

Articles

Optical Properties of $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ as a Function of Nonaqueous Environment

Rajesh B. Nair, Brian M. Cullum, and Catherine J. Murphy*

Department of Chemistry and Biochemistry, University of South Carolina,
Columbia, South Carolina 29208

Received July 19, 1996[®]

The complex $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ is not photoluminescent in water but does emit in nonaqueous solvents (alcohols, acetonitrile) and in the presence of hydrated polymers such as DNA. Here we examine the steady-state and time-resolved photoluminescence spectra of $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ in a series of nonaqueous solvents. We find that solvent polarity, as defined by the E_T scale, is the single most important parameter in predicting luminescence lifetime and intensity in nonaqueous systems. These results are compared to the data for DNA, and the sequence-dependent microenvironment of the complex bound to DNA also follows the trends observed herein. The addition of high concentrations of water to solutions of $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ dissolved in nonaqueous solvents leads to decreases in emission intensity that follow the Perrin sphere of quenching model. The nonradiative rate constants for luminescence decay increase as the solvent polarity increases, while the radiative rate constants are relatively unaffected by the local environment.

Introduction

There has been increasing demand for the design and development of transition metal complexes that can act as luminescent probes for various environments.¹ Ruthenium complexes are ideally suited for application as sensitive non-covalent probes because they absorb and emit light in the visible, are coordinatively saturated, and are inert to substitution.

Polypyridyl complexes of ruthenium(II) are colored due to an intense metal-to-ligand charge transfer (MLCT) band at ~440 nm and frequently display photoluminescence at ~610 nm upon excitation into this MLCT band. The complex $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ (Figure 1) and its cousin $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$ have MLCT states which are localized on the electron-withdrawing dipyrrophenazine (dppz) ligand.² In a dramatic departure from typical ruthenium(II) diimine complexes, these molecules show no photoluminescence at ~610 nm in aqueous solution at ambient temperatures but emit brightly in nonaqueous solvents such as acetonitrile or alcohol.³ Polymers in aqueous solution, including Nafion⁴ and DNA,⁵ can also provide local nonaqueous pockets for these complexes, and hence, luminescence is observed in these systems. Luminescence enhancements of $>10^4$ are esti-

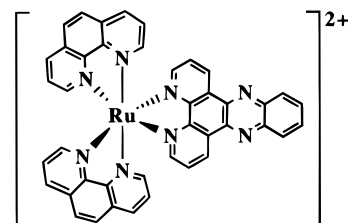


Figure 1. $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$.

mated upon binding of $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ to DNA.^{3,5} The dipyrrophenazine ligand, compared to the parent phenanthroline (phen) ligand, has an extended aromatic surface area which allows for tight binding to DNA via intercalative stacking. Dipyrrophenazine complexes of ruthenium (II) act as molecular "light switches" by allowing luminescence to occur only when the phenazine nitrogens are protected from water; in DNA, the metal complex, upon intercalation into the helix, is protected from the aqueous solvent, thereby preserving the luminescence.^{3,5} Accumulated evidence points to hydrogen bonding and/or excited-state proton transfer to the phenazine nitrogens as the mechanism of deactivation of the complex's excited state.^{3,5,6}

In principle, the local nonaqueous environment surrounding the phenazine nitrogen portion of $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ should influence the complex's spectroscopic properties, in terms of the local environment's hydrogen-bonding ability and polarity. In this paper, we report on the optical properties of $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ in various nonaqueous solvents and assess the ability of this complex to act as a molecular probe of local environment.

Experimental Section

Instrumentation and Materials. NH_4PF_6 , 1,10-phenanthroline, $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, $\text{CF}_3\text{SO}_3\text{H}$, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), formamide, pyridine, CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, trifluoroethanol

* To whom correspondence should be addressed: 803-777-3628 (phone); 803-777-9521 (fax); murphy@psc.sc.edu (e-mail).

[®] Abstract published in *Advance ACS Abstracts*, February 15, 1997.

- (1) (a) Demas, J. N.; DeGraff, B. A. *Anal. Chem.* **1991**, *63*, 829A. (b) Juris, A.; Balzani, V.; Barigelli, F.; Campagna, S.; Belser, P.; Von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.
- (2) (a) Chambron, J.-C.; Sauvage, J.-P.; Amouyal, E.; Koffi, P. *New J. Chem.* **1985**, *9*, 527. (b) Amouyal, E.; Homs, A.; Chambron, J. C.; Sauvage, J. P. *J. Chem. Soc., Dalton Trans.* **1990**, 1841. (c) Fees, J.; Kaim, W.; Moscherosch, M.; Matheis, W.; Klima, J.; Krejčík, M.; Zalis, S. *Inorg. Chem.* **1993**, *32*, 166. (d) Schoonover, J. R.; Bates, W. D.; Meyer, T. J. *Inorg. Chem.* **1995**, *34*, 6421.
- (3) Jenkins, Y.; Friedman, A. E.; Turro, N. J.; Barton, J. K. *Biochemistry* **1992**, *31*, 10809.
- (4) Sabatani, E.; Nikol, H. D.; Gray, H. B.; Anson, F. C. *J. Am. Chem. Soc.* **1996**, *118*, 1158.
- (5) (a) Friedman, A. E.; Chambron, J.-C.; Sauvage, J.-P.; Turro, N. J.; Barton, J. K. *J. Am. Chem. Soc.* **1990**, *112*, 4960. (b) Hartshorn, R. M.; Barton, J. K. *J. Am. Chem. Soc.* **1992**, *114*, 5919. (c) Dupureur, C. M.; Barton, J. K. *J. Am. Chem. Soc.* **1994**, *116*, 10286.

- (6) Turro, C.; Bossmann, S. H.; Jenkins, Y.; Barton, J. K.; Turro, N. J. *J. Am. Chem. Soc.* **1995**, *117*, 9026.

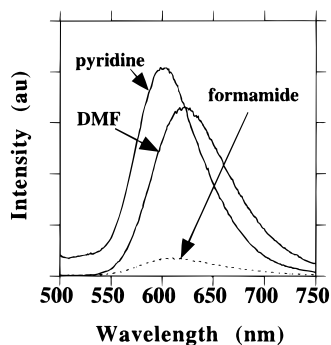


Figure 2. Photoluminescence spectra of 9.6×10^{-5} M $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ in several representative nonaqueous solvents in air.

(TFE), acetonitrile (MeCN), CH_2Cl_2 , and D_2O were obtained from Aldrich and were of the highest purity available. The water content of fresh solvents was obtained from the manufacturers and was less than 0.4% in all cases, with DMSO and MeCN having the most water and CH_2Cl_2 the least. Water was deionized and purified with a Continental Water system.

^1H NMR spectra were obtained on a Bruker AM-400 instrument. Absorption spectra of the complex were obtained on a Perkin-Elmer Lambda 14 UV–visible spectrophotometer. Steady-state luminescence spectra were measured on an SLM-Aminco 8100 spectrofluorometer with 4 nm resolution and excitation at 440 nm. Luminescence quenching studies of 9.6×10^{-5} M $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ dissolved in various nonaqueous solvents by H_2O were performed with the same instrument parameters.

Emission lifetimes were acquired using a N_2 laser (Laser Science, Inc., model VSL-337). The samples, contained in quartz cuvettes, were excited by the 337 nm fundamental beam of the laser. Luminescence signals were collected with a Spex monochromator (Model 1681), with 500 μm slits, giving a spectral resolution of 1.8 nm. The output of the detector, a Hamamatsu R2949 PMT, was sampled by a LeCroy 9350L digital sampling oscilloscope. To determine the lifetime of each sample, 1000 waveforms were averaged on the oscilloscope. The average waveform was then deconvoluted using Andre's fast Fourier transform (FFT) method⁷ and fitted to single exponential decays. Lifetimes obtained with a Q-switched Nd:YAG laser (Quintel) at 532 nm excitation were generally identical to those obtained with the nitrogen laser. The shortest lifetime reliably deconvoluted from our system is ~ 2 ns.

Sample Preparation. $[\text{Ru}(\text{phen})_2\text{dppz}](\text{PF}_6)_2$ was synthesized according to standard procedures^{8–10} and purified by alumina chromatography. Solutions for spectroscopy were either prepared in air or were purged with N_2 .

Quenching with H_2O and D_2O . The lifetime of 9.6×10^{-5} M $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ dissolved in DMSO was monitored as aliquots of H_2O and D_2O were added. Data were taken from 0 to 5 M quencher.

Results

The absorption spectra of $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ upon dissolution in various nonaqueous solvents and water are very similar. The emission spectra are somewhat solvatochromic, with the emission maximum shifting over a range of ~ 30 nm around the generic ~ 610 nm peak (Figure 2). The related complex $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$ has also been observed to have solvatochromic emission spectra in alcoholic (methanol through decanol) solutions.¹¹ There is no steady-state emission observed at all in water for either complex.

Luminescence lifetimes are collected in Table 1. All lifetimes

Table 1. Emission Characteristics of $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ in Nonaqueous Solvents at $T = 298$ K

| solvent | E_T , kcal/mol ^a | α^a | $\lambda_{\text{max}}^{\text{em}}$, nm | quantum yield | | τ , ns | |
|--------------------------|----------------------------------|------------|--|------------------|----------------|------------------|----------------|
| | | | | air ^b | N_2^b | air ^c | N_2^c |
| pyridine | 40.2 | 0.00 | 598 | 0.015 | 0.076 | 315 | 752 |
| CH_2Cl_2 | 41.1 | 0.22 | 592 | 0.012 | 0.037 | 257 | 456 |
| DMF | 43.8 | 0.00 | 625 | 0.011 | 0.023 | 207 | 399 |
| DMSO | 45.0 | 0.00 | 626 | 0.0077 | 0.013 | 232 | 330 |
| MeCN | 46.0 | 0.15 | 607 | 0.0073 | 0.033 | 177 | 663 |
| EtOH | 51.9 | 0.86 | 605 | 0.0046 | 0.027 | 91 | 93 |
| MeOH | 55.5 | 0.98 | 601 | 0.0031 | 0.0033 | 43 | 45 |
| formamide | 56.6 | 0.66 | 610 | 0.0012 | 0.0023 | 25 | 24 |
| TFE | 59.5 | 1.35 | <i>d</i> | <i>d</i> | <i>d</i> | <i>d</i> | <i>d</i> |
| water | 63.1 | 1.13 | <i>d</i> | <i>d</i> | <i>d</i> | <i>d</i> | <i>d</i> |

^a The E_T values, a measure of solvent polarity, and α values, a measure of the ability of the medium to donate hydrogen bonds, are from ref 12. ^b Relative quantum yield compared to $[\text{Ru}(\text{bpy})_3]^{2+}$ ($\phi = 0.042$ in deaerated aqueous solution and $\phi = 0.028$ in aerated aqueous solution).^{1b} Values are corrected for the refractive index of the solvent according to ref 13. The concentration of $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ was 9.6×10^{-5} M in air-saturated solutions and was 1.0×10^{-6} M in deaerated solutions. ^c Lifetimes are the average of three independent measurements and have an estimated error of $\pm 5\%$. ^d There is no emission observed in water or TFE.

were well-fit by single exponential decays, as expected for a pure species. Excitation in the dppz bands at 337 nm yields generally identical lifetimes as excitation in the MLCT band at 532 nm. Lifetimes and relative quantum yields are longer and higher, respectively, in deoxygenated solution compared to air. (We include the results in air since much of the data on this complex are reported in air). There is a reasonably linear correlation between the polarity of the solvent, as defined by the E_T parameter,¹² and both the lifetime and relative quantum yield of the complex (Figure 3). The E_T value corresponds to the energy absorption maximum for a solvatochromic organic dye that has a large dipole moment in the ground state and a smaller dipole moment in the excited state.¹² E_T incorporates both "pure" polarity and hydrogen-bond-donating parameters.¹²

In order to estimate radiative and nonradiative rate constants, we use the relations $\phi_r = k_r\tau$ and $\tau = 1/(k_r + k_{\text{nr}})$, where ϕ_r is the quantum yield of emission, corrected for the refractive index of the solvent (Table 1), k_r is the radiative rate constant in s^{-1} , τ is the observed luminescence lifetime in s, and k_{nr} is the sum of all the rate constants of processes that are nonradiative. We have implicitly assumed that, like $[\text{Ru}(\text{bpy})_3]^{2+}$, population of the triplet MLCT state occurs with a quantum yield of unity for $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$. We find that the radiative rates are essentially independent of emission energy, as seen for $[\text{Ru}(\text{bpy})_3]^{2+}$, but there is not a clean correlation of the rates of nonradiative decay with the energy gap between the ground and excited states as measured by the emission maximum energy, as has been observed for $[\text{Ru}(\text{bpy})_3]^{2+}$.¹³ We also find that radiative rates for $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ vary little as a function of E_T and α .

We have also examined the effect of water on $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ in a predominantly nonaqueous environment. Stern–Volmer plots of $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ emission intensity in nonaqueous solvents when quenched by rather large concentrations of water (steady-state conditions) are in general nonlinear and upward-curving. We find that the Perrin sphere of quenching model fits our data much better than the Stern–Volmer model (Figure 4 and Table 2). The Perrin sphere of quenching model assumes that the emitting molecules are

- (7) Andre, J. C.; Vincent, L. M.; O'Connor, D.; Ware, W. R. *J. Phys. Chem.* **1979**, *83*, 2285.
- (8) Howells, R. D.; McCown, J. D. *Chem. Rev.* **1977**, *77*, 69.
- (9) Sullivan, B. P.; Salmon, D. J. Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.
- (10) Yamaka, M.; Tanaka, Y.; Yoshimoto, Y.; Kuroda, S.; Shimao, I. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1006.
- (11) Chambron, J.-C.; Sauvage, J.-P. *Chem. Phys. Lett.* **1991**, *182*, 603.

- (12) Kamlet, M. J.; Abboud, J. L. M.; Taft, R. W. *Prog. Phys. Org. Chem.* **1981**, *13*, 485.
- (13) Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5583.

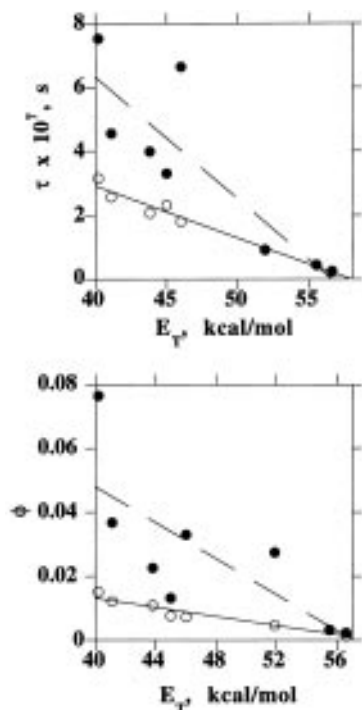


Figure 3. Top: Plot of $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ emission lifetime vs E_T , a measure of solvent polarity which also includes H-bond donation ability. The data taken in air (open circles) yield a correlation coefficient of 0.99 for the least-squares fit line (solid line). The data taken under N_2 (filled circles) yield a correlation coefficient of 0.87 for the least-squares fit line (dashed line). Bottom: Plot of $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ relative quantum yield vs E_T , a measure of solvent polarity which also includes H-bond donation ability. The data taken in air (open circles) yield a correlation coefficient of 0.96 for the least-squares fit line (solid line). The data taken under N_2 (filled circles) yield a correlation coefficient of 0.75 for the least-squares fit line (dashed line).

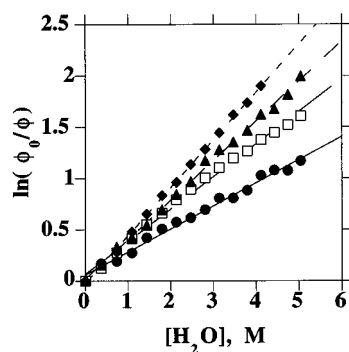


Figure 4. Representative Perrin plots for the quenching of $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ in several nonaqueous solvents by water, in air. Filled diamonds are the data for DMSO, filled triangles for DMF, open squares for EtOH, and filled circles for formamide.

Table 2. Perrin Fit Parameters for the Quenching of 9.6×10^{-5} M $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ in Nonaqueous Solvents^a by Water, in Air

| solvent | slope of Perrin plot (M^{-1}) | correlation coeff | r (\AA) |
|-----------|--|-------------------|----------------------|
| formamide | 0.225 | 0.995 | 4.5 |
| MeOH | 0.241 | 0.999 | 4.6 |
| EtOH | 0.318 | 0.997 | 5.0 |
| DMF | 0.386 | 0.999 | 5.4 |
| DMSO | 0.446 | 0.999 | 5.7 |

^a Dichloromethane is not miscible with water and was not investigated. Pyridine yielded nonlinear Stern–Volmer plots and nonlinear Perrin plots.

quenched completely if the quencher molecules are within a sphere of radius r , and any quenchers located outside this sphere

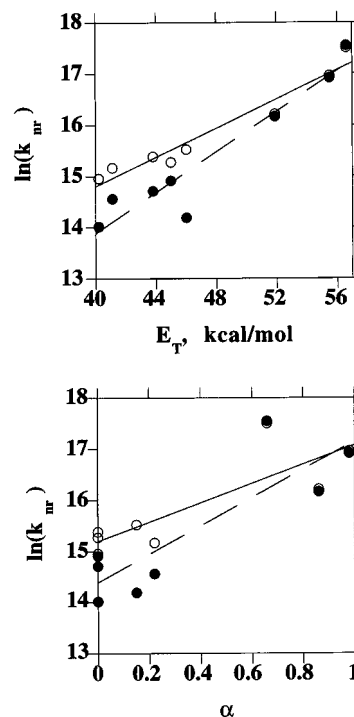


Figure 5. Top: Plot of $\ln k_{\text{nr}}$ vs E_T for $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ in various solvents. The data taken in air (open circles) yield a correlation coefficient of 0.97 for the least-squares fit line (solid line). The data taken under N_2 (filled circles) yield a correlation coefficient of 0.95 for the least-squares fit line (dashed line). Bottom: Plot of $\ln k_{\text{nr}}$ vs α for $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ in various solvents. The data taken in air (open circles) yield a correlation coefficient of 0.84 for the least-squares fit line (solid line). The data taken under N_2 (filled circles) yield a correlation coefficient of 0.86 for the least-squares fit line (dashed line).

do not quench the emission at all.¹⁴ The Perrin equation is $\ln(\phi_0/\phi) = N_0V[Q]$, where ϕ and ϕ_0 are the relative quantum yields of emission with and without quencher, respectively, N_0 is Avogadro's number, V is the volume of the quenching sphere, and $[Q]$ is the quencher concentration. Fit parameters and values for r ($V = (4/3)\pi r^3$) are listed in Table 2. We have also performed time-resolved quenching experiments in DMSO with H_2O and D_2O and find that D_2O is less effective at quenching the ruthenium complex emission than H_2O , yielding a significant isotope effect of 1.5 (from the relative slopes of the Perrin plots). This result agrees with, but is not as dramatic as, the reported isotope effect of 2.1 for H_2O vs D_2O Stern–Volmer quenching in acetonitrile.³

Discussion

One of the most interesting features we have gathered from our data is that the *polarity* of the medium correlates well with $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ optical properties, in particular luminescence lifetimes and relative intensities. This is a feature of the solvent medium that has received little attention for $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ in comparison to the medium's ability to hydrogen bond to the phenazine nitrogens of the complex. We find that the more polar the solvent as defined by E_T , the larger the $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ nonradiative rate constant (Figure 5). Significantly, the ability of the solvent to hydrogen bond to the ruthenium complex, as measured by the α parameter,¹² does not correlate as well with k_{nr} . The emission energy maximum of $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ also does not show a good linear correlation

(14) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin Cummings: Menlo Park, CA, 1978.

with solvent polarity, which might have been expected for a simple charge-transfer excited state.

If we examine the data for DNA, the correlation of environment polarity with emission lifetime and relative quantum yield holds up: $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ bound to poly[d(GC)]·poly[d(GC)] exhibits shorter lifetimes ($\tau_1 = 290$ ns and $\tau_2 = 70$ ns) and a weaker relative intensity of emission than when bound to poly[d(AT)]·poly[d(AT)] ($\tau_1 = 740$ ns and $\tau_2 = 120$ ns).^{3,15} G and C are more polar (dipole moments are 7.5 and 7.6 debyes respectively) than A and T (dipole moments are 2.9 and 4.6 D, respectively).¹⁶ Thus all these data are consistent with the notion that the more polar GC base pairs provide a more polar environment for the complex and, thus, reduce its lifetime and emission intensity. Even though GC-rich DNA is better-stacked than AT-rich DNA,¹⁶ leading one to expect that the complex once bound to GC-rich DNA would be better shielded from water and thus emit brighter and longer, the more polar GC environment seems, in our analysis, to dominate these effects and reduce emission intensities and lifetimes.

A recent report finds that $[\text{Ru}(\text{bpy})_3]^{2+}$ itself exhibits changes in lifetime and relative quantum yield that seem to track the polarity of alcoholic (methanol through decanol) solvents; the authors speculate that the diimine nitrogens are the most likely site of solvent association via hydrogen bonds and dipole forces.¹⁷ In the case of $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ the phenazine nitrogens are more solvent-accessible, but nonetheless the interaction of its diimine nitrogens with the local environment should not be neglected and may differ qualitatively from that of the phenazine nitrogens. From our data we cannot distinguish which sites are more affected by solvent.

Another initially peculiar feature of $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ is that its emission *energies* in different solvents do not track the

lifetimes and relative quantum yields. These results, however, have also been observed for $[\text{Ru}(\text{bpy})_3]^{2+}$, and temperature studies have concluded that the energy gap law (rates of *nonradiative* decay increase as the energy gap between ground and excited states decreases) does hold for this complex.¹³

The addition of high concentrations of water to the ruthenium complex dissolved in nonaqueous solvents leads to nonlinear Stern–Volmer plots. This implies that the quenching mechanism is not solely diffusional, and a comparison of steady-state and time-resolved Stern–Volmer plots suggests that static quenching contributes to the process.¹⁴ Fitting our data to the Perrin sphere of quenching model, we find that the radius of the sphere of water quenching is 4.5–6.0 Å depending on the host solvent (Table 2). Variations in the size of the Perrin sphere roughly correlate with the α parameter; the better the medium is at donating hydrogen bonds, the smaller the Perrin sphere. This size is consistent with, but is certainly not proof of, quenching of the ruthenium complex via hydrogen bonding to nearest-neighbor water molecules and agrees with our and others' results of a large isotope effect for the quenching of $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ emission by H_2O vs D_2O .³

Clearly, the emission maxima, lifetimes, and intensities of $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ are very sensitive to local environment. This complex is likely to be useful in optically probing nonaqueous environments, with the caveat that red shifts in the emission maximum do not correlate with the polarity of the medium as measured by the E_T parameter. Rather, luminescence lifetimes and relative intensities are better indicators of the polarity of the $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ local environment.

Acknowledgment. We thank the Department of Energy for funding. C.J.M. also gratefully acknowledges the National Science Foundation for a CAREER Award. We also thank Professors S. M. Angel and M. Berg for many helpful discussions and Prof. J. K. Barton for comments on the manuscript.

IC960862U

(15) Murphy, C. J.; Barton, J. K. *Meth. Enzymol.* **1993**, 226, 576.

(16) Saenger, W. *Principles of Nucleic Acid Structure*; Springer-Verlag: New York, 1984.

(17) Hartmann, P.; Leiner, M. J. P.; Draxler, S.; Lippitsch, M. P. *Chem. Physics* **1996**, 207, 137.