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Multiple Charge-Transfer Emissions from Different Metal–Ligand Pairs in Ruthenium Diimines

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Ruthenium diimines are unique in their emissivity. Optical excitation with light of less than 500 nm leads to a strong emission in the 600–700 nm range. All emissive ruthenium complexes appear to undergo intersystem crossing from the absorptive singlet metal-to-ligand charge-transfer (MLCT) state to an emissive triplet MLCT state localized on the lowest-energy metal–ligand pair. In contrast to this currently accepted model, in which a single emissive state is populated and then equilibrates among other states based on a particular set of conditions, the excitation-wavelength dependence of the [(bpy)$_2$RudppH]$^{3+}$ emission suggests two emissive pathways. One populates an emissive MLCT state localized on a bpy–Ru pair, and the other populates a lower-energy MLCT state localized on the dpp–Ru pair.

The syntheses of ruthenium(II) diimines with more elaborate conjugated ligand systems provide new insights into the partitioning of energy among the different components of the complex. Unlike the parent tris-analogues, where quantitative conversion occurs from the higher-energy excited states populated on absorption to the lowest-energy emissive state, many more structurally varied complexes exhibit multiple emissions. Multinuclear ruthenium(II) complexes show different emissions from distinct chromophores within the complex.[1,2] Generally found at low temperature, multiple emissions have been found from room temperature solutions of alkyne-linked (bpy)$_2$Ru^{II} bimetallics.[1] Multiple emissions from monometallic ruthenium(II) diimines possessing asymmetric coordination shells occur in low-temperature and/or rigid matrices.[3−6] Their temperature dependencies[7,8] suggest intersystem crossing to the lowest triplet metal-to-ligand charge-transfer (^{3}MLCT) and then thermal equilibration among different excited states. Two emissions have been observed from room temperature solutions of [Ru(bpy)$_2$-4-methyl-4′-[ρ-(dimethylamino)-α-styryl]-2,2′-bpy]$^{2+}$.[9] The strong electron-donating property of the asymmetric substituent suggests an intraligand charge-transfer (ILCT) emission that coexists with the ^{3}MLCT transition.[9]

This report describes the appearance of multiple emissions from room temperature aqueous solutions of [Ru(bpy)$_2$dpp]$^{2+}$ [dpp denotes 2,3-bis(2-pyridyl)pyrazine][10] as a result of the complex's acid−base chemistry. In contrast to other monometallic ruthenium(II) diimines, rapid intersystem crossing from the high-energy, spin-allowed absorptions, and a single emission from the lowest-energy spin-forbidden MLCT state, data presented here point to two emissions initiating from MLCT states localized on different ligands.[10]

Room temperature aqueous solutions of [Ru(bpy)$_2$dpp]$^{2+}$ exhibit MLCT absorptions at 430 and 470 nm corresponding to charge transfer to bpy and dpp ligands, respectively.[10] At pH = 7, excitation of either transition leads to an emissive MLCT state localized on the dpp ligand with an emission maximum at 705 nm[11] (Figure 1a). At room temperature, the quantum efficiency, Φ_{em}, is $(2.0 \pm 0.2) \times 10^{-3}$ and the emission decays exponentially with a lifetime of 115 ± 12 ns.

Increasing [H$^+$] from 0.1 to 1 M causes little change in the absorption spectrum, but NMR spectra as a function of [H$^+$] are consistent with the protonation of dpp's peripheral pyridine nitrogen.[12] Consistent with an increase in the positive charge, five protons shift downfield with increasing [H$^+$]. The changes in chemical shift yield a pK_a of 1.52 for protonation of the pendant pyridyl ring.

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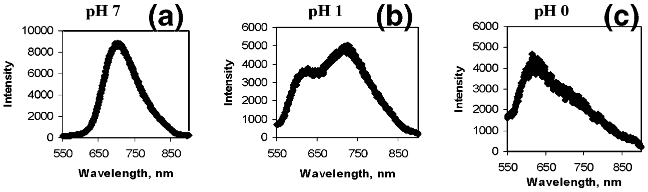

Figure 1. Emission spectra of $[Ru(bpy)_2dpp]^{2+}$ at different pHs; at 298 K with fixed $\lambda_{exc} = 457.9$ nm.

Previous studies[13,14] of the excited-state acid−base chemistry of $[Ru(bpy)_2dpp]^{2+}$ confirmed a loss of the 705-nm emission from the unprotonated complex with increasing $[H^+]$. However, because of a huge difference in emissivity, these experiments failed to detect that loss of the 705-nm emission occurs with the appearance of two much weaker emissions with maxima at 620 and 735 nm (Figure 1b). These emissions reach maximum intensities at pH = 1, at which the K_a values derived from the NMR data show that 78% of the complex exists in the protonated form, $[Ru(bpy)_2dppH]^{3+}$, with the proton attached to the peripheral pyridine nitrogen of dpp. The 620- and 735-nm emissions occur with quantum efficiencies of $(3 \pm 1) \times 10^{-8}$ and $(4 \pm 1) \times 10^{-9}$, and both decay within 16 ps.

Increasing $[H^+]$ beyond 2 M eliminates both emissions and dramatically changes the MLCT absorptions. In 10 M H_2SO_4, a single strong absorbance with a maximum at 575 nm replaces the 430- and 470-nm absorptions. The spectral changes occur at an acid concentration where protonation of coordinated pyrazine occurs[13] and are assigned to the conversion of $[Ru(bpy)_2dppH]^{3+}$ to $[Ru(bpy)_2dppH_2]^{4+}$. There is no indication that the diprotonated complex emits. Because *all* spectral changes can be quantitatively reversed by the addition of a base and the 620- and 735-nm emissions exhibit a maximum intensity at a $[H^+]$ at which the NMR indicates a predominance of the monoprotonated complex, the 735- and 620-nm emissions are assigned to those from $[Ru(bpy)_2dppH]^{3+}$.

Although both emissions arise from $[Ru(bpy)_2dppH]^{3+}$, the 735-nm emission intensity declines as $[H^+]$ increases from 0.1 to 2 M, whereas the 620-nm emission intensity is unchanged over the same $[H^+]$ (Figure 1c).[15] The acid dependence of the 735-nm emission points to an excited state localized on the monoprotonated dpp ligand because a vacant acid−base site remains at the peripheral dpp pyrazine nitrogen. The bipyridines do not possess an acid−base site and are not expected to exhibit an acid−base dependence.[13] Because the wavelength maximum of the 620-nm emission is equivalent to that of the parent analogue $Ru(bpy)_3^{2+}$, where the excited state is localized on an individual bpy ligand,[16,17] and is independent of $[H^+]$, the 620-nm emission is assigned to an excited state localized on the bpy ligand.

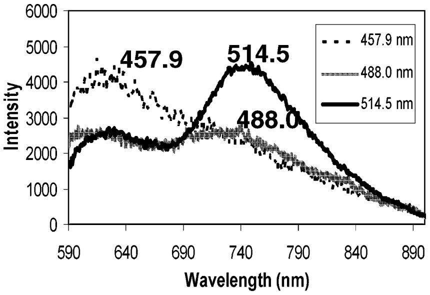

Figure 2. Emission spectra of $[Ru(bpy)_2dppH]^{3+}$ at pH = 0, 298 K, as a function of 457.9-, 488.0-, and 514.5-nm excitation wavelengths.

Additional evidence supporting the assignment of the 620- and 735- nm emissions to $[Ru(bpy)_2dppH]^{3+}$ is the excitation-wavelength dependence of the peaks. A 457.9-nm excitation increases the intensity of the 620-nm emission relative to the 735-nm emission, whereas a 514.5-nm excitation wavelength increases the intensity of the 735-nm emission relative to the 620-nm emission (Figure 2). This contrasts with $[Ru(bpy)_2dpp]^{2+}$, where the 705-nm emission is independent of the excitation wavelength.

Attributing the 620-nm emission to an impurity is not supported by the data. Chromatography yields a clean separation of $[Ru(bpy)_2dpp]^{2+}$. The 620-nm emission maximum occurs at the same wavelength as that from $Ru(bpy)_3^{2+}$, but the emission lifetime, ≤16 ps, is significantly smaller than the 600-ns lifetime of $Ru(bpy)_3^{2+}$ in a room temperature aqueous solution.[16] The double emission is not from traces of the dimer $[(bpy)_2Ru]_2dpp^{4+}$ because it emits at 755 nm with a lifetime of 54 ± 11 ns.[10] Emission from the diprotonated complex is also ruled out because diprotonation of the complex requires high acidity ($[H^+] \sim 5$ M) and $[Ru(bpy)_2(dppH_2)]^{4+}$ is nonemissive,[12,13] rather the 620- and 735-nm emissions arise from the intermediate monoprotonated complex with the proton attached to the peripheral dpp pyridine.

Vos and co-workers report that protonation switches excitation energy between two emitting states centered on different ligands within the same molecule.[18] In that case, double emissions occur only as the temperature is lowered and the two emitting states are believed to be weakly coupled. With an energy difference of 2200 cm^{-1}, thermal equilibration between the 620- and 735-nm emissive states in $[Ru(bpy)_2dppH]^{3+}$ at room temperature is unlikely. It is also not likely to invoke an ILCT transition to account for the $[Ru(bpy)_2dppH]^{3+}$ multiple emissions because neither the bpy nor dpp ligands possess the strong electron-donating properties needed for an ILCT transition.[9] However, our data indicate that excitation of $Ru(bpy)_2dppH^{3+}$ leads to the population of a bpy- and dpp-localized ^{3}MLCT state from which emissions occur. The detailed pathways by which the excitation energy decays to these emissive states remain to be established, but one finding can be noted. Resolution of the overlapping 430- and 470-nm ^{1}MLCT absorptions of $[Ru(bpy)_2dppH]^{3+}$ shows that the relative intensities of the 620- and 735-nm emissions correlate with the fractions of light

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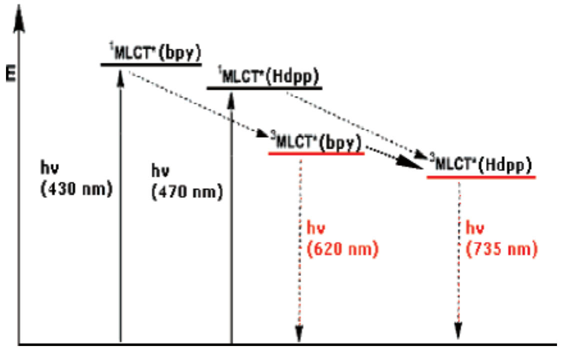

Figure 3. Energy-level diagram of $[Ru(bpy)_2dppH]^{3+}$. Solid lines represent energy absorption, and red dashed lines represent radiative transitions.

absorbed by the different MLCT absorptions. In this case, the ratio of the intensity of the 620-nm emission to that of the 735-nm emission is given by $I^{620}/I^{735} = \Phi^{620}f^{430}/\Phi^{735}f^{470}$, where Φ^{620} is the quantum efficiency of the emission at 620 nm, $(3 \pm 1) \times 10^{-8}$, f^{430} is the fraction of the excitation absorbed by the resolved 430-nm transition to the bpy-localized MLCT state, Φ^{735} is the quantum efficiency of the emission at 735 nm, $(4 \pm 1) \times 10^{-9}$, and f^{470} is the fraction of the excitation absorbed by the resolved 470-nm transition to the dppH-localized MLCT state. With 514-nm excitation, the I^{620}/I^{735} ratio is calculated to be 0.65 ± 0.42, which is within the experimental error of the ratio of the intensities of the emissions taken from Figure 2, 0.55. Similar results occur with 488-nm excitation; the calculated I^{620}/I^{735} ratio, 1.32 ± 0.42, is within the experimental error of that extracted from Figure 2. One possibility (Figure 3) is that all intersystem crossing from the singlets proceeds through the ^{3}MLCT (bpy), followed by internal conversion to the ^{3}MLCT (dppH). This is consistent with the available evidence for $Ru(bpy)_3^{2+}$, which undergoes internal conversion through the singlet manifold and then intersystem crossing to the luminescent ^{3}MLCT state with unitary or close to unitary efficiency. $[Ru(bpy)_2dppH]^{3+}$ differs in the availability of a dppH-localized ^{3}MLCT ca. 2000 cm^{-1} below the ^{3}MLCT(bpy). The quantum efficiencies of emissions from the ^{3}MLCT states and specifically the lifetime of the ^{3}MLCT(bpy) reflect the dynamics of internal conversion between these lower-energy states (Figure 3).[19]

Emission pathways localized on different ligands challenge the generally accepted idea that emission from ruthenium(II) diimines always derives from a state localized on the ligand possessing the lowest-energy acceptor orbitals. Relative to Φ_{em} for $[Ru(bpy)_2dpp]^{2+}$, the quantum yields of the multiple emissions indicate that relaxation to the lowest-energy metal–ligand pair remains the dominant process. Emissions from each metal–ligand pair in $[Ru(bpy)_2dppH]^{3+}$ are detectable because protonation of the peripheral dpp pyridine increases the nonradiative rate of relaxation so that the emissivity of the lowest-energy ^{3}MLCT(Hdpp) is comparable to that from the ^{3}MLCT(bpy) state. Alternatively, the ^{3}MLCT(bpy) is not always present as implied above but is available as a result of protonation itself.

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Supporting Information Available: Spectra showing Raman scattering peaks, resolved MLCT absorptions, and calculations correlating emission intensities to light absorbed. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) We thank the reviewers for pointing this out.