

## Turning the $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$ Light-Switch On and Off with Temperature

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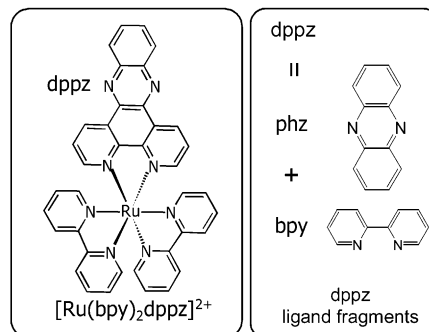
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**Abstract:** We report temperature-dependent excited-state lifetime measurements on  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$  in both protic and aprotic solvents. These experiments yield a unifying picture of the excited-state photophysics that accounts for observations in both types of solvent. Our measurements support the notion of bpy-like and phz-like states associated with the dppz ligand and show that the ligand orbital associated with the bright state is similar in size to the corresponding orbital in the <sup>3</sup>MLCT state of  $[\text{Ru}(\text{bpy})_3]^{2+}$ . In contrast to the current thinking, the experiments presented here indicate that the light-switch effect is not driven by a state reversal. Rather, they suggest that the dark state is always lowest in energy, even in aprotic solvents, and that the light-switch behavior is the result of a competition between energetic factors that favor the dark state and entropic factors that favor the bright (bpy) state.

### I. Introduction

There has been intense interest in  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$  (Figure 1) as a luminescent probe of DNA. In particular, this complex is brightly luminescent when bound to DNA, but is nonemissive in aqueous solution.<sup>1–3</sup> The “light-switch” effect stems from hydrogen bond formation with water, which quenches the excited-state luminescence and reduces the quantum yield by 2–3 orders of magnitude. In the bound form, the dppz ligand is intercalated into the DNA strand. Intercalation shields the phenazine nitrogens from the solvent and results in a luminescent excited state. The stark contrast between the dark and bright states of this molecule makes this complex useful for the study of DNA and other nonpolar microenvironments.<sup>4–11</sup>

The light-switch property does not require DNA for activation, and luminescence is observed in a number of aprotic



**Figure 1.** Chemical structure of the light-switch complex,  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$ , and ligand fragments discussed in the text.

environments. Consequently, this complex has been studied in a wide variety of solvents in an attempt to understand the origin of the light-switch mechanism.<sup>12–14</sup> The photophysical factors that govern this function are thought to arise from 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 of the dppz ligand and a dark, nonluminescent state localized largely on the phenazine (phz) portion. It has been suggested that in aprotic environments, the bright state is the lower energy state, and thus luminescence is observed. The light-switch is activated in protic solvents by hydrogen bond formation at the phz nitrogens, which lowers the energy of the dark state below the bright state. Because of

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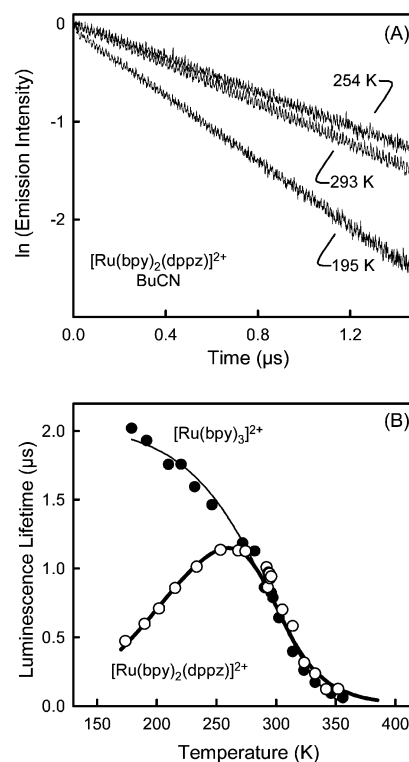
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this state reversal, excited-state relaxation is believed to progress rapidly through these two states to produce a quasi charge-separated state from which fast nonradiative relaxation back to the ground state occurs. The presence of two distinct states on the dppz ligand is supported by low-level molecular orbital calculations, electrochemical measurements on the ground-state complex, and recent ultrafast experiments.<sup>13,15–21</sup> While there is some evidence indicating that the dark state is localized primarily on the phz portion of the ligand, the connection of the bright state with the bpy fragment has not been experimentally confirmed, and a detailed description of the mechanism that leads to the light-switch behavior has remained elusive.

In this report, we describe temperature-dependent excited-state lifetime measurements on  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$  in both protic and aprotic solvents. These experiments yield a unifying picture of the excited-state photophysics that accounts for observations in both types of solvent. Not only do our measurements support the notion of bpy-like and phz-like states associated with the dppz ligand, but they also suggest that the bpy-like state is photophysically similar to the <sup>3</sup>MLCT state in  $[\text{Ru}(\text{bpy})_3]^{2+}$ . In contrast to the current thinking, the experiments presented here suggest that the dark (phz) state is always lowest in energy (even in aprotic solvents) and that the light-switch behavior is not driven by a state reversal but is governed by a competition between energetic factors that favor the dark (phz) state and entropic factors that favor the bright (bpy) state. These results also speak to the control of charge flow in molecular systems and point out that the excited-state charge distribution is dictated not just by excited-state energetics, but also by entropic factors. Such issues may become important in the design of functional electronic materials based on molecular systems, where the location of excited-state charge must be controlled.

## II. Experimental Section

Time-resolved measurements were conducted by time-correlated single photon counting (TCSPC). Picosecond laser pulses are produced by a mode-locked Ti:Sapphire laser whose output is frequency doubled to 423 nm. The repetition rate is selected to be at least 5 times the natural lifetime of the sample (190 kHz) using an acousto-optic modulator (AOM). After the AOM, the beam passes through an iris and illuminates, without focusing, a 10 mm quartz cuvette containing the sample. The emitted light is collected at 90° and focused onto the slit of a 240 mm focal length, single grating monochromator and subsequently delivered to a cooled, multichannel plate-photomultiplier tube (MCP, Hamamatsu R3809U-51). The intensity of the detected luminescence is varied by use of neutral density filters mounted before the monochromator. The signal from the MCP is amplified prior to sending it into a 200 MHz constant fraction discriminator (CFD, Tennelec 454) whose output serves as the start pulse for a time-to-amplitude converter (TAC, Tennelec 864). The stop pulse is obtained by focusing 10% of the excitation beam onto a Si:PIN photodiode, whose output is sent into a variable delay box, then to a CFD, and



**Figure 2.** (a) Decay in luminescence intensity at 620 nm for  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$  in butyronitrile (BuCN) at three different temperatures. Excitation was at 423 nm. (b) Compilation of luminescence lifetimes as a function of temperature for  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$  (○) and  $[\text{Ru}(\text{bpy})_3]^{2+}$  (●), also in BuCN. At all temperatures, BuCN presented is a liquid. The solid line through the  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$  data is the result of a fit to the equilibrium model described in the text.

finally to the TAC. The TAC's output is sent to a multichannel analyzer that is interfaced to a PC. The instrument response of the apparatus is 80 ps at the fwhm.

The sample temperature was varied using a homemade cryostat. The sample cuvette was placed in a quartz dewar. To cool the sample, nitrogen gas was passed through a coil submersed in liquid nitrogen and then into the dewar. The temperature of the sample was varied by altering the flow rate of the gaseous nitrogen and monitored using a thermocouple attached to the cuvette. Above 298 K, the sample temperature was controlled using a circulating water bath that warmed the cuvette holder.

The  $[\text{Ru}(\text{bpy})_2\text{dppz}](\text{PF}_6)_2$  and  $[\text{Ru}(\text{dppz})_3](\text{PF}_6)_2$  compounds were synthesized using methods described previously.<sup>17,22</sup> All solvents were distilled prior to use, and the samples were Ar sparged to remove dissolved oxygen. Sample concentrations used in the emission experiments were  $\sim 10^{-5}$  M, as determined by absorbance measurements.

## III. Results and Discussion

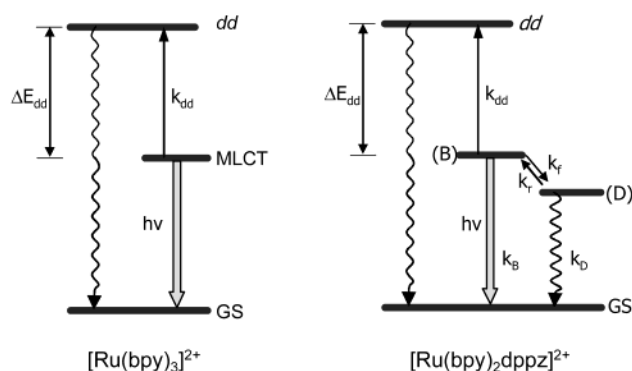
In room-temperature nitrile solvents,  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$  is brightly luminescent with a steady-state emission spectrum centered around 620 nm. The luminescent state is <sup>3</sup>MLCT in character and localized on the dppz ligand. This paper focuses on the emission lifetime as a function of temperature.

The decay in the luminescence intensity of  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$  in liquid butyronitrile (BuCN) is displayed in Figure 2A. Three transients are shown,<sup>23</sup> each corresponding to a different temperature. All are single exponential. The excited-state

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**Figure 3.** Energy level diagrams depicting excited states of  $[\text{Ru}(\text{bpy})_3]^{2+}$  and  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$ . (B) and (D) refer to the bright and dark states described in the text. Both are MLCT states associated with the dppz ligand. The bright state, (B), is entropically favored and thus is populated at high temperatures. The dark state, (D), is energetically favored and is therefore populated at low temperatures. In this scheme,  $k_B$  is the total relaxation rate, which reflects both radiative and nonradiative deactivation pathways. While  $k_D$  is taken to be largely nonradiative, it may have a small radiative component, as is evidenced by the observation of a short-lived red-shifted emission band in water.<sup>13</sup>

lifetime has a clear dependence on the sample temperature, increasing from 970 to 1130 ns as the system is cooled from 293 to 254 K. This increase is consistent with a large number of Ru(II) complexes (including  $[\text{Ru}(\text{bpy})_3]^{2+}$ ) that show similar behavior. However, unlike other Ru(II) compounds, a rollover in lifetime is observed as the system is cooled below 254 K, and by 195 K, the lifetime is only 595 ns.

As a benchmark for comparison, we have performed a similar series of measurements on  $[\text{Ru}(\text{bpy})_3]^{2+}$  (Figure 2B). At high temperatures, the excited-state lifetimes for  $[\text{Ru}(\text{bpy})_3]^{2+}$  and  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$  are nearly identical. This is not the case below 250 K. While the  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$  lifetime decreases, the  $[\text{Ru}(\text{bpy})_3]^{2+}$  lifetimes show a continual increase. These observations are inconsistent with the current photophysical model for  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$ , which has the dark state higher in energy than the bright state in aprotic solvents. If this were the case, then the photophysical behavior of  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$  should be more like  $[\text{Ru}(\text{bpy})_3]^{2+}$  at low temperatures, not high temperatures as is observed. In short, our data indicate that the dark state is lowest in energy, even in aprotic solvents.

To decipher the temperature dependence observed in the  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$  complex, we must first understand the photophysical factors that give rise to the temperature dependence in  $[\text{Ru}(\text{bpy})_3]^{2+}$ . These factors are well documented.<sup>24–27</sup> At elevated temperatures, the lifetime is influenced by metal-centered dd states situated 3000–3500  $\text{cm}^{-1}$  above the <sup>3</sup>MLCT state (Figure 3). Thermal population of these states leads to rapid nonradiative decay to the ground state. The presence of this additional deactivation pathway causes the lifetime to decrease as the temperature is increased above room temperature. At low temperatures, where thermal activation of the dd states is insignificant, the natural lifetime is determined by the population distribution in a manifold of low-energy <sup>3</sup>MLCT states.<sup>28,29</sup> Change in the population of these states with temperature leads

to a gradual increase in the excited-state lifetime as the temperature is decreased. As a result of these factors, at both high and low temperatures the lifetime of  $[\text{Ru}(\text{bpy})_3]^{2+}$  increases as the temperature is decreased. This is true not only for  $[\text{Ru}(\text{bpy})_3]^{2+}$ , but for a large number of polypyridyl Ru(II) compounds.

The rollover in the  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$  lifetimes (Figure 2B) is attributed to a dynamical interaction between a bright state (B) and a lower energy dark state (D). A diagram depicting these states is illustrated in Figure 3. Single-exponential decay kinetics are observed at all temperatures, consistent with a constant equilibrium between B and D. Recent ultrafast experiments support the notion of a rapid interconversion between these two states.<sup>13,18</sup> In particular, they show a fast (<20 ps) kinetic component that could correspond to the time it takes to establish the equilibrium populations. Although the kinetics of this equilibrium are certainly relevant to the photophysics, the light-switch mechanism itself is dictated by the thermodynamics of this equilibrium.

We have modeled the  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$  lifetime data using the kinetic scheme depicted in Figure 3. Our goal is not to extract exact values for the various rate constants – there are too many unknowns, and the model is too simple<sup>30</sup> – but rather to demonstrate that this kinetic model accounts (at least qualitatively) for the general features of the data. If the bright and dark states are in constant equilibrium, then the observed lifetime ( $1/k_{\text{obs}}$ ) can be written as a population-weighted average of the decay rates for the two excited states:

$$k_{\text{obs}} = \rho_B(k_B + k_{\text{dd}}(T)) + \rho_D k_D \quad (1)$$

where  $\rho_B$  and  $\rho_D$  are the relative populations in the bright and dark states,  $k_B$  and  $k_D$  are their relaxation rates back to the ground state, and  $k_{\text{dd}}$  is the rate constant for deactivation via the dd state. The emission lifetimes of  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$  and  $[\text{Ru}(\text{bpy})_3]^{2+}$  above 300 K are nearly indistinguishable. This suggests that the bright state in  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$  and the MLCT state in  $[\text{Ru}(\text{bpy})_3]^{2+}$  are photophysically similar. (This is discussed in more detail later.) It also suggests that the excited-state population in  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$  is completely shifted toward the bright state at high temperatures, that is,  $\rho_B \gg \rho_D$ .

The relative populations can be expressed in terms of the  $B \leftrightarrow D$  equilibrium constant, that is

$$K_{\text{EQ}} = \frac{\rho_D}{\rho_B} = \exp\left(-\frac{\Delta G}{k_B T}\right) = \exp\left(-\frac{\Delta H - T\Delta S}{k_B T}\right) \quad (2)$$

where  $\Delta H$  and  $\Delta S$  are the enthalpy and entropy changes for the  $B \rightarrow D$  process. The dark state is enthalpically favored ( $\Delta H$

(28) There are four low-lying triplet states lying within 500  $\text{cm}^{-1}$  of each other. The amount of singlet character increases from 0% for the lowest state to about 40% for the highest, and thus the higher energy states have shorter radiative lifetimes. Because the four <sup>3</sup>MLCT states are in rapid equilibrium, the emission intensity decays with single-exponential kinetics, and the lifetime is a Boltzmann-weighted average of the lifetimes of the different states. Therefore, as the temperature is decreased and the distribution shifts to lower energy, the excited-state lifetime increases.

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(30) The kinetic model shown in Figure 3 does not include low-lying triplets such as those found in  $[\text{Ru}(\text{bpy})_3]^{2+}$ , but instead treats the bright state (B) as a single MLCT state. Although the lowest three MLCT states in  $[\text{Ru}(\text{bpy})_3]^{2+}$  can be treated as a single state at these temperatures, the presence of the fourth MLCT state does contribute to the temperature dependence. Complications arising from additional low-lying states in the MLCT manifold of  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$  could be present, and they are not accounted for in the model.

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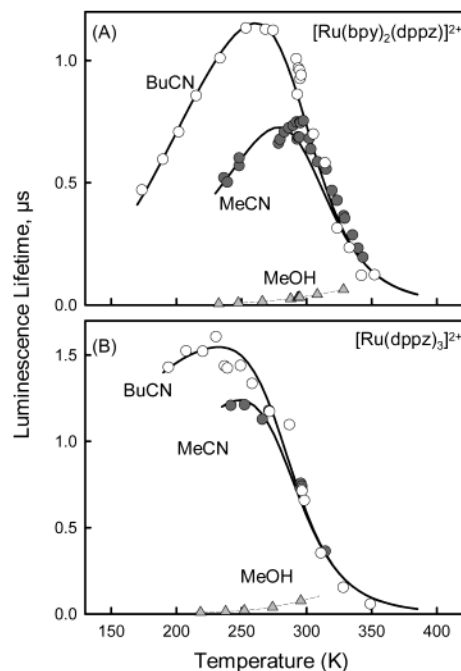
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$< 0$ ), even in aprotic solvents, and at low temperatures the population resides in that state (i.e.,  $K_{\text{EQ}} \gg 1$ ). As the temperature is increased, the population in the bright state increases, corresponding to a decrease in  $K_{\text{EQ}}$ . If  $\Delta S$  is *positive*, the population in the dark state will always be larger than the bright state (i.e.,  $\rho_{\text{D}} > \rho_{\text{B}}$ ), and thus a complete shift in the population will not occur. To shift the entire population to the bright state,  $\Delta S$  must be *negative*. Thus, while the dark state is always energetically preferred, the bright state is entropically favored and thus dominates at high temperatures. Lower entropy might be expected for the dark state because the greater amount of charge separation could induce more order in the surrounding solvent. We must point out that, in principle, our observations could stem from the temperature dependence of  $\Delta H$ . This would arise from a difference in heat capacities between the reactants and products,  $\Delta C_{\text{p}}$ . Because the “reaction” corresponds to the motion of charge from one portion of the dppz ligand to another,  $\Delta C_{\text{p}}$  is most likely small, and, for this reason, we dismiss it as the source of the observed temperature dependence.

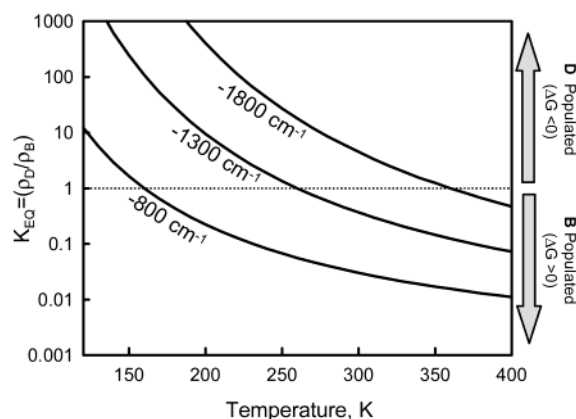
We have used eqs 1 and 2 to model our data numerically. In this analysis, the relaxation rates,  $k_{\text{B}}$  and  $k_{\text{D}}$ , are approximated to be temperature independent,<sup>31,32</sup> and  $k_{\text{dd}}$  is written using the usual Arrhenius type expression, that is,  $k_{\text{dd}}(T) = A \exp(-\Delta E_{\text{dd}}/k_{\text{B}}T)$ . The values for  $A$  and  $\Delta E_{\text{dd}}$  are obtained from an analysis of the high-temperature lifetime data. They were determined from the  $[\text{Ru}(\text{bpy})_3]^{2+}$  data to be  $6.0 \times 10^{12} \text{ s}^{-1}$  and  $3200 \text{ cm}^{-1}$ , respectively; both agree well with values measured by other groups.<sup>24,33,34</sup> The solid line shown in Figure 2B corresponds to the lifetimes ( $k_{\text{obs}}^{-1}$ ) calculated<sup>35</sup> using eqs 1 and 2 with  $\Delta H = -790 \text{ cm}^{-1}$ ,  $\Delta S = -5 \text{ cm}^{-1}/\text{K}$ ,  $k_{\text{B}} = (1800 \text{ ns})^{-1}$ , and  $k_{\text{D}} = (160 \text{ ns})^{-1}$ .

As a further test of this model, we have examined the excited-state photophysics of the  $[\text{Ru}(\text{bpy})_2(\text{dppz})]^{2+}$  complex in other solvents. Figure 4A shows lifetime data obtained in BuCN, MeCN (acetonitrile), and MeOH (methanol). The excited-state lifetime in methanol is greatly reduced, consistent with observations made by other groups.<sup>1,12</sup> Interestingly, in the alcohol solvent the lifetime increases with temperature between 230 and 308 K. In the case of methanol, and probably other protic solvents as well, it appears that the preferential stabilization of the dark state is so great that the temperature needed to shift the population to the bright state lies above room temperature and, in this case, above the boiling point of the solvent too.

The relative population of the bright and dark states (i.e., the light-switch) is the result of a competition between enthalpic ( $\Delta H$ ) and entropic ( $-T\Delta S$ ) contributions to the total free energy,  $\Delta G$ . To illustrate this, the equilibrium constant,  $K_{\text{EQ}}$ , is shown as a function of temperature in Figure 5 for different values of  $\Delta H$ . Because  $\Delta S$  is *negative*,  $K_{\text{EQ}}$  changes from values that exceed unity at low temperatures (dark state populated) to values that are less than 1 at high temperatures (bright state populated).



**Figure 4.** Excited-state lifetimes as a function of temperature in butyronitrile (BuCN), acetonitrile (MeCN), and methanol (MeOH). Panels A and B contain data for  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$  and  $[\text{Ru}(\text{dppz})_3]^{2+}$ , respectively. The solid lines drawn through the nitrile data are from eqs 1 and 2.



**Figure 5.** Equilibrium constant ( $K_{\text{EQ}}$ ) as a function of temperature for different values of  $\Delta H$ .  $K_{\text{EQ}}$  was calculated using  $\Delta H = -1800 \text{ cm}^{-1}$  and  $-800 \text{ cm}^{-1}$  and  $\Delta S = -5 \text{ cm}^{-1}$ . The smaller  $\Delta H$  value approximates that obtained from the analysis of our data in BuCN, an aprotic solvent. The larger values are likely comparable to those obtained in protic solvents.

If  $\Delta S$  were positive,  $K_{\text{EQ}}$  would be greater than 1 at all temperatures. In aprotic environments, the energy gap is small, and the minimum temperature needed to drive the equilibrium toward the bright state lies *below* room temperature. In protic solvents, the preferential stabilization of the dark state increases the energy gap and shifts the inversion point *above* room temperature. The light-switch effect is observed at room temperature, where the vast majority of measurements have been performed, because the entropy term dominates in aprotic solvents, and the energetic term dominates in protic ones.

The effect of solvent polarity on the light-switch mechanism can also be understood in the context of this equilibrium model. The luminescence lifetimes obtained in MeCN show an inversion temperature at approximately 290 K, as compared to 260 K in BuCN, suggesting that the energy gap in MeCN is greater

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(35) A nonlinear least-squares fit to eqs 1 and 2 was not possible due to a high correlation between several of the parameters. This problem could be solved by collecting data at lower temperatures, where the lifetime should approach a limiting value of  $1/k_{\text{D}}$ . However, we are prevented from doing this because of the freezing of the solvent. The solid lines in Figures 2 and 4 represent the best fits to the experimental data as determined by visual inspection.

than that in BuCN. Our model shows that a small change in the energy gap can have a profound effect on the equilibrium. The solid line drawn through the MeCN data was obtained from eqs 1 and 2 simply by increasing the energy gap from  $-790\text{ cm}^{-1}$  (the value used for the BuCN data) to  $-1010\text{ cm}^{-1}$ . The values for all other parameters were held constant.

The origin of the electrostatic stabilization most likely stems from the differences in the charge distribution for the bright and dark states. If the charge distribution in the dark state is located primarily on the phz portion of the ligand, then it will have a greater excited-state dipole moment than the bright state. Thus, when the polarity of the solvent is increased, the dark state will experience greater stabilization and lead to a larger energy gap. The notion of an extended charge distribution in the dark state and a more compact charge distribution in the bright state has been proposed before.<sup>15–17</sup> However, our experiments go a step further and suggest that the excited-state charge distribution in the bright state is similar in size to that present in the <sup>3</sup>MLCT state of  $[\text{Ru}(\text{bpy})_3]^{2+}$ .

The similarity in photophysical behavior at high temperatures places the bright state in  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$  at an energy similar to that of the <sup>3</sup>MLCT state in  $[\text{Ru}(\text{bpy})_3]^{2+}$ , at least with respect to its location relative to the dd states. Analysis of the high-temperature data suggests that the energy gap between the <sup>3</sup>MLCT and dd states is about  $3100\text{ cm}^{-1}$  in  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$  and about  $3200\text{ cm}^{-1}$  in  $[\text{Ru}(\text{bpy})_3]^{2+}$ . The energy gaps are remarkably similar, especially when compared to other substituted polypyridyl Ru(II) compounds.<sup>24,33,34</sup> Subtle differences in the chemical structure of the polypyridyl ligand can have a substantial effect on the excited-state energetics, and energy gaps ranging from  $2740\text{ cm}^{-1}$  in  $[\text{Ru}(\text{dmb})_3]^{2+}$  to  $4230\text{ cm}^{-1}$  in the

carboxylic acid functionalized complex,  $[\text{Ru}(\text{dcb})_3]^{2+}$ , have been observed.<sup>33,34,36</sup> In this context, the similarity in <sup>3</sup>MLCT/dd energy gaps for  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$  and  $[\text{Ru}(\text{bpy})_3]^{2+}$  is rather remarkable given the vastly different chemical structures of the two ligands. The logical conclusion is that the electron distribution in the bright state is similar to that in the <sup>3</sup>MLCT state of  $[\text{Ru}(\text{bpy})_3]^{2+}$ .

On the basis of the  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$  and  $[\text{Ru}(\text{bpy})_3]^{2+}$  data alone, the simplest interpretation of this observation is that the bright state is localized on one of the two bpy ligands and the dark state is associated with the dppz ligand. If this were true, however, then qualitatively different photophysical behavior would be expected for  $[\text{Ru}(\text{dppz})_3]^{2+}$ , which has no bpy ligands and hence cannot support such an equilibrium. Lifetime measurements for  $[\text{Ru}(\text{dppz})_3]^{2+}$  are shown in Figure 4B. The  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$  and  $[\text{Ru}(\text{dppz})_3]^{2+}$  complexes exhibit similar trends in all three solvents, indicating that the same dynamical process is occurring in both complexes. In other words, both the bright and the dark states must be associated with the dppz ligand, implying that the  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$  complex could be described as a  $[\text{Ru}(\text{bpy})_3]^{2+}$  core and a phz charge acceptor.

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(36) dmb = (4,4'-dimethyl-2,2'-bipyridine); dcb = (4,4'-dicarboxylate-2,2'-bipyridine).