Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Photochemistry and Photobiology A: Chemistry 164 (2004) 29–32

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

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

Tamotsu Horiuchi [a,*], Hidetoshi Miura [a], Satoshi Uchida [b]

[a] Technology Research Laboratory, Corporate Research Center, Mitsubishi Paper Mills Limited, 46 Wadai, Tsukuba 300-4247, Ibaraki, Japan
[b] Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, 1-1 Katahira 2-Chome,
Aoba-Ku, Sendai 980-8577, Japan

Received 19 September 2003; received in revised form 17 November 2003; accepted 8 December 2003

Abstract

A solar-to-electric conversion efficiency of 5.1% is achieved with this new dye, compared to 5.8% for N3 dye under the same experimental conditions. Although these indoline dyes are slightly less efficient than N3 dye [*cis*-Ru(II)(2,2′-bipyridil-4,4′-dicarboxilic acid) (NCS)], the cost would be expected much lower because it does not contain any noble, rare metals in the structure and also it is easy to prepare specially for the mass production. Furthermore, indoline dyes are shown to be highly stable to photoredox processes by cyclic voltammogram.

Keywords: Dye-sensitized solar cell; Metal-free organic dyes; J-aggregate

1. Introduction

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 N3 dye [*cis*-Ru(II)(2,2′-bipyridil-4,4′-dicarboxilic acid) (NCS)], are used in dye-sensitized solar cells containing titania nanocrystals, exhibit high performance and good stability. Due to the use of rare metals and the difficulty of purification, metal-free dyes such as perylene dyes [2], anthocyanine 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 efficient metal-free organic dye for solar cells, varieties of organic dyes were synthesized and investigated, in particular, photographic sensitizer. 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 dyes molecular structure.

2. Experimental

2.1. Synthesis of the dye

Indoline dye 1 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. A crystal was collected by filtration and washed two times with distilled water (2000 ml) and recrystallized in 1-propanol to give a 110.51 g. Yield: 110.51 g (91.8%, red crystals); LC (254 nm): 99.9%; m.p.: 236–238 °C; FD-MS: $m/e = 465$[M] (100), 466[M + 1] (30), 467[M + 2] (15); ^{1}H NMR ($CDCl_3$): δ 1.5–2.2 (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).

Indoline dye 2 was obtained by the same synthesis conditions for indoline dye 1 except replacing rhodanine-3-acetic acid to cyanoacetic acid. Subsequently, Indoline dye 2 was obtained by yellow crystals (64.9%). LC (254 nm): 99.9%; m.p.: 151–152 °C; FD-MS: $m/e = 359$[M] (100), 360[M+1] (35), 361[M + 2] (15); ^{1}H NMR ($CDCl_3$): δ 1.5–2.2 (8H, m), 3.77–3.82 (1H, m), 3.82 (3H, s), 4.77–4.84 (1H, m), 5.54 (1H, d), 6.55 (1H, d), 6.94 (2H, dd), 7.03–7.22 (4H, m), 7.27 (1H, d).

---

[*] Corresponding author. Tel.: +81-29-864-3530; fax: 81-29-864-3530.
E-mail address: horiuchi_tamotsu@mpm.co.jp (T. Horiuchi).

1010-6030/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2003.12.018

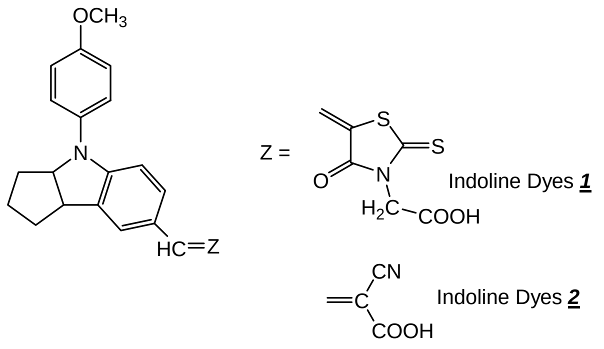

Fig. 1. Molecular structure of indoline dyes.

2.2. Cell assembly

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 1 h followed by heating at 550 °C for 30 min in air. Obtained TiO_2 film thickness was about 12 μm. All dye solutions were prepared in ethanol (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 titanium sheet. Two different electrolyte solutions were used. A mixture 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 of 0.1 M LiI, 0.05 M I_2, 0.5 M 1,3-dimethyl-3-imidazolinium iodine in 3-methoxypropionitrile was used for indoline dyes.

2.3. Photovoltaic property measurement

The photovoltaic performance of the solar cells based on indoline dyes was measured with a potentiostat (HA-501G, Hokutodenko Co. Ltd.) and employed AM1.5 solar simulator (XC-300, Optel Co. Ltd.) as a light source. A power/energy meter (13PEM001, Melles Griot KK) was used to ensure a constant illumination intensity of 100 mW cm^{-2}. Action spectra of the monoclomatic IPCEs for solar cells measured with a Hypermonoclolight (SM-25, Bunkoh-keiki Co. Ltd.).

3. Results and discussion

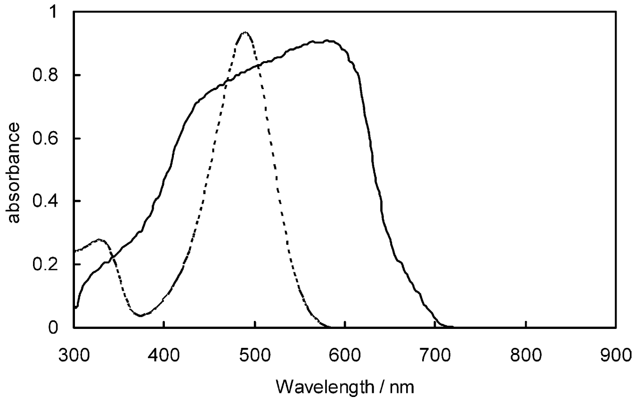

Fig. 2. UV-Vis spectra of indoline dye 1 in ethanol (dash line) and adsorbed on TiO_2 film (solid line).

Fig. 2a shows the light absorption spectra of 1 in ethanol and on a TiO_2 electrode, revealing peaks at 483 nm and about 600 nm, respectively. And Fig. 2b shows the light absorption spectra of 2 in ethanol and on a TiO_2 electrode, revealing peaks at 390 nm and about 415 nm, respectively. On TiO_2 electrode, indoline dyes 1 appear red, and dye 2 appears yellow. Adsorption of dye onto 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 benzotiazole 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 expected to the form of various aggregate on the TiO_2 electrode. Especially, absorption spectra on the red side of monomer were expected to be due to formation of J-aggregate. The molecular coefficients of 1 and 2 in ethanol was 43 300 M^{-1} cm^{-1} at 483 nm and 40 400 M^{-1} cm^{-1} at 390 nm, which is very high in comparison to 13 900 M^{-1} cm^{-1} at 541 nm for N3 dye [*cis*-Ru(II)(2,2′-bipyridil-4,4′-dicarboxilic acid) (NCS), Solaronix] under the same conditions.

Photovoltaic properties of the solar cells constructed from these electrodes were measured. Measured photocurrent and voltage curve shows Fig. 3 obtained short-circuit photocurrent density (J_{sc}), open-circuit photovoltage (V_{oc}), fill factor (ff) and solar-to-electric conversion efficiencies (η) for indoline dyes 1 and 2 were $J_{sc} = 14.8\,mA\,cm^{-2}$, $V_{oc} = 589\,mV$, ff $= 0.59$, $\eta = 5.11\%$ and $J_{sc} = 10.0\,mA\,cm^{-2}$, $V_{oc} = 622\,mV$, ff $= 0.65$, $\eta = 4.03\%$, respectively. In the same conditions, photovoltaic properties for N3 dye was $J_{sc} =$

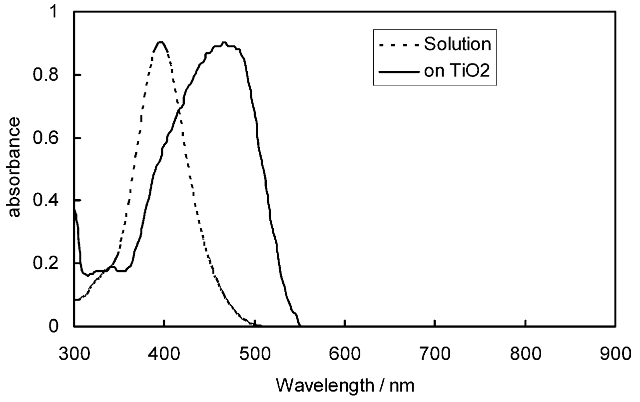

Fig. 3. UV-Vis spectra of indoline dye 2 in ethanol (dash line) and adsorbed on TiO_2 film (solid line).

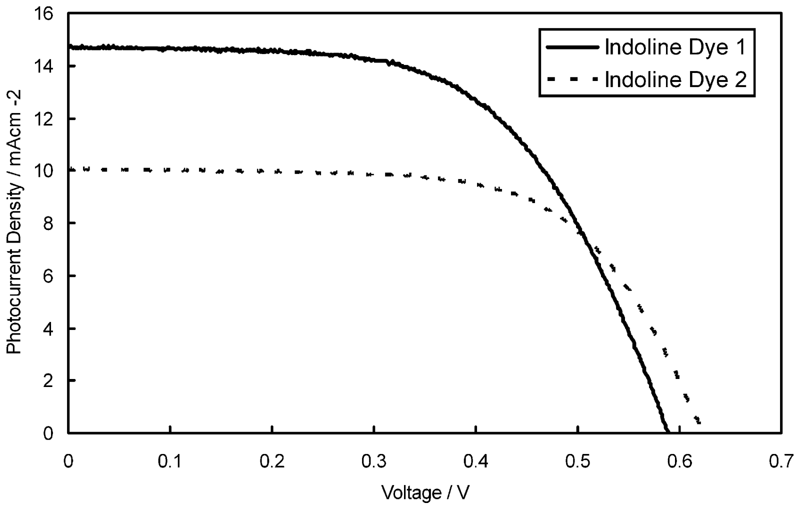

Fig. 4. A photocurrent voltage curve obtained with dye-sensitized solar cells based on indoline dyes 1 and 2 under AM 1.5 radiation (100 mW cm^{-2}).

13.1 mA cm^{-2}, $V_{\mathrm{oc}} = 699$ mV, ff = 0.63, $\eta = 5.75\%$ with 0.5 M TBP contained electrolyte. The solar-to-electric conversion efficiencies of these indoline dyes were very high for metal-free organic dyes. Fig. 4 shows action spectra of monochromatic incident photon-to-current conversion efficiencies (IPCEs) for indoline dyes 1 and 2. The IPCE for indoline dye 1 reached more than 70% in the range from 445 to 600 nm. On the other hand, IPCE for indoline dye 2 reached more than 80% in the range from 415 to 510 nm. Although indoline dyes have narrow absorption band in comparison to N3 dye, indoline dyes shows large photocurrent due to large amount of IPCEs. 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. 5 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 +0.82 V (versus SCE). Under the same conditions, N3 dye was found to be +0.90 V (versus SCE). On the other hand, the CV of 1 appeared to be reduction peaks (Fig. 6). This behavior is unusual for conventional dyes using for photographic process. Stability of the redox characteristic of the dye is very important because of one of the reasons in degradation of the performance is destroy of the dye. Therefore, stability of the radical cation state of the dye is very important. In Fig. 5, CV for MC-2 as conventional melocyanine dyes not shows reduction peak.

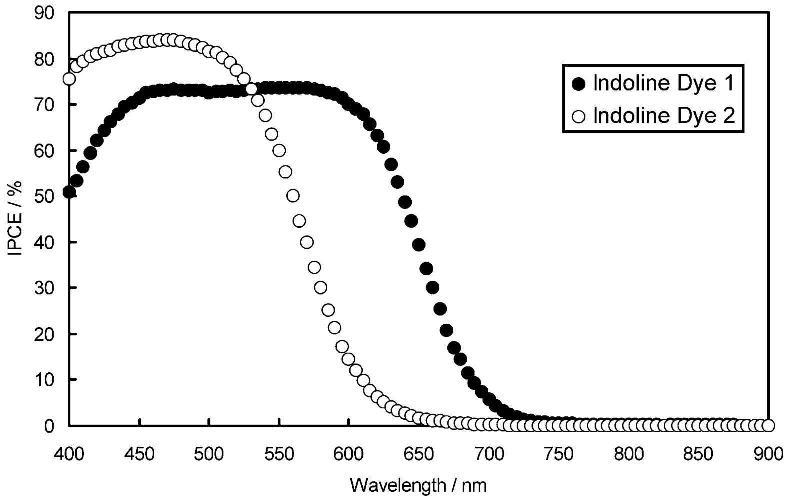

Fig. 5. IPCE action spectra of dye-sensitized solar cells based on indoline dyes 1 and 2.

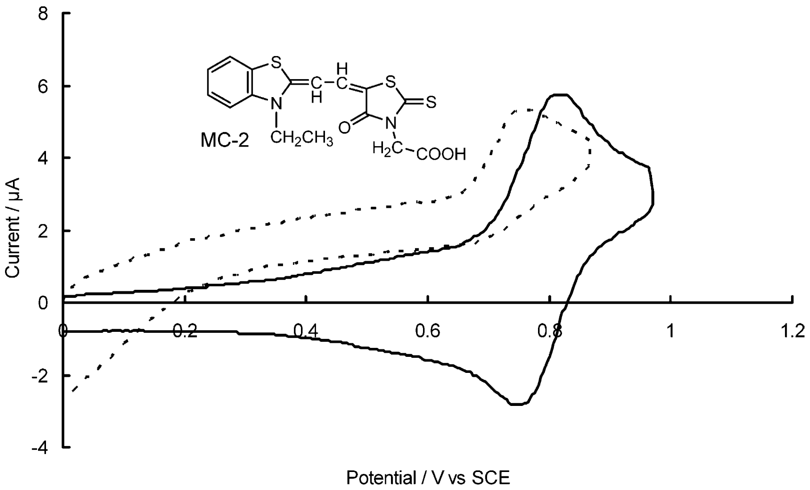

Fig. 6. Cyclic voltammograms of (a) indoline dye 1 and (b) MC-2 in acetnitrile.

Indoline dye would thus be expected to have a long life in solar cells.

4. Conclusion

A solar-to-electric conversion efficiency of 5.1% is achieved with this new dye, compared to 5.8% for N3 dye under the same experimental conditions. Although indoline dyes have narrow absorption band in comparison to N3 dye, indoline dyes shows large photocurrent due to large amount of IPCEs. Furthermore, indoline dyes are shown to be highly stable to photoredox processes by cyclic voltammogram.

References

[1] B. O' Regan, M. Grätzel, Nature 1991 (1991) 737.

[2] S. Ferrere, A. Zaben, B.A. Gregg, J. Phys. Chem. B 101 (1997) 4490.

[3] N.J. Cherepy, G.P. Smestad, M. Grätzel, J.Z. Zhang, J. Phys. Chem. B 101 (1997) 9342.

[4] K. Hara, T. Horiguchi, T. Kinoshita, K. Sayama, H. Sugihara, H. Arakawa, Chem. Lett. (2000) 316.

[5] A.C. Khazraji, S. Hotchandani, S. Das, P.V. Kamat, J. Phys. Chem. B 103 (1999) 4693.

[6] K. Sayama, K. Hara, N. Mori, M. Satsuki, S. Suga, S. Tsukagoshi, Y. Abe, H. Sugihara, H. Arakawa, Chem. Commun. (2000) 1173.

[7] K. Hara, K. Sayama, Y. Ohga, A. Shinpo, S. Suga, H. Arakawa, Chem. Commun. (2001) 569.

[8] F. Nüesch, J.E. Moser, V. Shklover, M. Grätzel, J. Am. Chem. Soc. 118 (1996) 5420.