Photovoltaic performance of dye-sensitized solar cells based on donor–acceptor π-conjugated benzofuro[2,3-c]oxazolo[4,5-a]carbazole-type fluorescent dyes with a carboxyl group at different positions of the chromophore skeleton

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Donor–acceptor π-conjugated benzofuro[2,3-c]oxazolo[4,5-a]carbazole-type fluorescent dyes **3a**, **3b**, **8a**, and **8b** with a carboxyl group at different positions of the chromophore skeleton have been designed and synthesized. The absorption and fluorescence spectra and cyclic voltammograms of the fluorescent dyes agree very well, showing that the position of the carboxyl group has a negligible influence on the photophysical and electrochemical properties of these dyes. When these dyes are used in dye-sensitized solar cells, however, their photovolatic performances are considerably different. The short-circuit photocurrents and energy conversion efficiencies under a simulated solar light increase in the order: **3a** (2.12 mA cm^{-2}, 1.00%) ≈ **3b** (2.10 mA cm^{-2}, 1.06%) > **8b** (1.50 mA cm^{-2}, 0.67%) > **8a** (0.84 mA cm^{-2}, 0.34%). Based on semi-empirical molecular orbital calculations (AM1 and INDO/S) together with spectral analyses and their photovolatic performance, the relationships between the observed photovolatic properties and the chemical structures of the benzofuro[2,3-c]oxazolo[4,5-a]carbazole-type fluorescent dyes are discussed. It is found that strong interaction between a TiO$_2$ surface and the electron accepting moiety of the dye leads to a high photovoltaic performance.

Introduction

Donor–acceptor π-conjugated dyes are useful as sensitizers of dye-sensitized solar cells (DSSCs)[1] and emitters of organic light emitting diodes (OLEDs)[2] because of their strong absorption and emission properties. Many donor–acceptor π-conjugated dyes with a carboxyl group, acting not only as the anchoring group for attachment to metal oxides but also as the electron acceptor, are synthesized and used as sensitizers of DSSCs.[3–5] A number of researchers have suggested that a carboxyl group can form an ester linkage with a TiO$_2$ surface to provide a strongly bound dye and good electronic communication between them. However,

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development of new donor–acceptor π-conjugated dyes for DSSCs is limited because a carboxyl group is required to combine with the π-conjugation system or the electron accepting moiety of dyes for the above reasons. To obtain new and efficient sensitizers for DSSCs, a novel molecular design such as forming a strong interaction between the electron accepting moiety of sensitizers and a TiO$_2$ surface is necessary. Therefore, we have designed and synthesized novel donor–acceptor π-conjugated benzofuro[2,3-c]oxazolo[4,5-a]carbazole-type fluorescent dyes **3a**, **3b**, **8a**, and **8b** with a carboxyl group at different positions of the chromophore skeleton (Fig. 1). In this paper, we report the photovoltaic performance of DSSCs based on benzofuro[2,3-c]oxazolo[4,5-a]carbazole-type fluorescent dyes **3a**, **3b**, **8a**, and **8b**. To elucidate the main differences in photovolatic performance among the fluorescent dyes **3a**, **3b**, **8a**, and **8b**, we performed semi-empirical
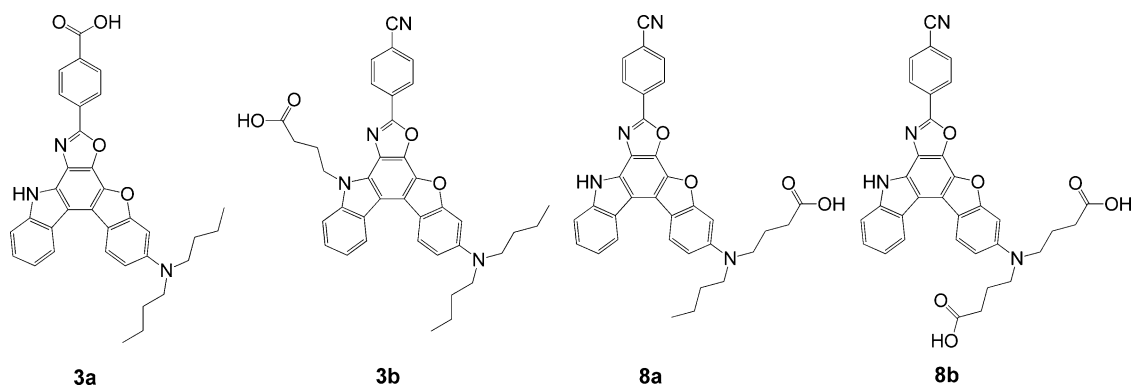

Fig. 1 Chemical structures of benzofuro[2,3-c]oxazolocarbazole-type fluorescent dyes.

molecular orbital calculations (AM1 and INDO/S). On the basis of the results of calculations, spectral analyses, and photovoltaic performance, the relationships between the observed photovoltaic properties and the chemical structures of the benzofuro[2,3-c]oxazolo[4,5-a]carbazole-type fluorescent dyes are discussed.

## Results and discussion

Synthesis of benzofuro[2,3-c]oxazolo[4,5-a]carbazole-type fluorescent dyes

The synthetic pathway is shown in Schemes 1–3. Compound **3a** was synthesized by hydrolysis of 7-(4-cyanophenyl)-3-dibutylaminobenzofuro[2,3-c]oxazolo[4,5-a]carbazole[6] (**1a**) under basic conditions (Scheme 1). Compound **3b** was also synthesized by hydrolysis of N-alkylated **2b** obtained by reaction of **1a** with ethyl 4-bromobutyrate using sodium hydride (Scheme 2). Synthesis of **8a** and **8b** is outlined in Scheme 3. Carbazole-1,2-dione was prepared according to the published procedure.[7] The compounds **4a** and **4b** were obtained by the reaction of carbazole-1,2,-dione with 4-[butyl-(3-hydroxyphenyl)amino]butyric acid ethyl ester and 4-[(3-ethoxycarbonylpropyl)-(3-hydroxyphenyl)amino]butyric acid ethyl ester in the presence of CuCl₂, respectively. Next, intramolecular oxidative-cyclization of **4a** and **4b** using Cu(OCOCH₃)₂ gave the quinones **5a** and **5b**, respectively. The quinones **5** were allowed to react with p-cyanobenzaldehyde to give the structural isomers of oxazolocarbazole-type fluorophores **6** and **7**. This is the first report of the preparation of this isomeric pair of
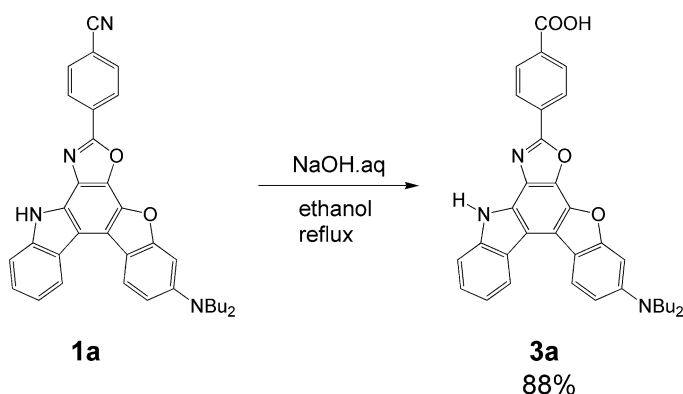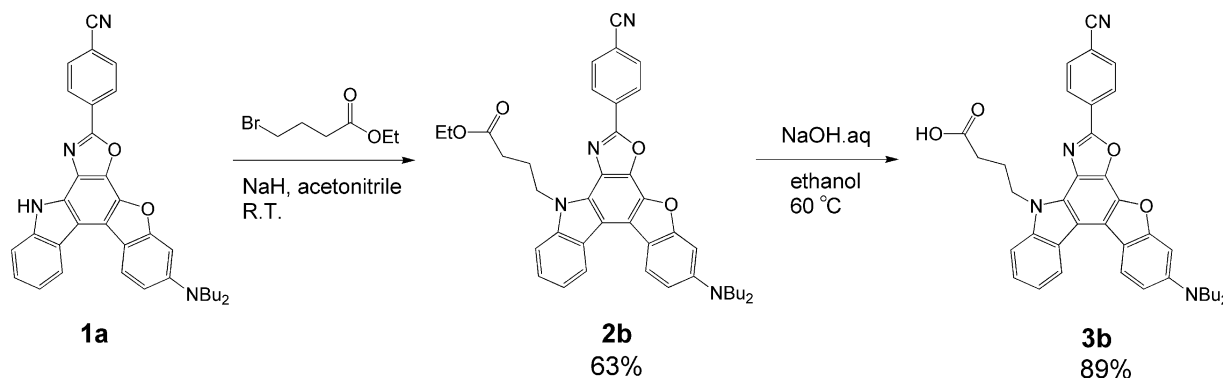
oxazole compounds using ammonium acetate. In this reaction, NH₃ resulting from CH₃COONH₄ in the initial stage is acting as the nucleophilic reagent to the 6- and/or 7-carbonyl carbon. In this case, NH₃ preferentially attacks the 7-carbonyl carbon rather than the 6-carbonyl in spite of the similar steric reactivity of the two carbonyls. It was considered that the conjugated linkage of the dialkylamino group to the 6-carbonyl group would make the 6-carbonyl carbon less electrophilic than the 7-carbonyl carbon, so that the nucleophilic reagents (NH₃) preferentially attack the electrophilic 7-carbonyl carbon. As the result, this reaction afforded preferentially the compounds **6**. The compounds **8a** and **8b** were prepared by hydrolysis of their precursors **6a** and **6b**, respectively.
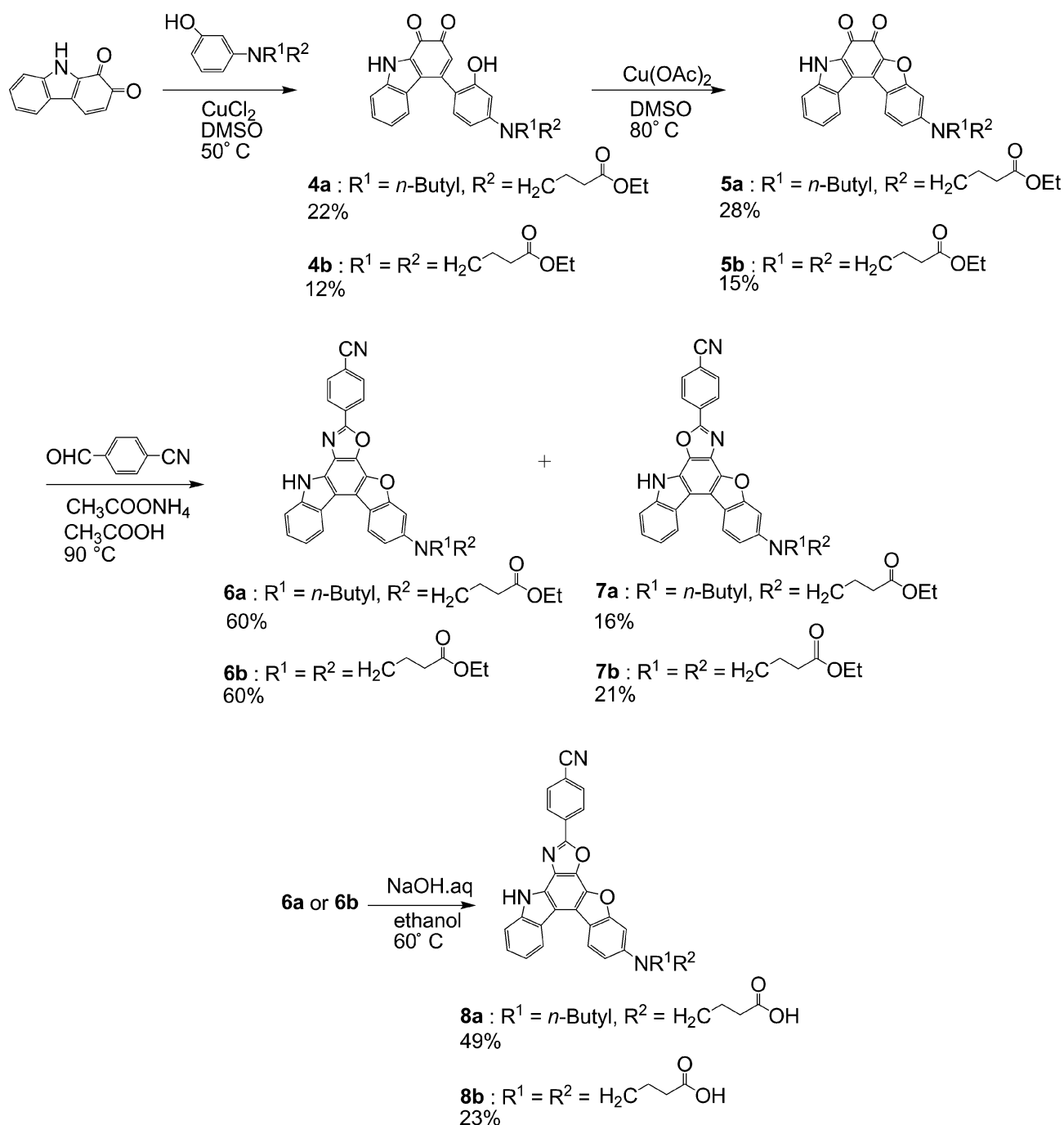
Spectroscopic properties of benzofuro[2,3-c]oxazolo[4,5-a]-carbazole-type fluorescent dyes in solution and on TiO₂ film

The absorption, excitation, and fluorescence spectra of **3a**, **3b**, **8a**, and **8b** in 1,4-dioxane are shown in Fig. 2 and their spectral data are summarized in Table 1. The absorption and fluorescence spectra of all these fluorescent dyes agree very well, showing that the effect of the position of the carboxyl group attached to the same chromophore skeleton on the photophysical properties of **3a**, **3b**, **8a**, and **8b** is negligible. All these fluorescent dyes exhibit intense absorption bands at around 420 and 350 nm, and an intense fluorescence at around 530 nm. The fluorescence quantum yields (Φ) of these dyes in 1,4-dioxane were close to 100%. From the measurement of the fluorescence excitation spectra of **3a**, **3b**, **8a**, and **8b**, it was found that two absorptions lead to the same efficiency for the emission (Fig. 2b). Absorption spectra of dyes adsorbed on TiO₂ film are shown in Fig. 3, where the amounts of adsorbed dyes on TiO₂ film are 6.8×10^{16}, 4.4×10^{16}, 3.9×10^{16}, and 6.6×10^{16} molecules cm⁻² for **3a**, **3b**, **8a**, and **8b**,

Table 1 Optical properties of the dyes in 1,4-dioxane

Dye	λ_{max}^{abs}/nm (ε_{max}/dm³ mol⁻¹ cm⁻¹)[a]	λ_{max}^{fl}/nm[b]	Φ	SS[c]/nm
3a	416 (25700), 347 (25400)	525	0.97	109
3b	425 (24400), 349 (27300)	537	0.99	112
8a	429 (21500), 353 (25500)	534	0.97	105
8b	424 (22200), 348 (23900)	541	0.97	117

[a] 2.0×10^{-5} M. [b] 2.0×10^{-6} M. [c] Stokes shift value.

Scheme 1 Synthesis of fluorophore **3a**.

Scheme 2 Synthesis of fluorophore **3b**.

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Scheme 3 Synthesis of fluorophores **8a** and **8b**.

respectively. No significant differences in the absorption properties are noted among the four dyes. Although the absorption peak wavelengths of adsorbed dyes on TiO$_2$ films are similar to those in 1,4-dioxane, the onset of absorption bands are red-shifted by 80–100 nm. Such a red-shift is attributable to dye aggregation on the TiO$_2$ electrode.[5,8] Further studies on the possible influence of the molecular arrangement of dyes adsorbed on TiO$_2$ surface, on the photovoltaic performance of DSSCs are now in progress in our group.

Electrochemical properties of benzofuro[2,3-*c*]oxazolo[4,5-*a*]-carbazole-type fluorescent dyes and their HOMO and LUMO energy levels

The electrochemical properties of **3a**, **3b**, **8a**, and **8b** were determined by cyclic voltammetry (CV) in acetonitrile containing 0.1 M Et$_4$NClO$_4$. As an example, the CV of **8a** is shown in Fig. 4. CV curves of these compounds showed three redox waves at similar potentials irrespective of the compounds, though the peaks of
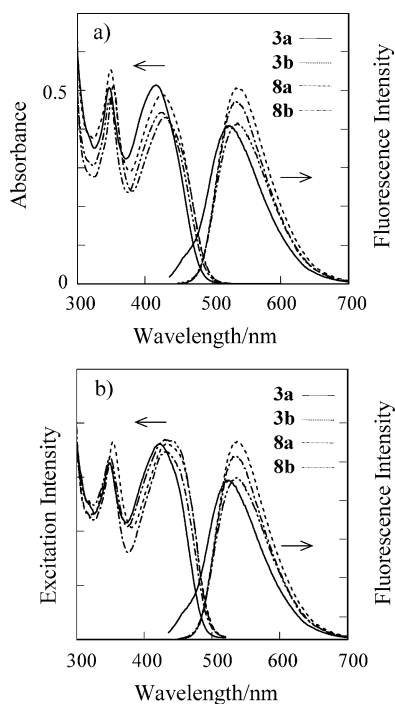
Fig. 2 a) Absorption and fluorescence spectra and b) excitation and fluorescence spectra of 3a, 3e, 8a, and 8b in 1,4-dioxane.

Fig. 4 Cyclic voltammogram of compound 8a in acetonitrile containing 0.1 M Et$_4$NClO$_4$ at a scan rate of 20 mV s^{-1}. The arrow denotes the direction of the potential scan.

3a were shifted in a negative direction compared with those of the other compounds (Table 2). Three oxidation peaks of these compounds are determined to be 0.31–0.37, 0.82–0.88, and 0.98–1.0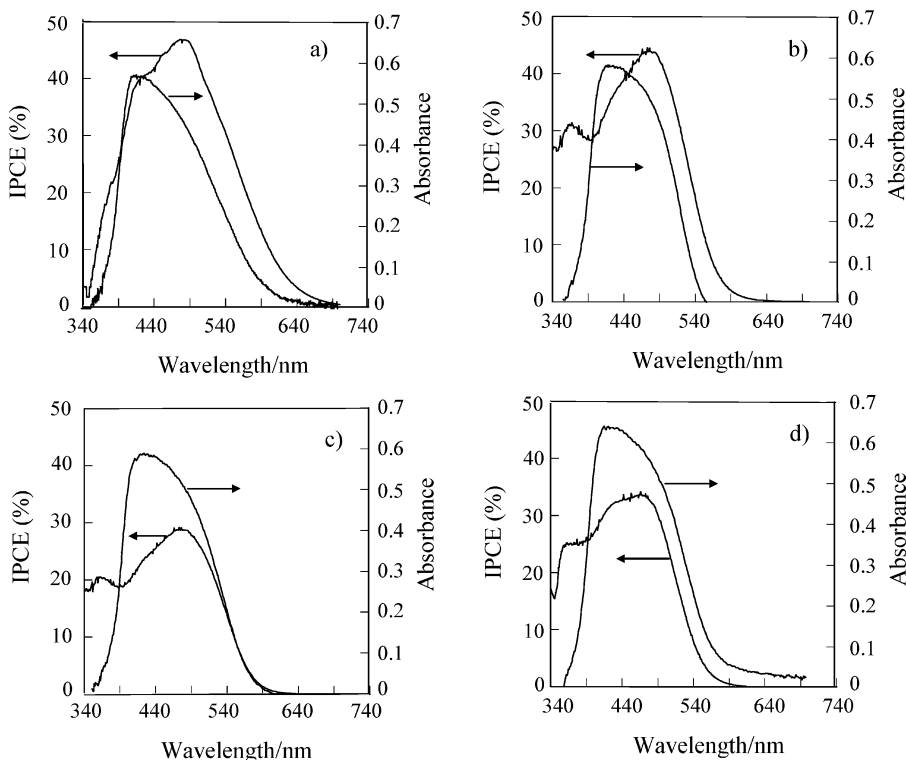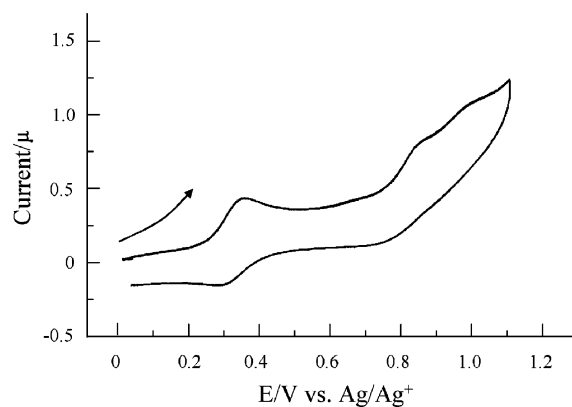2 V vs. Ag/Ag$^+$. The corresponding reduction peaks appear at 0.25–0.31 V for the first redox step. The first redox waves are clearly observed and the peak separations are ca. 60 mV, suggesting that the first oxidized states of the dyes are stable. On the other hand, ill-defined waves for the second and third oxidation processes indicate that the second and third oxidized states of the dyes are less stable than the first ones.

On the basis of the spectral analyses and CVs, we estimated the HOMO and LUMO energy levels of the four dyes. The HOMO energy levels for 3a, 3b, 8a, and 8b were evaluated to be 0.87, 0.91, 0.93, and 0.91 V with respect to NHE, respectively. The LUMO energy levels of the dyes were estimated from the first oxidation potential and an intersection of absorption and fluorescence spectra [480 nm (2.58 eV), 486 nm (2.55 eV), 485 nm

Fig. 3 Absorption spectra of the dyes adsorbed on TiO$_2$ film and the IPCE spectra for DSSCs based on the dyes: a) 3a, b) 3b, c) 8a, and d) 8b. The amount of adsorbed dyes on TiO$_2$ film is 6.8×10^{16}, 4.4×10^{16}, 3.9×10^{16}, and 6.6×10^{16} molecules cm^{-2} for 3a, 3b, 8a, and 8b, respectively.

Table 2 Electrochemical properties of **3a**, **3b**, **8a**, and **8b**

Compound	E_{pa}/V vs. Ag/Ag+ [a]	E_{pc}/V vs. Ag/Ag+ [b]	ΔE_p/mV	$E_{1/2}$/V vs. Ag/Ag+
3a	0.31, 0.82, 0.98	0.25, –, –	60, –, –	0.28, –, –
3b	0.35, 0.84, 0.98	0.28, 0.78, –	70, 60, –	0.32, 0.81, –
8a	0.37, 0.85, 1.02	0.31, 0.80, –	60, 50, –	0.34, 0.83, –
8b	0.35, 0.88, 0.99	0.30, –, –	50, –, –	0.33, –, –

[a] E_{pa} and E_{pc} are the anodic and cathodic peak potentials in acetonitrile (0.1 M Et$_4$NClO$_4$). [b] E_{pa} and E_{pc} are the anodic and cathodic peak potentials in acetonitrile (0.1 M Et$_4$NClO$_4$).

(2.56 eV), and 487 nm (2.54 eV) for **3a**, **3b**, **8a**, and **8b**, respectively] corresponding to the energy gap between HOMO and LUMO. The LUMO energy levels for these dyes were −1.71, −1.64, −1.63, and −1.63 V for **3a**, **3b**, **8a**, and **8b**, respectively. Evidently, they are higher than the energy level of TiO$_2$ conduction band (−0.5 V), showing that these dyes can efficiently inject electrons into the conduction band of the TiO$_2$ electrode. The results of absorption and fluorescence spectra and CV for these dyes demonstrate that all these dyes have similar HOMO and LUMO energy levels.

Semi-empirical MO calculations (AM1, INDO/S)

To understand the photophysical and electrochemical properties of benzofuro[2,3-c]oxazolo[4,5-a]carbazole-type fluorescent dyes, we have carried out semi-empirical molecular orbital (MO) calculations of **3a**, **3b**, **8a**, and **8b** using the INDO/S method[9] after geometrical optimizations using the MOPAC/AM1 method.[10] The calculated absorption wavelengths and the transition characters of the first absorption bands are collected in Table 3. The observed and calculated absorption spectra of the compounds (Tables 1 and 3) compare well with each other with respect to both the absorption wavelength and the absorption intensity, although the calculated absorption wavelengths are blue-shifted. The deviation of the INDO/S calculations, giving transition energies greater than the experimental values, has been generally observed.[11] The calculations showed that the longest excitation bands of the dyes were mainly assigned to the transition from HOMO to LUMO, where HOMOs were mostly localized on the 3-dibutylaminobenzofuro[2,3-c]oxazolo[4,5-a]carbazole moiety for all dyes, and LUMOs were mostly localized on the carboxyphenyl moiety for **3a** and the cyanophenyl moiety for **3b**, **8a**, and **8b**. The changes in the calculated electron density accompanying the first electron excitation are shown in Fig. 5, which reveals

Table 3 Calculated absorption spectra for **3a**, **3b**, **8a**, and **8b**

Compound	Absorption (calc.)		CI component[b]
	λ_{max}/nm	f [a]	
3a	402	0.92	HOMO → LUMO (75%)
	328	0.59	HOMO → LUMO + 1 (43%)
			HOMO-1 → LUMO (13%)
3b	404	0.90	HOMO → LUMO (77%)
	329	0.64	HOMO → LUMO + 1 (47%)
			HOMO-1 → LUMO (16%)
8a	398	0.95	HOMO → LUMO (78%)
	327	0.61	HOMO → LUMO + 1 (45%)
			HOMO-1 → LUMO (13%)
8b	394	0.96	HOMO → LUMO (79%)
	325	0.62	HOMO → LUMO + 1 (46%)
			HOMO-1 → LUMO (12%)

[a] Oscillator strength. [b] The transition is shown by an arrow from one orbital to another, followed by its percentage CI (configuration interaction) component.

a strong migration of intramolecular charge transfer from the 3-dialkylaminobenzofuro[2,3-c]oxazolo[4,5-a]carbazole moiety to the carboxylphenyl or cyanophenyl moiety for all dyes. The calculations showed that the second excitation bands of the dyes were mainly assigned to the transition from HOMO to LUMO + 1, where a moderate migration of charge from the 3-dialkylaminobenzofuro[2,3-c]oxazolocarbazole moiety to the carboxyphenyl moiety for **3a** and the cyanophenyl moiety for **3b**, **8a**, and **8b** is also observed. These calculation results suggest that the effects of the cyano and carboxyl groups and *N*-alkylation of the carbazole ring on the photophysical and electrochemical properties of these dyes are negligible, so that all dyes show similar absorption and fluorescence spectra and CV.
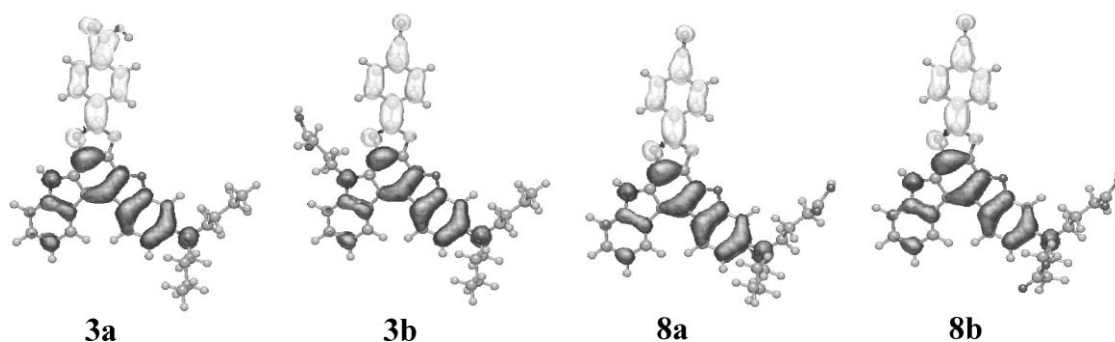

3a   **3b**   **8a**   **8b**

Fig. 5 Calculated electron density changes accompanying the first electronic excitation of **3a**, **3b**, **8a**, and **8b**. The black and white lobes signify decrease and increase in electron density accompanying the electronic transition respectively. Their areas indicate the magnitude of the electron density change.

Photovoltaic performance of DSSCs based on benzofuro[2,3-c]oxazolo[4,5-a]carbazole-type fluorescent dye

The incident photon-to-current conversion efficiency (IPCE) spectra for DSSCs are shown in Fig. 3. The IPCE is represented by the following equation:

$$\text{IPCE } (\%) = \frac{1240 \, (\text{eV nm}) \, J_{sc} \, (\text{mA cm}^{-2})}{\lambda \, (\text{nm}) \, \Phi \, (\text{mW cm}^{-2})} \times 100 \quad (1)$$

where J_{sc} is the short-circuit photocurrent density generated by monochromatic light, and λ and Φ are the wavelength and the intensity of the monochromatic light, respectively. When the performances of DSSCs fabricated using these dyes as sensitizers were examined, big differences in the IPCE spectra and the photocurrent–voltage (I–V) characteristics were observed. As shown in Fig. 5, the maximum IPCE value increases in the order of **3a** (46%) > **3b** (45%) > **8b** (34%) > **8a** (30%). Table 4 summarizes the photovoltaic performances of DSSCs based on the dyes under AM 1.5 irradiation (60 mW cm^{-2}). The solar energy-to-electricity conversion yield (η (%)) is expressed by the following equation:

$$\eta \, (\%) = \frac{J_{sc} \, (\text{mA cm}^{-2}) \, V_{oc} \, (\text{V}) \, ff}{I_o \, (\text{mW cm}^{-2})} \times 100 \quad (2)$$

where I_0 is the intensity of incident white light, V_{oc} is the open-circuit photovoltage, and ff represents the fill factor. Interestingly, the J_{sc} for **3b** (1.60 mA cm^{-2}), which has a nonconjugated linkage between the carboxyl group and the chromophore, is similar to that for **3a** (1.30 mA cm^{-2}) and higher than those of **8a** (0.80 mA cm^{-2}) and **8b** (0.75 mA cm^{-2}), when comparisons are made between similar amounts of dyes adsorbed on TiO$_2$ (*ca.* 3 × 10^{16} molecules cm^{-2}). The V_{oc}s for **3a**, **3b**, **8a**, and **8b** are 544 mV, 550 mV, 430 mV, and 485 mV, respectively, which were different among the dyes. On the other hand, when the amount of adsorbed dye on TiO$_2$ film increased to 6.8 × 10^{16}, 4.4 × 10^{16}, 3.9 × 10^{16}, and 6.6 × 10^{16} molecules cm^{-2} for **3a**, **3b**, **8a**, and **8b**, respectively, the I_{sc} and η values increased in the order: **3a** (2.12 mA cm^{-2}, 1.00%) ≈ **3b** (2.10 mA cm^{-2}, 1.06%) > **8b** (1.50 mA cm^{-2}, 0.67%) > **8a** (0.84 mA cm^{-2}, 0.34%). It is worth noting that the J_{sc} and η for **3b** are similar to those for **3a**, although the amounts of adsorbed dyes on TiO$_2$ film in **3b** is less than that in **3a**. This result also demonstrates that the molecular aggregation state of the dye on the TiO$_2$ electrode has a great influence on the I_{sc} and η of DSSCs. Furthermore, the V_{oc} values for **3a** (508 mV) and **3b** (530 mV) were higher than those of **8a** (435 mV) and **8b** (470 mV).

Table 4 Photovoltaic performances of DSSCs

Dye	× 10^{16} molecules cm^{-2} [a]	J_{sc}/mA cm^{-2}	V_{oc}/mV	ff	η (%)
3a	2.5	1.30	544	0.60	0.70
	6.8	2.12	508	0.57	1.00
3b	2.7	1.60	550	0.58	0.84
	4.4	2.10	530	0.58	1.06
8a	2.9	0.80	430	0.57	0.33
	3.9	0.84	435	0.57	0.34
8b	2.8	0.75	485	0.57	0.34
	6.6	1.50	470	0.58	0.67

[a] Adsorption amount per unit area of TiO$_2$ film.

Relationship between photovoltaic performance and chemical structure

To understand the differences in J_{sc}, we assumed that the dye molecule is standing perpendicular to the TiO$_2$ substrate as shown in Fig. 6. In **3a**, a carboxyl group can form an ester linkage with the TiO$_2$ surface, so that electrons will be injected from the dye to TiO$_2$ through the carboxyl group. For **3b**, **8a**, and **8b**, on the other hand, the carboxyl group acts as an anchoring group for attachment to the TiO$_2$ surface, but it cannot be the electron acceptor. From the molecular structure of **3b**, it was suggested that the phenylcyano group acting as electron acceptor is located in close proximity to the TiO$_2$ surface by interactions such as intermolecular hydrogen bonding between the cyano nitrogen of the dye and the hydroxyl proton of the TiO$_2$ surface. Consequently, dye **3b** can efficiently inject electrons from the phenylcyano group to the conduction band of the TiO$_2$ electrode through intermolecular hydrogen bonding. On the other hand, we presume that free rotation of the butyl group for **8a** and rigid linkages with the TiO$_2$ surface for **8b** prevent the phenylcyano moiety of the dye from being in close proximity to the TiO$_2$ surface. Fukuzumi *et al.* reported that for DSSC based on fluorescein derivatives, the xanthen moiety acting as an electron acceptor, which can inject electrons into the conduction band of the semiconductor, is located in close proximity to the semiconductor surface.[12] On the other hand, it is reported that the Fermi level of TiO$_2$ is affected by the adsorption of dyes with a permanent dipole.[13] If our model for dye adsorption is correct, the direction of the dipole moments of **3a** and **3b** in the adsorption state will be opposite to those of **8a** and **8b**. Thus, this will cause the difference in V_{oc}.
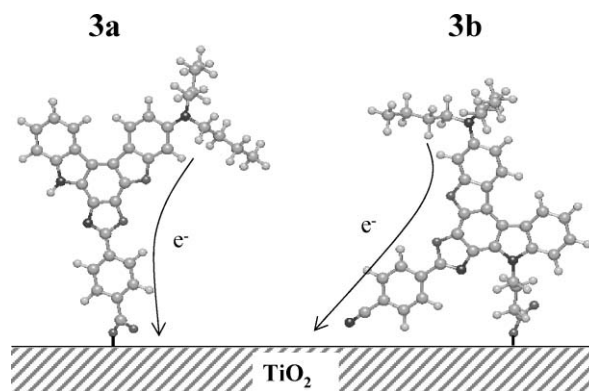

Fig. 6 Plausible configurations of **3a** and **3b** on a TiO$_2$ surface. Molecular structures of **3a** and **3b** are optimized by the MOPAC/AM1 method.

Conclusions

In conclusion, novel donor–acceptor π-conjugated benzofuro[2,3-c]oxazolo[4,5-a]carbazole-type fluorescent dyes with a carboxyl group at different positions of the chromophore skeleton have been designed and synthesized, and the photovoltaic performances of DSSCs based on these dyes were investigated. It was found that the distance between the electron acceptor moiety and TiO$_2$ will affect the efficiency of electron injection. Further studies on DSSCs based on these dyes are now in progress to elucidate the influence of the molecular arrangement of dyes adsorbed on a

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TiO$_2$ surface on the photovoltaic performances (J_{sc}, V_{oc}, and η) of DSSCs.

Experimental

Melting points were measured with a Yanaco micro melting point apparatus MP model. IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer by ATR method. Absorption spectra were observed with a Shimadzu UV-3150 spectrophotometer and fluorescence spectra were measured with a Hitachi F-4500 spectrophotometer. The fluorescence quantum yields (Φ) were determined by a Hamamatsu C9920-01 equipped with CCD by using a calibrated integrating sphere system (λ_{ex} = 325 nm). Cyclic voltammograms (CVs) were recorded in MeCN/Et$_4$NClO$_4$ (0.1 M) solution with a three-electrode system consisting of Ag/Ag$^+$ as the reference electrode, Pt plate as the working electrode, and Pt wire as counter electrode, by using a Hokuto Denko HAB-151 potentiostat equipped with a functional generator. Elemental analyses were recorded on a Perkin Elmer 2400 II CHN analyzer. ^{1}H NMR spectra were recorded on a JNM-LA-400 (400 MHz) FT NMR spectrometer with tetramethylsilane (TMS) as an internal standard. Column chromatography was performed on silica gel (KANTO CHEMICAL, 60N, spherical, neutral).

Synthesis of 7-(4-carboxyphenyl)-3-dibutylamino-benzofuro[2,3-c]oxazolo[4,5-a]-carbazole (3a)

To a solution of **1a** (1.0 g, 1.90 mmol) in ethanol (500 ml) was added dropwise aqueous NaOH (0.76 g, 19 mmol, 50 mL,) with stirring under reflux. After further stirring for 16 h under reflux, the solution was acidified to pH 4 with 2 M HCl, and concentrated under reduced pressure. The residue was dissolved in CH$_2$Cl$_2$, and washed with water. The organic extract was dried over MgSO$_4$, filtered, and concentrated. The residue was chromatographed on silica gel (CH$_2$Cl$_2$–ethyl acetate = 2 : 5 as eluent) to give **3a** (0.91 g, yield 88%); 296–297 °C (decomposition); IR (KBr): ν = 3240, 1692 cm^{-1}; ^{1}H NMR (DMSO-d$_6$, TMS) δ = 0.97 (6H, t), 1.37–1.43 (4H, m), 1.58–1.63 (4H, m), 3.38 (4H, t) overlap peak of dissolved water in DMSO-d$_6$, 6.94–6.96 (1H, m), 7.03–7.05 (1H, m), 7.33–7.38 (1H, m), 7.46–7.50 (1H, m), 7.66 (1H, d, J = 8.08 Hz), 8.20 (2H, d, J = 8.32 Hz), 8.38 (2H, d, J = 8.32 Hz), 8.46 (1H, d, J = 8.32 Hz), 8.60 (1H, d, J = 7.84 Hz), 12.50 (1H, s, –NH); elemental analysis calcd (%) for C$_{34}$H$_{31}$N$_3$O$_4$: C 74.84, H 5.73, N 7.70; found: C 74.72, H 5.63, N 7.67.

Synthesis of 7-(4-cyanophenyl)-3-dibutylaminobenzofuro[2,3-c]-oxazolo[4,5-a]carbazole-9-butyric acid ethyl ester (2b)

A solution of **1a** (1.0 g, 1.90 mmol) in dry acetonitrile was treated with sodium hydride (60%, 0.11 g, 2.85 mmol) and stirred for 1 h at room temperature. Ethyl 4-bromobutyrate (1.85 g, 9.49 mmol) was added in a dropwise manner over 20 min and the solution was stirred at room temperature for 10 h. After concentrating under reduced pressure, the resulting residue was dissolved in CH$_2$Cl$_2$, and washed with water. The organic extract was dried over MgSO$_4$, filtered, and concentrated. The residue was chromatographed on silica gel (CH$_2$Cl$_2$ as eluent) to give **2b** (0.77 g, yield 63%); mp 209–211 °C; IR (KBr): ν = 2228, 1738 cm^{-1}; ^{1}H NMR (acetone-d$_6$, TMS) δ = 1.04 (6H, t), 1.12 (3H, t), 1.48–1.52 (4H, m), 1.71–1.76

(4H, m), 1.89–1.92 (2H, m), 2.46–2.50 (2H, m), 3.51–3.54 (4H, m), 4.00–4.04 (2H, m), 5.07–5.11 (2H, m), 7.00–7.04 (2H, m), 7.39–7.46 (1H, m), 7.53–7.60 (1H, m), 7.81–7.86 (1H, m), 8.04–8.08 (2H, m), 8.51–8.58 (3H, m), 8.70–8.74 (1H, m); elemental analysis calcd (%) for C$_{40}$H$_{40}$N$_4$O$_4$: C 74.98, H 6.29, N 8.74; found: C 74.97, H 6.31, N 8.71.

Synthesis of 7-(4-cyanophenyl)-3-dibutylaminobenzofuro[2,3-c]-oxazolo[4,5-a]carbazole-9-butyric acid (3b)

To a solution of **2b** (0.1 g, 0.16 mmol) in ethanol (300 ml) was added dropwise aqueous NaOH (0.06 g, 1.6 mmol, 30 mL,) with stirring at 60 °C. After further stirring for 6 h under reflux, the solution was acidified to pH 4 with 2 M HCl, and concentrated under reduced pressure. The residue was dissolved in CH$_2$Cl$_2$, and washed with water. The organic extract was dried over MgSO$_4$, filtered, and concentrated. The residue was chromatographed on silica gel (CH$_2$Cl$_2$–ethyl acetate = 10 : 1 as eluent) to give **3b** (0.085 g, yield 89%); mp 260–262 °C; IR (KBr): ν = 2228, 1712 cm^{-1}; ^{1}H NMR (acetone-d$_6$, TMS) δ = 1.04 (6H, t), 1.46–1.53 (2H, m), 1.74–1.79 (4H, m), 1.88–1.91 (4H, m), 3.51–3.55 (2H, m), 3.61–3.64 (4H, m), 5.11–5.15 (2H, m), 6.98–7.05 (2H, m), 7.43–7.46 (1H, m), 7.56–7.60 (1H, m), 7.85 (1H, d, J = 8.76 Hz), 8.07 (2H, d, J = 8.76 Hz), 8.54 (2H, d, J = 9.04 Hz), 8.59 (1H, d, J = 8.80 Hz), 8.73 (1H, d, J = 8.08 Hz); elemental analysis calcd (%) for C$_{38}$H$_{36}$N$_4$O$_4$: C 74.49, H 5.92, N 9.14; found: C 74.29, H 5.83, N 9.09.

Synthesis of 4-{butyl-[4-(1,2-dioxo-2,9-dihydro-1H-carbazol-4-yl)-3-hydroxyphenyl]amino}butyric acid ethyl ester (4a)

To a solution of 9H-carbazole-1,2-dione (3.00 g, 15.2 mmol) and CuCl$_2$ (2.05 g, 15.2 mmol) in DMSO (150 ml) was added 4-[butyl-(3-hydroxyphenyl)amino]butyric acid ethyl ester (3.40 g, 15.2 mmol) with stirring at 50 °C. After further stirring for 1 h, the reaction mixture was poured into water. The resulting precipitate was filtered, washed with water and dried. The residue was chromatographed on silica gel (CH$_2$Cl$_2$–ethyl acetate = 3 : 1 as eluent) to give **4a** (1.62 g, yield 22%); mp 141–143 °C; IR (KBr): ν = 3266(br), 1708, 1603 cm^{-1}; ^{1}H NMR (acetone-d$_6$, TMS) δ = 0.98 (3H, t), 1.23 (3H, t), 1.38–1.44 (2H, m), 1.61–1.67 (2H, m), 1.94–2.00 (2H, m), 2.37–2.44 (2H, m), 3.25–3.47 (4H, m), 4.09–4.15 (2H, m), 5.88 (1H, s), 6.42–6.47 (2H, m), 6.99–7.03 (1H, m), 7.20–7.52 (4H, m), 8.01 (1H, s, –OH), 11.20 (1H, s, –NH); elemental analysis calcd (%) for C$_{28}$H$_{30}$N$_2$O$_5$: C 70.87, H 6.37, N 5.90; found: C 70.62, H 6.26, N 5.63.

Synthesis of 4-{butyl-[4-(1,2-dioxo-2,9-dihydro-1H-carbazol-4-yl)-3-hydroxyphenyl]amino}butyric acid ethyl ester (4b)

To a solution of 9H-carbazole-1,2-dione (5.00 g, 25.4 mmol) and CuCl$_2$ (3.41 g, 25.4 mmol) in DMSO (200 ml) was added 4-[(3-ethoxycarbonylpropyl)-(3-hydroxyphenyl)amino]butyric acid ethyl ester (8.56 g, 25.4 mmol) with stirring at 50 °C. After further stirring for 2 h, the reaction mixture was poured into water. The resulting precipitate was filtered, washed with water and dried. The residue was chromatographed on silica gel (CH$_2$Cl$_2$–ethyl acetate = 3 : 1 as eluent) to give **4b** (1.58 g, yield 12%); mp 88–89 °C; IR (KBr): ν = 3264(br), 1708, 1602 cm^{-1}; ^{1}H NMR (acetone-d$_6$, TMS) δ = 1.23 (6H, t), 1.93–2.00 (4H, m), 2.38–2.44 (4H, m), 3.40–3.48 (4H, m), 4.07–4.15 (4H, m), 5.88 (1H, s), 6.46–6.53 (2H,

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m), 6.99–7.03 (1H, m), 7.21–7.51 (4H, m), 8.50 (1H, s, –OH), 11.19 (1H, s, –NH); elemental analysis calcd (%) for $C_{30}H_{32}N_2O_7$: C 67.66, H 6.06, N 5.26; found: C 67.87, H 6.02, N 5.08.

Synthesis of 4-[butyl-(6,7-dioxo-7,8-dihydro-6*H*-5-oxa-8-aza-indeno[2,1-*c*]fluoren-3-yl)amino]butyric acid ethyl ester (5a)

A solution of **4a** (1.0 g, 2.11 mmol) and Cu(OCOCH$_3$)$_2$ (0.42 g, 2.11 mmol) in DMSO (100 ml) was stirred at 80 °C for 2 h. After the reaction was completed, the reaction mixture was poured into water. The resulting precipitate was filtered, washed with water and dried. The residue was chromatographed on silica gel (CH$_2$Cl$_2$–ethyl acetate = 3 : 1 as eluent) to give **5a** (0.28 g, yield 28%); mp 99–101 °C; IR (KBr): v = 3223, 1728, 1586 cm^{-1}; ^{1}H NMR (acetone-d$_6$, TMS) δ = 1.00 (3H, t), 1.25 (3H, t), 1.43–1.49 (2H, m), 1.67–1.72 (2H, m), 1.97–2.01 (2H, m), 2.46–2.50 (2H, m), 3.51–3.59 (4H, m), 4.12–4.17 (2H, m), 6.82 (1H, d, J = 2.44 Hz), 7.01 (1H, dd, J = 2.44 and 9.28 Hz), 7.26–7.31 (1H, m), 7.36–7.41 (1H, m), 7.55 (1H, d, J = 8.56 Hz), 8.18 (1H, d, J = 9.28 Hz), 8.21 (1H, d, J = 8.56 Hz), 11.21 (1H, s, –NH); elemental analysis calcd (%) for $C_{28}H_{28}N_2O_5$: C 71.17, H 5.97, N 5.93; found: C 71.33, H 5.67, N 5.72.

Synthesis of [(6,7-dioxo-7,8-dihydro-6*H*-5-oxa-8-aza-indeno[2,1-*c*]fluoren-3-yl)-(3-ethoxycarbonylpropyl)amino]butyric acid ethyl ester (5b)

A solution of **4b** (1.00 g, 1.88 mmol) and Cu(OCOCH$_3$)$_2$ (0.34 g, 1.88 mmol) in DMSO (100 ml) was stirred at 80 °C for 3 h. After the reaction was completed, the reaction mixture was poured into water. The resulting precipitate was filtered, washed with water and dried. The residue was chromatographed on silica gel (CH$_2$Cl$_2$–ethyl acetate = 3 : 1 as eluent) to give **5b** (0.15 g, yield 15%); mp 110–112 °C; IR (KBr): v = 3260, 1724, 1591 cm^{-1}; ^{1}H NMR (acetone-d$_6$, TMS) δ = 1.25 (6H, t), 1.99–2.01 (4H, m), 2.42–2.50 (4H, m), 3.57–3.61 (4H, m), 4.12–4.17 (4H, m), 6.94 (1H, d, J = 2.20 Hz), 7.16 (1H, dd, J = 2.20 and 9.28 Hz), 7.27–7.32 (1H, m), 7.37–7.41 (1H, m), 7.55 (1H, d, J = 8.56 Hz), 8.19 (1H, d, J = 9.28 Hz), 8.22 (1H, d, J = 8.56 Hz), 11.33 (1H, s, –NH); elemental analysis calcd (%) for $C_{30}H_{30}N_2O_7$: C 67.91, H 5.70, N 5.28; found: C 68.05, H 6.00, N 5.01.

Synthesis of 7-(4-cyanophenyl)benzofuro[2,3-*c*]oxazolo[4,5-*a*]-carbazole-3-butylaminobutyric acid ethyl ester (6a) and 7-(4-cyanophenyl)benzofuro[2,3-*c*]oxazolo[5,4-*a*]carbazole-3-butylaminobutyric acid ethyl ester (7a)

A solution of **5a** (0.15 g, 0.32 mmol), *p*-cyanobenzaldehyde (0.042 g, 0.32 mmol), and ammonium acetate (0.49 g, 6.35 mmol) in acetic acid (50 ml) was stirred at 90 °C for 1 h. After the reaction was completed, the reaction mixture was poured into water. The resulting precipitate was filtered, washed with water and dried. The residue was chromatographed on silica gel (toluene–acetic acid = 5 : 3 as eluent) to give **6a** (0.112 g, yield 60%) and **7a** (0.03 g, yield 16%); **6a**: mp 257–258 °C; IR (KBr): v = 3434, 2226, 1728 cm^{-1}; ^{1}H NMR (acetone-d$_6$, TMS) δ = 1.03 (3H, t), 1.27 (3H, t), 1.46–1.52 (2H, m), 1.70–1.75 (2H, m), 2.05–2.09 (2H, m) overlap peak of remaining acetone, 2.49–2.52 (2H, m), 3.52–3.61 (4H, m), 4.15–4.20 (2H, m), 7.09 (1H, dd, J = 2.44 and 9.04 Hz), 7.16 (1H, d, J = 2.44 Hz), 7.41–7.44 (1H, m), 7.51–7.55 (1H, m), 7.80 (1H, d,

J = 8.08 Hz), 8.06 (2H, d, J = 8.80 Hz), 8.50 (2H, d, J = 8.80 Hz), 8.55 (1H, d, J = 9.04 Hz), 8.71 (1H, d, J = 8.08 Hz), 11.52 (1H, s, –NH); elemental analysis calcd (%) for $C_{36}H_{32}N_4O_4$: C 73.95, H 5.52, N 9.58; found: C 74.12, H 5.24, N 9.38; **7a**: mp 267–269 °C; IR (KBr): v = 3276, 2230, 1702 cm^{-1}; ^{1}H NMR (acetone-d$_6$, TMS) δ = 1.03 (3H, t), 1.27 (3H, t), 1.46–1.52 (2H, m), 1.70–1.75 (2H, m), 2.05–2.09 (2H, m) overlap peak of remaining acetone, 2.48–2.52 (2H, m), 3.52–3.69 (4H, m), 4.14–4.20 (2H, m), 7.07 (1H, dd, J = 2.44 and 9.04 Hz), 7.18 (1H, d, J = 2.44 Hz), 7.42–7.46 (1H, m), 7.52–7.56 (1H, m), 7.77 (1H, d, J = 8.04 Hz), 8.07 (2H, d, J = 8.80 Hz), 8.49–8.53 (3H, m), 8.74 (1H, d, J = 8.08 Hz), 11.45 (1H, s, –NH); elemental analysis calcd (%) for $C_{36}H_{32}N_4O_4$: C 73.95, H 5.52, N 9.58; found: C 73.67, H 5.29, N 9.42.

Synthesis of ethoxycarbonylpropyl-{7-(4-cyanophenyl)benzofuro-[2,3-*c*]oxazolo-[4,5-*a*]carbazole}-3-aminobutyric acid ethyl ester (6b) and ethoxycarbonylpropyl-{7-(4-cyanophenyl)-benzofuro[2,3-*c*]oxazolo[5,4-*a*]carbazole}-3-aminobutyric acid ethyl ester (7b)

A solution of **5b** (0.20 g, 0.38 mmol), *p*-cyanobenzaldehyde (0.05 g, 0.38 mmol), and ammonium acetate (0.58 g, 7.54 mmol) in acetic acid (50 ml) was stirred at 90 °C for 1 h. After the reaction was completed, the reaction mixture was poured into water. The resulting precipitate was filtered, washed with water and dried. The residue was chromatographed on silica gel (toluene–acetic acid = 5 : 1 as eluent) to give **6b** (0.145 g, yield 60%) and **7b** (0.05 g, yield 21%); **6b**: mp 252–254 °C; IR (KBr): v = 3436, 2226, 1724 cm^{-1}; ^{1}H NMR (acetone-d$_6$, TMS) δ = 1.27 (6H, t), 2.01–2.06 (4H, m) overlap peak of remained acetone, 2.49–2.52 (4H, m), 3.58–3.62 (4H, m), 4.15–4.20 (4H, m), 7.16 (1H, dd, J = 2.44 and 9.04 Hz), 7.27 (1H, d, J = 2.44 Hz), 7.41–7.45 (1H, m), 7.51–7.55 (1H, m), 7.81 (1H, d, J = 8.32 Hz), 8.07 (2H, d, J = 8.80 Hz), 8.52 (2H, d, J = 8.80 Hz), 8.56 (1H, d, J = 9.04 Hz), 8.72 (1H, d, J = 7.80 Hz), 11.55 (1H, s, –NH); elemental analysis calcd (%) for $C_{38}H_{34}N_4O_6$: C 71.10, H 5.33, N 8.72; found: C 71.10, H 5.14, N 8.62; **7b**: mp 230–232 °C; IR (KBr): v = 3344, 2228, 1727 cm^{-1}; ^{1}H NMR (acetone-d$_6$, TMS) δ = 1.27 (6H, t), 2.02–2.10 (4H, m) overlap peak of remaining acetone, 2.48–2.52 (4H, m), 3.55–3.59 (4H, m), 4.15–4.20 (4H, m), 7.09 (1H, dd, J = 2.44 and 9.04 Hz), 7.22 (1H, d, J = 2.44 Hz), 7.41–7.44 (1H, m), 7.51–7.55 (1H, m), 7.74 (1H, d, J = 8.04 Hz), 8.00 (2H, d, J = 8.32 Hz), 8.39 (2H, d, J = 8.32 Hz), 8.47 (1H, d, J = 9.04 Hz), 8.70 (1H, d, J = 8.04 Hz), 11.55 (1H, s, –NH); elemental analysis calcd (%) for $C_{38}H_{34}N_4O_6$: C 71.10, H 5.33, N 8.72; found: C 71.26, H 5.14, N 8.48.

Synthesis of 7-(4-cyanophenyl)benzofuro[2,3-*c*]oxazolo[4,5-*a*]-carbazole-3-butylaminobutyric acid (8a)

To a solution of **6a** (0.10 g, 0.17 mmol) in ethanol (500 ml) was added dropwise aqueous NaOH (0.034 g, 0.86 mmol, 10 mL,) with stirring at 60 °C. After further stirring for 16 h under reflux, the solution was acidified to pH 4 with 2 M HCl, and concentrated under reduced pressure. The residue was dissolved in CH$_2$Cl$_2$, and washed with water. The organic extract was dried over MgSO$_4$, filtered, and concentrated. The residue was chromatographed on silica gel (CH$_2$Cl$_2$–ethyl acetate = 3 : 1 as eluent) to give **8a** (0.048 g, yield 49%); mp 269–271 °C; IR (KBr): v = 3235, 2223, 1704 cm^{-1}; ^{1}H NMR (acetone-d$_6$, TMS) δ = 1.03 (3H, t), 1.47–1.52 (2H, m), 1.72–1.76 (2H, m), 2.05–2.09 (2H, m) overlap peak of remained

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acetone, 2.49–2.53 (2H, m), 3.52–3.61 (4H, m), 7.11 (1H, dd, $J = 2.20$ and 9.04 Hz), 7.18 (1H, d, $J = 2.20$ Hz), 7.40–7.45 (1H, m), 7.51–7.55 (1H, m), 7.81 (1H, d, $J = 8.04$ Hz), 8.08 (2H, d, $J = 8.52$ Hz), 8.53 (2H, d, $J = 8.52$ Hz), 8.56 (1H, d, $J = 9.04$ Hz), 8.73 (1H, d, $J = 7.80$ Hz), 11.51 (1H, s, –NH); m/z (EI) 557 (M$^+$, 30%).

Synthesis of carboxypropyl-{7-(4-cyanophenyl)benzofuro[2,3-c]-oxazolo[4,5-a]carbazole)-3-aminobutyric acid (8b)

To a solution of **6b** (0.10 g, 0.16 mmol) in ethanol (500 ml) was added dropwise aqueous NaOH (0.062 g, 1.56 mmol, 20 mL,) with stirring at 60 °C. After further stirring for 22 h under reflux, the solution was acidified to pH 4 with 2 M HCl, and concentrated under reduced pressure. The residue was dissolved in CH$_2$Cl$_2$, and washed with water. The organic extract was dried over MgSO$_4$, filtered, and concentrated. The residue was chromatographed on silica gel (CH$_2$Cl$_2$–ethyl acetate = 3 : 1) to give **8b** (0.022 g, yield 23%); mp 259–261 °C; IR (KBr): $v = 3255, 2227, 1704$ cm^{-1}; ^{1}H NMR (DMSO-d$_6$, TMS) $\delta = 1.84$–1.89 (4H, m), 3.35–3.50 (4H, t) overlap peak of dissolved water in DMSO-d$_6$, 6.94–6.96 (4H, m), 7.06 (1H, dd, $J = 2.44$ and 9.04 Hz), 7.23 (1H, d, $J = 2.44$ Hz), 7.36–7.40 (1H, m), 7.48–7.52 (1H, m), 7.68 (1H, d, $J = 8.28$ Hz), 8.11 (2H, d, $J = 8.80$ Hz), 8.41 (2H, d, $J = 8.80$ Hz), 8.45 (1H, d, $J = 9.04$ Hz), 8.60 (1H, d, $J = 7.80$ Hz), 12.50 (1H, s, –NH); m/z (EI) 586 (M$^+$, 30%).

Computational methods

The semi-empirical calculations were carried out with the Win-MOPAC Ver. 3 package (Fujitsu, Chiba, Japan). Geometry calculations in the ground state were made using the AM1 method.[9] All geometries were completely optimized (keyword PRECISE) by the eigenvector following routine (keyword EF). Experimental absorption spectra of the eight compounds were compared with their absorption data by the semi-empirical method INDO/S (intermediate neglect of differential overlap/spectroscopic).[10] All INDO/S calculations were performed using single excitation full SCF/CI (self-consistent field/configuration interaction), which includes the configuration with one electron excited from any occupied orbital to any unoccupied orbital, where 225 configurations were considered [keyword CI (15 15)].

Preparation of the dye-sensitized solar cells based on benzofuro[2,3-c]oxazolo[4,5-a]carbazole-type fluorescent dyes

The TiO$_2$ electrodes used for dye-sensitized solar cells were prepared as follows. Into a powder (1.30 g) of TiO$_2$ (P-25, $d = 30$–40 nm) in mortar was added water (1.9 mL) in six portions with plenty of stirring. Then, three drops of 12 M nitric acid and polyethylene glycol (80 mg) were successively added, and the mixture was well-kneaded to a smooth paste. It was then applied to a fluorine-doped tin oxide (FTO) substrate and sintered for 30 min at 500 °C. The 7 µm thick TiO$_2$ electrode (0.5 × 0.5 cm^2 in the photoactive area) was immersed in a 0.3 mM tetrahydrofuran solution of the dye for a number of hours – long enough to adsorb the photosensitizer. The DSSCs were fabricated by using the TiO$_2$ electrode thus prepared, Pt-coated glass as a counter electrode, and a solution of 0.05 M iodine, 0.1 M lithium iodide,

and 1,2-dimethyl-3-n-propylimidazolium iodide in acetonitrile as electrolyte. The photocurrent–voltage characteristics were measured using a potentiostat under a simulated solar light (AM 1.5, 61 mW cm^{-2}). IPCE spectra were measured under monochromatic irradiation with a tungsten-halogen lamp and a monochromator. The dye-coated film was immersed in a solvent mixture of THF–DMSF–1 M NaOH aq (5 : 4 : 1), which was used to determine the amount of dye molecule adsorbed onto the film by measuring the absorbance. The quantification of each dye was made based on the λ_{max} and the molar extinction coefficient of each dye in the above solution. Absorption spectra of the dye-adsorbed TiO$_2$ films were measured in the diffuse-reflection mode by a JASCO UV-VIS spectrophotometer with a calibrated integrating sphere system ISV-469.

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