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$[Ru(bpy)_2dppz]^{2+}$ Light-Switch Mechanism in Protic Solvents as Studied through Temperature-Dependent Lifetime Measurements†

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Temperature-dependent excited-state lifetime measurements have been performed on four different Ru(II)-based dppz compounds in protic and aprotic solvents. This work supports the existence of a dynamic equilibrium between two MLCT states associated with the dppz ligand: one is a bright state with a ligand orbital similar in size to that associated with the ^{3}MLCT state of $[Ru(bpy)_3]^{2+}$, and the other is a dark phz-like state. Our results are consistent with a light-switch mechanism involving a competition between energetic factors that favor the dark (phz) state and entropic factors that favor the bright (bpy) state. This paper explores the photophysics of these light-switch compounds through a systematic variation of the equilibrium energetics. This is accomplished by (1) varying the dielectric strength of the solvent and (2) making chemical substitutions on the dppz ligand. Observations obtained from all four compounds in six different solvents can be explained using this equilibrium model.

I. Introduction

The polypyridyl Ru(II) compound $[Ru(bpy)_2dppz]^{2+}$ (Figure 1) has been identified as a luminescent probe of many aprotic environments,[1−3] including polymer films, micelles, and DNA. In aqueous solution, $[Ru(bpy)_2dppz]^{2+}$ is essentially nonemissive; however, in the presence of DNA, the molecule intercalates between adjacent base pairs in the double helix and becomes brightly luminescent.[4−9] This behavior, called the "light-switch" effect, is the basis for use of this compound as a probe of nonpolar microenvironments. As it turns out, DNA is not the only environment in which $[Ru(bpy)_2dppz]^{2+}$ emits, and luminescent excited states are observed in many protic and aprotic solvents. Because of their useful applications and unique photophysical properties, dppz-containing molecules have been studied in a range of solvents with the goal of understanding the origin of their emission.[10−15]

The light-switch mechanism has been attributed to the presence of two metal-to-ligand charge-transfer (MLCT) states on the dppz ligand: a bright (luminescent) state associated with the bipyridine (bpy) fragment and a dark (nonluminescent) state localized largely on the phenazine (phz) portion.[16] According to this model, the bright state is lowest in energy for aprotic solvents resulting in an emissive excited state. Protic solvents, on the other hand, hydrogen bond to the phz nitrogens, lower the energy of the dark state below that of the bright state, and shut off the luminescence. Although this environment-induced state reversal has been suggested as the basis for the light-switch property, direct confirmation has been elusive.

Our research effort concurs with the existence of two states associated with the dppz ligand: a dark phenazine-based state and a luminescent $[Ru(bpy)_3]^{2+}$-like ^{3}MLCT state. However, our data are inconsistent with the state reversal description of the light-switch behavior. Instead, the results of temperature dependence measurements show that, in $[Ru(bpy)_2dppz]^{2+}$, the dark state is always lowest in energy and the light-switch behavior is the result of a dynamic equilibrium between an enthalpically favored dark state and an entropically favored bright state.[17,18] A diagram depicting these states is presented in Figure 2. Lifetime data obtained at high temperatures indicate

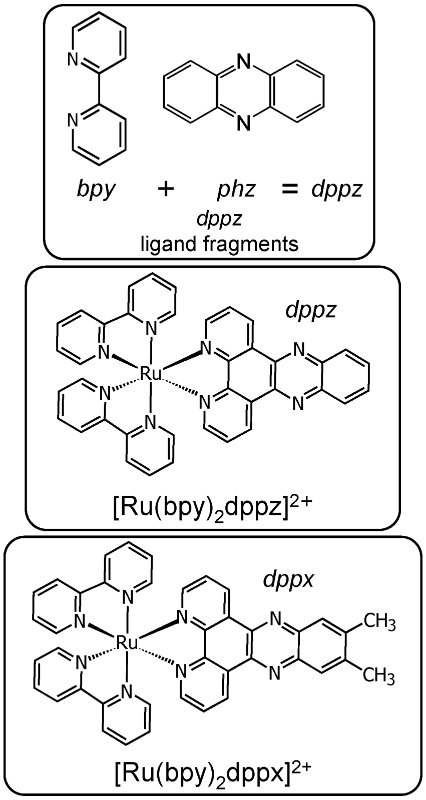

Figure 1. Chemical structures of light-switch complexes $[Ru(bpy)_2dppz]^{2+}$ and $[Ru(bpy)_2dppx]^{2+}$ and ligand fragments discussed in the text.

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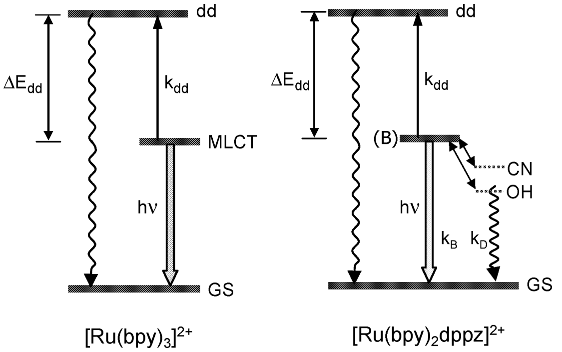

Figure 2. Energy level diagrams depicting the excited states of [Ru(bpy)$_2$dppz]$^{2+}$ and [Ru(bpy)$_3$]$^{2+}$. The bright state described in the text is denoted by B, and both OH and CN refer to the dark state. The dark state for protic solvents is represented by OH, whereas CN corresponds to the dark state in aprotic solvents. All three are MLCT states associated with the dppz ligand. The bright state, B, is entropically favored and is populated at high temperatures. The dark state is enthalpically favored and is therefore populated at low temperatures. In this scheme, k_B is the relaxation rate from the bright state, and k_D is the relaxation rate from the dark state.

that the bright state is an MLCT state in which the photoexcited electron is located on the bpy fragment of the dppz ligand. Measurements performed in different solvents provide an indication as to the nature of the dark state. They suggest that it has a greater degree of charge-transfer character than the bright state. On this basis, we assign it to an MLCT state in which the electron is localized more on the phz portion of the dppz ligand. Thus, the equilibrium corresponds to the transfer of the photoexcited electron between the inner and outer portions of the dppz ligand. Qualitatively speaking, our model describes the [Ru(bpy)$_2$dppz]$^{2+}$ complex as consisting of a [Ru(bpy)$_3$]$^{2+}$ core and a phz charge-acceptor.

This paper expands upon our previous work in two ways. We examine the luminescent properties of [Ru(bpy)$_2$dppz]$^{2+}$ in a series of linear alcohols. As observed in nitrile solvents, the photophysics in alcohols also appears to be governed by an excited-state equilibrium. Experiments performed in a range of solvents (protic and aprotic) suggest that several properties connected with the dark state correlate with the degree of solvent polarity. In particular, increasing the solvent polarity preferentially stabilizes the dark-state energy and increases the rate of nonradiative relaxation, the latter being consistent with observations made by Murphy and co-workers.[13] This correlation with the solvent dielectric strength strongly supports our contention that the dark state has significant charge-transfer character, in contrast to a recent theoretical calculation that the dark state is a ligand-centered $^3\pi\pi^*$ state.[19] We also examine a complex with a chemically modified dppz ligand, i.e., [Ru(bpy)$_2$dppx]$^{2+}$, where the addition of electron-donating methyl substituents destabilizes the π^* orbitals and pushes the phz state higher in energy. The effect of this substitution is clear in the experimental data. This equilibrium description of the light-switch mechanism accounts for a wide range of observations across multiple dppz-containing Ru(II) compounds in a series of solvents with differing chemical character and polarity.

II. Experimental Description

The time-resolved emission experiments were conducted by time-correlated single photon counting (TCSPC). Briefly, the 846-nm output from a mode-locked Ti:sapphire oscillator (Spectra Physics Tsunami) is frequency doubled in a BBO crystal to produce ~1-ps pulses at 423 nm with a pulse energy of ~0.2 nJ/pulse. The repetition rate of the 76-MHz pulse train is reduced using an acoustooptic modulator such that the time between excitation pulses is at least 5 times the natural lifetime of the sample (usually between 5 and 10 μs). Emission is collected at 90° with respect to excitation, passed through a 0.25-m monochromator and is directed onto a microchannel plate photomultiplier tube (MCP−PMT). The details regarding the TCSPC electronics are described elsewhere.[17,20] The instrument response is measured to be approximately 80 ps, fwhm.

Emission measurements were performed at a series of temperatures. Control over the sample temperature was achieved in one of two ways. Below 273 K, the temperature was maintained using a liquid-nitrogen-cooled cryostat (Janis 6NDT) with feedback controlling electronics that kept temperatures within ±0.1 K of the desired temperature. Above 273 K, a circulating water bath was used. The [Ru(bpy)$_2$dppz]$^{2+}$, [Ru(dppz)$_3$]$^{2+}$, [Ru(bpy)$_2$dppx]$^{2+}$, and [Ru(dppx)$_3$]$^{2+}$ complexes were synthesized per previous methods by our laboratory.[10,21] The (PF$_6^-$) salt of each complex was used for nitrile solvents, whereas the (Cl$^-$) salt was used for the alcohols.

III. Results and Discussion

This part of the paper is divided into four sections. In section A, we present steady-state spectroscopic data on [Ru(bpy)$_2$dppz]$^{2+}$ in ethanol (EtOH) at and below 298 K. Section B examines the temperature dependence of the luminescence lifetime in fluid solution. These experiments reveal the presence of a temperature-dependent equilibrium between a bright state (B) and a dark state (D). Both the high-temperature transients and the steady-state spectra at room temperature and in the low-temperature glass show that the bright state in [Ru(bpy)$_2$dppz]$^{2+}$ is photophysically similar to the ^{3}MLCT state in [Ru(bpy)$_3$]$^{2+}$. Section C extends the temperature dependence studies to other alcohol solvents and reveals that the luminescence properties correlate with the solvent polarity, suggesting that the dark state has significant charge-transfer character. Finally, section D examines the chemically modified compound [Ru(bpy)$_2$dppx]$^{2+}$, demonstrating that the equilibrium energetics can be tuned through chemical substitution.

A. [Ru(bpy)$_2$dppz]$^{2+}$ Steady-State Spectroscopy. There are at least three low-lying electronic states in [Ru(bpy)$_2$dppz]$^{2+}$ that have been postulated to play a role in determining its excited-state photophysical properties. Two are ^{3}MLCT states that correspond to the electron being localized separately on the bpy and phz fragments of the dppz ligand and the third is a long-lived, ligand-centered $^3\pi\pi^*$ state. In protic solvents, both the $^3\pi\pi^*$ and MLCT states have been observed in the *fac*-[Re(dppz)(CO)$_3$(Cl)] complex.[11] The state ordering in that complex depends on the rigidity of the solvent, with the emissive ^{3}MLCT state being lowest in fluid solutions and the $^3\pi\pi^*$ state being lowest in low-temperature glasses. The origin of this emission behavior is easily explained. In rigid environments (e.g., a 77 K glass), the solvent is frozen in a configuration appropriate for the ground electronic state, and the $^3\pi\pi^*$ state is lowest in energy. The state ordering is reversed in fluid solution, where the solvent reorganizes to stabilize the ^{3}MLCT state below the $^3\pi\pi^*$ state. Our observations indicate that, unlike *fac*-[Re(dppz)(CO)$_3$(Cl)], the luminescence in [Ru(bpy)$_2$dppz]$^{2+}$ originates from an MLCT state, both in fluid solution and in the low-temperature glass.

The basis for this conclusion comes from the steady-state emission properties, which are remarkably similar for [Ru(bpy)$_3$]$^{2+}$ and [Ru(bpy)$_2$dppz]$^{2+}$, especially given the significant

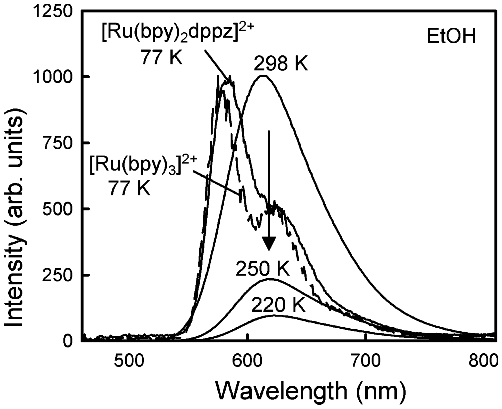

Figure 3. Steady-state emission spectra of $[Ru(bpy)_2dppz]^{2+}$ (—) in ethanol (EtOH) are shown for 77, 220, 250, and 298 K. A spectrum of $[Ru(bpy)_3]^{2+}$ (— — —) in EtOH at 77 K is also displayed for comparison.

differences in the chemical structures of the two complexes. Displayed in Figure 3 are emission spectra of $[Ru(bpy)_2dppz]^{2+}$ and $[Ru(bpy)_3]^{2+}$ in EtOH. $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_2dppz]^{2+}$ exhibit emission spectra with similar shapes and positions at both 77 and 298 K. At 298 K, they have broad, structureless emission bands that peak at 610 nm, consistent with the assertion that both compounds are ^{3}MLCT emitters at room temperature. At 77 K, both emission bands are blue shifted to 580 nm, show vibronic structure, and exhibit similar luminescence lifetimes (5.1 and 4.8 μs for $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_2dppz]^{2+}$, respectively). These observations indicate that the emission at 77 K does not originate from a $^3\pi\pi^*$ state, for $^3\pi\pi^*$ emission in dppz complexes occurs near 540 nm with a lifetime on the order of tens of microseconds. Instead, our data indicate that emission in $[Ru(bpy)_2dppz]^{2+}$ is from a ^{3}MLCT state that is photophysically similar to the $[Ru(bpy)_3]^{2+}$ ^{3}MLCT state, even in the low-temperature glass, and that the $^3\pi\pi^*$ state does not play a significant role.

As the temperature is decreased from room temperature, the intensity of the $[Ru(bpy)_2dppz]^{2+}$ emission band drops and continues to do so as long as the solvent remains fluid. This drop in emission intensity is the result of an excited-state equilibrium between two ^{3}MLCT states: an entropically favored *bright* state (B) localized on the bpy-fragment of the dppz ligand and an enthalpically favored *dark* state (D) localized primarily on the phz fragment. As the temperature is lowered, the entropic contribution to the free energy is diminished, and as a consequence, the population shifts from the bright state into the enthalpically favored dark state, and the emission intensity drops. Upon further cooling to 77 K, $[Ru(bpy)_2dppz]^{2+}$ becomes brightly luminescent. This reemergence of the emission stems from the rigid environment. In a 77 K glass, the solvent surrounding $[Ru(bpy)_2dppz]^{2+}$ is frozen in a configuration appropriate for the ground electronic state and is unable to reorganize structurally to solvate the charge-transfer state. In the absence of this energetic stabilization, the bright state, with its smaller excited-state dipole, is energetically favored. Because of these rigidity effects, we have chosen to focus on temperatures for which the solvent is clearly a fluid.

In fluid solution, there is no significant change in the band shape of the emission spectrum with decreasing temperature; however, there does appear to be a slight red shift (~9 nm) in the emission maximum at lower temperatures. Red shifts of this magnitude have been observed in the emission spectra of $[Ru(bpy)_3]^{2+}$ upon sample cooling for temperatures above the glass−fluid transition[22] and are attributed to the redistribution of population among the low-lying MLCT states in the triplet manifold. Observation of a shift of the emission band in $[Ru(bpy)_2dppz]^{2+}$ might suggest that, like $[Ru(bpy)_3]^{2+}$, the bright state is composed of a set of low-lying triplet states. This would be another indicator of its photophysical similarity with the $[Ru(bpy)_3]^{2+}$ ^{3}MLCT state. We note, however, that this explanation cannot account for the substantially larger shifts (40−75 nm) recently reported[15] for $[Ru(phen)_2dppz]^{2+}$ in more viscous solvents (e.g., glycerol), thereby suggesting that (at least in some cases) multiple factors could contribute to the spectral shift. The observations made in partially frozen environments notwithstanding, the steady-state emission spectra observed in fluid solvents suggest that the luminescent state in $[Ru(bpy)_2dppz]^{2+}$ is photophysically similar to that in $[Ru(bpy)_3]^{2+}$.

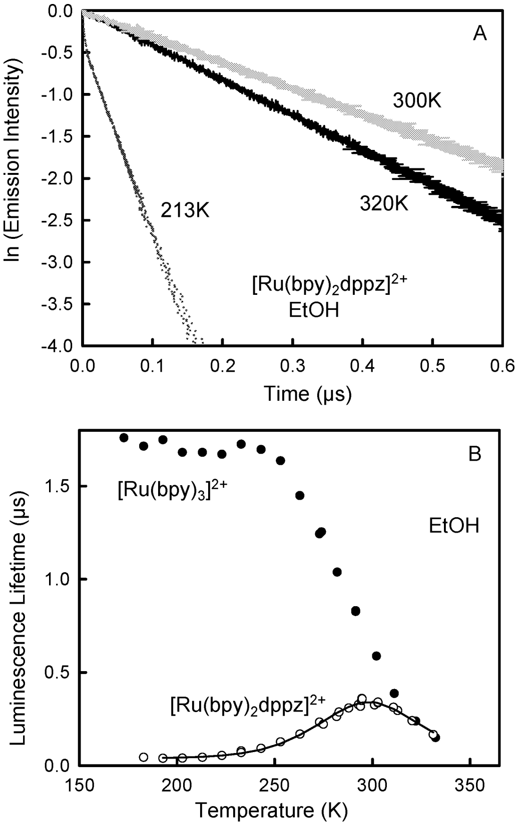

Figure 4. (A) Decay in luminescence intensity at 610 nm for $[Ru(bpy)_2dppz]^{2+}$ in EtOH at three different temperatures. Excitation was at 423 nm. (B) Compilation of luminescence lifetimes as a function of temperature for $[Ru(bpy)_2dppz]^{2+}$ (○) and $[Ru(bpy)_3]^{2+}$ (●) in EtOH. The solid line through the $[Ru(bpy)_2dppz]^{2+}$ data is the result of a fit to the equilibrium model described in the text.

B. Temperature Dependence of the Luminescence Lifetime. The presence of an excited-state equilibrium between two MLCT states is evident from the temperature dependence of the emission. The luminescence decay for $[Ru(bpy)_2dppz]^{2+}$ in EtOH is displayed at three different temperatures in Figure 4A. Just as was observed in the nitriles, the $[Ru(bpy)_2dppz]^{2+}$ emission decay obeys a single exponential; the fast component present in the data originates from a solvent impurity. The longest decay time is observed at the intermediate temperature (300 K), and at both higher and lower temperatures, the excited-state lifetime decreases.

We have made similar measurements at a series of temperatures, and the resulting lifetimes are displayed in Figure 4B. The experiments discussed in this section focus on the photophysics in the absence of rigid media effects, and thus, they are conducted at temperatures for which the solvent is a fluid.[23] Cooling the sample from 330 to 300 K increases the emission lifetime, as expected for most Ru(II) complexes. However, just as in nitrile solvents,[17] an unexpected rollover in the excited-state lifetime is observed at 300 K, and by 180 K, the lifetime of $[Ru(bpy)_2dppz]^{2+}$ shortens to 40 ns. Although the details differ, this general form of temperature dependence has been observed in all solvents (alcohols and nitriles) studied to date. Önfelt et al.[14] observed a similar trend in the temperature dependence of the $[Ru(phen)_2dppz]^{2+}$ lifetimes in glycerol. Their data however also showed a time-dependent shift of the emission spectrum to the red that is not apparent in our data,[24] possibly due to the faster solvent reorganization time for EtOH compared to glycerol. To describe the origin of the temperature-dependent behavior in $[Ru(bpy)_2dppz]^{2+}$, we must first understand the effect of temperature on $[Ru(bpy)_3]^{2+}$.

The temperature-dependent excited-state lifetimes of $[Ru(bpy)_3]^{2+}$ in EtOH are shown for comparison in Figure 4B. The lifetime of $[Ru(bpy)_3]^{2+}$ increases as the sample is cooled over the entire temperature range studied here. This temperature dependence is well understood and arises from two different sources.[25−33] One is metal-centered dd states situated 3000−3500 cm^{-1} above the ^{3}MLCT manifold. These states provide a rapid nonradiative decay pathway to the ground state when thermally populated and, therefore, are involved primarily at elevated temperatures. At low temperatures, where the dd states are thermally inaccessible, the observed lifetime is influenced by population redistribution among the manifold of low-energy ^{3}MLCT states. As temperature decreases, the population shifts toward the lowest-energy ^{3}MLCT, which has the highest degree of triplet character and the slowest radiative relaxation rate. This redistribution leads to a gradual increase in the excited-state lifetime as the temperature is decreased. Therefore, at both high and low temperatures, the lifetime of $[Ru(bpy)_3]^{2+}$ increases as the temperature is decreased. These observations are typical of a large number of polypyridyl Ru(II) compounds.[28,32,34,35]

At high temperatures, the emission lifetimes of $[Ru(bpy)_2dppz]^{2+}$ are nearly identical to those of $[Ru(bpy)_3]^{2+}$; however, at temperatures below 300 K, these lifetimes decrease, whereas those for $[Ru(bpy)_3]^{2+}$ increase. [This rollover in lifetimes is also observed in nitriles (i.e., aprotic solvents), although the maximum lifetime in that case is observed at a slightly lower temperature.] We attribute this lifetime rollover behavior to an excited-state equilibrium between a bright state (B) and a lower energy dark state (D). A diagram representing these states is illustrated in Figure 2.

The high-temperature data provide insight into the physical nature of the bright state (B). In particular, the similarity in the lifetimes observed at high temperatures for these two compounds suggests that the bright state in $[Ru(bpy)_2dppz]^{2+}$ and the ^{3}MLCT state in $[Ru(bpy)_3]^{2+}$ are photophysically similar. Although the simplest interpretation of this statement puts the bright state on one of the two bpy ligands in the $[Ru(bpy)_2dppz]^{2+}$ complex, this is not the case. If it were, then qualitatively different photophysical behavior would be expected for $[Ru(bpy)_2dppz]^{2+}$ than for $[Ru(dppz)_3]^{2+}$, which has no bpy ligands and hence cannot support such an equilibrium. The lifetimes measured for the $[Ru(dppz)_3]^{2+}$ complex also exhibit this rollover behavior at low temperatures (Figure 5B), suggesting that the bright state is confined to the bpy fragment of the dppz ligand and is not just simply localized on one of the two ancillary bpy ligands.

We have modeled $[Ru(bpy)_2dppz]^{2+}$ using the kinetic scheme depicted in Figure 2. Our goal is not to extract exact values for the various rate constants—there are too many unknowns, and the model is too simple—but rather to demonstrate that this kinetic scheme accounts for the general features of the data. This will provide a framework from which we can predict how alterations of different system properties affect the observed signals.

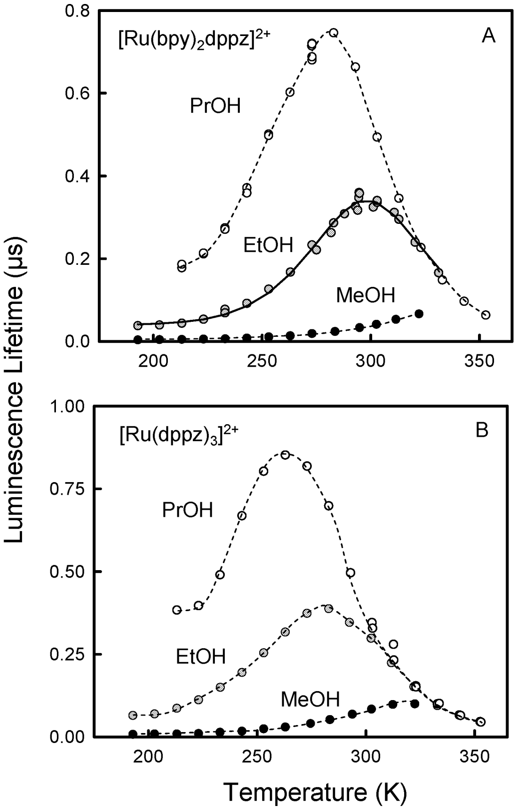

Figure 5. Excited-state lifetimes as a function of temperature in PrOH, EtOH, and MeOH for (A) $[Ru(bpy)_2dppz]^{2+}$ and (B) $[Ru(dppz)_3]^{2+}$. The solid line drawn through the EtOH data is from eqs 1 and 2; the dashed lines are included merely to guide the eye.

If the bright and dark states are in constant equilibrium, then the observed lifetime ($1/k_{obs}$) can be written as a population-weighted average of the decay rates of the two excited states

$$k_{obs} = \rho_B[k_B + k_{dd}(T)] + \rho_D k_D \tag{1}$$

where ρ_B and ρ_D are the relative populations in the bright and dark states, respectively, and k_B and k_D are their relaxation rates back to the ground state. The rate constant for deactivation via the dd state is k_{dd}. The relative populations can be expressed in terms of the B ⟺ D equilibrium constant

$$K_{EQ} = \frac{\rho_D}{\rho_B} = \exp\left(-\frac{\Delta G^\circ}{kT}\right) = \exp\left(-\frac{\Delta H^\circ - T\Delta S^\circ}{kT}\right) \tag{2}$$

where ΔH° and ΔS° are the enthalpy and entropy changes for the B ⟺ D process.

The similarity between the $[Ru(bpy)_2dppz]^{2+}$ and $[Ru(bpy)_3]^{2+}$ photophysics indicates that, at high temperatures, there is a complete shift in the excited-state population toward the higher-energy bright state, i.e., $\rho_B \gg \rho_D$. This leads to a definitive assignment regarding the relative entropies of the two states. A complete shift in population cannot occur if ΔS° is positive because the population in the dark state would then always be larger than the population in the bright state (i.e., $\rho_D > \rho_B$); therefore, ΔS° must be negative. A more ordered solvent configuration surrounding the dark-state charge distribution is consistent with the solvent interacting with a larger dipole. Thus, whereas the dark state is enthalpically preferred (and favored at low temperatures), the bright state is entropically favored (and dominant at high temperatures).

The temperature dependence in the lifetimes of [Ru(bpy)$_2$dppz]$^{2+}$ is the result of a competition between enthalpic ($\Delta H°$) and entropic ($-T\Delta S°$) contributions to the total free energy. At low temperatures, the population is shifted toward the dark state, and relaxation back to the ground state is rapid. As the temperature is increased, the entropic contribution begins to dominate, the population shifts toward the higher-energy bright state, and the photophysics shifts to mimic that of [Ru(bpy)$_3$]$^{2+}$.

We have used eqs 1 and 2 to model our data numerically. In this analysis, the relaxation rates, k_B and k_D, are approximated to be temperature-independent, and k_{dd} is written using the usual Arrhenius type expression, that is, $k_{dd}(T) = A \exp(-\Delta E_{dd}/kT)$. The values for A and ΔE_{dd} were obtained from [Ru(bpy)$_3$]$^{2+}$ data to be 5.1×10^{12} s^{-1} and 3200 cm^{-1}, respectively; both agree well with values measured by other groups.[28,30,31,34-36] The solid line in Figure 5 corresponds to the lifetimes calculated using eqs 1 and 2 with $\Delta H° = -2380$ cm^{-1}, $\Delta S° = -9.92$ cm^{-1}/K, $k_B = (1740\ \text{ns})^{-1}$, and $k_D = (40\ \text{ns})^{-1}$. A nonlinear least-squares fit of the luminescence data is not possible because of a high correlation among several of the parameters. This correlation arises partially because of the limited temperature range over which the measurements can be performed with the sample remaining as a fluid. Nevertheless, the kinetic scheme reproduces the general form of the temperature-dependent lifetimes.

The dark state appears to share some common features with the charge-separated state observed in Ru(II)-acceptor systems. In particular, it is interesting to note that relaxation to the ground state from the dark state is significantly faster than it is from the bright state. This might seem counterintuitive given that, in the dark state, the photoexcited electron is farther away from the metal center than it is in the bright state. However, it is consistent with the back-electron-transfer times observed in a number of Ru(II)-based charge-separated states. Photoexcitation of Ru(II) compounds with ligand bound acceptors can lead to the formation of a charge-separated state, i.e., [Ru$^+$ (L)$_3$•••(A•)$^-$]$^{2+}$. The back electron-transfer times for a number of dyads of this type have been measured to be in the *subnanosecond* regime, which are far faster than the electron–hole recombination times observed from the ^{3}MLCT excited state of [Ru(L)$_3$]$^{2+}$ (~1 μs).[37-39] Schanze and co-workers[40] have postulated that this fast back electron transfer is facilitated by a rapid triplet → singlet spin conversion process in the [Ru$^+$ (L)$_3$•••(A•)$^-$]$^{2+}$ charge-separated state. Regardless of the mechanism, the presence of a fast back electron transfer appears to be a typical feature of the charge-separated systems. A relaxation rate (k_D) that is higher than that of ^{3}MLCT state decay but lower than that of back electron transfer in Ru(II)-acceptor systems suggests that the dark state of [Ru(bpy)$_2$dppz]$^{2+}$ can be viewed as an intermediate point along a continuum that bridges states that are truly molecular in nature (e.g., a ^{3}MLCT state) on one end and fully charge-separated (e.g., [Ru$^{\oplus}$ (L)$_3$•••(A•)$^-$]$^{2+}$) on the other.

C. Solvent Tuning of the Equilibrium Energetics. We have examined the temperature dependence of the emission lifetimes for [Ru(bpy)$_2$dppz]$^{2+}$ and [Ru(dppz)$_3$]$^{2+}$ in both linear alcohols and linear nitriles.[17] Displayed in Figure 5 are the luminescence lifetimes for [Ru(bpy)$_2$dppz]$^{2+}$ and [Ru(dppz)$_3$]$^{2+}$ in 1-propanol (PrOH), EtOH, and methanol (MeOH). For both complexes, the temperature corresponding to the maximum lifetime (T_{max}) continuously shifts toward higher temperatures as the solvent polarity is increased. For [Ru(bpy)$_2$dppz]$^{2+}$, T_{max} increases from PrOH (280 K) to EtOH (300 K). A rollover does not appear in the MeOH data probably because the solvent boils before the shift in excited-state population to the bright state occurs; however, we estimate using eqs 1 and 2 that the maximum would appear at about 350 K. The similar temperature dependence seen between [Ru(bpy)$_2$dppz]$^{2+}$ and [Ru(dppz)$_3$]$^{2+}$ supports the notion that the excited-state population is shared between fragments of dppz and not between separate ligands. For a given solvent, T_{max} for [Ru(dppz)$_3$]$^{2+}$ is shifted to a lower temperature compared to T_{max} for [Ru(bpy)$_2$dppz]$^{2+}$. The origin of this difference is unclear, but it could be a difference in the packing of the solvent around the two chromophores.

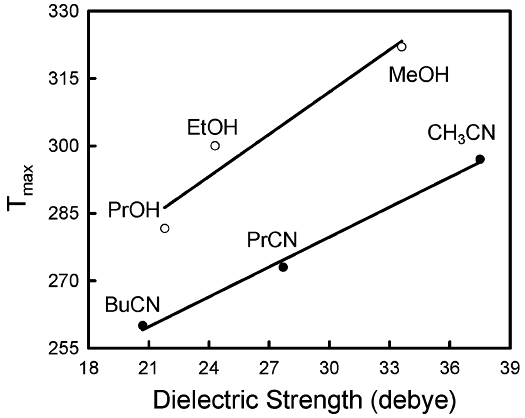

Figure 6. Temperature of maximum emission lifetime (T_{max}) of [Ru(bpy)$_2$dppz]$^{2+}$ as a function of solvent dielectric strength (ϵ). Both the alcohol and nitrile series are included. The correlation of dielectric strength with T_{max} suggests that the dark state has charge-separated character, not $^3\pi\pi^*$.

The temperature of the maximum lifetime (T_{max}) is displayed as a function of the solvent dielectric strength for [Ru(bpy)$_2$dppz]$^{2+}$ in both the nitriles and alcohols in Figure 6. There is a clear correlation between T_{max} and the solvent dielectric constant within each individual solvent series. The increase in T_{max} with increasing solvent polarity is consistent with a greater stabilization of the dark state in more polar solvents. If the charge distribution in the dark state is located primarily on the phz portion of the ligand (as was stated in section B), then it will have a greater dipole moment than the bright state. Dark-state stabilization could increase T_{max} in two ways. When the dark state is stabilized relative to the bright state, the larger energy gap (i.e., more negative $\Delta H°$) pushes the temperature at which the entropic term overcomes the enthalpic term to a higher value. Stabilization of the dark state would also decrease the energy gap between it and the ground state. On the basis of the energy gap law, one would then expect that this should *increase* the rate of nonradiative decay from the dark state (k_D), which, in turn, would shift T_{max} to higher temperatures. We do, in fact, observe larger k_D values in the more polar solvents. As seen in Figure 5, the lifetime at low temperature, which provides a direct measure of $(k_D)^{-1}$, decreases from MeOH to PrOH. Thus, the correlation of T_{max} and k_D with the solvent polarity indicates that there is a greater degree of charge separation in the dark state, suggesting that the dark state has charge-separated character and is not a ligand-centered $\pi\pi^*$ state.

The alcohol and nitrile series separate into two groups, with the nitriles having their maximum lifetimes at lower temperatures. The difference between the two series most likely stems from the ability of the alcohols to hydrogen bond to phz nitrogens, which would further stabilize the dark state more than electrostatic solvation alone.

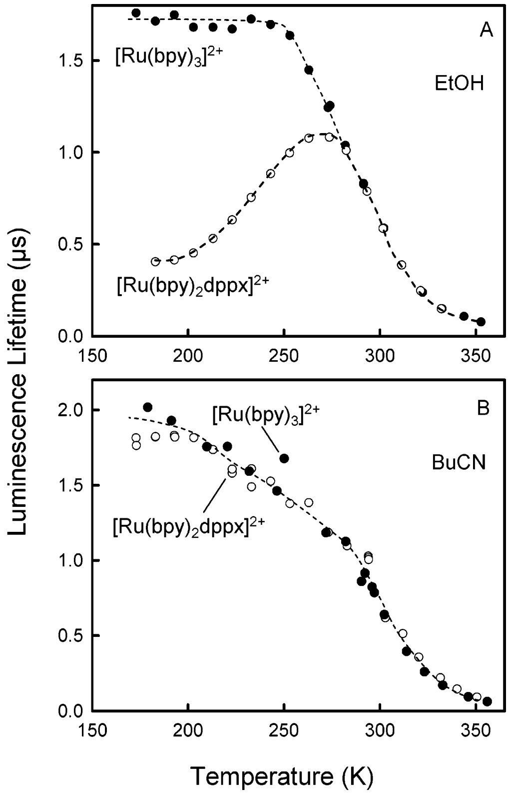

Figure 7. (A) Compilation of luminescence lifetimes as a function of temperature for $[Ru(bpy)_2dppx]^{2+}$ (○) and $[Ru(bpy)_3]^{2+}$ (●) in EtOH. (B) Luminescence lifetimes as a function of temperature for $[Ru(bpy)_2dppx]^{2+}$ (○) and $[Ru(bpy)_3]^{2+}$ (●) in butyronitrile (BuCN). The dashed lines are included to guide the eye.

D. Altering the Equilibrium Energetics via Chemical Modification. We performed similar experiments on a complex (Figure 1) with a chemically modified dppz ligand, $[Ru(bpy)_2dppx]^{2+}$. Figure 7A shows the temperature-dependent lifetimes of $[Ru(bpy)_2dppx]^{2+}$ in EtOH. Between 270 and 330 K, $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_2dppx]^{2+}$ exhibit similar luminescence. The shared photophysical behavior at high temperatures suggests that the same excited-state dynamics are responsible for the observed emission in both molecules. This also indicates that the additional methyl groups do not affect the energy of the bpy state dramatically. The decrease in lifetime below 270 K for $[Ru(bpy)_2dppx]^{2+}$ is evidence that the same general photophysical model can be used to describe both the substituted and unsubstituted molecules. However, there are some minor differences. The maximum lifetime for $[Ru(bpy)_2dppx]^{2+}$ occurs at a colder temperature than that of $[Ru(bpy)_2dppz]^{2+}$, which is indicative of a smaller energy gap between bright and dark states. Because the bright-state energy remains the same upon addition of the methyl groups, the energy gap must become smaller by raising the energy of the dark state. This is consistent with the expectation that the electron-donating substituents would raise the energy of the $\pi\pi^*$ orbital on the phz portion of the dppx ligand.

The luminescence lifetimes for both the $[Ru(bpy)_2dppx]^{2+}$ and $[Ru(dppx)_3]^{2+}$ complexes in the other alcohols (MeOH and PrOH) exhibit the same general trends as their unsubstituted analogues (Figure 8). Once again, this points to an excited-state equilibrium involving a bright state localized on the bpy fragment of the dppx ligand and not on one of the ancillary bpy ligands.

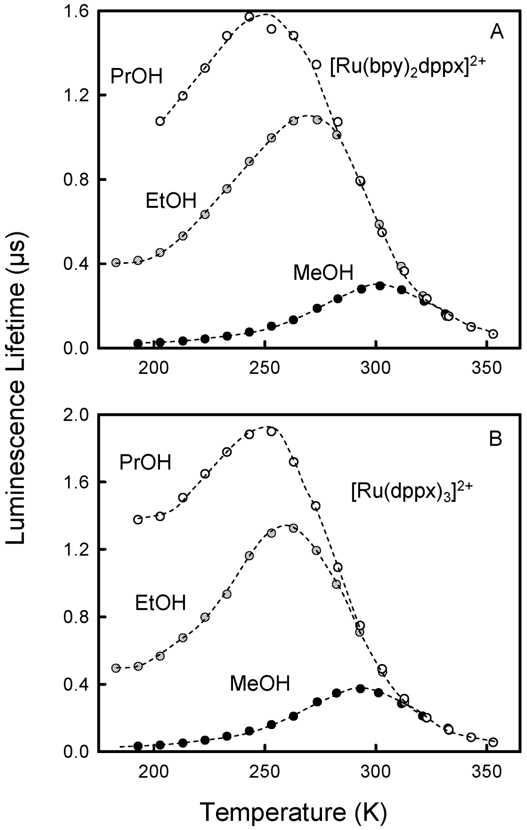

Figure 8. Excited-state lifetimes as a function of temperature in PrOH, EtOH, and MeOH for (A) $[Ru(bpy)_2dppx]^{2+}$ and (B) $[Ru(dppx)_3]^{2+}$. The dashed lines are included to guide the eye.

Although the $[Ru(bpy)_2dppx]^{2+}$ and $[Ru(bpy)_2dppz]^{2+}$ complexes show similar behavior in the alcohols, in the nitriles, they behave quite differently. Figure 7B shows the temperature-dependent emission lifetimes of $[Ru(bpy)_2dppx]^{2+}$ and $[Ru(bpy)_3]^{2+}$ in butyronitrile. Unlike in alcohols, $[Ru(bpy)_2dppx]^{2+}$ does not show the rollover at low temperature. The monotonic temperature dependence for $[Ru(bpy)_2dppx]^{2+}$ suggests that the excited-state population remains in the bright state throughout this temperature range. Perhaps the absence of a rollover arises because the energy gap has been decreased such that it can be overcome even at very low temperatures. It is also possible that the methyl groups have raised the energy of the phz state higher than that of the bpy state. Inverting the state order would make the bright state enthalpically favored. As a result, the population would remain in the bright state, and photophysics similar to that of $[Ru(bpy)_3]^{2+}$ would be observed at all temperatures.

IV. Conclusions

The temperature-dependent light-switch behavior observed in Ru(II)-dppz complexes results from a dynamic equilibrium between two MLCT states associated with the dppz ligand. One is a bright state with a ligand orbital similar in size to that associated with the ^{3}MLCT state of $[Ru(bpy)_3]^{2+}$, and the other moiety is a dark phz-like state. The light-switch mechanism stems from a competition between energetic factors that favor the dark (phz) state and entropic factors that favor the bright (bpy) state.

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(18) The dark state within our model is not required to be strictly nonemissive and, in light of a recent publication (ref 15), is probably partially emissive in certain instances. Nevertheless, because the bright and dark states of our model are in constant equilibrium, neither the analysis nor the conclusions presented in this work would be affected by this detail.

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(23) A number of groups have studied the photophysics of Ru(II) polypyridyl complexes in partially frozen solvents and reported on the complicated nature of the spectroscopy that arises in part from the slow solvent reorganization of these highly viscous environments. See: Chen, P.; Meyer, T. J. *J. Phys. Chem.* **1994**, *98*, 1439−1477 and references therein. Therefore, one must be careful in the assessment of any behavior near the fluid−glass transition temperature. In particular, it is unclear in a recent report by Olofsson et al. (ref15) what role the slowly reorganizing solvent plays in the photophysics.

(24) A time-dependent spectral shift to the red would manifest itself in the single-detection wavelength kinetics as (1) a transient *growth* in the emission at early times on the red edge of the emission band and (2) a fast *decay* component on the blue edge. Transients obtained at the red and blue edges of the emission spectrum decay with single-exponential kinetics after about 200 ps (earliest time with no contribution from our instrument response), indicating that there is no time-dependent shift in the emission band.

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