Design and Synthesis of Near-infrared-active Heptamethine–Cyanine Dyes to Suppress Aggregation in a Dye-sensitized Porous Zinc Oxide Solar Cell

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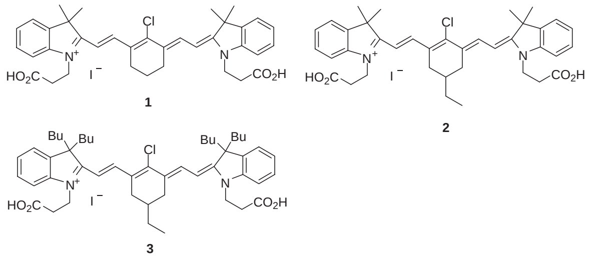
New heptamethine–cyanine dyes were synthesized and used for dye-sensitization of porous zinc oxide cells in the near-infrared region (800 nm). The introduction of alkyl groups into the cyclohexene and indolenium moieties remarkably prevented H-aggregation of the dyes. Consequently, the photovoltaic performance of the dye-sensitized zinc oxide cells with DCA was improved; a solar-to-electricity conversion efficiency (η) of 0.67%, a short-circuit current density of 2.22 mA cm^{-2}, an open-circuit photovoltage of 0.46 V, and a fill factor of 0.66 under standard AM 1.5 irradiation (100 mW cm^{-2}).

Dye-sensitized solar cells (DSSCs) using ruthenium–polypyridyl complexes as photosensitizers,[1] and various organic dyes[2] have been intensively studied as low-cost alternatives to conventional silicon cells. These compounds are very effective charge-transfer sensitizers for DSSCs in the visible region between 400–800 nm. However, these photosensitizers lack absorption in red/near-infrared (IR) region.

Although near-IR photosensitizers are quite important for use of the red/near-IR part of the spectrum of sunlight, until very recently, there have been only a few reports on near-IR sensitizers, such as squarylium dyes,[3] zinc–phthalocyanines,[4] and heptamethine–cyanine dyes.[5,6] Therefore, it would be very useful to develop effective new sensitizers in the near-IR region for the use of DSSCs as photovoltaic windows.

In our previous report,[5] some heptamethine–cyanine dyes were synthesized and used for the dye-sensitization of zinc oxide (ZnO) cells. However, the DSSCs gave a quite low incident photon to current conversion efficiency (IPCE) (4% at 804 nm) and solar energy-to-electricity conversion efficiency ($\eta =$ 0.16). Such low energy conversions could be attributable to the formation of H-aggregates, the inappropriate position of the carboxyl group as a binding group, and the absence of deoxycholic acid (DCA) as a co-adsorption reagent. In an attempt to further improve the efficiencies of the dyes, we describe here the design and synthesis of novel heptamethine–cyanine dyes **1**–**3** (Scheme 1), their use for the dye-sensitization of ZnO cells in the near-IR region, and an examination of the effect of DCA. In these novel heptamethine–cyanine dyes, the introduction of two types of alkyl groups in the cyclohexene and indolenium moieties as well as the position of the carboxyethyl group were designed to suppress aggregation and to strongly interact with the ZnO surface to improve the electronic coupling of the dyes in the near-IR region.

Dye **1** was synthesized as follows. 2-Chloro-3-(hydroxymethylene)cyclohexene-1-carbaldehyde was condensed with 1-(2-carboxyethyl)-2,3,3-trimethylindolenium iodide under reflux in a solvent of acetic acid with sodium acetate and purified by column chromatography using silica gel with a mixed solvent of dichloromethane, ethyl acetate, and methanol (v/v/v = 6:1:1) to give **1** in 25% yield. Dyes **2** and **3** were synthesized in respective yields of 28 and 33% by the same method.



Scheme 1. Molecular structures of the dyes **1**–**3**.

A porous ZnO layer (thickness: 3 μm) was electrodeposited onto F-doped SnO$_2$ (FTO)-coated glass (Asahi Glass, 10 Ω/sq.) using eosin Y as a template molecule.[7] After being dried at 100 °C for 1 h, the film was immersed in an ethanol solution of dyes **1**–**3** (0.1 mmol dm^{-3}) with or without various amounts of DCA and kept at room temperature for 1 h. Photovoltaic measurements were carried out for sandwich-type cells (two electrodes) consisting of a dye-coated ZnO electrode and a Pt-sputtered FTO glass counter electrode attached in a face-to-face configuration using a polymer film spacer. The electrolyte was 0.5 mol dm^{-3} tetrabutylammonium iodide and 0.05 mol dm^{-3} iodine in a mixed solvent of acetonitrile and ethylenecarbonate (v/v = 1:4). The cell area was regulated to 0.2 cm^2 using a

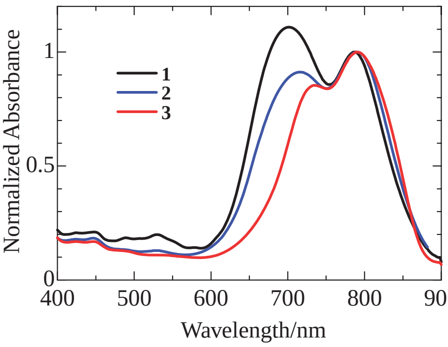


Figure 1. Absorption spectra of dyes **1**, **2**, and **3** absorbed on ZnO film, the absorbances of which are normalized.

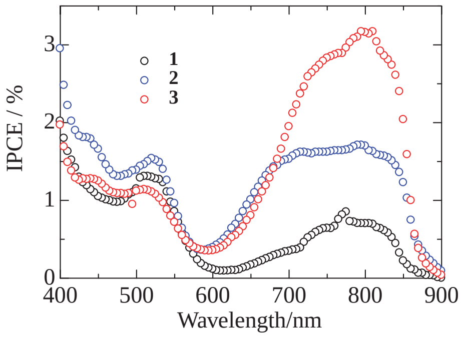


Figure 2. Action spectra obtained for ZnO solar cells that have been sensitized by dyes **1**, **2**, and **3**.

photo mask. The photocurrent action spectra were recorded at short circuit under monochromatic light illumination at a constant photon number ($5 \times 10^{14}\,\mathrm{cm^{-2}\,s^{-1}}$). Photovoltaic performance was measured under simulated AM 1.5 irradiation ($100\,\mathrm{mW\,cm^{-2}}$).

Figure 1 shows the absorption spectra of ZnO thin films on which are adsorbed dyes **1**–**3**. The absorption spectra show two kinds of absorption: monomeric absorption at around 780 nm and the absorption of H-aggregates at a shorter wavelength than the monomeric absorption. A comparison of the absorption spectra in Figure 1 reveals that the amount of H-aggregates with dyes **1**–**3** is in the order **1**, **2**, and **3**. The difference among dyes **1**–**3** was presumably due to steric hindrance. Thus, dye **2** shows greater steric hindrance than **1** due to the presence of an ethyl group on the cyclohexene linkage in **2**. In addition, the introduction of two butyl groups to the indolenium moiety of **3** to enhance steric hindrance was more effective for inhibiting H-aggregation than the dimethyl analogue in dye **2**. It is well known that H-aggregation usually quenches fluorescence efficiently and would consequently be a loss mechanism that competes with electron injection, resulting in lower IPCEs. As a result, the IPCEs for dyes **1**–**3** are in the order **3** (3%), **2** (2%), and **1** (1%), as shown in Figure 2.

Next, optimization of the DCA concentration to $1\,\mathrm{mmol\,dm^{-3}}$ under immersion conditions gave the best photovoltaic performance.[8] Figure 3 shows the absorption and action spectra of **3**-adsorbed ZnO thin films with DCA ($1\,\mathrm{mmol\,dm^{-3}}$). H-aggregates have been suppressed and the highest IPCE (26% at 805 nm) has been attained in the near-IR region. The *I*–*V* measurement of the cell under illumination with a simulated sunlight ($100\,\mathrm{mW\,cm^{-2}}$) yielded a short-circuit current density (J_{sc}) of 2.30 mA, an open-circuit photovoltage (V_{oc}) of 0.46 V, and a fill factor (*ff*) of 0.66. However, because the light generated by a simulator poorly matches with the sun light in the near-IR region, the current was also calculated from the overlap integral of the IPCE spectrum with the solar spectrum (AM 1.5). The corrected J_{sc} of 2.22 mA was obtained, so that a conversion efficiency (η) of 0.67% was estimated.

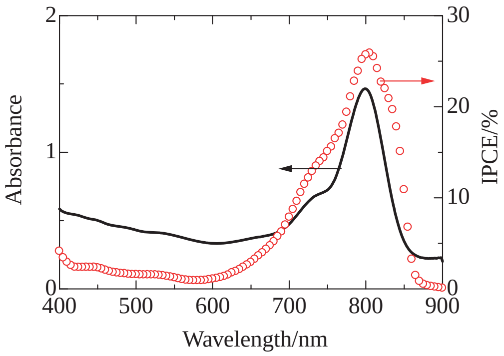


Figure 3. Absorption and action spectra obtained for ZnO solar glass cells sensitized by dye **3** with DCA ($1\,\mathrm{mmol\,dm^{-3}}$).

Finally, we have developed plastic DSSCs of ZnO with heptamethine–cyanine dye **3** using indium tin oxide (ITO)-coated plastic substrate in place of FTO-coated glass. As a result, the solar cell using ITO-coated plastic substrate sensitized by dye **3** with DCA ($2\,\mathrm{mmol\,dm^{-3}}$) achieved an IPCE of 23% at 800 nm, η of 0.61% with J_{sc} of $2.04\,\mathrm{mA\,cm^{-2}}$ (corrected as above), V_{oc} of 0.46 V, and *ff* of 0.65 under illumination with AM 1.5 simulated sunlight ($100\,\mathrm{mW\,cm^{-2}}$).

In conclusion, our findings demonstrated that new heptamethine–cyanine dyes **1**–**3**, which were designed to suppress H-aggregates, and the use of DCA as a co-adsorbent improved the conversion efficiency ($\eta = 0.67\%$) in the near-IR region. This should provide an opportunity to cover a wide range of the solar spectrum by mixing these dyes with the main dyes to give high energy conversion efficiency.

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