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Incorporation of Redox Couples into *p*-Chlorosulfonated Polystyrene Coated Electrodes by Chemical Binding

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Redox couples that contain unbound amine, hydroxy, or carboxylate groups can be incorporated at room temperature into *p*-chlorosulfonated polystyrene films via sulfonamide, sulfonester, or sulfonanhydride linkages, respectively. The *p*-chlorosulfonated polystyrene films can be cast onto virtually any surface, including platinum and glassy-carbon electrodes. The redox couples incorporated include polypyridyl complexes of iron, ruthenium, and osmium, an ammine complex of ruthenium, organics, a nickel macrocycle, and a nickel porphyrin. The modified films based on sulfonamide links were the most stable, and the films based on sulfonanhydride links were by far the least stable. The *p*-chlorosulfonated polystyrene films were used in a variety of applications including (1) co-incorporation of more than one redox site, (2) fabrication of bilayers in which different redox couples are held in separate films, (3) selectivity and directed charge transfer for redox couples in the external solution, (4) hydrolysis of the sulfonyl chloride groups followed by binding of cations in the resulting polysulfonate films by ion exchange, and (5) incorporation of emitting chromophores into the polymeric films.

Introduction

By now, a variety of approaches have been developed for the attachment of electroactive compounds to electrode or semiconductor surfaces.[1] The approaches include covalent binding to surface chemical sites,[2] electropolymerization on an electrode surface,[3] deposition of a preformed metallopolymer by evaporation,[4] and deposition of an electroinactive polymer followed by incorporation of electroactive compounds by electrostatic[5,6] or chemical binding.[2e] We report here a conceptually more general approach to the problem of preparing electroactive, metallopolymeric films on electrodes which is based on the formation of a stable chemical link to a preadsorbed polymeric film.

In the design of the particular system reported here, there were several critical requirements including (1) the availability of a low-molecular-weight, electroinactive polymeric backbone,

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(2) a chemical basis for the facile incorporation of a variety of redox couples into the polymer, (3) no significant alteration or modification in the chemical properties of the redox couple, and (4) the possibility of incorporation of redox sites by more than one type of binding.

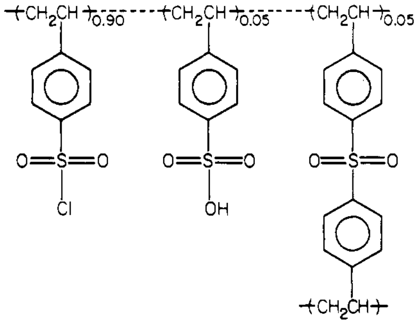
Polystyrene was chosen as the basic polymeric unit both because of the ease of preparing samples of controlled molecular weight over a wide molecular weight range[8] and because of its extensive background chemistry toward functionalization.[9] As an active site for chemical attachments, the chlorosulfonyl group is attractive because of its reactivity at room temperature toward a variety of functional groups, including amine, hydroxy, and carboxylate groups to give the sulfonamide ($-SO_2NHR$), sulfonester ($-SO_3R$), and sulfonanhydride ($-SO_3C(O)R$) links, respectively. In addition, the resulting sulfonyl-based links are expected to be much more stable than the analogous $-C(O)-$ links, which have been used to bind reagents directly to electrode and semiconductor surfaces[2a-d] and, in a directly related study, to bind (hydroxymethyl)ferrocene to a poly(methacrylyl chloride)-modified SnO_2 electrode.[2e] In addition, the incorporation chemistry is confined to the periphery of the redox site, resulting in an only slightly altered chemical environment. As a final point, the chlorosulfonyl groups can be hydrolyzed to sulfonic acid groups, which imparts cation-exchange properties to the polymer and allows cationic redox couples to be incorporated by electrostatic binding.[5,6]

Experimental Section

Materials. Tetraethylammonium perchlorate ($(NEt_4)ClO_4$; TEAP) was prepared by using a literature procedure,[10] purified by recrystallization from hot water four times, dried under vacuum at 100 °C for 10 h, and stored in a vacuum desiccator. Acetonitrile (Burdick and Jackson; distilled from CaH_2) and acetone (Burdick and Jackson; distilled from anhydrous Na_2CO_3) were bubble degassed for 1 h with argon that was purified by passage through a column packed with R3-11 catalyst (Chemical Dynamics Corp.) and were stored in an inert-atmosphere drybox. Alumina (Woehm Pharmaceutical; activity 1) was used as received. Aniline (Fisher) was vacuum distilled from CaH_2. *N,N′*-Dimethyl-*p*-phenylenediamine (DMPD; Eastman) was vacuum distilled and stored in a drybox. The complexes $(bpy)_{3-n}Ru(5\text{-phenNH}_2)_n{}^{2+}$ (n = 1–3; bpy is 2,2′-bipyridine; 5-phenNH$_2$ is 5-amino-1,10-phenanthroline), $(bpy)_2Ru(4\text{-pyNH}_2)_2{}^{2+}$ (4-pyNH$_2$ is 4-aminopyridine), and $(bpy)_2Ru(3\text{-pyNH}_2)_2{}^{2+}$ (3-pyNH$_2$ is 3-aminopyridine) were prepared as reported previously.[11] The following metal complexes were prepared by using literature procedures: $(bpy)_2Ru(4\text{-pyOH})_2{}^{2+}$ (4-pyOH is 4-hydroxypyridine,[11] $(bpy)_2Ru(3\text{-pyOH})_2{}^{2+}$ (3-pyOH is 3-hydroxypyridine),[11] $(bpy)_2Ru[4,4'\text{-bpy(COOH)}_2]^{2+}$ (4,4′-bpy(COOH)$_2$ is 4,4′-dicarboxy-2,2′-bipyridine),[11] $(bpy)_2Ru(4\text{-pyCOOH})Cl^+$ (4-pyCOOH is 4-carboxypyridine),[12] $(NH_3)_5Ru(4\text{-pyNH}_2)^{2+}$,[13] $Fe(5\text{-phenNH}_2)_3{}^{2+}$,[14] $Fe(5\text{-phenNH}_2)_2(CN)_2$,[11] and $(5\text{-phenNH}_2)_2Os(dppm)^{2+}$ (dppm is bis(diphenylphosphino)methane).[15] The following compounds were received as gifts: (Cp)Fe(Cp-4-phNH$_2$) (Cp is η^5-C_5H_5; Cp-4-phNH$_2$ is η^5-C_5H_4-4-$C_6H_4NH_2$; from Dr. R. H. Schmehl), nickel tetrakis(*o*-aminophenyl)porphyrin (from Ruth Freitag), and $[Ni\{(NH_2Ethi)_2Me_2[16]tetraeneN_2\}](PF_6)_2$[16] (from Professor Daryle H. Busch). All other materials and solvents were reagent grade and were used as received.

Preparation of Polystyrene (Mol Wt 3700 ± 200). Low-molecular-weight polystyrene was synthesized by polymerizing styrene with stannic chloride in ethylene dichloride at 23 °C.[8] The resulting polymer was characterized by elemental analysis (Anal. Calcd: C, 92.3; H, 7.7. Found: C, 90.9; H, 7.6) and by IR (the IR spectrum matches the spectrum of a polystyrene film) and ^1H NMR spectroscopies, as well as by vapor-pressure osmometry (mol wt 3700 ± 200).

Preparation of *p*-Chlorosulfonated Polystyrene. Polystyrene (mol wt 3700 ± 200) was chlorosulfonated by treatment with chlorosulfonic acid in carbon tetrachloride at 0 °C.[9] Chlorosulfonation at higher temperatures resulted in an insoluble polymer presumably due to a higher degree of sulfone cross-linkages. The *p*-chlorosulfonated polystyrene was characterized by IR (the spectrum is identical with a spectrum reported in the literature)[17] and ^1H NMR spectroscopies, as well as by potentiometric titrimetry of the sulfonyl chloride sites (4.0 ± 0.2 mequiv of Cl^-/g of polymer was released upon reaction with excess aniline at room temperature).[18] Elemental analysis data are consistent with a formulation of the *p*-chlorosulfonated polystyrene as follows:



(Anal. Calcd: C, 48.4; H, 3.6; S, 15.8; Cl, 16.1. Found: C, 47.9; H, 3.5; S, 15.5; Cl, 16.1.) It should be noted that we have had problems in getting reproducible values for carbon analyses for reasons that are not obvious. However, given the titrimetric data and the consistent values for H, S, and Cl analyses, we feel that the analysis quoted above is appropriate for the polymer sample used in the experiments described here. Comparison of the elemental analysis results with the potentiometric titrimetry results suggests that, as shown above, ca. 90% of the sulfonyl chloride sites present in the polymer reacted with excess aniline at room temperature to release Cl^-. The *p*-chlorosulfonated polystyrene was stored in a desiccator over P_2O_5.

Electrochemistry. Experiments were performed in acetonitrile with 0.1 M tetraethylammonium perchlorate supporting electrolyte in one-compartment cells in an inert-atmosphere drybox. Electrochemical potentials were recorded vs. the quasi-stable silver-wire reference electrode. Formal potentials for solution redox couples ($E°'_{soln}$) and for surface-bound couples ($E°'_{surf}$) were recorded outside the drybox vs. the saturated sodium chloride calomel electrode (SSCE, +0.23 V NHE) at ca. 23 °C (room temperature) and are uncorrected for junction-potential effects. Cyclic voltammograms were obtained without iR compensation at 200 mV/s with a Princeton Applied Research Model 175 universal programmer and a Model 173 potentiostat and were recorded on a Hewlett-Packard 7015B X-Y recorder. The electrodes used were either glassy-carbon rods or platinum disks with Teflon shrouds. The electrode surfaces were polished with 1-μm diamond paste (Buehler) on a Gould 550/1140 rpm polishing wheel (Buehler).

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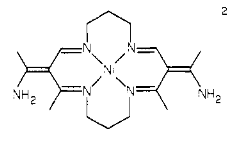
(16) The structure of this compound is



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Apparent surface coverages (Γ_{app}, mol/cm^2) were calculated by using the equation $\Gamma_{app} = Q_c/(nFA)$ (where n is the number of electrons per molecule reduced, F is Faraday's constant, A is the area of the electrode in cm^2, and Q_c is the charge (area) under the reductive component of the M$^{III/II}$ cyclic voltammetric wave as evaluated by planimetry). The procedure used may underestimate the actual quantity of monomer incorporated into the films because of slow electrochemical response on the time scale of the experiment and because of incomplete incorporation throughout the film, particularly in that part of the film closest to the electrode (see text).

The stability of the sulfonamide, sulfonester, and sulfonanhydride-linked films was investigated by scanning the electrode potential through the Ru$^{III/II}$ wave for the particular incorporated redox couple 10 times in a fresh 0.1 M TEAP/CH$_3$CN solution and observing the decrease in charge under the Ru^{III} → Ru^{II} wave. The potential scan limits were set 1.0 V apart and were centered such that each incorporated film spent approximately the same fraction of total time for a potential cycle in the Ru^{III} state. The first and tenth cyclic voltammograms were recorded and the areas under the reductive Ru$^{III/II}$ wave compared to give the percent remaining electroactivity.

Electrode-Coating Procedures. Electrodes were coated in an inert-atmosphere drybox by dissolving the *p*-chlorosulfonated polystyrene in dry acetone, placing 0.01 mL of the resulting solution onto the electrode surface, and allowing the acetone to evaporate. The thickness of the films was not determined exactly, although relatively thin to thick films could be prepared by using different solution concentrations or by depositing more than one coat from the same solution. A stock solution of *p*-chlorosulfonated polystyrene was prepared and diluted with dry acetone to give polymer solutions containing 6.67×10^{-4}, 1.11×10^{-5}, and 2.22×10^{-6} g/mL. Evaporation of 0.01 mL of the polymer solution containing 6.67×10^{-4} g/mL onto an electrode (ca. 0.15 cm^2) constituted a relatively thick film ($\Gamma_{app} = 2.6 \times 10^{-8}$ mol/cm^2; ca. 3000 Å).[19,20] Relatively thin films ($\Gamma_{app} = 5.5 \times 10^{-10}$ mol/cm^2; ca. 10 Å)[19,20] and films of intermediate thickness were prepared from polymer solutions containing 2.22×10^{-6} and 1.11×10^{-5} g/mL, respectively.

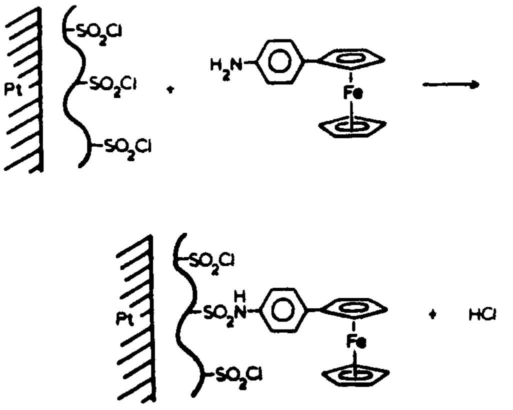
Incorporation Techniques. Redox couples were incorporated into the *p*-chlorosulfonated polystyrene coated electrodes in an inert-atmosphere drybox by using two general techniques: (1) The coated electrode was soaked in an acetonitrile solution containing the redox couple (3 mM) to be incorporated and (2) the potential of the coated electrode was cycled in 0.1 M TEAP/CH$_3$CN solution containing the redox couple (3 mM) in a negative-potential region where the redox couple is electroactive. The first technique is sufficient for incorporation of relatively small, neutral compounds all the way through even thick films. Incorporation of charged complexes all the way through all but thin films requires the latter technique (see text). The impregnated, polymer-coated electrodes were rinsed with acetonitrile to remove unincorporated complex and were allowed to dry.

Analytical Measurements. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Infrared spectra of thin films supported on NaCl plates were obtained with a Beckman 4250 spectrophotometer. The film of *p*-chlorosulfonated polystyrene was cast onto the inside face of one of the NaCl plates of a demountable IR solution cell (Barnes Analytical) in an inert-atmosphere drybox and the cell sealed to prevent hydrolysis of the sulfonyl chloride groups. Proton NMR spectra were recorded with a 60-MHz R-24B Hitachi Perkin-Elmer spectrometer with Me$_4$Si as an internal standard. The molecular weight of polystyrene was determined in toluene solution by using a 302B Hewlett-Packard vapor-pressure osmometer. The emission spectrum was recorded in air at 22 ± 2 °C on an SLM Instruments 8000 photon counting spectrofluorimeter. The excitation wavelength was 300 nm. Corrections for detector sensitivity were made by using data and programs supplied with the instrument. The sample consisted of a dry film containing the emitting chromophore which was coated on a platinum flag electrode. Laser-lifetime measurements were made by using a Molectron IL200 tunable dye laser pumped by a Molectron UV400 nitrogen laser. The excitation wavelength was 467 nm. As in the emission experiments, the samples were irradiated in air as dry films on platinum electrodes, on glassy carbon electrodes, or on glass slides. Microscopy was performed with an ETEC scanning electron microscope (SEM). Samples were prepared by evaporative deposition of the films directly onto the specimen mounts. Visible absorption spectra of films coated on glass slides were recorded by using a Varian Series 634 spectrophotometer.

Results and Discussion

Film Deposition and Soaking Incorporation Procedure. Films of *p*-chlorosulfonated polystyrene can be deposited by evaporation onto many surfaces, including glassy carbon and platinum electrodes. Thick films are not visually uniform in thickness but are microscopically free of holes greater than 150 Å as shown by 4000× magnification SEM experiments.

Once a film containing the reactive sulfonyl chloride groups is deposited on a surface, it is a simple matter to incorporate any redox couple that contains an unbound amine, hydroxy, or carboyxlate group into the film by soaking the coated electrode in an acetonitrile solution containing the redox couple to be incorporated, e.g., eq 1.



(1)

For the redox-active couples, the incorporation process can be conveniently monitored by cyclic voltammetry. However, it is important to realize that the electrochemical experiment relies on the presence of redox couples at the electrode/film interface while the incorporation of redox couples into the films occurs from the opposite direction and begins at the film solution interface. This is an important point since, in a simple soaking experiment, a decreasing concentration gradient could exist from the film/solution interface to the electrode/film interface. If no incorporation occurs at the electrode/film interface no response would be observed by cyclic voltammetry since *p*-chlorosulfonated polystyrene, being electrochemically *inactive*, would serve as an insulator between the electrode and the redox couples incorporated elsewhere in the film. If incorporation does occur at the electrode/film interface, cyclic voltammetry can be used to monitor the extent of incorporation by integration of the charge (area) under the reductive wave for the incorporated redox couple.

The simple soaking procedure is adequate for the incorporation of relatively small, neutral compounds, such as (Cp)Fe(Cp-4-phNH$_2$), throughout even thick *p*-chlorosulfonated polystyrene films as evidenced by a well-defined cyclic voltammetric response in solutions free of the redox couple (Figure 1).

The shape and characteristics of the waves in cyclic voltammograms depend upon the thickness of the resulting films. Thin films (Figure 1A) exhibit a linear dependence of peak current (i_p) on sweep rate (ν), and the potential difference between oxidative and reductive peak potentials approaches the diffusion-free theoretical value of zero at slow sweep rates; e.g., ΔE_p = 10 mV at a sweep rate of 20 mV/s for (Cp)Fe(Cp-4-phNHS(O)$_2$–). The voltammetric waves tail slightly as the sweep rate is increased from 20 to 200 mV/s although the oxidative and reductive waves remain symmetrical around the peak potentials $E_{p,a}$ and $E_{p,c}$, suggesting relatively fast charge transport through the thin films.[21] Thick films (Figure

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[19] The apparent surface coverage was determined for exhaustively incorporated (η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_4$-4-C$_6$H$_4$NH$_2$). The thin film was soaked for a day, whereas the thick film was soaked for several days.

[20] Ellis, C. D.; unpublished results.

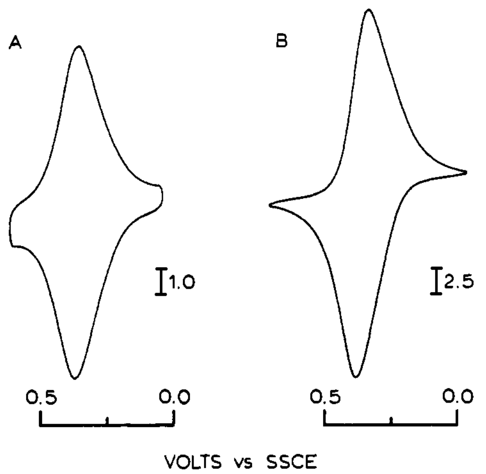

Figure 1. Cyclic voltammograms of a platinum electrode that was (A) coated with a thin film of *p*-chlorosulfonated polystyrene (see Experimental Section) and subsequently impregnated with (Cp)Fe(Cp-4-phNH$_2$) (Γ_{app} = 3.6 × 10^{-10} mol/cm^2) or (B) coated with a thick film of *p*-chlorosulfonated polystyrene (see Experimental Section) that was subsequently impregnated with (Cp)Fe(Cp-4-phNH$_2$) (Γ_{app} = 1.07 × 10^{-8} mol/cm^2). The current scales in μA are shown to the right of each voltammogram. The scan rate is 200 mV/s in (A) and 20 mV/s in (B).

1B) have a nonlinear dependence of i_p on sweep rate, greater ΔE_p values (ΔE_p = 35 mV at a sweep rate of 20 mV/s for the (Cp)Fe(Cp-4-phNHS(O)$_2$–) sites in Figure 1B), and significant tailing of the waves as the sweep rate is increased from 20 to 200 mV/s. All three observations suggest relatively hindered charge transport.[21]

Incorporation of Cations. Compared to small neutral molecules like (Cp)Fe(Cp-4-phNH$_2$), large cations like (bpy)$_2$Ru(5-phenNH$_2$)$^{2+}$ incorporated by soaking gave a greatly reduced cyclic voltammetric response under the same conditions. For example, for the Ru complex, Γ_{app} = 4.5 × 10^{-11} mol/cm^2 for a relatively thick film soaked for 1 min in a 3 mM acetonitrile solution (Figure 2A), while Γ_{app} = 5.6 × 10^{-9} mol/cm^2 for the ferrocene derivative under the same conditions. Incorporation of (bpy)$_2$Ru(5-phenNH$_2$)$^{2+}$ into the films is obvious because of the appearance of color in the films and, as noted below, because of their strong luminescence.

The limited degree of incorporation by soaking may be a consequence of the larger size of the Ru complex and of the creation of a polycationic, electrostatic "screen" on the outside of the film. Incorporation of cations throughout the film is possible for thin films by using extended soaking times (hours instead of minutes) or, in general, by cycling the potential of the coated electrode at negative potentials where ligand-based reductions occur. For example, (bpy)$_2$Ru(5-phenNH$_2$)$^{2+}$ (3 mM in 0.1 M (NEt$_4$)ClO$_4$/CH$_3$CN) is extensively incorporated (Γ_{app} = 1.7 × 10^{-9}) into a relatively thin film following 10 scans through the potential region where 2,2′-bipyridine is reduced (–1.0 to –1.5 V) at 200 mV/s (Figure 2B). The importance of the reductive cycling procedure was demonstrated by a series of experiments using the same conditions, a 50-s exposure time, and the same electrode but polished after each experiment and evaporating the same volume of polymer solution but attempting to incorporate the complex by (1) soaking, (2) cycling 10 times at 200 mV/s over a 0.5-V potential range that fell between the Ru(II) → Ru(III) oxidation and bpy-localized reductions, (3) cycling 10 times over a 0.5 V range that included the Ru(II) → Ru(III) oxidation, or (4) cycling 10 times over a 0.5 V range that included the bpy-localized reduction. For the four experiments the relative extent of incorporation was 1:2:5:17.

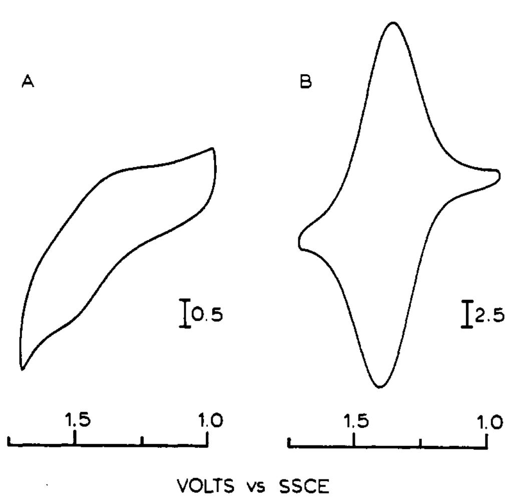

Figure 2. Cyclic voltammograms of a platinum electrode coated with *p*-chlorosulfonated polystyrene (0.01 mL of a polymer solution containing 6.67 × 10^{-4} g/mL of polymer—see Experimental Section) that was (A) soaked for 1 min in a 3 mM (bpy)$_2$Ru(5-phenNH$_2$)$^{2+}$/CH$_3$CN solution, rinsed with CH$_3$CN, and placed in a fresh 0.1 M TEAP/CH$_3$CN solution or (B) cycled 10 times at 200 mV/s from –1.0 to –1.5 V in a 0.1 M TEAP/CH$_3$CN solution containing 3 mM (bpy)$_2$Ru(5-phenNH$_2$)$^{2+}$, rinsed with CH$_3$CN, and placed in a fresh 0.1 M TEAP/CH$_3$CN solution. The scan rate is 200 mV/s. The current scales are shown below the voltammograms in μA.

Factors Controlling the Extent of Incorporation. For either soaking or potential cycling, the rate and/or extent of incorporation are dependent upon a number of factors, including (1) film thickness, (2) the concentration of reagent in the external solution, (3) the exposure time or number of cyclical potential scans, and (4) the size, charge, and cross-linking ability of the molecule to be incorporated.

Small neutral compounds are completely incorporated into even thick films simply by soaking, whereas larger, cationic complexes are not. Such observations are consistent with the fact that diffusion of electroactive molecules through polycationic metallopolymeric films is dependent upon both charge and molecular volume. Order of magnitude decreases in membrane-diffusion rates are induced by positive charge on the substrate or by increasing the size of the substrate from ferrocene to (bpy)$_2$RuCl$_2$.

Charge and volume effects also appear to dictate the maximum loading of redox sites into the polymer films. Soaking a film in 0.1 M (NEt$_4$)ClO$_4$/CH$_3$CN containing 3 mM (Cp)Fe(Cp-4-phNH$_2$) for an extended period resulted in the occupation of ~92% of the available sulfonyl chloride sites (4.0 × 10^{-3} site/g of polymer compared to a total of 4.5 × 10^{-3} site/g of polymer—Experimental Section). By contrast, ~55% of the available sulfonyl chloride sites (~49% of the total sites) become bound to (bpy)$_2$Ru(5-phenNH$_2$)$^{2+}$ when the reductive potential cycling procedure is used over an extensive period under the same conditions.

The extent of incorporation is probably additive and dependent upon the molecular volume of the redox sites. A relatively thin film was saturated with (bpy)$_2$Ru(5-phenNH$_2$)$^{2+}$ groups by reductive cycling, giving Γ_{app} = 3.3 × 10^{-10} mol/cm^2. After the film was soaked overnight in an acetonitrile solution containing 3 mM (Cp)Fe(Cp-4-phNH$_2$), cyclic voltammograms indicated that 2.7 × 10^{-10} mol/cm^2 of ferrocene sites had been added, showing, once again, that (bpy)$_2$Ru(5-phenNH$_2$)$^{2+}$ had occupied only 55% of the total number of sites in the film. It should be noted that the molecular volume of the polypyridyl complex (~1.5 × 10^3 Å^3)

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[21] Laviron, E.; Roullier, L.; DeGrand, C. *J. Electroanal. Chem. Interfacial Electrochem.* **1980**, *112*, 11.

Table I. Formal Potentials and Electrochemical Stabilities of Incorporated Redox Couples in 0.1 M $(NEt_4)NClO_4/CH_3CN$ at a Scan Rate of 200 mV/s

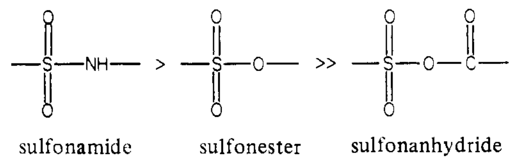
redox couple	$E^{\circ\prime}_{soln}$, V[a]	$E^{\circ\prime}_{surf}$, V[a]	Γ_{app}[b]	stability,[c] %
$(bpy)_2Ru(5\text{-}phenNH_2)^{2+}$	+1.31	+1.28	2.2×10^{-9}	94
$(bpy)_2Ru(5\text{-}phenNH_2)_2{}^{2+}$	+1.39[d]	+1.37	2.4×10^{-9}	99
$Ru(5\text{-}phenNH_2)_3{}^{2+}$	*e*	+1.53	8.3×10^{-10}	100
$(bpy)_2Ru(4\text{-}pyNH_2)_2{}^{2+}$	+0.99	+1.14[f]	1.8×10^{-9}	99
$(bpy)_2Ru(3\text{-}pyNH_2)_2{}^{2+}$	+1.18	+1.32	7.0×10^{-9}	94
$(bpy)_2Ru(4\text{-}pyOH)_2{}^{2+}$	+1.18[d]	+1.20	8.9×10^{-10}	88
$(bpy)_2Ru(3\text{-}pyOH)_2{}^{2+}$	+1.24	+1.25	2.2×10^{-9}	51
$(bpy)_2Ru[4,4'\text{-}bpy(COOH)_2]^{2+}$	+1.28	+1.25	1.3×10^{-9}	72
$(bpy)_2Ru(4\text{-}pyCOOH)Cl^{+}$	+0.75	+0.74	6.4×10^{-10}	39

[a] $E^{\circ\prime}$ is the average of the peak current potentials for the oxidative and reductive waves ($E_{p,a}$ and $E_{p,c}$, respectively); the potential is vs. the saturated sodium chloride electrode. [b] Γ_{app} is the apparent surface coverage in mol/cm^2 (see Experimental Section) of $Ru^{III/II}$ sites in a thick *p*-chlorosulfonated polystyrene film that was reductively cycled 10 times between −1.0 and −1.5 V in a 0.1 M $TEAP/CH_3CN$ solution containing 1–3 mM of the complex to be incorporated. The concentration of complex was varied so as to keep the concentration of potential linking sites constant (3 mM). Γ_{app} was determined in a fresh electrolyte solution. [c] Percent remaining electroactivity under the reductive $Ru^{III/II}$ surface wave after 10 cyclical potential scans centered around the $Ru^{III/II}$ redox couple (see Experimental Section). [d] The value is approximate due to overlap of ligand-based oxidative waves with the $Ru^{II/III}$ oxidative wave.[11] [e] The complex electropolymerizes too rapidly to see the $Ru^{III/II}$ wave for the solution couple.[11] [f] Another redox couple appears at ca. +1.03 V as shoulders on the main couple at +1.14 V.

is an order of magnitude larger than the volume of the ferrocene derivative (~1.3×10^2 Å^3).[22]

Characterization of Surface Couples. From the data in Table I, $E^{\circ\prime}_{surf}$ values for the polymer-bound redox couples are essentially the same as potentials for the corresponding solution redox couples, $E^{\circ\prime}_{soln}$. The two exceptions, $(bpy)_2Ru(4\text{-}pyNH_2)_2{}^{2+}$ and $(bpy)_2Ru(3\text{-}pyNH_2)_2{}^{2+}$, can be explained by the changes in electronic substituent effects at the Ru metal center in going from a strongly electron-donating amine group to a more electron-withdrawing sulfonamide group. The absence of similar shifts for the other couples in Table I suggests that differences in electronic effects are smaller, and as noted below, the polymeric environment may provide a compensating shift to more negative potentials compared to acetonitrile solution.

Of the three chemical links used in binding redox couples, the order of *decreasing* stability is



The relative stability of the sulfonamide linkages makes it the group of choice for the incorporation of redox couples into the films.

Another trend in the data is the increase in stability of films prepared from monomers in the order $(bpy)_2Ru(5\text{-}phenNH_2)^{2+}$ < $(bpy)Ru(5\text{-}phenNH_2)_2{}^{2+}$ < $Ru(5\text{-}phenNH_2)_3{}^{2+}$. Presumably, the role of multiple 5-phenNH$_2$ ligands is to provide a cross-linking which inhibits dissolution of the polymer by increasing the effective chain length.

It is clear from Table II that a variety of redox sites can be incorporated into the films and that the necessary requirement is the presence of a linking site, preferably an amine group. The complex $(NH_3)_5Ru(4\text{-}pyNH_2)^{2+}$ could be extensively incorporated simply by soaking, pointing out the importance of volume effects, while the nickel tetrakis(*o*-aminophenyl)porphyrin could be extensively incorporated only by allowing the complex to react with *dissolved* polymer before formation of the film. The free ligand, 5-phenNH$_2$, can be incorporated by soaking. Although the resulting film is electrochemically inactive, the presence of the ligand was shown by the appearance of the characteristic, ligand-based emission following UV excitation.

Table II. Formal Potentials for Unincorporated and Incorporated Redox Couples in 0.1 M $(Et_4N)ClO_4/CH_3CN$ at a Scan Rate of 200 mV/s

redox couple	$E^{\circ\prime}_{soln}$, V[a]	$E^{\circ\prime}_{surf}$, V[a]
$(NH_3)_5Ru(4\text{-}pyNH_2)^{2+}$	+0.12	−0.18
$Fe(5\text{-}phenNH_2)_3{}^{2+}$	*b*	+1.23
$Fe(5\text{-}phenNH_2)_2(CN)_2$	+0.40	+0.32
$(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4\text{-}4\text{-}C_6H_4NH_2)$	+0.31	+0.36
$(5\text{-}phenNH_2)_2Os(dppm)^{2+}$ [c]	*c*	+1.37
$[Ni\{(NH_2Ethi)_2Me_2[16]tetraeneN_4\}]^{2+}$ [16]	+1.16	+1.13
$H_2N\text{-}4\text{-}C_6H_4N(CH_3)_2$ (DMPD)	+0.78, +0.15	+0.55
nickel tetrakis(*o*-aminophenyl)porphyrin	−1.24, −1.74	−1.32, −1.83

[a] $E^{\circ\prime}$ is the average of $E_{p,a}$ and $E_{p,c}$; the potential is vs. the saturated sodium chloride electrode. [b] The complex electropolymerizes too rapidly to see the $Fe^{III/II}$ wave for the solution couple. [c] A value could not be obtained due to overlap of ligand-based oxidative waves with the $Os^{II/III}$ oxidative wave; dppm is bis(diphenylphosphino)methane, $Ph_2PCH_2PPh_2$.

Environmental Effects. The rather significant difference between $E^{\circ\prime}_{soln}$ and $E^{\circ\prime}_{surf}$ values for the $(NH_3)_5Ru(4\text{-}pyNH_2)^{2+}$ redox couple in Table II suggests that environmental effects can influence redox potentials in the films. $Ru^{III/II}$ potentials for complexes of the type $(NH_3)_5Ru(py)^{2+}$ (py is pyridine) are known to be solvent dependent with, for example, a potential shift of 0.36 V occurring between dimethyl sulfoxide and nitromethane.[23] Therefore, there may be a precedent for the −0.3 V shift in potential for the pentaammine couple in the film, which leads to a stabilization of the Ru^{III} state relative to Ru^{II}. Potentials for polypyridyl complexes of Ru, Os, and Fe are less dependent upon the environment because of the larger molecular volumes involved.[23]

Visible Spectra. Visible spectra for film-incorporated $(bpy)_2Ru(5\text{-}phenNH)^{2+}$ sites on a glass slide and for $(bpy)_2Ru(5\text{-}phenNH_2)^{2+}$ in an acetonitrile solution are shown in Figure 3. Compared to the solution spectrum, the spectrum of the attached chromophore in the film has the same basic features including a metal-to-ligand charge-transfer (MLCT) band at 452 nm with a higher energy shoulder at ca. 430 nm, but λ_{max} for the MLCT absorption band in the film is blue shifted by ca. 5 nm from 457 to 452 nm and the film spectrum

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(22) The volume of the ferrocene derivative was calculated on the basis of a 3.32 Å × 4.49 Å × 8.90 Å rectangular box, while the volume of the ruthenium complex was calculated on the basis of a sphere with a radius of 7.1 Å.

(23) Curtis, J. C.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 224.

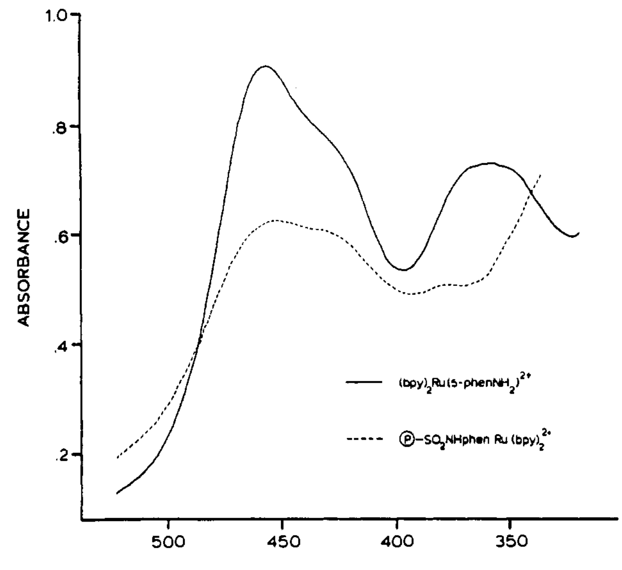

Figure 3. Visible absorption spectra for $(bpy)_2Ru(5\text{-}phenNH_2)^{2+}$ dissolved in CH_3CN (—) and for $(bpy)_2Ru(5\text{-}phenNH_2)^{2+}$ incorporated by soaking into a *p*-chlorosulfonated polystyrene coated glass slide (- - -).

is somewhat broadened compared to the solution spectrum.

The similarity between the spectra of the unincorporated and the incorporated complex suggests that the incorporation process involves reaction at only the amine group, leaving the rest of the ruthenium complex unaffected. The conversion of the amine substituent into a more electron-withdrawing sulfonamide substituent can account for the blue shift in the absorption maximum for the MLCT band. MLCT bands for polypyridyl complexes of Ru^{II} are sensitive to substituents on the bound ligands; e.g., λ_{max} for $(bpy)_2Ru(5\text{-}phenNO_2)^{2+}$ (5-phenNO$_2$ is 5-nitro-1,10-phenanthroline) in CH_3CN occurs at 448 nm.[20] The disappearance of the absorption band at 360 nm in the film, which is observed in the free amine complex, is also consistent with an amine → sulfonamide conversion since the band at 360 nm is thought to arise from a $\pi^* \leftarrow n$ transition involving the lone pair on the amine nitrogen.[24]

Co-incorporation. Co-incorporation of (Cp)Fe(Cp-4-phenNH$_2$) and $(bpy)_2Ru(5\text{-}phenNH_2)^{2+}$ was described in a previous section. The ability to achieve co-incorporation of different redox sites within the films is a general phenomenon. In order to obtain approximately equal concentrations of co-incorporated redox sites, it is necessary that they be of approximately the same volume and of the same charge type and that they have the same number of potential NH_2 binding sites in the ligands. For example, when an electrode film is soaked in acetonitrile solution containing (Cp)Fe(Cp-4-phNH$_2$) and *N*,*N*-dimethyl-*p*-phenylenediamine, both at 3 mM, redox couples appear at +0.55 and +0.36 V for the incorporated $DMPD^{+/0}$ and $(Cp)Fe(Cp\text{-}4\text{-}phNH)^{+/0}$ couples, respectively (Figure 4B). Similarly, as shown in Figure 4A, the cationic complexes $Ru(5\text{-}phenNH_2)_3{}^{2+}$ and $Fe(5\text{-}phenNH_2)_3{}^{2+}$ can be co-incorporated by reductively cycling the potential of a coated electrode through the 1,10-phenanthroline reduction region (−1.0 to −1.5 V) in 0.1 M TEAP/CH_3CN, 1 mM in both complexes, as shown by the appearance of waves at $E_{1/2}$ +1.50 and +1.24 V for the $Ru(5\text{-}phenNH_2)_3{}^{3+/2+}$ and $Fe(5\text{-}phenNH_2)_3{}^{3+/2+}$ couples, respectively.

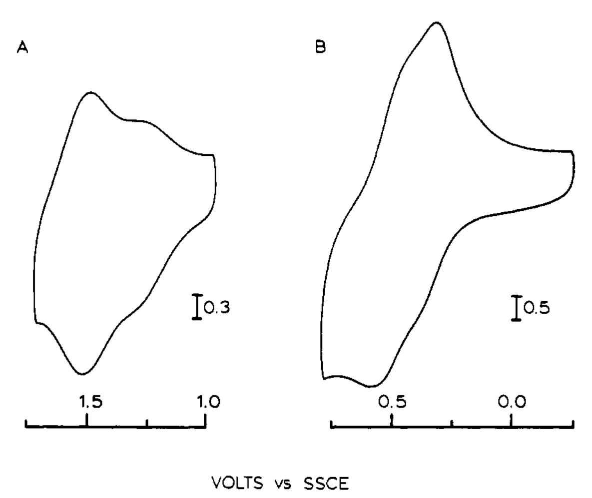

Figure 4. Cyclic voltammograms of a platinum electrode coated with *p*-chlorosulfonated polystyrene (0.01 mL of a polymer solution containing 1.11 × 10^{-5} g/mL—see Experimental Section) that was (A) cycled 10 times at 200 mV/s from −1.0 to −1.5 V in a 0.1 M TEAP/CH_3CN solution containing 1 mM $Ru(5\text{-}phenNH_2)_3{}^{2+}$ and 1 mM $Fe(5\text{-}phenNH_2)_3{}^{2+}$, rinsed with CH_3CN, and placed in a fresh 0.1 M TEAP/CH_3CN solution or (B) soaked for 30 s in an acetonitrile solution containing 3 mM (Cp)Fe(Cp-4-phNH$_2$) and 3 mM *N*,*N′*-dimethyl-*p*-phenylenediamine, rinsed with CH_3CN, and placed in a fresh 0.1 M TEAP/CH_3CN solution. The scan rate is 200 mV/s. The current scales are shown below the voltammograms in μA.

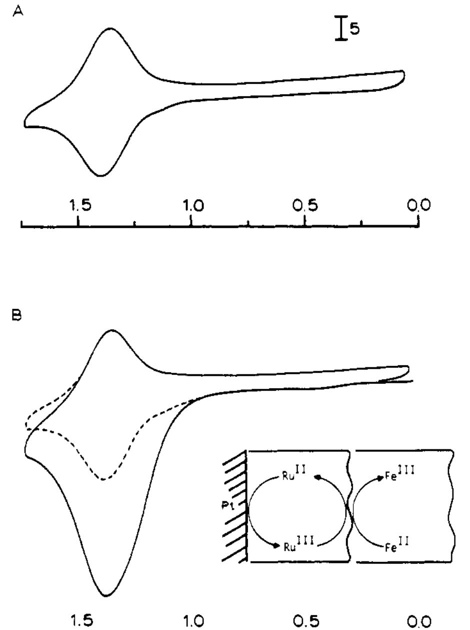

Figure 5. (A) Cyclic voltammogram of a platinum electrode coated with *p*-chlorosulfonated polystyrene (0.03 mL of a polymer solution containing 1.11 × 10^{-5} g/mL—see Experimental Section) that was cycled 10 times at 200 mV/s from −1.0 to −1.5 V in a 0.1 M TEAP/CH_3CN solution containing 3 mM $(bpy)Ru(5\text{-}phenNH_2)_2{}^{2+}$, rinsed with CH_3CN, and placed in a fresh 0.1 M TEAP/CH_3CN solution and (B) initial (—) and subsequent (- - -) cyclic voltammograms (+0.1 → +1.7 → +0.1 V) of the electrode in (A) coated with a second layer of *p*-chlorosulfonated polystyrene (0.02 mL of the same polymer solution used above) that was soaked for 5 min in a 3 mM (Cp)Fe(Cp-4-phNH$_2$)/CH_3CN solution, rinsed with CH_3CN, and placed in a fresh 0.1 M TEAP/CH_3CN solution. The current scale for both (A) and (B) is shown in the upper right-hand corner in μA. The scan rate is 200 mV/s.

Bilayer Films. The chlorosulfonated polystyrene films can be used to prepare bilayers. For example, a platinum electrode was coated with *p*-chlorosulfonated polystyrene (0.03 mL of a *p*-chlorosulfonated polystyrene solution containing 1.11 × 10^{-5} g/mL of polymer) and $(bpy)Ru(5\text{-}phenNH_2)_2{}^{2+}$ was in-

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[24] This assignment is consistent with the observation that the absorption band at 360 nm disappears when the amine group is protonated.[20]

troduced by reductive cycling, giving $E^{\circ\prime}_{surf} = +1.37$ V and $\Gamma_{app} = 1.1 \times 10^{-9}$ mol/cm^2 (Figure 5A). On top of the first film was evaporated another polystyrene film (0.02 mL of the same polymer solution), which was subsequently impregnated with (Cp)Fe(Cp-4-phNH$_2$) by soaking the electrode for 5 min in a 3 mM solution. The electrochemical response of the resulting bilayer film electrode was obtained by cycling the potential from +0.1 to +1.7 to +0.1 V. As shown by the solid line in Figure 5B, an electrochemical response for the (Cp)Fe(Cp-4-phNH-SO$_2$-) sites in the outer film ($E^{\circ\prime}_{surf} = +0.36$ V) is not observed in the initial voltammogram because the outer film is insulated from the electrode by the inner film, which is electrochemically inactive in the potential region for the [(Cp)Fe(Cp-4-phNH-SO$_2$-)]$^{+/0}$ couple. However, as the potential for oxidation of the inner film is approached (ca. 1 V), a three-stage pathway for oxidizing the outer film becomes available: (1) oxidation of Ru^{II} to Ru^{III} in the inner film at the electrode, (2) electron-hole migration through the inner film to the inner-film/outer-film interface by electron hopping between sites, and (3) oxidation of Fe^{II} to Fe^{III} in the outer film, which is favored by ca. 1 V. The existence of the pathway is shown by the current enhancement observed for the oxidative wave for the Ru$^{II/III}$ couple in the inner film. Re-reduction of the oxidized ferrocene sites in the outer film is not observed electrochemically because the inner-film to outer-film electron-transfer reaction, (bpy)Ru^{II}(5-phenNH-SO$_2$-)$_2^{2+}$ + (Cp)Fe(Cp-4-phNH-SO$_2$-)$^+$ $\rightarrow$ (bpy)Ru^{III}(5-phenNH-SO$_2$-)$_2^{3+}$ + (Cp)Fe(Cp-4-phNH-SO$_2$-), is unfavorable thermodynamically by ca. 1 V.

A bilayer electrode was also fabricated by electropolymerizing (bpy)$_2$Ru(vpy)$_2^{2+}$ (vpy is 4-vinylpyridine) onto a platinum electrode ($E^{\circ\prime}_{surf} = +1.23$ V; $\Gamma_{app} = 9.5 \times 10^{-10}$ mol/cm^2),[3a] which was subsequently coated with a *p*-chlorosulfonated polystyrene film and which was, in turn, impregnated with (Cp)Fe(Cp-4-phNH$_2$). A bilayer response much like that in Figure 6 was also obtained.

Selectivity and Directed Charge Transfer. As observed earlier with films prepared by reductive electropolymerization, the chlorosulfonated films containing redox sites can provide a basis for selective oxidation of couples in the external solution and act as a medium for indirect electron transfer from the external solution to the electrode. Selectivity was demonstrated at a film extensively impregnated with (bpy)Ru(5-phenNH)$_2^{2+}$ by reductive cycling ($E^{\circ\prime}_{surf} = +1.37$ V; $\Gamma_{app} = 6.2 \times 10^{-10}$ mol/cm^2). When the potential at the electrode was cycled from −0.1 to +1.1 V in a 0.1 M TEAP/CH$_3$CN solution containing 5 mM ferrocene ($E^{\circ\prime}_{soln} = +0.40$ V) and 5 mM (bpy)$_2$Ru(bpy)Cl$^+$ ($E^{\circ\prime}_{soln} = +0.78$ V), an electrochemical response for the diffusion of ferrocene through the film was observed but the magnitude of the diffusional wave for the (bpy)$_2$Ru(vpy)Cl$^{2+/+}$ couple was greatly reduced (see Figure 6B). As a consequence, because of the difference in the diffusional characteristics of the two reagents within the polycationic films, the ferrocene derivative can be selectively oxidized in the presence of the ruthenium cation at potentials where both reagents are oxidized at a bare electrode (see Figure 6A).

With thicker films, diffusion through the films is slow and indirect electron transfer can be observed. For example, in a film impregnated with (bpy)Ru(5-phenNH)$_2^{2+}$ ($E^{\circ\prime}_{surf}$ = +1.37 V; $\Gamma_{app} = 1.6 \times 10^{-9}$ mol/cm^2; Figure 6A) cycling from −0.1 to +1.7 V in a 0.1 M TEAP/CH$_3$CN solution containing 5 mM (bpy)$_2$Ru(vpy)Cl$^+$ ($E^{\circ\prime}_{soln} = +0.78$ V) gives no electrochemical response for diffusion of the redox couple through the film (see Figure 6C), but a sevenfold enhancement of the current for the Ru(III)/Ru(II) wave for the film-based couple is observed. The explanation is that oxidation of (bpy)$_2$Ru(vpy)Cl$^+$ can occur at higher potentials by electron transfer through the film. As in the bilayers, the net electron transfer is unidirectional. Electrons flow only from the external solution to the electrode because the reverse film/solution reaction, (bpy)Ru(5-phenNH-SO$_2$-)$_2^{2+}$ + (bpy)$_2$Ru(vpy)Cl^{2+} $\rightarrow$ (bpy)Ru(5-phenNH-SO$_2$-)$_2^{3+}$ + (bpy)$_2$Ru(vpy)Cl$^+$, is unfavorable by 0.6 V.

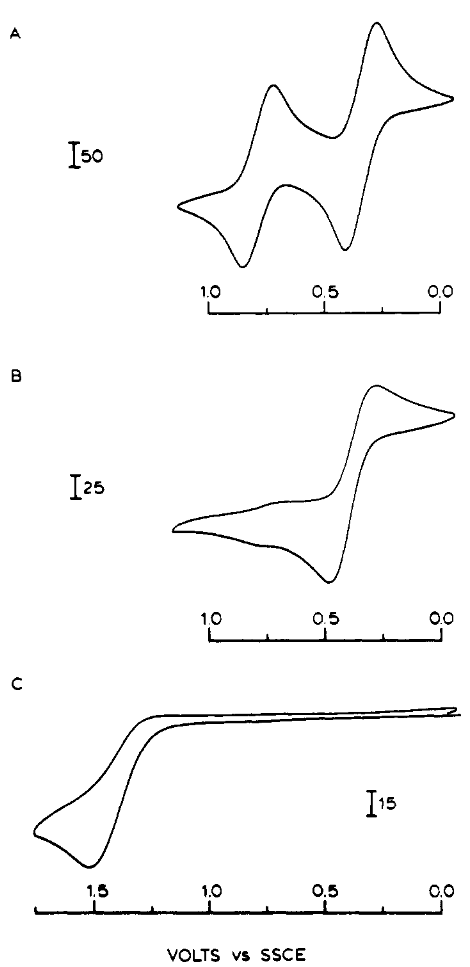
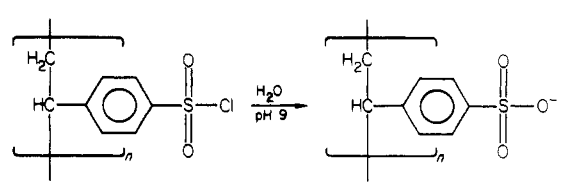


Figure 6. (A) Cyclic voltammogram of ferrocene (5 × 10^{-3} M) and (bpy)$_2$Ru(vpy)Cl$^+$ (5 × 10^{-3} M) in a 0.1 M TEAP/CH$_3$CN solution at a bare platinum electrode. (B) Cyclic voltammogram as in (A) except that the electrode was coated with *p*-chlorosulfonated polystyrene (0.04 mL of a polymer solution containing 1.11 × 10^{-5} g/mL—see Experimental Section) that was impregnated with (bpy)Ru(5-phenNH$_2$)$_2^{2+}$ ($\Gamma_{app} = 6.2 \times 10^{-10}$ mol/cm^2). (C) Initial cyclic voltammogram of (bpy)$_2$Ru(vpy)Cl$^+$ (5 × 10^{-3} M) in a 0.1 M TEAP/CH$_3$CN solution at the same electrode in (A) coated with *p*-chlorosulfonated polystyrene (0.01 mL of a polymer solution containing 6.67 × 10^{-4} g/mL—see Experimental Section) that was impregnated with (bpy)Ru(5-phenNH$_2$)$_2^{2+}$ ($\Gamma_{app} = 1.6 \times 10^{-9}$ mol/cm^2). The current scales in μA are shown to the left of the voltammograms in (A) and (B) and below the voltammogram in (C). The scan rate is 200 mV/s.

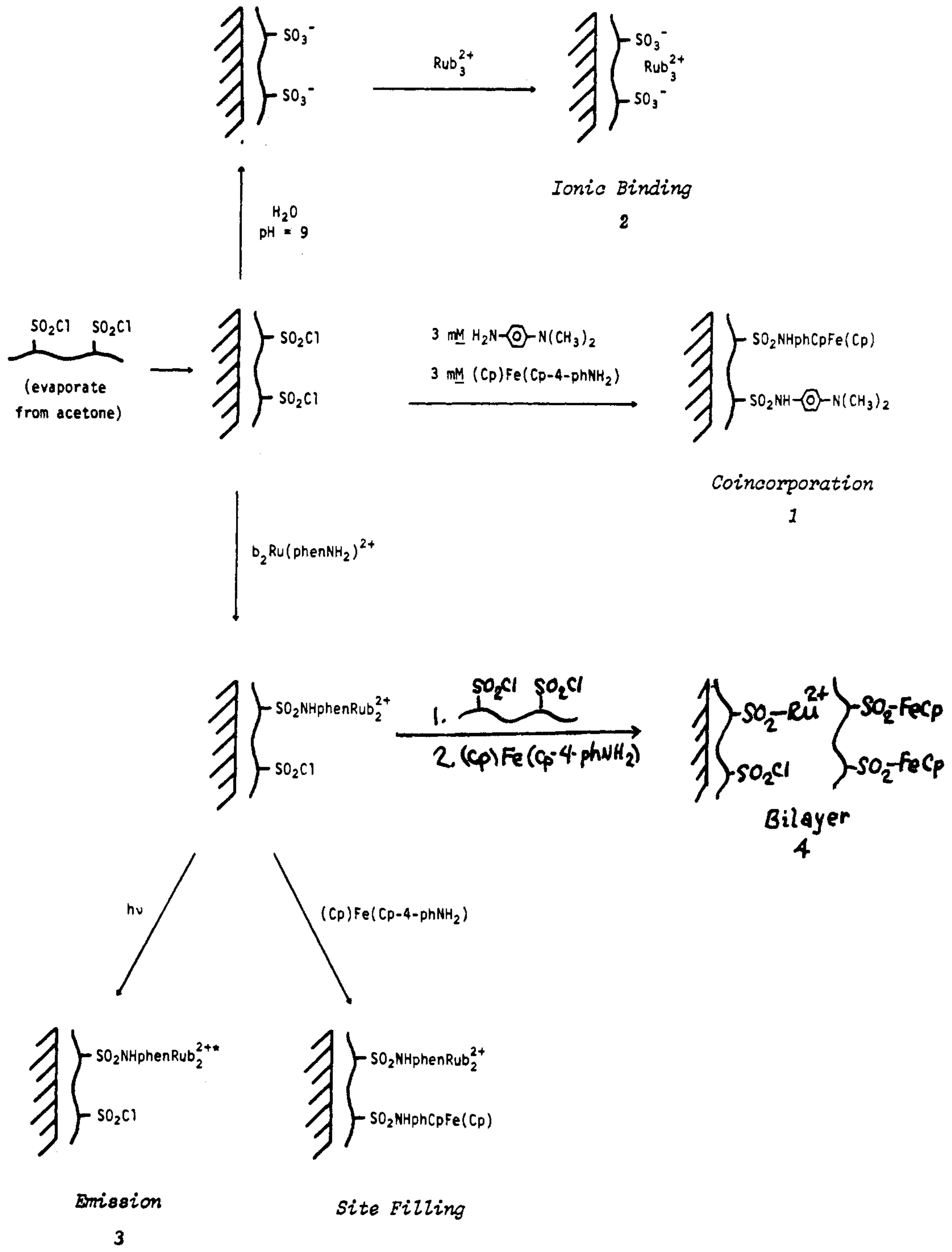
Hydrolysis and Ionic Binding. Exposure of the *p*-chlorosulfonated films to aqueous solutions buffered at pH 9 leads to polyanionic films by hydrolysis (eq 2), into which cations



(2)

like Ru(bpy)$_3^{2+}$ can be incorporated by ion exchange. For example, a film was prepared from 0.01 mL of a polymer solution containing 6.67 × 10^{-4} g/mL of polymer and hydrolyzed by soaking in an aqueous solution saturated in borax

Scheme I



buffer (pH 9). Soaking the resulting film for several hours in a 0.01 M $Ru(bpy)_3^{2+}/CH_3CN$ solution gave rise to the incorporation of $Ru(bpy)_3^{2+}$ as shown by an orange luminescence when the film was irradiated with UV light. In 0.1 M $(NEt_4)ClO_4$ an electrochemical response was obtained at $E^{\circ\prime}_{surf} = +1.23$ V, $\Gamma_{app} = 1.2 \times 10^{-10}$ mol/cm^2, both of which agree favorably with $Ru(bpy)_3^{2+}$ incorporated into Nafion films.[7a,b]

Emission. One desirable feature of the incorporation procedure described here is that it does not alter in a significant way the inner coordination spheres of the attached redox sites. An advantage offered for several of the polypyridyl complexes listed in Tables I and II is that they are relatively strong emitters when irradiated with UV light in solution, and that property is retained when the chromophores are incorporated into *p*-chlorosulfonated polystyrene films. In films on platinum or glassy-carbon electrodes, emission can only be observed for thicker films. A noticeable emission is not observed for thin films, presumably because of excited-state quenching by the electrode.[25]

An emission spectrum of $(bpy)_2Ru(5\text{-}phenNH)^{2+}$ in a film on a platinum flag electrode has $\lambda_{max}^{em} = 610$ nm. The excited-state lifetime is ca. 600 ns in air in a dry film. The emission is quenched when the redox sites are oxidized electrochemically or chemically to Ru^{III} as shown by the loss of emission when a film of medium thickness containing $(bpy)_2Ru(5\text{-}phenNH_2)^{2+}$ was potentiostated at +1.6 V in an 0.1 M $TEAP/CH_3CN$ solution for ca. 30 min. Complete quenching also occurs by soaking a similarly prepared electrode

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for ca. 5 min. in a 0.1 M $HClO_4/H_2O$ solution containing excess Ce^{IV}. Partial regeneration of the emission occurs on re-reduction of the redox sites in the film to Ru^{II} by electrochemical reduction—potentiostating at +0.5 V for ca. 30 min—or by soaking in a solution containing a chemical reductant—ca. 15 min in a 0.1 M $TEAP/CH_3CN$ solution containing excess $(bpy)_2Ru(py)Cl^+$ ($E°'_{soln} = +0.79$ V).

Conclusions

The results described here show that a variety of reagents can be incorporated into *p*-chlorosulfonated polystyrene films if the reagnet contains an appropriate site, preferably an amine group, because of the stability of the resulting sulfonamide link. In addition, the polystyrene films can be cast onto virtually any surface by evaporation. As a consequence, the results described here are notable since *they offer a broadly based, general approach to the controlled incorporation of redox sites and combinations of redox sites into the electrode–film interface.* As shown by electrochemical, spectral, and excited-state measurements, the bound redox sites retain many of the properties of their solution analogues.

Because of their properties, the films have found use in a number of applications, some of which are shown in summary form in Scheme I and which include the following: (1) the co-incorporation of two redox couples and of a potential excited state/quencher pair, $[(bpy)_2Ru(5\text{-phenNH-})^{2+}]/[(CH_3)_2(NC_6H_4NH\text{-})]$, (2) hydrolysis and subsequent binding of cationic complexes by ion exchange, (3) the preparation of films containing relatively strongly emitting excited states, and (4) the preparation of redox bilayers.

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Heteronuclear NMR Studies of Cobalamins. 2. ^{13}C and ^{31}P NMR Studies of $[^{13}C]$Cyanocobalamin[1]

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NMR observations of $[^{13}C]$cyanocobalamin (cyano-labeled) in sulfuric acid–water mixtures at 25 °C show that both the base-on and base-off species may be observed, and quantitated, in both ^{13}C and ^{31}P NMR spectra. Observation of the ^{13}C resonance of the base-off species has permitted, for the first time, assignment of the two ^{13}C resonances observed upon addition of 1 equiv of $K^{13}CN$ to diaquocobinamide and, by analogy, the two resonances observed upon addition of 2 equiv of $K^{13}CN$ to both diaquocobinamide and aquocobalamin. Correlation of the base-off ^{31}P chemical shifts of cyanocobalamin with a generalized acidity function for sulfuric acid–water mixtures leads to values of −1.57 and −0.04 for the two macroscopic pK_a's for phosphodiester deprotonation. A similar study of methylcobalamin gave values of −1.59 and −0.01 for these two macroscopic pK_a's. An upfield shift of 35.68 Hz in the ^{31}P chemical shift upon displacement of the axial base of cyanocobalamin by protonation is observed and attributed to changes in phosphodiester conformation upon base displacement. Analysis of the change in the relative amounts of base-on and base-off species as a function of acidity shows that the base-on–base-off pK_a of cyanocobalamin is relatively independent of the state of protonation of the phosphodiester moieties and has a value of 0.11 ± 0.01. At higher acidities a change in the ^{13}C chemical shift of base-off $[^{13}C]$cyanocobalamin is observed, which can be attributed either to a reversible protonation of coordinated cyanide ($pK_a = -1.87$) or to reversible loss of water from the lower coordination position due to the depressed activity of water at such acidities.

Introduction

The coenzymatic forms of vitamin B_{12} are well-known to be involved in the catalysis of about 15 enzymic reactions in various organisms, including the 1,2-intramolecular rearrangements catalyzed by 5′-deoxyadenosylcobalamin (AdoCbl) requiring enzymes[2–5] and the methyl-transfer reactions catalyzed by methylcobalamin requiring enzymes.[2,5,6] As is the case with most coenzymes, the intimate details of the structure of cobalamins, well-known from X-ray crystallographic studies,[7–10] are difficult to relate directly to what is known of the function of cobalamin coenzymes.

As a sensitive probe of solution structure, nuclear magnetic resonance spectroscopy offers the possibility of understanding both the structure of cobalamins in functioning environments and the nature of the carbon–cobalt bond, the unique feature of the cobalamin coenzymes. Given the size of the structures, the ^1H NMR spectra of cobalamins are, of course, quite complex. Nonetheless, significant progress has been made in assigning the proton resonances and probing solution structure and dynamics via ^1H NMR,[11–16] particularly at very high field,

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