

Excited State Interfacial Electron Transfer from a Compound with a Single Pyridine Ligand

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Received July 18, 2003

The coordination compound $\text{Ru}(\text{NH}_3)_5(\text{eina})(\text{PF}_6)_2$, where eina is ethyl isonicotinate, was synthesized and attached to optically transparent nanocrystalline (anatase) TiO_2 films, abbreviated $\text{Ru}(\text{NH}_3)_5(\text{eina})/\text{TiO}_2$. The metal-to-ligand-charge-transfer (MLCT) absorption was found to shift in wavelength with solvent. The absorption maximum of the low energy MLCT band was observed at 486 nm in acetonitrile and 528 nm in dimethylformamide for $\text{Ru}(\text{NH}_3)_5(\text{eina})(\text{PF}_6)_2$ and at 512 and 555 nm for $\text{Ru}(\text{NH}_3)_5(\text{eina})/\text{TiO}_2$, respectively. The compound was found to be nonemissive with an excited state lifetime <10 ns under all conditions studied. Light excitation in fluid solution and when attached to insulating ZrO_2 films resulted in a loss of the MLCT absorption, consistent with ligand field photochemistry. Pulsed light excitation of $\text{Ru}(\text{NH}_3)_5(\text{eina})/\text{TiO}_2$ yields an absorption difference spectrum consistent with an interfacial charge separated state, $\text{Ru}^{\text{III}}(\text{NH}_3)_5(\text{eina})/\text{TiO}_2(\text{e}^-)$. This state forms within 10 ns and returns cleanly to ground state product within milliseconds. The injection quantum yields were determined by comparative actinometry and were found to be excitation wavelength dependent: $\phi_{\text{inj}}(417 \text{ nm}) = 0.30 \pm 0.05$ and $\phi_{\text{inj}}(532.5 \text{ nm}) = 0.15 \pm 0.03$. Regenerative solar cells based on $\text{Ru}(\text{NH}_3)_5(\text{eina})/\text{TiO}_2$ with 0.5 M TBAI, where TBA is tetrabutylammonium, and 0.05 M I_2 in acetonitrile were very inefficient. Sluggish iodide oxidation is expected, on the basis of the negative $E^\circ(\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}) = +0.17$ (V vs Ag/AgCl) reduction potential, and this presumably allows a greater fraction of the injected electrons to recombine with the oxidized compound thereby lowering the solar cell efficiency.

There exists considerable interest in dye-sensitized semiconductor materials for applications in regenerative solar cells.¹ The most efficient materials are composed of nanocrystalline (anatase) TiO_2 thin films sensitized to visible light with Ru(II) polypyridine compounds.^{1–3} The polypyridine ligands play at least two important roles. First, they are

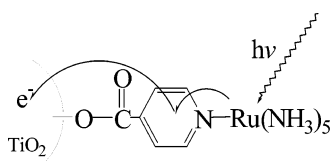
chromophoric and accept charge in the metal-to-ligand charge-transfer (MLCT) excited state. Second, they generally have functional groups, such as carboxylic acids,² acetylacetonates,³ or phosphonates,⁴ that bind the compounds to the semiconductor surface. Thus, sensitization with Ru(II) compounds usually involves interfacial charge-transfer from an electron localized on a surface bound bipyridyl or terpyridyl ligand to the TiO_2 acceptor states.⁵ The most successful ruthenium polypyridyl sensitizer is *cis*- $\text{Ru}(\text{dcb})_2(\text{NCS})_2$, where dcb is 4,4'-(COOH)₂-2,2'-bipyridine, anchored to TiO_2 surface via two or more of its carboxylic acid groups.^{2b,6} The carboxylic groups are believed to enhance the electronic coupling of the MLCT excited state with the $\text{Ti}^{\text{IV}}(3d)$ conduction band orbital manifold.^{2b,6,7} It is known that such interfacial charge-transfer processes can take place on a pico- to femtosecond time scale.⁸ What remains unknown is how many pyridine ligands are required for efficient dye sensitization. Here we report compelling evidence that this can be accomplished with a Ru(II) compound that contains a single pyridine ligand and carboxylic acid functional group, Scheme 1.

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Scheme 1



The compound of interest is $\text{Ru}(\text{NH}_3)_5(\text{eina})(\text{PF}_6)_2$, where eina is 4- CO_2Et -pyridine (ethyl isonicotinate). Hydrogen NMR and elemental analysis were consistent with the given formulation. We note that closely related compounds have been prepared and their ligand field (LF) photochemistry is well documented.^{9,10} The preparation of nanocrystalline TiO_2 and ZrO_2 thin films as well as the spectroscopic and electrochemical methods have been previously described.¹¹ The sensitizers were bound from acetonitrile solutions with pH 1 pretreated TiO_2 as previously published.¹¹ The concentration-dependent binding was well described by the Langmuir adsorption isotherm model, with limiting surface coverages of $3 \pm 2 \times 10^{-8} \text{ mol/cm}^2$ and adduct formation constant of $2 \times 10^5 \text{ M}^{-1}$, typical of Ru(II) compounds based on dcb ligands.^{1,12} The asymmetric C=O stretch is observed at 1720 cm^{-1} for the free compound and shifts to 1734 cm^{-1} upon surface binding. Surface coordination and solvent also have a profound impact on the $\text{Ru}^{\text{III/II}}$ reduction potentials. Cyclic voltammetry measurements gave quasireversible waves with $E_{1/2}(\text{Ru}^{\text{III/II}}) = 172 \text{ mV}$ in acetonitrile and -36 mV in dimethylformamide (vs Ag/AgCl) relative to 460 and 180 mV for the free compounds. In contrast, ruthenium trisbipyridyl compounds, such as $\text{Ru}(\text{bpy})_2(\text{dcb})^{2+}/\text{TiO}_2$, have $\text{Ru}^{\text{III/II}}$ reduction potentials that are within 50 mV of those measured in fluid acetonitrile electrolyte¹¹ while more environmentally sensitive compounds, such as $\text{Ru}(\text{dcb})(\text{CN})_4^{2-}/\text{TiO}_2$, display $E_{1/2}(\text{Ru}^{\text{III/II}})$ shifts of comparable magnitude to those observed here.¹³

The $\text{Ru}(\text{NH}_3)_5(\text{eina})(\text{PF}_6)_2$ compound has an intense MLCT absorption band centered at 486 nm ($\epsilon_{\text{max}} = 1.47 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) in acetonitrile. When anchored to TiO_2 , the MLCT absorption band broadens and the maximum shifts to lower

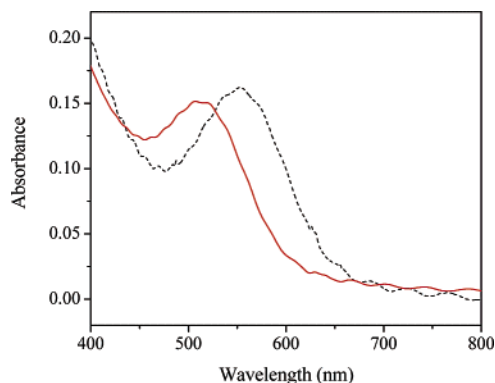


Figure 1. Absorption spectra of $[\text{Ru}(\text{NH}_3)_5(\text{eina})](\text{PF}_6)_2$ adsorbed on TiO_2 in neat acetonitrile (—) and dimethylformamide (---).

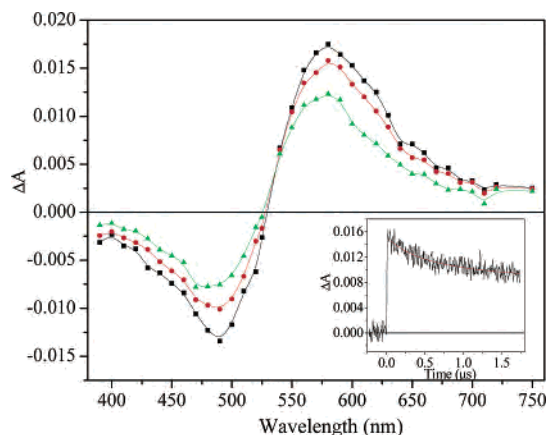


Figure 2. Absorption difference spectra observed after 532.5 nm laser light excitation ($\sim 12 \text{ mJ/pulse}$, 10 ns fwhm) of $\text{Ru}(\text{NH}_3)_5(\text{eina})/\text{TiO}_2$ in acetonitrile. The spectra are shown at delays of 0 ns (■), 200 ns (●), and 2 μs (▲). The inset shows an absorption transient monitored at 600 nm with an overlaid fit to a second-order equal-concentration kinetic model.

energy. The surface bound and free compound were highly solvatochromic.¹³ In dimethylformamide, the MLCT maximum red shifts to 555 nm, Figure 1. Previous studies have proposed that the solvatochromism in this class of compounds is due to the hydrogen bonding of the ammine ligands with solvent molecules.^{14,15}

$\text{Ru}^{\text{II}}(\text{NH}_3)_5(\text{eina})^{2+}$ was nonemissive with no evidence of long-lived excited states ($\tau < 10 \text{ ns}$) by time-resolved absorption spectroscopy under all conditions studied. This is consistent with previous reports and rapid nonradiative decay through low-lying ligand field (dd) states.¹⁰ For $\text{Ru}^{\text{II}}(\text{NH}_3)_5(\text{eina})/\text{ZrO}_2$, photochemical ligand loss was facile and clearly observed as a decreased MLCT absorption in the photolyzed region of the film.

On the other hand, pulsed 532.5 or 417 nm laser excitation of $\text{Ru}^{\text{II}}(\text{NH}_3)_5(\text{eina})/\text{TiO}_2$ leads to the immediate appearance of the transient difference absorbance spectra shown in Figure 2. The transient spectra are fully consistent with that expected for an interfacial charge separated state based on an electron in TiO_2 and an oxidized ruthenium center, abbreviated $\text{Ru}^{\text{III}}/$

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TiO₂(e⁻).¹⁶ Spectroelectrochemical studies demonstrated that a bleach was expected for the formation of Ru(III) and the positive band at ~580 nm is attributed to the electron in TiO₂.¹⁶ The injection quantum yield was determined by comparative actinometry¹⁷ on a per absorbed photon basis: $\phi_{\text{inj}}(417) = 0.30 \pm 0.05$ and $\phi_{\text{inj}}(532.5) = 0.15 \pm 0.03$. The reduction potential of the Franck–Condon excited state generated with 417 nm light is -2.80 V versus Ag/AgCl while that generated with green 532 nm excitation is a much weaker reductant, -2.16 V. The wavelength dependence is consistent with injection from vibrationally hot excited states.¹⁸ Recombination of the injected electron with the oxidized compound was well modeled by a second-order equal-concentration kinetic model with wavelength-independent observed rate constants of $(8 \pm 4) \times 10^8 \text{ s}^{-1}$ over the first microsecond, inset Figure 2. The Ru^{III}/TiO₂(e⁻) charge separated state returns cleanly to baseline on a millisecond time scale with no evidence for photochemistry after a thousand laser pulses.

When employed in regenerative solar cells with 0.5 M TBAI/0.05 M I₂ CH₃CN electrolyte (where TBA is tetrabutylammonium), a maximum monochromatic incident photon-

to-current efficiency (IPCE) of ~0.002 was observed for [Ru-(NH₃)₅(eina)]/TiO₂. The photocurrent was even lower when DMF was used in place of CH₃CN. This value is significantly less than the injection quantum yield measured spectroscopically. The low photocurrent is expected for sensitizers with such negative reduction potentials and almost certainly stems from sluggish iodide oxidation reactions that allow a greater fraction of Ru^{III}/TiO₂(e⁻) → Ru^{II}/TiO₂ recombination.¹⁹

In conclusion, we have demonstrated sensitization of TiO₂ to visible light with a solvatochromic transition metal compound that contains a single chromophoric pyridine ligand and surface binding group. The sensitization yield was found to be wavelength dependent and ~30% with blue light excitation, consistent with injection from hot excited states. While the presence of low-lying ligand field states and a negative Ru^{III/II} reduction potential probably preclude its use in practical dye-sensitized solar cells, the observation greatly increases the possible type of sensitizers that can be envisioned for energy conversion applications. In addition, the presence of only one chromophoric ligand removes any doubt as to where the excited state is localized and should facilitate data interpretation in fundamental excited-state interfacial electron-transfer studies.

Acknowledgment. The Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy, is gratefully acknowledged for research support.

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