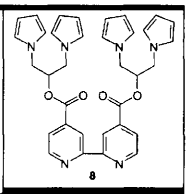

CHEMICAL
SOCIETY
REVIEWS

Conjugated polymers incorporating pendant functional groups—synthesis and characterisation

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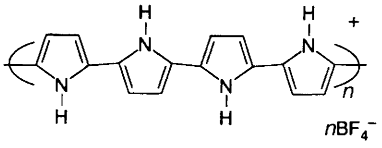
The subject of this review is the synthesis and electropolymerisation of pyrroles or thiophenes with pendant functional groups (metal complexes, ligands, biomolecules for protein binding *etc.*) to afford electrodes coated with a polymeric matrix containing the desired functionality. Such electrodes are being examined in electrocatalysis and in sensor fabrication. More recently, well-defined, soluble polythiophenes with receptor groups for alkali metal ions or for non-covalent binding of electron-deficient aromatics have been made chemically. These polymers can be spin-coated onto electrode surfaces. Their optical and redox properties are changed as a consequence of reversible binding in readily detectable ways. Chemical synthesis of polymers avoids the quite positive potentials usually required for electropolymerisation, which can be a problem for delicate or expensive functional groups. Another approach is to attach the functionality to a suitably reactive polymer after electropolymerisation. Electropolymerisation can also result in poorly adherent or inhomogeneous polymer coatings, and the review concludes with an approach to tackling this problem with another class of functionalised pyrroles—those designed for the fabrication of monolayers, self-assembled on gold electrodes.

1 Introduction

In 1979 a communication was published detailing how pyrrole, on electrooxidation in 0.1 M Et_4NBF_4 in 'wet' CH_3CN, gave a conducting film of polypyrrole (later shown to have the idealised structure **1**) on the working electrode surface.[1] Later, polythiophene (**2**) was prepared similarly. These materials, together with polyacetylene (synthesised chemically in the mid-1970s), have some remarkable properties which have stimulated a very large and increasingly interdisciplinary research effort since their discovery; early work is described in the two-volume book by Skotheim.[1] For example, they may be reversibly redox-cycled between the positively-charged, conducting (p-doped) state in which they are formed (shown in **1** and **2**) and a neutral, essentially insulating state; during this redox switch, ions must move into or out of the film to balance the charge. Their conductivity therefore varies with applied potential, in a manner reminiscent of inorganic semiconductors (the term 'doping' to describe oxidation to the conducting form was purloined, inaccurately, from that field). Moreover, as the electronic structures of the redox states are different, they have different colours (*i.e.* the polymers are electrochromic). Polythiophene, for instance, is blue in the conducting form and red in the insulating form.



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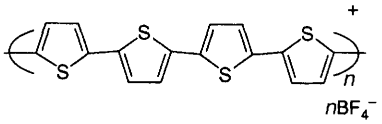

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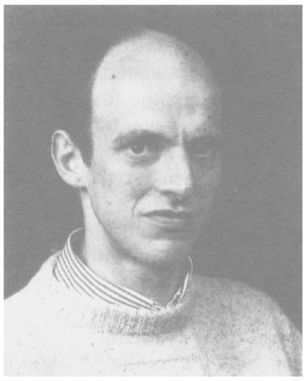

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Discovery of these materials came as electrochemists were increasingly becoming interested in modified electrodes, that is, in chemically anchoring electrocatalytic or other redox-active species to electrode surfaces in order to exert finer control over the reactivity of the electrode than could be obtained simply by varying the applied potential. The first account of deliberate electrode modification dates from 1973; the known strong adsorption of alkenes at platinum surfaces was used to coat a platinum electrode with a monolayer of a platinum complex of a pyridine ligand with a pendant alkene.[2]

Clearly, by using thiophenes or pyrroles bearing some functionality (for example, a metal complex, a metal ion binding site, an anionic or cationic group) as monomers for electropolymerisation, electrodes could be modified with a potentially conductive matrix containing these functional groups. It was perceived that such systems could be useful in, for example, electrosynthesis, novel types of sensor, or electrochromic devices.

The aim of this review is to highlight some important factors in the synthesis, characterisation and applications of functionalised polythiophenes and polypyrroles. Coverage is not restricted to polymers generated electrochemically, since chemical routes, to functionalised polythiophenes in particular, have now become useful.

Clearly, work in this field must begin with synthesis, of the monomer for electropolymerisation or of the polymer itself. The review too, therefore, begins with some general remarks about synthetic routes to monomers and polymers. Approaches to characterisation of conjugated polymer-modified electrodes are next discussed. The covalent incorporation of some specific classes of functional groups into polythiophenes and polypyrroles is then discussed in turn. Conjugated polymers bearing every conceivable type of functionality have been made, including C_{60} derivatives, optically active side-chains, perfluoroalkyl groups, electron donors such as phenothiazine, acceptors such as viologens (or combinations of the two), liquid crystalline groups *etc*. An apology is offered in advance to workers who feel that their contribution has been omitted unreasonably. However, it is hoped that coverage of a few types of functional group in appropriate detail should better illustrate the area than a mere catalogue of every possibility.

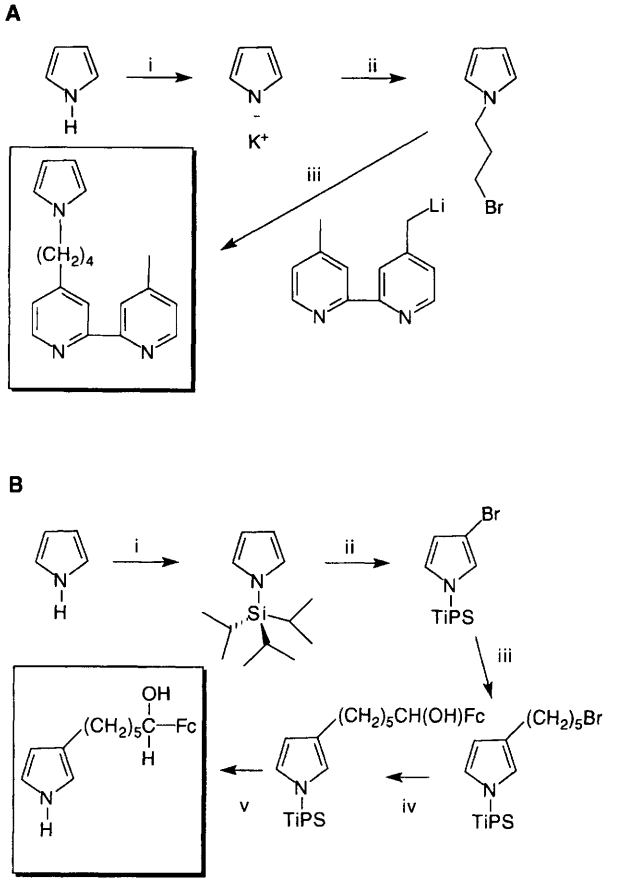
2 Synthetic routes to functionalised thiophenes, pyrroles and their polymers

Much effort has gone into the synthesis of new heterocyclic monomers based upon thiophene or pyrrole, in order to tune the electronic structures and hence the redox and optical properties of the resulting polymers; this fascinating area has been well reviewed very recently,[3] so this discussion will focus on the preparation of monomers bearing pendant functional groups.

Polypyrroles can be redox-cycled between insulating and conducting forms at potentials compatible with aqueous electrolytes, unlike polythiophenes,[1] a clear advantage in possible sensing applications. Moreover, the positive potentials needed to oxidise pyrroles to polypyrroles are not so extreme as those needed to oxidise thiophenes to polythiophenes. Clearly, this is a key point since, to incorporate a given functional group into a conducting polymer using electrooxidation, that functional group must be stable at the positive potential necessary to generate the polymer.

Another consideration is the nature of the connection between the functional group and the heterocyclic polymer backbone. In work with alkyl-substituted polythiophenes, it was shown that the incorporation of bulky groups reduced the conductivity of the doped form, and decreased the degree of conjugation, unless the bulky group was separated by at least a four-carbon chain from the polymer backbone.[4] Therefore, to incorporate bulky functional groups without affecting adversely the redox and optical properties of the polymer, a flexible chain must be employed as a linker between the heterocycle and the functional group; the bulkier the functional group, the longer this chain must be. Additionally, electropolymerisation proceeds *via* generation of heterocycle radical cations,[1] which are appreciably acidic; neither thiophenes nor pyrroles will electropolymerise in the presence of basic moieties[5] and this needs to be taken into account.

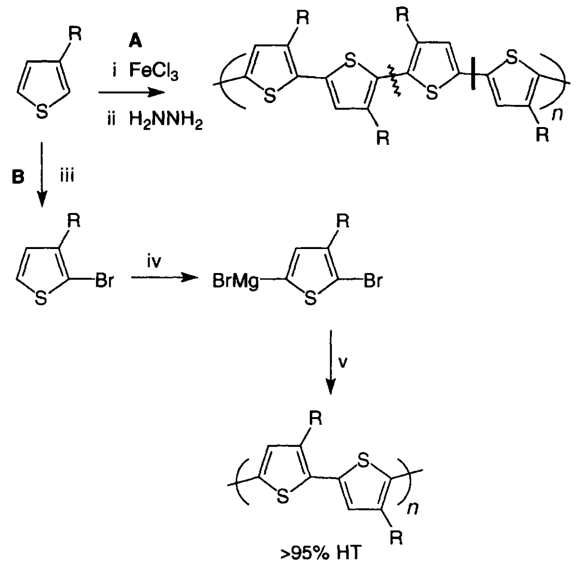
Treatment of pyrrole with potassium metal gives pyrrol-1-ylpotassium, which, although potentially an ambident nucleophile, usually undergoes electrophilic attack at nitrogen (Scheme 1, **A**).[6] Since this is the most straightforward way of functionalising pyrroles, the great majority of studies of functionalised polypyrroles involve *N*-functionalised pyrrole monomers. Unfortunately, in work with simple alkyl or aryl substituents, it was shown that the film-forming properties of pyrroles were diminished, and that the conductivity of the resulting polypyrroles was curtailed, by *N*-substitution; 3-substitution had a much less adverse effect.[7] Potentially, 3-functionalised pyrroles are therefore very attractive. Unfortunately, the syntheses of these are not trivial; the chemistry of pyrrole is heavily dominated by electrophilic substitution at the 2- (or 2,5-) position(s).[6] To obtain 3-functionalised pyrroles selectively, it is necessary to protect the 2- and 5-positions by attaching a bulky group to the nitrogen. Scheme 1, **B**, shows one approach that has been applied here.[8] An alternative is to use Friedel–Crafts acylation of pyrrole-*N*-toluene-*p*-sulfonamide, in which case deprotection must be performed by base hydrolysis.



Scheme 1 (**A**) Typical synthesis of a ligand with a pendant *N*-functionalised pyrrole:[12] (i) potassium metal, tetrahydrofuran (thf); (ii) excess Br(CH$_2$)$_3$Br; (iii) thf (treatment of 4,4′-dimethyl-2,2′-bipyridine with Bu^{n}Li affords the reagent shown). (**B**) Synthesis of a 3-functionalised pyrrole, illustrating a common protection strategy:[8] (i) BuLi, then triisopropylsilyl (TiPS) chloride; (ii) *N*-bromosuccinimide; (iii) BuLi, then excess Br(CH$_2$)$_5$Br; (iv) Mg, Et$_2$O, then ferrocene carbaldehyde (FcCHO); (v) Bu$_4$NF, thf–H$_2$O.

The syntheses of 3-functionalised thiophenes are more straightforward as suitable starting materials [*e.g.* 3-bromothiophene, 2-(3-thienyl)ethanol] are stable and commercially available, and one does not need protecting groups to manipulate them. Soluble polythiophenes can readily be made by FeCl$_3$ or [Fe(acetylacetonato)$_3$] oxidation of 3-alkylthiophenes, but, like electropolymerisation, this can give regiorandom polymers (*i.e.* a mixture of head-to-head, head-to-tail and tail-to-tail coupled monomer units; Scheme 2).[4] Recently, the synthesis of polyalkylthiophenes with a near-exclusive head-to-tail arrangement of monomers has been acheived.[9] These polymers also have relatively high average degrees of polymerisation and narrow molecular weight ranges. Interestingly, this chemistry has since been extended to the preparation of poly(ω-bromoalkyl)thiophenes,[9] which will doubtless find application in the preparation of structurally ordered, functionalised materials.

This is an important development because it is well-known that the key properties of polythiophenes (the redox potential for the p-doping/undoping process; the electronic absorption and luminescence emission maxima for the π to π* transition of the neutral polymer) depend on the degree of conjugation. In chemically-generated polythiophenes, this is controlled mainly by the inter-ring twist angle; the more twisted adjacent monomer units are with respect to each other, the lower is the degree of conjugation, the higher is the redox potential, and the higher is the energy of the π to π* transition.[4] The inter-ring twist angle is controlled in the first instance by the size of neighbouring substituents in 3- (or 3,4-) substituted polymers. This effect is well illustrated by recent work on polythiophene-based light-emitting diodes; the energy of electroluminescence could be controlled across the visible region simply by varying the size of the substituents.[10] Blue electroluminescence could be obtained using chemically-generated poly-3-methyl-4-cyclohexylthiophene, in which the very bulky cyclohexyl groups reduce the degree of conjugation enough to raise the π to π*



Scheme 2 (**A**) Chemical oxidation of 3-R-thiophene (R = *n*-hexyl or longer) gives a soluble polythiophene, but this may have head-to-tail, head-to-head (zig-zag line) and tail-to-tail (bar) linkages.[4] (**B**) Synthesis of regioregular, soluble polythiophenes:[9] (iii) *N*-bromosuccinimide, dmf; (iv) Bu^{n}Li, then $MgBr_2{\cdot}2Et_2O$, Et_2O, −78 °C; (v) 5 mol% $[NiCl_2(Ph_2P\{CH_2\}_3PPh_2)]$ catalyst.

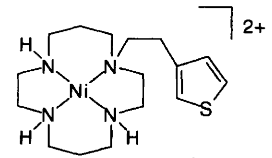
absorption energy into the UV, and hence the emission energy into the blue.

3 Conjugated polymer-modified electrode preparation and characterisation

Electrodeposition of conjugated polymers is usually best performed using repetitive scan cyclic voltammetry (RSCV), with the anodic limit just beyond the potential at which the monomer becomes irreversibly oxidised (to polymer) and the cathodic limit at a potential just negative of the polymer redox chemistry. Chronoamperometry (*i.e.* stepping the potential to a value at which monomer oxidation takes place for a fixed length of time, while monitoring current flow) or chronopotentiometry (*i.e.* passing a known current for a fixed length of time while monitoring electrode potential) can also be employed.[11] Control over film thickness can be exerted by controlling the amount of charge passed during electrodeposition. However, control over other factors, such as the morphology of the films, is less easily exercised; some recent advances in this area are discussed in the final section. Spin-casting a film onto the electrode is an alternative to electrodeposition, if the polymer is soluble and can be chemically prepared.

Cyclic voltammetry is easy to perform, with equipment which is widely available.[11] It can be used to assess, in a preliminary way, whether the redox chemistry of the functional group has been affected by incorporation into the polymer matrix. For instance, one question that immediately arises is: if the functional group has a redox process at a potential where the polymer matrix is in its neutral (insulating) state, can electron transfer still occur between the electrode surface and the functional group? Sometimes, if for example the functional group is a charged metal complex, there is sufficient ionic conductivity within the film to allow electron transfer by a hopping mechanism even when the polymer backbone is electronically insulating.[12,13] In favourable cases, differences between the electrochemistry of the polymer-trapped functional group, and that of the same functional group in solution, are due only to the fact that the former has the characteristics of a surface-localised process and the latter has the characteristics of a solution process, coupled with the fact that, since a redox group within the polymer undergoes electron transfer, charge-balancing ions will need to enter or leave the polymer film. The latter process results in kinetic limitations, evident on studying the voltammetry as a function of scan rate.

Electrochemists have devised ways to apply many spectroscopic and physical techniques to electrode surfaces *in situ* under potential control, and conducting polymer-modified electrodes in particular have been much studied.[11,15] When coupled with the electrochemical data, these techniques can give invaluable information. Electronic spectroscopy is particularly useful for metal complex-containing polymers. The development of Fourier transform infrared (FTIR) spectrometers, coupled with advances in thin-layer reflectance and attenuated total internal reflection techniques, has made IR spectroscopy a valuable tool for examining the nature of the charge carriers in conducting polymers[15] The power of *in situ* spectroscopic techniques for studying functionalised conducting polymers has recently been applied to electrodeposited copolymers of **3** (perchlorate salt) with 3-methylthiophene.[14,15]



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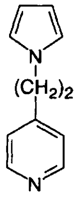
In situ electronic spectroscopy showed that the energy of the π–π* transition for the neutral form of the copolymer was higher than that for poly-3-methylthiophene (P3MT) itself, indicating a shorter mean conjugation length. *In situ* FTIR spectra further showed that P3MT has very uniform conjugation lengths; the lowest-energy electronic transition of the oxidised form of conducting polymers can be seen in the IR, and the energy of this transition did not appreciably change with potential for P3MT.[15] The corresponding band in the copolymer was at lower energy, and its maximum did vary with potential. This is probably due to a combination of the shorter mean conjugation length, and a higher static dielectric constant for this copolymer incorporating ionic moieties. Thus, incorporation of the metal complex into P3MT could be achieved while maintaining the redox activity of the polymer, but at a significant cost in terms of important conjugated polymer properties such as the degree of conjugation.

4 Electropolymerisation of polypyridine metal complexes bearing pendant pyrroles

Metal complexes of polypyridine and porphyrin ligands often display both metal- and ligand-centred redox processes, and have been intensively studied as electrocatalysts. Much effort has therefore gone into incorporating these into polymer-modified electrodes. The majority of studies here involve pyrroles; work until 1990 has been already reviewed.[12] Work on the immobilisation of metalloporphyrins in electropolymerised films has more recently been reviewed by one of the main groups in this field,[13] so these will not be dealt with here.

Early work on incorporating metal–polypyridine complexes into polypyrrole showed that with coordinatively saturated complexes such as $[Ru(bpy)_2(L)_2]^{2+}$ (bpy = 2,2′-bipyridine; L = **4** or **5**) or $[Ru(bpy)_n(L\text{–}L)_{3-n}]^{2+}$ (L–L = **6** or **7**), the film-forming ability of the complexes, and the stability to repetitive



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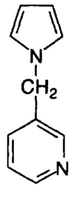

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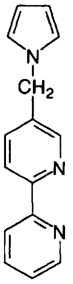

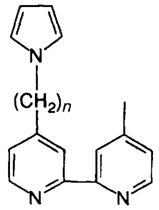

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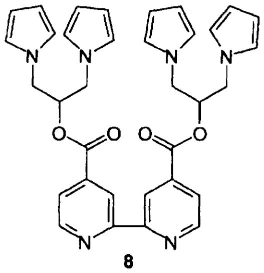
$n = 2,3,4$

voltammetry of the films once prepared, improved on increasing the number of pyrrole groups per metal centre.[13] In fact, with only one pendant pyrrole per metal centre, stable films could rarely be generated at all. Clearly, complexes bearing more than one pendant pyrrole can cross-link through the metal centres, giving more insoluble and therefore more robust polymer films; similar results are obtained when forming ionically conducting polymer films by electroreduction of 4-vinyl-4′-methylbipyridine complexes.[16] This lesson resulted in the synthesis of complexes with ligands bearing additional pyrrole groups, for instance **8** and **9**.



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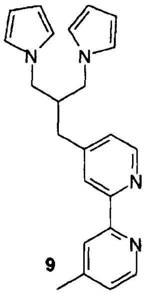

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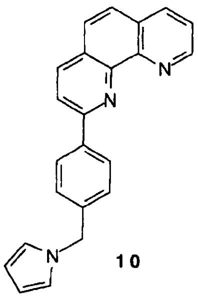

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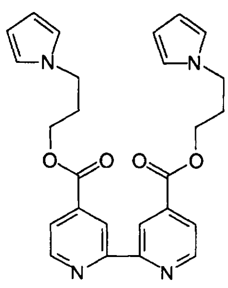
The fate of the ‘polypyrrole’ formed on electrooxidation of Ru^{II} complexes of ligands bearing pendant pyrroles is an important question.[12] Usually, workers in this area grew films by repetitive cyclic voltammetry, with a very negative potential limit to allow the ligand-based reductions to be observed and the positive potential limit just beyond the Ru^{II}/Ru^{III} redox wave, *i.e.* about +1.3 V (*vs.* Ag/10 mM Ag^+). Although films could successfully be grown by this protocol, the poly(*N*-functionalised)pyrrole redox chemistry expected at +0.6 V was never seen. Only when films were grown by RSCV with the anodic limit just positive of the onset of pyrrole oxidation, *i.e.* +0.75 V, was a redox-active polypyrrole obtained.[17] If the Ru^{II}/Ru^{III} process was subsequently scanned, again the polypyrrole electrochemistry vanished; a broad wave superimposed on the Ru^{II} oxidation was assigned to the irreversible oxidation of the polypyrrole backbone. Thus, electropolymerisation of pyrroles can often be used to modify an electrode with a polymer-encapsulated metal complex even if the ‘polypyrrole’ itself is irreversibly destroyed by oxidation as it forms; presumably there is enough residual ionic conductivity within such films to allow continued pyrrole electrooxidation on top of the irreversibly oxidised material on successive scans.

The problem with complexes of the type $[M(bpy)_3]^{n+}$ (M = 4d or 5d transition metal) is that, for electrocatalysis, one is limited to outer-sphere electron transfer processes because these complexes are inert to ligand substitution. More recent work has focussed on metal centres having potential free coordination sites which could participate in inner-sphere processes, and on more reactive organometallic complexes. The coordination chemistry of the metal sites within films can often be manipulated electrochemically. For example, $[RuCl_2(\mathbf{7})_2]$ (n = 4) readily electropolymerised in acetonitrile to afford poly-$[RuCl_2(\mathbf{7})_2]$.[18] This had a reversible Ru^{II}/Ru^{III} redox wave at +0.3 V (*vs.* standard calomel electrode, SCE). When repeatedly redox cycled over the Ru^{II}/Ru^{III} wave in aqueous CF_3SO_3H, conversion, *via* poly-$[RuCl(H_2O)(\mathbf{7})_2]^+$, to poly-*cis*-$[Ru(H_2O)_2(\mathbf{7})_2]^{2+}$ occurred. Irradiation of the latter with visible light caused isomerisation to poly-*trans*-$[Ru(H_2O)_2(\mathbf{7})_2]^{2+}$. It is known that, in solution, *cis*-$[Ru(bpy)_2(H_2O)_2]^{2+}$ undergoes successive pH-dependent stepwise two-electron oxidations to unstable *cis*-$[Ru^{VI}(O)_2(bpy)_2]^{2+}$, which rapidly loses bpy to form *trans*-$[Ru^{VI}(O)_2(OH)_2(bpy)]$. The latter reaction was inhibited in polymer films.[18] This is of some importance because *cis*-$[Ru^{VI}(O)_2(bpy)_2]^{2+}$, though unstable, is a good oxidation catalyst. A poly-*cis*-$[Ru(H_2O)_2(\mathbf{7})_2]^{2+}$ film was used to oxidise benzyl alcohol to benzaldehyde at +1.15 V with 89% current efficiency and 2200 turnovers. Related Ru^{II} complexes have been used in homogeneous conditions in organic synthesis for the catalysis of olefin epoxidation by oxo-transfer reagents like PhIO (including asymmetric examples); it would be interesting to develop electrocatalytic methods for these important reactions.

The complex $[(Cp^*)RhCl(bpy)]^+$ (Cp^* = η-C_5Me_5) is a homogeneous catalyst for the reduction of the important redox enzyme cofactor NAD^+ to 1,4-NADH, which is kinetically slow. Electrodes modified with $[(Cp^*)RhCl(bpy)]^+$ might therefore be valuable in enzyme-based sensors. In acetonitrile solution the 18-electron $[(Cp^*)RhCl(L–L)]^+$ (L–L = various substituted bpy and 1,10-phenanthroline ligands) are reduced in a slow two-electron process, at *ca.* −1.0 V (Ag/10 mM Ag^+) to unstable, formally 20e species, which are in equilibrium with the 18e Rh^I $[(Cp^*)Rh(bpy)]$ formed by chloride ion loss; this is confirmed by the behaviour of this redox wave in the presence of added Cl^-.[19] At < −2.0 V, successive one-electron reductions of L–L occur, with loss of any remaining Cl^-; on sweeping positive, the two-electron oxidation of $[(Cp^*)Rh^I(L–L)]$ is seen, at more positive potentials than for oxidation of $[(Cp^*)RhCl(L–L)]^-$. Using the ligands L–L = **8**, **9** and **10**, polypyrrole films incorporating $[(Cp^*)RhCl(L–L)]^+$ were grown. In this work, the polypyrrole backbone retained its redox activity because modest positive potentials (+0.7 to +0.9 V) were used to prepare the films. Interestingly, the charge under the Rh^{III}/Rh^I redox wave for a film of $[(Cp^*)RhCl(\mathbf{8})]^+$ was smaller than that for the polypyrrole redox process. Presumably, electron transfer is inhibited by the polymer backbone being electronically insulating in the Rh^{III}/Rh^I potential region, coupled with low redox conductivity. By either repetitive cyclic voltammetry over the Rh^{III}/Rh^I redox wave, or by poising the potential of the film just negative of this process, the reactive, coordinatively unsaturated species $[(Cp^*)Rh(L–L)]^{2+}$ could be accumulated in the film on reoxidation. When the ligand-based reduction process was accessed, a sharp current spike was seen at the foot of the cathodic wave; presumably, the remaining Rh^{III} complex became accessible to the electrode as the ligand-based reduction made the film more ionically conducting. In aqueous solution, a catalytic wave due to hydrogen evolution occurred (at low pH), at the onset of the Rh^{III}/Rh^I wave. Presumably, the mechanism of H_2 evolution involves the reaction of the electron-rich $[(Cp^*)Rh^I(bpy)]$ with H^+ to generate the hydride $[(Cp^*)Rh^{III}H(bpy)]^+$.

Platinum metal–phosphine complexes have been used in many homogeneously-catalysed organic reactions. Recently, efforts have been made to couple this chemistry with electrochemical processes *via* electrode modification. This has also stimulated progress in the study of the electrochemistry of platinum metal–phosphine complexes, which had previously been rather neglected. For instance, the complexes *cis,trans*-$[Rh(H)_n(Cl)_{2-n}(PR_3)_2(L–L)]$ (n = 0, 1, 2; PR_3 = PPh_3, $PEtPh_2$; L–L = bpy, 2,2′-bipyridyl-4,4′-isopropylcarboxylate, **8**, **11**) have been the subject of a detailed voltammetric and spectroscopic study.[20] Like the Cp* complexes described above, irreversible two-electron reduction at *ca.* −1.0 V (*vs.* Ag/10 mM Ag^+, in acetonitrile) is coupled with loss of chloride ions, to give $[Rh^I(PR_3)_2(L–L)]^+$; broad waves on sweeping the potential positive again were attributed to two-electron oxidations to $[Rh^{III}(PR_3)_2(L–L)(CH_3CN)_2]^{3+}$ and $[RhCl_2(PR_3)_2(L–L)]^+$. If the experiments were conducted in the presence of a proton source (formic acid or water), $[Rh(H)_2(PR_3)_2(L–L)]^+$ complexes were formed. It is interesting that hydride ligands so stabilise Rh^{III} that no metal-centred reduction was seen for these species; only the reversible ligand-based reductions at < −2.0 V were evident. However, the hydrides were irreversibly oxidised, at *ca.* +1.0 V, to $[Rh(PR_3)_2(L–L)(CH_3CN)_2]^{3+}$ with evolution of protons (detected by pH measurement after exhaustive electrolyses). Polypyrrole films incorporating these metal centres were grown using the ligands **8** and **11**. The metal-based redox processes within films were generally similar to



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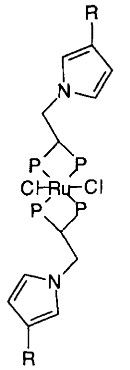

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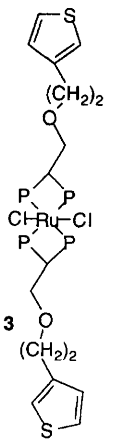

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R = n-hexyl; phenyl groups on phosphorus omitted for clarity

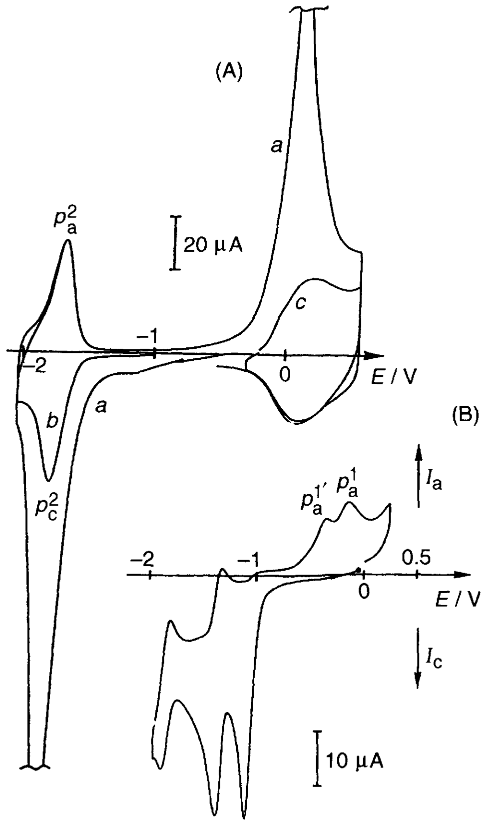


Fig. 1 (A) Cyclic voltammograms, in CH_3CN + 0.1 M tetrabutylammonium perchlorate (TBAP), of a glassy carbon electrode (5 mm diameter, surface coverage 7×10^{-9} mol cm^{-2} Rh, 100 mV s^{-1}) prepared by the oxidative electropolymerisation of 1 mM $[RhCl_2(PEtPh_2)_2(\mathbf{8})]^+$ in CH_3CN + 0.1 M TBAP. Curve (*a*), first negative-going scan, −0.5 to −2.0 to +0.6 to −0.5 V, showing the current 'spikes' due to combined bpy and Rh^{III} reductions at *ca.* −1.8 V, and to the combined polypyrrole and Rh^I oxidations at +0.2 V; curves (*b*) and (*c*), scans restricted to the negative and positive potential regions respectively (initial scans not shown). Here, the redox processes seen are due only to the bpy ligands and the polypyrrole backbone respectively; the complex is trapped as Rh^I {probably poly-$[Rh(PEtPh_2)_2(\mathbf{8})]^+$} or Rh^{III} {probably poly-$[Rh(PEtPh_2)_2(\mathbf{8})(CH_3CN)_2]^{3+}$} respectively. (B) Cyclic voltammogram (5 mm diameter glassy carbon electrode, CH_3CN + 0.1M TBAP) of $[RhCl_2(PEtPh_2)_2(L\text{–}L)]^+$ (L–L = 4,4′-bis(isopropoxycarbonyl)-2,2′-bipyridine) in solution, illustrating the Rh^{III}/Rh^I redox processes (cathodic wave at −1.1 V; anodic waves labelled $Pa^{I\prime}$ and Pa^I) expected for the metal centre in (A), but suppressed by the insulating polymer film. The two anodic waves associated with the Rh^{III}/Rh^I process are assigned[20] to the formation of $[RhCl_2(PEtPh_2)_2(L\text{–}L)]^+$ ($p_a{}^I$) and $[Rh(PEtPh_2)_2(L\text{–}L)(CH_3CN)_2]^{3+}$ ($p_a{}^{I\prime}$) respectively. The two reversible redox processes at more negative potentials are due to the successive bpy ligand-based reductions. (Reproduced from ref. 20. Copyright Elsevier Science SA, 1995.) Potentials *vs.* Ag/10^{-2}M Ag^+.

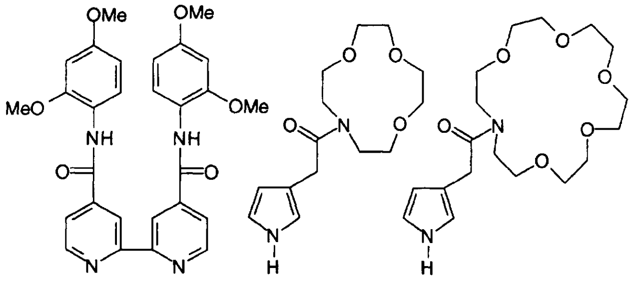
those in solution, except for slower kinetics for chloride ion uptake and loss. However, one remarkable finding was that in films of poly-$[RhCl_2(PEtPh_2)_2(\mathbf{8})]^+$, in which the electroactivity of the polypyrrole backbone is again maintained, the film imposes a form of chemical rectification on the complex (Fig. 1). On sweeping the potential negative, the expected Rh^{III}/Rh^I wave was not present, but on accessing the first bpy-based reduction process (onset *ca.* −1.5 V) a sharp cathodic current spike was seen, due to the combined ligand and Rh^{III}/Rh^I reductions. If the scan range was subsequently maintained between −1.0 and −2.0 V, only the ligand-based, reversible redox process was seen; the complex was 'locked' in its Rh^I form. If the positive potential limit was then extended to +0.6 V, a sharp anodic current spike at *ca.* 0.0 V, at the onset of polypyrrole oxidation, was seen, due to combined polypyrrole and Rh^I/Rh^{III} oxidations. The explanation for this phenomenon is presumably the same as for the current spike seen for the Cp* complex described above; in the potential region where the polypyrrole is in its electronically insulating state, and prior to the onset of the bpy-based reduction where the ionic conductivity of the film will rise, the film is too insulating to mediate electron transfer between the metal centres and the electrode surface.

The dichloride complexes could be transformed into the dihydrides within the polymer films by redox-cycling in the presence of a proton donor. Polypyrrole-modified carbon electrodes containing the dihydride complexes were tried in the electrocatalytic reduction of activated alkenes, and ketones.[20] Product yields and Coulombic efficiencies were low, but the principle was demonstrated; using poly-$[RhCl_2(PEtPh_2)_2(\mathbf{11})]^+$, cyclohexanone was produced from cyclohex-2-enone at −1.4 V (*vs.* SCE) in 14.5% yield (47% current yield).

A limitation with this chemistry is the reliance on pyrrole-functionalised bpy ligands. Routes to phosphine ligands bearing pendant pyrroles or thiophenes would enable the incorporation of metal–phosphine complexes into polymer-modified electrodes without bpy co-ligands. It has been shown that nucleophilic addition to the double bond of coordinated $(Ph_2P)_2C{=}CH_2$ can furnish platinum metal complexes of functionalised diphosphine ligands in one step.[21] Recently, we have used this chemistry to prepare complexes such as **12** and **13**, which can be used as monomers for electropolymerisations.

If any metal complex is to be electropolymerised, clearly the metal centre must be stable at the positive potential necessary to grow the polymer film, and this can pose problems. Recently, it has been found that ligands such as **7** (*n* = 4) and **11** can themselves be electropolymerised in acetonitrile media, providing that deprotonation of the intermediate pyrrole radical cation by the bpy is suppressed by the presence of strong acid ($HClO_4$).[22] Care needs to be taken that acid-catalysed pyrrole oligomerisation[6] (to non-conjugated oligomers) is avoided. Voltammograms of the resulting films (on Pt electrodes) show an irreversible reduction at *ca.* −1.0 V (*vs.* Ag/10 mM Ag^+) due to reduction of bpy-bound protons to H_2, and the usual pair of one-electron reductions of the $bpy^{\bullet-}$ to bpy^{2-} at very negative potentials. Whereas Mn^{II} complexes of ligands like **8** and **11** could not be obtained by electropolymerisation of $[Mn(L\text{–}L)_3]^{2+}$ (the Mn^{II} centre underwent irreversible oxidation at the potentials required to oxidise the pendant pyrroles), modified electrodes incorporating $[Mn(L\text{–}L)_3]^{2+}$ could be made simply by soaking the poly-$(H_2\mathbf{8})^{2+}$ or poly-$(H_2\mathbf{11})^{2+}$ electrodes in a dimethyl sulfoxide (dmso) solution of $MnCl_2$. Poly-$[M(diene)(L\text{–}L)]^+$ (M = Rh, Ir; diene = cycloocta-1,5-diene or norbornadiene) films could similarly be prepared, by soaking previously-deprotonated films of poly-**8** or poly-**11** in solutions of $[\{M(diene)Cl\}_2]$ in dmso–$Bu^n{}_4NClO_4$. Complexes such as these are precursors to homogeneous catalysts, and it will be interesting to see whether electrocatalytic reactions can be developed using these modified electrodes.

Attempts to develop sensor applications for polypyrrole–bipyridine complex films have been described. The complex $[Ru(\mathbf{7})_2(\mathbf{14})](BF_4)_2$ (n = 4) has two pendant pyrroles available for electropolymerisation, and a diamide-functionalised bpy ligand.[17] The amide groups in Ru^{II} complexes of **14** have been demonstrated to act as a receptor for halide ions in solution; the ^1H chemical shift of the amide protons changes as a function of halide ion concentration, and the first ligand-based reduction potential moves by up to 50 mV to negative potential in the presence of Cl^- ions. There are complications with the growth of films containing $[Ru(\mathbf{7})_2(\mathbf{14})](BF_4)_2$ because pyrrole oxidation almost coincides with an irreversible peak due to the oxidation of the dimethoxybenzene units. It is possible that the polymerisation involves the latter as well as the pyrroles, and the 'polypyrrole' generated was not, in any case, electroactive. However, what is beyond doubt is that the electrochemistry of the film so formed does depend upon the electrolyte anion; a shift in the potential of the first ligand-based reduction (localised on the amide-functionalised bpy) is seen in the presence of Cl^-, but not in the presence of Br^- or I^-. Using solution electronic spectroscopy, with $[Ru(bpy)_2(\mathbf{14})]^{2+}$ as a model complex, the association constant for chloride ion binding was 1.7×10^6 mol^{-1} l. However, the films did not slavishly mimic the solution behaviour of $[Ru(bpy)_2(\mathbf{14})]^{2+}$; low levels of F^- had no measurable effect upon the solution redox chemistry of $[Ru(bpy)_2(\mathbf{14})]^{2+}$ but did greatly perturb the electrochemistry of films of poly- $[Ru(\mathbf{7})_2(\mathbf{14})]^{2+}$.



14 **15** **16**

5 Host–guest chemistry in conjugated polymers

The archetypal example of host–guest chemistry was the development of crown ethers (hosts) for selective complexation of alkali metal ions (guests). More recently, much effort has been expended in designing crown ethers with additional functionality which allows straightforward detection of metal ion binding, for example a ferrocenyl group whose redox potential changes as a function of metal ion binding. By building crown ether functions into conjugated materials, the possibility exists that the properties of the polymer might change in a detectable way as a function of metal ion binding by the crown ethers, allowing the design of potentially simple sensors. One obvious property to use is the redox switching potential of the polymer; it might be expected that this would be affected by the presence of ions within the neutral film as a consequence of cation binding by the pendant crown ethers.

Early attempts did not seem to give much ground for optimism. For instance, an *N*-functionalised pyrrole bearing a 15-crown-5 substituent gave a polymer, the electrochemistry of which did not vary appreciably as a function of the presence of alkali metal cations in the bathing electrolyte.[23] However, this is an instance where the synthesis of 3-functionalised pyrroles, though more difficult, was worthwhile. Monomers **15** and **16** could be electropolymerised on Pt discs (CH_3CN, $LiClO_4$ electrolyte) to give polypyrrole films with high conductivities (1 S cm^{-1}) which could be redox-cycled in both aqueous and non-aqueous (acetonitrile) media with much lower redox potentials than the *N*-functionalised materials.[24] The redox wave for the doping/undoping process for poly-**15** did not change appreciably as a function of electrolyte cation (Li^+, Na^+ or K^+), perhaps because this amide derivative of 12-crown-4 is not a particularly good ligand for any alkali metal ion. However, if poly-**16** was grown in $LiClO_4$ electrolyte, then cycled in $NaClO_4$ or $KClO_4$, the anodic peak for polypyrrole oxidation shifted positive, irreversibly, by up to 0.4 V in CH_3CN (Fig. 2).

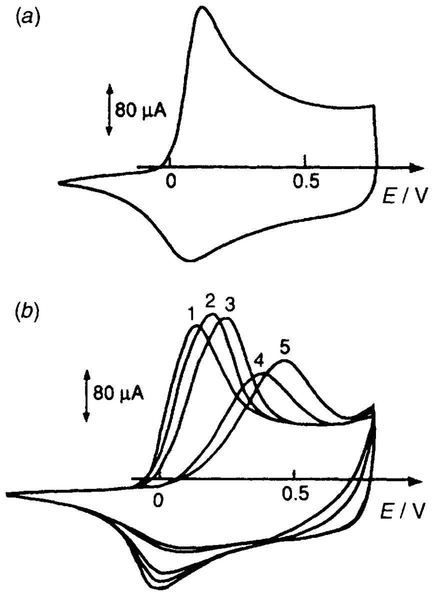
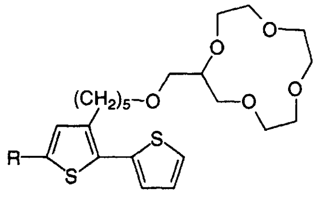


Fig. 2 (*a*) Cyclic voltammogram (*E vs.* SCE) of a poly-**16** film, polymerisation charge 0.1 C cm^{-2}, platinum electrode, sweep rate 50 mV s^{-1}, CH_3CN, electrolyte 0.1 M $LiClO_4$. (*b*) Successive voltammograms of the same film after transfer to CH_3CN–0.1 M $NaClO_4$. From ref. 24.

Presumably the binding of Na^+ or K^+ by the larger crown in poly-**16** makes it thermodynamically harder to generate the oxidised form of the polymer than when Li^+ (weakly bound by larger crown ether cavities) is the electrolyte cation. This may be due to changes to the polymer secondary structure caused by cation binding, which make doping less favourable, as will be discussed further below. The advantage often enjoyed by polypyrroles of water compatibility was of no use in this instance as a similar cation response was not observed in aqueous electrolytes.

Polythiophenes incorporating pendant 12-crown-4 sites have also been prepared, by electrooxidising **17** and **18** in CH_3CN–$Bu^n{}_4NPF_6$. In contrast to poly-**16**, these respond most strongly to the presence of Li^+ ions, as expected given the binding preference of this smaller crown.[25] Even very low concentrations ($\geqslant 5 \times 10^{-5}$ M) of Li^+ in CH_3CN were enough to cause obvious changes in the voltammetry of poly-**17** (Fig. 3). With increasing [Li^+], the polymer redox wave shifted positive, broadened, and decreased in area. Significantly, model poly-3-alkylthiophenes showed no change in their redox properties in the presence of Li^+ and 12-crown-4; the binding site must be covalently anchored to the polymer for the effect to be apparent.



R = H; **17**

R = 2-thienyl; **18**

Among the most interesting developments in this area have been reports of some soluble polythiophenes, generated chemically.[26] Scheme 3 shows the syntheses of polythiophenes

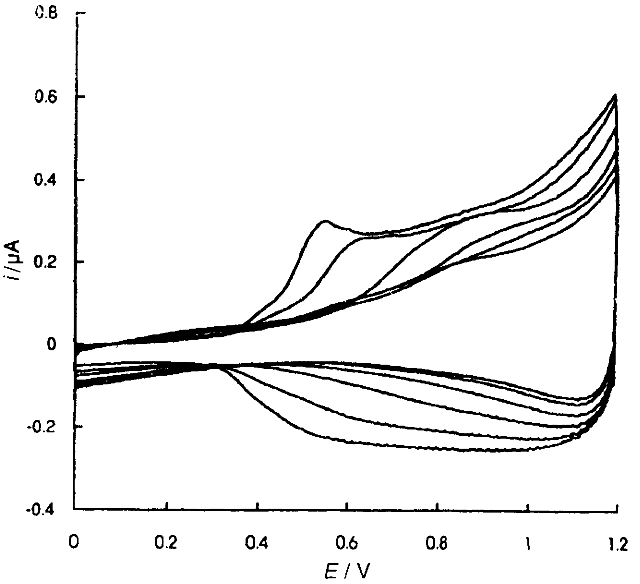
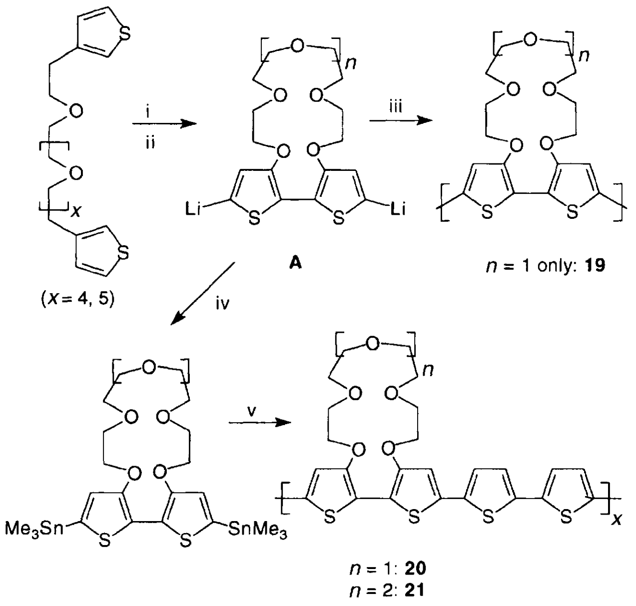


Fig. 3 Cyclic voltammograms (*E vs.* Ag/AgCl) of a poly-**17** film (sweep rate 100 mV s^{-1}) in CH_3CN, 0.1 M TBAP in the absence of $LiClO_4$, then successively increasing concentrations; 10^{-4}, 2×10^{-4}, 3×10^{-4}, 4×10^{-4}, 5×10^{-4} M, of $LiClO_4$. The polymer redox process moves to more positive potentials and diminishes as $LiClO_4$ is added. (Reproduced from ref. 25. Copyright 1993, VCH Publishing Group).



Scheme 3 Synthesis of ionoresponsive polythiophenes:[26] (i) $CuCl_2$ oxidative coupling (*ca.* 20% yield); (ii) Bu^{n}Li (**A** not isolated); (iii) [Fe(acetylacetonato)$_3$] oxidation; (iv) Me_3SnCl; (v) 5,5′-dibromo-2,2′-bithiophene, Pd^0 catalyst.

designed such that the binding of alkali metal ions by the crown-like oligooxyethylene moieties would alter the degree of inter-ring twisting in the polymer chain (see Fig. 4), and hence alter the colour of the polymer, as well as its redox properties. The potential advantage of the polythiophene acting as a 'reporter' of cation binding is that even if only a single binding site is occupied on a given polythiophene chain, the 'twisting' effect could be transmitted significantly to neighbouring rings, thus amplifying the response at low concentration of cation. One would predict a blue shift in the π–π* transition on cation binding, as the degree of conjugation is lowered with twisting, and this was indeed observed for these polymers. The magnitude of the shift also showed size selectivity. By analogy with known binding constants for crown ethers, Na^+ is expected to fit best the pentaoxy receptor, and K^+ the hexaoxy receptor. The data supported this picture. Also notable was that the shifts were very large even though binding constants, measured for the monomers, were smaller than those found for crown ethers themselves, lending support to the idea that although binding is weak, it affects more of the chain than the immediate bithiophene unit concerned. One disadvantage of these otherwise elegant systems is the length (and overall yields) of the syntheses (Scheme 3), and it is interesting that similar findings have also been reported for regioregular poly[3-oligo(oxyethylene)-4-methylthiophene]s.[27]

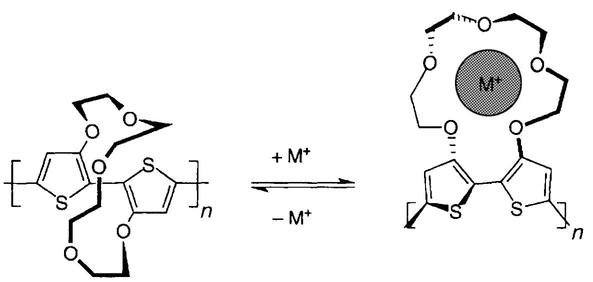
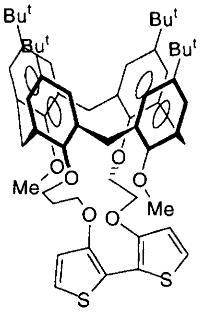


Fig. 4 The principle behind the design of the ionoresponsive polymers of ref. 26. Binding of an alkali metal cation causes twisting of the polythiophene chain away from optimum conjugation.



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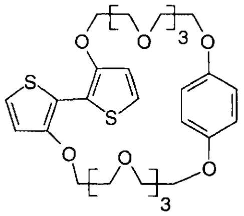


23

Calixarenes give very high binding constants for alkali metal ions, and as a result of their greater rigidity are also more size-selective than crown ethers. The calixarene-functionalised bithiophene **22** was therefore synthesised, characterised crystallographically, and its copolymer with 3,3′-bis(2-methoxyethoxy)-2,2′-bithiophene prepared.[26] In this instance, the bithiophene exhibited considerable twisting in the absence of cation binding (inter-thiophene ring angle 68°), and a red shift was seen for the polymer in the presence of Na^+; in this instance, binding of Na^+ by the calixarene improved the conjugation of the polymer. Interestingly, the redox potential of the polymer, cast as a film onto interdigitated Pt microelectrodes, increased in the presence of Na^+ in spite of this. Moreover, using a bipotentiostat and maintaining a small potential difference between two adjacent Pt microelectrodes overlapped by the polymer film, it was possible to monitor the current flowing as the polymer was redox-cycled, which is related to the conductivity; it was found that the conductivity of the film was almost completely suppressed in the presence of Na^+ (Fig. 5). Even though Li^+ and K^+ had no significant effect upon either the electronic spectrum of the polymer or its redox potential, they also significantly suppressed film conductivity. It was suggested that these results could be accounted for by localisation of charge carriers *via* electrostatic repulsion from occupied binding sites. In this respect, the *in situ* monitoring of polymer conductivity provided the best detection route for cation binding. The suppression of film conductivity on cation binding has been termed a 'chemoresistive' response. Unlike the behaviour of polythiophenes with pendant crowns, the binding of Na^+ was reversible; holding the polymer in its oxidised form resulted in expulsion of the Na^+, and the voltammogram and

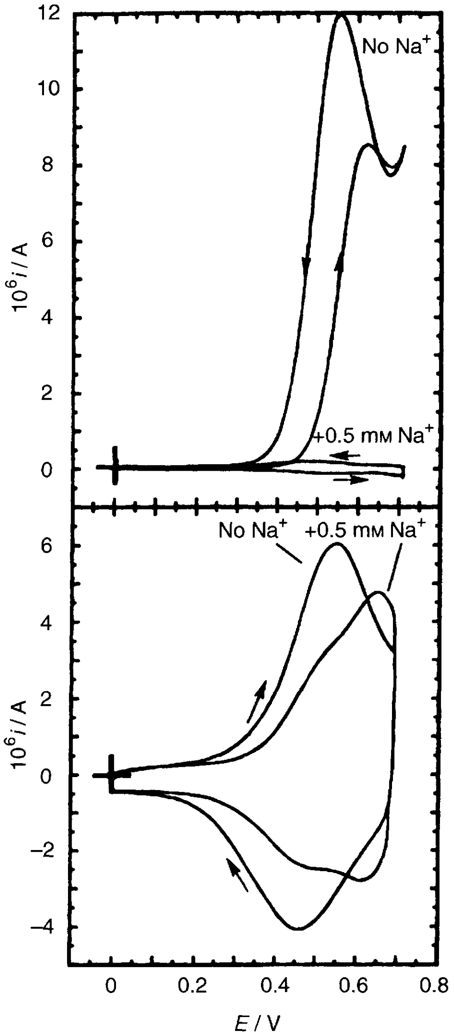
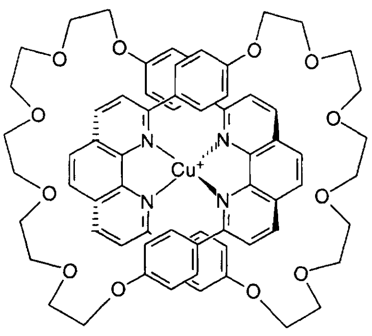


Fig. 5 (Bottom) Cyclic voltammogram (drain current, 20 mV offset, 10 mV s^{-1}, 0.1 M Bu_4NPF_6, CH_3CN) of a film of AB copolymer of **22** with 3,3′-bis(2-methoxyethoxy)-2,2′-bithiophene in the absence and presence of 0.5 mM Na^+ recorded, using a bipotentiostat, on two interdigitated microelectrodes 10 μm apart, connected by the film. (Top) Current flowing between the microelectrodes, due to the potential difference (20 mV) maintained between them (200 mV s^{-1} 0.1 M Bu_4NPF_6, CH_3CN). Note that while the presence of this small concentration of Na^+ has some effect on the voltammogram, it completely suppresses the conductivity of the film as determined by the latter technique. Potentials are *vs.* a silver quasi-reference electrode. (Reproduced from ref. 26. Copyright 1995, American Chemical Society).

conductivity response of the original polymer film were restored.

Recently, there has been much interest in the complexation of viologen-related molecules (which are electron-poor aromatic molecules) by electron-rich 1,4-dialkoxyaryls incorporated in polyether rings. Interlocked rings (so-called catenanes) can be synthesised utilising the self-assembly of such individual electron-poor and -rich building blocks, and a new sub-field of supramolecular chemistry has developed recently from this finding.[28] Thiophenes are also suitably electron-rich; an AB copolymer of **23** with 3,3′-bis(2-methoxyethoxy)-2,2′-bithiophene has been successfully demonstrated as a sensor for the paraquat (4,4′-dimethylbipyridinium) cation using a very similar approach to that described for the alkali metal-sensing polythiophenes.[26] Once again the most sensitive form of detection of paraquat binding in the receptor sites of these polymers was monitoring, *in situ*, the conductivity of cast films using interdigitated electrodes.

Another class of interlocked molecules which has attracted interest are those prepared from reactive 1,10-phenanthrolines by formation of a tetrahedral metal complex, followed by ring closure with oligooxyethylene chains, to give complexes of the general structure **24**. The electropolymerisation of the pyrrole-bearing copper complexes **25** has been used to modify electrode surfaces with similarly interlocked metal coordination sites, the interlocking in this instance being due to polypyrrole cross-linking.[29] That these sites, once formed, are rigidly anchored within the polymer matrix was demonstrated by removal of the copper(I) by treatment of the polymer film with CN^- or SCN^-, followed by treatment with a different metal ion [*e.g.* cobalt(II), zinc(II)]; the voltammetry of the film changed to reflect whichever rigid tetrahedral bis(1,10-phenanthroline) metal complex was present within the film. Moreover, when the free bis-(pyrrolyl)phenanthroline ligands themselves were electropolymerised, then soaked in solutions of metal ions, no metal ion complexation could be detected voltammetrically. Clearly, a metal ion must be present to preserve the tetrahedral cavity during electropolymerisation for the films subsequently to undergo metal ion exchange. The approach has since been extended to 3-functionalised pyrroles and to pre-formed rotaxane complexes.[29] These systems could be utilised for transition metal ion sensing, as the later 3d metal ions all form tetrahedral complexes with the intertwined ligands that have distinctive redox properties which can be distinguished voltametrically. Particularly with nickel and cobalt, the redox properties are also interesting in that the rigid enforcement of tetrahedral geometry by the interlocked 1,10-phenanthroline ligands stabilises the unusual M^I oxidation state, and electrocatalytic applications can also be forseen for these modified electrodes.



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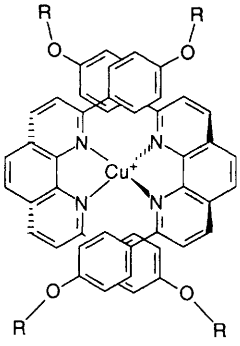
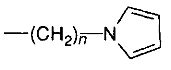


25

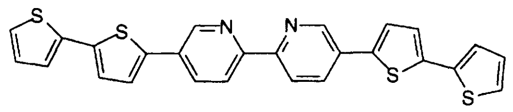
R =



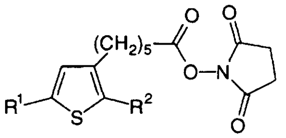
n = 3,6,11

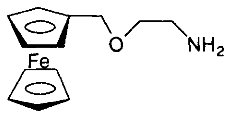
Related work, with polythiophenes, has focussed on more direct electronic coupling between the metallorotaxane receptor site and the conjugated polymer backbone. By combining a preformed cyclo-oligooxyethylene-1,10-phenanthroline ligand, the ligand **26** and Cu^I or Zn^{II} as the ‘templating’ metal ion, rotaxane complexes with two pendant bithiophene units were prepared, and these have been electropolymerised to afford alternating quaterthiophene–bpy complex copolymers with threaded cyclic phenanthroline units.[30]

Nature is still supreme in the area of host–guest chemistry. Various dipeptides and tripeptides, known to be specifically recognised and bound by appropriate proteins, have been attached to pyrrole, *via* the reaction of pyrrol-3-ylacetic acid with the amine-terminal end of the peptide in the presence of dicyclohexylcarbodiimide.[31] Some of the peptides were used with the carboxy terminus in the free acid form, and some as the methoxy esters. The peptide-functionalised pyrroles were electropolymerised and the cyclic voltammograms of the polymers were examined in the presence of varying concentrations of the proteins concerned. The selective binding of a given



26





27 $R^1 = R^2 = H$
$R^1 = H, R^2 =$ 2–thienyl
$R^1 = R^2 =$ 2–thienyl

28

protein to its specific peptide could be detected by a shift to more positive potential and a diminution of current response for the redox process of the polymers. Moreover, once the protein was bound by the peptide, it could subsequently be released (if the peptide was in the free acid form) by electrooxidation of the polypyrrole backbone. This occurred because on oxidation, protons were released from the carboxy terminal groups to balance the positive charge of the polymer backbone; this pH change causes peptide binding to weaken.

6 Attaching biomolecules to conjugated polymers, *via* post-polymerisation modification

Many attempts to fix redox enzymes to electrode surfaces using polymers of various kinds have been described. Although the idea of 'wiring' a redox enzyme to an electrode *via* a conducting polymer, as in Fig. 6, is attractive from the point of view of sensor construction, the conflicting requirements of preserving enzyme activity while preparing a truly conductive polymer mean that it is extremely difficult to achieve in practice. The difficulties are well illustrated by the following example. Glucose oxidase oxidises β-D-glucose to δ-gluconolactone, at the same time reducing O_2 to H_2O_2. This enzyme has been functionalised by attaching 3-carboxymethylpyrrole to protein surface lysyl (*i.e.* pendant NH_2) groups by amide bond formation.[32] This did not impair enzyme activity. The pyrrole-functionalised enzyme could only be attached to an electrode surface by co-polymerisation with pyrrole itself. Moreover, the voltammetry suggested strongly that the electroactivity, and therefore the conductivity, of the 'polypyrrole' is destroyed as the polymer forms, as a consequence of the concentrations of monomers used (1 mM) and the necessity for using buffered media (pH 7) to preserve enzyme activity. Therefore 'wiring' as in Fig. 6 has not been achieved—the enzyme is merely anchored to the electrode surface. Nevertheless, the activity of enzyme films formed by covalent anchoring in this way (maintained at +0.7 V *vs.* SCE) was over six times as high as films formed by simply entrapping glucose oxidase, as a charge-balancing anionic species, within a growing polypyrrole film.

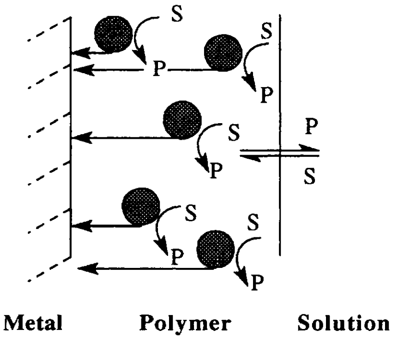


Fig. 6 'Wiring' an enzyme (shaded circle) to an electrode *via* a conducting polymer matrix. The substrate (S) partitions into the polymer from solution and is oxidised by the enzyme to the product (P); the electrons released are shuttled to the electrode by the conducting polymer backbone.

If it is desired to prepare a polymer-modified electrode bearing a particularly sensitive or expensive functional group, it may be preferable to attach this after the electrode modification step, and methods for doing this are now being developed. These are particularly appropriate for the attachment of biomolecules to conducting polymers. For example, glucose oxidase has been attached to the surface of conducting polymer films formed by the electrooxidation of *N*-(4-aminophenyl)-2,5-di(2-thienyl)pyrrole and *N*-(2-aminoethyl)-2,5-di(2-thienyl)pyrrole, using protein surface carboxy groups to form amides in this instance.[33] The activity of the resulting polymer-anchored enzyme electrodes was measured as a function of the number of scans in the RSCV experiment to grow the polymer; the optimum number of scans was around 50. Beyond this, activity fell off, due to diffusion limitations within the polymer. The mechanism was thought to involve formation of H_2O_2 and its diffusion through the polymer layer to become reduced at the underlying Pt electrode, rather than charge transport *via* the polymer film, however. The response time of the electrode was fast as the enzyme was only attached at the polymer-electrolyte interface, rather than dispersed within the film.

Polythiophenes have been derivatised similarly. Activated ester–functionalised polythiophene films made by electropolymerisation of the monomers **27** have been shown to react with the aminoethoxymethyl **28** to give polythiophenes bearing the corresponding pendant amidoferrocene groups, using cyclic voltammetry.[33] The technique was extended to the attachment of amine-bearing biomolecules.

7 Self-assembled monolayers and conjugated polymers

Much of the chemistry covered in this brief review relies on an electropolymerisation step to fabricate a modified electrode. The morphology of electrodeposited conducting polymers, and how well they adhere to the electrode surface, are important questions likely to have a bearing on the utility of polymer-modified electrodes, and it seems appropriate to end this article by discussing a class of functionalised monomer whose purpose is to enable some control to be exercised over the electrode–polymer interface.

Interest in the monolayer-modified electrodes referred to in the Introduction revived recently with the discovery that very well-ordered, close-packed monolayers could be fabricated by the adsorption of alkanethiols on to gold electrodes. These are referred to as self assembled monolayers (SAMs) since they form spontaneously if a gold electrode is soaked in a solution of the alkanethiol RSH (or dialkyl disulfide RSSR). Many different redox-active molecules, from simple ferrocenyl groups to organometallic clusters or enzymes, can thus be attached a fixed distance from a gold surface by an alkylthio pendant group of known length. Several studies have been reported recently on the behaviour of pyrrole- or aniline-terminated SAMs; thiophenes are not useful here, as their oxidation potentials are well positive of that for the oxidative desorption of thiols from gold surfaces (> *ca.* +1.3 V *vs.* SCE).

Simultaneous *in situ* ellipsometry and electrochemical quartz crystal microbalance (EQCM) measurements have been used to examine the growth of polyaniline films on gold electrodes, either bare, or pre-coated with a SAM of either 4-aminothiophenol (4-ATP), or other alkane- or arene-thiols.[34] Ellipsometry provides a measurement of the complex refractive index and thickness of surface films. EQCM, in its simplest manifestation, measures changes in the mass of a film on an electrode surface as a function of potential. The results showed that on bare gold, or on gold coated with alkane- or arene-thiols, an optically diffuse film (*i.e.* one containing much solvent) is deposited in the early stages of growth. On gold pre-coated with 4-ATP, optically much denser films formed, although the amount of material deposited as a function of time was not greatly different. Subsequent voltammetry and AC impedance measurements showed that films grown on 4-ATP-coated gold switched more rapidly between the conducting and insulating states. The 4-ATP film evidently aids the process of nucleation, the initial event in the deposition of conjugated polymer films. It may also, as evidenced by the switching experiments, impose some order on the initial film formation process.

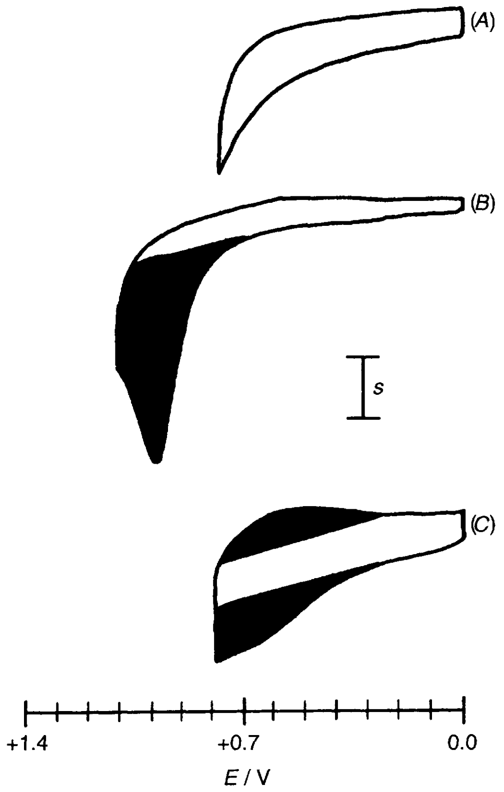
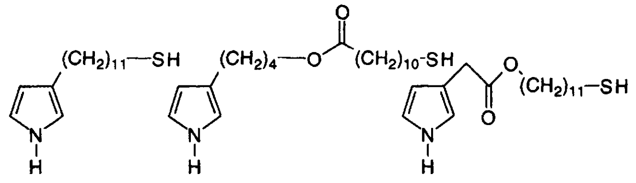


Fig. 7 Cyclic voltammograms of (*A*) gold electrode coated with a SAM of ω-pyrrol-1-ylhexanethiol scanned between 0 and +0.75 V (*vs.* sodium standard calomel electrode); (*B*) between 0 and +1.1 V showing the charge due to the irreversible oxidation of the pyrrole moieties (shaded area); (*C*) between 0 and +0.75 V after the potential excursion shown in *B*, showing the charge due to the electrochemistry of the thiol-anchored polypyrrole strands formed in *B* (shaded area). Area of electrode 1.96 × 10^{-3} cm^2, scan rate 100 mV s^{-1}, current scale *S* = 5 μA cm^{-2} for (*A*) and (*C*), 13 μA cm^{-2} for *B*. (Reproduced from ref. 35. Copyright 1994, American Chemical Society).

Similar conclusions were reached when poly-3-ethylpyrrole was grown on gold pre-coated with monolayers of **29**, **30** or **31**.[35] Much more adhesive, denser and more conductive films were produced on the SAM-coated gold than on bare gold, and poly-3-ethylpyrrole grown on gold coated with a simple alkanethiol was similar to that grown on bare gold. Again, this suggests that the presence of the pyrrole-terminated SAM results in the growing polypyrrole becoming chemically bonded to the surface, as the terminal pyrrole is involved in the electropolymerisation.



29 **30** **31**

Attempts were also made to electrooxidise these pyrrole-terminated SAMs in the absence of additional pyrrole monomer in solution. Although the SAMs of **29–31** became irreversibly oxidised at the expected potentials, the products were electroinactive, suggesting that the electrogenerated pyrrole radical cations react with trace nucleophiles rather than undergoing coupling to form polymer. However, similar monolayers of *N*-(ω-thioalkyl)pyrroles can be electropolymerised, to give an electroactive, polypyrrole-like material (see Fig. 7).[35] Presumably, the pendant pyrroles knit together to form strands of polymer held parallel to the surface by the alkanethiol tethers. Evidence for this comes from competitive displacement experiments. Alkanethiol SAMs undergo exchange with thiols in solution. When the unpolymerised *N*-(ω-thioalkyl)pyrrole SAMs were treated with solutions of ferrocenylalkanethiols, they were displaced; the increasing surface concentration of ferrocenylalkanethiol as a function of time could easily be monitored using the surface-anchored ferrocene redox chemistry. However, once the pyrrole groups had been electrooxidised, the ferrocenylalkanethiol failed to displace the 'polypyrrole-knitted' SAM.

The use of monolayers of anchored heterocycle monomers to fix conjugated polymer layers to electrode surfaces predates the discovery of alkanethiol SAMs, however. As long ago as 1982, when polypyrrole was being examined as a protective coat for n-doped silicon in photoelectrochemistry, it was found that it did not adhere well to the surface. Silicon is inevitably covered by a thin layer of oxide. The surface was therefore first treated with 1-pyrrol-1-yl-3-(trimethoxysilyl)propane; trialkoxysilanes are known to anchor firmly to oxides by reaction with surface hydroxy groups with elimination of alcohol. Subsequent electropolymerisation gave a polypyrrole layer which was so adherent that it could not be peeled off the surface with adhesive tape.[35]

8 Conclusions and prospects

This review commenced with conjugated polymers incorporating metal complexes. The range of metal complexes which has been anchored to electrode surfaces by the electropolymerisation of a pendant pyrrole group has been extended over the last few years to include coordinatively unsaturated or organometallic species,[17–20,22] which are likely to prove more interesting as electrocatalysts. Developments in applications, such as in sensing, may be forthcoming for these systems, but these will probably be in 'niche' areas. That there is a role for well-designed, chemically-prepared conjugated materials in sensor applications has been well-demonstrated for calixarene-, crown ether- and rotaxane-containing polythiophenes.[26] Chemical synthesis avoids some of the additional variables inevitably encountered in electropolymerisation experiments, but at a cost—the synthetic effort involved is substantial. Another important pointer from this work is that changes in the voltammetry of polymer films may not be the most sensitive parameter for detecting a response to binding by the polymer; conductivity and optical properties offer other possibilities. It may be useful to see if the same concepts can be applied to the detection of enzymes or oligonucleotides using polypyrroles bearing short polypeptide or RNA side-chains respectively.[31]

Finally, the use of self-assembled monolayers of pyrrole-terminated alkanethiols offers a good way of preparing extremely thin yet dense conjugated polymer films by electropolymerisation. It will be interesting to examine such processes using *in situ* techniques such as scanning tunnelling microscopy, to see if more ordered polymer chains also result, and to apply this idea to the preparation of thin, functionalised conjugated polymer films.

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