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LETTERS

Photochemically Reversible Luminescence Lifetime Switching in Metal−Organic Systems

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We use a diarylethene with solution-stable open and closed forms (1,2-bis(2-methylbenzo[*b*]thiophen-3-yl) hexafluorocyclopentene), BTF6, as a photochromic energy transfer quencher of the metal-to-ligand charge-transfer (MLCT) based luminescence in $[Ru(dpp)_3]^{2+}$, dpp = 4,7-diphenyl-1,10-phenanthroline. As only the closed form of BTF6 serves as a quencher for the MLCT luminescence, and the read (390 nm), write ($\lambda <$ 360 nm), and erase ($\lambda >$ 500 nm) wavelengths are well-separated, this system potentially represents an economic alternative to covalent systems. For the first time, we demonstrate the concept of using luminescence lifetimes to transduce the photochromic binary state of the quencher as opposed to the intensity-based readout schemes that are traditionally employed. The luminescence quenching process is described in terms of Förster-type resonance energy transfer (RET) enhanced by diffusion.

Photochromic materials are potentially useful for advanced optoelectronic devices such as optical memory, optical switching, and displays. Organic photochromes are promising memory media due to their fast response and potential for atomic scale processing. The diarylethene family of photochromes are amenable for such applications and provide photochemically reversible yet thermally irreversible photochromism.[1,2] Diarylethenes also possess excellent fatigue resistance, picosecond switching times, high photochemical quantum yields, in addition to large wavelength changes in their "open" and "closed" (conjugated) forms.[1−3] Different types of signal outputs can be utilized for memory and switching devices, including refractive index changes,[4] luminescence,[5−13] optical rotation,[6] electrochromism,[14] and magnetic interactions.[15] Photochromic materials utilizing photoluminescence readout, where the emission properties are used to interrogate the binary state of the photochrome, are of interest because of the sensitivity afforded by fluorescence technologies and the ability for "all optical" read−write−erase cycles. In general, the diarylethene parent compounds do not display significant luminescence, but several systems appended with various chromophores have shown reversible changes in emission intensity which rely on intramolecular quenching processes.[5,6,8,16] An alternative approach to these sophisticated syntheses is to harness intermolecular energy transfer processes between noncovalently linked fluorophore/photochromic quencher pairs, as recently shown using coumarin or BODIPY dyes dispersed in a polymer matrix along with the photochrome *cis*-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethane.[17] Upon irradiation of these polymer films, good fluorescence intensity contrasts have been realized, but the small Stokes shift which is typical for these fluorescent materials volatilizes the reading cycle of these potential devices.

In the present study, we use a diarylethene with solution-stable open and closed forms (1,2-bis(2-methylbenzo[*b*]thiophen-3-yl) hexafluorocyclopentene), BTF6, as a photochromic energy transfer quencher of the metal-to-ligand charge-transfer (MLCT) based luminescence in $[Ru(dpp)_3]^{2+}$, dpp = 4,7-diphenyl-1,10-phenanthroline. These structures are presented in Figure 1. As only the closed form of BTF6 serves as a quencher for the MLCT luminescence, and the read (390 nm), write ($\lambda <$ 360

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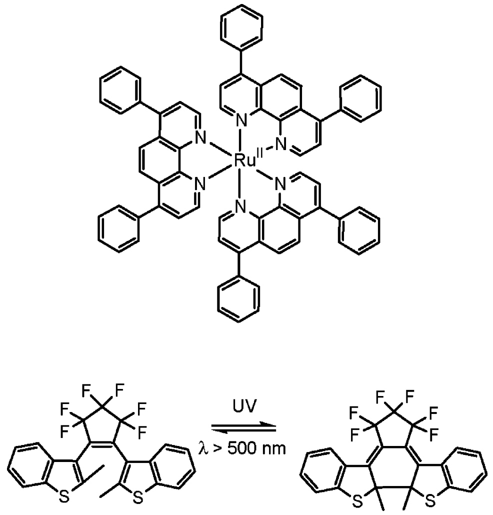

Figure 1. Molecular structures of $[Ru(dpp)_3]^{2+}$(top), the open form (left) and closed form (right) of BTF6. The photochromic action of BTF6 is also displayed.

nm), and erase (λ > 500 nm) wavelengths are well-separated, this system potentially represents an economic alternative to covalent systems. For the first time, we demonstrate the concept of using luminescence lifetimes to transduce the photochromic state of the quencher as opposed to the intensity-based readout schemes that are typically employed. The advantage of using MLCT complexes is that simple and cost-effective time-resolved measurements are feasible because of the long excited-state lifetimes and Stokes shifts exhibited by these luminophores. This opens the possibility for new optical memory devices operating on the principle of binary lifetime discrimination.

$[Ru(dpp)_3](PF_6)_2$ and BTF6 were prepared in one and three steps, respectively; their structures were consistent with that already published by other investigators.[18,19] The luminescence quantum yield and excited-state lifetime of $[Ru(dpp)_3]^{2+}$ in CH_3CN were determined to be 0.37 ± 0.04 and 6.0 ± 0.30 μs. This complex also possesses exceptional photostability and solubility in polar organic solvents.[20] The emission of this compound is bright orange ($\lambda_{max} = 610$ nm), originating from MLCT excited states.[20,21] Because the emission properties of $[Ru(dpp)_3]^{2+}$ are extremely sensitive to the presence of dissolved dioxygen, it has been utilized as an oxygen sensor.[22] BTF6 represents one of the earliest examples of a highly fatigue-resistant photochromic material.[19] Although a recent report on a unique intramolecular Ru(II)−DTE system suggests that ligand-localized triplet states can sensitize the ring-closing reaction,[23] we see no evidence for intermolecular MLCT sensitization of this reaction in BTF6.

Figure 2 shows the absorption spectra of open and closed forms of BTF6 as well that of $[Ru(dpp)_3]^{2+}$ in CH_3CN. It can be clearly seen that the low energy MLCT band of $[Ru(dpp)_3]^{2+}$ and the absorption of the BTF6 open form do not overlap, whereas the closed form's absorption minimizes in the same wavelength region (~390 nm), providing a window for preferential $[Ru(dpp)_3]^{2+}$ excitation. Upon irradiation with UV light (λ < 360 nm) colorless solutions of BTF6 become bright red with new absorption bands appearing at 350 and 525 nm. These bands arise from increased conjugation in the closed form and correspond to a photostationary state of BTF6 consisting of a mixture of both open and closed forms. The ratio between these two isomers after UV irradiation was determined previously by Irie et al. and equals 45:55, respectively.[19] The quantum yield of photoisomerization depends on solvent properties, particularly on viscosity.[24,25] The photochemistry is relatively fast and occurs in the picosecond time range.[25,26] Upon visible light irradiation, the closed form quantitatively converts back to the open form and coloration/decoloration cycles can be repeated as many as 1.3×10^4 times in aerated solutions without significant degradation.[19]

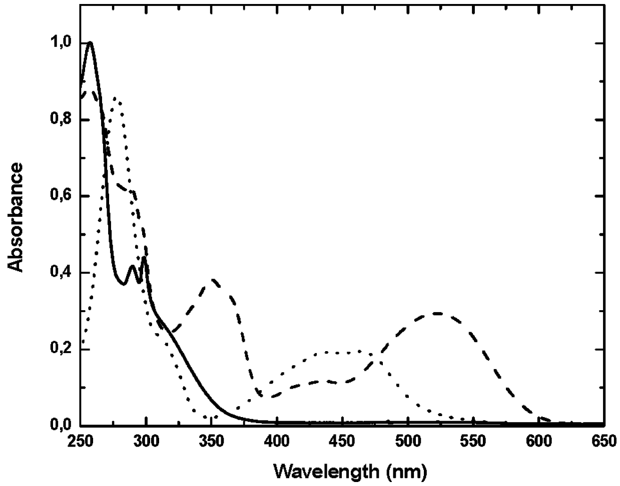

Figure 2. Absorption spectra of $[Ru(dpp)_3]^{2+}$ (····) and open BTF6 (—) along with the photostationary state of BTF6 produced with 254 nm irradiation (- - -), measured in CH_3CN.

Typical experiments employed degassed CH_3CN solutions containing 7×10^{-6} M of $[Ru(dpp)_3]^{2+}$ and 5×10^{-4} M BTF6 which were prepared and sealed under argon in a 1 cm path length quartz optical cell. All steady state and time-resolved luminescence experiments performed in the present study have been described in detail previously,[27] and in all cases, an excitation wavelength of 390 nm was employed to minimize excitation of the closed form of BTF6. In the reported data, the experimental errors for the absorption and emission maxima are ±2 nm and ±5% for the luminescence intensities and excited-state lifetimes. Control experiments showed that the luminescence lifetime and emission intensity of $[Ru(dpp)_3]^{2+}$ were unaffected by the open form of BTF6 and that the photochemistry of BTF6 proceeded smoothly in the presence of $[Ru(dpp)_3]^{2+}$. Irradiation of these solutions using the 254 nm output (760 $\mu W/cm^2$) of a standard blacklight lamp in a darkened room converts the open form of BTF6 to the colored closed form. The full solution volume (3.5 mL) can be converted to the photostationary state under these conditions in 3 min. Figure 3 shows that upon increasing concentration of the closed form (via 254 nm photolysis) the luminescence intensity and lifetimes originating from $[Ru(dpp)_3]^{2+}$ gradually decrease. The luminescence lifetimes were adequately modeled using single exponentials over the entire range of acceptor concentrations employed. Linear Stern−Volmer plots obtained for both lifetimes and intensity changes indicate that the quenching process is purely dynamic in nature (Figure 4). The quenching constant of 3.23×10^9 $M^{-1}s^{-1}$ indicates that the quenching approaches diffusion limits and no significant deviations from linear Stern−Volmer behavior was observed up to millimolar concentrations of the closed form of BTF6.

The luminescence quenching process can be described in terms of Förster-type resonance energy transfer (RET) enhanced by diffusion. Good spectral overlap between the $[Ru(dpp)_3]^{2+}$ emission and the low energy absorption band of the closed form of BTF6 allows efficient RET to take place, and we calculated a Forster distance (R_0) of 28.2 Å. Several theoretical models have been developed in order to include the diffusion into the

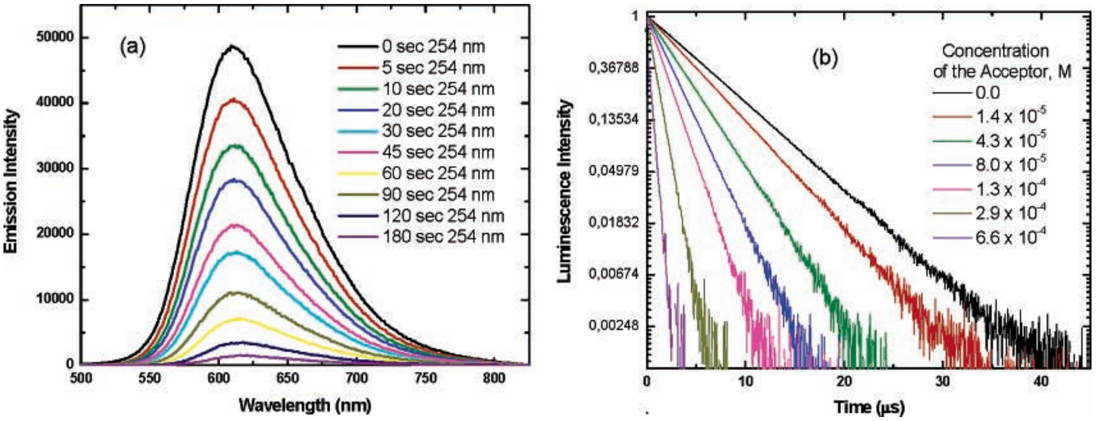

Figure 3. Luminescence intensity (a) and lifetime quenching (b) of $[Ru(dpp)_3]^{2+}$ by the closed form of BTF6 in degassed CH_3CN solution. All data was obtained with 390 nm excitation. The data in part b were detected at 610 nm and represent averages of 64 transients.

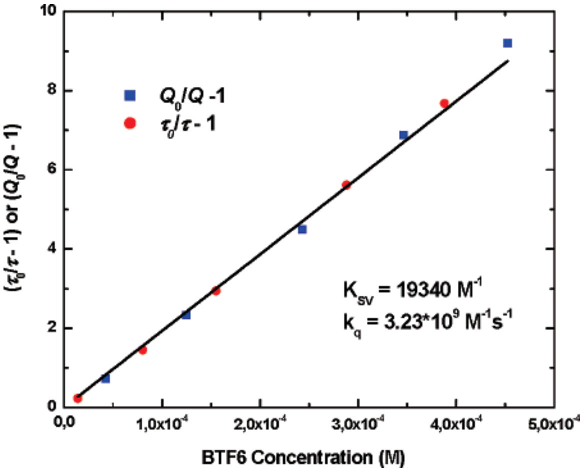

Figure 4. Stern−Volmer plot of luminescence intensity and lifetime quenching of $[Ru(dpp)_3]^{2+}$ by the closed form of BTF6 in degassed CH_3CN solution. Data taken from Figure 3.

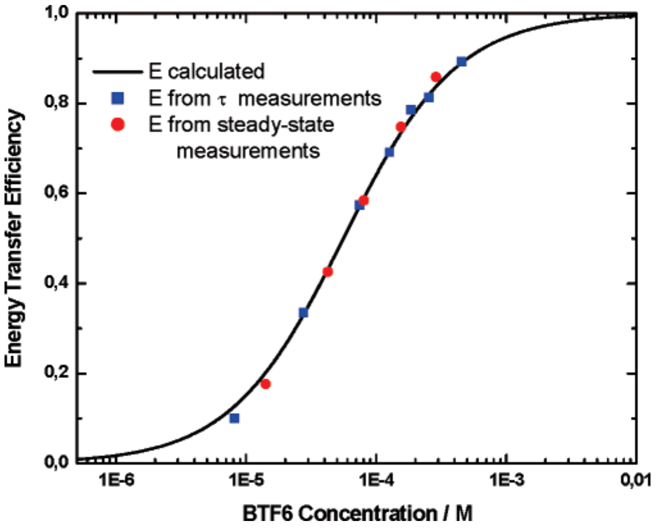

Figure 5. Intermolecular energy transfer efficiencies in the $[Ru(dpp)_3]^{2+}$/BTF6 system in CH_3CN. The data points are from Figures 3 and 4 and efficiencies calculated using eqs 1 and 2. The solid line was calculated using eqs 3 and 4 with a value of $a = 4.1$ Å.

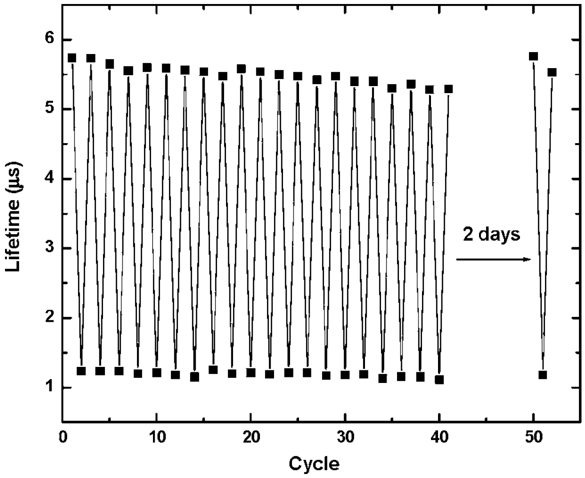

Figure 6. Reversible binary luminescence lifetime switching of the $[Ru(dpp)_3]^{2+}$/BTF6 system in degassed CH_3CN ($\lambda_{ex} = 390$ nm). Note that 21 complete photochemical cycles are shown.

RET process.[28−32] One of the limiting cases is RET in the rapid diffusion limit, first introduced by Stryer.[28,29] This model was successfully applied to luminescence quenching of long-lived Tb^{3+} and Eu^{3+} complexes with millisecond lifetimes,[33−35] and the same approach was utilized here. Figure 5 presents the energy transfer efficiency from $[Ru(dpp)_3]^{2+}$ to the BTF6 closed form obtained from lifetime and integrated luminescence intensity measurements. The energy transfer efficiencies (E) were calculated from the quenching data (Figures 2 and 3) using eqs 1 and 2, where Q, Q_0, τ, and τ_0 are quantum yields and lifetimes of donor in the presence and absence of acceptor, respectively. The theoretical curve (solid line in Figure 5) was obtained using eqs 3 and 4, where ρ is the density of acceptors, τ_0 is the donor lifetime, and a is the distance of closest approach.[29] All parameters are known except for a, which was varied until the best agreement between theory and experiment was achieved, when $a = 4.1$ Å. Although small in magnitude, such values of a are reasonable for small molecules freely diffusing in solution.[36]

$$E = 1 - Q/Q_0 \tag{1}$$

$$E = 1 - \tau/\tau_0 \tag{2}$$

$$E = k_r/(k_0 + k_r) \tag{3}$$

$$k_r = 4\pi\rho R_0^{\,6}/3\tau_0 a^3 \tag{4}$$

In the interest of binary memory applications, we measured the reversible photochemical modulation of luminescence lifetimes (and intensities) in the $[Ru(dpp)_3]^{2+}$/BTF6 system, Figure 6. In alternate cycles, the closed form of BTF6 was converted to its open form using a 50 W flood light bulb. This photolysis completely regenerated the open form of BTF6 in 3 min. In all cases, the luminescence intensity and lifetime could be repetitively cycled between two extremes 20 times without significant degradation in performance. Following this repetitive cycling, the sample was maintained under ambient conditions in the dark for 2 days at which time the photochemical cycling process was performed again, yielding similar results. This simple experiment illustrates the compatibility and potential long term stability of the two components. We believe that the performance of this solution-based system will ultimately be limited by the fatigue resistance properties of BTF6 photochrome but also note that complete separation of "read" and "erase" wavelengths is required for ultimate success in real-world applications. Another issue worth further exploration in related systems is to understand whether nonradiative RET contributes to destructive readout. In the present work, destructive readout appears to be largely minimized, even though 390 nm excitation is sufficient for direct photochemical ring-opening. Although we cannot completely rule out contributions from RET in ring-opening, a recent literature report utilizing singlet−singlet RET does not provide any evidence of energy transfer sensitization of the photochromic reaction.[17]

In conclusion, the new concept of luminescence lifetime binary switching was demonstrated using $[Ru(dpp)_3]^{2+}$ and photochromic BTF6. This intermolecular system displayed excellent switching performance over a reasonable period of time in solution without significant degradation, suggesting its possible use in "all-optical" read−write−erase memory systems. The photochromic state of BTF6 was indirectly interrogated through the lifetime response of $[Ru(dpp)_3]^{2+}$ and represents to the best of our knowledge the first example of binary lifetime discrimination. The quenching process was adequately modeled using RET in the rapid-diffusion limit. If translated into the solid state, the current system can potentially be used for long-term optical data or image storage utilizing luminescence lifetime and/or intensity readout schemes.

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