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

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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)<sup>1</sup> 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  $(\eta)$  of over 11% for AM1.5-simulated solar light (100 mW cm<sup>-2</sup>, 1 sun).<sup>2</sup> 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 highefficiency DSCs have been reported; new organic dyes with efficiencies over 5% are hemicyanine dye ( $\eta = 5.1\%$ ),<sup>3a</sup> polyene–diphenylaniline dye ( $\eta = 5.1\%$ ),<sup>3b</sup> thienylfluorene dye,  $(\eta = 5.23\%)^{3c}$  phenothiazine dye  $(\eta = 5.5\%)^{3d}$ thienothiophene-thiophene-derived dye ( $\eta = 6.23\%$ ),<sup>3e</sup> phenylconjugated polyene dye ( $\eta = 6.6\%$ , <sup>3f</sup> 6.8%<sup>3g</sup>), N,N-dimethylaniline–cyanoacetic acid ( $\eta = 6.8\%$ ),<sup>3h</sup> porphyrin dye ( $\eta = 7.1\%$ ),<sup>3i</sup> oligothiophene dye ( $\eta = 7.7\%$ ),<sup>3j</sup> coumarin dye ( $\eta =$ 8.2%),<sup>3k</sup> indoline dye (D149, see Scheme 1:  $\eta = 9.03\%)^{3l}$  and oligo-phenylenevinylene-unit dye ( $\eta = 9.1\%$ ).<sup>3m</sup>

In order to improve the  $\eta$  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,  $\pi$ -stacked aggregation (D and/or H aggregation<sup>4</sup>) on the nanocrystalline-TiO<sub>2</sub> 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).

 $TiO_2$  surface and thus act as filters.<sup>5</sup> Some ruthenium complexes (black dye<sup>2a</sup> and N719<sup>2b</sup>) have shown the best results using chenodeoxycholic acid (CDCA), which functions as an antiaggregation reagent to improve the photovoltaic effect.<sup>6</sup> On the contrary, indoline dyes and coumarin dyes form photoactive aggregates on nanocrystalline-TiO<sub>2</sub> electrodes for DSCs, known as J-aggregation.<sup>7,8</sup> 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.<sup>9</sup> In this report, we disclose the synthesis method of D205 and show high-efficiency DCSs using volatile electrolytes. In particular, with the use of chenodeoxycholic acid (CDCA), the DSCs with D205 on nanocrystalline-TiO<sub>2</sub> electrodes exhibited a high open-circuit photovoltage at 710 mV. The best resulting photopowerconversion 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-cyclo-penta[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),<sup>10</sup> 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 CHCl<sub>3</sub> 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.†

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**Fig. 2** Absorption spectra in DMF (a) and incident photonto-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.<sup>11</sup> The cell conditions of this report are described below. The thicknesses of the transparent nanocrystalline-TiO<sub>2</sub> layer and the scattering layer were 14 and 5  $\mu$ m, respectively. For the dye uptake, the TiO<sub>2</sub> electrodes were immersed into the D149<sup>31</sup> 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 dveadsorbed TiO<sub>2</sub> 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).<sup>3/</sup> A self-adhesive, antireflection, UV cut-off film  $(\lambda < 380 \text{ nm}, \text{Arctop}, \text{Asahi Glass}, \text{Japan})$  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<sup>-2</sup>) 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
$J_{\rm sc}/{\rm mA~cm^{-2}}$	$19.08\pm0.26$	$18.99\pm0.19$	$19.86\pm0.10$	$18.68\pm0.08$
V <sub>oc</sub> /V FF	$0.638 \pm 0.05$ $0.682 \pm 0.06$	$0.656 \pm 0.11$ $0.678 \pm 0.09$	$0.644 \pm 0.13$ $0.694 \pm 0.06$	$0.710 \pm 0.07$ $0.707 \pm 0.09$
$\eta/\%$	$8.26 \pm 0.09$	$8.43 \pm 0.16$	$8.85 \pm 0.18$	$9.40 \pm 0.12$

reduce the scattered light from the edge of the glass electrodes of the dyed  $\text{TiO}_2$  layer, light-shading masks were attached onto the DSCs.<sup>12</sup> 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%.<sup>13</sup>

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 shortwavelength 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 TiO<sub>2</sub> electrodes, which will be presented in a forthcoming paper.

Fig. 3 shows the photovoltaic characteristics of dyesensitized 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.*<sup>14</sup> 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-TiO<sub>2</sub> 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  $\eta$  from D149 to D205 was only by 2.1%. With CDCA, the improvement in  $\eta$  from D149 to D205 by 6.2% was significant. The resulting average  $\eta$  value of D205 with CDCA was an outstanding 9.40% (Table 1). The highest  $\eta$  value of 9.52% was achieved with a DSC based on D205 ( $J_{SC}$ : 18.56 mA cm<sup>-2</sup>,  $V_{OC}$ : 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  $\eta$  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<sup>-2</sup>). This efficiency rivals the highest value (11.18%) obtained with a DSC based on the Ru dve N719 under the same measurement conditions.<sup>2b</sup> It was confirmed that the control of dyeaggregation 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 dyeaggregation 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.

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## Notes and references

- † (2) IR (KBr):  $\nu$  1534, 1676, 1744, 1767, 2852, 2922, and 2955 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  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; <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  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 (CHCl<sub>3</sub>):  $\lambda_{max} = 554$  nm;  $\varepsilon = 7.47 \times 10^4$ ; ESI-TOFMS: m/z calcd for C<sub>48</sub>H<sub>47</sub>N<sub>3</sub>O<sub>4</sub>S<sub>3</sub> [M]<sup>+</sup>: 825.2723; meas.: 825.2697; IR (KBr):  $\nu$  1486, 1508, 1541, 1564, 1576, 1675, 1702, 2855 and 2925 cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$  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; <sup>13</sup>C NMR (DMSO-d<sub>6</sub>):  $\delta$  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), 39.4 (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.

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