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Microstructures in Thin Polymeric Films. Photochemically Produced Molecular Voids

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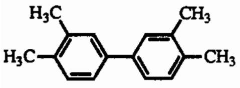
Ligand loss photochemistry in copolymerized films of poly-*cis*-[Ru(Me$_4$bpy)$_2$(vpy)$_2$]$^{2+}$[Os(vbpy)$_3$]$^{2+}$ (Me$_4$bpy is 4,4′,5,5′-tetramethyl-2,2′-bipyridine, vpy is 4-vinylpyridine, vbpy is 4-methyl-4′-vinyl-2,2′-bipyridine) on Pt electrodes results in loss of ⊦Ru(Me$_4$bpy)$_2$]$^{2+}$ and the creation of molecular voids. The vpy binding sites in the poly[Os(vbpy)$_3$]$^{2+}$,vpy films which remained were used to coordinate ⊦Os(PMe$_2$Ph)$_3$Cl$_2$] following reduction of *mer*-Os(PMe$_2$Ph)$_3$Cl$_3$ at the underlying electrode. By using masking techniques, it was possible to incorporate the Os^{II} complex with spatial control.

Introduction

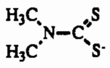
Recently it was reported that photochemical ligand loss[1] occurred in thin, polymeric films of poly-*cis*-[Ru(Me$_4$bpy)$_2$(vpy)$_2$]$^{2+}$ (Me$_4$bpy is 4,4′,5,5′-tetramethyl-2,2′-bipyridine, vpy is 4-vinylpyridine) prepared by reductive electropolymerization of *cis*-[Ru(Me$_4$bpy)$_2$(vpy)$_2$]$^{2+}$ on Pt electrodes.[2]

$$\text{poly-}cis\text{-}[\mathrm{Ru(Me_4bpy)_2(vpy)_2}]^{2+} + 2\mathrm{L} \xrightarrow{h\nu} cis\text{-}[\mathrm{Ru(Me_4bpy)_2(L)_2}]^{n+} + \text{poly(vpy)} \quad (1)$$

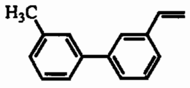
$$\mathrm{L = CH_3CN,\ ^1/_2\ dmtc^-,\ etc}$$



(Me$_4$bpy)



(dmtc$^-$)



(vbpy)

In the films, the photochemical removal of the cross-linking fragment ⊦Ru(Me$_4$bpy)$_2$]$^{2+}$ [3] led to loss of the polymer from the underlying substrate and provided a means for creating images and novel microstructures. The photochemistry has been extended to copolymeric films of poly-cis-[Ru(Me$_4$bpy)$_2$(vpy)$_2$]$^{2+}$,[M(vbpy)$_3$]$^{2+}$ (M is Os^{II} or Ru^{II}; vbpy is 4-methyl-4′-vinyl-2,2′-bipyridine).[4] In the copolymerization procedure the vpy groups are incorporated into the network that is formed by poly-[M(vbpy)$_3$]$^{2+}$. Photolysis of the films leads to the selective removal of the photolabile fragment, ⊦Ru(Me$_4$bpy)$_2$]$^{2+}$.

$$\text{poly-}cis\text{-}[\mathrm{Ru(Me_4bpy)_2(vpy)_2}]^{2+},[\mathrm{M(vbpy)_3}]^{2+} \underset{\mathrm{dmtc^-}}{\xrightarrow{h\nu}} \text{poly}[\mathrm{M(vbpy)_3}]^{2+},\mathrm{vpy} + cis\text{-}[\mathrm{Ru(Me_4bpy)_2(dmtc)}]^{+} \quad (2)$$

In this case the vpy groups remain after photolysis and provide a basis for carrying out chemical reactions within the "molecular voids" that are produced by photolysis. We report here an example where these groups are used as binding sites for a complex of Os^{II}. We have also utilized the spatial control offered by combining masking techniques with the photochemical procedure to create a structure in which the new metal complex is incorporated only in spatially well-defined regions of a film.

Experimental Section

Materials. Synthetic procedures for the preparations of 4-methyl-4′-vinyl-2,2′-bipyridine (vbpy),[5a] *cis*-[Ru(Me$_4$bpy)$_2$(vpy)$_2$](PF$_6$)$_2$,[2] [Os(vbpy)$_3$](PF$_6$)$_2$,[2] and *mer*-Os(PMe$_2$Ph)$_3$Cl$_3$[5b] were as described elsewhere.

Measurements. Preparation and Characterization of the Films. Cyclic voltammetric experiments were carried out by using a Princeton Applied Research Model 173 Potentiostat and a homebuilt wave form generator. Voltammograms were recorded on either a Hewlett Packard 7015B or a Soltec VP-6414S X-Y recorder. All potentials are relative to the Ag/AgNO$_3$ reference electrode[6] unless otherwise noted. The supporting electrolyte in electrochemical experiments was 0.1 M [N(*n*-Bu)$_4$](PF$_6$) in acetonitrile. The electrodes used in the electrochemical experiments were 0.12-cm^2 Teflon-shrouded Pt. These were polished by using 1-μm micron diamond paste (Buehler) and rinsed with water and acetone prior to use. Surface analytical measurements utilized either a Pt flag or a 0.18-cm^2 Teflon-shrouded Pt disk electrode.

The preparation of the polymeric films by reductive electropolymerization was carried out in a one-compartment cell containing acetonitrile solutions of the monomer(s) in the range 0.5–1.0 mM under N$_2$. The films were deposited by cycling the potential of the working electrode between −1.0 and −2.0 or −2.1 V at 50 or 100 mV/s. The surface coverages of polymer on the electrodes (Γ_M) (M is Os^{II} or Ru^{II}) in mol/cm^2 was determined by measuring the charge associated with the M$^{III/II}$ oxidation wave by using triangulation to measure the area of the wave in the recorded cyclic voltammogram. In copolymeric films the total surface coverage of polymer on the electrode was calculated by summing the Γ_M values measured for each component of the film. The ratios of the two components in the copolymeric films were varied by controlling the ratios of the two monomers in the electropolymerization solution.[7] The ratios of Ru^{II} to Os^{II} in copolymeric films of poly-*cis*-[Ru(Me$_4$bpy)$_2$(vpy)$_2$]$^{2+}$,[Os(vbpy)$_3$]$^{2+}$ were determined by measuring the area under the Ru$^{III/II}$ and Os$^{III/II}$ waves as described above.

Photolysis of the Films. Photolysis of the films on Pt electrodes was carried out by using a Bausch & Lomb SP200 mercury lamp. The output of the lamp was passed through a Pyrex UV cutoff filter before reaching the sample. The electrodes were suspended in a glass cell which contained a 0.1 M aqueous solution of dmtc$^-$. Typically, the films were irradiated for 30 min to 1 h. After exposure, the films were rinsed in water and acetonitrile.

Incorporation of *mer*-Os(PMe$_2$Ph)$_3$(vpy)Cl$_2$ in the Films. After photolysis, an electrode coated with a copolymeric film was immersed in a 0.37 mM solution of *mer*-Os(PMe$_2$Ph)$_3$Cl$_3$ in 0.2 M [N(*n*-Bu)$_4$](PF$_6$)/

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[1] (a) Durham, B.; Walsh, J. L.; Carter, C. L.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 860. (b) Pinnick, D. V.; Durham, B. *Inorg. Chem.* **1984**, *25*, 1440.

[2] Gould, S.; O'Toole, T. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 9490.

[3] The notation ⊦is used to indicate a fragment of the polymeric film.

[4] Gould, S.; Meyer, T. J. *J. Am. Chem. Soc.* **1991**, *19*, 7442.

[5] (a) Abruña, H. D.; Breikess, A. I.; Collum, D. B. *Inorg. Chem.* **1985**, *24*, 987. (b) Chatt, J.; Leigh, G. J.; Mingos, D. M. P.; Paske, R. J. *J. Chem. Soc. A* **1968**, 2636.

[6] The Ag/AgNO$_3$ reference electrode was 0.01 M in AgNO$_3$ in 0.1 M [NEt$_4$](ClO$_4$)/acetonitrile. The potential of this electrode vs SSCE is +0.3 V.

[7] (a) Typically the mole fraction of Ru^{II} and Os^{II} in the copolymeric films of poly[Ru(Me$_4$bpy)$_2$(vpy)$_2$]$^{2+}$,[Os(vbpy)$_3$]$^{2+}$ prepared by using this method were found to be within 5% of the composition of the solution from which they were prepared.[7b] (b) Gould, S. Ph.D. Thesis. The University of North Carolina at Chapel Hill, 1991.

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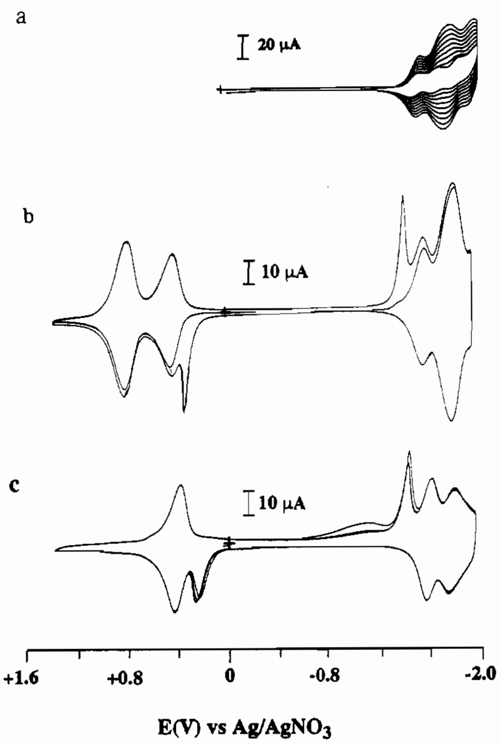

Figure 1. (a) Repetitive cyclic voltammograms of a solution 0.37 mM in $[Os(vbpy)_3]^{2+}$ and 0.37 mM in *cis*-$[Ru(Me_4bpy)_2(vpy)_2]^{2+}$ in acetonitrile that was 0.1 M in $[N(n\text{-}Bu)_4](PF_6)$ at a Pt disk electrode of surface area 0.12 cm^2. Scan rate = 100 mV/s. (b) Cyclic voltammogram of the poly-*cis*-$[Ru(Me_4bpy)_2(vpy)_2]^{2+}$,$[Os(vbpy)_3]^{2+}$ film that resulted from the scans in part a in a fresh electrolyte solution. $\Gamma_{Ru} = 4.2 \times 10^{-9}$ mol/cm^2; $\Gamma_{Os} = 3.2 \times 10^{-9}$ mol/cm^2. Scan rate = 100 mV/s. (c) Cyclic voltammogram of the film in part b under the same conditions after photolysis in 0.1 M aqueous Na(dmtc) for ~45 min. $\Gamma_{Os} = 3.1 \times 10^{-9}$ mol/cm^2. The scan shown was recorded after an initial conditioning cycle.

CH_2Cl_2. The potential of the electrode was repeatedly scanned from +0.2 to −1.1 V vs Ag/AgNO$_3$ at 100 mV/s for 10 min.

Surface Analysis. X-ray photoelectron spectroscopy (XPS) studies were carried out by using a Perkin-Elmer Physical Electronics Model 5400 system. The operating conditions were as follows: MgKα anode (15 kV, 400 W); hemispherical analyzer pass energy of 35 eV; angle of collection of 45°; analysis area of 1 mm^2 or 600 μm^2. All reported binding energies were charge referenced to the C 1s polymer peak at 285.0 eV. The Ru 3d/C 1s, Os 4f, and P 2p spectra were processed by using a Gaussian–Lorentzian curve-fit routine (80% Gaussian) with a Shirley background subtraction.[8]

Results

Electrochemistry. In Figure 1a are shown a series of cyclic voltammograms recorded during the reductive electrocopolymerization of *cis*-$[Ru(Me_4bpy)_2(vpy)_2]^{2+}$ and $[Os(vbpy)_3]^{2+}$. The electropolymerization solution contained 0.37 mM *cis*-$[Ru(Me_4bpy)_2(vpy)_2]^{2+}$ and 0.37 mM $[Os(vbpy)_3]^{2+}$. In the initial voltammogram waves were observed at −1.56, −1.74, −1.90, and −2.05 V, which arise from reversible, bpy ligand-centered reductions for $[Os(vbpy)_3]^{2+}$ and $[Ru(Me_4bpy)_2(vpy)_2]^{2+}$. In subsequent scans the current for the reversible couples increased in magnitude as the electroactive polymeric film accumulated on the electrode surface. Visual inspection of the electrode surface after an acetonitrile rinse revealed the presence of an orange coating.

A cyclic voltammogram of the intact copolymeric film recorded in a fresh electrolyte solution is shown in Figure 1b. The voltammogram is the sum of typical voltammetric responses observed for separate, single-component films of poly$[Os(vbpy)_3]^{2+}$ and poly$[Ru(Me_4bpy)_2(vpy)_2]^{2+}$.[2] In the copolymeric films, a $Ru^{III/II}$ metal-centered oxidation for poly-*cis*-$[Ru(Me_4bpy)_2(vpy)_2]^{2+}$ was observed at +0.81 V and an $Os^{III/II}$ metal-centered oxidation for poly$[Os(vbpy)_3]^{2+}$ at +0.45 V. A voltammetric wave for the first bpy-based reduction of poly-$[Os(vbpy)_3]^{2+}$ appeared at −1.6 V. The second bpy-based reduction of $[Os(vbpy)_3]^{2+}$ ($E_{1/2}$ = −1.76 V) and first Me$_4$bpy-based reduction of $[Ru(Me_4bpy)_2(vpy)_2]^{2+}$ ($E_{1/2}$ = −1.89 V) overlap and together gave rise to the wave observed at −1.85 V. The sharp prepeaks that appeared at the onset of both the $Os^{III/II}$ oxidation wave and the first ligand reduction wave disappeared if cycling was restricted to either the metal-based oxidations or ligand-based reductions. The appearance of prepeaks of this type has been noted previously in films of this type.[9] The ratio of Ru^{II} to Os^{II} in the film, 57:43, was slightly enriched in Ru^{II} compared to the electropolymerization solution where the ratio was 50:50.

Photochemistry. Photolysis of a copolymeric film of poly-*cis*-$[Ru(Me_4bpy)_2(vpy)_2]^{2+}$,$[Os(vbpy)_3]^{2+}$ in the presence of a 0.1 M aqueous solution of dmtc$^-$, followed by water and acetonitrile rinsing, led to a change in the electrochemical response of the still intact copolymeric film. In Figure 1c is shown a cyclic voltammogram for the poly-*cis*-$[Ru(Me_4bpy)_2(vpy)_2]^{2+}$, $[Os(vbpy)_3]^{2+}$ copolymer in Figure 1b after photolysis. In this voltammogram the $Ru^{III/II}$ wave for poly-*cis*-$[Ru(Me_4bpy)_2(vpy)_2]^{2+}$ at 0.81 V has disappeared. Remaining are the $Os^{III/II}$ wave at +0.42 V and two ligand-based reductions at −1.62 and −1.81 V which are now equal in magnitude. These observations are consistent with the photochemical reaction in eq 2. The soluble photoproduct, $[Ru(Me_4bpy)_2(dmtc)]^+$, is lost from the film while the vinylpyridine groups are retained. They are expected to be copolymerized and incorporated in the photoinert network formed by the polymerized vinylbipyridine groups of the photoinert poly-$[Os(vbpy)_3]^{2+}$.

X-ray photoelectron spectroscopy (XPS) confirmed that loss of the electrochemical response for poly-*cis*-$[Ru(Me_4bpy)_2(vpy)_2]^{2+}$ was indeed due to the removal of a Ru-containing fragment. A copolymeric film of poly-*cis*-$[Ru(Me_4bpy)_2(vpy)_2]^{2+}$,$[Os(vbpy)_3]^{2+}$ ($\Gamma = 1.4 \times 10^{-9}$ mol/cm^2) of composition $\chi_{Ru} = 0.49$ was prepared on a Pt electrode. The XPS spectra exhibited photoelectron peaks for Os 4f$_{7/2}$ at a binding energy of 50.7 ± 0.2 eV, Ru 3d$_{5/2}$ at 280.9 ± 0.1 eV, and N 1s at 400.0 ± 0.2 eV as well as a signal from the Pt substrate (Pt 4f$_{7/2}$ at 70.4 ± 0.2 eV). After photolysis, peaks for the Ru, Os, N, and Pt photoelectrons were still observed; however, the Ru3d$_{5/2}$ peak at 280.6 eV was diminished in intensity confirming that there was a loss of a Ru-containing species from the film.

Coordination of $[\text{-}Os(PMe_2Ph)_3Cl_2]$ to Photochemically Generated vpy Sites in the Copolymeric Films. Certain halide-containing transition metal complexes are unstable with respect to halide loss upon electrochemical or chemical reduction.[10] We have taken advantage of this chemistry to incorporate a complex of Os^{II} into the molecular voids created by the photochemical extrusion of $[Ru(Me_4bpy)_2(dmtc)]^+$. The initial complex was *mer*-$Os(PMe_2Ph)_3Cl_3$ and the sequence of reactions that led to loss of Cl$^-$ are shown in Scheme I, where S is a coordinating solvent molecule such as CH_3CN or pyridine. Previous work by Calvert et al. revealed that when this reaction was carried out electrochemically at an electrode that had been coated with a polymeric film of poly(4-vinylpyridine) (PVP), it led to the

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(8) Shirley, D. A. *Phys. Rev. B* **1972**, *5*, 4709.

(9) Denisevich, P.; Abruña, H. D.; Leidner, C. R.; Meyer, T. J.; Murray, R. W. *Inorg. Chem.* **1982**, *21*, 2153.

(10) Calvert, J. M.; Sullivan, B. P.; Meyer, T. J. In *Chemically Modified Surfaces in Catalysis and Electrocatalysis*, Miller, J., Ed.; ACS Symposium Series 192; American Chemical Society: Washington DC, 1982; p 159.

(11) An increase in Γ_{Os} after photolysis was not typically observed. This result may be due to an underestimation of Γ_{Os} for the film prior to photolysis due to slow electron hopping or counterion diffusion across this relatively thick film.

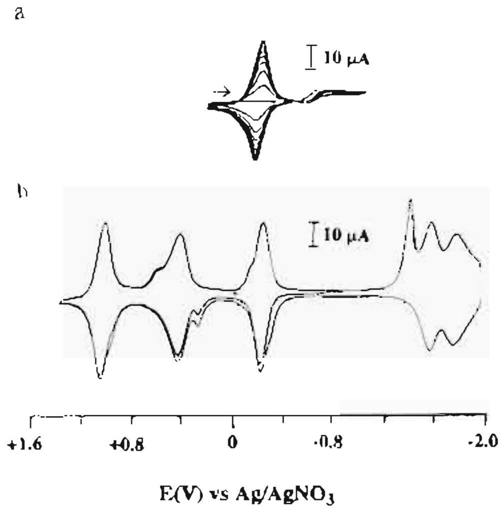


Figure 2. (a) Repetitive cyclic voltammograms of a solution 3.7 mM in Os(PMe$_2$Ph)$_3$Cl$_3$ in methylene chloride that was 0.2 M in [N(*n*-Bu)$_4$](PF$_6$). The working electrode was the copolymeric film-coated Pt disk from Figure 1c. Scan rate = 100 mV/s. (b) Cyclic voltammogram of the poly[Os(vbpy)$_3$]$^{2+}$,Os(PMe$_2$Ph)$_3$(vpy)Cl$_2$ film that resulted from the scans in part a in acetonitrile that was 0.1 M in [N(*n*-Bu)$_4$](PF$_6$). Scan rate = 100 mV/s.

incorporation of the complex as Os(PMe$_2$Ph)$_3$(PVP)Cl$_2$ with Os^{II} bound to a pyridyl group of PVP.[10]

Scheme I

$$\mathrm{Os^{III}(PMe_2Ph)_3Cl_3} + e^- \rightleftharpoons [\mathrm{Os^{II}(PMe_2Ph)_3Cl_3}]^- \quad (3)$$

$$[\mathrm{Os^{II}(PMe_2Ph)_3Cl_3}]^- + \mathrm{S} \rightarrow \mathrm{Os^{II}(PMe_2Ph)_3(S)Cl_2} + \mathrm{Cl}^- \quad (4)$$

$$\mathrm{Os^{II}(PMe_2Ph)_3(S)Cl_2} = \mathrm{Os^{III}(PMe_2Ph)_3(S)Cl_2} + e^- \quad (5)$$

In Figure 2a are shown cyclic voltammograms recorded for a copolymeric film-coated Pt electrode in a methylene chloride solution 0.37 mM in Os(PMe$_2$Ph)$_3$Cl$_3$. The initial copolymeric film before photolysis was poly-*cis*-[Ru(Me$_4$bpy)$_2$(vpy)$_2$]$^{2+}$,[Os(vbpy)$_3$]$^{2+}$ (χ_{Ru} = 0.57, $\Gamma = 7.4 \times 10^{-9}$ mol/cm^2). The [-Ru(Me$_4$bpy)$_2$]$^{2+}$ was removed photochemically as described above. The irreversible reduction, which has an onset at ~-0.7 V, is the Os$^{III/II}$ metal-centered reduction for *mer*-Os(PMe$_2$Ph)$_3$Cl$_3$, eq 3. The reduction current was low (compared to the response at a bare electrode) and reached a plateau at -0.75 V due to slow diffusion of the complex through the film to the electrode surface. On subsequent scans a new wave appeared at -0.23 V. This wave continued to grow in magnitude as the electrode was cycled repeatedly between +0.2 and -1.2 V. The new wave corresponds to the reversible Os$^{III/II}$ couple of poly[Os(PMe$_2$Ph)$_3$(vpy)Cl$_2$]. The cyclic voltammogram shown in Figure 2b was recorded in a fresh electrolyte solution after the electrode had been removed and rinsed in acetonitrile. The presence of poly[Os(PMe$_2$Ph)$_3$(vpy)Cl$_2$] is obvious from the new, reversible waves that appear at -0.22 and +1.08 V. They correspond to the Os$^{III/II}$ and Os$^{IV/III}$ couples of the incorporated complex. After incorporation, the complex was stable to subsequent cycling. No changes in electrochemical response were observed when the films were dried and stored under ambient conditions for several days. There was no evidence for incorporation of Os(PMe$_2$Ph)$_3$Cl$_3$ by cyclic voltammetry in a control experiment that followed the same procedure but on an *unphotolyzed* film of poly-*cis*-[Ru(Me$_4$bpy)$_2$(vpy)$_2$,[Os(vbpy)$_3$]$^{2+}$.

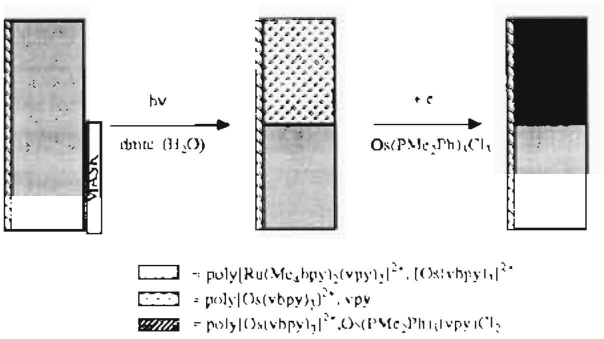
The extent to which Os(PMe$_2$Ph)$_3$Cl$_3$ was incorporated into the sites initially occupied by poly-*cis*-[Ru(Me$_4$bpy)$_2$(vpy)$_2$]$^{2+}$ was investigated for a series of copolymeric films of poly-*cis*-[Ru(Me$_4$bpy)$_2$(vpy)$_2$]$^{2+}$,[Os(vbpy)$_3$]$^{2+}$ whose compositions varied from χ_{Ru} = 1.0 to 0.2. From the results of these experiments (Table I), the extent of incorporation reached a maximum of ~80%[12] at χ_{Ru} ~ 0.5 with the percent of sites occupied decreasing at both higher and lower values of χ_{Ru}. An estimate of the extent of the loss of the polymeric network as a function of χ_{Ru} was obtained by measuring the change in the surface coverage of poly[Os(vbpy)$_3$]$^{2+}$ before and after photolysis as a function of film composition. The results are presented in Table I.

Table I. Incorporation of *mer*-Os(PMe$_2$Ph)$_3$(vpy)Cl$_2$ into Copolymeric Films of Poly-*cis*-[Ru(Me$_4$bpy)$_2$(vpy)$_2$]$^{2+}$,-[Os(vbpy)$_3$]$^{2+}$ after Photolysis

before photolysis		after photolysis	after incorporation	
χRu^a	$10^9\Gamma^b$ (mol/cm^2)	$\Delta\Gamma_{Os}{}^c$ (%)	$10^9\Gamma_{Os(2)}{}^d$ (mol/cm^2)	incorporation^e (%)
0.18	3.1	1		trace
0.34	3.2	15	0.1	9
0.40	7.3	0	2.1	78
0.42	12.8	*f*	2.4	42
0.57	4.1	20	1.4	59
0.57	6.1	14	2.3	66
0.57	7.4	1	2.9	69
0.58	4.7	19	0.7	26
0.60	4.1	20	0.8	31
0.60	4.3	20	1.5	61
0.64	3.4	24	1.4	64
0.68	4.4	30	0.5	16
0.73	3.9	28	0.8	29
0.86	4.2	71	0.04	1
1.00	6.5		0.03	<1

^{a} Calculated as Γ_{Ru}/Γ where $\Gamma = \Gamma_{Os} + \Gamma_{Ru}$. ^{b} Initial surface coverage $\Gamma = \Gamma_{Os} + \Gamma_{Ru}$. ^{c} Percent decrease in Γ_{Os} for poly[Os(vbpy)$_3$]$^{2+}$ following photolysis. ^{d} Surface coverage of bound Os(PMe$_2$Ph)$_3$(vpy)Cl$_2$. ^{e} Percent of potential binding sites (estimated as the number of initial Ru^{II} sites, Γ_{Ru}) occupied by Os(PMe$_2$Ph)$_3$(vpy)Cl$_2$. Calculated as $(\Gamma_{Os(2)}/\Gamma_{Ru}) \times 100$. ^{f} A 10% increase in Γ_{Os} was observed.[11]

Scheme II



Spatially Resolved Incorporation. By using masking techniques, it was possible to carry out the incorporation of the Os^{II} complex with spatial control. This experiment was carried out on a Pt flag electrode by using the sequence of reactions illustrated in Scheme II. The initial poly[Ru(Me$_4$bpy)$_2$(vpy)$_2$]$^{2+}$,[Os(vbpy)$_3$]$^{2+}$ film ($\Gamma = 6.2 \times 10^{-9}$ mol/cm^2, χ_{Ru} = 0.41) was masked such that only half was exposed during the photolysis step. In Figures 3 and 4 are shown spatially resolved XPS spectra recorded for the unphotolyzed and photolyzed regions of the film, respectively. In the masked region photoelectron peaks were observed at for Os 4f$_{7/2}$ of poly[Os(vbpy)$_3$]$^{2+}$ at 50.8 ± 0.2 eV, Ru 3d$_{5/2}$ of poly[Ru(Me$_4$bpy)$_2$(vpy)$_2$]$^{2+}$ at 280.9 ± 0.2 eV, and P 2p of the PF$_6^-$ counterion at 136.4 ± 0.2 eV. In the photolyzed region the peak for Ru 3d$_{5/2}$ did not appear, confirming the loss of that

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[12] The percent incorporation was calculated as $(\Gamma_{Os(2)}/\Gamma_{Ru}) \times 100$ where $\Gamma_{Os(2)}$ was the surface coverage of bound Os(PMe$_2$Ph)$_3$(vpy)Cl$_2$ in the final film and Γ_{Ru} was the surface coverage of poly[Ru(Me$_4$bpy)$_2$(vpy)$_2$ in the film before photolysis.

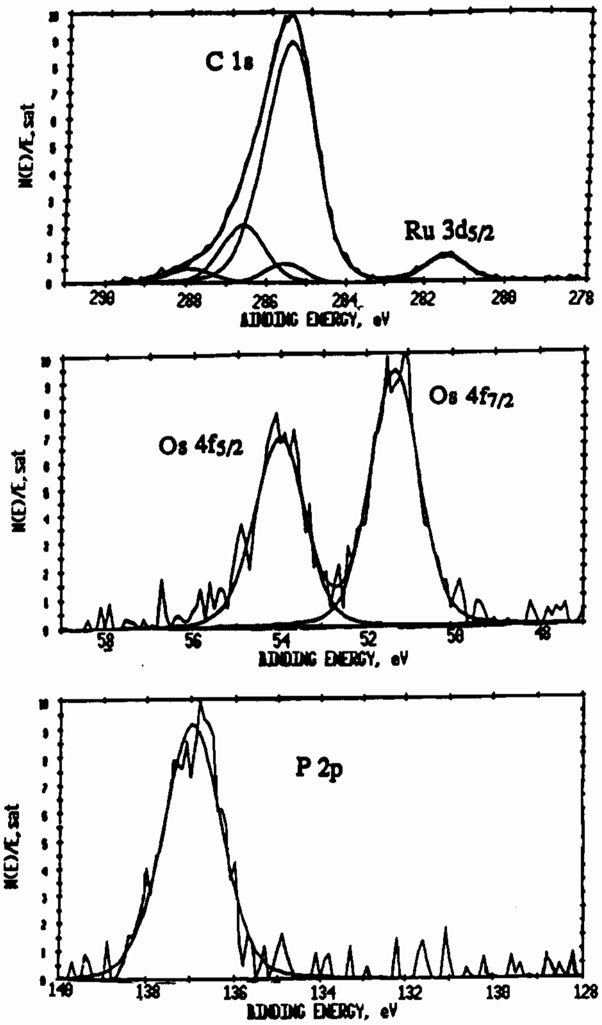

Figure 3. Top to bottom: (a) Ru 3d/C 1s, (b) Os 4f, and (c) P 2p curve fit XPS windows for the region of a copolymeric film of poly-*cis*-[Ru(Me_4bpy)$_2$(vpy)$_2$](PF_6)$_2$,[Os(vbpy)$_3$](PF_6)$_2$ (Γ = 6.2 × 10^{-9} mol/cm^2, χ_{Ru} = 0.41) that was masked during photolysis.

species upon photolysis. New peaks were observed at 52.0 ± 0.2 and 131.8 ± 0.2 eV for Os $4f_{5/2}$ and P 2p of Os(PMe_2Ph)$_3$(vpy)Cl_2.

Discussion

Photochemical ligand loss from polypyridyl complexes of Ru^{II} in solution is well documented.[1,13,14] The mechanism involves initial metal to ligand charge transfer (Ru^{II} → bpy) excitation followed by population of a lowlying dd state or states. It is the dd state (or states) that is responsible for the ligand loss photochemistry. Photochemical loss of pyridine from *cis*-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ occurs by stepwise displacement of py by an added ligand L (where L is a coordinating anion such as Cl$^-$, NCS$^-$, etc. or the solvent) to give *cis*-[Ru(bpy)$_2$(L)$_2$]$^{2+}$.[1a] The ligand loss photochemistry does not appear for related complexes of Os^{II} since 10*Dq* is higher and the dd states are often inaccessible at room temperature.[15]

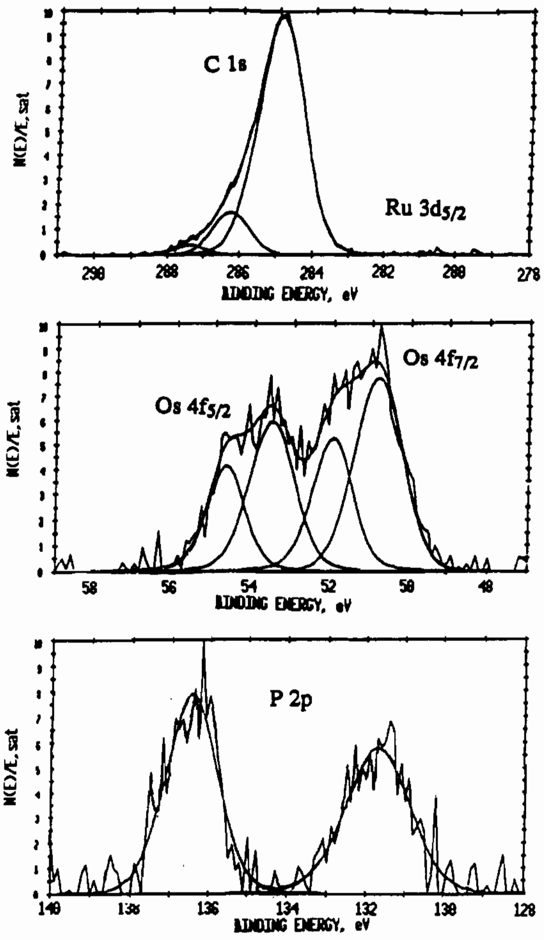

Figure 4. Top to bottom: (a) Ru 3d/C 1s, (b) Os 4f, and (c) P 2p curve fit XPS windows for the region of a copolymeric film of poly-*cis*-[Ru(Me_4bpy)$_2$(vpy)$_2$(PF_6)$_2$,[Os(vbpy)$_3$](PF_6)$_2$ film that had been photolyzed and into which Os(PMe_2Ph)$_2$(vpy)Cl_2 had been incorporated by electrochemical reduction.

In previous work it was shown that the ligand loss photochemistry also occurred in thin, polymeric films of poly-[Ru(Me_4bpy)$_2$(vpy)$_2$]$^{2+}$. In these films, photolysis in aqueous solutions containing dmtc$^-$ led to the appearance of [Ru(Me_4bpy)$_2$(dmtc)]$^+$ as a photoproduct (eq 1). The decrease in cross-linking that resulted from the photochemical cleavage of the ruthenium–vpy bonds led to the eventual loss of the film from the underlying substrate.

The results of the electrochemical and XPS experiments presented here show that an analogous photochemical reaction occurs in copolymeric films of poly-*cis*-[Ru(Me_4bpy)$_2$(vpy)$_2$]$^{2+}$,[Os(vbpy)$_3$]$^{2+}$. The loss of the electrochemical response for poly[Ru(Me_4bpy)$_2$(vpy)$_2$]$^{2+}$ as well as the significant decrease in the Ru peaks in the XPS point to the loss of Ru^{II} from the initial film. After complete photolysis, {Ru(Me_4bpy)$_2$]$^{2+}$ fragments were selectively removed from the film as the soluble photoproduct [Ru(Me_4bpy)$_2$(dmtc$^-$)]$^+$, leaving behind an intact copolymer of poly[Os(vbpy)$_3$]$^{2+}$, vpy as described in eq 2. In this case the film is maintained on the electrode surface by the cross-linking provided by the polymerized tris-vbpy complex of Os^{II}. The selective loss of the Ru^{II} fragment and the more open structure that results on photolysis are illustrated by step i in Scheme III.

In an earlier paper the more open structure created by the appearance of the molecular voids produced in the photolysis procedure were utilized to achieve size selective transport to the underlying electrode. An equally interesting point was to ascertain whether or not it was possible to utilize the molecular voids as size exclusive volumes for carrying out chemical reactions. In principle, the photochemical technique offers considerable latitude in controlling both the concentration and size of the voids which

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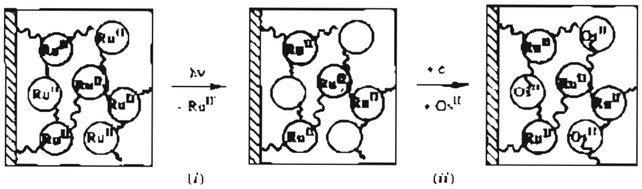
Scheme III



are produced, and this could be exploitable in shape selective chemistry, the formation of small clusters, etc. The film matrix itself is electroactive at well-defined potentials and has the capacity to transfer oxidative or reductive equivalents from the underlying electrode throughout the film matrix.

We chose to explore a relatively simple reaction, the refilling of the molecular voids with a second complex, by exploiting the vpy groups that were released in the photochemical procedure, eq 2. The complex chosen for study was $Os(PMe_2Ph)_3Cl_3$. Reduction of this complex past the irreversible $Os^{III/II}$ reduction wave at −0.7 V results in labilization and loss of Cl^-, Scheme I. When the reduction occurs at a Pt disk substrate coated with poly$[Os(vbpy)_3]^{2+}$,vpy, the complex must diffuse through the film to reach the electrode. Following reduction at the electrode-film interface and Cl^- loss, capture of Os^{II} occurs by binding to vpy, eq 6.

$$\text{poly}[Os(vbpy)_3]^{2+},(vpy)_n + m[Os^{II}(PMe_2Ph)_3Cl_3]^- \rightarrow (\text{poly}[Os(vbpy)_3]^{2+},Os(PMe_2Ph)_3(vpy)Cl_2)_m,vpy_{(n-m)} + mCl^- \quad (6)$$

The efficiency of the incorporation of the Os^{II} complex, defined as the percentage of initial poly-*cis*-$[Ru(Me_4bpy)_2(vpy)_2]$ sites occupied by $Os(PMe_2Ph)_3(vpy)Cl_2$ in the final film,[12] was found to depend on the composition of the initial copolymeric film. Incorporation was greatest for poly-*cis*-$[Ru(Me_4bpy)_2(vpy)_2]^{2+}$,$[Os(vbpy)_3]^{2+}$ films with $\chi_{Ru} \sim 0.5$, Table I. For $\chi_{Ru} < 0.5$ the decrease in percent incorporation may be a consequence of an incompletely formed trans-film diffusional network. This would create "pockets" where the diffusing complex is unable to reach a molecular void during its residual time as Os^{II} in the film. It is also true that the permeability of the copolymeric films toward external reagents depends on the composition of the polymer with permeabilities decreasing as the content in poly$[Ru(Me_4bpy)_2(vpy)_2]^{2+}$ decreases.[7b] Finally, the apparent decrease may be partly artifactual. As the concentration of added complex decreases, there is a likelihood that not all the sites are in sufficiently close contact to undergo site-to-site electron transfer hopping. Thus, the electrochemical measurement may not sample all of the $Os(PMe_2Ph)_3(vpy)Cl_2$ sites in the films.

For $\chi_{Ru} > 0.5$, it is possible that the decrease in percent incorporation was due to an increase in the number of vpy sites lost from the film along with the $[Ru(Me_4bpy)_2(dmtc)]^+$ photoproduct during the photochemical procedure. This would occur because the structural integrity of the films relies to a greater extent on the crosslinking provided by poly-$[Ru(Me_4bpy)_2(vpy)_2]^{2+}$ in films where the Ru^{II} polymer is the major component. An overall loss of polymeric network as the initial χ_{Ru} is increased can be found in the data in Table I by the decrease in Γ_{Os} as χ_{Ru} is increased.

Masking techniques were used to demonstrate that the coordination of $Os(PMe_2Ph)_3(vpy)Cl_2$ within the films could be carried out with spatial control. Photolysis of a copolymeric film of $[Ru(Me_4bpy)_2(vpy)_2]^{2+}$,$[Os(vbpy)_3]^{2+}$ through a mask resulted in loss of Ru^{II} and creation of vpy binding sites only in exposed regions of the film. This provided a basis for the spatially selective incorporation of $Os(PMe_2Ph)_3(vpy)Cl_2$ into films which occurred only where they had been photolyzed. This opens some interesting possibilities for the preparation of microstructures. By exploiting masking techniques appropriately, it will be possible to control the spatial arrangement of the molecular voids that serve as the reactive sites within the films.

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