scan rates, and that the rate constant for heterogeneous electron transfer for Ru(bpy)$_3^{2+}$ incorporated in the polymer is somewhat smaller than that at a bare electrode.

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Registry No. Ru(bpy)$_3^{2+}$, 15158-62-0; C, 7440-44-0; H_2SO_4, 7664-93-9; Me-*p*-$C_6H_4SO_3H$, 104-15-4; K_2SO_4, 7778-80-5; Ru(bpy)$_3^{3+}$, 18955-01-6; Nafion, 39464-59-0.

Electrochemical Control of the Luminescent Lifetime of Ru(bpy)$_3^{2+*}$ Incorporated in Nafion Films on Graphite Electrodes

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Abstract: The formal potential of the Ru(bpy)$_3^{3+/2+}$ redox couple incorporated in a Nafion film was measured spectroelectrochemically. An electrochemical (Stern–Volmer) method is presented that can be used to determine the rate of quenching of the luminescence of one half of a redox couple by the other half. The method is also shown to give qualitative information about cases in which the quenching is by an independent redox couple. The kinetics of the quenching process yield information on the Nafion film structure. The magnitude of the rate constant for quenching of the Ru(bpy)$_3^{2+}$ excited state by Ru(bpy)$_3^{3+}$ is used to elucidate the mechanism of production of this excited state in the electrochemiluminescent reaction of Ru(bpy)$_3^{3+}$ with oxalate.

The increasing popularity of polyelectrolyte coatings as matrices for binding redox complexes to the surfaces of electrodes[1-8] has enhanced the need for studies of the effects of the polyelectrolyte environment on the thermodynamic properties and kinetic behavior of the incorporated redox reagents. Rubinstein and Bard[5,6] recently described the use of polyanion films of Nafion[9] to bind Ru(bpy)$_3^{2+}$ (bpy = 2,2′-bipyridine) to the surface of pyrolytic graphite, glassy carbon, and Pt electrodes to study the chemiluminescence of Ru(bpy)$_3^{2+*}$ that was electrogenerated by oxidizing Ru(bpy)$_3^{2+}$ to Ru(bpy)$_3^{3+}$ in the presence of oxalate ions. The time and potential dependence of the luminescence could be accounted for by either of two alternative mechanisms that were difficult to choose between on the basis of the data obtained.[6] We have also been investigating the properties of cationic redox complexes electrostatically bound in Nafion films.[4] By measuring the lifetime of photogenerated Ru(bpy)$_3^{2+*}$ ions in Nafion coatings on graphite electrodes as a function of the electrode potential it has been possible to measure the rate at which Ru(bpy)$_3^{3+}$ quenches Ru(bpy)$_3^{2+*}$ within the polyelectrolyte film. The results point to the likely mechanisms by which Ru(bpy)$_3^{2+*}$ was generated in the experiments of Rubinstein and Bard[6] as well as provide information on the internal structure of Nafion films cast on graphite electrodes.

Experimental Section

Materials. A 5.2 wt % solution of relatively low molecular weight Nafion (in the sulfonic acid form) in a 5/1 mixture of 2-propanol/water was available from a sample supplied by Du Pont a number of years ago. Commercially available Ru(bpy)$_3$Cl$_2$ and Ru(NH$_3$)$_6$Cl$_3$ were recrystallized from water prior to use. Basal plane pyrolytic graphite (BPG) electrodes (Union Carbide Co., Chicago, IL) were cut and mounted as previously described.[10] The antimony-doped tin oxide optically transparent electrodes (OTE) were available in these laboratories. The electrochemical cell used in the emission experiments with the BPG electrodes was a standard 1-cm emission cell joined at the top to a reference compartment. The cell used in the spectroelectrochemical and lifetime measurements, shown in Figure 1, was fabricated from a block of Kel-F. A hole was cut through the center of the block, and a glass microscope slide was glued to one side of the block and the OTE to the other to form a watertight compartment. The glue was type S-804 epoxy (Saunders Corp., Los Angeles, CA). The reference and auxiliary electrodes were introduced into the cell through two holes drilled through the top. The connection to the OTE was made by clamping an electrical connector directly to the electrode. The reference electrode was Ag/AgCl(KCl, sat), with respect to which all potentials are quoted. The supporting electrolyte was 0.1 M CF$_3$COOH–0.1 M CF$_3$COONa.

Procedures and Instrumentation. Nafion films on graphite electrodes were prepared by carefully syringing microliter amounts of the 5.2 wt % stock solution onto a freshly cleaved electrode, making sure that the polymer solution completely covered the surface. The solvent was allowed to evaporate at room temperature until the films were dry (approximately 5 min). Incorporation of Ru(bpy)$_3^{2+}$ into the films was accomplished by exposing the coated electrodes to 1 mM aqueous solutions of Ru(bpy)$_3$Cl$_2$ for times determined by the extent of incorporation desired. The electrodes were then washed and soaked for at least 30 min in pure water. The soaking step helped to provide a more uniform distribution of the complex within the coating and enhanced the reproducibility of the results. The quantity of electroactive complex present in the coatings was determined either by integration of cyclic voltammograms recorded at low scan rates (2 mV s^{-1}) or by absorbance measurements with the optically transparent electrode. Nafion films on OTE's were prepared prior to cell assembly by evaporating aliquots of the solution applied to the electrode surface. The resulting film does not have a uniform thickness. The outer quarter of the film is about 3–5 times thicker than its central portion.[11,12] Much of the Ru(bpy)$_3^{2+}$ that enters this thicker portion of the film is not in electronic contact with the underlying electrode and is thus electroinactive. This becomes clearly evident if the electrode potential is adjusted to 1.3 V, where all of the electroactive complexes in the film are oxidized to Ru(bpy)$_3^{3+}$, which shows no luminescence under irradiation. Illumination of such oxidized films with

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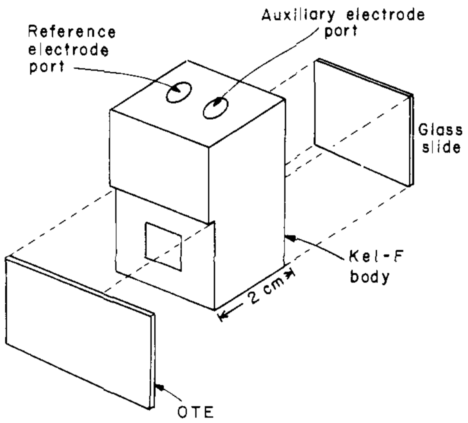

Figure 1. Exploded view of the Kel-F cell used in the spectroelectrochemical (Nernst plot) and lifetime measurements.

blue light produces a bright orange emission from the outer, thicker portion of the film with none from the central portion.

The outermost quarter of each film was carefully removed with a scalpel before the electrode was mounted in order to obtain films of more uniform thickness. Thicknesses of the coatings were monitored with a Dektak Profilometer (Sloan Co.). The coated electrode was glued to the Kel-F cell and placed in an oven at 100 °C for 10 min to set the glue. Ru(bpy)$_3^{2+}$ was incorporated in the coating by filling the cell with a 1 mM solution of the complex and allowing incorporation to proceed until the desired quantity of complex had entered the film. Electrochemical measurements were conducted with a Princeton Applied Research (PAR) 173 potentiostat driven by a PAR 175 universal programmer. The luminescence measurements employed a Perkin-Elmer Model MPF-3 emission spectrophotometer or a locally constructed instrument with a tungsten light source.[13] For spectroelectrochemical measurements the Kel-F cell was mounted in a Hewlett-Packard Model 8450A spectrophotometer.

Emission lifetimes were measured by the following procedure: The absorbance of the Nafion–Ru(Bpy)$_3^{2+}$ coating on an OTE mounted in the spectroelectrochemical cell was monitored spectrophotometrically while the electrode was adjusted to each potential of interest. The absorbance changes accompanying each change in potential were usually complete within 60 s, but the electrode was held at each potential for 20 additional min to assure uniformity of the concentrations of Ru(bpy)$_3^{2+}$ and Ru(bpy)$_3^{3+}$ in the films. The cell was then disconnected from the potentiostat and quickly transferred to a computer-controlled pulsed laser apparatus to be described.[14] Spectral monitoring of the coating after the approximately 2 min required for the transfer showed that none of the Ru(bpy)$_3^{3+}$ was reduced by reaction with H_2O in the acidic electrolytes employed. The coated electrode was irradiated with 8-ns pulses of 532-nm radiation that was filtered so as to deliver ca. 1 mJ of energy per pulse. The temporal decay of the resulting luminescence in the coating was monitored, and the lifetime of the emitting complex was computed by fitting the data to a simple exponential function.[14]

Results

Spectroelectrochemistry on Tin Oxide Electrodes. Curve A in Figure 2 is the spectrum of Ru(bpy)$_3^{2+}$ incorporated in a Nafion film approximately 2 × 10^{-5} cm thick deposited on a transparent tin oxide electrode immersed in a supporting electrolyte solution (0.1 M CF_3COOH–0.1 M CF_3COONa). Curve B is the spectrum that resulted when the electrode was held at 1.3 V for 10 min to oxidize the incorporated complex to Ru(bpy)$_3^{3+}$. Since the molar absorptivity of Ru(bpy)$_3^{3+}$ at 450 nm is 4% that of Ru(bpy)$_3^{2+}$,[12] the two spectra in Figure 2 show that over 95% of the Ru(bpy)$_3^{2+}$ incorporated by the film is susceptible to electrooxidation. The total cross-sectional concentration of the electroactive complex in the film, Γ_T, was evaluated from the difference in absorbances at 450 nm for the two spectra in Figure 2, ΔA, and the molar absorptivity of Ru(bpy)$_3^{2+}$, ϵ_{450}, according to eq 1, which is valid

$$\Gamma_T = \Delta A/\epsilon_{450} \qquad (1)$$

so long as the diameter of the transmitted light beam is smaller than that of the film whose absorbance is being measured. The value of ϵ_{450} was set equal to its value in homogeneous solutions of Ru(bpy)$_3^{2+}$ (ϵ_{450} = 1.46 × 10^4 [15]) because curve A in Figure 2 exhibits no features that distinguish it from the spectrum recorded with a homogeneous solution of the complex. This procedure gave Γ_T = 2.2 × 10^{-8} cm^{-2}. For a uniform film thickness of 2 × 10^{-5} cm, this would correspond to a concentration of 1.1 M.

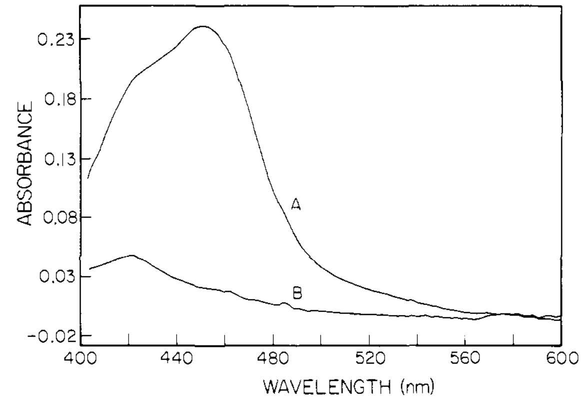

Figure 2. (A) Absorption spectrum of Ru(bpy)$_3^{2+}$ incorporated in a Nafion film on a transparent tin oxide electrode. The average film thickness was 2 × 10^{-5} cm, and 2.2 × 10^{-8} mol cm^{-2} of complex was incorporated in it. (B) Absorption spectrum of the film after the electrode potential was held at 1.3 V for 10 min. Supporting electrolyte: 0.1 M CF_3COOH–0.1 M CF_3COONa.

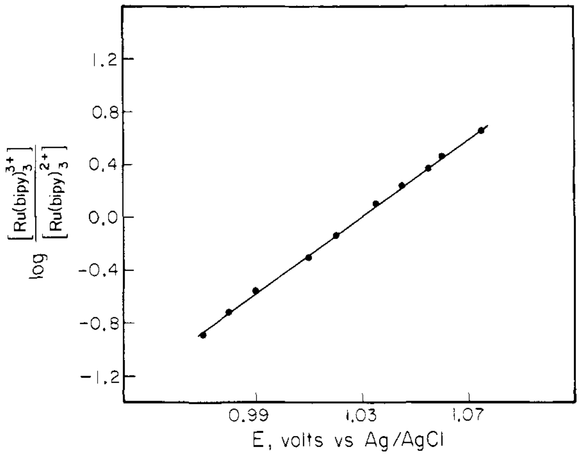

Figure 3. Nernst plot for the Ru(bpy)$_3^{3+/2+}$ couple incorporated in the Nafion film of Figure 2.

To evaluate the formal potential of the Ru(bpy)$_3^{3+/2+}$ couple within the Nafion film, we measured its absorbance at a series of electrode potentials. At each potential the absorbance was monitored until it became constant (1–2 min). At this point the current passing had fallen to background levels. The applied potentials were varied randomly to verify that the final absorbances depended only on the electrode potential and not on the direction from which it was approached. The absorbance–potential data were used to prepare Nernst plots of log ([Ru(bpy)$_3^{3+}$]/[Ru(bpy)$_3^{2+}$]) vs. the electrode potential. The concentrations of the two complexes were calculated at each potential from the absorbance at 450 nm compared with its value in the two curves of Figure 2. A typical plot is shown in Figure 3 from which a formal potential, E_f, of 1.03 V was obtained after correction for a 30-mV junction potential measured between the reference and working electrode compartments in the cell. This value is very close to the value (1.02 V) that has been reported for homogeneous solutions of the complex.[15] Experiments conducted with films containing (0.5–2.2) × 10^{-8} mol cm^{-2} of Ru(bpy)$_3^{2+}$ gave the same value for E_f.

The slope of the Nernst plot in Figure 3 is 70 mV, significantly larger than the 59 mV expected for an ideal redox couple. This

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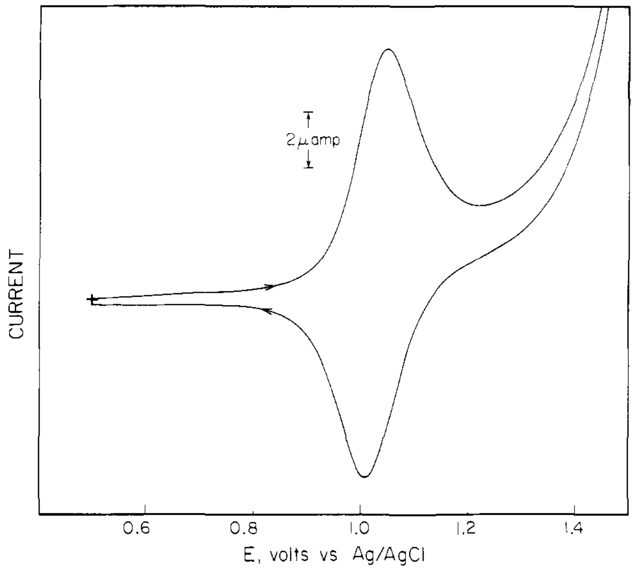

Figure 4. Cyclic voltammogram for 2.5 × 10^{-8} mol cm^{-2} of $Ru(bpy)_3^{2+}$ incorporated in a Nafion film (~2 × 10^{-5} cm thick) on a pyrolytic graphite electrode. Scan rate: 2 mV s^{-1}. Supporting electrolyte: 0.1 M CF_3COOH–0.1 M CF_3COONa.

difference is not unexpected, considering the large effective concentration (1.1 M) of the highly charged reactants. Fortunately, the nonideal behavior did not destroy the linearity of the Nernst plots, which were used to evaluate the concentrations of $Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{3+}$ at each electrode potential of interest in the luminescence lifetime experiments.

Cyclic Voltammetry on Pyrolytic Graphite Electrodes. A cyclic voltammogram for $Ru(bpy)_3^{2+}$ incorporated in a Nafion film on a basal plane pyrolytic graphite electrode is shown in Figure 4. The film was prepared with the same quantity of Nafion as those on the tin oxide electrodes of Figures 2 and 3. The quantity of electroactive $Ru(bpy)_3^{2+}$ incorporated by the film was measured as $\Gamma_T = 2.5 \times 10^{-8}$ mol cm^{-2} from the area under the reductive half of the voltammogram between 1.1 and 0.7 V at scan rates sufficiently low to obtain peak currents that varied linearily with scan rate. At higher scan rates the waves develop "diffusional tails" showing that significant reactant concentration gradients exist within the film.[16] Rubinstein and Bard have reported essentially identical behavior.[5,6]

At low scan rates (v <10 mV s^{-1}) where the peak currents are linearly dependent on v, it follows that the concentrations of $Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{3+}$ remain essentially uniform throughout the film during the potential scan. The concentrations were determined by measuring the area under the voltammogram up to each potential of interest.

Luminescence from $Ru(bpy)_3^{2+*}$ in Nafion Films. As was true of the absorption spectrum on tin oxide electrodes, the emission and excitation spectra of $Ru(bpy)_3^{2+}$ incorporated in Nafion films on graphite electrodes were essentially identical with those observed in homogeneous solution. The emission lifetime of $Ru(bpy)_3^{2+*}$ in a film on the tin oxide electrode, measured as described in the Experimental Section, was 0.68 μs, in reasonable agreement with a value reported for the same ion in a bulk Nafion membrane under somewhat different conditions.[17] Figure 5 shows how the intensity of the luminescence due to $Ru(bpy)_3^{2+}$ changed when the potential of the irradiated electrode was scanned slowly (2 mV s^{-1}) from 0.5 to 1.50 V and back. The luminescence decreases rapidly when the electrode reaches potentials where the $Ru(bpy)_3^{2+}$ is oxidized to $Ru(bpy)_3^{3+}$, which does not luminesce. The luminescence falls to a small, potential-independent value that represents the emission by the small fraction of the $Ru(bpy)_3^{2+}$ present in the film that is electroinactive and cannot be converted to the nonemitting oxidation state.

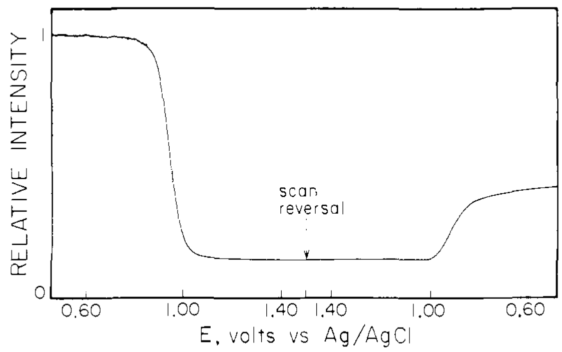

Figure 5. Intensity of the luminescence of the film of Figure 4 relative to its value at 0.5 V vs. the potential of the graphite electrode on which the film resides.

Note that the intensity of the luminescence grows again during the reverse potential scan as the $Ru(bpy)_3^{3+}$ is re-reduced to $Ru(bpy)_3^{2+}$, but it reaches only about 30% of its initial value at potentials where the corresponding cyclic voltammogram (Figure 4) shows that all of the complex has been reduced to $Ru(bpy)_3^{2+}$. However, if the electrode was allowed to stand at open circuit or was held at potentials less than 0.8 V, the luminescence gradually increased until it reached its initial value (>95%) in ca. 10 min. This pattern of rapid loss followed by slow recovery of the luminescence was repeated 40–50 times without any qualitative change in the luminescent response. There was, however, a slow decay in the total emission intensity with cycling that appeared to result from a loss of the complex while it was in the 3+ oxidation state.[11,12]

Experiments with films containing less incorporated complex behaved similarly except that the fraction of the luminescence that returned rapidly upon re-reduction of the complex was greater. For example, 50% of the luminescence reappeared rapidly with a film containing 3.2 × 10^{-9} mol cm^{-2} of $Ru(bpy)_3^{2+}$ in a 2 × 10^{-5} cm Nafion film, and the remaining 50% required ca. 10 min to reappear. If the illuminated electrode potential was scanned more rapidly or stepped from 0.5 to 1.3 to 0.5 V, the luminescence decayed during the oxidation and then regained its initial value almost immediately upon re-reduction of the complex. Thus, the temporary decrease in emission intensity is related to the time the complex spends as $Ru(bpy)_3^{3+}$ within the Nafion film as well as to its concentration. If only a portion of the $Ru(bpy)_3^{2+}$ was oxidized by restricting the electrode potential to values on the rising portion of the voltammogram before returning to 0.5 V, the return of the luminescence was somewhat more rapid than when all of the incorporated complex was oxidized. The possible origin of this interesting behavior will be addressed in the Discussion section.

As the total quantity of $Ru(bpy)_3^{2+}$ incorporated in a Nafion film was decreased, the fraction of the initial luminescence that remained when the electrode was stepped to 1.3 V increased. Thus, the fraction of electroinactive complex increases as its concentration in the Nafion film is decreased. Martin et al.[18] have reached a similar conclusion on the basis of electrochemical assays of Nafion films containing known amounts of $Ru(bpy)_3^{2+}$.

A plot of the fraction of $Ru(bpy)_3^{2+}$ in the film as a function of the electrode potential was prepared for comparison with the luminescence–potential curve of Figure 5. The two curves are plotted together in Figure 6, from which it is apparent that the luminescence decreases much more rapidly than does the concentration of $Ru(bpy)_3^{2+}$. We propose that the quenching of $Ru(bpy)_3^{2+*}$ by the $Ru(bpy)_3^{3+}$ that is introduced into the film as $Ru(bpy)_3^{2+}$ is oxidized is responsible for the separation between the two curves in Figure 6.

Electrochemical Stern–Volmer Plots. The proposal is that curve B in Figure 6 represents the luminescence that would result at any potential if $Ru(bpy)_3^{3+}$ did not quench the emission from

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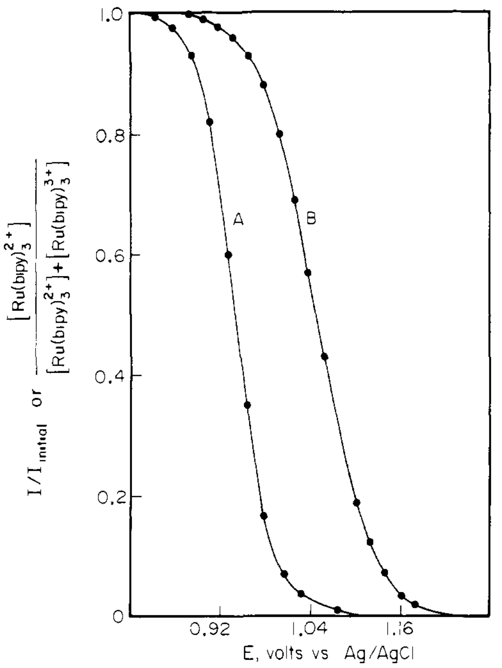

Figure 6. Potential dependence of (A) the relative luminescence intensity of Figure 5 (corrected by subtracting the residual intensity at 1.5 V); (B) the fraction of the total complex incorporated in the Nafion film that is present as $Ru(bpy)_3^{2+}$.

$Ru(bpy)_3^{2+*}$ while curve A gives the observed luminescence. Thus, the ratio of the ordinate values for curves B and A at each potential, I_B and I_A, gives the ratio of the quantum yields for emission or of the lifetimes of the excited state, in the absence and presence of quencher:

$$I_B/I_A = \Phi_0/\Phi_q = \tau_0/\tau_q \qquad (2)$$

where Φ and τ are the quantum yield and lifetime, respectively, in the absence (Φ_0, τ_0) and presence (Φ_q, τ_q) of quencher. These are just the data needed to evaluate the quenching of $Ru(bpy)_3^{2+*}$ by $Ru(bpy)_3^{3+}$ by means of the Stern–Volmer equation:[19]

$$I_B/I_A = 1 + k_q\tau_0 C_{Ru(III)} \qquad (3)$$

where k_q is the quenching rate constant and $C_{Ru(III)}$ is the concentration of the proposed quencher, $Ru(bpy)_3^{3+}$. The value of $C_{Ru(III)}$ was determined at each potential by integration of the current that flowed when the fully reduced film was scanned to that potential. (The film thickness must also be known.) Note that since the ratio of the luminescence in the presence and absence of quencher is evaluated at each potential, eq 3 should be applicable to the experiments of Figure 6 even though the concentrations of both the emitter and quencher are different at each electrode potential.

Stern–Volmer plots[19] of I_B/I_A vs. $C_{Ru(III)}$ for two films containing different total quantities of incorporated complex are shown in Figure 7. The good linearity of the data supports the proposal that the luminescence of $Ru(bpy)_3^{2+*}$ is quenched by $Ru(bpy)_3^{3+}$. The values of k_q obtained from the slopes of lines in Figure 7A,B are 5×10^7 and 1×10^7 M^{-1} s^{-1}, respectively. This degree of reproducibility in measured values of k_q for runs with different electrodes and coatings was typical.

Quenching constants were also evaluated from excited-state lifetime measurements with films in which the concentrations of $Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{3+}$ were controlled by holding the electrode for several minutes at each potential of interest and then quickly transferring the electrode to the lifetime-measuring apparatus (Experimental Section). Figure 8 shows the resulting Stern–Volmer plot of τ_0/τ_q vs. $C_{Ru(III)}$, which was evaluated from Figure 3 and a knowledge of Γ_T. The slope of the line corresponds to $k_q = 0.5 \times 10^7$ M^{-1} s^{-1}. This value is in reasonable agreement with the values obtained from Figure 7, and we believe it to be the most reliable for several reasons: (i) The Nafion film was cast on a smooth tin oxide electrode so that its thickness could be measured with the profilometer. With the pyrolytic graphite electrode, the thickness was calculated rather than measured. (ii) Lifetimes were measured at open circuit with films that had been fully equilibrated at each potential. (iii) Lifetime measurements are superior to steady-state luminescent measurements for evaluating second-order quenching constants because the lifetime is an intrinsic property of the excited state while the steady-state intensity is a function of both the experimental apparatus and the properties of the ground-state emitter, as, for example, in static quenching.[19]

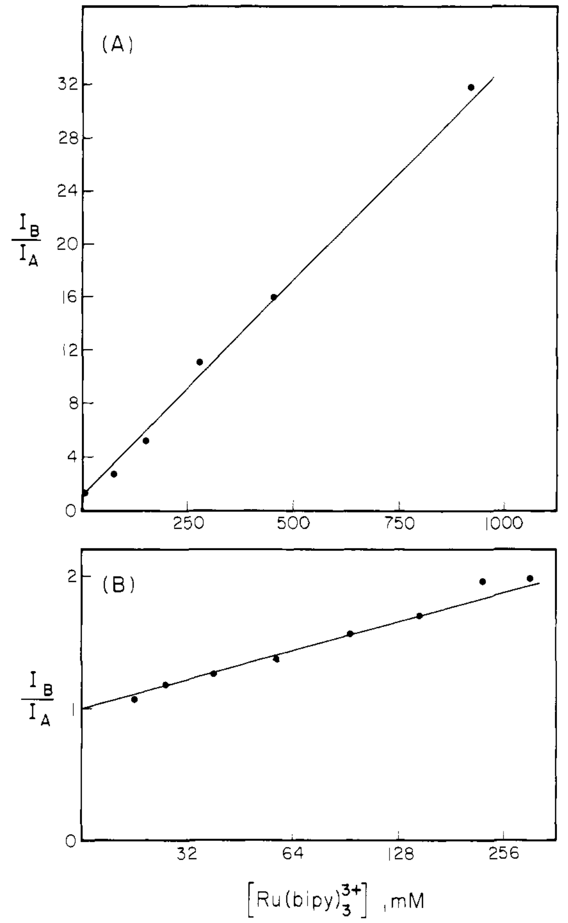

Figure 7. Stern–Volmer plots of the ratio of the ordinate values at each potential in Figure 6 (see text) vs. the concentration of $Ru(bpy)_3^{3+}$ in the film. The films contained (A) 2.5×10^{-8} and (B) 3.2×10^{-9} mol cm^{-2} of complex.

Quenching of $Ru(bpy)_3^{2+*}$ by $Ru(NH_3)_6^{3+/2+}$. It is also possible to monitor the potential dependence of the quenching of $Ru(bpy)_3^{2+*}$ by independent redox couples co-incorporated into the Nafion films. For example, Figure 9 shows a quenching experiment in which both $Ru(bpy)_3^{2+}$ and $Ru(NH_3)_6^{3+}$ were present in the Nafion film. The potential where $Ru(NH_3)_6^{3+}$ is reduced to $Ru(NH_3)_6^{2+}$ ($E_f = -0.28$ V in Nafion) is far removed from E_f for the $Ru(bpy)_3^{3+/2+}$ couple (1.03 V) so that the relative quenching rates for $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_6^{2+}$ can be easily determined by scanning the electrode potential over the wave for the $Ru(NH_3)_6^{3+/2+}$ couple while the luminescence from $Ru(bpy)_3^{2+*}$ on the irradiated electrode is being observed. It is clear from Figure 9 that $Ru(NH_3)_6^{2+}$ is a better quencher than $Ru(NH_3)_6^{3+}$. Interestingly, this is the opposite order from that observed in experiments with the same reagents in homogeneous solution.[20]

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(20) Creutz, C.; Sutin, N. *Inorg. Chem.* **1976**, *15*, 496.

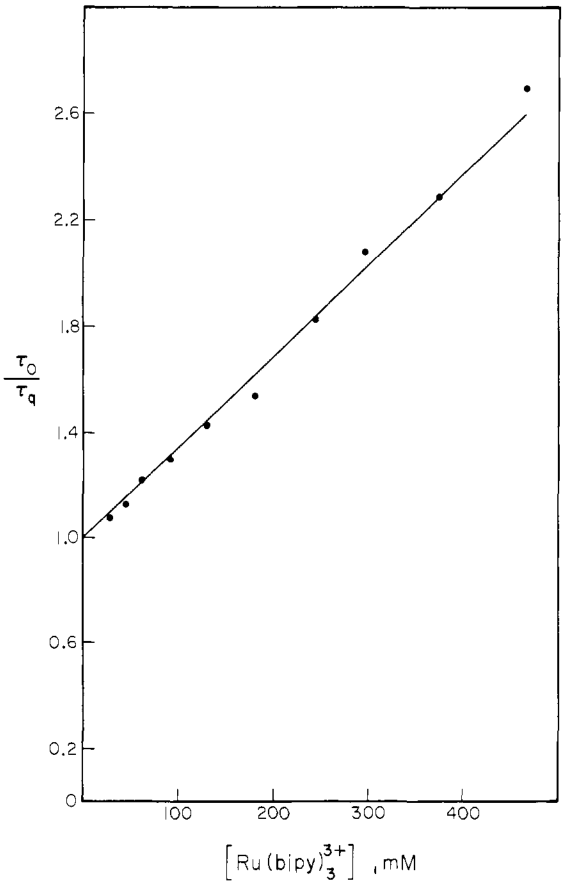

Figure 8. Stern–Volmer plots of the ratio of the lifetimes of $\mathrm{Ru(bpy)_3^{2+*}}$ in a Nafion film in the presence and absence of $\mathrm{Ru(bpy)_3^{3+}}$ as a function of the concentration of $\mathrm{Ru(bpy)_3^{3+}}$. The film was that described in Figure 2.

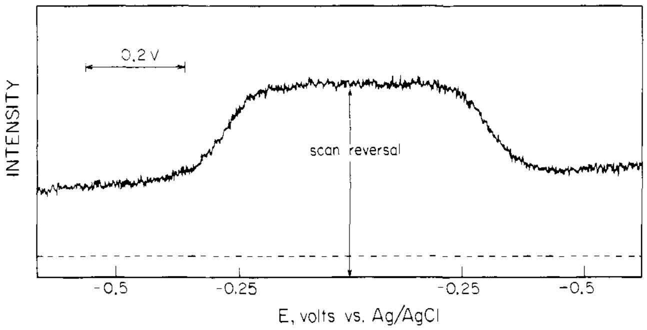

Figure 9. Intensity of the luminescence (arbitrary units) from a Nafion film on a graphite electrode in which ca. 5×10^{-9} mol cm^{-2} of both $\mathrm{Ru(bpy)_3^{2+}}$ and $\mathrm{Ru(NH_3)_6^{3+}}$ had been incorporated. The electrode potential was scanned between −0.65 and 0 V at 2 mV s^{-1}. The dashed line is the residual luminescence when the electrode is held at 1.3 V. Other conditions as in Figure 3.

It is also noteworthy that Figure 9 shows there is no lag in the change in luminescence as the quencher is cycled between $\mathrm{Ru(NH_3)_6^{3+}}$ and $\mathrm{Ru(NH_3)_6^{2+}}$. Any changes in the local environment surrounding these two quenchers that result from the change in their charges are apparently without effect on their quenching rates. The contrasting results obtained with $\mathrm{Ru(bpy)_3^{3+}}$ as quencher (Figure 5) indicates that changes in the local environment of the emitting species are responsible for the much greater lag between the changes in potential and luminescence in this case.

Discussion

The luminescence of $\mathrm{Ru(bpy)_3^{2+*}}$ incorporated in Nafion films has provided a useful means of detecting apparent changes in the local environment experienced by the reactant when it is oxidized from $\mathrm{Ru(bpy)_3^{2+}}$ to $\mathrm{Ru(bpy)_3^{3+}}$. The delay in the restoration of the full initial luminescence from $\mathrm{Ru(bpy)_3^{2+}}$ after it has been cycled through the $\mathrm{Ru(bpy)_3^{3+}}$ state (Figure 5) seems best interpreted as arising from differences between the initial local environment of $\mathrm{Ru(bpy)_3^{2+}}$ produced by reduction of $\mathrm{Ru(bpy)_3^{3+}}$ and the equilibrium environment that results when the $\mathrm{Ru(bpy)_3^{2+}}$ is introduced by allowing the ion to diffuse into the Nafion film. The slow recovery of the initial luminescence cannot be attributed to some residual $\mathrm{Ru(bpy)_3^{3+}}$ that temporarily escapes re-reduction and acts as a quencher because the faradaic charges consumed in the oxidation and re-reduction steps (as determined from the area under the cyclic voltammogram by extrapolating the current ahead of the wave to correct for the background current) are essentially equal (>95%), so that the maximum possible quantity of unreduced $\mathrm{Ru(bpy)_3^{3+}}$ is far too small to quench the luminescence by the extent that is observed. Instead, we believe that the increase in "electrostatic cross-linking"[21] produced by the association of each $\mathrm{Ru(bpy)_3^{3+}}$ complex with three sulfonate groups within the Nafion polyelectrolyte film results in a significant change in the local structure of the polymer. The effective local concentration of sulfonate may become larger, and this may lead to alterations in the degree of solvation of the complex. It is well-known that luminescence lifetimes are dependent on the nature of the solvent.[22]

Previous studies[17,18,23] have reported evidence of at least two kinds of binding sites in Nafion membranes, one type being more hydrophilic and the other more hydrophobic. We believe that our luminescence experiments reveal the presence of a similar kind of site anisotropy that is induced by the electrochemical increase in the charge of the cations that occupy the sites. Note that the measurements of the emission lifetime of $\mathrm{Ru(bpy)_3^{2+*}}$ as a function of electrode potential (Figure 8) are not expected to have been influenced by the slow restoration of the luminescence because the experiments were conducted with fully equilibrated films.

A study of the luminescence from $\mathrm{Ru(bpy)_3^{2+*}}$ incorporated in bulk Nafion membranes and its quenching by methylviologen cations (*N*,*N*′-dimethyl-4,4′-bipyridine) has been previously reported.[17] Nonlinear Stern–Volmer plots were obtained in this case that were interpreted in terms of inhomogeneous concentrations of the incorporated cations arising from the anisotropic cluster structure of bulk Nafion membranes.[24,25] The analysis of Lee and Meisel[17] indicates that with $k_q \sim 10^7$ M^{-1} s^{-1} and the wide range of quencher (i.e., $\mathrm{Ru(bpy)_3^{3+}}$) concentrations available in the electrochemical Stern–Volmer experiment ($\sim 10^{-2}$–1 M) inhomogeneous concentrations of the quencher caused by clustering within the Nafion films should produce significant nonlinearities in Stern–Volmer plots. Thus, the good linearity we observed in Figures 7 and 8 indicates that the films cast on tin oxide or graphite surfaces from solutions of the soluble form of Nafion adopt internal structures that are more homogeneous than those present in bulk Nafion membranes. The cast films may also be considerably more porous than bulk Nafion, which could account for the otherwise surprising observation of Rubinstein and Bard[6] that oxalate anions easily penetrated their Nafion films. The structures available from Nafion polyelectrolytes seem to depend strongly on the conditions employed in the preparation of membranes and the casting of films.

The extraordinary (and highly useful) stability of Nafion films on graphite and tin oxide electrodes contrasts with their behavior on glass: films cast on microscope slides are dislodged by immersion in water. The great stability on the other substances may arise from the formation of covalent bonds to the surface by reaction of the sulfonic acid groups in the soluble form of the Nafion polyelectrolyte with receptive functional groups (carboxyl,

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hydroxyl, etc.) on the electrode surfaces.[26]

The value of k_q evaluated in this work can be used to help distinguish among the various schemes considered by Rubinstein and Bard in discussing the potential dependence of the electrochemiluminescence they observed when $Ru(bpy)_3^{2+}$ in Nafion films was oxidized to $Ru(bpy)_3^{3+}$ in the presence of oxalate anions.[6] The digital simulation procedure they employed produced acceptable fits of the experimental data for three alternative sets of rate constants for several of the key reactions, so that an unambiguous mechanistic assignment was not possible. The values of k_q producing the three best fits were 0, 5×10^7, and 2×10^9 $M^{-1}\,s^{-1}$. The second is closest to the values measured in these experiments, and this prompts us to assign the mechanistic scheme that corresponds to this value in the digital simulation of ref 6 as the correct one. One consequence of this assignment is that the $Ru(bpy)_3^{2+*}$ generated in the experiments of Rubinstein and Bard[6] must have arisen from the reduction of $Ru(bpy)_3^{3+}$ by both CO_2^- and $Ru(bpy)_3^+$.

Conclusions

The spectroelectrochemical procedure employed here to measure the concentrations of $Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{3+}$ in Nafion films on transparent tin oxide electrodes is reliable and especially useful in cases where redox couples that do not adhere to the Nernst equation are under study. The use of polymer films on electrodes to house emitting and quenching species in Stern–Volmer experiments is attractive because the concentration of quencher can be varied continuously by control of the electrode potential. In favorable cases, data for an entire Stern–Volmer plot can be obtained in a single experiment. The example presented in these experiments involved the quenching of the luminescence from one half of a redox couple by the other half of the same couple, but the procedure is also applicable to cases in which the quenching is by an independent redox couple (Figure 9).

The results of luminescence quenching experiments proved useful in probing the structures of Nafion films as the earlier work of Lee and Meisel[17] suggested they might be. The experiments indicate that cast Nafion films have more homogeneous structures than bulk membranes of Nafion. They also show that significant changes in the local polyelectrolyte environment accompany the oxidation of $Ru(bpy)_3^{2+}$ to $Ru(bpy)_3^{3+}$ in Nafion films. The magnitude of the quenching rate constant measured in the Nafion films allows a choice to be made among possible mechanistic schemes proposed previously[6] for the generation of electrochemiluminescence at Nafion-coated electrodes.

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Registry No. $Ru(bpy)_3^{3+}$, 18955-01-6; $Ru(bpy)_3^{2+}$, 15158-62-0; Nafion, 39464-59-0; oxalate, 144-62-7.

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Intramolecular Potential Functions from Observed Crystal Structures. 1. 1,3,5-Triphenylbenzene, *p*,*p*′-Bitolyl, 1,1′-Binaphthyl, and *o*-Terphenyl[1]

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Abstract: The crystal structures of the title compounds were reproduced by minimizing the energies of computational models with respect to lattice parameters, molecular rotations and translations, and the intramolecular torsion angles between rigid phenyl or naphthyl groups. The energies of the models were calculated by using potential functions that include terms for intermolecular and intramolecular nonbonded interactions and a conjugation energy or π-bonding term that is a function of the phenyl–phenyl or naphthyl–naphthyl torsion angles. The values of these angles computed for the crystals were shown to depend on the coefficients of the latter terms, and these coefficients were adjusted to reproduce the experimental torsion angles as well as possible. The adjusted values obtained for the four compounds are similar but not identical, and they are bracketed by various values reported from theoretical calculations on biphenyl. *o*-Terphenyl was represented by a more complicated model, which allows for bond-angle and out-of-plane distortions of the phenyl–phenyl bonds. Potential energy curves and equilibrium conformations were calculated for the isolated molecules. Four published nonbonded potentials for hydrocarbons were tested, and a 6–exp–1 function was selected as best for this work.

The conformation of a molecule in the crystalline state differs from that of the isolated molecule because of effects that may be attributed to intermolecular forces. For small molecules, such forces are now very well-known,[2] and even for large molecules, they have been fairly well characterized. For hydrocarbons, for example, potentials have been developed that are able to reproduce the observed crystal structures, heats of sublimation, and external vibrational frequencies to a good approximation.[3-10]

Intramolecular potentials, on the other hand, have been used extensively for predicting the conformations and energies of isolated molecules.[11-13] Most of these potentials have been designed

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