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Photoelectrochemistry of Tris(bipyridyl)ruthenium(II) Covalently Attached to n-Type SnO_2

Pushpito K. Ghosh and Thomas G. Spiro*

*Contribution from the Department of Chemistry, Princeton University,
Princeton, New Jersey, 08544.* *Received December 10, 1979*

Abstract: $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridyl) has been covalently attached to n-type SnO_2 via condensation of surface hydroxyl groups with ruthenium (4-(trichlorosilylethyl)-4′-methyl-2,2′-bipyridine)bis(2,2′-bipyridine) bis(hexafluorophosphate)). A thick coating (~1000 layers, based on the surface hydroxyl group concentration) was produced, presumably via oligomerization of hydrolyzed $-SiCl_3$ groups. The coating, which was stable to organic solvents as well as to aqueous acids and bases, gave reversible cyclic voltammograms, with peak potentials shifted slightly from those of aqueous $Ru(bpy)_3^{2+}$, but the number of electroactive molecules corresponded only to a few layers. The coated electrode gave a photocurrent about twice that observed for SnO_2 in contact with aqueous 4 mM $Ru(bpy)_3^{2+}$, with a slightly red-shifted excitation spectrum. Only a small fraction of the electroactive molecules appeared to participate in excited-state electron transfer, although a steady-state current was supported, presumably by slow electron transfer from the outer layers. Prolonged illumination produces extensive hydrolysis of the outer layers of the coating, but a modest reduction of electroactivity, and only a slight decrease in photocurrent. The photocurrent increases with applied potential, then reaches a plateau, and falls off again near the reduction potential of $Ru(bpy)_3^{2+*}$; the falloff is attributed to back-electron transfer via tunnelling through the thin space charge layer.

Introduction

Much of the recent work on photochemical systems for solar energy conversion has focused on the complex $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridyl).[1-6] It is thermally and photolytically stable in aqueous solutions and has advantageous spectral properties.[7-14] Excitation in its intense (ϵ_{max} 1.4 × 10^4 M^{-1} cm^{-1}) visible (λ_{max} ~455 nm) absorption band produces a relatively long-lived (~0.5 μs) excited state with high quantum efficiency (>0.9), thanks to efficient intersystem crossing induced by the heavy Ru atom. This state readily donates[13] or accepts[15] an electron, producing a powerful oxidant ($Ru(bpy)_3^{3+}$) or reductant ($Ru(bpy)_3^{+}$). The energies are adequate for the simultaneous oxidation and reduction of H_2O to give O_2 and H_2,[16] if kinetic barriers could be overcome. At one point simultaneous O_2 and H_2 generation was observed when a $Ru(bpy)_3^{2+}$-containing fatty acid film in contact with water was irradiated,[1a] but this result has not been reproduced.[1b]

Another important theme in photochemical energy conversion studies is the use of semiconductor electrodes[17-24] to convert photons to electricity or electrochemical reaction products. Fujishima and Honda[17] and Wrighton and co-workers[18] demonstrated that excitation of n-type TiO_2 above its band gap (3 eV) led to photoassisted O_2 generation, the counterelectrode producing H_2. Most semiconductors with band gaps in the visible region suffer from photodecomposition,[25] but progress is being made on protecting them with suitable electrolytes[26-29] or coatings.[30-32] Another approach to visible photochemistry is to use large band gap semiconductors in conjunction with photosensitizers,[33-42] materials that absorb light in the visible region and transfer electrons to or from the electrode. $Ru(bpy)_3^{2+}$ itself is a good photosensitizer.[40-42] However, only a small fraction of the light incident on the electrode can be absorbed by photosensitizer molecules that are close enough to transfer electrons.

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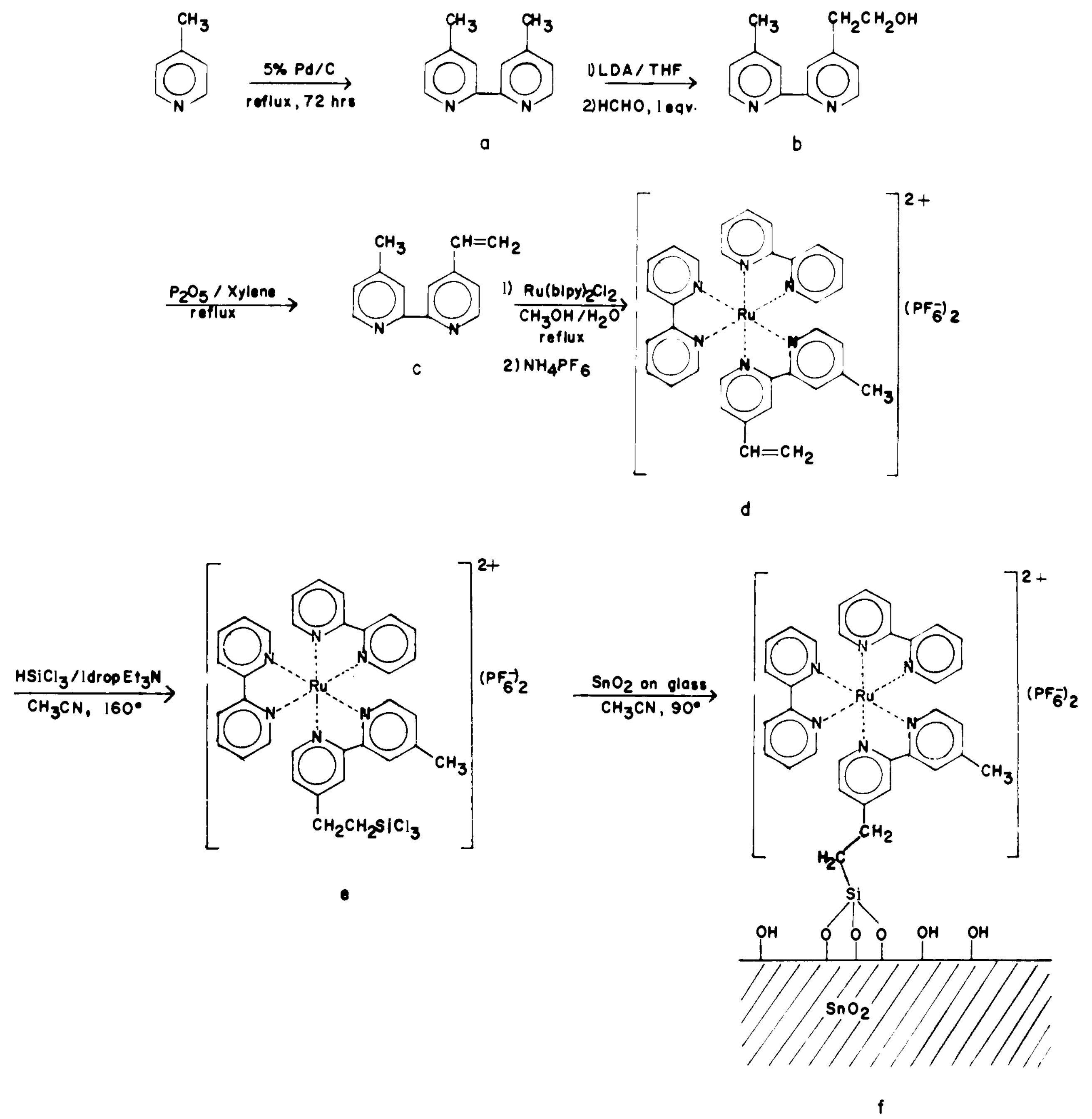

Figure 1. Synthetic scheme for the covalent attachment of $Ru(bpy)_3^{2+}$ to SnO_2 electrodes.

This limitation might be alleviated by increasing the surface concentration of photosensitizer molecules by attaching them to the electrode. Surface attachment of electroactive molecules to modify electrode properties is also of much current interest.[43-46] Silylating agents offer an effective general method, because of the strong Si-O bonds that can be formed with ubiquitous surface hydroxyl groups.[32,43,46,47] We have used this approach to attach $Ru(bpy)_3^{2+}$ to n-type SnO_2, and have studied the electrochemistry and photoelectrochemistry of the coated electrodes. We have found that a thick hydrolytically stable coating is formed, only the first few layers of which are electroactive. A small fraction of the electroactive molecules are photoactive, but the photocurrent is relatively stable under prolonged illumination, while the outer layers of the coating are lost, apparently via photoinduced hydrolysis.

Experimental Section

All chemicals were of reagent grade. Dry solvents were used wherever necessary. $Ru(bpy)_3Cl_2$ was purchased from G. F. Smith Chemical Co. and used without purification.

Synthesis of Covalently Bound Ruthenium Complex (Figure 1). 4,4′-Dimethyl-2,2′-bipyridine[16] (a). 4-Picoline (200 mL) was twice distilled from KOH and then refluxed with 8.93 g of 5% Pd/C under an inert atmosphere. After 70 h, 75 mL of benzene was added and the refluxing continued for another 30 min. The hot solution was vacuum filtered and white crystals precipitated out. Most of the solvent was vacuum distilled, and the solid was recrystallized from ethyl acetate. Yield of recrystallized product was 2 g/g of 5% Pd/C (lit. yield[1b] 1.4 g/g

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of 10% Pd/C). NMR (60 MHz, $CDCl_3$): δ 8.3, (d, 2 H), 8.06 (s, 2 H), 6.95 (d, 2 H), and 2.33 (s, 6 H).

4-Hydroxyethyl-4′-methyl-2,2′-bipyridine (b). BuLi (24.0 mL of 2.35 M) was added to a solution of 8.0 mL of diisopropylamine in 30 mL of tetrahydrofuran, and the resulting mixture was stirred for 15 min; 10 g of a in 250 mL tetrahydrofuran was then slowly added from a dropping funnel, and the color changed to orange-brown. After 2 h, 1.7 g of gaseous formaldehyde was bubbled through the solution, whose color slowly turned green. After an additional 1 h of stirring, the reaction mixture was quenched with ice water and extracted with ether. Viscous product (8.2 g) was recovered from the ether layer, yield 70%. NMR (60 MHz, $CDCl_3$): δ 8.0 (2 H), 7.75 (2 H), 6.7 (2 H), 4.35 (s, 1 H), 3.45 (t, 2 H), 2.45 (t, 2 H), and 1.95 (s, 3 H).

4-Vinyl-4′-methyl-2,2′-bipyridine (c). b (8.7 g) in 200 mL of xylene was gently refluxed with 30 g of phosphorus pentoxide (P_2O_5) for 2 h (the solid P_2O_5 turned yellow). The mixture was then cooled to 5 °C and crushed ice was slowly added to decompose the excess P_2O_5. The aqueous layer was then separated and the pH gradually raised to 5.0. The product was extracted with methylene chloride. Evaporation of solvent and subsequent purification gave 6.0 g of a white solid, yield 75%. NMR (60 MHz, $CDCl_3$): 8.45–8.05 (4 H), 7.15–6.80 (2 H), 6.65–5.25 (3 H, vinylic protons, AMX spin system), and 2.30 (s, 3 H).

$Ru(bpy)_2Cl_2$ was prepared as desribed in ref 1b.

Ruthenium (4-Vinyl-4′-methyl-2,2′-bipyridine)bis(2,2′-bipyridine) Bis(hexafluorophosphate) (d). $Ru(bpy)_2Cl_2$ (1.315 g), 0.5009 g of c, and 0.76 g of sodium bicarbonate were refluxed together in 60 mL of 2:3 methanol–water solution, until the $Ru(bpy)_2Cl_2$ was used up, as indicated by the absorption spectrum. Aqueous 3 M ammonium hexafluorophosphate (4 mL) was added and a red solid precipitated out. Recrystallization from acetone/dichloromethane gave 1.9 g of product, yield 77%. Absorption spectrum: λ_{max} 452 nm. NMR (60 MHz, acetone-d_6): δ 8.3–6.9 (22 H, aromatic protons), 6.4–5.0 (3 H, vinylic AMX spin system), and 2.0 (s, 3 H).

Ruthenium (β-(4-Trichlorosilylethyl)-4′-methyl-2,2′-bipyridine)bis(2,2′-bipyridine) Bis(hexafluorophosphate) (e). d (1.69 g), 0.19 g of freshly distilled trichlorosilane, 0.012 mL of triethylamine, and 10 mL of dry acetonitrile were heated in a pressure vessel for 3 h at 165 °C. A small-scale reaction using acetonitrile-d_3 was carried out simultaneously in a NMR tube. Some polymerization occurred during this reaction. NMR (90 MHz, acetonitrile-d_3): δ 8.5–7.1 (22 H, aromatic protons), 3.2–2.5 (m, 2 H, αCH_2), 2.3 (s, 3 H), 2.1–1.7 (m, 2 H, βCH_2). The multiplets in the upfield region have a pattern similar to that of β-(4-pyridylethyl)trichlorosilane.[48]

Immobilization of e. Clean, dry NESA glass[49] (fluorine-doped n-type SnO_2 glass) was placed in a rack in a reaction flask filled with the crude mixture from the previous reaction, diluted with 100 mL of dry acetonitrile, and allowed to stand for 8 h at 90 °C under an inert atmosphere (Ar). The flask was then placed in a glovebag and the NESA plates were removed and throughly rinsed with acetonitrile, benzene, and acetone. Repeated rinsing with aqueous solutions of acids and bases failed to remove the bound material.

Electrochemical and Photoelectrochemical Measurements. Optically transparent SnO_2 was the working electrode in a three-electrode configuration, with Pt counterelectrode and Ag/AgCl reference electrode (+0.277 V vs. NHE). The cell body was made of Lucite and the cell design was similar to the one described by Hawkridge and Kuwana.[50] Cyclic voltammograms (without ohmic compensation) were obtained with a Bioanalytical Systems Inc. CV-1 instrument equipped with a X-Y recorder. Photocurrent measurements were made under potentiostatic conditions. Monochromatic light from a Spectra Physics Model 166 argon laser was mechanically chopped and then defocused so that the beam incident on the SnO_2 working electrode was approximately 1 cm^2 in area. The current was measured as the voltage drop across a known resistor in series with the working electrode. The modulated voltage signal was detected with a PAR Model HR-8 lock-in amplifier.

Results and Discussion

A. Covalent Attachment of $Ru(bpy)_3^{2+}$. The derivatization of $Ru(bpy)_3^{2+}$ to provide functionalities for covalent attachment was accomplished via the preparation of 4,4′-dimethyl-2,2′-bipyridine. Initial approaches involved oxidation of the methyl groups to carboxylic acids and attachment to surface OH groups either directly, via a dehydration catalyst[51] (dicyclohexylcarbodiimide), or indirectly, via amidation of $(EtO)_3Si(CH_2)_3NH_2$.[51,52] The coatings formed in this way, although resistant to organic solvents, were hydrolytically unstable, washing off readily in water.[53]

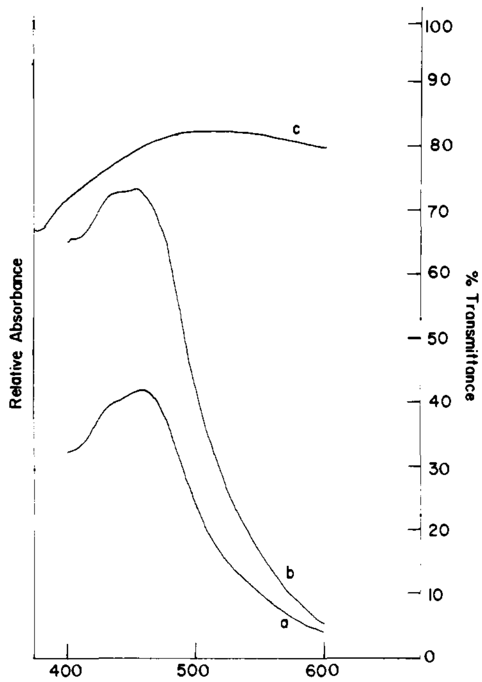

Figure 2. Absorption spectra of (a) aqueous solution of $Ru(bpy)_3^{2+}$ and (b) $Ru(bpy)_3^{2+}$ bound to SnO_2 electrode; (c) transmission spectrum (right scale) of unmodified SnO_2 electrode.

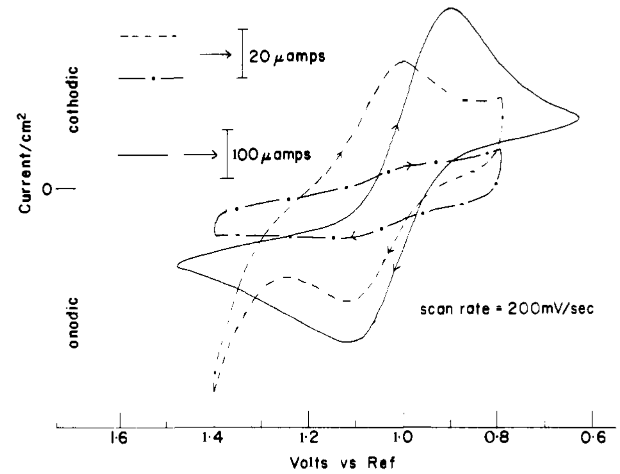

Figure 3. Cyclic voltammogram of SnO_2 electrode (i) in 10^{-3} M $Ru(bpy)_3^{2+}$ (—), (ii) in electrolyte only (—·—), and (iii) covalently coated with $Ru(bpy)_3^{2+}$ (-----). The electrolyte in all cases was 0.1 N H_2SO_4.

These results led us to the approach outlined in Figure 1, in which a $-SiCl_3$ group is separated from the heterocyclic ring by two methylene groups in order to improve the hydrolytic stability of the subsequent surface OH attachment. This objective was achieved, as the resultant coating was not removed by prolonged exposure to aqueous solutions including dilute acids and bases. The synthetic sequence was lithiation and formaldehyde addition to a methyl group, followed by dehydration of the resulting alcohol, and hydrosilylation of the vinyl group, a catalytic amount of triethylamine being added to promote β-addition.[54]

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[53] The attachment of $Ru(bpy)_3^{2+}$ on platinum oxide electrodes by these methods has been very recently reported[52] to be stable in organic solvents. Stability toward aqueous solutions was not reported.

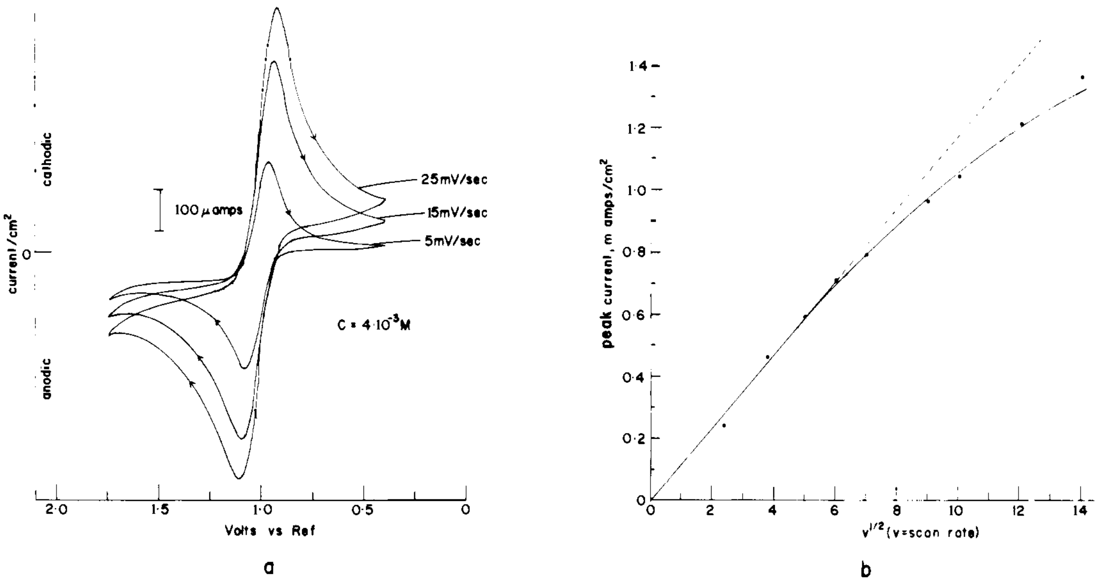

Figure 4. (a) Voltammograms at various scan rates for SnO_2 in 4 × 10^{-3} M $Ru(bpy)_3^{2+}$ and 0.1 N H_2SO_4; (b) plot of peak current vs. $v^{1/2}$ (v = scan rate).

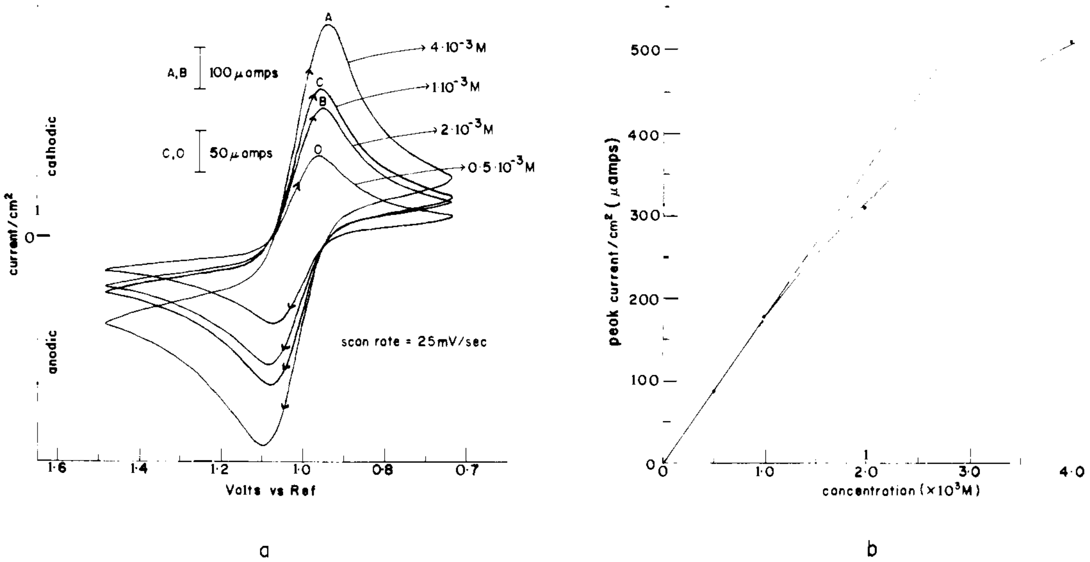

Figure 5. (a) Voltammograms (scan rate = 25 mV/s) for SnO_2 at various concentrations of $Ru(bpy)_3^{2+}$ in 0.1 N H_2SO_4; (b) plot of peak current vs. concentration.

The absorption spectrum of the dried coated electrode (Figure 2) was the same as that of $Ru(bpy)_3^{2+}$ in solution. Assuming that the molar absorptivity of $Ru(bpy)_3^{2+}$ was the same in the coating as in solution, the absorbance corresponded to a surface concentration of 8.3 × 10^{-7} mol/cm², which is about 1000 times the coverage expected from the number of surface hydroxyl groups, $\sim 10^{-9}$–10^{-10} mol/cm².[55] The thick coating no doubt resulted from oligomerization reactions of the trifunctional $-SiCl_3$ groups, as postulated by Wrighton and co-workers to account for thick ferrocene coatings[46] obtained by similar silylation procedures.

B. Cyclic Voltammetry. Because of its high carrier concentration, the SnO_2 electrode gave well-developed cyclic voltammograms when in contact with aqueous $Ru(bpy)_3^{2+}$, as shown in Figure 3 (solid curve). The coated electrode in contact with aqueous electrolyte gave similar voltammograms (dashed curve), although there is a +0.05-V shift in the $E°$ value and the peak-to-peak separation is smaller for a given scan rate. Another interesting difference is an irreversible anodic wave, beginning at about +1.3 V, which is not seen for unmodified electrodes. This might be due to catalysis of H_2O oxidation, although oxidation of an unidentified constituent of the modified electrode surface is also a possibility.

Figures 4a and 5a show the response of the voltammograms for unmodified SnO_2 to variations in scan rate and $Ru(bpy)_3^{2+}$ concentration, respectively. For a reversible electrode process with linear diffusion, the variation in the peak current is given by[56]

$$i_{pa}/A = 0.452(nF)^{3/2}C_R(D_R v/RT)^{1/2} \qquad (1)$$

where v is the scan rate and the other terms have their usual meanings. Figure 4b shows that the predicted linearity with $v^{1/2}$ is obeyed at low v, while Figure 5b likewise shows the predicted linearity with C_R at low C_R. Moreover, the slopes of the straight-line portions are in agreement with those calculated with eq 1, if a reasonable diffusion constant, D_R 1 × 10^{-5} cm^{-2}/s, is used. The deviations from linearity are attributable to uncompensated cell resistance associated with the semiconductor character of the electrode. At high scan rates or concentrations

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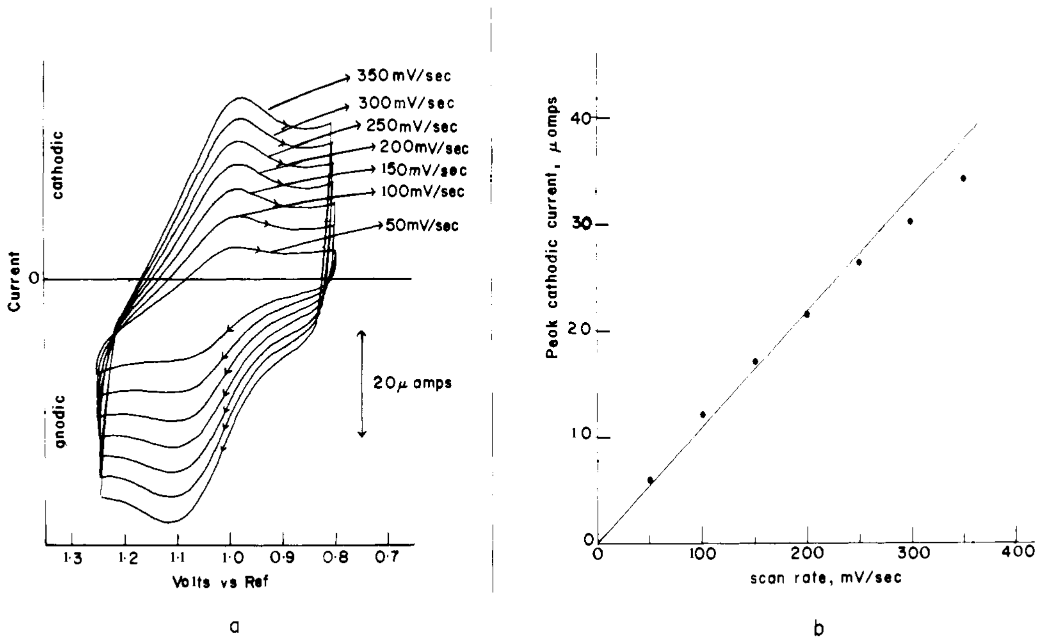

Figure 6. (a) Voltammograms for covalently bound $Ru(bpy)_3^{2+}$ at various scan rates; (b) plot of peak current vs. v. The electrolyte was 0.1 N H_2SO_4.

the lag in the electrode potential from its reversible value increases the peak separation of the voltammograms and lowers the peak current. From the peak separations we estimate a cell resistance of 67 Ω, using the equation[57]

$$\psi = [(nF/RT)nFA(\pi a D_R)^{1/2}C_R R]^{-1} \quad (2)$$

where R is the cell resistance, $a = nFv/RT$, and ψ is a parameter, the value of which can be obtained from the peak-to-peak separation. The resistance accounts quantitatively for the deviations from linearity in Figures 4b and 5b, via the equations[58]

$$v' = v(1 + i_pR/\Delta E)^{-1} \quad (3)$$

$$(i_p)_{v'} = (i_p)_v(1 + i_pR/\Delta E)^{-1/2} \quad (4)$$

in which ΔE is the potential range (associated with each sweep) within which v' (sweep rate for significant deviation from linearity) deviates considerably from v (the corrected sweep rate). Thus the electrode behaves as expected for a reversible process with linear diffusion, but with a substantial cell resistance. We see no evidence for $Ru(bpy)_3^{2+}$ adsorption at SnO_2, as reported by Gleria and Memming.[40] Perhaps differently prepared electrodes have different adsorption properties.

Figure 6a shows voltammograms at various scan rates for $Ru(bpy)_3^{2+}$, bound covalently to SiO_2. In this case the peak current is directly proportional to v (Figure 6b), as expected from

$$i_p = n^2C_RF^2v/4RT \quad (5)$$

where C_R is the surface concentration, in mol/cm^2. Equation 5 is a modification of the relation derived by Hubbard and Anson[59] for diffusionless processes in thin-layer cells. It can be used to estimate the surface concentration of electroactive species. An independent estimate is available from the area under the voltammograms (after correction for the background current) which gives the total numbers of coulombs passed through the electrode. Both methods give essentially the same result, 2.2×10^{-10} and 2.0×10^{-10} mol/cm^2, respectively. This value corresponds to only a few layers of electrode coverage, and is 1/400 of the $Ru(bpy)_3^{2+}$ in the attached film, as measured spectrophotometrically. We conclude that only those $Ru(bpy)_3^{2+}$ centers that are in the immediate vicinity of the electrode are electroactive on the voltammetric time scale. This is in contrast to the finding for ferrocene bonded to Pt or Au electrodes[46] via silyl attachment that the electroactive species correspond to coverages of 10–100 layers and involve essentially all the bound ferrocene. Apparently, rapid electron transfer is supported by the ferrocene network but not by the $Ru(bpy)_3^{2+}$ network of the present study. This may be related to the point of Si attachment: directly on the cyclopentadienyl ring of ferrocene, but two saturated carbon atoms away from the pyridine ring of $Ru(bpy)_3^{2+}$. An additional difference is that the ferrocene coating is neutral, while the $Ru(bpy)_3^{2+}$ coating contains dications, presumably interspersed with counterions (PF_6^- in the present case). The resulting ionic lattice may impede rapid electron transfer.

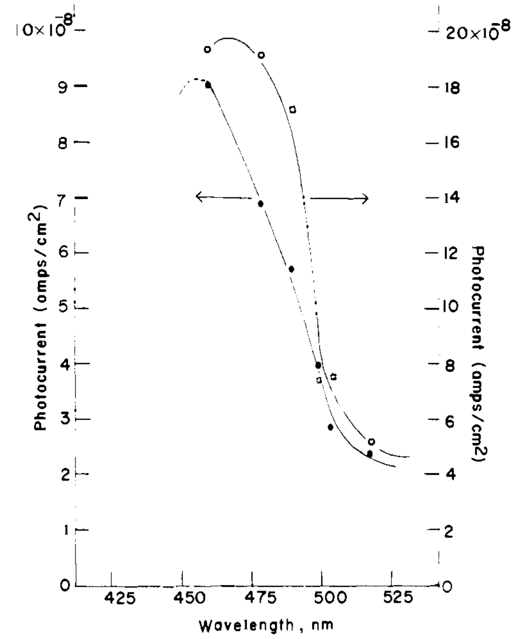

Figure 7. Action spectrum of (i) 4×10^{-3} M $Ru(bpy)_3^{2+}$ in 0.1 N H_2SO_4 (●) and (ii) covalently bound $Ru(bpy)_3^{2+}$ in 0.1 N H_2SO_4 (□). Light intensity (8×10^{-8} einstein cm^2 s^{-1}) and applied potential (0.2 V vs. reference) were identical for both cases. The cell configuration allowed introduction of light through the SnO_2 working electrode.

C. Photocurrents. When n-type SnO_2 in contact with aqueous $Ru(bpy)_3^{2+}$ is illuminated with visible light, a detectable anodic photocurrent results. Figure 7 (filled circles) shows that the excitation spectrum tracks the $Ru(bpy)_3^{2+}$ absorption spectrum,

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(57) Nicholson, R. S. *Anal. Chem.* **1965**, *37*, 1351.

(58) Delahay, P. "New Instrumental Methods in Electrochemistry"; Interscience: New York, 1954.

(59) Hubbard, A.; Anson, F. C. *Anal. Chem.* **1966**, *38*, 58.

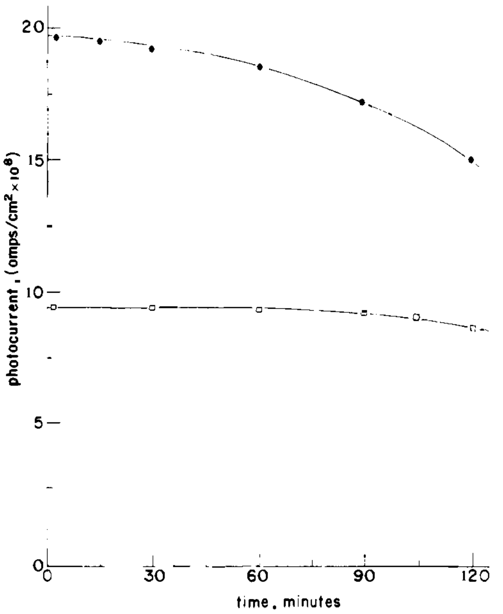

Figure 8. Variation of photocurrent with time for (i) 4 × 10^{-3} M Ru(bpy)$_3^{2+}$ in 0.1 N H_2SO_4 (□) and (ii) covalently bound Ru(bpy)$_3^{2+}$ in 0.1 N H_2SO_4 (●).

as expected if Ru(bpy)$_3^{2+}$* electrons are injected into the SnO_2 conduction band. With more complete data Gleria and Memming[40] observed a ~10-nm red shift of the photoexcitation spectrum relative to the absorption spectrum, suggesting a slight perturbation of the excited state by the electrode. They also observed a shoulder in the excitation spectrum at ~520 nm, interpreted as reflecting direct singlet–triplet excitation.

The covalently modified electrode likewise gave visible photocurrents (Figure 7), with an excitation spectrum red shifted by ~10 nm relative to that of aqueous Ru(bpy)$_3^{2+}$, presumably reflecting a stronger interaction with the electrode. (Saturation effects were ruled out by monitoring the laser power dependence of the photocurrent which was found to be linear at the levels used in this study.) The peak photocurrent was about twice that obtained for 4 mM Ru(bpy)$_3^{2+}$ at unmodified SnO_2.

For SnO_2 in aqueous Ru(bpy)$_3^{2+}$, we can estimate the quantum efficiency of the photocurrent from the incident photon flux, I_0 (calculated from the laser power and the illuminated area), and the absorptivity, ϵ. At 457.9 nm, near the peak of the photoexcitation spectra, these were 8 × 10^{-8} (einstein·cm^{-2})/s^{-1} and 1.4 × 10^7 mol^{-1} cm^{-2}. In the linear absorbance range (no saturation) the flux of excited-state molecules is I_0 $(1 - 10^{-\epsilon m})$, where m is the number of moles of Ru(bpy)$_3^{2+}$/cm^{-2}. We are interested only in those excited-state molecules which are capable of electron transfer to the electrode, i.e., the molecules in the diffusion layer defined by the thickness $(2D\tau)^{1/2}$ ~ 315 Å, where D is the diffusion coefficient (~10^{-5} cm^{-2}/s) and τ is the excited-state lifetime (~0.5 μs in air-staurated solution).[60] At the concentration employed, 4 mM, 0.4% of the light was absorbed in this layer, giving an excited-state flux of 3.2 × 10^{-11} mol cm^{-2} and a maximum expected current of 3.1 μA cm^{-2}, 30 times greater than the observed peak current. The low apparent quantum efficiency is probably due to the quenching of Ru(bpy)$_3^{2+}$* by surface states within the band gap of the heavily doped SnO_2.

For the covalently attached Ru(bpy)$_3^{2+}$ the photocurrent is doubled, but, if the photoactive region corresponds to the electroactive material, 2.1 × 10^{-10} mol cm^{-2}, as determined by cyclic voltammetry, then the excited-state flux is 5.4 × 10^{-10} mol cm^{-2} s^{-1}, corresponding to a current of 52 μA cm^{-2}, 260 higher than observed. However, this flux could only have been maintained for 0.4 s before all 2.1 × 10^{-10} mol cm^{-2} of electroactive material was oxidized to Ru(bpy)$_3^{3+}$. The steady-state photocurrent must

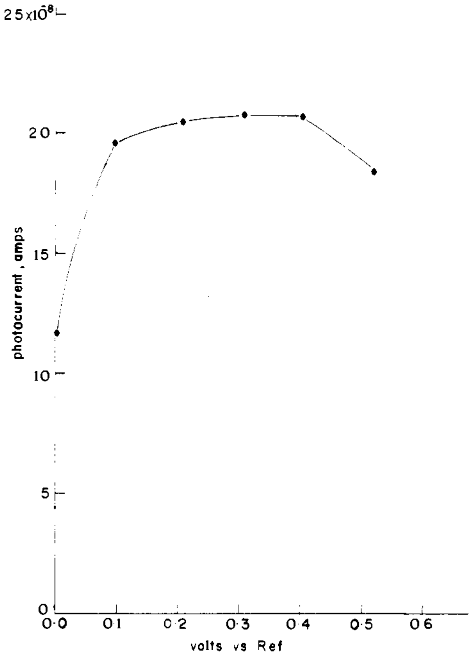

Figure 9. Variation of photocurrent with applied potential for covalently bound Ru(bpy)$_3^{2+}$ in 0.1 N H_2SO_4. Similar results were obtained for the solution redox couple.

therefore be limited by slow electron transfer from outer layers of the Ru(bpy)$_3^{2+}$ coating, or other redox reactions which may be taking place in the interstitial electrolyte. We observed no initial surge of photocurrent when the light was turned on, but only a rapid rise leveling off to the steady-state current. It therefore appears likely that only a small fraction of the electroactive molecules participate in excited-state electron transfer.

Under constant illumination for 2 h the photocurrent of the covalently attached Ru(bpy)$_3^{2+}$ falls by about 15%, as shown in Figure 8. (The photocurrent of uncoated SnO_2 in aqueous Ru(bpy)$_3^{2+}$, run as a control, shows essentially no change.) Interestingly, the amount of electroactive material, as determined by cyclic voltammetry (Figure 6) after the 2-h illumination, falls to less than half its initial value. Thus the apparent quantum efficiency actually increases somewhat. During the illumination the color of the electrode faded markedly, and at the end of the 2-h period we estimate that less than 10% of the original Ru(bpy)$_3^{2+}$ was left. Apparently, the outer layers of the coating are rapidly shed, presumably via photoactivated hydrolysis, but the layer next to the electrode is relatively stable, as judged by the photocurrent.

Over the 2-h illumination period, the integrated photocurrent amounted to 1.3 × 10^{-3} C/cm^2 or 1.3 × 10^{-8} mol of electrons/cm^2. This is about 65 times the initial amount of electroactive material, as determined by cyclic voltammetry. The excess electrons could have been provided by the Ru(bpy)$_3^{2+}$ in the outer layers of the coating. The amount of material is much too small for spectrophotometric determination. These experiments do not enable us to tell whether the coated electrode is capable of oxidizing the electrolyte under illumination. In acidic solutions the rate of H_2O oxidation by Ru(bpy)$^{3+}$ is negligibly small,[16] but Memming et al.[61] have recently reported that it is greatly accelerated for photolytically generated Ru(bpy)$^{3+}$.

D. Applied Potential. Figure 9 shows that the photocurrent of the coated electrode rises rapidly with applied positive potential, then plateaus between +0.1 and +0.4 V vs. Ag/AgCl, and then falls again. The initial rise is attributable to increased electrode efficiency due to band bending, as illustrated in Figure 10, since n-type SnO_2 has a flat-band potential near 0.0 V[62] at pH 1. What

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[60] Results obtained with solutions flushed with argon failed to show any significant differences.

[61] Memming, R.; Schröppel, F.; Bringmann, U. *J. Electroanal. Chem.* **1979**, *100*, 307.

[62] Möellers, F.; Memming, R. *Ber. Bunsenges. Phys. Chem.* **1972**, *76*, 469.

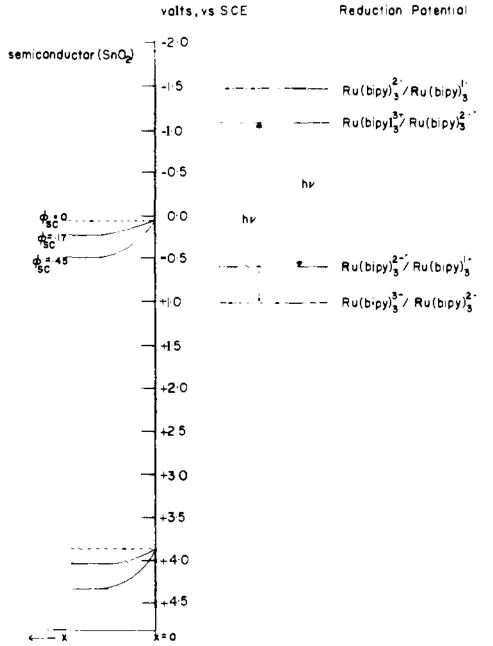

Figure 10. Correlation diagrams showing relative positions of semiconductor energy bands[61] with respect to the redox couples.[63] The SnO_2 flat-band potential is close to 0.0 V vs. SCE at pH 1; band bending (φ_{sc}) is indicated to occur in response to different applied potentials. x is the distance into the semiconductor from the solution interface.

is surprising is the falloff beyond +0.4 V. We suggest that it is caused by back-electron transfer from the electrode, via relatively facile tunnelling through the space charge layer, which is quite thin for heavily doped SnO_2; the Debye length[63] is estimated to be only 10 Å for our electrodes. Similar tunnelling is apparent in the cathodic photocurrents reported by Memming et al.[61] for heavily doped SnO_2 in contact with $Ru(bpy)_3^{2+}$. Excited-state molecules are electron acceptors as well as electron donors, and the potential of the $Ru(bpy)_3^{2+*}/Ru(bpy)_3^{+}$ couple is at ~0.57 V vs. Ag/AgCl. Thus the reduced anodic photocurrent beyond 0.4 V can reasonably be attributed to competing electron donation and acceptance by $Ru(bpy)_3^{2+*}$, once the bottom of the SnO_2 conduction band is lowered to the region of the $Ru(bpy)_3^{2+}$ reduction potential. This competition may be a general phenomenon in photosensitization experiments with heavily doped semiconductors; both donor and acceptor energy levels should be taken into account in interpreting the photocurrents.

Conclusions

1. Introduction of $-SiCl_3$ two methylene groups away from the pyridine ring of $Ru(bpy)_3^{2+}$ allows formation of a coating on SnO_2 which is about 1000 layers thick, as judged from the concentration of surface hydroxyl groups. This coating is stable in contact with aqueous solutions, but hydrolyzes extensively upon illumination.
2. The coating is electroactive, with a midpoint potential shifted slightly from that of aqueous $Ru(bpy)_3^{2+}$, but the number of electroactive molecules, determined by cyclic voltammetry, corresponds to only a few layers.
3. The coated electrode produces a photocurrent about twice as large as that observed for SnO_2 in contact with 4 mM $Ru(bpy)_3^{2+}$, for which a quantum efficiency of ~3% is estimated. Only a small fraction of the electroactive molecules in the coating appear to participate in excited-state electron transfer, but a steady-state current is supported, presumably by slow electron transfer from $Ru(bpy)_3^{2+}$ in the outer layers. Prolonged illumination produces a slow reduction in the photocurrent, a faster loss of electroactivity, and a much faster loss of absorbance, presumably due to photoinduced hydrolysis of the outer layers.
4. The photocurrent rises with applied potential, as band bending increases, reaches a plateau, and then falls again, near the reduction potential of $Ru(bpy)_3^{2+*}$. The falloff is attributable to back-electron transfer, via tunnelling through the space charge layer.

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(63) The Debye length is given by $(\epsilon_{sc}kT/4\pi e^2 n_0)^{1/2}$, where ϵ_{sc} = dielectric constant of the semiconductor (~10 for SnO_2), n_0 = carrier concentration (~10^{20} cm^{-3} for the electrode under study), and e is the electronic change.

(64) Meyer, T. J. *Acc. Chem. Res.* **1978**, *11*, 94.