Oligothiophene-Containing Coumarin Dyes for Efficient Dye-Sensitized Solar Cells

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We have developed oligothiophene-containing coumarin dyes fully functionalized for dye-sensitized nanocrystalline TiO₂ solar cells (DSSCs). DSSCs based on the dyes gave good performance in terms of incident photon-to-current conversion efficiency (IPCE) in the range of 500–800 nm. A solar energy-to-electricity conversion efficiency (η) of 7.4% was obtained with a DSSC based on 2-cyano-3-[5′-(1,1,6,6-tetramethyl-10-oxo-2,3,5,6-tetrahydro-1H,4H,10H-11-oxa-3e-aza-benzof[e]anthracen-9-y1)-[2,2′]bithiophenyl-5-y1]-acrylic acid (NKKX-2677) under simulated AM 1.5G irradiation (100 mW cm⁻²) with a mask: short-circuit current density (Jₛ𝑐) = 13.5 mA cm⁻²; open-circuit voltage (Vₒ𝑐) = 0.71 V; fill factor (FF) = 0.77. Transient absorption spectroscopy measurements indicated that electron injection from NKKX-2677 to the conduction band of TiO₂ is very rapid (<100 fs), which is much faster than the emission lifetime of the dye (1.0 ns), giving a highly efficient electron injection yield of near unity.

1. Introduction

Recently there has been significant interest in organic devices for application in the fields of light-emitting diodes,† field effect transistors,‡ and photovoltaic cells (PVCs).§ The performance of these devices depend mainly on the properties of functionalized organic molecules and polymers. In a nanostructured dye-sensitized solar cell (DSSC), they have several advantages as photosensitizers: (a) they are cheaper than Ru complexes, (b) they have large absorption coefficients due to intramolecular transitions, and (c) there are no concerns about limited resources, because they do not contain noble metals such as ruthenium. DSSCs based on metal-free organic dyes, porphyrin dyes, and natural dyes have been studied and developed. Coumarin derivatives have been used successfully as organic dye photosensitizers in DSSCs: we have attained maximum η values of up to 6.0% with DSSCs based on a coumarin dye, NKKX-2311, in which the coumarin moiety is connected to a cyanoacetic acid (CAA) moiety (=C(-C≡N)) through a methine (-CH≡CH-) backbone. To achieve higher η values, such as those observed with DSSCs based on Ru-complex photosensitizers, however, sophisticated molecular design of coumarin dyes is required. For example, Horiuchi et al. recently achieved high η of up to 8.0% under AM 1.5G (100 mW cm⁻²) with DSSCs based on novel merocyanine dyes. The molecular structure of the dye results in a broad absorption spectrum and prevents excess dye aggregation on the TiO₂ surface.

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One promising approach to improving the performance of coumarin-dye photosensitizers would be to expand the \( \pi \)-conjugation system by increasing the number of methine units in NKX-2311. Although such an elongation 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 decrease the stability of the dye molecule, due to the possibility of isomer formation. The introduction of \( \pi \)-conjugated ring moieties such as benzene, thiophene, pyrrole, or furan into the methine backbone of NKX-2311 simultaneously expands the \( \pi \)-conjugation system and improves the stability of the dye molecule relative to dyes that have a long methine chain unit, in our experience. Therefore, we designed new coumarin dyes by introducing thiophene moieties into the methine moiety of NKX-2311 rather than by elongating the methine moiety itself (Chart 1). Preliminary experiments showed that thiophene modification of coumarin-dye photosensitizers markedly improved the performance of DSSCs based on common dyes.\(^{45}\) In this paper, we report detailed characterizations of novel coumarin dyes modified with thiophene moieties and their high performance in DSSCs. Our results strongly suggest that organic dye photosensitizers can be successfully modified for use in DSSCs and demonstrate the promising performance of DSSCs based on organic dye photosensitizers.

2. Experimental Section

Synthesis of the Dyes. The molecular structures of the coumarin dyes NKX-2587, NKX-2677, and NKX-2697 are shown in Chart 1. Detailed synthesis procedures for the dyes are shown in the Supporting Information.

Characterization of the Dyes. \(^1H\) NMR spectra of the coumarin dyes were recorded with a JEOL JNM-AL300 spectrometer. High-resolution mass spectra and electrospray ionization mass spectra were obtained with a Hitachi M-80 B spectrometer and a Micromass Quattro II mass spectrometer, respectively. The absorption spectra of the dyes in solution and adsorbed on TiO\(_2\) films were measured with a Shimadzu UV-3101PC. FT-IR absorption spectra were measured with a Perkin-Elmer Spectrum One spectrometer in transmission mode with an ATR system equipped with a ZnSe prism. The oxidation potential of the dye in acetonitrile (AN) was measured in a normal one-compartment cell with a glassy carbon working electrode, a Pt counter electrode, and a Ag/Ag\(^+\) reference electrode in an AN solution that included 0.01 M AgNO\(_3\) and 0.1 M tetrabutylammonium perchlorate (TBAP). The measurements were performed with an electrochemical analyzer (ALS, model 610B). The potential was calibrated against the ferrocene redox couple. The oxidation potential of the dye adsorbed on a TiO\(_2\) film was measured by differential pulse voltammetry using a dye-coated TiO\(_2\) electrode as the working electrode in 0.1 M TBAP/AN. The fluorescence lifetime was measured using a time-correlated single-photon counting fluorometer (IBH, TBX-04). Thermogravimetric (TG) analysis of the dyes was performed with a Rigaku, TG8120 analyzer. The amount of the dye adsorbed on the TiO\(_2\) surface was estimated spectroscopically after the dye had been desorbed in a 0.1 M solution of NaOH in 50:50 (vol \%) ethanol–H\(_2\)O.

The light source for the femtosecond pump–probe transient absorption measurements was a regenerative amplifier system of a Ti:sapphire laser (800 nm wavelength, 160 fs fwhm pulse width, 1.0 mJ/pulse intensity, 1 kHz repetition; Spectra Physics, Hurricane) combined with two optical parametric amplifiers (OPAs; Quantronix, Topas). For a pump pulse, the output of the OPA at a wavelength of 540 nm with an intensity of several microjoules per pulse at a 500 Hz modulation frequency was used; and for a probe pulse, the output of the other OPA at 4 \( \mu \)m was used. The probe beam was focused at the center of the pump beam on the sample and then detected with an MCT photodetector (Hamamatsu, P3257-10) after passing through a monochromator (Acton Research, SpectraPro-300).

Density functional theory (DFT) calculations were performed with the Gaussian 98 program package. The geometry of the dye was optimized by means of the B3LYP method in combination with the 6-31G* basis set. The nature of the stationary points and the theoretical IR absorption spectra were assessed by means of vibrational-frequency analysis. Vibrational frequencies predicted at the B3LYP/6-31G* level were scaled by 0.9614.\(^{46}\) The calculations were run on the Quantum Chemistry Grid/Gaussian Portal system at the Tsukuba Advanced Computing Center.

Preparation of Dye-Sensitized TiO\(_2\) Electrodes. Nanocrystalline TiO\(_2\) photoelectrodes were prepared by a screen printing technique. TiO\(_2\) nanoparticles and an organic TiO\(_2\) paste for screen printing were prepared by methods reported by Grätzel and co-workers.\(^{10,47}\) The TiO\(_2\) paste consisted of TiO\(_2\) nanoparticles, large TiO\(_2\) particles (average 100 nm) as scattering centers, ethyl cellulose as a binder, and \( \alpha \)-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 thickness of the TiO\(_2\) thin films, measured with an Alpha-Step 300 profilometer (Tencor Instruments), was ca. 15 \( \mu \)m.

The coumarin dyes were dissolved in a mixed solvent of 50:50 (vol \%) tert-butyl alcohol (t-BuOH, Kanto Chemical) and AN (Kanto, dehydrated for organic synthesis). These solvents were used as obtained from the suppliers without further purification. A coadsorbate, deoxycholic acid (DCA) was added to the dye solution as employed by Kay and Grätzel.\(^{32}\) The TiO\(_2\) films were immersed in the dye solutions and then kept at 25 °C for more than 12 h to allow the dye to adsorb to the TiO\(_2\) surface.

Photovoltaic Measurements of the Solar Cells. The electrochemical cell (two-electrode type) used for photovoltaic measurements consisted of a dye-sensitized TiO\(_2\) electrode, a counter electrode, a film spacer (30 \( \mu \)m thick), and an organic electrolyte. We used two types of cells. In the case of the not-sealed cell (type A), we used black binder clips to hold two electrodes. Because these clips are held near the edge of the
dye-sensitized TiO2 electrode, they diminished partially the influence of incident light from the side: it was difficult to attach a mask onto the top of this type of cell. The other type is a sealed cell (type B) with a black mask (aperture area: 0.58 cm × 0.58 cm). The counter electrode was a Pt film (ca. 200 nm thick) sputtered onto a TCO-coated glass plate. The apparent surface area of the TiO2 film electrode, measured by an optical microscope, LEICA M420, equipped with a digital camera (Nikon DXM1200), was 0.25–0.26 cm2.

The electrolyte was 0.6 M 1,2-dimethyl-3-n-propylimidazolium iodide (DMPImI)−0.1 M LiI−0.05 M I2 in methoxyacetonitrile (MAN) or 0.6 M DMPImI−0.1 M LiI−0.05 M I2−1.0 M 4-tert-butylpyridine (TBP) in AN. Reagent-grade LiI (Wako) and I2 (Wako) were used for the electrolyte. MAN (Aldrich and Tokyo Kasei) and TBP (Aldrich) were distilled before use. DMPImI was purchased from Tomiyama Pure Chemical Industries Ltd.

The photovoltaic performance of the solar cells was measured with a source meter (Advantest, R6246). We employed an AM 1.5G solar simulator (Yamashita Denso Co., YSS-150A with a 1000-W Xe lamp and an AM filter) as the light source. The incident light intensity was calibrated by using a standard solar cell composed of a crystalline silicon solar cell and an IR cutoff filter (Schott, KG-5), giving the photosresponse range of an amorphous silicon solar cell (produced and calibrated by Japan Quality Assurance Organization). Action spectra of the monochromatic incident photon-to-current conversion efficiency (IPCE) of the solar cell were measured with a CEP-99W system (Bunkoh-keiki Co., Ltd.).

3. Results and Discussion

Absorption, Emission, and Electrochemical Properties of the Dyes. Figure 1 shows the absorption spectra of the coumarin dyes NKX-2587, NKX-2677, and NKX-2697 both in t-BuOH−AN (50:50 (vol %)) solution and adsorbed on a transparent TiO2 film. The number of thiophene moieties did not affect the absorption properties of the dye in solution (Figure 1a). Absorption peaks (λmax) were observed at 507 nm for NKX-2587, 511 nm for NKX-2677, and 501 nm for NKX-2697 (Table 1). The molar absorption coefficient (ε at λmax) was 54 300 M−1 cm−1 for NKX-2587, 64 300 M−1 cm−1 for NKX-2677, and 73 300 M−1 cm−1 for NKX-2697 (Table 1).

The absorption peaks of the dyes were blue-shifted by adsorption on the TiO2 surface (Figure 1b). These blue shifts of the absorption spectra by adsorption on the TiO2 surface were also observed in other organic dyes.30 Nazeeruddin et al. reported that the MLCT transition bands of the black dye are blue-shifted as the pH of the solution increased.11 They concluded that the blue shift is due to formation of the deprotonated form (i.e., the carboxylate anion), whose π* orbital of the terpyridyl ligand is higher than the protonated form. In the case of the coumarin dyes, therefore, the blue shifts of absorption spectra were probably due to deprotonation of the dyes by adsorption on the TiO2 surface.

When the absorption spectra of the dyes on the TiO2 film (Figure 1b) is normalized by the ε at λmax to compare briefly the amount of the dyes on the TiO2 film, the normalized value of the peak became larger as the number of thiophene moieties increased. There are probably intermolecular π−π stacking interactions due to the thiophene moieties of the adsorbed dyes, as has been observed in substituted oligothiophenes.28 This π−π stacking interaction appears to increase the amount of adsorbed dye. For example, the amounts of dye adsorbed on the TiO2 film (10 μm thick) were 1.6 × 10−7 mol cm−2 for NKX-2587 and 2.0 × 10−7 mol cm−2 for NKX-2677, which were higher than the amounts of other dyes: e.g., 1.3 × 10−7 mol cm−2 for N3 dye.8 These results suggest that strong interactions between the thiophene moieties of the dyes result in a highly ordered adsorption of the dyes to the TiO2 surface.

The emission properties and the oxidation potential (Eox) of the dyes are summarized in Table 1. The λmax for emission increased with increasing number of thiophene moieties. The emission lifetime decreased with increasing number of thiophene moieties. The Eox of the dyes in solution was not strongly affected by the number of thiophenes.

The Eox of the dyes adsorbed on a nanocrystalline TiO2 film is summarized in Table 2. The Eox of the dyes was shifted negatively as the number of thiophene moieties increased. These negative shifts in the Eox levels of the dyes on the TiO2 surface are probably caused by intramolecular π−π stacking interactions. In DSSCs, the oxidized dyes formed after electron injection into TiO2 accept electrons from I− ions, regenerating the ground state of the dye. Therefore, the HOMO level of the dye must be more positive than the iodine redox potential to accept electrons effectively, as mentioned in the Introduction. As shown in Table 2, the oxidation potentials corresponding to the HOMO levels of NKX-2587, -2677, and -2697 adsorbed

### Table 1: Absorption, Emission, and Electrochemical Properties of the Coumarin Dyes

<table>
<thead>
<tr>
<th>Dye</th>
<th>λmax/nm</th>
<th>ε at λmax</th>
<th>λmax/nm</th>
<th>Lifetime/ns</th>
<th>Eox/NHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>NKX-2587</td>
<td>507</td>
<td>54 300</td>
<td>556</td>
<td>2.4</td>
<td>1.02</td>
</tr>
<tr>
<td>NKX-2677</td>
<td>511</td>
<td>64 300</td>
<td>572</td>
<td>1.0</td>
<td>1.05</td>
</tr>
<tr>
<td>NKX-2697</td>
<td>501</td>
<td>73 300</td>
<td>577</td>
<td>0.8</td>
<td>1.04</td>
</tr>
</tbody>
</table>

E: Absorption, emission spectra, and emission lifetime were measured in t-BuOH−AN (50:50 (vol %)) solution at 25 °C. Oxidation potential (Eox) of dye was measured in 0.1 M TBAP in AN (working electrode, glassy carbon; reference electrode, Ag/AgCl; counter electrode, Pt).
TABLE 2: Electrochemical Properties of the Coumarin Dyes Absorbed on a TiO2 Film

<table>
<thead>
<tr>
<th>dye</th>
<th>$E_{ox}$/V vs NHE</th>
<th>$E_{red}$/eV</th>
<th>$E_{ox} - E_{red}$/V vs NHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>NKX-2587</td>
<td>1.01</td>
<td>1.86</td>
<td>−0.85</td>
</tr>
<tr>
<td>NKX-2677</td>
<td>0.93</td>
<td>1.82</td>
<td>−0.89</td>
</tr>
<tr>
<td>NKX-2697</td>
<td>0.91</td>
<td>1.68</td>
<td>−0.77</td>
</tr>
</tbody>
</table>

* Conditions: working, a dye-coated TiO2 electrode; counter, a Pt electrode; reference, an Ag/Ag+ in 0.1 M AgNO3−0.1 M TBAP in AN; electrolyte, 0.1 M TBAP in AN. * $E_{ox}$ was estimated by differential pulse voltammetry. * $E_{ox}$ was estimated from the onset of absorption spectra of the dyes adsorbed on a transparent TiO2 film.

on TiO2 were sufficiently more positive than the iodine redox potential value.5,6

The $0\rightarrow0$ energies ($E_{0\rightarrow0}$) of the dyes adsorbed on a nanocrystalline TiO2 film (Table 2) were estimated from the maximum wavelengths of the UV−visible absorption spectra. The $E_{ox} - E_{0\rightarrow0}$ values, which correspond to the LUMO level of the dyes, are more negative than the $E_{cb}$ of the TiO2 electrode (−0.5 V vs NHE)5,6, meaning that efficient electron injection from the dyes to TiO2 should occur.

Structure of NKX-2677 Adsorbed on TiO2 Surface.

Generally, photosensitizers in DSSCs are adsorbed to the TiO2 surface through anchoring groups. Such anchoring to the TiO2 surface gives rise to a large electronic coupling, which results in ultrafast electron injection. Coumarin dyes appear to anchor to the TiO2 surface through their carboxyl group; indeed, a dye with a coumarin group and thiophene moieties but no carboxyl group was not adsorbed on the TiO2 surface (data not shown).

To determine the detailed structure of NKX-2677 adsorbed to the TiO2 surface, we measured its FT-IR absorption spectra and calculated the molecular structure of NKX-2677.

In the FT-IR absorption spectrum of neat NKX-2677 (Figure 2a, −COOH type), the absorption peak at 2213 cm−1 is assigned to the C≡N stretching band. Absorption peaks at 1711 and 1686 cm−1 were assigned to the C=O stretching bands of the coumarin-framework carbonyl group and the carbonyl group, respectively. In the spectrum of adsorbed NKX-2677 (Figure 2b), the C=O stretching band (1686 cm−1) has disappeared, and a new absorption band is observed at 1590 cm−1. This band is assigned to asymmetric O−C−O stretching in the carboxylate (−COO−) group.49 The theoretical IR absorption spectrum of NKX-2677 sodium salt as a model for the dye adsorbed on TiO2 (i.e., a bidentate carboxylate form) obtained by vibrational-frequency analysis (Figure 2c) agrees better with the spectrum of adsorbed NKX-2677 (Figure 2b) than with that of neat NKX-2677 (Figure 2a). These spectra strongly suggest that NKX-2677 is adsorbed onto the TiO2 surface by bidentate carboxylate coordination, rather than by ester-like bonding. It has been observed by FT-IR spectroscopic measurements that Ru complexes having carboxyl groups also are adsorbed onto a TiO2 surface by bidentate carboxylate coordination.49

Figure 3 shows the optimized molecular structure of the NKX-2677 sodium salt (as a model for the dye’s structure on the TiO2 surface) and the electron distributions of its HOMO and LUMO. Comparison of the electron distributions in the frontier MOs reveals that HOMO−LUMO excitation slightly moved the electron distribution from the coumarin moiety (the donor) to the cyanoacetic acid (CAA) moiety (the acceptor), whereas the main distribution was observed on the thiophene backbone connecting the thiophene and CAA moieties. Moreover, a HOMO is located at the C=≡C double bonds in the thiophene backbone, whereas a LUMO is located at the C=−C single bonds and the S atoms, as observed for HOMO and LUMO distribution of polythiophene.50 This is related to the fact that the aromatic form of thiophenes has a lower total energy, which causes it to be preferred in the ground state, than the quinoid form.50 It is clear that whole electron distribution in the HOMO and LUMO of NKX-2677 is strongly affected by the aromatic quinoid structural change of the thiophene moieties. After excitation, the excited electrons are apparently injected into TiO2 via the CAA moiety directly connected to the TiO2 surface.

Photovoltaic Performance of DSSCs Based on the Dyes.

Action spectra of IPCEs for DSSCs (type A) composed of a...
nanocrystalline TiO\textsubscript{2} electrode, the coumarin dyes, and an iodine redox (I\textsuperscript{-}/I\textsubscript{3}\textsuperscript{-}) electrolyte are shown in Figure 4 (electrolyte: 0.6 M DMPImI\textsuperscript{-}0.1 M LiI\textsuperscript{-}0.05 M I\textsubscript{2} in MAN). IPCEs are represented by the following equation:

$$\text{IPCE} = \frac{[1240(\text{eV nm})]J_{ph}}{\lambda\Phi}$$

where $J_{ph}$ (mA cm\textsuperscript{-2}) is the short-circuit photocurrent density for the monochromatic irradiation and $\lambda$ (nm) and $\Phi$ (mW cm\textsuperscript{-2}) are the wavelength and the intensity, respectively, of the monochromatic light.

The onset wavelengths of the IPCE spectra for DSSCs based on NKX-2587 and NKX-2677 were 780 and 820 nm, respectively. IPCE values higher than 70\% were observed in the range of 430–640 nm with a maximum value of 77\% at 498 nm for the DSSC based on NKX-2677. When the reflection and absorption losses in the TCO substrate are considered, the net photon-to-current conversion efficiency in this range exceeds 90\%, which indicates the highly efficient performance of these solar cells. The onset wavelength of the IPCE spectrum of a DSSC based on NKX-2677 was 900 nm, which is the most red-shifted among all DSSCs based on organic dye photosensitizers. This value is almost equal to that for a DSSC based on a ruthenium–terpyridyl complex (called black dye),\textsuperscript{11} although the maximum IPCE value of the DSSC based on NKX-2677 (62\% at 490 nm) is slightly lower than the efficiencies of the DSSCs based on NKX-2587 and -2677. The lower IPCE value of the DSSC based on NKX-2677 is probably due to its lower LUMO level (i.e., $E_{\text{ox}} - E_{\text{o-}}$), which leads to decreased electron injection yield relative to that of other dyes (Table 2).

In addition, the use of DCA as a coadsorbate, which was simultaneously adsorbed on the TiO\textsubscript{2} electrode during the dye adsorption process, improved the IPCE performance of the DSSC based on NKX-2677. Cholic acid derivatives were first employed as coadsorbates in DSSCs based on porphyrins to suppress dye aggregation on the TiO\textsubscript{2} surface.\textsuperscript{32} The IPCE performance of the DSSC based on NKX-2677 was also improved in the presence of DCA as a coadsorbate.\textsuperscript{31} Aggregation of NKX-2697 may be a factor that decreases electron injection yield, due to energy quenching processes occurring between molecules in the absence of DCA.

The solar energy-to-electricity conversion efficiency, $\eta$ (%), under white-light irradiation (e.g., AM 1.5G) can be obtained from the following equation:

$$\eta = \frac{J_{sc} V_{oc} \text{FF}}{I_{0}} \times 100$$

where $I_{0}$ (mW cm\textsuperscript{-2}) is the photon flux (e.g., ca. 100 mW cm\textsuperscript{-2} for AM 1.5G), $J_{sc}$ (mA cm\textsuperscript{-2}) is the short-circuit current density under irradiation, $V_{oc}$ (V) is the open-circuit voltage, and FF represents the fill factor. An $\eta$ value of 7.4\% ($J_{sc} = 13.5$ mA cm\textsuperscript{-2}, $V_{oc} = 0.71$ V, and FF = 0.77) was obtained with a DSSC (type B) based on NKX-2677 under AM 1.5G irradiation (100 mW cm\textsuperscript{-2}) with a mask (Figure 5). For a DSSC (type A) based on NKX-2677, the $\eta$ value was 8.1\% ($J_{sc} = 14.8$ mA cm\textsuperscript{-2}, $V_{oc} = 0.71$ V, and FF = 0.77), which can be compared to the previous data.\textsuperscript{45} In this DSSC, TBP as an additive in the electrolyte played an important role in the high solar-cell performance. The $V_{oc}$ and FF values for a DSSC based on NKX-2677 were remarkably improved by the addition of TBP in the electrolyte and, consequently, the total conversion efficiency was improved,\textsuperscript{51} as was observed in DSSCs based on Ru dyes.\textsuperscript{9,52} High $\eta$ values were also obtained with the DSSCs (type A) based on other dyes: 5.8\% ($J_{sc} = 12.1$ mA cm\textsuperscript{-2}, $V_{oc} = 0.66$ V, and FF = 0.73) for NKX-2587 and 6.4\% ($J_{sc} = 14.3$ mA cm\textsuperscript{-2}, $V_{oc} = 0.70$ V, and FF = 0.64) for NKX-2679, respectively.

When we measured the performance of a DSSC (type B with a mask) based on a Ru dye, N719 dye, under similar conditions for the DSSC based on NKX-2677, the $\eta$ value was 8.9\% ($J_{sc} = 16.5$ mA cm\textsuperscript{-2}, $V_{oc} = 0.75$ V, and FF = 0.72). We consider that the lower performance of the DSSC based on NKX-2677 relative to one based on N719 dye is probably due to lower voltage generated in the DSSC based on NKX-2677. That is, we need to employ an electrolyte containing a high concentration of TBP (1.0 M), which decreases the $J_{sc}$,\textsuperscript{51} to obtain high $V_{oc}$ and FF in DSSC based on NKX-2677: e.g., the $\eta$ was 3.6\% ($J_{sc} = 17.1$ mA cm\textsuperscript{-2}, $V_{oc} = 0.47$ V, and FF = 0.45) without TBP.\textsuperscript{31} In the case of N719 dye, we could obtain a high $V_{oc}$ value, 0.75 V with an electrolyte containing 0.5 M TBP. This suggests that recombination between the injected electrons in TiO\textsubscript{2} and I\textsubscript{3}\textsuperscript{-} ions in the electrolyte easily occurs in the DSSC based on NKX-2677 compared to one based on N719 dye, although the detailed mechanism is not clear at present.

**Electron-Transfer Processes in DSSCs Based on NKX-2677.** Figure 6 shows (a) transient absorption monitored at 4000 nm for a NKX-2677-adsorbed TiO\textsubscript{2} film after excitation at 540 nm and (b) an energy diagram for a DSSC based on NKX-2677. In Figure 6a, the increasing absorption after photocexcitation of NKX-2677 is attributed to the injected electrons into the conduction band of TiO\textsubscript{2}. Since there was no vibrational absorption band around 4000 nm in our FT-IR absorption measurement, we can rule out a possibility of observing transient absorption due to vibrational bands of the dye molecule (note that a vibrational band in the electronic excited state generally appears near that in the ground state). The increase of the transient absorption clearly indicates that electron injection from the dye into the conduction band of TiO\textsubscript{2} occurs very rapidly (within \textless100 fs), a rate that is much faster than the emission lifetime (1.0 ns; Table 1). Therefore, high electron injection yield, which is nearly unity, from the dye to TiO\textsubscript{2} was achieved in the system. Recently, Kitamura et al. reported that electron injection from organic oligoene dyes into the conduction band of TiO\textsubscript{2} occurs very rapidly (within \textless100 fs).\textsuperscript{30} Thus, ultrafast, highly efficient electron injection from organic dyes to TiO\textsubscript{2} is accomplished as well as in DSSCs based on N3 dye.\textsuperscript{13,53} After the electron injection, the oxidized dye molecules must accept electrons from the I\textsuperscript{-} redox mediator, regenerating the
ground state of the dye (Figure 6b). The rereduction of N3 dye cations by I$^-$ is reported to occur within 100 ns, which is faster than the recombination between the injected electrons and the N3 dye cations.\textsuperscript{54} In addition, when the energetic driving force for rereduction of the dye, which is estimated from the difference in the oxidation potentials of the dye and I$^-$ ions, is sufficiently large (e.g., $\Delta G > 0.3$ eV), the reaction yield is near 100%.\textsuperscript{55} Taking into consideration these points, rereduction of NKX-2677 cations by I$^-$ must occur efficiently, just as in the N3 dye system.

**Stability of the Dye and Solar Cell Performance.** As shown above, DSSCs based on coumarin dyes showed efficient solar-cell performance similar to those based on N3 or N719 dyes. The eventual commercialization of DSSCs requires long-term stability of the dye molecule itself and of the cell or module. DSSCs based on N3 or N719 dyes are reported to have good long-term stability under continuous irradiation.\textsuperscript{56--58} For example, a long-term stability of more than 10 000 h achieved with a cell under in the absence of UV light at 17 °C at 2.5 sun.\textsuperscript{57} We therefore investigated the thermal stability of NKX-2677 and the stability of cell performance of DSSCs based on NKX-2677.

In TG analysis of NKX-2677 under an O$_2$ atmosphere, an 8% drop in mass was observed around 278 °C. In another coumarin dye, NKX-2311, a similar mass drop was observed around 230 °C under a N$_2$ atmosphere.\textsuperscript{42} FT-IR absorption spectroscopic analysis clearly indicated that this mass drop was due to decomposition of the dye by decarboxylation.\textsuperscript{42} From these results, decarboxylation of NKX-2677 may occur around 278 °C, which indicates that NKX-2677 is much more thermally stable than NKX-2311. It has been reported that decarboxylation of N3 dye occurs at temperatures higher than 290 °C under N$_2$ and higher than 260 °C in air.\textsuperscript{59} We conclude that NKX-2677 has thermal stability that is as good as that of N3 dye.

We investigated the long-term stability of a sealed DSSC based on NKX-2677 under continuous AM 1.5G irradiation through a UV (\textless 420 nm) cutoff filter (80 mW cm$^{-2}$, 25 °C). No signs of dye degradation and no decrease in solar-cell performance was observed during the first 5 days: the stability of cell performance seemed to depend more on the quality of the sealing of the cell than on the stability of the dye. This suggests that the dye is relatively stable under irradiation in the cell, where redox electrolyte ions are present, although the long-term stability of the cell performance must be investigated in further detail. When we employed an electrolyte containing a high concentration of TBP, however, a change in the color due to desorption of the dyes from the TiO$_2$ electrode was gradually observed during the continuous irradiation. To obtain further long-term stability of DSSCs based on NKX-2677, we need to develop an electrolyte with low TBP.

**4. Conclusion**

We have developed novel coumarin dyes functionalized for use in DSSCs, where they performed well as photosensitizer. A solar energy-to-electricity conversion efficiency of 7.4% was obtained with a DSSC (type B) based on NKX-2677 under AM 1.5G irradiation (100 mW cm$^{-2}$) with a mask. Transient absorption spectroscopy analysis indicated that electron injection from NKX-2677 into the conduction band of TiO$_2$ occurs very rapidly (within \textless 100 fs), which is much faster than the emission lifetime of the dye (1.0 ns), giving a highly efficient electron injection yield of almost unity. The dye molecule of NKX-2677 has high thermal stability; the first degradation step (decarboxylation) occurred at 278 °C. In a preliminary long-term stability test under continuous AM 1.5G irradiation through a UV (\textless 420 nm) cutoff filter, no degradation of the solar-cell performance of a DSSC based on NKX-2677 was observed.
suggesting that the dye is relatively stable under irradiation in the cell. Our results strongly suggest that the organic dye photosensitizers show promise for application in DSSCs.

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**Supporting Information Available:** Synthesis procedures for the dyes. This material is available free of charge via the Internet at http://pubs.acs.org.

**References and Notes**


Supporting Information

Synthesis of 2-cyano-3-[5-(1,1,6,6-tetramethyl-10-oxo-2,3,5,6-tetrahydro-1H,4H,10H-11-oxa-3a-aza-benzo[de]anthracen-9-yl)-thiophen-2-yl]-acrylic acid (NKX-2587):

8-hydroxy-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline-9-carbaldehyde (126 g) and thiophene-2-yl-acetonitrile (59 g) were dissolved in 125 mL of N,N-dimethylformamide (DMF) and then acetic acid (79 mL) and piperidine (152 mL) were added to the solution, which was then kept at 170 °C for 3 h. Addition of ethanol (480 mL) afforded crystals of 1,1,6,6-tetramethyl-9-thiophen-2-yl-2,3,5,6-tetrahydro-1H,4H-11-oxa-3a-aza-benzo[de]anthracen-10-one (84 g); 1H NMR (CDCl₃) δ (TMS, ppm): 1.32 (6H, s), 1.58 (6H, s), 1.74–1.84 (4H, m), 3.21–3.33 (4H, m), 7.08 (1H, dd), 7.15 (1H, s), 7.29 (1H, dd), 7.65 (1H, dd), 7.84 (1H, s).

1 (20 g) was dissolved in 200 mL of DMF and then phosphorus oxychloride (14.7 mL) was added into the solution, which was then kept at 35 °C for 1.5 h. After neutralization with 25% (wt/wt) NaOH solution, the solution was kept at 50 °C for 0.5 h. After recrystallization of the resulting precipitates from 2-propanol, crystals of 5-(1,1,6,6-tetramethyl-9-thiophen-2-yl-2,3,5,6-tetrahydro-1H,4H-11-oxa-3a-aza-benzo[de]anthracen-10-one 1 (84 g) were obtained; 1H NMR (CDCl₃) δ (TMS, ppm): 1.32 (6H, s), 1.59 (6H, s), 1.75–1.84 (4H, m), 3.21–3.38 (4H, m), 7.08 (1H, dd), 7.15 (1H, s), 7.29 (1H, dd), 7.65 (1H, dd), 7.84 (1H, s).

An acetonitrile solution (180 mL) of 2 (9.0 g) and cyanoacetic acid (2.8 g) was refluxed at 115 °C in the presence of piperidine (4.4 mL) for 4 h. Recrystallization of the resulting precipitates from chloroform (110 mL)–triethylamine (2.2 mL) mixed solvent by adding acetic acid (22 mL) and acetonitrile (110 mL) afforded dark green crystals (8.7 g) of 2-cyano-3-[5-(1,1,6,6-tetramethyl-10-oxo-2,3,5,6-tetrahydro-1H,4H,10H-11-oxa-3a-aza-benzo[de]anthracen-9-yl)-thiophen-2-yl]-acrylic acid (NKX-2587). mp 266–270 °C. 1H NMR (DMF-d₇) δ (TMS, ppm): 1.47 (6H, s), 1.70 (6H, s), 1.9–2.0 (4H, m), 3.5–3.7 (4H, m),
7.70 (1H, s), 8.09 (1H, d), 8.20 (1H, s), 8.83 (1H, s). IR (neat)/cm⁻¹: 2957, 2219, 1693, 1677, 1607, 1513, 1410, 1261, 1033, 806. MS–ESI (m/z): 473.4 (M – H)⁻. HRMS–EI (m/z): (M – CO₂)⁺ calcd for C₂₆H₂₆N₂O₂S, 430.1714, found, 430.1740.

Synthesis of 2-cyano-3-[5′-(1,1,6,6-tetramethyl-10-oxo-2,3,5,6-tetrahydro-1H,4H,10H-11-oxa-3a-aza-benzo[de]anthracen-9-yl)-[2,2′]bithiophenyl-5-yl]-acrylic acid (NKX-2677):

1 (20 g) was dissolved in 140 mL of DMF and then 38 mL of DMF solution including 9.6 g of N-bromosuccinimide was added to the solution, which was then kept for 0.5 h. After adding methanol (200 mL) and water (50 mL), and cooling, crystals of 9-(5-bromo-thiophen-2-yl)-1,1,6,6-tetramethyl-2,3,5,6-tetrahydro-1H,4H,11-oxa-3a-aza-benzo[de]anthracen-10-one 3 (21.7 g) were obtained; ¹H NMR (CDCl₃) δ (TMS, ppm): 1.31 (6H, s), 1.57 (6H, s), 1.74–1.83 (4H, m), 3.21–3.33 (4H, m), 7.01 (1H, d), 7.13 (1H, s), 7.32 (1H, d), 7.76 (1H, s).

3 (21 g), 2-thiopheneboronic acid (7.6 g), Pd(PPh₃)₄ (1.6 g), and K₂CO₃ (19 g) were dissolved in 420 mL of DMF and then kept at 120 °C for 4 h under an Ar atmosphere. After filtration, the filtrate was extracted with chloroform and then washed with aqueous saturated NaCl solution and then dried over dehydrated MgSO₄. After filtration and evaporation of the solvent, the resulting precipitates were recrystallized from chloroform–methanol mixed solvent, resulting in 9-[2,2′]bithiophenyl-5-yl-1,1,6,6-tetramethyl-2,3,5,6-tetrahydro-1H,4H-11-oxa-3a-aza-benzo[de]anthracen-10-one 4 (13.3 g); ¹H NMR (CDCl₃) δ (TMS, ppm): 1.32 (6H, s), 1.58 (6H, s), 1.7–1.9 (4H, m), 3.2–3.4 (4H, m), 7.02 (1H, t), 7.13–7.18 (2H, m), 7.18–7.23 (2H, m), 7.56 (1H, d), 7.82 (1H, s).

4 (1.0 g) was dissolved in 10 mL of DMF and then Vilsmeier reagent, which was prepared from 1 mL of DMF and 0.3 mL of phosphorus oxychloride, was added to the solution, which was then kept at 70 °C for 3 h (Vilsmeier–Haack reaction). The resulting solution was added to 100 mL of water. After neutralization with 25% NaOH solution, the
solution was extracted with ethyl acetate. The organic layer was washed with aqueous saturated NaCl solution and then dried over dehydrated MgSO4. After filtration and evaporation of the solvent, the resulting precipitates were purified by silica gel column chromatography and then recrystallized from methanol, resulting in 5′-(1,1,6,6-tetramethyl-10-oxo-2,3,5,6-tetrahydro-1H,4H,10H,11-oxa-3a-aza-benzo[de]anthracen-9-yl)-[2,2"]bithiophenyl-5-carbaldehyde 5 (0.44 g); 1H NMR (CDCl3) δ (TMS, ppm): 1.32 (6H, s), 1.58 (6H, s), 1.75–1.84 (4H, m), 3.24–3.36 (4H, m), 7.17 (1H, s), 7.28 (1H, d), 7.34 (1H, d), 7.55 (1H, d), 7.67 (1H, d), 9.85 (1H, s).

5 (0.75 g) and cyanoacetic acid (0.20 g) were reacted in acetonitrile (75 mL) in the presence of piperidine (0.05 mL) for 3 h by a similar procedure as for NKX-2587. Recrystallization of resulting precipitates from chloroform (33 mL)–triethylamine (0.2 mL) mixed solvent by adding acetic acid (1.5 mL) and acetonitrile (33 mL) afforded dark green crystals (0.5 g) of 2-cyano-3-[5′-(1,1,6,6-tetramethyl-10-oxo-2,3,5,6-tetrahydro-1H,4H,10H,11-oxa-3a-aza-benzo[de]anthracen-9-yl)-[2,2"]bithiophenyl-5-yl]-acrylic acid (NKX-2677); mp 285–288 °C. 1H NMR (CDCl3/DMSO-d7) δ (TMS, ppm): 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), 8.23 (1H, s), 9.23 (1H, s). IR (neat)/cm–1: 2928, 2213, 1711, 1686, 1604, 1565, 1519, 1408, 1277, 1152, 1041, 805. MS–ESI (m/z): 555.1 (M – H)–. HRMS–EI (m/z): (M – CO2)+ calcd for C30H28N2O2S2, 512.1591, found, 512.1670.

Synthesis of 2-cyano-3-[5"-(1,1,6,6-tetramethyl-10-oxo-2,3,5,6-tetrahydro-1H,4H,10H,11-oxa-3a-aza-benzo[de]anthracen-9-yl)-[2,2';5',2"]terthiophen-5-yl]-acrylic acid (NKX-2697):

4 (16 g) was dissolved in 160 mL of DMF and then 24 mL of DMF solution containing 6.0 g of N-bromosuccinimide was added to the solution, which was then kept at room temperature for 1 h using a similar procedure as for 3. After the resulting solution was added to 1200 mL of methanol, water (125 mL) was added to the solution and then cooled.
After recrystallization of the resulting precipitates from methanol (75 mL), crystals of 9-(5'-bromo-[2,2']bithiophenyl-5-yl)-1,1,6,6-tetramethyl-2,3,5,6-tetrahydro-1H,4H-11-oxa-3a-aza-benzo[de]anthracen-10-one 6 (14.3 g) were obtained; $^1$H NMR (CDCl$_3$) $\delta$ (TMS, ppm): 1.32 (6H, s), 1.57 (6H, s), 1.74–1.84 (4H, m), 3.22–3.34 (4H, m), 6.94 (1H, d), 6.97 (1H, d), 7.08 (1H, d), 7.15 (1H, s), 7.52 (1H, d), 7.82 (1H, s).

6 (14 g), 2-thiopheneboronic acid (5 g), Pd(PPh$_3$)$_4$ (0.9 g), and K$_2$CO$_3$ (11 g) were dissolved in 280 mL of DMF and then kept at 120 °C for 3 h under an Ar atmosphere using a similar procedure as for 4. After filtration, the filtrate was extracted with ethyl acetate and then washed with aqueous saturated NaCl solution and then dried over dehydrated MgSO$_4$. After filtration and evaporation of the solvent, the resulting precipitates were purified by silica gel column chromatography and then were recrystallized from chloroform–methanol mixed solvent, resulting in 1,1,6,6-tetramethyl-9-[2,2';5',2"]terthiophen-5-yl-2,3,5,6-tetrahydro-1H,4H-11-oxa-3a-aza-benzo[de]anthracen-10-one 7 (7.5 g); $^1$H NMR (CDCl$_3$) $\delta$ (TMS, ppm): 1.32 (6H, s), 1.58 (6H, s), 1.75–1.84 (4H, m), 3.22–3.34 (4H, m), 7.02 (1H, dd), 7.09 (1H, d), 7.12 (1H, d), 7.15 (1H, d), 7.15 (1H, s), 7.17 (1H, dd), 7.21 (1H, dd), 7.56 (1H, d), 7.82 (1H, s).

7 (7.3 g) was dissolved in 110 mL of DMF and then Vilsmeyer reagent, which was prepared from 38 mL of DMF and 3.8 mL of phosphorus oxychloride, was added to the solution, which was then kept at 70 °C for 1 h using a similar procedure as for 5 (Vilsmeyer–Haack reaction). The resulting solution was added to 1000 mL of water. After neutralization with 25% NaOH solution, the solution was extracted with ethyl acetate. The organic layer was washed with aqueous saturated NaCl solution and then dried over dehydrated MgSO$_4$. After filtration and evaporation of the solvent, the resulting precipitates were purified by column chromatography on silica gel. Recrystallization of the precipitates from chloroform–methanol mixed solvent afforded 5"-(1,1,6,6-tetramethyl-10-oxo-2,3,5,6-tetrahydro-1H,4H,10H-11-oxa-3a-aza-benzo[de]anthracen-9-yl)-[2,2';5',2"]terthiophene-5-carbaldehyde 8 (0.44 g); $^1$H NMR (CDCl$_3$) $\delta$ (TMS, ppm): 1.32 (6H, s), 1.58 (6H, s),
8 (1.7 g) and cyanoacetic acid (1.9 g) were reacted in acetonitrile (17 mL)–chloroform (34 mL) mixed solvent in the presence of piperidine (0.45 mL) for 5 h using a similar procedure as for NKX-2587. Acetic acid (3 mL) was added to the reaction solution, and the resulting precipitates were recrystallized from DMF. Recrystallization of the precipitates from chloroform (20 mL) containing triethylamine (0.2 mL) and acetic acid (1.5 mL) afforded purple crystals of 2-cyano-3-[5"-(1,1,6,6-tetramethyl-10-oxo-2,3,5,6-tetrahydro-1H,4H,10H,-11-oxa-3a-aza-benzo[de]anthracen-9-yl)-[2,2';5',2"]terthiophen-5-yl]-acrylic acid (NKX-2697); mp 293–296 °C. 

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\text{\textbf{1H NMR (CDCl}_3/\text{DMSO-d}_7\text{)}} \delta \text{(TMS, ppm): 1.33 (6H, s), 1.59 (6H, s), 1.76–1.86 (4H, m), 3.25–3.37 (4H, m), 7.18 (1H, s), 7.19 (1H, d), 7.22 (1H, d), 7.25 (1H, d), 7.32 (1H, d), 7.56 (1H, d), 7.66 (1H, d), 7.88 (1H, s), 8.25 (1H, s).}
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IR (neat)/cm⁻¹: 2949, 2211, 1709, 1685, 1607, 1575, 1513, 1410, 1301, 1214, 1042, 775. MS–ESI (m/z): 637.5 (M – H)⁻. HRMS–EI (m/z): (M – CO₂)⁺ calcd for C₃₄H₃₀N₂O₂S₃, 594.1468, found, 594.1417.