Communication

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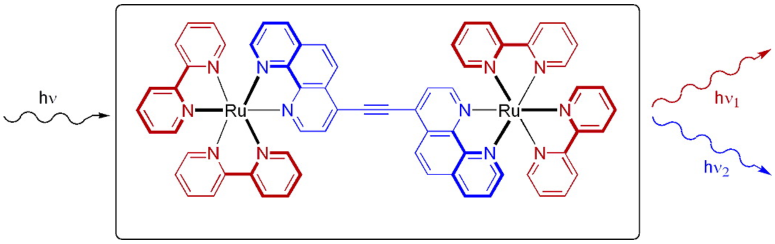

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Dual Emission from a Family of Conjugated Dinuclear Ru^{II} Complexes

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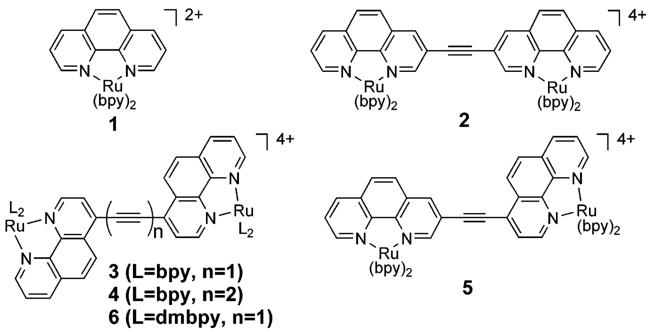
The structural and functional sophistication of photosynthetic light-harvesting complexes have inspired chemists to fabricate devices capable of light-induced functions.[1] Ru^{II} polypyridyl complexes have become key components in such systems due to their chemical stability, as well as their favorable excited-state photophysical and redox characteristics.[2,3] While the general behavior of these "classical" coordination compounds is well understood,[4] recent findings indicate that certain fundamental assumptions concerning their photophysics are too restrictive. A basic tenet of standard photophysics is the idea that only one excited state, at most, can be sufficiently long-lived to luminesce or participate in significant chemical processes. This is the foundation of Kasha's rule,[5] but recent findings indicate that it is not always valid. One example is the discovery of ^{1}MLCT-based emission.[6] Dual emission[7] has also been observed in other systems. Although nearly all Ru^{II} heteroleptic complexes exhibit a single emissive excited state, a few isolated systems have been found to possess two simultaneously emissive excited states.[8]

Dual emission has been reported for small molecules almost exclusively at low temperature and in rigid media,[9] where thermal energy is insufficient to surmount even low-energy barriers. Alternatively, with sufficiently large, supramolecular complexes, two chromophores may behave independently, coupled only by weak, long-distance interactions. In contrast to these cases, we report here the discovery of a family of small coordination compounds that exhibit two emissive states, both with charge-transfer character, in which the two excited states coexist for long times at room temperature in fluid solution.

A family of simple alkyne-linked, isomeric dimetallic (bpy)$_2$Ru^{II} complexes was studied, with the only variable being the substitution position on the bridging 1,10-phenanthroline (phen) ligand (Chart 1). Both symmetric systems (linked at the 3- or 4-positions of the phen ring) were investigated, along with an asymmetric dimer linking a 3-substituted complex to a 4-substituted system.[10,11] Comparing the UV/vis absorption spectra of dimers **2** and **3** to that of the parent complex [(bpy)$_2$Ru(phen)]$^{2+}$ **1** reveals significant differences (Figure 1a). Although all systems evidence the $\pi-\pi^*$ transition for the auxiliary bpy ligands at 286 nm, the dimer linked at the 3-position (**2**) possesses additional prominent transitions between 340 and 360 nm, which have been assigned as $\pi-\pi^*$ transitions on the extended phenanthroline.[11,12] These transitions are present, but far less intense, in the dimer linked at the 4-position (**3**). In contrast to the single broad transition observed in the MLCT region above 400 nm for **2** (as with the parent complex **1**), there are two well-resolved bands for **3**; one at 440 and the other at 520 nm.[13] To determine the origin of these transitions, the metal-free bridging phen ligands that correspond to complexes **2** and **3** were synthesized and characterized. In both isomeric systems, the ligand-localized transitions result in absorptions below 400 nm (see Figure S5, Supporting Information (SI)).[14] Thus, the transitions at 440 and 520 nm for **3** have been assigned as MLCT in nature.

Chart 1. Structures of Ru^{II} Complexes Included in This Study



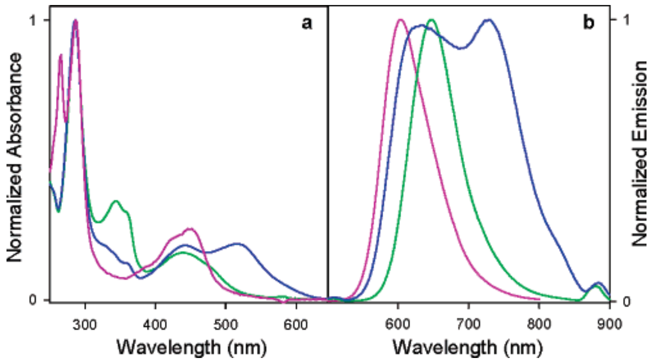


Figure 1. Normalized UV/vis absorption (a) and steady-state emission spectra (b) of **1** (purple), **2** (green), and **3** (blue) in acetonitrile at 22 °C. The excitation wavelength is 450 nm in all emission spectra.

The steady-state emission profile of the parent complex **1** and complex **2** each exhibit single emission peaks, with λ_{em} of 607 and 648 nm, respectively (see Figure 1b); the later is shifted to lower energy relative to the parent complex due to the extended conjugation of the phen ligand. In remarkable contrast to these systems, the emission spectra of the isomeric dimer **3** shows two broad, well resolved features, one around 620 and another around 720 nm, signifying the presence of two emitting states.

Excitation spectra for the two emission features of **3** show that the two excited states have different absorption profiles (see Figure S4, SI). Emission at 620 nm is stimulated by absorption into the MLCT centered at 440 nm, while emission at 720 nm is produced by absorption both at 440 and 520 nm. Consistent with this observation, excitation at 450 nm, as in Figure 1b, produces comparable areas for the two peaks, as detected with an uncorrected, but red-sensitive (R928), photomultiplier. Corrected spectra show somewhat greater emission near 800 nm. Excitation in the green (530 nm), however, produces predominately the longer-wavelength emission (see Table 1). It appears that each emission feature correlates primarily with one of the ^{1}MLCT absorption features. Thus, there is a notable degree of selectivity in accessing the different emissive states.

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Table 1. Emissive Characteristics of Ru^{II} Complexes[a]

cmpd	λ_{em1} (nm)[b]	τ_{em1} (ns)[c]	λ_{em2} (nm)[b]	τ_{em2} (ns)[c]	$I_{720}/(I_{620} + I_{720})$[d]		
					$\lambda_{ex} = 355$	$\lambda_{ex} = 450$	$\lambda_{ex} = 530$
1	610	147 ± 2					
2	648	225 ± 2					
3	620	141 ± 4	730	280 ± 6	0.56	0.19	0.87
4	620	143 ± 3	730	265 ± 10	0.63	0.09	0.96
5	620	143 ± 10	680	320 ± 15	0.69	0.13	0.91
6	620	125 ± 10	740	255 ± 10	0.34	0.22	0.74

[a] Measurements were performed in $2-8 \times 10^{-6}$ M solutions in air-equilibrated acetonitrile. [b] Emission maximum determined following excitation at 450 nm. [c] Lifetimes determined following pulsed excitation at 443 nm. [d] Represents the approximate fraction of the initial population of the two ^{3}MLCT states that is in the lower-energy state. Calculated as the initial amplitudes of the curve fitting to the respective components from the luminescence decays, corrected for the detector sensitivity ratio between 620 and 720 nm.

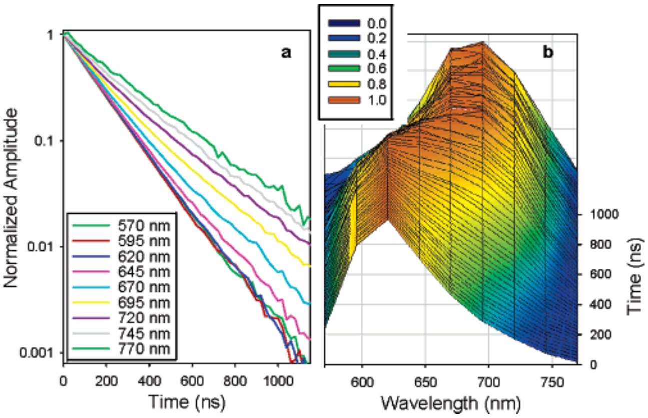

Figure 2. (a) Normalized emission decays of complex **3** monitored at different wavelengths following pulsed excitation ($\lambda_{ex} = 443$ nm) in air-equilibrated acetonitrile. (b) Evolution of the luminescence spectrum of **3** over time following pulsed excitation ($\lambda_{ex} = 530$ nm). Individual spectra were normalized to the same peak intensity.

Time-resolved emission studies on **3** resulted in biexponential decays. The contributions of the two emissive components to the decay were found to vary with detection wavelength (Figure 2a). The decays at the wavelength extremes are essentially monoexponential, while the intermediate wavelengths contain both components. The shorter lifetime (140 ns in the presence of air, 1 μs when deoxygenated) component characterizes the higher-energy emission, and a longer lifetime (280 ns in air or 3 μs when deoxygenated) is associated with the lower-energy emission.[15,16] Note that the corresponding decays for **1** and **2** are monoexponential and do not vary with detection wavelength (see Table 1 and Figure S1, SI).

The evolution of the emission spectrum for **3** is shown in Figure 2b. The spectra have been normalized to show that the short-lived, high-energy component is relatively more prominent at short times, and the lower-energy component, at long times. There is an isosbestic point, proving that two independent states are emitting, as opposed to a single state slowly evolving toward lower energies and a longer lifetime.

The deoxygenated quantum yield[17] for the integrated emission in **3** is approximately 0.006 for each transition,[18] about 10-fold lower than for **1**, although the fraction in each component is dependent on excitation wavelength. This implies either that population of the emitting states is less than quantitative or that the radiative lifetime of **3** is about 10-fold longer than that of **1**, of order 100 μs.

As the luminescent behavior of **3** was so unexpected, both in light of the rarity of dual emission and its contrast to the behavior of its isomer, dimer **2**, three additional systems were synthesized and characterized: a butadiyne-linked dimer **4**, an asymmetrically substituted dimer **5**, and an analogue to **3** that contains 4,4′-dimethyl 2,2′-bipyridine coligands (**6**). The anomalous emissive behavior of **3** was validated by the results for these systems, which also possessed two emission features readily discernible at room temperature in fluid solution, as summarized in Table 1.[11] This series demonstrates that the excited states on either the bridging ligand or co-ligands may be tuned by structural modification.

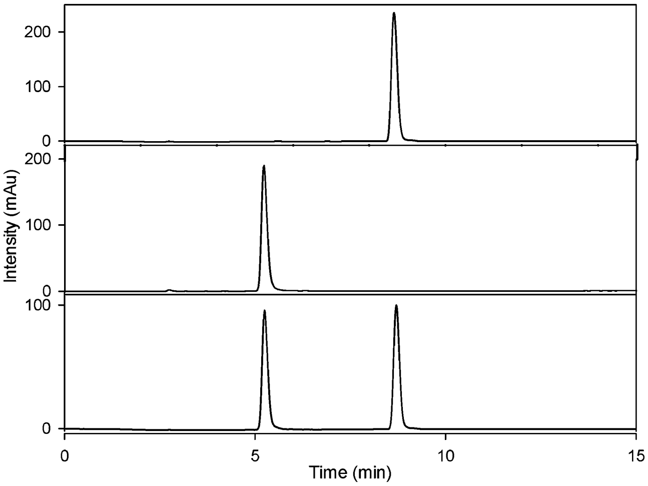

Figure 3. Analytical HPLC of **3** (top), $Ru(bpy)_3$ (middle), and a 1:1 mixture of the two (bottom). See SI for expanded chromatograms and experimental details.

As most other Ru^{II} polypyridyl complexes that have been characterized as having two emissive features have been shown to exhibit dual emission that is of the "distinct orbital" type,[19] it was important to determine the orbital parentage of the two excited states. Considering the excited state lifetimes and energies of the two components in these 4-substituted complexes, both emissive states would appear to be MLCT-based. This is supported by the emission spectra of the uncoordinated bridging ligand, which indicates that a ligand-centered transition would occur at higher energies, as expected (see Figure S6, SI). In addition, the radiative lifetime determined for the two emissive processes, although possibly longer than in most Ru^{II} complexes, could be due to nothing but ^{3}MLCT states in coordination compounds of this sort.

The consensus in the field is that in complexes such as **1** excited states are localized on one ligand on the time scale of emission,[20] albeit with some hopping probability. We propose that the excited states we observe are "spatially isolated," with emission from both the coordinated bpy and bridging phen ligands, but with a large energy barrier to crossing between the localized states. The bpy-localized state is assigned as the higher-energy feature. The higher-energy state may be decaying into the lower state; however, while in standard Ru^{II} complexes this occurs on an extremely fast time scale, in our system, if it occurs, it is only at a very slow rate. The "spatially isolated" type of dual emission is extremely uncommon,[8b] and most clearly deviates from the rules for nonradiative decay, as it involves emission from orbitals of the same parentage.

Other possible rationales for the observed behavior have been explored extensively and discounted. The most likely alternative explanation for our results is that one of the emission features results from the presence of an impurity. No evidence for contaminations was found through any characterization techniques, however, and analytical HPLC indicates extremely high purity (see Figure 3 and Figure S7, SI). Dual emission was found in **3**, **4**, **5**, and **6**, despite the fact that each dimer was produced by a different synthetic pathway. The synthesis chosen likewise eliminated the possibility of contamination by a structural isomer (see SI). The possibility of a persistent trace luminescent impurity from a common source (such as the solvent) has been eliminated as the luminescent components are not present in the blank or the other complexes studied. Last, we have examined and eliminated the possibility that the second emission feature results from the product of thermal or photodegredation; see SI for a discussion of these experiments.

While the spectral evolution shown in Figure 2b is reminiscent of energy transfer, this cannot be the explanation for the observed anomalous emission. The emission was measured as a function of concentration, and aside from an inner-filter effect that attenuated the blue edge at high concentrations, there was no concentration effect. In addition, there is no rise time (>1 ns) for either emission feature, as would be expected in the case of energy transfer. Alternatively, unexpected long-wavelength emission is sometimes due to excimers or stable dimers. The absence of both concentration effects and a rise time observed in the time-resolved studies similarly excludes such excimer or dimer formation.

In summary, we have found that a family of simple alkyne-linked Ru^{II} dimers exhibit dual emission that is well resolved both in energy and lifetime at room temperature and in fluid solution. Furthermore, this anomalous emissive behavior is a result of changing the substitution position by one carbon. This minor structural modification results in the failure of standard nonradiative decay pathways that usually result in relaxation to a single emissive state. Intriguingly, structurally analogous Ru^{II} dimers linked through bpy ligands show no such anomalous emissive features,[21,22] indicating the behavior is correlated to the specific position and ligand.[23] These results are unprecedented and in conflict with the emissive behavior of nearly all coordination complexes. The Ru^{II} systems characterized provide a unique opportunity to investigate the structural and electronic features that result in decoupling of excited states. We currently have underway the syntheses and spectroscopic characterization of additional compounds with which we shall explore the structure requirements in more detail. In addition, as the dual emission occurs at room temperature, there is potential for useful application. The implications of such systems that avoid standard nonradiative decay pathways extend from the creation of photosensitizers with enhanced efficiency to the design of new biluminescent materials.

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Supporting Information Available: Synthetic details, analytical HLPC chromatograms, and additional spectroscopic data, including emission decays of compound **2**, emission decays of compound **3** in methylene chloride, excitation spectra, and absorption and emission spectra of the metal-free dimers. This information is available free of charge via the Internet at http://pubs.acs.org.

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(10) Note the dinuclear complexes studied are a mixture of diastereoisomers.

(11) See Supporting Information for additional experimental details.

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(13) The presence of two distinct transitions, while not uncommon in heteroleptic complexes, is somewhat surprising given the simple spectrum for isomer **2**.

(14) Excess Zn^{2+} was added to simulate the effect of binding the divalent Ru^{2+} ion; the absorption spectra was red-shifted, as expected, but the longest wavelength absorption remained below 400 nm (see Figure S5).

(15) While many Ru^{II} complexes exhibit diminished lifetimes associated with lower-energy emission, consistent with the energy gap law, enhanced lifetimes have been observed with highly conjugated ligands, which decrease distortion in the excited state. See Boyde, S.; Strouse, G. F.; Jones, W. E.; Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 7395−7396.

(16) Similar results were obtained for the time-resolved studies in other solvents; see Figure S2 for the emission decays of **3** in methylene chloride.

(17) Quantum yields were measured according to the guidelines of Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991−1024.

(18) This value is approximate due to the low quantum yield, and the fact that the two emissive states possess overlapping excitation spectra.

(19) Dual emission of the "distinct orbital" type has been reported in coordination complexes that contain appended organic fluorophores, but are not true violations of Kasha's rule, as they are considered "composite molecules." See refs 8c−e and (a) Simon, J. A.; Curry, S. L.; Schmehl, R. H.; Schatz, T. R.; Piotrowiak, P.; Jin, X., Thummel, R. R. *J. Am. Chem. Soc.* **1997**, 110122−11022. (b) Tyson, D. S.; Henbest, K. B.; Bialecki, J.; Castellano, F. N. *J. Phys. Chem. A* **2001**, *105*, 8154−8161.

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(22) The absence of additional emission features in these systems may be related to the flexibility of the bpy-linked systems. Dual emission results from avoidance of standard radiationless decay pathways, and studies on classical systems, such as biphenyl and 9,10-dihydrophenanrthrene, show that a reduction in radiationless decay occurs with increased structural rigidity. See Nijegorodov, N. I.; Downey, W. S. *J. Phys. Chem.* **1994**, *98*, 5639−5643.

(23) Although there are no reports of dual emission from 4-substituted phenanthrolines in the literature, there is a mention of unpublished results that provided evidence for dual emission from a 4,7-substituted phenanthroline complex at low temperature. See Blakley, R. L.; Myrick, M. L.; DeArmond, M. K. *J. Phys. Chem.* **1990**, *94*, 4804−4809.

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