Synthesis, processing and properties of conjugated polymer networks

Christoph Weder*

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Despite the diverse research activities focused on the chemistry, materials science and physics of conjugated polymers, the feature of conjugated cross-links, which can provide electronic communication between chains, has received little attention. This situation may be a direct consequence of the challenge to introduce such links while retaining adequate processability. Focusing on recent studies of materials for which charge transport or electrical conductivity data are available, this feature article attempts to present an overview of the synthesis, processing and electronic properties of conjugated polymer networks. For the purpose of this discussion, two distinctly separate architectures—featuring covalent cross-links on the one hand and non-covalent organometallic bridges on the other—are treated in separate sections. The available data indicate that cross-linking can have significant benefits for intermolecular charge transfer if the polymers are carefully designed.

Introduction: why conjugated polymer networks are of interest

Charge transport in conjugated polymers

Since the discovery of electrical conductivity in π-conjugated polymers three decades ago,[1] semiconducting polymers have become the focus of major research and development activities around the globe.[2] The excitement for this new generation of polymeric materials reflects their potential to combine the processibility and outstanding properties of polymers with the exceptional, readily-tailored electronic and optical properties of functional organic molecules. Their potential applications, especially as synthetic metals,[3] and as organic semiconductors in light-emitting diodes,[4] field-effect transistors,[5] photovoltaic cells,[6] sensors[7] and other devices have motivated the development of synthesis and processing methods of conjugated polymers with unique electronic properties. Breathtaking progress has been made, and "plastic electronics" technology has matured beyond the onset of commercial exploitation[8] of conjugated polymers into a variety of applications that range from corrosion control[9] to light-emitting diodes.[4] One key problem for the full technological exploitation of polymer semiconductors, however, is that they display generally a much lower charge carrier mobility, μ, than inorganic materials,[10] and hence also a decreased electrical conductivity σ (which is proportional to μ). This limitation is related to the fact that the charge transport in conjugated polymers is a function of *intra*-chain charge diffusion and *inter*-chain interactions, *i.e.* hopping.[11] The charge carrier mobility in these materials is usually limited by disorder effects, which prevent efficient inter-chain coupling and lead to materials with one-dimensional electronic properties.[12–15] Exciting progress has been documented for polymers with high degrees of supramolecular order, and in some cases orientation.[16–22] For example, disordered, amorphous samples of poly(3-alkylthiophene)s (PATs) display a hole mobility in the order of $\sim 10^{-5}$ cm^2 V^{-1} s^{-1}; this value is increased up to ~ 0.2 cm^2 V^{-1} s^{-1} in semi-crystalline films of PATs in which π-stacked conjugated polymer lamellae are organized parallel to a substrate and allow for highly efficient in-plane charge transport.[16,17,21,22] At the same time, a significant improvement is observed in the electrical conductivity. For example, the electrical conductivity of iodine-doped poly(2,5-dimethoxy-*p*-phenylene vinylene) fibers was shown to increase from 20 to 1200 S cm^{-1} upon uniaxial orientation by tensile deformation.[23] In another exemplary study, Sirringhaus *et al.* exploited the liquid crystalline (LC) character of a 9,9-dioctylfluorene-bithiophene copolymer.[19] In this case, the LC polymer was uniaxially oriented with the help of an alignment layer, and the polymer was quenched into a nematic glass that displayed significantly enhanced carrier mobilities of up to 0.02 cm^2 V^{-1} s^{-1} along the alignment direction. Thus, the process of ordering/orienting conjugated polymers indeed affords materials with significantly improved charge carrier

Department of Macromolecular Science and Engineering, Case Western Reserve University, 2100 Adelbert Road, Cleveland, OH 44106-7202, USA. E-mail: christoph.weder@case.edu; Fax: (+1) 216 368 4202; Tel: (+1) 216 368 6374

Christoph Weder is Associate Professor of Macromolecular Science and Engineering at Case Western Reserve University in Cleveland, Ohio. Weder was educated at the Swiss Federal Institute of Technology (ETH) in Zürich where he earned his academic degrees from the Departments of Chemistry (Dipl. Chem.) in 1990 and Materials (Dr. sc. nat.) in 1994. After an appointment as a postdoctoral fellow at the Massachusetts Institute of Technology, Weder returned to ETH in 1995 when the Department of Materials appointed him firstly as head-assistant and lecturer, and then in 1999 after completion of his 'Habilitation', as an independent lecturer. He moved to Case in 2001, where he established the Functional Polymer Laboratory. Weder's primary research interests are the design, synthesis and investigation of the structure–property relationships of novel functional polymers, in particular, materials with advanced optic or electronic properties.

mobility and electrical conductivity. It should be noted, however, that many of the processing protocols employed for the fabrication of materials with a high degree of order and orientation[24] are incompatible with the preferred low-cost processes of plastic electronic manufacturing, for example spin-coating,[25] inkjet[26] and screen printing.[27] On the other hand, there are important exceptions to this notion; a prominent example is the inkjet printing of the aforementioned thermotropic LC materials, which has allowed the fabrication of all-polymer transistors with appreciable device characteristics.[26a]

An orthogonal approach for improved charge transport

The introduction of π-conjugated cross-links between conjugated macromolecules represents an attractive alternative approach for the designing of semiconducting polymers with improved charge transport characteristics.[28] Indeed, in an ideal π-conjugated macromolecular network that features *conjugated* cross-links (Fig. 1), intra-chain diffusion may become the predominant mechanism for charge transport, while inter-chain processes—if at all—only play a subordinate role. An important prerequisite for this mechanism is that the electronic potentials of the cross-links (*i.e.*, HOMO and LUMO or electron affinity and ionization potential) match those of the linear segments, so that these moieties do not serve as traps or barriers for the charge carriers, but rather allow for adequate electronic coupling. As shown in Fig. 1, the networks can be designed to rely on either covalent or non-covalent interactions. The first case is based on the introduction of a conjugated tri-functional (or higher functionalized) monomer along with the conventional bi-functional monomers (Fig. 1a, left). Obviously, this approach ultimately leads to an intractable polymer network, which has to be processed prior to or during network formation. A variation of this strategy is a two-stage process, in which linear precursor macromolecules with cross-linkable functionalities are first prepared, processed and subsequently cross-linked (Fig. 1a, right). Networks based on physical cross-links (*e.g.*, hydrogen bonds, electrostatic interactions or chain entanglements) represent architectures in which non-covalent interactions lead to potentially very useful properties,[28b] but the exact nature and influence of the cross-links is often ill-defined and makes the elucidation of structure–property relationships difficult. Therefore, the present review emphasizes the important class of organometallic networks that are formed through coordination bonds between ligand sites comprised in the organic semiconductor and metallic cross-links (Fig. 1b). These metallopolymers are also intractable but are accessible either *via* ligand-exchange reactions (Fig. 1b, left) or, alternatively, by the polymerization of pre-fabricated ligand–metal complexes (Fig. 1b, right).

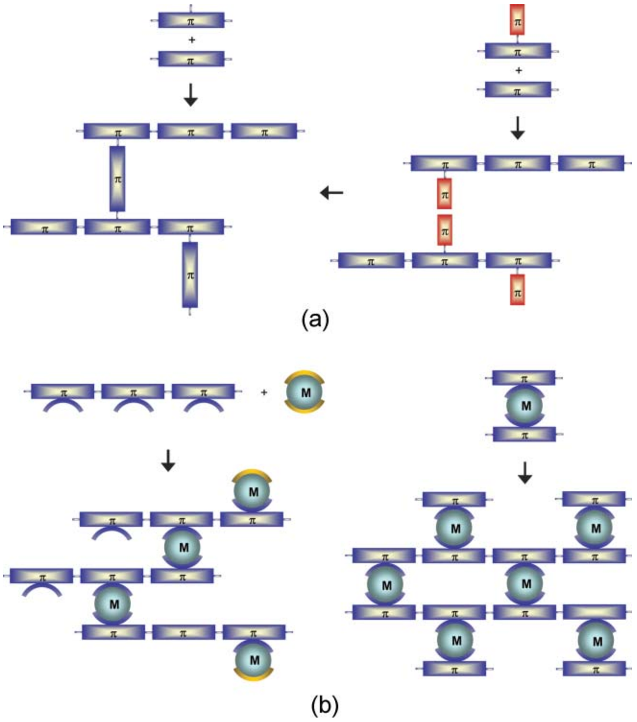


Fig. 1 Simplified schematic representation of cross-linked conjugated polymer networks with covalent (a) and non-covalent organometallic cross-links (b). In the case of covalent networks, one-step (left) and two-step protocols (precursor approach, right) are commonly employed. Organometallic networks can be prepared by ligand-exchange reactions (left) or the polymerization of a pre-fabricated ligand–metal complex (right).

Scope of this review

Interestingly, despite the diverse research activities focused on the chemistry, materials science and physics of conjugated polymers, the feature of conjugated cross-links has received little attention, at least as far as systematic studies and well-defined materials are concerned. This situation may be a direct consequence of the challenge of introducing such cross-links and retaining adequate processability. On the other hand, in many cases, the exact structure of the cross-linked semiconducting polymers is not known. While conjugated polymer-based networks featuring *non-conjugated* cross-links based on covalent[29] or non-covalent bonds[30] have been deliberately prepared and studied by a number of research groups, examples of cross-links that might allow adequate electronic transport between chains are rather rare, and in many cases have been obtained serendipitously and/or lack unambiguous characterization. Focusing on selected recent examples of materials for which charge transport or electrical conductivity data are available, and whose chemical structure has been appropriately established, this review attempts to present a concise overview of the synthesis, processing and electronic properties of conjugated polymer networks. For the purpose of discussion, two distinctly separate architectures—featuring covalent cross-links on the one hand and non-covalent organometallic bridges on the other—are treated in separate sections. The available data indicate that cross-linking can have significant benefits for intermolecular charge transfer if the polymers are carefully designed.

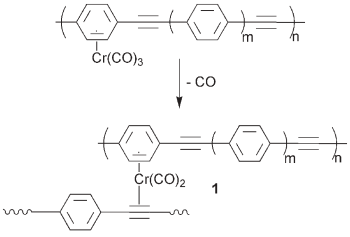
Networks based on organometallic cross-links

Electronic communication between metal and polymer

The general approach of introducing transition metals into conjugated polymers has received considerable attention, in particular due to the potential of manipulating the electronic properties of these materials.[31–36] Conventional concepts for the design of π-conjugated metallopolymers rely on either the incorporation of metal centers into the polymer backbone, their coordination to the conjugated backbone, or their attachment *via* conjugated or non-conjugated spacer units in the form of side groups. The different mechanisms of electrical conduction in metallopolymers have recently been discussed in a scholarly manner by Swager and Holliday.[37] Classic electron transfer theory[38] distinguishes two different situations—outer and inner sphere transfer—depending on the electronic coupling between the orbitals of the transition metal and those of the conjugated macromolecules. In the case of outer sphere transfer, the metal and delocalized polymer orbitals lack significant mixing (systems in which the metal is attached to the conjugated polymer backbone *via* a non-conjugated spacer typically fall into this category), and as a result, the transition metals may not be intimately involved in the overall charge transport. By contrast, inner sphere transfer, which is of interest here, is observed for systems with strong overlap between the orbitals of the metal and conjugated macromolecules.[39] This can be the case if the metal centers form part of the polymer backbone or coordinate directly with the latter. Importantly, a matching of the energies of the involved orbitals (macroscopically manifested by matched redox potentials or valence and conduction bands) is important for efficient transport through the polymer–metal complex; this mechanism is also referred to as superexchange.[33,40] Mismatched energies, in contrast, can deteriorate the charge transport, since charge localization caused by the metal centers may lead to charge trapping.

Networks prepared by ligand-exchange reactions

As mentioned heretofore, cross-linked organometallic polymers are intractable, *i.e.* non-melting and insoluble materials. Ligand-exchange reactions between a linear conjugated polymer that comprises adequate ligand sites and a metal complex with, ideally weakly bound, low-molecular weight ligands represents one important possibility for preparing thin films of these polymers (Fig. 1b, left). Another possibility is the polymerization of pre-fabricated ligand–metal complexes (Fig. 1b, right). One of the earlier examples of the formation of organometallic conjugated networks by the ligand-exchange approach was reported by Wright.[41] His experiments suggested that upon thermal treatment or UV irradiation of solid thin films of poly(arylene ethynylene)s containing the $Cr(CO)_3$–benzene moiety, cross-linking occurred upon loss of CO with the formation of phenylene–$Cr(CO)_2$–ethynyl moieties (**1**, Scheme 1). Speculating that multi-coordination permits electronic communication between the metals through the π-conjugated chains, Hirao *et al.* described, among other systems,[42] the synthesis of organometallic networks of poly(*o*-toluidine) with Pd^{2+} or Cu^{2+} coordinating to the imine moieties in the polymer (**2**, Chart 1).[43] Unfortunately, the electronic properties of these polymers have remained largely unexplored.



Scheme 1 Cross-linking reaction proposed to occur in solid thin films of poly(arylene ethynylene)s containing the $Cr(CO)_3$–benzene moiety upon heating.[41]

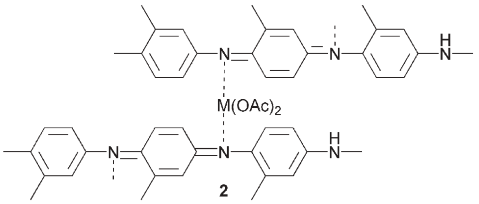
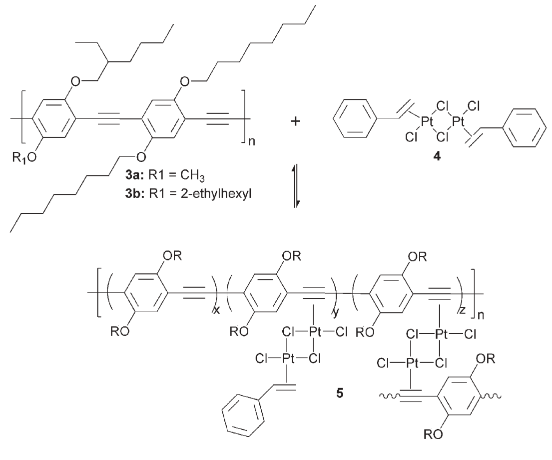


Chart 1

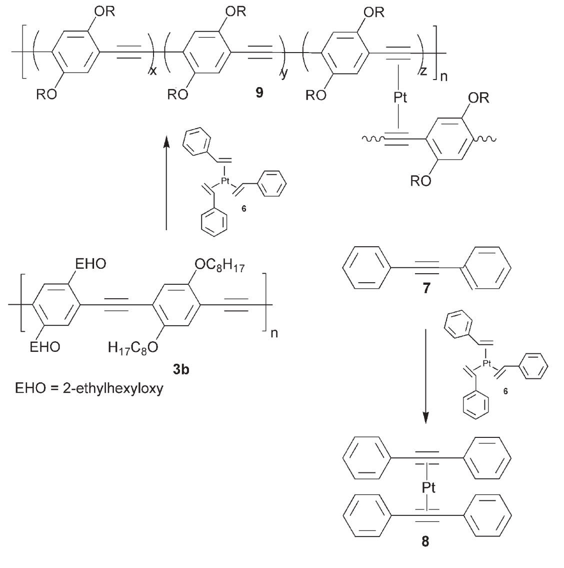
In another study, we demonstrated that the unsaturated carbon–carbon bonds in the backbone of poly(*p*-phenylene ethynylene)s (PPEs) can be utilized as quite a versatile binding motif.[44–46] The conjugated polymers employed were the alkoxy-substituted PPEs, **3**,[47,48] which are representative of this family of conjugated polymers with well-documented optoelectronic properties,[49] and offer two ethynylene moieties per repeating unit as potential ligand sites (Scheme 2). In the initial experiments dinuclear $[Pt\text{-}(\mu\text{-}Cl)Cl(PhCH{=}CH_2)]_2$ (**4**)[50] was employed as the cross-linker. The ethynylene groups comprised in the PPE were shown to readily coordinate to Pt^{2+} in exchange for weakly-bound styrene ligands.[44] An extensive *in situ* ^{195}Pt NMR study revealed that in dilute $CHCl_3$ solutions the equilibrium of the investigated PPE–Pt systems dictates non-cross-linked structures (Scheme 2, **5**, $z \approx 0$). Importantly, under these conditions, the system remains homogeneous and therefore processible. Evaporation of the solvent leads to a shift of the equilibrium to PPE–Pt network structures (Scheme 2, **5**, $z > 0$), and due to its volatile nature, the liberated styrene ligand is also removed during this process.[44] Spin-coating resulted in films of good optical



Scheme 2 Ligand-exchange reaction between PPE **3a** and $[Pt\text{-}(\mu\text{-}Cl)Cl(PhCH{=}CH_2)]_2$ (**4**), leading to cross-linked metallopolymers **5**.[44]

quality that were unequivocally cross-linked. As expected, the coordination of Pt^{2+} markedly influences the photophysical characteristics of the PPE; the photoluminescence is quenched upon complexation, and at high Pt contents, the absorption maximum experiences a hypsochromic shift. Clearly, the Cl-bridged dinuclear cross-links originally employed cannot be expected to provide significant π-conjugation between chains. Indeed, time-of-flight (TOF) measurements conducted as a function of carrier type, electric field, sample thickness and Pt content[51] suggest that the photocurrents observed for thin films of **5** (**3b**–Pt^{2+}) are range-limited, indicating trapping of both electrons and holes in this material. In earlier work on linear Pt^{2+}-containing poly-ynes, π-conjugation was found to be preserved through the metal atom; however the hybridization between the π-orbitals of the polymer ligand and the platinum 5d orbitals was found to be weak.[52]

In subsequent experiments, Pt^0 was chosen as the cross-linker, since it forms stable bis(ethynylene) complexes,[53] which due to the interaction of the π bond of the ligand with the $d_{x^2-y^2}$ orbital of the Pt or *via* π-backbonding from the d_{xz} orbital of Pt to π* orbitals of the ligands, may allow for electronic conjugation.[52,54] A styrene solution of $Pt(styrene)_3$ (**6**) served as the Pt^0 source,[55] and model reactions with diphenylacetylene (DPA, **7**) confirmed that even in the presence of a ~150-fold excess of styrene, the ligands of **6** are quantitatively replaced by **7**, and the only product formed is $Pt(DPA)_2$ (Scheme 3, **8**).[56] The analogous reaction between PPE **3b** and **6** was accomplished by combining styrene solutions of these reactants (Scheme 3);[45,46] the ratio of the molar concentrations of Pt^0 and phenylene ethynylene (PE) moieties, $[Pt^0]/[PE]$, was varied between 0.016 : 1 and 0.34 : 1; in the following such ratios are expressed as single numbers, *e.g.* 0.016 and 0.34. Spin-coating and solution casting yielded homogeneous thin films of the cross-linked metallopolymer **9** (Scheme 3). The carrier mobility of a series of metallopolymers **9**[46] and the uncomplexed PPE **3b**[57] was determined by TOF measurements as a function of carrier type, electric field and Pt^0 content. The shape of the photocurrent transients of **3b** and **9** ($[Pt^0]/[PE]$ = 0.17), shown in Fig. 2, is characteristic of dispersive transport.[58] This mechanism is typical for materials with a high degree of spatial and/or energetic disorder, and is concomitant with a wide variation of local transport rates.[59] High electron (1.9×10^{-3} cm^2 $V^{-1}s^{-1}$) and hole (1.6×10^{-3} cm^2 V^{-2} s^{-1}) mobilities were found at low electric field strength (3.8×10^4 V cm^{-1}) for the neat **3b**. The data shown in Fig. 2 and Fig. 3 demonstrate that the carrier mobility strongly increases upon introduction of Pt^0. A distinct enhancement of the mobility was observed for **3b**–Pt^0 with a small $[Pt^0]/[PE]$ value, but the effect levels off at a $[Pt^0]/[PE]$ ratio of ~0.17 when charge carrier mobilities of 1.6×10^{-2} cm^2 V^{-1} s^{-1} (electrons) and 1.4×10^{-2} cm^2 V^{-1} s^{-1} (holes) are reached. These values are an order of magnitude higher than those of the neat PPE. Interestingly, the enhancement is similarly pronounced for electron and hole transport; thus the metallopolymers **9** are very effective ambipolar semiconductors. The charge carrier mobility of polymers **9** was found to decrease with increasing bias (Fig. 3). This behavior is consistent with a hopping transport model that accounts for off-diagonal (positional) disorder caused by variations in the inter-site distances, in addition to diagonal (energetic) disorder in the transport manifold.[60] The large



Scheme 3 Ligand-exchange reaction between $Pt(styrene)_3$ (**6**) and PPE **3b** or diphenylacetylene (**7**), leading to cross-linked metallopolymers **9** and model compound bis(diphenylacetylene)platinum (**8**), respectively.[46,56]

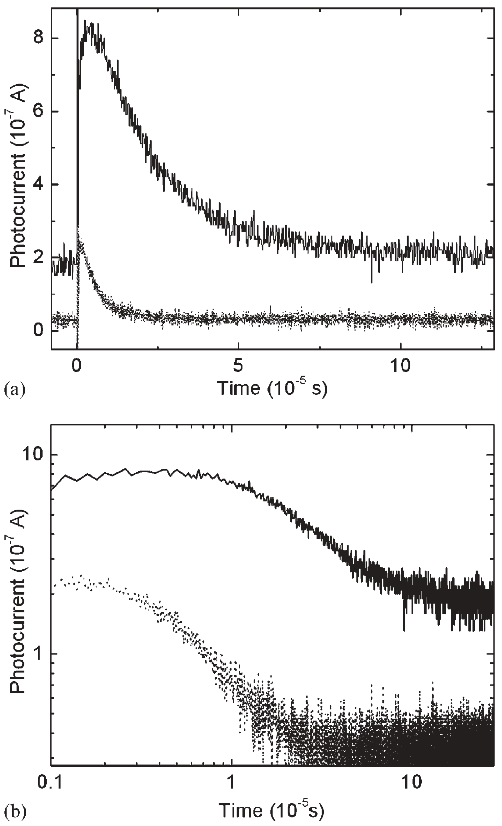


Fig. 2 Electron TOF photocurrent transients of PPE **3b** (solid line, film thickness L = 8 μm) and metallopolymer **9** (dotted line, L = 30 μm, $[Pt^0]/[PE]$ = 0.17) films in linear (top) and logarithmic (bottom) plots, measured at a temperature of 295 K and an electric field of 1.5×10^5 V cm^{-1}. Reproduced with permission from Ref. 46.

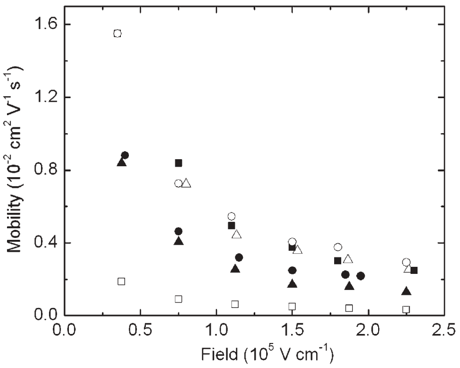
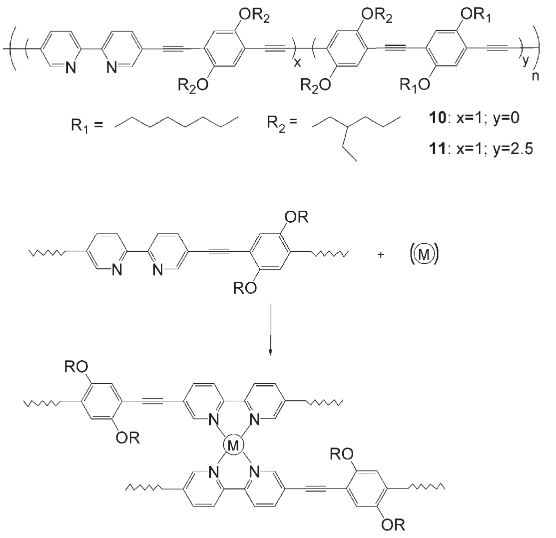


Fig. 3 Electron mobility of metallopolymer **9** as function of [Pt^0]/[PE] and electric field ([Pt^0]/[PE]: □ = 0, ▲ = 0.016, ● = 0.086, △ = 0.17, ■ = 0.25, ○ = 0.34). Reproduced with permission from Ref. 46.

off-diagonal disorder results in a negative field dependence of the mobility at low fields, because a stronger field favors forward hopping and inhibits faster routes for carriers involving hops transverse to the applied electric field.

With the notion that other examples of suitable bis-(η^2-diphenyl ethynylene)metal complexes, which could provide electronic conjugation between chains, are rare,[61] 2,2′-bipyridine (Bipy) moieties were introduced as auxiliary ligands into the backbone of PPEs.[62] This versatile ligand[63] has already been introduced into a plethora of macromolecules that form the basis of a number of metallo-supramolecular systems.[34] Pioneering work on PPEs with Bipy groups in the polymer backbone and *linear* metal complexes of these polymers has been carried out by the groups of Schanze[64] and Klemm.[65] Interestingly, the metal-complexed PPEs investigated in these studies were almost exclusively prepared by polymerizing metal-complexed monomers, rather than by complexation of the Bipy-containing polymer with metals. However, the latter framework, which—mainly with sensor applications in mind and not under consideration of potential network formation—has been applied by a number of groups for a variety of other conjugated polymers,[66–71] is formidably suited to preparing metallo-supramolecular PPE networks. Systematic ligand-exchange reactions were conducted with PPEs containing different fractions of the Bipy moiety (BipyPPEs **10**, **11**) and a variety of metal complexes (Scheme 4).[62] For example, BipyPPE–Cu^+ networks were prepared *via* the complexation of **10** (a copolymer featuring phenylene ethynylene and bipyridine moieties in an alternating fashion) with $[Cu^I(CH_3CN)_4]PF_6$. UV-vis absorption and photoluminescence (PL) emission spectra, acquired upon titrating **10** with $[Cu^I(CH_3CN)_4]PF_6$ in $CHCl_3$–CH_3CN (15 : 1 v/v), are shown in Fig. 4. The intensity of the characteristic π–π* transition around 423 nm, associated with the conjugated backbone of **10**, systematically weakened upon addition of Cu^+, and a new band at *ca.* 452 nm developed that was interpreted as being due to a metal-to-ligand charge transfer complex.[62] As can be seen from the inset in Fig. 4a, the intensity of the transition at 452 nm steadily intensified with increasing [Cu^+] : [Bipy] ratio, before levelling off at a [Cu^+] : [Bipy] ratio of about 0.5. Similarly, the polymer's PL was gradually quenched upon



Scheme 4 Schematic representation of the formation of metallo-supramolecular networks through the complexation of 2,2′-bipypridine-containing poly(2,5-dialkyloxy-*p*-phenylene ethynylene)s **10** and **11** with transition metals.

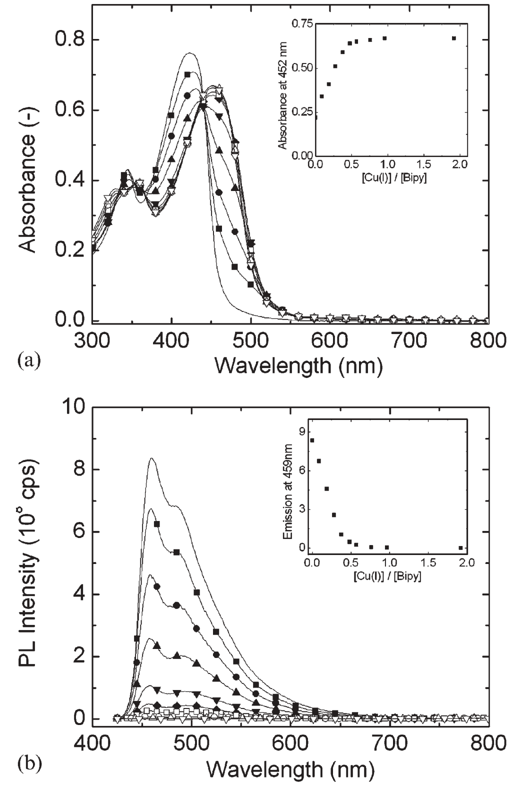


Fig. 4 UV-vis absorption (top) and PL emission (bottom) spectra acquired upon addition of tetrakis(acetonitrile)Cu^I-hexafluorophosphate to BipyPPE **10** (concentration of polymer-bound Bipy = 1.93 × 10^{-5} M) in $CHCl_3$–CH_3CN (15 : 1 v/v). Shown are spectra at selected [Cu^+] : [Bipy] ratios of 0 (—), 0.09 (■), 0.19 (●), 0.28 (▲), 0.38 (▼), 0.48 (◆), 0.57 (□), 0.76 (○), 0.96 (△) and 1.92 (▽). The insets show the absorption at 452 nm (a) and the emission at 459 nm (b) as a function of [Cu^+] : [Bipy] ratio.

addition of $[Cu^I(CH_3CN)_4]PF_6$ (Fig. 4b). Scatchart plots of the data presented in Fig. 4 are characteristic of positive cooperative binding,[72] and the observed changes in the UV-vis and PL spectra were fully reversible upon addition of a competing ligand, such as free bipyridine, to the system. Thus, these results are consistent with the (reversible) formation of BipyPPE–Cu^+–BipyPPE cross-links between the conjugated macromolecules and point to relatively large binding constants. The fact that changes in the optical spectra level off at a metal–ligand ratio of 0.5 clearly indicates the formation of 2 : 1 ligand–metal complexes, which in turn suggests the formation of well-defined network structures. The fact that the partially metallated polymer retained a significant extent of PL emission (Fig. 4b) is indicative of a limited exciton migration along the polymer to the non-radiative low band gap sites. This feature appears to be related to the "de-conjugated" nature of uncomplexed, twisted Bipy moieties that cause "optical insulation" and allow the coexistence of multiple chromophores on the same macromolecule. Their weak electronic coupling is in marked contrast to the PPE-based polymer systems reported by Swager and co-workers, which act as "molecular wires" and display energy migration through conjugated segments that comprise up to ~50 repeat units.[73] The complexation of BipyPPEs **10** and **11** with the perchlorates of Co^{2+} and Ni^{2+} led to very similar optical changes to those found in the case of Cu^+. Interestingly, the addition of $Zn(ClO_4)_2$ or $Cd(ClO_4)_2$ caused a somewhat more pronounced change to the absorption band than did Cu^+, Ni^{2+} or Co^{2+}, and in the case of both metals, broad structure-less emission bands centered at 619 (Zn^{2+}) and 591 nm (Cd^{2+}) developed. These results reflect the fact that Zn^{2+} and Cd^{2+} both exhibit a fully occupied d-orbital (Zn^{2+}: $3d^{10}$, Cd^{2+}: $4d^{10}$) that frequently displays a weak tendency for the formation of metal-to-ligand charge transfer.[74] Hence, the complexation of these metals with Bipy-containing polymers does not usually lead to MLCT complexes.[70] Rather, the optical changes appear to be related to a significant reduction of the polymers' π–π* transition on account of a planarization of the Bipy moiety,[67,68] as well as an electron density variation upon complexation with the electron-poor metals.[70] In view of the fully occupied d-orbital of the metal, the observed emission cannot be related to a d–d transition, but appears to be caused by intra-ligand π–π* transitions.

Networks prepared by polymerization of pre-fabricated metal–ligand complexes

The polymerization of pre-fabricated metal–ligand complexes (Fig. 1b, right) represents another framework for the synthesis of cross-linked metallopolymers. If no co-monomer is employed as a linear chain extender, the cross-link density of the resulting materials is usually very high. As will become evident from the examples presented here, virtually all materials synthesized by this approach were prepared by electrochemical polymerization; the thiophene (or oligothiophene) moiety, which can usually be polymerized by electrochemical means through oxidative coupling at the α (strongly favored) or β position,[35] has been the most popular motif as far as the organic conjugates segment is concerned. It should be noted that the electrochemical polymerization method is a very convenient general methodology that allows the facile preparation of laboratory-scale thin films of high quality, but its usefulness appears to be more limited when it comes to the commercial production of electronic polymers.

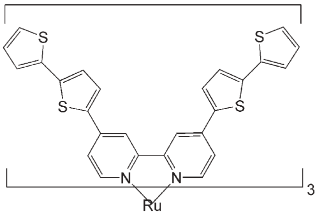

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Chart 2

Swager's group has reported the investigation of a series of polythiophene–$Ru(bpy)_3$ hybrid materials.[75] These polymers were synthesized by the electrochemical polymerization of $Ru(bpy)_3$ derivatives that were appended with bithienyl moieties (*e.g.*, **12**, Chart 2). The choice of $Ru(bpy)_3$ centers as the redox component is the result of the broad manifold of reversible redox processes associated with this type of complex that make redox matching with the polymer likely. On the other hand, the electrochemical polymerization of the bipy-bridged bithienyl monomers was found to proceed smoothly for both the free ligand as well as the metal complex. Comparative experiments led to the conclusion that cross-linking in these polymers is an important contributor to high conductivity. Indeed, the highest electrical conductivity (3.3×10^{-3} S cm^{-1}, determined as in many of studies reviewed in this section, by *in situ* conductivity experiments[76]) was reported for poly-**12** (Chart 2).[75b] The cyclic voltammograms of poly-**12** display both metal-centered and thiophene-based electroactivity, and similarly high redox conductivities were observed for the thiophene-based oxidation and metal-based reduction processes. Poly-**12** is highly cross-linked and, in contrast to other members of the investigated series, possesses a 4,4′-substitution pattern of the Bipy moiety that allows effective orbital overlap between the polythiophene segments and the d_{xz} and d_{yz} orbitals of the ruthenium centers, and therefore electronic transport through the organometallic segments.

Wolf *et al.*[35,77] studied a series of polythiophenes that were cross-linked *via* different Pd complexes. In this case, the approach relied on the electropolymerization of monomers **13–15** (Chart 3), in which 3′-diphenylphosphino-2,2′:5′2″-terthiophene moieties were coordinated in three different modes with the metal. All three monomers could be polymerized to yield thin films that displayed an *in situ* conductivity of between 10^{-4} (poly-**15**) and 10^{-3} S cm^{-1} (poly-**13**) when oxidized. Based on comparative studies with analogous monomers, in which one or both of the terthiophene's α-positions were blocked with methyl groups and—where possible—oligomers thereof, the authors concluded that the role of the metal is largely inductive in case of poly-**13**, which features a dinuclear Pd complex. Charge transport in this material presumably results from delocalization along the extended polythiophene chains and π-stacking, rather than

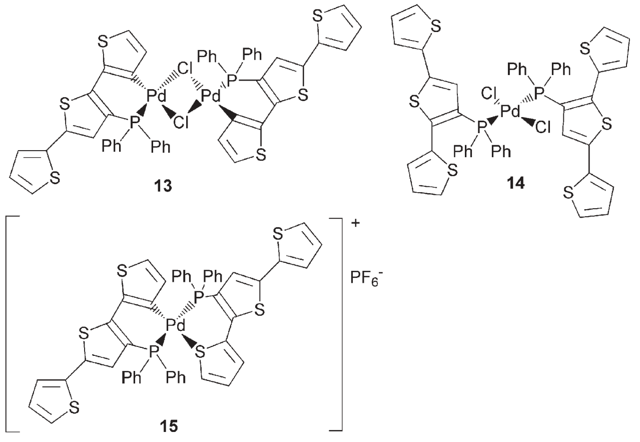


Chart 3

through the metal cross-links. On the other hand, the conductivity is thought to involve a contribution from cross-metal delocalization in the case of poly-**15**, but the effect appears to be rather small.

The groups of Pickup[78] and Skabara[79] have electropolymerized bis[1,2-di(2-thienyl)-1,2-ethenedithiolene]nickel[78] (**16**) and bis[(terthiophene)dithiolene]complexes[79] containing Ni^{2+}, Pd^{2+} or Au^{3+} (**17**) (Chart 4). The conductivities of this series of metallopolymers, determined by impedance spectroscopy, are in the range of *ca.* 10^{-6} to 10^{-5} S cm^{-1} in a potential range of 0 to +1 V, and around 10^{-4} S cm^{-1} (poly-**16**) in a potential regime where the polymer is oxidized. Films of poly-**17** show only one redox wave for the metal dithiolene unit, which is less reversible than in the monomer, suggesting that there is little electronic communication between adjacent metal units.[78]

Vidal *et al.* investigated polythiophenes that comprised the 1,10-phenanthroline moiety as a ligand.[80] Entwined architectures around copper ions were obtained by dimerizing monomers **18** and **19** by complexation with Cu^+ and electropolymerization of the entwined intermediates **20** and **21** (Scheme 5). Interestingly, electrochemical studies coupled with *in situ* conductivity experiments and X-ray absorption spectroscopy revealed rather different electronic properties for poly-**20** and poly-**21**. In their oxidized states, poly-**18** and poly-**20** display similar conductivities, in the order of 10^{-4} S cm^{-1}. The experiments clearly demonstrated that the conductivity of poly-**20** is related to transport through the conjugated organic segments and that no significant electronic interactions between the metal and the polymer occur. The case of poly-**21** clearly contrasts with that of poly-**20**. The cyclic voltammograms (CVs) of poly-**21** suggest a mixing of the redox processes associated with the copper and the conjugated organic parts. *In situ* conductivity experiments revealed a stable potential window of high conductivity that corresponds to the oxidation of the polymer; the level of conductivity (9×10^{-4} S cm^{-1}) was found to be an order of magnitude higher than that of poly-**18**, poly-**19** or poly-**20**. De-metallated films of poly-**21** showed a significant decrease in conductivity. Thus, the work nicely demonstrates charge transport between chains through the copper centers.

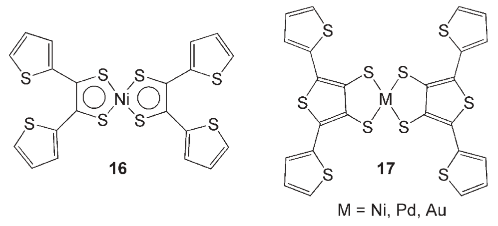
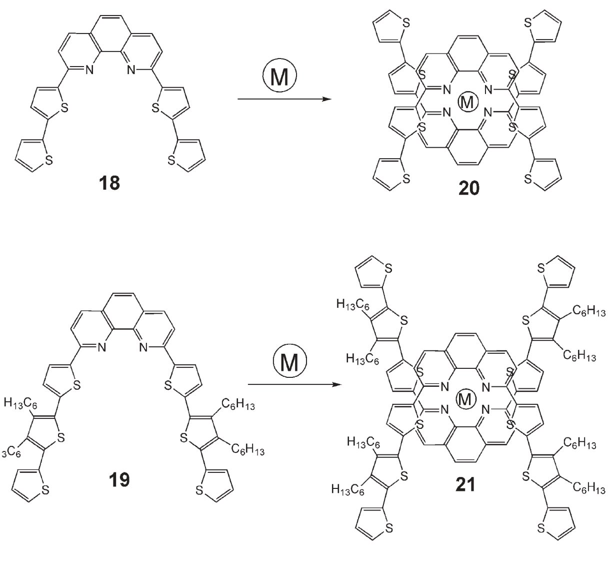


Chart 4

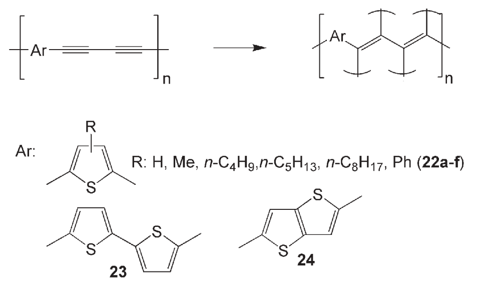


Scheme 5 Schematic representation of the formation of entwined precursors *via* dimerization of **18** and **19** through complexation with Cu^+.

Networks based on conjugated covalent cross-links

Precursor approach

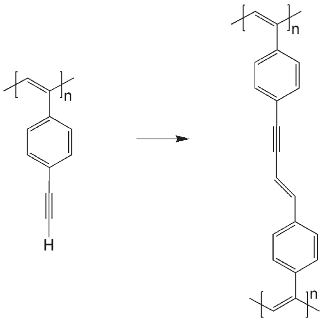
Conjugated polymer networks with covalent cross-links can be synthesized and processed into the scientifically but also technologically-relevant shape of thin films (and other shapes), using different strategies. One approach is the so-called precursor approach, a two-stage process, in which well-defined linear precursor macromolecules with cross-linkable functionalities are first prepared, processed and subsequently cross-linked (Fig. 1a). Some of the earlier comprehensive studies on the synthesis and characterization of "hypercross-linked" conjugated polymers by this approach were reported by the groups of Whitesides[81] and Stille.[82] Their work was based on low-molecular weight conjugated precursor polymers and oligomers comprising thermally cross-linkable diacetylene groups and a variety of different aromatic moieties. As far as electronic transport is concerned, the most comprehensive data sets are available for the poly(2,5-ethynylenethiophene)s, **22**, and the related materials **23** and **24** shown in Scheme 6.[82] Derivatives of **22**, in which the aromatic moiety was additionally derivatized with alkyl chains, were soluble and could be appropriately characterized and processed into thin films by spin-coating or solution casting. Thermal treatment allowed for solid state cross-linking at moderate temperatures (150–200 °C). Based on ^{13}C CP-MAS studies, the principal structure of the resulting cross-links was identified as



Scheme 6 Formation of diene-containing, hypercross-linked networks by thermal cross-linking of poly(2,5-ethynylenethiophene)s **22** and related materials **23** and **24**.[82]

a diene-containing material (Scheme 6). The intrinsic conductivities of the un-doped linear (*i.e.* not cross-linked) polymers **22–24** were in the range 10^{-13}–10^{-11} S cm^{-1}, *i.e.*, at the lower end of the semiconducting regime. Doping with iodine led to a modest increase in conductivity (10^{-11}–10^{-8} S cm^{-1}), while the use of arsenic pentafluoride, which is a stronger oxidant than I_2, afforded semiconducting materials with conductivities in the range of 10^{-8}–10^{-6} S cm^{-1}. Rather interestingly, the conductivities of the cross-linked products of **22–24** in their un-doped states varied over several orders of magnitude; in some cases, the cross-linked product displayed a significantly higher conductivity than the un-reacted parent (*e.g.*, **22a**, 10^{-8} *vs.* 10^{-13} S cm^{-1}). This behavior is consistent with the formation of defects upon thermal cross-linking that may act as charge carriers. On the other hand, the doping of cross-linked materials with AsF_5 did not increase their conductivity beyond the values observed for the similarly-doped linear polymers. This result was explained by the lack of interaction between the polymers and the dopant due to a relatively high oxidation potential of the polymer on the one hand, and the potential inability of the counterion (AsF_6^-) to become incorporated in the polymer matrix on the other. The data, unfortunately, do not allow a conclusion to be drawn about whether or not the cross-linking imparts the charge transport between chains.

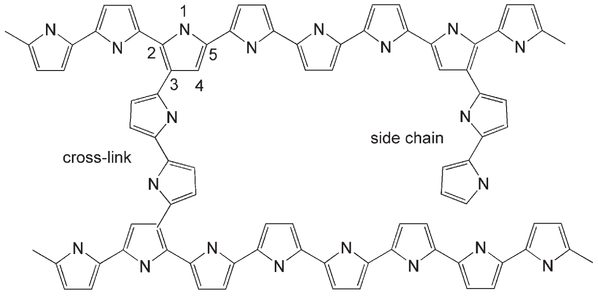
Another example for the precursor approach comes from Lavastre *et al.*, who reported the formation of conjugated polymer networks through the heat treatment of poly[(4-ethynyl)phenylacetylene] (Scheme 7).[83] The cross-linking reactions were studied *via* thermoanalytical techniques (DSC and TGA) and the resulting insoluble products characterized by means of infrared spectroscopy. Based on the IR data and by comparison with earlier work, the generation of ene–yne fragments was suggested as the result of the cross-linking reaction. Unfortunately however, no charge mobility or conductivity data have been reported for this system.



Scheme 7 Cross-linking reaction proposed to occur in poly[(4-ethynyl)phenylacetylene] upon thermal treatment.[83]

Conjugated polymer networks by one-step protocols

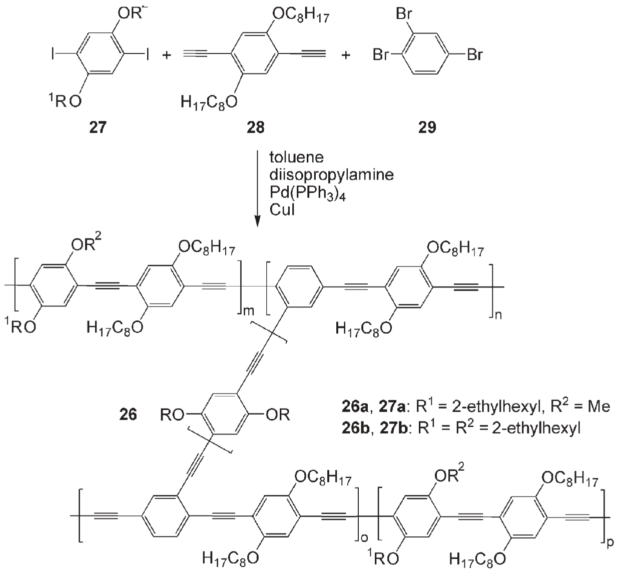
A variety of protocols have been employed for the preparation of cross-linked conjugated polymer thin films by one-step protocols, including electrochemical methods and the processing of dispersions. In an important study, Joo *et al.* have compared the electronic characteristics of different polypyrrole samples that were synthesized electrochemically and chemically, and feature different degrees of conjugated side chains and/or cross-links (**25**, Chart 5).[84] X-ray photoelectron spectroscopy suggests that a significant fraction of the pyrrole units not only react in the 2,5 positions to form linear macromolecules, but that side reactions in the 3-position lead to branching or cross-linking between chains (Chart 5). While the analytical techniques employed in this study did not allow an unambiguous discrimination to be made between (originally unintentionally introduced) side chains and cross-links, a clear difference between the investigated samples was evident; about 20% of the pyrrole moieties of chemically prepared, dodecylbenzenesulfonic acid (DBSA)-doped polypyrrole were incorporated in side chains or cross-links, while that fraction was increased to about 33% in the case of electrochemically prepared, PF_6^--doped polypyrrole. In a systematic study, the authors have related these structural differences to the electronic properties of these polymers. For chemically synthesized polypyrrole samples that were doped with DBSA or naphthalenesulfonic acid (NSA) the dc conductivity was $\leqslant 0.1$ S cm^{-1} at room temperature, and their temperature dependence displayed a strong localization behavior. By contrast, the dc conductivity of electrochemically synthesized polypyrrole doped with hexafluorophosphate (PF_6^-) was in the critical or even metallic regime (50 S cm^{-1}) and displayed a much higher density of states than the chemically synthesized samples. Thus, the highest conductivities were found for the material (electrochemically prepared, PF_6^--doped polypyrrole) for which the highest density of cross-links and side chains was observed. The results suggest improved inter-chain interactions for this system and agree with the expectation of percolation of the metallic state with increasing cross-link density.



25

Chart 5

We recently embarked on the synthesis of poly(*p*-phenylene ethynylene)[49] networks with covalent cross-links.[85,86] These polymers (**26**) were synthesized by the palladium-catalyzed cross-coupling polycondensation of 1,4-diiodo-2,4-dialkoxybenzenes (**27**), 1,4-diethynyl-2,5-bis-(octyloxy)benzene (**28**) and various quantities (ratio of **27** : **29** = 0.1–10) of 1,2,4-tribromobenzene (**29**) as a cross-linker (Scheme 8).[85] The reaction may allow linear PPE segments of appreciable molecular length to grow before cross-linking, because the reactivity of the aryl bromide in the cross-coupling reaction is lower than that of the aryl iodide.[87] If the polymerization was carried out under conventional reaction conditions (*i.e.* in homogeneous toluene–diisopropylamine solutions), the reaction mixtures gelled after a relatively short reaction time. Consistent with the anticipated network structure, the products thus prepared did not dissolve but swelled significantly (between *ca.* 300–600% w/w) in chloroform and toluene, both of which are good solvents for the linear polymer. These conjugated polymer networks were highly luminescent when swollen and their photoluminescence spectra were very similar to those of their parent linear PPE. As mentioned heretofore, the potential usefulness of the cross-linked polymers under investigation in actual devices depends on the ability to process these materials into thin films (and possibly other shapes). One approach to accomplishing this objective follows the general framework routinely employed for standard thermoset polymers, and is based on the simultaneous polymerization and processing of the material into the desired shape. Indeed, it was shown that cross-linked coherent thin films can be produced by casting the reaction mixture and conducting the polymerization reaction while shaping the object.[85] An alternative to overcoming the problem of processing is to synthesize the cross-linked target polymers in the form of spherical particles that can be processed from (aqueous) dispersions. By applying concepts employed for the preparation of dispersions of *linear* conjugated polymers[88] and exploiting the fact that some metal-catalyzed cross-coupling reactions are tolerant to the presence of water,[89] it was shown that cross-linked conjugated polymer particles can be conveniently produced by polymerization in aqueous emulsions.[86] The size of the resulting particles could be readily tuned over a wide range (nm to mm) by modifying the reaction conditions (Fig. 5). For example, micrometer-sized particles were obtained by carrying out the polymerization of monomers **27–29** in a vigorously-stirred water–toluene–diisopropylamine mixture, utilizing sodium dodecyl sulfate (SDS) as a surfactant. The mixture formed an oil-in-water emulsion and most of the reactants and catalysts were presumably dissolved in the organic phase. The polymer produced was precipitated and isolated as a dry powder, but the product could readily be re-dispersed into well-separated particles by ultrasonication in solvents such as toluene (without further surfactant addition), as shown by the micrographs in Fig. 5. As can be seen from Fig. 5, the size distribution of the polymer particles produced was relatively narrow, with an average diameter of ~4.7 μm. The chemical composition of the polymer was comparable to that of the homogenous reaction product, and elemental analysis revealed that the SDS content of the final product was very low.[86] To further reduce the average particle size, the polymerization reaction was conducted under the emulsion conditions outlined above, but with an ultrasonic bath employed instead of a mechanical stirrer and the concentration of the surfactant was increased. Scanning electron microscopy pictures (Fig. 5) confirm that



Scheme 8 Synthesis of cross-linked PPEs **26** by the palladium-catalyzed cross-coupling reaction of 1,4-diiodo-2,4-dialkoxybenzenes (**27**), 1,4-diethynyl-2,5-bis-(octyloxy)benzene (**28**) and various amounts (ratio of **27** : **29** = 0.1–10) of 1,2,4-tribromobenzene (**29**). **26a**, **27a**: R1 = 2-ethylhexyl, R2 = Me; **26b**, **27b**: R1 = R2 = 2-ethylhexyl.[85,86]

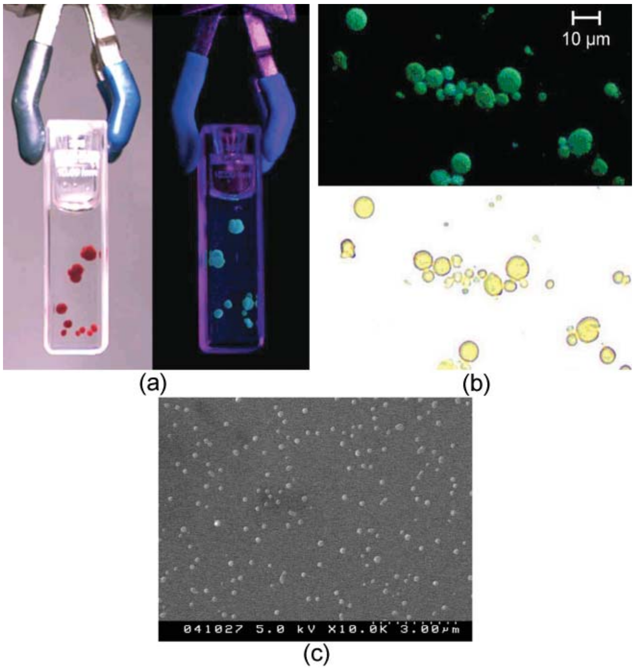


Fig. 5 Photograph (a), optical micrograph (b) and scanning electron micrograph (c) of cross-linked conjugated milli- (a) micro- (b), and nanoparticles (c) prepared by emulsion polymerization according to Scheme 8. Photographs and optical micrographs were taken in fluorescence mode under excitation at 366 nm and in transmission/reflection mode, with the polymer particles dispersed in toluene. (a) and (b) are reproduced with permission from Ref. 86.

cross-linked nanospheres with a diameter between *ca.* 50 and 400 nm and a narrow size distribution can be produced by this method. The resulting polymer particles were processed into homogeneous thin films by casting dispersions of these materials in toluene.[51] It appears that this general approach is universally applicable to many polymer systems. Preliminary TOF measurements revealed a charge carrier mobility of *ca.* 7×10^{-3} cm^2 V^{-1} s^{-1} for holes and 9×10^{-3} cm^2 V^{-1} s^{-1} for electrons at low electric field strength (3.8×10^4 V cm^{-1}) for polymer **26b**.[51] These values are significantly higher than those of the linear polymer **3b** at the same field strength (1.6×10^{-3} cm^2 V^{-2} s^{-1} for holes and 1.9×10^{-3} cm^2 V^{-1} s^{-1} for electrons), suggesting that the cross-linking gives rise to improved inter-chain interactions for this system.

Concluding remarks

In view of the fact that intermolecular charge transport has long been recognized as an important factor for the overall conductivity of conjugated polymers, and with the notion that much of the early work on these materials was directed at developing a fundamental understanding of the structure–property relationships in these materials—in particular the factors which promote high electrical conductivity—it is quite surprising that the knowledge base regarding the effect of conjugated cross-links is still rather limited. However, the experimental examples compiled in this review demonstrate that conjugated polymer networks with well-defined chemical structures can be synthesized and processed by a variety of approaches. The available data indicate that this structural motif can have significant benefits for the electronic communication between chains if the polymers are carefully designed. Future work in this area may further exploit this potential and lead to the next generation of higher performance organic semiconducting materials.

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