Research Article

A New Heteroleptic Biquinoline Ruthenium(II) Sensitizer for Near-IR Sensitization of Nanocrystalline TiO₂

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Ruthenium(II) complex containing *cis*-[Ru(H₂dcbiq)(L)(NCS)₂], where H₂dcbiq = 4,4'-dicarboxy-2,2'-biquinoline and L = 4,4'-di-*tert*-butyl-2,2'-dipyridyl coded as **SPS-02**, was synthesized and fully characterized. This complex showed appreciably broad absorption range. The new complex was used as photosensitizer in nanocrystalline TiO₂ dye-sensitized solar cell application. *cis*-[Ru(H₂dcbiq)(L)(NCS)₂] (**SPS-02**) achieved efficient sensitization of nanocrystalline TiO₂ over the whole visible range, extending into the near-IR region (ca. 1000 nm) with superior short-circuit photocurrent density ($J_{sc} = 9.13 \text{ mA cm}^{-2}$) and conversion efficiency ($\eta = 2.09\%$) compared with complex *cis*-[Ru(H₂dcbiq)₂(NCS)₂] (**1**) under an irradiation of full sunlight (100 mW cm^{-2}).

1. Introduction

Dye-sensitized solar cells (DSSCs) have been developed as an efficient, low-cost alternatives to the silicon technology during the last years [1–6]. Based on dye-sensitized nanocrystalline titanium dioxide as photoelectrode, power conversion efficiencies of over 11% have been reached [7]. In order to improve the efficiency of DSSCs, the sensitizer should absorb photons in the near-IR region as well as over the entire visible region of the solar spectrum. Considerable efforts have been made on 2,2'-bipyridine- and 2,2':6',2''-terpyridine-based ruthenium complexes to improve the light-harvesting properties through introduction of extended π -conjugated system [6]. 2,2'-biquinoline has low π -energy level than both 2,2'-bipyridine and 2,2':6',2''-terpyridine and has potential to improve IR absorbance with its analogues Ru complexes. Arakawa and coworkers studied solar cells based on TiO₂ sensitized with homoleptic ruthenium complexes containing 4,4'-dicarboxy-2,2'-biquinoline

cis-[Ru(H₂dcbiq)₂(NCS)₂] (**1**) and reported that these solar cells have an enhanced red response in the near-IR region, but the solar cell performance was decreased due to the poor electron injection efficiency on to TiO₂ [8]. As a part of our research program in the development of new photosensitizers [9–14], we have strategically designed a heteroleptic dye SPS-02 (Figure 1) having both 4,4'-di-*tert*-butyl-2,2'-dipyridyl and 4,4'-dicarboxy-2,2'-biquinoline in the same molecule, which exhibits better performance in the IR region.

2. Experimental

2.1. Synthesis of SPS-02. [RuCl₂(*p*-cymene)]₂ (0.228 g, 0.37 mmol) was dissolved in DMF (30 mL), and 4,4'-di-*tert*-butyl-2,2'-dipyridyl (0.20 g, 0.74 mmol) was added. The reaction mixture was heated at 80°C under nitrogen for 2 h, and then 4,4'-dicarboxy-2,2'-biquinoline (0.313 g, 0.74 mmol) was added. The reaction mixture was refluxed at 160°C for

FIGURE 1: Chemical structures of **1** and **SPS-02**.

another 4 h under reduced-light conditions to avoid light-induced cis to trans isomerization. An excess of NH_4NCS (1.78 g, 23.4 mmol) was then added to the reaction mixture, which was then heated at 130°C for a further 5 h. The solvent was removed with a rotary evaporator. Water was added to the resulting semisolid to remove excess NH_4NCS . The water insoluble product was collected, washed first with distilled water and then with diethyl ether, and dried. The crude complex was dissolved in a solution of sodium hydroxide (0.4 g) in water (10 mL). The concentrated solution was charged onto a Sephadex LH-20 column and eluted with water. The main brown band was collected and concentrated to 3 mL. The required complex was isolated upon addition of a few drops of 0.01 M aqueous HNO_3 . Complex **SPS-02** was obtained after membrane filtration as brownish solid 78 mg. Anal. calcd for $\text{C}_{40}\text{H}_{36}\text{N}_6\text{O}_4\text{RuS}_2$: C, 57.89; H, 4.37; N, 10.13. Found: C, 57.43; H, 4.52; N, 9.93.

2.2. Preparation of TiO_2 Electrode. Nanocrystalline TiO_2 photoelectrodes of about $20\ \mu\text{m}$ thickness (area: $0.25\ \text{cm}^2$) were prepared using a variation of a method reported by Nazeeruddin et al. [15]. Fluorine-doped tin oxide-coated glass electrodes (Nippon Sheet Glass Co., Japan) with a sheet resistance of $8\text{--}10\ \text{ohm}^{-2}$ and an optical transmission of $>80\%$ in the visible range were used. Anatase TiO_2 colloids (particle size $\sim 13\ \text{nm}$) were obtained from commercial sources (Ti-Nanoxide D/SP, Solaronix). The nanocrystalline TiO_2 thin films of approximately $20\ \mu\text{m}$ thickness were deposited onto the conducting glass by screen printing. The film was then sintered at 500°C for 1 h. The film thickness was measured with a Surfcom 1400A surface profiler (Tokyo Seimitsu Co. Ltd.). The electrodes were impregnated with a 50 mM titanium tetrachloride solution and sintered at 500°C . The dye solutions ($2 \times 10^{-4}\ \text{M}$) were prepared in 1 : 1 acetonitrile and *tert*-butyl alcohol solvents. Deoxycholic acid as a coadsorbent was added to the dye solution at

a concentration of 20 mM. The electrodes were immersed in the dye solutions and then kept at 25°C for 20 h to adsorb the dye onto the TiO_2 surface.

2.3. Fabrication of Dye-Sensitized Solar Cell. Photovoltaic measurements were performed in a two-electrode sandwich cell configuration. The dye-deposited TiO_2 film was used as the working electrode and a platinum-coated conducting glass as the counter electrode. The two electrodes were separated by a surlyn spacer ($40\ \mu\text{m}$ thick) and sealed up by heating the polymer frame. The electrolyte was composed of 0.6 M dimethylpropyl-imidazolium iodide (DMPII), 0.05 M I_2 , and 0.1 M LiI in acetonitrile.

2.4. Photovoltaic Characterization. The working electrode was illuminated through a conducting glass. The current-voltage characteristics were measured using the previously reported method [16] with a solar simulator (AM-1.5, $100\ \text{mW}/\text{cm}^2$, WXS-155S-10: Wacom Denso Co. Japan). Monochromatic incident photon-to-current conversion efficiency (IPCE) for the solar cell, plotted as a function of excitation wavelength, was recorded on a CEP-2000 system (Bunkoh-Keiki Co. Ltd.).

3. Results and Discussion

Heteroleptic ruthenium(II) complex **SPS-02** was prepared by direct treatment of $[\text{RuCl}_2(p\text{-cymene})]_2$, 4,4'-Di-*tert*-butyl-2,2'-dipyridyl and 4,4'-dicarboxy-2,2'-biquinoline in refluxing DMF. Figure 2 shows the absorption spectrum of complex **SPS-02** in ethanol.

The strong absorption band of the complex **SPS-02** in the region between 250 and 350 nm are due to $\pi\text{--}\pi^*$ transitions. An intense and broad MLCT band at 619 nm with a shoulder at about 500 nm was observed for **SPS-02**. This enhanced red

FIGURE 2: UV absorption spectra of **SPS-02** in ethanol. FIGURE 3: Photocurrent action spectra for **SPS-02**-sensitized and **1**-sensitized films of TiO_2 .

absorption of complex **SPS-02** with MLCT band at 619 nm renders it attractive candidate as a panchromatic charge-transfer sensitizer for DSC application.

Figure 3 shows the photocurrent action spectra for complex **SPS-02** where the incident photon-to-current conversion efficiency (IPCE) values are plotted as a function of wavelength. The photoresponse of thin films extends upto 1000 nm. We observed an IPCE of 45% in **SPS-02** at about 610 nm, while in the case of complex **1**, the IPCE was 20%. The DSC sensitized with complex **SPS-02** exhibits superior light-harvesting properties in the near-IR region. The superior performance of **SPS-02** was attributed to the superior light-harvesting efficiency of high- and low-energy photons.

FIGURE 4: Photocurrent density-voltage characteristics of device **SPS-02** and device **1** under air mass 1.5 (100 mW cm^{-2}).TABLE 1: Photovoltaic performance of complex **SPS-02** and **1**.

Dye	J_{sc} (mA/cm^2)	V_{oc} [V]	F.F.	Eff. (%)
SPS-02	9.13	0.35	0.65	2.09
1	6.88	0.29	0.50	1.04

Figure 4 shows a photocurrent density-voltage curve of a sealed solar cell based on complex **SPS-02** and **1** under AM 1.5 G simulated solar light at a light intensity of 100 mW cm^{-2} with a metal mask of 0.25 cm^2 . The photovoltaic performance of complex **SPS-02** and **1** on nanocrystalline TiO_2 electrode was studied using an electrolyte with a composition of 0.6 M dimethylpropyl-imidazolium iodide (DMPPI), 0.05 M I_2 , and 0.5 M LiI in acetonitrile. The short-circuit photocurrent density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and overall cell efficiencies (η) for test cells constructed from each dye are summarized in Table 1. The test cell sensitized with complex **SPS-02** showed a photocurrent density of 9.13 mA cm^{-2} , an open circuit potential of 0.35 V, and a fill factor of 0.65, corresponding to an overall conversion efficiency (η) of 2.09%. Under similar fabrication and evaluation conditions, complex **1** gives $J_{sc} = 6.88 \text{ mA cm}^{-2}$, $V_{oc} = 0.29 \text{ V}$, and FF = 0.50, corresponding to an overall conversion efficiency (η) 1.04%. Though the new Ru complex has spectral response in a wide energy range (400–1000) the low value of short-circuit photocurrent (J_{sc}) and cell efficiency (η) are attributed to its low LUMO level which inhibits efficient electron injection on to the conduction band of TiO_2 .

4. Conclusions

A new ruthenium(II) complex containing *cis*-[Ru(H_2dcbiq)(L)(NCS) $_2$], where $\text{H}_2\text{dcbiq} = 4,4'$ -dicarboxy-2,2'-biquinoline and L = 4,4'-Di-*tert*-butyl-2,2'-dipyridyl coded as

SPS-02, was synthesized and characterized. This new dye exhibited efficient light-harvesting efficiency in a wide energy range (400–1000) which makes it as a potential photosensitizer for nanocrystalline TiO₂ dye-sensitized solar cells. The performances of the dye-sensitized solar cells exhibited superior in terms of short-circuit photocurrent density ($J_{sc} = 9.13 \text{ mA cm}^{-2}$) and conversion efficiency ($\eta = 2.09\%$) compared with complex **1**.

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