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Conjugated metallopolymers. Redox polymers with interacting metal based redox sites

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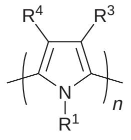
Hybrid materials which combine the electronic conductivity of conjugated polymers and the redox and optical properties of metal complexes are being developed to take advantage of synergistic electronic interactions. Many systems show a splitting of the metal redox wave analogous to that in dinuclear complexes with through-ligand metal–metal interactions (superexchange). The influence of the conjugated backbone on electron transport between metal centres has been the focus of much work, and the existence of a superexchange pathway has been demonstrated. Several systems have been shown to exhibit catalytic and photocatalytic activities, and a number of applications in sensors have been described.

Introduction

Widespread interest in redox polymers dates from the early 1980s when it was realized that the chemical modification of electrode surfaces would open up important new areas of science and technology.[1] The coating of electrodes with electroactive polymers was found to be a versatile and convenient strategy for endowing them with new electrocatalytic, optical, electronic, sensing, and charge/information storage properties.[2–4]

The first generation of redox polymers[2] included the following five main groups of materials:
(a) conjugated organic polymers such as polypyrroles **1**, polythiophenes **2**, and polyanilines **3**;[5,6]
(b) saturated organic polymers with pendent transition metal complexes, such as polyvinylferrocene **4** and metal complexes of polyvinylpyridine[7] **5**;



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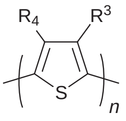

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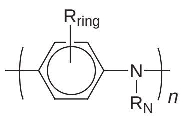

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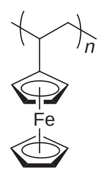

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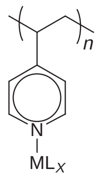

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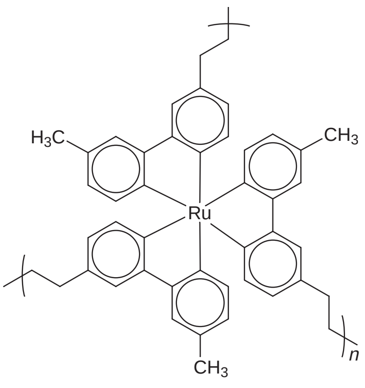

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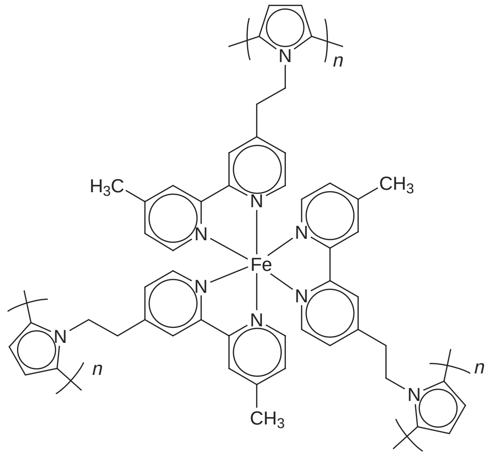

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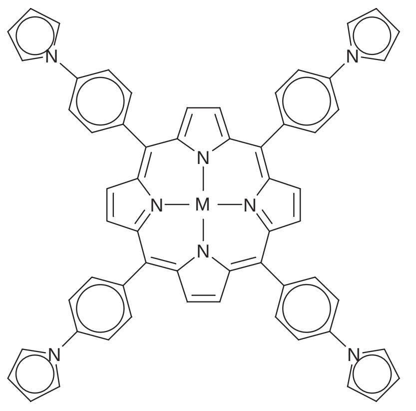
(c) electrochemically polymerized transition metal complexes with multiple polymerizable ligands, such as poly[ruthenium(4-vinyl-4′-methyl-2,2′-bipyridine)$_3$$^{2+}$] **6**,[8] poly[iron(4-(2-pyrrol-1-ylethyl)-4′-methyl-2,2′-bipyridine)$_3$$^{2+}$] **7**,[9] and poly-[tetra(4-pyrrol-1-ylphenyl)porphyrin] (poly-**8**).[10] These differ from the polymers in group (b) in that they do not contain extended organic chains. The complexes are linked in a 3-D network primarily by intermolecular dimerization of the ligands;
(d) saturated organic polymers with pendent electroactive organic moieties,[2] such as poly(4-nitrostyrene) **9**;
(e) ion exchange polymers containing electrostatically bound electroactive ions, such as Nafion containing $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine), and quaternized polyvinylpyridine containing $Fe(CN_6)^{3-/4-}$.

More recently, there has been growing interest in a new type of redox polymer that is a hybrid of materials from groups (a) and (b) and will be referred to as conjugated metallopolymers. Examples include metal complexes of poly(2,2′-bipyridine) **10** and the polyferrocenes **11**. The key feature of this class of material is that the metal is coordinated directly to the conjugated backbone of the polymer, or forms a link in the backbone, such that there is an electronic interaction between the electroactive metal centres and the electroactive polymer backbone. As will be illustrated in this article, this can enhance electron transport in the polymer, enhance its electrocatalytic activity, and lead to novel electronic



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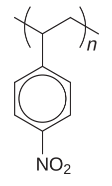

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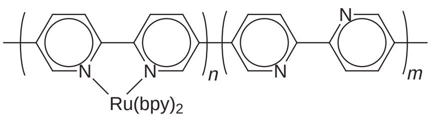

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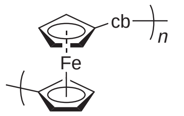

cb = conjugated bridge

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and electrochemical properties. A broad review of this class of material has recently appeared.[11]

Electron transport pathways

The primary rationale for creating conjugated metallopolymers is that electronic interactions between the polymer's π-system and the metal's d-orbitals will modulate the properties of both components in interesting and potentially useful ways. One of the anticipated benefits is fast electron transport to/from the metal centres so that multiple electrons can be rapidly exchanged with a substrate (*e.g.* O_2) during electrocatalysis. The source/sink of the extra electrons can be the polymer backbone itself, if it is electroactive over the appropriate potential range, or other nearby metal centres (or their ligands). d–π Interactions would be expected to enhance the rate of electron transfer in both cases.

Electron transfer between immobilized metal centres in a polymer film can occur by three mechanisms (Fig. 1); outer sphere electron transfer between metal sites, as in conventional redox polymers,[12,13] electron transfer through the polymer backbone *via* a metal–metal electronic interaction (superexchange pathway), and *via* polymer based charge carriers (polymer mediated pathway).

Electron transfer *via* polymer based charge carriers requires the polymer backbone to be electronically conductive and therefore either p-doped or n-doped at potentials close to the formal potential of the metal centre. The significance of this pathway can be assessed to some extent by cyclic voltammetry which will show the degree to which the backbone's redox waves overlap with that of the metal complex. This is illustrated in Fig. 2, which compares voltammograms of two different conducting ion exchange polymers loaded with $Fe(CN)_6^{3-/4-}$.[14] Polymer A exhibits a p-doping wave at a formal potential ($E°'$) of *ca.* 0.7 V that does not overlap significantly with the $Fe(CN)_6^{3-/4-}$ wave at $E°'=0.2$ V. Consequently, electron exchange between Fe centres is solely by the outer sphere mechanism, and so the $Fe(CN)_6^{3-/4-}$ wave exhibits features typical of a slow diffusion controlled process (peak separation >0 and a square root dependence of peak currents on scan speed). In contrast, the p-doping wave of polymer B ($E°' \approx -0.1$ V) does overlap with the $Fe(CN)_6^{3-/4-}$ wave, and consequently electron exchange between Fe centres can occur *via* p-type charge carriers on the polymer backbone. The $Fe(CN)_6^{3-/4-}$ wave is symmetric and peak currents scale linearly with scan speed, indicating that

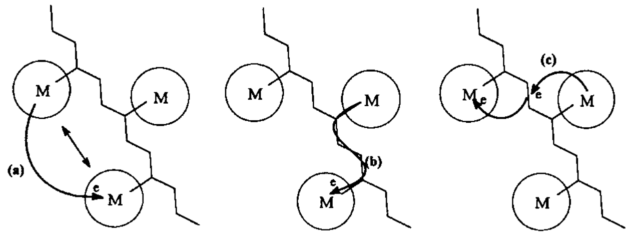


Fig. 1 Schematic diagram of the three electron transfer pathways between metal centres in redox polymers. (a) Outer sphere electron transfer; (b) superexchange pathway; (c) polymer mediated pathway.

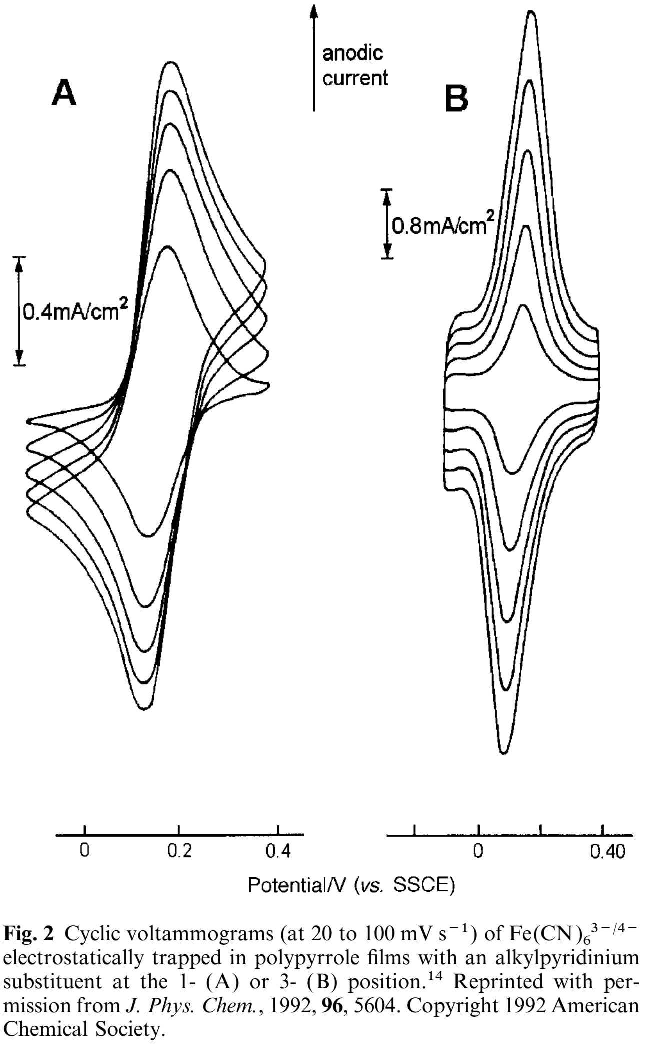


Fig. 2 Cyclic voltammograms (at 20 to 100 mV s^{-1}) of $Fe(CN)_6^{3-/4-}$ electrostatically trapped in polypyrrole films with an alkylpyridinium substituent at the 1- (A) or 3- (B) position.[14] Reprinted with permission from *J. Phys. Chem.*, 1992, **96**, 5604. Copyright 1992 American Chemical Society.

electron transport between Fe centres is much faster than in Fig. 2A.

Although the data in Fig. 2 show a clear connection between the overlap of the polymer and metal wave and the existence of the polymer mediated pathway, care must be taken in the interpretation of voltammetric data because a significant number of polymer based charge carriers can be present at potentials many hundreds of millivolts before the polymer's p-doping voltammetric peak. For example, poly(3-methylthiophene) exhibits a p-type conductivity of *ca.* 10^{-7} S cm^{-1} at a potential (+0.1 V *vs.* SCE) 500 mV prior to its voltammetric peak for p-doping, and a 0.3 μm thick layer can mediate the oxidation of solution species at mass transport limited rates at this potential.[15]

Electron transfer through the polymer backbone *via* a metal–metal electronic interaction (superexchange pathway) can occur *via* two mechanisms,[16] electron-type superexchange and hole-type superexchange, as illustrated in Fig. 3. In the former, mixing of the π* LUMO of the polymer and the metal d orbitals is the major contributor to the metal–metal interaction, while in the latter mixing of the π HOMO of the polymer and the metal d orbitals is the major contributor. The extensive literature[17] on electron transfer between ligand bridged metal centres is relevant to assessing the significance of superexchange pathways in metallopolymers.

The extent of d–π interactions in conjugated metallopolymers will depend in part on the relative energies of these orbitals, which can conveniently be assessed from electrochemical studies. The redox potentials for p-doping and n-doping of the polymer indicate the energies of its π and π* orbitals respectively, while the redox potential of the complex provides a relative measure of the energy of its d-orbitals. Strong metal–metal interactions in a metallopolymer will cause a splitting of the metal redox wave into multiple waves, as observed in complexes with bridging ligands.[17]

The question of whether electron transfer between metal sites is more efficient through a conjugated linkage than by electron hopping *via* a conducting conjugated polymer segment has been addressed by Zotti *et al.*,[18] although their results are not unambiguous. Their *in situ* conductivity measurements on polymers **12** and **13** are shown in Fig. 4. The constant conductivity at high potentials in both cases is due to the polymer backbone, while the shoulder for **12** and the peak for **13** at the ferrocene formal potential are due to electron transfer between ferrocene sites (redox conductivity[19]). The fact that the redox conductivity due to the ferrocene sites is higher than the backbone conductivity for **13** (which has a conjugated linkage between the ferrocene and the backbone) but not for **12** (which has a saturated linkage) suggests that electronic comunication though a conjugated linkage is more effective than electron hopping *via* conducting conjugated polymer segments (since it could not be expected that the latter would provide a larger conductivity than the backbone's conductivity). However, a problem with these data is that for some unexplained reason **12** had a much larger backbone conductivity than **13**, and this casts some uncertainty on the validity of the conclusions.

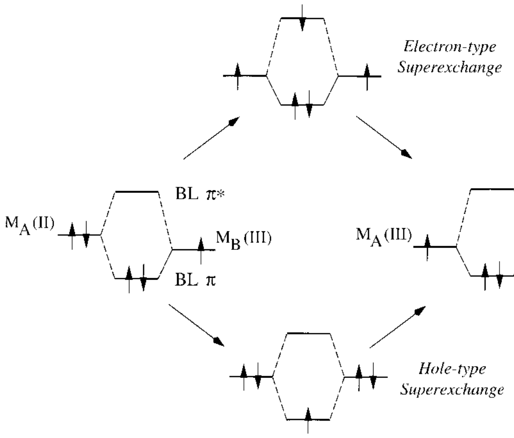
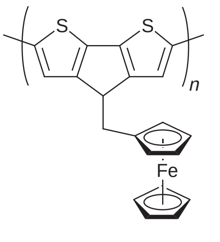


Fig. 3 Superexchange mechanisms. BL = bridging ligand.



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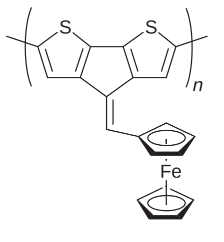

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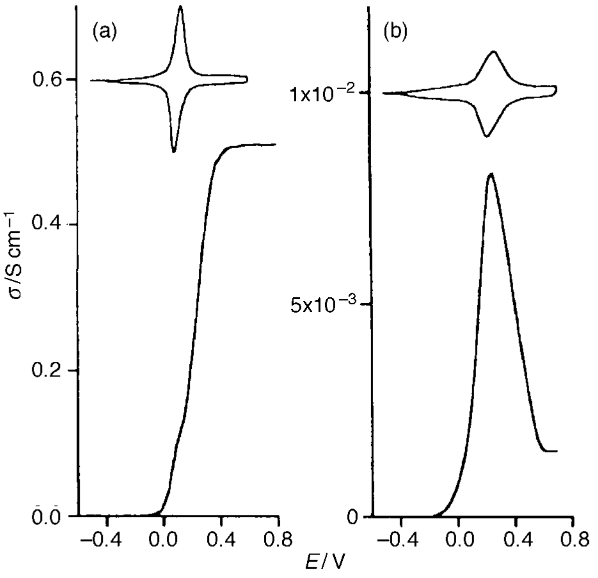


Fig. 4 *In situ* conductivities of **12** and **13** in acetonitrile + Et_4NClO_4. Upper: CVs for comparison.[18] Reprinted with permission from *Synth. Met.*, 1996, **76**, 255. Copyright 1996 Elsevier Sciences S.A.

2,2′-Bipyridine based materials

Poly(2,2′-bipyridine) (poly-bpy)

The first bipyridine based conjugated metallopolymer was a $Ru(bpy)_2^{2+}$ complex of poly-bpy **10**.[20,21] The poly-bpy was prepared by the Ni(0) catalysed coupling of 5,5′-dibromo-2,2′-bipyridine, and subsequently metallized by refluxing with $Ru(bpy)_2Cl_2$ in water. The resulting water-insoluble product consisted of a methanol-soluble fraction, with a UV-visible absorption at *ca.* 450 nm characteristic of the $Ru(bpy)_3^{2+}$ chromophore and a Ru : poly-bpy ratio of *ca.* 0.2, and a poorly characterized intractable material with a Ru : poly-bpy ratio of *ca.* 0.014. When electrodes coated with poly-bpy were reacted with $Ru(bpy)_2Cl_2$, 10–15% coordination of the $Ru(bpy)_2^{2+}$ moiety occurred and intriguing cyclic voltammograms were observed (Fig. 5(*a*)). Compared to the monomer complex (Fig. 5(*c*)), the ligand reduction waves (originally in the −1.5 to −2.5 V region) appear to have moved positively, while the Ru(III/II) wave (at *ca.* +1.0 V in $Ru(bpy)_3^{2+}$) appears to have moved negatively. All waves are broadened considerably in the metallopolymer into a wide charge envelope with multiple peaks. The broadening and multiple peaks suggest that there are strong interactions between the poly-bpy π-system and the Ru d-orbitals. However, these effects are not seen in more regular and well characterised systems (*e.g.* poly-[Ru(**15**)$_3$] and **24b** below). Therefore, given the lack of characterization of the

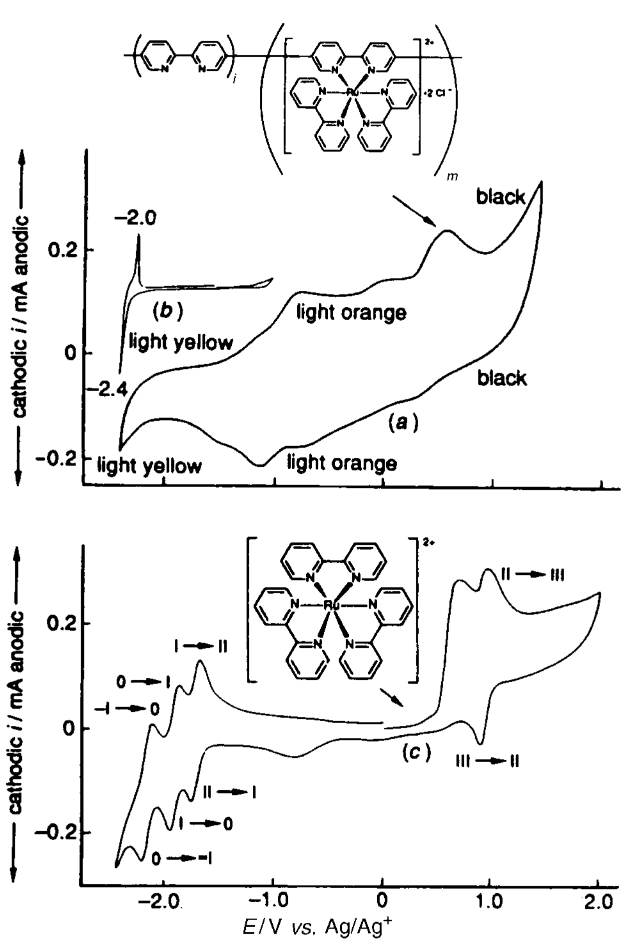


Fig. 5 CV curves for (*a*) a poly-bpy–Ru(bpy)$_2$ **10** film on a Pt electrode, (*b*) poly-bpy, and (*c*) Ru(bpy)$_3^{2+}$, in acetonitrile solutions containing 0.1 M Bu$_4$NClO$_4$.[21] Reprinted with permission from *J. Am. Chem. Soc.*, 1994, **116**, 4832. Copyright 1994 American Chemical Society.

Ru(bpy)$_2$ complexed poly-bpy sample used for the voltammetry in Fig. 5(*a*), the result must be viewed with some doubt. The broadening can perhaps be explained by the low utilization of bpy sites along the polymer chain, which will lead to a wide range of different polymer based (different lengths of uncomplexed polymer between Ru centres) and metal based (different distances from adjacent Ru sites) redox sites.

Complexation of poly-bpy with RuCl$_3$,[21] Ni(II),[21] Pt(bpy)$_2^{2+}$,[22] PtCl$_4^{2-}$,[22] and of poly(6,6′-dihexyl-2,2′-bipyridine) with Cu(II)[23] and Fe(bpy)$_2$Cl$_2$,[21] have also been reported. The RuCl$_3$ and Pt complexes were found to be active catalysts for the photochemical generation of H$_2$,[21,22] and the Ni complex was reported to catalyze the electrochemical reduction of CO$_2$.[21] As shown in Fig. 6 the complex with Pt(bpy)$_2^{2+}$, which is formed photochemically in the photolysis cell, is the most active catalyst for photochemical H$_2$ generation. Spectroscopic monitoring of bpy release and XPS measurements indicated almost stoichiometric binding of the Pt(bpy) moiety to the polymer, which was in large excess.

Bipyridine–thiophene copolymers

Swager and coworkers[24–26] have taken an approach to metal–bipyridine containing polymers that involves the electrochemical polymerization of preformed complexes with thiophene end groups on a bipyridine ligand (Scheme 1). This produces polymers with higher metal loadings (100%) than those produced from poly-bpy, and with the metal centre in a more well defined and well characterized site. The introduction of oligothiophene segments into the bipyridine backbone will stabilize the HOMO (valence band) and should lead to stronger hole superexchange interactions between metal sites. An added advantage is that these metallopolymers are conveniently formed by anodic polymerization as thin films on electrodes.

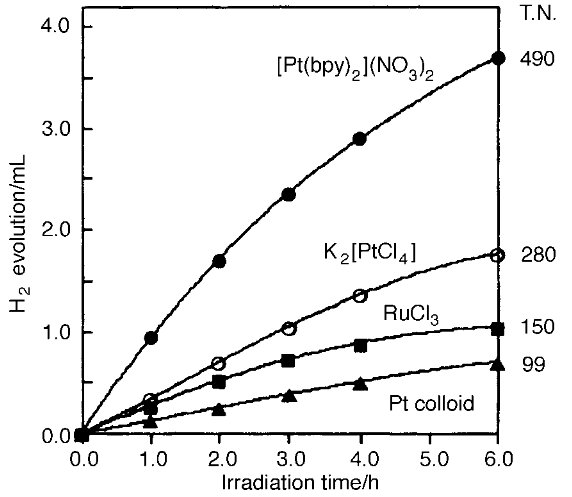


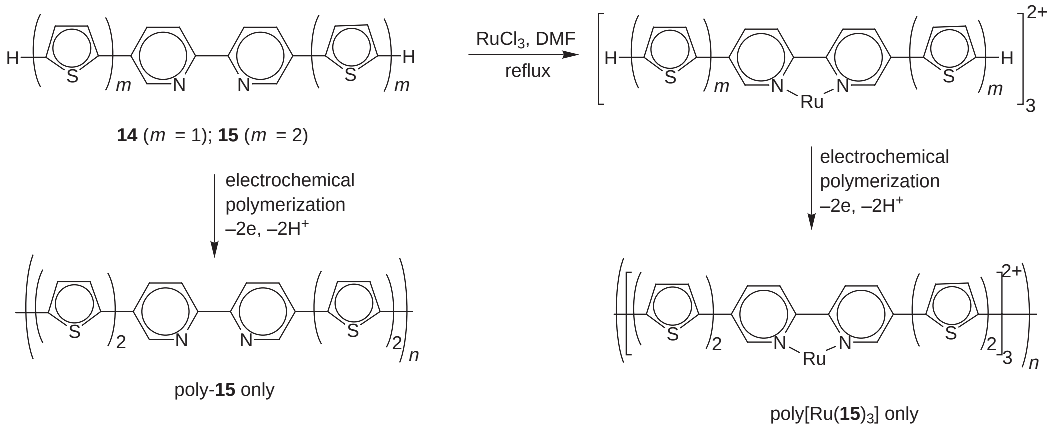
Fig. 6 Photoreductive H$_2$ evolution catalyzed by poly-bpy in an aqueous NEt$_3$/MeOH solution in the presence of various metal complexes. T.N. = turnover number per Pt or Ru atom.[22] Reprinted with permission from *J. Phys. Chem. B*, 1997, **101**, 3806. Copyright 1997 American Chemical Society.

Surprisingly, the ligand with single terminal thiophenes **14** and its tris complex with Ru both failed to polymerize.[24] However, extending the terminal groups to bithiophenes **15** did give a polymerizable ligand and Ru complex. Cyclic voltammograms and *in situ* conductivity (I_d in plot c is proportional to conductivity) *vs.* potential plots for both poly-**15** and poly[Ru(**15**)$_3$] are shown in Fig. 7.

The metal-free polymer shows the expected p-doping and n-doping voltammetric waves at *ca.* +1.0 V and −2.0 V, respectively (Fig. 7A). It is non-conducting in the potential region between the two doping waves (the band gap) and exhibits a maximum p-type conductivity of *ca.* 2×10^{-3} S cm^{-1} at *ca.* +1.0 V, and a maximum n-type conductivity of *ca.* 4×10^{-3} S cm^{-1} at *ca.* −2.0 V. It is interesting that the maximum n-type conductivity is higher than the maximum p-type conductivity, since polythiophenes normally have much higher p-type than n-type conductivities. It would suggest that the bipyridine segments are not strongly involved in the delocalization and mobility of the p-type charge carriers, as would be expected based on their π-electron deficiency and the fact that polypyridines can not be p-doped within the normally accessible potential range.[21]

Cyclic voltammetry of the Ru polymer (Fig. 7B) shows anodic electrochemistry to +1.2 V that is characteristic of the polymer backbone, with little perturbation from the coordinated Ru centres. This is consistent with the inference that the bipyridine segments are not strongly involved in p-doping. They will be even more π deficient when coordinated to Ru, and therefore even more weakly involved in p-doping. It would have been interesting to see the Ru(III/II) electrochemistry of the polymer, which would be expected at potentials slightly higher than those used in Fig. 7, but there was no mention of the existence of additional waves at higher potentials.

The cathodic electrochemistry of the Ru polymer shows two reversible waves at −1.23 V and −1.39 V respectively, that are typical of bpy based reductions observed for Ru complexes (*e.g.* see reversible waves at −1.6, −1.9, and −2.2 V in Fig. 5(*b*)). Similar waves were observed at slightly lower potentials (−1.34 and −1.54 V) for the monomer complex (Ru(**15**)$_3^{2+}$) before polymerization and were strangely assigned to Ru(II/I) and Ru(I/0) processes. Cycling of the potential of the Ru polymer through these reduction waves generates a conductivity profile (Fig. 7B) that is characteristic



Scheme 1

of redox conductivity (*i.e.* driven by concentration gradients of reduced sites rather than an electric field),[19] showing peaks (a shoulder for the first wave) at the voltammetric peak potentials. This is very similar to the ligand-based redox conductivity observed for the non-conjugated polymer poly[Os(bpy)$_2$(4-vinylpyridine)$_2$].[19] Taken together, these observations suggest that the n-type charge carriers corresponding to the two reduction waves shown in Fig. 7B for the Ru polymer reside predominantly on the bipyridine segments of the polymer. The small shifts in potential relative to Ru(bpy)$_3$ and the monomer complex (Ru(**15**)$_3{}^{2+}$), and the somewhat higher conductivity relative to poly[Os(bpy)$_2$(4-vinylpyridine)$_2$], indicate that there is weak delocalization over the oligothiophene segments. Reduction of the oligothiophene segments does occur, but at lower potentials than shown in Fig. 7B, and it leads to degradation of the polymer.

Polymerizable Cu$^+$ and Zn^{2+} complexes of **15** (**18a** and **19a**)[25] and the analogous dioxyethylene substituted ligand **17** (**18b** and **19b**)[26] have been prepared with the aid of the macrocyclic ligand **16** (Scheme 2). As well as aiding the formation of well defined complexes of **15** and **17**, this ligand also allows the formation of 'polymetallorotaxanes' in which the polymer chain is threaded through the macrocycle.[27,28] The metal ion can subsequently be removed to leave the macrocyle physically associated with the polymer in a way that facilitates the binding of metal ions for sensor applications.[25–28] The use of the dioxyethylene substitutents in poly-**18b** and poly-**19b** has the advantage of lowering the energy of

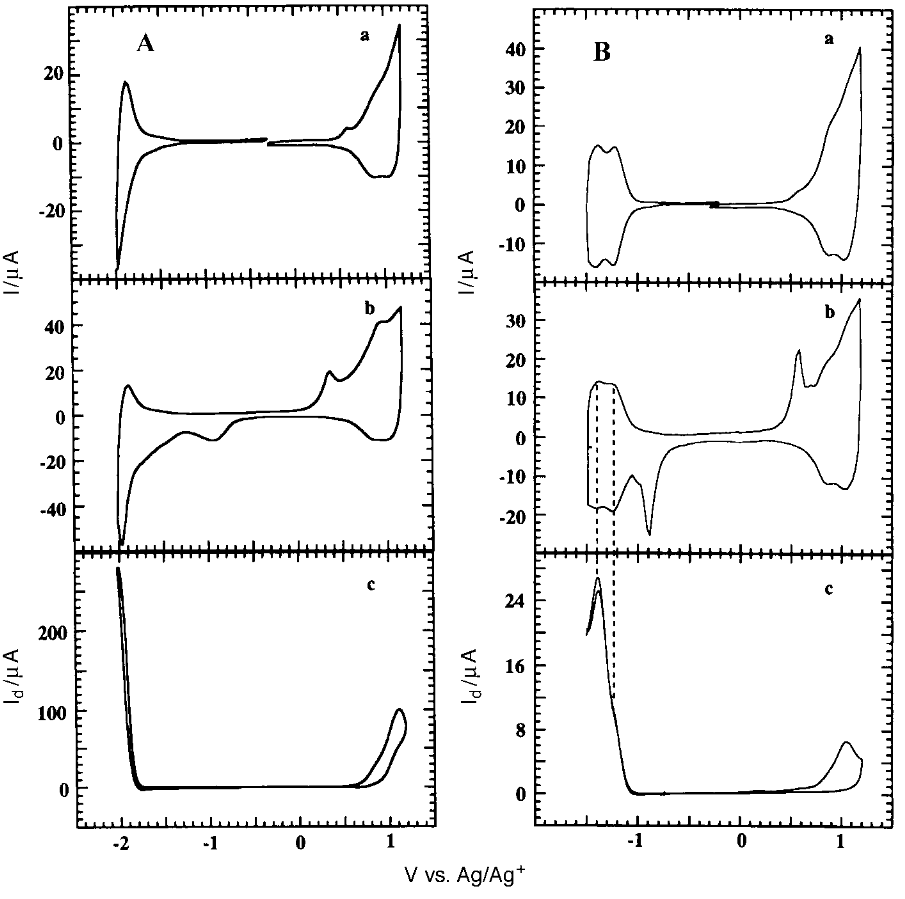
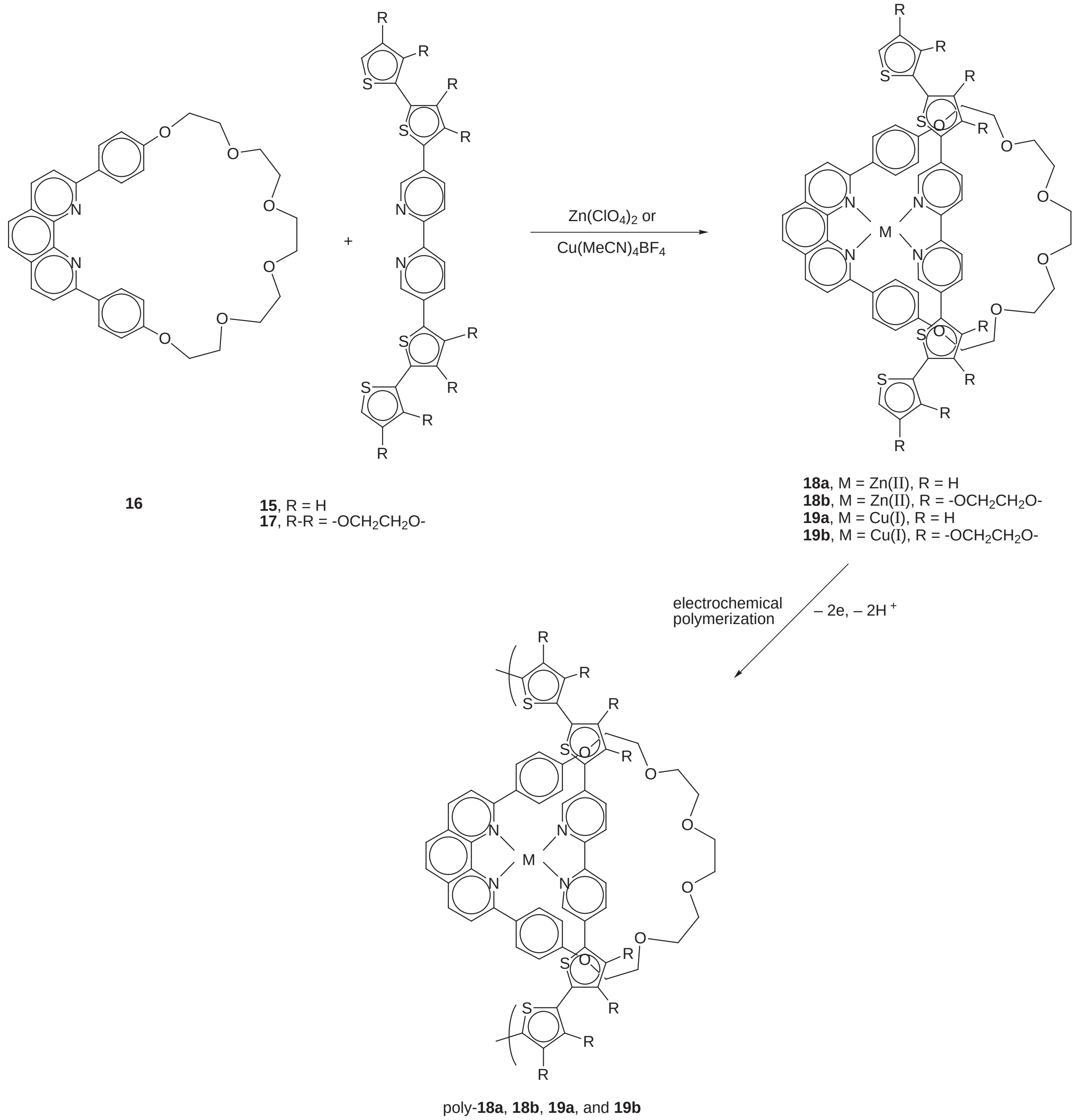
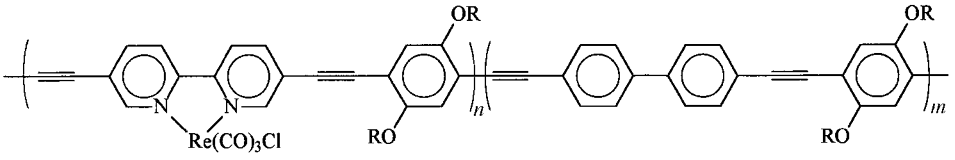


Fig. 7 Cyclic voltammograms at 100 mV s^{-1} (a and b) and drain current ($I_d \propto$ conductivity) plots (c) for poly-**15** (A) and poly[Ru(**15**)$_3$] (B) films in acetonitrile containing Bu$_4$NPF$_6$. The central panels (b) show charge trapping peaks that are observed when the potential scan limits include both oxidation and reduction of the polymer.[24] Reprinted with permission from *Adv. Mater.*, 1996, **8**, 497. Copyright 1996 VCH Publishers.



Scheme 2



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the polymer's valence band, thereby facilitating p-doping. It also increases the affinity of the polyrotaxane for metal ions by increasing the donor character of the bipyridine segments and localizing the macrocycle close to the bipyridine segments.

Electrochemical and *in situ* conductivity studies of the polymetallorotaxanes prepared from **18a**, **18b**, **19a**, and **19b** have revealed rich insight into the effects of metal ion binding on the electronic structure of the polymer backbone.[25,26] Fig. 8 shows repesentative data for poly-**17** and its rotaxane complexes with Zn^{2+} (poly-**18b**) and Cu^+ (poly-**19b**). The uncomplexed polymer is somewhat unusual in that it shows two well defined redox waves rather than the broad envelope of p-doping current (compare Fig. 8A with Fig. 7A) normally observed for conducting polymers. This difference has been assumed to indicate increased charge localization in poly-**17**, which is reasonable given the strong donor character of the tetra(ethylenedioxythiophene) segments and the strong acceptor character of the bipyridine segments. The p-type charge carriers would be expected to be strongly lozalized on the tetra(ethylenedioxythiophene) segments, with the two voltammetric peaks corresponding to polaron (cation) and then bipolaron (dication) formation as observed in methyl capped

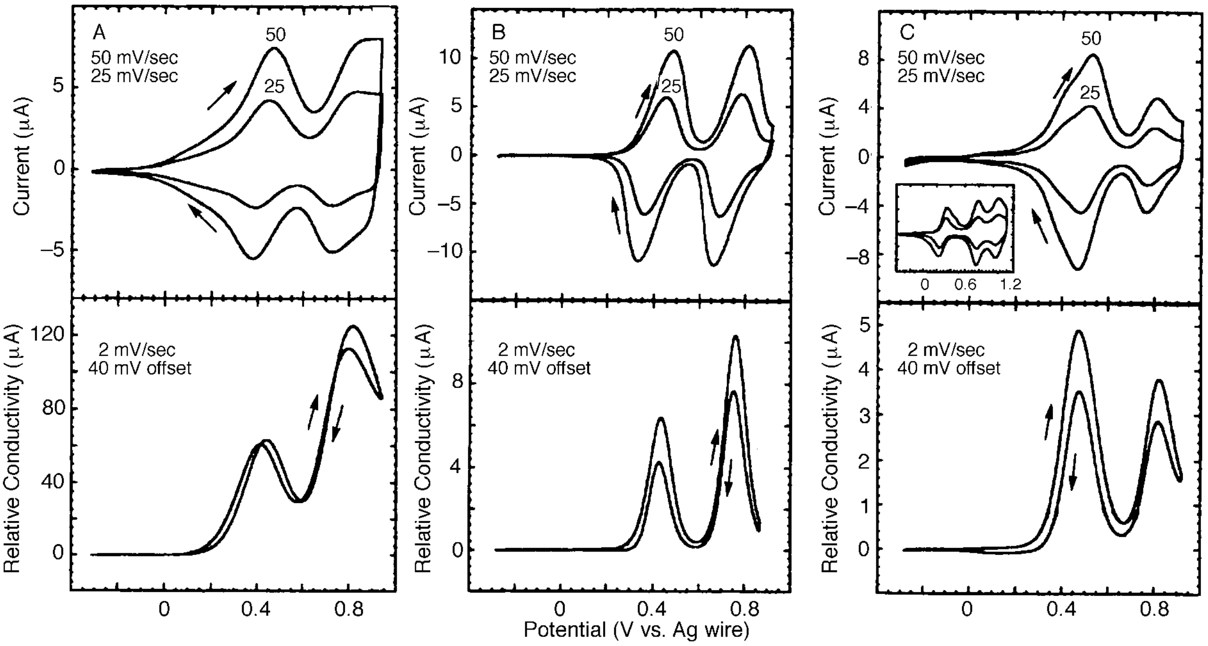


Fig. 8 Cyclic voltammograms (a) and relative conductivity plots (b) for poly-**17** (A), poly-**18b** (B), and poly-**19b** (C) films in CH_2Cl_2 containing Bu_4NPF_6.[26] Reprinted with permission from *J. Am. Chem. Soc.*, 1997, **119**, 12568. Copyright 1997 American Chemical Society.

hexathiophene.[29] Complexation of Zn^{2+} to poly-**17** causes a sharpening of its two voltammeric waves and a substantial decrease in the conductivity associated with them (compare Fig. 8A and B), indicating further localization of the p-type charge carriers. Cu^+ has a similar effect (Fig. 8C), but also produces a new redox wave due to the Cu(II/I) couple ($E^{\circ\prime} \approx 0.4$ V) just before the first polymer wave, and increases the conductivity associated with the first wave relative to the second wave. In poly-**19a**, where the Cu(II/I) wave ($E^{\circ\prime} = 0.48$ V) is well separated from the first polymer wave ($E^{\circ\prime} = 0.96$ V), there is no significant conductivity associated with the Cu(II/I) couple and the presence of the Cu^{2+} does not enhance the conductivity associated with the first polymer wave. It seems clear therefore that in poly-**19b** the Cu(II/I) is involved in the mediation of electron transport between singly oxidized tetra(ethylenedioxythiophene) segments. Conversely, the tetra(ethylenedioxythiophene) segments can be viewed as mediating electron transport between metal centres. However, the mechanism of electron transport, and the relative importance of the superexchange and polymer mediated pathways (Fig. 1), are not clear from the available data.

The reversible binding of metal ions by poly-**15** and poly-**17** rotaxanes has been investigated with the goal of developing sensory materials.[26] The Zn^{2+} can be extracted from poly-**18a** by ethylenediamine treatment and partially replaced with Zn^{2+} in acetonitrile. Immersion of the demetallated polymer in a Cu^+ solution produces a large voltammetric wave for bound $Cu^{2+/+}$, but use of a Cu^{2+} solution results in relatively little Cu^{2+} binding, clearly showing that the polymer has a higher affinity for Cu^+ over Cu^{2+}. Reversible extraction/binding of Zn^{2+} and Cu^{2+} from/to poly-**18b** and poly-**19b** was also observed, and due to the electron donating nature of the dioxyethylene substituents stronger coordination was observed. Treatment of a demetallated film with Cu^{2+} was found to produce a dramatic decrease in its dry resistance (by $>10^6$), by binding to and oxidizing the polymer backbone. However, the binding of the Cu^{2+} is probably incidental to its oxidizing ability.

Other bipyridine based systems

Copolymer **20**, in which $Re(CO)_3Cl$ groups are coordinated to bpy segments of an aryleneethynylene backbone, has been used to explore interactions between the photophysics of the metal centres and the backbone.[30,31] Surprisingly, the two chromophores do not seem to be strongly coupled, with inefficient quenching of the backbone's fluorescence by the metal centres, and the absence of MLCT$\rightarrow{}^3\pi,\pi^*$ energy transfer.

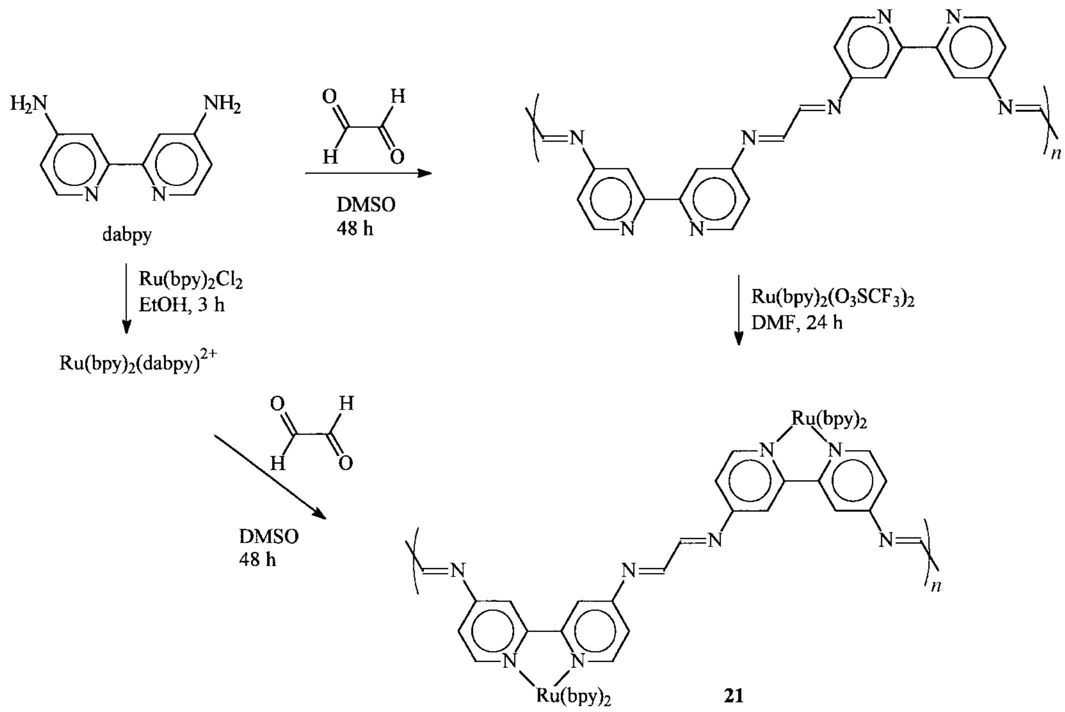
Petersen and coworkers[32] have developed a potentially very versatile route to a metallated poly(bipyridinyl–diazabutadienediyl) **21**, as illustrated in Scheme 3. The condensation polymerization can be performed either prior to, or following, reaction of the diamino-bipyridine ligand with the metal, to give polymers with 100% coordination of the bpy sites and identical characteristics. In principle, it can also be carried out in a stepwise manner to produce materials with controlled chain lengths, sequences of different metal complexes along the chain, and other custom designs.

2,2′-Bithiazole based materials

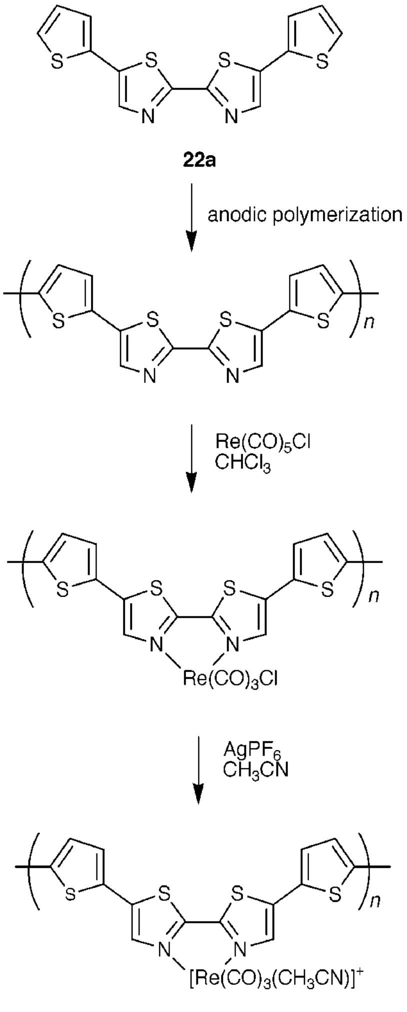
2,2′-Bithiazole is a more attractive ligand than bpy for use in p-doped materials because it is less π deficient and therefore its polymers are more easily oxidized. However, it suffers the disadvantage that reduced back donation from coordinated metal centres into its π system causes it to bind metals less strongly.

Although there have been a number of reports of the synthesis of polythiazoles and polybithiazoles, only one[33] mentions the formation of a metal complex (the reaction of $Ru(bpy)_2Cl_2$ with poly(4,4′-dimethyl-2,2′-bithiazole) is described in the Supporting Information), and little information is provided. An approach analogous to that used by Swager's group for preparing bipyridine based metallopolymers, namely the use of electrochemically polymerizable thiophene end groups, has been more widely explored.

Thus Wolf and Wrighton[34] have complexed $Re(CO)_3Cl$ groups to electrochemically formed films of poly[5,5′-bis(2-thienyl)-2,2′-bithiazole] (poly-**22a**), and subsequently converted these to $Re(CO)_3(CH_3CN)^+$ groups (Scheme 4). Approximately 60–75% of the available bithiazole N,N coordination sites in the polymer could be functionalized in this way. The resulting metallopolymer (**23**) exhibited a maximum p-type conductivity of *ca.* 2×10^{-3} S cm^{-1}, which is two orders of magnitude lower than that of the uncomplexed polymer



Scheme 3



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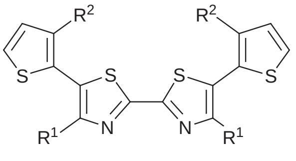
Scheme 4

(poly-**22a**). As with the analogous bpy polymers (poly-**15** and poly-**17**), complexation of the metal appears to cause localization of the p-type carriers within the oligothiophene segments. This conclusion was supported by IR spectroscopy which showed, *via* changes in the carbonyl stretching frequencies of 4–6 cm^{-1}, that the modulation of the electron density on the Re by p-doping of the polymer was minor.



22a (R^1=R^2=H)
22b (R^1=Me, R^2=H)
22c (R^1=Me, R^2=OMe)

In order to obtain bis(thienyl)bithiazole polymers with 100% coordination of the bithiazole segments, we have prepared

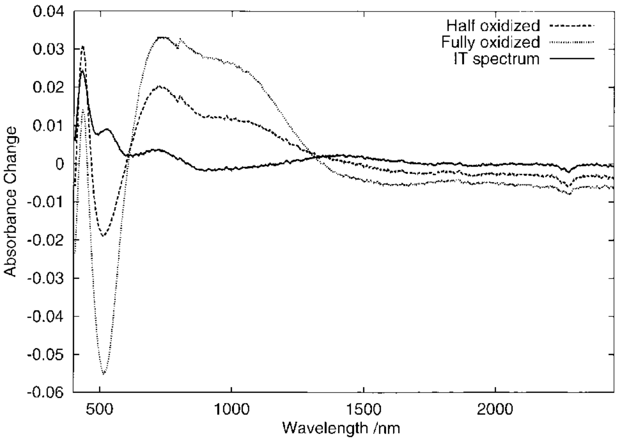


Fig. 9 Difference spectra (*vs.* Ru(II) form) of the half (a) and fully (b) oxidized (Ru(III)) forms of **24b** (*ca.* 80% metallated), and an intervalence charge transfer spectrum obtained by subtracting 50% of the absorbance in (b) from that in (a).[39]

Ru(bpy)$_2{}^{2+}$ and Os(bpy)$_2{}^{2+}$ complexes of **22a** and the methyl and methoxy substituted analogues **22b** and **22c**.[35,36] However, as with complexes of the bipyridine analogue with single terminal thiophenes (**14**), these complexes could not be polymerized, and thus far we have been unable to synthesize the bithiazole analogue of **15** with terminal bithiophenes. However, complexes of **22a**, **22b**, and **22c** could be copolymerized with 3-methylthiophene and bithiophene, suggesting that their failure to give sustained polymerization alone is due to steric factors.

Polybenzimidazoles

Polybenzimidazoles (*e.g.* **24**) are an attractive choice for the synthesis of conjugated metallopolymers for a number of reasons. They tend to be very robust, remaining stable under considerable thermal and chemical stress, and studies of binuclear benzimidazole complexes (*e.g.* ref. 37) have shown them to possess notable coupling between the two metals. In addition, removal of the imidazole proton allows pH control of the electron density along the polymer backbone.

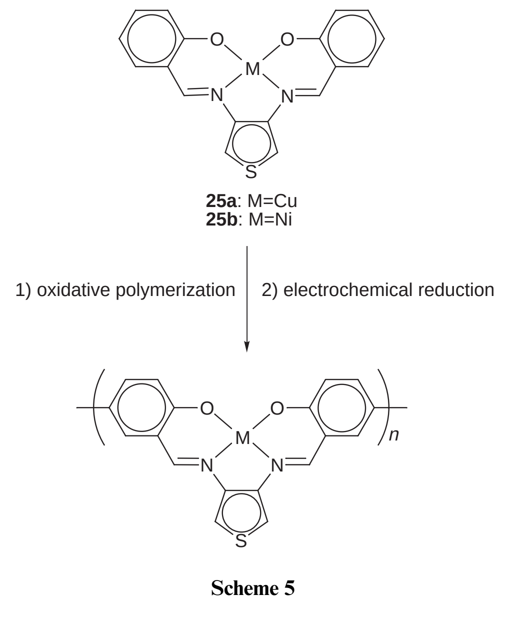
Evidence of metal–metal coupling in a Ru(bpy)$_2{}^{2+}$ complex of **24a** (**24b** with *ca.* 80% metallation) has been provided by near-IR spectroelectrochemistry and electron transport studies.[38,39] Fig. 9 shows difference spectra (following subtraction of a spectrum recorded in the reduced state) for the half and fully oxidized states of **24b**, and an intervalence transfer (IT) spectrum. The IT spectrum, which shows a clear IT band at 1370 nm, was obtained by the subtraction of one-half the absorbance of the spectrum of the fully oxidized form from the spectrum of the half-oxidized form. The degree of electronic coupling between neighbouring metal sites, H_{AB}, was estimated to be *ca.* 50 cm^{-1}, which is similar to values obtained for similar binuclear complexes.[37]

The diffusion coefficient for electron hopping between metal sites in **24b**, D_e, was measured by several different methods in both acidic and basic media.[39] Significantly higher values were obtained in base (*ca.* 2×10^{-8} cm^2 s^{-1} *vs.* *ca.* 6×10^{-9} cm^2 s^{-1} in acid), implicating the polymer backbone in the conduction mechanism (superexchange pathway in Fig. 1) since deprotonation of the benzimidazole has been shown to increase the extent of Ru–Ru coupling in an analogous binuclear complex.[37] Further evidence that D_e is enhanced by a superexchange pathway, even in acid, was provided by a comparison with D_e values for non-conjugated polymer–Ru(bpy)$_2{}^{2+}$ complexes. Thus, D_e is only 7×10^{-10} cm^2 s^{-1} for poly[Ru(bpy)$_2$(4-vinylpyridine)$_2$]$^{3+/2+}$, and only 2×10^{-10} cm^{-2} s^{-1} for poly[Ru(bpy)$_2$(3-{pyrrol-1-ylmethyl}pyridine)$_2$]$^{3+/2+}$. Given the structural rigidity of **24b**, electron hopping *via* outer sphere electron transfer between metal sites would be expected to be even slower than in these non-conjugated polymers, for which it is the sole electron transport mechanism. The fact that D_e values are more than a factor of 10 higher in **24b** indicates that the superexchange pathway is dominant. The polymer mediated pathway can be ruled out in this case because of the lack of polymer based electroactivity and conductivity in the potential region of the Ru(III/II) formal potential.

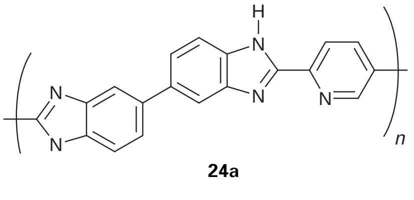
Schiff base systems

A variety of Schiff base metal complexes have been electrochemically polymerized to form films on electrodes.[40,41] In these systems the metal can form an integral part of the conducting backbone or can be peripheral, and the differences in the properties of materials of these two types were compared in a recent study by Reddinger and Reynolds.[41,42] The former type was exemplified by polymers formed by the electrochemical polymerization of **25a** and **25b**, which form linkages *via* the phenyl rings (Scheme 5) because of steric crowding around the thiophene. The resulting polymers, which lack conjugation at the thienyl linkage, display a single (oxidative) redox wave and electrochromic properties that are strongly dependent on the metal (Ni or Cu). In contrast, the polymer formed from **26** (Scheme 6) shows two separate redox process, one attributable to the polythiophene backbone, and another due to the pendent Schiff base complex. Absorption changes associated with the backbone electrochemistry tend to obscure the electrochromism of the complex.

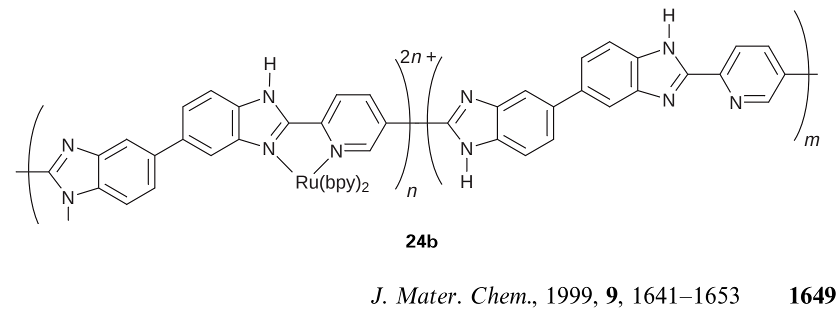
A better example of the involvement of the metal in the conjugation system comes from recent work by Kingsborough and Swager.[40] Schiff base **27** was found to be very difficult to oxidize, with a redox potential close to that of thiophene, and could not be electrochemically polymerized. The lack of conjugation at the ethylene diimine linkage clearly causes the two halves of the molecule to be electronically independent. On the other hand, the analogous Co complex **28** was easily oxidized and polymerized, suggesting the existence of electronic communication between the two halves of the ligand through the Co. The resulting metallopolymer showed separate voltammetric waves due to the cobalt centres and the polymer backbone (Fig. 10a), with only the latter redox process produc-



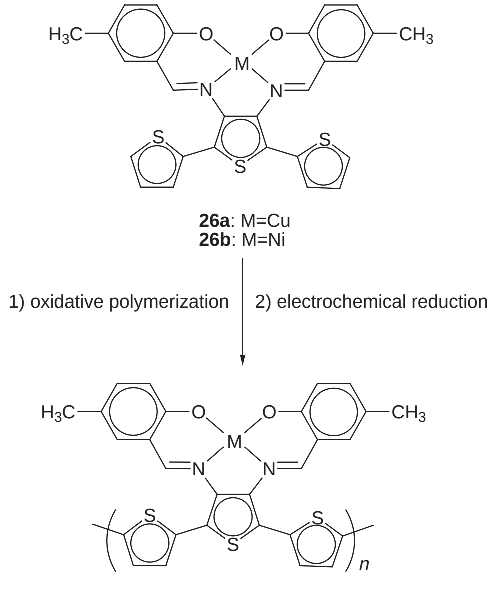
Scheme 5



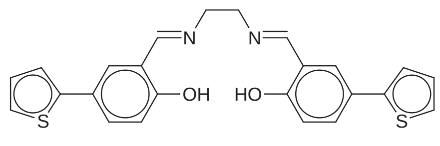
24a



24b



Scheme 6



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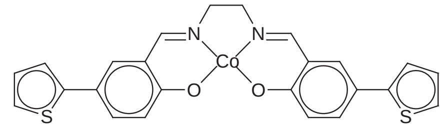

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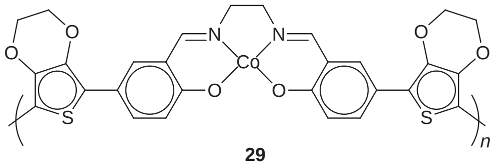

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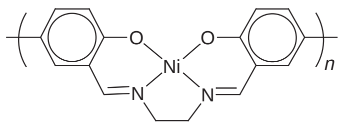

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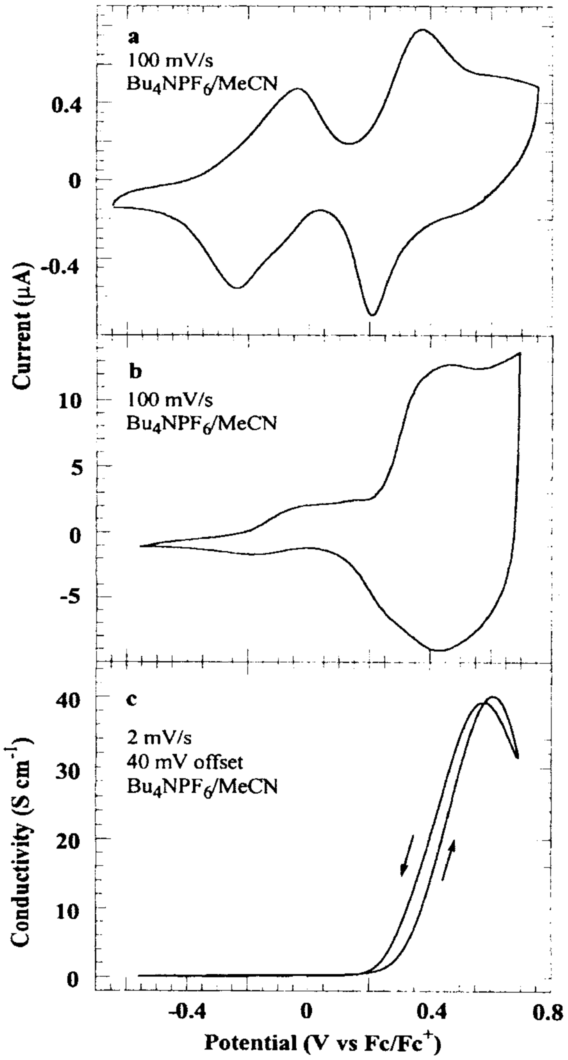
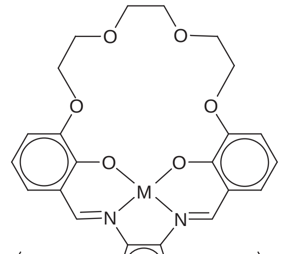


Fig. 10 Cyclic voltammograms of thin (a) and thick (b) films of poly-**28** in 0.1 M Bu_4NPF_6/MeCN (a), and *in situ* conductivity *versus* electrochemical potential (c).[40] Reprinted with permission from *Adv. Mater.*, 1998, **10**, 1100. Copyright 1998 VCH Publishers.

ing significant electronic conductivity (Fig. 10c). Shifting the backbone electrochemistry to overlap the Co electochemistry, by employing ethylenedioxy substituents on the thiophenes (**29**), enhanced the electronic conductivity of the metallopolymer significantly, although the mechanism is unclear.

A convincing description of the role of the metal in electrochemically formed films of poly[*N*,*N*′-ethylenebis(salicylideneaminato)nickel(II)] (**30**, poly[Ni(salen)]) has recently been provided by Vilas-Boas *et al.*[43] Their combination of electrochemical and spectroscopic techniques highlights the need to fully characterize new materials if a sound understanding of their properties is desired. They conclude that oxidation of **30** produces polarons (paramagnetic radicals), and then bipolarons (diamagnetic dications) as the potential is increased, associated with biphenyl linkages but delocalized through the metal bridges. Thus **30** behaves like a polyphenylene type organic conductor with the metal ion acting as a conjugating bridge between biphenyl moieties. As would be expected, based on the need for *para* (or *ortho*) linkages at the phenyl rings to effect long range conjugation, the conduction path in the doped state appears to be through the phenoxide ligands (*i.e.* -Ph-O-Ni-O-Ph-).



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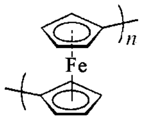
Several Schiff base metallopolymers have been proposed as active materials in sensors. The Co metallopolymer **29** shows a significant decrease in conductivity when exposed to pyridines, presumably as a result of binding to the Co in an axial position, suggesting possible applications in the sensing of Lewis bases.[40] The crown ether substituted polymer **31** shows a shift in its formal potential on binding alkali and alkaline earth metal ions that is characteristic of the ion.[44] A partially reversible loss of electrochemical activity in the presence of pyridine (5 nM) was also noted for this system.

Polyferrocenes

Polyferrocenes (structure **11**) are the most widely studied class of conjugated metallopolymers. Elegant synthetic methods based on ring opening polymerization have made a wide variety of well-defined systems available,[45] and have provided considerable insight into the factors influencing the strength of metal–metal interaction along the chain. A full discussion of this class of material is beyond the scope of this article and so I will focus on recent work concerning Fe–Fe interactions, and the involvement of the metal centres in the conjugated π system. An introduction to the full literature can be obtained from the cited references.



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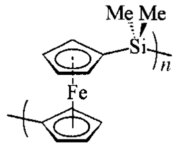

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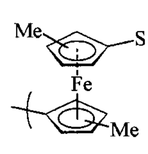

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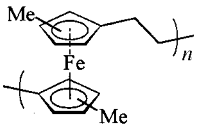

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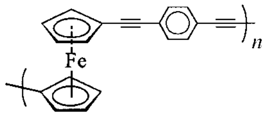

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Polyferrocene itself (**32**) does not appear to have been extensively studied, presumably due to the difficulty of preparing well defined, high molar mass samples.[46] Cyclic voltammetry of a low molar mass (*ca.* 900 g mol^{-1}) sample (Fig. 11) gave multiple peaks covering a potential range of *ca.* +0.2 to +0.8 V, indicating that there are strong interactions between Fe sites along the chain.[47] This conclusion was supported by Mössbauer spectroscopy which demonstrated rapid electron exchange between Fe(II) and Fe(III) sites in partially oxidized samples. The appearance of more than two waves in the cyclic voltammogram of this material is a consequence of its low molar mass (it should properly be described as a mixture of oligomers).[48]

Electrochemical data for high molar mass poly(ferrocenylsilanes) (*e.g.* **33**) indicate that there are also quite strong Fe–Fe interactions, with the appearance of two reversible oxidation waves in cyclic voltammetry (*e.g.* Fig. 12) with potential separations of 0.21 to 0.29 V.[49] Electrochemical studies of a series of oligomers have confirmed that the first wave for the polymers corresponds to the oxidation of alternating Fe sites along the chain.[48] The remaining sites, which are harder to oxidize because of their interaction with the adjacent oxidized sites, are oxidized in the second wave. The separation of the two waves ($\Delta E_{1/2}$) therefore provides a measure of the strength of this interaction. Table 1 lists values for a variety of other bridges between the ferrocene units. As would be expected $\Delta E_{1/2}$ is small (90 mV) for the saturated ethane bridge (**35**), although that there is any coupling with this bridge is surprising. In this case, a through-space interaction would appear to be more likely than an interaction through the bridge. This is supported by the fact that there is only very weak coupling in **36** (despite the conjugated linkage) where the ferrocene groups are held further apart. The weak coupling in **36** also illustrates that there are only weak interactions between the Fe sites and the conjugated π system of the bridge. The Fe linkages do not appear to allow significant delocalization of the π system beyond the bridging group.[50]

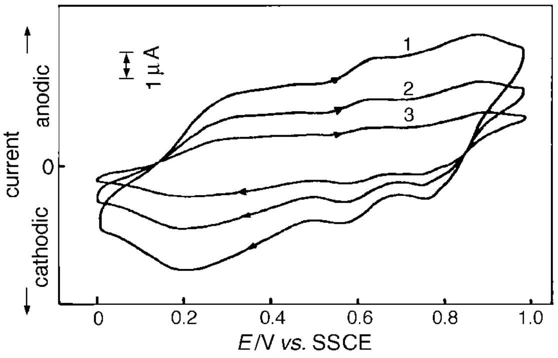


Fig. 11 Cyclic voltammograms (380, 190, and 74 mV s^{-1}) for **32** (1 mM) at a gold electrode in CH_2Cl_2 containing Bu_4NBF_4.[47] Reprinted with permission from *Denki Kagaku*, 1998, **56**, 781.

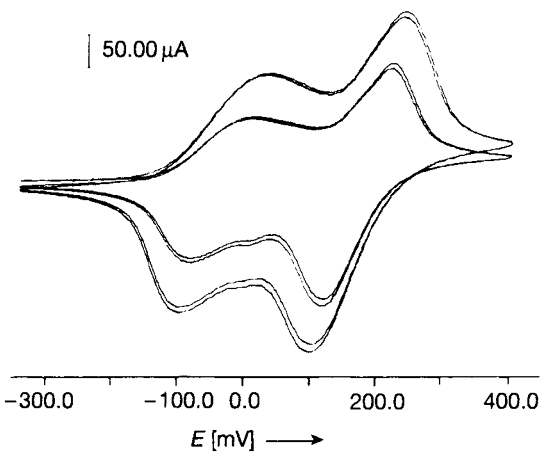


Fig. 12 Cyclic voltammograms of **33** in CH_2Cl_2 (+0.1 M Bu_4NPF_6) at 500 and 1000 mV s^{-1}.[49] Reprinted with permission from *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1709. Copyright 1993 Wiley.

The relative strength of the Fe–Fe interactions in the absence of a bridging group (*i.e.* with a direct link between the cyclopentadienyl rings of adjacent ferrocenes) is difficult to determine because of the absence of electrochemical data on high molar mass samples of **32**. However, since the spread of the waves in Fig. 11 (*ca.* 600 mV) is significantly larger than the spread for 4 to 6 unit oligo(ferrocenyldimethylsiliane)s (*ca.* 250 mV), they are clearly much stronger than in the silane bridged polymers.

Metal complexes of polyaniline and polypyrrole

There have been a number of reports of the complexation of metal ions with conventional conducting polymers such as polyaniline (*e.g.* ref. 51), polypyrrole (*e.g.* ref. 52), and polythiophene,[53] although none of these complexes have been well characterized. The primary evidence for coordination comes from UV-vis spectroelectrochemistry. Fig. 13 and 14 show, respectively, the effect of $CuCl_2$ on the UV-vis spectrum and cyclic voltammogram of polyaniline. The observed changes strongly suggest that the Cu(II) complexes with the polymer, although the nature of the resulting complex is unknown.

Further investigation of this and similar systems can be

Table 1 Separation of the two voltammetric half-wave potentials ($\Delta E_{1/2}$) for polyferrocenes with various bridging groups[45]

Bridging group	Structure	$\Delta E_{1/2}$ (mV)
$-SiMe_2-$	**33**	210
–S–	**34**	310–330
$-CH_2-CH_2-$	**35**	90
–C≡C–Ph–C≡C–[a]	**36**	<30[b]

[a] Ref. 50. [b] Too small to measure.

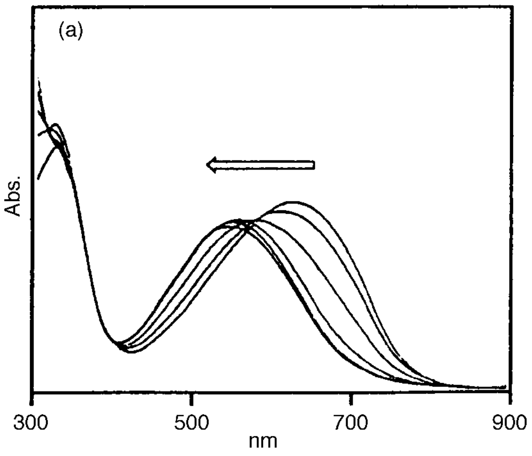
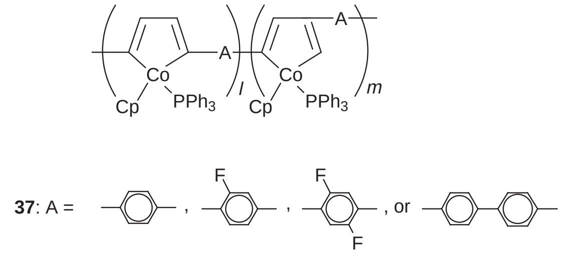


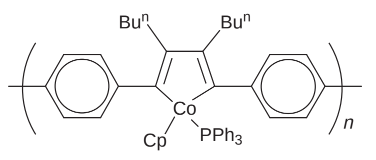
Fig. 13 UV-visible spectra of undoped polyaniline in 1-methyl-2-pyrrolidinone on successive additions of $CuCl_2$ to *ca.* 0.3 per aniline ring.[54] Reprinted with permission from *J. Org. Chem.*, 1997, **62**, 1072. Copyright 1997 American Chemical Society.

expected to provide valuable insight into the influence of metal coordination on the properties of conjugated polymers, and the occurrence of metal–metal interactions through conjugated polymers. There is already evidence that new catalytic and electrocatalytic systems can be developed. For example, polyaniline, polypyrrole, and their derivatives have been found to be effective catalysts, in the presence of various metal ions, for the oxidation of a number of types of organic molecule,[54,55] including the Wacker oxidation of olefins.[51]

Poly(arylene cobaltacyclopentadienylene)s

The poly(arylene cobaltacyclopentadienylene)s represented by structures **37**[56] and **38**[57] are interesting because they are organometallic analogues of polypyrroles and polythiophenes, which are two of the most widely studied classes of conducting (conjugated) polymer. There have been several theoretical studies of the effect of changing the heteroatom in these systems (and experimental work on polymers with O, Se, and Te as the heteroatom), but none have yet considered the use of metal heteroatoms.[58] UV-vis and voltammetric data for **37** indicate that these materials are significantly conjugated, and that they are easily n-doped. They have band gaps (*ca.* 2.2 eV from UV-vis spectroscopy) similar to those commonly observed for polythiophenes. Their oxidation occurs at relatively low potentials, but does not appear to involve the conjugated π-system significantly. A broadening of the Co based oxidation peaks in cyclic voltammetry indicates that there are weak interactions between adjacent Co centres.[57] Further work is needed to elucidate the electron transport characteristics of these materials and the nature of the oxidized state.





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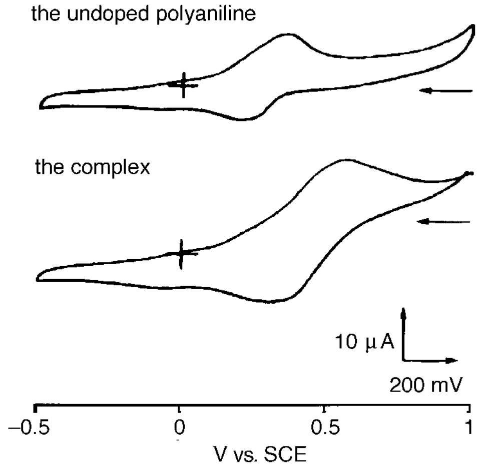

Fig. 14 Cyclic voltammetry of undoped polyaniline in 1-methyl-2-pyrrolidinone ($+Bu_4NClO_4$) in the absence and presence of $CuCl_2$ (0.02 per aniline ring). Scan rate $= 5\ mV\ s^{-1}$.[54] Reprinted with permission from *J. Org. Chem.*, 1997, **62**, 1072. Copyright 1997 American Chemical Society.

Coordination polymers

Polymers formed by coordination of metals to bi- or multifunctional ligands are receiving growing attention,[11,46] and have the potential to become an important class of redox polymer. However, despite the excellent prospect of developing materials with strong metal–metal interactions, I have not found any electrochemical studies of coordination polymers relevant to this article.

Concluding remarks

The primary motivation behind the development of conjugated metallopolymers is to obtain synergistic electronic effects between the metal centres and the polymer backbone. Such effects have been seen in most cases, but are often disappointingly weak. The strongest coupling is seen in ferrocene based systems where the metal forms part of the backbone. There may also be strong coupling in Ru complexes of poly(2,2′-bipyridine) **10**, although the evidence for this is inconclusive. Further work is clearly needed to ascertain the conditions necessary for strong coupling between metal centers through a conjugated polymer backbone.

Important applications in electrocatalysis, sensors, and molecular electronics are envisaged for conducting metallopolymers. There have been some encouraging reports of electrocatalysis and some sensor concepts have been demonstrated. It can be expected there will be increasing focus on such applications as the field develops and important new active materials are discovered.

Acknowledgments

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