Black MLCT Absorbers

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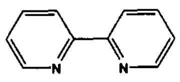
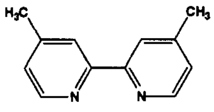
Polypyridyl complexes of ruthenium(II) have been used extensively in studies of photoinduced electron and energy transfer.[1] We recently reported the development of a general procedure for synthesis of tris(heteroleptic) complexes which contain bidentate ligands,[2] e.g. $[\mathrm{Ru(bpy)(Me_2bpy)\{(Et_2CO_2)_2bpy\}}]^{2+}$ (bpy is 2,2′-bipyridine, Me_2bpy is 4,4′-dimethyl-2,2′-bipyridine, and $(EtCO_2)_2$bpy is 4,4′-bis(carboxyethyl)-2,2′-bipyridine), based on sequential addition of the ligands to oligomeric $[\mathrm{Ru(CO)_2Cl_2}]_n$ and the earlier work of Deacon *et al.*[3] We report here application of this methodology to a specific target: *viz.* the systematic design of chromophores with appreciable absorption throughout the near-UV and visible spectral regions. Initial photophysical studies indicate that the metal-to-ligand charge transfer (MLCT) excited states that result can be sufficiently long-lived to undergo efficient electron and energy transfer and they tend to be photochemically inert compared with $[\mathrm{Ru(bpy)_3}]^{2+}$.


bpy



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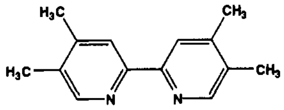
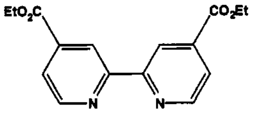


Me₄bpy



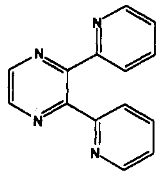
(EtCO₂)₂bpy

Visible light absorptivity in these complexes arises primarily from charge transfer transitions from $d\pi(\mathrm{Ru^{II}})$ to multiple, low-lying π^*(polypyridyl) levels, e.g. eq 1.[4]

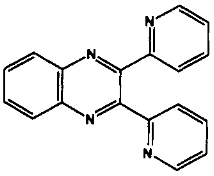
$$\mathrm{Ru^{II}(bpy)_3}^{2+} \xrightarrow{h\nu} \mathrm{Ru^{III}(bpy^{\bullet-})(bpy)_2}^{2+*} \qquad (1)$$

In this example, $d\pi \rightarrow \pi_1^*$ occurs at 450 nm and $d\pi \rightarrow \pi_2^*$ at 243 nm in CH_3CN.[1] Ligand-based, $\pi \rightarrow \pi^*$ transitions with absorptivities >40 000 $m^2\ mol^{-1}$ dominate the near-UV region.[5] The MLCT transitions produce excited states that are largely singlet, e.g. $^1(d\pi^6) \rightarrow {}^1(d\pi^5\pi^{*1})$, but which possess significant triplet character due to spin–orbit coupling.[4] In mixed-chelate complexes, separate transitions occur to each of the ligands, but rapid intramolecular electron transfer leads ultimately to a triplet MLCT state in which the excited electron is localized on the ligand having the lowest π^*-acceptor orbital.[6] Our design strategy for black absorbers was to find ways to systematically shift the $d\pi \rightarrow \pi^*$ bands toward the red region of the spectrum. There are two approaches to this problem. One is to add electron-withdrawing groups to a polypyridyl ligand to lower π^*,[7] and the other is to stabilize the "hole" at $\mathrm{Ru^{III}}$ in the MLCT state by introducing electron-donating ligands.[8]

We have explored the effect of decreasing π^* energies in the series $[\mathrm{Ru(Me_2bpy)(Me_4bpy)(BL)}]^{2+}$ (Me_4bpy is 4,4′,5,5′-tetramethyl-2,2′-bipyridine) where BL is 2,3-bis(2-pyridyl)pyrazine (dpp), 6,7-dimethyl-2,3-bis(2-pyridyl)quinoxaline (Me_2dpq), 2,3-bis(2-pyridyl)quinoxaline (dpq), or 2,3-bis(2-pyridyl)-1,4-diazaanthracene (dpa).[9] Electrochemical measurements show that in this series $E_{1/2} = -1.09$, -0.91, -0.83, and -0.67 V, respectively (in acetonitrile versus ssce), for the first (ligand-based) reduction. Since the BL ligands are more easily reduced than either Me_2bpy or Me_4bpy, the potentials indicate the order of increasing electron-acceptor ability to be dpa > dpq > Me_2dpq > dpp. This ordering tracks the lowest-energy MLCT bands (Figure 1a), and is consistent with earlier observations on related complexes.[10]



dpp



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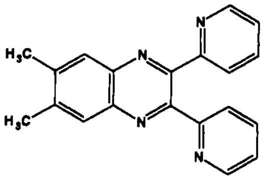
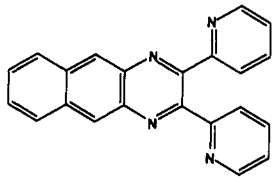


Me₂dpq



dpa

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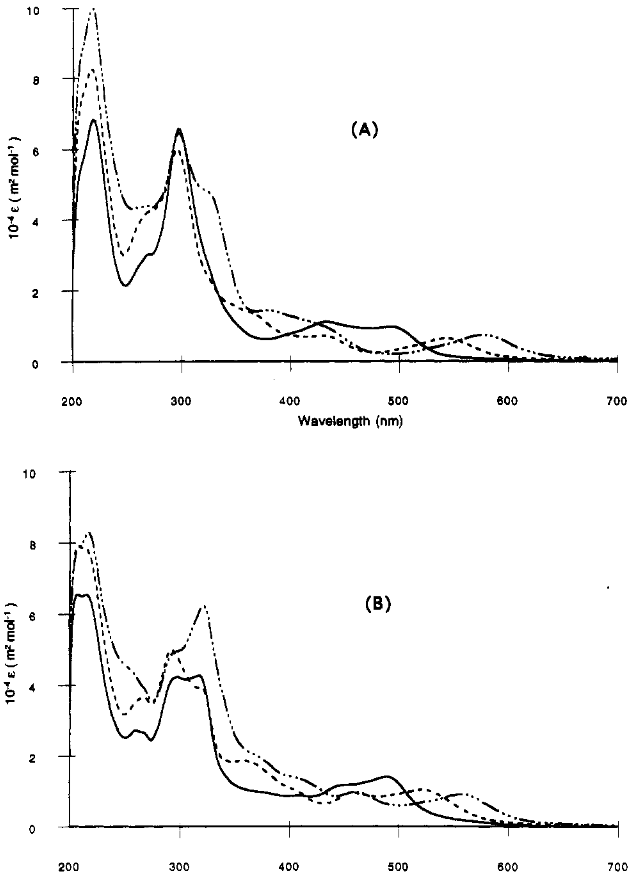

Figure 1. UV-visible absorption spectrum of (A) $[Ru(Me_2bpy)(Me_4bpy)(BL)]^{2+}$, and (B) $[Ru(Me_2bpy)\{(EtCO_2)_2bpy\}(BL)]^{2+}$ in acetonitrile solution BL = dpa (–····–), dpq (- - -), dpp (—).

The shift to lower energy reaches λ_{max} = 568 nm for BL = dpa, but at the expense of creating a "spectral gap" with a minimum at ~470 nm. The gap can be filled by using a ligand with an intermediate π^*-acceptor orbital. This is illustrated in Figure 1b for the series $[Ru(Me_2bpy)\{(EtCO_2)_2bpy\}(BL)]^{2+}$. With BL = dpa, bands arising from $d\pi \rightarrow \pi_1^*$ are observed at 548, ~452, and ~410 nm (to dpa, $(EtCO_2)_2bpy$, and Me_2bpy, respectively), while bands from $d\pi \rightarrow \pi_2^*$ appear at higher energy.

It is possible to extend MLCT absorption to even lower energies by incorporating an electron-donating ligand that possesses significant σ- and π-donating character; we have used diethyldithiocarbamate anion, Et_2dtc^-.[11] Anionic ligands stabilize the excited states by electron donation to Ru^{III} (eq 1) causing a general red shift in the MLCT bands. Absorption spectra for $[Ru\{(EtCO_2)_2bpy\}(dpa)(Et_2dtc)]^+$ and $[Ru(Me_2bpy)\{(EtCO_2)_2bpy\}(Et_2dtc)]^+$ are shown in Figure 2. In the former, significant visible light absorption ($\epsilon > 3000$ m² mol⁻¹) is extended past 700 nm. Both exhibit significant light absorption throughout the visible.

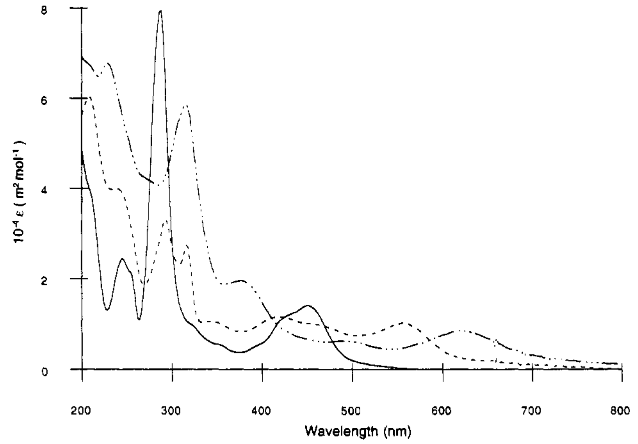

Figure 2. UV-visible absorption spectra of $[Ru\{(EtCO_2)_2bpy\}(dpa)(Et_2dtc)]^+$ (–····–) and $[Ru(Me_2bpy)\{(EtCO_2)_2bpy\}(Et_2dtc)]^+$ (- - -) in acetonitrile solution. The spectrum of $[Ru(bpy)_3]^{2+}$ is shown for comparison (—).

These low-energy broad-band absorbers may have useful excited state properties as well. For instance, $[Ru(Me_2bpy)\{(EtCO_2)_2bpy\}(dpa)]^{2+*}$ is a near-IR emitter ($\lambda_{max} > 850$ nm in CH_3CN at 298 K) with $\tau = 98(\pm 5)$ ns ($k = 1.02 \times 10^7$ s⁻¹),[12] as determined by transient absorption measurements (3–4 mJ/pulse). Emission from $[Ru(Me_2bpy)\{(EtCO_2)_2bpy\}(Et_2dtc)]^{+*}$ occurs at λ_{max} = 1100 nm (in CH_3CN at 298 K) with $\tau = 12(\pm 4)$ ns, as measured by transient absorption (λ_{ex} = 532 nm, <5 mJ/pulse).[13] All of these complexes are photochemically inert. In the future we will extend the overlapping band strategy and known approaches for extending excited state lifetimes to prepare a family of black absorbers which can be used as sensitizers.

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(9) Satisfactory elemental analyses (±0.4% for C,H,N) were found for all the complexes reported in this manuscript.

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(12) We acknowledge Dr. S. L. Mecklenburg for this measurement.

(13) We acknowledge Dr. J. V. Caspar for this measurement.

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