

## Synthesis and Characterization of a Novel Ruthenium Complex Bearing a Curcumin Derivative Ligand and Its Application to Dye-sensitized Solar Cells

Hironobu Ozawa, Hiroki Kawaguchi, Yu Okuyama, and Hironori Arakawa\*  
 Department of Industrial Chemistry, Faculty of Engineering, Tokyo University of Science,  
 12-1 Ichigaya Funagawara-machi, Shinjuku-ku, Tokyo 162-0826

(Received March 25, 2011; CL-110255; E-mail: h.arakawa@ci.kagu.tus.ac.jp)

A novel ruthenium complex bearing a bisdemethoxycurcumin, which is a natural dye exhibiting a strong absorption around 410 nm, as a ligand has been synthesized and characterized for application to dye-sensitized solar cells (DSCs). The DSC with this sensitizer showed about 55% incident photon-to-current conversion efficiency at the wavelength region between 450 and 600 nm, and 5.76% conversion efficiency under AM 1.5 (100 mW cm<sup>-2</sup>) irradiation.

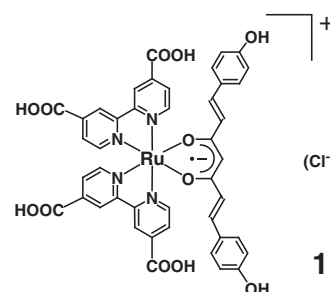
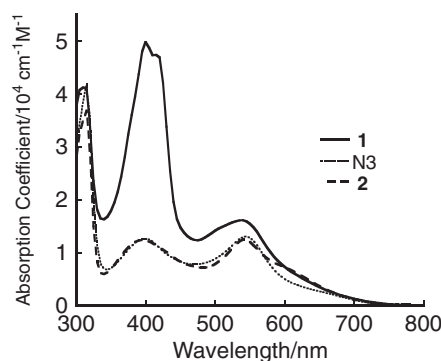


Chart 1.



**Figure 1.** Molar absorptivity spectra of **1** (solid line), **2** (dashed line), and N3 (dotted line) in DMF.

Dye-sensitized solar cells (DSCs) have attracted much attention due to higher light-to-electrical energy conversion efficiency and lower fabrication cost.<sup>1</sup> Recently 10–11% efficiencies have been achieved by employing polypyridyl ruthenium complexes as sensitizers.<sup>2</sup> Extensive studies on the development of highly efficient ruthenium sensitizers have been thus far carried out since the photovoltaic performances of DSCs are entirely depend on the sensitizing abilities of dyes. Both increase of the molar absorption coefficient and extension of the onset of the absorption spectrum into near the IR region are required to improve the sensitizing abilities of ruthenium dyes. The former is achieved by expansion of the  $\pi$ -conjugated systems of the ligand or introduction of chromophore units.<sup>3</sup> On the other hand, to accomplish the latter is relatively difficult since the onset of the absorption spectrum of the polypyridyl ruthenium complex is closely related to their redox potential.

Most efficient ruthenium sensitizers, such as N719  $\{(TBA)_2[*cis*-Ru(Hdcbpy)_2(NCS)_2]\}$  (TBA: tetrabutylammonium, dcbpy: 4,4'-dicarboxy-2,2'-bipyridine) or black dye  $\{(TBA)_3-[Ru(Htcterpy)(NCS)_3]\}$  (tcterpy: 4,4',4''-tricarboxy-2,2':6',2''-terpyridine), possess two or three isothiocyanate ligands to adjust their redox potentials for both the electron injection into the conduction band of TiO<sub>2</sub> and the reduction of the resulting one-electron-oxidized form of the dye by a redox mediator in the electrolyte. Although isothiocyanate ligand is useful for such redox-potential engineering of ruthenium sensitizers, it is known that isothiocyanate ligand gradually undergoes ligand-substitution under irradiation, resulting in the degradation of the photovoltaic performance of DSCs.<sup>4</sup> For the long-term stability of DSCs, various bidentate or tridentate ligands which can bind to ruthenium atom stronger than monodentate isothiocyanate ligand have been explored, and several ruthenium sensitizers bearing such multidentate ligands have been reported.<sup>5</sup> In this context, we previously reported that  $\beta$ -diketonate ligands are useful for the redox-potential engineering of ruthenium and osmium complexes, and these sensitizers, such as  $[Ru(dcbpy)_2(acac)]Cl$  (**2**, acac: acetylacetonate), exhibit higher sensitizing ability.<sup>6</sup> Han et al. also showed the effectiveness of  $\beta$ -diketonate ligands for the development of efficient sensitizers.<sup>7</sup>

On the other hand, curcumin is well known as a natural orange dye contained in turmeric and ginger. Curcumin and its derivatives exhibit strong absorption around 420 nm<sup>8</sup> and possess a  $\beta$ -diketone unit, which can serve as a bidentate ligand. In this study, a novel ruthenium complex **1** (Chart 1) bearing a bisdemethoxycurcumin (bdmc) has been synthesized and characterized. This complex is the first example of a ruthenium sensitizer bearing a natural dye as a ligand. Here we communicate photo- and electrochemical properties of **1**, and the photovoltaic performance of the DSC with **1**.

The novel dye **1** was synthesized by the reaction of *cis*- $[RuCl_2(dcbpy)_2]$ <sup>9</sup> with bdmc in the presence of Na<sub>2</sub>CO<sub>3</sub>. The crude product was purified on a Sephadex LH-20 column using methanol as an eluent, and the pure complex was obtained as a chloride salt.<sup>10</sup>

The molar absorptivity spectra of **1** and  $[Ru(dcbpy)_2(acac)]^+$  (**2**), together with that of *cis*- $[Ru(dcbpy)_2(NCS)_2]$  (N3) are shown in Figure 1. A quite strong absorption mainly attributed to the  $\pi$ - $\pi^*$  transition of the bdmc unit was observed for **1** around 410 nm. In addition, the molar absorptivity of **1** at the MLCT band region was moderately increased compared to that

**Table 1.** Electrochemical properties of dyes<sup>a</sup>

Entry	$E_{\text{HOMO}}$		$E_{0-0}^{\text{d}}$ /V	$E_{\text{LUMO}}^{\text{c}}$ /V vs. SCE
	/V vs. SCE			
<b>1</b>	0.79 <sup>b</sup>	0.82 <sup>c</sup>	1.64	-0.82
<b>2</b>	0.66 <sup>b</sup>	0.82 <sup>c</sup>	1.66	-0.84
N3	0.69 <sup>b</sup>	0.82 <sup>c</sup>	1.68	-0.86

<sup>a</sup>All potentials are given vs. SCE. <sup>b</sup>Oxidation potentials in CH<sub>3</sub>OH containing 5 mM TBAOH. <sup>c</sup>Oxidation potentials of dyes adsorbed on the TiO<sub>2</sub> film, measured in 0.1 M LiClO<sub>4</sub> acetonitrile solution. <sup>d</sup> $E_{0-0}$  was estimated from the onset of the absorption spectrum measured in DMF. <sup>e</sup>Calculated from the equation:  $E_{\text{LUMO}} = E_{\text{HOMO}} - E_{0-0}$ .

**Table 2.** Photovoltaic performance of DSCs under AM1.5 (100 mW cm<sup>-2</sup>) irradiation<sup>a</sup>

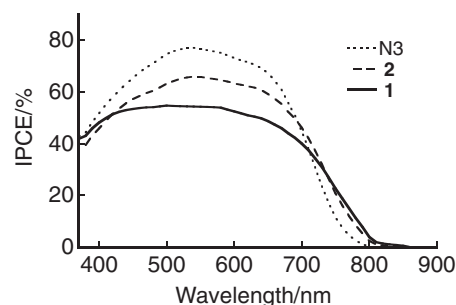
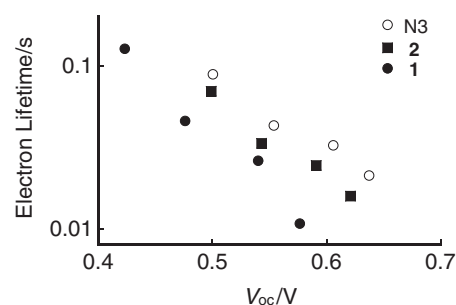
Entry	$J_{\text{sc}}$ /mA cm <sup>-2</sup>	$V_{\text{oc}}$ /V	FF	$\eta$ /%	Amount of dye
					adsorption /10 <sup>-7</sup> mol cm <sup>-2</sup>
<b>1</b>	12.55	0.62	0.74	5.76	1.6
<b>2</b>	14.61	0.65	0.72	6.81	2.4
N3	15.75	0.67	0.74	7.87	1.7

<sup>a</sup>The electrolyte was an acetonitrile solution containing of 0.05 M I<sub>2</sub>, 0.1 M LiI, 0.6 M DMPIImI, and 0.5 M TBP (TiO<sub>2</sub> film thickness: 24 μm, active area: 0.25 cm<sup>2</sup>).

of **2**. Since bdmc has no absorption at this region (Figure S1),<sup>11</sup> this enhancement is attributed to the formation of a hybridized orbital between the bdmc orbital and the Ru-based orbital. Such a hybridized orbital spread over the Ru–bdmc framework was observed as LUMO+4 (Figure S5).<sup>11</sup> On the other hand, both the absorption maximum of the MLCT band and the onset wavelength of **1** were almost the same as those of **2**, indicating that the electrochemical properties of **1** are similar to those of **2**.

Electrochemical properties of **1**, **2**, and N3 are summarized in Table 1. As expected from the similarity of the absorption feature in the MLCT band region, the first oxidations of **1** and **2** adsorbed on TiO<sub>2</sub> electrode occurred at the same potential (0.82 V vs. SCE). The lowest transition energy ( $E_{0-0}$ ) of **1** was estimated from the onset of the absorption spectrum since **1** was found to be a nonemissive compound under N<sub>2</sub> at room temperature.  $E_{0-0}$  for **1** was estimated to be 1.64 V, and the energy level of the LUMO was calculated to be -0.82 V vs. SCE. These HOMO–LUMO energy levels of **1** were suitable as a sensitizer of the nanocrystalline TiO<sub>2</sub> solar cell.

Photovoltaic performance of the DSCs based on **1**, **2**, and N3 is summarized in Table 2. The DSC with **1** showed lower  $J_{\text{sc}}$  and  $V_{\text{oc}}$  values than those of **2**, resulting in the lower conversion efficiency (5.76%). As for the amount of dye adsorbed on TiO<sub>2</sub> film, **1** was much less than that of **2**. This might be one reason for the observed lower  $J_{\text{sc}}$  value of **1**. On the other hand, the DSC with **1** exhibited about 55% incident photon-to-current conversion efficiency (IPCE) in the wavelength range between 450 and 600 nm (Figure 2). Although slight enhancement of the IPCE value around 400 nm was observed, characteristic strong absorption of **1** at this region was not reflected in the IPCE value. It seems probable that effective electron injection from the bdmc ligand did not take place because bdmc ligand locates

**Figure 2.** Incident photon-to-current conversion efficiency (IPCE) spectra of DSCs with **1** (solid line), **2** (dashed line), and N3 (dotted line) measured under AM1.5 irradiation (100 mW cm<sup>-2</sup>) (thickness of TiO<sub>2</sub>: 24 μm, active areas of the cells: 0.25 cm<sup>2</sup>).**Figure 3.** Electron lifetime in the TiO<sub>2</sub> film vs.  $V_{\text{oc}}$  for the DSCs with **1** (closed circle), **2** (square), and N3 (open circle) (thickness of TiO<sub>2</sub>: 7 μm).

away from TiO<sub>2</sub> film after **1** was adsorbed. Although lower IPCE values were observed for **1** in the visible-light region, higher IPCE values than that for N3 were observed at wavelengths longer than 700 nm, as observed for **2**. This enhancement reflects the higher molar absorption coefficient of **1** and **2** in the MLCT band region.

To gain further insight into the observed lower  $J_{\text{sc}}$  and  $V_{\text{oc}}$  values for **1**, the electron lifetime and electron density of the TiO<sub>2</sub> film were measured by stepped light-induced transient measurements of photocurrent and photovoltages (SLIM-PCV) method. Figure 3 shows the electron lifetimes in the TiO<sub>2</sub> photoelectrodes of the DSCs with **1**, **2**, and N3 as a function of  $V_{\text{oc}}$ . The electron lifetime decreased in the order N3 > **2** > **1**. This trend was also observed in  $V_{\text{oc}}$  values. Although the energy level of the conduction band of TiO<sub>2</sub> for **1** was slightly lower than those for **2** and N3 (Figure S6),<sup>11</sup> the shorter electron lifetime is considered to be the major reason for the lower  $V_{\text{oc}}$  value for **1**. The observed lower  $J_{\text{sc}}$  value of **1** can be reasonably explained by this shorter electron lifetime. On the other hand, the electron lifetime of **2** was also shorter than N3, although the amount of dye adsorption of **2** was much larger. Moreover, the electron lifetime of **1** was much shorter than N3, even though the amount of dye adsorption of **1** was almost the same. These results suggest that the shorter electron lifetimes of **1** and **2** were mainly due to the enhancement of the backward electron transfer to the one-electron-oxidized forms of dyes. It is likely that the higher positive charge of the one-electron-oxidized forms of **1** and **2** (2+) compared to that of N3 (1+) facilitates the backward

electron transfer, resulting in the shorter electron lifetimes of the ruthenium dyes bearing  $\beta$ -diketonate ligand.

In summary, we have succeeded in the preparation of the first example of a ruthenium sensitizer bearing a natural dye as a ligand. The DSC with this novel dye exhibited 5.76% conversion efficiency under AM 1.5 (100 mW cm<sup>-2</sup>) irradiation.

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- 10 Anal. Calcd for C<sub>43</sub>H<sub>35</sub>N<sub>4</sub>O<sub>14</sub>ClRu ([M]<sup>+</sup>Cl·2H<sub>2</sub>O): C, 53.34; H, 3.64; N, 5.79%. Found: C, 53.19; H, 4.14; N, 5.57%. ESI-TOF-MS *m/z*: [M]<sup>+</sup> 897.09.
- 11 Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.