Synthesis and Application of Ruthenium(II) Tricarboxyterpyridyl Complex with a Nitrogen Chelete Ligand for Solar Cells Based on Nanocrystalline TiO$_2$ Films

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The ethylenediamine Ru(II) tricarboxyterpyridine complex [Ru(tctpy)(en)(NCS)]Cl (1) was newly synthesized, and its photophysical and photovoltaic properties were characterized. Solar cells based on nanocrystalline TiO$_2$ films sensitized with 1 exhibited efficient sensitization over the visible and near-infrared region. These solar cells generated a large short-circuit photocurrent of 17.7 mA cm^{-2} and an open-circuit potential of 0.68 V under simulated AM 1.5 solar irradiation (100 mW cm^{-2}) with a solar energy conversion efficiency of 8.5%.

Dye-sensitized solar cells (DSSCs) consist of a dyed nanoporous semiconductor photoelectrode permeated with a redox electrolyte.[1] Ruthenium(II) polypyridine charge transfer complexes have attracted great interest for use in DSSCs ever since Grätzel and co-workers reported the successful use of charge transfer sensitizer Ru(dcbpy)$_2$(NCS)$_2$ (N3 dye, 2) (dcbpy = 4,4'-dicarboxy-2,2'-bipyridine).[2] They also reported that [Ru(tctpy)(NCS)$_3$](TBA)$_3$ (black dye, 3) (tctpy = 4,4',4''-tricarboxy-2,2':6',2''-terpyridine, TBA = tetra-*n*-butylammonium) can be used as a panchromatic sensitizer for DSSCs.[3] Because Ru(II) terpyridine complexes have an expanded π-conjugated field, they can generally absorb a wider range of light than Ru(II) bipyridine complexes. Nonetheless, few ligands for Ru(tctpy)L$_3$ complexes have been studied.[3,4] Recently, we reported π-diketonato ruthenium(II) tricarboxyterpyridine complexes that can absorb a wider range of light than black dye.[4] However, when used in DSSCs, these β-diketonato complexes have not shown high open-circuit voltage, probably because their LUMO energy, ≈-0.9 V vs a saturated calomel electrode (SCE), are too close to the TiO$_2$ conduction band edge, ≈-0.7 V vs SCE.[5,6] Therefore, we investigated ruthenium(II) tricarboxyterpyridine dye complexes with more-negative LUMO energy. In this paper, we present the synthesis and application of the ethylenediamine ruthenium(II) tricarboxyterpyridine complex [Ru(tctpy)(en)(NCS)]Cl (1) as a new sensitizer for DSSCs.

Complex 1 was synthesized using microwave synthesis techniques, which shortened the duration of the ligand replacement reactions (Scheme 1).[7] However, when used for the ester hydrolysis reaction, microwave heating resulted mainly in decomposition; therefore we used a conventional method to hydrolyze the ester groups on the terpyridine ligand. The reaction mixture contained 1,[8] a linkage isomer of 1 (1-SCN),[9] and some other by-products. Complex 1 and 1-SCN were separated and purified on a Sephadex LH-20 column and by preparative HPLC using diluted TBA(OH) aqueous solution as an eluent. After purification, 1 was precipitated out by the addition of 0.5 M HCl. The UV–vis absorption spectra of 1 and 3 exhibit intense, broad metal-to-ligand charge transfer (MLCT) bands with absorption maxima at 560 nm (Figure 1), which enhanced absorption in
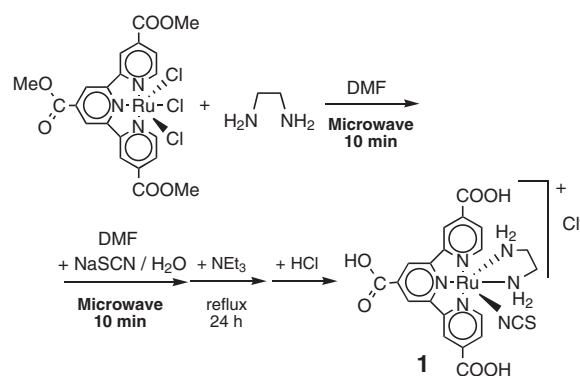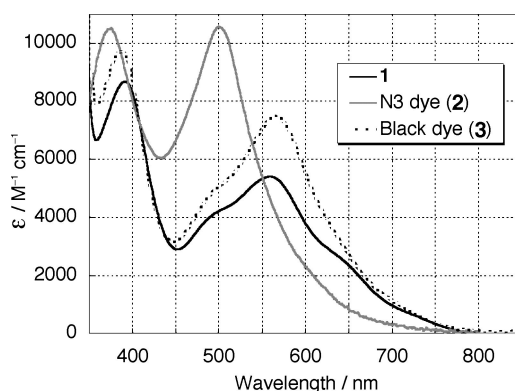

Scheme 1.

Figure 1. Absorption spectra of dye complexes in aqueous NaOH (pH = 12).

the red region of solar light compared to 2. The cyclic voltammogram of 1 measured in ethanol containing 2 equiv. of TBA(OH) and 0.1 M TBA(ClO$_4$) shows one irreversible wave for the Ru^{3+}/Ru^{2+} couple at +0.60 V vs SCE. An emission maximum was observed at around 800 nm, when 1 was measured in ethanol at 298 K, and the lifetime was 47 ns. The 0–0 transition energy (E^{00}) of 1 was approximately 1.63 eV,[10] which was 0.32 eV smaller than that of 2.[2] Therefore, the excited-state oxidation potential (E_{ox}^*) of 1 was estimated to be -1.03 V vs SCE, which was 0.08 eV more negative than that of 3.[11] This negative shift of the excited-state energy level is desirable for injection of an electron into the conduction band[5] of nanocrystalline TiO$_2$.

TiO$_2$ nanocrystalline films (thickness, 19 μm,[12] area 0.25 cm^2) were dipped into a 2 × 10^{-4} M ethanolic solution of 1 containing 4 × 10^{-4} M TBA(OH) for 12–48 h. Photoelectrochemical experiments on the dye-sensitized semiconductor electrode films were performed in a sandwich-type solar cell[3] in conjunc-
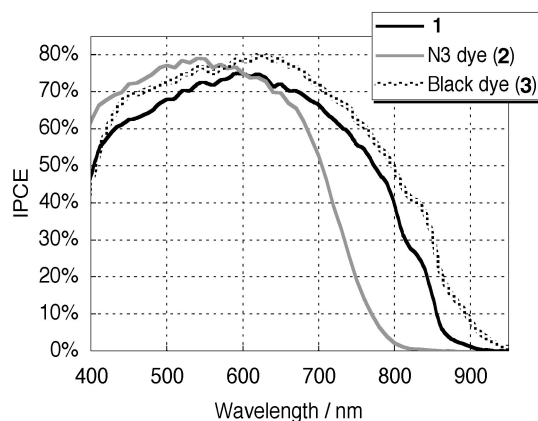
Figure 2. Photocurrent action spectra of dye-sensitized TiO_2 films. The electrolyte solution was a mixture of 0.6 M dimethyl-propyl-imidazolium iodide, 0.05 M I_2, and 0.1 M LiI in CH_3CN. The cell area of the TiO_2 electrode was 0.25 cm^2.

Table 1. Photovoltaic performance of the **1**-sensitized TiO_2 solar cells using electrolytes with different TBP concentrations

Amount of TBP	J_{sc} / mA cm^{-2}	V_{oc} / V	ff	η / %
0 M	19.6	0.57	0.69	7.8
0.1 M	17.7	0.68	0.71	8.5
0.3 M	15.7	0.70	0.74	8.1
0.5 M	14.5	0.69	0.73	7.4

tion with a redox electrolyte consisting of a solution of 0.6 M di-methylpropyl-imidazolium iodide, 0.05 M I_2, 0.5 M *tert*-butyl-pyridine (TBP), and 0.1 M LiI in acetonitrile. Complex **1** exhib-ited efficient sensitization of nanocrystalline TiO_2 solar cells over the entire visible range, displaying a maximum at around 600 nm, where incident photon-to-current conversion efficiency (IPCE) approached a high value of about 75% (Figure 2).

The photovoltaic performance parameters of the **1**-sensi-tized cells using electrolytes with various TBP concentrations are listed in Table 1. The short-circuit photocurrent (J_{SC}) de-creased as the TBP concentrations increased. In contrast, the open-circuit voltage (V_{OC}) increased significantly at a TBP con-centration of 0.1 M, and the fill factor (ff) increased slightly. A solar cell sensitized with **1** showed an overall solar light-to-elec-trical energy conversion efficiency (η) of 8.5% with the electro-lyte containing 0.1 M TBP. In contrast, DSSCs sensitized with compounds **2** and **3** showed the highest efficiency when 0.5 M TBP was employed. Figure 3 shows the I–V characteristics of DSSCs sensitized with **1** and **3**, after optimization of the TBP content in the electrolyte. The conversion efficiency could be further improved by changing the substituents on the diamine chelate so as to expand the spectral response in the lower-energy part of the solar spectrum. Optimization of the cell efficiency and stability under long-term irradiation is in progress.
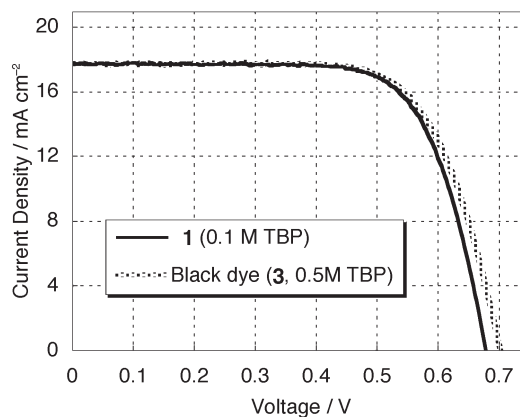
Figure 3. I–V curves of DSSCs sensitized with **1** and **3**, after optimization of TBP content in the electrolyte.

References and Notes
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7 Ru(4,4′,4″-trimethoxycarbonyl-2,2′:6′,2″-terpyridine)Cl$_3$[3] (310 mg, 0.5 mmol) in DMF (40 mL) was added to ethylenediamine (50 mL, 0.75 mmol). The reaction mixture was heated at reflux for 10 min by means of a microwave synthesizer. To the resulting solution 5 mL of an aqueous solution of NaSCN (50 mg, 0.6 mmol) was added. After the reaction mixture was refluxed for 10 min, 10 mL of Et$_3$N was added, and the solution was refluxed for 24 h to hydrolyze the ester groups on the terpyridine ligand. The reaction mixture was allowed to cool, and the volatiles were removed under reduced pressure. The residue was extracted with 0.1 M TBA(OH) aqueous solution, and the extract was filtered through a membrane filter. [Ru(tctpy)(en)-(NCS)]Cl (**1**) and some by-products were precipitated out by the ad-dition of 0.5 M HCl and were then filtered off and washed several times with water. Complex **1** was purified by column chromatography on Sephadex LH-20 and by recycling preparative HPLC. In both cas-es, 1×10^{-3} M TBA(OH) aqueous solution was used as the eluent.
8 Data for **1**: ^{1}H NMR (400 MHz, D_2O-NaOD): δ 8.95 (d, 2H), 8.77 (s, 2H), 8.75 (s, 2H), 8.00 (d, 2H), 5.70 (t, 2H), 3.23 (t, 2H), 2.45 (t, 2H). MS (ESI-MS): *m/z*: 585 (M)$^+$. Anal. Found: C, 40.98; H, 3.17; N, 13.27%. Calcd for $C_{21}H_{19}ClN_6O_6RuS$: C, 40.68; H, 3.09; N, 13.56%.
9 Data for **1-SCN**: ^{1}H NMR (400 MHz, D_2O-NaOD): δ 8.92 (d, 2H), 8.81 (s, 2H), 8.78 (s, 2H), 8.02 (d, 2H), 5.61 (t, 2H), 3.23 (t, 2H), 2.47 (t, 2H). MS (ESI-MS): *m/z*: 585 (M)$^+$.
10 The 0–0 transition energy was determined from the 5% level of the emission spectrum at room temperature.
11 E_{ox}^* of **3** was estimated to be -0.95 V vs SCE. CV and emission spectrum of **3** were measured in our laboratory.
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