Emission Spectroscopy of $Ru(bpy)_2dppz^{2+}$ in Nafion. Probing the Chemical Environment in Cast Films

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Abstract: The incorporation of $Ru(bpy)_2dppz^{2+}$ (dppz = dipyrido[3,2-*a*:2′,3′-*c*]phenazine) into Nafion coatings was monitored *in situ* by electronic absorption, steady-state emission, and lifetime measurements. Whereas the aqueous loading solution does not show any luminescence (the emission of $Ru(bpy)_2dppz^{2+}$ in nonaqueous solvents is completely quenched by water), strong emission was detected immediately after immersion of the Nafion coating. The emission decay is triexponential, with two long-lived components ($\tau = 900$ and 300 ns) dominating a fast decay ($\tau = 50$ ns). Emission intensities, lifetimes, and lifetime distributions depend strongly on the loading level, owing both to self-quenching and environmental changes brought about by increases in the concentration of the complex in the film. Owing to the remarkable efficiency of excited-state deactivation attributable to dppz−H_2O hydrogen bonding, $Ru(bpy)_2dppz^{2+}$ is an extremely sensitive probe of accessible water structures in Nafion.

Introduction

Ionomers (ion-containing polymers) are of considerable interest because of their importance in ion-exchange and separation chemistry.[1−3] Nafion, the perfluorinated ionomer manufactured by E.I. duPont de Nemours and Co., has attracted particular attention because of its thermal stability (up to 200 °C), mechanical strength, easy handling, and, especially, its chemical and biological inertness. As a supporting matrix for electrode coatings,[2,4,5] Nafion is a useful material for electroanalysis, electrosynthesis, electrocatalysis, and sensor technology.[2,5] Many studies directed at the characterization of Nafion and the correlation of its behavior with its structure have been made.[2] X-ray and light-scattering experiments have shown that the structure of Nafion includes semicrystalline portions mixed with noncrystalline areas in which the anionic sulfonate groups are aggregated.[2] It is generally accepted that the interior of Nafion membranes and coatings consists of a continuous ionic network of interconnected hydrophilic ionic clusters embedded in a hydrophobic fluorocarbon matrix.[2,3] Support for this model has been obtained from neutron scattering and from IR and NMR spectroscopic measurements.[2] Additional information about the interior structure has come from electrochemical[4] and photochemical[5,6] studies in which electroactive and luminescent probe molecules were imbedded in Nafion membranes and films. One of the most studied probe molecules has been $Ru(bpy)_3^{2+}$, mainly because of its rich redox and luminescence properties.[7] Lee and Meisel[5a] reported that the luminescence of $Ru(bpy)_3^{2+}$ in Nafion is somewhat enhanced relative to its luminescence in pure water and resembles that in the presence of sodium perfluorooctanoate micelles. They suggested that the similarity is an indication of hydrophobic interactions of $Ru(bpy)_3^{2+}$ ions with the fluorocarbon chains and concluded that the complex resides in an interfacial region that separates the fluorocarbon regions from the ionic clusters within Nafion membranes. Emission spectroscopic evidence for hydrophobic interactions between Nafion and $Ru(bpy)_3^{2+}$ also has been reported by Prieto and Martin,[5d] Lin et al.,[5f] and most recently by Colón and Martin.[6] Because of interference from the luminescence of the complex in the loading solution, however, the $Ru(bpy)_3^{2+}$ luminescence was not monitored in any of these studies during the time required for its incorporation within the Nafion.

The luminescence of $Ru(bpy)_3^{2+}$ in Nafion films is only moderately sensitive to the outer-sphere environment of the complex cation. Previous interpretations of the interactions of $Ru(bpy)_3^{2+}$ with a Nafion host were based on rather small changes in the luminescence intensities (20−50%) and band maxima. We have found that a mixed-ligand ruthenium complex, $Ru(bpy)_2dppz^{2+}$ (dppz = dipyrido[3,2-*a*:2′,3′-*c*]phenazine), is a more sensitive probe than $Ru(bpy)_3^{2+}$ of internal morphology and electronic properties of the environment of cations in Nafion coatings. Although the absorption originating in metal-to-ligand charge transfer (MLCT) of $Ru(bpy)_2dppz^{2+}$ is similar to that of $Ru(bpy)_3^{2+}$, the luminescence of the dppz complex is strongly quenched in aqueous solutions.[8,9] The

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efficient quenching of the Ru(bpy)$_2$dppz^{2+} luminescence has been attributed to coupling of water molecules to the MLCT excited state[10] via hydrogen bonds to the phenazine nitrogens.[8,9] The quenching is diminished when the phenazine nitrogens are shielded from water, as appears to result from intercalation into DNA[9,11] or incorporation into micellar superstructures.[12]

We anticipated that Ru(bpy)$_2$dppz^{2+} would behave similarly upon incorporation into Nafion. If the complex resides in the hydrophobic portions of the film, where the concentration of water is low, strong luminescence should be observed; and at sites where higher concentrations of water are present, the luminescence of the complex should be weak or totally quenched. Indeed, we have found that the luminescence properties of Ru(bpy)$_2$dppz^{2+} can be employed to probe the different environments experienced by cationic complexes in Nafion. Of particular interest are the changes we were able to observe in the environment experienced by the complex during its incorporation into the host polymer coating.

Experimental Section

Materials. Nafion 1100 was purchased from Aldrich as a 5 wt % solution. [Ru(bpy)$_3$]Cl$_2$ was obtained from Strem. [Ru(bpy)$_2$dppz](PF$_6$)$_2$ and [Ru(phen)$_2$dppz](PF$_6$)$_2$ (gifts from Prof. J. K. Barton) were purified by chromatography on an alumina column. Analytical grade solvents were used as received. Deionized water was further purified by passing through a Millipore Q-plus train. Indium tin oxide (ITO) electrodes on glass were from Donnelly Corp.

Film Preparation. Nafion films with thicknesses that vary across their surfaces exhibit non-uniform emission patterns that complicate luminescence studies. We found that the use of casting solutions with a relatively high water content minimized this problem. Therefore, stock solutions were prepared by diluting the commercial Nafion solution with water to a final concentration of 1 wt %. The alcohol: water ratio in the final solution was 20:80 by weight. These solutions remained clear and could be stored for long periods of time with no apparent precipitation. Nafion films were prepared by placing 2 μL of the stock solution on the surface of ITO electrodes and by using a microsyringe tip to spread the solution over an area of about 0.3 cm^2 and allowing the solvent to evaporate at room temperature. The films produced in this way contained 78 nmol cm^{-2} of Nafion sulfonate groups. From profilometric measurements the films prepared in this manner were found to have thicknesses of 0.6 ± 0.1 μm. The dried films were dipped in aqueous 0.1 M LiCl for 3 h to replace the protons with lithium cations because the lithium-exchanged Nafion yielded more reproducible results. The ruthenium complexes were incorporated into the Li−Nafion coatings by immersing the coatings in 20 μM aqueous solutions for varying time periods. The loading levels were determined from differences in the MLCT absorbances in the loading solutions before and after completing the loading (ϵ values: Ru(bpy)$_3{}^{2+}$, 1.5 × 10^4;[7b] Ru(bpy)$_2$dppz^{2+}, 1.6 × 10^4 M^{-1} cm^{-1} [8]).

Instrumentation. A Sloan DecTak 3030 Profilometer was used to measure the thicknesses of Nafion films. UV−vis absorbance spectra were obtained with a PC-controlled HP8450A spectrometer with the ITO/Nafion samples placed in a 10 × 10 mm quartz cuvette in the beam path. The probe beam was limited to a cross sectional area of 1 mm^2. Steady-state luminescence experiments were conducted with an SLM 8000C fluorimeter. The excitation beam at 440 nm wavelength was 90° polarized to avoid the so-called Wood's anomaly.[13] The ITO-supported film was placed in the cuvette at a 45° angle to the excitation beam and to the detector axis. The reported luminescence intensities were normalized with respect to the emission of rhodamine-B, measured simultaneously, to compensate for any instrumental instability. Luminescence lifetime measurements were obtained using an excimer-pumped dye laser.[14a] Sample excitation at 480 nm (coumarin 480 dye, Exciton) employed 10 Hz laser pulses (1.2−2.0 mJ); the resulting emission was monitored at 620 nm.

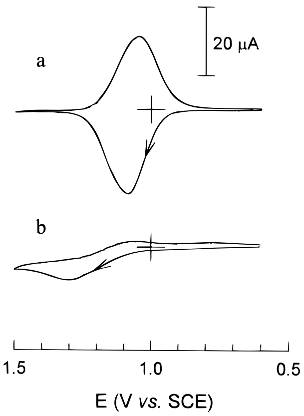

Figure 1. Steady-state cyclic voltammograms for Nafion films on ITO electrodes containing (a) ca. 26 nmol cm^{-2} Ru(bpy)$_3{}^{2+}$ and (b) ca. 33 nmol cm^{-2} Ru(bpy)$_2$dppz^{2+}. The films were loaded by immersion for 20 h in a 20 μM solution of the Ru complex. The voltammograms were recorded in aqueous 0.1 M LiClO$_4$ solutions where the pH was adjusted to 2.25 by addition of concentrated HClO$_4$. Scan rate: 5 mV s^{-1}.

Results

Cyclic Voltammetry. The cyclic voltammogram recorded with a Nafion film containing 26 nmol cm^{-2} of Ru(bpy)$_3{}^{2+}$ in 0.1 M LiClO$_4$ as supporting electrolyte is shown in Figure 1a. The voltammogram was obtained after repetitive cycling of the electrode potential with a film that had been saturated with Ru(bpy)$_3{}^{2+}$ (i.e., the film initially contained one Ru(bpy)$_3{}^{2+}$ for every two sulfonate groups). The well-defined, nearly symmetric waves in the voltammogram (Figure 1a) represent the steady-state response from coatings containing one Ru(bpy)$_3{}^{3+/2+}$ for every three sulfonate groups.

The voltammetric response obtained after repetitive cycling of a Nafion film containing ca. 33 nmol cm^{-2} of Ru(bpy)$_2$dppz^{2+} is quite different (Figure 1b). The peak currents are much smaller than those obtained with Ru(bpy)$_3{}^{2+}$ and the peaks are broader and farther apart. The difference in the behavior of the two complexes indicates that electron transfer between the Nafion-bound Ru(bpy)$_2$dppz^{2+} and the electrode surface is extremely slow. Either very slow electron self-exchange between adjacent complexes or slow diffusion of the complex could account for the observed behavior. Whatever its origin, the dramatic difference in the electrochemical responses of Ru(bpy)$_3{}^{2+}$ and Ru(bpy)$_2$dppz^{2+} suggests that other properties of the two complexes might differ as well.

Electronic Absorption and Emission Spectroscopy. One of our primary goals was to observe the luminescence of the metal complexes in real time as they were incorporated into Nafion films. At first, we followed this process from unstirred, relatively dilute solutions (e.g., 20 μM) so that the concentration of the complex at the film/solution interface was diminished by the incorporation. Under these conditions, the incorporation

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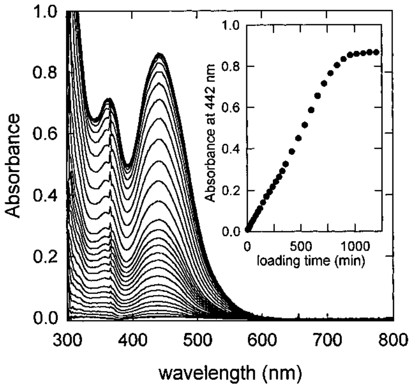

Figure 2. UV−vis absorption spectra of $Ru(bpy)_2dppz^{2+}$ in a 0.6 μm Nafion film at various times between 5 and 1320 min after immersion in the loading solution (aqueous 20 μM $Ru(bpy)_2dppz^{2+}$). The spectra represent the difference between the spectrum recorded immediately after introducing the ITO/Nafion sample into the solution and those recorded at later times (see text). Inset: absorbance of the MLCT band as a function of loading time.

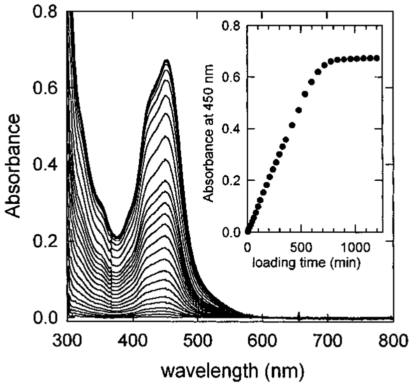

Figure 3. UV−vis absorption spectra of $Ru(bpy)_3^{2+}$ in a 0.5 μm Nafion film at various times between 5 and 1200 min after immersion in the loading solution (aqueous 20 μM $Ru(bpy)_3^{2+}$). The spectra represent the difference between the spectrum recorded immediately after introducing the ITO/Nafion sample into the solution and those recorded at later times (see text). Inset: absorbance of the MLCT band as a function of loading time.

reaction was slow enough so that the guest complex had time to explore most of the thin film volume during the time required to reach equilibrium. Figure 2 shows a series of absorption spectra of $Ru(bpy)_2dppz^{2+}$ in a Nafion/ITO coating measured during the loading of the complex from a 20 μM aqueous solution. A spectrum taken immediately after the coated electrode was placed in the solution was subtracted from each spectrum recorded at later times to compensate for the contribution from the complex in the loading solution.[14b] Thus, the spectra in Figure 2 reflect only the $Ru(bpy)_2dppz^{2+}$ that has been incorporated (and concentrated) by the coating. The MLCT feature at 442 nm and the phenazine intraligand band at 365 nm are clearly resolved in the absorption spectrum of the film. The intensities of the bands increase continuously as the loading of the complex proceeds. The insert in Figure 2 shows this increase of the MLCT band maximum as a function of time. The absorbance increases linearly with time until it reaches a plateau after ca. 900 min of loading. Qualitatively similar behavior was observed with $Ru(bpy)_3^{2+}$ (Figure 3).

The incorporation of $Ru(bpy)_2dppz^{2+}$ and $Ru(bpy)_3^{2+}$ into Nafion was also monitored by following the characteristic emission of the two complexes during loading (Figures 4 and 5, respectively). The 20 μM solution of $Ru(bpy)_2dppz^{2+}$ exhibited essentially no luminescence, but as the complex partitioned into the Nafion coating it began to luminesce and the intensity of the emission increased to a maximum value in about 300 min, after which it decreased and leveled off (Figure 4). The steady intensity reached after ca. 1000 min of loading was about 20% of the maximum intensity. Also shown in Figure 4 is the substantial red shift of the emission maximum with loading time.

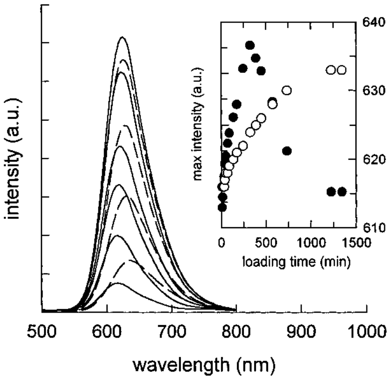

Figure 4. Steady-state luminescence spectra of ITO/Nafion films measured at various times after immersion in 20 μM $Ru(bpy)_2dppz^{2+}$. The solid lines from lower to higher are the responses after 10, 30, 70, 135, 245, and 325 min. The dashed lines from higher to lower correspond to 390, 575, 735, and 1225 min. Inset: luminescence intensity (●) and λ_{max} (○) as a function of loading time.

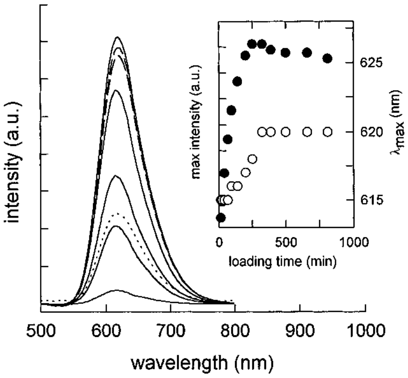

Figure 5. Steady-state luminescence spectra of ITO/Nafion films measured at various times after immersion in 20 μM $Ru(bpy)_3^{2+}$. The solid lines from lower to higher are the response after 14, 67, 40, 140, and 250 min. The dashed lines from higher to lower correspond to 500 and 800 min. The dotted line is the response of the fresh loading solution. The emission spectra of the coating represent the difference between the spectrum recorded immediately after introducing the ITO/Nafion sample into the solution and those recorded at later times (see text). Inset: luminescence intensity (●) and λ_{max} (○) as a function of loading time.

The luminescence behavior exhibited by $Ru(bpy)_2dppz^{2+}$ (Figure 4) was remarkably different from that of $Ru(bpy)_3^{2+}$ during a similar loading experiment (Figure 5). The luminescence of the 20 μM $Ru(bpy)_3^{2+}$ loading solution masked the luminescence from the Nafion during the early stages of incorporation. The emission intensities plotted in Figure 5 are the differences between the initial intensity from the solution[14] and the intensity measured from the coating and the solution at subsequent times. Unlike the situation with $Ru(bpy)_2dppz^{2+}$, subtraction of the solution emission was essential in the case of $Ru(bpy)_3^{2+}$ because of the significant emission in the loading solution. The luminescence from the Nafion coating increased initially at a rate similar to that observed with $Ru(bpy)_2dppz^{2+}$ (Figure 4) and reached a maximum at about the same time, but the subsequent decrease in luminescence was much smaller (Figure 5). The red shift in the band maximum was also somewhat smaller.

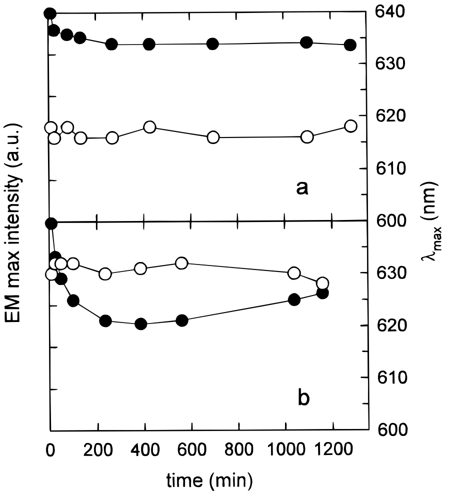

Figure 6. Time-dependent luminescence intensity (●) and λ_{max} (○) for Ru(bpy)$_2$dppz^{2+} in Nafion films dipped in pure water. The films were loaded from 20 μM aqueous solutions of Ru(bpy)$_2$dppz^{2+} for (a) 45 min, resulting in 1.5 nmol cm^{-2} of incorporated complex, and (b) 270 min, resulting in 8.9 nmol cm^{-2} of incorporated complex.

To try to resolve the possible reasons for the observed decrease in the emission intensity after ca. 300 min of loading, the luminescences from two Nafion coatings containing different quantities of Ru(bpy)$_2$dppz^{2+} were monitored over a period of 1200 min with the films immersed in pure water. The results show that at low loading there is little change in the luminescence intensity or λ_{max} (Figure 6a), while a significant decrease in intensity occurs with the more highly loaded coating (Figure 6b).

The absorbances of both films remained essentially constant throughout the experiments so that loss of Ru(bpy)$_2$dppz^{2+} from the Nafion was not responsible for the decrease in luminescence in Figure 6b. The decrease seems more likely to be the result of the redistribution of the water remaining in the film. The very low mobility of the Ru(bpy)$_2$dppz^{2+} cations within the film, as is evident from the voltammogram in Figure 1b, could produce an inhomogeneous distribution of counterions inside the film with higher concentrations of hydrated lithium counterions near the electrode/Nafion interface and higher concentrations of Ru(bpy)$_2$dppz^{2+} counterions near the Nafion/solution interface. As the two counterions slowly diffuse across the film in response to the concentration gradients, water molecules carried by the hydrated lithium cations would be transported toward the Ru(bpy)$_2$dppz^{2+} cations to produce the decrease in their luminescence shown in Figure 6b. The absence of such a decrease in more lightly loaded films (Figure 6a) might then be attributed to the presence of more hydrated lithium counterions in the vicinity of the Ru(bpy)$_2$dppz^{2+} complexes; in this partially aqueous environment the Ru(bpy)$_2$dppz^{2+} cations would exhibit a smaller but more constant luminescence.

Additional information about the origin of the temporal variations of the luminescence was obtained by monitoring *in situ* lifetimes during loading with the coated electrodes immersed in a solution of Ru(bpy)$_2$dppz^{2+}. Shown in Figure 7 are representative emission decay curves obtained during such an experiment for a coating that had been loaded with Ru(bpy)$_2$dppz^{2+} for 0.5, 212, and 426 min. It is interesting to note that the small amount of complex incorporated after 0.5 min, which is practically undetectable by UV−vis absorbance (using conventional methods), was enough to obtain decay curve (a) in Figure 7. The three curves in Figure 7 clearly demonstrate that the emission lifetime decreases as the Ru(bpy)$_2$dppz^{2+} loading of the Nafion coating increases.

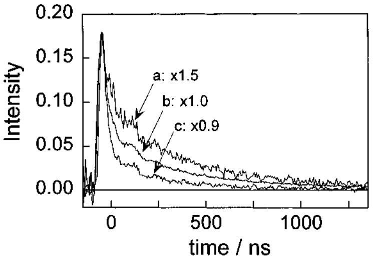

Figure 7. Luminescence decay curves for Ru(bpy)$_2$dppz^{2+} in an ITO/Nafion film immersed in a 20 μM Ru(bpy)$_2$dppz^{2+} solution. The traces were recorded after (a) 0.5, (b) 212, and (c) 426 min of loading. The intensities were normalized as shown.

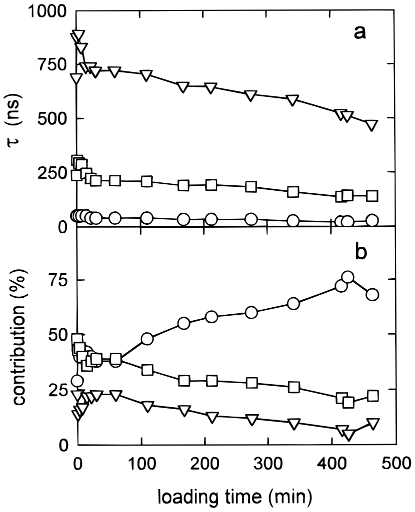

Figure 8. Dependence of the lifetimes (a) and contributions (b) of the long- (▽), medium- (□), and short-lived (○) components responsible for the luminescence of Ru(bpy)$_2$dppz^{2+} in an ITO/Nafion film on loading time. The lifetimes and component populations were evaluated by deconvolution and fitting of decay curves (see Figure 7) to a triexponential function (see text).

In an attempt at a more quantitative analysis, the decay curves were deconvoluted from the instrument response ($<$10 ns). None of the emission decay curves could be fitted satisfactorily to single exponential or biexponential functions. Only triexponential functions yielded acceptable fits. Although Colón and Martin[6] used a dispersed kinetic model to describe the emission decay of Ru(bpy)$_3$$^{2+}$ in Nafion, we prefer a triexponential model for two reasons: (1) the intriguing inconsistencies between steady-state emission and lifetimes pointed out by Colón and Martin are practically nonexistent in the case of Ru(bpy)$_2$dppz^{2+}; and (2) the emission of Ru(bpy)$_2$dppz^{2+} (unlike Ru(bpy)$_3$$^{2+}$) can be quenched substantially in the presence of water, producing more distinctive lifetimes.

As illustrated in Figure 8, the emission lifetimes and the fractions of the incorporated complex that exhibit each of the three lifetimes (determined from the preexponential factors) change with loading. After a brief increase and fast decrease early in the loading (first 15 min), the lifetimes of the two longer-lived components decrease steadily by ca. 30% over the next 450 min. The lifetime of the short-lived component decreases by about 60% over the same period (Figure 8a). These changes in lifetimes are accompanied by changes in the distribution of the three emitting components (Figure 8b). At low loading (up to 60 min loading time), the decay traces consist mostly of the two long-lived components, while the short-lived one participates to only a small extent. As the loading continues, the short-lived component becomes increasingly important and eventually accounts for about 75% of the overall decay. It is

Table 1. Emission Lifetimes (ns) and Maxima (nm; in Parentheses) of Ruthenium Complexes in Various Media

complex	medium H_2O	 CH_3CN	 DNA/H_2O	 Nafion
$Ru(bpy)_3^{2+}$	620 (613)[a]	870 (615)[a]	650 (617)[b]	680 (610)[c] 250/800 (610)[d]
$Ru(dppz)_3^{2+}$	*e*	730 (615)[f]	*e*	*e*
$Ru(bpy)_2dppz^{2+}$	*g*	180 (622)[h] 770 (620)[d]	90/340 (621)[h]	50/300/900 (620)[d]
$Ru(phen)_2dppz^{2+}$	*g*	180 (619)[h] 770 (620)[d]	120/770 (617)[h]	50/300/900 (620)[d]

[a] Reference 7b. [b] Reference 17. [c] References 5a and 5c. [d] This work. [e] Not reported. [f] Reference 18. [g] Emission below the detection limit. [h] Reference 9a.

worth noting that the contributions of the two long-lived components decrease at the same rate during loading, suggesting that the same phenomenon is responsible for quenching their emissions.

Analogous to the steady-state emission experiments (Figure 6), changes in the emission lifetimes of films with different fixed quantities of $Ru(bpy)_2dppz^{2+}$, while immersed in pure water, were monitored with time. The emission lifetimes and distributions were essentially constant when the quantity of the complex in the film was relatively low, but at higher loading levels the contribution of the short-lived component increased considerably with time at the expense of the longer-lived components.

Discussion

Our finding that $Ru(bpy)_2dppz^{2+}$ exhibits luminescence when incorporated in Nafion is important because it clearly shows that the cationic complex can reside in an environment inside the coating where the dppz ligand is efficiently prevented from hydrogen bonding with the water. This finding is remarkable in view of the fact that the films we employed were cast from a solvent mixture consisting of 80% water, which leads to a high water content in the initially cast films.[15] However, it has recently been demonstrated that large quantities of water are ejected from Nafion films during the incorporation of complexes of hydrophobic ligands.[16] Such ejection of water and hydrated counterions as $Ru(bpy)_2dppz^{2+}$ is incorporated in Nafion would result in the initially incorporated cation's experiencing a dehydrated environment where its luminescence is enhanced. However, water molecules and the remaining hydrated counterions located elsewhere in the films diffuse much more rapidly than the large $Ru(bpy)_2dppz^{2+}$ cations so that water can be reintroduced into the regions of the film initially occupied by the $Ru(bpy)_2dppz^{2+}$ cations. This is the process that we believe is responsible for the unusual time dependence of the emission intensity in the inset in Figure 4.

Additional evidence supporting this conclusion is given in Table 1 where emission lifetimes of $Ru(bpy)_2dppz^{2+}$ and related complexes in Nafion are compared with lifetimes measured in other media. The lifetime of $Ru(bpy)_2dppz^{2+}$ in dry, carefully deoxygenated acetonitrile, 770 ns, is considerably longer than that obtained previously in the presence of O_2[9a] and is comparable to that reported for $Ru(dppz)_3^{2+}$.[18] The similarity of the lifetimes for the mixed-ligand and the homo-ligand complexes accords with the report by Sauvage et al.[8] that the MLCT transition is to dppz.

The three emission lifetimes for $Ru(bpy)_2dppz^{2+}$ in Nafion (Table 1) were obtained by fitting decay curves (similar to those in Figure 7) for films that had been loaded for 4 min. The lifetime of 900 ns is significantly longer than the values reported for this complex in other media (Table 1), including the 770-ns lifetime in dry, degassed acetonitrile, as well as those measured in the presence of DNA.[9,11] This emission enhancement is logically attributable to a reduction of the quenching by the water in Nafion films. The intermediate lifetime of 300 ns can be assigned to incorporated complex molecules that are only partially protected from interaction with water. We assume that the short lifetime (50 ns) is the signature of complexes that are associated with hydrophilic ionic clusters.[2]

When RuL_4dppz^{2+} complexes are intercalated in DNA,[9,11] the nature of L plays an important role in determining the luminescence lifetime. For RuL_4dppz^{2+} in Nafion, however, L has little effect on the lifetimes (for example, $Ru(bpy)_2dppz^{2+}$ and $Ru(phen)_2dppz^{2+}$ exhibit similar lifetimes; Table 1). It was suggested that the longer lifetime of $Ru(phen)_2dppz^{2+}$ when intercalated in DNA is due to additional shielding provided by the more hydrophobic (relative to bpy) phen ligand.[9a] The similarity of the bpy and phen complexes in Nafion could mean that dppz is so well shielded from water in the film that additional protection is inconsequential.

At low $Ru(bpy)_2dppz^{2+}$ loading levels in Nafion, the two longer-lived components constitute 60−70% of the emitting centers (Figure 8). This behavior suggests that in the beginning of the loading process a large portion of the incorporated complex is located in the hydrophobic region of the film with the phenazine interacting strongly with the perfluorinated backbone of the polymer. Additional evidence for such interactions are the small peak currents and large separations of peak potentials observed in the cyclic voltammogram (Figure 1b). Similar behavior observed for other complexes of hydrophobic ligands has been attributed to their low mobility in the film.[4c] Strong interaction of the protruding phenazine ligand with perfluorocarbon chains of the polymer could result in decreased mobility of the complex. Such immobilization, which also could lead to enhancement of emission lifetimes,[7b] might account for the longer lifetime of $Ru(bpy)_2dppz^{2+}$ in Nafion relative to acetonitrile.

The emission properties of both $Ru(bpy)_3^{2+}$ and $Ru(bpy)_2dppz^{2+}$ depend on the loading time. The data in Figures 2−5 show that the emission intensity per molecule incorporated decreases with loading time for both complexes. The observed decrease is larger than an inner filter effect, which is expected as a result of the increasing absorption of the sample with increasing concentration in the film. Bimolecular self-quenching would be expected to lower the emission per molecule and lead to saturation behavior with loading time (as seen for $Ru(bpy)_3^{2+}$ in Figure 5). The sharp drop in the emission intensity of $Ru(bpy)_2dppz^{2+}$ after ∼300 min (Figure 4), however, suggests that an additional process is responsible for the quenching in Nafion. The increased contribution of the short-lived component (Figure 8b) indicates that $Ru(bpy)_2dppz^{2+}$ undergoes a gradual change in its environment during loading. The red shift of the emission maximum (Figure 3) is additional evidence of that change and suggests further that it is accompanied by an increase in the polarity of the medium.[7b] The diffusional redistibution of the water remaining in the film, as discussed above, could result in an increase in the water activity in the vicinity of the complex with a corresponding increase in polarity. The emission of $Ru(bpy)_2dppz^{2+}$ is much more sensitive to water

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than is that of $Ru(bpy)_3^{2+}$. In acetonitrile the emission of $Ru(bpy)_2dppz^{2+}$ exhibits Stern−Volmer quenching by added water.[9a] Thus, slight changes in the water activity experienced by the complex inside Nafion could lead to pronounced differences in quenching and thus to the distinctive behavior of the two complexes (as seen in Figures 4 and 5, respectively).

Restructuring of the polymer and dehydration of the polymer interior are other features that may affect the distribution of the complex and its exposure to water. Since the quenching of the luminescence depends upon the coupling between the exposed nitrogen atoms of dppz and the OH groups of water molecules, any interference with this H-bond coupling would diminish the quenching. As the data in Figure 6 demonstrate, such effects are more significant at moderate loading levels than at low loading levels.

In summary, $Ru(bpy)_2dppz^{2+}$ luminesces strongly in Nafion films with a remarkably long lifetime. The protruding phenazine moiety of the complex appears to interact strongly with the hydrophobic fluorocarbon matrix that interferes with hydrogen bonding to water molecules in the polymer film. The emission intensity and lifetime are regulated by the degree of self-quenching as well as the quenching attributable to environmental changes imposed by the level of loading.

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