Synthesis, Characterization, and Properties of a Series of Osmium- and Ruthenium-Containing Metallopolymers

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ABSTRACT: A series of metallopolymers, based on poly(4-vinylpyridine) (PVP) and poly(*N*-vinylimidazole) (PVI), has been prepared containing both osmium and ruthenium bis(2,2′-bipyridyl) centers. The polymers have been characterized by using UV–vis and emission spectroscopies. The results obtained are compared with those obtained for the metallopolymers containing only osmium or ruthenium centers as well as model monomeric complexes. Some electrochemical and photochemical properties of glassy carbon electrodes modified with these materials are also reported.

Introduction

Metallopolymers constitute a class of materials that is attracting increasing attention because of their potentially widespread application.[1-5] In particular, polymers containing covalently bound ruthenium complexes have been investigated in some detail, and the application of these materials as redox catalysts, photosensitizers, and molecular diodes has been proposed.[6-14] In these studies, the materials are often investigated as thin layers on solid electrode surfaces. Ruthenium-containing metallopolymers are of interest because of their long-lived excited state and facile electron-exchange dynamics, which can be exploited in areas such as photosensitization. However, photochemically induced ligand-exchange reactions are frequently a feature of these materials.[11,13]

In this paper we describe the synthesis and characterization of a series of novel metallopolymers of poly(4-vinylpyridine) (PVP) and poly(*N*-vinylimidazole) (PVI) containing two different redox centers based on ruthenium and, more photostable, osmium bis(2,2′-bipyridyl) moieties. The effect of the presence of two redox centers in the same polymer on ground- and excited-state properties is explored by using electrochemical and spectroscopic techniques.

Experimental Section

Equipment. UV–visible spectra were recorded on Hewlett-Packard 342A diode array and Shimadzu UV 240 spectrophotometers. Emission spectra were recorded by using a Perkin-Elmer LS-5 luminescence spectrometer equipped with a red-sensitive Hamamatsu R928 detector. Spectra were recorded by using an emission slit width of 10 nm at room temperature and 2.5 nm at 77 K and are not corrected for photomultiplier response. Electrochemical measurements were performed by using an E.G. and G PAR 273 potentiostat/galvanostat. A visible 100-W light source was used for the photochemical experiments. Glassy-carbon electrodes of 7 mm were modified by pipetting the required quantity of a methanolic 1% (w/v) solution of the metallopolymer directly onto their surface. The solvent was then allowed to evaporate slowly in a solvent-saturated chamber followed by air drying. All potentials are quoted versus a potassium-saturated calomel electrode (SCE) without regard for liquid junction potentials. Peak positions for the redox couples of the metallopolymer coatings were obtained at slow sweep rates where the anodic and cathodic peaks typically converge. Potential step chronoamperometry was used to determine Os(II/III) charge transport rates by stepping from −0.4 V to 200 mV past the formal potential of the redox couple. Charge transport rates for Ru(II/III) oxidation were calculated by stepping from −0.4 to 1.3 V and then substracting out the current contribution from the Os(II/III) oxidation. Alternatively by initially holding the potential past the formal potential of the osmium couple, until the osmium oxidation is complete, and then stepping to 1.3 V, the charge transport rate could be assessed without an osmium contribution. These transient current/charge measurements were made over the time range 0–40 ms by means of a Philips 3311 digital storage oscilloscope interfaced to a BBC microcomputer for data interrogation and by allowing signal-averaged results to be obtained. This regime has been discussed previously.[15] Differential scanning calorimetry (DSC) was performed by using 2-mg samples of vacuum-dried materials using a Stanton Redcroft CPC 706 temperature programmer, a DSC Lineariser, and a DC amplifier. Experiments were carried out in static air with a heating rate of 10 °C/min up to temperatures of 350 °C.

Materials. $[Ru(bipy)_2Cl_2]$,[16] $[Ru(bipy)_2(H_2O)_2](PF_6)_2$,[17] $[Ru(bipy)_2(PVP)_{10}Cl]Cl$ (**1**),[10b] $[Ru(bipy)_2(PVP)_{10}](Cl)_2$ (**2**),[10b] $[Ru(bipy)_2(PVI)_{10}Cl]Cl$ (**3**),[11] and $[Ru(bipy)_2(PVI)_{10}]Cl_2$ (**4**)[11] were prepared as described previously. $[Os(bipy)_2Cl_2]$ was prepared as described by Buckingham et al.[18]

Poly(4-vinylpyridine). Poly(4-vinylpyridine) was prepared by bulk polymerization of freshly distilled 4-vinylpyridine under a nitrogen atmosphere using 2,2′-azobis(isobutyronitrile) as initiator at 70 °C. The product was purified by repeated precipitation in diethyl ether from methanol. The resulting polymer was fractionated by partial precipitation from methanol solutions by addition of toluene to cloud point followed by raising the temperature. The molecular weight of the precipitant at 40 °C was determined by viscometry measurements in ethanol in conjunction with the Mark–Houwink equation to be approximately 430 000 g/mol.[19]

Poly(*N*-vinylimidazole). Poly(*N*-vinylimidazole) was prepared from freshly distilled monomer as described above for PVP and similarly fractionated. The molecular weight as determined by viscometry in ethanol was 110 000 g/mol.[19]

For $[Os(bipy)_2(Pol)_nCl]Cl$ [Pol = poly(4-vinylpyridine) or poly(*N*-vinylimidazole)], n = 5, 10, 15, and 25. PVP polymers are labeled as compounds **5–8** and PVI polymers as compounds **9–12**. For the polymers containing high metal loadings, elemental analyses were obtained. These are of limited value, as only the chloride content shows appreciable variation with metal loading. The metallopolymers were prepared as the analogous ruthenium polymers[10b,11] except that longer reflux times were required. $[Os(bipy)_2Cl_2]$ and the appropriate amount of the polymer were heated at reflux in ethanol for periods up to 6 days. The reaction was monitored by UV–visible spectroscopy and cyclic voltammetry. Although no photochemical reactions were observed, the reactions were routinely carried out in the dark. The metallopolymers were isolated by precipitation into diethyl ether and purified by repeated precipitation (3×) in diethyl ether from methanol. In a typical synthesis of $[Os(bipy)_2(PVP)_{10})Cl]Cl$, 40 mg (0.07 mM) of $[Os(bipy)_2Cl_2]$ was dissolved in 30 cm^3 of ethanol and refluxed for 30 min. A total of 73 mg (0.7 mM) of PVP in 10 cm^3 of ethanol was then added and refluxing continued for 72 h. The metallopolymer was recovered by precipitation into diethyl ether and vacuum dried; yield 104 mg, 92%. The perchlorate salts of these polymers were prepared by addition of 2 M equiv of lithium perchlorate to the ethanol solution of the metallopolymer. The precipitant polymer was recovered by filtration

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and purified as for the materials where chloride was the anion. These materials are labeled as **5a**, **6a**, **7a**, and **8a** for the PVP polymers and **9a**, **10a**, **11a**, and **12a** for the PVI polymers.

$[Os(bipy)_2(PVP)_{10}]Cl_2$, Compound 13. $[Os(bipy)_2Cl_2]$ (57 mg, 0.1 mmol) and PVP (104 mg, 1 mmol) were heated at reflux in 75 cm^3 ethanol/water (50:50) in the dark for 8 days. The metallopolymer was recovered by solvent stripping and subsequent dissolution in methanol, followed by precipitation into diethyl ether and vacuum drying. The reaction could also be carried out in ethylene glycol/water mixtures with some reduction in the reflux time; yield 146 mg, 91%.

$[Os(bipy)_2(PVI)_{10}]Cl_2$, Compound 14. This polymer was prepared as reported above for the analogous PVP polymer; yield 87%.

$[Os(bipy)_2(PVP)_{10}Cl]Cl/[Ru(bipy)_2(PVP)_{10}Cl]Cl$, Compound 15. To 57 mg (0.035 mmol) of $[Os(bipy)_2(PVP)_{10}Cl]Cl$ (**6**) in methanol was added $[Ru(bipy)_2Cl_2]$ (17 mg, 0.035 mmol), and the solution was refluxed in the dark for 3 days. The resulting metallopolymner was recovered by precipitation into diethyl ether and vacuum dried; yield 68 mg, 92%.

$[Os(bipy)_2(PVI)_{10}Cl]Cl/[Ru(bipy)_2(PVI)_{10}Cl]Cl$, Compound 16. To 53 mg (0.035 mmol) of $[Os(bipy)_2(PVI)_{10}Cl]Cl$ (**10**) in methanol was added $[Ru(bipy)_2Cl_2]$ (17 mg, 0.035 mmol), and the solution was refluxed in the dark for 24 h. The resulting metallopolymer was recovered by precipitation into diethyl ether and vacuum dried; yield 62 mg, 88%.

$[Ru(bipy)_2(PVP)_{10}](Cl)_2/[Os(bipy)_2(PVP)_{10}Cl]Cl$, Compound 17. To 62 mg (0.04 mmol) of $[Ru(bipy)_2(PVP)_{10}](Cl)_2$ (**2**) dissolved in methanol was added 23 mg (0.04 mmol) of $[Os(bipy)_2Cl_2]$. The resulting solution was refluxed in the dark for 3 days. The product was recovered as described above and purified by precipitating three times in diethyl ether from methanol; yield 67 mg, 80%.

$[Ru(bipy)_2(PVI)_{10}](Cl)_2/[Os(bipy)_2(PVI)_{10}Cl]Cl$, Compound 18. This mixed ruthenium/osmium metallopolymer was prepared from compound **4** and purified as given above for compound **17**; yield 85%.

$[Os(bipy)_2(PVP)_{10}](Cl)_2/[Ru(bipy)_2(PVP)_{10}](Cl)_2$, Compound 19. To $[Os(bipy)_2(PVP)_{10}](Cl)_2$ (**13**, 50 mg, 0.03 mmol) in methanol was added $[Ru(bipy)_2(H_2O)_2](ClO_4)_2$ (19 mg, 0.03 mmol). The resulting solution was refluxed in the dark for 3 days. The product was recovered by precipitation in diethyl ether and vacuum dried; yield 60 mg, 86%.

$[Os(bipy)_2(PVI)_{10}](Cl)_2/[Ru(bipy)_2(PVI)_{10}](Cl)_2$, Compound 20. This metallopolymer was prepared as given above for compound **19** by using $[Os(bipy)_2(PVI)_{10}](Cl)_2$ (**14**) as starting material; yield 82%.

Synthesis of Mononuclear Model Compounds. The following compounds were synthesized by using literature methods from $Os(bipy)_2Cl_2$;[8,10b,20] pic = 4-methylpyridine, mim = *N*-methylimidazole. $[Os(bipy)_2(pic)Cl](PF_6)$ (**21**). Calcd for $C_{26}ClF_6H_{23}N_5OsP$: C, 40.22; H, 2.96; N, 9.02. Found: C, 40.57; H, 3.02; N, 9.07. $[Os(bipy)_2(pic)_2](PF_6)_2$ (**22**). Calcd for $C_{32}F_{12}H_{30}N_6OsP_2$: C, 39.26; H, 3.06; N, 8.58. Found: C, 39.32; H, 3.10; N, 8.59. $[Os(bipy)_2(mim)Cl](PF_6)$ (**23**). Calcd for $C_{24}ClF_6H_{22}N_6OsP$: C, 37.66; H, 2.87; N, 10.98. Found: C, 37.32; H, 2.74; N, 10.51. $[Os(bipy)_2(mim)_2](PF_6)_2$ (**24**). Calcd for $C_{28}F_{12}H_{28}N_8OsP_2$: C, 35.14; H, 2.92; N, 11.71. Found: C, 35.16; H, 2.87; N, 11.79.

Results and Discussion

General Procedures. To our best knowledge, the osmium polymers reported here are the first examples of their kind. In the literature some reports of osmium polypyridyl containing polymeric materials have appeared; however, in these cases heavily cross-linked materials were formed by electropolymerization at electrode surfaces.[21] This procedure typically gives rise to insoluble products in which the ratio of metal centers/polymer units is difficult to control or determine.

The synthetic approach used is to react the appropriate metal complexes with preformed PVP or PVI, so that cross-linking can be avoided and soluble polymers are obtained. In this manner the materials can be characterized in solution as well as thin films on electrode surfaces.

The formation of the different metallopolymers is based on the well-documented lability of the chloride ions in the complex $[M(bipy)_2Cl_2]$, M = Ru, Os. Extensive studies have shown that the first chloride ion is easily removed by refluxing in methanol or ethanol, whereas the removal of the second chloride occurs only in aqueous solutions or with high boiling solvents.[10b,11,16,17,22] Therefore, in syntheses that aimed to prepare monosubstituted materials such as $[Os(bipy)_2(PVP)_{10}Cl]Cl$, ethanol was used as a solvent (see reactions 1 and 2), whereas for the synthesis of species such as $[Os(bipy)_2(PVP)_{10}]Cl_2$, water was added to the reaction mixture (see reactions 1–4, S = solvent).

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

$$[Ru(bipy)_2(S)Cl]^+ + Pol \rightarrow [Ru(bipy)_2(Pol)Cl]^+ + S \quad (2)$$

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

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

The osmium polymers are prepared in a similar way to the corresponding ruthenium polymers, but because of the inertness of osmium complexes, longer reflux times are needed. The synthetic flexibility of the procedure is evident since materials with different metal to polymer ratios can be prepared easily by adding the appropriate amounts of reactants. The polymer backbone can be changed provided it has a pendant coordinating group, and the nature of the metal center can also be varied. The metal loading of the materials reported here is based on the quantity of starting material employed, assuming complete reaction. This assumption is supported by the continuous monitoring of the reactions using spectroscopic and electrochemical techniques. The coordination around the metal ions was examined by comparison of the spectroscopic and electrochemical properties of the polymers with those of appropriate model compounds (vide infra). Approximate extinction coefficients have also been evaluated. This is, however, complicated by problems as to the degree of hydration of the homopolymers and the subsequent metallopolymers. The extinction coefficients, however, remain useful for examining the ratio of metal centers to polymer units.

Glass Transition Temperature. The effect of metal loading and the nature of the counterion in the $[Os(bipy)_2(PVP)_nCl]X$ and $[Os(bipy)_2(PVI)_nCl]X$ metallopolymers, where the counterion X is chloride or perchlorate, has been examined. The thermal stability of the metal centers in these materials means that it is possible to examine T_g as a function of redox site loading; $[Ru(bipy)_2Cl]Cl$ units have been used previously as probes of structure and dynamics in quaternized poly(4-vinylpyridine).[14] The glass transition temperature is clearly sensitive to the metal loading, with T_g increasing considerably over the homopolymer values with increasing metal loading (see Table I). Thoroughly dried poly(4-vinylpyridine) has a glass transition temperature of approximately 142 °C, which is largely independent of molecular weight.[23] The higher glass transition temperature with increasing metal content most likely reflects a greater difficulty in obtaining fluidlike motion within the metallopolymers, as the molecular weight is increased by addition of metal

Table I
Glass Transition Temperatures for Polymers of the Type $[Os(bipy)_2(Pol)_nCl]X$

compd	T_g, °C	compd	T_g, °C
PVP	143	PVI	182
	X = Cl^-		
5	230	9	260
6	205	10	226
7	192	11	207
8	180	12	193
	X = ClO_4^-		
5a	252	9a	278
6a	223	10a	240
7a	209	11a	217
8a	189	12a	198

centers. We have attempted to correlate these observations with thermodynamic parameters observed for charge transport through films of these materials immobilized on electrode surfaces in contact with aqueous electrolyte.[15,24] The activation energy for charge transport does indeed increase with redox site loading. Under certain circumstances two activation energies are observed. So far it has been assumed that these observations are connected with the internal polymer organization. However, the temperature at which the change in activation energy occurs, 285 K, is significantly different from the glass transition temperatures reported here and cannot therefore be connected. This is probably not too surprising as during the electrochemical measurements the films are in contact with an aqueous electrolyte.

PVP is thermally stable in a nitrogen atmosphere up to 300–350 °C. On conversion to the acid salt or 1-alkylpyridinium salt, the thermal stability decreases, the decrease being a function of the extent of quaternization. For the materials described here, however, no loss of thermal stability via DSC measurements is observed and both spectroscopic and electrochemical measurements suggest that the metallopolymers do not decompose at temperatures of up to 300 °C. The degradation in the polymeric 1-alkylpyridinium salts is generally accepted as occurring in two stages: loss of the 1-alkyl group and scission of the polymer backbone.[25] That these metal-containing polymers remain stable suggests a strong coordination between the metal and polymer nitrogen.

The glass transition temperature of the perchlorate salt of these polymers shows an increase over those values obtained when chloride is the counterion. For quaternized PVP films containing ferrocyanide, in contact with perchlorate-containing solutions,[26] it has been proposed recently that an almost completely dehydrated material results, with consequential loss of internal fluidlike motion. It seems likely that such a process is also occurring in these polymers and that this is being reflected in the T_g measurements.

Absorption and Emission Spectroscopy. Electronic spectroscopy has proved useful in the characterization of ruthenium-containing polymers.[10,11] In particular, the position of the lowest absorption maxima and the wavelength of emission are often characteristic for a particular ruthenium moiety, and by comparison with mononuclear model compounds, the coordination sphere of the metal ion bound to the polymer backbone can be established. The data obtained for the absorption and emission spectra of the metallopolymers, together with data obtained for some model compounds, have been given in Table II. The spectral features observed are typical of osmium and ruthenium compounds. A detailed analysis of the spectroscopic features of osmium and ruthenium compounds has been given elsewhere[10,11,16,17,20] and will not be considered here. The electronic transitions observed in the visible region are attributed to metal-to-ligand charge-transfer bands (MLCT), while the emission is throught to occur from a ligand-based triplet state. The spectra obtained for the polymers **5–12** do agree well with those observed for the model compounds **21** and **23** (see parts a and b of Figure 1). For these model compounds and metallopolymers no emission was observed. This suggests for these polymers a coordination of $[OsN_5Cl]Cl$. Due to the spectral complexity, however, no definite assignment of the coordination sphere around the osmium ion can be made from the absorption data alone. The absorption spectra of the osmium polymers **13** and **14** are very similar to those observed for the model compounds **22** and **24**, respectively. A significant feature of the UV/visible data is the similarity of the extinction coefficients between the polymeric and monomeric species. Also for both sets of compounds emission signals at about 750 nm are observed. This strongly suggests the presence of the $[OsN_6]Cl_2$ moiety in these polymers, so that two nitrogen units from the polymer backbone are bound to the osmium center. These observations are in agreement with the synthetic conditions employed.

The spectra obtained for the mixed metal compounds show the presence of both metal centers, but the complexity of the spectra prevents a conclusive analysis of the composition of the materials. More specific information can be obtained from the emission spectra. For the mixed polymers **15** and **16** the presence of an emission maximum at about 700 nm can, by comparison with analogous compounds,[27] be explained by the presence of a $[RuN_5Cl]Cl$ moiety. As anticipated no evidence for an osmium-based emission was observed in these materials. For the polymers **17** and **18** an emission at about 625 nm at 77 K is indicative of the presence of $[RuN_6]Cl_2$ groupings.[9,10] For these compounds no osmium-based emission was observed. For polymer **19** emission signals at room temperature are observed at 618 nm with a shoulder at 730 nm. At 77 K emission maxima at 600 and 750 nm are observed for these materials. The positions of these maxima, and the rather large difference in the high-energy band between room temperature and 77 K, suggest that this band is due to emission from the $[RuN_6]Cl_2$ moiety, while the temperature-insensitive band at 750 nm most likely represents emission from the $[OsN_6](Cl)_2$ unit. The response observed for $[Os(bipy)_2(PVI)_{10}](Cl)_2/[Ru(bipy)_2(PVI)_{10}](Cl)_2$ (**20**) is similar, with a ruthenium emission occurring at 650 and 633 nm for room temperature and 77 K, respectively. The osmium emission occurs at 750 nm at 77 K. This behavior is illustrated in Figure 2. Where significant excited-state interaction exists between metal centers, e.g., in dimeric complexes,[28] a single emission is observed from the lowest energy state. The fact that both centers in these materials emit (at least at this loading and in solution) suggests that significant excited-state interaction is absent.

Electrochemical Properties. The materials obtained were further characterized by using electrochemical techniques. The formal potentials of the M(II/III) redox couple of the metallopolymers coated as thin films on glassy carbon electrodes have been listed in Table II. A typical cyclic voltammogram of a mixed metal metallopolymer (**15**) has been given in Figure 3. As expected the osmium analogues of previously reported ruthenium metallopolymers show reversible redox couples at less positive potentials.[20,22] The redox potentials obtained for compounds **5–12** did not show any variation with the metal

Table II
Spectroscopic and Electrochemical Data for the Metallopolymers and Monomeric Model Compounds

compd	λ_{max}(absorpn)[a] nm (log ϵ)	λ_{max}(emission) at rt,[a] nm	λ_{max}(emission) at 77 K,[a] nm	$E_{1/2}^{ox}$,[b] mV	$E_{1/2}^{red}$,[b] mV
1	498 (3.92), 440 (3.87)	704	680	0.75	−1.50, −1.55
2	455 (4.01), 464 (4.05)	604	594	1.25	−1.36, −1.54
3	502 (3.75), 347 (3.73)		685	0.57	−1.48, −1.60
4	485 (3.97), 345 (3.86)	635	617	0.86	−1.40, −1.51
5	364 (4.05), 431 (4.08)			0.35	−1.47
	486 (4.04), 730 (3.45)				
9	364 (3.72), 431 (3.65)			0.23	−1.57
	524 (3.67)				
13	354 (4.23), 444 (4.08)	764	750	0.75, 2.15	−1.15, −1.65
	616 (3.46)				
14	344 (3.67), 404 (3.59)	758	748	0.48	−1.30, −1.59
	496 (3.88), 666 (3.07)				
15	358 (4.28), 486 (4.18)	716	684	0.35, 0.75	−1.52
16	354 (4.14), 506 (4.13)	700	684	0.25, 0.67	−1.60
17	352 (4.35), 432 (4.21)	650	616	0.33, 1.15	−1.48
	486 (4.20)				
18	346 (3.94), 488 (3.93)	643	626	0.22, 0.88	−1.62
19	352 (4.28), 432 (4.33)	618	600	0.75, 1.15	−1.15, −1.60
	480 (4.22)	730 (sh)	750		
20	344 (4.14), 488 (4.03)	650	632, 754	0.48, 0.95	
21	358 (4.07), 428 (4.09)			0.33, 1.78	−1.46, −1.70
	506 (4.08), 730 (3.49)				
22	358 (4.24), 390 (4.02)	766	750	0.73, 2.20	−1.32, −1.55
	422 (4.09), 610 (3.50)				
23	365 (3.92), 430 (4.12)			0.23	−1.57
24	346 (3.86), 416 (3.80)	754	750	0.95	−1.30, −1.69
	512 (3.85), 686 (3.37)				

[a] Measured in methanol. [b] Electrolyte is 0.1 M TEAP/acetonitrile. [c] Measured in acetonitrile.

loading. When examined as surface deposits, these metallopolymers show surface behavior[29] at slow sweep rates, with peak currents directly proportional to the scan rate. At scan rates higher than 20 mV/s semiinfinite diffusion[29] is observed, with the peak current being proportional to the square root of the scan rate. These metallopolymers show considerable potential as electrode modifiers, and the rate of charge transport for polymer **6** has recently been extensively examined as a function of electrolyte, pH, redox site loading, and temperature.[15]

Table II shows that the position of the Os(II/III) oxidation is sensitive to the nature of the osmium moiety and that the synthetic conditions outlined here result in the formation of only one electroactive product. By comparison of the redox potentials obtained for the metallopolymers with those of analogous polymeric[9,10] and mononuclear model compounds, assignments about the nature of the polymer-bound moieties can be made. These assignments are in total agreement with those given above based on the absorption and emission results. The redox potentials obtained for the ruthenium groups in the mixed metal polymers are in close agreement with those reported earlier for polymers only containing ruthenium. This coupled with the fact that the wave form remains undistorted suggests that little interaction exists between the metal centers.[30] A similar behavior has been reported for electropolymerized metal bipyridyl systems.[21] The redox potentials observed for a particular osmium or ruthenium moiety in different metallopolymers are the same within experimental error. For some of the osmium-containing polymers an additional irreversible oxidation was observed at around 2 V vs SCE. This oxidation has, by comparison with data reported for analogous compounds, been assigned to the Os(III/IV) redox couple.[20] Also data for the first reduction potentials were obtained. As in other similar compounds these reductions are thought to be bipyridyl based.[31] No detailed analysis of these reductions was, however, carried out; as in most cases only one, rather ill-defined, reduction wave is observed. It is not possible to definitely assign these reductions to either the osmium or ruthenium moieties.

The nature of any ground-state interaction can also be investigated by evaluating charge-transport rates through thin films of these materials. Chronoamperometry was used to evaluate homogeneous charge-transport rates, given as D_{CT}, for both Os(II/III) and Ru(II/III) oxidation for glassy-carbon electrodes modified with films of the mixed osmium/ruthenium polymers. The Cottrell behavior for electrodes modified with $[Os(bipy)_2(PVP)_{10}Cl]Cl/[Ru(bipy)_2(PVP)_{10}Cl]Cl$ (**15**) in 0.1 M tetraethylammonium perchlorate is illustrated in Figure 4. This clearly shows that the rate of charge propogation through the polymer phase via the osmium centers is more rapid than that through the ruthenium centers; D_{CT} is 2.1×10^{-9} and 9.8×10^{-10} $cm^2\ s^{-1}$ for the osmium and ruthenium centers, respectively. The same values were obtained for the corresponding polymers containing only osmium or ruthenium centers, i.e., compounds **6** and **1**, where the redox center concentration is the same. This suggests that little interaction exists between the redox centers. The activation energies for these mixed metal polymers are also similar to their single metal analogues. In the above electrolyte the osmium activation energy is 20 kJ/mol while the ruthenium activation energy is 15 kJ/mol; these values are the same to within experimental error as those obtained for compounds **6** and **1**. The reaction entropy, which has proven to be sensitive to changes in redox center solvation,[32] remains constant at a value of 19.5 J/mol·K on going from the monometallic to the bimetallic polymers.

Photochemical Properties. Earlier work on ruthenium-based metallopolymers has shown that these polymers can be photolabile, and the photochemically induced ligand-exchange reactions have been studied in some detail.[13,33] Because of the presence of two different absorbing species in the mixed metal polymers, the use of absorption spectroscopy is of little value for monitoring such ligand-exchange reactions. However, cyclic voltammetry can be used to examine the photochemistry of thin

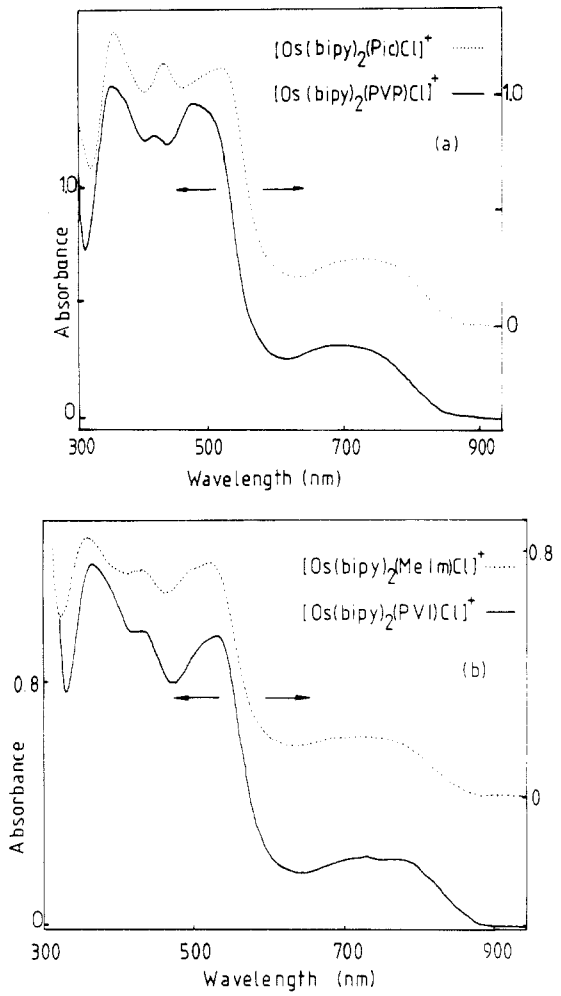

Figure 1. UV/visible spectra of (a) metallopolymer **5** and model compound **21** and (b) metallopolymer **9** and model compound **23**. Spectra of the metallopolymers were recorded in methanol and model compounds in acetonitrile. Sample concentration is 10^{-4} mol dm^{-3}.

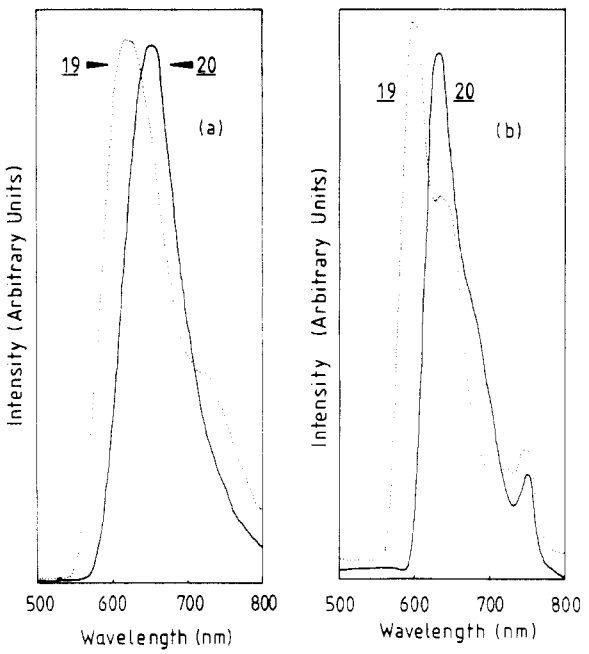

Figure 2. (a) Room temperature and (b) 77 K emission spectra of metallopolymers **19** and **20** in methanol. Sample concentration is 10^{-4} mol dm^{-3}.

films of the polymers reported here. It was found that metallopolymers containing only osmium centers are photo-

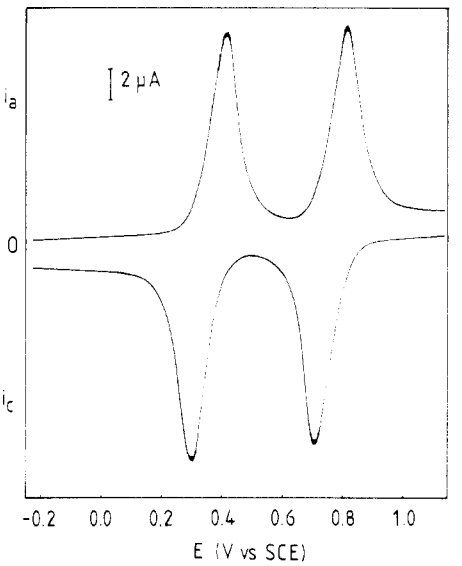

Figure 3. Cyclic voltammogram of metallopolymer **15** deposited as a thin film on a glassy-carbon electrode. Electrolyte is 0.1 M TEAP/acetonitrile. Surface coverage as obtained from CV measurements at low sweep rates is 1×10^{-8} mol cm^{-2}. Electrode area is 0.0706 cm^{-2}. Scan rate is 10 mV/s.

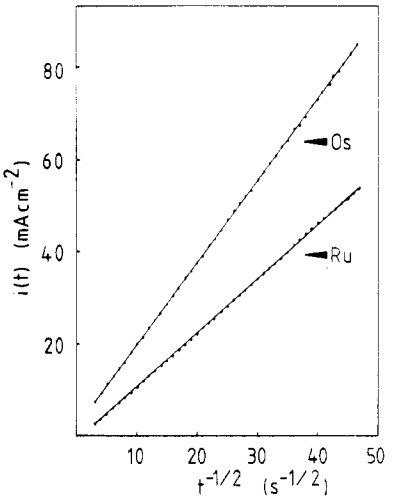

Figure 4. Chronoamperometric response presented as Cottrell plots for the Os(II/III) and Ru(II/III) oxidation, for compound **15**. Tetraethylammonium perchlorate (0.1 mol dm^{-3}) is the supporting electrolyte. Surface coverage is 2×10^{-8} mol cm^{-2}.

stable both in methanol solution and as thin films on glassy-carbon electrode surfaces in a wide variety of electrolyte salts and solvents. This photostability of osmium compounds with respect to the analogous ruthenium compounds is generally accepted to arise because of the increased energy of the antibonding dd orbitals, responsible for the photochemically induced ligand-exchange reactions.[34] Both the $[RuN_5Cl]Cl$ and the $[RuN_6]Cl_2$ moieties showed photochemically induced photosubstitution, with the product in both cases having a redox potential of about 800 mV vs SCE. A typical example of cyclic voltammograms taken during the photolysis of an electrode modified with polymer **15** has been given in Figure 5. It can be seen that the osmium redox couple remains stable but that the signal originally observed for the ruthenium redox couple shifts upon photolysis from 650 to about 800 mV vs SCE. Such a shift has in other ruthenium-containing polymers been explained by a ligand-exchange reaction (reaction 5). The shift in potential observed here is in agreement with such a ligand exchange.[13,33] The photochemically induced ligand

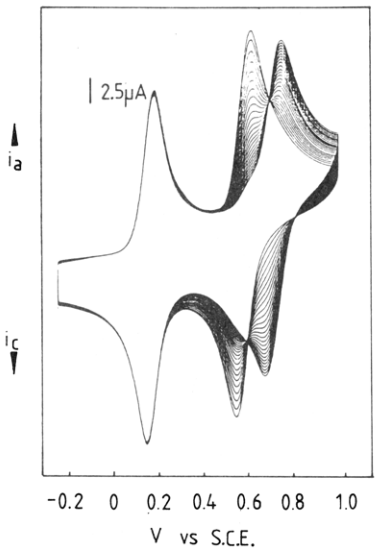

Figure 5. Photochemically induced ligand-exchange reactions in a thin, electrode-bound film of metallopolymer **15** using 1 mol dm^{-3} aqueous $HClO_4$ as electrolyte. Scan rate is 100 mV/s. Surface coverage is 1×10^{-8} mol cm^{-2}. Interval between scans is 30 s.

$$[Ru(bipy)_2(PVP)_nCl]^+ \xrightarrow{h\nu/H_2O} [Ru(bipy)_2(PVP)_nH_2O]^{2+} + Cl^- \quad (5)$$

substitution of the ruthenium metallopolymers provides a convenient means of changing the redox potential of the surface-immobilized species. This has potential applications in sensor development and information storage while the photostable osmium center can act as an internal standard. It is also important to realize that the clear difference in redox potential between the $[RuN_5H_2O]$-Cl_2 and other moieties strongly suggests that no significant amounts of this aquo species are present in the polymers prepared. Since the photochemically induced ligand exchange goes to completion, it is a convenient way of preparing a pure species that cannot be synthesized by direct methods.

Concluding Remarks

The synthetic strategy developed here allows the stepwise formation of multifunctional polymers. The metallopolymers can be readily characterized by UV/visible and emission spectroscopies and can be prepared with controlled loadings by varying the stoichiometric ratio of the starting polymer in metal complex. Electrochemical measurements and emission spectroscopy confirm that the excited-state and redox properties of the metal centers are maintained upon polymeric attachment. This is significant since one can identify a suitable metal complex for a given application and then synthesize a polymeric analogue with the same properties.

The T_g measurements suggest that the rigidity of the metallopolymers increases with increasing metal loading. Electrochemical and emission data suggest that at best a weak interaction exists between the different redox centers. This is perhaps somewhat unexpected, especially as with the metal loadings used; the coordination spheres are expected to be in very close contact, and the difference between the metal centers will be on the order of 15 Å.

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References and Notes

(1) Kaneko, M.; Tsuchida, E. *J. Macromol. Sci., Rev. Macromol. Chem.* **1981**, *16*, 397.
(2) Chauvin, D.; Commereuc, D.; Dawans, F. *Prog. Polym. Sci.* **1977**, *5*, 95.
(3) Davydova, S. L.; Plate, N. A. *Coord. Chem. Rev.* **1975**, *16*, 195.
(4) Murray, R. W.; Ewing, A. G.; Durst, R. A. *Anal. Chem.* **1987**, *59*, 379A.
(5) Redepenning, J. G. *Tr. Anal. Chem.* **1987**, *6*, 18.
(6) (a) Chidsey, E. D.; Murray, R. W. *Science* **1986**, *231*, 25. (b) Westmoreland, T. D.; Calvert, J. M.; Murray, R. W.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1983**, *65*. (c) Abruna, H. D.; Denisevich, M.; Umana, M.; Meyer, T. J.; Murray, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 1.
(7) (a) Kaneko, M.; Yamada, A.; Kurimura, Y. *Inorg. Chim. Acta* **1980**, *45*, L73. (b) Kaneko, M.; Yamada, A.; Tsuchida, E.; Kurimura, Y. *J. Phys. Chem.* **1984**, *88*, 1061. (c) Kaneko, M.; Okada, T.; Teratani, S.; Taya, K. *Electrochim. Acta* **1987**, *32*, 1405. (d) Kaneko, M. *J. Macromol. Sci., Chem.* **1987**, *24*, 357. (e) Kaneko, M.; Nakamura, H. *Macromolecules* **1987**, *20*, 2265.
(8) Murao, K.; Suzuki, K. *J. Chem. Soc., Chem. Commun.* **1984**, 238.
(9) Potts, K. T.; Usifer, D. A. *Macromolecules* **1988**, *21*, 1985.
(10) (a) Clear, J. M.; Kelly, J. M.; Vos, J. G. *Makromol. Chem.* **1983**, *184*, 613. (b) Clear, J. M.; Kelly, J. M.; O'Connell, C. M.; Vos, J. G. *J. Chem. Res., Miniprint* **1981**, 3039. (c) Haas, O.; Vos, J. G. *J. Electroanal. Chem.* **1980**, *113*, 139.
(11) Geraty, S. M.; Vos, J. G. *J. Chem. Soc., Dalton Trans.* **1987**, 3073.
(12) McHatton, R. C.; Anson, F. C. *Inorg. Chem.* **1984**, *23*, 3935.
(13) (a) Haas, O.; Kriens, M.; Vos, J. G. *J. Am. Chem. Soc.* **1981**, *103*, 1318. (b) Haas, O.; Zumbrunnen, H. R.; Vos, J. G. *Electrochim. Acta* **1985**, *30*, 1551.
(14) Oh, S.-M.; Faulkner, L. R. *J. Am. Chem. Soc.* **1989**, *111*, 5613.
(15) Forster, R. J.; Kelly, A. J.; Vos, J. G.; Lyons, M. E. G. *J. Electroanal. Chem.* **1989**, *270*, 365.
(16) Sullivan, B. P.; Salmon, P. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.
(17) Johnson, E. C.; Sullivan, B. P.; Salmon, S. A.; Adeyemi, S. A.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 2211.
(18) Buckingham, D. A.; Dwyer, F. P.; Goodwin, H. A.; Sargeson, A. M. *Aust. J. Chem.* **1964**, *17*, 325.
(19) (a) Berkowitz, J. B.; Yamin, M.; Fuoss, R. M. *J. Polym. Sci.* **1958**, *28*, 69. (b) Bamford, C. H.; Schofield, E. *Polymer* **1981**, *22*, 1227.
(20) Kober, E. M.; Caspar, J. V.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 4587.
(21) (a) Calvert, J. M.; Schmehl, R. H.; Sullivan, B. P.; Facci, J. S.; Meyer, T. J.; Murray, R. W. *Inorg. Chem.* **1983**, *22*, 2151. (b) Schmehl, R. H.; Murray, R. W. *J. Electroanal. Chem.* **1983**, *152*, 97. (c) Facci, J. S.; Schmehl, R. H.; Murray, R. W. *J. Am. Chem. Soc.* **1982**, *104*, 4959.
(22) (a) Kober, E. M.; Marshall, J. L.; Dressick, W. L.; Sullivan, B. P.; Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 2755. (b) Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 3722.
(23) Brandrup, J., Immergut, E. H., Ed. *Polymer Handbook*; Wiley: New York, 1975; p 111.
(24) Lyons, M. E. G.; Fay, H. G.; Vos, J. G.; Kelly, A. J. *J. Electroanal. Chem.* **1988**, *250*, 207.
(25) Haas, H. C.; Moreau, R. D. *J. Polym. Sci.* **1977**, *15*, 1225.
(26) (a) Oh, S. M.; Faulkner, L. R. *J. Electroanal. Chem.* **1989**, *269*, 77. (b) Niwa, K.; Doblhofer, K. *Electrochim. Acta* **1986**, *31*, 549.
(27) Moyer, B. A.; Meyer, T. J. *Inorg. Chem.* **1981**, *20*, 444.
(28) Doppelt, P.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 2027.
(29) Hillman, A. R. *Electrochemical Science and Technology of Polymers*; R. G., Linford, Ed.; Elsevier: Essex, U.K., 1987, p 241.
(30) (a) Daifuku, H.; Aoki, K.; Tokuda, K.; Matsuda, H. *J. Electroanal. Chem.* **1985**, *183*, 1. (b) Brown, A. P.; Anson, F. C. *Anal. Chem.* **1977**, *49*, 1589. (c) Gerischer, H.; Scherson, D. A. *J. Electroanal. Chem.* **1985**, *188*, 33. (d) Laviron, E.; Roullier, L. *J. Electroanal. Chem.* **1980**, *115*, 65.
(31) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.
(32) Forster, R. J.; Lyons, M. E. G.; Vos, J. G., submitted for publication in *J. Phys. Chem.*
(33) Calvert, J. M.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 3978.
(34) Casper, J. V.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 2444