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Chemical Gating of a Molecular Bilayer Rectifier at Clay-Modified Electrodes

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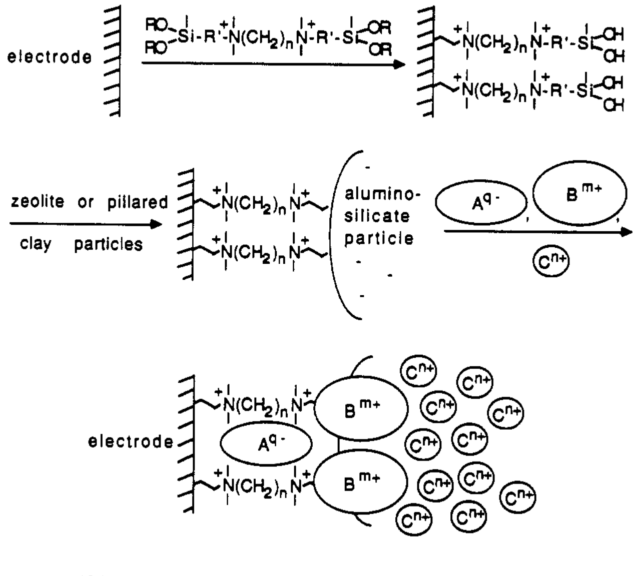
Conductive SnO_2 electrodes modified with a 1-2 monolayer thick coating of a cationic silane bind $Al_{13}O_4(OH)_{28}{}^{3+}$-pillared montmorillonite. The cationic polymer provides binding sites, which are electrochemically accessible to the SnO_2 electrode, for iron(III) tetrakis(4-sulfonatophenyl)porphyrin ($FeTPPS^{3-}$) anions. Electroactive cations such as $Ru(NH_3)_6{}^{3+}$ and $Os(bpy)_2pyCl^+$ adhere to the clay surface, at sites too remote for direct electron transfer with the electrode, and oxidation/reduction of these ions is mediated by $FeTPPS^{3-}$. The axial ligation of the metalloporphyrin anions changes reversibly with solution pH, and in weakly basic solutions electron transfer between these anions and the electrode is very slow. Cyclic voltammetry and UV-visible spectroscopy show that the $FeTPPS^{3-}$ contained within the silane film behaves as a pH-sensitive gate for electron transfer to and from the cations bound to the clay surface. When the formal potential of the clay-bound cation is sufficiently different from that of $FeTPPS^{3-}$, proton-gated current rectification can be observed electrochemically.

Introduction

Electrode surfaces coated with monolayer and polymeric films have been studied extensively as molecular analogues of electronic device elements. Langmuir-Blodgett deposition of electron donor-acceptor amphiphiles,[1,2] layering of redox- or electronically conducting-polymer films,[3-8] and deposition of single-component films onto two or more closely spaced electrodes[9] have been explored as means for creating molecular assemblies with diode- or transistor-like current-voltage characteristics. Previously, we have reported the electrochemistry and photoresponse of zeolite- and pillared clay-modified electrodes (CME), in which aluminosilicate particles are bound to an oxide electrode surface by cationic polymers, which can themselves bind redox-active anions.[10,11] These cationic polymer/anionic aluminosilicate bilayer films offer the advantage of self-assembly of various molecular "devices" via simple ion-exchange reactions. With the appropriate combination of electroactive anions and cations, chains of redox-active molecules can be created, as shown in Scheme I. Trilayer assemblies are formed by combining electroactive anions with multiply charged cations B^{m+} and C^{n+}, which are respectively size-excluded from and intercalated into the bulk of the microporous aluminosilicate. Bilayers may also be generated from a combination of only two ions, such as A^{q-} and B^{m+}. Depending on the identity of the electroactive species, these electrodes display the characteristics of diodes[10] and/or photodiodes.[11]

Scheme I. Fabrication of a Cationic Polymer/Aluminosilicate Bilayer Electrode and Self-Assembly of Electroactive Layers via Ion-Exchange



Rectifying electrodes based on redox polymer bilayers,[3] and similar two-terminal devices based on microelectrode arrays[12]

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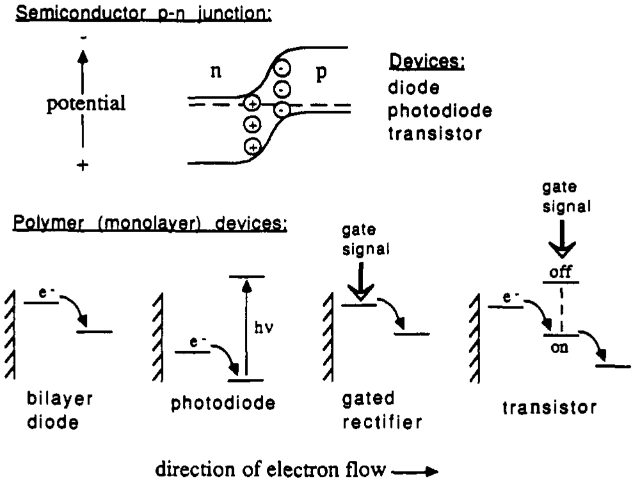
Scheme II. Semiconductor-Based and Molecular Electronic Devices



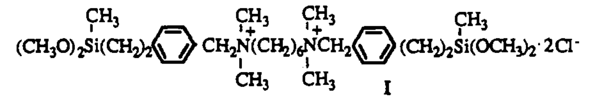
and donor–spacer–acceptor monolayers,[1,2] operate as electrochemical analogues of semiconductor p–n junctions, as illustrated in Scheme II. With the bilayer electrode potential poised between the formal potentials of the two molecular layers, at equilibrium the inner layer is oxidized and the outer layer is reduced. Current may pass easily in the "forward bias" direction, by making the inner layer more negative and the outer layer more positive, provided the applied voltage (in a two-terminal device) approaches the difference in formal potentials of the two layers. Current flow in the "reverse bias" direction is inhibited by the built-in electrochemical potential gradient at the bilayer interface, much as it is inhibited in the p–n junction device by a built-in electric field. This analogy may be extended as well to that of bilayer molecular devices containing photoactive components,[11,13] also shown in Scheme II, with p–n junction photodiodes.

After diodes and photodiodes, the next level of complexity in molecular devices is switching in response to stimulus of an electrochemical "gate". This problem has been attacked in a number of ways. Wrighton and co-workers have shown that switching of conducting polymers and some metal oxides between conductive and nonconductive states can form the basis of transistor-like microelectrode arrays.[9] While the response time of these electrochemical devices is too slow for conventional transistor-based applications, their ability to interface with chemical systems nevertheless makes them quite interesting as sensor elements. Since electrochemical switching in these devices is coupled both to the motion of nonelectroactive counterions (such as H^+) and to electroactive agents that poise the "gate" potential, they respond to either kind of reagent. Ion-gated electrodes based on structural changes in insulating lipid multilayers[14,15] and clays[16] have also been described. In this case a nonelectroactive analyte, such as an alkali or alkali earth cation, induces an electrochemical response. An interesting question, addressed in part in this paper, is whether or not chemically responsive gated rectifiers or transistors might also be fabricated from layers of redox-active molecules, according to the designs shown in Scheme II. In these examples, one layer must be switched on and off (i.e., made a better or poorer conductor) in response to an externally applied chemical signal. If this "gate" layer is a redox-active ion or redox polymer, one might imagine switching by ligation of a nonelectroactive molecule that modulates either its electron self-exchange rate constant or its formal potential. Changing the self-exchange (and therefore cross-exchange) rate should allow switching of either a bilayer or trilayer device, whereas modulation of the formal potential of the middle layer should effect switching in the trilayer case.

The electron-transfer properties of metalloporphyrin complexes have been extensively reported in the literature.[17] The formal potential, the electrochemical reversibility, as well as the heterogeneous rate constant for metal-centered redox reactions are dependent on the nature of the axial ligands. The pH dependence of the electrochemical characteristics of iron porphyrins in particular makes them interesting candidates as gate molecules for molecular bilayer and trilayer devices. In aqueous solutions, in the presence of poorly coordinating electrolytes, their axial ligands are represented as HO^- and/or H_2O, depending upon the solution pH. We report in this paper the reversible chemical gating of bilayer rectifier CME's, based on the axial ligation chemistry of iron porphyrin anions.

Experimental Section

Materials. Texas montmorillonite (STx-1) was obtained from the Source Clay Minerals Repository (University of Missouri, Columbia, MO). It was ion-exchanged and pillared as described previously.[11] Hexaammineruthenium (III) chloride, obtained from Aldrich Chemical Co., and iron(III) tetrakis(4-sulfonatophenyl)porphyrin (trisodium salt), obtained from Midcentury Chemicals, Posen, IL, were used as received. $[Os(bpy)_2pyCl]ClO_4$ (bpy = 2,2′-bipyridine, py = pyridine) was prepared and purified by the method of Buckingham et al.[18] Acetonitrile (HPLC grade) was freshly distilled from P_2O_5 before use. The silane compound I used to couple the pillared clay particles to the electrode surface was available from previous experiments.[10,11] All other chemicals were of reagent grade quality and were obtained from commercial sources.


$$(CH_3O)_2\overset{CH_3}{Si}(CH_2)_2C_6H_4CH_2\overset{CH_3}{\underset{CH_3}{\overset{+}{N}}}(CH_2)_6\overset{CH_3}{\underset{CH_3}{\overset{+}{N}}}CH_2C_6H_4(CH_2)_2\overset{CH_3}{Si}(OCH_3)_2\cdot 2Cl^-$$

I

Electrode Preparation and Ion Exchange. Conductive SnO_2-on-glass (100 Ω/square) was obtained from Delta Technologies, Ltd. The preparation and modification of electrodes with pillared montmorillonite have been described previously.[11] Prior to ion-exchange with electroactive ions, the cationic polymer contains chloride counterions, and the clay is in the sodium form. Ion exchange was carried out by immersing the electrode for several hours in unbuffered, aqueous solutions of compounds containing the appropriate ions: $Ru(NH_3)_6Cl_3$ (1 mM), $[Os(bpy)_2pyCl]ClO_4$ (1 mM), and $Na_3FeTPPS$ (0.1 mM). The degree of ion exchange of $Ru(NH)_3{}^{3+}$ and $Os(bpy)_2pyCl^+$ in the pillared clay was determined by exposing bulk samples to excess quantities of 1 mM solutions of the appropriate salts and then determining the concentration in the supernatant by UV–visible spectroscopy.

Apparatus. Cyclic voltammetry experiments were done with an EG&G/PAR Model 175 universal programmer and a Model 363 potentiostat/galvanostat. Voltammograms were recorded on a Soltec VP-6423S X-Y recorder. Electrochemical experiments were carried out in a one-compartment, three-electrode cell. Aqueous solutions were 10 mM acetic acid:sodium acetate (HAc:NaAc = 1:1) or pure sodium acetate in 18.3 MΩ·cm deionized water and were thoroughly deaerated with nitrogen prior to the experiments. All potentials are referred to the

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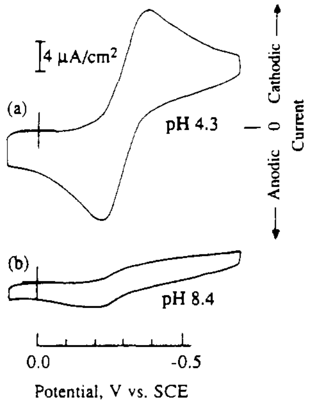

Figure 1. Cyclic voltammetry of 0.4 mM FeTPPS^4 in aqueous 10 mM (a) HAc/NaAc, pH 4.3, and (b) NaAc, pH 8.4 (SnO_2 electrode, scan rate = 50 mV/s).

saturated calomel electrode (SCE) and are uncorrected for *IR* drop and liquid-junction potentials. UV–visible spectra of transparent SnO_2/glass electrodes were obtained on a Hewlett Packard 8452A diode array spectrophotometer. Diffuse-reflectance UV–vis spectra were taken with a DMS-300 instrument equipped with an integrating sphere attachment.

Results and Discussion

Cyclic Voltammetry of Polymer/Clay Bilayer Electrodes. The pH dependence of the electrochemical reactions of $FeTPPS^{3-/4-}$ at a bare SnO_2 electrode can be seen in Figure 1. In HAc/NaAc solution (pH 4.3), $FeTPPS^{3-/4-}$ shows quasireversible oxidation/reduction waves, indicating that the heterogeneous electron-transfer reaction 1 is relatively fast. In a solution containing 10 mM NaAc as the electrolyte (pH 8.4), reaction 1 is kinetically slow, and the peak current at an SnO_2 electrode is reduced dramatically. In metalloporphyrins such as $FeTPPS^{3-}$, the porphyrin ring is essentially planar and ligates the iron atom through its four nitrogen atoms. In the presence of electron donor ligands, the iron atom can add two further axial ligands above and below the plane of the ring. These axial ligands may affect both the formal potential and the kinetics of the metal-centered oxidation/reduction. In acidic aqueous media and in the absence of more strongly coordinating molecules, the axial ligands for $FeTPPS^{3-}$ are two H_2O molecules, whereas in weakly basic media, the ligands are one H_2O and one OH^-. Thus the electrode response in the two media is quite different.[19]

$$FeTPPS^{3-} + e^- = FeTPPS^{4-} \qquad (1)$$

Shown in Figure 2 is a typical cyclic voltammogram for surface-confined $FeTPPS^{3-/4-}$ at a CME prepared as outlined in Scheme I. In the acidic HAc/NaAc buffer (trace a), small but discernible cathodic and anodic peaks at –0.4 and –0.2 V vs SCE are attributed to reduction and oxidation of silane polymer-bound $FeTPPS^{3-/4-}$. Depending on preparation conditions, the thickness of the silane polymer is typically 1–4 monolayer,[10] and the surface coverage of $FeTPPS^{3-/4-}$ obtained by integrating the current passed in Figure 2a is ca. 4×10^{-11} equiv/cm², consistent with ion-exchange into a film of roughly monolayer coverage. When the same electrode is cycled in NaAc at pH 8.4 (trace b), the corresponding waves are essentially absent. The lost electroactivity is almost completely recovered when the electrode is again examined in HAc/NaAc (trace c), showing that the decrease in peak current density in weakly basic solution is due to a reversible change, such as protonation/deprotonation of the axial OH^- ligand, and not to decomposition of the $FeTPPS^{3-/4-}$.

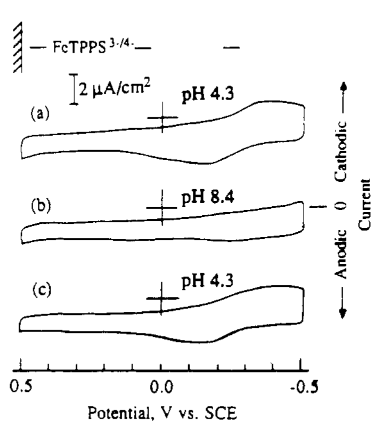

Figure 2. Cyclic voltammetry of a CME prepared according to Scheme I and ion-exchanged with $FeTPPS^{3-}$ in 10 mM (a) HAc/NaAc, pH 4.3, (b) NaAc, pH 8.4, and (c) again in HAc/NaAc (scan rate 50 mV/s).

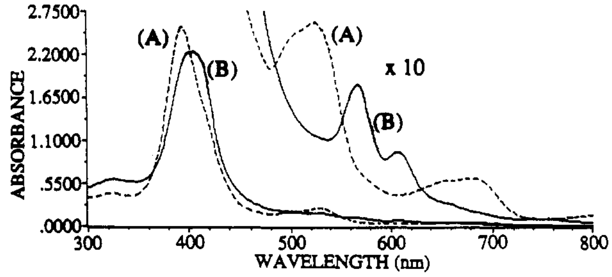

Figure 3. UV–visible spectra of 1.4×10^{-5} M $FeTPPS^{3-}$ in (A) 10 mM HAc/NaAc and (B) 10 mM NaAc. Reference spectra were the same solutions without $FeTPPS^{3-}$.

The pH dependence of the current response at the CME is quite similar to that of $FeTPPS^{3-/4-}$ in fluid solution and is therefore attributed to the same changes in axial ligation. We note that the attenuation of cyclic voltammetric waves at high pH can be interpreted in terms of slowing of the kinetics for heterogeneous charge transfer and not to shifting of the formal potential of the $FeTPPS^{3-/4-}$ couple. Changes in the UV–visible spectrum of the complex, both in the Soret and Q-band regions, also reflect reversible protonation/deprotonation of an axial hydroxide/water ligand (Figure 3).

Cyclic voltammetric curves for a CME equilibrated with $Ru(NH_3)_6^{3+}$ and no other electroactive ions are shown in Figure 4a. While heterogeneous electron transfer between $Ru(NH_3)_6^{3+/2+}$ and electrode surfaces is normally quite facile at either pH 4.3 or 8.4, in this case no electroactivity is observed either in HAc/NaAc or NaAc. Under these conditions the loading of $Ru(NH_3)_6^{3+}$ (determined by exchanging a bulk sample of pillared montmorillonite with excess 1.0 mM $Ru(NH_3)_6^{3+}$) is 6×10^{-5} mol/gram, consistent with occupation of sites on both the internal and external surfaces of the pillared clay. The $Ru(NH_3)_6^{3+/2+}$ ions that are ion-exchanged into and onto the clay are held at sites sufficiently distant that direct electron transfer between $Ru(NH_3)_6^{3+/2+}$ and the electrode surface does not occur. Nonelectroactive acetate ions situated in the cationic silane layer close to the electrode surface cannot mediate electron transfer to the $Ru(NH_3)_6^{3+/2+}$ couple, and the oxidation and reduction of clay-bound $Ru(NH_3)_6^{3+/2+}$ are therefore extremely slow under these conditions.

When this electrode is exchanged with both $Ru(NH_3)_6^{3+}$ and $FeTPPS^{3-}$, significantly larger currents are observed than with either ion alone, as shown in Figure 4b–d. In weakly acidic HAc/NaAc (trace b), because the formal potentials of $Ru(NH_3)_6^{3+/2+}$ and $FeTPPS^{3-/4-}$ are nearly coincident, mediated oxidation and reduction of $Ru(NH_3)_6^{3+/2+}$ by $FeTPPS^{3-/4-}$ can both occur, according to the following mechanism:

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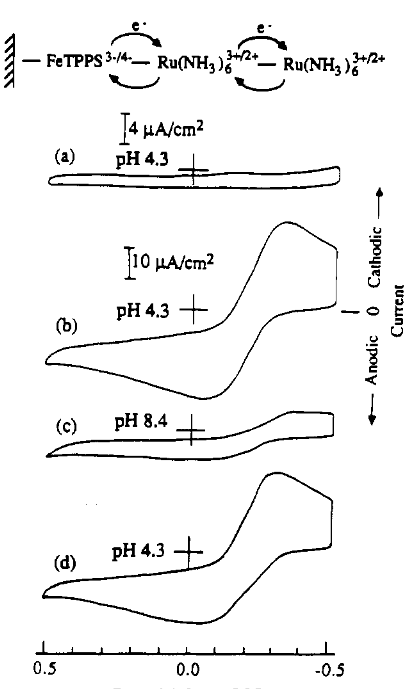

Figure 4. (a) Cyclic voltammetry of a CME ion-exchanged with $Ru(NH_3)_6^{3+}$ in 10 mM HAc/NaAc, pH 4.3. (b–d) Cyclic voltammetry of a CME ion-exchanged with both $Ru(NH_3)_6^{3+}$ and $FeTPPS^{2-}$ in 10 mM (b) HAc/NaAc, (c) NaAc, and (d) again in HAc/NaA c (scan rate = 50 mV/s). Scans were initiated at –0.5 V.

anodic process:

$$FeTPPS^{4-} \rightarrow FeTPPS^{3-} + e^- \quad (2)$$

$$FeTPPS^{3-} + Ru(NH_3)_6^{2+} \rightarrow FeTPPS^{4-} + Ru(NH_3)_6^{3+} \quad (3)$$

cathodic process:

$$FeTPPS^{3-} + e^- \rightarrow FeTPPS^{4-} \quad (4)$$

$$FeTPPS^{4-} + Ru(NH_3)_6^{3+} \rightarrow FeTPPS^{3-} + Ru(NH_3)_6^{2+} \quad (5)$$

The large current enhancement, relative to the $FeTPPS^{3-/4-}$ CME shown in Figure 2, arises because of the much higher loading of $Ru(NH_3)_6^{3+}$, which is made accessible to the electrode surface via mediation reactions 2–5.

Proton-Gating of the Electrochemical Response. Interestingly, both the anodic and cathodic peaks are significantly suppressed if the cyclic voltammetry is performed in weakly basic NaAc solution (trace c in Figure 4). Since the electrochemistry of $Ru(NH_3)_6^{3+/2+}$ is independent of the solution pH, one may conclude that, in basic solution, reactions 2 and 4 (and possibly 3 and 5 as well) are too slow to allow mediated electron transfer between $Ru(NH_3)_6^{3+/2+}$ and the electrode. Consistent with this conclusion, we find that the electrochemical response is restored (trace d) upon returning to the weakly acidic HAc/NaAc buffer. The key point is that altering the solution pH changes a porphyrin axial ligand from H_2O to OH^-, which in turn switches the mediation current reversibly from "on" to "off", as shown in Scheme II. The chemical (proton) signal gates electron flow in much the same way as modulation of the gate potential switches the source-drain current on and off in a field effect transistor.

In order to test our assertion that the electron transfers to and from $Ru(NH_3)_6^{3+/2+}$ occur exclusively via mediation by the gate molecule $FeTPPS^{3-/4-}$, electrodes were prepared containing $Os(bpy)_2pyCl^+$ instead of $Ru(NH_3)_6^{3+}$. The important difference between these two ions is their formal potentials, that of $Ru(NH_3)_6^{3+/2+}$ being nearly coincident (at –0.20 V vs SCE) with that of $FeTPPS^{3-/4-}$, and that of $Os(bpy)_2pyCl^{2+/+}$ being significantly more positive (+0.30 V). In this case we would predict current rectification, with rapid electron transfer occurring only in the cathodic direction, and gating of this cathodic current via protonation/deprotonation of $FeTPPS^{3-/4-}$.

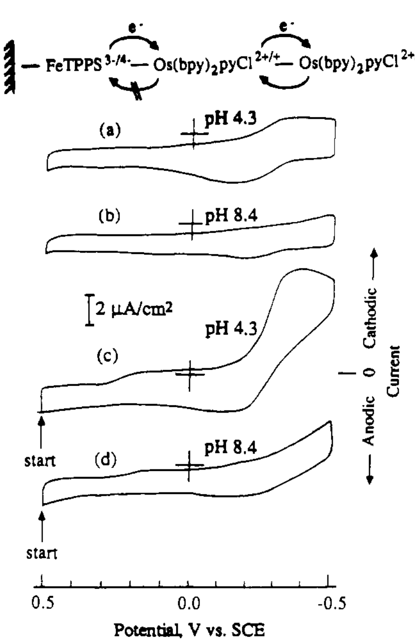

Figure 5. Cyclic voltammetry of a CME (a) exchanged with $FeTPPS^{3-}$ in 10 mM HAc/NaAc and 10^{-5} M $FeTPPS^{3-}$, (b) same electrode as (a) in 10 mM NaAc and 10^{-5} M $FeTPPS^{3-}$, (c) exchanged with both $FeTPPS^{3-}$ and $Os(bpy)_2pyCl^+$ in 10 mM HAc/NaAc and 10^{-5} M $FeTPPS^{3-}$, and (d) same electrode as (c) in 10 mM NaAc and 10^{-5} M $FeTPPS^{3-}$ (scan rate = 50 mV/s). The electrode was held at +0.5 V for 1 min prior to initiation of scans (c) and (d).

Cyclic voltammetry of a $FeTPPS^{3-/4-}/Os(bpy)_2pyCl^{2+/+}$ CME is shown as a function of pH in Figure 5. Like $Ru(NH_3)_6^{3+}$, the $Os(bpy)_2pyCl^+$ ions exchange onto both the internal and external surfaces of the pillared clay, at a loading of 7×10^{-5} mol/g. This ion is slightly smaller in size than $Ru(bpy)_3^{2+}$ and $Os(bpy)_3^{2+}$, which were shown previously[11,20] to exchange only onto external sites at approximately loadings of 1×10^{-5} mol/g. Rudzinski and Bard measured the diffusion constants of metal tris(bipyridyl) complexes and $Ru(NH_3)_6^{3+/2+}$ in pillared clays and found that, because of their smaller size, the latter had diffusion constants 1–2 orders of magnitude higher than the former. A similar effect seems to be operative with the relatively large $Os(bpy)_2pyCl^+$ ions, as evidenced by the smaller current densities observed in Figure 5, compared to Figure 4.

Leaching of $FeTPPS^{3-/4-}$ from $FeTPPS^{3-/4-}/Os(bpy)_2pyCl^{2+/+}$ electrodes occurs upon long exposure to acetate-containing electrolyte, and for this reason the experiments represented in Figures 5–7 were carried out in solutions containing 1×10^{-5} M $FeTPPS^{3-}$. This amount of $FeTPPS^{3-}$ has a negligible effect on the electrochemical response of polymer-confined $FeTPPS^{3-/4-}$, as seen by comparison of traces a and b in Figure 5 with corresponding cyclic voltammograms in Figure 2. Repetitive cycling of $FeTPPS^{3-/4-}/Ru(NH_3)_6^{3+/2+}$ electrodes in acetate electrolyte showed no evidence for leaching of either electroactive component.

Figure 5c shows the cyclic voltammetry of a $FeTPPS^{3-/4-}/Os(bpy)_2pyCl^{2+/+}$ CME in the acidic HAc/NaAc electrolyte. Prior to this scan, the electrode was held for 1 min at the positive potential limit, in order to effect oxidation of both $FeTPPS^{4-}$ and $Os(bpy)_2pyCl^+$. Apart from a small "leakage" current near the $Os(bpy)_2pyCl^{2+/+}$ formal potential, ascribed to

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(20) Rudzinski, W. E.; Bard, A. J. *J. Electroanal. Chem.* **1986**, *199*, 323.

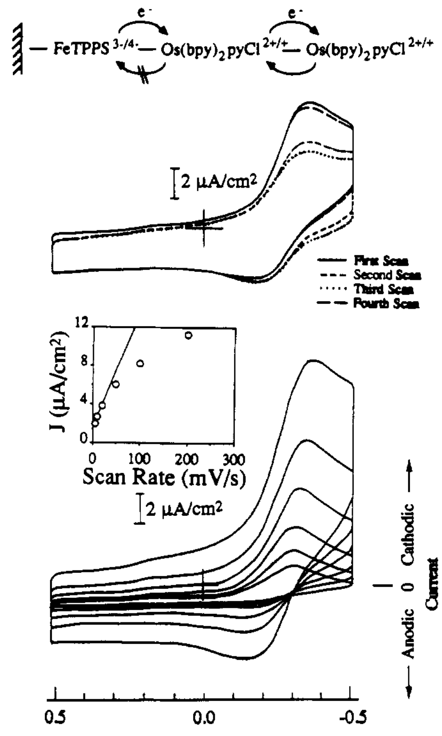

Figure 6. Top: Repetitive cycling of a FeTPPS^{3-}/Os(bpy)$_2$pyCl$^+$ CME in 10 mM HAc/NaAc and 10^{-5} M FeTPPS^{3-} (scan rate = 100 mV/s). The electrode was held 1 min at +0.5 V prior to first and fourth scans. Bottom: Cyclic voltammetry of the same electrode at 200, 100, 50, 20, and 10 mV/s. The electrode was held 1 min at +0.5 V between scans. Inset: Plot of cathodic peak current density vs scan rate.

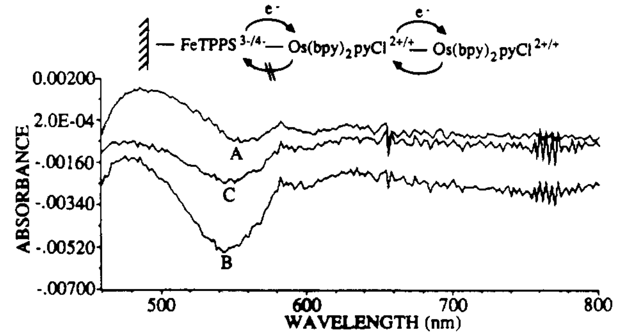

Figure 7. Visible difference spectra of a CME ion-exchanged with both FeTPPS^{3-} and Os(bpy)$_2$pyCl$^+$. The reference spectrum is the same electrode held at –0.5 V vs SCE. Electrolyte is 10 mM HAc/NaAc and 10^{-5} M FeTPPS^{3-}. Spectra A and B are recorded 1–2 s and 1 min after the electrode potential is stepped abruptly to +0.5 V. Spectrum C is recorded 1–2 s after stepping abruptly back to –0.5 V.

clay particles in direct contact with the electrode surface,[11] most of the cathodic current onsets at the FeTPPS$^{3-/4-}$ potential and is not reversed in the anodic sweep. This asymmetric voltammetric peak is essentially absent if the scan is initiated at the negative limit. By analogy to previously reported experiments with polymer bilayer electrodes[3] and CME's containing electroactive ions with different formal potentials,[11] we can assign the cathodic peak to trapping of electrons on clay-bound Os(bpy)$_2$pyCl$^{2+/+}$. The direct interconversion of Os(bpy)$_2$pyCl$^{2+/+}$ is slow because these ions are bound to the clay surface at sites remote from the electrode surface. However, the reduction of Os(bpy)$_2$Cl^{2}py$^+$ by FeTPPS^{4-} ions produced in the cathodic sweep is rapid, because the cross-exchange reaction 6 is thermodynamically favorable by ca. 550 mV. The combination of reactions 4 and 6 causes the enhancement of the cathodic current. However, the reverse of (6) is unobservably slow because it is thermodynamically unfavorable. As expected, there is very little mediation of the Os(bpy)$_2$pyCl$^{2+/+}$ interconversion in either direction if the scan is carried out in the wealy basic NaAc electrolyte (traced in Figure 5). This electrode therefore functions as the gated rectifier shown in Scheme II, the gate signal being supplied by electrolyte protons.

$$\mathrm{FeTPPS^{4-} + Os(bpy)_2pyCl^{2+} = FeTPPS^{3-} + Os(bpy)_2pyCl^{+}} \quad (6)$$

Charge Trapping/Detrapping. Further evidence for charge-trapping in the FeTPPS$^{3-/4-}$/Os(bpy)$_2$pyCl$^{2+/+}$ CME is obtained from cyclic voltammetry shown in Figure 6. Repetitive cycling of the electrode (top of Figure 6) results in loss of the cathodic current attributed to mediated Os(bpy)$_2$pyCl^{2+} reduction. Since the reverse of reaction 6 is slow, the oxidized form of this couple is depleted in the clay during the cathodic sweep but not replenished during the ca. 5-s excursion to positive potential. However, holding the electrode for 1 min at +0.5 V causes slow oxidation of Os(bpy)$_2$pyCl$^+$, and so the cathodic current is restored. At slow scan rates the cathodic peak current density is linear with scan rate (bottom of Figure 6), as expected for charge "detrapping" mediation reactions in thin redox-active bilayers.[3a] Nonlinearity at higher scan rates is consistent with slow charge-transfer diffusion of Os(bpy)$_2$pyCl$^+$ in the pillared clay; that is, the layer of Os(bpy)$_2$pyCl$^+$ produced within the clay during the 1-min hold at +0.5 V is reduced at a diffuction-controlled rate during the cathodic sweep at fast scan rates.

A spectroelectrochemical experiment, shown in Figure 7, supports the assigment of cathodic peaks in Figures 5 and 6 to the mediation reaction 6 and also demonstrates the difference in time scales for oxidation and reduction of Os(bpy)$_2$pyCl$^{2+/+}$. In this experiment the reference spectrum is a fully reduced electrode film. The electrode is stepped abruptly to +0.5 V (positive of the Os(bpy)$_2$pyCl$^{2+/+}$ formal potential), and spectrum A is recorded immediately. Since the diffuse-reflectance UV–visible spectrum of Os(bpy)$_2$pyCl$^+$/pillared montmorillonite shows an absorbance maximum at about 540 nm, a negative absorption at that position in the difference spectra is due to the loss (i.e., oxidation) of Os(bpy)$_2$pyCl$^+$. There is only a small negative absorbance, corresponding to oxidation of a small fraction of the Os(bpy)$_2$pyCl$^+$ in the film, 1–2 s after the electrode potential is stepped to +0.5 V (spectrum A). Os(bpy)$_2$pyCl$^+$ is slowly oxidized as the potential is held at +0.5 V, and after 1 min significant bleaching of the Os(bpy)$_2$pyCl$^+$ absorbance is evident (spectrum B). When the electrode potential is returned to –0.5 V, the reduction of Os(bpy)$_2$pyCl^{2+} is rapid; about 60% of the Os(bpy)$_2$pyCl^{2+} generated in 1 min at 0.5 V is reduced within 1–2 s, as evidenced by spectrum C. These difference spectra affirm the slow rate of oxidation and rapid mediated reduction of Os(bpy)$_2$pyCl$^{2+/+}$ in the CME, consistent with the observation of current rectification of cyclic voltammetry.

Conclusions

This study has demonstrated that axial ligation of a metalloporphyrin, and consequent modulation of its electrochemical properties, can act to gate electron transfer in bilayer devices composed a cationic silane polymer and an anionic pillared clay. In the example presented here, protonation/deprotonation of an axial hydroxide ligand switches the gate molecule "on" or "off" by controlling its rate of electron exchange with the electrode surface. At present it would be unrealistic to suggest that these devices could form the basis of practical pH sensors, since better and simpler sensors for H$^+$ exist and since interferences such as dissolved O$_2$ would interfere with the amperometric response under ordinary conditions. We note, however, that the example presented here suggests new possibilities for the preparation of microelectrochemical devices that are sensitive to ligands (other than H$^+$) that bind metalloporphyrins. Other device designs based on this chemistry may also be more suitable for chemical sensing. Among the most obvious of these are two-terminal devices in which the polymer and clay layers connect to sandwich or side-by-side microelectrodes and trilayer devices in which binding of an electron donor ligand such as a halogen, pseudohalogen, or amine modulates the redox conductivity of the film through changes in the formal potential of the metalloporphyrin gate-molecule. These possibilities will be explored in future experiments.

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