Letter

Design of new coumarin dyes having thiophene moieties for highly efficient organic-dye-sensitized solar cells

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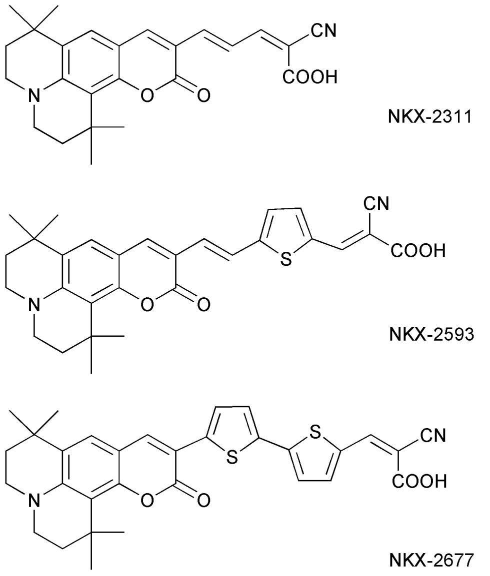
We have developed new coumarin dyes having thiophene moieties in order to improve the photovoltaic performance of dye-sensitized nanocrystalline TiO_2 solar cells based on the organic dyes as photosensitizers. A solar-energy-to-electricity conversion efficiency (η) of 7.7% was attained under AM 1.5 irradiation (100 mW cm^{-2}) with a short-circuit current density (J_{sc}) of 14.3 mA cm^{-2}, an open-circuit voltage (V_{oc}) of 0.73 V, and a fill factor (*ff*) of 0.74.

Dye-sensitized nanocrystalline TiO_2 solar cells (DSSCs) based on Ru complex photosensitizers have been intensively studied because of both their high performance as unconventional solar cells and the possibility for low-cost production of such devices.[1–5] In addition to Ru complexes, organic dyes have also been utilized as photosensitizers in DSSCs. Recently, the performance of DSSCs based on organic dyes has been remarkably improved.[6–12] For example, coumarin dye derivatives have been successfully used as organic dye photosensitizers for DSSCs. We have attained maximum solar-energy-to-electricity conversion efficiencies, η, of up to 6.0% with DSSCs based on NKX-2311.[9–11] In addition, we have developed other efficient polyene dye photosensitizers for nanocrystalline TiO_2 solar cells that produce an η value of 6.8% under AM 1.5 irradiation (100 mW cm^{-2}).[12] These dyes have an *N*,*N*′-dimethylaniline moiety instead of the coumarin framework as the donor moiety. In order to achieve η values higher than 7%, like those obtained with DSSCs based on the Ru complexes, however, it is necessary to improve the molecular design of organic dye photosensitizers.

One of approaches to improve peformance of the coumarin dyes would be to increase π-conjugation by extending the methine unit (–CH=CH–) of NKX-2311. Although such an extension would contribute to a red shift in the absorption spectrum, it would simultaneously cause two problems: first, it would complicate the synthetic procedure and, second, it would increase the instability of the dye molecule, owing to the possibility of isomer formation. The introduction of π-conjugated ring moieties, such as benzene, thiophene, pyrrole, or furan, into the methine chain of NKX-2311 would simultaneously extend π-conjugation and improve the stability of the dye molecule relative to the dyes, which have a long methine chain unit, according to our experience. Therefore, we designed new coumarin dyes by introducing thiophene moieties into the methine chain of NKX-2311 rather than by extending the methine unit itself (Scheme 1). This modification has improved the solar cell performance remarkably. We achieved an η value of 7.7% (short-circuit current density, J_{sc}, of 14.3 mA cm^{-2}, open-circuit voltage, V_{oc}, of 0.73 V, and fill factor, *ff*, of 0.74) under AM 1.5 irradiation (100 mW cm^{-2}), with a DSSC based on NKX-2677. We attribute the improved solar cell performance mainly to both a broadening of the absorption spectra and relatively negative positions of the LUMO levels of the dyes upon introduction of the thiophene moieties.

Fig. 1 shows the absorption spectra of NKX-2311, NKX-2593, and NKX-2677 both in *tert*-butyl alcohol–AN (50:50) solution and adsorbed on a TiO_2 film measured in the diffuse reflectance mode for NKX-2311 and NKX-2677. Introduction of the thiophene moieties produced no marked change in the absorption spectra of the dyes in the solution: the λ_{max} values are 507 nm for NKX-2311, 507 nm for NKX-2593, and 510 nm for NKX-2677 [Fig. 1(a)]. In contrast, the absorption spectrum of NKX-2677 adsorbed on the TiO_2 surface is remarkably broadened relative to that of NKX-2311 [Fig. 1(b)]: the absorption spectrum of NKX-2593 adsorbed on the TiO_2 surface is almost the same as that of NKX-2677. The thiophene moieties seem to contribute to the broadening of the absorption spectrum of the dye on the TiO_2 surface. This might be because of dye-dye and/or dye-TiO_2 interactions, for example, although the detailed mechanism is unclear at the present



Scheme 1 Molecular structures of NKX-2311, NKX-2593, and NKX-2677.

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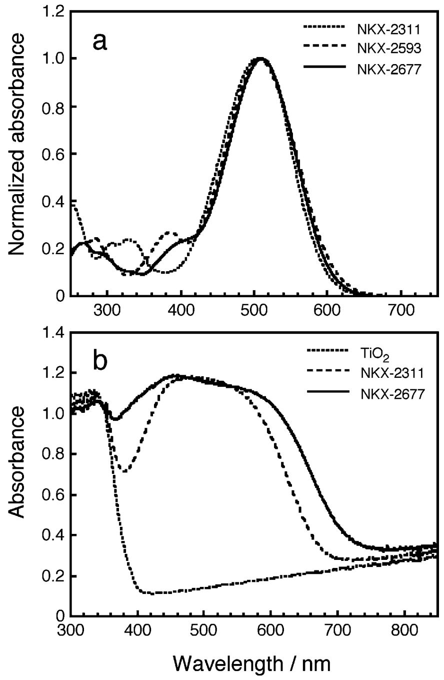

Fig. 1 (a) Absorption spectra of NKX-2311, NKX-2593, and NKX-2677 in *tert*-butyl alcohol–acetonitrile (50:50): (···) NKX-2311, (---) NKX-2593, (—) NKX-2677. (b) Absorption spectra of NKX-2311 and NKX-2677 adsorbed on a TiO_2 film: (···) TiO_2, (---) NKX-2311, (—) NKX-2677. The spectra were measured in the diffuse reflectance mode.

stage. This broadening of the absorption spectrum is desirable for harvesting the solar spectrum and leads to a large photocurrent. The molar absorption coefficients ε at λ_{max} are 55 700 M^{-1} cm^{-1} for NKX-2593 and 64 300 M^{-1} cm^{-1} for NKX-2677.

Fig. 2 shows action spectra of monochromatic incident photon-to-current conversion efficiencies (IPCEs) for DSSCs based on NKX-2311, NKX-2593, and NKX-2677 (electrolyte: 0.6 M 1,2-dimethyl-3-*n*-propylimidazolium iodide (DMPImI)–0.1 M LiI–0.05 M I_2 in methoxyacetonitrile). The onset of the IPCE spectra for DSSCs based on NKX-2593 and NKX-2677 is at 850 nm, which is red-shifted relative to the onset for the DSSC based on NKX-2311 (*ca.* 750 nm), and is almost equal to the onset for the DSSC based on the N3 dye.[3–5] This IPCE spectrum clearly indicates that introducing the thiophene moieties into the methine unit of NKX-2311 broadened the IPCE spectrum of NKX-2311 and thus led to an improved photocurrent under white light irradiation.

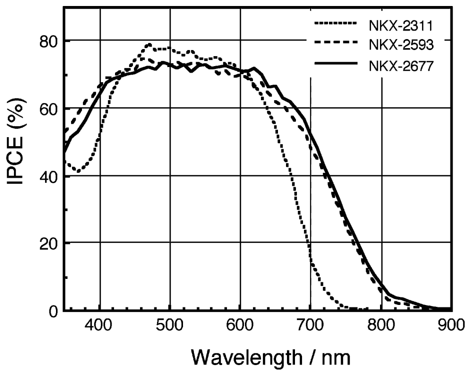

Fig. 2 Spectra of monochromatic incident photon-to-current conversion efficiencies (IPCEs) for DSSCs based on coumarin dyes: (···) NKX-2311, (---) NKX-2593, (—) NKX-2677. The electrolyte was the mixture 0.6 M DMPImI–0.1 M LiI–0.05 M I_2 in methoxyacetonitrile.

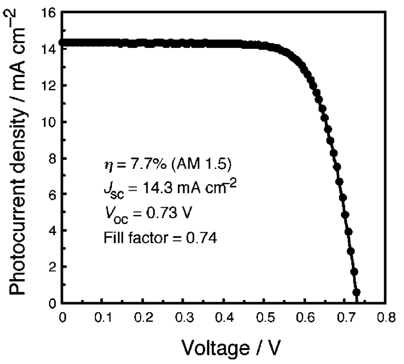

Fig. 3 A photcurrent voltage curve obtained with a DSSC based on NKX-2677 under AM 1.5 radiation (100 mW cm^{-2}; 7.7% efficiency). The electrolyte was the mixture 0.6 M DMPImI–0.1 M LiI–0.05 M I_2–1.0 M TBP in acetonitrile. Deoxycholic acid (40 mM) was employed as a co-adsorbate.

Fig. 3 shows a photocurrent voltage curve for the maximum performance of a DSSC based on NKX-2677 under AM 1.5 irradiation (100 mW cm^{-2}), with an electrolyte of 0.6 M DMPImI–0.1 M LiI–0.05 M I_2–1.0 M 4-*tert*-butylpyridine (TBP) in acetonitrile (AN). An η value of 7.7%, which is the highest efficiency obtained so far among DSSCs based on organic dye photosensitizers, was achieved under AM 1.5 radiation (J_{sc} = 14.3 mA cm^{-2}, V_{oc} = 0.73 V, and ff = 0.74). We can obtain good reproducible efficiencies from 7.5% to 7.7% with the solar cell based on NKX-2677. This efficiency is almost the same as that (7.8–8.0%) obtained with the DSSC based on the Ru dye N719 under the same measurement conditions. The performance of the DSSC based on NKX-2593 under AM 1.5 radiation also exceeded 7% with an η_{max} = 7.2% (J_{sc} = 14.7 mA cm^{-2}, V_{oc} = 0.67 V, and ff = 0.73).

One of factors that contributes to the improved solar cell performance upon the introduction of the thiophene moieties is the broadening of the absorption spectra of the dyes, which results in a large photocurrent. In addition to this, employing TBP in the electrolyte (1.0 M) markedly improves the cell voltage and, consequently, the total efficiency. TBP adsorbed on the TiO_2 surface negatively shifts the conduction band level of TiO_2. In addition, it prevents recombination between the injected electrons and I_3^- ions on the TiO_2 surface by the blocking effect, resulting in an improved voltage.[1,3] The reduction potentials of NKX-2593 and NKX-2677 measured electrochemically in DMF are −0.91 and −0.87 V *vs.* NHE, respectively. These values are more negative than the value of −0.82 V for NKX-2311, which suggests that the strong electron-donating ability of the thiophene moieties affects the relatively negative reduction potentials of the dyes. These relatively negative reduction potentials allow the use of TBP, because of the relatively large energy gaps between the LUMO levels of the dyes and the conduction band edge level (E_{cb}) of the TiO_2 electrode, −0.5 V *vs.* NHE,[3] as observed in DSSCs based on several polyene dyes.[12] In contrast, employing TBP in a system with a small energy gap between the LUMO level and E_{cb}, such as NKX-2311, leads to a remarkable decrease in photocurrent owing to a decreased electron injection yield.[10]

As shown above, the design of new coumarin dyes by the introduction of thiophene moieties remarkably improves the performance of the DSSC based on coumarin dye photosensitizers. We expect that the thiophene moieties in the methine chain should also improve the stability of the dye under irradiation. No sign of dye degradation in a DSSC based on NKX-2677 was observed by means of a brief experiment under continuous white light irradiation (*ca.* 80 mW cm^{-2}, < 420 nm cut-off) for 5 days: both the J_{sc} and V_{oc} increased about 5%

during the term. This suggests that the dye is relatively stable in the cell under irradiation, while the long-term stability of the cell performance must be investigated further. Our results strongly indicate that the application of organic dye photosensitizers in DSSCs is promising. We are now investigating the detailed mechanisms for DSSCs based on these coumarin dyes, including the broadening of the absorption spectra of the dyes on the TiO_2 surface and the effect of TBA on cell performance.

Experimental

Synthesis of dyes

1,1,6,6-Tetramethyl-9-(2-thiophen-2-ylvinyl)-2,3,5,6-tetrahydro-1*H*,4*H*-11-oxa-3*a*-azabenzo[*de*]anthracen-10-one (**1**) was prepared from 1,1,6,6-tetramethyl-10-oxo-2,3,5,6-tetrahydro-1*H*,4*H*,10*H*-11-oxa-3*a*-azabenzo[*de*]anthracene-9-carbaldehyde and potassium *tert*-butoxide. 5-[2-(1,1,6,6-Tetramethyl-10-oxo-2,3,5,6-tetrahydro-1*H*,4*H*,10*H*-11-oxa-3*a*-azabenzo[*de*]anthracen-9-yl)vinyl]thiophene-2-carbaldehyde (**2**) was synthesized from **1** by the Vilsmeyer–Haack reaction. An acetonitrile solution including **2** and cyanoacetic acid was refluxed in the presence of piperidine for 3.5 h. Purification of the resulting precipitates by column chromatography and recrystallization afforded dark green crystals of 2-cyano-3-{5-[2-(1,1,6,6-tetramethyl-10-oxo-2,3,5,6-tetrahydro-1*H*,4*H*,10*H*-11-oxa-3*a*-azabenzo[*de*]anthracen-9-yl)vinyl]thiophen-2-yl}acrylic acid (NKX-2593). Mp 263–267 °C. ^{1}H NMR (DMF-d_7) δ: 1.28 (6H, s), 1.51 (6H, s), 1.73–1.79 (4H, m), 3.32 (2H, t), 3.39 (2H, t), 7.19 (1H, d), 7.38–7.42 (2H, m) 7.81–7.90 (2H, m), 8.12 (1H, s), 8.41 (1H, s). MS-ESI m/z: 499.1 $(M-H)^-$.

1,1,6,6-Tetramethyl-9-thiophen-2-yl-2,3,5,6-tetrahydro-1*H*,4*H*-11-oxa-3*a*-azabenzo[*de*]anthracen-10-one (**3**) was prepared from 8-hydroxy-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinoline-9-carbaldehyde and thiophene-2-ylacetonitrile in DMF in the presence of acetic acid and piperidine. 9-(5-Bromothiophen-2-yl)-1,1,6,6-tetramethyl-2,3,5,6-tetrahydro-1*H*,4*H*-11-oxa-3*a*-azabenzo[*de*]anthracen-10-one (**4**) was obtained by bromination of **3** with *N*-bromosuccinimide in DMF. 9-[2,2′]Bithiophenyl-5-yl-1,1,6,6-tetramethyl-2,3,5,6-tetrahydro-1*H*,4*H*-11-oxa-3*a*-azabenzo[*de*]-anthracen-10-one (**5**) was prepared from **4** and 2-thiopheneboronic acid in the presence of $Pd(PPh_3)_4$ and K_2CO_3 (Suzuki coupling). 2-Cyano-3-[5′-(1,1,6,6-tetramethyl-10-oxo-2,3,5,6-tetrahydro-1*H*,4*H*,10*H*-11-oxa-3*a*-azabenzo[*de*]anthracen-9-yl)-[2,2′]bithiophenyl-5-yl]acrylic acid (NKX-2677) was synthesized from **5** by a similar procedure as for NKX-2593 *via* the Vilsmeyer–Haack reaction. NKX-2677 was purified by recrystallization from acetonitrile in the presence of acetic acid, yielding dark green crystals. Mp 285–288 °C. ^{1}H NMR ($CDCl_3$–DMF-d_7) δ: 1.32 (6H, s), 1.57 (6H, s), 1.75–1.85 (4H, m), 3.25–3.44 (4H, m), 7.18 (1H, s), 7.28 (1H, d), 7.37 (1H, d), 7.56 (1H, d), 7.65 (1H, d), 9.23 (1H, s), 8.23 (1H, s). MS-ESI m/z: 555.1 $(M-H)^-$.

Preparation of solar cells and photovoltaic measurement

A nanocrystalline TiO_2 photoelectrode (area: 0.25 cm^2; thickness: 14 μm) was prepared by screen printing. Both TiO_2 nanoparticles and an organic TiO_2 paste for screen printing were prepared by the methods reported by Grätzel and co-workers.[13,14] The TiO_2 paste consisted of the TiO_2 nanoparticles, large TiO_2 particles (average diameter 100 nm) as scattering centers, ethyl cellulose as a binder, and α-terpineol as a solvent. The TiO_2 paste was printed on a glass substrate coated with transparent conducting oxide (TCO, F-doped SnO_2), and subsequently sintered at 500 °C in air for 1 h. The dyes were dissolved in a mixture of *tert*-butyl alcohol, AN, and ethanol (2:2:1) at a concentration of 0.3 mM ($M = mol\ dm^{-3}$). Deoxycholic acid as a co-adsorbate was added into the dye solution at a concentration of 40 mM to improve photovoltaic performance as reported by Grätzel and co-workers.[15] The TiO_2 thin films were immersed in the dye solution at 25 °C for 12 h to adsorb the dye onto the TiO_2 surface. Photovoltaic measurements were carried out with a sandwich-type unsealed cell (two electrodes) consisting of a dye-coated TiO_2 photoelectrode, a Pt counter electrode, a polymer film spacer (25 μm thick), and an organic electrolyte. The electrolyte was either 0.6 M DMPImI–0.1 M LiI–0.05 M I_2–methoxyacetonitrile or 0.6 M DMPImI–0.1 M LiI–0.05 M I_2–1.0 M TBP–AN. The photovoltaic performance of the solar cells was measured under simulated AM 1.5 irradiation (*ca.* 100 mW cm^{-2}) using a solar simulator (Yamashita, YSS-150A).

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