

# Efficient Light-to-Electrical Energy Conversion with Dithiocarbamate–Ruthenium Polypyridyl Sensitizers

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New Ru(dcbH)(dcbH<sub>2</sub>)(L) sensitizers, where L is diethyldithiocarbamate, dibenzylthiocarbamate, or pyrrolidinedithiocarbamate, dcbH is 4-(COOH)-4'-(COO<sup>-</sup>)-2,2'-bipyridine, and dcbH<sub>2</sub> is 4,4'-(COOH)<sub>2</sub>-2,2'-bipyridine, have been synthesized, characterized, and anchored to nanocrystalline TiO<sub>2</sub> films for light to electrical energy conversion in regenerative photoelectrochemical cells with I<sup>-</sup>/I<sub>2</sub> acetonitrile electrolyte. The sensitizers have intense metal-to-ligand charge-transfer (MLCT) bands centered ~380 and 535 nm that sensitize TiO<sub>2</sub> over a notably broad spectral range. The photophysical and photoelectrochemical studies of these materials are contrasted with *cis*-Ru(dcbH<sub>2</sub>)<sub>2</sub>(NCS)<sub>2</sub>, which is one of the most efficient sensitizers reported to date. Photophysical measurements show that the high photocurrent observed for *cis*-Ru(dcb)<sub>2</sub>(NCS)<sub>2</sub>/TiO<sub>2</sub> is due to efficient and rapid iodide oxidation.

## Introduction

Regenerative solar cells based on wide band gap semiconductors sensitized to visible light with inorganic coordination compounds have recently experienced an order of magnitude increase in light-to-electrical energy conversion efficiency.<sup>1</sup> Remarkably, at discrete wavelengths of light these materials convert photons into electrons with efficiencies close to unity.<sup>1–3</sup> An important goal for the next generation of solar cells based on this technology is to prepare sensitizers that increase the spectral response in the red portion of the solar spectrum.

An accepted model for dye sensitization of wide band gap semiconductors in photoelectrochemical cells has emerged.<sup>1–3</sup> A sensitizing dye molecule absorbs visible or near infrared light and injects an electron into the semiconductor from its excited state(s). Once the electron is in the solid it proceeds through the semiconductor to an external circuit. The oxidized sensitizer accepts an electron from an electron donor, such as iodide, present in the electrolyte. The net process allows an electrical current to be generated with light of lower energy than the semiconductor band gap. The solar cells reported here are termed regenerative because the iodide is regenerated at a platinum counter electrode and no net chemistry occurs.

For ruthenium diimine sensitizers, the metal-to-ligand charge transfer (MLCT) absorption can be extended to longer wavelengths by appropriate substituent changes on chromophoric ligands or by decreasing the  $d\pi-\pi^*$  back-bonding donation to nonchromophoric ligands.<sup>4</sup> In previous studies, we employed

the former approach and utilized substituted diimine ligands with lower  $\pi^*$  accepting orbitals than the commonly utilized 4,4'-(COOH)<sub>2</sub>-2,2'-bipyridine, abbreviated dcbH<sub>2</sub>, ligand.<sup>5,6</sup> While some spectral enhancement was observed, the sensitizers did not perform as efficiently as those based on dcbH<sub>2</sub>. Photoelectrochemical and photophysical measurements indicated that the decreased solar conversion efficiency was largely due to a lower quantum yield for interfacial charge separation.<sup>5,6</sup>

In this manuscript, we have invoked the latter approach and utilized dithiocarbamates as nonchromophoric chelating ligands to tune sensitizer absorption properties. We report here the synthesis, photophysical, and photoelectrochemical properties of three Ru(dcbH)(dcbH<sub>2</sub>)(L) sensitizers, where L is one of the three dithiocarbamate ligands shown in Chart 1: diethyldithiocarbamate (dedtc), dibenzylthiocarbamate (dbtc), and pyrrolidinedithiocarbamate (pdtc). The approach was successful, and these violet coordination compounds efficiently sensitize TiO<sub>2</sub> beyond 700 nm. The photoelectrochemical properties are contrasted with those of *cis*-Ru(dcbH<sub>2</sub>)<sub>2</sub>(NCS)<sub>2</sub>, which is one of the most efficient sensitizers for this application reported to date.<sup>7</sup>

## Experimental Section

**Preparations.** The syntheses of the Ru(dcbH)(dcbH<sub>2</sub>)(L) sensitizers are described below. We note that similar dithiocarbamate compounds with unsubstituted bipyridines have been reported in the literature.<sup>8</sup>

Sensitizers were prepared by refluxing Ru(dcbH<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub><sup>5</sup> with a 10-fold excess of the sodium dithiocarbamates (ammonium for pdtc, Fluka) for 2 h in the dark in methanol. The reaction mixture was then rotary

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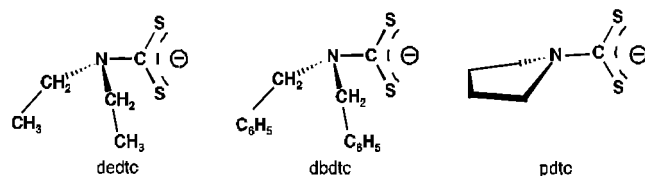
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Chart 1



evaporated to dryness and the solid dissolved in water (except for the dibenzyl complex as described below). The solution was acidified with HCl at pH = 2 and the solid precipitated was washed twice with aqueous HCl at pH = 2 and then with distilled water.

Since dibenzylidithiocarbamic acid (Hdbdte) is insoluble in water, the excess of Na(dbdte) in the preparation of Ru(dcbH<sub>2</sub>)(dcbH)(dbdte) was eliminated by washing the solid with acetone prior to precipitation of the acidic form with HCl from water.

Elemental analyses were performed with a Carlo Erba Model 1110 Instrument. <sup>1</sup>H NMR were obtained on a 400 MHz Bruker spectrometer.

**Ru(dcbH<sub>2</sub>)(dcbH)(dedtc)·H<sub>2</sub>O.** <sup>1</sup>H NMR of the fully deprotonated complex (400 MHz, CD<sub>3</sub>OD/NaOD): δ 9.7 (2 H, d, 6), 9.0 (2 H, s, 3), 8.88 (2 H, s, 3'), 8.21 (2 H, d, 5), 7.78 (2 H, d, 6'), 7.57 (2 H, d, 5'), 3.79 (4 H, q, -CH<sub>2</sub>), 1.22 (6 H, t, -CH<sub>3</sub>). Anal. Calcd for the neutral complex: C, 46.15; N, 9.28; H, 3.61; S, 8.50. Found: C, 46.32; N, 9.35; H, 3.75; S, 8.10.

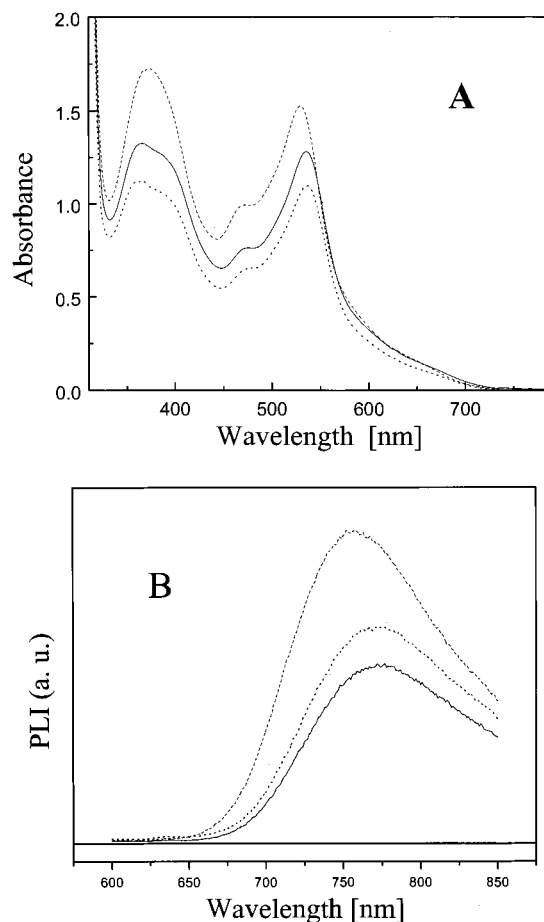
**Ru(dcbH<sub>2</sub>)(dcbH)(dbdte).** <sup>1</sup>H NMR of the fully deprotonated complex (400 MHz, CD<sub>3</sub>OD/NaOD): δ 9.72 (2 H, d, 6), 9.02 (2 H, s, 3), 8.89 (2 H, s, 3'), 8.18 (2 H, d, 5), 7.80 (2 H, d, 6'), 7.59 (2 H, d, 5'), 7.36 (6 H, m, 8 and 10), 7.24 (4 H, d, 9), benzyl protons presumably buried under solvent peak. Anal. Calcd for the neutral complex: C, 54.41; N, 8.14; H, 3.40; S, 7.45. Found: C, 53.83; N, 8.16; H, 3.20; S, 7.28.

**Ru(dcbH<sub>2</sub>)(dcbH)(pdte).** <sup>1</sup>H NMR of the fully deprotonated complex (400 MHz, CD<sub>3</sub>OD/NaOD): δ 9.79 (2 H, d, 6), 9.01 (2 H, s, 3), 8.85 (2 H, s, 3'), 8.18 (2 H, d, 5), 7.83 (2 H, d, 6'), 7.61 (2 H, d, 5'), 3.28 (4 H, t, 7), 2.01 (4 H, t, 8). Anal. Calcd for the neutral complex: C, 47.41; N, 9.53; H, 3.16; S, 8.73. Found: C, 47.40; N, 9.72; H, 2.87; S, 8.34.

*cis*-Ru(dcbH<sub>2</sub>)<sub>2</sub>(NCS)<sub>2</sub> was available from previous studies.<sup>5</sup>

Nanocrystalline TiO<sub>2</sub> (anatase) electrodes were prepared by a previously published procedure.<sup>9</sup> The sensitizers were anchored to the TiO<sub>2</sub> surface by soaking in millimolar methanol solutions of the sensitizers overnight.

**Spectroscopic Measurements. Absorbance.** UV-vis absorbance measurements were made on a Hewlett-Packard 8451A diode array spectrophotometer. Measurements were carried out on the apparatus previously described.<sup>9</sup> Briefly, excitation was carried out using the 532 nm laser pulses, ca. 8 ns and 10 mJ/pulse, from a Nd:YAG (Continuum Surelite). The approximately 5 mm diameter excitation beam was expanded to ca. 3 cm using a quartz plano-concave lens (JML Direct, -50 mm EFL, 25.4 mm diameter), resulting in a fluence of around 3 mJ cm<sup>-2</sup>. The absorbance change of the laser irradiated sample was probed at 90° to the excitation pulse using an Applied Photophysics 150 W Xe arc lamp operating in pulsed mode. The sample was protected from the probe light using a fast shutter, 10 ms pulse width, and appropriate UV and heat absorbing glass and solution filter combinations. The probe light was focused onto the sample and again onto the entrance slit of a *f*/3.4 Applied Photophysics monochromator, typically under conditions such that the effective bandwidth was 2–3 nm. The probe beam was monitored after the monochromator using a Hamamatsu R928 photomultiplier. The photomultiplier was protected from scattered laser light using appropriate glass filters positioned between the sample and monochromator. Kinetic traces were



**Figure 1.** Absorption (A) and emission (B) spectra of Ru(dcb)<sub>2</sub>(dedtc)<sup>3-</sup> (—), Ru(dcb)<sub>2</sub>(dbdte)<sup>3-</sup> (---), and Ru(dcb)<sub>2</sub>(pdte)<sup>3-</sup> (···) in basic methanol solution. The emission spectra were obtained with 535 ± 2 nm light excitation. PLI is the photoluminescence intensity.

recorded on a LeCroy 9450 digital oscilloscope using a 50 Ω input and operating at 350 MHz. In general, kinetic traces represent the average of 40–100 laser shots. Excitation was directed to the front face of the TiO<sub>2</sub> film, oriented at a ca. 45° angle, such that the predominant Rayleigh scattering was directed away from the monochromator. Cuvettes were stoppered with a PTFE plug, argon purged by bubbling through a glass tube and maintained under a premoistened argon flow.

**Photoluminescence.** Photoluminescence (PL) spectra were obtained with a Spex Fluorolog which had been calibrated with a standard NBS tungsten-halogen lamp. Emission lifetimes were measured by correlated, single-photon counting with a PRA 3000 fluorescence spectrometer equipped with a Model 510B pulsed lamp and a Model 1551 cooled photomultiplier tube.

**Electrochemistry.** Electrochemistry was performed in 0.1 M tetrabutylammonium hexafluorophosphate (Aldrich, TBAH) methanol or acetonitrile electrolyte. The TBAH was recrystallized from ethanol. A BAS Model CV27 potentiostat was used in a standard three-cell arrangement consisting of a Pt working electrode, a Pt gauze counter electrode, and a SCE reference electrode. Approximately millimolar concentrations of the compounds were dissolved in the electrolyte.

**Photoelectrochemistry.** Photoelectrochemical measurements were performed in a 2 electrode sandwich cell arrangement as previously described.<sup>9</sup> Briefly, ~10 μL of electrolyte was sandwiched between a TiO<sub>2</sub> electrode and a Pt-coated tin oxide electrode. The TiO<sub>2</sub> was illuminated with a 450 W Xe lamp coupled to a *f*/0.22 m monochromator for IPCE measurements. Light excitation was through the FTO glass substrate of the photoanode. Photocurrents were measured under short circuit conditions with a Keithly model 617 digital electrometer. Incident irradiances were measured with a calibrated silicon photodiode

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**Table 1.** Spectroscopic Properties of Sensitizers<sup>a</sup>

sensitizer <sup>b</sup>	absorption <sup>c</sup>		emission <sup>d</sup>	
	$\lambda_{\max}$ , nm (MLCT)	$\lambda_{\max}$ , nm (MLCT)	$\lambda_{\max}$ , nm	$\tau$ , ns
Ru(dcb) <sub>2</sub> (dedtc) <sup>3-</sup>	366	535	775	17
Ru(dcb) <sub>2</sub> (dbdte) <sup>3-</sup>	372	530	757	13
Ru(dcb) <sub>2</sub> (pdte) <sup>3-</sup>	361	536	773	19
Ru(dcb) <sub>2</sub> (NCS) <sub>2</sub> <sup>4-</sup>	380	518	795	20

<sup>a</sup> Spectroscopic properties of the sensitizers measured in basic methanol solution. <sup>b</sup> Sensitizer specified where dcb is 4,4'-(COO<sup>-</sup>)<sub>2</sub>-2,2'-bipyridine, dedtc is diethyldithiocarbamate, dbdte is dibenzylthiocarbamate, and pdte is pyrrolidinedithiocarbamate. <sup>c</sup> The absorption maximum are  $\pm 2$  nm. <sup>d</sup> The emission maximum is  $\pm 4$  nm, and the lifetimes are  $\pm 0.3$  ns.

**Table 2.** Electrochemical Properties of Sensitizers<sup>a</sup>

sensitizer	$E_{1/2}$ ( $\Delta E_{pa,pc}$ ), mV (CH <sub>3</sub> OH)	$E_{1/2}$ ( $\Delta E_{pa,pc}$ ), mV (CH <sub>3</sub> CN)
Ru(dcbH <sub>2</sub> )(dcbH)(dedtc)	723 (95)	<i>b</i>
(TBA) <sub>3</sub> [Ru(dcb) <sub>2</sub> (dedtc)]	598 (105)	443 (75)
Ru(dcbH <sub>2</sub> )(dcbH)(dbdte)	665 (130)	<i>b</i>
(TBA) <sub>3</sub> [Ru(dcb) <sub>2</sub> (dbdte)]	600 (100)	475 (90)
Ru(dcbH <sub>2</sub> )(dcbH)(pdte)	658 (135)	<i>b</i>
(TBA) <sub>3</sub> [Ru(dcb) <sub>2</sub> (pdte)]	538 (125)	425 (90)
Ru(dcbH <sub>2</sub> ) <sub>2</sub> (NCS) <sub>2</sub>	800 <sup>c</sup>	850 <sup>d</sup>
(TBA) <sub>4</sub> [Ru(dcb) <sub>2</sub> (NCS) <sub>2</sub> ]	720 <sup>c</sup>	710 <sup>c</sup>

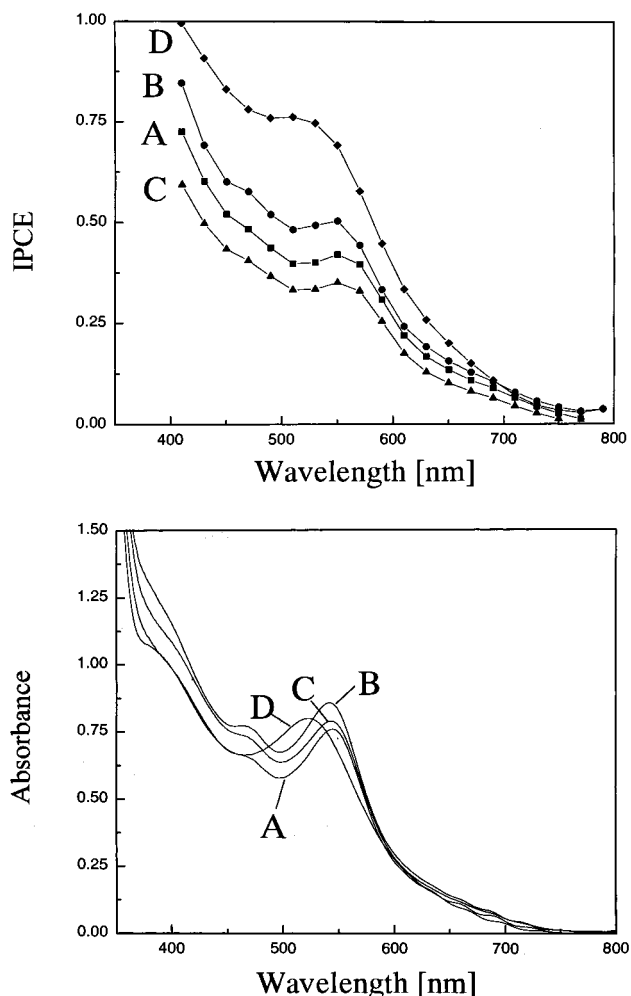
<sup>a</sup>  $E_{1/2}$  measured in mV versus the SCE reference by cyclic voltammetry. The potential is assigned to the Ru<sup>III/II</sup> couple.  $\Delta E_{pa,pc}$  is the peak-to-peak separation between cathodic and anodic peak potentials uncompensated for cell resistance and measured at a 100 mV/s scan rate. <sup>b</sup> Poor solubility precluded electrochemical analysis. <sup>c</sup> Irreversible process; anodic peak potential given. <sup>d</sup> Data taken from ref 7.

from UDT Technologies. The supporting electrolyte was 0.5 M LiI/0.05 M I<sub>2</sub> in acetonitrile.

## Results and Discussion

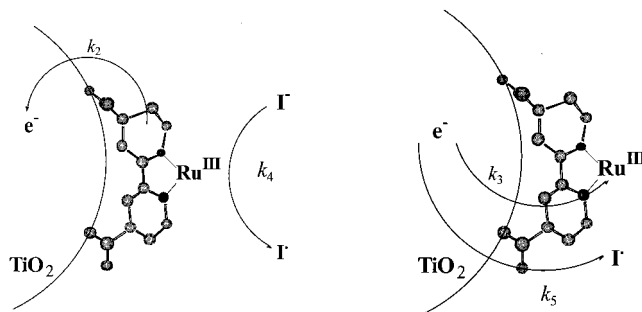
Shown in Figure 1 are the absorption spectra of the violet dithiocarbamate sensitizers in basic methanol solution. Two broad MLCT absorption bands are observed at  $\sim 380$  and 535 nm for all three compounds. The fully deprotonated forms of these complexes show weak room-temperature photoluminescence in methanol, as shown in the figure. The excited-state lifetimes were measured by single photon counting, Table 1. In methanol electrolyte, the neutral and anionic forms of these compounds display quasi-reversible Ru(III/II) voltammetry, Table 2. In acetonitrile, the anionic forms of the dithiocarbamate sensitizers also display quasi-reversible behavior. However, the poor solubility of the neutral and fully protonated forms precluded voltammetric analysis. The voltammetry is termed quasi-reversible because the anodic and cathodic currents are equal within experimental error, while the peak-to-peak splitting is typically  $\sim 100$  mV. In methanol, the oxidations of [*cis*-Ru(dcb)<sub>2</sub>(NCS)<sub>2</sub>]<sup>4-</sup> and *cis*-Ru(dcbH<sub>2</sub>)<sub>2</sub>(NCS)<sub>2</sub> are irreversible.

Photoaction spectra of the sensitizers, incident photon-to-current efficiency (IPCE) versus wavelength, anchored to nanocrystalline anatase films in a regenerative solar cell with 0.5 M LiI/0.05 M I<sub>2</sub> are shown in Figure 2. These sensitizers convert light to electricity across the entire visible region, 400–750 nm. For comparison, the photoaction spectrum of *cis*-Ru(dcb)<sub>2</sub>(NCS)<sub>2</sub>/TiO<sub>2</sub> is also shown. This sensitizer gave the highest photocurrent efficiency measured and is known to produce photocurrents with a quantum yield near unity on TiO<sub>2</sub> materials and electrolytes better optimized for energy conversion.<sup>5,7</sup> In best case scenarios the dithiocarbamate dyes were 10% less efficient at individual wavelengths of light from 400



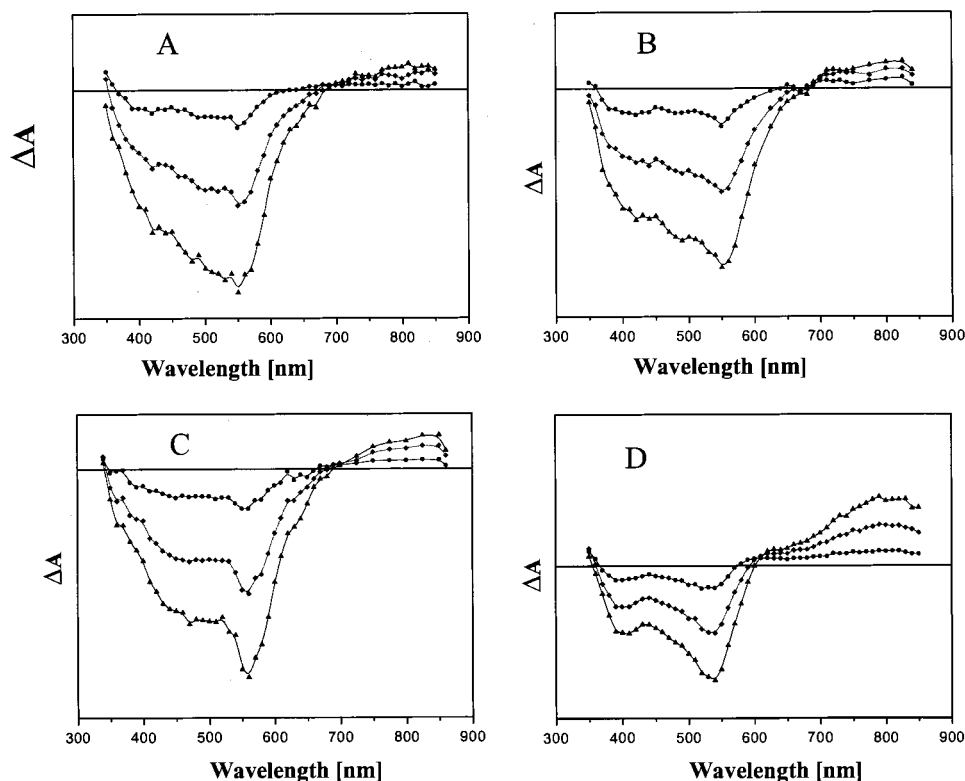
**Figure 2.** Upper panel: Photoaction spectra of (A) Ru(dcb)<sub>2</sub>(dedtc)/TiO<sub>2</sub> (squares), (B) Ru(dcb)<sub>2</sub>(dbdte)/TiO<sub>2</sub> (circles), (C) Ru(dcb)<sub>2</sub>(pdte)/TiO<sub>2</sub> (triangles), and (D) *cis*-Ru(dcb)<sub>2</sub>(NCS)<sub>2</sub>/TiO<sub>2</sub> (diamonds) in regenerative solar cells with 0.5 M LiI/0.05 M I<sub>2</sub> acetonitrile electrolyte. IPCE is the incident photon-to-current efficiency. Lower panel: Absorption spectra of (A) Ru(dcb)<sub>2</sub>(dedtc)/TiO<sub>2</sub>, (B) Ru(dcb)<sub>2</sub>(dbdte)/TiO<sub>2</sub>, (C) Ru(dcb)<sub>2</sub>(pdte)/TiO<sub>2</sub>, and (D) *cis*-Ru(dcb)<sub>2</sub>(NCS)<sub>2</sub>/TiO<sub>2</sub> in acetonitrile.

## Scheme 1



to 500 nm but were consistently lower. The increased photocurrent efficiency for *cis*-Ru(dcb)<sub>2</sub>(NCS)<sub>2</sub>/TiO<sub>2</sub> is not due simply to the amount of light absorbed. Rather, it must result from the dynamics of the electron-transfer processes that convert the MLCT excited states to an electrical current.

The desirable electron-transfer processes that convert the energy stored in the MLCT excited state of an idealized sensitizer to an electrical current are shown on the left-hand side of Scheme 1. Electron injection into the empty states of TiO<sub>2</sub>,  $k_2$ , and subsequent oxidation of iodide by the Ru(III)



**Figure 3.** Absorption difference spectra of (A)  $\text{Ru(dcb)}_2(\text{dedtc})/\text{TiO}_2$ , (B)  $\text{Ru(dcb)}_2(\text{dbdtc})/\text{TiO}_2$ , (C)  $\text{Ru(dcb)}_2(\text{pdctc})/\text{TiO}_2$ , and (D)  $\text{cis-Ru(dcb)}_2(\text{NCS})_2/\text{TiO}_2$  in a 1.0 M  $\text{LiClO}_4$  acetonitrile electrolyte after pulsed laser excitation ( $\lambda_{\text{exc}} = 532$  nm, 8–10 ns,  $\sim 10$  mJ/pulse). The spectra were recorded 10 ns (triangles), 100 ns (diamonds), and 1.5  $\mu\text{s}$  (circles) after the laser pulse.

complex,  $k_4$ , must occur with a quantum yield near unity in efficient solar cells. Further, the energy wasting recombination of the injected electron with the oxidized sensitizer,  $k_3$ , or the oxidized iodide product(s),  $k_5$ , shown on the right-hand side, must occur with quantum yields near zero. We explored these processes by nanosecond transient absorption spectroscopy.

Shown in Figure 3 are absorption difference spectra recorded after pulsed 532 nm excitation of the sensitizers bound to  $\text{TiO}_2$  in an argon-saturated 1.0 M  $\text{LiClO}_4$  solution. We assign the absorption difference spectra to the oxidized dye. Contributions from the MLCT excited states should be negligible since the lifetimes of these sensitizers are very short, no positive absorptions from the MLCT excited state are observed in the UV region,<sup>9</sup> and the observed kinetics are wavelength independent. The difference spectra for the dithiocarbamate sensitizers bound to  $\text{TiO}_2$  display a broad bleach in the visible region with a weak positive absorption in the red. The difference spectra for  $\text{cis-Ru(dcb)}_2(\text{NCS})_2/\text{TiO}_2$  are qualitatively similar; however, the positive absorption in the red is more pronounced. This positive absorption has been previously observed and assigned to ligand-to-metal charge-transfer transitions,  $\text{SCN} \rightarrow \text{Ru(III)}$ .<sup>10</sup>

Shown in Figure 4 are single-wavelength absorption transients for the different sensitizers anchored to  $\text{TiO}_2$ . The transients correspond to formation and loss of the oxidized sensitizer. In all cases, the formation of the oxidized sensitizer occurs within the instrument response function indicative of rapid interfacial charge separation,  $k_2 > 10^8 \text{ s}^{-1}$ . Fast and efficient charge injection is expected for this class of sensitizers.<sup>10–14</sup> The regeneration of the ground-state sensitizer occurs by back interfacial electron transfer from  $\text{TiO}_2$  to the  $t_{2g}$  orbitals of  $\text{Ru(III)}$ ,  $k_3$ . As shown, about 80% of the initial amplitude recovers

in 1.5  $\mu\text{s}$ . Complete recovery requires tens of microseconds, consistent with previous reports for related sensitizers.<sup>15</sup> These transients could not be fit to a simple first-order process but can be described by the Kohlrausch–Williams Watts function or a sum of two exponentials.<sup>9</sup> Average recombination rates based on this model are the same for the dithiocarbamate sensitizers within experimental error,  $k_3 = (2.5 \pm 0.2) \times 10^6 \text{ s}^{-1}$  and  $k_3 = 2.8 \times 10^6 \text{ s}^{-1}$  for  $\text{cis-Ru(dcb)}_2(\text{NCS})_2/\text{TiO}_2$ .

An important point is that the recombination rates,  $k_3$ , occur on approximately the same time scale for all four sensitizers. In fact, recombination is slightly faster after light excitation of  $\text{cis-Ru(dcb)}_2(\text{NCS})_2/\text{TiO}_2$  under these conditions. Therefore, the lower photocurrent efficiency of the dithiocarbamate sensitizers when compared to  $\text{cis-Ru(dcb)}_2(\text{NCS})_2$  does not result from differences in charge recombination rate constants.

Also shown in Figure 4 are the decay signals of the nascent  $\text{Ru(III)}$  in the presence of 0.05 M  $\text{LiI}$  and 0.95 M  $\text{LiClO}_4$ . The addition of iodide to the external electrolyte provides an alternative pathway for regeneration of the sensitizer, iodide oxidation,  $k_4$ . The kinetics of iodide oxidation are complex in these systems and appear to involve static and/or dynamic processes. Nevertheless, iodide addition does result in a decreased concentration of the oxidized sensitizer as expected, Figure 4. Stern–Volmer analysis of the integrated area under the absorption transients at different iodide concentrations yields  $K_{\text{sv}} = 100 \text{ M}^{-1}$  for  $\text{cis-Ru(dcb)}_2(\text{NCS})_2/\text{TiO}_2$  and  $K_{\text{sv}} = 30 \pm 20 \text{ M}^{-1}$  for the three dithiocarbamate sensitizers.

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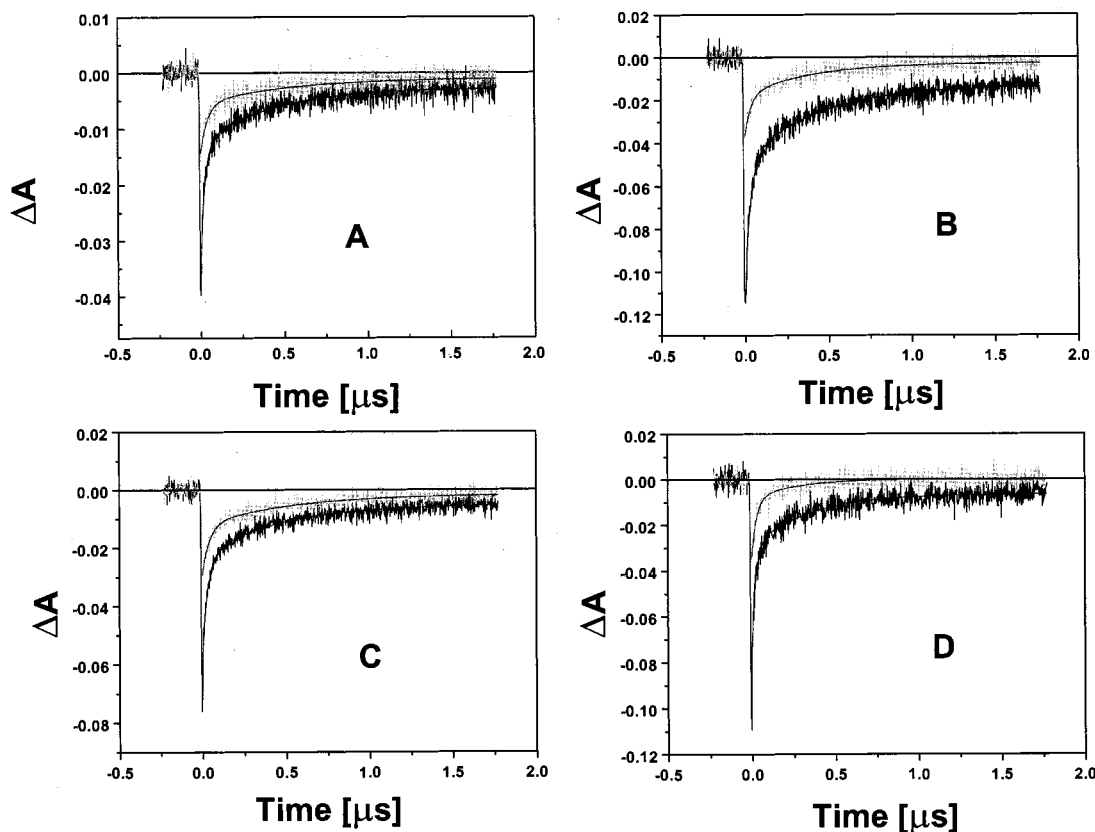
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**Figure 4.** Single wavelength absorption transients recorded in 1.0 M LiClO<sub>4</sub> acetonitrile electrolyte (black signal) and in 0.95 M LiClO<sub>4</sub>/0.05 M LiI acetonitrile electrolyte (gray signal), where (A) is Ru(dcb)<sub>2</sub>(dedtc)/TiO<sub>2</sub>, (B) is Ru(dcb)<sub>2</sub>(dbdtc)/TiO<sub>2</sub>, (C) is Ru(dcb)<sub>2</sub>(pdte)/TiO<sub>2</sub>, and (D) is *cis*-Ru(dcb)<sub>2</sub>(NCS)<sub>2</sub>/TiO<sub>2</sub>. The solid lines are fits to a biexponential model.

The finding that *cis*-Ru(dcb)<sub>2</sub>(NCS)<sub>2</sub>/TiO<sub>2</sub> oxidizes iodide more efficiently than the blue sensitizers after light excitation rationalizes, at least in part, the higher photocurrent measured for this sensitizer. After electron injection,  $k_2$ , a competition is setup between charge recombination,  $k_3$ , and iodide oxidation,  $k_4$ . For dithiocarbamate sensitizers located in portions of the nanocrystalline film where the iodide concentration is depleted, charge recombination efficiently competes with iodide oxidation and a lower photocurrent results.

On the basis of the measured Ru<sup>III/II</sup> potentials, we expect the rates of iodide oxidation to be comparable for all the dithiocarbamate sensitizers. The irreversible nature of *cis*-Ru(dcbH<sub>2</sub>)<sub>2</sub>(NCS)<sub>2</sub> oxidation in methanol and the insolubility of the protonated forms of the dithiocarbamate complexes in acetonitrile preclude a direct comparison of these reduction potentials. The values in acetonitrile are particularly important since the photoelectrochemical measurements were performed in this solvent. Furthermore, oxidation of *cis*-Ru(dcbH<sub>2</sub>)<sub>2</sub>(NCS)<sub>2</sub> is reported to be reversible in CH<sub>3</sub>CN,  $E_{1/2} = 0.85$  V vs SCE.<sup>7</sup> However, the measured potentials in methanol for the series of dithiocarbamate sensitizers show that going from the anionic to the protonated forms there is a maximum increase in  $E_{1/2}$ (Ru<sup>III/II</sup>) of ~120 mV. If the same increase occurs in acetonitrile, than the maximum values for the Ru<sup>III/II</sup> potentials in this solvent should be in the range of 550–600 mV. This is ~250 mV less positive than the known potential for *cis*-Ru(dcbH<sub>2</sub>)<sub>2</sub>(NCS)<sub>2</sub>, thereby providing a larger driving force for I<sup>-</sup> oxidation that is consistent with the larger  $K_{sv}$  measured. Furthermore, for the anionic forms of the sensitizers in aceto-

nitrile,  $E_{1/2}$  increases in the same order as the IPCE: Ru(dcb)<sub>2</sub>(pdte)/TiO<sub>2</sub> < Ru(dcb)<sub>2</sub>(dedtc)/TiO<sub>2</sub> < Ru(dcb)<sub>2</sub>(dbdtc)/TiO<sub>2</sub> < *cis*-Ru(dcb)<sub>2</sub>(NCS)<sub>2</sub>/TiO<sub>2</sub>.

### Conclusion

Violet ruthenium polypyridyl sensitizers have been synthesized and characterized with dithiocarbamate nonchromophoric ligands. When anchored to nanocrystalline TiO<sub>2</sub> films, these sensitizers efficiently convert light into electricity in regenerative solar cells over the entire visible region. Photophysical studies show that the photocurrent is limited by iodide oxidation. This finding combined with our earlier studies underscores the difficulty in realizing efficient semiconductor sensitization with black ruthenium diimine compounds. Stabilization of the  $\pi^*$  levels of the diimine ligands can result in a poor interfacial charge separation yield,<sup>5,6</sup> while decreasing the metal-based reduction potential can result in sluggish iodide oxidation rates. Further improvements for the dithiocarbamate sensitizers reported here will require new strategies to increase iodide (or other electron donors) oxidation efficiency.

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