Dual Electron Injection from Charge-Transfer Excited States of TiO_2-Anchored Ru(II)-4,4′-Dicarboxy-2,2′-biquinoline Complex

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Dual electron injection phenomenon observed for the first time in dithiocyanato bis(4,4′-dicarboxy-2,2′-biquinoline)-ruthenium(II) when anchored to nanocrystalline TiO_2 film indicates an ultrafast rate of electron injection into the conduction band of TiO_2 which is competitive to internal conversion and/or intersystem crossing between the two lowest excited MLCT states.

There has been an increasing interest in solar-to-electrical energy conversion with dye-sensitized photoelectrochemical cells based on wide bandgap oxide semiconductors.[1-3] Grätzel and coworkers reported solar cells of remarkable energy conversion efficiency (exceeding 10%) based on a porous TiO_2 semiconductor electrode sensitized with ruthenium-based polypyridyl-type complexes, making practical applications feasible.[1,2] In these systems, after absorption of a photon, the adsorbed dye molecule undergoes a transition from ground state to an excited state located energetically above the conduction band of the semiconductor. Subsequently, an efficient and rapid electron transfer occurs from dye excited state to the conduction band of semiconductor. Thermodynamic driving force[4] and electronic coupling[5] between dye molecules and semiconductor are found to dictate a large extent the kinetics of the electron transfer processes and thus control the device efficiency. A detailed understanding of the mechanism and time scale of the electron injection from surface-adsorbed dyes to the conduction band of the semiconductors is indispensable to develop the devices. Studies of ultrafast dynamics show that electron injection occurs within femtosecond time scale.[6-8] Here, we report a direct observation of efficient electron injection from an ultra-short-lived, higher lying MLCT excited state of $Ru(dcbiq\underline{H})_2(NCS)_2(TBA)_2$ ($dcbiq\underline{H}_2$ =4,4′-dicarboxy-2,2′-biquinoline, TBA= tetrabutylammonium) into the conduction band of TiO_2, suggesting electron injection occurs near the sub-picosecond domain. Recently, Ferrere and Gregg reported an ultrafast electron injection in iron-based sensitizing dye *cis*-$[Fe^{II}(4,4'\text{-dicarboxy-2,2'-bipyridine})_2(CN)_2]$.[9]

The complex $[Ru(dcbiq\underline{H})_2Cl_2]Na_2$ was synthesized by adding Na_2dcbiq (350 mg) to a clear hot solution of dichlorotetrakis(dimethylsulfoxide)ruthenium[10] (220 mg) in ethylene glycol (40 mL). The reaction mixture was heated nearly to reflux for approximately 5 min until the solution became deep green, cooled and crude chloro-complex was precipitated by the addition of 0.1 M HNO_3. The complex $Ru(dcbiq\underline{H})_2(NCS)_2$ $(TBA)_2$ **1** was synthesized from $Ru(dcbiq\underline{H})_2Cl_2Na_2$ according to the literature procedure.[2]

The absorption spectrum of complex **1** in ethanol (Figure 1a) shows two intense intraligand π-π* transitions between 250 and 400 nm and two MLCT bands with maxima at 630 nm (ε= 9800 dm^3 mol^{-1} cm^{-1}) and 500 nm. The complex **1** in ethanol-methanol glass matrix at 77 K emits a broad emission from the lowest excited MLCT state with a peak at 880 nm (Figure 1b). The emission lifetimes of lowest excited MLCT state of complex **1** in ethanol-methanol at 298 K and 77 K are 34 ns and 590 ns, respectively.

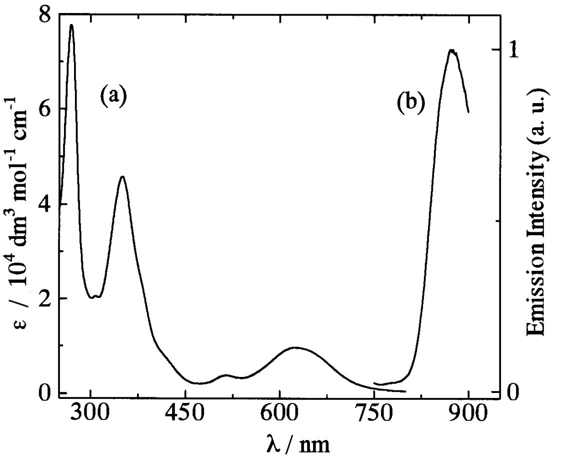

Figure 1. Absorption and emission spectra of *cis*-$Ru(dcbiq\underline{H})_2(NCS)_2(TBA)_2$: (a) absorption spectrum in ethanol solution; (b) emission spectrum in ethanol-methanol glass (4:1,v/v) at 77 K (instrument limit is 900 nm).

The cyclic voltammogram of complex **1** measured in acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate shows one quasi-reversible wave at 0.92 V vs SCE for the $Ru^{3+/2+}$ couple. A ligand-based reduction potential was observed at -0.85 V vs SCE. Coating of TiO_2 and SnO_2 nanocrystalline films[2,11] with complex **1** was carried out by soaking the films for overnight in a 10^{-4} M ethanolic solution. Photoelectrochemical experiments of the dye sensitized semiconductor electrode films were performed into a sandwich-type solar cell[2] in conjunction with a redox electrolyte consisted of a solution of 0.6 M dimethylpropylimidazolium iodide, 0.05 M I_2, 0.5 M *tert*-butylpyridine, and 0.1 M LiI in methoxyacetonitrile. A short-circuit photocurrent of 2.5 mA cm^{-2} for TiO_2 film and 2.12 mA cm^{-2} for SnO_2 film were obtained under simulated AM 1.5 solar irradiation.

Figure 2 shows the photocurrent action spectra for complex **1** adsorbed on TiO_2 and SnO_2 films where the incident photon to current conversion efficiency (IPCE) is plotted as a function of wavelength and along with the absorption spectra of the

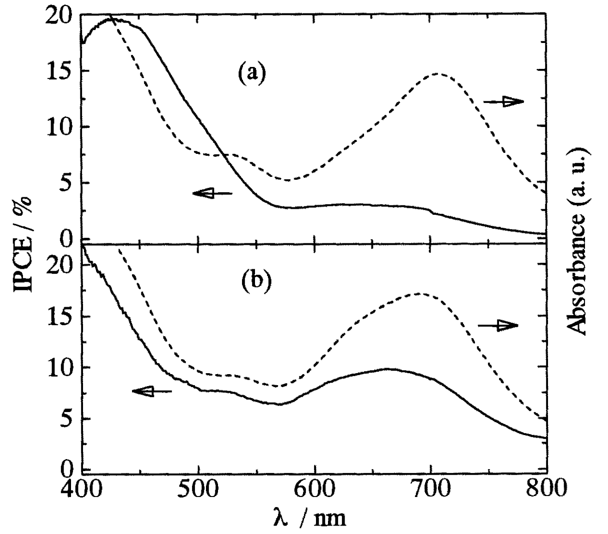

Figure 2. Absorption spectra (------) of *cis*-Ru(dcbiqH)$_2$(NCS)$_2$(TBA)$_2$ anchored to transparent films of TiO_2 (a) and SnO_2 (b); spectra are corrected for corresponding undyed films. Photocurrent action spectra (——) of the same dyed films of TiO_2 (a) and SnO_2 (b). The incident photon to current conversion efficiency is plotted as a function of wavelength. A sandwich type cell configuration was used to measure these spectra.

adsorbed dye. It is observed that in the dye**1**-sensitized TiO_2 film (Figure 2a), a relatively efficient injection (IPCE ≈20%) occurs from the higher lying excited MLCT state (λ_{max}≈ 550 nm, adsorbed dye) but injection is much less efficient (IPCE ≈3%) from the lowest excited MLCT state (λ_{max}≈ 700 nm, adsorbed dye). The energy level of the lowest excited state is estimated to be about 0.1 eV[12] lower than the conduction band edge of TiO_2 (≈ -0.65 V vs SCE, pH >4).[13] Hence, the lowest excited MLCT state is not energetically favorable to inject an electron into the conduction band of TiO_2. The IPCE spectrum for complex **1** on SnO_2 film (Figure 2b), which has a conduction band edge ~0.5 V[14] more positive than TiO_2, qualitatively trace the dye's absorbance feature and the cell efficiency (IPCE) increased to 10% at 670 nm. These results indicate that the lowest excited MLCT state is energetically allowed to enable transfer of an electron into the conduction band of SnO_2 but not into TiO_2. Although the lowest excited state is not thermodynamically favorable for electron injection in the dye**1**-sensitized TiO_2 film, the small IPCE value (≈3%) observed between 550 nm to 800 nm may be due to injection from upper vibrational level, where both electron injection and vibrational relaxation processes are competing with each other. For the dye**1**-sensitized TiO_2 film, an efficient electron injection from the ultra-short-lived,[15,16] higher lying excited MLCT state occurs prior to the internal conversion event between the two lowest excited states. From femtosecond time-resolved spectroscopy experiment on $[Ru(bpy)_3]^{2+}$, McCusker et al. revealed that formation of the lowest excited state occurs by ~300 fs after the initial excitation.[16] Thus, dual electron injection from the metal-to-ligand charge transfer excited states observed in the dye**1**-sensitized TiO_2 film indicates an ultrafast rate of electron injection to TiO_2, and agrees with the findings of femtosecond dynamical studies. Although the dye **1** injects electrons near the subpicosecond domain to TiO_2 and SnO_2, the low cell efficiency (IPCE) may be due to dye aggregation on the films or fast recombination of injected electron with the oxidized dye.[8]

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12 The excited state oxidation potential of **1** is estimated to be about –0.5 V with the electrochemical data and the excited state energy, for the 0-0 transition (850 nm) estimated from the rise of absorption spectrum (adsorbed on TiO_2, Figure 2a).
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