Electrogenerated Chemiluminescence. 53. Electrochemistry and Emission from Adsorbed Monolayers of a Tris(bipyridyl)ruthenium(II)-Based Surfactant on Gold and Tin Oxide Electrodes

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Cyclic voltammetric surface waves were found for monolayers of $Ru(bpy)_2(bpy')^{2+}$, where bpy' is 4-methyl-4'-(dodecyl-1-thiol)-2,2'-bipyridine, which spontaneously adsorbs onto conducting substrates (indium tin oxide, polycrystalline gold). On polycrystalline gold, the monolayer, probably attached via the thiol functional group, is oxidized in an aqueous oxalate medium to produce electrogenerated chemiluminescence (ecl). The derivatized gold surface exhibited an ecl emission maximum from the excited surfactant at 650 nm. This represents a red shift compared to the solution phase luminescence of the complex in acetonitrile (λ_{max} = 629 nm) or its aggregates with Triton-X100 micelles in aqueous media (λ_{max} = 639 nm).

Introduction

Electrogenerated chemiluminescence (ecl) involves the reaction of electrogenerated species that react to form excited species, usually via an energetic redox reaction.[1] In most cases the precursors and reactants are soluble in the electrolyte phase, with the emission occurring in the diffusion layer near the electrode surface. However, ecl has been generated in films constrained to the surface of an electrode, e.g., as multilayer polymer films.[2] Emission via ecl in a monolayer film was recently demonstrated with a $Ru(bpy)_3^{2+}$ (bpy = 2,2'-bipyridine) molecule modified by addition of a C_{19} hydrocarbon chain via an amide linkage and coated on gold and indium tin oxide (ITO) substrates by Langmuir–Blodgett techniques.[3] The ecl was generated in an aqueous medium by oxidation of the Ru(II) species in the presence of oxalate. The detection of emission of monolayer films on metallic and degenerate semiconductor surfaces showed that emission from the excited states generated by electron transfer could compete with quenching by the electrode. Potential applications of such films include active displays[4] and means of trace analysis. Solution ecl processes have already been studied with analytical applications in mind, e.g., for determination of oxalate or $Ru(bpy)_3^{2+}$ tagged molecules.[5] By adsorption of the ecl-active molecule on the surface of the electrode, significant increases in sensitivity should be possible.

In this paper we describe studies with a $Ru(bpy)_3^{2+}$ type complex in which one bpy was derivatized to produce complex (I) $[Ru(bpy)_2(bpy')^{2+}$, where bpy' is 4-methyl-4'-(dodecyl-1-thiol)-2,2'-bipyridine] which spontaneously adsorbs on solid surfaces. The well-documented affinity of thiols for such metals as gold, platinum, silver, and mercury allowed the strong chemisorption of complex I

onto polycrystalline gold electrodes.[6] Thus we aimed to study the electrochemistry and ecl of a monolayer in which the resultant modified electrode is more stable than the previously studied Ru(II)-based monolayer[3] toward both leaching and such side reactions as hydrolysis of the substituent side chain.[7]

Complex (I)
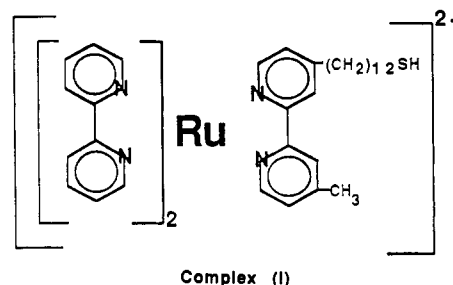
Experimental Section

All organic solvents were obtained from J. T. Baker (Phillipsberg, NJ) or Fisher Scientific. These solvents and the supporting electrolytes were used without further purification. Milli Q water (18 MΩ, Millipore) was used in all washings and aqueous solution preparations.

Ligand Synthesis. 4,4'-Dimethyl-2,2'-bipyridine (Aldrich Chemicals) was recrystallized from ethyl acetate and the crystals were then vacuum dried overnight at 25 °C. The bromide precursor to the thiol derivative was prepared by the method of Ellison and Iwamoto.[8] The thiol was obtained by reacting the bromide precursor with sodium hydrosulfide (Aldrich) in aqueous DMSO overnight[9] and was purified by vacuum distillation on a Kugelrohr system (Aldrich). The product was identified by its 300-MHz (General Electric) ^{1}H NMR: δ 1.25 (br s, 24, bpy–CH_2–(CH_2)$_{10}$–CH_2–SH), δ 2.48 (s, 3, bpy–CH_3), δ 7.12–8.52 (comp., 6, bpy–H).

Preparation of (bpy)$_2$Ru(bpy') Complex. Complex I, was prepared by adapting published procedures.[10] The product was partially purified by column chromatography on neutral alumina

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with a 3:2 toluene–acetonitrile (or 1:9 methanol–dichloromethane) mixture as the eluent, by discarding the leading purplish band and the brownish band that stuck to the stationary phase. Thin-layer chromatography of the isolated product showed a single spot, but solution-phase cyclic voltammetry (CV) in acetonitrile showed waves at potentials other than complex oxidation indicating that the desired complex was contaminated, with what appears to be a solvato complex. The contaminant was removed as the leading band on an α-cellulose column with a 3:1 toluene-dichloromethane mixture. The complex of interest (I) was washed from the column with a 1:1 dichloromethane–absolute methanol mixture. Solvent was removed at 40 °C and reduced pressure. Anal. Calcd for $C_{42}H_{50}N_6SP_2F_{12}Ru$: C, 47.47; H, 4.75; N, 7.91; S, 3.02. Found: C, 48.86; H, 4.93; N, 7.80; S, 3.16. The higher-than-calculated carbon and hydrogen microanalytical results are due to traces of cellulose microfibers in the sample taken for the analyses.

Preparation of Solid Substrates. In-doped tin oxide (ITO) on glass (1.25 by 3.75 cm rectangles) (Delta Technologies, Ltd., White Bear Lake, MN) were sonicated in 10% Alconox detergent solution for 10 min after an overnight soak in 10% KOH in ethanol. The pieces were then sonicated sequentially for 10 min each in water, absolute ethanol, and propanol. The cleaned pieces were kept under absolute methanol in plastic containers and were rinsed with water just before use.

Gold, 99.99%, was either sputtered (MRC Model 8620) or vapor deposited (Vacuum Engineering Co., North Billerica, MA) onto pretreated glass (vide infra), with the substrate at ambient temperature. Inspection by scanning tunneling microscopy (STM) (Nanoscope II, Digital Instruments, Santa Barbara, CA) of the gold films showed the sputtered samples to be much smoother than the vapor-deposited samples. However, the degree of roughness did not seem to affect the experimental results; hence the different samples were used interchangeably. The polycrystalline gold films were washed with hexane, absolute ethanol, and water just before use.

Spontaneous Adsorption and Langmuir–Blodgett Transfer of Films onto Solid Substrates. The ruthenium complex was allowed to self-adsorb onto the solid supports by soaking substrates in 2 mM solutions in dichloromethane for at least 2 h. Langmuir–Blodgett film preparations were conducted on a Lauda preparative film balance, while film transfers onto pre-cleaned substrates were done with a Lauda Filmlift (Brinkmann Instruments Co., Westbury, NY) at 20 dyn/cm. All transfers were done at room temperature with 1.0 mM NH_4PF_6 solution as the subphase. The subphase was filtered through 0.2 μM Nylon-66 filters (Rainin Instruments, Woburn, MA) before use on the trough.

Pretreatment of Glass for Gold Coating. As described elsewhere,[3] the ecl of the $Ru(bpy)_3^{2+}$–oxalate system is activated by biasing the working electrode to about 1.25 V vs SCE. At these potentials we observed that gold on untreated glass tended to peel off the support. In an attempt to circumvent this problem, we adapted Majda's[11] approach of "gluing" the gold layer onto the glass support. Microscope glass slide pieces (1.25 by 3.75 cm) were cleaned by sonicating in detergent solution for 30 min, rinsing with water, resonication for 10 min in absolute ethanol and 30 min in hexane, and then boiling for 3 h in a 1:1 HNO_3–HCl mixture. The glass was then rinsed copiously with water and stored under absolute methanol overnight. The silanation of the glass was conducted in a rigorously anhydrous environment with mercaptotrimethoxysilane (Petrarch Systems, Bristol, PA) for 24 h, in dry benzene, by following published procedures.[12] The glass pieces were handled in air after conditioning and were used as substrates for gold deposition.

Ecl and Electrochemical Measurements. Electrochemical measurements were made with a Model 175 universal programmer, a Model 173 potentiostat (Princeton Applied Research, PAR, Princeton, NJ), and an Ominigraphic 2000 X-Y recorder (Houston Instruments, Houston, TX). A saturated calomel reference electrode (SCE) was used for all measurements in aqueous media, while a silver wire was used as a quasireference electrode (Ag

QRE) in nonaqueous media. The Ag QRE was calibrated in every case by determining the cyclic voltammetric behavior of ferrocene added to the analyte solution. A platinum gauze was utilized as an auxiliary electrode. Aqueous phase measurements were conducted in N_2-deaerated 0.2 M Na_2SO_4 (pH = 4.5, adjusted with dilute sulfuric acid) or in 0.5 M H_2SO_4. Ecl experiments were conducted in a solution containing 0.1 M $Na_2C_2O_4$ and 0.4 M Na_2SO_4 of pH 4.7. Although the solutions used for all experiments were deaerated, replicate measurements made without deaeration showed essentially the same results. Total ecl emission was monitored at room temperature with a Hamamatsu PMT Model R958 (Hamamatsu Photonics, Hamamatsu City, Japan) connected to PM Photometer (American Instrument Co., Silver Springs, MA). The meter output was fed into the Y axis of an X-Y recorder while the signal from the potentiostat was fed into the X axis to afford ecl intensity versus bias potential displays. Ecl was also imaged with a CCD series 200 camera (Model CH210, Photometrics Ltd., Tucson, AZ, with camera cooled to –110 °C) interfaced to a Dell System (Austin, TX) Model 200 personal computer. Ecl spectra were obtained by beam dispersion with a Chemspec 100S concave holographic diffraction grating (American Holographic, Littleton, MA) and detected by the CCD camera. The camera was operated in a binning mode and a satisfactory signal to noise ratio was obtained by accumulating spectra for 10 min. Pixel numbers were converted to wavelengths by calibration with a mercury-argon test lamp (Ultra-Violet Products, San Gabriel, CA). The details of this instrumentation will be described elsewhere.[13]

Solution-Phase Luminescence. Solution-phase luminescence measurements were made with a Spex fluorometer, with a 550-W xenon lamp source and a Hamamatsu R508 photomultiplier tube. Spectral data were corrected for lamp and photomultiplier response.

Contact Angle Measurements. Contact angle measurements were made with a Ramé-Hart goniometer, with Milli Q water, under ambient conditions. Water drops (0.01 mL) were placed at four different spots on the substrate surface and three measurements of contact angles (two at 0° and one at a 45° angle of platform inclination) were made on each spot. The mean of these measurements, over the four spots, is reported. Receding angles were made at a 45° angle of platform inclination, and the mean difference between the angles measured at that plane inclination is reported as the contact angle hysteresis.

Results and Discussion

Purification and Characterization of the Ruthenium Complex. The synthetic route employed in the synthesis of I can, in principle, yield a number of side products. Of these, probably the most important results from the cis–trans isomerization of the ruthenium starting material $(Ru(bpy)_2Cl_2)$.[14] This is especially true if the solution was not properly degassed nor adequately protected from light. The trans isomer cannot yield product I; however given the high affinity of ruthenium for sulfur-containing ligands, it can undergo intramolecular ligand exchange in which the thiol on the modified bipyridyl ligand (bpy') will displace a preexisting bipyridyl ligand (bpy) to yield a bis(bipyridine) complex with a sulfur and a solvent molecule occupying the other two coordination sites. Such a product will be favored by entropy[15] over the other potential byproducts and will not be very different from I in its chromatographic properties. However, it can be easily distinguished from I by its electrochemical behavior. The product of the synthesis purified only on alumina chromatography was shown to be contaminated with an easily oxidized material ($E_{1/2}$ = 0.90 V vs Ag QRE, $E_{1/2}$(ferrocene) = 0.375 in 0.1 M tetra-

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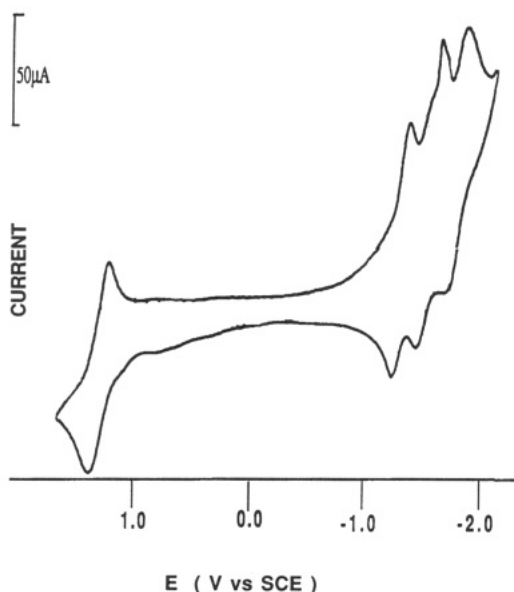
Figure 1. Cyclic voltammogram of 2.0 mM solution of I in 0.1 M TBAP in MeCN at a platinum disk working electrode (area = 0.05 cm²): scan rate, 200 mV/s.

n-butylammonium perchlorate (TBAP) in MeCN). The contaminant was separated from I on a cellulose column and was identified by ^{1}H NMR to be the intramolecular ligand exchange product.

Figure 1 is the cyclic voltammogram of a 2 mM solution of I in MeCN, 0.1 M TBAP. The effect of the modification of a bipyridine ligand on the electronic properties of the resultant complex is illustrated by comparing the redox potentials for the 3+ and 2+ oxidation of I, which showed $E_{1/2}$ = 1.185 V vs Ag QRE, ΔE_p = 103 mV, and $i_{p,c}/i_{p,a}$ = 0.8 ($E_{1/2}$(ferrocene) = 0.375 V, ΔE_p = 60 mV) with those for Ru(bpy)$_3^{2+}$, where $E_{1/2}$ = 1.35 V vs Ag QRE and ΔE_p = 60 mV in 0.1 M TBAP, MeCN. The modification on the ligand significantly increases the electron density on the metal center, with the –(CH$_2$)$_{12}$SH substituent acting as an electron-releasing group,[16] thus making the potential for the metal-based one-electron oxidation less positive. The observed separation of the cathodic and anodic peaks, ΔE_p, of 103 mV indicates that the electron transfer process of the Ru$^{2+/3+}$ couple is not as reversible as in the parent complex.

In acetonitrile, I exhibits an absorption band at 454 nm (ϵ = 13 600 mol L^{-1} cm^{-1}), which is very slightly red shifted compared to Ru(bpy)$_3^{2+}$ in the same medium (λ_{max} = 450 nm, ϵ = 14 000). The emission spectrum of I in undegassed MeCN at room temperature shows a maximum at 615 nm, which is again red shifted in comparison with the parent complex (λ_{max} = 607 nm), when these are excited at their respective absorbance bands. This is in agreement with the observations of Cook et al. that 4-substituted ligands lead to a red shift in the luminescence in such complexes.[17] Complex I was quite insoluble in water, but it could be dissolved in aqueous micellar solutions. The solution of I in a 5% (w/v) Triton-X100 solution exhibited an absorbance spectrum identical with that in MeCN; however, its emission spectrum showed a red shift with respect to the latter (λ_{max} = 639 nm).

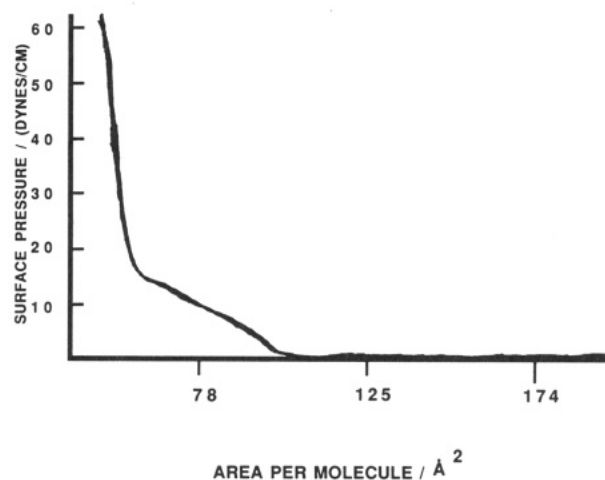**Surfactant Properties of the Ruthenium Complex.** The length of the aliphatic chain substituted on the

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Figure 2. Surface pressure–molecular area isotherm of I at the air–water interface, at room temperature, on a 1.0 mM NH$_4$PF$_6$ subphase.
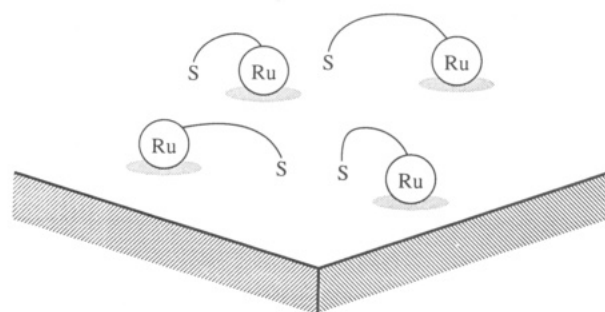

Figure 3. Schematic view of possible configuration of I at the air–water interface in a compressible film.

modified bipyridyl ligand confers surfactant properties to I. Hence the complex could be spread at air–water interfaces and transferred as a Langmuir–Blodgett (L-B) film onto solid substrates, in addition to its being spontaneously adsorbed at solution–solid interfaces.[7,18] Figure 2 shows the surface pressure–molecular area isotherm of I at an air–water interface, with 1.0 mM NH$_4$PF$_6$ as the subphase. The spread molecules start to form a coherent film at about 100 Å²/molecule, then form a relatively incompressible film at about 40 Å²/molecule. These properties depended strongly on the subphase composition. Very low limiting areas were obtained in the absence of a subphase electrolyte, presumably due to increased solubility of the spread molecules in water at elevated surface pressures.

The thiol functional group on the surfactant tail of I distinguishes this complex from other known ruthenium surfactant complexes,[7] since it conveys some hydrophilic character to the surfactant tail. Hence, the surface activity of I is determined in part by a balance between the hydrophilicities of the head and thiol groups and the hydrophobicity of the methylene groups in the aliphatic tail. Thus, at the air–water interface both hydrophilic groups can be associated with the water phase, while the hydrophobic chain is in the air, as illustrated in Figure 3. Thus, the films are less organized than the usual L-B films, and this behavior may be responsible for experimental difficulties encountered when attempts were made to transfer the film from the air–water interface to solid substrates by lifting substrates through a preformed monolayer on the trough. Such a transfer usually results in the

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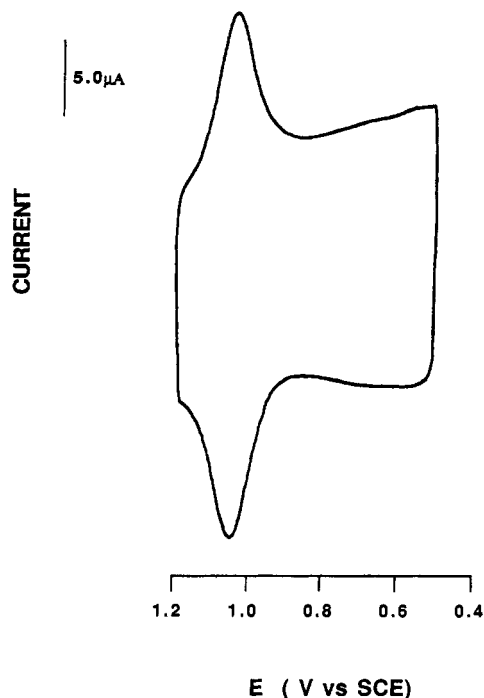
Figure 4. Cyclic voltammogram of a self-adsorbed monolayer of I on ITO (area = 6.2 cm²), in 0.5 M H₂SO₄: scan rate, 200 mV/s.

head group against the substrate and the tails sticking out.[3,18] Transfers were only achieved when the substrate was first dipped through the preformed monolayer and then lifted. Although a bilayer would be expected under such conditions, less than a monolayer was transferred, as indicated by the transfer ratio (about 0.5) and the coverage estimated by cyclic voltammetry (CV). This unusual behavior introduces ambiguities about the orientation of the immobilized molecules in the L-B films.

Spontaneous Adsorption of I on Solid Substrates. Solid substrates, such as ITO or polycrystalline gold, when immersed in 2 mM solutions of I in dichloromethane developed a yellow coloration after soaking for about 2 h. When these substrates were removed from the solution, washed well with water, and examined electrochemically in 0.2 M Na₂SO₄ or 0.5 M H₂SO₄, they showed surface CV redox waves due to the adsorbed materials. A typical cyclic voltammogram of an ITO electrode treated with I is shown in Figure 4. The voltammogram is characteristic of a surface-immobilized electroactive species.[19] Integration of the redox peaks (3.44 μC/cm² after correcting for charging current) indicated that less than 10% (based on 100 Å²/molecule) of the electrode surface was covered with the complex. The complex appears to adsorb strongly on the substrate, since the integrated areas under the cyclic voltammetric waves did not change over several hours of continuous cycling in aqueous media. Prolonged washing of the coated substrates with chloroform and methanol or ethanol, however, removed most of the initial yellow coloration and greatly reduced the peak current magnitude in the cyclic voltammograms. However, such electrodes continued to exhibit ecl, albeit at a reduced intensity. Sonication of the ITO substrates in organic solvents essentially removed all the adsorbed materials, as ecl imaging and cyclic voltammetry of such treated substrates did not reveal much signal above the background current.

Figure 5 is the cyclic voltammogram at different scan rates (v) of a Langmuir–Blodgett film of the complex
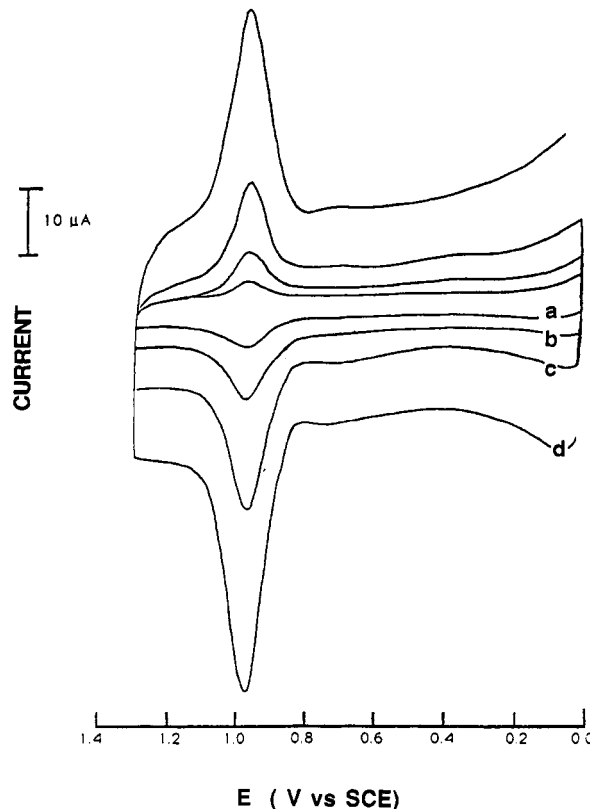
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E (V vs SCE)

Figure 5. Cyclic voltammogram of a Langmuir–Blodgett film of I, transferred at 20 dyn/cm to ITO, in 0.5 M H₂SO₄. Scan rates (mV/s) were as follows: a, 50; b, 100; c, 200; d, 500. Electrode area was 3 cm².

transferred at 20 dyn/cm surface pressure on a clean ITO electrode. The monolayer was transferred by dipping and lifting the ITO electrode through the film at 5 cm/min and 10 cm/min, respectively. Although the shapes of the waves are closer to those of ideal surface waves, the coverage, as calculated from the charge under the peaks (11.3 μC/cm² after correcting for charging current), is only about 30% of a monolayer. The surface concentration decreased with decreasing film transfer pressure, and only 5% coverage was obtained at zero pressure. Furthermore, at lower transfer pressures the surface wave characteristics (ΔE_p and width of peaks at half-height) approached those of the spontaneously adsorbed films. The differences between the characteristics of the cyclic voltammograms of the self-adsorbed and the Langmuir–Blodgett (L-B) films may be due to differences in the packing conformations on the electrode. Pressure probably forces molecules in the L-B film into a more ordered and closely packed or uniform configuration on the surface so that the L-B films transferred at higher pressures will have a partially ordered orientation while the molecules in the spontaneously adsorbed films may be randomly oriented. The observed CV waves of the latter will be a composite for different orientations and hence may be somewhat broader.[19] Very highly ordered films can however show double peaks.[20]

The peak potential, E_{pa}, of the immobilized complex of 1.06 V vs SCE is identical with that observed for an L-B monolayer of the amide-linked complex.[3] The difference of about 170 mV between the redox potential of Ru(bpy)₃²⁺ in aqueous acidic solutions and of the immobilized species

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Table I. Contact Angles of Substrate and Films of I

nature of substrate	contact angle, deg	hysteresis, deg
clean ITO	8 ± 1	0
spontaneously adsorbed I on ITO	44 ± 3	21 ± 2
clean polycrystalline gold on glass	57 ± 6	16 ± 3
spontaneously adsorbed I on gold	59 ± 3	16 ± 4
L-B film of I transferred at 15 dyn/cm on gold	39 ± 2	19 ± 5

suggests strong interaction between the complex molecules and the ITO surface. The perturbation of the electronic structure of the complex, as a consequence of the adsorption, may be similar to that suggested in ref 3, as the same magnitude of peak potential shift was observed. In ref 3, the head group was, by design, in direct contact with the electrode surface. If the perturbation depends on the orientation of the head group with respect to the surface, then it could be inferred that in the present case the head group is also against the electrode surface. Both the head and tail groups of the present complex are hydrophilic and thus will have affinities for the substrate. Under such circumstances the molecule probably has both ends in contact with the electrode surface, thus constraining it to lie flat. Flat lying molecules do not form organized films.[21] Moreover, interhead repulsions will also hinder the formation of a compact layer; such an orientation would explain in part the 425 Å^2/molecule coverage calculated from the CV results.

Well-defined cyclic voltammograms could not be obtained with gold substrates. This can be attributed to the relatively low coverage of I on gold and contributions to the CV anodic current by formation of gold oxide at potentials characteristic of the oxidation of I. Attempts at covering the exposed gold by adsorbing the alkyl thiol $C_{12}H_{25}SH$ after the ruthenium complex was adsorbed did not improve the CV response. Similarly, voltammograms obtained in MeCN, 0.1 M TBAP of adsorbed I on gold were dominated by the cathodic current due to the reduction of gold oxide. However, as described below, ecl was obtained from such films, indicating adsorption and immobilization of some I on the gold surface.

Contact Angles as Probe of Film Structure. Contact angles are known to be sensitive to surface polarity, while the contact angle hysteresis is an index of the surface uniformity.[22] Both the head group and the tail terminal of I are polar; hence if either is at the outside of the films, the contact angles with water on the films will be lowered compared to films with exposed hydrocarbon tails. Contact angles were measured on the substrates just before and after exposure to the complex, in an attempt to gain information about the orientation of the immobilized molecules of I. The results are summarized in Table I. The contact angles on the bare electrode substrates indicated that they were clean. The value of 57 ± 6° on polycrystalline gold agrees fairly well with literature values,[22,23] while the hysteresis of 16 ± 3° may be indicative of the relative smoothness of the gold films used. When I self-adsorbs on the polycrystalline gold film, the contact

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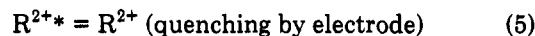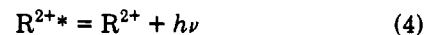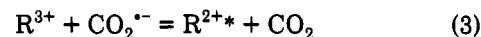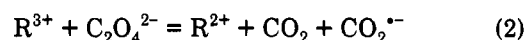
angle does not appear to change much, which is reasonable since less than 10% coverage is achieved. In contrast, the contact angle drops considerably on the same substrate with the L-B film, indicating the exposure of either the $Ru(bpy)_3^{2+}$ head group or the thiol terminal, and the increased hysteresis in contact angles implies that the LB film surface is less uniform than that of the bare gold surface. Visual inspection of the LB film, under bright light, as well as imaging of the emitted ecl, as described below, show the film to be patchy. A thiol surface is expected to have a polarity similar to an alcohol or a carboxylate surface; such films show contact angles of about 70°,[22] while the I L-B surface shows a value of 39 ± 2°. This indicates that this surface is more polar than expected for a thiol. The ruthenium(II) head group is therefore implicated as the exposed functionality, which is reasonable given the strong affinity of gold for thiol.[23]

When these observations are taken in conjunction with the low surface coverage observed by CV, a qualitative picture of the film emerges. The film transfer only occurs on dipping the solid substrate through the preformed monolayer on the trough, yet the amount of material actually transferred is controlled by an interplay of intermolecular repulsions of the head groups and the stability of the gold–thiol bond. The patchy nature of the transferred film may thus be a consequence of this competition which allows the less strongly bound molecules to be stripped off during the lifting stage of the film transfer process. The large size of the $Ru(bpy)_3^{2+}$ head group compared to the hydrocarbon chain prevents close packing of the molecules and a high degree of order in the films.

Although similar conclusions can be drawn for the films on ITO, weaker chemisorption is expected on this substrate. Given the hydrophilic nature of the head and terminal groups, the molecules could lie flat on the surface. Such an orientation is consistent with the higher contact angles observed with ITO substrates, as more methylene groups will be exposed in such a configuration.

Ecl of the Surface Film. Inspection of the ecl emitted with the electrodes biased at 1.25 V vs SCE showed the adsorbed material formed "islands" or "patches" of high concentrations. Long "soaks" usually left substrates with a yellow coloration, indicating the formation of multilayers. Such samples used in ecl or electrochemical experiments were washed copiously with water, until the washings were colorless to the eye and the electrode surface was colorless. Polycrystalline gold soaked in millimolar solutions of I in dichloromethane, even after washing with water and three cycles of absolute ethanol, chloroform, ethanol, and water, sonicating for about a minute in 1:1 ethanol–chloroform mixture, and then rewashing with ethanol and water, still showed ecl. The ecl of layers of I on both gold and ITO persisted for at least 30 min under continuous electrolysis in oxalate media.

Light emission occurs when $Ru(bpy)_3^{2+}$-based species are oxidized in the presence of certain solution components, such as oxalate. This ecl is attributed to the following set of reactions, where R^{2+} represents the $Ru(bpy)_3^{2+}$ group:

$$R^{2+} - e^- = R^{3+} \text{ (at electrode)} \qquad (1)$$

$$R^{3+} + C_2O_4^{2-} = R^{2+} + CO_2 + CO_2^{\cdot-} \qquad (2)$$

$$R^{3+} + CO_2^{\cdot-} = R^{2+*} + CO_2 \qquad (3)$$

$$R^{2+*} = R^{2+} + h\nu \qquad (4)$$

$$R^{2+*} = R^{2+} \text{ (quenching by electrode)} \qquad (5)$$

Ecl of this type has been shown to occur in an L-B monolayer with the R^{2+} head group presumably facing the ITO
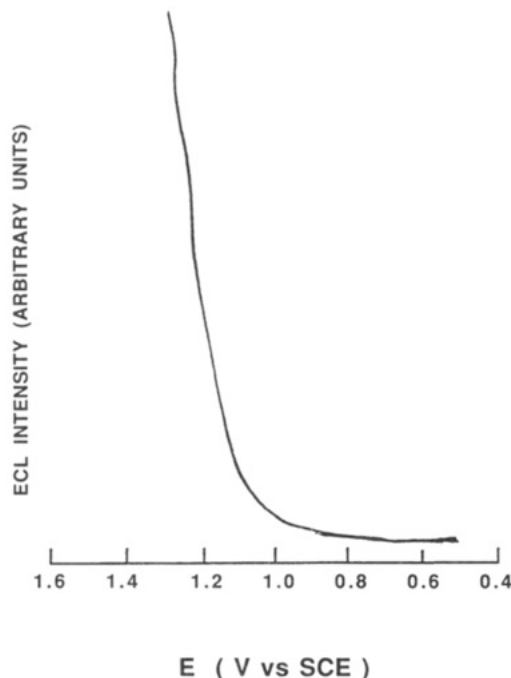
Figure 6. Photomultiplier tube response representing total ecl emission as a function of bias potential of a spontaneously adsorbed monolayer of I on ITO, in 0.1 M $Na_2C_2O_4$ and 0.4 M Na_2SO_4 (pH = 4.7).

or gold substrates, indicating that emission (4) can compete with quenching (5), even with this group in close proximity to the metal or degenerate semiconductor surface. Similar ecl experiments were undertaken with electrodes with adsorbed I. Figure 6 shows the PMT response (in arbitrary units) as a function of the bias potential of the ITO electrode coated with self-adsorbed I after an overnight soak of the substrate in a millimolar solution of I in dichloromethane. The ecl starts at potentials characteristic of the oxidation of I and shows a typical ecl intensity–potential wave. Oxalate oxidation directly at the electrode, although thermodynamically possible, is known to be kinetically slow. The presence of adsorbed I probably further hinders direct oxidation of oxalate. Figure 7 compares photos of the same electrode before and after stepping the potential to 1.25 V vs SCE, in a mixture of 0.1 M NaC_2O_4 and 0.2 M Na_2SO_4. Inspection of Figure 7b reveals nonuniform clusters of the emitters on the electrode. Similar patterns were observed with L-B films on ITO and on polycrystalline gold on glass.

Figure 8 shows the PMT response as a function of potential applied to a gold electrode treated with the complex after (a) thoroughly rinsing with water and ethanol and (b) sonication in 1:1 CH_2Cl_2–MeCN for 5 min followed by three ethanol–water wash cycles. The emission from complex I chemisorbed on gold was quite low but sufficient to be dispersed into the spectrum shown in Figure 9. We estimate the emission intensity observed here to be roughly the same as that of a 10^{-8} M solution of $Ru(bpy)_3^{2+}$ in MeCN subjected to annihilation ecl. The emission peak at 650 nm can be compared with the 680-nm peak obtained for the amide-linked complex.[3] The red shift in the emission maximum for surface species compared with dissolved component has been attributed to interactions among the adsorbed molecules. Thus the small red shift found with I suggests that the interaction between the chemisorbed species may not be as strong as in the compact monolayers (about 96% coverage) in the earlier work.[3] The ecl band for adsorbed I in aqueous solution, however, is at much lower energy than the solution
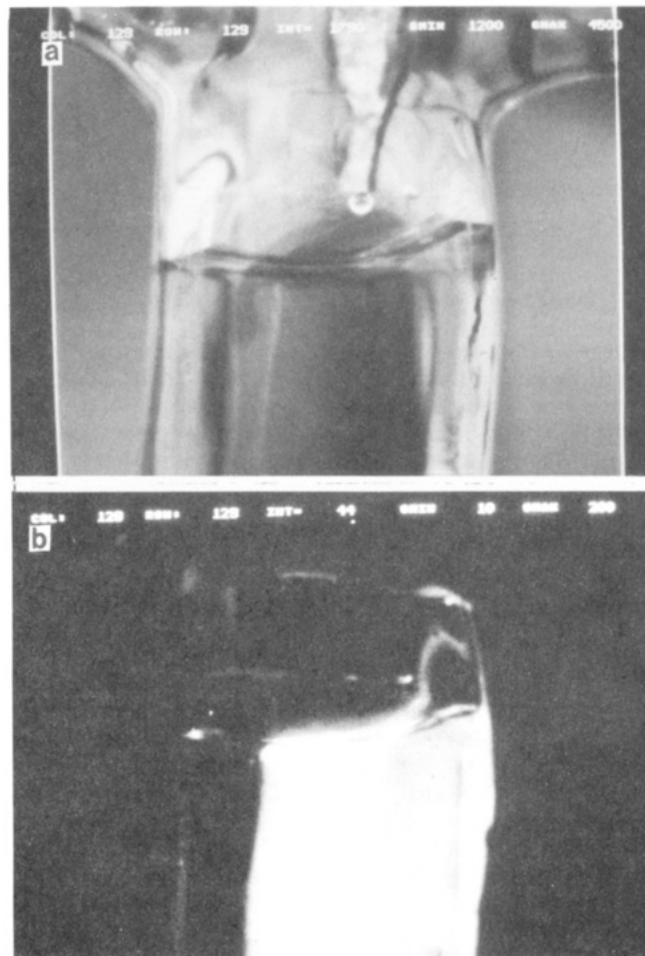

Figure 7. CCD camera images of a self-adsorbed monolayer of I on ITO in 0.1 M $Na_2C_2O_4$ and 0.4 M Na_2SO_4 (pH = 4.7): (a) before electrochemical excitation, electrode illuminated by room light; (b) ecl emission upon electrochemical excitation at 1.25 V vs SCE.
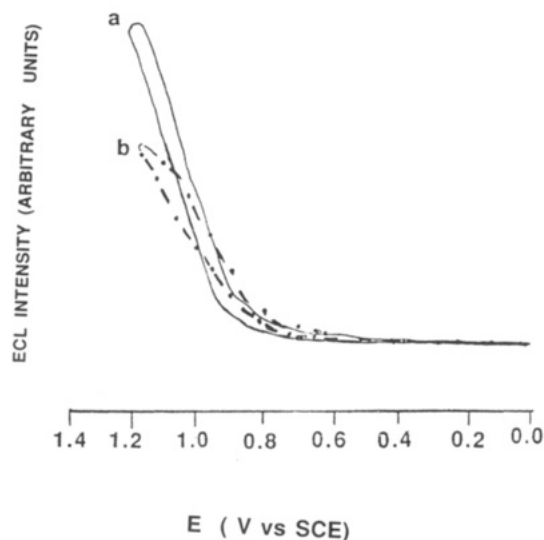

Figure 8. Photomultiplier tube response (total ecl emission) as a function of bias potential of a spontaneously adsorbed I on polycrystalline gold film on glass in 0.1 M $Na_2C_2O_4$ and 0.4 M Na_2SO_4 (pH = 4.7) after the indicated treatments: (a) substrate washed thoroughly with water after 12 h immersion in 1 mM solution of I in dichloromethane; (b) same substrate as in (a) after 5 min of sonication in 1:1 CH_2Cl_2–MeCN mixture, followed by liberal rinsing with absolute ethanol–water.

phase luminescence peak of 629 nm in undegassed MeCN, as well as a 639-nm peak observed in aqueous micellar
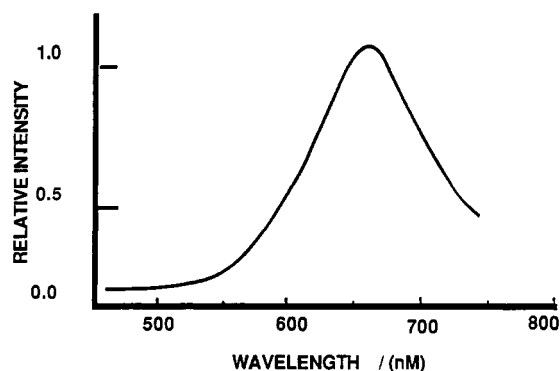
Figure 9. Spectrum of the ecl of a chemisorbed monolayer of I on polycrystalline gold in 0.1 M $Na_2C_2O_4$ and 0.4 M Na_2SO_4 (pH = 4.7) biased to 1.25 V vs SCE obtained with CCD camera and monochromator (integrated over 10 min).

solution (5% (w/v) Triton-X100 in Milli-Q water). This indicates that some interaction between the immobilized molecules exists. The fact that there is a red shift of the emission maximum upon immobilization[7,24] is a good indication that the emission observed is not due to solution species. Thus the ecl found here for adsorbed species with the $Ru(bpy)_3^{2+}$ group on or near the gold surface supports

the earlier study[3] showing emission under these conditions and suggests that the rate of the emission process is sufficiently fast to compete with quenching by the metal via energy and electron transfer processes.

Conclusion

$[Ru(bpy)_2(bpy')](PF_6)_2$, where bpy is 2,2'-bipyridine and bpy' is 4-methyl-4'-(dodecyl-1-thiol)-2,2'-bipyridine adsorbs on conducting substrates (indium doped tin oxide (ITO) and polycrystalline gold) to provide chemically modified electrodes that can be used in the electrogeneration of chemiluminescence in oxalate solutions. The chemisorption of this ruthenium tris(bipyridine) complex onto polycrystalline gold, probably via the thiol group, affords chemically modified electrodes that are stable in acidic, basic, and organic media.

(24) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 218, and references (257–265) therein.