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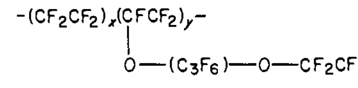
Polymer Films on Electrodes. 4. Nafion-Coated Electrodes and Electrogenerated Chemiluminescence of Surface-Attached Ru(bpy)$_3^{2+}$

Sir:

A pyrolytic graphite electrode coated with the perfluorinated ion-exchange polymer Nafion (**1**)[1] and containing Ru(bpy)$_3^{2+}$ (bpy = 2,2′-bipyridine) was prepared. Electrogenerated chemiluminescence at the polymer layer is produced upon oxidation of the 2+ Ru species in the presence of oxalate ion.



$$\begin{array}{l} -(\mathrm{CF_2CF_2})_x(\mathrm{CFCF_2})_y- \\ \qquad | \\ \mathrm{O-(C_3F_6)-O-CF_2CF_2-SO_3^-Na^+} \end{array}$$

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Electroactive groups can be bound quite readily to an electrode surface in the form of a polymer layer,[2-4] where either the polymer itself is electroactive [e.g., poly(vinylferrocene)][2a] or the electroactive molecules are later attached into the polymer [e.g., Ru(NH$_3$)$_6^{2+}$ on polyacrylic acid].[4b,c] In the latter example, Oyama and Anson demonstrated that ions from solution could be bound to the polymer by exploiting its ion-exchange properties (electrostatic binding).[4c]

Nafion (**1**), an ion-exchange polymer which is very resistant to chemical attack, even by strong oxidants at elevated temperatures, has found increasing use as a membrane material. We have found that a pyrolytic graphite (PG) electrode can be coated with this material. In a typical experiment, a layer of ~1.4 mg of Nafion polymer/cm^2 of electrode surface was prepared by dip coating. The electrode was dipped into a solution of ~2% Nafion (equiv wt ~970) in ethanol, then taken out and dried in the air, leaving the polymer film on the surface. The film thickness can be estimated by using the density of dry commercial Nafion membranes (~2 g cm^{-3}) as ~7 μm (dry). The polymer-coated electrode was then immersed for 10–15 min in a solution of 5 mM Ru(bpy)$_3$Cl$_2$ in 0.1 M H$_2$SO$_4$, rinsed thoroughly with distilled water, and transferred to the electrochemical cell. Electrodes prepared in this manner acquire a deep orange color, demonstrating the large amount of Ru(bpy)$_3^{2+}$ incorporated into the polymer.

Such an electrode, denoted as PG/Nafion, Ru(bpy)$_3^{2+}$, shows the cyclic voltammetric behavior characteristic of the Ru(bpy)$_3^{3+/2+}$ couple when immersed in a solution containing only supporting electrolyte (Figure 1a). However, the observed oxidation and reduction peaks are broad and separated by 170 mV at this scan rate, markedly deviating from the expected behavior of a surface-confined electroactive species.[2a,5a] Such deviations are caused by limitations in the overall rate of the redox process by mass transfer within the film, charge transfer at the substrate/film interface, and associated chemical reactions of the electroactive forms, as well as by nonidealities in the film structure.[2,3,4a,5b] For these films, the peak currents, measured over a range of scan rates (v) of 0.01–1 V/s, were proportional to $v^{1/2}$, indicating that the current was controlled by diffusion in these thick polymer layers.[2a,3b]

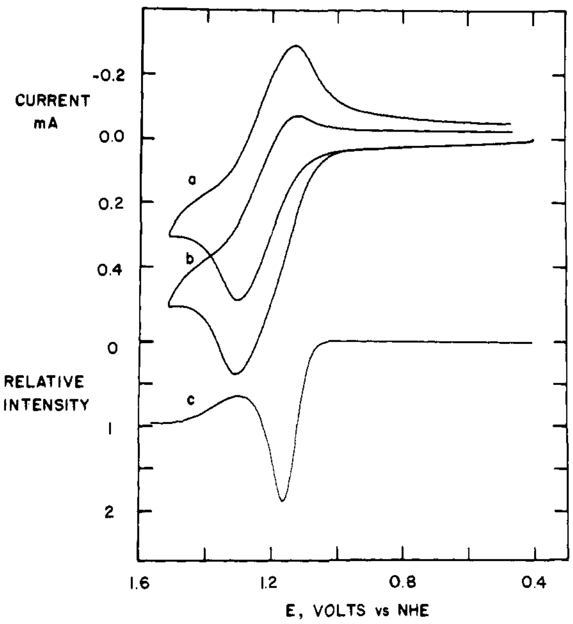

Figure 1. (a) Current-potential curve (sweep rate, 0.1 V/s) for a PG/Nafion, Ru(bpy)$_3^{2+}$ electrode in 0.2 M Na$_2$SO$_4$. (b) Same as (a), with addition of 50 mM Na$_2$C$_2$O$_4$. (c) ecl intensity vs. potential, in the same solution as (b) (anodic scan only). The electrode was a PG (Union Carbide Corp.) cylinder, 0.5-cm diameter, with the basal plane as the active surface.

The amount of Ru(bpy)$_3^{2+}$ attached to the surface was determined by first oxidizing the film at +1.60 V, and then determining the charge required to reduce the film when the potential was stepped to +0.60 V until the current dropped to zero (several minutes). For typical films, the surface concentration of Ru(bpy)$_3^{2+}$ is (2–4) × 10^{-6} mol/cm^2.

The behavior of the same electrode in an aqueous solution containing 50 mM sodium oxalate is shown in Figure 1b. In the absence of Ru(bpy)$_3^{2+}$ on the Nafion-coated electrode, oxalate itself is oxidized at potentials more positive than Ru(bpy)$_3^{2+}$. However, on the modified electrode, oxalate is catalytically oxidized by the Ru(bpy)$_3^{3+}$ attached to the surface. This is clearly seen in Figure 1b by the increase in the anodic peak current and decrease in the cathodic peak current, caused by the reaction of Ru(III) with C$_2$O$_4^{2-}$. Basically, the same catalysis is also observed when a solution containing Ru(bpy)$_3^{2+}$ and C$_2$O$_4^{2-}$ is oxidized on Pt or carbon electrodes in aqueous solution.[6]

When the potential of a PG/Nafion, Ru(bpy)$_3^{2+}$ electrode in an aqueous solution containing 50 mM Na$_2$C$_2$O$_4$ and 0.2 M Na$_2$SO$_4$ (pH ~6) is stepped to +1.4 V, a constant, very intense orange luminescence is observed, clearly visible to the non-dark-adapted eye. The ecl intensity upon scanning the potential in the positive direction is shown in Figure 1c. The detailed shape of the intensity–potential and intensity–time curves is currently under further investigation. The ecl spectrum is identical with the known luminescence spectrum of Ru(bpy)$_3^{2+*}$.[6,7] The mechanism of the ecl reaction is very likely the same as that previously proposed for the simultaneous oxidation of dissolved

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$Ru(bpy)_3^{2+}$ and oxalate in acetonitrile (MeCN)[8] and aqueous[6] solutions, where oxidation of oxalate produces a strong reductant, $CO_2^{-}\cdot$, which ultimately causes reduction of $Ru(bpy)_3^{3+}$ and excited-state production.

The PG/Nafion, $Ru(bpy)_3^{2+}$ electrode shows remarkable stability. The coating did not come off when the electrode was immersed at open circuit in water or aqueous solution for 3 weeks, and occasional cyclic voltammograms taken during this period were perfectly reproducible. The ecl intensity with occasional operation slowly decreased with time, although even after 3 weeks light emission was clearly seen when applying the positive potential steps. When the potential was repetitively cycled between 0.65 and 1.45 V at 100 mV/s, the peak current decreased by ~5% after 350 cycles and by ~16% after 1500 cycles. However, if the electrode was left in the solution overnight at open circuit after this cycling, the peak current recovered to over 90% of its initial value. If the electrode was left to dry in the air and then transferred back to the solution, the ecl intensity decreased sharply or even disappeared.

We have also shown[6] that ecl can be produced by the alternate electrogeneration of $Ru(bpy)_3^{3+}$ and $Ru(bpy)_3^{+}$ in an aqueous solution containing ≥20% MeCN, in a process similar to that found in dry aprotic media.[7] Generation of ecl (in the absence of oxalate) at the PG/Nafion, $Ru(bpy)_3^{2+}$ electrode in aprotic media is complicated by the rapid dissolution of the polymer film in these solutions. However, if the modified electrode is transferred to an aqueous solution containing 20% MeCN and 0.1 M tetrabutylammonium fluoroborate and the potential is repetitively pulsed between the oxidation and the reduction potentials of the adsorbed complex, a very intense luminescence is generated. This ecl rapidly decays upon continued pulsing because of dissolution of the film.[9] This experiment is especially interesting because it provides unique evidence for mobility within the polymer and the possibility of charge transfer and chemical reactions between attached groups, as suggested by Kaufman and Engler.[3c]

Finally, we ran a preliminary experiment to examine the possibility of producing chemiluminescence in membranes. A piece of Nafion membrane (1200 E.W., 10 mil thickness, supplied by duPont de Nemours and Co.) was immersed for 1 h in 5.0 mM $Ru(bpy)_3Cl_2$ in 0.1 M H_2SO_4. The membrane turned orange, indicating that a large amount of $Ru(bpy)_3^{2+}$ was incorporated into it. When this membrane was immersed for ~15 min in an acidic $KMnO_4$ solution, the membrane turned green, signaling production of $Ru(bpy)_3^{3+}$. When the oxidized membrane was transferred to a concentrated aqueous $Na_2C_2O_4$ solution in a dark room and shaken, a weak but definite orange luminescence was observed from the membrane. This preliminary experiment indicates the possibility of electrostatically attaching large amounts of metal complex into Nafion membranes, and carrying out chemical reactions in the membrane or at the interface with the solution.

Because of its stability, Nafion represents a potentially very useful coating at an electrode, and the electrostatic binding technique[4c] offers a simple way of incorporating charged reactants into it. The observation of ecl and its time and potential dependence may be valuable in probing the nature of the charge- and mass-transfer events within polymer layers. Moreover, such electrodes might also be useful for electrocatalytic purposes and in photochemical experiments.[10]

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(9) We have been informed through private communication that annihilation ecl from polymer-coated electrodes has been recently observed by D. Buttry and F. C. Anson (California Institute of Technology) and by K. Iwasa and S. Toshima (Tohoku University).

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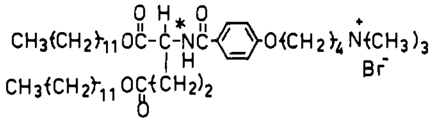
Unique Properties of Chromophore-Containing Bilayer Aggregates: Enhanced Chirality and Photochemically Induced Morphological Change[1]

Sir:

A variety of synthetic single chain[2–4] and double chain (dialkyl)[5–10] amphiphiles produce stable monolayer and bilayer membranes in dilute aqueous solution. These totally synthetic membranes possess structural characteristics which are common to the biolipid membrane, such as molecular alignment and phase transition. These characteristics are readily used for developing unique functional systems. We describe in this communication two examples of the unique property of the chromophore-containing synthetic bilayer membrane.

It has been shown that chiral dialkylammonium amphiphiles as synthesized from alanine and glutamic acid produce well-developed bilayer membranes in water.[11] We subsequently prepared chiral membranes with the aromatic chromophore.

Dialkyl amphiphile L-**1**[12] similarly produces bilayer vesicles in water as probed by electron microscopy. The layer width inferred from an electron micrograph of a negatively stained sample was ca. 50 Å. Interestingly, the magnitude of the optical activity was sensitive to the temperature of measurement. Figure 1 shows the temperature dependence of the CD spectrum of L-**1** in dilute aqueous solution (1.0×10^{-4} M).[13] At temperatures above 31–32 °C, which is the phase-transition temperature (T_c), the CD spectrum possesses a maximum at 245 nm with $[\theta]_{245} = +6000$. This spectrum is identical with that observed in methanol. At temperatures below T_c, there are observed extremely large maxima at 220 and 260 nm with a shoulder extending beyond 700 nm; $[\theta]_{220} = +360\,000$ and $[\theta]_{260} = -400\,000$. The temperature dependence of $[\theta]_{max}$ near 260 nm is shown in Figure 2. The $[\theta]_{max}$ value changes at T_c drastically. These spectral changes are reversible; however, when the temperature is lowered, aging is required to fully regain the low-temperature spectrum. Similar spectral changes are observed for D-**1** in the mirror image.



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The CD enhancement is highly dependent on the amphiphile concentration. When the concentration is lowered from 1.0×10^{-4} M to 5.0×10^{-6} M, $[\theta]_{260}$ decreases from $-400\,000$ to $-22\,000$. The $[\theta]_{260}$ value is not sensitive to the amphiphile concentration

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(12) This compound was prepared by condensation of didodecyl L-glutamate and *p*-(4-bromobutoxy)benzoic acid and the subsequent quaternization with trimethylamine; mp 45–220 °C (the liquid crystalline behavior was observed in this temperature range), $[\alpha]^{20}_{D}$ +7.46° (*c* 2.00, $CHCl_3$). D-**1** and DL-**1** were similarly prepared. The purity was confirmed by elemental analysis, thin-layer chromatography, and ^1H NMR spectroscopy.

(13) Sonication of an aqueous suspension of **1** was carried out by using a Branson ultrasonic cleaner 12 (bath type) for 3–5 min. The aggregate weight was 6×10^9. When L-**1** was sonicated with the cell disruptor for 5–10 min, the low-temperature CD spectrum could not be observed even after aging for 10 h at 0 °C.

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