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Highly-efficient metal-free organic dyes for dye-sensitized solar cells

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A solar-to-electric conversion efficiency of 6.1% is achieved with this new dye, compared to 6.3% for N3 dye under the same experimental conditions. Although these indoline dyes are slightly less efficient than N3 dye, the cost of indoline dye is much less than for N3 due to ease of preparation. Furthermore, indoline dyes are shown to be highly stable to photoredox processes by cyclic voltammogram.

Dye-sensitized solar cells (Grätzel cells) have attracted a great deal of interest, as they offer high energy-conversion efficiencies at low cost.[1] Ru dyes, such as [*cis*-Ru(II)(2,2′-bipyridyl-4,4′-dicarboxylic acid)(NCS)], are used in dye-sensitized solar cells containing titania nanocrystals, exhibit high performance and good stability. However, Ru dyes are very expensive due to the rarity of the metal. As Ru dyes are expensive, metal free dyes such as perylene dyes,[2] anthrocyanine dyes,[3] xanthene dyes,[4] melocyanine dyes[5,6] and coumarin dyes[7] have been investigated. As yet, however, organic dyes have not been able to efficiently convert solar energy.

To prepare an efficient metal-free organic dye for solar cells, a variety of organic dyes were synthesized and investigated, in particular, photographic sensitizers. Eventually, a novel indoline dye exhibiting very good performance in dye-sensitized solar cells was found. These new dyes are easily prepared, exhibit high efficiencies, and are relatively cheap due to the simple preparation procedures. Novel indoline dyes that exhibit extraordinary performance as solar cells are presented.

Fig. 1 shows the indoline dye synthesis scheme. Indoline dye **3** was produced by heating a mixture of 1,2,3,3a,4,8b-hexahydro-4-(4-methoxyphenyl)cyclopento[*b*]indole-7-carboxaldehyde (75.69 g), rhodanine-3-acetic acid (54.69 g), ammonium acetate (6.73 g) and acetic acid (180 ml) to 120 °C. The reaction came to completion after 30 min, and the reaction mixture was allowed to cool to room temperature. Crystals were collected by filtration, washed two times with distilled water (2000 ml) and recrystallized in 1-propanol to give a yield of 110.51 g.†

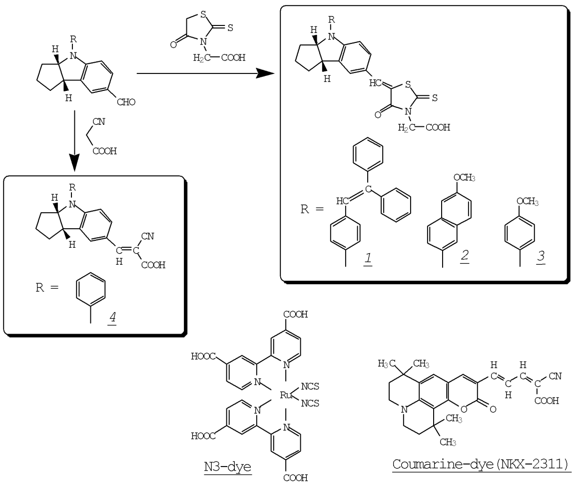

Fig. 1 Indoline dye synthesis scheme and molecular structure of indoline dyes, N3 dye and coumarin dye.

Fig. 2 shows the light absorption spectra of **1** in *tert*-butyl alcohol/acetnitrile (1/1) and on a TiO_2 electrode, revealing peaks at 491 nm and 540 nm, respectively. Similar absorption spectra have been observed in indoline dye **2** in solution and on a TiO_2 electrode. On a TiO_2 electrode, indoline dyes **1–3** appear bright red, and dye **4** appears yellow. Adsorption of dye onto a TiO_2 electrode was observed to broaden the absorption spectrum and to red shift the absorption peak. Similar broadening and red shifts have been reported in thiazole melocyanines on TiO_2 electrodes,[6,8] which has been suggested to be due to the formation of J-aggregate on the TiO_2 electrode. The indoline dyes were thus supposed to have formed J-aggregate on the TiO_2 electrodes. The molecular coefficient of **1** was 55800 $mol^{-1}\cdot cm^{-1}$ at 491 nm, which is very high in comparison to 13900 $mol^{-1}\cdot cm^{-1}$ at 541 nm for N3 dye [*cis*-Ru(II)(2,2′-bipyridyl-4,4′-dicarboxilic acid)(NCS), Solaronix] under the same conditions.

Titania paste was prepared by mixing HPW-25 (Catalyst and Chemicals Ind. Co., Ltd.) and HPW-200 at a weight ratio of 8 : 2, and depositing this onto a 0.25 cm^2 piece of F-doped tin oxide coated glass (Nihon Sheet Glass Co., Ltd.). The resulting layer was dried at 100 °C for 15 min 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 17 h. The counter electrode consisted of Pt coated on titanium sheet. Two different electrolyte solutions were used. A mixture (A) of 0.1 M LiI, 0.05 M I_2, 0.5 M 1,3-dimethyl-3-imidazolinium iodine and 0.6 M 4-*tert*-butyl pyridine (TBP) in 3-methoxypropionitrile was used for N3 dye, and a mixture (B) of 0.1 M LiI, 0.05 M I_2, 0.5 M 1,3-dimethyl-3-imidazolinium iodide in 3-methoxypropionitrile was used for coumarin and indoline dyes.

To evaluate solar cell performance, a 300 W Xe lamp (Hyper Xenone Exciter, Bunkoh Keiki Co., Ltd.) was equipped to filter out the IR (over 700 nm) and UV (under 400 nm) spectral region.[9] Illumination intensity was held constant at 100 $mW\cdot cm^{-2}$ using a pyranometer (LI-200SB, LI-COR) and also

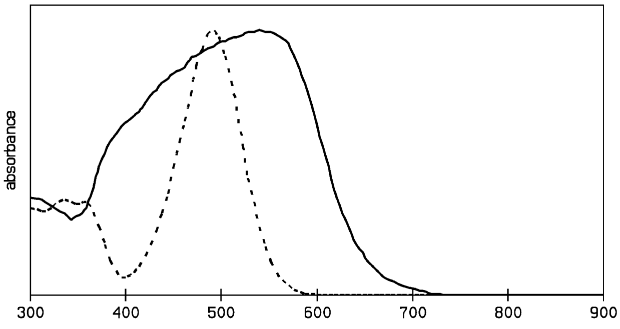

Fig. 2 UV/vis spectra of indoline dye **1** in *t*-BuOH/CH_3CN (dashed line) and adsorbed on TiO_2 film (solid line).

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calibrated by a Si second order PV reference cell. A pyranometer was used to ensure a constant illumination intensity of 100 mW·cm^{-2}. Experimental photocurrent and voltage data were measured by a PC *via* a 12-bit A-D converter and a set of variable resistors.

Photovoltaic properties of the solar cells constructed from these electrodes were measured. Measured short-circuit photocurrent density (J_{sc}), open-circuit photovoltage (V_{oc}), fill factor (*ff*) and solar-to-electric conversion efficiencies (η) are listed Table 1. The solar-to-electric conversion efficiencies of these indoline dyes were very high for metal-free organic dyes. It is known that conversion efficiency for N3 dye generally increases when using an electrolyte containing TBP. Therefore, TBP was added for evaluation with N3 dye. However, efficiencies of the indoline dyes when degraded by the addition of TBP were the same as for coumarin dyes. By optimizing the electrolyte used with the indoline dyes, higher solar cell performance is hoped for.

In addition to high efficiencies, indoline dye was also found to be highly stable to photoredox processes. Dye **1** was observed to be stable to redox processes by cyclic voltammogram (CV) tests. Voltammograms were recorded using a Pt disk working electrode in acetonitrile containing 0.1 M tetra-n-butylammonium perchlorate. Scans started at 0 V *versus* saturated calomel electrode (SCE), increasing at a rate of 200 mV·s^{-1}. Fig. 3 shows the CV of indoline dye **1** measured in acetonitrile containing 0.1 M tetra-n-butylammonium perchlorate, which exhibits an oxidation potential (E_{ox}) of +0.88 V (*vs*. SCE). Under the same conditions, E_{ox} of **4**, N3 dye and coumarin dyes were found to be +1.04 V, +0.90 V and +0.86 V (*vs*. SCE). Although the oxidation potential of indoline dye **4** is higher than of N3 dye, **1** was almost the same as N3 dye. Further, the CV of **1** and **4** appeared to be reduction peaks. This means that indoline dyes **1** and **4** are highly stable in the radical cation state. This behavior is unusual for melocyanine dyes used for photographic process. In Fig. 3, the CV for MC-2, typical of melocyanine dyes, does not show a reduction peak. Indoline dyes would thus be expected to be long lived in solar cells.

Table 1 Photovoltaic performance of dye-sensitized solar cells containing indoline-dyes **1** and **2**, compared to N3 dye and coumarin dye (NKX-2311)

	V_{oc} (mV)	J_{sc} (mA·cm^{-2})	*ff*	η (%)	Electrolyte
N3 dye	698	16.77	0.54	6.3	A
Coumarin dye	491	16.10	0.41	3.3	B
Indoline dye **1**	604	17.76	0.57	6.1	B
2	559	18.07	0.55	5.5	B

Experiments were conducted using a TiO$_2$ photoelectrode of approx. 15 μm thickness and 0.25 cm^2 working area.

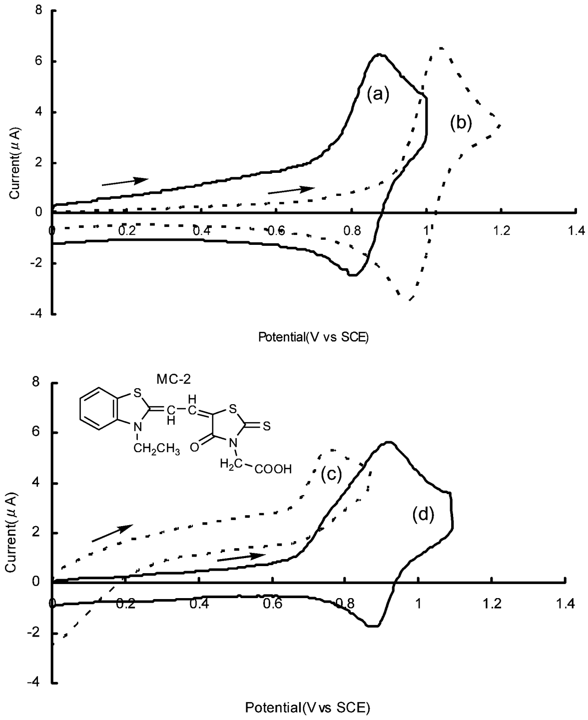

Fig. 3 Cyclic voltammograms of (a) indoline dye **1**, (b) indoline dye **4**, (c) MC-2 and (d) N3 dye in acetonitrile.

Notes and references

† Yield: 110.51 g (91.8%, red crystals); LC (254 nm): 99.9%; m.p.: 236 ~ 238 °C; ^{1}H-NMR (CDCl$_3$):δ1.5 ~ 2.2 (8H, m), 3.84 (3H, s), 3.84 ~ 3.88 (1H, m), 4.84 ~ 4.89 (1H, m), 4.93 (2H, s), 6.61 (1H, d), 6.95 (2H, d), 7.19 ~ 7.24 (5H, m), 7.70 (1H, s).

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