Novel polyene dyes for highly efficient dye-sensitized solar cells

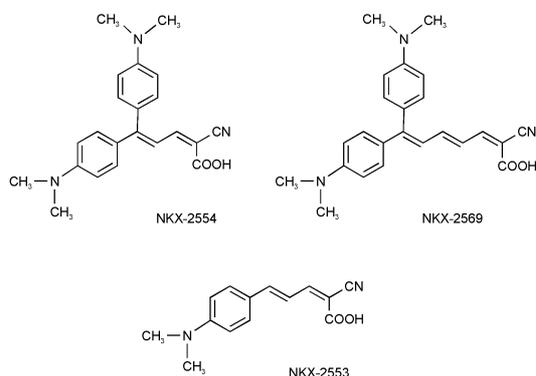Kohjiro Hara,[a] Mitsuhiko Kurashige,[a] Shunichiro Ito,[b] Akira Shinpo,[b] Sadaharu Suga,[b] Kazuhiro Sayama[a] and Hironori Arakawa*[a]

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We have developed an efficient and novel polyene-dye-sensitized nanocrystalline TiO_2 solar cells producing a 6.8% solar energy-to-electricity conversion efficiency (η) under AM 1.5 irradiation (100 mW cm^{-2}): short-circuit current density (J_{sc}), 12.9 mA cm^{-2}, open-circuit photovoltage (V_{oc}), 0.71 V, fill factor (ff), 0.74.

There has been an increasing interest in dye-sensitized nanocrystalline TiO_2 solar cells (DSSCs) because of their high solar-cell performance and a possibility of low-cost production. DSSCs based on several Ru-complex photosensitizers such N3 and Black dyes produced efficient solar energy-to-electricity conversion efficiencies, η, of up to 10%.[1–4] Organic dyes have been also utilized as photosensitizers in DSSCs. Recently, the solar-cell performance of DSSCs based on organic-dye photosensitizers has been remarkably improved.[5–8] One class of successful organic-dye photosensitizers are coumarin-dye derivatives. The absorption spectrum of one of them, NKX-2311, is expanded up to *ca.* 700 nm, which leads to wide light harvesting property and consequently large photocurrents.[7,8] A maximum η of up to 6.0% was attained with a DSSC based on NKX-2311.[8] In order to accomplish η values higher than 6.0% to outperform DSSCs based on the Ru dyes, sophisticated molecular design of organic dyes is requested. Expansion of the methine moiety of NKX-2311, which results in a red shift in the absorption spectrum of the dye, would simultaneously cause several problems in terms of a complicated synthesis procedure and chemical instability of the dye. Considering these points, we have designed and synthesized novel polyene-dye photosensitizers for use in DSSC. They contain the *N,N*-dimethylaniline (DMA) moiety as the donor part and a methine (–CH=CH–) unit connecting with the cyano (–CN) and carboxyl (–COOH) groups as the acceptor part (Scheme 1). Consequently, we have succeeded in construction of a DSSC with η = 6.8% under AM 1.5 irradiation. In addition to their high solar-cell performance, their prospective low-cost production owing to their simple molecular structure and synthesis procedure suggest a possibility of promising applications of organic-dye photosensitizers in DSSCs.

An acetonitrile solution of 4-dimethylaminocinnamaldehyde and cyanoacetic acid was refluxed in the presence of piperidine for 1 h. Recrystallization of the resulting precipitates from methanol–triethylamine by adding acetic acid afforded purple crystals of 2-cyano-5-(4-dimethylaminophenyl)penta-2,4-dienoic acid (NKX-2553).† 2-Cyano-5,5-bis(4-dimethylaminophenyl)penta-2,4-dienoic acid (NKX-2554) and 2-cyano-7,7-bis(4-dimethylaminophenyl)hepta-2,4,6-trienoic acid (NKX-2569) were synthesized from the corresponding aldehyde intermediates and cyanoacetic acid by a similar procedure as for NKX-2553. Expansion of the methine unit in the aldehyde intermediate was carried out by Vilsmeyer–Haack reaction. NKX-2554 and 2569 were purified by recrystallization.

Nanocrystalline TiO_2 photoelectrodes (area: 0.245 cm², thickness: 14 μm) were prepared by screen printing. TiO_2 nanoparticles and an organic TiO_2 paste for screen printing were prepared by methods reported by Grätzel and coworkers.[9,10] The TiO_2 paste consisted of TiO_2 nanoparticles, large TiO_2 particles (av. 100 nm) as scattering centers, ethyl cellulose as binder, and α-terpineol as 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 polyene dyes were dissolved in *tert*-butyl alcohol–acetonitrile (50:50) with a concentration of 0.3 mM. The TiO_2 thin films were immersed into the dye solution and then kept at 25 °C for 12 h so that the dye could be adsorbed onto the TiO_2 surface. Photovoltaic measurements were carried out with a sandwich-type cell (two electrode) consisting of a dye-coated TiO_2 electrode, a Pt counter electrode, a polymer film spacer, and an organic electrolyte. The electrolyte was 0.6 M 1,2-dimethyl-3-*n*-propylimidazolium iodide (DMPImI)–0.1 M LiI–0.05 M I_2–methoxyacetonitrile or 0.6 M DMPImI–0.1 M LiI–0.05 M I_2–0.56 M 4-*tert*-butylpyridine (TBP)–acetonitrile (AN). The photovoltaic performance of the solar cells were measured under simulated AM 1.5 irradiation (100 mW cm^{-2}).

Absorption spectra of the novel polyene dyes, NKX-2553, 2554 and 2569 in *tert*-butyl alcohol–AN (50:50) solution are shown in Fig. 1. The absorption peak of NKX-2553, which has a DMA moiety, is at 457 nm and that of NKX-2554 is slightly
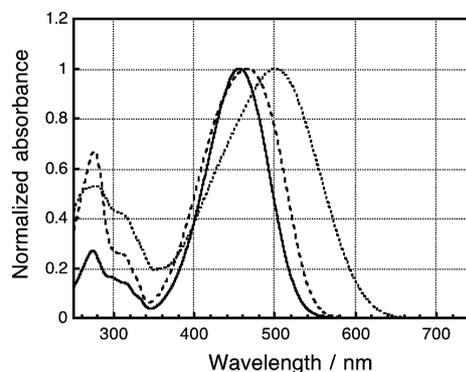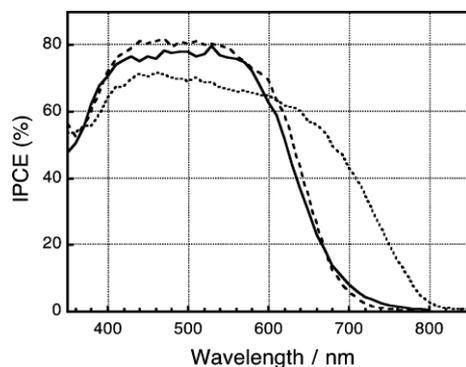

Scheme 1 Molecular structures of novel polyene dyes.

Fig. 1 Absorption spectra of novel polyene dyes in *tert*-butyl alcohol–acetonitrile (50:50): solution: (—) NKX–2553, (- - -) NKX–2554, (···) NKX–2569.

red-shifted by introducing a DMA moiety into NKX-2553. Moreover, the absorption spectrum of NKX-2569 (λ_{max} = 502 nm) is red-shifted compared to that of NKX-2554 by expanding the methine unit of NKX-2554. Thus, introduction of a DMA moiety and expanding the methine unit both contribute to a red shifting of the absorption spectra of the dyes. Such red shift in the absorption spectra are desirable for harvesting the solar spectrum. The molar absorption coefficient, ε, for these dyes in methanol are 33500–41200 M^{-1} cm^{-1}. The reduction potential of NKX-2553, 2554 and 2569 in DMF are −1.0, −1.1 and −0.90 V vs. NHE, respectively. These values are more negative than the −0.82 V for NKX-2311, leading to larger energy gaps between the LUMO levels of dyes and the conduction band edge level (E_{cb}) of the TiO$_2$ electrode (−0.5 V vs. NHE).[3] These relatively negative reduction potentials for the polyene dyes are considered to be due to a strong electron-donating ability of the DMA moiety. Relatively large energy gaps between the LUMO and E_{cb} enable addition of TBP in the electrolyte (0.56 M), improving the photovoltage and consequent total efficiency. TBP adsorbed on the TiO$_2$ surface shifts the conduction band level of TiO$_2$ negatively and prevents recombination between injected electrons and I$_3^-$ ions on the TiO$_2$ surface, resulting in an improved photovoltage.[1,3,4] By contrast, employing TBP in a system which has a small energy gap between the LUMO level and E_{cb}, leads to substantial decrease in the photocurrent due to a decreasing electron injection yield.

Fig. 2 shows action spectra of monochromatic incident photon-to-current conversion efficiencies (IPCEs) for DSSCs based on a nanocrystalline TiO$_2$ electrode, novel polyene dyes, and an iodine redox (I$^-$/I$_3^-$) electrolyte. The onset of IPCE spectra for DSSCs based on NKX-2553 and 2554 was ca. 760 nm. IPCE values higher than 70% were observed in the range from 460 to 600 nm with a maximum value of 82% at 468 nm for the DSSC based on NKX-2554. When the reflection and absorption losses in the TCO substrate are considered, the net photon-to-current conversion efficiency in this range reaches more than 90%, which indicates highly efficient performance of these solar cells. The onset of the IPCE spectrum of a DSSC based on NKX-2569 reached 820 nm. This is almost equal to that for the DSSC based on the N3 dye, although its IPCE values are slightly lower than the efficiencies for DSSCs based on NKX-2553 and 2554 (the maximum is 72% at 460 nm). When we employed deoxycholic acid (DCA) as a co-adsorbate, the IPCE performance of a DSSC based on NKX-2569 was improved. To suppress dye aggregation on the TiO$_2$ surface, DCA derivatives have been employed as co-adsorbates in DSSCs.[11] It is suggested that aggregation of NKX-2569 decreases electron injection yield without DCA.

Table 1 shows photovoltaic performance for DSSCs based on NKX-2553, 2554 and 2569 under AM 1.5 irradiation (100 mW cm^{-2}). High efficiencies of > 5% were attained by DSSCs based on these dye photosensitizers. A maximum η value of 6.8% was achieved under AM 1.5 irradiation with a DSSC

based on NKX-2569 (short-circuit photocurrent density, J_{sc}, 12.9 mA cm^{-2}, open-circuit photovoltage, V_{oc}, 0.71 V, fill factor, ff, 0.74). This efficiency shows the highest value so far among solar cells based on organic dyes and approaches the η values of 7.5–7.8% for the DSSC of N3 (or N719) dye under the same measurement conditions of the DSSC of NKX-2569. These results strongly indicate the prospect for promising application of organic dye photosensitizers in DSSCs concerning both high solar-cell performance and a possibility of low-cost production. No degradation of the dye or cell performance were observed under white light irradiation (< 420 nm cut off, 80 mW cm^{-2}) for several days, suggesting that the dye is relatively stable under irradiation. Long term stability of the dye and cell performance will be investigated in detail.

Table 1 Photovoltaic performance of polyene dye-sensitized nanocrystalline TiO$_2$ solar cells

Dye	J_{sc}/mA cm^{-2}	V_{oc}/V	Fill factor	η (%)
NKX-2553	10.4	0.71	0.74	5.5
NKX-2554	9.9	0.74	0.74	5.4
NKX-2569	12.9	0.71	0.74	6.8

Conditions: irradiated light, AM 1.5 (100 mW cm^{-2}); photoelectrode, TiO$_2$ (14μm thickness and 0.245 cm^2 area); electrolyte, 0.6 M 1,2-dimethyl-3-*n*-propylimidazolium iodide–0.1 M LiI–0.05 M I$_2$–0.56 M 4-*tert*-butylpyridine in acetonitrile. Co-adsorbate: 5 mM deoxycholic acid.

Notes and references

† NKX-2553: mp 221–223 °C, ^{1}H NMR (DMF-d_7): δ 3.07 (12H, s), 6.81 (2H, d), 7.04 (1H, dd), 7.55 (1H, d), 7.61 (2H, d), 8.05 (1H, d). HRMS–EI (*m/z*): [M]$^+$ calc. for C$_{14}$H$_{14}$N$_2$O$_2$, 242.1054, found 242.1042 (4%); [M − CO$_2$]$^+$ calc. for C$_{13}$H$_{14}$N$_2$, 198.1156, found, 198.1112 (100%).

NKX-2554: mp 205–208 °C, ^{1}H NMR (CDCl$_3$): δ 3.05 (6H, s), 3.06 (6H, s), 6.65 (2H, d), 6.73 (2H, d), 7.01 (1H, d), 7.13 (2H, d), 7.36 (2H, d), 8.00 (1H, d). HRMS–EI (*m/z*): [M]$^+$ calc. for C$_{22}$H$_{23}$N$_3$O$_2$, 361.1789, found, 361.1845 (4%); [M − CO$_2$]$^+$ calc. for C$_{21}$H$_{23}$N$_3$, 317.1891, found, 317.1800 (100%).

NKX-2569: mp 218–220 °C, ^{1}H NMR (DMF-d_7): δ 3.01 (6H, s), 3.03 (6H, s), 6.75 (2H, d), 6.82–6.85 (3H, m), 7.01 (1H, d), 7.12 (2H, d), 7.24–7.31 (1H, m), 7.32 (2H, d), 7.92 (1H, d). HRMS–EI (*m/z*): [M]$^+$ calc. for C$_{24}$H$_{25}$N$_3$O$_2$, 387.1945, found, 387.2127 (15%); [M − CO$_2$]$^+$ calc. for C$_{23}$H$_{25}$N$_3$, 343.2047, found, 343.2358 (100%).

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Fig. 2 Spectra of monochromatic incident photon-to-current conversion efficiencies (IPCEs) for DSSCs based on novel polyene dyes: (— NKX-2553, (---) NKX-2554, (···) NKX-2569. The electrolyte was a solution of 0.6 M DMPImI–0.1 M LiI–0.05 M I$_2$ in methoxyacetonitrile.