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# Synthesis of new-type donor–acceptor π-conjugated benzofuro[2,3-*c*]oxazolo[4,5-*a*]carbazole fluorescent dyes and their photovoltaic performances of dye-sensitized solar cells

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**Abstract**—New-type donor–acceptor π-conjugated benzofuro[2,3-*c*]oxazolo[4,5-*a*]carbazole fluorescent dyes with various lengths of non-conjugated alkyl chains containing a carboxyl group at the end position have been developed and their photovoltaic performances of dye-sensitized solar cells are investigated. It is found that in spite of the lengths of the alkyl chains, due to flexibility of alkyl chain, the cyano group of the dyes is located in close proximity to $TiO_2$ surface and thus a good electron communication between the dyes and $TiO_2$ surface is established.

Dye-sensitized solar cells (DSSCs) based on nanocrystalline $TiO_2$ electrodes have received considerable attention because of high incident solar light-to-electricity conversion efficiency and low cost of production.[1–8] Recently, much research has focused on the development of new metal-free organic dyes. In particular, donor–acceptor π-conjugated organic dyes possessing broad and intense spectral features are useful as sensitizers. Many donor–acceptor π-conjugated dyes with carboxyl group, acting as not only the anchoring group for attachment on metal oxide but also the electron acceptor, have been synthesized and used as sensitizers of DSSCs.[2–6] A number of studies have suggested that a carboxyl group can form an ester linkage with $TiO_2$ surface to provide a strongly bound dye and a good electron communication between them. However, development of new donor–acceptor π-conjugated dyes for DSSCs is limited because a carboxyl group is required to combine with π-conjugation system or electron acceptor moiety of dyes for the above reasons.

In our previous study, to clarify the influence of the position of a carboxyl group attached to the same chromophore skeleton on photovoltaic performances of DSSCs,[9] we have designed and synthesized novel donor–acceptor π-conjugated benzofuro[2,3-*c*]oxazolo[4,5-*a*]carbazole-type fluorescent dyes **1a**, **3c**, **4a** and **5a** (Scheme 1), where the electron acceptor is a carboxyl group for **1a** and a cyano group for **3c**, **4a** and **5a**. The photovoltaic performance of **3c** having a non-conjugated linkage between a carboxyl group and a chromophore is similar to that of **1a** and higher than those of **4a** and **5a**. To understand the differences in the photovoltaic performance, it was assumed that the dye **3c** is standing perpendicularly to the $TiO_2$ substrate as shown in Figure 1, and that the dye **3c** can efficiently inject electrons from the phenylcyano group to the conduction band of $TiO_2$ electrode through an intermolecular hydrogen bonding between a cyano nitrogen of the dye and a hydroxyl proton of the $TiO_2$ surface. To provide a further confirmation for this view, we have designed and synthesized new-type donor–acceptor π-conjugated benzofuro[2,3-*c*]oxazolo[4,5-*a*]carbazole fluorescent dyes **3a–f** with different lengths of non-conjugated alkyl chains containing a carboxyl group at the end position.

In this Letter, we report photovoltaic performances of DSSCs based on the fluorescent dyes **3a–f** and discuss a relationship between chemical structures of the dyes and their photovoltaic properties.

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*Keywords*: Heterocycles; Dye-sensitized solar cells; Fluorescence; Donor–acceptor π-conjugated fluorophores.

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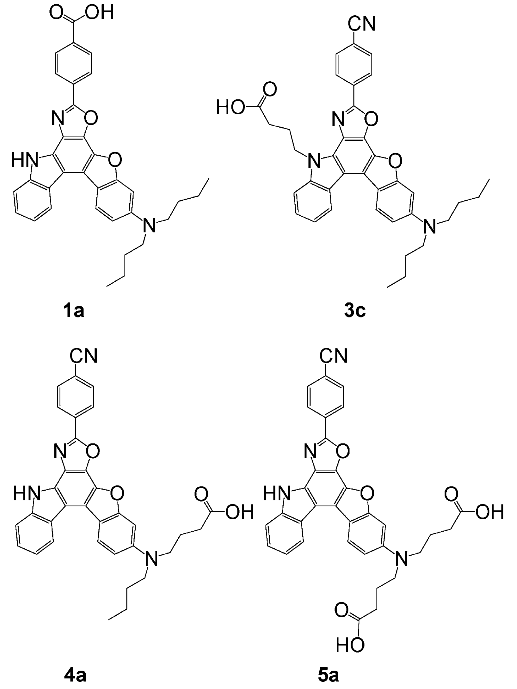


**Scheme 1.** Chemical structures of benzofuro[2,3-*c*]oxazolocarbazole-type fluorescent dyes.

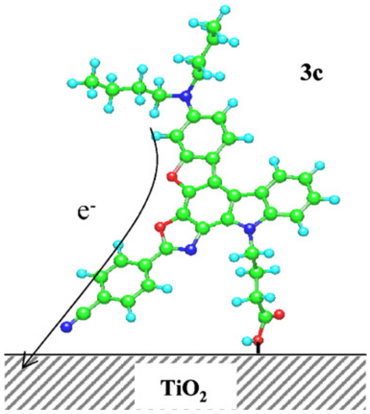


**Figure 1.** Plausible configuration of **3c** on TiO$_2$ surface. Light blue, green, blue, and red balls correspond to hydrogen, carbon, nitrogen, and oxygen atoms, respectively.

The synthetic pathway of benzofuro[2,3-*c*]oxazolo[4,5-*a*]-carbazole-type fluorescent dyes **3a**–**f** is shown in Scheme 2. We used compound **1**[9] as a starting material. The reaction of **1** with alkylhalide using sodium hydride yielded **2a**–**f**. The compounds **3a**–**f** were obtained by hydrolysis of **2a**–**f**.

The absorption and fluorescence spectra of **3a**–**f** in 1,4-dioxane are shown in Figure 2 and their spectral data are summarized in Table 1. All these fluorescent dyes exhibit intense absorption bands at around 430 and 350 nm, and an intense fluorescence at around 530 nm. The fluorescence quantum yields ($\Phi$) of these dyes in 1,4-dioxane are close to 100%. Absorption spectra of dyes adsorbed on TiO$_2$ film are shown in Figure 3, where the amounts of adsorbed dyes are $4.4\times10^{15}$, $6.6\times10^{16}$, $5.5\times10^{16}$, $7.8\times10^{16}$, $7.2\times10^{16}$, and $7.4\times10^{16}$ molecules cm$^{-2}$ for **3a**–**f**, respectively. The absorbance and absorption peak wavelengths of adsorbed dyes on TiO$_2$ films are very similar to one another, but only the absorbance of **3a** is lower than those of the other dyes. Undoubtedly, the low absorbance of **3a** is ascribable to the small amount of **3a** adsorbed on TiO$_2$ film. In all the dyes except **3a**, the onsets of absorption bands of adsorbed dyes are red-shifted by 50–80 nm relative to those in 1,4-dioxane. Such a red-shift is attributable to aggregation of the dyes on TiO$_2$ electrode.[5c,10,11]

The electrochemical properties of **3a**–**f** were determined by cyclic voltammetry (CV) in acetonitrile containing 0.1 M Et$_4$NClO$_4$. CV curves of these compounds showed three redox waves at similar potentials irrespective of the sort of the dyes. The first oxidation peaks for

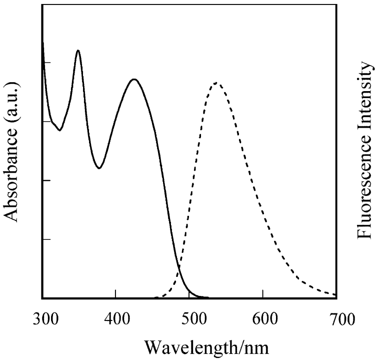
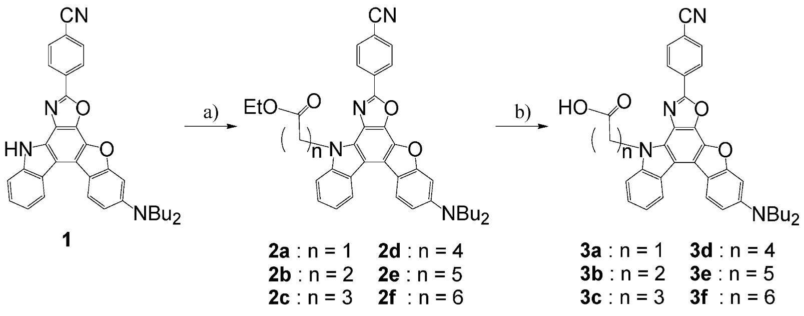


**Figure 2.** (a) Absorption (—) and (b) fluorescence (- - -) spectra of **3c** in 1,4-dioxane.



**Scheme 2.** Synthesis of fluorescent dyes **2a**–**f** and **3a**–**f**. Reagents and conditions: (a) NaH, alkylhalide, acetonitrile, rt, 1–12 h, 72% for **2a**, 39% for **2b**, 63% for **2c**, 74% for **2d**, 76% for **2e**, and 69% for **2f**; (b) NaOH aq, ethanol, 60 °C, 2–12 h, 54% for **3a**, 25% for **3b,** 89% for **3c**, 39% for **3d**, 63% for **3e**, and 77% for **3f**.

**Table 1.** Optical properties of **3a–f** in 1,4-dioxane and their energy levels of HOMO and LUMO

| Dye | $\lambda_{max}^{abs}$/nm ($\varepsilon_{max}$/dm$^3$ mol$^{-1}$ cm$^{-1}$)[a] | $\lambda_{max}^{fl}$ (nm)[b] | $\Phi$ | SS[c] (nm) | HOMO[d] (V) | LUMO[d] (V) |
|---|---|---|---|---|---|---|
| **3a** | 427 (26,700), 350 (26,100) | 540 | 0.97 | 113 | 0.87 | −1.71 |
| **3b** | 425 (25,300), 350 (26,900) | 532 | 0.96 | 107 | 0.90 | −1.70 |
| **3c** | 427 (24,400), 349 (27,300) | 537 | 0.99 | 112 | 0.91 | −1.64 |
| **3d** | 430 (26,900), 354 (33,000) | 534 | 0.97 | 104 | 0.89 | −1.66 |
| **3e** | 430 (28,900), 354 (35,000) | 534 | 0.95 | 104 | 0.89 | −1.66 |
| **3f** | 431 (26,100), 354 (31,000) | 533 | 0.95 | 103 | 0.86 | −1.75 |

[a] $2.0 \times 10^{-5}$ M.
[b] $2.0 \times 10^{-6}$.
[c] Stokes shift value.
[d] Versus a normal hydrogen electrode (NHE).

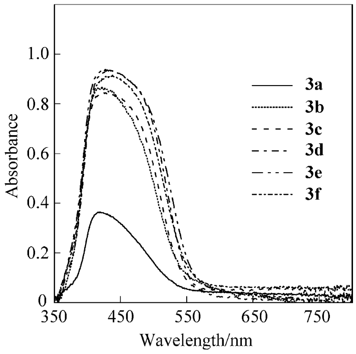


**Figure 3.** Absorption spectra of **3a–f** adsorbed on $TiO_2$ film.

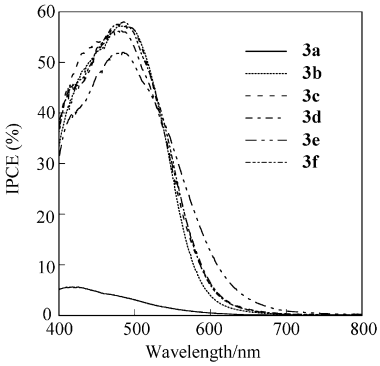


**Figure 4.** IPCE spectra of DSSCs based on **3a–f**.

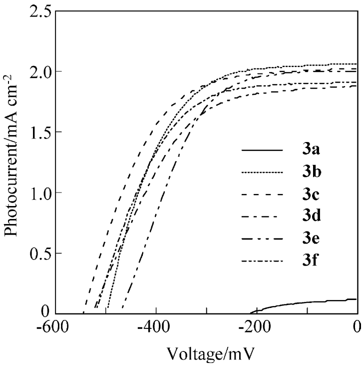


**Figure 5.** Photocurrent–voltage curves of DSSCs based on **3a–f**.

**3a–f** were determined to be 0.33–0.36 V versus Ag/Ag$^+$. The corresponding reduction peaks appeared at 0.25–0.31 V for the first redox step (see Supplementary data for details). On the bases of the spectral analyses and CVs, we estimated the HOMO and LUMO energy levels of the six dyes. All these dyes have similar HOMO and LUMO energy levels (Table 2). Evidently, the LUMO energy levels for these dyes are higher than the energy level of $TiO_2$ conduction band (−0.5 V), showing that these dyes can inject efficiently electrons to conduction band of $TiO_2$ electrode.

The DSSCs were fabricated by using the $TiO_2$ electrode, Pt-coated glass as a counter electrode, and an acetonitrile solution with 0.05 M iodine, 0.1 M lithium iodide, and 1,2-dimethyl-3-*n*-propylimidazolium iodide as electrolyte. The photocurrent–voltage characteristics were measured using a potentiostat under a simulated solar light (AM 1.5, 61 mW cm$^{-2}$). The incident photon-to-current conversion efficiency (IPCE) spectra were measured under monochromatic irradiation with a tungsten–halogen lamp and a monochromator. IPCE spectra and photocurrent–voltage curves are depicted in Figures 4 and 5, respectively. The maximum IPCE values are very similar except for **3a**: 6% for **3a**, 57% for **3b**, 58% for **3c**, 56% for **3d**, 52% for **3e**, and 58% for **3f**. The photocurrent–voltage curves for **3b–f** resemble also very well. For these dyes, the short-circuit photocurrent densities ($J_{sc}$) are 1.9–2.1 mA cm$^{-2}$, and the solar energy-to-electricity conversion yield ($\eta$) values are 0.85–1.00%. As shown in Table 2, no significant differences are also seen for the other photovoltaic parameters such as photovoltage ($V_{oc}$) and fill factor (ff) among the dyes except **3a**. The close agreements of all the photovoltaic features for **3b–f** demonstrate that the π-conjugated skeletons of these dyes lie on the $TiO_2$ surface in a similar fashion irrespective of different lengths of alkyl chains with a carboxyl group acting as an anchor. In view of highly efficient charge injection probabilities as suggested by IPCE values over 50%

**Table 2.** Photovolatic performances of DSSCs based on **3a–f**

| Dye | Molecules[a] (cm$^{-2}$) | $J_{sc}$ (mA cm$^{-2}$) | $V_{oc}$ (mV) | ff | $\eta$ (%) |
|---|---|---|---|---|---|
| **3a** | $4.4 \times 10^{15}$ | 0.12 | 216 | 0.42 | 0.02 |
| **3b** | $6.6 \times 10^{16}$ | 2.06 | 500 | 0.57 | 1.00 |
| **3c** | $5.5 \times 10^{16}$ | 2.01 | 548 | 0.56 | 1.00 |
| **3d** | $7.8 \times 10^{16}$ | 1.88 | 524 | 0.53 | 0.86 |
| **3e** | $7.2 \times 10^{16}$ | 2.00 | 468 | 0.55 | 0.84 |
| **3f** | $7.4 \times 10^{16}$ | 1.91 | 520 | 0.57 | 0.90 |

[a] Adsorption amount per unit area of $TiO_2$ film.

for **3b–f**, it is likely that the electron-accepting phenylcyano groups are attached to the $TiO_2$ as shown in Figure 1, so that the dyes **3b–f** can efficiently inject electrons from the dye skeleton to the conduction band of the $TiO_2$ through the phenylcyano groups. The lower photovoltaic performance of **3a** is attributable to the small amount of **3a** adsorbed on $TiO_2$ film compared with those for the other dyes because of a steric hindrance between the phenylcyano moiety of **3a** and $TiO_2$ surface. The $\eta$ values of DSSCs based on the dyes **3a–f** are relatively small compared with those of other organic dyes because the π-conjugated system of **3a–f** does not have an intense absorption band over a long-wavelength region of the solar spectrum.

In conclusion, to develop the molecular design and synthetic strategy of donor–acceptor π-conjugated dyes for DSSCs, we have designed and synthesized new-type donor–acceptor π-conjugated fluorescent dyes **3a–f** and their photovoltaic performances of dye-sensitized solar cells are studied. It is found that in spite of the lengths of alkyl chains, due to the flexibility of alkyl chains, the cyano groups of the dyes are located close to $TiO_2$ surface and a good electron communication is established between the cyano group and $TiO_2$ surface. It is concluded that a carboxyl group of donor–acceptor π-conjugated sensitizer is necessary not as the electron acceptor, but only as the anchoring group for attachment on $TiO_2$ surface. The most important point for developing new and efficient donor–acceptor π-conjugated sensitizers for DSSCs is to design dye molecules capable of forming a strong interaction between the electron acceptor moiety of sensitizers and $TiO_2$ surface.

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## Supplementary data

Supplementary data (synthetic and experimental details) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.10.107.

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