High Efficiency of Dye-Sensitized Solar Cells Based on Metal-Free Indoline Dyes

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Dye-sensitized solar cells (Grätzel cells) have attracted a great deal of interest, as they offer high energy-conversion efficiencies at low cost.[1−3] Ruthenium dyes are used in dye-sensitized solar cells containing titania nanocrystals, i.e., *cis*-bis(isothiocyanato)-bis(2,2′-bipyridil-4,4′-dicarboxylate) ruthenium(II) (referred to as N3 dye) was reported in 1993,[4] and *cis*-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylate)ruthenium(II) bis-tetra-*n*-butylammonium (referred to as N719 dye) was reported in 1999.[5] A metal-free organic dye that is environmentally friendly and easily synthesized from widely available has been long awaited, while there was no successor regarding the photovoltaic properties against the ruthenium dye since it was reported in 1993. We already reported metal-free indoline dyes for dye-sensitized solar cells, which have a good performance.[6] Furthermore, to obtain much higher conversion efficiency, the structures of the indoline dyes were modified. In general, the extension of the methine chain in the cyanine and melocyanine dyes was a very effective method for a red shift in the absorption spectra. However, the band gaps between the highest occupied molecular orbitals (HOMO) and lowest occupied molecular orbitals (LUMO) are remarkably smaller with the increased methine chain length. We found that the molecular design of the rhodanine ring contributed to the red shift in the absorption spectrum. Here we report organic dyes with a new type of indoline structure that exhibit high efficiencies.

Figure 1 shows the molecular structure for indoline dyes **1−4**. All the indoline dyes were synthesized under similar conditions as described before.[6] Figure 2 shows the light absorption spectra of indoline dye **1** in *tert*-butyl alcohol/acetonitrile (1/1) and on the TiO$_2$ electrode, revealing peaks at 526 and 541 nm, respectively. The molecular coefficient of indoline dye **1** was 68700 M^{-1} cm^{-1} at 526 nm in *tert*-butyl alcohol/acetonitrile (1/1), which is very high in comparison to 13 900 M^{-1} cm^{-1} at 541 nm for the N3 dye under the same conditions. Indoline dyes **2** and **3** show similar absorption spectra peaks as indoline dye **1**, at 532 and 531 nm, respectively. Indoline dye **4** has a slightly red-shifted absorption spectra peak in comparison to indoline dyes **1−3**, because indoline dye **4** has three rhodanine rings. On the TiO$_2$ electrode, indoline dyes **1−3** appear purple, and indoline dye **4** appears black. Although adsorptions of these new indoline dyes onto the TiO$_2$ electrode were found to broaden the absorption spectrum peaks, these dyes hardly produced a red shift in the absorption peak. Already-reported indoline dyes have a one-unit rhodanine ring, which has a large red shift on the TiO$_2$ electrode because of J-aggregate on the TiO$_2$ electrode.[6] This means these new indoline dyes have a moderate interaction between the dyes on the TiO$_2$ surface.
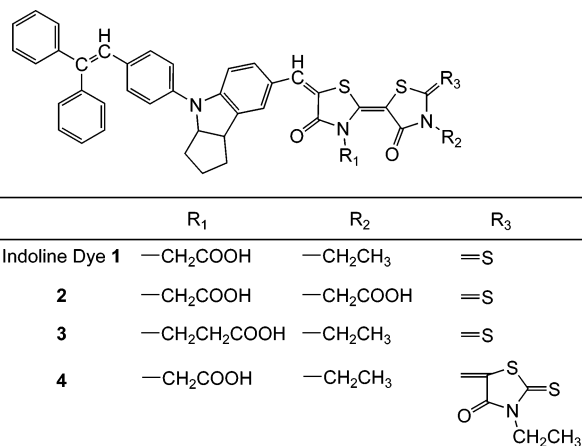
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Figure 1. Molecular structures of indoline dyes **1−4**.

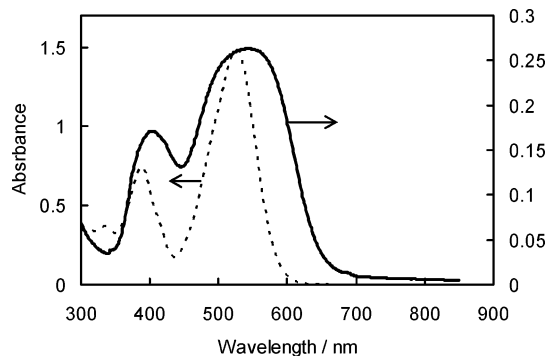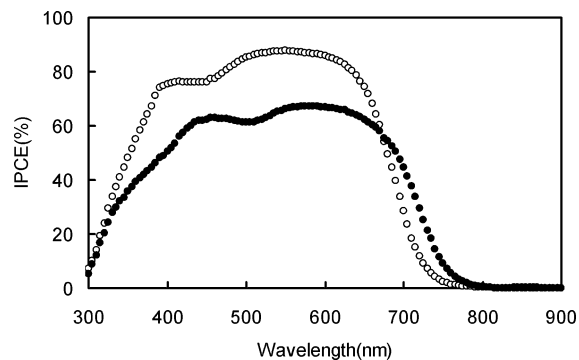|	R$_1$	R$_2$	R$_3$
Indoline Dye **1**	—CH$_2$COOH	—CH$_2$CH$_3$	=S
2	—CH$_2$COOH	—CH$_2$COOH	=S
3	—CH$_2$CH$_2$COOH	—CH$_2$CH$_3$	=S
4	—CH$_2$COOH	—CH$_2$CH$_3$	(rhodanine ring)

Figure 2. Absorption spectra of indoline dye **1** in *tert*-butyl alcohol/acetonitrile (1:1) (− − −) and on the TiO$_2$ films (−−−). All the absorption spectra were measured by transparent mode using a UV−vis spectrometer (JASCO, VX-800).

Titania paste was prepared by mixing HPW-25 (Catalyst and Chemicals Ind. Co., Ltd.) and HPW-200 at a weight ratio of 7:3 and depositing this onto a 0.16-cm^2 piece of F-doped tin oxide coated glass (Nihon Sheet Glass Co., Ltd.). The resulting layer was dried at 100 °C for 1 h followed by heating at 550 °C for 2 h in air. Dye solutions were prepared in *tert*-butyl alcohol/acetonitrile (1/1, 5 × 10^{-4} M) with titania electrodes prepared by immersion in the dye solution for 15 h. The counter electrode consisted of Pt coated on glass. Two different electrolyte solutions were used. A mixture of 0.1 M LiI, 0.05 M I$_2$, 0.6 M 1,3-dimethyl-3-imidazolinium iodine, and 0.5 M 4-*tert*-butyl pyridine (TBP) in 3-methoxypropionitrile was used for the N3 dye and N719 dye. In general, it is known that the composition of this electrolyte is the best recipe for the N3 dye and N719 dye. Also, a mixture of 0.1 M LiI, 0.05

Figure 3. Incident photon-to-current conversion efficiencies spectra for dye-sensitized solar cells based on indoline dye **1** (○) and indoline dye **4** (●). The electrolyte was a mixture of 0.1 M LiI, 0.05M I_2, and 0.6 M DMPII in 3-methoxypropionitrile.

Table 1. Photovoltaic Performance of Dye-Sensitized Solar Cells Based on the Indoline Dyes **1**−**4**, Compared to the N3 Dye and N719 Dye[a]

	Voc (mV)	Jsc (mAcm^{-2})	ff	η (%)
indoline dye **1**	645	18.75	0.538	6.51
2	584	17.50	0.538	5.50
3	628	17.38	0.513	5.60
4	569	19.56	0.533	5.93
N3 dye	699	18.06	0.625	7.89
N719 dye	754	16.68	0.657	8.26

[a] Experiments were conducted using TiO_2 photoelectrode with approximately 12-μm thickness and 0.16-cm^2 working area.

M I_2, and 0.6 M 1,3-dimethyl-3-imidazolinium iodine in 3-methoxypropionitrile was used for the indoline dyes for the best result. The photovoltaic performances were measured with a potentiostat (HSV-100, Hokutodenko Co., Ltd.) and employed an AM1.5 solar simulator (YSS-40S, Yamashita Denso Co.) as the light source. The illumination intensity was held constant at 100 mW cm^{-2} using a power/energy meter (13PEM001, Melles Griot KK) and also calibrated by a grating spectroradiometer (LS-100, EKO Instruments Co., Ltd.). The action spectra of the monochromatic incident photon-to-current conversion efficiency (IPCE) for solar cells were measured with a Hypermonolight (SM-25, Bunkoh-keiki Co., Ltd.).

The photovoltaic properties of the solar cells constructed from these electrodes were measured. The measured open-circuit photovoltage (Voc), short-circuit photocurrent density (Jsc), fill factor (ff), and solar-to-electric conversion efficiencies (η) are listed in Table 1. The solar-to-electric conversion efficiencies of the indoline dyes **1**−**4** were high for the dye-sensitized solar cells based on the metal-free organic dyes. Figure 3 shows the action spectra of the monochromatic IPCEs for indoline dyes **1** and **4**. The IPCE for indoline dye **1** reached more than 85% in the range from 445 to 600 nm, and indoline dye **4** reached more than 60% in the range from 415 to 510 nm. These indoline dyes show a large photocurrent due to large IPCEs, and the absorption band of the indoline dyes is almost the same as the N3 and N719.

By optimizing dye **1** using cholic acid derivatives, such as chenodeoxycholic acid, a much higher photovoltaic performance is achieved. It is known that cholic acid derivatives[7] and phosphonic acid[8] prevent aggregation for dyes on the TiO_2 surface. It has been
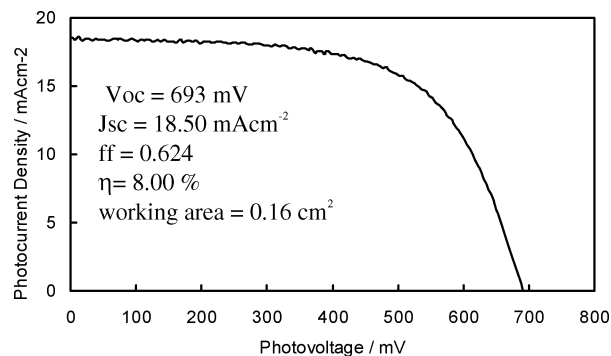
Figure 4. Photocurrent voltage curve obtained with dye-sensitized solar cell based on indoline dye **1** under AM 1.5 radiation (100 mW cm^{-2}), which has 1 mM chenodeoxy cholic acid and 0.05 M TBP in electrolyte.

reported that black dye[9] and coumarin dyes[10] obtained a much higher efficiency by adding 20 mM cholic acid derivatives to the dye solutions. It was found that chenodeoxycholic acid as a coadsorbent added to a solution of indoline dye **1** showed the best performance at 2 times higher concentration than that of indoline dye. A 0.05 M concentration of TBP was added to the electrolyte as a result of optimizing the electrolyte composition. Although LiI in the electrolyte was changed to NaI, KI, CeI, (n-butyl)$_4$NI, and LiI showed the best photovoltaic performance in comparison to the other iodides. Finally, the optimized evaluation condition for indoline dye **1** was determined as follows. (a) Dye solution: 5 × 10^{-4} M indoline dye **1** and 1 × 10^{-3} M chenodeoxy cholic acid as a coadsorbent in *tert*-butyl alcohol/acetonitrile (1/1). (b) Electrolyte: mixture of 0.1 M LiI, 0.05 M I_2, 0.6 M 1,3-dimethyl-3-imidazolinium iodine, and 0.05 M TBP in 3-methoxypropionitrile. As a result, indoline dye **1** showed an excellent photovoltaic performance (Figure 4, Voc = 693 mV, Jsc = 18.50 mAcm^{-2}, ff = 0.624, η = 8.00%). This is the highest value for dye-sensitized solar cells based on metal-free organic dyes without antireflection layer. By TG-DTA analysis, indoline dye **1** showed enough thermal resistivity up to 300 °C.

Supporting Information Available: Synthesis and characterization procedures for the indoline dye **1** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737.
(2) Grätzel, M. *J. Photochem. Photobiol., C* **2003**, *4*, 145.
(3) Grätzel, M. *J. Photochem. Photobiol., A* **2004**, *164*, 3.
(4) Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Müller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382.
(5) Nazeeruddin, M. K.; Zakeeruddin, S. M.; Humphry-Baker, R.; Jirousek, M.; Liska, P.; Vlachopoulos, N.; Shklover, V.; Fischer, C.-H.; Grätzel, M. *Inorg. Chem.* **1999**, *38*, 6298.
(6) Horiuchi, T.; Miura, H.; Uchida, S. *Chem. Commun.* **2003**, 3036.
(7) Kay, A.; Grätzel, M. *J. Phys. Chem.* **1993**, *97*, 6272.
(8) Wang, P.; Zakeeruddin, S. M.; Humphry-Baker, R.; Moser, J. E.; Grätzel, M. *Adv. Mater.* **2003**, *15*, 2101.
(9) Nazeeruddin, M. K.; Péchy, P.; Renouard, T.; Zakeeruddin, S. M.; Humphry-Baker, R.; Comte, P.; Liska, P.; Cevey, L.; Costa, E.; Shklover, V.; Spiccia, L.; Deacon, G. B.; Bignozzi, C. A.; Grätzel, M. *J. Am. Chem. Soc.* **2001**, *123*, 1613.
(10) Hara, K.; Kurashige, M.; Dan-oh, Y.; Kasada, C.; Shinpo, A.; Suga, S.; Sayama, K.; Arakawa, H. *New J. Chem.* **2003**, *27*, 783.

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