Control of Metallocene Electroactivity by Thin-Film Metallopolymer Permeation

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Introduction:

Redox-active metallopolymeric films have an extensive range of applications that includes electrocatalysis, electronic devices, and molecular and ionic sensing.[1] Polymer permeability plays an important role in these applications.[2]

In principle, polymer film permeability can be controlled both electrostatically and sterically. It follows that if permeants are electroactive molecular species, their electroactivity can be modulated extensively via the permeation process.[3] Conversely, the extent of permeant electroactivity itself can be used to measure film permeation properties.

Our goal in the present study is to control the permeation process, and therefore the electroactivity of the permeant, entirely via steric factors. We attempt this by varying both the size of the molecular permeant and the effective polymer film pore size. To accomplish the latter, we make use of an oxidative electrochemical film synthesis scheme.[4,5] The oxidative polymerization of ruthenium-phenanthroline complexes, developed primarily in our lab, permits linkages between film redox sites to be varied in both length and composition, resulting in polymer "cavity" size variations of molecular dimensions.

Polymer film precursors used are of the type $[Ru(phen)_2(L_2)](PF_6)_2$ where L=4,4'-bipyridine (4,4'-bpy), 1,2-bis(4-pyridyl)ethylene (BPE), 1,2-bis(4-pyridyl)ethane (BPA), 4,4'-trimethylenedipyridine (TMP), and ß,ß'-bis(4-pyridyl)-1,4-diethylbenzene (BPEB). The mechanism of polymerization appear to involve nucleophilic attack by the uncoordinated pyridyl nitrogen portion of a dipyridyl ligand at the phenanthroline of an adjacent monomer, where the coordinated phenanthroline ligand is activated electrochemically by oxidation of Ru(II) to Ru(III). The resulting linkage is between pyridyl and phenanthroline. Varying the length of the spacer in the parent dipyridyl ligand enables a series of cross-linked electroactive films with site-to-site linkages of 12-30Å to be prepared. Idealized linkage structures are shown in Figure 1.[6]

Experimental:

Starting materials and spacer ligands were purchased from GFS Chemicals. Molecular permeants (with the exception of Fe(vbpy)$_2$(CN)$_2$) (vbpy=4-vinyl-4'-methyl-2,2'-bipyridine) were purchased from Aldrich. Fe(vbpy)$_2$(CN)$_2$ was prepared by a literature method[7] and ß,ß'-bis(4-pyridyl)-1,4-diethylbenzene (BPEB) was prepared by a method developed in our lab.[8] Acetonitrile was distilled under nitrogen over CaH$_2$.

[Ru(phen)$_2$(L$_2$)](PF$_6$)$_2$ (L=4,4'bpy, BPE, BPA, TMP, BPEB) species were prepared as in earlier work.[4]

Oxidative electropolymerization was achieved by using a 1mM monomer solution and cycling continuously between 0.7V and 1.7V at 100mV/s using a 1mm Pt disk electrode as a working electrode.

Permeabilities were determined from rotating disk electrode (RDE) voltammetry, where the steady-state limiting currents for oxidation of the permeant were reached at various rotation rates, at a scan rate of 5mV/s.

Results and Discussion:

Consecutive cyclic voltammograms for Ru(phen)$_2$(TMP)$_2^{2+}$ are shown in Figure 2. The current from the oxidation and reduction of metal center increases with each scan. Upon termination of cycling, an adherent, orange film is observed on the electrode surface. After rinsing and placing the electrode into a fresh solution containing no monomer, the current behavior is retained indicating the presence of an immobilized, oxidatively assembled, stable, electroactive film. Similar responses are found for 4,4'-bpy, BPA and BPE containing complexes. (Ru(phen)$_2$(BPEB)$_2^{2+}$ experiments are in progress.)

The limiting rate (or current, i_{lim}) for solute oxidation depends on the rate of permeation of the polymer film by the solute. If these are viewed as consecutive rate processes then:

$$i_{lim}^{-1} = i_{mass\ transport}^{-1} + i_{permeation}^{-1} \qquad (1)$$

The individual terms are further defined as:

$$i_{mass\ transport} = 0.620nFAD^{2/3}\omega^{1/2}v^{-1/6}C_{soln} \qquad (2)[9]$$

$$i_{permeation} = nFAPD_{film}C_{soln}/d \qquad (3)[10]$$

where ω is the rotation rate, v is the kinematic viscosity, n is the number of electrons transferred per permeant, F is the Faraday, A is the electrode area, C_{soln} is the solute concentration, and d is the polymer film thickness. The permeability PD$_{film}$ is the product of the solute partition coefficient P and its diffusion coefficient D$_{film}$ within the film.

The rotating disk electrode technique provides control of the first term in (1) via rotation-rate dependent convective mass transport. The permeation contribution is then obtained from the intercept of a Koutecky-Levich plot, i.e. a plot of i_{lim}^{-1} vs. $\omega^{-1/2}$. With $i_{mass\ transport}$ proportional to the square root of rotation rate,

the limiting current for permeation is found from the intercept of the plot and PD is determined from (3).

Permeabilities of a prototypical compound, ferrocene, through the various films were first determined. Unexpectedly, permeation was found to diminish with increased polymer site linkage length. A reductively polymerized film of $Ru(5\text{-Cl-}phen)_3^{2+}$[11] was used to observe effects in a film with no pyridyl spacer. From multiple replications, PD was largest for the films with no spacer and smallest for films derived from $Ru(phen)_2(TMP)_2^{2+}$. This pattern is tentatively attributed to enhanced polymer cross-linking with increased linkage length.

Larger ferrocene derivatives were employed in a search for molecular sieving effects deriving from permeant size. As expected, diminished permeabilities accompanied increases in steric bulk. Such behavior was observed for films derived from both $Ru(phen)_2(TMP)_2^{2+}$ and $Ru(phen)_2(4,4'\text{-bpy})_2^{2+}$. (Studies with $Ru(phen)_2(BPEB)_2^{2+}$ are in progress.)

To place the study on more quantitative grounds, the solution phase diffusion coefficient (determined electrochemically by measuring currents at bare electrodes) was used as an inverse measure of molecular size.[12] Figure 3 compares permeabilities of several solutes ($Ru(phen)_2(TMP)_2^{2+}$-based films) to values for D (or inverse size). Selectivity is obviously lacking for larger species such as $Fe(vbpy)_2(CN)_2$ and some of the bulky ferrocenes. (The small residual responses observed are probably due to pinhole transport, rather than true permeation.) There is, however, significant permeability by smaller species. Ultimately, as shown in Figure 3, we observed a sharp size selection or "molecular sieving" by metallopolymeric films. Slightly different results were found with $Ru(phen)_2(4,4'\text{-bpy})_2^{2+}$-based films, but the sharp "cutoff" in current response with increasing permeant size was again observed. Preliminary results seem to suggest that the sieving or molecular size "cutoff" can be synthetically tuned. We also find evidence, however, for a possible secondary permeability dependence on extent of film cross-linking (see above). Further permeation-controlled studies using films with larger cavities (such as those derived from $Ru(phen)_2(BPEB)_2^{2+}$) should establish more clearly the viability of tunable molecular selectivity based on film "cavity" size and permeant size.

References:
(1) Westmoreland, T.D.; Calvert, J.M.; Murray, R.W.; Meyer, T.J., *Chem. Soc., Chem. Commun.*, **1983**, 65.

(2) Swalen, J.D.; Allara, D.L.; Andrade, J.D.; Chandross,E.A.; Garoff, S.; Israelachvili, J.; McCarthy, T.J.; Murray, R.; Pease, R.F.; Robolt, J.F.; Wynne, K.J.; Yu, H., *Langmuir*, **1987**, *3*, 932.

(3) McCarley, R.L.; Irene, E.A.; Murray, R.W., *J. Phys. Chem.*, **1991**, *95*, 2492.

(4) Fussa-Rydel, O.; Hupp, J.T., *J. Electroanal. Chem.*, **1988**, *251*, 417.

(5) Calvert, J.M.; Peebles, D.L.; Nowak, R.J., *Inorg. Chem.*, **1985**, *24*, 3111.

(6) Skeens-Jones, L.; Ibers, J.A.; Subramanian, P.; Hupp, J.T., unpublished work.

(7) (a)Abruña, H.D.; Breikss, A.I.; Collum, D.B., *Inorg. Chem.*, **1985**, *24*, 987.
(b)Schilt, A.A., *J. Am. Chem. Soc.*, **1960**, *82*, 3000.

(8) Yoon, D., personal communication.

(9) Bard, A.J.; Faulkner, L.K., *Electroanalytical Methods*; Wiley: New York, **1980**.

(10) Ewing, A.G.; Feldman, B.J.; Murray, R.W., *J. Phys. Chem.*, **1985**, *89*, 1263.

(11) Fussa-Rydel, O.; Zhang, H.T.; Hupp, J.T.; Leidner, C.R., *Inorg. Chem.*, **1989**, *28*, 1533.

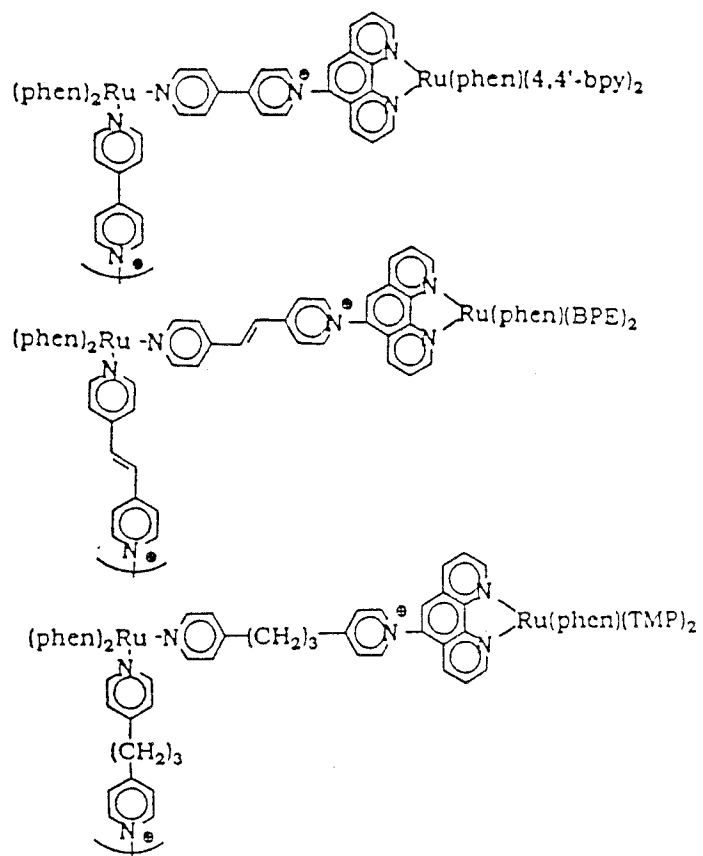(12) Koval, C.A.; Ketterer, M.E.; Reidsema, C.M., *J. Phys. Chem.*, **1986**, *90*, 4201.

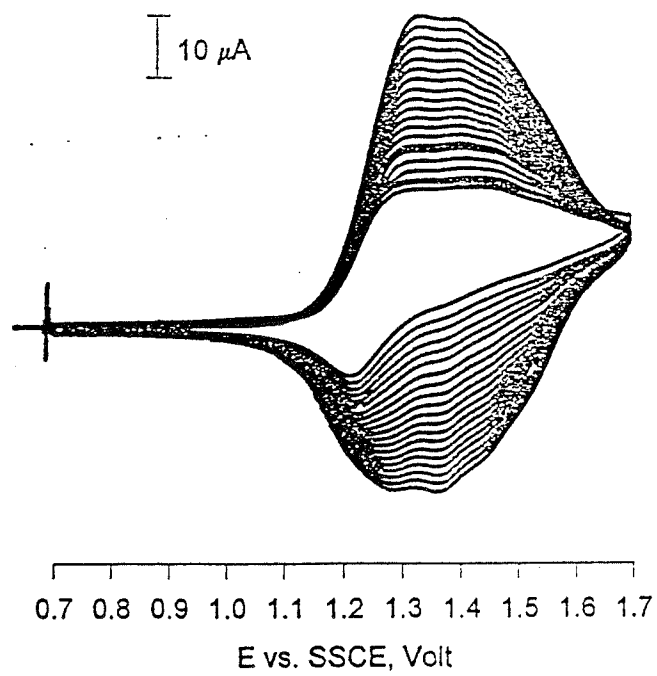Figure 1. Linkage structures based on 4,4'bpy, BPE, and TMP as spacers.

Figure 2. Cyclic voltammetric response of 1mM Ru(phen)$_2$(TMP)$_2$$^{2+}$
in 0.1M TBAP/acetonitrile at Pt disk (sweep rate 100 mV/s).

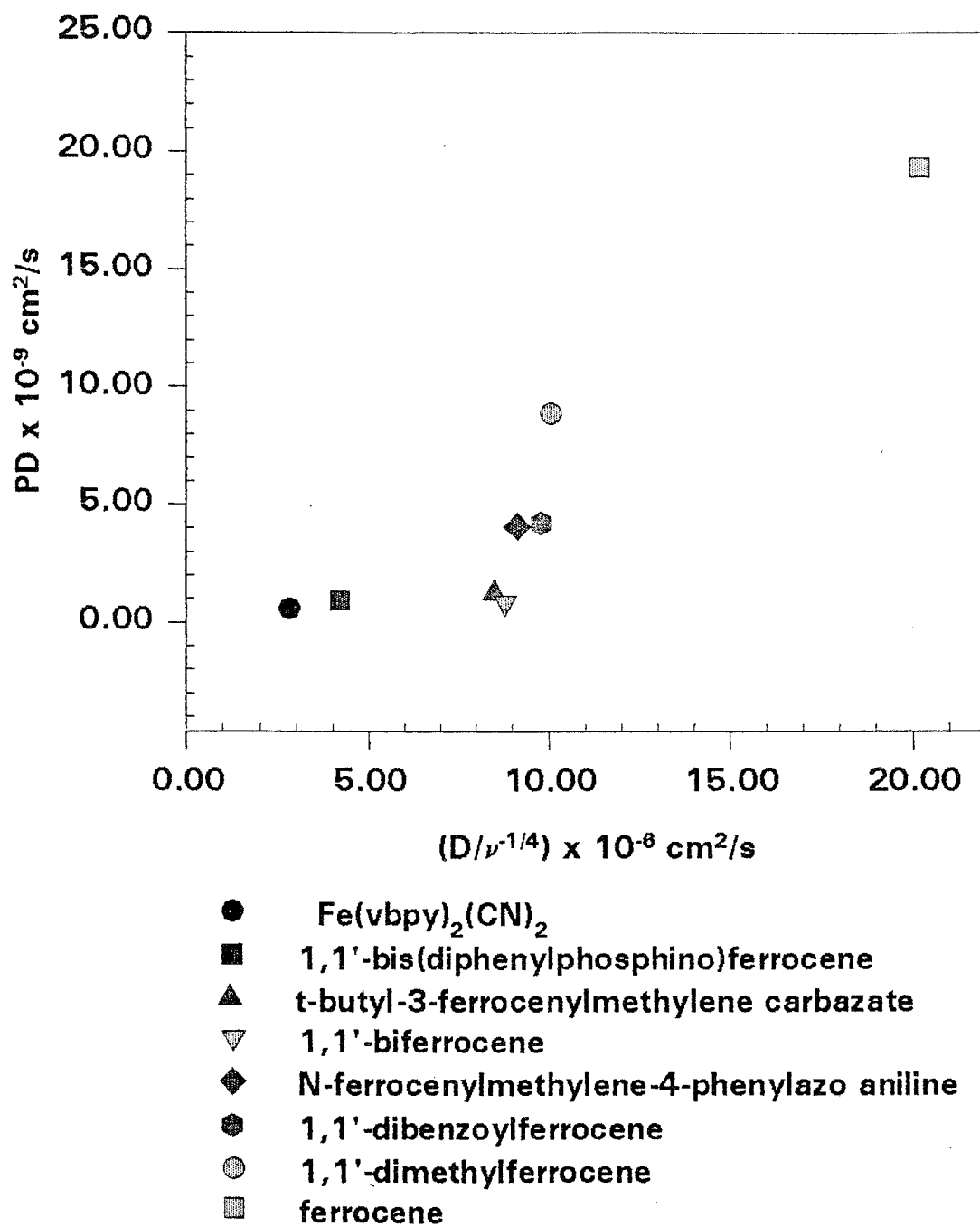Figure 3. Permeabilities vs. Diffusion coefficients of permeants through films of poly-Ru(phen)$_2$(TMP)$_2^{2+}$.