Ruthenium(II) Tricarboxyterpyridyl Complex with a Fluorine-substituted β-Diketonato Ligand for Highly Efficient Dye-sensitized Solar Cells

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We have developed a new β-diketonato Ru(II) complex, Ru(4,4′,4″-tricarboxy-2,2′:6′,2″-terpyridine) [4,4,4-trifluoro-1-(4-fluorophenyl)butane-1,3-dionato](NCS)$[(C_4H_9)_4N]_2$ (**1**) which shows very efficient panchromatic sensitization of nanocrystalline TiO_2 solar cell over the whole visible range extending into the near IR region (ca. 950 nm). A solar energy conversion efficiency of 8.9% was attained under standard AM 1.5 irradiation (100 mW cm^{-2}) with a short-circuit photocurrent density of 20.4 mA cm^{-2}, an open-circuit photovoltage of 0.65 V, and a fill factor of 0.67.

There has been an increasing interest in dye-sensitized nanocrystalline TiO_2 solar cells (DSCs) owing to their high efficiency and a possibility of low-cost production of such devices.[1–3] The most efficient metal complex photosensitizers employed so far in DSCs are Ru(II) polypyridyl complexes because of their intense charge-transfer absorption in the whole visible range and the ease of tunability of redox properties by choosing an appropriate ligand in a controlled manner.[4] Grätzel and co-workers reported thiocyanato-Ru(II) polypyridyl sensitizer Ru(tctpy)-$(NCS)_3(TBA)_3$ (**2**) (tctpy = 4,4′,4″-tricarboxy-2,2′:6′,2″-terpyridine, TBA = tetra-*n*-butylammonium) which achieve over 10% power conversion efficiency.[5] The monodentate thiocyanato ligands destabilized the ground state by electron donation to the metal t_{2g} orbital causing a red shift in the MLCT bands relative to $[Ru(2,2'{:}6',2''\text{-terpyridine})_2]^{2+}$ complex.

Many groups have utilized nonchromophoric chelating ligands such as dithiocarbamates, dithiolates and ethylenediamine donor ligands to tune sensitizer absorption properties and efficiently sensitize TiO_2.[6–8] Recently, Sugihara et al. reported an efficient Ru(II) 4,4′-dicarboxy-2,2′-bipyridine sensitizer containing one chelating β-diketonato ligand.[9] In addition, β-diketonato Ru(II) sensitizer of Ru(tctpy)(tfac)(NCS) (tfac = 1,1,1-trifluoropentane-2,4-dionato) showed efficient panchromatic sensitization of nanocrystalline TiO_2 solar cell.[10] However, this complex did not show the expected improvement in the solar cell efficiency because of low open-circuit voltage. In this letter, we report a new fluorine substituted β-diketonato Ru(II) sensitizer, Ru(tctpy)(tffpbd)(NCS)$(TBA)_2$ (**1**) (tffpbd = 4,4,4-trifluoro-1-(4-fluorophenyl)butane-1,3-dione[11]) that yields power conversion efficiency of 8.9% under standard AM 1.5 condition.

Complex **1** was synthesized by the same procedure to that of Ru(tctpy)(tfac)(NCS).[12] Complex **1** shows an intense and broad electronic absorption with two absorption peaks at 413 and 586 nm and a distinct shoulder at 680 nm covering entire visible region assigned to metal-to-ligand charge-transfer (MLCT) transitions (Figure 1a). The lowest energy MLCT band at 586 nm ($\varepsilon = 7000\ \text{mol}^{-1}\ \text{cm}^{-1}$) is blue-shifted compared to those of **2**. Substitution of two thiocyanato ligands by fluorine-substituted tffpbd chelating ligand stabilizes the ground state by electron withdrawn from Ru causing a decrease in the energy of the t_{2g} metal orbital and thus blue-shift the lowest energy MLCT band. The enhanced red absorption of complex **1** renders it attractive candidates as a panchromatic charge-transfer sensitizer for DSCs. When excited within the charge-transfer absorption band of complex **1** in ethanol–methanol (4:1, v/v) at 298 K exhibits a broad emission band with a maximum at 920 nm as shown in Figure 1b, attributed to the luminescence from the lowest energy ^{3}MLCT state. The excited-state lifetime of complex **1** was estimated to be 13 and 358 ns at 298 and 77 K, respectively. The cyclic voltammogram of complex **1** coated on TiO_2 electrode measured in 0.1 M $LiClO_4$ acetonitrile solution shows one quasi-reversible wave at +0.73 V vs SCE for the $Ru^{3+/2+}$ couple. The 0–0 transition energy (E^{0-0}) of **1** was approximately 1.59 eV.[13] Therefore, the excited-state reduction potential (E^*) of **1** was calculated to be −0.86 V vs SCE, which was 0.09 eV more positive than that of **2**.[8,13]

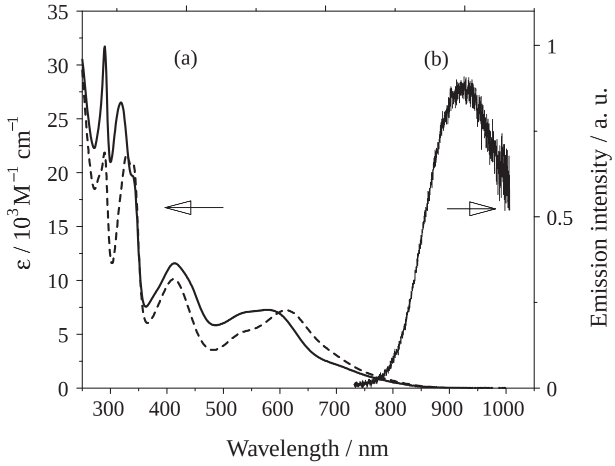


Figure 1. (a) Absorption spectra of complex **1** (———) and **2** (- - - - -) and (b) corrected emission spectra of complex **1** in ethanol-methanol (4:1, v/v) at 298 K.

A nanocrystalline TiO_2 photoelectrode (area: 0.25 cm^2; thickness: 20 μm) was prepared by screen printing on conducting glass as previously described.[3] The dye was dissolved in a mixture of *tert*-butyl alcohol and acetonitrile (1:1) at a concentration of 2×10^{-4} M. Deoxycholic acid as a coadsorbent was added into the dye solution at a concentration of 20 mM to prevent aggregation of the dye molecules. The TiO_2 films were immersed into the dye solution and then kept at 25 °C for 20 h to adsorb the dye

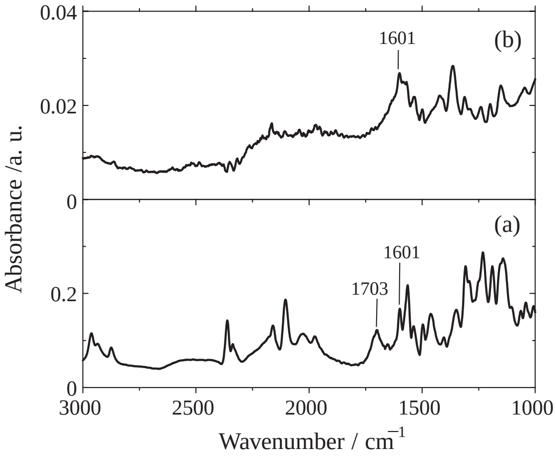


Figure 2. ATR-FTIR spectra of complex **1** obtained using solid sample (a) and adsorbed on the TiO_2 film (b).

onto the TiO_2 surface. The ATR-FTIR spectra of the complex **1** measured as a solid and in the adsorbed form onto TiO_2 films are shown in Figure 2. The complex **1** that contains one carboxylic acid and two carboxylate groups shows bands at 1703 and 1601 cm^{-1} due to υ(–C=O) and υ(–COO$^-$ asymmetric), respectively.[14] After grafting onto the TiO_2 surface, the intense band at 1703 cm^{-1} for the carboxylic acid mode is disappeared (Figure 2b). This indicates that the carboxylic acid is dissociated on the surface and implicated in the surface attachment of the dye.

Figure 3 shows a photocurrent–voltage curve for the maximum performance of a sandwich-type sealed solar cell based on complex **1** under standard AM 1.5 irradiation (100 mW cm^{-2}), with an electrolyte of 0.6 M dimethylpropylimidazolium iodide (DMPII), 0.05 M I_2, 0.1 M LiI, and 0.05 M *tert*-butylpyridine (TBP) in acetonitrile. A short-circuit photocurrent density (J_{sc}) obtained was 20.4 mA cm^{-2}, the open-circuit photovoltage (V_{oc}) was 0.65 V, and the fill factor (*ff*) was 0.67 corresponding to an overall conversion efficiency (η) of 8.9%. The inset of Figure 3 shows the action spectrum of monochromatic incident photon to current conversion efficiency (IPCE) of such a cell (electrolyte: 0.6 M DMPII, 0.05 M I_2, and 0.1 M LiI in acetonitrile). Complex **1** achieved efficient sensitization of nanocrystalline TiO_2 over the whole visible range extending into the near IR region (ca. 950 nm) with a maximum IPCE value of 78% at around 550 nm. Taking into account the reflection and absorption losses by the conducting glass, the photon to current conversion efficiency in this range reaches about 90%. Long term stability and cell performance will be investigated in detail.

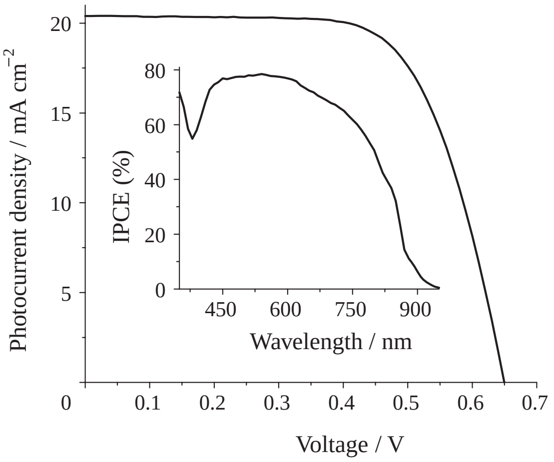
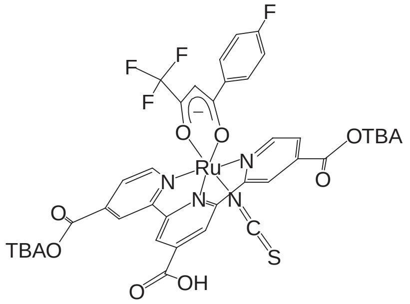


Figure 3. Photocurrent–voltage characteristics of DSCs sensitized with the complex **1** at AM 1.5 illuminations. The redox electrolyte consisted of a solution of 0.6 M DMPII, 0.05 M I_2, 0.1 M LiI, 0.05 M TBP in acetonitrile. The inset shows IPCE spectrum of nanocrystalline TiO_2 film sensitized by complex **1**. The IPCE is plotted as a function of wavelength.



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12 Ru(tctpy)(tffpbd)(SCN)$(TBA)_2$ (**1**) was prepared according to a literature method.[5,10] Yield 35%. MS (ESIMS): m/z: 413.5 $(M - 3H)^{3-}$, 620.7 $(M - 2H)^{2-}$, 1242.5 $(M - H)^{-}$. ^{1}H NMR (270 MHz, DMSO): δ 9.16 (H, ss), 8.77 (H, d), 8.72 (H, d), 8.46 (H, m), 8.21 (H, d), 8.15 (H, d), 7.51 (H, m), 7.32 (H, m), 6.97 (H, t), 6.53 (0.5H, s), 6.49 (0.5H, s), 3.26 (16H, t) 1.64 (16H, m), 1.41 (16H, m), 1.02 (24H, t). Anal. Calcd for $C_{61}H_{89}F_4N_6O_8RuS$: C, 58.92; H, 7.21; N, 6.76%. Found: C, 57.32; H, 7.01; N, 6.70%.

13 $E^{0\text{–}0}$ transition energy was determined from the 5% emission intensity of the emission spectrum at 298 K. E^* is calculated from $E^*\ (Ru^{3+/2+}) = E\ (Ru^{3+/2+}) - E^{0\text{–}0}$.

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