

## Long-Lived Photoinduced Charge Separation across Nanocrystalline TiO<sub>2</sub> Interfaces

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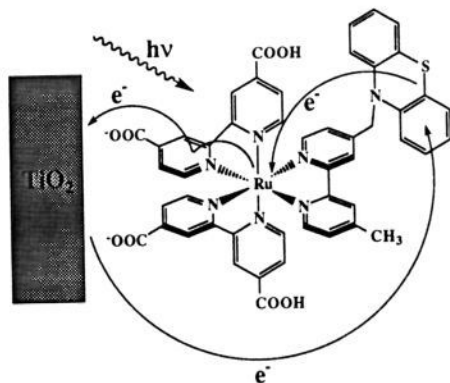
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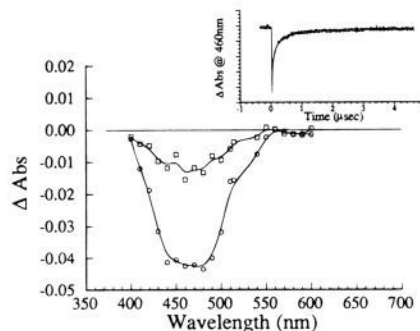
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Recently there has been considerable research effort to convert light into electricity with nanometer-sized semiconductor clusters.<sup>1–4</sup> These efforts have largely been motivated by the impressive solar energy devices developed by Grätzel and co-workers with ruthenium polypyridyl sensitizers anchored to porous colloidal TiO<sub>2</sub> films.<sup>1</sup> As in natural photosynthesis, these materials convert light into useful energy by efficiently separating charge: the electronically excited sensitizer injects an electron into the solid to form a charge-separated pair with the hole localized on the sensitizer. Recombination of the electron and hole to give ground state products represents a detrimental process which may reduce the efficiency of a regenerative solar cell. It is therefore worthwhile to explore the performance of a more complex molecular sensitizer with a covalently bound electron donor and to develop a clear picture of the interfacial electron transfer processes which dictate charge separation efficiencies.

With this objective, we have designed and synthesized a novel sensitizer, [Ru(4-(CO<sub>2</sub><sup>-</sup>)-4'-(CO<sub>2</sub>H)-2,2'-bipyridine)<sub>2</sub>(4-CH<sub>3</sub>-4'-CH<sub>2</sub>-PTZ)-2,2'-bipyridine)] (abbreviated Ru(dcbH)<sub>2</sub>(bpy-PTZ)), where PTZ is phenothiazine, shown below.



The strategy in the design of this sensitizer was to vectorially translate the "hole" away from the interface by intramolecular electron transfer as shown schematically. In this communication, we report the preparation and photoelectrochemical and redox properties of Ru(dcbH)<sub>2</sub>(bpy-PTZ) and [Ru(4-(CO<sub>2</sub><sup>-</sup>)-



**Figure 1.** Excited state absorption difference spectra of Ru(dcbH)<sub>2</sub>(dmb) anchored to a transparent TiO<sub>2</sub> film in neat propylene carbonate. Spectra are shown 50 ns (○) and 500 ns (□) after excitation with a 10 mJ, 5 ns pulse of 532 nm light. The data represents the average of 10 laser pulses. Inset: The kinetics of absorbance at 460 nm, assigned to the recombination of the TiO<sub>2</sub> (e<sup>-</sup>)|–Ru<sup>III</sup> charge-separated pair.

4'-(CO<sub>2</sub>H)-2,2'-bipyridine)<sub>2</sub>(4,4'-(CH<sub>3</sub>)<sub>2</sub>-2,2'-bipyridine)], abbreviated Ru(dcbH)<sub>2</sub>(dmb), which serves as a model. The excited state absorption and photoelectrochemical properties of the sensitizers bound to porous nanocrystalline TiO<sub>2</sub> films demonstrate how molecular level modification can tune interfacial dynamics and efficiencies in operational solar cells.

The sensitizers were prepared by refluxing Na<sub>4</sub>[Ru(4,4'-(CO<sub>2</sub><sup>-</sup>)-bpy)<sub>2</sub>Cl<sub>2</sub>]<sup>2b</sup> (100 mg) with a stoichiometric amount of either bpy-PTZ<sup>5</sup> or dmb (Aldrich) in 60 mL of 1:1 MeOH/H<sub>2</sub>O for 3 h in the dark under argon. The solution was concentrated to ~5 mL, loaded onto a silica column, and eluted with NaCl-saturated methanol. The first fraction was collected, evaporated to dryness, and redissolved in water. The neutral form was precipitated by addition of dilute HCl. Characterization was satisfactory.<sup>6</sup> Electrochemical properties of the two sensitizers in fluid solution were explored by cyclic voltammetry in MeOH. The model compound displays a reversible Ru<sup>III/II</sup> wave at +1.05 V and an irreversible ligand reduction at E<sub>pc</sub> = –1.34 V vs SCE. For Ru(dcbH)<sub>2</sub>(bpy-PTZ) an irreversible ligand reduction, E<sub>pc</sub> = –1.33, an irreversible metal oxidation, E<sub>pa</sub> = +1.08, and a reversible oxidation assigned to PTZ<sup>+0</sup> at +0.72 V vs SCE are observed. The preparation of porous nanocrystalline TiO<sub>2</sub> films,<sup>1b</sup> surface attachment, and photoelectrochemical measurements have been previously described.<sup>2</sup>

Electron transfer dynamics at nanocrystalline TiO<sub>2</sub> interfaces were explored by excited state absorption spectroscopy in propylene carbonate. The TiO<sub>2</sub> films were sufficiently transparent that measurements could be made in a transmission mode at wavelengths greater than 400 nm.<sup>7</sup> Excitation of the model compound anchored to TiO<sub>2</sub> results in the formation of a charge-separated pair with the electron in TiO<sub>2</sub> and the hole localized on the ruthenium metal center, abbreviated TiO<sub>2</sub> (e<sup>-</sup>)|–Ru<sup>III</sup>. Interfacial electron transfer from the charge-separated state to ground state products, eq I, is monitored by the recovery of the Ru(II) metal-to-ligand charge transfer (MLCT) absorption, Figure 1. Kinetics of the recovery, shown in the inset, were



modeled as a biexponential decay, which yields rates of  $k_1 = 8.5 \times 10^6 \text{ s}^{-1}$  and  $k_2 = 5.1 \times 10^5 \text{ s}^{-1}$  with relative amplitudes of 0.77 and 0.23, respectively.

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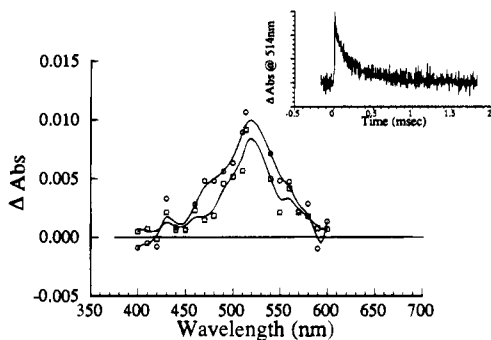
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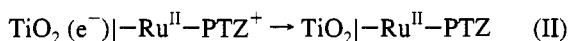
(6) Elemental anal. Calcd for Na<sub>4</sub>RuC<sub>36</sub>H<sub>30</sub>N<sub>6</sub>O<sub>11</sub>Cl<sub>2</sub> (Na salt of model × 3H<sub>2</sub>O): C, 43.8; H, 3.06; N, 8.52. Found: C, 42.7; H, 2.98; N, 8.34. Calcd for RuC<sub>48</sub>H<sub>33</sub>N<sub>7</sub>O<sub>8</sub>S (Ru(dcbH)<sub>2</sub>(bpy-PTZ)): C, 59.5; H, 3.43; N, 10.12. Found: C, 56.7; H, 3.50; N, 9.60.

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**Figure 2.** Excited state absorption difference spectra of Ru(dcbH)<sub>2</sub>-(bpy-PTZ) anchored to a transparent TiO<sub>2</sub> film in neat propylene carbonate. Spectra are shown 500 ns (○) and 5 μs (□) after excitation with a 10 mJ, 5 ns pulse of 532 nm light. The data represents the average of 10 laser pulses. Inset: The kinetics measured at 514 nm, assigned to the recombination of the TiO<sub>2</sub> (e<sup>-</sup>)-Ru<sup>II</sup>-PTZ<sup>+</sup> charge-separated pair recorded with ~2 μs resolution.

Under the same conditions, excitation of Ru(dcbH)<sub>2</sub>(bpy-PTZ) anchored to TiO<sub>2</sub> results in the immediate appearance of an absorption typical of PTZ<sup>+</sup>,<sup>5</sup> Figure 2. It is apparent that after visible excitation, electron injection into TiO<sub>2</sub> and electron transfer from PTZ occur although these processes cannot be time resolved by our instrumentation.<sup>8</sup> Intramolecular electron transfer from PTZ to Ru(III) is thermodynamically downhill by ~360 mV, and in less than 30 ns an interfacial charge-separated pair is created, TiO<sub>2</sub> (e<sup>-</sup>)-Ru<sup>II</sup>-PTZ<sup>+</sup>, where the electron is in the solid and the hole is localized on PTZ. This state recombines to ground state products, eq II, with a rate constant of 3.6 × 10<sup>3</sup> s<sup>-1</sup>, Figure 2 (inset). The increased noise



in this decay is a result of the smaller extinction coefficient of PTZ<sup>+</sup> with respect to the difference between the Ru(II) and Ru(III) absorption bands.<sup>5,9</sup> The lifetime of PTZ<sup>+</sup> is therefore ~10<sup>3</sup> times greater than that observed in fluid solution for this<sup>10</sup> and related<sup>11</sup> phenothiazine-containing donor-acceptor compounds. Furthermore, recombination of the electron-hole pair is slowed by a factor of ~2 × 10<sup>3</sup> compared to the model compound.

Both sensitizers efficiently convert light into electricity in regenerative solar cells with NaI/I<sub>2</sub>. The incident photon to current efficiency (IPCE) plotted against wavelength strongly resembles the absorption spectrum of the sensitizers. With these more transparent TiO<sub>2</sub> films, both sensitizers convert light to electricity with a maximum monochromatic efficiency of 45 ± 5%. However, the open-circuit photovoltage, V<sub>oc</sub>, under white

(8) As pointed out by a reviewer, an alternative mechanism is plausible in the presence of iodide: After electron injection, Ru(III) is reduced by I<sup>-</sup> and the resulting radical (or some derivative form) is reduced by PTZ. While we cannot exclude the possibility that some fraction of PTZ<sup>+</sup> is formed by this pathway, this mechanism would require that the pseudo-first-order rate constant for the reduction of Ru(III) by I<sup>-</sup> be competitive with intramolecular reduction by PTZ. The intramolecular rate in the absence of iodide is >5 × 10<sup>7</sup> s<sup>-1</sup>, which represents our instrument response function. We note that the mechanism proposed by the reviewer also translates the hole away from the chromophore to PTZ.

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light illumination is consistently 100 mV greater for Ru(dcbH)<sub>2</sub>-(bpy-PTZ) than for the model compound. This is important as V<sub>oc</sub> defines the maximum free energy produced by a solar cell under constant light irradiance conditions.

The maximum open-circuit photovoltage attainable in devices of this type is the energetic difference between the Fermi level of the solid under illumination and the Nernst potential of the redox couple in the electrolyte. However, for these devices this limitation has not been realized and V<sub>oc</sub> is in general much smaller. It appears that V<sub>oc</sub> is kinetically limited by electron tunneling through the solid to acceptors at the interface or in the electrolyte.<sup>1c</sup> For an n-type semiconductor in a regenerative cell, eq III holds,<sup>12,13</sup> where I<sub>inj</sub> is the electron injection flux, n is the concentration of electrons in TiO<sub>2</sub>, and the summation is for all electron transfer rates to acceptors A. In the absence of

$$V_{oc} = \left( \frac{kT}{e} \right) \ln \left( \frac{I_{inj}}{n \sum_i k_i [A]_i} \right) \quad (\text{III})$$

impurities and O<sub>2</sub>, electron acceptors could be iodide oxidation products, Ru(III), and for Ru(dcbH)<sub>2</sub>(bpy-PTZ), PTZ<sup>+</sup>. The measured kinetics described above can be used in conjunction with eq III to predict the open-circuit voltages. If one assumes that I<sub>inj</sub> and n are the same for the two sensitizers, then V<sub>oc</sub> for Ru(dcbH)<sub>2</sub>(bpy-PTZ) should be 200 mV larger than for the model compound. To test this we measured the open-circuit voltage in a 0.1 M tetrabutylammonium perchlorate/propylene carbonate electrolyte in the absence of iodide. Versus a Pt or Ag quasi reference electrode, V<sub>oc</sub> is 500 mV for Ru(dcbH)<sub>2</sub>-(bpy-PTZ) and 325 mV for Ru(dcbH)<sub>2</sub>(dmb). For a larger number of samples a 175 ± 10 mV larger photovoltage was measured for Ru(dcbH)<sub>2</sub>(bpy-PTZ) in good agreement with the calculated difference. The fact that an increased V<sub>oc</sub> is also measured for Ru(dcbH)<sub>2</sub>(bpy-PTZ) in the presence of iodide is gratifying. This may signal that recombination of electrons in the solid with Ru(III) competes with iodide oxidation in the model compound, as suggested by kinetic observations.<sup>2,7</sup> Alternatively, if iodide oxidation occurs farther from the interface for Ru(dcbH)<sub>2</sub>(bpy-PTZ), the products may be less efficient acceptors for electrons in TiO<sub>2</sub>.

In summary, a novel sensitizer has been designed to vectorially translate the oxidizing equivalent (the hole) away from the nanostructured semiconducting interface. The decreased electronic coupling between the surface and the hole results in an extremely long-lived charge-separated pair which directly leads to an increased open-circuit photovoltage in a regenerative solar cell. Further, the measured interfacial molecular level kinetics applied to a solid state model quantitatively predict the increased efficiency. The general strategy of vectorial translation of photogenerated holes away from interfaces is successful and may be applied to other assemblies to prevent charge recombination and increase solar conversion efficiencies.

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