

High-conversion-efficiency organic dye-sensitized solar cells with a novel indoline dye

Seigo Ito,^{*ab} Hidetoshi Miura,^c Satoshi Uchida,^d Masakazu Takata,^e
Koichi Sumioka,^e Paul Liska,^b Pascal Comte,^b Peter Péchy^b and Michael Grätzel^b

Received (in Cambridge, UK) 29th May 2008, Accepted 31st July 2008

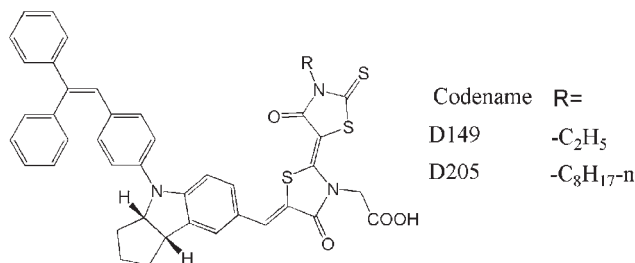
First published as an Advance Article on the web 12th September 2008

DOI: 10.1039/b809093a

An indoline dye (D205), the synthesis method of which is disclosed in this report, gave high-efficiency organic dye-sensitized solar cells (9.52%) using an anti-aggregation reagent (chenodeoxycholic acid).

Dye-sensitized solar cells (DSCs)¹ have been investigated extensively as potential candidates for renewable-energy systems. By using ruthenium complexes through novel molecular design, Sharp and our group have reported DSCs with high photoenergy-conversion efficiencies (η) of over 11% for AM1.5-simulated solar light (100 mW cm⁻², 1 sun).² However, ruthenium complex dyes are not suitable for cost-effective environmentally-friendly photovoltaic systems, because ruthenium is a rare and expensive metal, which limits the potentially wide application of these complexes. Therefore, the investigation of DSCs using metal-free organic dyes is very important for practical applications. Recently, numerous organic dyes for high-efficiency DSCs have been reported; new organic dyes with efficiencies over 5% are hemicyanine dye ($\eta = 5.1\%$),^{3a} polyene-diphenylamine dye ($\eta = 5.1\%$),^{3b} thienylfluorene dye, ($\eta = 5.23\%$),^{3c} phenothiazine dye ($\eta = 5.5\%$),^{3d} thienothiophene-thiophene-derived dye ($\eta = 6.23\%$),^{3e} phenyl-conjugated polyene dye ($\eta = 6.6\%$,^{3f} 6.8%^{3g}), *N,N*-dimethyl-aniline-cyanoacetic acid ($\eta = 6.8\%$),^{3h} porphyrin dye ($\eta = 7.1\%$),³ⁱ oligothiophene dye ($\eta = 7.7\%$),^{3j} coumarin dye ($\eta = 8.2\%$),^{3k} indoline dye (D149, see Scheme 1: $\eta = 9.03\%$)^{3l} and oligo-phenylenevinylene-unit dye ($\eta = 9.1\%$).^{3m}

In order to improve the η values, it is necessary to remodel the molecular design of organic dye photosensitizers. One of the new design concepts is to control aggregation between dye molecules. To obtain a dye with efficient photocurrent generation, π -stacked aggregation (D and/or H aggregation⁴) on the nanocrystalline-TiO₂ electrodes should normally be avoided. Aggregation may lead to intermolecular quenching or molecules residing in the system that are not functionally attached to the



Scheme 1 The structures of indoline dyes (D149 and D205).

TiO₂ surface and thus act as filters.⁵ Some ruthenium complexes (black dye^{2a} and N719^{2b}) have shown the best results using chenodeoxycholic acid (CDCA), which functions as an anti-aggregation reagent to improve the photovoltaic effect.⁶ On the contrary, indoline dyes and coumarin dyes form photoactive aggregates on nanocrystalline-TiO₂ electrodes for DSCs, known as J-aggregation.^{7,8} Therefore, controlling dye-aggregation is an important issue for high-efficiency DSCs.

In order to control the aggregation between dye molecules, a new indoline dye was designed by introducing an *n*-octyl substitute onto the rhodanine ring of D149 for use in DSC: D205 (Scheme 1). D205 gave 7.2% conversion efficiency using an ionic-liquid electrolyte.⁹ In this report, we disclose the synthesis method of D205 and show high-efficiency DSCs using volatile electrolytes. In particular, with the use of chenodeoxycholic acid (CDCA), the DSCs with D205 on nanocrystalline-TiO₂ electrodes exhibited a high open-circuit photovoltage at 710 mV. The best resulting photopower-conversion efficiency was 9.52% under 1 sun irradiation. This is the best photopower-conversion efficiency published for an organic dye-sensitized solar cell to date.

Fig. 1 shows the synthesis route for D205. Indoline dye (D205, **3**) was produced by heating a mixture of 4-[4-(2,2-diphenyl-vinyl)-phenyl]-1,2,3,3a,4,8b-hexahydro-cyclopenta[b]indole-7-carbaldehyde (**1**) (0.53 g, 1.2 mmol), octyl-5-(4-oxo-thiazolidin-2-ylidene)-rhodanine-3-acetic acid (**2**) (0.53 g, 1.3 mmol),¹⁰ ammonium acetate (0.01 g) and acetic acid (10 mL) at 120 °C for 5 h. After cooling the red-brown precipitate was filtered and washed twice with MeOH and then dried, yielding 0.89 g of crude dye. The crude dye was subjected to silica gel column chromatography, using CHCl₃ and MeOH (20 : 1) as the eluent, and 0.80 g (78%) of pure dye was obtained as a brown powder. The analytical data are given in the footnote.†

^a Department of Electrical Engineering and Computer Sciences, Graduate School of Engineering, University of Hyogo, 2167 Shosha, Himeji, Hyogo, 671-2280, Japan. E-mail: itou@eng.u-hyogo.ac.jp

^b Laboratoire de Photonique et Interfaces, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

^c Tsukuba Research Center, Chemireca Inc., D-14 2-1-6, Sengen, Tsukuba, Ibaraki, 305-0047, Japan

^d Research Center for Advanced Science and Technology (RCAST), The University of Tokyo, 4-6-1, Komaba, Meguro, Tokyo, 153-8904, Japan

^e Technology Research laboratory, Corporate Research Center, Mitsubishi Paper Mills Limited, 46, Wadai, Tsukuba-city, Ibaraki, 300-4247, Japan

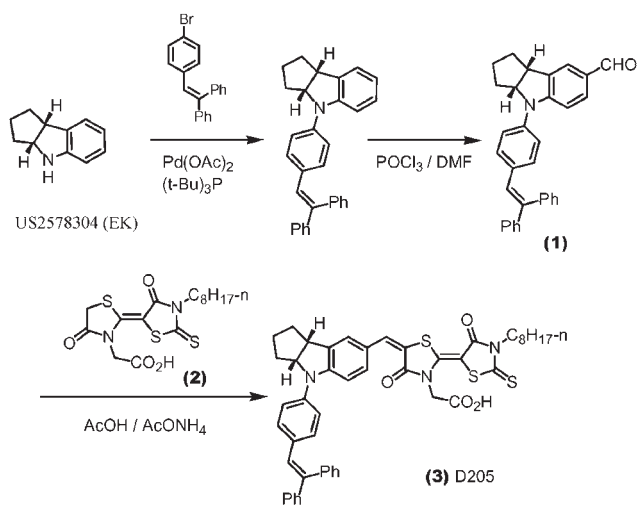


Fig. 1 Synthesis route of D205.

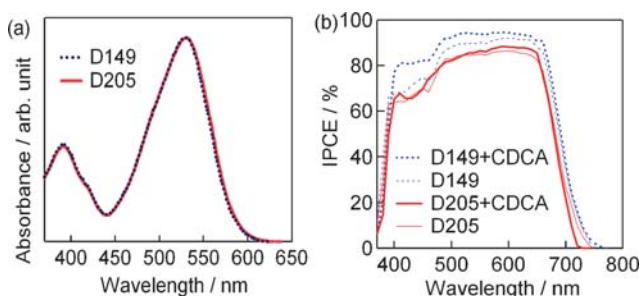


Fig. 2 Absorption spectra in DMF (a) and incident photon-to-electron conversion efficiency (IPCE) (b) of indoline dyes (D149 and D205). The IPCEs were measured with/without chenodeoxycholic acid (CDCA). A sheet of Arctop (an anti-reflecting UV cut-off film, Asahi Glass, Japan) was attached to each DSC surface for IPCE.

For DSC fabrication, the procedure for dye-sensitized nanocrystalline-TiO₂ and Pt electrodes was described in detail in a previous report.¹¹ The cell conditions of this report are described below. The thicknesses of the transparent nanocrystalline-TiO₂ layer and the scattering layer were 14 and 5 μm, respectively. For the dye uptake, the TiO₂ electrodes were immersed into the D149³¹ or D205 solutions [0.5 mM in a mixture of acetonitrile and *tert*-butyl alcohol (v/v, 1 : 1)], and kept at room temperature for 4 h. For the coadsorption, chenodeoxycholic acid was added (1.0 mM). The dye-adsorbed TiO₂ electrode and Pt counter electrode were assembled into a sealed sandwich-type cell by heating with a hot-melt ionomer film (Surlyn 1702, 25 μm thick, DuPont). A drop of the electrolyte solution was placed on a drilled hole in the counter electrode of the assembled cell, and was driven into the cell by means of vacuum backfilling. Finally, the hole was sealed using an additional hot-melt film (Bynel 4164, 35 μm thick, DuPont) and a cover glass (0.1 mm thick). The electrolyte was composed of 0.10 M lithium iodide, 0.60 M butylmethylimidazolium iodide, 0.05 M I₂, and 0.05 M 4-*tert*-butylpyridine in acetonitrile : valeronitrile (v/v, 85 : 15).³¹ A self-adhesive, antireflection, UV cut-off film ($\lambda < 380$ nm, Arctop, Asahi Glass, Japan) was attached to the DSC surface after the cell was assembled. In order to

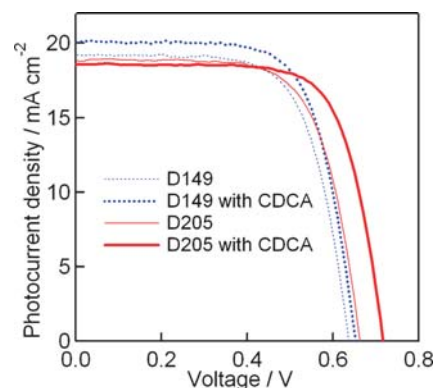


Fig. 3 Current density vs. voltage characteristics for DSCs with indoline dyes (D149 and D205) as sensitizers with/without CDCA under AM1.5 simulated sunlight (100 mW cm⁻²) illumination.

Table 1 Photovoltaic characteristics of DSCs with the indoline dyes shown in Fig. 3. Each result was obtained from three DSCs

Photovoltaic characteristics	Without CDCA		With CDCA	
	D149	D205	D149	D205
$J_{sc}/\text{mA cm}^{-2}$	19.08 ± 0.26	18.99 ± 0.19	19.86 ± 0.10	18.68 ± 0.08
V_{oc}/V	0.638 ± 0.05	0.656 ± 0.11	0.644 ± 0.13	0.710 ± 0.07
FF	0.682 ± 0.06	0.678 ± 0.09	0.694 ± 0.06	0.707 ± 0.09
$\eta/\%$	8.26 ± 0.09	8.43 ± 0.16	8.85 ± 0.18	9.40 ± 0.12

reduce the scattered light from the edge of the glass electrodes of the dyed TiO₂ layer, light-shading masks were attached onto the DSCs.¹² The power of the AM1.5 solar simulator was calibrated using a reference Si photodiode equipped with an IR cut-off filter (KG-3, Schott) in order to reduce the mismatch in the region of 350–750 nm between the simulated light and the AM1.5 to less than 2%.¹³

Fig. 2 shows absorption spectra in DMF and incident photon-to-electron conversion efficiency (IPCE) spectra of D149 and D205. The IPCEs under 380 nm are deteriorated, because sheets of anti-reflecting UV cut-off film (Arctop, Asahi Glass, Japan) attached to DSCs reduced the values in the short-wavelength region (< 380 nm). It should be noted that although the absorption spectra of D149 and D205 were identical, the IPCEs of D149 and D205 are different. We are currently studying dye-aggregation phenomena with CDCA on TiO₂ electrodes, which will be presented in a forthcoming paper.

Fig. 3 shows the photovoltaic characteristics of dye-sensitized solar cells using D149 and D205. Table 1 summarizes the results where J_{sc} is the short-circuit photocurrent density under irradiation, V_{oc} is the open-circuit voltage and FF represents the fill factor. Comparisons between D149 and D205 show that *n*-octyl substitution increased the V_{oc} regardless of the presence of CDCA. The presence of CDCA increased the V_{oc} of D205 by approximately 0.054 V, but had little effect on D149 (improvement of only 0.006 V). It is significant that the combination of CDCA and the *n*-octyl chain (D205) improves the V_{oc} up to 0.710 V, which is 0.066 V higher (10.2%) than that of D149 with CDCA. Kroeze *et al.*¹⁴ showed that alkyl substitution of dyes improved the V_{oc} ,

due to the blocking effect of the charge recombination between I_3^- and electrons injected in the nanocrystalline-TiO₂ electrodes. Therefore, the V_{OC} variation observed in Fig. 3 indicates that the charge recombination was impeded by the blocking effect, due to the combination of the *n*-octyl chain and CDCA.

Without CDCA, the variation of J_{SC} by *n*-octyl substitution on the rhodanine ring was small (0.5% of J_{SC}). However, with CDCA, the effect of the *n*-octyl chain was apparent and the substitution of the *n*-octyl chain (from D149 to D205) with CDCA decreased the J_{SC} by 5.9%. The effect of *n*-octyl substitution and CDCA on the *FF* was similarly small. Without CDCA, the *n*-octyl substitution decreased the *FF* by 0.6%. With CDCA, the *n*-octyl substitution increased the *FF* by 1.9%.

Without CDCA, the improvement in η from D149 to D205 was only by 2.1%. With CDCA, the improvement in η from D149 to D205 by 6.2% was significant. The resulting average η value of D205 with CDCA was an outstanding 9.40% (Table 1). The highest η value of 9.52% was achieved with a DSC based on D205 (J_{SC} : 18.56 mA cm⁻², V_{OC} : 0.717 V, and *FF*: 0.716). Reproducible efficiencies from 9.3% to 9.5% were obtained with the solar cell based on D205.

In summary, a new indoline dye exhibiting an η value of 9.52% has been demonstrated, which is the highest efficiency obtained so far among DSCs based on organic dye photosensitizers under AM 1.5 radiation (100 mW cm⁻²). This efficiency rivals the highest value (11.18%) obtained with a DSC based on the Ru dye N719 under the same measurement conditions.^{2b} It was confirmed that the control of dye-aggregation by the combination between CDCA and substitution of the *n*-octyl chain on the rhodanine ring was the key factor in obtaining a high-efficiency organic dye-sensitized solar cell. These results strongly indicate that the application of organic dye photosensitizers in DSCs is promising with regard to high solar cell performance, low-cost production and recyclability. However, the detailed mechanisms of dye-aggregation for DSC photovoltaics are still undetermined. In order to supersede the results of ruthenium complexes (11%),² advanced studies to understand molecular aggregation with an electron-dynamics study (*e.g.* photovoltage decay) will be presented in a forthcoming paper.

This work was supported by a grant from the Swiss Federal Energy Office (OFEN) and Nissan Science Foundation.

Notes and references

† (2) IR (KBr): ν 1534, 1676, 1744, 1767, 2852, 2922, and 2955 cm⁻¹; ¹H NMR (CDCl₃): δ 0.88 (3H, t, J = 6.9 Hz), 1.26–1.33 (10H, m), 1.35 (3H, t, J = 7.2 Hz), 1.64–1.71 (2H, m), 3.89 (2H, s), 4.05 (2H, t, J = 7.7 Hz), 4.31 (2H, q, J = 7.2 Hz), and 4.68 (2H, s) ppm; ¹³C NMR (CDCl₃): δ 14.1 (1C), 14.1 (1C), 22.6 (1C), 26.8 (1C), 26.8 (1C), 29.1 (1C), 29.1 (1C), 31.2 (1C), 31.7 (1C), 44.9 (1C), 45.3 (1C), 62.9 (1C), 94.8 (1C), 150.0 (1C), 165.9 (1C), 167.5 (1C), 172.6 (1C), and 189.3 (1C) ppm. (3) mp: >250 °C; UV-Vis (CHCl₃): λ_{max} = 554 nm; ϵ = 7.47 × 10⁴; ESI-TOFMS: m/z calcd for C₄₈H₄₇N₃O₄S₃ [M]⁺: 825.2723; meas.: 825.2697; IR (KBr): ν 1486, 1508, 1541, 1564, 1576, 1675, 1702, 2855 and 2925 cm⁻¹; ¹H NMR (DMSO-d₆): δ 0.85 (3H, t, J = 6.8 Hz), 1.25–1.28 (11H, m), 1.60–1.69 (4H, m), 1.75–1.84 (2H, m), 1.99–2.12

(1H, m), 3.84–3.89 (1H, m), 3.95–3.98 (2H, m), 4.74 (2H, s), 4.95–4.99 (1H, m), 7.02–7.04 (3H, m), 7.09 (1H, s), 7.14–7.16 (2H, m), 7.20–7.22 (2H, m), 7.29–7.37 (5H, m), 7.41–7.49 (5H, m) and 7.71 (1H, s) ppm; ¹³C NMR (DMSO-d₆): δ 14.0 (1C), 22.1 (1C), 23.9 (1C), 26.2 (1C), 26.3 (1C), 28.5 (1C), 28.6 (1C), 31.2 (1C), 32.9 (1C), 34.9 (1C), 44.0 (1C), 44.3 (1C), 46.1 (1C), 68.6 (1C), 92.7 (1C), 108.1 (1C), 112.5 (1C), 119.4 (2C), 123.8 (1C), 126.9 (2C), 127.1 (1C), 127.4 (1C), 127.7 (1C), 128.4 (3C), 129.2 (2C), 129.7 (2C), 130.4 (2C), 131.5 (1C), 132.9 (1C), 134.9 (1C), 136.6 (1C), 139.4 (1C), 140.2 (1C), 140.3 (1C), 142.6 (1C), 146.2 (1C), 149.0 (1C), 166.1 (1C), 166.2 (1C), 168.0 (1C) and 189.0 (1C) ppm.

- B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737; M. Grätzel, *Nature*, 2001, **414**, 338; F. Gao, Y. Wang, J. Zhang, D. Shi, M. Wang, R. Humphry-Baker, P. Wang, S. M. Zakeeruddin and M. Grätzel, *Chem. Commun.*, 2008, 2635.
- (a) Chiba A. Islam, Y. Watanabe, R. Komiya, N. Koide and L. Han, *J. Appl. Phys.*, 2006, **45**, L638; (b) Md. K. Nazeeruddin, F. De Angelis, S. Fantacci, A. Selloni, G. Viscardi, P. Liska, S. Ito, B. Takeru and M. Grätzel, *J. Am. Chem. Soc.*, 2005, **127**, 16835.
- (a) Z.-S. Wang, F.-Y. Li and C.-H. Huang, *J. Phys. Chem. B*, 2001, **105**, 9210; (b) D. P. Hagberg, T. Edvinsson, T. Marinado, G. Boschloo, A. Hagfeldt and L. Sun, *Chem. Commun.*, 2006, 2245; (c) K. R. J. Thomas, J. T. Lin, Y.-C. Hsueh and K.-C. Ho, *Chem. Commun.*, 2005, 4098; (d) H. Tian, X. Yang, R. Chen, Y. Pan, L. Li, A. Hagfeldt and L. Sun, *Chem. Commun.*, 2007, 3741; (e) S.-L. Li, K.-J. Jiang, K.-F. Shao and L.-M. Yang, *Chem. Commun.*, 2006, 2792; (f) T. Kitamura, M. Ikeda, K. Shigaki, T. Inoue, N. A. Anderson, X. Ai, T. Lian and S. Yanagida, *Chem. Mater.*, 2004, **16**, 1806; (g) K. Hara, M. Kurashige, S. Ito, A. Shinpo, S. Suga, K. Sayama and H. Arakawa, *Chem. Commun.*, 2003, 252; (h) K. Hara, T. Sato, R. Katoh, A. Furube, T. Yoshihara, M. Murai, M. Kurashige, S. Ito, A. Shinpo, S. Suga and H. Arakawa, *Adv. Funct. Mater.*, 2005, **15**, 246; (i) W. M. Campbell, K. W. Jolley, P. Wagner, K. Wagner, P. J. Walsh, K. C. Gordon, L. Schmidt-Mende, Md. K. Nazeeruddin, Q. Wang, M. Grätzel and D. L. Officer, *J. Phys. Chem. C*, 2007, **111**, 11760; (j) N. Koumura, Z.-S. Wang, S. Mori, M. Miyashita, E. Suzuki and K. Hara, *J. Am. Chem. Soc.*, 2006, **128**, 14256; (k) Z.-S. Wang, Y. Cui, Y. Dan-oh, C. Kasada, A. Shinpo and K. Hara, *J. Phys. Chem. C*, 2007, **111**, 7224; (l) S. Ito, S. M. Zakeeruddin, R. Humphry-Baker, P. Liska, R. Charvet, P. Comte, Md. K. Nazeeruddin, P. Pèchy, M. Takata, H. Miura, S. Uchida and M. Grätzel, *Adv. Mater.*, 2006, **18**, 1202; (m) S. Hwang, J. H. Lee, C. Park, H. Lee, C. Kim, C. Park, M.-H. Lee, W. Lee, J. Park, K. Kim, N.-G. Park and C. Kim, *Chem. Commun.*, 2007, 4887.
- E. E. Jelly, *Nature*, 1936, **138**, 1009T. H. James, *The Theory of the Photographic Process*, Macmillan Inc., London–New York, 1977, p. 219.
- A. C. Khazraji, S. Hotchandani, S. Das and P. V. Kamat, *J. Phys. Chem. B*, 1999, **103**, 4693.
- A. Kay and M. Grätzel, *J. Phys. Chem.*, 1993, **97**, 6272.
- T. Horiuchi, H. Miura, K. Sumioka and S. Uchida, *J. Am. Chem. Soc.*, 2004, **126**, 12218.
- K. Sayama, S. Tsukagoshi, K. Hara, Y. Ohga, A. Shinpo, Y. Abe, S. Suga and H. Arakawa, *J. Phys. Chem. B*, 2002, **106**, 1363.
- D. Kuang, S. Uchida, R. Humphry-Baker, S. M. Zakeeruddin and M. Grätzel, *Angew. Chem., Int. Ed.*, 2008, **47**, 1923.
- J. D. Mee (Eastman Kodak Co.), *US Pat.*, 5 679 795, 1997.
- S. Ito, T. N. Murakami, P. Comte, P. Liska, C. Grätzel, Md. K. Nazeeruddin and M. Grätzel, *Thin Solid Films*, 2008, **516**, 4613.
- S. Ito, M. K. Nazeeruddin, P. Liska, P. Comte, R. Charvet, P. Pèchy, M. Jirousek, A. Kay, S. M. Zakeeruddin and M. Grätzel, *Prog. Photovoltaics: Res. Appl.*, 2006, **14**, 589.
- S. Ito, H. Matsui, K. Okada, S. Kusano, T. Kitamura, Y. Wada and S. Yanagida, *Sol. Energy Mater. Sol. Cells*, 2004, **82**, 421.
- J. E. Kroeze, N. Hirata, S. Koops, Md. K. Nazeeruddin, L. Schmidt-Mende, M. Grätzel and J. R. Durrant, *J. Am. Chem. Soc.*, 2006, **128**, 16376.