Synthesis, Characterisation, and Photochemical Properties of a Series of Ruthenium containing Metallopolymers based on Poly-*N*-vinylimidazole

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A series of polymeric materials has been prepared by treating poly-*N*-vinylimidazole (pnvi) with hydrated bis(2,2′-bipyridyl)ruthenium dichloride. The mole ratio of poly-*N*-vinylimidazole to $[Ru(bipy)_2Cl_2]\cdot 2H_2O$ (pnvi:Ru ratio) was varied from 5:1 to 50:1. From spectroscopic and electrochemical studies, both in solution and as thin films, it is shown that depending on the reaction conditions, different types of ruthenium–pnvi complexes are formed. The spectroscopic and electrochemical properties of the metallopolymers obtained are compared to those of mononuclear *N*-methylimidazole compounds of bis(2,2′-bipyridyl)ruthenium(II). An unusual, photochemically induced, reversible ligand-exchange process is observed for thin polymer layers in sulphuric acid.

The modification of electrode surfaces with thin films of electroactive polymeric materials continues to be an active area of research. Much attention has been paid to the preparation and characterisation of new polymers,[1–4] the theory of electrocatalysis,[2,5] and to the understanding of the charge-transport processes in these films.[6–8] A number of polymeric materials have been prepared based on polypyridyl compounds of ruthenium. These metallopolymers have well established photochemical and electrochemical transfer properties which provide a basis for catalytic applications.[3,9–14] Earlier studies have shown that the electrochemical properties of the modified electrodes are strongly related to the nature of the polymer backbone and in particular to the polymer electrolyte interface. To investigate the influence of the polymer backbone on the electrochemical properties of electrodes modified with these materials we have prepared a range of ruthenium containing polymers.[4] In this work we report the synthesis and characterisation of a series of bis(2,2′-bipyridyl)ruthenium(II) complexes of poly-*N*-vinylimidazole (pnvi). The materials were studied both in solution and as thin coatings on electrode surfaces using spectroscopic and electrochemical techniques. To determine the nature of the polymer-bound metal complexes the properties of the materials obtained were compared with those of a series of mononuclear model compounds.

Results and Discussion

General.—In a series of experiments hydrated bis(2,2′-bipyridyl)ruthenium(II) dichloride was treated with pnvi using different reaction solvents and reaction times. The stoicheiometric ratio of pnvi to ruthenium was varied from 5:1 to 50:1. The metallopolymers were either left in solution or isolated by evaporation of most of the solvent and subsequent precipitation in diethyl ether. The solids obtained were then dried *in vacuo* at room temperature. The metallopolymers isolated were found to be soluble immediately after their isolation but in most cases, on storing for longer periods, would only partly redissolve. The characterisation of the series of polymer-bound complexes was accomplished by applying several techniques to each sample. The data obtained were compared with those for the mononuclear model compounds $[Ru(bipy)_2(mim)_2][PF_6]_2$, $[Ru(bipy)_2(mim)Cl]PF_6$, and $[Ru(bipy)_2(mim)(H_2O)][PF_6]_2$ (mim = *N*-methylimidazole, bipy = 2,2′-bipyridyl), chosen as model compounds for the expected polymer-bound complexes $[Ru(bipy)_2(pnvi)_2]^{2+}$, $[Ru(bipy)_2(pnvi)Cl]^{+}$, and $[Ru(bipy)_2(pnvi)(H_2O)]^{2+}$ respectively. Spectroscopic and electrochemical data suggest (see later) that the species $[Ru(bipy)_2(pnvi)Cl]^{+}$ and $[Ru(bipy)_2(pnvi)_2]^{2+}$ are both present in most metallopolymers prepared from $[Ru(bipy)_2Cl_2]\cdot 2H_2O$, their ratios depending on the reaction conditions.

Reaction of $[Ru(bipy)_2(CO_3)]$ with pnvi yields, as expected, only the disubstituted product.[3] The formation of the different species from $[Ru(bipy)_2Cl_2]\cdot 2H_2O$ probably occurs as shown in equations (1)—(4).

$$[Ru(bipy)_2Cl_2] + S \longrightarrow [Ru(bipy)_2(S)Cl]^+ + Cl^- \quad (1)$$

$$[Ru(bipy)_2(S)Cl]^+ + pnvi \longrightarrow [Ru(bipy)_2(pnvi)Cl]^+ + S \quad (2)$$

$$[Ru(bipy)_2(pnvi)Cl]^+ + H_2O \longrightarrow [Ru(bipy)_2(pnvi)(H_2O)]^{2+} + Cl^- \quad (3)$$

$$[Ru(bipy)_2(pnvi)(H_2O)]^{2+} + pnvi \longrightarrow [Ru(bipy)_2(pnvi)_2]^{2+} + H_2O \quad (4)$$

In these reactions S is either methanol or water. The extent to which these reactions occur depends on the reaction conditions which, along with the elemental analysis of the materials obtained, are given in Table 1. The elemental analyses of metallopolymers are known to be rather inconsistent. It should therefore be pointed out that the pnvi:Ru ratios calculated should only be taken as an indication of the composition of the products obtained. The ratios calculated are mainly based on the chloride content.

Electronic Spectra.—The absorption and emission maxima of the metallopolymers together with the values obtained for the model compounds have been listed in Table 2. In Figures 1 and 2 absorption and emission spectra of some representative materials have been given. In the absorption spectra two bands are observed in the visible region of the spectrum. As in similar bis(2,2′-bipyridyl)ruthenium(II) compounds these bands have been assigned to metal-to-ligand charge-transfer transitions (m.l.c.t.) of the type $\pi^*(bipy) \longleftarrow d\pi(Ru)$.[15] Because of the strong similarities of the electronic spectra of the metallopolymers with those of analogous mononuclear ruthenium complexes emission in the metallopolymers is also thought to originate from bipy based ^{3}m.l.c.t. states.[15] The absorption maxima in the visible region do vary with the ligand composition of the complexes and they are therefore generally used for the identification of the complexes. To ascertain the coordination around the central metal ion in the polymer-bound materials their absorption spectra were compared with those of the mononuclear model compounds. A similar approach has

Table 1. Reaction conditions and elemental analyses for ruthenium containing poly-*N*-vinylimidazole metallopolymers

Sample	pnvi:Ru[a] (mg)	Mol ratio	Solvent	Reaction time (h)	Elemental analysis (%)				pvni:Ru ratio obtained
					C	H	N	Cl	
(A)	470:478	5:1	Methanol	72	51.4	4.9	18.2	7.7	4.4:1
(B)	470:486	5:1	Ethanol	24	50.9	5.0	18.0	7.8	4.2:1
(C)	470:484	5:1	Methanol	24	50.6	4.9	17.7	8.1	4.0:1
(D)	470:486	5:1	Methanol	48	50.4	4.8	18.0	8.4	4.0:1
(E)	235:243	5:1	Methanol–H_2O (1:1)	72					
(F)	470:97	25:1	Methanol	72	55.4	5.8	23.7	3.4	14:1
(G)	470:28	10:1	Methanol	72					
(H)	471:48	50:1	Methanol	72					
(I)[b]	48:48	5:1	Methanol–H_2O (1:1)	72					

[a] Metallopolymers prepared using $[Ru(bipy)_2Cl_2]\cdot 2H_2O$. [b] Prepared using $[Ru(bipy)_2(CO_3)]$.

Table 2. Spectroscopic and electrochemical data for metallopolymers and mononuclear model compounds

Sample	$\lambda_{max.}$(absorption)/ nm[a]	$\lambda_{max.}$(emission, r.t.)/nm[a]	$\lambda_{max.}$(emission, 77 K)/nm[b]	$E_{\frac{1}{2}}$/mV[c]	Product ratio[d]
$[Ru(bipy)_2(mim)_2][PF_6]_2$	492, 340	640	626	965[e]	
$[Ru(bipy)_2(mim)Cl][PF_6]$	512, 352		682	660[e]	
$[Ru(bipy)_2(mim)(H_2O)][PF_6]_2$	487, 338			995[e]	
(A)	502, 347	638	630 (685)	570 (805)	5.7
(B)	507, 352	643	686	545 (835)	7.5
(C)	502, 348	633	689	570 (805)	>8
(C)				677[e]	
(D)	500, 348	630	682	535 (810)	6.5
(E)	485, 345	637	628	825 (610)	<0.15
(F)	485, 345	626	617	590 (835)	2.0
(G)	487, 343	637	619	860	
(H)	481, 340	636	618	840	
(I)	482, 340	640	618	855 (1 025[e])	
$[Ru(bipy)_2(pnvi)(H_2O)]^{2+}$				730 (1 020[e])	

[a] Solvent methanol. [b] Measured in ethanol glass at 77 K, value in parentheses indicates a shoulder. [c] Electrolyte 1 mol dm^{-3} H_2SO_4 unless otherwise stated, minor redox couples present are given in parentheses; scan rate 50 mV s^{-1}, reference electrode s.c.e. [d] See text. [e] Electrolyte acetonitrile–0.1 mol dm^{-3} NEt_4ClO_4.

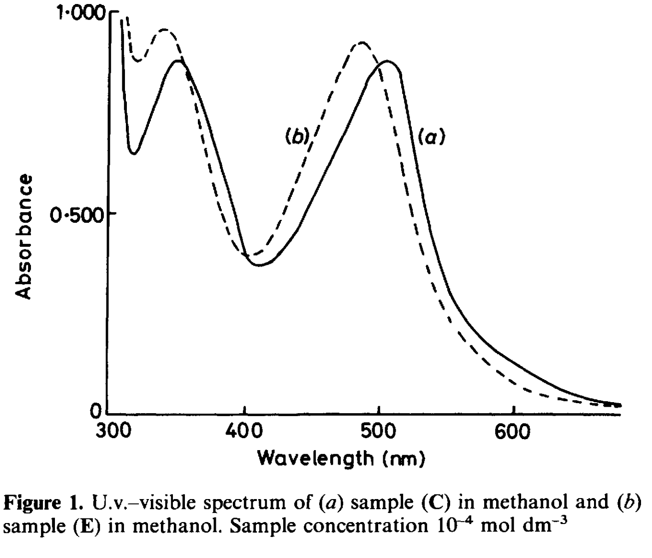

Figure 1. U.v.–visible spectrum of (*a*) sample **(C)** in methanol and (*b*) sample **(E)** in methanol. Sample concentration 10^{-4} mol dm^{-3}

been made before in the case of poly-4-vinylpyridine ruthenium complexes.[3,4a] However in our case the absorption maxima of the different compounds are very close together (see Table 2) and from these data alone no definite conclusions can be drawn. The absorption maxima obtained for the metallopolymers do however suggest the presence of $[Ru(bipy)_2(pnvi)Cl]^+$ as the main species for the polymers **(A)**—**(D)**, whereas $[Ru(bipy)_2(pnvi)_2]^{2+}$ and possibly $[Ru(bipy)_2(pnvi)(H_2O)]^{2+}$ appear to be the most adundant species in the materials **(E)**—**(I)**. The absorption maxima of the polymeric materials are observed at slightly higher energy than those of the corresponding mononuclear model compounds.

Emission spectra were obtained in fluid solution at room temperature and in methanol glasses at 77 K. Because the mono-substituted complexes are very weak emitters it was necessary to obtain low-temperature spectra to identify the different species. At 77 K the complexes $[Ru(bipy)_2(mim)_2]^{2+}$ and $[Ru(bipy)_2(mim)Cl]^+$ emit at 626 nm and 682 nm respectively, while for the species $[Ru(bipy)_2(mim)(H_2O)]^{2+}$ no emission is observed.

By comparison with the model compounds one can, from low-temperature emission spectra, clearly distinguish between $[Ru(bipy)_2(pnvi)Cl]^+$ which emits at 685 nm [samples **(A)**—**(D)**] and $[Ru(bipy)_2(pnvi)_2]^{2+}$ which emits at 620 nm [samples **(E)**—**(I)**]. At room temperature an emission at *ca.* 635 nm was observed for all the polymeric materials while at lower temperatures an emission band at *ca.* 685 nm appears [see Figure 2(*a*)]. This suggests that at room temperature emission from $[Ru(bipy)_2(pnvi)_2]^{2+}$ is much stronger, while at liquid nitrogen temperature the emission intensities of the compounds are more alike. With this in mind it can be explained that at room temperature metallopolymers with only a small amount of $[Ru(bipy)_2(pnvi)_2]^{2+}$ show emission at *ca.* 635 nm, with only a weak shoulder at 700 nm arising from the presence of the main species, $[Ru(bipy)_2(pnvi)Cl]^+$.

An analysis of the data in Table 2 suggests that for polymer to metal ratios of > 10 $[Ru(bipy)_2(pnvi)_2]^{2+}$ is obtained as the

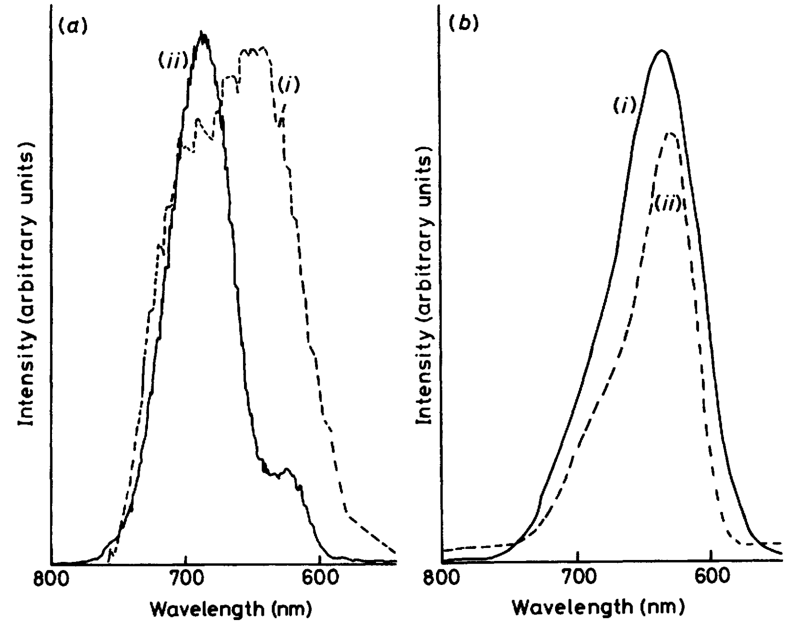

Figure 2. Room-temperature emission spectrum of (*a*)(*i*) sample (**C**) in methanol (*b*)(*i*) sample (**E**) in methanol. 77-K Emission spectrum of (*a*)(*ii*) sample (**C**) in ethanol and (*b*)(*ii*) sample (**E**) in ethanol. Sample concentration 10^{-4} mol dm^{-3}

Table 3. Effect of different electrolytes on the $E_{\frac{1}{2}}$ values of the species $[Ru(bipy)_2(pnvi)Cl]^+$ [sample (**C**)] and $[Ru(bipy)_2(pnvi)_2]^{2+}$ [sample (**I**)]*

	$E_{\frac{1}{2}}$	
Electrolyte	(**C**)	(**I**)
H_2SO_4	585 (30)	860 (60)
HCl	605 (50)	925 (50)
NaCl	660 (55)	920 (60)
$HClO_4$	550 (100)	825 (100)
$CH_3CN-NEt_4ClO_4$	665 (125)	1 025 (90)

* Measurements taken using polymer modified glassy carbon electrodes. Surface coverage 3×10^{-8} mol cm^{-2}, scan rate 50 mV s^{-1}. All potentials mV *vs.* s.c.e. Values in parentheses are peak-to-peak separations. Electrolyte concentration 1 mol dm^{-3}; $CH_3CN-NEt_4ClO_4$ 0.1 mol dm^{-3}.

main product [samples (**F**)—(**H**)]. For a 5:1 polymer to metal ratio the products obtained depend on the reflux time and the reaction solvent. When water is added to the reaction mixture the disubstituted complex is obtained [sample (**E**)]. In methanol the main product is $[Ru(bipy)_2(pnvi)Cl]^+$ with the amount of $[Ru(bipy)_2(pnvi)_2]^{2+}$ increasing with reaction time. The absorption and emission data do not yield conclusive information about the presence of the aqua species $[Ru(bipy)_2(pnvi)(H_2O)]^{2+}$.

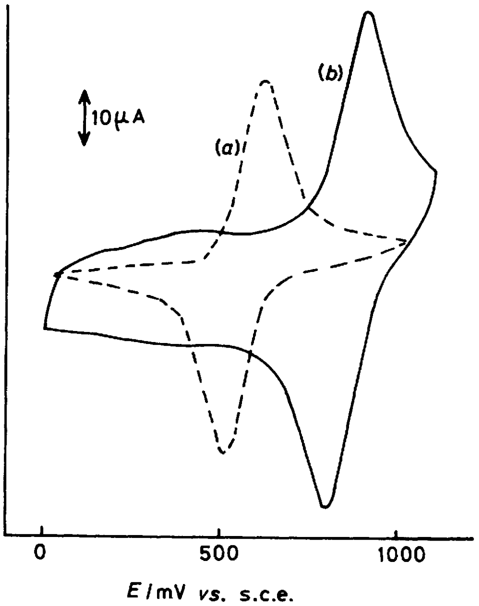

Figure 3. Cyclic voltammogram of a glassy carbon electrode coated with (*a*) sample (**C**) and (*b*) sample (**I**). Scan rate 50 mV s^{-1}, electrolyte 1 mol dm^{-3} $HClO_4$. Surface coverage: (*a*) 2.0×10^{-8} mol cm^{-2}, (*b*) 2.4×10^{-8} mol cm^{-2}

Electrochemical Measurements.—Electrochemical studies were used both for the characterisation of the metallopolymers and for the investigation of the photochemical properties of the polymer films. The data obtained are listed in Table 2. Poly-*N*-vinylimidazole bound $Ru(bipy)_2$ complexes were attached to glassy carbon and pyrolytic graphite electrodes according to literature procedures.[1,14] The modified electrodes produced were studied by cyclic voltammetry in a series of electrolytes (see Table 3). Typical examples of cyclic voltammograms are given in Figure 3. The cyclic voltammograms obtained were found to show a decrease in peak-to-peak separation with decreasing scan rate and for scan rates up to 200 mV s^{-1} a linear dependence of the peak current on the scan rate. In general the polymer films show the electrochemical behaviour that is expected for surface bound, fast electron exchanging species.[1,8]

As indicated by the results given in Table 2 the position of the $Ru^{II}-Ru^{III}$ redox couple was found to depend strongly on the nature of the ligands bound to the ruthenium centre. From the redox potentials obtained for the modified electrodes it can be concluded that, depending on the reaction conditions, two different ruthenium species are obtained. The influence of the reaction conditions on the products obtained can be judged from the ratio of the peak currents of the two redox couples (see

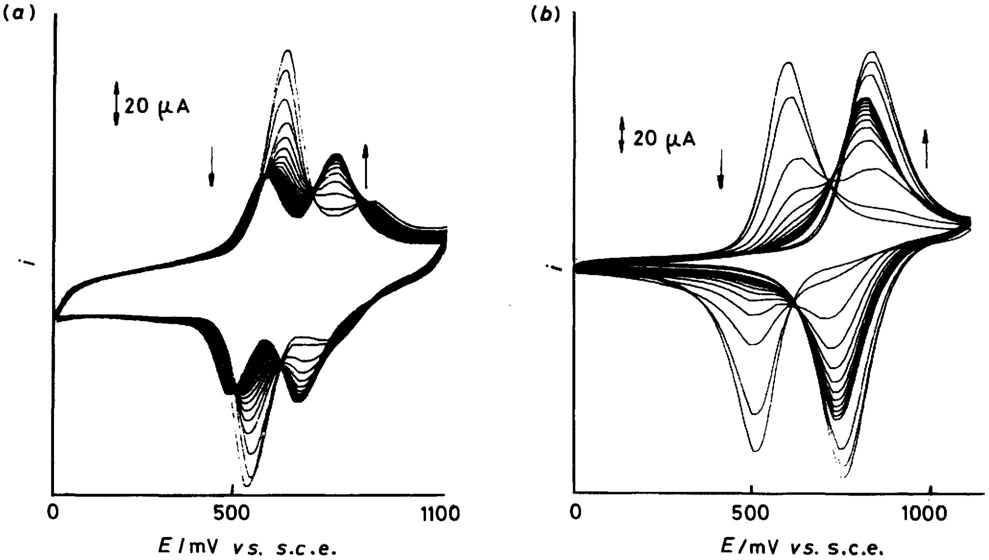

Figure 4. Photochemically induced ligand-exchange reactions in thin, electrode bound: (*a*) films of sample (C) using 1 mol dm^{-3} H_2SO_4 as electrolyte and (*b*) coatings of sample (C) using 1 mol dm^{-3}, $HClO_4$ as electrolyte. Scan rate 50 mV s^{-1}. Electrode coverage 2.0×10^{-8} mol cm^{-2}. For a detailed description of the experiments see text

Table 2). This ratio shows that for a synthesis using methanol as solvent, short reflux times (*i.e.* 12 h), and a low pnvi:Ru ratio (*i.e.* 5:1) a product with a redox couple of 570 mV is obtained. This redox couple has been assigned to $[Ru(bipy)_2(pnvi)Cl]^+$ by comparison of the redox potentials obtained for the model compounds (see Table 3) and other similar metallopolymers.[1,16,17]

Longer reflux times [*i.e.* sample (A)], addition of water to the reaction [sample (E)], and a higher pnvi:Ru ratio, lead to the formation of a product with a redox couple of *ca.* 850 mV. This redox couple has been assigned to the complex $[Ru(bipy)_2(pnvi)_2]^{2+}$, again by comparison with analogous compounds.

The redox potentials obtained depend on the electrolyte used (see Table 3); in aqueous solution the redox potential varies from 550 mV in $HClO_4$ to 640 mV in Na_2SO_4 for $[Ru(bipy)_2(pnvi)Cl]^+$. The influence of the electrolytes used is also reflected in the shape of the cyclic voltammograms obtained, *i.e.* much broader bands with larger peak-to-peak separations are obtained in high pH and perchlorate media than in low pH sulphate or chloride media. This is most likely explained by the nature of the metallopolymer electrolyte interface. Because of protonation of the polymer backbone the metallopolymer is more easily penetrated by an acidic electrolyte, 1 mol dm^{-3} H_2SO_4, and this may lead to a lower redox potential in acidic media. More detailed investigations on the electrochemical properties of these modified electrodes are in progress. Some of the metallopolymers, *e.g.* $[Ru(bipy)_2(pnvi)_2]^{2+}$, were found to be soluble in some of the acidic media used, particularly H_2SO_4, and films of $[Ru(bipy)_2(pnvi)_2]^{2+}$ came off the electrode surface when H_2SO_4 was used as electrolyte. This process did not occur when $HClO_4$ was used probably due to the insolubility of the metallopolymer in this medium.

As stated above the solubility of the metallopolymers changes with time. This process is conveniently monitored using electrochemical methods. Over a period of several months electrodes were periodically modified with an ageing polymer solution. With time a redox couple with a potential of 730 mV was found to develop at the cost of the original signal at 570 mV. This clearly indicates a change in the co-ordination chemistry of the polymer-bound metal complex. On the basis of the photochemical studies discussed below this redox couple has been assigned to $[Ru(bipy)_2(pnvi)(H_2O)]^{2+}$. This compound is most likely formed according to equation (3). One point to note is that only the monosubstituted species $[Ru(bipy)_2(pnvi)Cl]^+$ is unstable in solution. So increased concentration of $[Ru(bipy)_2(pnvi)Cl]^+$ relative to $[Ru(bipy)_2(pnvi)_2]^{2+}$ leads to formation of increased amounts of $[Ru(bipy)_2(pnvi)(H_2O)]^{2+}$. As the aqua complex can easily form the disubstituted species the formation of this complex in the solid state would lead to crosslinking and a decrease in solubility as is indeed observed.

Photochemistry.—Earlier experiments with poly-4-vinylpyridine (pvp) based metallopolymers have shown that these materials undergo photoinduced ligand substitutions.[18,19] Such reactions are of great interest as they provide an elegant way to change the redox potential of electroactive metallopolymer films coated on electrode surfaces. Furthermore, compounds can be formed that are not easily prepared by normal synthetic methods.

The photochemical properties of thin films of pnvi based metallopolymers on glassy carbon were investigated by electrochemical means. Photolysis was carried out in the electrolytes 1 mol dm^{-3} H_2SO_4 and 1 mol dm^{-3} $HClO_4$. On photolysis of sample (C) {which contains mainly $[Ru(bipy)_2(pnvi)Cl]^+$} in H_2SO_4 the intensity of the wave at 570 mV, corresponding to the starting material, decreased with the appearance of two new signals, one at the 730 mV and a second one at 540 mV [see Figure 4(*a*)]. It was found that within a few minutes an equilibrium was reached with the peak heights of the two waves at 540 mV and 730 mV remaining the same. It was found that the photosubstitution process was slower when the electrode was continuously cycled through the oxidation potential during the photolysis. If the electrode, still in solution, was then placed in darkness total conversion to a single species at 730 mV, with no loss of product from the electrode surface, was observed. On re-irradiation of the coated electrode the system was found to revert back to the equilibrium situation with two redox couples. The conversions from one state to another are fast and reversible. Clearly the species at 730 mV is more stable in the dark while the species with a redox couple at 540 mV is stabilised by photolysis. By comparison with redox potentials obtained for similar metallopolymers and with model compounds the species at 730 mV was identified as $[Ru(bipy)_2(pnvi)(H_2O)]^{2+}$, while the redox couple at 540 mV is possibly explained by the presence of $[Ru(bipy)_2(pnvi)(SO_4)]$.

Upon irradiation of sample (**C**) in $HClO_4$, $[Ru(bipy)_2(pnvi)Cl]^{2+}$ undergoes a quantitative conversion to the aqua species with a redox potential at 750 mV as illustrated in Figure 4(*b*). This is a very useful method for the preparation of the aqua complex and allows the study of $[Ru(bipy)_2(pnvi)(H_2O)]^{2+}$, a compound that cannot be prepared easily by other means.

The electrochemical behaviour of the species $[Ru(bipy)_2(pnvi)(H_2O)]^{2+}$, as prepared by photochemical means, was studied in various electrolytes. After photolysis [electrode film made from sample (**C**)] in $HClO_4$ the electrode, now coated with $[Ru(bipy)_2(pnvi)(H_2O)]^{2+}$, was placed in a series of electrolytes. In 1 mol dm^{-3} H_2SO_4 the complex was stable and exhibited, as expected from the photochemical experiments carried out in this electrolyte, a redox couple at *ca.* 750 mV. In 1 mol dm^{-3} HCl the complex transformed immediately to $[Ru(bipy)_2(pnvi)Cl]^+$ as evidenced by the appearance of a redox couple at *ca.* 590 mV. In CH_3CN–NEt_4ClO_4 the band intensity at a redox potential of 1 020 mV, corresponding to the $[Ru(bipy)_2(pnvi)(H_2O)]^{2+}$ redox couple, was found to decrease with time with the development of a new band at 1 150 mV which can be attributed to the formation of $[Ru(bipy)_2(pnvi)(CH_3CN)]^{2+}$. This is in agreement with some previously published results for $[Ru(bipy)_2(pvp)(H_2O)]^{2+}$ where, in acetonitrile, a redox couple at 1 135 mV was assigned to $[Ru(bipy)_2(pvp)(CH_3CN)]^{2+}$.[18]

At this stage it is important to point out that in cyclic voltammograms of films prepared from freshly prepared metallopolymers no appreciable amounts of the aqua species are found, with possible exceptions for samples (**E**) and (**F**). The presence of a redox couple at *ca.* 600 mV in both materials might suggest the presence of both the chloro and the aqua compound. The absence of an emission signal at 77 K that can be attributed to the chloro compound in sample (**F**) might also suggest that the electrochemical signal at 600 mV is not just due to the chloro compound.

Photolysis of $[Ru(bipy)_2(pnvi)_2]^{2+}$ [sample (**I**)] in H_2SO_4 leads to the loss of the electroactive centre from the electrode surface.

In $HClO_4$, however the same sample was found to be photostable with no formation of any new products and no loss of material from the electrode surface. As no photosubstitution is observed here $[Ru(bipy)_2(pnvi)_2]^{2+}$ might have interesting properties as a photosensitizer under these conditions. The photostability of the pnvi based metallopolymer, in this electrolyte, seems to be greater than observed for the analogous metallopolymer $[Ru(bipy)_2(pvp)_2]^{2+}$.[11,19]

Concluding Remarks.—The results reported here show that the nature of the polymer-bound metal complex obtained from the reaction between $[Ru(bipy)_2Cl_2]{\cdot}2H_2O$ and poly-*N*-vinylimidazole depends strongly on the reaction conditions. This is quite contrary to results obtained with poly-4-vinylpyridine, where $[Ru(bipy)_2(pvp)Cl]^+$ was obtained as the only product up to pvp : Ru ratios of 100 : 1.[4a] It is furthermore important that the nature of the polymer-bound metal complex changes with time, both in solution and in the solid state. The ligand-exchange process is much faster under irradiation. A very efficient formation of the aqua complex from the chloro compound is observed in perchloric acid. The photochemical process is electrolyte dependent and an interesting photochemically induced ligand-exchange reaction is observed in sulphuric acid. As this reaction is reversed in the dark, such a process could find application in information storage devices. The photostability of $[Ru(bipy)_2(pnvi)_2]^{2+}$ in perchloric acid makes the use of thin films of this material in solar energy devices possible. We are at present investigating a number of possible applications. To obtain materials suitable for a particular application the reaction conditions will have to be controlled carefully. To ascertain the nature of the metal centres the use of different techniques is important. Electrochemical techniques are most useful to obtain a product ratio, while emission experiments can be used to detect small amounts of (strongly emitting) by-products.

Experimental

U.v.–visible spectra were recorded on Pye-Unicam SP8-200 and Shimadzu UV 240 spectrophotometers. Emission spectra were recorded using a Perkin-Elmer LS-5 luminescence spectrometer. Spectra were recorded using an emission slit width at 10 nm at room temperature and 2.5 nm at 77 K and are not corrected for photomultiplier response. Electrochemical measurements were carried out using an E.G. and G. Par model 174A polarographic analyser with an E.G. and G. Par 175 Universal programmer. A slide projector was included as a light source for photochemical investigations. Glassy carbon or pyrolytic graphite electrodes were coated with a known amount of a 10^{-3} mol dm^{-3} solution (based on Ru) of the polymer in methanol. The electrodes were then left to dry for several days. A saturated potassium calomel electrode (s.c.e.) was used as a reference electrode. All potentials given in this contribution are *vs.* s.c.e. Redox potentials reported for modified electrodes are average values obtained for different coatings. Variations of both peak potentials and peak-to-peak separations of up to 25 mV are observed for different electrodes coated with the same sample. Elemental analyses were carried out at the Microanalytical Laboratory of University College Dublin.

$[Ru(bipy)_2Cl_2]{\cdot}2H_2O$[20] and $[Ru(bipy)_2(CO_3)]$[21] were prepared according to literature procedures. *N*-Vinylimidazole was obtained from Aldrich and distilled before use. Reagent-grade solvents were used without further purification.

*Poly-*N*-vinylimidazole.*—Freshly distilled *N*-vinylimidazole was polymerised with 2,2′-azoisobutyronitrile as an initiator in a 20 : 1 ratio. The bulk polymerisation was carried out *in vacuo* at 70 °C for 2 h. The product obtained was dissolved in methanol and precipitated in acetone. Using gel-permeation chromatography and polystyrene reference compounds it was estimated that the number average molecular weight, $\bar{M}_n$, of the sample obtained is *ca.* 40 000. The filtered product was then dried under vacuum at room temperature [Found: C, 59.0; H, 7.0; N, 27.2. $(C_5H_6N_2{\cdot}0.5H_2O)_n$ requires C, 58.3; H, 6.8; N, 27.2%].

Reaction of pnvi with $[Ru(bipy)_2Cl_2]$.—Methanolic solutions of pnvi and the ruthenium complex were heated at reflux for up to 3 d. The reaction conditions are given in Table 1. The materials were isolated by precipitation in diethyl ether or acetone and the solids obtained dried *in vacuo*. In some cases only half of the product was isolated; the remaining half was used to investigate the changes that occur in solution with time.

The polymer pnvi was treated with $[Ru(bipy)_2(CO_3)]$ as described in the literature for the corresponding poly-4-vinylpyridine complex.[3]

$[Ru(bipy)_2(mim)_2][PF_6]_2$.—$[Ru(bipy)_2Cl_2]{\cdot}2H_2O$ (255 mg, 0.5 mmol) and *N*-methylimidazole (246 mg, 3 mmol) were heated at reflux in 150 cm^3 ethanol–water (75:25) for 3 h. The product was then isolated as the PF_6 salt by addition of an excess of NH_4PF_6 in water. The solid obtained was recrystallised from acetone–water mixtures and dried *in vacuo*. Yield 332 mg, 75% (Found: C, 38.9; H, 3.0; N, 12.5. $C_{28}H_{28}F_{12}N_8P_2Ru$

requires C, 38.7; H, 3.2; N, 12.95%). U.v.-visible (methanol): λ (log ε) 492 (3.99) and 340 (3.89).

$[Ru(bipy)_2(mim)Cl]PF_6$.—$[Ru(bipy)_2Cl_2]\cdot 2H_2O$ (255 mg, 0.5 mmol) and mim (40 mg) were heated at reflux in ethanol (150 cm^3) for 7 h. The product was isolated by the addition of aqueous NH_4PF_6. The solid obtained was recrystallised from acetone–water mixtures and dried *in vacuo*. Yield 240 mg, 70% (Found: C, 42.4; H, 3.3; Cl, 5.7; N, 12.0. $C_{24}H_{22}ClF_6N_6PRu$ requires C, 42.6; H, 3.3; Cl, 5.3, N, 12.4%). U.v.-visible (methanol): λ (log ε) 512 (3.84) and 352 (3.83).

$[Ru(bipy)_2(mim)(H_2O)][PF_6]_2\cdot H_2O$.—$[Ru(bipy)_2(mim)Cl][PF_6]$ (69.9 mg, 0.103 mmol) was heated at reflux in water (10 cm^3) until dissolved, which took *ca.* 5 min. The product was then precipitated by addition of NH_4PF_6 in water. The filtered product (78 mg, 94%) was dried under vacuum overnight (Found: C, 35.4; H, 3.0; N, 10.0. $C_{24}H_{26}F_6N_6OPRu$ requires C, 35.1; H, 3.2; N, 10.2%). U.v.-visible (methanol): λ (log ε) 487 (3.94) and 338 (3.98).

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