Molecular Design of Coumarin Dyes for Stable and Efficient Organic Dye-Sensitized Solar Cells

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A series of coumarin dyes (NKX-2593, NKX-2807, and NKX-2883) with one or two -CN groups as electron acceptors were synthesized and applied as dye sensitizers for dye-sensitized solar cells. Compared with the dye containing one -CN group, linking one more -CN group to the π-conjugation bridge positively shifts the lowest unoccupied molecular orbital and thus red-shifts the maximum absorption band, harvesting more photons in the long-wavelength region for photoelectric conversion. Among the three dyes studied, NKX-2883 showed the best photovoltaic performance, yielding 7.6% power conversion efficiency using a volatile electrolyte and demonstrating good photostability under visible light soaking with 6% of power conversion efficiency for 1000 h using a nonvolatile electrolyte.

Introduction

Dye sensitized solar cells (DSSCs) have been attracting considerable attention due to the potential of low cost and high efficiency as compared to the conventional p−n junction solid-state inorganic solar cells. So far ruthenium polypyridyl complexes are the most promising sensitizers for DSSCs, achieving power conversion efficiency (η) >10% and good long-term stability.

In addition to metal complex dye sensitizers, metal-free organic dye sensitizers are also promising due to their higher extinction coefficients and facile molecular design. In the past decades, various kinds of organic dyes have been designed and employed as dye sensitizers in DSSCs, achieving gradual improvement of η through wise molecular design. Among the organic dyes employed for DSSCs so far, coumarin dyes are one kind of promising dye stuff and have been studied systematically in our group. On the basis of the concept of the donor−π-conjugation-bridge−acceptor (D−Π−A) structure, we have synthesized a series of coumarin dyes by inserting different numbers of thiophene and/or methine units as π-conjugation bridge between a coumarin derivative as the donor and cyanoacrylic acid as the acceptor. With two or three π-conjugation units, the reported coumarin dyes show maximum absorption peak around 500 nm and appropriate highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels, respectively, matching the redox potential of the I3−/I− redox couple and the conduction band edge. As a consequence, η has been achieved to 8.2% with a coumarin dye. One factor that limits the DSSC performance is the short-circuit photocurrent (Jsc), which is determined by how well the absorption window of the dye overlaps the solar emission spectrum. The reported coumarin dyes absorb light poorly above 700 nm, and little success was gained to further extend photoresponse to the longer wavelength region by expanding π-conjugation via increasing the number of π-conjugation units more than three. Therefore, efficiently harvesting incident photons in the longer wavelength region still remains a big challenge for coumarin dyes.

In the light of the concept of the D−Π−A structure, increasing the electron-withdrawing ability of acceptors would red shift the absorption peak. Our preliminary results indicate that linking two -CN groups to the π-conjugation bridge was successful in extending the photoresponse to longer wavelength. In this work, we report on the detailed physicochemical properties of the designed coumarin dyes with two -CN groups and comparison of coumarin dyes with one or two -CN groups (Figure 1) in terms of solar-cell performance. The effect of one more -CN group in the dye on absorption properties and photovoltaic performance of DSSCs is discussed. As compared
experimental Section

Materials and Reagents. Regent-grade Lil (Wako Pure Chemical Industries Ltd.), I₂ (Wako), LiClO₄ (Wako), TiCl₄ (Wako), N-methylbenzimidazole (NMBl, Aldrich), acetonitrile (AN, Wako), and deoxycholic acid (DCA, Tokyo Kasei Kogyo Co. Ltd.) were used without further purification. Dimethyl-n-propylimidazolium iodide (DMPImI), 4-tert-butylpyridine (TBP), and tert-butanol were purchased from Tomiyama Pure Chemical Industries Ltd. Transparent conducting oxide (TCO, F-doped SnO₂, 10 Ω/□, Nippon Sheet Glass Co.) was washed with basic solution, ethanol, and acetone successively under sonaparisonation for 10 min each before use.

Syntheses of Dyes. The syntheses of NKX-2593 and NKX-2883 were reported previously.⁴⁻⁷ The synthesis of NKX-2807 is described as follows. 1,1,6,6-Tetramethyl-10-oxo-2,3,5,6-tetrahydro-1H,4H,10H-11-oxa-3a-azabenzene[de]anthracen-9-carbaldehyde (15 g) and thiophene-2-yiactonitrile (30 g) were dissolved in 30 mL of N,N-dimethylformamide (DMF), and then acetic acid (7.9 mL) and piperidine (15.2 mL) were added to the solution, which was then kept at 90 °C for 1 h. Moreover, thiophene-2-yiactonitrile (2.6 mL) was added to the solution, which was then kept at 90 °C for 30 min. Addition of methanol (90 mL) and cooling afforded crystals of 3-[1,1,6,6-tetramethyl-10-oxo-2,3,5,6-tetrahydro-1H,4H,10H-11-oxa-3a-azabenzene[de]anthracen-9-yl]-2-thiophen-2-ylacrylonitrile (1: 11.2 g). ¹H NMR (CDCl₃; TMS; ppm): δ1.31 (6H, s), 1.55 (6H, s), 1.76 (2H, t), 1.81 (2H, t), 3.29 (2H, t), 3.37 (2H, t), 7.05 (1H, dd), 7.19 (1H, s), 7.28 (1H, dd), 7.33 (1H, dd), 7.70 (1H, s), 7.78 (1H, dd), 7.73 (1H, dd), 7.70 (1H, s), 8.58 (1H, s).

Compound 1 (1 g) was dissolved in 15 mL of DMF, and then phosphorus oxychloride (0.65 mL) was added into the solution, which was then kept at 40 °C for 1 h. Moreover, phosphorus oxychloride (0.65 mL) dissolved in 2 mL of DMF was added into the solution. After stirring at 40 °C for 1 h, 0.65 mL of phosphorus oxychloride was added into the solution, which was then kept at 70 °C for 30 min. The resulting solution was added to iced water. After neutralization with 25% (w/w) NaOH solution, the solution was kept at 50 °C for 20 min. After recrystallization of the resulting precipitates from 40 mL of methanol, crude crystals of 2-[5-formylthiophen-2-yl]-3-[1,1,6,6-tetramethyl-10-oxo-2,3,5,6-tetrahydro-1H,4H,10H-11-oxa-3a-azabenzene[de]anthracen-9-yl]acrylonitrile (2: 0.94 g) were obtained. The crude crystals were purified by column chromatography using silica gel and then recrystallized from chloroform and methanol. ¹H NMR (CDCl₃; TMS; ppm): δ1.31 (6H, s), 1.55 (6H, s), 1.74 (2H, t), 1.82 (2H, t), 3.32 (2H, t), 3.41 (2H, t), 7.19 (1H, s), 7.40 (1H, d), 7.70 (1H, d), 7.93 (1H, s), 8.67 (1H, s), 9.87 (1H, s).

A chloroform solution (14 mL) of 2 (0.7 g) and cyanoacetic acid (0.2 g) was refluxed in the presence of piperidine (0.05 mL) for 1.5 h. Moreover, cyanoacetic acid (0.2 g) and piperidine (0.05 mL) were added to the solution, which was then kept for 1 h: this procedure was repeated 3 times. Recrystallization of the resulting precipitates from chloroform—triethylamine mixed solvent by adding acetic acid and acetonitrile afforded crystals (0.38 g) of 2-cyano-3-[5-[1-cyano-2-(1,1,6,6-tetramethyl-10-oxo-2,3,5,6-tetrahydro-1H,4H,10H-11-oxa-3a-azabenzene[de]anthracen-9-yl]vinyl]thiophen-2-yl]acrylic acid (NKX-2807); mp 261.8 °C. ¹H NMR (DMSO-d₆; TMS, ppm): δ 1.27 (6H, s), 1.47 (6H, s), 1.7–1.8 (4H, m), 3.3–3.5 (4H, m), 7.41 (1H, s), 7.54 (1H, d), 7.76 (1H, s), 7.99 (1H, d), 8.48 (1H, s), 8.58 (1H, s). MS-ESI (m/z): 524.05, (M−H)⁻.

Fabrication of the Dye-Sensitized TiO₂ Films. A screen printing method was used to fabricate TiO₂ films on TCO glass. TiO₂ nanoparticles (ca. 20 nm), large particles (ca. 100 nm), were prepared by the method reported previously.⁸ TiO₂ nanoparticles and a mixture of nanoparticles and scattering large particles at a ratio of 6:4 were dispersed in ethanol. The TiO₂ pastes were prepared by mixing TiO₂ suspension, ethyl cellulose, and α-terpinolene in ethanol followed by the removal of the solvent with rotary evaporator at 40 °C under vacuum of 40 hPa. Pastes N and M consisted of nanoparticles and mixed particles (20 and 100 nm particles at a ratio of 6:4), respectively. Transparent TiO₂ films, fabricated on TCO glass or glass slides using paste N, were used for characterizations such as electrochemical and spectroscopic measurements. Double-layer (NM) TiO₂ films (12 μm), employed for photovoltaic measurements, were prepared by printing the transparent layer (7 μm) first with paste N followed by further coating with paste M (5 μm). The TiO₂ films were fired at 525 °C for 2 h with a rising rate of 10 °C/min. All the films were immersed in 0.05 M TiCl₄ solution for 30 min at 70 °C followed by calcinations at 450 °C for 30 min. The film thickness was measured with a Tencor Alpha-Step 500 surface profiler. The film size is apparently 0.5 × 0.5 cm². Dye-sensitized TiO₂ photoelectrodes were obtained by immersing the TiO₂ films in dye solution overnight when they were at ~100 °C cooled from the heating.

Characteristics. The UV−vis absorption spectra of the dye-loaded transparent film and the dye solutions were recorded on a Shimadzu UV-3101PC spectrophotometer. Cyclic voltammetry (CV) was measured with a three-electrode electrochemical cell on a CH 610 electrochemical analyzer. Dye-loaded film, platinum, and Ag/Ag⁺ (0.01 M AgNO₃ + 0.1 M TBAP in AN) were employed as working, counter, and reference electrodes, respectively. The supporting electrolyte was 0.1 M LiClO₄ in AN, which was degassed with N₂ for 20 min prior to the scan. The potential of the reference electrode is 0.49 V vs NHE and calibrated with ferrocene immediately after CV measurement.

Photovoltaic Measurement. Sealed cells, the sealing procedure published elsewhere,⁹ were employed for photovoltaic measurements. The current−voltage characteristics of the cells were measured on a computer-controlled voltage−current source meter (Advantest, R6243), under illumination of simulated AM1.5G solar light from an AM1.5 solar simulator (Wacom Co., WXS-80C-3 with a 300 W Xe lamp and an AM1.5 filter). 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 photosponse range of amorphous silicon solar cell. The standard solar cell was produced and calibrated by Japan Quality Assurance Organization. Photocurrent action spectra were recorded on a CEP-99W system (Bunkoh-Keiki Co., Ltd.). The sealed DSSC device at open circuit equipped with a 420 nm cutoff filter was subjected to continuous light soaking (100 mW cm⁻²; device surface temperature, 50–55 °C), and I−V curves were measured regularly. To avoid the diffuse light penetrating into the active dye loaded film, a black mask with an aperture area of 0.2354 cm², measured with an optical microscope, LEICA M420, equipped with a digital camera (Nikon DXM1200), was employed to test photovoltaic performance. We did not calculate the mismatch factor for calibration of current and efficiency. However, considering that the Jsc of DSSCs in this work at 100 mW cm⁻² simulated AM1.5G light is almost the same as the
Organic Dye-Sensitized Solar Cells

Results and Discussion

In this work is reliable.

TABLE 1: UV–Vis Absorption and Redox Properties of the Three Dyes

| Dye        | λmax/nm | ε(10^4 M⁻¹ cm⁻¹) | Eon/V vs NHE | gap/a V vs NHE | LUMO/Evis absorption spectra for the dye-sensitized 1.5 m thick (Table 1), thus reducing the gap between HOMO and LUMO. However, when the two -CN groups were separated by two thiophenes (the case of NKX-2883), the maximum absorption blue-shifted from 566 nm for NKX-2807 to 552 nm for NKX-2883. The second -CN group would enhance the electron-withdrawing ability of cyanoacrylic acid, but such an enhancement may weaken if the -CN group is far away from the cyanoacrylic acid. As compared to NKX-2807, NKX-2883 showed more negative LUMO due to the relatively lower electron-withdrawing ability of acceptors (Table 1). The above data indicate that the addition of one more -CN group to the π-conjugation bridge is effective in red-shifting the photocurrent density from IPCE spectrum and AM1.5G solar emission spectrum, we suggest that the measured efficiency in this work is reliable.

Results and Discussion

Figure 2 shows the UV–vis absorption spectra for the three dyes in ethanol. All three coumarin dyes show one strong and broad π–π* transition peak in the visible region between 500 and 600 nm. The molar extinction coefficients at each maximum absorption wavelength are 7.18 × 10^4 (510 nm), 5.76 × 10^4 (566 nm), and 9.74 × 10^4 dm³ mol⁻¹ cm⁻¹ (552 nm) for NKX-2593, NKX-2807, and NKX-2883, respectively, which are summarized in Table 1. It is attractive that NKX-2883 has pretty high extinction coefficient, rendering efficient light harvesting.

This work aims at extension of photoreponse to a longer wavelength region through linking of one more electron acceptor (i.e., -CN) to the dye molecule. It is found from Figure 2 that the molar extinction coefficients at the maximum absorption wavelength are 7.18, 5.76, and 9.74 × 10^4 (510 nm), 5.76, and 9.74 × 10^4 (552 nm) for NKX-2593, NKX-2807, and NKX-2883, respectively, which are summarized in Table 1. It is attractive that NKX-2883 has pretty high extinction coefficient, rendering efficient light harvesting.

Figure 3 shows the UV–vis absorption spectra for the dye-loaded films as detailed in the Experimental Section. a The gap is estimated from the absorption onset of dye-loaded TiO₂, as shown in Figure 3.

Figure 2. UV–vis absorption spectra for NKX-2593, NKX-2807, and NKX-2883 in ethanol, respectively.

Figure 3. UV–vis absorption spectra for the dye-sensitized 1.5 µm TiO₂ film using a bare TiO₂ as the reference.

Figure 4. CV of NKX-2883-loaded TiO₂ film (0.25 cm², 6 µm thick) using 0.1 M LiClO₄ in acetonitrile as the supporting electrolyte. The scan rate was 0.1 V s⁻¹.

One more acceptor is effective in realizing this goal. NKX-2593 has the typical D–π–A structure, comprising a coumarin derivative as the electron donor, methine-thiophene as the π-conjugation linkage, and cyanoacrylic acid as the electron acceptor. When the other electron acceptor (-CN) was linked to the opposite side of the thiophene unit relative to cyanoacrylic acid in NKX-2593, forming NKX-2807, the maximum absorption was red-shifted significantly from 510 to 566 nm. The significant red shift of the maximum absorption peak arises from the fact that one more electron acceptor (-CN) enhances the electron-withdrawing ability of electron acceptors and lowers the LUMO (Table 1), thus reducing the gap between HOMO and LUMO. However, when the two -CN groups were separated by two thiophenes (the case of NKX-2883), the maximum absorption blue-shifted from 566 nm for NKX-2807 to 552 nm for NKX-2883. The second -CN group would enhance the electron-withdrawing ability of cyanoacrylic acid, but such an enhancement may weaken if the -CN group is far away from the cyanoacrylic acid. As compared to NKX-2807, NKX-2883 showed more negative LUMO due to the relatively lower electron-withdrawing ability of acceptors (Table 1). The above data indicate that the addition of one more -CN group to the π-conjugation bridge is effective in red-shifting the photocurrent density as compared to the coumarin dyes with one -CN group. Although we do not have evidence how the second -CN group enhances the electron-withdrawing ability of the A part in the D–π–A structure, it seems that electrons first move from the donor part to the -CN group linked to the π-conjugation bridge, upon excitation, and then move to the ending A part (i.e., cyanoacrylic acid). As a consequence, the electron-withdrawing ability of the A part in the D–π–A structure would be enhanced by linking one more -CN group to the π-conjugation bridge.

Figure 3 shows the UV–vis absorption spectra for the dye-loaded TiO₂ films (~1.5 µm) with a bare TiO₂ film as the reference. Upon dye adsorption onto the TiO₂ surface, the maximum absorption respectively blue-shifted by 42, 35, and 32 nm for NKX-2593, NKX-2807, and NKX-2883 as compared to the spectra in solution (Figure 2). Such blue shifts would result from the solvent effect, deprotonation of carboxylic acid upon dye attachment to the TiO₂ surface,¹⁰ and/or H-aggregation of dye molecules.¹¹

We can see from Figure 3 that the maximum absorbance is greater than 1 for the three dye-loaded films of 1.5 µm. The light harvesting efficiency (LHE) is therefore almost unity when we use 6 µm or thicker TiO₂ films for solar cell fabrications.
The absorbance ratio of the three dyes in Figure 3 is almost equal to the corresponding ratio of extinction coefficient, suggesting their similar dye amount on the TiO$_2$ surface. This is further confirmed by the spectral determination of dye solutions obtained by detaching the dye on the TiO$_2$ surface into basic solutions.

The energy levels of the dye were determined by CV of dye-loaded TiO$_2$. On the TiO$_2$ surface, NKX-2883 displayed a well-resolved CV curve while the other two dyes did not give good CV signal. Figure 4 shows the CV data for NKX-2883-loaded TiO$_2$ film using 0.1 M LiClO$_4$ in AN as supporting electrolyte. NKX-2883 bonded to the TiO$_2$ surface can be electrochemically oxidized and reduced in a quasi-reversible fashion. Two one-electron oxidation waves respectively located at the half-wave potentials of 0.97 and 1.45 V vs NHE were observed. The first oxidative process generates a cation radical, while the second oxidative process produces a dication by oxidation of the π-system. With increasing applied potential up to 2 V vs NHE, the dye was stepwise oxidized to the cation and the original neutral state by reversing the potential scan. The first oxidation potential of 0.97 V is taken as the HOMO, and the LUMO is calculated using the expression of $LUMO = HOMO - \Delta E$, where the gap is derived from the absorption onset of the dye-loaded TiO$_2$ films (Figure 3). The data for HOMO, LUMO, and gap are also listed in Table 1. It is evident that the LUMOs of the three dyes are more negative than the conduction band edge ($-0.50$ V vs NHE at pH = 1) and HOMOs are more positive than the potential of I$_3^-$/I$^-$, ensuring electron injection from the excited dye molecules to the conduction band of TiO$_2$ and dye regeneration by iodide being thermodynamically favorable.

Figure 5a shows incident photon-to-electron conversion efficiency (IPCE) as a function of incident wavelength for DSSCs based on one of the three dyes using electrolyte A containing 0.1 M LiI, 0.05 M I$_2$, and 0.6 M DMPImI. In good agreement with the UV-vis absorption result, IPCE action spectra for DSSCs based on NKX-2807 and NKX-2883 are broader than that of a DSSC with NKX-2593 (Figure 5a). The maximum IPCEs for the three DSSCs increased in the order of NKX-2807 $<$ NKX-2883 $<$ NKX-2593. The difference of maximum IPCE arises from the different driving force for electron injection (i.e., the difference between LUMO and the conduction band edge). Assuming that the conduction band edge is independent of the dye, the driving force of the electron injection follows the order of NKX-2807 $<$ NKX-2883 $<$ NKX-2593, consistent with the order of the maximum IPCE. These results indicate that the driving force for electron injection of NKX-2807 and NKX-2883 is not sufficiently high, but that of NKX-2593 is sufficiently high at the used condition. Since it is difficult to determine the conduction band edge of TiO$_2$ in the presence of dye and electrolyte, which is the case of the DSSC device, we discuss the driving force for electron injection qualitatively.

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### Table 2: Current–Voltage Characteristics for DSSCs Based on the Three Dyes

<table>
<thead>
<tr>
<th></th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NKX-2593</td>
<td>16.71</td>
<td>0.52</td>
<td>0.67</td>
<td>5.8$^a$</td>
</tr>
<tr>
<td></td>
<td>14.89</td>
<td>0.58</td>
<td>0.73</td>
<td>6.3$^a$</td>
</tr>
<tr>
<td></td>
<td>13.37</td>
<td>0.63</td>
<td>0.77</td>
<td>6.5$^a$</td>
</tr>
<tr>
<td>NKX-2807</td>
<td>14.32</td>
<td>0.51</td>
<td>0.73</td>
<td>5.3$^b$</td>
</tr>
<tr>
<td></td>
<td>10.93</td>
<td>0.53</td>
<td>0.75</td>
<td>4.3$^b$</td>
</tr>
<tr>
<td>NKX-2883</td>
<td>17.46</td>
<td>0.52</td>
<td>0.69</td>
<td>6.3$^a$</td>
</tr>
<tr>
<td></td>
<td>16.90</td>
<td>0.58</td>
<td>0.74</td>
<td>7.3$^a$</td>
</tr>
</tbody>
</table>

$^a$ Electrolyte A, $^b$ Electrolyte A + 0.1 M TBP, $^c$ Electrolyte A + 0.5 M TBP.
IPCE is the product of LHE, electron injection efficiency (EIE), and the efficiency for charge collection (CCE) at the conducting glass support. Considering the LHE is unity for DSSCs based on the three dyes, and assuming that the CCE is the same for the three DSSCs, the IPCE depends on the EIE, which depends on the driving force for electron injection. For the three DSSCs, only NKX-2593 produced unity maximum IPCE but the other two dyes produced maximum IPCE lower than unity at 0.1 M Li$^+$. Judged from the LUMO levels shown in Table 1 and based on the above analysis, it is affirmed that the different driving forces for electron injection should account for the different IPCE for the three dyes.

For a given dye, the driving force of the electron injection depends on the position of the conduction band edge, which can be affected by the adsorption of cations such as Li$^+$. Since Li$^+$ as a potential determining ion is usually used in the redox electrolyte for efficient DSSCs, we investigated the influence of Li$^+$ content on IPCE. With increasing Li$^+$ content in the electrolyte, the conduction band edge would shift positively due to the cation adsorption on and/or intercalation into the TiO$_2$, and thus improvement of IPCE is expected for NKX-2807 and NKX-2883, which showed relatively low IPCE at 0.1 M Li$^+$. For NKX-2593, the maximum IPCE increased successively with increasing concentration of Li$^+$ up to 0.5 M. At 0.5 M Li$^+$, the maximum IPCE is still lower than 80%, indicating that the driving force for electron injection is insufficient for NKX-2807 at or below 0.5 M Li$^+$. For NKX-2883, the maximum IPCE increased to $\sim$80% when the concentration of Li$^+$ increased to 0.2 M and remained unchanged with further increasing the concentration of Li$^+$ to 0.5 M. These data indicate that the driving force for electron injection is sufficient at or above 0.2 M Li$^+$ but insufficient at or below 0.1 M Li$^+$ for NKX-2883. Red shift of the photoresponse onset in IPCE spectra was observed for all the three DSSCs with increasing Li$^+$ concentration due to the interaction of Li$^+$ ions with the carbonyl group in the dye. The gradual decrease in $V_{oc}$ with increasing Li$^+$ content further indicates that the conduction band edge shifts positively by increasing the Li$^+$ content. Therefore the driving force for electron injection is enhanced by increasing Li$^+$ concentration.

We conclude from the above data that there is a threshold for the driving force of electron injection, above which electron injection yield is unity but below which electron injection yield is lower than unity. Such a driving force can be tuned by adjusting the Li$^+$ concentration in the electrolyte.

The performance parameters for the DSSCs using electrolyte A or A plus x M TBP are summarized in Table 2. The $J_{sc}$ increases in the order of NKX-2807 < NKX-2593 < NKX-2883. Although NKX-2807 has wider photoresponse than NKX-2593, the former produced lower $J_{sc}$ due to the low IPCE as seen in Figure 5a. NKX-2883 produced high IPCE in a wide range of wavelength as compared to the other two dyes, thus resulting in the highest $J_{sc}$. On the basis of the above data, wise
molecular design should take into account both wide absorption properties and suitable HOMO and LUMO energy levels, well-matching the redox potential of the redox couple and the conduction band edge, respectively.

Contrasting to the Li\(^+\) effect on the conduction band edge, the addition of TBP to the electrolyte shifts the conduction band edge negatively, which increases open-circuit photovoltage (\(V_{oc}\)) but decreases \(J_{sc}\) simultaneously. For NKX-2807 with the lowest LUMO, addition of 0.1 M TBP to electrolyte A decreased \(J_{sc}\) dramatically but slightly improved \(V_{oc}\) and the fill factor (FF), resulting in a significant decrease in \(\eta\). For the other two dyes with relative high LUMO, addition of 0.1 M TBP to electrolyte A could improve \(V_{oc}\) and FF significantly, sufficiently compensating for the \(J_{sc}\) loss, resulting in significant improvement of \(\eta\). For example, a DSSC based on NKX-2883 produced \(\eta = 6.3\%\) (\(J_{sc} = 17.46\) mA cm\(^{-2}\), \(V_{oc} = 0.52\) V, and FF = 0.69) using electrolyte A, and the efficiency was improved to 7.3\% (\(J_{sc} = 16.90\) mA cm\(^{-2}\), \(V_{oc} = 0.58\) V, and FF = 0.74) when 0.1 M TBP was added to electrolyte A. Since \(J_{sc}\) and \(V_{oc}\) (FF) vary oppositely with increasing TBP content, the DSSC must have an optimal TBP concentration for the highest \(\eta\), depending on the LUMO of the dye. It was found that the optimal TBP concentrations were 0, 0.1, and 0.5 M for NKX-2807, NKX-2883, and NKX-2593, respectively. The more negative of LUMO, the higher optimal TBP concentration. At each optimal TBP concentration, NKX-2883 produced the highest \(\eta\) among the three dyes.

Similar to the other coumarin dyes we reported, coadsorption of DCA with NKX-2883 is also effective in retarding charge recombination and hence improving \(V_{oc}\) and \(\eta\).\(^{15}\) When 30 mM DCA was included in the solution of NKX-2883, the best performance was achieved as shown in Figure 6a. Upon coadsorption of DCA, \(J_{sc}\) decreased a little due to the reduced dye adsorption, whereas \(V_{oc}\) and FF increased due to the retarded charge recombination, as evidenced by the dark current observation (Figure 6b). As a consequence, \(\eta = 7.6\%\) was achieved (\(J_{sc} = 16.50\) mA cm\(^{-2}\), \(V_{oc} = 0.61\) V, and FF = 0.76) using 0.6 M DMPImL, 0.2 M LiI, 0.05 M I\(_2\), and 0.1 M TBP as a redox electrolyte. As compared to the coumarin dyes with one -CN group, we reported previously,\(^{5,6}\) NKX-2883 showed higher \(J_{sc}\) due to the wider photoresponse but lower \(V_{oc}\) due to the lower LUMO. Consequently, NKX-2883 showed a small increase in \(\eta\) from 7.4 to 7.6\% as compared to its counterpart dye NKX-2677 containing one -CN group at each optimal condition.\(^{5}\)

The feature of NKX-2883 with very high extinction coefficient is attractive for fabrication of efficient thin film DSSCs. For example, DSSC with 6 \(\mu\)m TiO\(_2\) film produced 15.08 mA cm\(^{-2}\) of \(J_{sc}\) and 6.7\% of \(\eta\) for NKX-2883 (\(\varepsilon = 9.74 \times 10^4\) M\(^{-1}\) cm\(^{-1}\)) but 10.10 mA cm\(^{-2}\) of \(J_{sc}\) and 6.1\% of \(\eta\) for NT719 (\(\varepsilon = 1.42 \times 10^4\) M\(^{-1}\) cm\(^{-1}\)). Unfortunately, \(\eta\) for coumarin dyes could not be improved as significantly as for NT719 when thick film was used because the former has a lower electron lifetime and hence the electron diffusion length.\(^{16}\) The future molecular design for efficient organic dye would focus on how to enhance the electron lifetime and hence the electron diffusion length. If the electron lifetime of coumarin dye can be enhanced to the level of Ru dyes and meanwhile has appropriate LUMO for electron injection, the \(V_{oc}\) would be improved significantly and therefore \(\eta\) can be boosted to \(>10\%\). In addition, thin film DSSCs are favorable for flexible plastic DSSCs because cracking of thick film is difficult to avoid during roll-to-roll production. Therefore, organic dyes with high extinction coefficient have great potential application in flexible DSSCs.

Figure 7 shows the stability data for a NKX-2883-based DSSC subjected to continuous visible-light soaking at 50–55 \(^\circ\)C in open-circuit mode using nonvolatile electrolyte comprising 0.6 M DMPImL, 0.1 M I\(_2\), and 0.1 M NMBI instead of the volatile electrolyte. \(J_{sc}\) did not change much for the first 150 h and then increased gradually up to 800 h, followed by a plateau up to 1000 h. The increase in photocurrent from the initial value is calculated to be \(\sim 15\%\). Contrasting to the \(J_{sc}\) increase under illumination, \(V_{oc}\) dropped by \(\sim 50\) mV. FF first increased due to the accelerated diffusion of electrolyte and then decreased probably ascribed to the increased resistance under light soaking. As a consequence, the \(\eta\) first increased from 5.9 to 6.2\% and then remained almost constant until 1000 h. As the temperature increases during light soaking, electrolyte diffusion becomes faster and the conduction band edge moves downward relative to the \(I^-/I_3^+\) couple;\(^{17}\) both effects result in the enhancement of \(J_{sc}\), and the latter effect leads to a decrease in \(V_{oc}\). The initial increase in FF up to 150 h is also due to the faster electrolyte diffusion as the temperature rises. The \(J_{sc}\) gain compensates the loss of \(V_{oc}\) and FF well, resulting in almost constant efficiency during light soaking. These data indicate that metal-free organic dyes also show good photostability and are able to compete with ruthenium poly(pyridine) complexes after careful optimization.

Conclusion

Organic dyes with a coumarin derivative as the electron donor, connected with methine and thiophene as the \(\pi\)-conjugation linkage and two -CN groups as the electron acceptor, have been synthesized as sensitizers for DSSCs. Compared with the coumarin dye with one -CN group, the dyes with two -CN groups, NKX-2807 and NKX-2883, showed photoresponse extended to the longer wavelength region as a result of lowering of LUMO. The LUMOs for NKX-2807 and NKX-2883 with two -CN groups are not sufficiently high for electron injection at 0.1 Li\(^+\), but the IPCE is significantly improved by simply increasing the Li\(^+\) concentration due to the positive shift of the conduction band edge with increasing Li\(^+\) content. NKX-2883 not only produced \(\eta\) as high as 7.6\% using a volatile electrolyte but also was stable for 1000 h with \(\eta = 6\%\) using nonvolatile electrolyte.

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References and Notes