Efficient Panchromatic Sensitization of Nanocrystalline TiO_2-based Solar Cells Using 2-Pyridinecarboxylate-substituted Ruthenium(II) Complexes

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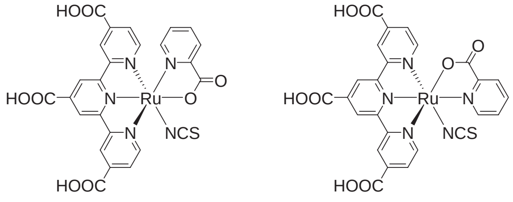
Ruthenium(II) complexes containing a 2-pyridinecarboxylate ligand (**1** and **2**) were synthesized as sensitizers for dye-sensitized solar cells (DSCs). The solar cells containing **2** exhibited efficient panchromatic sensitization over the entire visible wavelength range, extending into the near-IR region. An overall solar light-to-electrical conversion efficiency of 9.66% was achieved under standard air mass (AM) 1.5 irradiation ($100\,mW\,cm^{-2}$). This efficiency was superior to that of black dye (9.58%) under the same cell fabrication and measuring procedure.

Ruthenium(II) polypyridyl complexes as sensitizers for DSCs have received much attention since Grätzel and coworkers reported successful use of Ru(4,4′-dicarboxy-2,2′-bipyridine)$_2$(NCS)$_2$ (N3 dye)[1] and Ru(4,4′,4″-tricarboxy-2,2′:6′,2″-terpyridine)(NCS)$_3$ (black dye).[2] To increase the stability and performance of DSCs, modifications of 2,2′-bipyridine ligands have been widely investigated. However, a drawback of ruthenium(II) bis(2,2′-bipyridyl) complexes is a lack of absorption in the red region of the visible spectrum. In contrast, black dye exhibits better absorption properties in the red and near-IR region than the N3 dye, because of its expanded π-conjugated field. There have been few modifications of 2,2′:6′,2″-terpyridine ligand owing to difficulties in its synthesis.[3,4]

To tune electronic absorption properties of ruthenium(II) 2,2′:6′,2″-terpyridyl complexes, bidentate ligands have been utilized as the donor ligand instead of the two NCS ligands of black dye. The chelating structure of these ligands makes complexes resistant to ligand loss reactions. Moreover, this type of ruthenium(II) complex has been enhanced with additional functions by modifications of bidentate ligands.[5] We have investigated ruthenium(II) complexes with β-dicatonato ligands,[5] an ethylenediamine ligand,[6] 2-phenylpyridinato ligands,[7] and a 2-quinolinecarboxylate ligand[8] as bidentate ligands. The complexes containing these ligands exhibit efficient panchromatic sensitization. In this letter, we report an application of ruthenium(II) complexes containing a 2-pyridinecarboxylate ligand (**1** and **2**) (Scheme 1) as sensitizers for DSCs.

Complexes **1** and **2** were synthesized by the same procedure as the complex containing a 2-quinolinecarboxylate ligand.[8,9] The structural difference between **1** and **2** is the orientation of the coordinated 2-pyridinecarboxylate ligand. The absorption spectra of **1** and **2** in 1×10^{-3} M aqueous NaOH solution are compared to that of black dye in Figure 1. Both **1** and **2** show intense and broad absorption over the entire visible region. The lowest energy bands at 532 nm (**1**) and 518 nm (**2**) are blue-shifted compared with that of the black dye. The blue shifts might be caused by the replacement of two NCS ligands with a 2-pyridinecarboxylate ligand, since the electron-donating ability of a single 2-pyridinecarboxylate ligand is inferior to that of two NCS ligands.[10] Cyclic voltammograms of **1** and **2** were measured in methanol solution containing 0.1 M tetrabutylammonium perchlorate using a three-electrode apparatus comprising a platinum wire counter electrode, a platinum working electrode, and an Ag/AgCl (saturated aqueous KCl) reference electrode in contact with an NaCl salt bridge. Ferrocene was added to each sample solution at the end of the experiments, and a ferrocenium/ferrocene redox couple was used as an internal potential reference. A quasi-reversible wave for the $Ru^{3+/2+}$ couple between 0.4 and 0.9 V versus a saturated calomel electrode (SCE) was obtained. The peak potential of differential pulse voltammograms for **1** and **2** were 0.77 and 0.73 V vs. SCE, respectively. The observed potentials were sufficiently low for rapid electron transfer from iodide/triiodide couple to the oxidized complex. Emission spectra were measured in acetonitrile/*N*,*N*-dimethylformamide (99:1, v/v) solution at 25 °C. The solutions were deoxygenated by bubbling with argon for 10 min and excited at 405 nm using



1 **2**

Scheme 1. Structures of the complexes.

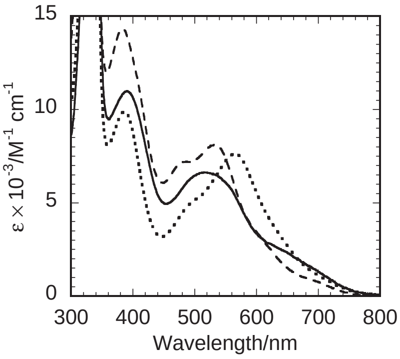


Figure 1. Absorption spectra of **1** (dashed line), **2** (solid line), and black dye (dotted line). Spectra of these complexes were measured in 1×10^{-3} M aqueous NaOH solution.

a picosecond diode. The emission maxima of **1** and **2** were observed at 940 and 920 nm, and the excited-state lifetimes were estimated to be 8 and 20 ns, respectively. The 0–0 transition energies (E^{0-0}) of **1** and **2** are approximately 1.65 and 1.68 eV, respectively.[11] Therefore, the excited-state redox potential ($E_{ox}{}^*$) was calculated to be -0.88 and -0.95 V vs. SCE. The $E_{ox}{}^*$ value of **1** was 0.07 eV more positive than that of **2**. Complexes **1** and **2** showed slightly different properties, resulting from the structural difference of these complexes.

Nanocrystalline TiO_2 photoelectrodes (area 0.25 cm^2; thickness 36 µm), prepared as previously described,[12] were immersed into an ethanol solution of dye for 24 h at 25 °C. The concentration of **1** and **2** was 1×10^{-4} M containing 2×10^{-4} M tetrabutylammonium hydroxide (TBA(OH)) in the dye solution, and that of black dye was 2×10^{-4} M. Each solution contains a deoxycholic acid as a coadsorbate to suppress dye aggregation on TiO_2 surfaces.[13] The concentrations of deoxycholic acid in the solutions were 1×10^{-2} M for **1** and **2** and 2×10^{-2} M for black dye. Photoelectrochemical measurements were performed using a two-electrode solar cell consisting of the dye-coated TiO_2 electrode, a platinum film counter electrode, a polypropylene film spacer (thickness: 60 µm), and an electrolyte solution consisting of 0.6 M 1,2-dimethyl-3-propylimidazolium iodide, 0.05 M iodine, 0.1 M lithium iodide, and 0.1–0.5 M *tert*-butylpyridine (TBP) in acetonitrile.

Some preliminary photovoltaic experiments of the DSCs were investigated under AM 1.5 irradiation (100 mW cm^{-2}); the results are summarized in Table 1. The highest performances of DSCs containing **1** and **2** were obtained at the concentration of TBP in electrolyte was 0.1 M. In contrast, DSCs containing black dye showed the highest conversion efficiency when 0.5 M TBP was employed. The DSC containing **1** had an efficiency of 6.16%, which is 64.3% of the DSC containing black dye that has a 9.58% efficiency under the same cell fabrication and measuring procedure. The amounts of adsorbed **1** and black dye on TiO_2 film were almost the same (Table 1). One of the reasons for this result might be positive-shifted $E_{ox}{}^*$ of **1**. On the contrary, the DSC containing **2** showed a 9.66% efficiency, which is 56% higher than that of **1**. Note that the DSC containing **2** exhibits a higher efficiency than that of black dye. Figure 2 shows the photocurrent action spectra of the maximum performance of DSCs containing **1**, **2**, and black dye. The IPCE for each DSC is plotted as a function of the wavelength. The maximum IPCE values of DSCs containing **1**, **2**, and black dye are 58%, 73%, and 71%, respectively. As expected from photovoltaic experiments, the DSC containing **1** shows slightly lower IPCE values. The DSC containing **2** exhibits efficient panchromatic sensitization over the entire visible wavelength range extending into the near-IR region. Moreover, **2** showed higher IPCE values than that of black dye in the 400–780 nm regions. This is consistent with the results obtained from photovoltaic experiments, as the DSC containing **2** has a higher J_{sc} value than that of black dye. We are currently investigating a modification of the 2-pyridinecarboxylate ligand, optimization of cell fabrication, and long-term stability of the cells.

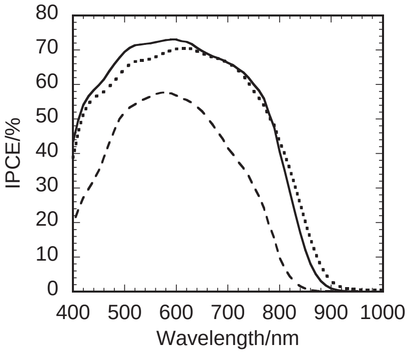


Figure 2. Photocurrent action spectra for DSCs containing **1** (dashed line), **2** (solid line), and black dye (dotted line).

Table 1. Photovoltaic performances of DSCs containing **1**, **2**, and black dye

Complex	$\Gamma^a \times 10^7$ /mol cm^{-2}	TBP /M	$J_{sc}{}^b$ /mA cm^{-2}	$V_{oc}{}^c$ /V	ff^d	η^e /%
1	1.7	0.1	13.25	0.629	0.739	6.16
2	2.1	0.1	19.81	0.677	0.721	9.66
Black dye	1.8	0.5	19.03	0.713	0.707	9.58

[a]Amount of adsorbed complex on TiO_2 film.[14] [b]Short-circuit photocurrent. [c]Open-circuit voltage. [d]Fill factor. [e]Overall solar light-to-electrical conversion efficiency.

We are grateful to Dr. Ryuzi Katoh, Dr. Motohiro Kasuya, and Dr. Satoshi Kodate for the measurement of the emission spectrum. This work was supported by the Incorporated Administrative Agency New Energy and Industrial Technology Development Organization (NEDO), under the Ministry of Economy, Trade and Industry (METI).

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9 Complexes **1** and **2** were purified by column chromatography (Sephadex LH20, 5×10^{-3} M aqueous TBA(OH) solution). The structures of **1** and **2** were identified by nuclear magnetic resonance (NMR) spectroscopy analysis. The signals of 2-pyridinecarboxylato ligand were different between **1** and **2**. The strong downfield shifts of **1** were obtained by a ring current effect of 2,2′:6′,2″-terpyridine ligand.
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Published on the web (Advance View) December 6, 2008; doi:10.1246/cl.2009.62