stabilization energy of the thiophene ring.⁹⁷

Other interesting systems (**105**,⁹⁸ **106**,⁹⁹ **107**¹⁰⁰) in which the

oligoarylene moiety acts as “molecular wire” are depicted in Fig. 12. The electronic structure of the bridge component in these donor–bridge–acceptor (DBA) systems play a critical role in the determination of the ease of electron transfer.

Vollmer *et al.* have studied the photophysical properties of



104

Fig. 11 D–A system in which a bithiophene acts as spacer between the donor dialkylaniline and the acceptor C_{60} .

the energy transfer in system **105**, in which a quinquethiophene bridge is terminally linked to the 5-position of a porphyrin and to the 9-position of an anthracene group.⁹⁸ The use of the quinquethiophene spacer provides a supermolecule with retention of the identity of individual electronic levels of the donor and acceptor moieties thus providing a highly selective excitation of the anthracene donor which leads to quantitative

energy transfer to the emitting porphyrin acceptor *via* the quinquethiophene bridge. Furthermore, in contrast to other previously studied polyenes used as spacers, in the oligothiophenes neither radiationless deactivation of the excitation energy through the conjugated chain nor quenching of the acceptor emission could be observed. The mechanism of the observed ultrafast (< 10 ps) intramolecular singlet–singlet energy transfer can be explained with different theories like Försters, Dexters, superexchange or intramolecular relaxation. However, from the experimental results presented, no clear distinction can be made.

Davis *et al.* have synthesized a series of structurally well-defined DBA molecules (**106**) that incorporate tetracene as the donor and pyromellitimide as the acceptor, linked by phenylenevinylene oligomers of various lengths.⁹⁹ Photoinduced electron transfer in this series exhibits very weak distance dependence for donor–acceptor separations as large as 40 Å, with rate constants of 10^{11} s^{-1} . The experimental data obtained in the study show the critical role that the energy gap from donor-to-bridge charge injection plays in promoting molecular-wire behavior in DBA molecules that possess highly

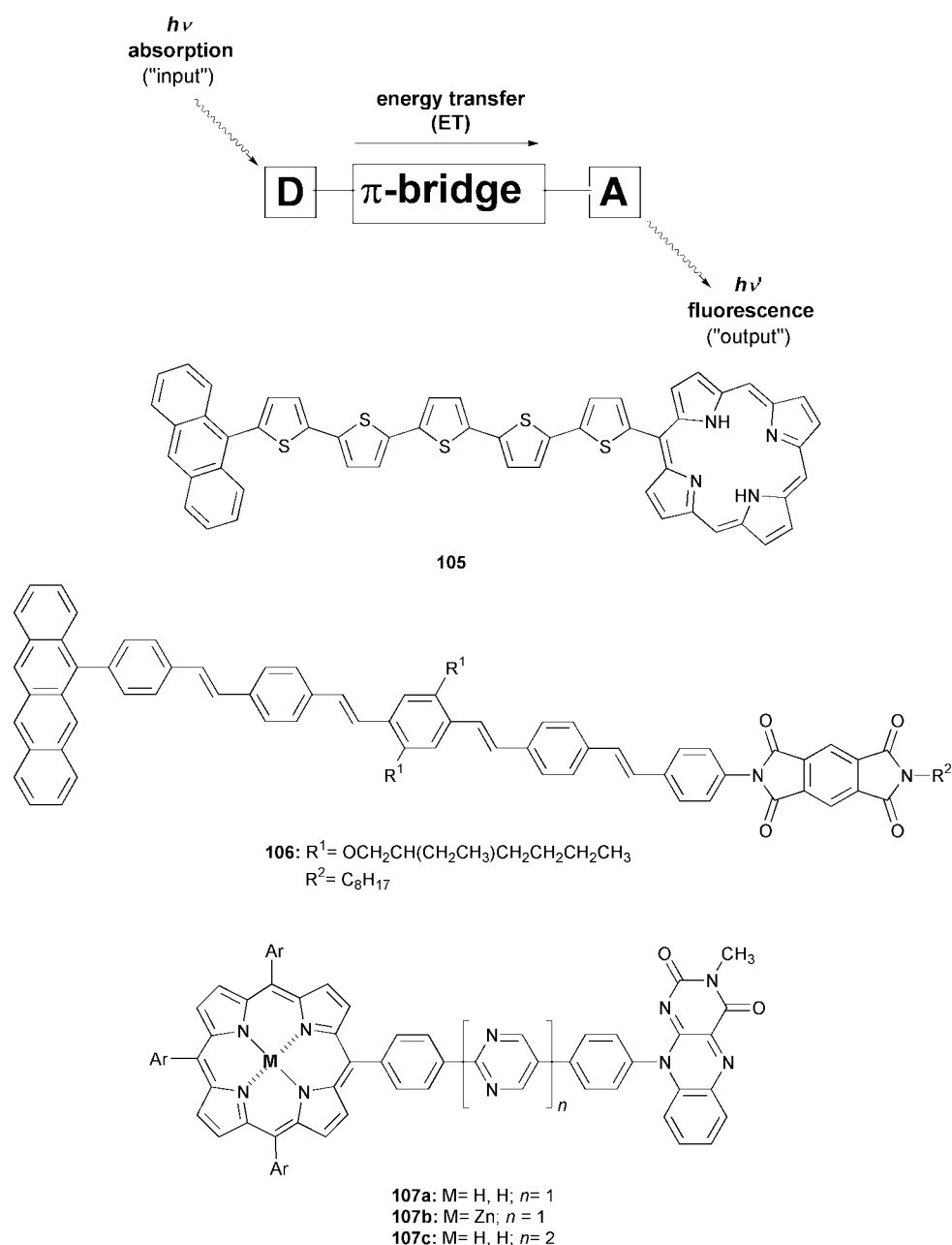
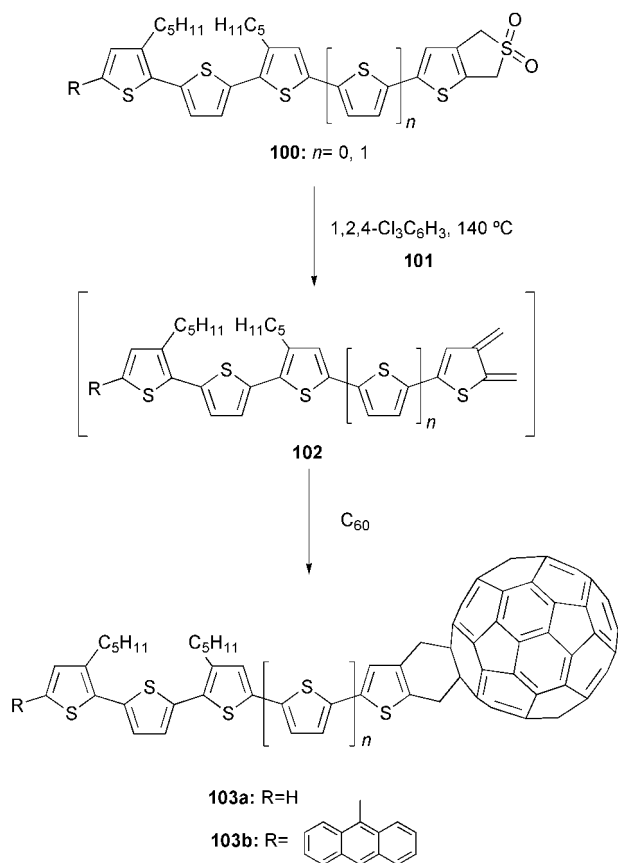


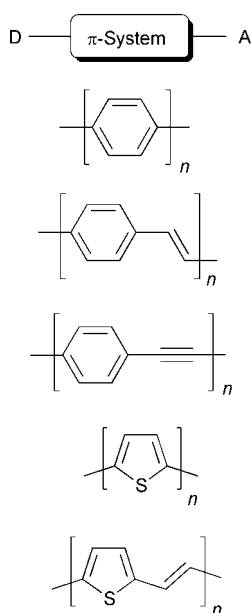
Fig. 12 DBA systems in which conjugated oligomers act as molecular wires.



Scheme 13

conjugated bridges. Moreover, due to the unusually high electron and hole mobilities displayed by PPV polymers, the ability to exercise photochemical control over charge injection into well-defined oligo(phenylenevinylene)-containing systems may lead to molecular electronic devices based on these materials.

Hermann *et al.* have introduced oligo(diazaphenylene) bridges as spacers in DBA systems containing porphyrins as donor moieties and flavins as the acceptor unit (**107**).¹⁰⁰ This type of heterocyclic oligophenylene analogues were chosen as



Scheme 14

spacers because of their rigid structure, their excellent chemical stability, the easy control of their length and their transparency in the visible and near-UV spectroscopic region. Thus, their absorption does not interfere with that of the porphyrin. The results of the experimental observations indicate that a charge-separated state can be populated after excitation of the flavin moiety, which relaxes to the ground state on the subnanosecond time scale.

From all of the above, it can be concluded that a great deal of work is still to be done in this area. The recent development of synthetic routes towards functionalized monodisperse oligoarylenes with multinanometre dimensions incorporating different carbo- and heterocycles opens up the way to their incorporation in complex DBA systems. By means of the chemical synthesis, the great control achieved on the band-gap of the system, wavelength of absorption, electron donor and electron acceptor ability will allow the choice of the appropriate oligoarylene to offer the best performances as linkers in combination with a variety of donor and acceptor moieties.

4 Oligoarylenes as building blocks for the synthesis of materials for optoelectronics and photonic applications

The notion that altering the structure of a material can profoundly alter its electromagnetic properties has enabled new technologies that offer control over light. These new materials, often referred to somewhat imprecisely as “photonic materials”, have in common the property of strong interaction with light.¹⁰¹ With the emergence of photonic technologies in areas such as telecommunications where information is coded, transported and routed optically, there is a strong technological demand for this kind of material.¹⁰²

The interaction of light with a material can be described by the material's refractive index or relative permittivity. An important type of material for photonic or optoelectronic applications are the so called second-order nonlinear optical (NLO) materials that exhibit the linear electrooptic effect by which the refractive index of the material can be controlled through the application of an external electric field.¹⁰³ Other

Fig. 13 Conjugated oligoarylenes as π -conjugated segments in D- π -A compounds with second order nonlinear optical applications.

Table 1

| Compound | R | Fig. | $\mu\beta/10^{-48}$ esu | Ref. |
|----------|---|------|-------------------------|------|
| 112 | CH ₃ CH ₂ | | 1100 | 114 |
| 113 | CH ₃ CH ₂ | | 1300 | 114 |
| 114 | CH ₃ CH ₂ | | 2300 | 114 |
| 115 | CH ₃ (CH ₂) ₂ CH ₂ | | 3800 | 114 |
| 116 | CH ₃ CH ₂ | | 6200 | 97 |
| 117 | | | 6900 | 97 |
| 118 | CH ₃ CH ₂ | | 7400 | 97 |
| 119 | | | 1150 | 109c |

important materials due to their potential photonic applications are (i) those exhibiting photorefractive effect, (ii) molecules with a large two-photon absorption cross section or (iii) light driven molecular switches.

The role that the chemistry of molecular and polymeric organic materials has played in the development of new systems with potential photonic and optoelectronic applications has increased within the last decade.¹⁰⁴ In the next sections we will present a short overview of some of these compounds that include conjugated oligoarylenes on their structures.

4.1 Oligoarylene-containing molecular materials exhibiting NLO behavior

As a result of intensive research efforts, some fundamental relationships between properties and the molecular structure of NLO organic materials have emerged. Thus, second-order NLO chromophores need a push-pull structure, which means that π - π conjugated segments must be end-functionalized by strongly electron conjugated donor and acceptors, respectively. It has been well recognized that NLO activity of chromophores is determined not only by donor-acceptor (D-A) strength but more subtly by conjugated electron relays. Thus, the relay activities of oligophenylenes, oligo(phenylenevinylene)s, oligo(phenyleneethynylene)s, oligothiophenes and oligo(thienylenevinylene)s (Fig. 13) have been compared with those exhibited

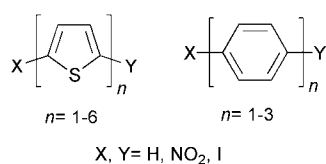


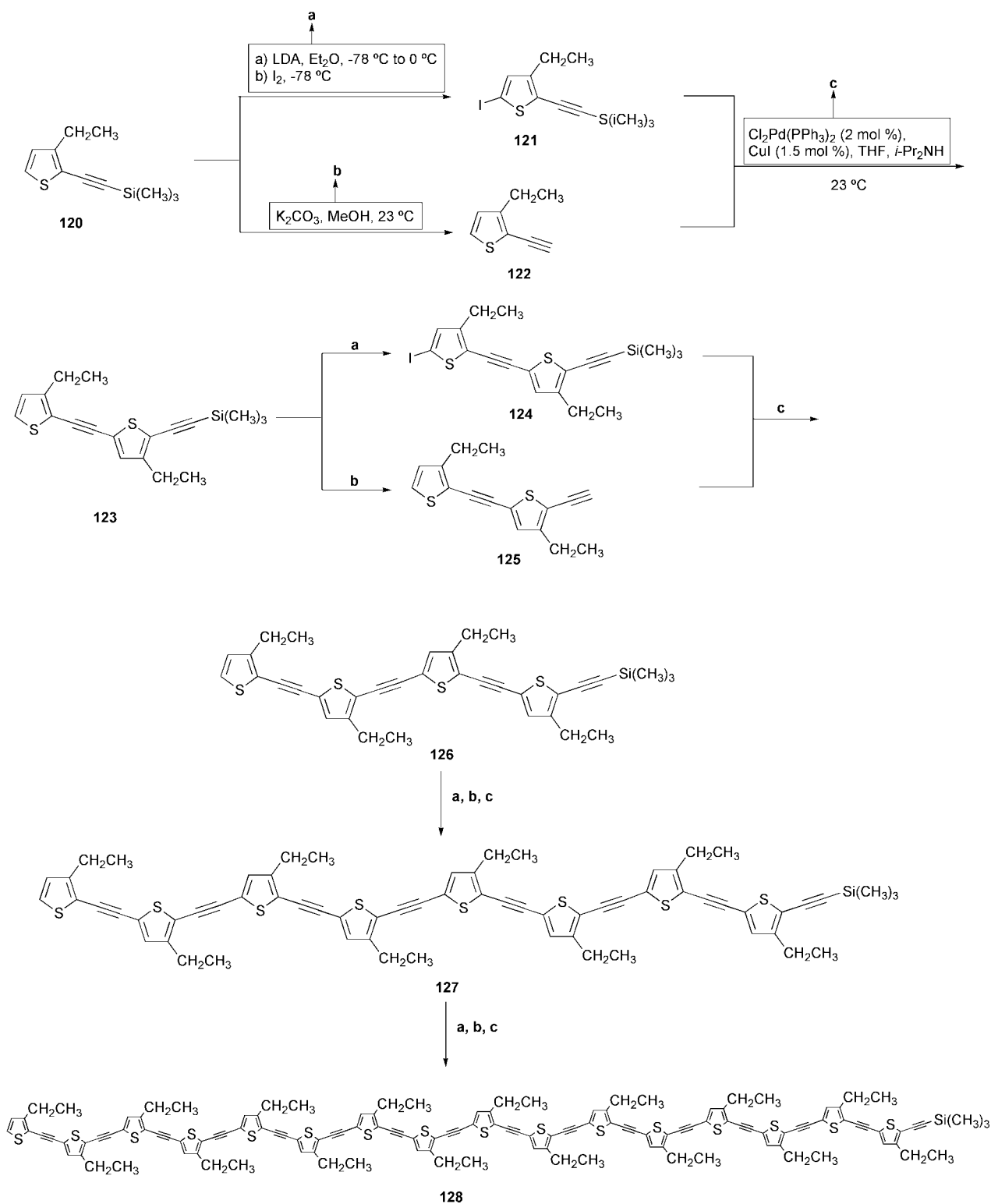
Fig. 14 Oligothiophenes and oligophenylenes with third-order nonlinear optical properties.

for typical relays such as a polyene bearing the same D-A pairs and the same conjugation length.¹⁰⁵

Experimental data as well as theoretical calculations have shown that polyene systems display a relay activity highly superior to that of an oligophenyl system. Experimental measurements on donor-acceptor-substituted oligophenyl derivatives demonstrate that these systems present absorption maxima that are greatest for bi- or terphenyls for a given donor-acceptor combination. This fact is in agreement with the decrease of the β values observed for the three-phenyl system in comparison with the two-phenyl containing analogue and suggests that although oligophenylene systems impart to this kind of materials enhanced thermal stability, they are not appropriate candidates as π -spacers for NLO.¹⁰⁶

On the other hand, a high degree of conjugation has been observed between the donor and acceptor end groups along a conjugated bridge containing three or four thiophene units and a strong tendency to increase $\mu\beta(0)$ values have been observed with an increasing number of thiophene units. The difference between these conjugated bridges and those containing phenylene units has been explained by a reduced aromaticity of the oligothiophene which allows greater electronic interactions of the end groups (quinonoid resonance structure) as well as an enhanced π -overlap between the preferentially coplanar thiophene units in comparison to the preferentially twisted phenylene units.^{107,108} The different degrees of planarity of these π -chain molecules are a result of the more pronounced steric interactions of the two *ortho* hydrogens in oligophenylenes. As thiophene-derived chromophores have been recently developed with enhanced thermal stability,¹⁰⁹ oligothiophenes might be good candidates to be used as π -spacers in NLO derivatives.

Effenberg and coworkers have developed a synthetic route towards the preparation of different donor/acceptor substituted ter- and quaterthiophenes (**111**) in the search for



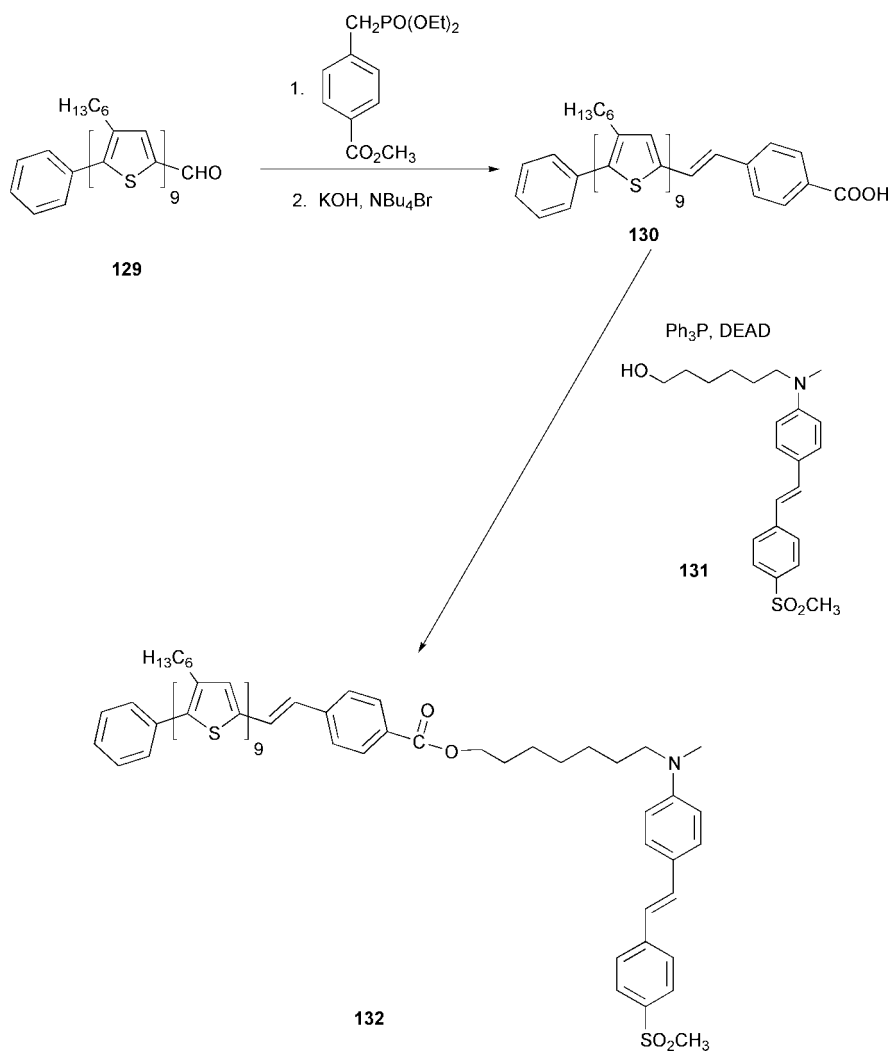
Scheme 15

solvatochromic materials.^{107b} This synthetic route starts from the donor substituted bi- or terthiophenes (**108**) and involves a Pd-catalyzed cross coupling reaction *via* organozinc compounds as depicted in Scheme 14.

The solvatochromic shift of the charge-transfer (CT) band of some of these push-pull oligothiophenes extends almost over the whole visible range, indicating a large electronic interaction between the two α,α' -substituents and full electron delocalization over the π -conjugated bridge. Because of the strict connection between solvatochromism and first hyperpolarizability,¹¹⁰ and taking into account the recent synthesis of highly

efficient and stable NLO chromophores containing thiophene,¹¹¹ bithiophene^{109c,112} and other easily delocalizable heteroaromatics^{105,113} as spacers, more work should be devoted to the incorporation of efficient donor and acceptor groups in appropriate conjugated oligo(het)arylenes in order to study their second order NLO response.

Oligoarylenevinylene spacers lay in the frontier between oligoarylene and polyene systems. Jen and coworkers have shown that chromophores containing thienylenevinylene linkers exhibit a significantly larger $\mu\beta(0)$ value compared to those containing phenylenevinylene linkers, and the $\mu\beta(0)$ value



Scheme 16

increases noticeably with increasing the number of thienylenevinylene units in the homologues.¹¹⁴ On the other hand, due to the presence of the vinylene moiety, dimeric and trimeric thienylenevinylene derivatives are known to have a lower band-gap relative to the corresponding oligothiophenes, namely bithiophene and terthiophene, respectively. Thus, thienylenevinylene derivatives have been the spacer of choice in different NLO derivatives.^{97,105,109c,113–115} Some representative examples of NLO molecular materials together with their $\mu\beta$ values are collected in Table 1.

Some of the trends outlined above for NLO materials can be confirmed by comparison between appropriate NLO systems in Table 1. Thus, it can be seen how replacement of the phenylene moiety in **112** ($\mu\beta = 1100 \times 10^{-48}$) by the thiophene system in **113** ($\mu\beta = 1300 \times 10^{-48}$) produces an increase in the $\mu\beta$ value similar to that observed for **118** in comparison with **116**. By comparison of derivatives **113**, **114** and **115** containing the same donor and acceptor groups, the beneficial effect of an increase in the number of vinylthiophene units in the spacer can be observed. The same effect can be appreciated when comparing **116** with **117**. By suppression of the vinylene linkages, a decrease in the $\mu\beta$ value is observed. Therefore, a $\mu\beta$ value of 2300×10^{-48} esu is observed for the derivative with two vinylthiophene units (**114**) while a $\mu\beta$ value of 1150×10^{-48} esu was measured for the parent **119** bearing two thiophene units. Finally, the effect of the replacement of the final donor or acceptor group can be seen when comparing those derivatives with a final dicyanovinyl acceptor group (**113**,

114) with the analogues containing the stronger tricyanovinyl group (**116** and **117** respectively).

Derivatives containing oligo(aryleneethynylene) spacers have been also used for NLO. It has been observed that the presence of the acetylenic bridging unit reduces significantly the molecular charge-transfer giving rise to materials with improved optical transparency.¹¹⁶ However, the penalty for this transparency is a decrease in β for these derivatives. Improvement in the second order nonlinearity while maintaining good optical transparency can be envisaged for these derivatives *via* lengthening of the π -conjugated network.¹¹⁷ Thus, $\mu\beta$ values of up to 1200×10^{-48} esu have been measured for D–A substituted oligo(phenyleneethynylene)s containing three benzene units linked by two acetylene bridges.¹¹⁷

Considering these synthetic possibilities, good prospects can be foreseen for optimizing the $\mu\beta$ values and transparency of second order NLO systems by using a variable number of carbocyclic and heterocyclic units either directly attached or linked through vinylene or acetylene spacers and combined with appropriate donor and acceptor functionalities.

Other interesting types of organic materials for nonlinear optics are those exhibiting cubic polarizability.¹¹⁸ The potential applications of these materials include optical switching and information processing. Compared to the extensive amount of research conducted on synthesis and characterization of new molecular structures for second order nonlinear processes, the scope of synthesis of new molecular materials and their characterization for third-order nonlinear optical properties

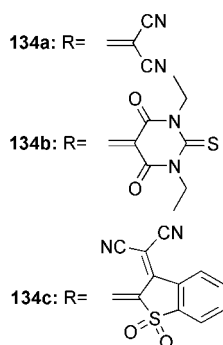
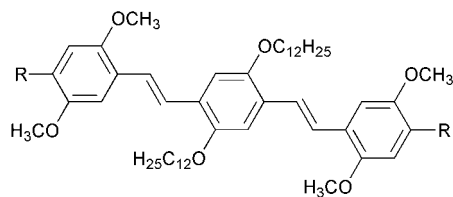
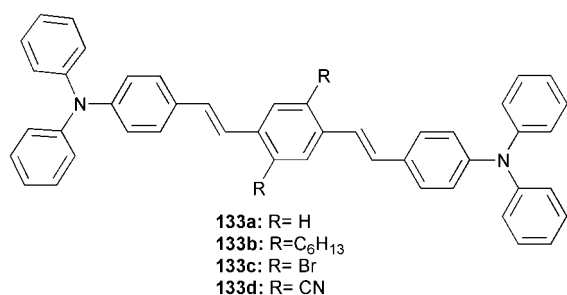


Fig. 15 Functionalized oligoarylenes which present two-photon absorption.

has received rather limited attention. Consequently, there is an even greater need for the study of structure–property relationship for third-order NLO processes using systematically derivatized and sequentially built new structures.

The study of families of conjugated oligomers is an important means of gaining experimental information about the scaling of γ value with chain length. With this aim, Samuel *et al.* have reported measurements of γ as a function of n , where n is the number of repeating units in a series of conjugated oligo(3-ethylthiopheneethynylene)s **123**, **126–128**.¹¹⁹ The oligomers were synthesized by the novel convergent/divergent iterative approach depicted in Scheme 15, giving a doubling of the oligomer length at each stage.^{15,120}

It was observed in this series of compounds that γ/n values increase strongly up to $n=8$ but tend to level off for $n=16$, demonstrating the effects of saturation. The authors suggest that the saturation arises as a result of incomplete electron delocalization due to the presence of triple bonds. There is a mismatch of electronic orbitals between the sp^2 -hybridized carbon atoms in the thiophene rings and the sp -hybridized carbon atoms between the rings. This mismatch causes the

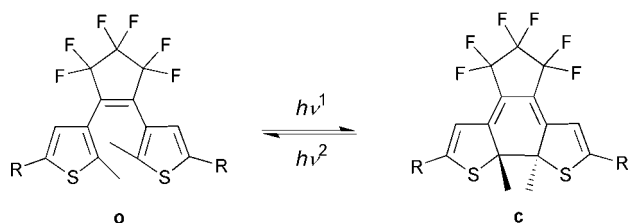


Fig. 16 Diarylethenes as photochromic materials. Reversible electrocyclic interconversion between the unconjugated (open, o) state and the colored (closed, c) takes place under irradiation.

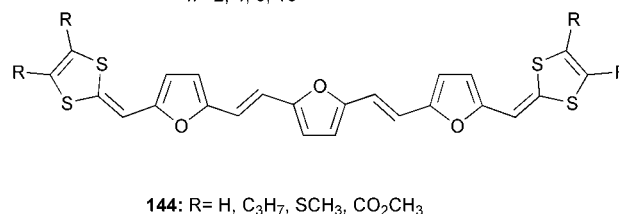
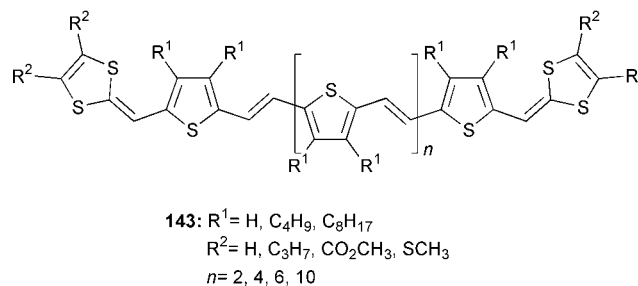
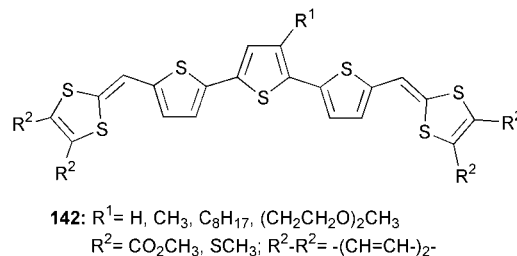
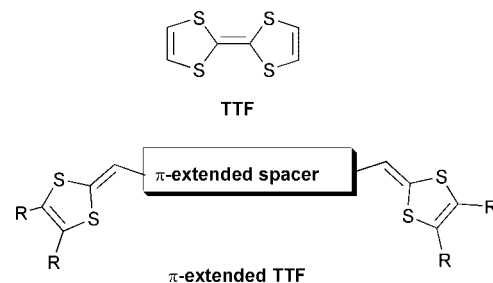


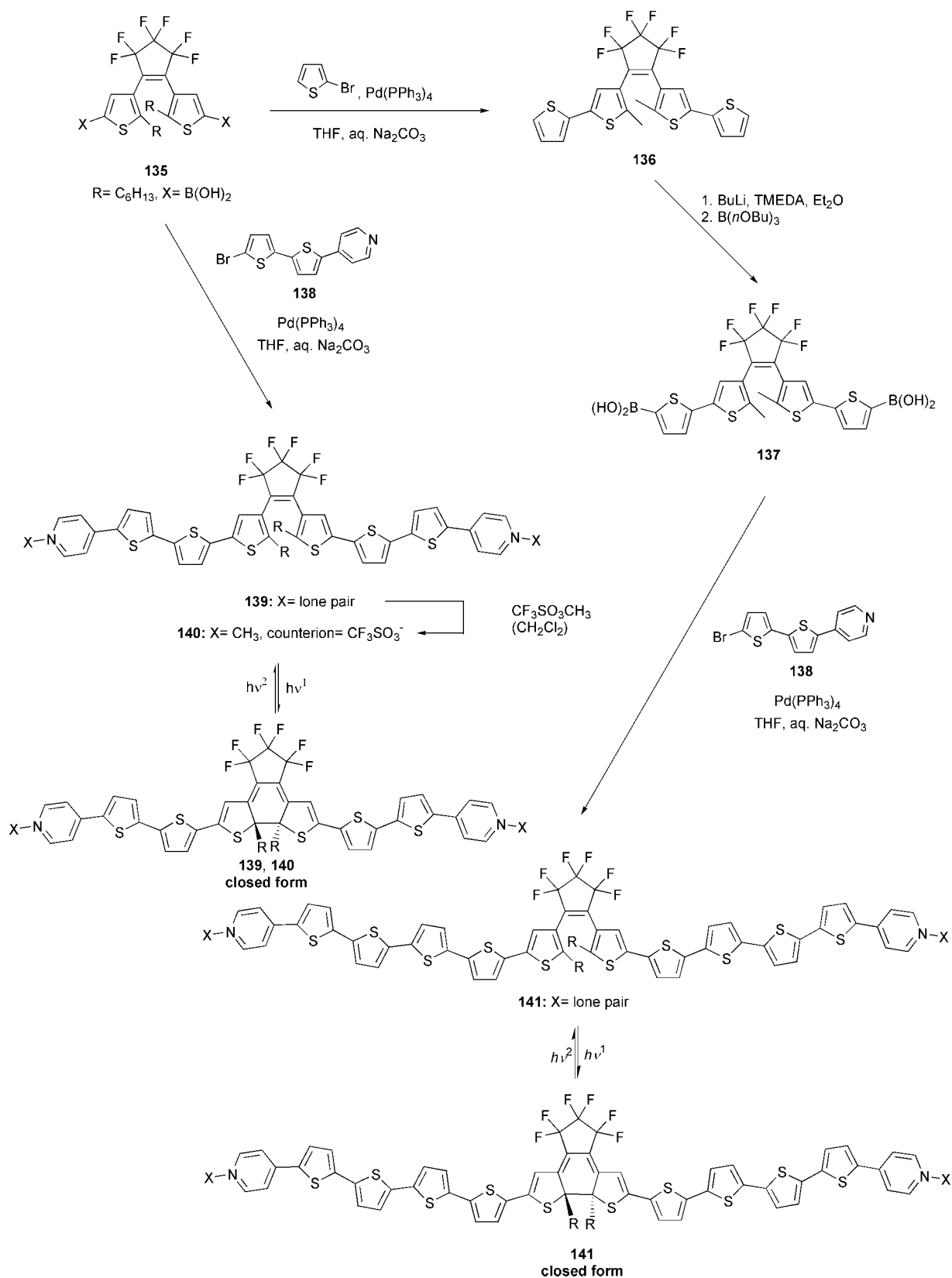
Fig. 17 Selected examples of π -extended TTF analogues containing oligoheteroarylene spacers.

saturation and therefore limits the cubic hyperpolarizability. However, as mentioned above, the presence of the acetylene bridge contributes to the large energy gap of these molecules, giving them improved transparency. These findings make them useful at wavelengths where polyenes are too strong absorbing.

Zhao *et al.* investigated the third-order nonlinearity of systematically derivatized and sequentially built oligothiophenes and oligophenylenes (Fig. 14).¹²¹

These authors found that, as for second-order NLO materials, the increase in the γ value with the number of phenylene units appears to level off at $n>3$ while no convergence γ value was observed for the oligothiophene series due, again, to the much more effective conjugation through the thiophene unit.¹²¹ On the other hand, the experimental results suggest that substitution by nitro and iodo groups enhances the third-order optical nonlinearity of the thiophene units.

Although other functionalized oligothiophenes,¹²² oligophenylenes¹²³ and oligo(phenylenevinylene)s¹²⁴ have been used as third-order NLO materials, and some preliminary structure–property correlations have been proposed, much work remains to be done to clarify and optimize the understanding of the structure–property relationships in order to provide the right tools to efficiently design novel



Scheme 17

structures to play an important role in the development of third-order NLO materials.

4.2 Photorefractive materials containing oligoarylene moieties

There are some materials that combine second-order NLO effects with photoconducting properties. They are the so-called photorefractive (PR) materials which have potential

application in holographic data storage. Storing information throughout the volume of a medium, rather than just on the surface, is an intriguing high-capacity alternative.¹²⁵ Recently, the photorefractive effect has been observed both in molecular organic systems¹²⁶ and polymeric materials.¹²⁷

A convenient approach to prepare PR polymers is to mix all the necessary molecular components into a polymer matrix, thus forming a composite. However, one major drawback of

these composite materials is their phase separation, caused, as mentioned earlier, by the incompatibility between small molecules and the polymer hosts. To minimize phase separation and, simultaneously, utilize the advantage of orientational enhancement, Yu and coworkers have designed and synthesized (Scheme 16) a simple, small molecular system (**132**) that connects covalently an NLO chromophore to a 3-alkylsubstituted oligothiophene.¹²⁸

The oligothiophene moiety plays a dual role as both the photocharge generator and the charge transporter while the electrooptic effect can be generated by aligning the dipoles of the NLO chromophore (D–A stilbene moiety) under an applied electric field. Furthermore, an amorphous film of this material can be prepared by sandwiching it between two indium tin oxide (ITO) glass slides. The films can be maintained in the amorphous state for a long time. This single molecular system exhibits large net optical gain coefficient and diffraction energy and studies of the dynamics of holographic gratings reveal that this material also has a fast response time to optical signals. In comparison with the parent polymeric materials, this type of multifunctional molecular system shows advantages in defining molecular structures and in the ease of purification and sample preparation.¹²⁸ This work paves the way for the future functionalization of new photoconductive oligoarylenes with different NLO chromophores.

4.3 Oligoarylene-containing organic molecules with large two-photon absorption cross sections

Molecular two-photon absorption (TPA) has found many applications over recent years, including optical power limitation,¹²⁹ three-dimensional optical data storage,¹³⁰ micro-fabrication¹³¹ and two-photon-excited fluorescence microscopy.¹³² In the presence of intense laser pulses, molecules can simultaneously absorb two or more photons, and the transition probability for absorption of two identical photons is proportional to I^2 where I is the intensity of the laser pulse.¹³³ It has been observed that the peak of two-photon absorption occurs at wavelengths significantly shorter than two times the one-photon absorption maximum, thus indicating that the two-photon state is energetically above the lowest B_u one-photon state. Furthermore, two-photon excited state absorption generates a larger 'effective' two-photon absorptivity when ns pulses are compared to ps pulses. Thus, there is an entry into the same excited state manifold as for one-photon optical limiting. This may have a profound influence on design criteria and the possibility that one chromophore may provide optical power limiting throughout the visible region, but by two different mechanisms.¹³⁴

The design of new chromophores with enhanced two-photon cross-sections, δ , has been lacking. However, in the last few years two groups have attempted to address the lack of such design paradigms. Reinhardt's group designed a series of molecules for use at 800 nm, and recognized the salient problem of how to increase the two-photon cross-section while maintaining λ_{\max} of the chromophores constant.¹³⁵ Thus, they identify as important parameters for an increase in the molecular two-photon absorption: (i) the extension of the conjugation length; (ii) the change in the identity of the conjugated bridge; (iii) the increase in the π -donor strength; (iv) the incorporation of more polarizable double bonds and (iv) the increase in the planarity of the chromophore.

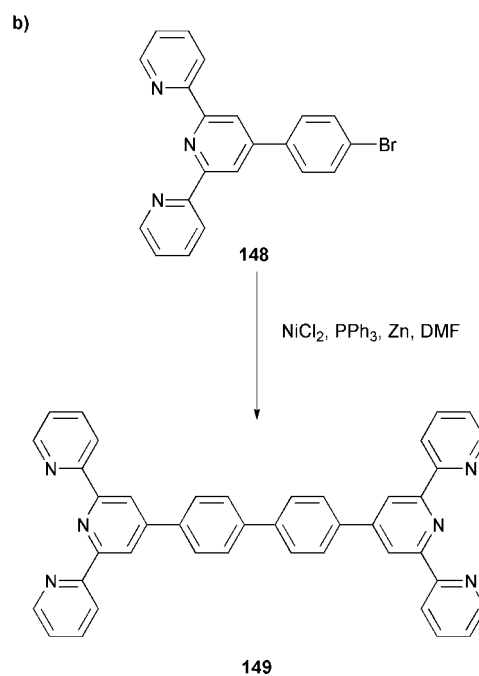
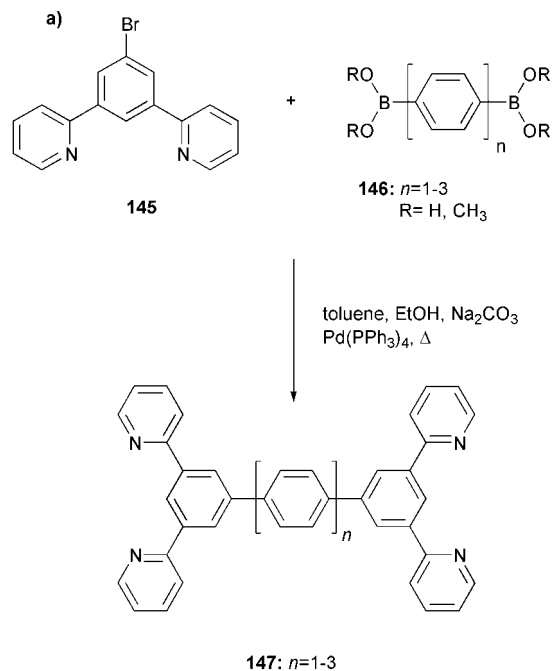
Perry, Marder and coworkers have identified similar design parameters, but based on their observation of the effect of strong donor substitution on stilbene derivatives.^{129b,133,136}

Two distinct chromophore types emerge from these studies:

Type 1: D–A–D

Type 2: A–D–A

Both types can be typified by suitable substituted oligo(phenylenevinylene) derivatives. Some representative examples of



Scheme 18

type 1 (**133**) and type 2 (**134**) oligomeric derivatives are depicted in Fig. 15.

Stimulated by the research work carried out by the above mentioned groups, other research groups have examined the two-photon-absorption properties in the conjugated oligoarylene series.^{134,137} However, some additional work should be dedicated to the synthesis of other oligomeric analogues following the design criteria outlined above (longer oligomers, more planar systems like ladder polymers, the incorporation of more polarizable spacers like the thiophene moiety) which will probably lead to systems with enhanced two-photon absorption properties. Moreover, as most of the chromophores recently reported as effective optical power limiters employed ns pulses and they will be probably ineffective against lasers employing microsecond pulses, the new chromophores should

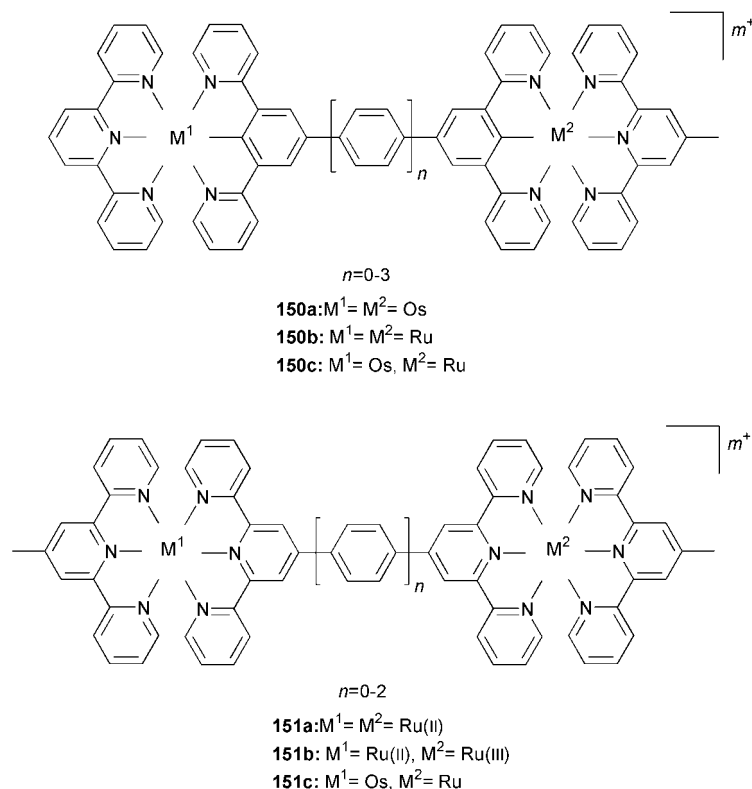


Fig. 18 Ruthenium and osmium complexes containing oligophenylene bridges.

be designed in order to be tested in the μs time domain. However, for two-photon absorptions (and other third-order nonlinear optical applications) conjugated oligomer-based systems probably cannot compete with “fully conjugated” polymers, but may rather be used as model systems.

4.4 Conjugated oligoarylenes as light driven molecular switches

Light-driven molecular switches have been recently reported to be interesting for numerous applications.¹³⁸ Of special interest is their use in optical information storage systems.¹³⁹ Materials used for these applications allow reversible modulation of a given electronic property by an external trigger which, in this case, is the light.

Among other interesting photochromic materials, diarylethenes, namely those bearing two thiophene derived groups, deserve special attention since they undergo a reversible electrocyclic interconversion between an unconjugated (open,

o) state and a colored, conjugated state (closed, c) under irradiation at well separated wavelengths (Fig. 16).¹⁴⁰

Lehn and coworkers have recently described the synthesis and some physicochemical properties of diarylethene-derived molecular switches containing functionalized oligothiophenes (**139–141**, Scheme 17).¹⁴¹ These systems represent a combination within the same entity of both the switching and the oligothiophene features and display, in the closed (c) form a total conjugation corresponding to about eight connected thiophenes (**141**).

The key compound **135** gives access to more complicated switch molecules with fewer steps by use of the well known palladium-catalyzed carbon–carbon bond formation. The presence of the pyridine moiety in peripheral positions of these molecular switches allows the synthesis of either neutral molecules (**139**, **141**) or, by methylation, to the parent pyridinium salt derivatives (**140**). In the case of compounds **139** and **141**, UV light was not necessary to

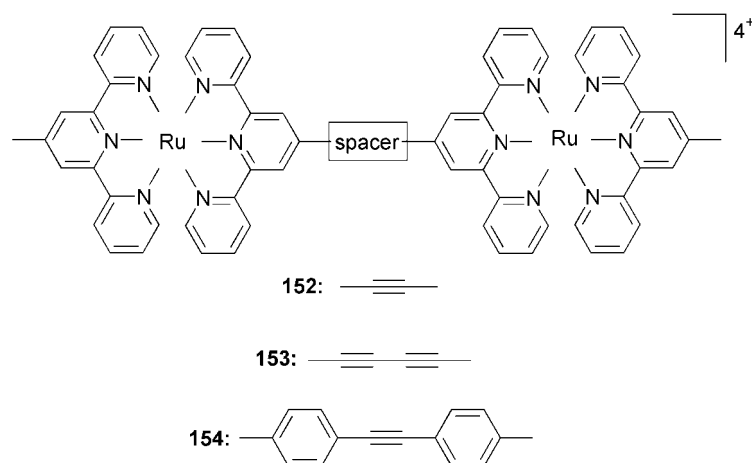
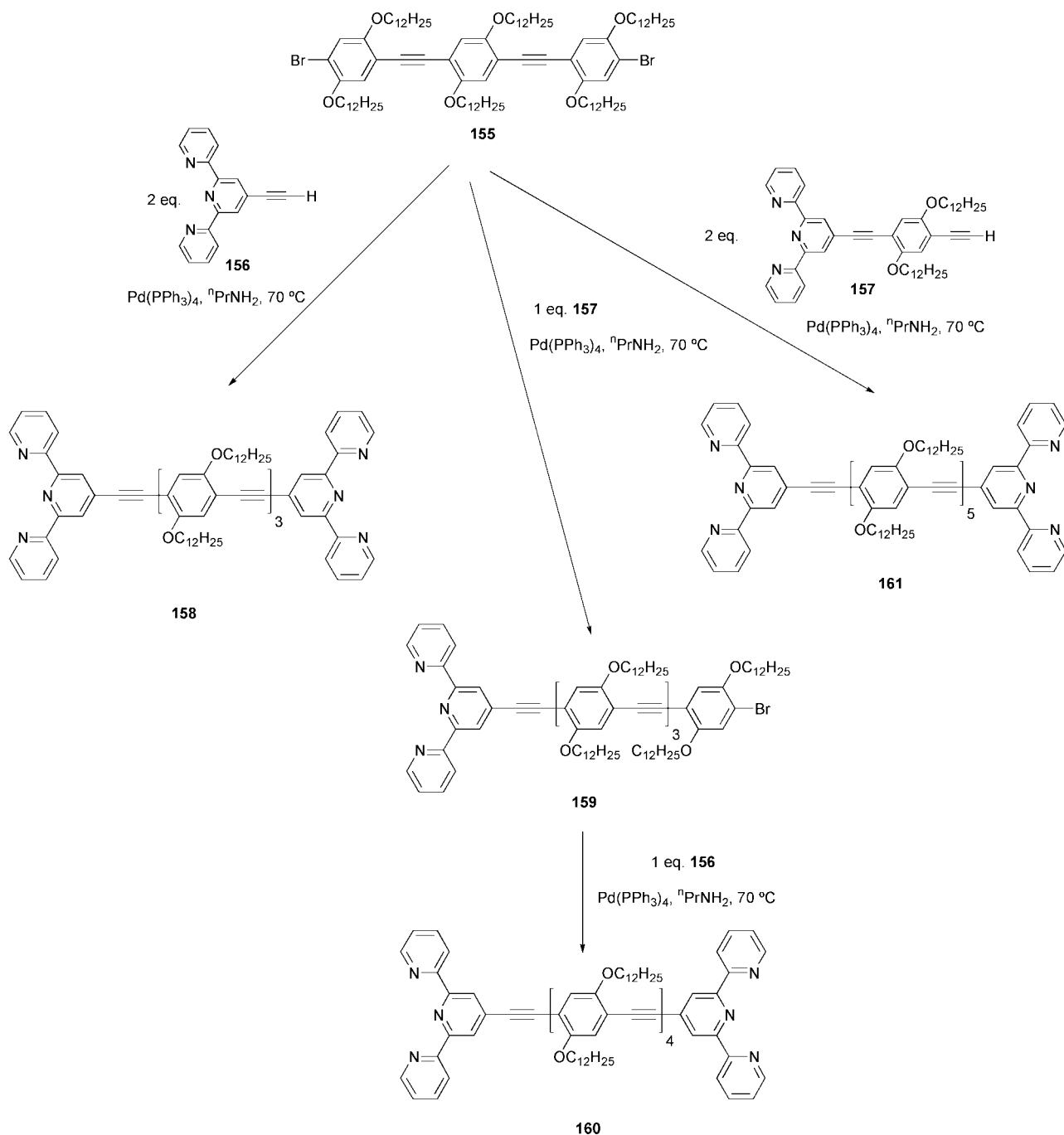


Fig. 19 Oligopyridine based ditopic ligands bridged by alkyne-containing spacers.



Scheme 19

obtain the closed forms: photoswitching between the open and closed forms could be achieved by irradiation with two different wavelengths of the visible region. Thus, the open forms could be generated by irradiation of the closed forms at a wavelength > 600 nm while subsequent irradiation of the open forms at a wavelength < 450 – 500 nm returned the compounds quantitatively. In the case of the methylated compounds, they opened quantitatively upon irradiation at a wavelength > 600 nm, but conversion to the closed forms could only be achieved by irradiation at around 330 nm. These molecular switches are found to display very large changes in fluorescence and in electrochemical properties in the open and closed forms due to the different levels of conjugation. Such changes represent photocontrol of electrochemical properties in the fashion of a photoswitched molecular wire.

Of special interest for their potential use in optical data storage would be compounds which absorb light strongly in the

near-infrared (NIR) region of the spectrum given that reading and writing is performed by diode lasers which operate in this region.¹⁴² Thus, the absorption wavelength tunability offered by the chemistry of conjugated oligomers should be considered in order to synthesize this type of molecular photoswitches exhibiting absorption in the NIR region.

5 Linearly extended tetrathiafulvalene (TTF) analogues with bridged π -conjugated oligoarylene spacers.

The study of tetrathiafulvalene (TTF, Fig. 17) and its derivatives has been the subject of unabated interest since it was first reported by Wudl in 1970.¹⁴³ For almost two decades TTF derivatives have been used as strong electron-donor moieties in charge-transfer (CT) complexes and ion radical salts exhibiting interesting electrical conducting and super-

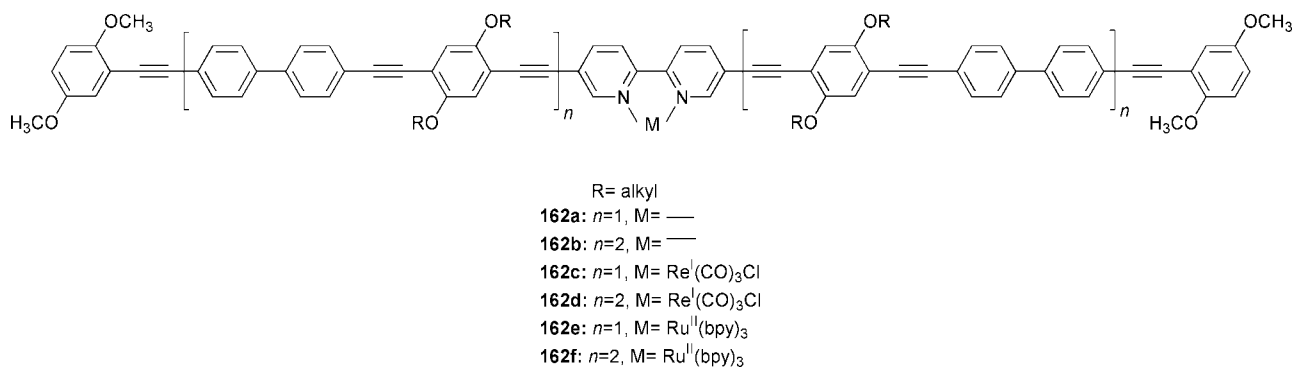


Fig. 20 Monodisperse oligo(phenyleneethynylene) derivatives containing metal–organic sites.

conducting properties. However, during the last few years, the utility of TTF (i) as a building block in macromolecular and supramolecular structures, (ii) as molecule-based ferromagnetic compounds, (iii) as synthetic intermediates in organic chemistry, (iv) as a donor moiety in intramolecular donor (D)–acceptor (A) systems including NLO materials and the important association with the fullerene core and (v) in the preparation of liquid crystalline materials and Langmuir–Blodgett (LB) films, has made of TTF one of the most extensively studied molecules.¹⁴⁴

Although different chemical modifications have been carried out on the TTF unit in order to prepare building blocks for macro- and supramolecular chemistry, the “classical” chemical modifications carried out on the TTF skeleton are aimed at increasing electrical conductivity.¹⁴⁵ Thus, one of the most effective strategies to produce CT complexes with high electrical conductivity involves the synthesis of TTF derivatives that allow enhanced dimensionality in the charge-transfer complexes.¹⁴⁶

TTF analogues with extended π -conjugation (Fig. 17) have been successfully used in the preparation of CT complexes with enhanced dimensionality. This specific approach has been considered in detail by Roncali¹⁴⁷ who has reviewed the synthesis of TTF analogues with polyalkene, heterocyclic, heterocyclic π -conjugated and other rigid π -conjugated spacers. Roncali points out that by precise control of the spacer length it should be possible to tune the conduction mechanism between the “vertical” mixed valence conduction of TTF charge-transfer salts and the “horizontal” polaron/bipolaron conduction on linear systems.

A logical extension of this strategy consists in the use of long conjugated oligoarylenes as spacer groups in order to achieve further improvement of π -donor ability and to increase the number of accessible cationic states. In Fig. 17 are depicted some representative examples (**142–144**) of TTF-analogues containing oligoheteroarylene spacers which can be easily synthesized by Wittig–Horner olefination reaction from the corresponding diformylsubstituted-conjugated oligomers and differently substituted phosphonate esters.

The use of oligothiophenes as π -spacers in π -extended TTF derivatives (**142**) decreases the oxidation potential and HOMO–LUMO gap of both constitutive building blocks.¹⁴⁸ However, interannular rotational disorder in the oligothiophene spacers appears to be a major obstacle to extensive π -delocalization. Consequently, more rigid spacers were incorporated between the thiophene units in order to increase effective conjugation. With this aim, derivatives **143** were synthesized.¹⁴⁹ Long alkyl chains were incorporated into the thiophene units in order to make soluble even the longer TTF analogues. Contrary to that observed for the parent analogues containing the oligothiophene spacers (**142**), the lengthening of the thienylenevinylene spacer does not lead to any apparent saturation of the effective conjugation up to the longest spacers analyzed. This fact is due to the more planar and more rigid

geometry of the oligo(thienylenevinylene) spacers. Interestingly, electrochemical studies carried out on derivatives **143** show that an increase in the number of thienylenevinylene units produces a positive shift of E_{red1} whereas E_{ox1} is quite independent of the chain length and remains at constant values. This result is due to the fact that the HOMO level of conjugated TTF analogs is essentially determined by the end 1,4-dithiafulvenyl groups. This means that the decrease in the HOMO–LUMO gap is caused only by a lowering of the LUMO level and therefore, as shown by the optical data in solution, a faster approach to the convergence limit of the effective conjugation length (ECL) takes place when compared with that observed for oligo(thienylenevinylene) analogues without the 1,4-dithiafulvenyl groups.

Preliminary attempts to synthesize radical cation salts of some of the shorter members of these series of compounds by using galvanostatic electrocrystallization produce an insulating material. This electrical behavior is due to the intercalation of the anion between donor dimers stacked which do not allow intra-stack-electron delocalization.¹⁴⁷ Further studies should be directed towards the influence of the length of the spacers on the crystal structure of these materials as well as on their potential electrically conducting behavior.

Another interesting approach has been the replacement of the thiophene-containing oligomers by furan-2,5-diylvinylene oligomers (**144**). The smaller aromatic resonance energy of furan should allow a further decrease of the overall aromatic character of the spacer and hence a better π -electron delocalization over the whole conjugated system may be expected.¹⁵⁰ In contrast to the oligo(thienylenevinylene) analogues, electrogenerated cation radical salts of some of these materials show a weak but significant electrical conductivity ($10^{-4} \text{ S cm}^{-1}$) probably due to the ease of formation of the dicationic state in these compounds which can contribute to some intrastack delocalization.

We have recently reported the use of naphthalene spacers to prepare π -extended TTF derivatives which form CT-complexes in combination with acceptor molecules such as TCNQ or DDQ.¹⁵¹ As we have recently developed a synthetic strategy towards the preparation of appropriately functionalized oligo(2,6-naphthylenevinylene)s,⁹² oligomeric analogues of the above molecules should be considered as a realistic goal. The structural study of these and other carbocyclic-containing π -extended TTF derivatives [like oligo(phenylenevinylene)s or oligo(phenyleneethynylene)s] will enable the determination of the influence of these π -extended systems on the solid state properties of these materials, including electrical conductivity.

6 Conjugated oligoarylenes incorporating ligand binding sites

Transition metal complexes are known to participate in a variety of processes involved in, for example, (i) solar light energy conversion, (ii) photocatalysis, (iii) artificial photo-

synthesis, (iv) chemosensors and ferromagnets. To be effective, it is necessary to optimize the choice of both the metal center and the coordinated organic framework.¹⁵² Thus, due to the interesting electronic properties exhibited by conjugated oligomers, the preparation of derivatives which incorporate metal ions as integral structural units represent especially interesting synthetic targets for further materials science applications. Substrates of this type would be expected to display a rich variety of physicochemical properties such as, for example, multiple redox behavior and optical, magnetic, mechanical, sensing and catalytic activity. The unique characteristics of particular metal ions may be harnessed to fine-tune the electronic properties of the conjugated organic component in order to perform a desired function.¹⁵³

Pyridine/benzene rods with biscyclometalating binding sites were reported by Sauvage and coworkers who first prepared 3,3',5,5'-tetra(2-pyridyl)biphenyl.¹⁵⁴ This group¹⁵⁵ also extended this rod by incorporating one, two or three phenylene spacers (**147**) using aromatic cross-coupling reactions between the diboronic acid derivatives (**146**) of the respective phenylene bridge and the brominated dipyridylbenzene (**145**) or its ruthenium complex¹⁵⁶ yielding the assembled dinuclear complex directly (Scheme 18a). Derivative **149** containing two terpyridyl units could be obtained *via* Ni(0)-promoted homo-coupling of 4'-(*p*-bromophenyl)-2,2':6',2''-terpyridyl (**148**, Scheme 18b).¹⁵⁷

Diosmium and diruthenium complexes **150a,b** could be subsequently prepared from **147** in which the metals are attached to the 4 and 4' positions of biphenyl and stabilized by the surrounding pyridine units. On the other hand, both the dinuclear Ru(II)/Ru(II) complexes **151a** and the mixed valence species **151b** (Fig. 18) were prepared from the complete tridentate terpyridyl-based series **149** with metal-to-metal distances of 7–20 Å.¹⁵⁸ Barigletti *et al.* used these rods to assemble the mixed-metal complexes (**151c**) and investigated both their luminescence and electrochemical properties.¹⁵⁹

It was observed that the much higher electron donor character of the anionic phenyl bridging ligands and the short Ru–C(phenyl) bonds lead to substantially increased metal–metal interactions in derivatives **150** relative to the analogous systems in which the *meta*-terpyridine moieties are chosen for metal coordination **151**.¹⁶⁰

During the last decade, Ziessel and coworkers have been very active in the design and synthesis of multitopic ligands.^{152,161} They have been specially engaged with the development of oligopyridine-based ditopic ligands bridged by alkyne spacers comprising several ethynyl groups (**152**, **153**, Fig. 19). The spacer serves as both a rigid girder to maintain structural integrity and a conduit for electron flow. The alkyne bridge actively promotes long-range electronic coupling between remote cationic units, especially under illumination with visible light. They have observed that the level of electronic communication along the molecular wire can be controlled by insertion of suitable insulating groups into the bridge. Thus, the presence of phenyl rings between the acetylenic units (**154**) severs electron delocalization along the wire.

By careful design, it has been possible to introduce directionality and selectivity in this type of photoactive dyads being consequently able to modulate the rate of triplet energy transfer by several orders of magnitude.¹⁶² An emerging problem of increasing the size of the system is the lowering of solubility. Thus, Ziessel and Khatyr have achieved solubility and tunability for an increasing number of oligophenyleneethynylene derivatives containing two back-to-back terpyridines (**158**, **160**, **161**) by functionalizing the phenylene rings with two dodecylene moieties (Scheme 19).¹⁶³

The synthetic strategy used to synthesize these derivatives involves the use of palladium promoted coupling reactions of terminal alkynes (**156**, **157**) with oligophenyleneethynylenes end-capped with bromine atoms (**155**, **159**). This family of

ditopic ligands allow to tune the edge-to-edge distance between the two central pyridine rings from 16 to 44 Å. To the best of our knowledge, there are no reports about the metal-to-metal interactions in metal complexes of the longest members of this series. The introduction of other carbocyclic units between the acetylenic bridges should be studied in order to tune the electronic coupling between orbitals on the acetylenic function and other arylene units which will allow to tune the metal–metal interaction in this type of system.

Other researchers have been engaged with the study of conjugated oligomers containing more than two metal ion-binding sites. Thus, Schanze and coworkers have recently synthesized a series of π -conjugated polymers that incorporate a metal–bipyridine chromophore directly into a poly(phenyleneethynylene) polymer.¹⁶⁴ In order to better understand the optical properties of these metal–organic π -conjugated materials they have also synthesized a series of monodisperse oligo(phenyleneethynylene) derivatives containing metal–organic sites (**162a–f**, Fig. 20) as models for the structurally related polymers.¹⁶⁵

Comparison of the UV–Vis spectra of the free oligomers (**162a,b**) with those of the corresponding (L)Re(CO)₃Cl (**162c,d**) and (L)Ru(bpy)₂²⁺ (**162e,f**) complexes demonstrates that metallation induces a substantial red-shift of the lowest absorption. The low energy band likely arises from a long-axis polarized π, π^* transition localized predominantly on the chromophore defined by the bis(dioctadecyloxyphenylethynyl)-capped bipyridine segment. The transition is red-shifted because metallation forces the bipyridyl unit into a planar conformation, thereby effectively increasing the conjugation length. Thus, the use of a variety of metal cations in combination with conjugated oligomers comprising electronically communicating ion-binding sites can be envisaged as a new tool for synthetic chemists to efficiently tune the physicochemical properties of these compounds for specific materials science applications.

7 Outlook

The very large number of studies dedicated to the synthesis of conjugated oligoarylenes and to the examination of their properties has made it possible to choose oligomers according to need to a degree that is amazing in some occasions. By choice of the appropriate arylene units, linkages and number of repeating units, an extraordinary control on the photophysical and electrochemical properties of these materials can be achieved. Synthetic strategies have been also developed that allow enhanced solubility, thermal stability and processability of these materials and therefore, in addition to serving as models for higher polymeric forms, these oligomeric structures have become more important in their own right.

The incorporation of different low molecular weight oligoarylenes either as side chains or as a part of the main chain in conjugated–non-conjugated block copolymers has already proved to be an effective way to combine the control of the conjugation length characteristic of molecular systems with processability properties of polymeric materials. They have been successfully used in the fabrication of light emitting devices in which the emission color, electron affinity and ionization potential can be tuned by choice of appropriate conjugated oligomers and non-conjugated spacers.

Only a few examples of oligoarylenes functionalized with dendritic substituents have been reported. Nevertheless, these systems present high interest given that they may allow supramolecular control of interchain interaction which will permit the development at will of either compact materials favoring interstack interactions or, in contrast, avoid interstack interactions thus favoring the behavior of the systems as single molecular wires.

Synthetic strategies have been developed that allow the incorporation of different functionalities in oligoarylenes for specific applications. Photoinduced electron and energy transfer have been reported for molecular dyads and triads bearing conjugated oligoarylenes covalently linked to electron acceptor systems like C₆₀ or porphyrin systems and donor moieties like anthracene or dialkylamines.

As a result of intensive research efforts, some fundamental relationships between properties and the molecular structure of oligoarylene-containing materials have emerged. Thus, the bases for the development of improved oligoarylene-based materials for NLO and two-photon absorption have been settled and certainly a lot of work will be devoted to this task in the next few years.

A number of tasks still remain to be performed before the bright prospects of conjugated oligoarylenes can be realized. Of the wide variety of systems that have become available, only a few have been extensively studied, and the best materials for each specific application are yet to be identified. The study of most of these applications is a multidisciplinary area and, consequently, the efforts of synthetic chemists to prepare a variety of materials exhibiting any specific property have to be complemented by the work of applied physicists and materials scientists in order to find the optimum device structures to maximize device performances.

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