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Evidence for Static Quenching of MLCT Excited States by Iodide

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The metal-to-ligand charge-transfer (MLCT) excited states of $Ru(deeb)(bpy)_2(PF_6)_2$ [where bpy is 2,2-bipyridine and deeb is 4,4′-$(CO_2CH_2CH_3)_2$-2,2′-bipyridine] in acetonitrile or dichloromethane were found to be quenched by iodide at room temperature. The ionic strength dependence of the optical spectra gave evidence for ion pairing. Iodide is found to quench the photoluminescence (PL) intensity and influence the spectral distribution of the emitted light. A static component to the time-resolved PL quenching provided further evidence for ground-state adduct. Stern–Volmer analysis of the static component provided an estimate of the iodide–$Ru(deeb)(bpy)_2^{2+}$ adduct equilibrium constant in dichloromethane, $K_{sv} = 40\,000$ M^{-1}. Transient absorption studies clearly demonstrate that an electron-transfer quenching mechanism is operative and that $I_2^{-\bullet}$ can be photoproduced in high yield, $\phi = 0.25$. For $Ru(bpy)_3(PF_6)_2$ in acetonitrile, similar behavior could be observed at iodide concentrations >100 times that required for dichloromethane.

Electron-transfer quenching of metal-to-ligand charge-transfer (MLCT) excited states by iodide is generally found to be an inefficient process.[1] For example, Demas and Addington reported Stern−Volmer quenching constants of <0.5 M^{-1} for $Ru(bpy)_3^{2+*}$ quenching by iodide.[1] This observation presumably reflects the very positive formal iodine reduction potential, $E°(I^{\bullet/-}) = 1.3$ V vs NHE, and the fact that most MLCT excited states are simply not strong enough oxidants.[2] Here, we communicate experimental conditions where Ru(II) polypyridyl excited states efficiently oxidize iodide. We provide strong evidence for a static electron-transfer mechanism, wherein ruthenium(II) bipyridine iodide adducts are formed with favorable energetics for light-induced electron transfer. We provide an estimate of the adduct formation constant and show that visible-light excitation efficiently produces long-lived charge-separated products. The implications of these observations for solar energy conversion are also discussed.

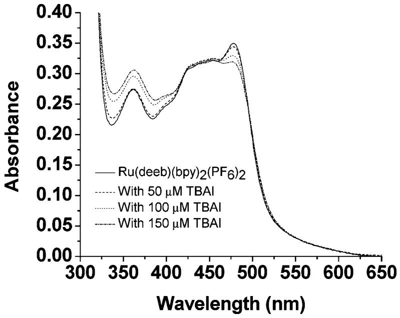

Figure 1. Visible absorption spectra of $Ru(deeb)(bpy)_2(PF_6)_2$ in CH_2Cl_2 and with the indicated concentrations of tetrabutylammonium iodide.

Shown in Figure 1 is the absorption spectrum of Ru(deeb)-$(bpy)_2(PF_6)_2$ in CH_2Cl_2, where bpy is 2,2′-bipyridine and deeb is 4,4′-$(CO_2CH_2CH_3)_2$-2,2′bipyridine. The Ru → bpy and Ru → deeb charge-transfer bands are not well resolved; however, the latter accounts for most of the oscillator strength on the lower-energy side, $\lambda \approx 500$ nm.[3] The addition of TBAI (tetrabutylammonium iodide) resulted in isosbestic changes in the absorption spectra to about 100 μM. With 50 μM $Ru(deeb)(bpy)_2^{2+}$ and iodide, Job plots revealed a 1:1 stoichimetry.[4] At higher iodide concentrations, the isosbestic points were lost. A decrease in intensity and shift of the Ru → deeb MLCT band was observed, as well as an increase in intensity around 365 nm. These spectral changes could be largely reversed if the ionic strength was increased with excess $TBAPF_6$. The same behavior was observed in acetonitrile, although the iodide concentration had to be increased by greater than 2 orders of magnitude. $Ru(bpy)_3$-$(PF_6)_2$ showed smaller spectral changes with added iodide in dichloromethane.

The steady-state photoluminescence (PL) intensity from $Ru(deeb)(bpy)_2^{2+*}$ in CH_2Cl_2 was quenched by the addition of iodide, and the spectral distribution of the emitted light was changed (Figure 2). The normalized spectra show that the long-wavelength region of the emission was unchanged by the addition of iodide whereas the relative intensity in the blue region was enhanced. Therefore, the full width at half-maximum (fwhm) increased by 670 cm^{-1} when the

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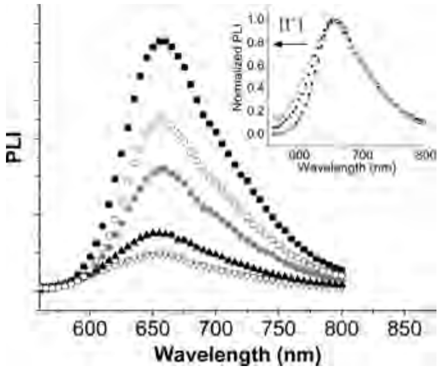

Figure 2. Steady-state photoluminescence spectra of Ru(deeb)(bpy)$_2^{2+*}$ (■) in CH_2Cl_2 and with (gray dot) 15, (▲) 25, and (▽) 55 μM tetrabutylammonium iodide. The spectra are largely reversible upon addition of excess tetrabutylammonium hexafluorophosphate (○). The inset depicts the normalized spectra (with the 15 μM data point removed for clarity) and the observed blue shift of the high-energy-band side as the iodide concentration increases.

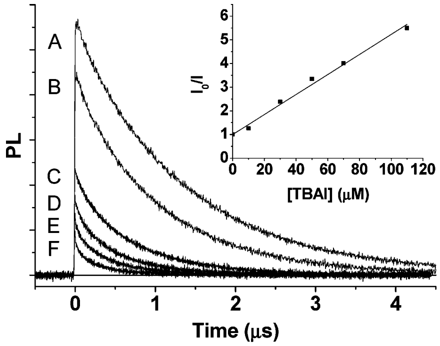

Figure 3. Time-resolved PL decays of Ru(deeb)(bpy)$_2^{2+}$ as a function of TBAI concentration: (A) 0, (B) 10, (C) 30, (D) 50, (E) 70, and (F) 110 μM in dichloromethane. The solution was excited with 532.5-nm light (8−10 ns fwhm, 4.1 mJ/pulse), and the emission was observed at 650 nm. The inset shows a Stern−Volmer plot of (■) the initial ($t = 0$ s) amplitudes and (—) the best-fit line, $K_{sv} = 40\,000$ M^{-1}.

iodide concentration was increased to 55 μM. The PL intensity was enhanced by the addition of excess TBAPF$_6$, and the spectral distribution was restored to the same values as observed in neat dichloromethane. Ru(bpy)$_3^{2+*}$ showed similar quenching with added iodide in dichloromethane, although the PL spectral shifts were not observed.

In time-resolved PL studies, it was found that the initial amplitude and the lifetimes were quenched by iodide, consistent with both static and dynamic processes (Figure 3).[5] Interestingly, the lifetimes were nonexponential in the presence of iodide. The origin of this effect will be the subject of future studies but might reflect solution heterogeneity and/or more complex dynamic processes. The static component cannot be explained by trivial spectral changes and was well described by the Stern−Volmer model from which an adduct formation constant was abstracted. The Figure 3 inset gives representative data where I is the observed amplitude at $t = 0$ s.[5] We emphasize that this is a preliminary analysis and that the time-resolved PL data also show evidence for complex dynamic quenching pathways whose origins are not yet fully understood.

In nanosecond time-resolved absorption studies, pulsed 532.5-nm light excitation (8−10 ns fwhm, 2.5 mJ/pulse) of 14 μM Ru(deeb)(bpy)$_2^{2+}$ in 10 mM TBAI in dichloromethane resulted in the appearance of the well-known absorption spectra of $I_2^{-\bullet}$ and Ru(deeb$^-$)(bpy)$_2^+$ with a quantum yield of ~0.25.[6] The formation of $I_2^{-\bullet}$ occurs within our instrument response time, ~10 ns, with no measurable recombination on a tens-of-microseconds time scale at the concentrations used in these studies. Therefore, the iodine atom is not observed spectroscopically as an intermediate in this photochemistry; however, $I^\bullet$ is known to react with iodide to form $I_2^{-\bullet}$, with $K_{eq} = 1.2 \times 10^4$ M^{-1} in H_2O at room temperature.[7]

The changes to the MLCT absorption and the appearance of static components in the time-resolved emission provide compelling evidence for a ground-state adduct between the Ru(II) compounds and iodide. The isosbestic points and Job plots are consistent with a 1:1 adduct at low iodide concentrations (eq 1).

$$\mathrm{Ru(deeb)(bpy)_2}^{2+} + \mathrm{I}^- \rightleftharpoons [\mathrm{Ru(deeb)(bpy)_2, I}]^+ \qquad (1)$$

The fact that the spectral changes can be reversed by addition of an inert electrolyte is also consistent with this conclusion.

A molecular-level description of the [Ru(deeb)(bpy)$_2$, I]$^+$ adduct is uncertain; however, precedence for both ion pairing and specific π interactions with the diimine ligands can be found in the literature.[8−12] Stufkens has prepared Ru(II) compounds with coordinated iodide and bpy ligands that display absorption bands that are iodide → bpy charge transfer in nature.[10−13] Of particular relevance to this report is the work of Elliott, who has provided X-ray crystallographic and optical data of Cr(III) compounds that clearly demonstrate bipyridine−iodide adduct formation.[9] A variety of aromatic compounds are also well-known to form π adducts with iodide, many of which display well-defined iodide → π^* absorption bands.[14−17] In the present case, the intense MLCT absorptions preclude the direct analysis of any charge-transfer bands that might be present (Figure 1).

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It is unclear whether the absorption changes with iodide result from underlying iodide → deeb (or bpy) transitions or if the iodide adducts simply perturb the energetics of the MLCT absorption bands. In either case, the static emission quenching does provide an estimate of the adduct formation constant for $[\mathrm{Ru(deeb)(bpy)_2, I}]^+$ of 40 000 M^{-1}.

In the dye-sensitized solar cells of Gratzel and co-workers, iodide redox mediators are by far the most efficient.[18] In this regard, the adducts described herein might lower the excited-state electron injection yields and be detrimental for energy conversion. However, if static charge-transfer quenching occurs in the Gratzel solar cell, an alternative energy conversion mechanism could occur that might be as efficient as excited-state injection (eq 2)[19−22]

$$[\mathrm{TiO_2/S, I^-}]^{+*} \rightarrow [\mathrm{TiO_2/S', I^\bullet}]^+ \rightarrow [\mathrm{TiO_2(e^-)/S'', I^\bullet}]^+ \quad (2)$$

where S represents $\mathrm{Ru^{III}(deeb^-)(bpy)_2}^{2+*}$, S′ represents $\mathrm{Ru^{II}(deeb^-)(bpy)_2}^+$, and S″represents $\mathrm{Ru^{II}(deeb)(bpy)_2}^{2+}$. Photoinitiated static electron transfer yields $\mathrm{Ru^{II}(deeb^-)(bpy)_2}^+$, and the reduced deeb ligand injects an electron into $\mathrm{TiO_2}$. Such a dye sensitization mechanism has been observed spectroscopically with other electron donors and is directly relevant to the celebrated photogalvanic cells that were popular in the 1960s.[22]

As described by Kamat and others,[23−25] high iodide concentrations and the semiconductor surface can facilitate charge-transfer processes with iodide. An advantage of reductively quenching the excited state is that the reduced ruthenium polypyridyl sensitizer is a stronger reductant than the MLCT excited states by ∼400 mV.[19] In principle, this additional energy can be abstracted to give larger open-circuit photovoltages in regenerative solar cells.[19] Therefore, efficient reductive charge transfer through ion pairs followed by electron transfer to a semiconductor surface might be an attractive approach for solar energy conversion.

In conclusion, we have demonstrated a static electron-transfer quenching mechanism for iodide photooxidation by ruthenium bipyridyl compounds for the first time. The static mechanism results from the light excitation of ground-state adducts formed between the Ru(II) cations and iodide. With micromolar concentrations in dichloromethane at room temperature, a 1:1 adduct is formed with $K_{\mathrm{sv}} = 40\,000\ \mathrm{M}^{-1}$. The spectroscopic data strongly suggest that the adducts involve interactions between iodide and the diimine ligand(s) as well as ion pairing. Pulsed-light excitation of these adducts ultimately yields $[\mathrm{Ru(deeb^-)(bpy)_2}^+, \mathrm{I_2}^{-\bullet}]$ charge-separated states with quantum yields of 0.25. Thus, for solar energy conversion applications, a green photon can store ∼1.7 eV of free energy for tens of microseconds.

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