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

Yaw S. Obeng and Allen J. Bard*

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

Received April 2, 1990. In Final Form: June 21, 1990

Cyclic voltammetric surface waves were found for monolayers of Ru(bpy)₂(bpy')⁺, 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 electro-generated species that react to form excited species, usually via an energetic redox reaction. 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. Emission via ecl in a monolayer film was recently demonstrated with a Ru(bpy)₄ molecule modified by addition of a C₁₉ hydrocarbon chain via an amide linkage and coated on gold and indium tin oxide (ITO) substrates by Langmuir–Blodgett techniques. 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 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)₄ tagged molecules. 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⁺ type complex in which one bpy was derivatized to produce complex (I) [Ru(bpy)₂(bpy')⁺, 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. 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 toward both leaching and such side reactions as hydrolysis of the substituent side chain.

Experimental Section

All organic solvents were obtained from J. T. Baker (Phillipsburg, 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. The thiol was obtained by reacting the bromide precursor with sodium hydrosulfide (Aldrich) in aqueous DMSO overnight and was purified by vacuum distillation on a Kugelrohr system (Aldrich). The product was identified by its 300-MHz (General Electric) ¹H NMR: δ 1.25 (br s, 24, bpy-CH₂-CH₂-CH₂SH), δ 2.48 (s, 3, bpy-CH₃), δ 7.12–8.52 (comp., 6, bpy-H).

Preparation of (bpy)₂Ru(bpy') Complex. Complex I was prepared by adapting published procedures. The product was partially purified by column chromatography on neutral alumina.
with a 3:2 toluene–acetone (or 1:3 methanol–dichloromethane) mixture as the eluent, by discarding the leading purplish band with dilute sulfuric acid) or in 0.5 M H2SO4. Ecl experiments were conducted in a solution containing 0.1 M Na2CO3 and 0.4 M Na2SO3 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 Champsic 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 instrumentations 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)2Cl2).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') 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 entropy16 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 (E1/2 = 0.90 V vs Ag QRE, E1/2(ferrrocene) = 0.375 in 0.1 M tetra-

---

(11) Majda, M. Private communication.
Electrogenerated Chemiluminescence

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.

The contaminant was separated from I on a cellulose column and was identified by 1H 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 E1/2 = 1.185 V vs Ag QRE, ΔEₚ = 103 mV, and iₚ/c_iₚ, = 0.8 (E₁/₂(ferrocene) = 0.375 V, ΔEₚ = 60 mV) with those for Ru(bpy)₃²⁺, where E₁/₂ = 1.35 V vs Ag QRE and ΔEₚ = 60 mV in 0.1 M TBAP, MeCN. The modification on the ligand significantly increases the electron density on the metal center, with the -(CH₂)₁₂SH substituent acting as an electron-releasing group, thus making the potential for the metal-based one-electron oxidation less positive.

The 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. Figure 2 shows the surface pressure–molecular area isotherm of I at an air–water interface, with 1.0 mM NH₄PF₆ 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, 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

![Figure 2](image-url)

**Figure 2.** Surface pressure–molecular area isotherm of I at the air–water interface, at room temperature, on a 1.0 mM NH₄PF₆ subphase.

![Figure 3](image-url)

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

**Surfactant Properties of the Ruthenium Complex.**

The length of the aliphatic chain substituted on the

---


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. 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 (ν) of a Langmuir–Blodgett film of the complex 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 50% of a monolayer. The surface concentration decreased with decreasing film transfer pressure, and only 2% coverage was obtained at zero pressure. Furthermore, at lower transfer pressures the surface wave characteristics (ΔEₚ 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.

The peak potential, Eₚₑ, 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. The difference of about 170 mV between the redox potential of Ru(bpy)₃²⁺ in aqueous acidic solutions and of the immobilized species

Figure 4. Cyclic voltammogram of a self-adsorbed monolayer of I on ITO (area = 0.2 cm²), in 0.5 M H₂SO₄; scan rate, 200 mV/s.

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.
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 A^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, ecI 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 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 L-B 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°,24 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 intramolecular 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 semiluminance 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 ecI 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 ecI. The ecI 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 ecI is attributed to the following set of reactions, where R^2+ represents the Ru(bpy)_3^{2+} group:

\[
R^{2+} + e^- \rightarrow R^{3+} \quad \text{(at electrode)}
\]

\[
R^{3+} + C_2O_4^{2-} = R^{2+} + CO_2 + CO_2^{-*} \quad \text{(2)}
\]

\[
R^{3+} + CO_2^{-*} = R^{2+*} + CO_2 \quad \text{(3)}
\]

\[
R^{2+*} = R^{2+} + h\nu \quad \text{(4)}
\]

\[
R^{2+*} = R^{2+} (quenching by electrode) \quad \text{(5)}
\]

Ecl of this type has been shown to occur in an L-B monolayer with the R^2+ head group presumably facing the ITO.
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 NaC2O4 and 0.2 M Na2SO4. 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 CH2Cl2-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)₃²⁺ 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. 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. The ecl band for adsorbed I in aqueous solution, however, is at much lower energy than the solution phase luminescence peak of 629 nm in undegassed MeCN, as well as a 639-nm peak observed in aqueous micellar
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 immobilization7,24 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$^8$ 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')]$_2$(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.

**Acknowledgment.** The support of the Robert A. Welch Foundation (F-079) and the National Science Foundation (CHE 8901450) is gratefully acknowledged. We also appreciate helpful discussions and assistance by Professor T. E. Mallouk, Paul McCord, Kim R. Cousins, Kim R. Dean, and Andrienne C. Friedli.

**Registry No.** I, 130882-88-1; ITO, 50926-11-9; Au, 7440-57-5; Na$_2$C$_2$O$_4$, 62-76-0.

---