A coumarin-derivative dye sensitized nanocrystalline TiO$_2$ solar cell having a high solar-energy conversion efficiency up to 5.6%

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It is found that newly synthesized coumarin derivatives work as highly efficient photosensitizers for dye-sensitized nanocrystalline TiO$_2$ solar cells producing a 5.6% solar-light-to-electricity conversion efficiency, the highest efficiency so far among organic dye-sensitized solar cells, with a short-circuit current density of 13.8 mA cm^{-2}, an open-circuit photovoltage of 0.63 V, and a fill factor of 0.63 under standard AM 1.5 irradiation (100 mW cm^{-2}).

Dye-sensitized solar cells have been extensively investigated since Grätzel and coworkers reported a highly efficient solar-energy-to-electricity conversion efficiency, η, of 10%.[1] Transition metal complexes, *e.g.* *cis*-di(thiocyanato)bis(4,4′-dicarboxy-2,2′-bipyridine)ruthenium(II) [Ru(dcbpy)$_2$(NCS)$_2$], have been mainly applied, so far, in dye-sensitized solar cells as photosensitizers.[1–4] Organic dyes have been also used as photosensitizers for dye-sensitized solar cells.[5–9] Recently we reported a dye-sensitized TiO$_2$ solar cell, using special merocyanine dye aggregates as the photosensitizer, which showed a highly efficient η of 4.2%.[7] This result encouraged us to look for more efficient organic dye photosensitizers for dye-sensitized TiO$_2$ solar cells.

Coumarin dyes, *e.g.* coumarin 343 (C343) (Scheme 1), are recognized as good organic dye photosensitizers, injecting electrons effectively into the conduction band of semiconductors.[10,11] For example, Murakoshi *et al.* observed an ultrafast electron injection (< 20 fs) from C343 into the conduction band of TiO$_2$.[11] The η values of nanocrystalline semiconductor solar cells using conventional coumarin dyes such as C343 as the photosensitizer is, however, much lower than that of solar cells sensitized by Ru complex photosensitizers because of the narrow absorption area in the visible

region. A wide absorption range in the visible region for the coumarin dye is required to attain highly efficient solar-energy-to-electricity conversion. We have synthesized new coumarin derivatives which are able to absorb visible light from 400 up to 700 nm and prepared highly efficient dye-sensitized nanocrysalline TiO$_2$ solar cells using such new coumarin photosensitizers. The value of η increased up to 5.6%, the highest efficiency among organic dye-sensitized solar cells so far, using 2-cyano-5-(2,3,6,7-tetrahydro-1,1,7,7-tetramethyl-11-oxo-1H,5H,11H-[1]benzopyrano[6,7,8-*ij*]quinolizin-10-yl)penta-2,4-dienoic acid **2** as the photosensitizer. It should be noted that the photocurrent performance of a TiO$_2$ solar cell composed of this dye (compound **2**) is almost equal to that of the Ru(dcbpy)$_2$(NCS)$_2$ system.

Compound **1**† was synthesized by refluxing an acetonitrile solution containing 2,3,6,7-tetrahydro-1,1,7,7-tetramethyl-11-oxo-1H,5H,11H-[1]benzopyrano[6,7,8-*ij*]quinolizin-10-carbaldehyde **3** and cyanoacetic acid in the presence of piperidine, and purified by column chromatography using silica gel and a chloroform–methanol mixed solvent as the eluting solution. Recrystallization of **1** from acetonitrile solution in the presence of triethylamine afforded a red purple crystalline triethylammonium salt. 3-(2,3,6,7-Tetrahydro-1,1,7,7-tetramethyl-11-oxo-1H,5H,11H-[1]benzopyrano[6,7,8-*ij*]quinolizin-10-yl)propenal **4** was prepared from **3** by Wittig reaction and then Vilsmeier–Haack reaction. Compound **2**† was synthesized starting from **4** and cyanoacetic acid by a similar procedure for **1**. Resulting precipitates of **2** were dissolved in DMF and a bright purple crystalline compound was obtained upon recrystallization.

TiO$_2$ nanoparticles were prepared by hydrolysis of Ti tetraisopropoxide as described elsewhere.[12,13] TiO$_2$ thin films were prepared by screen printing on transparent conducting oxide (TCO, F-doped SnO$_2$) and then sintered at 500 °C for 1 h. Nanocrystalline TiO$_2$ films (10–13 μm thick) were coated with dyes by dipping the film in 3 × 10^{-4} mol dm^{-3} dye solutions in ethanol or *tert*-butyl alcohol–acetonitrile (1:1). The dye-coated TiO$_2$ electrode was incorporated into a thin-layer sandwich-type cell with a Pt sputtered TCO as the counter electrode, a spacer film, and an organic electrolyte solution to measure the solar cell performance. The electrolyte was 0.6 mol dm^{-3} 1,2-dimethyl-3-propylimidazolium iodide (DMPImI)–0.1 mol dm^{-3} LiI–0.05 mol dm^{-3} I$_2$ in methoxyacetonitrile. η Values for solar cells were measured using a standard AM 1.5 solar simulator and a digital sourcemeter.

Absorption spectra of C343, compounds **1** and **2** in ethanol and compound **2** adsorbed on a transparent TiO$_2$ film (4 μm thick) are shown in Fig. 1. The threshold wavelengths of absorption spectra for compounds **1** and **2** are 570 and 630 nm, respectively, while that for C343 was 500 nm, indicating that introducing the –CH=CH– unit into the coumarin framework expanded the conjugation in the dye resulting in wide absorption in the visible region. This wide absorption and red shift of absorption maximum in the visible region for photosensitizers is desirable for light harvesting of solar energy. The absorption spectrum of compound **2** adsorbed on a TiO$_2$ film is
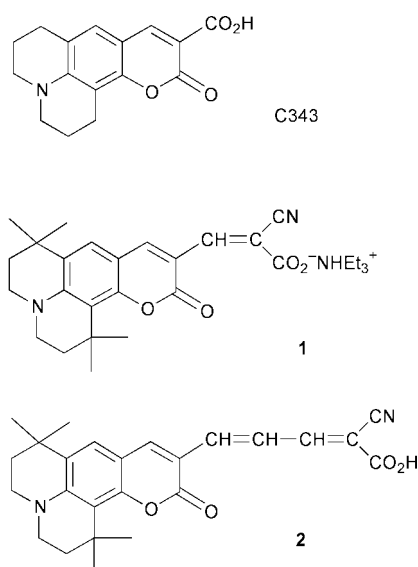
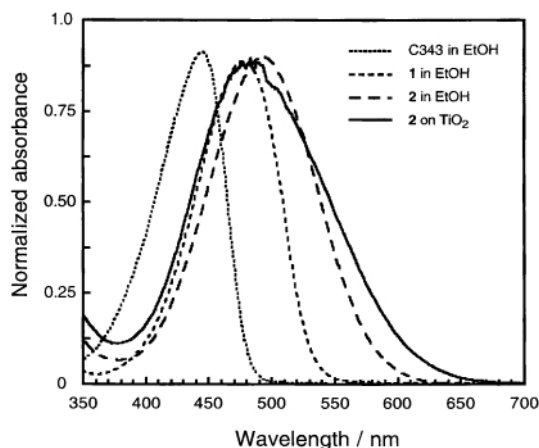Scheme 1 Molecular structure of new coumarin derivatives.

Fig. 1 Absorption spectra of C343, **1** and **2** in EtOH, and of **2** adsorbed on a TiO$_2$ film whose absorbance is normalized: (- - - - - -) C343, (– – –) **1** in ethanol, (— —) **2** in ethanol, (—) **2** adsorbed on TiO$_2$.

slightly expanded compared with that in ethanol. A long tail of absorption up to 670 nm was observed, indicating a strong electronic coupling between compound **2** and TiO$_2$. The absorption spectrum of compound **2** absorbed on TiO$_2$ films thicker than 10 μm gave an absorption band edge which tailed up to 750 nm, the deep purple film being similar to that of the Ru complex.
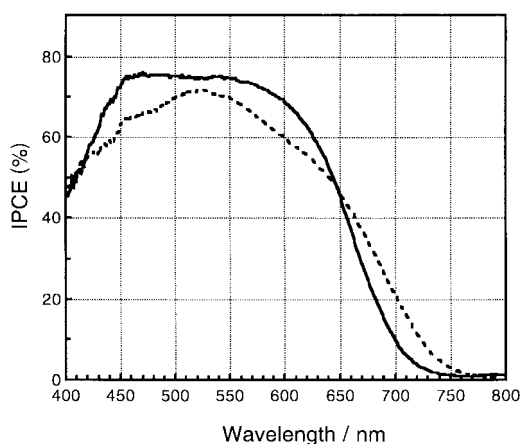
Fig. 2 shows typical action spectra of incident photon-to-current conversion efficiencies (IPCE) obtained from nanocrystalline TiO$_2$ solar cells sensitized by compound **2** as well as Ru(dcpby)$_2$(NCS)$_2$(TBA)$_2$. Visible light (400–750 nm) can be converted to current with a maximum of 76% at 470 nm by the solar cell composed of compound **2**, producing a large photocurrent.

Taking into consideration light absorption loss by TCO-coated glass, the light-to-current conversion efficiency is close to 100% from 450 to 550 nm. Both a large amount of compound **2** adsorbed on to a TiO$_2$ film (10 μm thick), 1×10^{-7} mol cm^{-2}, and the large absorption coefficient of dye (compound **2**) itself, *e.g.* 52 500 dm^3 mol^{-1} cm^{-1} at 504 nm in methnol, increased the light harvesting efficiency. The coverage of the TiO$_2$ surface with the dye was *ca.* 70% as derived from the roughness factor of the film, 1000, and the cross sectional area of one dye molecule, 1.2 nm^2. It should be noted that the IPCE performance of the solar cell with **2** is almost equal to that of the Ru(dcbpy)$_2$(NCS)$_2$ system, as shown in Fig. 2. The maximum short-circuit photocurrent density (J_{sc}) for a **2**-sensitized TiO$_2$ solar cell reached 15 mA cm^{-2} under AM 1.5 irradiation (100 mW cm^{-2}).

The lowest unoccupied molecular orbital (LUMO) of **2** (measured electrochemically) at −0.8 V *vs.* NHE, is able to inject electrons into the conduction band of the TiO$_2$ electrode (−0.5 V *vs.* NHE).[13] Good stability of the dye under irradiation for 2 days, with a turnover number of 100 000, was observed by a brief experiment using an opened cell, indicating effective cycling from the ground state of compound **2** to the oxidized form with efficient electron transfer from the dye to TiO$_2$ and from I$^-$ ions to the oxidized dyes. Detailed investigation of the long term stability of the dye using a sealed cell will be carried out.

The maximum efficiency for the **2**-sensitized TiO$_2$ solar cell was 5.6% with a J_{sc} of 13.8 mA cm^{-2}, an open-circuit photovoltage (V_{oc}) of 0.63 V, and a fill factor (*ff*) of 0.63 under standard AM 1.5 irradiation, which is the highest solar cell performance, so far, among organic dye-sensitized solar cells. Our results strongly support the prospect for promising application of organic dye photosensitizers in dye-sensitized nanocrystalline semiconductor solar cells, and indicate the importance of molecular structure design for tuning photosensitizers to produce high efficiency dye-sensitized solar cells. If electron injection occurs through chemical bonding of the carboxyl group, the structures of compound **1** and **2**, whose carboxyl group is directly connected to the conjugated methine chain, is advantageous for improving the injection of electrons into semiconductors. In addition, the cyano group (–CN) connected to the methine chain and the carboxyl group might be effective for electron injection due to their strong electron acceptability. We are currently synthesizing new dyes absorbing in a wider visible region and studying solar cell performance and mechanisms in detail.

Notes and references

† Compound **1**: mp 186–192 °C, δ_H(CDCl$_3$): 1.28 (6H, s), 1.32 (9H, t), 1.54 (6H, s), 1.74 (2H, t), 1.80 (2H, t), 3.13 (6H, q), 3.23 (2H, t), 3.36 (2H, t), 7.19 (1H, s), 8.38 (1H, s), 8.75 (1H, s).

Compound **2**: MS (ESI) *m/z*: 419.1 (M + H), 436.0 (M + H$_2$O), 450.8 (M + CH$_3$OH), 482.9 (M + 2CH$_3$OH), 490.8 (M + THF); mp 270–275 °C, δ_H(CDCl$_3$): 1.31 (6H, s), 1.53 (6H, s), 1.74–1.85 (4H, m), 3.41–3.49 (4H, m), 7.47 (2H, m), 7.75 (1H, dd), 8.08 (1H, d), 8.22 (1H, s).

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Fig. 2 Typical action spectra of incident photon-to-current conversion efficiencies (IPCE) obtained for nanocrystalline TiO$_2$ solar cells sensitized by **2** (—) and Ru(dcbpy)$_2$(NCS)$_2$(TBA)$_2$ (- - - -).