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# High-Extinction Ruthenium Compounds for Sunlight Harvesting and Hole Transport

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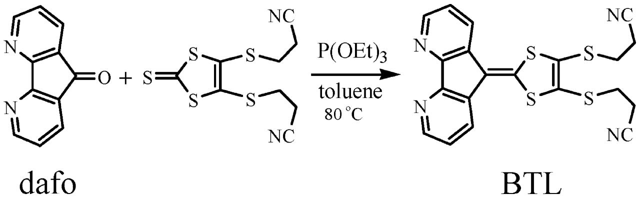
The compounds $Ru(bpy)_2(BTL)(PF_6)_2$ and $Ru(deeb)_2(BTL)(PF_6)_2$, where bpy is 2,2′-bipyridine, deeb is 4,4′-$(C_2H_5CO_2)_2$-bpy, and BTL is 9′-[4,5-bis(cyanoethylthio)]-1,3-dithiol-2-ylidene]-4′,5′-diazafluorene, were found to have very high extinction coefficients in the visible region. In an acetonitrile solution, the extinction of $Ru(deeb)_2(BTL)(PF_6)_2$ was $\epsilon = 44\,000 \pm 1000$ $M^{-1}$ $cm^{-1}$ at $\lambda = 470$ nm. Two quasi-reversible oxidation waves, $E_{1/2} = +0.88$ and $+1.16$ V, and an irreversible reduction, $E_{pr} = -1.6$ V, were observed versus ferrocene ($Fc^{+/0}$). At −40 °C, a state was observed with spectroscopic properties characteristic of a metal-to-ligand charge-transfer excited state, $\tau = 25$ ns. This same compound was found to photoinject electrons into $TiO_2$ with a quantum yield $\Phi = 0.3 \pm 0.2$ for 532.5 or 417 nm light excitation in a 0.1 M $LiClO_4$/acetonitrile electrolyte. In regenerative solar cells, a sustained photocurrent was observed with a maximum incident photon-to-current efficiency of 0.4. The photocurrent action and absorptance spectra were in good agreement, consistent with injection from a single excited state.

Coordination compounds that efficiently harvest solar energy are of great importance in inorganic chemistry. Ruthenium tris(bipyridine) has attracted much interest in this regard with metal-to-ligand charge-transfer (MLCT) absorption bands in the visible region and a molar extinction coefficient ($\epsilon$) of about 15 000 $M^{-1}$ $cm^{-1}$.[1] Substitution on the bipyridine rings and/or coordination of nonchromophoric ligands allow the absorption to be tuned throughout the visible and near-IR regions with modest extinction coefficient changes.[2–6] In contrast, natural and synthetic organic pigments also absorb solar photons but with extinctions that are often in excess of 200 000 $M^{-1}$ $cm^{-1}$.[7] The low extinction of ruthenium polypyridyl compounds precludes their application in many energy conversion assemblies. We recently discovered that the ruthenium(II) coordination compounds with the bpy-dithioline (BTL) ligand shown are intensely colored. The spectroscopic and redox properties of $Ru(bpy)_2(BTL)(PF_6)_2$ as well as a derivative with functional groups for binding to mesoporous nanocrystalline (anatase) $TiO_2$ thin films are reported herein. The yields for interfacial charge transfer have also been quantified by spectroscopic and photoelectrochemical methods.

**Scheme 1**



The ligand of interest, 9′-[4,5-bis(cyanoethylthio)]-1,3-dithiol-2-ylidene]-4′,5′-diazafluorene abbreviated as BTL, was recently communicated in *Inorganic Chemistry* for applications in supramolecular chemistry.[8] The preparative procedure employed here was similar and involved a phosphite-mediated coupling to the “dafo” bpy ligand shown in Scheme 1. Coordination to *cis*-$Ru(bpy)_2(Cl)_2$ or *cis*-$Ru(deeb)_2Cl_2$ (where deeb is 4,4′-$(C_2H_5CO_2)_2$-bpy), isolation, and purification yielded the desired $Ru(bpy)_2(BTL)^{2+}$ and $Ru(deeb)_2(BTL)^{2+}$ compounds usually as $PF_6^-$ salts. $^1H$ NMR, elemental analysis, and spectroscopic data were consistent with the proposed formulations.

Figure 1 shows the UV–visible absorption spectrum in a $CH_3CN$ solution. The inset displays the concentration dependence of the $Ru(deeb)_2(BTL)(PF_6)_2$ compound. The normalized absorption spectra were concentration-indepen-

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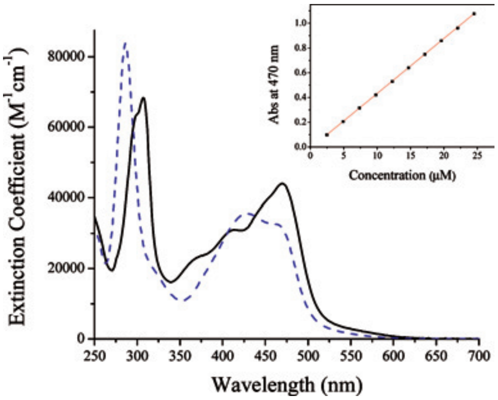

**Figure 1.** Absorption spectra of $Ru(deeb)_2(BTL)(PF_6)_2$ (solid line) and $Ru(bpy)_2(BTL)(PF_6)_2$ (dashed line) in neat acetonitrile. The inset shows the concentration dependence of the $Ru(deeb)_2(BTL)(PF_6)_2$ absorbance at 470 nm. The best-fit line yielded an extinction coefficient of 44 300 $M^{-1}$ $cm^{-1}$.

dent, and multiple measurements yielded $\epsilon = 44\,000 \pm 1000$ $M^{-1}$ $cm^{-1}$ at $\lambda = 470$ nm. The corresponding bpy compound showed properties similar to those of the deeb analogue $\epsilon = 32\,000 \pm 2000$ $M^{-1}$ $cm^{-1}$ at $\lambda = 468$ nm. The free BTL ligand has an extinction coefficient of 34 700 $M^{-1}$ $cm^{-1}$ at 416 nm but did not absorb light appreciably beyond 450 nm. The visible absorption spectrum of the ruthenium(II) compounds is complicated with overlapping intraligand transitions[9] on the BTL ligand as well as Ru → BTL and Ru → bpy MLCT transitions. The higher extinction for the $Ru(deeb)_2(BTL)^{2+}$ compound was expected because it is known that substituents with low-lying $\pi$ orbitals (such as aromatics, esters, carboxylic acids, or unsaturated organics) can enhance MLCT extinction coefficients relative to unsubstituted bpy.[10–12] Interestingly, 4 and 4′ disubstitution of 2,2′-bipyridine increases $\epsilon$ more effectively than does substitution in the 5 and 5′ positions.[11,12] The ester groups also allowed for binding to mesoporous nanocrystalline $TiO_2$ thin films from an acetonitrile solution.

The redox properties of the compounds were characterized by cyclic voltammetry in 0.1 M $LiClO_4$/acetonitrile solutions. Two quasi-reversible oxidation waves were observed for $Ru(deeb)_2(BTL)(PF_6)_2$, $E_{1/2} = +0.88$ and +1.16 V, and one for $Ru(bpy)_2(BTL)(PF_6)_2$, $E_{1/2} = +0.85$ V versus ferrocene ($Fc^{+/0}$). The first oxidation is assigned to the BDT ligand and the second to the ruthenium(II) metal center. Our inability to resolve the metal-centered oxidation for the bpy compound probably stems from insolubility of the oxidized product. Both compounds showed an irreversible reduction at $E_{pr} \sim -1.6$ V versus $Fc^{+/0}$. Attempts to obtain the absorption spectra of the reduced and oxidized forms were frustrated by sample decomposition.

The compounds were only weakly emissive at room temperature with excited-state lifetimes near our instrumental response, $\tau < 10$ ns. At −40 °C in $CH_3CN$, a longer-lived state was observed with spectroscopic properties characteristic of an MLCT excited state (Figure 2). The excited state decayed to the ground state with first-order kinetics, $\tau = 25$ ns.

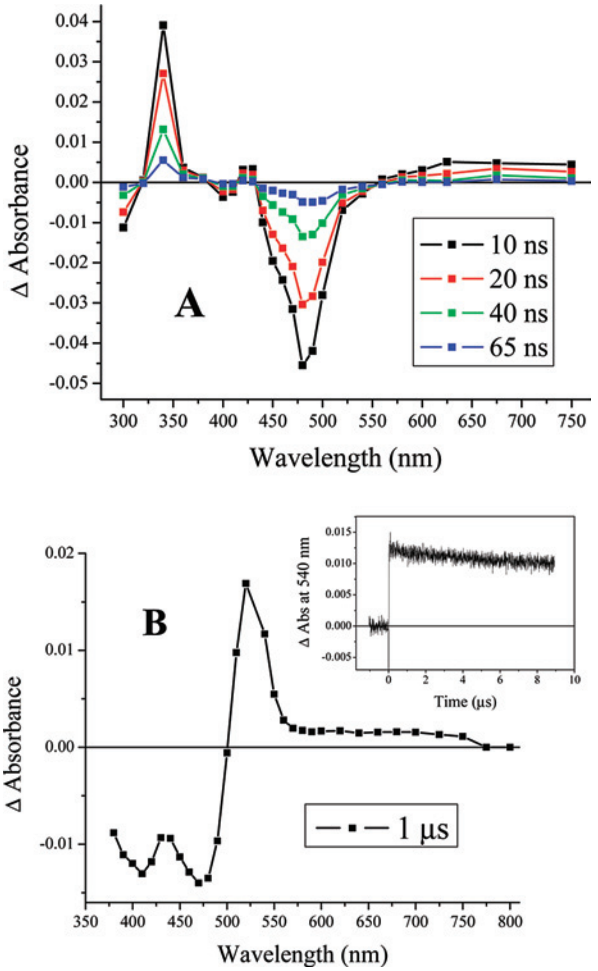

**Figure 2.** Absorption difference spectrum observed 1 $\mu$s after pulsed 532.5 nm light excitation of $Ru(deeb)_2(BTL)(PF_6)_2$ (A) in neat acetonitrile at −40 °C and (B) anchored to a nanocrystalline $TiO_2$ thin film in 0.1 M $LiClO_4$/$CH_3CN$ at room temperature. The inset in part B shows a single wavelength absorption change monitored at 540 nm.

Pulsed-light excitation of a $Ru(deeb)_2(BTL)/TiO_2$ thin film immersed in 0.1 M $LiClO_4/CH_3CN$ resulted in the appearance of a single product assigned to a charge-separated state comprised of the oxidized sensitizer and an electron in $TiO_2$, $Ru(deeb)_2(BTL^+)/TiO_2(e^-)$. The weak absorption in the red was expected for $TiO_2(e^-)$,[13] and the positive absorption near 520 nm was assigned to the oxidized dithioline ligand.[14] Thus, within 10 ns of light excitation, an electron is injected into $TiO_2$ and the hole is translated from the metal center to the dithioline-containing BTL ligand. The driving force for hole transfer after injection is −280 mV but was slightly uphill from the MLCT excited state, which presumably explains why it was not observed in a fluid solution (Figure 2A). We note that, after electron injection by the N3 sensitizer, *cis*-$Ru(dcb)_2(NCS)_2$, a similar hole transfer from ruthenium(III) to the thiocyanate ligands has been pro-

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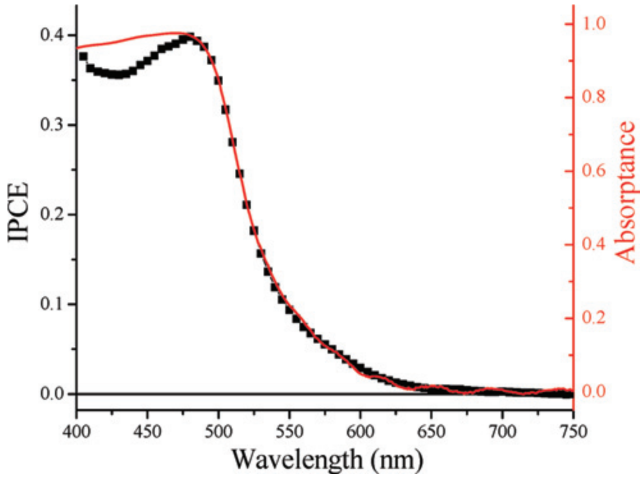

**Figure 3.** IPCE and absorptance spectrum of a Ru(deeb)$_2$(BTL)/TiO$_2$ thin film. The photocurrent action spectrum was measured in 0.50 M LiI and 0.50 M I$_2$/acetonitrile, while the absorptance spectrum was measured in 0.1 M LiClO$_4$/acetonitrile.

posed.[15] Hole transfer to more weakly coupled electron donors has been demonstrated at sensitized interfaces.[16–18]

Irradiance data demonstrated that the yields for excited-state injection and hole transfer were the same for 532.5 and 417 nm light excitation. We have developed thin film actinometers that allow absolute measurement of the quantum yield(s) from data like that shown in Figure 2B.[19] The analysis, however, requires knowledge of the change in the extinction coefficient that accompanies charge transfer, data that could not be obtained because of the poor stability of the oxidized forms of Ru(deeb)$_2$(BTL)(PF$_6$)$_2$. If one starts with the poor assumption that the oxidized sensitizer does not absorb light at 420 nm, the yield would be $\Phi = 0.1$ and increases to 0.5 if the extinction were 34 000 M$^{-1}$ cm$^{-1}$. When the literature value for the dithioline radical cation extinction coefficient was used, the yield was $\Phi = 0.2$.[14]

The incident photocurrent efficiency (IPCE) was measured in regenerative photoelectrochemical cells with a platinum counter electrode and 0.5 M LiI and 0.05 M I$_2$/acetonitrile solutions (Figure 3). The maximum IPCE was 40%, and the photocurrent action and absorptance spectra were in good agreement, consistent with injection from a single excited state. In other words, even though there was evidence for Ru$^{II}$ → deeb, Ru$^{II}$ → BTL, and $\pi \rightarrow \pi^*$ intraligand BTL transitions in the absorption spectrum of this compound, there was no evidence for preferential injection from any one of these excited states in the regenerative solar cell. This is consistent with the fact that injection and hole transfer yields were, within experimental error, the same with green and blue light excitation. It is likely that the less than 0.5 photocurrent efficiency results from the poor injection yields inferred from the spectroscopic measurements. Rapid sensitizer regeneration through iodide oxidation is indeed expected because of the positive ground-state reduction potential.[20]

A complete understanding of the factors that influence the injection and hole transfer yields for Ru(deeb)$_2$(BTL)/TiO$_2$ is absent. The weak emission and short excited-state lifetime of Ru(deeb)$_2$(BTL)$^{2+*}$ and Ru(bpy)$_2$(BTL)$^{2+*}$ at room temperature in a fluid solution are consistent with the presence of low-lying ligand-field (LF) states.[1] Previous studies of ruthenium(II) bipyridyl “dafo” compounds have shown that the bridge opens the bite angle between the pyridyl nitrogens, which thereby reduces the metal−nitrogen $\sigma$ overlap and stabilizes the LF states.[21,22] We have previously presented compelling evidence that MLCT deactivation by LF states in ruthenium and iron sensitizers can lower the electron injection yields into TiO$_2$.[23–25] One method by which this can be avoided is to utilize coordination compounds that have LF states at much higher energy, such as those based on osmium(II).[1]

In conclusion, a ruthenium(II) bipyridine dithioline compound with a notably high extinction coefficient in the visible region was found to photoinject electrons into TiO$_2$ and support intramolecular hole transfer away from the ruthenium center. While distinct intraligand and MLCT absorptions were apparent in the electronic spectrum of Ru(deeb)$_2$(BTL)$^{2+}$, the photophysical and electron-transfer behavior near room temperature on nanosecond and longer time scales was consistent with the presence of a single MLCT excited state. The approach of utilizing intraligand charge transfer to enhance extinction coefficients *and* promote hole transfer was successful. The dithioline ligands bridging the 3 and 3′ positions of bipyridine represent a viable alternative to the more traditional and widely pursued approach of introducing conjugated groups in the 4 and 4′ positions. High extinction sensitizers would enable the production of efficient solar cells based on thinner nanocrystalline TiO$_2$ films or alternative geometries with inherently low surface areas. It is notable that these first derivative dithioline compounds have extinctions comparable to the highest ever reported based on 4,4′-disubstituted bipyridylruthenium(II) compounds. Fine-tuning of the dithioline ligand and the coordination environment about ruthenium and osmium is expected to lead to further improvements. Such studies are underway in our laboratories.

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