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ELECTROCHEMISTRY AND PHOTOELECTROCHEMISTRY OF TRANSITION METAL COMPLEXES IN WELL-ORDERED SURFACE LAYERS

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SUMMARY

Two methods for preparing organized, multicomponent assemblies of electroactive complexes are described. Using a cationic silane reagent, a thin layer of zeolite or pillared clay particles can be tethered to an electrode surface. The silane provides a binding site for anionic complexes such as $Fe(CN)_6{}^{4-}$ and $Mo(CN)_8{}^{4-}$, while the zeolite or clay component binds electroactive cations such as $Os(bpy)_3{}^{2+}$, $Ru(bpy)_3{}^{2+}$, and metallocenes. These assemblies act as rectifiers electrochemically because of spatial ordering of their electroactive anionic and cationic components. Clay-modified electrodes containing $Ru(bpy)_3{}^{2+}$ and $Mo(CN)_8{}^{4-}$ or $Fe(CN)_6{}^{4-}$ can also act as photodiodes, because of efficient electron transfer quenching of photoexcited $Ru(bpy)_3{}^{2+}$ by the film-bound anions.

Another strategy for preparing organized electroactive films on surfaces involves the sequential adsorption of the components of the zirconium phosphonate structure from aqueous solution. Films produced in this way are morphologically similar to Langmuir-Blodgett multilayers. By incorporating both organic phosphonate and inorganic phosphate groups into the film, pillared materials with molecular sieving properties can be synthesized. These films bind electroactive cations smaller than the pillar height (ca. 10 Å) and exclude larger cations. Spatially organized cation/anion electrode assemblies can thus be prepared which also act as current rectifiers.

INTRODUCTION

The problem of artificial photosynthesis requires a system which is multifunctional -- capable of efficient light absorption, charge separation, vectorial electron transport, and multielectron catalysis. This problem provides a challenge to our skill in both molecular and supramolecular synthesis. The molecular part involves the preparation of compounds with the right photochemical and electrochemical properties to act as photosensitizers and electron relays. These molecules must be stable in at least two oxidation states and must undergo billions of turnovers in a photocatalytic cycle without undesirable side reactions. Thanks to extensive work over the past decade, a number of promising photosensitizers and electron relays, which fulfill these requirements, are available[1].

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The supramolecular part of the problem is largely one of controlling the rates of electron transfer (ET) between the molecular components of the assembly. We seek to modulate ET rates (as nature does so well in redox-active proteins and photosynthetic systems) by controlling such parameters as intramolecular distance and orientation, the polarity, dynamics and reorganization energy of the medium, and superexchange pathways through intervening solvent molecules or bridging groups. The dependance of ET rates on these parameters is now well understood from kinetic experiments with donor-acceptor molecules[2-4], proteins[5,6], polymers[7], and natural photosynthetic systems[8-10]. Since these ground rules are established, it is largely the supramolecular problem which prevents us from creating practical artificial photosynthetic systems.

Supramolecular assemblies which incorporate several molecular and/or solid state components in a well-defined spatial arrangement are potentially interesting not only for artificial photosynthesis, but also as catalysts, chemical sensors, and components of nanometer-scale electronic devices. Despite considerable motivation, from both a fundamental and practical point of view, to study these systems, the techniques available to us for their synthesis are still relatively few in number. Most of these rely on phenomena of self-organization (as with, for example, self-assembling monolayers, Langmuir-Blodgett films, and biphasic polymers such as Nafion), or molecular recognition, using templating media such as cyclodextrins, clays, and zeolites.

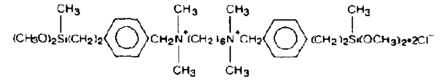
In this paper we describe two new techniques for preparing well-ordered, multicomponent electrode films. We have constructed very simple systems (containing only two or three redox-active components) in which supramolecular organization is achieved with a solid state template -- a zeolite, clay, or layered metal phosphonate. By choosing molecules of the right charge, size, and redox potential, a vectorial electron transport chain, which can be driven either photochemically or electrochemically, organizes spontaneously at the electrode surface.

ZEOLITE- AND CLAY-MODIFIED ELECTRODES

Large pore zeolites and pillared clays have internal void networks which admit molecules of appropriate size and charge. These aluminosilicates bind small cations such as Na^+, NH_4^+, K^+, etc., which may be exchanged for larger electroactive cations. Both materials are microcrystalline and have molecular sieving properties: cations larger than a well-defined "window" size cannot enter the internal void space. For example, zeolite Y has openings which admit molecules of critical dimension 7.4 Å or less. Montmorillonite clay pillared with

$Al_{13}O_4(OH)_{28}^{3+}$ or $Zr_4(OH)_{16-x}^{x+}$ has a free gallery height of about 9 Å[11]. Cations larger than these openings, such as metal polypyridyl complexes and metalloporphyrins, are excluded from the intracrystalline volume. Smaller electroactive cations, for example metallocenes and viologens, diffuse freely into the pores[12].

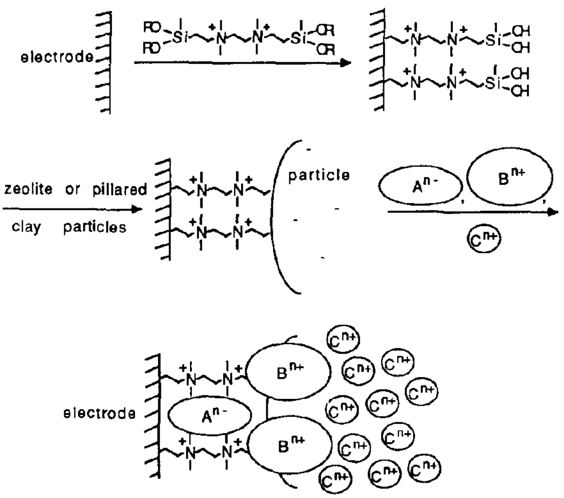
One strategy for binding zeolite or pillared clay particles to an electrode surface is shown in Scheme I. Using the silanol molecule I,



$(CH_3O)_2Si(CH_3)(CH_2)_2C_6H_4CH_2N^+(CH_3)_2(CH_2)_6N^+(CH_3)_2CH_2C_6H_4(CH_2)_2Si(CH_3)(OCH_3)_2 \cdot 2Cl^-$

I

an oxide electrode is functionalized with a thin layer of polymer. I polymerizes via hydrolysis of $Si-OCH_3$ groups and formation of siloxane



Scheme I. Derivatization of an oxide electrode surface with silane I, followed by binding of zeolite or clay particles and exchange of electroactive ions A^{n-}, B^{n+}, and C^{n+}.

(Si-O-Si) linkages. The electrode is then immersed in an acetonitrile slurry or zeolite or clay particles. The polymer, which is typically a few monolayers thick, still contains enough free silanol groups to bind the surface of the particles (presumably also through Si-O-Si bonds[13]), and a "monolayer" of micron-size particles is covalently attached. The particles provide binding sites for cations, while the fixed positive charges of the siloxane polymer act as binding sites for electroactive anions.

When an electrode modified according to Scheme I is soaked in a solution containing both electroactive anions and cations, the anions tend to occupy positions closer to the electrode surface because of their association with the cationic polymer. The cations, which bind electrostatically to the zeolite or clay particles, are sited farther from the electrode surface and, in some cases, cannot exchange electrons with it directly. The situation is reminiscent of polymer bilayer electrodes[14], polymer coatings containing both "fast" and "slow" redox couples[15,16], and polymer-modified electrodes in which one electroactive group is attached only the outer surface of the film[17]. In these assemblies one sees current rectification and charge trapping effects because one electroactive component can only exchange electrons with the electrode through oxidation or reduction of the other[12-17].

Figure 1 shows cyclic voltammograms obtained with electrodes modified according to Scheme I, using $Al_{13}O_4(OH)_{28}{}^{3+}$-pillared montmorillonite.

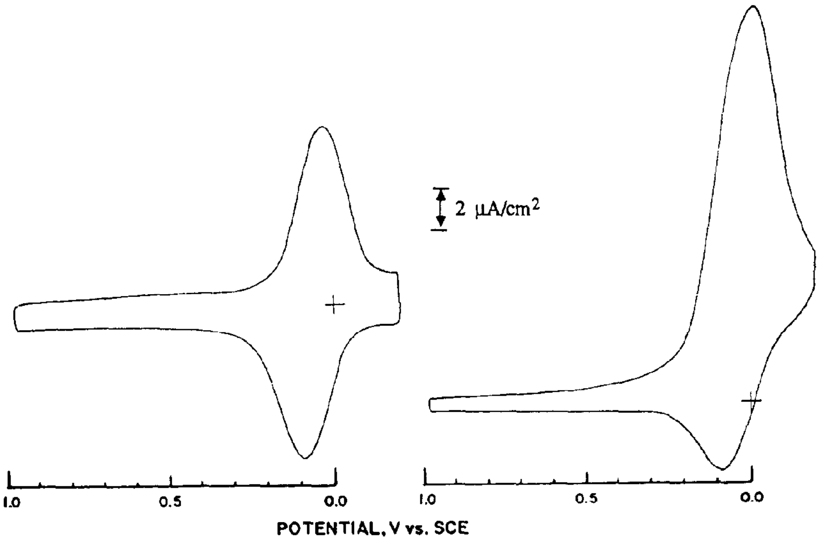


Figure 1. Cyclic voltammetry of SnO_2 electrodes modified according to Scheme I, using Al-pillared montmorillonite, and ion-exchanged with both $Fe(CN)_6{}^{4-}$ and $Os(bpy)_3{}^{2+}$. Left: scan initated at -0.2 V vs. SCE; right: scan initiated after 5 min. at +1.0 V. Scan rate 100 mV/sec.

The experiment is carried out in a blank electrolyte (1 mM KH_2PO_4) after soaking the electrode in a solution containing both $Fe(CN)_6{}^{4-}$ and

$Os(bpy)_3^{2+}$. Inititially, the electrode is held at potentials negative of both the $Fe(CN)_6^{4-/3-}$ and $Os(bpy)_3^{2+/3+}$ potentials, and only a reversible $Fe(CN)_6^{4-/3-}$ wave is seen. When the electrode is held positive of the $Os(bpy)_3^{2+/3+}$ potential for a prolonged period, the clay-bound $Os(bpy)_3^{2+}$ is slowly oxidized via reactions (1) and (2):

$$Os(bpy)_3^{2+} + Fe(CN)_6^{3-} \xrightarrow{\text{slow}} Os(bpy)_3^{3+} + Fe(CN)_6^{4-} \quad (1)$$

$$Fe(CN)_6^{4-} \xrightarrow{\text{fast}} Fe(CN)_6^{3-} + e^- \quad (2)$$

By sweeping the electrode negative (to the $Fe(CN)_6^{3-/4-}$ potential), the oxidized $Os(bpy)_3^{2+}$ ions are reduced according to (3) and (4):

$$Fe(CN)_6^{4-} + Os(bpy)_3^{3+} \xrightarrow{\text{fast}} Fe(CN)_6^{3-} + Os(bpy)_3^{2+} \quad (3)$$

$$Fe(CN)_6^{3-} + e^- \xrightarrow{\text{fast}} Fe(CN)_6^{4-} \quad (4)$$

Since reaction (3) is several orders of magnitude faster than its reverse reaction, (1), the reduction of $Os(bpy)_3^{3+}$ at the $Fe(CN)_6^{4-/3-}$ potential is rapid. The large reduction wave (right side of Fig. 1) therefore represents reduction of both $Fe(CN)_6^{3-}$ and $Os(bpy)_3^{3+}$, whereas the corresponding oxidation wave represents only the $Fe(CN)_6^{4-/3-}$ interconversion.

Analogous experiments carried out with zeolite Y electrodes show evidence for ion pairing between $Fe(CN)_6^{3-}$ and $Os(bpy)_3^{2+}$. The ion pair is not confined to the surface of the zeolite particles, and diffuses through the thin polymer film to the electrode surface. In this case, direct oxidation and reduction of $Os(bpy)_3^{2+/3+}$ occurs near its formal potential (+0.5 V)[13]. With the clay-modified electrodes (Fig. 1), the lack of current near the $Os(bpy)_3^{2+/3+}$ potential shows that ion pairing does not occur within the polymer. This complex apparently binds more tightly to the pillared clay than it does to the zeolite Y surface.

PHOTOACTIVE ANION-CATION DIADS

The vectorial nature of facile electron transport (reactions 3 and 4) at the pillared clay-modified electrode suggests the possibility of photochemically driven electrode reactions. What is needed is an anion-cation pair in which one ion is a photosensitizer and the other is a good electron donor (or acceptor) quencher. The quencher must not only oxidize or reduce the photoexcited sensitizer, but must also "escape" before back electron transfer can occur, regenerating the ground state.

Recent flash photolysis experiments carried out with $Ru(bpy)_3^{2+}$ derivatives and multiply charged anions have shown that $Mo(CN)_8^{4-}$ and $W(CN)_8^{4-}$ are superior electron donor quenchers in aqueous solution[18]. Quantum efficiencies for separation of the oxidized donor/$Ru(bpy)_3^+$ geminate ion pair are as high as 70-80%. Figure 2 shows a typical set of transient spectra recorded after an 11 ns laser flash which excites $Ru(bpy)_3^{2+}$. Rapid quenching by $W(CN)_8^{4-}$, and cage escape to form $W(CN)_8^{3-}$ and $Ru(bpy)_3^+$, is evidenced by the immediate appearance of spectral features at 450 and 510 nm, which correspond to bleaching of $Ru(bpy)_3^{2+}$ and formation of $Ru(bpy)_3^+$. Decay of spectral transients via equal concentration, second order kinetics can be attributed to the recombination reaction (5), which is energetically favorable by ca. 1.3 V and occurs at a diffusion controlled rate:

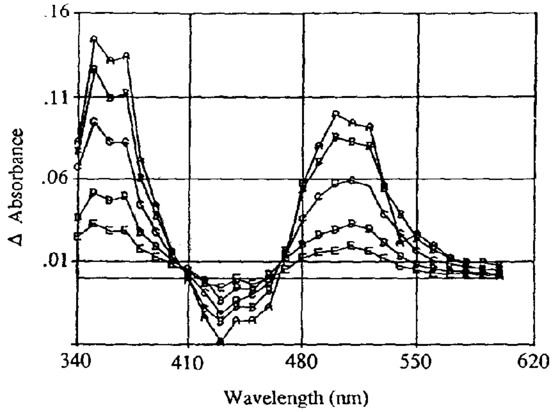


Figure 2. Transient absorbance spectra of an aqueous $Ru(bpy)_3^{2+}/W(CN)_8^{4-}$ solution. Spectra A-E were recorded 0.4-13.5 µs after a 532 nm laser flash, and show the formation and decay of $Ru(bpy)_3^+$ (maxima at 360 and 510 nm). Reproduced from ref. 18 with permission of the copyright owner.

$$W(CN)_8^{3-} + Ru(bpy)_3^{+} \longrightarrow W(CN)_8^{4-} + Ru(bpy)_3^{2+} \qquad (5)$$

Pillared clay-modified electrodes which are ion-exchanged with $Mo(CN)_8^{4-}$ and $Ru(bpy)_3^{2+}$ show photocurrents which are consistent with quenching of $Ru(bpy)_3^{2+*}$ by $Mo(CN)_8^{4-}$, and separation of the $Mo(CN)_8^{3-}$/$Ru(bpy)_3^+$ geminate ion pair. Figure 3 shows current/time transients recorded when the photoelectrode is illuminated with UV-filtered white light. Small photocurrents are observed, which onset at the $Mo(CN)_8^{4-/3-}$

formal potential and reach a maximum value at more negative potentials where photogenerated $Mo(CN)_8^{3-}$ is rapidly reduced. The cathodic photocurrent is a consequence of vectorial reduction of $Ru(bpy)_3^{2+*}$ by $Mo(CN)_8^{4-}$, and is not observed in the absence of either componenent. These current transients translate into a quantum efficiency of 0.01 per photon absorbed, which is markedly less than the value of 0.8 obtained

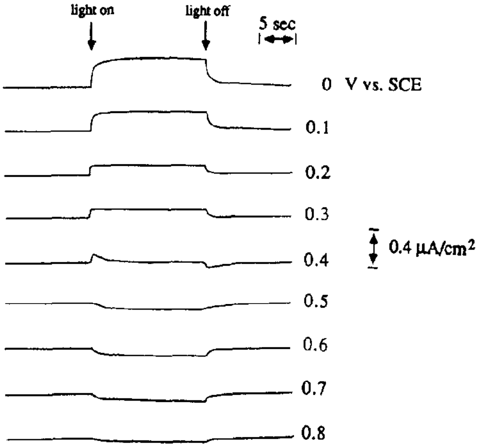
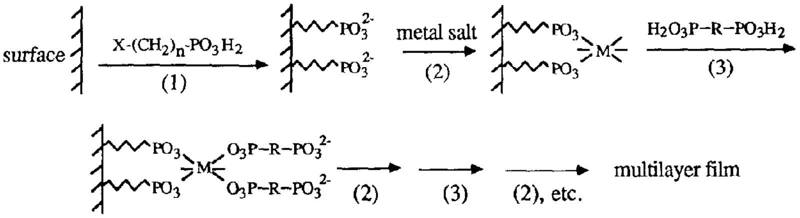


Figure 3. Current-time transients for $Mo(CN)_8^{4-}/Ru(bpy)_3^{2+}$/pillared clay electrodes in 1 mM aqueous KH_2PO_4.

with the same donor/sensitizer diad in fluid solution. It is nevertheless quite interesting that such photocurrents can be attained, in the absence of any sacrificial reagents and in a self-assembling system. Analogous systems in which the surface roughness and/or photosensitizer extinction coefficient are increased should yield larger photocurrents. Figure 3 is recorded from an electrode with a surface coverage of 2.5×10^{-9} moles $Ru(bpy)_3^{2+}/cm^2$, which absorbs only about 1% of the incident light power.

ELECTROACTIVE MULTILAYER ASSEMBLIES

A second strategy for preparing supramolecular electrode "nanostructures" is shown in Scheme II. In this scheme "X" is a surface-active group (i.e., a silanol for oxide surfaces such as silicon, SnO_2, and oxidized platinum, or a disulfide for gold) which anchors a layer of phosphonate groups to the surface. Onto this "primer" monolayer, a tetravalent (Zr^{4+}, Hf^{4+}) or trivalent (Y^{3+}, lanthanide^{3+}) metal ion is adsorbed, and then another organic phosphonate or phosphate layer. In this way a multilayer structure can be built up, one layer at a time, by sequential adsorption reactions.



Scheme II. Sequential adsorption technique for growing metal phosphonate multilayers on surfaces.

In our initial studies of this process we showed that well-ordered films could be grown on planar surfaces if R was an alkyl group[19]. The films adopt the structure of the highly insoluble tetravalent[20] and trivalent[21] metal phosphonates, which is morphologically similar to the alternating polar/nonpolar layered structure of Langmuir-Blodgett (LB) films. Recently, we have found that well-ordered metal phosphonate films can also be grown on high surface are substrates such as fumed silica[22]. In this respect, these and similarly adsorbed multilayer films[23,24] offer a significant advantage over LB films, which are applied to planar surfaces (only) via monolayer transfer techniques[25].

The tetravalent metal phosphonate structure is closely related to that of α-$Zr(HPO_4)_2 \cdot H_2O$[26]. In both structures one finds the same pseudohexagonal net of Zr atoms linked together by bridging $-PO_3$ groups. The ionic bonding within this net is sufficiently strong to cause essentially the same structure to form withany R group of projected area 25 Å^2 or less. This structure-directing property, which is common to many layered metal-organic compounds and their intercalated derivatives[20,21,27-29] is very advantageous from the standpoint of supramolecular synthesis, because it allows one to tailor the size of void spaces in the microporous layered solid. For example, reaction of zirconyl chloride with a mixture of alkyl- or arylphosphonic acid and H_3PO_4 is known to produce a single solid phase in which the phosphonate R and phosphate OH groups are randomly distributed over the planar Zr-O-P net[30]. The phosphonate groups prop open the layers leaving void spaces of well defined size. Since these voids contain the acidic phosphate OH groups, they can act as cation exchange sites. Therefore mixed phosphate/phosphonate zirconium salts are molecular sieving cation exchangers, much the same as zeolites and pillared clays.

When these mixed phosphate/phosphonates are prepared as layered films on electrodes, according to Scheme II (using a 1/1 molar ratio of H_3PO_4 and $H_2O_3PC_{10}H_{20}PO_3H_2$ in step 3), molecular sieving effects are manifested in the electrochemistry. Figure 4 shows the cyclic voltammetry of three-layer (50-60 Å thick) films ion-exchanged with a cationic ferrocene and $Os(bpy)_3^{2+}$. The $FcCH_2NMe_3^+$ cation is small enough to fit into the ca. 10 Å void space creatd by the pillaring decanebisphosphonate groups, and it can be clearly seen electrochemically. Similar results are obtained with other small electroactive cations, e.g. methylviologen. On the other hand, $Os(bpy)_3^{2+}$ is too big (diameter 12-13Å) to exchange into the 10 Å spaces within the film, and no electrochemistry is seen. The deep green color associated with $Os(bpy)_3^{2+}$-exchanged zeolite and clay electrodes is not observed, indicating that none of the complex is adsorbed. Anionic complexes such as $Fe(CN)_6^{4-}$ are likewise not bound by these thin-film cation exchangers.

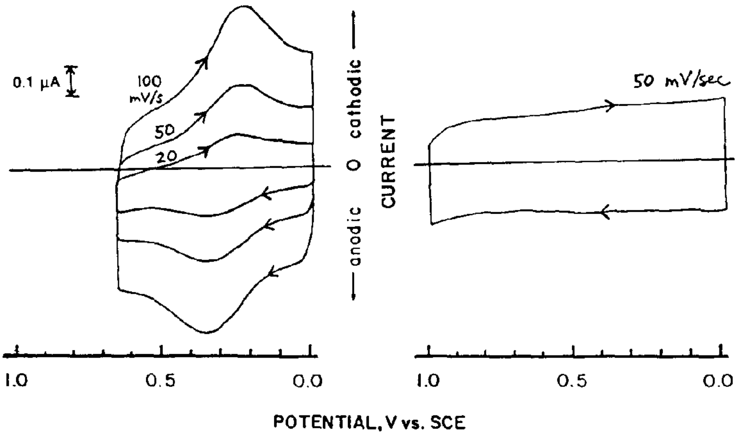


Figure 4. Cyclic voltammetry of three-layer zirconium phosphate/ decanebisphosphonate (1/1)/ SnO_2 electrodes in 1 mM aqueous KH_2PO_4, (left) after ion exchange with $CpFeCpCH_2NMe_3^+$, and (right) after ion exchange with $Os(bpy)_3^{2+}$.

By increasing the ratio of phosphate to pillaring phosphonate (Scheme II, step 3), a multilayer film which admits larger cations can be prepared. Figure 5 shows electrochemical data obtained with a 10-layer film which contains no pillaring phosphonate (i.e., a $Zr(HPO_4)_2 \cdot nH_2O$ film), grown on SnO_2. Without electroactive cations exchanged into it, the $Zr(HPO_4)_2 \cdot nH_2O$ coating is impervious to anions such as $Fe(CN)_6^{4-}$. Since this film is relatively thick and pinhole-free, no current is seen upon cycling through the $Fe(CN)_6^{4-/3-}$ potential. Exposing this electrode to a solution of $Os(bpy)_3^{2+}$ results in the uptake of the complex, and the electrode surface acquires its characteristic green color. Cyclic voltammetry of this electrode in a blank electrolyte clearly shows the presence of the bound $Os(bpy)_3^{2+}$ ions.

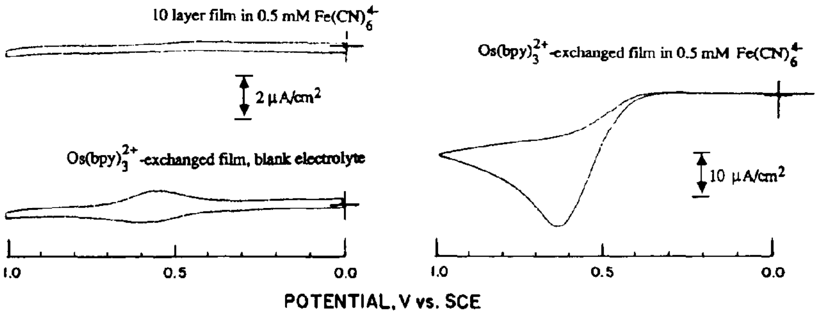


Figure 5. Cyclic voltammetry of a 10-layer zirconium phosphate/ SnO_2 electrode (upper left) in aqueous $Fe(CN)_6^{4-}$, (lower left) in a blank electrolyte after ion-exchange with $Os(bpy)_3^{2+}$, and (right) in aqueous $Fe(CN)_6^{4-}$ after ion-exchange with $Os(bpy)_3^{2+}$.

When the $Os(bpy)_3^{2+}$-exchanged $Zr(HPO_4)_2 \cdot nH_2O$ electrode is cycled in a solution containing $Fe(CN)_6^{4-}$, a large anodic wave, which onsets near the $Os(bpy)_3^{2+/3+}$ potential, is observed; however, there is no corresponding cathodic wave. The anodic process is clearly oxidation of $Fe(CN)_6^{4-}$, since the wave is much larger than can be accounted for by $Os(bpy)_3^{2+}$ in the film. We can interpret the irreversibility of this oxidation to spatial ordering of $Os(bpy)_3^{2+}$ and $Fe(CN)_6^{4-}$, much as we did for pillared clay electrodes (Fig. 1). The difference is that in this case the $Os(bpy)_3^{2+}$ ions are nearest to the electrode surface, so that reactions (2) and (4) are replaced by (6) and its reverse reaction:

$$Os(bpy)_3^{2+} \overset{\text{fast}}{\longleftrightarrow} Os(bpy)_3^{3+} + e^- \qquad (6)$$

As before, reaction (3) will be fast, since it is thermodynamically favorable, and (1) will be slow. The anodic process, therefore, can be represented by (6) + (3), the net reaction being oxidation of $Fe(CN)_6^{4-}$.

On the cathodic sweep, direct reduction of electrogenerated $Fe(CN)_6^{3-}$ (via (4)) is not possible, and reaction (1) is too slow to allow mediated reduction to take place at an observable rate.

Since this self-organizing two component system shows current rectification, as did the clay-based system, one might expect to be able to prepare molecular photodiodes using, e.g., $Ru(bpy)_3^{2+}$ ions exchanged into the film and an electron donor such as $Mo(CN)_8^{4-}$ in solution. In this case the polarity of the photodiode should be reversed, relative to Figure 2. Experiments along these lines are in progress.

CONCLUSIONS

While we have presented data obtained with only the simplest multicomponent (multi ≡ 2) supramolecular assemblies, we are optimistic that the techniques we have described can be applied to the fabrication of more complex systems. The growth of multilayers via adsorption reactions (Scheme II) appears to be particularly promising in this regard since electroactive molecules can be incorporated either by ion-exchange or by binding them covalently into the film. Additionally, this system allows the possibility of varying the rates of electron transfer between components by varying the distance between layers (i.e., the pillar height). These avenues are currently being explored.

ACKNOWLEDGMENT

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