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Long-Lived Near-Infrared MLCT Emitters

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Knowledge about metal-to-ligand charge transfer (MLCT) absorption and MLCT excited states in polypyridyl complexes of Ru^{II}, Os^{II}, and Re^{I} continues to evolve. The use of new acceptor ligands and heteroleptic synthetic strategies have allowed a new set of issues to be explored.[1] One is the design of complexes which are intense low energy light absorbers and of "black" absorbers, which absorb throughtout the visible based on the manipulation of the ligands.[2] Delocalization and rigidity in the acceptor ligand decrease structural changes in the excited state. This decreases the nonradiative decay rate constant (k_{nr}) and can greatly enhance excited-state lifetimes (τ), even for small ground/excited-state energy gaps.[3] We report here application of these findings to the design of a new class of near-infrared emitters in which τ and emission energies (E_{em}) can be tuned systematically.

In the complexes $[Ru(Me_2bpy)(Me_4bpy)(dpq)]^{2+}$ (Me_2bpy is 4,4′-dimethyl-2,2′-bipyridine; Me_4bpy is 4,4′,5,5′-tetramethyl-2,2′-bipyridine; dpq is 2,3-bis(2-pyridyl)quinoxaline), $[Ru(Me_2bpy)(bpy(COOEt)_2)(dpb)]^{2+}$ ($bpy(COOEt)_2$ is 4,4′-dicarboxy-2,2′-bipyridine, diethyl ester; dpb is 2,3-bis(2-pyridyl)benzoquinoxaline), $[Ru(bpy(COOEt)_2(dpb)(Et_2dtc)]^{+}$ (Et_2dtc is *N*,*N*-diethyldithiocarbamate anion), $[Ru(bpy)_2(dpop)]^{2+}$ (bpy is 2,2′-bipyridine; dpop is dipyrido[2,3-a;2′,3′-h]phenazine), $[(Ru(bpy)_2)_2(dpop)]^{4+}$, and $[Os(bpy)_2(dpb)]^{2+}$, there are low-lying π^* acceptor orbitals on dpq, dpb, and dpop (Figure 1). Low-energy MLCT absorption bands appear at 534, 548, 620, 530, and 664 nm, respectively, in CH_3CN at RT for the PF_6^- salts and emission maxima at λ_{max} = 838, 1030, 1440, 802, 1070, and 1130 nm, respectively. In Figure 2 are shown emission spectra of $[(Ru(bpy)_2)_2(dpop)](PF_6)_4$ and $[(Ru(bpy)_2)_2(dpop)](PF_6)_4$ in CH_3CN at RT overlaid with fits obtained by application of a standard Franck−Condon analysis, which assumes the average mode approximation and uses a single medium-frequency coupled mode.[4,5] These results are summarized along with excited-state lifetimes in Table 1. Lifetimes were measured by laser flash photolysis with transient absorption monitoring.[6]

In these complexes, the emission has been tuned progressively into the infrared by application of synergistic ligand effects. In the formation of MLCT excited states, there is partial oxidation at the metal and partial reduction at the acceptor ligand, e.g.,

$$Ru^{II}(bpy)_3{}^{2+} \xrightarrow[h\nu]{} Ru^{III}(bpy^{\bullet})(bpy)_2{}^{2+*}$$

The relatively electron rich ligands Me_2bpy, Et_2dtc^-, and Me_4bpy stabilize the excited-state hole at $*Ru^{III}$ by electron donation. Low-energy π^* acceptor orbitals on ligands such as dpq, dpb, and dpop stabilize the excited electron. A combination of the two results in a small excited-to-ground-state energy gap and a family of near-IR emitters.

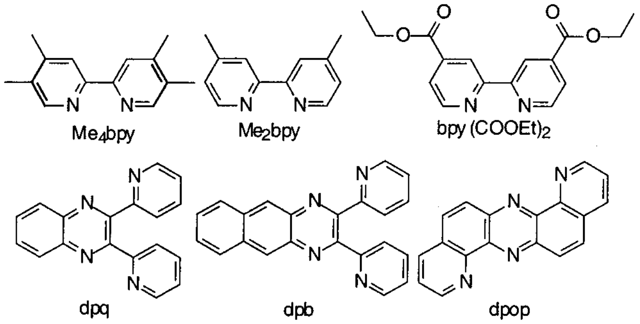

Figure 1. Structures of the polypyridyl ligands.

There are important design considerations in achieving low-energy emission. 1) Acceptor ligands with electron withdrawing substituents, such as $-CF_3$ and $-CO_2Et$, provide low-energy acceptor levels but they also destabilize the metal-centered hole. Low energy gaps require the simultaneous use of electron donor ligands as in entries 1−3 in Table 1. 2) Extending the π/π^* framework of the acceptor ligand lowers the energy of the acceptor level without significantly decreasing σ electron donor ability. 3) Coulombic stabilization of the excited electron by using π^*-(bridge) orbitals in ligand-bridged complexes decreases the energy gap, entry 4. 4) In equivalent coordination environments, Os^{III} is

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(4) (a) The spectra, $I(\bar{\nu})$, were fit by using the equation

$$I(\bar{\nu}) = \sum_{\upsilon=0}^{5} \{(E_0 - \upsilon \cdot \hbar\omega/E_0)^3 (S^{\upsilon}/\upsilon!) \times \exp[-4 \ln 2(\bar{\nu} - E_0 + \upsilon \cdot \hbar\omega/\Delta\bar{\nu}_{1/2})^2]\}$$

with υ, the vibrational quantum number from 0 to 5, E_0 the $\upsilon^* = 0 \rightarrow \upsilon = 0$ ground/excited-state energy gap, $\Delta\bar{\nu}_{1/2}$ the full-width at half-maximum intensity for each vibronic component, $\hbar\omega$ the quantum spacing for the average mode, and S the electron-vibrational coupling constant. For $[Ru(bpy)_2(dpop)]^{2+}$, E_0 = 12 400 cm^{-1}, S = 0.21, and $\Delta\bar{\nu}_{1/2}$ = 1 842 cm^{-1}. For $[(Ru(bpy)_2)_2(dpop)]^{4+}$, E_0 = 9 470 cm^{-1}, S = 0.26, and $\Delta\bar{\nu}_{1/2}$ = 1600 cm^{-1}. (b) Ballhausen, C. J. *Molecular Electronic Structures of Transition Metal Complexes*; McGraw-Hill: New York, 1979. (c) Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 3722. (d) Claude, J. P.; Meyer, T. J. *J. Phys. Chem.* **1995**, *99*, 51. (e) Murtaza, Z.; Graff, D. K.; Zipp, A. P.; Worl, L. A.; Jones, W. E. Jr.; Bates, W. D.; Meyer, T. J. *J. Phys. Chem.* **1994**, *98*, 10504.

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(6) Transient absorption spectra were acquired by using an apparatus described in Younathan, J. N.; Jones, W. E.; Meyer, T. J. *J. Phys. Chem.* **1991**, *95*, 488. Excitation intensity was limited to 1.4−2.2 mJ/pulse. All samples were freeze−pump−thaw degassed (4 cycles, 10^{-5} Torr) in sealed 1 cm cuvettes prior to measurement. Excitation was carried out at 355 nm and repeated at 532 nm to check for consistency.

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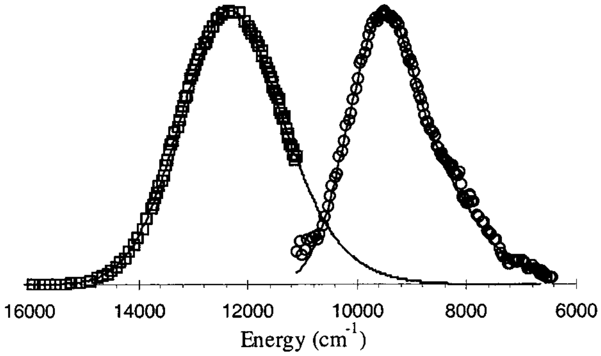

Figure 2. Emission spectra of [Ru(bpy)$_2$(dpop)](PF$_6$)$_2$ (squares) and [(Ru(bpy)$_2$)$_2$(dpop)](PF$_6$)$_4$ (circles) in CH$_3$CN at room temperature. The spectra are overlaid with theoretical fits based on a standard Franck−Condon analysis of the line shapes (lines). The raw data have been sparsed for increased clarity.

Table 1. Emission Maxima and Excited-State Lifetimes for Near-Infrared Emitters in Deaerated CH$_3$CN at RT

entry	salt	$\lambda_{\max}^{em}$, nm[a]	τ, ns[b]
1	[Ru(Me$_2$bpy)(Me$_4$bpy)(dpq)](PF$_6$)$_2$	838	322
2	[Ru(Me$_2$bpy)(bpy(COOEt)$_2$)(dpb)](PF$_6$)$_2$	1030	106
3	[Ru(bpy(COOEt)$_2$)(dpb)(Et$_2$dtc)](PF$_6$)	1440	−
4	[Ru(bpy)$_2$(dpop)](PF$_6$)$_2$	802	150
5	[(bpy)$_2$Ru(dpop)Ru(bpy)$_2$](PF$_6$)$_4$	1070	100
6	[Os(bpy)$_2$(dpb)](PF$_6$)$_2$	1130	~5

[a] ±3 nm. [b] ±3% except for entry 6.

less oxidizing than Ru^{III} by 0.4−0.5 eV, which results in a significant shift to the red for Os complexes compared to Ru, entry 6 (the emission maximum for [Ru(bpy)$_2$(dpb)](PF$_6$)$_2$ is at 916 nm).

Given the difficulty of measuring emission lifetimes in the near-infrared, we used transient absorption monitoring to determine τ. For [Ru(Me$_2$bpy)(Me$_4$bpy)(dpq)]$^{2+*}$, whose emission extends into the visible, $\tau = 324 \pm 10$ ns by emission monitoring and 322 ±16 ns by absorption monitoring. The lifetimes in Table 1 represent the average of at least five measurements differing by no more than 3% at different monitoring wavelengths. Care was taken to ensure that the lifetimes of the characteristic MLCT excited-state bleaches in the region of 420−600 nm matched the positive excited-state absorption features at ~380 nm, which characterize the polypyridyl radical anions.

As discussed previously, the lifetimes of these excited states are up to 100 times longer than would otherwise be expected if bpy were the acceptor ligand.[3a] Their decay is dominated by nonradiative processes. The decrease in the rate constant for nonradiative decay, k_{nr}, is a consequence of the delocalized nature of the π^* framework in the dpq and dpb acceptor ligands and delocalization and rigidity in dpop. At a fixed energy gap, these two features decrease changes in equilibrium displacement for the vibrations that couple the ground and excited states and with it, vibrational overlap and k_{nr}.

For [M(bpy)$_3$]$^{2+}$ (M = Ru, Os) the lowest lying MLCT excited "state" is actually a manifold of closely spaced levels of common orbital origin, which are in rapid thermal equilibrium.[7] A quantitative evaluation of the synergistic ligand effects would demand a detailed study of the temperature dependence of both emission spectra and lifetimes. However, the manifold of low-lying states acts dynamically as a single state at or near room temperature, and it is possible to discuss the results based on the results of emission spectral fitting. In the single mode approximation, this procedure gives the electron-vibrational coupling constant or Huang−Rhys factor, S.[8] It is related to the change in equilibrium displacement, ΔQ_e, by $S = 1/2\ M\omega/\hbar\ (\Delta Q_e)^2$, in which M is the reduced mass, ω (= $2\pi\nu$) the angular frequency for the average coupled vibration, and $\hbar$ is Planck's constant. For the polypyridyl complexes, S and $\hbar\omega$ are average quantities reflecting contributions from a series of medium-frequency ring-stretching modes.[9]

According to the energy gap law for nonradiative decay, k_{nr} is predicted to vary with the $v^* = 0 \rightarrow v = 0$ energy gap, E_0, as shown in eq 1, with S appearing in the vibrational overlap factor γ.

$$k_{nr} \propto \exp\left(-\frac{\gamma E_0}{\hbar\omega}\right) \tag{1a}$$

$$\gamma = \ln\left(\frac{E_0}{S\hbar\omega}\right) - 1 \tag{1b}$$

Typical values of S for bpy complexes are in the range 0.9−1.2 (e.g., 1.12 for [Ru(bpy)$_3$]$^{2+}$ in CH$_3$CN at 300 K) with $h\omega = 1300$ cm^{-1}.[4c−e,9] For the near-IR emitters, $S = 0.46$ for [Ru(Me$_2$bpy)(bpy(COOEt)$_2$(dpb)]$^{2+}$, $S = 0.21$ for [Ru(bpy)$_2$(dpop)]$^{2+}$, and $S = 0.26$ for [(Ru(bpy)$_2$)$_2$(dpop)]$^{4+}$, all under the same conditions. According to eq 1, at an energy gap of 1 000 nm (10 000 cm^{-1}) and quantum spacing of $h\omega = 1300$ cm^{-1}, a decrease in S from 1.0 to 0.4 is sufficient to decrease k_{nr} by a factor of ~10^3.

An additional contribution to enhanced lifetimes for the Ru^{II} complexes comes from the low energies of the MLCT excited states. For a higher energy, Ru^{II}-based MLCT emitter, a contribution to decreased lifetimes occurs by thermal population and nonradrative decay through low-lying, metal-centered dd states.[10] These states are too high in energy to be thermally populated for the near-IR emitters. Indeed, the quantum yields for photodecomposition of the salts in Table 1 at 25 °C in deaerated acetonitrile solution with excess tetrabutylammonium chloride were immeasurably small ($\Phi_{decomp} < 10^{-5}$).

There are limited examples in the literature of near-infrared emitters. They include singlet oxygen,[11] coordinatively labile complexes of the lanthanide and actinide ions,[12] photosensitive, highly conjugated organics, especially those based on porphyrins or cyanines,[13] and anionic complexes of Mo(III) and Re(IV).[14] Our results are important in pointing to the possibility of creating a family of near-IR emitters based on MLCT excited states whose emission energies can be tuned systematically by varying the metal, the acceptor ligand, and the ancillary ligands. Unlike other near-IR dyes, the excited-state lifetimes of these complexes can be controlled systematically by appropriate chemical changes, and they are photochemically stable.

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