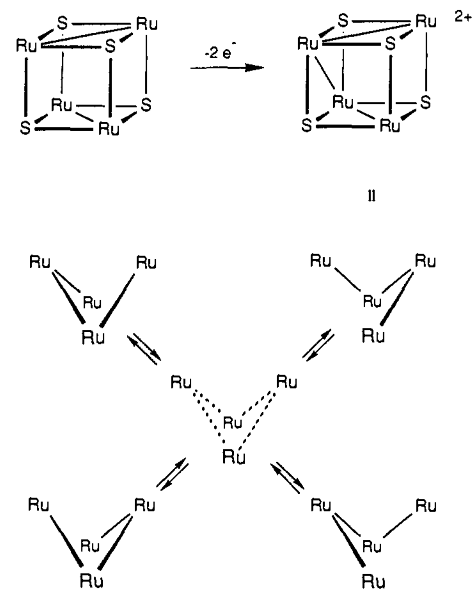
Scheme I



In summary, the clusters $[(\text{MeCp})_4\text{Ru}_4\text{E}_4]^{2+}$ (E = S, Se, Te) have dynamic structures which arise from mobile Ru–Ru bonds. The dynamic process was monitored through the ^{1}H NMR signals of the MeCp ligands which report on the time-averaged stereochemical environment about each metal. The manipulation of dynamic metal–metal bonds presents some novel opportunities in stereochemistry.

Acknowledgment. This research was supported by the National Science Foundation through Grant CHE 87-11460. Dr. Mary Frances Leopold is thanked for her assistance with the NMR measurements.

Supplementary Material Available: For [**1**]$(\text{TCNQ})_2$ tables of bond distances and angles and positional and thermal parameters and an ORTEP drawing for the $(\text{TCNQ})_2{}^{2-}$ anion (9 pages); table of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

Size-Selective Electrochemistry

Sharon Gould and Thomas J. Meyer*

Department of Chemistry
University of North Carolina at Chapel Hill
Chapel Hill, North Carolina 27599-3290

Received May 2, 1991

In a recent paper we reported that photochemical loss of 4-vinylpyridine (vpy) from poly$[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{vpy})_2]^{2+}$ (Me_4bpy is 4,4′,5,5′-tetramethyl-2,2′-bipyridine), reaction 1, occurred in thin polymeric films prepared by reductive electropolymerization of *cis*-$[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{vpy})_2]^{2+}$ on Pt electrodes.[1,2] As a result

$$\text{poly}[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{vpy})_2]^{2+} \xrightarrow[\text{dmtc}^-]{h\nu} [\text{Ru}(\text{Me}_4\text{bpy})_2(\text{dmtc})]^+ + 2\ \text{poly(vpy)} \quad (1)$$

of the photochemistry, the cross-linking fragment $[\text{-Ru}(\text{Me}_4\text{bpy})_2]^{2+}$ was removed from the films, which led to a loss of the polymer from the electrode and provided a means for creating images and novel microstructures.[2] We report here that photolysis of *copolymeric films* of poly$[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{vpy})_2]^{2+}$,$[\text{Ru}(\text{vbpy})_3]^{2+}$ (vbpy is 4-methyl-4′-vinyl-2,2′-bipyridine) leads to the selective removal of the fragment $[\text{-Ru}(\text{Me}_4\text{bpy})_2]^{2+}$. The poly$[\text{Ru}(\text{vbpy})_3]^{2+}$ film that remains acts as a size-selective transport barrier toward diffusion, which creates a basis for size-selective electrochemistry at the underlying electrode.

Copolymeric films of poly$[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{vpy})_2]^{2+}$,$[\text{M}(\text{vbpy})_3]^{2+}$ (M is Ru^{II} or Os^{II}) were prepared on Pt disk electrodes by reductive electropolymerization.[3] The ratio was varied by controlling the compositions of the solutions used for electropolymerization. In most cases the composition of the copolymeric films was the same as that of the solutions from which they were prepared. In cyclic voltammograms of the films, reversible $\text{Ru}^{\text{III/II}}$ couples for poly$[\text{Ru}(\text{vbpy})_3]^{3+/2+}$ (+0.91 V) and poly$[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{vpy})_2]^{3+/2+}$ (+0.80 V) appeared as a single, unresolved wave at $E_{1/2}$ = +0.88 V vs Ag/AgNO$_3$,[4] and the $\text{Os}^{\text{III/II}}$ couple for poly$[\text{Os}(\text{vbpy})_3]^{2+}$ appeared at +0.42 V. For M = Ru^{II} there were reversible, bipyridine-based reductions at −1.66 V for poly$[\text{Ru}(\text{vbpy})_3]^{2+}$ and an overlapping reduction at −1.88 V for poly$[\text{Ru}(\text{vbpy})_3]^{2+}$ (−1.86 V) and poly$[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{vpy})_2]^{2+}$ (−1.88 V). For M = Os^{II} there were reversible, bipyridine-based reductions at −1.60 V for poly$[\text{Os}(\text{vbpy})_3]^{2+}$ and an overlapping reduction at −1.85 V for poly$[\text{Os}(\text{vbpy})_3]^{2+}$ (−1.76 V) and poly$[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{vpy})_2]^{2+}$.

Photolysis of ~1:1 copolymeric films (H_2O, 0.1 M in sodium dimethyldithiocarbamate with a 200-W high-pressure Hg lamp for 45 min, followed by rinses in water and acetonitrile) led to equal peak currents for the ligand-based reduction waves. For M = Ru^{II}, the peak current for the $\text{Ru}^{\text{III/II}}$ wave decreased by about half. For M = Os^{II}, the $\text{Ru}^{\text{III/II}}$ wave disappeared. Under these conditions, films of poly$[\text{M}(\text{vbpy})_3]^{2+}$ are photoinert. These observations are consistent with reaction 2. Analysis of the

$$\text{poly}[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{vpy})_2]^{2+},[\text{M}(\text{vbpy})_3]^{2+} \xrightarrow[\text{dmtc}^-]{h\nu} [\text{Ru}(\text{Me}_4\text{bpy})_2(\text{dmtc})]^+ + \text{poly}[\text{M}(\text{vbpy})_3]^{2+},2\ \text{vpy} \quad (2)$$

copolymeric films by X-ray photoelectron spectroscopy (XPS) before and after photolysis confirmed that the Ru^{II} complex was lost from the films as a result of the photochemical reaction. A typical spectrum for a copolymeric film of poly$[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{vpy})_2]^{2+}$,$[\text{Os}(\text{vbpy})_3]^{2+}$ exhibited peaks for the Ru 3d, N 1s, and Os 4f photoelectrons. After photolysis, the peaks for Ru 3d were significantly attenuated, indicating that species had been lost from the polymer. The existence of free vpy sites in the films after photolysis was shown independently by chemical binding studies; see below. From the results of initial angle-dependent XPS studies on ~1:1 poly$[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{vpy})_2]^{2+}$,$[\text{Os}(\text{vbpy})_3]^{2+}$ (surface coverage (Γ) = 6.6×10^{-10} to 8.4×10^{-10} mol/cm^2), the films had decreased in thickness by 0–10% after photolysis. Profilometry experiments on thick films ($\Gamma = 0.7 \times 10^{-8}$ to 1.5×10^{-8} mol/cm^2) suggested decreases of 20–40%.

The photochemical reaction changes the transport properties of the films. The ability of the resulting microstructure to discriminate between ferrocene derivatives on the basis of molecular volume was investigated by oxidation at a rotated disk electrode. The data were treated by using eq 3, which describes the limiting current at a rotated disk electrode by assuming that mass transport through the films can be treated as a membrane-diffusional process.[5] This equation relates the limiting current (i_{lim}) to the

$$\frac{1}{i_{\text{lim}}} = \frac{1}{0.62nFAD_s^{2/3}\nu^{-1/6}\omega^{1/2}C_s} + \frac{1}{nFAD_{s,\text{pol}}PC_s/d} \quad (3)$$

---

[1] (a) Gleria, M.; Minto, F.; Beggiato, G.; Bortolus, P. *J. Chem. Soc., Chem. Commun.* **1978**, 285. (b) Durham, B.; Walsh, J. L.; Carter, C. L.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 860. (c) Pinnick, D. V.; Durham, B. *Inorg. Chem.* **1984**, *23*, 1440.

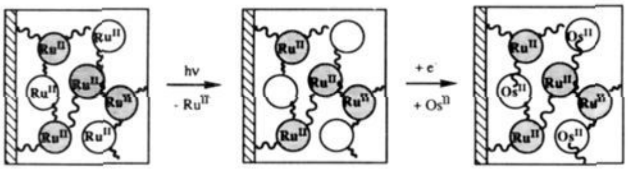
[2] Gould, S.; O'Toole, T. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 9490.

[3] (a) Denisevich, P.; Abruña, H. D.; Leidner, C. R.; Meyer, T. J.; Murray, R. W. *Inorg. Chem.* **1982**, *21*, 2153. (b) Abruña, H. D.; Denisevich, P.; Umana, M.; Meyer, T. J.; Murray, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 1. (c) Calvert, J. M.; Schmehl, R. H.; Sullivan, B. P.; Facci, J. S.; Meyer, T. J.; Murray, R. W. *Inorg. Chem.* **1983**, *22*, 2151.

[4] The reference was Ag/0.01 M AgNO$_3$ in 0.1 M $[\text{NEt}_4](\text{ClO}_4)$/acetonitrile. The potential of this electrode is +0.3 V vs the saturated sodium chloride calomel electrode.

0002-7863/91/1513-7442$02.50/0 © 1991 American Chemical Society

Scheme I



rotation rate (ω) and allows the constant $D_{s,pol}P$, the product of the diffusion coefficient of the electroactive species through the film and its partition coefficient into the film, to be evaluated from plots of i_{lim}^{-1} vs $\omega^{-1/2}$.[6] The kinetic model assumes that the rate of partitioning of the ferrocene into the film is rapid. Permeation measurements carried out for several of the ferrocenes by using a series of copolymeric films of ~1:1 poly$[Ru(Me_4bpy)_2(vpy)_2]^{2+}$,$[Ru(vbpy)_3]^{2+}$ that varied in thickness from 240 to 600 Å suggest that this assumption is valid.[5e]

The model also assumes that the film is not electroactive at the potential where the ferrocenes are oxidized. If this were not the case, oxidation of the ferrocene at the film/solution interface by electron-transfer mediation would result in currents that were insensitive to the mass transport properties of the film. The potential for the $Ru^{III/II}$ couple for the polymeric films was sufficiently removed from the potential for oxidation of the ferrocenes to avoid this complication.

In Figure 1 is shown a plot of $D_{s,pol}P$ vs molecular volume[7] for the oxidation of a series of ferrocene derivatives before and after photolysis of a copolymeric film initially 40% in poly$[Ru(Me_4bpy)_2(vpy)_2]^{2+}$ and 60% in poly$[Ru(vbpy)_3]^{2+}$.[10] The thickness of the film was ~440 Å.[11] From these data, photolysis greatly enhances diffusional transport to the underlying electrode. In the photolyzed film there is a discrimination based on size up to a threshold of ~300 $Å^3$ with $D_{s,pol}P$ varying by a factor of ~14 from the largest ferrocene derivative (500 $Å^3$) to the smallest (150 $Å^3$). The volume of the fragment $[-Ru(Me_4bpy)_2](PF_6)_2$ is ~1250 $Å^3$.[12] The enhancements in $D_{s,pol}P$ are far greater than could be accounted for by the effect on diffusion of the relatively small changes that occur in film thickness. Photolysis increases permeability toward the ferrocenes probably by decreased cross-linking and the creation of molecular-sized voids that increase porosity.

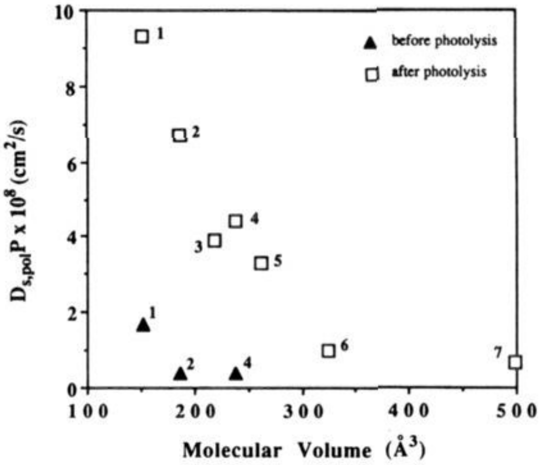


Figure 1. A plot of $D_{s,pol}P$ vs molecular volume for ferrocene (**1**), 1,1′-dimethylferrocene (**2**), *n*-butylferrocene (**3**), *p*-tolylferrocene (**4**), (2-methyl-4-nitrophenyl)ferrocene (**5**), decamethylferrocene (**6**), and 1,1′,2,2′-tetrakis(phenylmethyl)ferrocene (**7**). Rotated disk voltammograms were recorded in 0.14–0.17 mM solutions of the ferrocene in acetonitrile with 0.1 M tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte. They were recorded at rotation rates that varied from 300 to 3000 rpm at a scan rate of 20 mV/s. A value of $D_{s,pol}P$ for **3** before photolysis was not obtained since, under these conditions, i_{lim} appeared to be independent of ω. Measurements were not made for **5** or **6** before photolysis.

Size-selectivity effects have been observed at other film-coated electrodes[14] where the films were modified by chemical etching,[14a] by γ irradiation,[14b] or by controlling the conditions for electropolymerization.[14c-g] The approach taken here is unique in creating discrete molecular voids in an intact film structure. We have been able to "refill" the molecular voids (and perhaps more importantly, to demonstrate that chemical reactions can be carried out within them) by binding external reagents to the vpy groups that are released in the photochemical reaction in eq 2.

The complex $Os(PMe_2Ph)_3Cl_3$ undergoes an irreversible reduction at $E_{p,c} = -0.8$ V, which results in loss of chloride and formation of $Os(PMe_2Ph)_3(L)Cl_2$ (L is CH_3CN, pyridine, etc.).[15] Reduction of this complex in a methylene chloride solution that was 0.2 M in $[N(n\text{-}Bu)_4](PF_6)$ at a photolyzed film initially 60% in poly$[Ru(Me_4bpy)_2(vpy)_2]^{2+}$ ($d \sim 360$ Å) led to the incorporation of $Os(PMe_2Ph)_3(vpy)Cl_2$ as shown by the appearance of waves for the $Os^{III/II}$ ($E_{1/2} = -0.22$ V) and $Os^{IV/III}$ ($E_{1/2} = +1.08$ V) couples. In the best cases, 80% incorporation of Os^{II} into the sites vacated by Ru^{II} was achieved. In an experiment where only 15% of the sites were reoccupied, $D_{s,pol}P$ decreased by a factor of 3 for diffusion of ferrocene. The overall sequence of reactions is illustrated in Scheme I.

Acknowledgement is made to the Army Research Office for support of this work through Grant No. DAALO3-90-G-0062, to Prof. William F. Little for providing samples of substituted ferrocenes, and to Kimberly Hooker for providing XPS results. XPS instrumentation was funded by an instrumentation grant (R. W. Linton, principal investigator) from the Office of Naval Research, ONR No. N00014-86-G-0200. We also thank Prof. Royce W. Murray for helpful discussions.

---

(5) (a) Gough, D. A.; Leypoldt, J. K. *Anal. Chem.* **1979**, *51*, 439. (b) Leddy, J. A.; Bard, A. J. *J. Electroanal. Chem.* **1983**, *153*, 223. (c) Ikeda, T.; Schmehl, R.; Denisevich, P.; Willman, K.; Murray, R. W. *J. Am. Chem. Soc.* **1982**, *104*, 2683. (d) Ewing, A. G.; Feldman, B. J.; Murray, R. W. *J. Phys. Chem.* **1985**, *89*, 1263. (e) Leddy, J. A.; Bard, A. J.; Maloy, J. T.; Saveant, J. M. *J. Electroanal. Chem.* **1985**, *187*, 205.

(6) In eq 3, D_s and C_s are the diffusion coefficient and concentration of the electroactive species in solution, ν is the kinematic viscosity of the solvent, A is the electrode area, and d is the film thickness.

(7) The molecular volume for ferrocene was taken from the literature.[8] The molecular volumes of the substituted ferrocenes were estimated by correcting the volume of ferrocene for the additional substituents by estimating their van der Waals volumes by using atomic increments.[9]

(8) Chidsey, C. E. D.; Bertozzi, C. R.; Putvinski, T. M.; Mujsce, A. M. *J. Am. Chem. Soc.* **1990**, *112*, 4301.

(9) (a) Edwards, J. T. *Chem. Ind.* **1956**, 774. (b) Edwards, J. T. *J. Chem. Educ.* **1970**, *47*, 261. (c) Bondi, A. *J. Phys. Chem.* **1954**, *58*, 929.

(10) Experiments that measured $D_{s,pol}P$ for a series of copolymeric films of poly$[Ru(Me_4bpy)_2(vpy)_2]^{2+}$,$[Ru(vbpy)_3]^{2+}$ where the ratio of the monomers was varied revealed that the permeability of the copolymeric films (before and after photolysis) was dependent on the composition of the polymer. Higher rates of permeation were observed for films rich in poly$[Ru(Me_4bpy)_2(vpy)_2]^{2+}$. This is expected since films containing more poly$[Ru(vbpy)_3]^{2+}$ sites (with three polymerizable ligands) should be more highly cross-linked than films containing more poly$[Ru(Me_4bpy)_2(vpy)_2]^{2+}$ sites (with two polymerizable ligands). These results will be presented in a future publication. The purpose of the present work was to demonstrate photochemical manipulation of the structure and properties of the films.

(11) Film thicknesses, d, were calculated from surface coverage measurements made prior to photolysis by assuming that the concentration of ruthenium sites in the films was 1 M.

(12) This volume was estimated from the known crystal structure of $[Ru(bpy)_3]^{2+}$,[13] including the van der Waals extensions for the terminal H atoms, subtracting $^1/_3$ of this volume, adding the van der Waals volumes of the methyl substituents,[9] and including the volumes of the PF_6^- anions (~100 $Å^3$).

(13) Rillema, P. D.; Jones, D. S.; Levy, H. A. *J. Chem. Soc., Chem. Commun.* **1979**, 849.

(14) (a) Wang, J.; Hutchins, L. D. *Anal. Chem.* **1985**, *55*, 1536. (b) De Castro, E. S.; Huber, E. W.; Villarroel, D.; Galiatsatos, C.; Mark, J. E.; Heineman, W. R. *Anal. Chem.* **1987**, *59*, 134. (c) Wang, J.; Chen, S.-P.; Lin, M. S. *J. Electroanal. Chem.* **1989**, *273*, 231. (d) Ohsaka, T.; Hirokawa, T.; Miyamoto, H.; Oyama, N. *Anal. Chem.* **1987**, *59*, 1758. (e) Presspich, K. A.; Marbury, S. G.; Thomas, R. E.; Linton, R. W.; Irene, E. A.; Murray, R. W. *J. Phys. Chem.* **1989**, *93*, 5568. (f) McCarley, R. L.; Irene, E. A.; Murray, R. W. *J. Phys. Chem.* **1991**, *95*, 2492. (g) Ohnuki, Y.; Matsuda, H.; Ohsaka, T.; Oyama, N. *J. Electroanal. Chem.* **1983**, *158*, 55.

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