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Electrosynthesis and co-ordination chemistry of polymer films coated on electrode surfaces from pyrrole polypyridyls

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New functionalized polypyrrole films containing transition-metal complexes of the type $[Mn(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine) and $[M^IL(diene)]^+$ (M = Rh or Ir, L = 2,2′-bipyridine or 1,10-phenanthroline, diene = cycloocta-1,5-diene or norborna-2,5-diene) have been synthesized and characterized by electrochemical techniques and UV/VIS spectroscopy. The strategy is based on the complexation of Mn^{2+} cations and $[\{M^I(diene)Cl\}_2]$ precursor complexes in polymer films, coated on platinum and carbon electrodes by oxidative electropolymerization of pyrrole-substituted 2,2′-bipyridine and 1,10-phenanthroline monomers in acidic MeCN electrolyte. The redox behaviour of poly$[M^IL(diene)^+]$ is strongly dependent on the size of the cation of the supporting electrolyte. This appears to be a consequence of its permeation through the film to maintain electroneutrality in the polymer.

The oxidative electrochemical polymerization of pyrrole-substituted transition-metal complexes is an efficient way to assemble in one step stable metallopolymer films on electrode surfaces, with a view to developing new materials for electrocatalysis, electroanalysis and photoelectrochemistry.[1] However, this general strategy is not always suitable. Its main limitations are the transformation and/or the irreversible degradation of the metal complex in the polymerization step due to its redox instability, or chemical reactivity towards organic electrolytes able to perform efficiently pyrrole polymerization. An alternative route to polypyrrole-based materials is to trap metal complexes as counter ions in oxidized polypyrrole, or in polypyrroles substituted with anionic or cationic moieties.[1] Compared with films containing covalently bound metal complexes, the operational stability of these materials is rather poor, owing to exchange of dopant ions with counter ions of the electrolyte. Thus, it appears necessary to develop new strategies for the synthesis of stable metallopolymer films on electrode surfaces.

In this context, electropolymerization of metal-free compounds followed by *in situ* complexation of a free or chelated metal centre appears to be a straightforward strategy. It avoids the initial synthesis of the polymerizable complex, side reactions due to redox instability during electropolymerization and would allow the construction of stable materials. Surprisingly, only a few examples can be found in the literature. Iron–sulfur clusters have been bound to polypyrrole-containing pendant cysteinyl groups,[2–4] and Ni^{2+} cations have been complexed to electropolymerized pyrrole–bipy ligands (bipy = 2,2′-bipyridine) to give poly[tris(bipyridine)nickel(II)] films.[5] Direct reductive electropolymerization of bromomethyl-substituted derivatives of bipy followed by *in situ* complexation of Fe^{2+} cations has also been briefly reported.[6] Only very thin films were obtained, since electrode passivation occurred during ligand polymerization. Thus, the polypyrrole approach appears more attractive, since it allows one to grow thicker, conducting films of metal-free compounds.

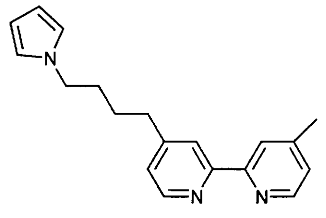
Here we report some examples illustrating the versatility of the strategy based on the electropolymerization of pyrrole-substituted 2,2′-bipyridine (L^1 and L^3) and 1,10-phenanthroline (L^2), followed by complexation of Mn^{2+} cations and $[\{M^I(diene)Cl\}_2]$ {M = Rh or Ir, diene = cycloocta-1,5-diene (cod) or norborna-2,5-diene (nbd, bicyclo[2.2.1]hepta-2,5-diene)} precursor complexes. It must be emphasized that the poly$[Mn(bipy)_3{}^{2+}]$ and poly$[M^I(diene)(bipy)^+]$ films synthesized in this way cannot be obtained from direct electropolymerization of pyrrole-substituted complexes, owing to their redox instability.

Results and Discussion

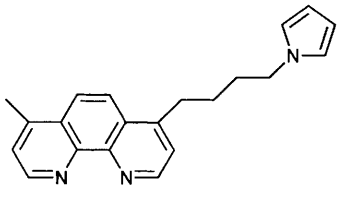
Electrosynthesis of polymer films

As previously reported for pyrrole-substituted pyridine[7] and 2,2′-bipyridine,[8] the oxidative electropolymerization of pyrrole polypyridyls is inefficient in 0.1 mol dm^{-3} tetrabutylammonium perchlorate–acetonitrile electrolyte. However, each of the monomers L^1–L^3 undergoes facile electropolymerization in acidic ($HClO_4$) acetonitrile. For example, cyclic voltammetry shows that the pyrrole irreversible oxidation is abnormally weak for L^1 [Fig. 1(*a*)] in neutral MeCN–$NBu^n{}_4ClO_4$ electrolyte. This is probably due to the formation of an insulating thin film on the electrode surface following deprotonation by the pyridyl groups of the first-formed pyrrole radical cation, preventing regular pyrrole polymerization. Similar inhibition phenomena have been observed for the polymerization of pyrrole in the presence of pyridine.[9] In contrast, a well developed pyrrole oxidation wave ($E_p \approx 1.1$ V) is observed after the addition of a ten-fold excess of perchloric acid [Fig. 1(*b*)]. Under these experimental conditions clean electropolymerization of pyrrole takes place because the N atoms of the pyridyl moieties are complexed by protons. For example, Fig. 2 shows the growth on a platinum-disc electrode of a film formed from 5 mmol dm^{-3} L^1 in MeCN–$NBu^n{}_4ClO_4$ electrolyte containing 50 mmol dm^{-3} $HClO_4$, upon repeated scans in the range 0–0.9 V. Formation of a conducting polypyrrolic film on the electrode surface is evidenced by the growth of its quasi-reversible redox peak system centred around 0.3 V.

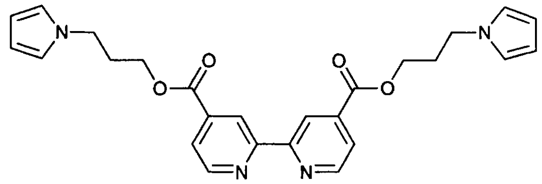
In the following experiments films were usually grown on platinum- and carbon-disc electrodes in MeCN–0.1 mol dm^{-3} $NBu^n{}_4ClO_4$ containing 5–10 mmol dm^{-3} of monomer and a ten-fold molar excess of perchloric acid, by controlled-potential oxidation at the threshold of the pyrrole oxidation wave, *i.e.* 0.80 to 0.85 V. All the resulting modified electrodes exhibit upon transfer into pure MeCN–$NBu^n{}_4ClO_4$ electrolyte the regular electroactivity of *N*-substituted polypyrroles [see for example Fig. 1(*c*)]. Apparent surface coverages Γ_L (mol cm^{-2}) can be determined from the charge under the polypyrrole



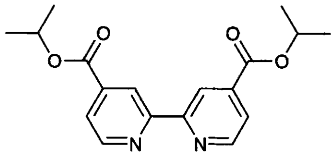
L^1



L^2



L^3



L^4

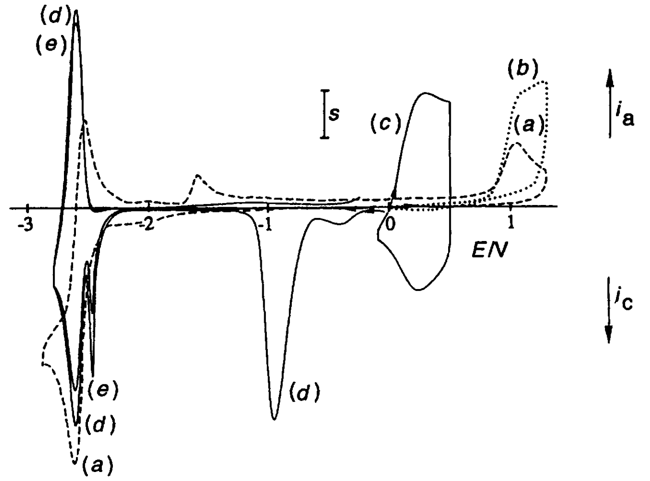


Fig. 1 Cyclic voltammograms in 0.1 mol dm^{-3} $NBu^n{}_4ClO_4$–MeCN of 0.01 mol dm^{-3} L^1 at a carbon electrode (diameter 3 mm) in the absence (*a*) and in the presence (*b*) of 0.1 mol dm^{-3} $HClO_4$; scan rate 0.1 V s^{-1}; s = 40 μA. A platinum–poly[$(H_2L^1)^{2+}$]-modified electrode (Γ_L = 3.4 × 10^{-8} mol cm^{-2}, scan rate 0.02 V s^{-1}) was employed: scans restricted to the positive potential region [(*c*); s = 4 μA]; first and second scans between 0 and −2.8 V [(*d*) and (*e*); s = 20 μA]; potentials are referred to Ag–0.01 mol dm^{-3} Ag$^+$

oxidation wave, assuming that one in three pyrrole units is oxidized.[10] Thin films with Γ_L from 10^{-9} to 5 × 10^{-8} mol cm^{-2} were obtained with electropolymerization yields from 40 to 80%. As expected, the polymerization yield increases with monomer concentration, and is almost quantitative for a concentration around 20 mmol dm^{-3}. Electropolymerization in aged monomer solutions, *i.e.* a few hours after their preparation, is less efficient and produces lower-quality films for the incorporation of metals ions and complexes. This behaviour can be attributed to the acid-catalysed, non-oxidative polymerization of the pyrrole-substituted compounds. This results in a decrease of the concentration of polymerizable monomer, and in the formation of partially saturated oligomers[11] which could be incorporated in the polypyrrole coating.

The polymerized compounds are obtained in their protonated H_2L^{2+} forms. When coated on a platinum surface they are fully deprotonated on the first cyclic voltammetry scan in the negative potential region. This is illustrated by the cyclic voltammetry curves for a platinum–poly[$(H_2L^1)^{2+}$]-modified electrode transferred with thorough rinsing to pure MeCN–$NBu^n{}_4ClO_4$ electrolyte. The large reduction peak which is seen around −1 V corresponds to reduction of the complexed protons [Fig. 1(*d*)]. As a consequence, the reversible one-electron reduction peak system for the free, deprotonated bipy moieties [(L^1)–$(L^1)^{\bullet-}$] appears at more negative potentials. On the second reduction scan [(*e*)] only this reversible wave

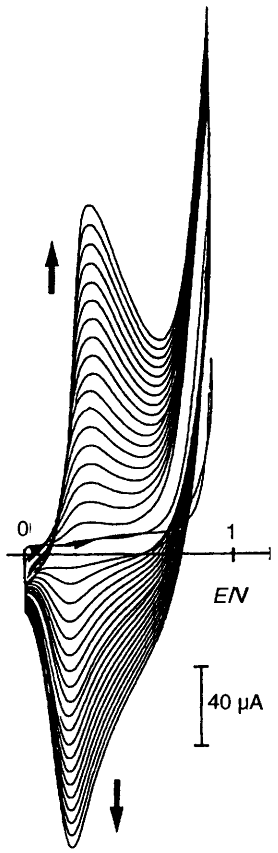


Fig. 2 Oxidative electropolymerization of L^1 (5 mmol dm^{-3}) in 0.1 mol dm^{-3} $NBu^n{}_4ClO_4$–0.05 mol dm^{-3} $HClO_4$–MeCN by repeated scans between 0 and 0.9 V; scan rate 0.1 V s^{-1}

remains. Its half-wave potential ($E_{\frac{1}{2}}$ = −2.63 V) compares well with that of the monomer [$E_{\frac{1}{2}}$ = −2.58 V, Fig. 1(*a*)].

Reductive deprotonation of poly[($H_2L^1)^{2+}$] films coated on a carbon electrode appeared quite inefficient. In contrast, the less basic poly(L^2) and poly(L^3) films coated on platinum or carbon surfaces can be readily deprotonated upon electrochemical reduction. The potential for the reversible one-electron reduction of the polypyridyl ligand in poly(L^3) films ($E_{\frac{1}{2}}$ = −2.10 V) is similar to that for the L^3 monomer in fluid solution ($E_{\frac{1}{2}}$ = −2.04 V). The reduction of L^2 appeared poorly reversible under our experimental conditions, as well in fluid solution (E_p = −2.56 V) as in poly(L^2) films (E_p = −2.70 V). Poly[($H_2L)^{2+}$] films are also readily deprotonated when soaked in Me_2SO for a few minutes. This was demonstrated by the absence of any reduction wave for protons on the cyclic voltammogram recorded after transfer with thorough rinsing to a MeCN electrolyte.

The apparent surface concentration of ligand Γ_L, can be measured from the charge under the L–$L^{\bullet -}$ reduction wave on first scans. The value determined in this way closely corresponds with that measured from the charge under the polypyrrole oxidation wave (see above). Owing to the degradation of the electroactivity of the films which occurs upon reductive scanning, we generally used the latter method to evaluate film thickness.

Complexation of Mn^{2+} cations in poly(L^1) films

Manganese(II) cations are effectively co-ordinated in poly(L^1) films by soaking the modified electrodes in Me_2SO solutions containing 10 mmol dm^{-3} $MnCl_2$. The complexation reaction in the film is slow, and takes several hours. *In situ* formation of $[MnL^1_3]^{2+}$ species is evidenced by recording in the negative potential region the cyclic voltammogram of the resulting modified electrode transferred with thorough rinsing to clean MeCN–$NBu^n_4ClO_4$ electrolyte. An initial broad, ill defined reduction wave is replaced after a few scans by three stable, reversible waves [$E_{\frac{1}{2}}$ = −1.72, −1.91 and −2.10 V; Fig. 3(*a*)] corresponding to the three successive one-electron ligand-centred reductions for the $[MnL^1_3]^{2+}$ complex. Such behaviour suggests that repeated scans force the permeation of the counter ions in the film, and thus the associated charge transfer in the polymer.[12] The half-wave potentials of the surface couples are in close correspondence with those for the model complex $[Mn(dmbipy)_3]^{2+}$ [dmbipy = 4,4′-dimethyl-2,2′-bipyridine; $E_{\frac{1}{2}}$ = −1.77, −1.95 and −2.16 V; Fig. 3(*b*)]. Moreover, the cyclic voltammetry curve is essentially the same as that observed in separate experiments[13] with films coated on platinum electrodes by reductive electropolymerization of the $[Mn(mvbipy)_3]^{2+}$ complex (mvbipy = 4-methyl-4′-vinyl-2,2′-bipyridine). The large difference in the responses for the three bipy-based reversible reductions, as compared with the solution behaviour, can be explained by different rates of charge propagation in the film. Similar phenomena have also been observed with poly[ML(diene)$^+$] films and will be discussed in detail below. On the basis of the charge under the ligand-centred reduction waves, we can assume that complete complexation of all bipy sites occurred in these rather thick films, taking into account that one Mn^{2+} cation is bound to three bipy moieties in the film. For instance, $\Gamma_L = 4.7 \times 10^{-8}$ and $\Gamma_{Mn} = 1.7 \times 10^{-8}$ mol cm^{-2} for the modified electrode presented in Fig. 2.

The efficient synthesis of poly($MnL^1_3{}^{2+}$) film-modified electrodes clearly demonstrates the interest of this approach. In a separate experiment[13] we found that this electrode material cannot be easily obtained from direct electropolymerization of $[MnL^1_3]^{2+}$. This behaviour is due to the irreversible transformation of polypyridyl manganese(II) complexes upon oxidation. It is known that their quasi-reversible oxidation is followed by a chemical reaction with ligand release, leading to a di-μ-oxo-dimanganese(IV) complex.[14] For the parent $[Mn(dmbipy)_3]^{2+}$ complex this oxidation (E_p = 1.03 V) occurs at a potential similar to that for pyrrole oxidation. In addition, the ligand released could be responsible for an inhibition of the polymerization.[13] Another complication arises from the easy protonation of the $[Mn(bipy)_3]^{2+}$ core;[13] here protons come from the pyrrole polymerization process. A similar lack of oxidative electropolymerization has been observed[15] with $[Mn(tterpy)_2]^{2+}$ [tterpy = 4′-(*p*-pyrrolylmethylphenyl)-2,2′-6′,2″-terpyridine].

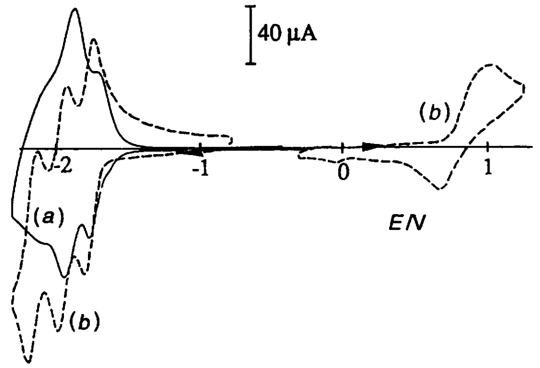


Fig. 3 Cyclic voltammograms in 0.1 mol dm^{-3} $NBu^n_4ClO_4$–MeCN: (*a*) Pt–poly[($MnL^1_3)^{2+}$]-modified electrode ($\Gamma_{Mn} = 1.7 \times 10^{-8}$ mol cm^{-2}; scan rate 0.02 V s^{-1}); (*b*) 2 mmol dm^{-3} $[Mn(dmbipy)_3]^{2+}$, scan rate 0.1 V s^{-1}

Complexation of chelated Rh^I and Ir^I in poly(L) films

In situ formation of metal complexes in preformed poly(L) films (L = L^1–L^3) was then applied to the synthesis of poly[M^IL(diene)$^+$] materials (M = Rh or Ir; diene = cod or nbd). This was accomplished by treating poly(L) films with [{M^I(diene)Cl}$_2$] complexes. From a structural point of view it was expected that the *in situ* formation of these square-planar complexes would take place more easily than the synthesis of $[Mn(bipy)_3]^{2+}$ units in poly(L^1) films, since they simply require the complexation of the metal centre with one bipy unit of the film. However, limitations due to the difficult permeation of the bulky [{M(diene)Cl}$_2$] precursor complexes to the binding sites in the film could limit the efficiency of the complexation reaction. The construction of the [Rh(bipy)(cod)]$^+$ complex in a poly(L^1) modified electrode ($\Gamma_L = 2.1 \times 10^{-8}$ mol cm^{-2}) soaked in Me_2SO–$NBu^n_4ClO_4$ electrolyte containing 1 mmol dm^{-3} [{Rh(cod)Cl}$_2$] is rapid as evidenced by the continuous increase upon cycling in the size of the cyclic voltammetry peaks for the [Rh(bipy)(cod)]$^{+/0}$ redox couple (Fig. 4). In a separate experiment we have verified that [{M(diene)Cl}$_2$]$^+$ complexes show no reduction waves out to potentials as low as −2 V.

Cyclic voltammetry curves for C–poly[RhL^1(cod)$^+$] modified electrodes prepared in this way and transferred to fresh MeCN–$NBu^n_4ClO_4$ electrolyte show stable, well behaved waves [Fig. 5(*i*)(*a*)]. The potentials of the surface couples are in good correspondence with those for the model complex [Rh(dmbipy)(cod)]$^+$ (see Table 1). The loading of the complex, and thus the apparent surface concentration of immobilized complex Γ_{Rh} (mol cm^{-2}), were determined from the charge under the first one-electron reduction wave. The incorporation ratio was defined as the ratio of the amount of immobilized complex to the amount of bipy units in the film, taking into account that one metal centre must be bound to one bipy ligand in the polymer. It varied from 75 to 40% in films with Γ_{L^1} from 10^{-8} to 4×10^{-8} mol cm^{-2}. The complexation process was slower and slower as the film thickness increased. No electrochemical response for [Rh(bipy)(cod)] complexes was observed when poly(L^1) films of $\Gamma_L \geqslant 5 \times 10^{-8}$ mol cm^{-2} were soaked in [{Rh(cod)Cl}$_2$] solutions. Evidently, the precursor complex cannot diffuse in a thick film to react with bipy

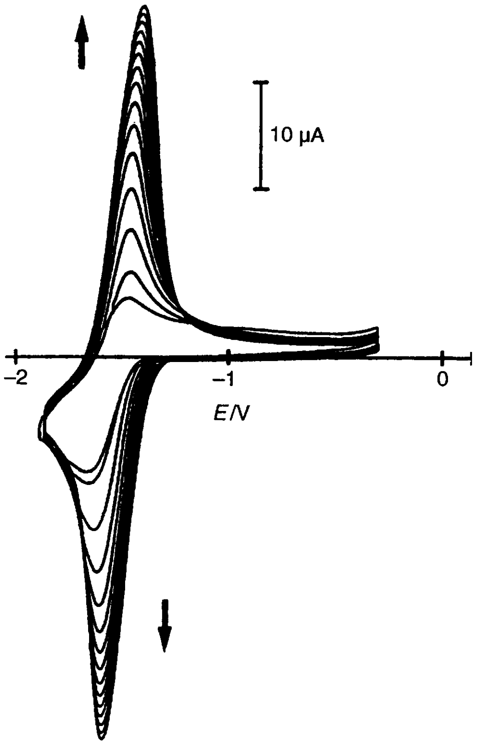


Fig. 4 Growth of a poly[RhL^1(cod)$^+$] film by cycling a Pt–poly(L^1) electrode (Γ_L = 2.1 × 10^{-8} mol cm^{-2}) in 0.1 mol dm^{-3} NBu$^n_4$ClO$_4$–Me$_2$SO containing 1 mmol dm^{-3} [{Rh(cod)Cl}$_2$]; scan rate 0.1 V s^{-1}

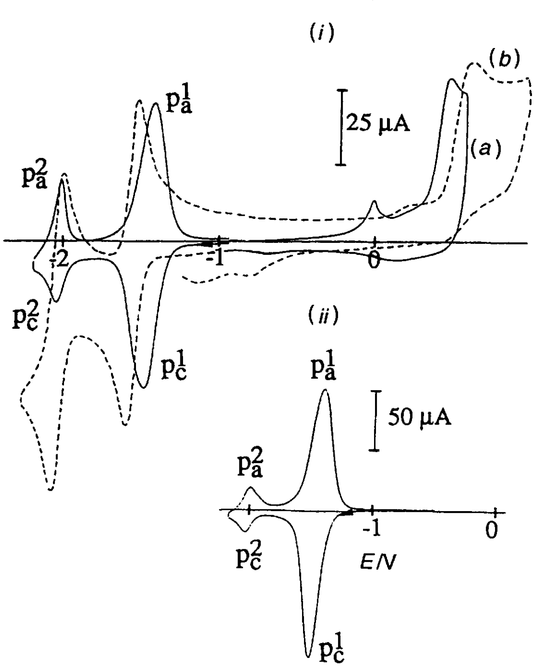


Fig. 5 Cyclic voltammograms of C–poly[RhL^1(cod)$^+$] modified electrodes in 0.1 mol dm^{-3} NBu$^n_4$ClO$_4$–MeCN: (i) (a) Γ_{Rh} = 10^{-8} mol cm^{-2}; (ii) Γ_{Rh} = 2.9 × 10^{-8} mol cm^{-2}. Curve (b) in (i) is that for 1 mmol dm^{-3} [Rh(dmbipy)(cod)$^+$]; scan rate 0.05 V s^{-1}

moieties close to the electrode–polymer interface. Poly[RhL^1(cod)$^+$] films could also be synthesized in MeCN–NBu$^n_4$ClO$_4$ electrolyte containing [{Rh(cod)Cl}$_2$], provided that the poly [(H$_2$L^1)$^{2+}$] films have been previously soaked for a few minutes in pure Me$_2$SO. In contrast, films deprotonated by electrochemical reduction in MeCN electrolyte appeared fully inert. We have no clear explanation at the present time for this surprising behaviour.

Table 1 Redox potential data^a for various complexes in fluid solution, or immobilized as an electrode film

	Reduction		Oxidation^b
Complex	$E_{\frac{1}{2}}^1$/V	$E_{\frac{1}{2}}^2$/V	$E_p{}^c$
[Rh(dmbipy)(cod)]$^+$	−1.58	−2.02	0.66
[RhL^4(cod)]$^+$	−1.12	−1.55	0.52
poly[RhL^1(cod)$^+$]	−1.52	−2.04	0.42
poly[RhL^1(nbd)$^+$]	−1.52	−2.10	*d*
poly[RhL^2(cod)$^+$]	−1.57	−2.09	*d*
poly[RhL^2(nbd)$^+$]	−1.56	−2.11	*d*
poly[RhL^3(cod)$^+$]	−1.04	−1.58	0.47
poly[RhL^3(nbd)$^+$]	−1.08	−1.53	*d*
[Ir(dmbipy)(cod)]$^+$	−1.40	−1.87	0.35
[IrL^4(cod)]$^+$	−1.01	−1.40	−0.01
poly[IrL^2(cod)$^+$]	−1.29	−1.86	0.30
poly[IrL^3(cod)$^+$]	−0.90	−1.38	0.27

^{a} Values *vs.* Ag–10 mmol dm^{-3} Ag$^+$, determined by cyclic voltammetry on a carbon-disc electrode in MeCN–NBu$^n_4$ClO$_4$ electrolyte. ^{b} Irreversible process. ^{c} Measured on the first scan. ^{d} Not determined.

There is a striking difference in the voltammetric responses for the two reversible bipy-based one-electron reductions,[16] as compared with the solution behaviour [Fig. 5(*i*)(*b*)]. The importance of film thickness in determining the differential response of the two redox couples is illustrated in Fig. 5(*ii*) for example, by the voltammogram obtained with a thicker film (Γ_{Rh} = 2.9 × 10^{-8} mol cm^{-2}). This differential response can be evaluated from the ratio of the peak currents ($i_{p_c^1}/i_{p_c^2}$) for the two reduction waves. At a moderate scan rate (v = 0.05 V s^{-1}) the smallest $i_{p_c^1}/i_{p_c^2}$ ratio (1.9 : 1) was observed with thin films ($\Gamma_{Rh} \approx$ 3.3 × 10^{-9} mol cm^{-2}), while it reached 11 : 1 with thicker films ($\Gamma_{Rh} \approx$ 3 × 10^{-8} mol cm^{-2}). However, this ratio decreases substantially with the scan rate.† For example, with a poly(L^1) film containing 1.3 × 10^{-8} mol cm^{-2} of immobilized [Rh(bipy)(cod)]$^+$ complex, $i_{p_c^1}/i_{p_c^2}$ decreased from 13 to 3 : 1 when the scan rate was decreased from 0.2 V s^{-1} to 2 mV s^{-1}. Obviously, the disparate voltammetric behaviour of the singly and doubly reduced forms of the complex within the polymer film is a consequence of different rates of charge propagation. A similar behaviour has been observed with double-stage redox polymers such as poly(vinylpyridinium)[17] and poly(pyrrole–bipyridinium)[18] films for example. Changes in the electroactivity of poly[Fe(bipy)$_3$$^{2+}$] films induced by counter-ion size have also been reported.[19] The rate constants for the successive electron transfers appeared dominated by counter ions diffusivity in the films, ion-trapping effects and also by characteristics of the polymer phase such as site–site separation. We found that the size of the cation of the supporting electrolyte has only a slight influence on the [Rh(bipy)(cod)]$^{+/0}$ redox peak system, and a large one on the [Rh(bipy)(cod)]$^{0/-}$ peak current. This is illustrated in Fig. 6 which shows the response of a C–poly[RhL^1(cod)$^+$] modified electrode in various electrolytes, *i.e.* in MeCN containing NBu$^n_4$ClO$_4$ (*a*), tetraethylammonium perchlorate (*b*) and tetramethylammonium tetrafluoroborate (*c*). The first reduction process leading to [Rh(bipy)(cod)] is likely to be associated with anion release from the polymer phase to the bulk solution, and thus not very sensitive to the use of ClO$_4$$^-$ or BF$_4$$^-$ which have similar size. In the second reduction step of [Rh(bipy)(cod)] to [Rh(bipy)(cod)]$^-$ cations from the electrolyte should be incorporated into the film to maintain electroneutrality. Therefore, electron transfer is definitively faster if the small NMe$_4$$^+$ cation, and to a lesser extent NEt$_4$$^+$, is used instead of the bulkier NBu$^n_4$$^+$. In MeCN–NMe$_4BF_4$ electrolyte the $i_{p_c^1}/i_{p_c^2}$

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† As expected for surface-confined redox couples, cyclic voltammetry of the poly[RhL^1(cod)]$^+$ film-modified electrode at scan rates < 0.05 V s^{-1} showed a peak *vs.* current response for the primary reduction which varied linearly with the scan rate under these experimental conditions. At faster scan rates the response is non-linear.

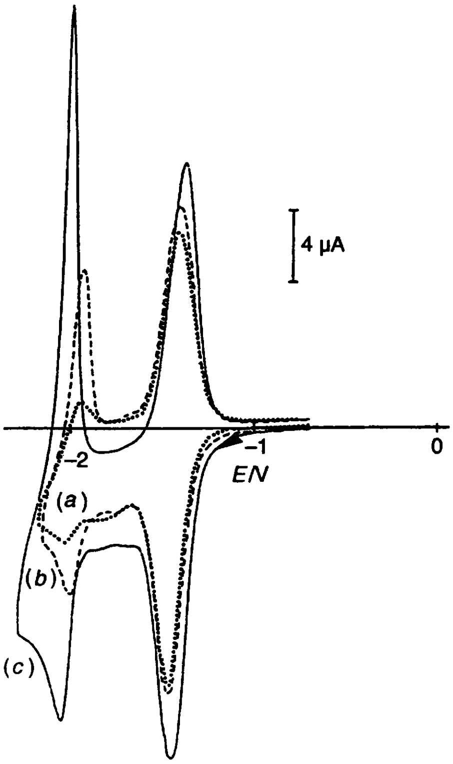

Fig. 6 Cyclic voltammograms of a C–poly[RhL^1(cod)$^+$]-modified electrode (Γ_{Rh} = 1.8 × 10^{-8} mol cm^{-2}) in MeCN containing 0.1 mol dm^{-3} NBu$^n_4$ClO$_4$ (*a*), NEt$_4$ClO$_4$ (*b*) and NMe$_4$BF$_4$ (*c*); scan rate 0.02 V s^{-1}

ratio remained small and almost identical (≈2:1) in the scan rate range 2 mV s^{-1} to 0.5 V s^{-1}. It should be noted that at slow potential scans the charge under the poly[RhL^1(cod)$^{+/0}$] and poly[RhL^1(cod)$^{0/-}$] reduction waves is nearly the same.

As for the parent complex [Rh(dmbipy)(cod)]$^+$ studied in fluid solution [Fig. 5(*i*)(*b*)]. the cyclic voltammetry curve for the imobilized complex is characterized in the positive potential region by an irreversible oxidation peak which adds to the polypyrrole oxidation wave [Fig. 5(*i*)(*a*)]. This oxidation goes with the irreversible transformation of the film electroactivity.

Various metallopolymers of Rh^I and Ir^I have been synthesized from [{Rh(cod)Cl}$_2$], [{Rh(nbd)Cl}$_2$] and [{Ir(cod)-Cl}$_2$] precursor complexes in different poly(L) films (L = L^1–L^3). In contrast with that observed with poly(L^1), the complexation reactions are effective in poly(L^2) and poly(L^3) films deprotonated by electrochemical reduction in MeCN electrolyte, and thus do not require the use of Me$_2$SO as electrolyte. Table 1 lists redox potential data measured for various complexes of Rh^I and Ir^I synthesized in poly(L) films, together with corresponding data determined for the parent complexes in fluid solution. As expected,[16,20] the reduction potentials are poorly sensitive to changes of diene (cod or nbd) and of polypyridyl ligand [bipy or 1,10-phenanthroline (phen), *i.e.* L^1 or L^2]. In contrast, substitution of the bipy ligand with carboxyester groups (L = L^3 or L^4) caused the reduction potentials to shift ≈0.4–0.5 V to more positive potentials. As for other polypyridinyl complexes of ruthenium,[21] rhodium[22] or rhenium,[23] the presence of electron-withdrawing substituents has a marked stabilizing effect on low formal oxidation states in these iridium and rhodium complexes. This observation confirms that the redox orbital involved in the reduction process is predominantly Π^*_{bipy}. It should be noted that the potential of the first reduction for the immobilized complexes is shifted by ≈0.1 V to more positive potentials as compared with that for the model complexes. A similar behaviour has been observed[24] with films coated on a platinum electrode by reductive electropolymerization of [M(mvbipy)(cod)]$^+$ complexes (M = Rh^I or Ir^I).

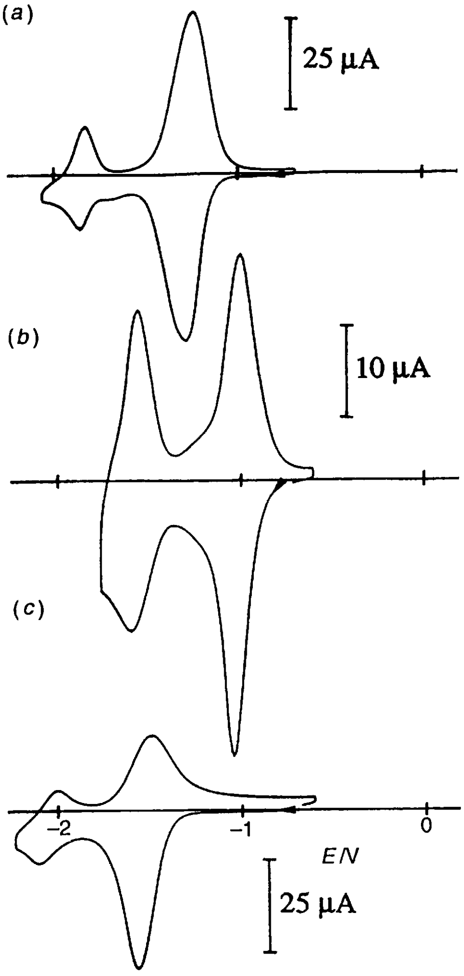

Fig. 7 Cyclic voltammograms in 0.1 mol dm^{-3} NBu$^n_4$ClO$_4$–MeCN of (*a*) poly[IrL^1(cod)$^+$] (Γ_{Ir} = 1.1 × 10^{-8} mol cm^{-2}), (*b*) poly-[RhL^3(nbd)$^+$] (Γ_{Rh} = 6.3 × 10^{-9} mol cm^{-2}) and (*c*) poly[Rh-L^2(cod)$^+$] (Γ_{Rh} = 1.2 × 10^{-8} mol cm^{-2}) films coated on a carbon electrode; scan rate 0.05 V s^{-1}

Cyclic voltammograms for various poly[ML(diene)$^+$] film-modified electrodes in MeCN–NBu$^n_4$ClO$_4$ electrolyte are shown in Fig. 7. The poly[IrL^1(cod)$^+$] [Fig. 7(*a*)] and poly[RhL^2(cod)$^+$] [Fig. 7(*c*)] films present the same features as poly[RhL^1(cod)$^+$]-modified electrodes. In contrast, poly(L^3)-based metallopolymer films [see Fig. 7(*b*) for example] are characterized by a markedly large wave for the second reduction step. This is probably due to a higher diffusivity of the NBu$^n_4$$^+$ counter ions in poly(L^3) films. As seen above for poly[RhL^1(cod)$^+$] films [Fig. 5(*i*)], the cyclic voltammograms for the various immobilized complexes present in the positive potential region an irreversible oxidation peak (E_p ≈ 0.3–0.5 V, see Table 1) which overlaps the polypyrrole oxidation wave. The peak potential for this irreversible oxidation process does not vary significantly whatever the complex, in contrast with what is found for the model complexes in fluid solution. This is clearly shown by the large potential difference for the oxidation of [IrL^4(cod)]$^+$ and poly[IrL^3(cod)$^+$] (E_p = −0.01 and 0.27 V respectively). In addition, no oxidation peak is observed when the polymeric matrix is non-conductive, *i.e.* when the polypyrrole conductivity has been destroyed following its overoxidation,[25] by potentiostatting the poly[(H$_2$L)$^{2+}$] electrode at 1.2 V for a few minutes prior to the incorporation of the metal complex. Obviously, this oxidation is mediated through the polypyrrole(0/+) redox system. As for [M(bipy)(diene)]$^+$

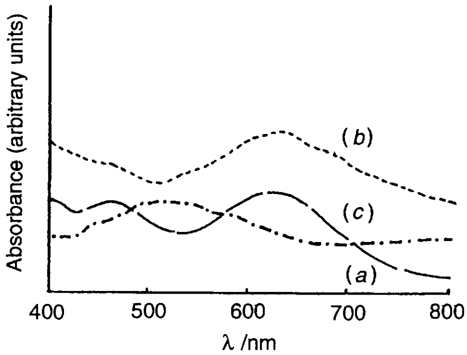

Fig. 8 Absorption spectra at an indium tin oxide (ITO)-coated glass electrode of (*a*) a poly(L^3) film ($\Gamma_L = 6.0 \times 10^{-9}$ mol cm^{-2}); (*b*) after soaking in 1 mmol dm^{-3} [{Ir(cod)Cl}$_2$]-MeCN solution and (*c*) of [IrL^4(cod)][BF$_4$] in MeCN

complexes studied in solution,[26] oxidation of immobilized complexes is accompanied by an irreversible transformation which leads to complete loss of the film electroactivity in the negative potential area.

The effective build-up of [M^{I}L(diene)]$^+$ complexes in polymer films was also established from UV/VIS experiments. For example, Fig. 8 presents the visible absorption of a poly(L^3) film grown on an optically transparent electrode (OTE) before (*a*) and after (*b*) its reaction in Me_2SO with [{Ir(cod)Cl}$_2$]. The appearance of a broad absorption band at 660 nm which compares well with that for [IrL^4(cod)]$^+$ in fluid solution (*c*) confirms the effective build-up of the iridium(I) complex in the preformed poly(L^3) film.

Conclusion

Polymer electrodes to which various metal complexes are bound within preformed poly(pyrrole–polypyridyl) polymer films have been synthesized and characterized by cyclic voltammetry and UV/VIS spectroscopy. This straightforward procedure for building metallopolymer films on electrode surfaces does not require the preliminary synthesis of polymerizable complexes. In addition, it allows the elaboration of functionalized polypyrroles which cannot be synthesized by direct electropolymerization of a pyrrole-substituted complex. Finally, we note that reduction processes in poly[M^I(bipy)(diene)] films (M = Rh or Ir) are strongly dependent on the size of the counter ions of the supporting electrolyte. These results illustrate how the electrochemical behaviour of redox polymers may be disturbed by counter ion diffusivity.

Experimental

General

All electrochemical experiments were run under an argon atmosphere in a glove-box, using a standard three-electrode electrochemical cell. All potentials are referred to a Ag–0.01 mol dm^{-3} Ag$^+$ reference electrode in MeCN–NBu$^n{}_4$ClO$_4$ electrolyte. The potential of the ferrocene–ferrocenium couple under our experimental conditions was 0.07 V. The working electrode was either a platinum disc (0.2 cm^2) or a vitreous carbon disc (0.2 or 0.07 cm^2) polished with 1 µm diamond paste. The electrolyte was a 0.1 mol dm^{-3} solution of supporting electrolyte in MeCN (Rathburn, HPLC grade S) or Me_2SO (SDS, pure on 4 Å molecular sieves). The salts tetra-*n*-butylammonium perchlorate (recrystallized from dichloromethane–cyclohexane), tetraethylammonium perchlorate (recrystallized from water) and tetramethylammonium tetrafluoroborate (used as recieved) were obtained from Fluka (puriss), dried under vacuum at 80 °C for 3 d before use, and stored under argon. Electrochemical measurements were carried out using an EG & G PAR model 173 potentiostat equipped with a model 179 digital coulometer and a model 175 programmer with output recorded on a Sefram TGM 164 X-Y recorder. For UV/VIS measurement, films were grown on ITO-coated transparent glass electrodes (Baltracon 220 from Balzers; $A = 1$ cm^2). Spectra were recorded using a Hewlett-Packard HP 8452A diode-array spectrophotometer. The cuvette, or the optically transparent electrode (OTE), was inserted in an optical translator connected with the spectrophotometer through an optical fibre system (Photonetics Spectrofip). The optical fibres are passed through the wall of the glove-box by means of seals.

Materials

The compounds L^1,[27] L^2,[28] L^3,[29] L^4,[30] [Mn(dmbipy)$_3$][BF$_4$]$_2$,[14] [{Rh(cod)Cl}$_2$],[31] [{Rh(nbd)Cl}$_2$][32] and [{Ir(cod)Cl}$_2$][33] were synthesized by published methods. The compounds [Rh(dmbipy)(cod)][BF$_4$] and [Ir(dmbipy)(cod)][PF$_6$] were prepared following the procedures described for the corresponding 2,2′-bipyridine derivatives[34,35] and characterized by FAB mass spectrometry; [ML^4(cod)][BF$_4$] (M = Rh or Ir) were synthesized in the same way in MeCN electrolyte but not isolated.

References

1 A. Deronzier and J.-C. Moutet, *Coord. Chem. Rev.*, 1996, **147**, 339.
2 C. J. Pickett, K. S. Ryder and J.-C. Moutet, *J. Chem. Soc., Chem. Commun.*, 1992, 694.
3 C.-J. Pickett, K. S. Ryder and J.-C. Moutet, *J. Chem. Soc., Dalton Trans.*, 1993, 3695.
4 C. J. Pickett and K. S. Ryder, *J. Chem. Soc., Dalton Trans.*, 1994, 2181.
5 F. Daire, F. Bedioui, J. Devynck and C. Bied-Charreton, *J. Electroanal. Chem. Interfacial Electrochem.*, 1986, **205**, 309.
6 S. Gould, G. F. Strouse, T. J. Meyer and B. P. Sullivan, *Inorg. Chem.*, 1991, **30**, 2942.
7 G. Bidan, A. Deronzier and J.-C. Moutet, *Nouv. J. Chim.*, 1984, **8**, 501.
8 E. Labbe, F. Bedioui and J. Devynck, *J. Electroanal. Chem. Interfacial Electrochem.*, 1989, **274**, 271.
9 N. J. Morse, D. R. Rosseinsky, R. J. Mortimer and D. J. Walton, *J. Electroanal. Chem. Interfacial Electrochem.*, 1988, **255**, 119.
10 G. K. Chandler and D. Pletcher, *Electrochemistry, Specialist Periodical Reports*, Royal Society of Chemistry, London, 1986, pp. 117–150.
11 G. F. Smith, *Adv. Heterocycl. Chem.*, 1963, **2**, 287.
12 A. Deronzier and J.-C. Moutet, *J. Am. Chem. Soc.*, 1994, **116**, 5019.
13 M.-N. Collomb Dunand-Sauthier and A. Deronzier, unpublished work.
14 M. M. Morrison and D. T. Sawyer, *Inorg. Chem.*, 1978, **17**, 333.
15 J.-P. Collin, A. Jouaiti and J. P. Sauvage, *J. Electroanal. Chem. Interfacial Electrochem.*, 1990, **286**, 75.
16 W. A. Fordyce, K. H. Pool and G. A. Crosby, *Inorg. Chem.*, 1982, **21**, 1027.
17 T. Takiguchi, T. Nonaka and T. Fuchigami, *J. Electroanal. Chem. Interfacial Electrochem.*, 1985, **195**, 177.
18 E. F. Dalton and R. W. Murray, *J. Phys. Chem.*, 1991, **95**, 6383.
19 L. A. Lyon, M. A. Ratner and J. T. Hupp, *J. Electroanal. Chem. Interfacial Electrochem.*, 1995, **387**, 109.
20 G. Costa, C. Tavagnacco, G. Balducci, G. Mestroni and G. Zassinovich, *J. Electroanal. Chem. Interfacial Electrochem.*, 1989, **261**, 189.
21 C. M. Elliot and E. J. Ershenhart, *J. Am. Chem. Soc.*, 1982, **104**, 7519.
22 I. M. F. de Oliveira and J.-C. Moutet, *J. Electroanal. Chem. Interfacial Electrochem.*, 1993, **361**, 203.
23 S. Cosnier, A. Deronzier and J.-C. Moutet, *New J. Chem.*, 1990, **14**, 831.
24 T. J. Meyer, B. P. Sullivan and J. V. Caspar, *Inorg. Chem.*, 1987, **26**, 4145.
25 S. Cosnier, A. Deronzier and J.-F. Roland, *J. Electroanal. Chem. Interfacial Electrochem.*, 1990, **285**, 133.
26 E. Makrlik, J. Hanzlik, A. Camus, G. Mestroni and G. Zassinovich, *J. Organomet. Chem.*, 1977, **142**, 95.
27 S. Cosnier, A. Deronzier and J.-C. Moutet, *J. Electroanal. Chem. Interfacial Electrochem.*, 1986, **207**, 315.

28 S. Chardon-Noblat, I. M. F. de Oliveira, J.-C. Moutet and S. Tingry, *J. Mol. Catal. A*, 1995, **99**, 13.

29 I. M. F. de Oliveira, J.-C. Moutet and N. Vlachopoulos, *J. Electroanal. Chem. Interfacial Electrochem.*, 1990, **291**, 243.

30 G. Sprintschnik, H. X. Sprintschnik, P. P. Kirsch and D. G. Whitten, *J. Am. Chem. Soc.*, 1977, **99**, 4947.

31 J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1957, 4735.

32 E. W. Abel, M. A. Bennett and G. Wilkinson, *J. Chem. Soc.*, 1959, 3179.

33 J. L. Herde and C. V. Senoff, *Inorg. Nucl. Chem. Lett.*, 1971, **7**, 1029.

34 C. Cocevar, G. Mestroni and A. Camus, *J. Organomet. Chem.*, 1972, **35**, 389.

35 G. Mestroni, A. Camus and G. Zassinovich, *J. Organomet. Chem.*, 1974, **73**, 119.

Received 2nd January 1996; *Paper* 6/00029K