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#### **Donor-Acceptor Systems**



 $\mathsf{CH_3CN}\ \mathsf{CH_2Cl_2}\ \mathsf{CH_2Br_2}\ \mathsf{CH_2I_2}$  Specific solvatochromic D- $\pi$ -A dyes with a pyridinium ring as electron-withdrawing group, which can lead to a large bathochromic shift of absorption band in halo-

CH<sub>3</sub>CN CH<sub>2</sub>Cl<sub>2</sub> CH<sub>2</sub>Br<sub>2</sub> CH<sub>2</sub>l<sub>2</sub> genated solvents, have been developed and applied as a photosensitizers to dye-sensitized solar cells.

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Synthesis of Specific Solvatochromic D- $\pi$ -A Dyes with Pyridinium Ring as Electron-Withdrawing Group for Dye-Sensitized Solar Cells

Keywords: Donor-acceptor systems / Solar cells / Solvatochromism / Dyes/pigments / Sensitizers





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### Synthesis of Specific Solvatochromic D- $\pi$ -A Dyes with Pyridinium Ring as Electron-Withdrawing Group for Dye-Sensitized Solar Cells

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Keywords: Donor-acceptor systems / Solar cells / Solvatochromism / Dyes/pigments / Sensitizers

Specific solvatochromic D- $\pi$ -A-type pyridinium dyes were designed and developed as photosensitizers for dye-sensitized solar cells (DSSCs). The dyes have N-sulfobutylpyridinium or N-(carboxybutyl)pyridinium bromide as an electron-withdrawing anchoring group. The two dyes show specific solvatochromism, leading to a large bathochromic shift of the absorption band in halogenated solvents. Moreover, a dye-adsorbed TiO<sub>2</sub> film immersed into halogenated solvents exhibits specific solvatochromism, as does a dye solution of halogenated solvents. DSSCs based on specific solvatochromic D- $\pi$ -A-type pyridinium dyes and halogenated solvents as elec-

#### Introduction

Dye-sensitized solar cells (DSSCs) based on dye-adsorbed TiO<sub>2</sub> electrodes have gained increasing attention from chemists, physicists, and engineers because of enormous scientific interest in not only their construction and operational principles, but also in their high incident-solarlight-to-electricity conversion efficiency and low cost of production.<sup>[1–5]</sup> To develop high-performance DSSCs, many kinds of ruthenium (Ru) complex dyes and organic dyes have been designed and developed. Consequently, DSSCs have achieved solar energy-to-electricity conversion yields (*n*) of up to 12%.<sup>[6]</sup> To obtain further new and efficient dve sensitizers for DSSCs, novel molecular designs are required to fully utilize the photophysical and electrochemical characteristics of the dyes themselves, and also form effective interactions between dyes and TiO2 surface and between dyes and electrolyte solution. For this purpose, we focused on the solvatochromism of organic dyes. Some organic dyes show positive solvatochromism (i.e., bathochromic shift of

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trolyte solvent were prepared and their photovoltaic performance investigated. It was found that the appropriate combination of solvatochromic dyes with electrolyte solution and the effective interaction between solvatochromic dyes and  $TiO_2$  surface can lead to not only an enhancement of lightharvesting efficiency (LHE), but also efficient electron injection from the dye to the conduction band (CB) of  $TiO_2$ . This work demonstrates that the solvatochromism of organic dyes is a key consideration for high-performance DSSCs based on organic dye sensitizers.

the absorption band with increasing solvent polarity) or negative solvatochromism (i.e., hypsochromic shift of absorption band with increasing solvent polarity).<sup>[7]</sup> Among the various types of solvatochromic dyes, donor- $\pi$ -acceptor  $(D-\pi-A)$  type pyridinium dyes having a diphenyl- or dialkylamino group as electron donor and a pyridinium ring as electron acceptor linked by a  $\pi$ -conjugated bridge are well known to show negative solvatochromism.<sup>[8-11]</sup> On the other hand, we have mentioned the specific solvatochromism of D- $\pi$ -A-type pyridinium dyes, leading to a large bathochromic shift of the absorption band in halogenated solvents; the bathochromic shifts of the intramolecular chargetransfer (ICT) absorption band in halogenated solvents are larger than those in nonhalogenated solvents of similar solvent polarity. We have demonstrated that the enhanced ICT characteristics of the D-π-A pyridinium dye in halogenated solvents are responsible for the large bathochromic shifts of the ICT band in halogenated solvents.<sup>[11]</sup>

In this work, to utilize the solvatochromic characteristics of a D- $\pi$ -A-type pyridinium dye, we prepared DSSCs based on newly synthesized D- $\pi$ -A-type pyridinium dyes (**OD5** and **OD6**) and electrolyte solutions of halogenated solvents (Scheme 1). The dyes **OD5** and **OD6** have *N*-(sulfobutyl)pyridinium and *N*-(carboxybutyl)pyridinium bromide, respectively, as an electron-withdrawing anchoring group. It was found that dye-adsorbed TiO<sub>2</sub> films immersed into halogenated solvents exhibit specific solvatochromism, as does a dye solution of halogenated solvents. Here, we report the impact of specific solvatochromic characteristics of D- $\pi$ -A-type pyridinium dyes on the photovoltaic performance

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Scheme 1. Synthesis of D- $\pi$ -A-type pyridinium dyes OD5 and OD6.

of DSSCs and demonstrate that the solvatochromism of organic dyes is one of the most important factors for highperformance DSSCs based on organic dye sensitizers.

#### **Results and Discussion**

#### Synthesis of D- $\pi$ -A-Type Pyridinium Dyes OD5 and OD6

The D- $\pi$ -A-type pyridinium dyes **OD5** and **OD6** were synthesized from diphenyl{7-[5-(pyridin-4-yl)thiophen-2-yl]-9*H*-carbazol-2-yl}amine (1)<sup>[12]</sup> and 1,4-butanesultone or 5-bromopentanoic acid (Scheme 1).

#### Photoabsorption Properties of OD5 and OD6 in Solution

The absorption spectra of OD5 and OD6 in various solvents are shown in Figure 1, and their spectroscopic data are summarized in Table 1. The two dyes show absorption maxima at around 435-495 nm, which are assigned to the ICT excitation from the electron-donor moiety (diphenylamino group) to the electron-acceptor moiety (pyridinium ring). The ICT absorption bands of the two dyes exhibit a general negative solvatochromism in nonhalogenated solvents (Figure 1a and b); with increasing solvent polarity from 1,4-dioxane [dielectric constant ( $\varepsilon_r$ ) = 2.22] to acetonitrile (MeCN,  $\varepsilon_r = 36.64$ ), for example, the ICT absorption band of **OD6** shows a hypsochromic shift from 470 to 440 nm. On the other hand, the two dyes showed specific solvatochromism, leading to a large bathochromic shift of the ICT absorption band in halogenated solvents; although the  $\varepsilon_r$  value ( $\varepsilon_r = 7.77$ ) of dibromomethane (DBM) is very close to that of tetrahydrofuran (THF;  $\varepsilon_r$  = 7.52), the ICT absorption bands of OD5 and OD6 in DBM show bathochromic shifts of 35 and 19 nm, respectively, compared with those in THF. It is noteworthy that the bathochromic shifts of the ICT band in diiodomethane (DIM) are larger than those in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) and

DBM. Moreover, as shown in Figure 1c and d, the ICT absorption bands in the mixed solvents of MeCN and halogenated solvent ( $CH_2Cl_2$ , DBM and DIM) are still redshifted compared with that in MeCN, although the ICT



Figure 1. Absorption spectra of (a) **OD5** and (b) **OD6** in various solvents and absorption spectra of (c) **OD5** and (d) **OD6** in mixed solvents of acetonitrile and halogenated solvent.

Table 1. Solvatochromic spectroscopic data of OD5 and OD6.

$\lambda_{\max}^{abs}[nm] (\epsilon [M^{-1} cm^{-1}])$	
OD5	OD6
454 (- <sup>[b]</sup> )	470 (- <sup>[b]</sup> )
444 (- <sup>[b]</sup> )	461 (- <sup>[b]</sup> )
437 (27100)	440 (22700)
471 (27000)	474 (19300)
479 (27200)	480 (18100)
484 (- <sup>[b]</sup> )	493 (- <sup>[b]</sup> )
454 (27900)	454 (22900)
460 (28000)	460 (21700)
463 (- <sup>[b]</sup> )	463 (- <sup>[b]</sup> )
	$\begin{array}{c} \lambda_{\max}^{abs}[nm] \\ \hline \textbf{OD5} \\ \hline 454 \; (-^{[b]}) \\ 444 \; (-^{[b]}) \\ 437 \; (27100) \\ 471 \; (27000) \\ 479 \; (27200) \\ 484 \; (-^{[b]}) \\ 454 \; (27900) \\ 460 \; (28000) \\ 463 \; (-^{[b]}) \end{array}$

[a] Acetonitrile (MeCN), dibromomethane (DBM) and diiodomethane (DIM). Solvent ratios given in v/v. [b] Poorly soluble. FULL PAPER

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absorption bands are blueshifted compared with those in pure halogenated solvents (Table 1).

#### Semiempirical MO Calculations (AM1, INDO/S)

The photophysical properties of **OD5** and **OD6** were analyzed by using semiempirical molecular orbital (MO) calculations. The molecular structures were optimized by using the MOPAC/AM1 method,<sup>[13]</sup> and then the INDO/S method.<sup>[14]</sup> The MO calculations reveal that the longestwavelength excitation bands are mainly attributable to the transition from HOMO to LUMO, and for both **OD5** and **OD6** the HOMO is mostly localized on the diphenylamino group, whereas the LUMO is mostly localized on the pyridinium ring (Figure 2a and b). The changes in the calculated electron density accompanied by the first electron excitations for the two dyes reveal a strong ICT nature from the diphenylamino group to the pyridinium ring upon photoexcitation (Figure 2c).



Figure 2. (a) HOMO and (b) LUMO of **OD5** (above) and **OD6** (below). The red and blue lobes denote the positive and negative phases, respectively, of the coefficients of the MOs. The size of each lobe is proportional to the MO coefficient. (c) Calculated electrondensity changes accompanying the first electronic excitation of **OD5** (top) and **OD6** (bottom). The black and white lobes signify the decrease and increase in electron density accompanying the electronic transition, respectively. Their areas indicate the magnitude of the electron-density change. Light-blue, green, blue, and red spheres correspond to hydrogen, carbon, nitrogen, and oxygen atoms, respectively.

#### **Electrochemical Properties of OD5 and OD6**

The electrochemical properties of OD5 and OD6 were determined by cyclic voltammetry (CV) in acetonitrile containing 0.1 M tetrabutylammonium perchlorate (Bu<sub>4</sub>N-ClO<sub>4</sub>). The potentials were referenced to internal ferrocene/ ferrocenium ( $Fc/Fc^+$ ) (Figure 3). The oxidation peaks for OD5 and OD6 were observed at 0.50 and 0.53 V vs. ferrocene/ferrocenium (Fc/Fc<sup>+</sup>), respectively. The corresponding reduction peaks for **OD5** and **OD6** appeared at 0.42 and 0.46 V, respectively, thus showing that the oxidized states of the two dyes are stable. The HOMO energy levels of the two dyes were evaluated from the half-wave potential for oxidation  $(E_{1/2}^{\text{ox}} = 0.46 \text{ and } 0.50 \text{ V} \text{ for OD5 and OD6},$ respectively). The HOMO energy levels for OD5 and OD6 were 1.09 and 1.13 V vs. the normal hydrogen electrode (NHE), respectively, thus indicating that the HOMO energy levels are more positive than the  $I_3^{-}/I^{-}$  redox potential (0.4 V). This assures an efficient regeneration of the oxidized dyes by electron transfer from the  $I_3^{-}/I^{-}$  redox couple

in the electrolyte. The LUMO energy levels of the two dyes were estimated from the  $E_{1/2}^{\text{ox}}$  and the onset of the absorption band in acetonitrile (530 nm; 2.34 eV for both **OD5** and **OD6**). The LUMO energy levels for **OD5** and **OD6** were -1.25 and -1.21 V, respectively. Evidently, the LUMO energy levels are higher than the energy level of the conduction band (CB) of TiO<sub>2</sub> (-0.5 V), suggesting that an electron injection to the CB of TiO<sub>2</sub> is thermodynamically feasible.



Figure 3. Cyclic voltammograms of (a) **OD5** and (b) **OD6** in acetonitrile containing 0.1  $\times$  Bu<sub>4</sub>NClO<sub>4</sub> at a scan rate of 100 mV s<sup>-1</sup>. The arrow denotes the direction of the potential scan.

## Photoabsorption Properties of OD5 and OD6 Adsorbed on TiO<sub>2</sub> Nanoparticles

The absorption spectra of dye-adsorbed TiO<sub>2</sub> films in air (no solvent) and immersed in solvents are shown in Figure 4. For both OD5 and OD6, the absorption bands of the dye-adsorbed TiO<sub>2</sub> film in air and immersed in MeCN appear in almost the same wavelength region as those of the two dyes in MeCN, but are blueshifted by ca. 25 nm, compared with those of the two dyes in THF (Figure 1a and b). The blueshifts of the absorption bands for the dye-adsorbed TiO<sub>2</sub> films relative to dye solutions may be attributed to the high polarity of the TiO<sub>2</sub> surface. It was found that the dyeadsorbed TiO<sub>2</sub> films immersed in mixed solvents of MeCN and halogenated solvent (CH<sub>2</sub>Cl<sub>2</sub>, DBM and DIM) exhibit specific solvatochromism; the absorption bands of dye-adsorbed TiO<sub>2</sub> films in the mixed solvents are still redshifted compared with those immersed in MeCN, as are the the absorption spectra of the dye solutions (Figure 1). For the dye OD5 immersed in MeCN/DIM, the absorption maximum was slightly redshifted compared with those of dyes immersed in other mixed solvents. These results indicate that the light-harvesting efficiency (LHE) of the dye-adsorbed TiO<sub>2</sub> film can be controlled by appropriate combination of solvatochromic dyes and electrolyte solutions for



Solvatochromic D-π-A Dyes

DSSCs; for example, positive solvatochromic dyes are advantageous to the bathochromic shift of the absorption band of the dye-adsorbed  $TiO_2$  film, because the  $TiO_2$  surface has a high polarity, as well as polar solvents such as MeCN, which is usually used to dissolve the electrolyte (iodine, lithium iodide, and imidazolium salt) for DSSCs.



Figure 4. Absorption spectra of (a) **OD5** and (b) **OD6** adsorbed on  $TiO_2$  film (9  $\mu$ m) in air (no solvent) and immersed in acetonitrile or mixed solvents of acetonitrile and halogenated solvent.

# FTIR Spectra of OD5 and OD6 Adsorbed on TiO<sub>2</sub> Nanoparticles

To elucidate the adsorption states of dyes OD5 and OD6 on TiO<sub>2</sub> nanoparticles, we measured the FTIR spectra of the dye powders and the dyes adsorbed on TiO<sub>2</sub> nanoparticles (Figure 5). For powders of OD5, the S=O stretching vibrations of the sulfonate group were observed at 1170 and  $1050 \text{ cm}^{-1}$ . On the other hand, for powders of **OD6**, the C=O stretching vibration of the carboxy group was observed at 1715 cm<sup>-1</sup>. When dye **OD5** was adsorbed on the TiO<sub>2</sub> surface, the S=O stretching vibrations weakened significantly; this suggests the formation of a bidentate bridging linkage between the sulfonate group of the dye and Lewis acid sites (exposed  $Ti^{n+}$  cations) on the  $TiO_2$  surface.<sup>[15,16]</sup> On the other hand, when **OD6** was adsorbed on the TiO<sub>2</sub> surface, the C=O stretching vibration of the carboxy group disappeared; this indicates the formation of a bidentate bridging linkage between the carboxy group of the dye and Brønsted acid sites (surface-bound hydroxy groups, Ti-OH) on the TiO2 surface. These observations indicate that OD5 is adsorbed on the TiO2 surface through

bidentate bridging linkages at Lewis acid sites on the  $TiO_2$  surface, whereas **OD6** is adsorbed on the  $TiO_2$  surface through bidentate bridging linkages at Brønsted acid sites.

## Photovoltaic Performance of DSSCs Based on OD5 and OD6

The DSSCs were prepared by using the dye-adsorbed TiO<sub>2</sub> electrode, Pt-coated glass as a counter electrode, and a solution containing iodine (0.05 M), lithium iodide (0.1 M), and 1,2-dimethyl-3-propylimidazolium iodide (0.6 M) as electrolyte, in which MeCN or the mixed solvent of MeCN and halogenated solvent (CH<sub>2</sub>Cl<sub>2</sub>, DBM and DIM) was used to dissolve the electrolyte. The photocurrent–voltage (*I–V*) characteristics were measured under simulated solar light (AM 1.5, 100 mW cm<sup>-2</sup>). The incident-photon-to-current conversion efficiency (IPCE) spectra and the *I–V* curves are shown in Figures 6 and 7, respectively. The pho-



Figure 6. IPCE spectra of DSSCs based on (a) **OD5** and (b) **OD6** employing various electrolyte solutions.



Figure 5. FTIR spectra of the dye powders and dyes adsorbed on  $TiO_2$  nanoparticles for (a) OD5 and (b) OD6.

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tovoltaic performance parameters are collected in Table 2. Overall, the maximum IPCE, the short-circuit photocurrent density  $(J_{sc})$ , and  $\eta$  for **OD5** are higher than those for **OD6**. The superior photovoltaic performance of OD5 may be attributed to efficient electron injection by the formation of the bidentate bridging linkage between the sulfonate group of the dye and the Lewis acid sites on the TiO<sub>2</sub> surface. For both OD5 and OD6, it is worth mentioning that the IPCE maxima for DSSCs based on the electrolyte solution of MeCN/DIM are redshifted compared with those of the other mixed solvents, which reflects the results of the absorption spectra of the dye-adsorbed TiO<sub>2</sub> film immersed in the mixed solvents, although the maximum IPCE, the  $J_{\rm sc}$ , and the  $\eta$  values are the lowest of the electrolyte solutions used. Interestingly, the open-circuit photovoltage  $(V_{oc})$ for DSSCs based on the electrolyte solution of MeCNe/ DBM is higher than those of the other mixed solvents. The IPCE value of DSSC based on OD5 employing the electrolyte solution of MeCN/CH<sub>2</sub>Cl<sub>2</sub> exceeds 80% in the range



Figure 7. I-V curves of DSSCs based on (a) **OD5** and (b) **OD6** employing various electrolyte solutions.

Table 2. DSSC performance parameters of OD5 and OD6.[a]

Dye	Electrolyte <sup>[b]</sup>	$J_{ m sc}$ [mA cm <sup>-2</sup> ]	V <sub>oc</sub> [mV]	ff	η [%]
OD5	MeCN	5.52	552	0.63	1.93
	MeCN/CH2Cl2[b]	6.64	528	0.63	2.21
	MeCN/DBM <sup>[b]</sup>	6.08	660	0.59	2.36
	MeCN/DIM <sup>[b]</sup>	4.26	464	0.59	1.17
OD6	MeCN	4.54	468	0.66	1.41
	MeCN/CH2Cl2[b]	5.20	488	0.61	1.56
	MeCN/DBM <sup>[b]</sup>	5.16	625	0.59	1.90
	MeCN/DIM <sup>[b]</sup>	4.20	433	0.60	1.09

[a] The photovoltaic performance of DSSCs based on the adsorption amount per unit area of the TiO<sub>2</sub> electrode is ca. 9.68-9.87 molecules cm<sup>-2</sup> under simulated solar light (AM 1.5, 100 mW cm<sup>-2</sup>). [b] Ratio 1:1 (v/v).

of 410–515 nm, which is higher than those of DSSCs based on the other electrolyte solutions (Figure 6a). The  $J_{sc}$  and  $\eta$  values were 6.64 mA cm<sup>-2</sup> and 2.21%, respectively (Figure 7a and Table 2). The higher photovoltaic performance of DSSCs based on the electrolyte solution of halogenated solvents relative to commonly used MeCN are attributed to the enhanced ICT characteristics of the D- $\pi$ -A pyridinium dyes in halogenated solvents, leading to efficient electron injection from the dye to the CB of TiO<sub>2</sub>.

#### Conclusions

To assess the impact of solvatochromic characteristics of dye sensitizers on the photovoltaic performance of DSSCs, we have designed and synthesized the specific solvatochromic D- $\pi$ -A-type dyes **OD5** and **OD6**, which have N-(sulfobutyl)pyridinium and N-(carboxybutyl)pyridinium bromide, respectively, as an electron-withdrawing anchoring group. The DSSCs based on specific solvatochromic D- $\pi$ -A-type pyridinium dyes and halogenated solvents as electrolyte solvent were prepared and their photovoltaic performances investigated. It was found that the appropriate combination of solvatochromic dye with electrolyte solution and the effective interaction between solvatochromic dye and TiO<sub>2</sub> surface can lead to not only an enhancement of LHE, but also efficient electron injection from the dye to the CB of TiO<sub>2</sub>. Thus, we demonstrate that the solvatochromism of organic dyes is a key consideration for high-performance DSSCs based on organic dye sensitizers. Further studies on the design and development of efficient solvatochromic dyes for high-performance DSSCs are in progress, and we hope to gain greater insight into the impact of solvatochromic characteristics of dye sensitizers on the photovoltaic performance of DSSCs.

#### **Experimental Section**

**General:** IR spectra were recorded with a Perkin–Elmer Spectrum One FTIR spectrometer by using the ATR method. High-resolution mass spectrometric data were acquired with a Thermo Fisher Scientific LTQ Orbitrap XL. <sup>1</sup>H NMR spectra were recorded with a Varian-400 (400 MHz) FT NMR spectrometer. Absorption spectra were recorded with a Hitachi U-2910 spectrophotometer. Cyclic voltammetry (CV) curves were recorded in acetonitrile/Bu<sub>4</sub>NClO<sub>4</sub> (0.1 M) solution with a three-electrode system consisting of Ag/Ag<sup>+</sup> as reference electrode, Pt plate as working electrode, and Pt wire as counter electrode, by using an AMETEK Versa STAT 4 potentiostat. The HOMO and LUMO energy levels of **OD5** and **OD6** were evaluated from spectral analyses and the CV data. HOMO energy levels were evaluated from  $E_{1/2}^{\text{ox}}$ . LUMO energy levels were estimated from  $E_{1/2}^{\text{ox}}$  and an onset of the absorption band (530 nm; 2.34 eV for both **OD5** and **OD6**).

**4-{4-[9-Butyl-7-(diphenylamino)-9***H***-carbazol-2-yl]pyridin-1-ium-1-yl} Butane-1-sulfonate (OD5):** A solution of  $1^{[12]}$  (0.35 g, 0.75 mmol) and 1,4-butanesultone (1.0 g, 7.3 mmol) in anhydrous toluene (20 mL) was stirred at 100 °C for 4 d. The resultant precipitate was washed with diethyl ether to give **OD5** (0.16 g, 33%) as a yellow solid. IR (ATR):  $\tilde{v} = 16214$ , 1177, 1035 cm<sup>-1</sup>. <sup>1</sup>H NMR

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(400 MHz, [D<sub>6</sub>]DMSO):  $\delta = 0.78$  (t, J = 7.2 Hz, 3 H), 1.15–1.21 (m, 2 H), 1.59–1.68 (m, 4 H), 2.00–2.06 (m, 2 H), 3.2–3.4 (m, 2 H, overlapping peak of dissolved water in [D<sub>6</sub>]DMSO), 4.35 (t, J = 7.2 Hz, 2 H), 4.59 (t, J = 6.8 Hz, 2 H), 6.88 (d, J = 6.8 Hz, 1 H), 7.05–7.09 (m, 6 H), 7.15 (s, 1 H), 7.31–7.35 (m, 4 H), 7.90 (d, J = 8.4 Hz, 1 H), 8.13 (d, J = 8.4 Hz, 1 H), 8.26 (d, J = 8.4 Hz, 1 H), 8.35 (s, 1 H), 8.66 (d, J = 6.8 Hz, 2 H), 9.07 (d, J = 6.8 Hz, 2 H) ppm. HRMS (ESI): calcd. for C<sub>37</sub>H<sub>37</sub>N<sub>3</sub>O<sub>3</sub>SNa [M + Na<sup>+</sup>] 626.24478; found 626.24469.

4-[9-Butyl-7-(diphenylamino)-9H-carbazol-2-yl]-1-(4-carboxybutyl)pyridin-1-ium Bromide (OD6): A solution of 1<sup>[12]</sup> (0.10 g, 0.21 mmol) and 5-bromopentanoic acid (0.038 g, 0.21 mmol) in anhydrous DMF (20 mL) was stirred at 90 °C for 3 h. After concentrating under reduced pressure, the resulting residue was washed with acetone and then toluene to give OD6 (0.012 g, 9%) as a yellow solid. IR (ATR):  $\tilde{v} = 1715$ , 1620 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz,  $[D_6]DMSO$ :  $\delta = 0.78$  (t, J = 7.6 Hz, 3 H), 1.15–1.21 (m, 2 H), 1.51-1.55 (m, 2 H), 1.64-1.68 (m, 2 H), 1.94-1.99 (m, 2 H), 2.30 (t, J = 7.2 Hz, 2 H), 4.36 (t, J = 7.2 Hz, 2 H), 4.58 (t, J = 6.8 Hz, 2 H), 6.89 (dd, J = 2.0, 8.4 Hz, 1 H), 7.05–7.09 (m, 6 H), 7.15 (d, J = 2.0 Hz, 1 H), 7.30–7.35 (m, 4 H), 7.91 (dd, J = 1.6, 8.4 Hz, 1 H), 8.14 (d, J = 8.8 Hz, 1 H), 8.26 (d, J = 8.0 Hz, 1 H), 8.35 (s, 1 H), 8.67 (d, J = 7.2 Hz, 2 H), 9.07 (d, J = 7.2 Hz, 2 H), 12.14 (s, 1 H) ppm. HRMS (ESI): calcd. for  $C_{38}H_{38}N_3O_2$  [M - Br]<sup>+</sup> 568.29585; found 568.29596.

**Computational Methods:** Semiempirical calculations were carried out with the WinMOPAC (Ver. 3.9) package (Fujitsu, Chiba, Japan). Geometry calculations in the ground state were made by using the AM1 method.<sup>[13]</sup> All geometries were completely optimized (keyword PRECISE) by the eigenvector-following routine (keyword EF). HOMO and LUMO of the compounds were evaluated from INDO/S calculations.<sup>[14]</sup> All INDO/S calculations were performed by using single excitation full SCF/CI (self-consistent field/configuration interaction), which included the configuration with one electron excited from any occupied orbital to any unoccupied orbital, where 225 configurations were considered [keyword CI (15 15)].

Fabrication of the Dye-Sensitized Solar Cells Based on Dyes OD5 and OD6: TiO<sub>2</sub> paste (JGC Catalysts and Chemicals Ltd., PST-18NR) was deposited on a fluorine-doped-tin-oxide (FTO) substrate by doctor-blading, and sintered at 450 °C for 50 min. The 9 µm thick TiO<sub>2</sub> electrode ( $0.5 \times 0.5$  cm<sup>2</sup> in photoactive area) was immersed into a 0.05 mM dye solution in dichloromethane for sufficient time to allow the electrode to adsorb the photosensitizer. The DSSCs were fabricated by using the TiO<sub>2</sub> electrode thus prepared, Pt-coated glass as a counter electrode, and a solution of 0.05 M iodine, 0.1 M lithium iodide, and 0.6 M 1,2-dimethyl-3-propylimidazolium iodide in acetonitrile, dichloromethane/acetonitrile, dibromomethane/acetonitrile, or diiodomethane/acetonitrile as electrolyte. The photocurrent-voltage characteristics were measured by using a potentiostat under simulated solar light (AM 1.5, 100 mW cm<sup>-2</sup>). IPCE spectra were measured under monochromatic irradiation with a tungsten-halogen lamp and a monochromator. The amount of adsorbed dye on TiO<sub>2</sub> nanoparticles was determined by absorption spectral measurement of the concentration change of the dye solution before and after adsorption. Absorption spectra of the dyes adsorbed on TiO<sub>2</sub> nanoparticles were recorded

on the dye-adsorbed  $TiO_2$  film in the transmission mode with a calibrated integrating sphere system.

**Supporting Information** (see footnote on the first page of this article): Copies of <sup>1</sup>H NMR spectra for **OD5** and **OD6**.

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