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A Red-Emitting Light Switch Based on a Heteroleptic Ruthenium(II) Complex Containing a Tridentate dppz Analogue

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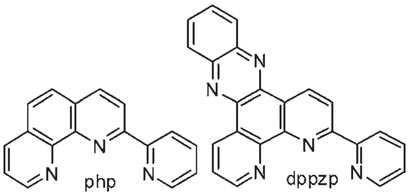
Delocalization of the charge-transfer excitation in the series [Ru(NNN)(bpy)CN]$^+$ [bpy = 2,2′-bipyridine; **1**, NNN = 2,2′:6′,2″-terpyridine; **2**, NNN = 2-(2′-pyridyl)-1,10-phenanthroline or php; **3**, NNN = 6′-(2″-pyridyl)dipyrido[3,2-*a*:2′,3′-*c*]phenazine or dppzp] proves to be an effective way of tuning photophysical properties. Red-emitting **3** functions as a DNA "light switch", shows emission from a state with charge-transfer-to-phenazine character, and exhibits a significantly enhanced emission signal relative to **1** and other dppzp-containing ruthenium(II) complexes.

Scheme 1. Chemical Structures of php and dppzp



Interest in ruthenium(II) polypyridine complexes remains high because of their photophysical properties[1] as well as their potential for applications in water oxidation,[2] artificial photosynthesis,[3] solar energy conversion,[3a,4] and DNA chemistry.[5] In the latter regard, Ru(bpy)$_2$(dppz)$^{2+}$ (dppz = dipyrido[3,2-*a*:2′,3′-*c*]phenazine) has been extensively studied as a luminescent DNA-binding probe.[6] The complex functions as a DNA "light switch" because interaction with water quenches the emission until the complex intercalates between DNA base pairs and becomes brightly luminescent. In other solvents, the complex also exhibits a dimmer-switch function in that the lifetime and emission yield drop as the temperature decreases.[7] Explanations of the switching effects revolve around a compartmentalization of the dppz ligand and two distinct metal-to-ligand charge-transfer (MLCT) states. One is an emitting bright state in which the excitation localizes on the bpy portion of the dppz ligand, proximal to the coordinated ruthenium center. In the other dark, nonluminescent state, the excitation localizes instead on the distal phenazine (phz) moiety.[7a,8]

Studies of chemically modified forms have provided new insight and helped to elucidate the energies and dynamics of the states involved. For example, extending the dppz ligand and introducing a second chelating site provide for the possibility of sensing metal ions in solution.[9] On the other hand, introducing sterically active methyl groups adjacent to the phz N atoms blocks the light-switch effect.[10] Substituents on the phz end of the dppz ligand can have an important electronic influence on the states involved,[11] as does replacing

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Table 1. Photophysical[a] and Electrochemical[b] Properties of Selected Complexes

					$E_{1/2}$/V	
complex	λ_{abs}/nm	λ_{em}/nm	Φ_{em}	τ/ns	oxidation	first reduction
1, Ru(trpy)(bpy)CN^+	487	674	3.1×10^{-4}	~8	0.62	−1.82
2, Ru(php)(bpy)CN^+	463/514	738	1.5×10^{-3}	90	0.64	−1.65
3, Ru(dppzp)(bpy)CN^+	488	755	1.8×10^{-3}	61	0.67	−1.34
$Ru(trpy)_2^{2+}$	476[c]	629[d]	$\leq 5.0 \times 10^{-6}$[c]	~0.3[d]	0.92[e,f]	−1.67[e,f]
$Ru(trpy)(dppzp)^{2+}$[d]	475	698	2.1×10^{-4}	~5	1.01[f]	−1.23[f]
$Ru(bpy)_3^{2+}$	452[g]	615[g]	6.2×10^{-2}[h]	1100[g]	0.79[i]	−1.72[i]
$Ru(bpy)_2(dppz)^{2+}$	450[j]	620[k]	2.1×10^{-2}[j]	770[k]	0.85[f,l]	−1.36[l]

[a] In CH_3CN unless otherwise noted. [b] Potentials vs the $Fc^{+/0}$ couple with 0.1 M Bu_4NPF_6 as the supporting electrolyte and in DMF unless otherwise noted. Potentials originally given vs SCE were converted to $Fc^{+/0}$ using ref 13. [c] Reference 14. [d] Reference 12b. [e] Reference 15. [f] In CH_3CN. [g] Reference 16. [h] Reference 17. [i] Reference 18. [j] Reference 19. In EtOH. [k] Reference 20. [l] Reference 21.

a CH group with a N atom in the back ring of the phz moiety.[8c] A recently described tridentate dppz derivative, denoted as dppzp (Scheme 1), provides new directions for exploration.[12] A published report reveals that $Ru(trpy)(dppzp)^{2+}$ exhibits the DNA light-switch effect.[12b] However, the lifetime (~5 ns) and emission quantum yield (2.1×10^{-4}) of the complex are both small. This report describes complex **3**, a ruthenium(II) complex of the dppzp ligand that exhibits much improved photophysical properties. Perhaps an even more interesting result is that photophysical studies of **3** show no evidence of a dark state.

Complexes structurally related to $Ru(trpy)_2^{2+}$ are virtually nonemissive in a fluid solution, because thermally assisted deactivation via ^{3}MC excited states is very efficient, even in systems involving carbometalated ligands.[22] The mixed-ligand complex Ru(trpy)(bpy)CN^+ is a better starting point because it exhibits a weak emission signal and offers multiple possibilities for electronic tuning.[23] In that context, the electrochemical properties of a complex often provide useful insight into the energetics of charge-transfer processes,[14,24] and Table 1 includes the relevant electrochemical properties of **1**−**3**. Each complex shows an anodic wave attributable to metal-centered oxidation, although there is little change in the potential (50 mV). In contrast, the first ligand reduction occurs with a much larger shift in the potential. Thus, the reduction processes for **2** and **3** are respectively 170 and 480 mV more positive than that of **1**. In light of the fact that the cathodic process becomes easier as the size of the π system of the NNN ligand increases, reduction clearly occurs at php in **2** and at dppzp in **3** (Scheme 1).

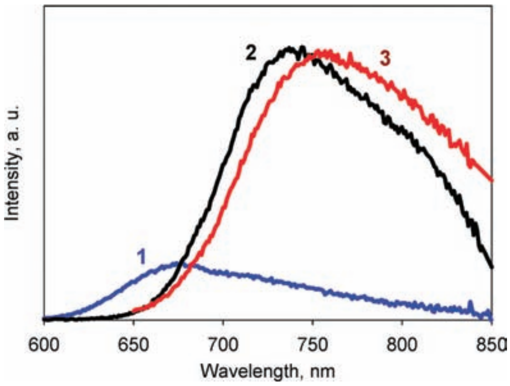

Figure 1. Corrected emission spectra of **1**−**3** in CH_3CN. Areas reflect quantum yields.

Interestingly, the influence of the reduction potential shows up more clearly in the emission data as compared with the absorbance data. Absorption spectra (Supporting Information) reveal that all three complexes show ligand-centered $\pi\pi^*$ transitions in the UV region, with the transition at ca. 330 nm in the spectrum of **3** being characteristic of a dppzp complex.[12] As described earlier for **1**,[23] the broad transitions above 450 nm correspond to Ru(dπ) → ligand(π^*) MLCT excitations. A compilation of luminescence maxima, quantum yields, and lifetimes obtained in CH_3CN appears in Table 1. Spectra in Figure 1 show that the emission maxima of **2** (738 nm) and **3** (755 nm) are red-shifted relative to **1** (674 nm) *and* the prototypical "light-switch" $Ru(bpy)_2(dppz)^{2+}$ (620 nm). Both the lifetimes and quantum yields of **2** and **3** are larger than those of **1**, and **3** shows a ~10-fold increase in both values relative to previously reported dppzp-containing ruthenium(II) complexes.[12b]

In each case, the emission maximum shifts to longer wavelength as the solvent polarity increases, from CH_2Cl_2 to $(CH_3)_2SO$, but the shift varies significantly from 8 nm for complex **1** to 29 nm for **2** and 48 nm for **3**. The stabilizing influence of a polar solvent is understandable in terms of enhanced charge displacement in the emissive MLCT excited state as the extension of the ligand increases. Turro and coworkers observed a similar effect with a $Ru(bpy)_2(dppz)^{2+}$ derivative that has a N atom in place of a CH group in the back ring of the phz moiety.[8c] They concluded that in the emissive charge-transfer excited state the electron is distal to the metal center, on the substituted phz moiety, whereas the electron resides closer to the ruthenium core in the emissive

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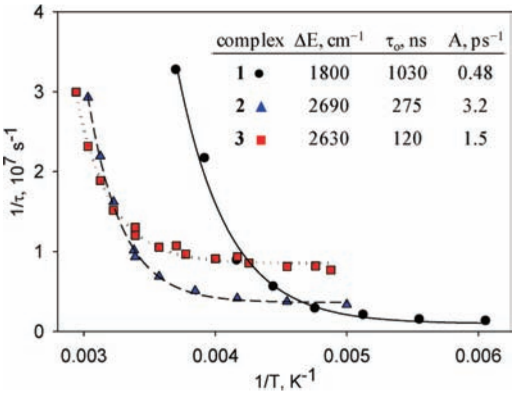

Figure 2. Inverse luminescent lifetime vs $1/T$ for **1**−**3** in 4:5 (v/v) PrCN/BuCN. Fits are described in the text.

state of the original dppz complex. Likewise, the large solvent dependence of the emission from **3** indicates an excited state largely localized on the distal compartment but with enough proximal character to support luminescence.

Further insight into the excited-state dynamics within the present series comes from temperature dependence studies, which show that both the lifetime (Figure 2) and emission intensity (Supporting Information) increase as the temperature decreases. The temperature dependence of the rate of decay of the excited state conforms to eq 1, where τ is the observed lifetime, A is a frequency factor, ΔE is the barrier from the emitting ^{3}MLCT state to the deactivating ^{3}MC state, and τ_0 is the intrinsic, or limiting, lifetime of the ^{3}MLCT state.

$$1/\tau = A\mathrm{e}^{-\Delta E/RT} + 1/\tau_0 \qquad (1)$$

The values for A, ΔE, and τ_0 appear in the inset in Figure 2. The frequency factors obtained ($A \approx 10^{12}$ s^{-1}) are typical of ruthenium(II) polypyridine complexes that decay via thermally accessible ^{3}MC states.[1a,25] The extremely low value of ΔE for **1** accounts for the relatively short lifetime of the complex at 298 K. On the other hand, **1** exhibits the longest τ_0 of the series because the limiting lifetimes trend according to the energy gap law. The balancing act involved is evident from the fact that at room temperature **1** decays via the ^{3}MC state 99% of the time, whereas **3** uses that channel only 49% of the time. However, the rate of direct nonradiative decay to the ground state is 8.6 times faster in the latter complex.

The increases in the lifetime and emission intensity of **3** with decreasing temperature contrast sharply with the results obtained with Ru(bpy)$_2$(dppz)$^{2+}$, in which the influence of a low-lying, phz-oriented dark state becomes evident at lower temperatures.[7a] The charge-transfer excited state of **3** is bright even though the electrochemical results, as well as solvent- and temperature-dependent studies of the emission, establish that the excited-state electron largely localizes on the distal phz fragment of the dppzp ligand. Also consistent with that view, complex **3** functions effectively as a DNA "light switch". In particular, data reported in the Supporting Information show that **3** exhibits virtually no emission signal in an aqueous buffer solution, but the complex becomes emissive and exhibits a 25 ns excited-state lifetime when it intercalates into double-helical DNA. Therefore, as with studies of Ru(bpy)$_2$(dppz)$^{2+}$[6a] and Ru(trpy)(dppzp)$^{2+}$,[12b] binding to DNA shields the phz N atoms from a potent solvent-assisted quenching mechanism.

In summary, several conclusions are worth noting: (1) The close agreement among the charge-transfer absorbance spectra of **1**−**3** suggests that the proximal part of the dppzp ligand is mainly responsible for the oscillator strength in the visible region. (2) On the other hand, emission studies are indicative of a luminescent state largely localized on the phz moiety of the dppzp ligand. There is also no sign of a dark state; indeed, the estimated radiative decay rates (calculated as Φ/τ) of **1** and **3** are very similar. Nevertheless, complex **3** still functions effectively as a DNA "light switch" and offers good prospects for obtaining a mechanistic understanding of water-induced quenching. (3) With a weak σ-bonding ligand like trpy or dppzp present in the coordination sphere, the key to obtaining a favorable room-temperature lifetime is to reduce the rate of nonradiative decay via ^{3}MC excited states without overly accelerating the rate of direct decay to the ground state, which is an exponential function of the triplet charge-transfer energy. In light of the two conflicting constraints, the emission yield of red-emitting **3** is quite respectable. Certainly, Ru(dppzp)(bpy)CN$^+$ compares favorably with Os(phen)$_2$(dppzp)$^{2+}$[26] and exhibits a much improved lifetime and emission quantum yield vis-à-vis Ru(trpy)(dppzp)$^{2+}$.[12b] (4) Finally, further elaboration is possible because the net charge, chirality, and spectator ligands of **3** are all variable.

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Supporting Information Available: X-ray crystallographic data in CIF format, listings of experimental details, compound characterization, solvent-, temperature-, and DNA-dependent emission spectra, and crystallographic results of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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