

Dye-Sensitized Solar Cells Based on D- π -A Fluorescent Dyes with Pyridine Ring Forming Strong Interaction with Nanocrystalline TiO₂

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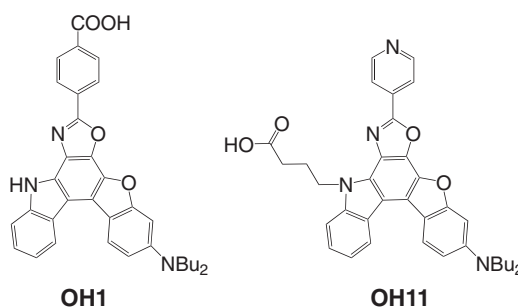
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New-type donor-acceptor π -conjugated (D- π -A) fluorescent dyes **OH11**, **OH14**, and **OH15** with pyridine, 4-phenylpyridine, and quinoline rings, respectively, as electron-accepting groups have been developed and their photovoltaic performance as dye-sensitized solar cells (DSSCs) are investigated. The short-circuit photocurrent densities (J_{sc}) of DSSCs using **OH11**, **OH14**, and **OH15** are 4.88, 3.91, and 1.72 mA cm⁻², and the solar energy-to-electricity conversion yields (η) are 1.62, 1.30, and 0.56%, respectively, under a simulated solar light (AM 1.5, 100 mW cm⁻²). The IR spectra of **OH11** and **OH14** adsorbed on TiO₂ indicate the formation of hydrogen bonding between the pyridine ring of dyes and the hydroxy group of TiO₂ surface and the formation of strong coordinate bonding between the pyridine ring of dyes and the Lewis acid site of TiO₂ surface. On the other hand, in the IR spectra of **OH15** adsorbed on TiO₂, only the formation of weak hydrogen bonding was observed. This work suggests that the pyridine rings forming a strong coordinate bonding with the Lewis acid site of TiO₂ surface are promising candidates as electron-accepting groups of new D- π -A dye sensitizers for DSSCs.

Donor-acceptor π -conjugated (D- π -A) dyes which have both the electron-donating (D) and electron-accepting (A) groups linked by a π -conjugated bridge, are one of the most promising organic sensitizers in dye-sensitized solar cells (DSSCs). Most of the D- π -A dyes such as coumarin dyes,¹ polyene dyes,² thiophene dyes,³ and indoline dyes⁴ have dialkylamine or diphenylamine moiety as electron donor, and carboxylic acid, cyanoacrylic acid, or rhodanine-3-acetic acid moiety which acts as electron acceptor as well as anchoring group for attachment on a TiO₂ surface. The carboxyl group can form an ester linkage with a TiO₂ surface to provide a strongly bound dye and good electron communication between them.

On the other hand, in our previous study, a novel fluorescent dye **OH11** with pyridine ring as an electron-accepting group, as a new D- π -A dye sensitizer, has been designed and synthesized (Scheme 1).⁵ The dye **OH11** has a non-conjugated alkyl chain containing a carboxyl group at the end position, so that the carboxyl group as an anchoring group is separated from the electron acceptor moiety. The photovoltaic performance of **OH11** is similar to that of **OH1** having a carboxyl group acting as not only anchoring group for attachment on TiO₂ surface but also the electron acceptor. It was suggested that the pyridine ring acting as electron acceptor is located in close proximity to the TiO₂ surface by the formation of a strong interaction such as the hydrogen bonding between the pyridine ring of **OH11** and the TiO₂ surface. Consequently, the dye **OH11** can inject efficiently electrons from the pyridine ring to the conduction band of TiO₂ electrode through their electronic interaction. However, it is necessary to give reliable evidence for the interaction between the pyridine ring of dye and the TiO₂ surface.

Therefore, in order to provide further confirmation for the effects of the interaction between the pyridine ring and the TiO₂ surface on the photovoltaic performances of DSSCs, we have

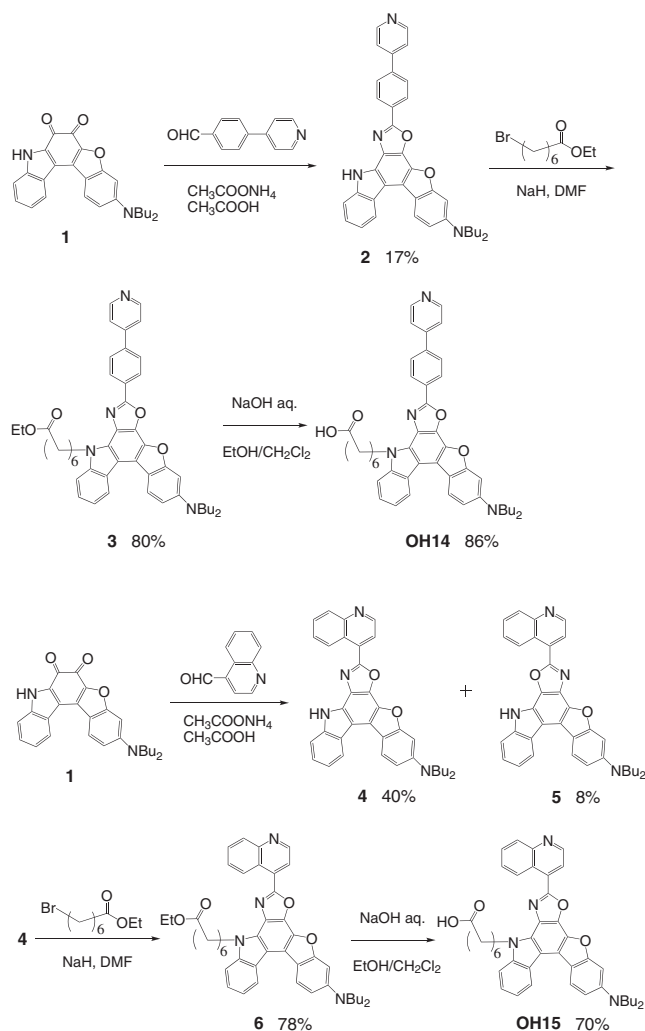


Scheme 1. Chemical structures of fluorescent dyes **OH1** and **OH11**.

designed and synthesized new D- π -A fluorescent dyes **OH14** and **OH15** with 4-phenylpyridine and quinoline rings, respectively, as electron-accepting groups. Similarly to **OH11**, the two dyes have a non-conjugated alkyl chain containing a carboxyl group as an anchoring group at the end position. In this paper, on the basis of the IR spectra of the dyes adsorbed on TiO₂ particles, it was demonstrated that the dyes **OH11** and **OH14** can inject electrons efficiently from the pyridine ring to the conduction band of the TiO₂ electrode through the strong coordinate bonding rather than the hydrogen bonding between the pyridine ring of dye and the TiO₂ surface.

Results and Discussion

Synthesis of D- π -A Fluorescent Dyes OH11, OH14, and OH15. As shown in Scheme 2, 3-dibutylaminobenzofuro[2,3-*c*]-6,7-carbazoledione (**1**)¹⁰ was used as a starting material. The reaction of quinone **1** with 4-(4-pyridinyl)benzaldehyde in the presence of ammonium acetate gave the dye **2**. On the other hand, the quinone **1** was allowed to react with 4-quinoline-



carboxaldehyde in the presence of ammonium acetate to give the structural isomers of **4** and **5**. The reaction of **2** and **4** with ethyl 7-bromoheptanoate using sodium hydride yielded **3** and **6**, respectively. The D- π -A fluorescent dyes **OH14** and **OH15** were obtained by hydrolysis of **3** and **6**, respectively.

Spectroscopic Properties of OH11, OH14, and OH15 in Solution and Adsorbed on TiO₂ Particles. The absorption and fluorescence spectra of **OH11**, **OH14**, and **OH15** in THF are shown in Figure 1 and their spectral data are summarized in Table 1. The three dyes show two absorption maxima: a sharp band at 350 nm is ascribable to $\pi \rightarrow \pi^*$ transition and another band at 410–450 nm to intramolecular charge transfer (ICT) excitation from the dibutylamino group to pyridine ring for **OH11**, to phenylpyridine for **OH14**, and to the quinoline ring for **OH15**. The ICT band of **OH15** occurs at a longer wavelength than those of **OH11** and **OH14**. The corresponding fluorescence bands for **OH11**, **OH14**, and **OH15** are observed at around 533, 556, and 593 nm, respectively. The fluorescence quantum yield increases in the order of **OH14** ($\Phi_F = 0.55$) < **OH15** ($\Phi_F = 0.61$) < **OH11** ($\Phi_F = 0.86$).

Absorption spectra of the dyes adsorbed on TiO₂ particles are shown in Figure 2. The absorption peak wavelengths are red-shifted by 38 nm for **OH11**, 38 nm for **OH14**, and 40 nm

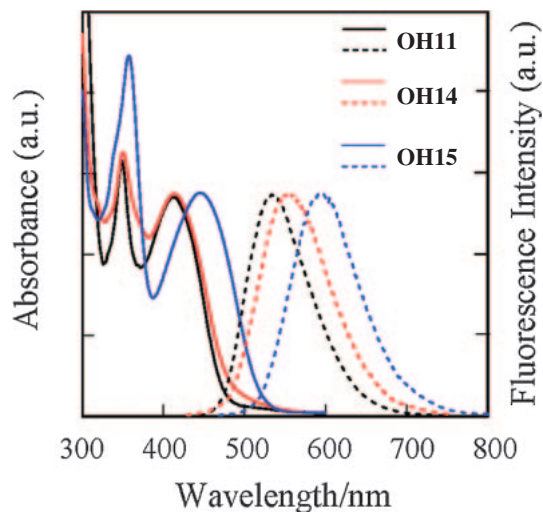


Figure 1. Absorption (—) and fluorescence (···) spectra of **OH11**, **OH14**, and **OH15** in THF.

Table 1. Spectroscopic Properties of **OH11**, **OH14**, and **OH15** in THF

Dye	$\lambda_{\max}^{\text{abs}}/\text{nm}$ ($\epsilon_{\max}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)	$\lambda_{\max}^{\text{fl}}/\text{nm}$	$\Phi_F^{\text{a)}$	SS ^{b)} /nm
OH11	349 (31000), 412 (26600)	533	0.86	121
OH14	350 (24200), 413 (20400)	556	0.55	143
OH15	358 (21500), 446 (13300)	593	0.61	147

a) The Φ values were determined by using a calibrated integrating sphere system ($\lambda_{\text{ex}} = 325 \text{ nm}$). b) Stokes shift value.

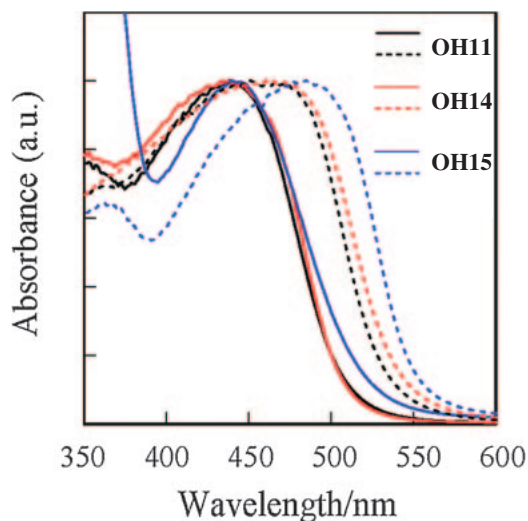


Figure 2. Absorption spectra of **OH11**, **OH14**, and **OH15** adsorbed on TiO₂ particles with CDCA (—) and without CDCA (···) as coadsorbent.

for **OH15** compared with those in THF. Chenodeoxycholic acid (CDCA) has been employed as coadsorbent to prevent dye aggregation on the TiO₂ surface. When CDCA is coadsorbed with **OH11** and **OH14** on TiO₂, the absorption peak wavelengths are blue-shifted by 8 nm for **OH11** and 16 nm for **OH14**, compared to without CDCA. The peak wavelengths are

still red-shifted compared with those in THF. In contrast, the absorption peak wavelength of **OH15** adsorbed on TiO_2 with coadsorption of CDCA is similar to that in THF. These results show that the red-shiftings of **OH11** and **OH14** by adsorption on TiO_2 are due to the interaction between the dye and TiO_2 surface, which will be discussed later again along with the IR spectra of the dyes adsorbed on TiO_2 .

IR Spectra of OH11, OH14, and OH15 Adsorbed on TiO_2 Particles. Figure 3 shows the FT-IR spectra of the dye powders and the dyes adsorbed on TiO_2 . For the dye powder, the C=O stretching band of carboxyl group was observed at 1711 cm^{-1} for **OH11**, 1719 cm^{-1} for **OH14**, and 1710 cm^{-1} for **OH15**, and the C=N or C=C stretching band due to the oxazole ring was observed at 1634 and 1622 cm^{-1} for **OH11**, 1623 cm^{-1} for **OH14**, and 1623 cm^{-1} for **OH15**. The characteristic stretching bands for the C=N or C=C of pyridine moiety were clearly observed at 1607 , 1599 , 1479 , 1460 , and 1412 cm^{-1} for **OH11**, 1602 , 1472 , 1460 , and 1412 cm^{-1} for **OH14**, and 1584 , 1472 , 1462 , and 1412 cm^{-1} for **OH15**.

When the dye was adsorbed on TiO_2 surface, the C=O stretching bands at 1711 , 1719 , and 1710 cm^{-1} for **OH11**, **OH14**, and **OH15**, respectively, disappeared and instead a new band appeared at 1550 cm^{-1} for **OH11**, 1545 cm^{-1} for **OH14**, and 1538 cm^{-1} for **OH15**, assignable to the asymmetric mode of carboxylate. The observations indicate that the carboxyl groups of the dyes form a bidentate chelation with the TiO_2 surface.^{1d} On the other hand, in the IR spectra of both **OH11** and **OH14** adsorbed on TiO_2 , the band at around 1600 cm^{-1} was broadened and the bands at around 1470 and 1460 cm^{-1} became weaker, indicative of the formation of hydrogen bonding between nitrogen of pyridine rings and hydroxy protons of the TiO_2 surface. Furthermore, a new band appeared at 1618 cm^{-1} for both **OH11** and **OH14**, which is assignable to pyridine rings coordinated to the Lewis acid sites of the TiO_2 surface. This indicates that **OH11** and **OH14** are adsorbed on the TiO_2 surface by hydrogen bonding as well as coordinate bonding. It is well known that pyridine is adsorbed on the TiO_2 surface by hydrogen bonding with the hydroxy group of TiO_2 surface and/or by coordinate bonding with the Lewis acid site of TiO_2 surface; when the pyridine is adsorbed on the TiO_2 surface by hydrogen bonding with the hydroxy group of the TiO_2 surface, the bands at around 1580 – 1600 cm^{-1} become broader and the bands at around 1460 – 1480 cm^{-1} become weaker, on the other hand, when the pyridine is adsorbed on the TiO_2 surface by coordinate bonding with the Lewis acid site of TiO_2 surface, new bands appear at 1600 – 1630 cm^{-1} .^{7,8} In the IR spectra of **OH15** adsorbed on TiO_2 , on the other hand, the 1462 cm^{-1} band became weaker and no sign of coordinate bonding was observed, suggesting that **OH15** is adsorbed on TiO_2 surface by weak hydrogen bonding alone. Accordingly, the large red-shift of absorption peak for **OH11** or **OH14** on TiO_2 (Figure 2) is ascribable to a strong interaction of the dye and TiO_2 due to coordinate bonding.

Electrochemical Properties of OH11, OH14, and OH15 and Their HOMO and LUMO Energy Levels. The electrochemical properties of three dyes were determined by cyclic voltammetry (CV) in DMF containing 0.1 tetraethylammonium perchlorate (Et_4NClO_4) for **OH11** and in CH_2Cl_2 containing 0.1 M tetrabutylammonium perchlorate (Bu_4NClO_4)

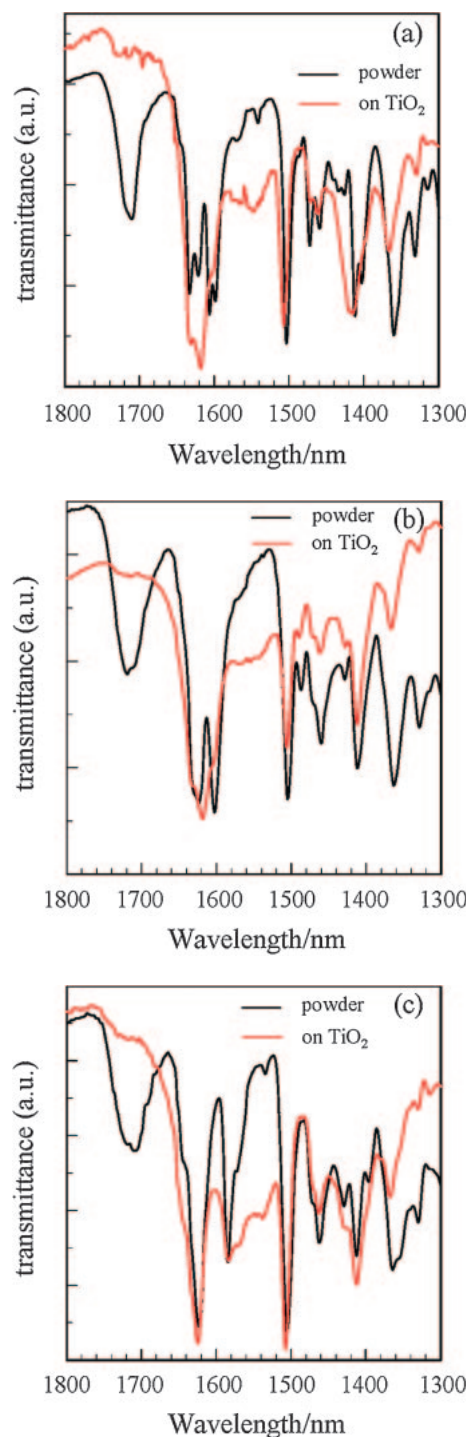


Figure 3. FT-IR spectra of the dye powders and the dyes adsorbed on particles for (a) **OH11**, (b) **OH14**, and (c) **OH15**.

for **OH14** and **OH15**. The potentials were referred to ferrocene/ferrocenium (Fc/Fc^+) as an internal reference. A typical CV curve of **OH14** is shown in Figure 4. The CV data are summarized in Table 2. The oxidation peaks of **OH11**, **OH14**, and **OH15** were observed, respectively, at 0.31 , 0.24 , and 0.28 V vs. Fc/Fc^+ , whereas the corresponding reduction peaks appeared at 0.26 , 0.18 , and 0.22 V . These results show that the oxidized states of the three dyes are stable.

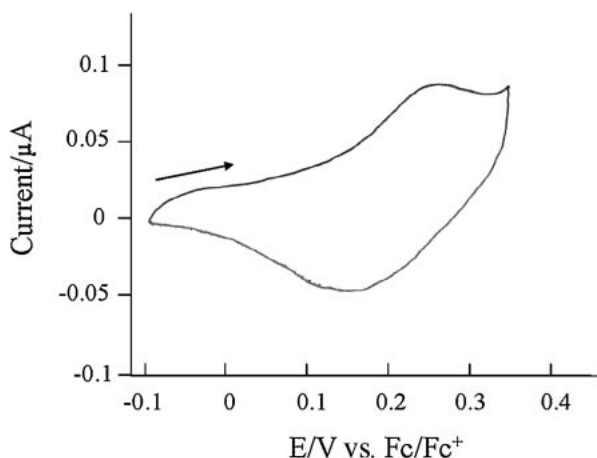


Figure 4. Cyclic voltammogram of **OH14** in CH_2Cl_2 containing 0.1 M Bu_4NClO_4 at a scan rate of 50 mV s^{-1} . The arrow denotes the direction of the potential scan.

Table 2. Electrochemical Properties of **OH11**, **OH14**, and **OH15** and Their Energy Levels of HOMO and LUMO

Dye	$E_{\text{pa}}/\text{V}^{\text{a}}$	$E_{\text{pc}}/\text{V}^{\text{a}}$	HOMO/ V^{b}	LUMO/ V^{b}
OH11	0.31	0.26	0.96	−1.62
OH14	0.24	0.18	0.89	−1.65
OH15	0.28	0.22	0.93	−1.45

a) E_{pa} and E_{pc} are the anodic and cathodic peak potentials vs. Fc/Fc^+ . b) vs. normal hydrogen electrode (NHE).

The HOMO and LUMO energy levels of the three dyes were evaluated from the spectral analyses and CV data. The HOMO energy levels for **OH11**, **OH14**, and **OH15** are evaluated, respectively to be 0.96, 0.89, and 0.93 V with respect to a normal hydrogen electrode (NHE). It can be presumed from the same HOMO energy levels among the three dyes that the rate of the dye regeneration by electron donation from I^- in redox mediator to the oxidized dye is comparable in the three dyes. The LUMO energy levels of the dyes are estimated from the oxidation potential and an intersection of absorption and fluorescence spectra (480 nm (2.58 eV) for **OH11**, 490 nm (2.54 eV) for **OH14**, and 520 nm (2.38 eV) for **OH15**) corresponding to the energy gap between HOMO and LUMO. The LUMO energy levels of **OH11**, **OH14**, and **OH15** are −1.62, −1.65, and −1.45 V, respectively. The LUMO level of **OH15** is lower than those of **OH11** and **OH14**, which lead to the decrease of the energy gap between the HOMO and LUMO responsible for the red-shift of ICT absorption band for **OH15**, relative to **OH11** and **OH14**. The LUMO energy levels for the three dyes are higher than the energy level of the TiO_2 conduction band (−0.5 V), suggesting that an efficient electron injection to the TiO_2 conduction band is thermodynamically possible. On the other hand, the rate (0.1–100 ps) of the electron injection from the excited dyes to TiO_2 conduction band is much faster than that of the fluorescence decay (1–5 ns) of the dyes,^{6g} which suggests that the electron injection into the TiO_2 conduction band is also kinetically possible.

Semiempirical MO Calculations (AM1, INDO/S) of OH11, OH14, and OH15. To understand the photophysical

Table 3. Calculated Absorption Spectra for **OH11**, **OH14**, and **OH15**

Dye	Absorption (calcd)		CI component ^{b)}
	$\lambda_{\text{max}}/\text{nm}$	f^{a}	
OH11	420	0.74	HOMO → LUMO (79%)
OH14	413	0.98	HOMO → LUMO (71%)
OH15	426	0.75	HOMO → LUMO (73%)

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

and electrochemical properties of **OH11**, **OH14**, and **OH15**, we carried out semiempirical molecular orbital (MO) calculations. The molecular structures were optimized by using the MOPAC/AM1 method,⁹ and then the INDO/S method¹⁰ using the SCRF Onsager Model was used for spectroscopic calculations in THF. The calculated torsion angles between the pyridine, 4-phenylpyridine, and quinoline rings and the oxazole ring of **OH11**, **OH14**, and **OH15** are ca. 8, 5, and 30°, respectively. The large torsion angle for **OH15** is attributed to steric hindrance between oxygen and/or nitrogen atoms of the oxazole ring and hydrogen atom of the quinoline ring. On the other hand, the calculated torsion angle between the pyridine ring and phenyl ring of **OH14** was ca. 40°, which is attributed to steric hindrance between a hydrogen atom of the pyridine ring and a hydrogen atom of the phenyl ring. The calculated absorption wavelengths and the transition characters of the first absorption bands are collected in Table 3. The longest excitation bands of **OH11**, **OH14**, and **OH15** show red-shifts in the order of **OH14** (413 nm) < **OH11** (420 nm) < **OH15** (426 nm), which are comparable to the observed spectra in THF, although the calculated absorption wavelength of **OH14** is shifted to longer wavelength than that of **OH11**. The calculations show that the longest excitation bands of **OH11**, **OH14**, and **OH15** are mainly assigned to the transition from HOMO to LUMO, where HOMOs are mostly localized on the 3-dibutylaminobenzofuro[2,3-*c*]oxazolo[4,5-*a*]carbazole moiety for the three dyes, and LUMOs are mostly localized on the pyridine ring for **OH11**, the 4-phenylpyridine ring for **OH14**, and the quinoline ring for **OH15**. The changes in the calculated electron density accompanying the first electron excitation are shown in Figure 5, which reveals an intramolecular charge transfer (ICT) from the 3-dibutylaminobenzofuro[2,3-*c*]oxazolo[4,5-*a*]carbazole moiety to the pyridine, 4-phenylpyridine, or quinoline rings for the three dyes.

Photovoltaic Performance of DSSCs Based on OH11, OH14, and OH15. The DSSCs were prepared by using the dye-adsorbed 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 0.6 M 1,2-dimethyl-3-propylimidazolium iodide as electrolyte. CDCA was employed as coadsorbent. The photocurrent–voltage (I – V) characteristics were measured under a simulated solar light (AM 1.5, 100 mW cm^{-2}). The incident photon-to-current conversion efficiency (IPCE) spectra were measured under with a tungsten–halogen lamp and a monochromator. IPCE spectra and I – V curves are depicted in Figures 6 and 7, respectively. The IPCE is calculated by the following equation:

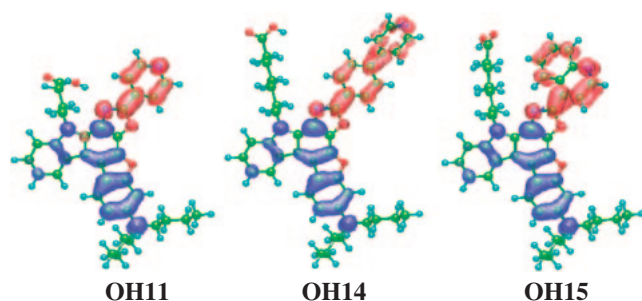


Figure 5. Calculated electron density changes accompanying the first electronic excitation of **OH11**, **OH14**, and **OH15**. The blue and red lobes signify decrease and increase in electron density accompanying the electronic transition, respectively. Their areas indicate the magnitude of the electron density change (light blue, green, blue, and red balls correspond to hydrogen, carbon, nitrogen, and oxygen atoms, respectively).

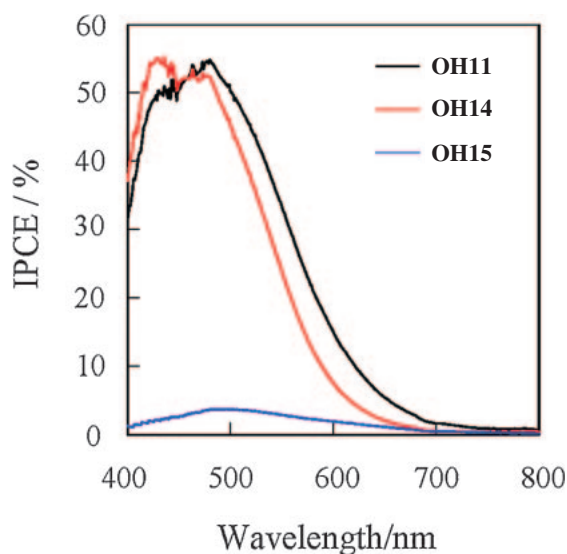


Figure 6. IPCE spectra of DSSCs based on **OH11**, **OH14**, and **OH15**.

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

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. The maximum IPCE value increases in the order of **OH15** (4% at 496 nm) $\ll$ **OH14** (53% at 480 nm) $\leq$ **OH11** (55% at 485 nm). Table 4 summarizes photovoltaic performances of DSSCs based on the **OH11**, **OH14**, and **OH15**, together with the one for **OH1** having a carboxyl group acting as not only anchoring group for attachment on TiO_2 surface but also the electron acceptor. The solar energy-to-electricity conversion yield $\eta/\%$ is expressed by the following equation:

$$\eta/\% = \{J_{\text{sc}}/(\text{mA cm}^{-2}) \times V_{\text{oc}}/\text{V}\} \times ff / \{I_0/(\text{mW cm}^{-2})\} \times 100 \quad (2)$$

where I_0 is the intensity of incident white light, V_{oc} is the open-circuit photovoltage, and ff represents the fill factor. The J_{sc} for

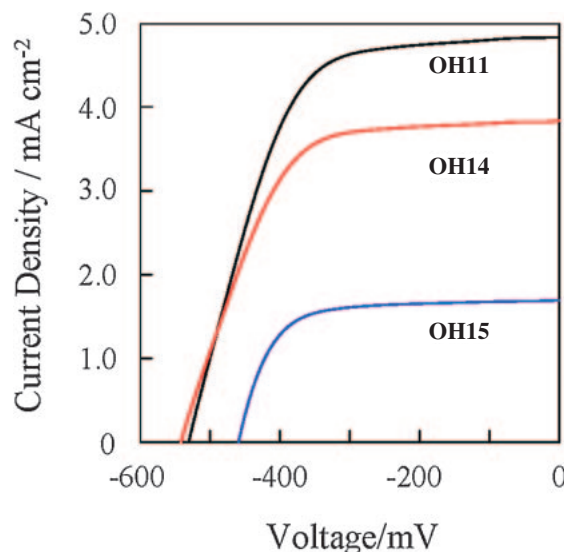


Figure 7. Photocurrent–voltage curves of DSSCs based on **OH11**, **OH14**, and **OH15**.

Table 4. Photovoltaic Performances of DSSCs Based on **OH1**, **OH11**, **OH14**, and **OH15**

Dye	$J_{\text{sc}}/\text{mA cm}^{-2}$	V_{oc}/mV	ff	$\eta/\%$
OH11	4.88	532	0.61	1.62
OH14	3.91	544	0.62	1.30
OH15	1.72	457	0.70	0.56
OH1	4.09	524	0.66	1.45

OH11 (4.88 mA cm^{-2}) is similar to that for **OH1** (4.09 mA cm^{-2}) and higher than that of **OH14** (3.91 mA cm^{-2}). On the other hand, the J_{sc} for **OH15** (1.72 mA cm^{-2}) shows a moderate value. The η values increase in the order of **OH15** (0.56%) $<$ **OH14** (1.30%) $<$ **OH1** (1.45%) $<$ **OH11** (1.62%). The values of V_{oc} for **OH1**, **OH11**, **OH14**, and **OH15** are 524, 532, 544, and 457 mV, respectively, which are different among the dyes. In addition, when 4-*tert*-butylpyridine (TBP) was added to the electrolyte, the V_{oc} was enhanced in all the cases. For example, the DSSC based on **OH11** yielded the η value of 2.51% with $J_{\text{sc}} = 5.52 \text{ mA cm}^{-2}$, $V_{\text{oc}} = 665 \text{ mV}$, and $ff = 0.67$.

It should be noticed, however, that the J_{sc} value of **OH15** obtained from the I – V curve does not correspond to that obtained from the IPCE spectrum. More recently, we found that the mismatches in the J_{sc} values between the I – V curve and the IPCE spectrum are observed in some of the D– π –A dye sensitizers with pyridine rings as electron-accepting groups. Further studies on the DSSCs based on the D– π –A dye sensitizers with pyridine rings as electron-accepting groups are now in progress to elucidate some effect on the J_{sc} values obtained from the I – V curve and the IPCE spectrum and will be reported in the next paper.

Consideration of a Relationship between Photovoltaic Performance and Configuration of Dye on TiO_2 Surface. The FT-IR spectra of **OH11** and **OH14** adsorbed on TiO_2 indicate the formation of hydrogen bonding between the nitrogen of pyridine ring and the hydroxy proton of TiO_2 surface as well as the formation of the strong coordinate bonding between the nitrogen lone-pair of pyridine and Lewis

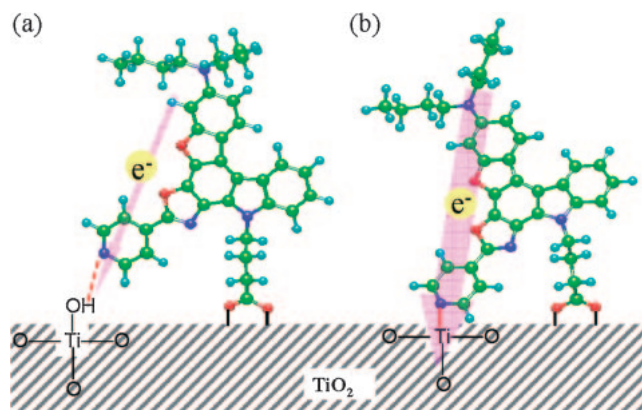


Figure 8. Configurations of **OH11** on TiO_2 surface; (a) hydrogen bonding and (b) coordinate bonding. Light blue, green, blue, and red balls correspond to hydrogen, carbon, nitrogen, and oxygen atoms, respectively.

acid sites of TiO_2 surface. In contrast, only the formation of weak hydrogen bonding was observed in the IR spectra of **OH15** adsorbed on TiO_2 . It is inferred from the molecular structure of **OH15** that the sterically hindered quinoline ring prevents the formation of the coordinate bonding between the nitrogen lone-pair of quinoline ring and the Lewis acid site of TiO_2 surface. According to our previous studies,^{5,6} it may be safe to assume that the dye molecules are standing perpendicular to the TiO_2 substrate as shown in Figure 8. Consequently, in view of highly efficient charge injection probabilities as suggested by IPCE values over 50%, the dyes **OH11** and **OH14** can inject electrons efficiently from the pyridine ring to the conduction band of the TiO_2 electrode through the strong coordinate bonding (Figure 8b) rather than the hydrogen bonding (Figure 8a). The slightly low photovoltaic performance for **OH14** is ascribable to the weakened ICT characteristics by the large twisting between the pyridine ring and phenyl ring, which leads to reduction in electron-injection yield. On the other hand, for **OH15**, the absence of the coordinate bonding between the quinoline ring and the Lewis acid site of TiO_2 surface might be responsible for lower electron injection yield (the low J_{sc} value) than those of **OH11** and **OH14**. Thus, it was suggested that the formation of strong coordinate bonding between the pyridine ring of dyes and the Lewis acid site of TiO_2 surface leads to an efficient electron injection owing to a good electron communication between them. As additional evidence, the dye **2** (see Ref. 5) with butyric acid removed from the carbazole moiety of **OH11**, so that it does not have a carboxyl group as anchoring group for attachment on TiO_2 surface, can be strongly adsorbed on the TiO_2 surface. It took about two months for the dye **2** to reach saturated adsorption, but only two days for **OH11**. The DSSC based on the dye **2** without CDCA yielded the η value of 0.96% with $J_{\text{sc}} = 3.65 \text{ mA cm}^{-2}$, $V_{\text{oc}} = 429 \text{ mV}$, and $ff = 0.62$. The η value for the dye **2**-DSSC is slightly lower than that (1.33%) for **OH11**-DSSC without CDCA. The maximum IPCE value for the dye **2** is 6% at 468 nm, and the mismatch in the J_{sc} values between the I - V curve and the IPCE spectrum was also observed. Therefore, our results demonstrate that the pyridine rings are one of the most promising candidates as electron-

accepting groups of D- π -A dye sensitizers for DSSCs, which induces the possibility of the epoch-making molecular design and synthesis of a variety of D- π -A dye sensitizers beyond the traditional D- π -A dye sensitizers with a carboxyl group as electron acceptor.

Conclusion

As a new type of D- π -A dye sensitizers for DSSCs, we have designed and synthesized the fluorescent dyes **OH11**, **OH14**, and **OH15** with pyridine, 4-phenylpyridine, and quinoline rings, respectively, as electron-accepting groups. The J_{sc} of DSSCs using **OH11** and **OH14** are higher than that of **OH15**. The FT-IR spectra of **OH11** and **OH14** adsorbed on TiO_2 particles indicate the formation of hydrogen bonding between the pyridine ring of dyes and the hydroxy group of TiO_2 surface and the formation of strong coordinate bonding between the pyridine ring of dyes and the Lewis acid site of TiO_2 surface. On the other hand, only the formation of weak hydrogen bonding was observed in the IR spectra of **OH15** adsorbed on TiO_2 . Consequently, it was suggested that the dyes **OH11** and **OH14** can inject electrons efficiently from the pyridine ring to the conduction band of the TiO_2 electrode through the strong coordinate bonding rather than the hydrogen bonding. Our results demonstrate that a carboxyl group of D- π -A dye sensitizers is necessary not as the electron acceptor, but only as an anchoring group for attachment on the TiO_2 surface. Therefore, we propose that the pyridine rings forming a strong coordinate bonding with the Lewis acid site of TiO_2 surface are promising candidates as electron-accepting groups of a new type of D- π -A dye sensitizers for 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 with a Hamamatsu C9920-01 equipped with CCD by using a calibrated integrating sphere system ($\lambda_{\text{ex}} = 325 \text{ nm}$). CVs were recorded in $\text{CH}_2\text{Cl}_2/\text{Bu}_4\text{NClO}_4$ (0.1 M) solution or in DMF/ Et_4NClO_4 (0.1 M) solution with a three-electrode system consisting of Ag/Ag^+ as reference electrode, Pt plate as 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 2400II CHN analyzer. ^1H NMR spectra were recorded on a JNM-LA400 (400 MHz) FT NMR spectrometer with tetramethylsilane as an internal standard. Column chromatography was performed on silica gel (KANTO CHEMICAL, 60N, spherical, neutral).

Preparation of 7-(4-Pyridin-4-ylphenyl)-3-dibutylamino-benzofuro[2,3-c]oxazolo[4,5-a]carbazole (2). A solution of **1** (0.50 g, 1.21 mmol), 4-(4-pyridinyl)benzaldehyde (0.22 g, 1.21 mmol), and ammonium acetate (2.33 g, 28.9 mmol) in acetic acid (50 mL) was stirred at 90 °C for 2 h. After the reaction was complete, the reaction mixture was condensed. The resulting precipitate was washed with water and dried. The

residue was chromatographed on silica gel (dichloromethane–ethyl acetate = 3:1 as eluent) to give **2** (0.12 g, yield 17%) as a yellow powder; mp 258–260 °C; IR (ATR): $\tilde{\nu}$ = 3058, 1622, 1597 cm^{-1} ; ^1H NMR (DMSO- d_6 , TMS): δ 0.96 (6H, t, J = 7.37 Hz), 1.35–1.43 (4H, m), 1.60–1.64 (4H, m), 3.40 (4H, t, J = 7.21 Hz) overlap with peak of dissolved water in DMSO- d_6 , 6.96 (1H, d, J = 8.80 Hz), 7.06 (1H, s), 7.37 (1H, t, J = 6.83 Hz), 7.49 (1H, t, J = 9.06 Hz), 7.68 (1H, d, J = 6.84 Hz), 7.85 (2H, d, J = 5.88 Hz), 8.14 (2H, d, J = 7.80 Hz), 8.43 (2H, d, J = 7.80 Hz), 8.48 (1H, d, J = 8.80 Hz), 8.62 (1H, d, J = 8.80 Hz), 8.71 (2H, d, J = 5.88 Hz), 12.47 (1H, s, –NH); FABMS m/z 579 (M^+).

Preparation of 7-(4-Pyridin-4-ylphenyl)-3-dibutylaminobenzofuro[2,3-*c*]oxazolo[4,5-*a*]carbazole-9-heptanoic Acid Ethyl Ester (3**).** A solution of **2** (0.12 g, 0.2 mmol) in DMF (150 mL) was treated with sodium hydride (60%, 0.01 g, 0.25 mmol) and stirred for 1 h at room temperature. Ethyl 7-bromoheptanoate (0.27 g, 1.15 mmol) was added dropwise over 20 min and the solution was stirred at room temperature for 2 h. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane, and washed with water. The organic extract was dried over MgSO_4 , filtered, and concentrated. The residue was chromatographed on silica gel (dichloromethane–ethyl acetate = 3:1 as eluent) to give **3** (0.12 g, yield 80%) as a yellow powder; mp 188–191 °C; IR (ATR): $\tilde{\nu}$ = 1732, 1622, 1595 cm^{-1} ; ^1H NMR (CD_2Cl_2 , TMS): δ 0.95 (6H, t, J = 6.95 Hz), 1.09 (3H, t, J = 6.95 Hz), 1.23–1.28 (2H, m), 1.35–1.64 (12H, m), 1.96–1.98 (2H, m), 2.16–2.21 (2H, m), 3.36 (4H, t, J = 7.61 Hz), 3.92–4.01 (2H, m), 4.90 (2H, t, J = 6.83 Hz), 6.82 (1H, d, J = 9.76 Hz), 6.89 (1H, s), 7.31 (1H, t, J = 7.67 Hz), 7.46 (1H, t, J = 7.31 Hz), 7.54–7.57 (3H, m), 7.79 (2H, d, J = 8.80 Hz), 8.30–8.38 (3H, m), 8.52–8.64 (3H, m); FABMS m/z 734 (M^+).

Preparation of 7-(4-Pyridin-4-ylphenyl)-3-dibutylaminobenzofuro[2,3-*c*]oxazolo[4,5-*a*]carbazole-9-heptanoic Acid (OH14**).** A solution of **3** (0.07 g, 0.10 mmol) in a mixed solvent (ethanol 300 mL and dichloromethane 25 mL) was added dropwise to aqueous NaOH (0.03 g, 0.7 mmol, 30 mL) with stirring at 70 °C. After further stirring for 12 h under reflux, the solution was acidified to pH 4 with 2 M HCl, and concentrated under reduced pressure. The residue was dissolved in dichloromethane, and washed with water. The organic extract was dried over MgSO_4 , filtered, and concentrated. The resulting residue was reprecipitated from dichloromethane–hexane to give **OH14** (0.06 g, yield 86%) as a dark red powder; mp 231–234 °C; IR (ATR): $\tilde{\nu}$ = 3050, 1718, 1623, 1602 cm^{-1} ; ^1H NMR (DMSO- d_6 , TMS): δ 0.97 (6H, t, J = 6.89 Hz), 1.37–1.48 (12H, m), 1.60–1.63 (2H, m), 1.91–2.02 (2H, m), 2.18 (2H, t, J = 6.83 Hz), 3.44 (4H, t, J = 4.53 Hz) overlap with peak of dissolved water in DMSO- d_6 , 4.95 (2H, t, J = 6.64 Hz), 6.93 (1H, d, J = 8.80 Hz), 7.02 (1H, s), 7.39 (1H, t, J = 6.77 Hz), 7.55 (1H, t, J = 6.77 Hz), 7.81 (1H, d, J = 7.80 Hz), 7.84 (2H, d, J = 5.88 Hz), 8.10 (2H, d, J = 6.84 Hz), 8.37 (2H, d, J = 6.84 Hz), 8.44 (1H, d, J = 8.80 Hz), 8.61 (1H, d, J = 6.84 Hz), 8.71 (2H, d, J = 4.88 Hz); FABMS m/z 706 (M^+).

Preparation of 7-(Quinolin-4-yl)-3-dibutylaminobenzofuro[2,3-*c*]oxazolo[4,5-*a*]carbazole (4**) and 7-(Quinolin-4-yl)-3-dibutylaminobenzofuro[2,3-*c*]oxazolo[5,4-*a*]carbazole**

(5). A solution of **1** (0.50 g, 1.21 mmol), 4-quinolinecarboxaldehyde (0.19 g, 1.21 mmol), and ammonium acetate (2.33 g, 28.9 mmol) in acetic acid (50 mL) was stirred at 90 °C for 2 h. After the reaction was complete, the reaction mixture was condensed. The resulting precipitate was washed with water and dried. The residue was chromatographed on silica gel (dichloromethane–THF = 3:1 as eluent) to give **4** (0.28 g, yield 40%) as an orange powder and **5** (0.06 g, yield 8%) as a red powder; **4**: mp 288–291 °C; IR (ATR): $\tilde{\nu}$ = 3058, 1622, 1587 cm^{-1} ; ^1H NMR (DMSO- d_6 , TMS): δ 0.99 (6H, t, J = 7.85 Hz), 1.39–1.45 (4H, m), 1.61–1.67 (4H, m), 3.44 (4H, t, J = 9.00 Hz) overlap with peak of dissolved water in DMSO- d_6 , 6.99 (1H, d, J = 8.80 Hz), 7.10 (1H, s), 7.40 (1H, t, J = 7.85 Hz), 7.52 (1H, t, J = 8.76 Hz), 7.74 (1H, d, J = 7.80 Hz), 7.91–7.99 (2H, m), 8.23 (1H, d, J = 8.80 Hz), 8.45 (1H, d, J = 4.88 Hz), 8.53 (1H, d, J = 8.80 Hz), 8.65 (1H, d, J = 7.80 Hz), 9.22 (1H, d, J = 3.92 Hz), 9.73 (1H, d, J = 7.80 Hz), 12.62 (1H, s, –NH); FABMS m/z 553 (M^+); **5**: mp 282–284 °C; IR (ATR): $\tilde{\nu}$ = 3064, 1622, 1586 cm^{-1} ; ^1H NMR (DMSO- d_6 , TMS): δ 0.99 (6H, t, J = 7.61 Hz), 1.39–1.45 (4H, m), 1.61–1.67 (4H, m), 3.41 (4H, t, J = 7.79 Hz) overlap with peak of dissolved water in DMSO- d_6 , 6.94 (1H, d, J = 8.80 Hz), 7.11 (1H, s), 7.40 (1H, t, J = 6.77 Hz), 7.54 (1H, t, J = 8.03 Hz), 7.73 (1H, d, J = 8.80 Hz), 7.91–7.98 (2H, m), 8.23 (1H, d, J = 7.80 Hz), 8.41 (1H, d, J = 4.88 Hz), 8.47 (1H, d, J = 8.80 Hz), 8.66 (1H, d, J = 7.80 Hz), 9.23 (1H, d, J = 3.92 Hz), 9.65 (1H, d, J = 8.80 Hz), 12.53 (1H, s, –NH); FABMS m/z 553 (M^+).

Preparation of 7-(Quinolin-4-yl)-3-dibutylaminobenzofuro[2,3-*c*]oxazolo[4,5-*a*]carbazole, 9-Heptanoic Acid Ethyl Ester (6**).** A solution of **4** (0.12 g, 0.22 mmol) in DMF (150 mL) was treated with sodium hydride (60%, 0.01 g, 0.25 mmol) and stirred for 1 h at room temperature. Ethyl 7-bromoheptanoate (0.26 g, 1.08 mmol) was added dropwise over 20 min and the solution was stirred at room temperature for 2 h. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane, and washed with water. The organic extract was dried over MgSO_4 , filtered, and concentrated. The resulting residue was reprecipitated from dichloromethane–hexane to give **6** (0.12 g, yield 78%) as an orange powder; mp 157–159 °C; IR (ATR): $\tilde{\nu}$ = 1732, 1622, 1584 cm^{-1} ; ^1H NMR (acetone- d_6 , TMS): δ 1.04 (6H, t, J = 7.07 Hz), 1.13 (3H, t, J = 7.61 Hz), 1.19–1.24 (2H, m), 1.42–1.74 (14H, m), 2.20–2.35 (2H, m), 3.53 (4H, t, J = 3.20 Hz), 3.97–4.09 (2H, m), 5.05 (2H, t, J = 7.25 Hz), 6.97 (1H, d, J = 8.80 Hz), 7.02 (1H, s), 7.43 (1H, t, J = 7.67 Hz), 7.58 (1H, t, J = 7.67 Hz), 7.83 (1H, d, J = 7.84 Hz), 7.87–7.96 (2H, m), 8.24 (1H, d, J = 8.80 Hz), 8.44 (1H, d, J = 3.92 Hz), 8.49 (1H, d, J = 8.80 Hz), 8.70 (1H, d, J = 7.80 Hz), 9.18 (1H, d, J = 3.92 Hz), 9.78 (1H, d, J = 7.80 Hz); FABMS m/z 709 (M^+).

Preparation of 7-(Quinolin-4-yl)-3-dibutylaminobenzofuro[2,3-*c*]oxazolo[4,5-*a*]carbazole, 9-Heptanoic Acid (OH15**).** A solution of **6** (0.12 g, 0.17 mmol) in a mixed solvent (ethanol 300 mL and dichloromethane 25 mL) was added dropwise to aqueous NaOH (0.03 g, 0.7 mmol, 30 mL) with stirring at 70 °C. After further stirring for 12 h under reflux, the solution was acidified to pH 4 with 2 M HCl, and concentrated under reduced pressure. The residue was dissolved in dichloromethane, and washed with water. The organic

extract was dried over MgSO_4 , filtered, and concentrated. The resulting residue was reprecipitated from dichloromethane–hexane to give **OH15** (0.08 g, yield 70%) as a dark red powder; mp 232–234 °C; IR (ATR): $\tilde{\nu}$ = 3050, 1708, 1622, 1584 cm^{-1} ; ^1H NMR ($\text{DMSO}-d_6$, TMS): δ 0.97 (6H, t, J = 7.73 Hz), 1.38–1.62 (14H, m), 1.98–2.10 (2H, m), 2.13 (2H, t, J = 6.71 Hz), 3.44 (4H, t, J = 6.28 Hz) overlap with peak of dissolved water in $\text{DMSO}-d_6$, 4.98 (2H, t, J = 5.80 Hz), 6.93 (1H, d, J = 8.80 Hz), 7.04 (1H, s), 7.41 (1H, t, J = 7.79 Hz), 7.57 (1H, t, J = 6.71 Hz), 7.87 (1H, d, J = 8.80 Hz), 7.92–7.96 (2H, m), 8.20 (1H, d, J = 8.80 Hz), 8.39 (1H, m), 8.47 (1H, d, J = 8.80 Hz), 8.63 (1H, d, J = 8.80 Hz), 9.16 (1H, d, J = 3.92 Hz), 9.64 (1H, d, J = 7.80 Hz); FABMS m/z 679 (M^+).

Computational Methods. The semiempirical calculations were carried out with the WinMOPAC Ver. 3.9 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 four compounds were compared with their absorption data by the semiempirical method INDO/S (intermediate neglect of differential overlap/spectroscopic)¹⁰ using the SCRf Onsager Model. 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 Dyes OH1, OH11, OH14, and OH15. The TiO_2 paste (JGC Catalysts and Chemicals Ltd., PST-18NR) was deposited on a fluorine-doped tin oxide (FTO) substrate by doctor-blading, and sintered for 50 min at 450 °C. The 9 μm thick TiO_2 electrode ($0.5 \times 0.5 \text{ cm}^2$ in photoactive area) was immersed into a 0.1 mM dye solution in the presence of 10 mM (**OH11** and **OH14**), 3 mM (**OH1**), or 1 mM (**OH15**) chenodeoxycholic acid (CDCA) in tetrahydrofuran for a sufficient number of hours 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 0.6 M 1,2-dimethyl-3-propylimidazolium iodide in acetonitrile as electrolyte. The photocurrent–voltage characteristics were measured using a potentiostat under a simulated solar light (AM 1.5, 100 mW cm^{-2}). IPCE spectra were measured under monochromatic irradiation with a tungsten–halogen lamp and a monochromator. The amount of adsorbed dye on TiO_2 particles 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_2 particles were measured in the diffuse-reflection mode with a Shimadzu UV-3150 spectrophotometer with a calibrated integrating sphere system ISR-3100.

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References

- a) K. Hara, K. Sayama, H. Arakawa, Y. Ohga, A. Shinpo, S. Suga, *Chem. Commun.* **2001**, 569. b) K. Hara, T. Sato, R. Katoh, A. Furube, Y. Ohga, A. Shinpo, S. Suga, K. Sayama, H. Sugihara, H. Arakawa, *J. Phys. Chem. B* **2003**, *107*, 597. c) K. Hara, M. Kurashige, Y. Dan-oh, C. Kasada, A. Shinpo, S. Suga, K. Sayama, H. Arakawa, *New J. Chem.* **2003**, *27*, 783. d) Z.-S. Wang, K. Hara, Y. Dan-oh, C. Kasada, A. Shinpo, S. Suga, H. Arakawa, H. Sugihara, *J. Phys. Chem. B* **2005**, *109*, 3907. e) K. Hara, Z.-S. Wang, T. Sato, A. Furube, R. Katoh, H. Sugihara, Y. Dan-oh, C. Kasada, A. Shinpo, S. Suga, *J. Phys. Chem. B* **2005**, *109*, 15476. f) A. Furube, R. Katoh, K. Hara, T. Sato, S. Murata, H. Arakawa, M. Tachiya, *J. Phys. Chem. B* **2005**, *109*, 16406. g) K. Hara, K. Miyamoto, Y. Abe, M. Yanagida, *J. Phys. Chem. B* **2005**, *109*, 23776. h) Z.-S. Wang, Y. Cui, K. Hara, Y. Dan-oh, C. Kasada, A. Shinpo, *Adv. Mater.* **2007**, *19*, 1138. i) Z.-S. Wang, Y. Cui, Y. Dan-oh, C. Kasada, A. Shinpo, K. Hara, *J. Phys. Chem. C* **2008**, *112*, 17011.
- a) I. Jung, J. K. Lee, K. H. Song, K. Song, S. O. Kang, J. Ko, *J. Org. Chem.* **2007**, *72*, 3652. b) D. P. Hagberg, J.-H. Yum, H. Lee, F. D. Angelis, T. Marinado, K. M. Karlsson, R. Humphry-Baker, L. Sun, A. Hagfeldt, M. Grätzel, M. K. Nazeeruddin, *J. Am. Chem. Soc.* **2008**, *130*, 6259. c) K. R. J. Thomas, J. T. Lin, Y.-C. Hsu, K.-C. Ho, *Chem. Commun.* **2005**, 4098. d) G. Zhou, N. Pschirer, J. C. Schöneboom, F. Eickemeyer, M. Baumgarten, K. Müllen, *Chem. Mater.* **2008**, *20*, 1808. e) W. Xu, B. Peng, J. Chen, M. Liang, F. Cai, *J. Phys. Chem. C* **2008**, *112*, 874. f) Z. Ning, Q. Zhang, W. Wu, H. Pei, B. Liu, H. Tian, *J. Org. Chem.* **2008**, *73*, 3791. g) G. Li, K.-J. Jiang, Y.-F. Li, S.-L. Li, L.-M. Yang, *J. Phys. Chem. C* **2008**, *112*, 11591.
- a) N. Koumura, Z.-S. Wang, S. Mori, M. Miyashita, E. Suzuki, K. Hara, *J. Am. Chem. Soc.* **2006**, *128*, 14256. b) S. Kim, J. K. Lee, S. O. Kang, J. Ko, J.-H. Yum, S. Fantacci, F. D. Angelis, D. D. Censo, M. K. Nazeeruddin, M. Grätzel, *J. Am. Chem. Soc.* **2006**, *128*, 16701. c) Z.-S. Wang, N. Koumura, Y. Cui, M. Takahashi, H. Sekiguchi, A. Mori, T. Kubo, A. Furube, K. Hara, *Chem. Mater.* **2008**, *20*, 3993. d) H. Choi, C. Baik, S. O. Kang, J. Ko, M.-S. Kang, M. K. Nazeeruddin, M. Grätzel, *Angew. Chem., Int. Ed.* **2008**, *47*, 327. e) H. Qin, S. Wenger, M. Xu, F. Gao, X. Jing, P. Wang, S. M. Zakeeruddin, M. Grätzel, *J. Am. Chem. Soc.* **2008**, *130*, 9202. f) H.-Y. Yang, Y.-S. Yen, Y.-C. Hsu, H.-H. Chou, J. T. Lin, *Org. Lett.* **2010**, *12*, 16. g) H. Choi, I. Raabe, D. Kim, F. Teocoli, C. Kim, K. Song, J.-H. Yum, J. Ko, M. K. Nazeeruddin, M. Grätzel, *Chem.—Eur. J.* **2010**, *16*, 1193.
- a) T. Horiuchi, H. Miura, S. Uchida, *Chem. Commun.* **2003**, 3036. b) T. Horiuchi, H. Miura, K. Sumioka, S. Uchida, *J. Am. Chem. Soc.* **2004**, *126*, 12218. c) L. Schmidt-Mende, U. Bach, R. Humphry-Baker, T. Horiuchi, H. Miura, S. Ito, S. Uchida, M. Grätzel, *Adv. Mater.* **2005**, *17*, 813. d) S. Ito, S. M. Zakeeruddin, R. Humphry-Baker, P. Liska, R. Charvet, P. Comte, M. K. Nazeeruddin, P. Péchy, M. Takata, H. Miura, S. Uchida, M. Grätzel, *Adv. Mater.* **2006**, *18*, 1202. e) W. H. Howie, F. Claeysens, H. Miura, L. M. Peter, *J. Am. Chem. Soc.* **2008**, *130*, 1367. f) D. Kuang, S. Uchida, R. Humphry-Baker, S. K. Zakeeruddin, M. Grätzel, *Angew. Chem., Int. Ed.* **2008**, *47*, 1923. g) S. Ito, H. Miura, S. Uchida, M. Takata, K. Sumioka, P. Liska, P. Comte, P. Péchy, M. Grätzel, *Chem. Commun.* **2008**, 5194.
- Y. Ooyama, S. Inoue, R. Asada, G. Ito, K. Kushimoto, K. Komaguchi, I. Imae, Y. Harima, *Eur. J. Org. Chem.* **2010**, 92.
- a) Y. Ooyama, Y. Harima, *Chem. Lett.* **2006**, 35, 902. b) Y. Ooyama, Y. Kagawa, Y. Harima, *Eur. J. Org. Chem.* **2007**, 3613.

- c) Y. Ooyama, A. Ishii, Y. Kagawa, I. Imae, Y. Harima, *New J. Chem.* **2007**, 31, 2076. d) Y. Ooyama, Y. Shimada, Y. Kagawa, I. Imae, Y. Harima, *Org. Biomol. Chem.* **2007**, 5, 2046. e) Y. Ooyama, Y. Shimada, Y. Kagawa, Y. Yamada, I. Imae, K. Komaguchi, Y. Harima, *Tetrahedron Lett.* **2007**, 48, 9167. f) Y. Ooyama, Y. Shimada, A. Ishii, G. Ito, Y. Kagawa, I. Imae, K. Komaguchi, Y. Harima, *J. Photochem. Photobiol., A* **2009**, 203, 177. g) Y. Ooyama, Y. Kagawa, H. Fukuoka, G. Ito, Y. Harima, *Eur. J. Org. Chem.* **2009**, 5321.
- 7 a) N. Sheppard, in *Vibrational Spectroscopy of Adsorbates*, ed. by R. F. Willis, Springer, Berlin, **1980**, pp. 165–176. b) H.-P. Boehm, H. Knözinger, in *Catalysis: Science and Technology*, ed. by J. R. Anderson, M. Boudart, Springer, Berlin, **1983**, Vol. 4, pp. 40–189. c) J. B. Peri, in *Catalysis: Science and Technology*, ed. by J. R. Anderson, M. Boudart, Springer, Berlin, **1984**, Vol. 5, pp. 171–220. d) A. A. Davydov, in *Infrared Spectroscopy of Adsorbed Species on the Surface of Transition Metal Oxide*, ed. by C. H. Rochester, Wiley, Chichester, **1984**. e) A. T. Bell, *Methods of Surface Characterization*, in *Vibrational Spectroscopy of Molecules on Surfaces*, ed. by J. T. Yates, Jr., T. E. Madey, Plenum Press, New York, **1987**, Vol. 1, pp. 105–133. f) M. W. Urban, *Vibrational Spectroscopy of Molecules and Macromolecules on Surfaces*, Wiley, Chichester, **1993**, pp. 171–185.
- 8 a) M. I. Zaki, M. A. Hasan, F. A. Al-Sagheer, L. Pasupulety, *Colloids Surf., A* **2001**, 190, 261. b) T. J. Dines, L. D. MacGregor, C. H. Rochester, *Spectrochim. Acta, Part A* **2003**, 59, 3205. c) T. Bezrodna, G. Puchkovska, V. Shimanovska, I. Chashechnikova, T. Khalyavka, J. Baran, *Appl. Surf. Sci.* **2003**, 214, 222. d) V. Vishwanathan, H.-S. Roh, J.-W. Kim, K.-W. Jun, *Catal. Lett.* **2004**, 96, 23. e) S. Wang, X. Ma, H. Guo, J. Gong, X. Yang, G. Xu, *J. Mol. Catal. A: Chem.* **2004**, 214, 273. f) X. Ma, S. Wang, J. Gong, X. Yang, G. Xu, *J. Mol. Catal. A: Chem.* **2004**, 222, 183. g) G. Neri, G. Rizzo, S. Galvagno, G. Loiacono, A. Donato, M. G. Musolino, R. Pietropaolo, E. Rombi, *Appl. Catal., A* **2004**, 274, 243. h) A. P. Kulkarni, D. S. Muggli, *Appl. Catal., A* **2006**, 302, 274. i) X. Wang, J. C. Yu, P. Liu, X. Wang, W. Su, X. Fu, *J. Photochem. Photobiol., A* **2006**, 179, 339. j) M. M. Mohamed, W. A. Bayoumy, M. Khairy, M. A. Mousa, *Micro-porous Mesoporous Mater.* **2007**, 103, 174.
- 9 M. J. S. Dewar, E. G. Zoeibisch, E. F. Healy, J. J. P. Stewart, *J. Am. Chem. Soc.* **1985**, 107, 3902.
- 10 a) J. E. Ridley, M. C. Zerner, *Theor. Chim. Acta* **1973**, 32, 111. b) J. E. Ridley, M. C. Zerner, *Theor. Chim. Acta* **1976**, 42, 223. c) A. D. Bacon, M. C. Zerner, *Theor. Chim. Acta* **1979**, 53, 21. d) H. A. Kurtz, J. J. P. Stewart, K. M. Dieter, *J. Comput. Chem.* **1990**, 11, 82.