Synthesis, optical, electrochemical and photovoltaic properties of a D–π–A fluorescent dye with triazine ring as electron-withdrawing anchoring group for dye-sensitized solar cells

Yousuke Ooyama,* Koji Uenaka and Joji Ohshita*

The D–π–A fluorescent dye OUJ-1 with 1,3,5-triazine ring as electron-withdrawing anchoring group and (diphenylamino)carbazole containing a thiophene ring as D–π moiety have been newly developed and their optical and electrochemical properties, adsorption states on TiO₂ nanoparticles, and photovoltaic performance in dye-sensitized solar cell (DSSC) were investigated. The absorption maximum (λ_{abs}) for the intramolecular charge-transfer (ICT) absorption band of the D–π–A dye OUJ-1 occurs at a longer wavelength than those of D–π–A dye NI-6 with a pyridyl group and D–π–A dye OUK-1 with a pyrazyl group. Moreover, the dye OUJ-1 exhibits significant fluorescence solvatochromic properties, that is, a bathochromic shift of the fluorescence band and a decrease in the fluorescence quantum yield (Φ) due to a change from the ICT excited state to the twisted intramolecular charge transfer (TICT) excited state with increasing solvent polarity were observed. The photovoltaic performance of a DSSC based on OUJ-1 is lower than those of NI-6 and OUK-1 due to the low dye loading of OUJ-1 on TiO₂ electrode. It was found that the dye OUJ-1 is adsorbed onto the TiO₂ surface through the formation of triazainium ions at the Brønsted acid sites (surface-bound hydroxyl groups, Ti-OH) on the TiO₂ surface, although the dye NI-6 was predominantly adsorbed on the TiO₂ through coordinate bonding between the pyridyl group of the dye and the Lewis acid sites (exposed Ti₃⁺ cations) on the TiO₂ surface, and the dye OUK-1 was adsorbed on the TiO₂ surface through both the formations of hydrogen bonding of pyrazyl groups and triazainium ions at Brønsted acid sites on the TiO₂ surface. This work revealed that the binding mode of D–π–A dye sensitzers with azine rings on the TiO₂ surface can be changed by control of the basicity and electron density of the azine rings.

Introduction

Donor-acceptor π-conjugated (D–π–A) fluorescent dyes having both electron-donating (D) and -accepting (A) groups linked by π-conjugated bridges are useful as emitters for organic light emitting diodes (OLEDs),¹⁻² photosensitizers for dye-sensitized solar cells (DSSCs),³⁻⁴ and fluorescence sensors for a variety of applications,⁵⁻⁸ because of their strong absorption and emission properties originating from the intramolecular charge transfer (ICT) excitation from the donor to acceptor moiety in the D–π–A structures. As a noteworthy structural feature of D–π–A dyes, the highest occupied molecular orbital (HOMO) is localized over the π-conjugated system close to the donor part, and the lowest unoccupied molecular orbital (LUMO) is localized over the acceptor part. In the light of the D–π–A structure concept, the expansion of π conjugation and the increase in the electron-donating and electron-accepting abilities of donors (D) and acceptors (A), respectively, leads to the decrease in the energy gap between the HOMO and LUMO. Thus, the photophysical, electrochemical, and ICT properties of a D–π–A dye strongly depend on the electron-donating ability of D and the electron-accepting ability of A, as well as on the electronic characteristics of the π bridge, that is, they should be strategically tunable through chemical modification on each component (D, A, or π bridge) to suit the requirements for efficient optoelectronic devices and optical, biochemical, and medicinal sensors.

In this work, D–π–A fluorescent dye OUJ-1 with 1,3,5-triazine ring as electron-withdrawing anchoring group and (dipheny lamino)carbazole containing a thiophene ring as D–π moiety have been newly developed and their optical and electrochemical properties, adsorption states on TiO₂ nanoparticles, and photovoltaic performances in DSSC were investigated (Scheme 1). The absorption maximum (λ_{abs}) for the ICT absorption band of the D–π–A dye OUJ-1 occurs at a longer wavelength than those of D–π–A dye NI-6 with a pyridyl group⁹ and D–π–A dye OUK-1 with a pyrazyl group.¹⁰ Moreover, the dye...
OUJ-1 exhibits significant fluorescence solvatochromic properties. It was found that the dye OUJ-1 is adsorbed onto the TiO₂ surface through the formation of trizainium ion at the Brønsted acid sites (surface-bound hydroxyl groups, Ti–OH) on TiO₂ surface, although the dye NI-6 was predominantly adsorbed on the TiO₂ surface through coordinate bonding between the pyridyl group of the dye and the Lewis acid site (exposed Ti₃⁺ cations) on the TiO₂ surface, and the dye OUK-1 was adsorbed on the TiO₂ surface through both the formations of hydrogen bonding of pyrazyl group and pyrazinium ion at Brønsted acid sites on the TiO₂ surface. The photovoltaic performance of DSSC based on OUJ-1 is lower those of NI-6 and OUK-1 due to low dye loading of OUJ-1 on TiO₂ electrode. On the basis of the experimental results and molecular orbital calculations, the differences of optical and electrochemical properties, adsorption states on TiO₂ nanoparticles, and photovoltaic performances in DSSC among these D–π–A dyes with azine rings are discussed.

Results and discussion

Synthesis

The synthesis of NI-6 and OUK-1 have been reported elsewhere.10,11 The synthetic pathway of D–π–A fluorescent dye OUJ-1 is shown in Scheme 2. The dye OUJ-1 was prepared by Stille coupling of stannyl compound 1 (ref. 11) with 2,4-dichloro-1,3,5-triazine.

Optical properties

The absorption and fluorescence spectra of NI-6, OUK-1, OUJ-1 in various solvents are summarized in Table 1. The three dyes in 1,4-dioxane show the absorption maximum (λₐₚₜₜₜ) at around 395–430 nm, which is assigned to the ICT excitation from electron donor moiety (diphenylamino group) to electron acceptor moiety (pyridyl, pyrazyl or triazyl group) (Fig. 1a). The λₐₚₜₜₜ for ICT band of the D–π–A dye OUJ-1 with 2-chloro-1,3,5-triazyl group occurs at a longer wavelength by 35 nm and 29 nm, respectively, than those of D–π–A dye NI-6 with a pyridyl group and D–π–A dye OUK-1 with a pyrazyl group, because of stronger electron-withdrawing ability of 2-chloro-1,3,5-triazyl group relative to pyridyl and pyrazyl groups. The molar extinction coefficient (ε) for the ICT band is 49 600 M⁻¹ cm⁻¹ for NI-6, 45 400 M⁻¹ cm⁻¹ for OUK-1 and 36 500 M⁻¹ cm⁻¹ for OUJ-1, respectively. The corresponding fluorescence maxima (λₕₚₜₜₜ) of OUJ-1 also occurs at a longer wavelength than those of NI-6 and OUK-1. Interestingly, the dye OUJ-1 exhibits significant fluorescence solvatochromic properties compared with NI-6 and OUK-1, that is, bathochromic shift of fluorescence band and a decrease in the fluorescence quantum yields (Φ) with increasing solvent polarity were
observed, although the absorption spectra are nearly independent of solvent polarity (Fig. 1b–d). In low polar solvent such as 1,4-dioxane and THF, the dye OUJ-1 exhibits fluorescence band at 547 nm in 1,4-dioxane and 600 nm in THF, respectively, arising from the 1ICT excited state. In polar solvent such as acetone, on the other hand, a new fluorescence band with the a significant decrease in the $\Phi$ value appeared at 638 nm, arising from the twisted intramolecular charge transfer (TICT) excited state which is due to the twisting between the triazyl group and the (diphenylamino)carbazole moiety, leading to non-radiative deactivation. Moreover, in highly polar solvent such as DMSO, owing to significant non-radiative deactivation from the TICT excited state leading to a decrease in the $\Phi$ value, the fluorescence band from only the $^1$ICT excited state was observed at 516 nm. Consequently, this result suggested that the predominant excited state for the D–π–A fluorescent dye OUJ-1 with triazyl group, which possesses stronger electron-withdrawing ability than those of pyridyl and pyrazyl groups, changes from the $^1$ICT state to the TICT state with increasing solvent polarity, resulting in a significant fluorescence solvatochromism.12–14

The absorption spectra of NI-6, OUK-1 and OUJ-1 adsorbed on TiO$_2$ film are shown in Fig. 1e. The absorption band of OUJ-1 are broadened compared with those of NI-6 and OUK-1. However, the absorption peak wavelengths of the three dyes adsorbed on TiO$_2$ are similar to those in 1,4-dioxane, although the absorption bands of the three dyes adsorbed on the TiO$_2$ film are broadened compared with those in 1,4-dioxane. Thus, this result indicates that the three dyes form weak $\pi$-stacked aggregates on TiO$_2$ surface.

**Electrochemical properties**

The electrochemical properties of NI-6, OUK-1 and OUJ-1 and were determined by cyclic voltammetry (CV). The CV curve of the three dyes are shown in Fig. 2. The reversible oxidation waves for the three dyes were observed at 0.37 V for NI-6, 0.42 V for OUJ-1, 0.45 V for OUJ-1, respectively, vs. ferrocene/ferrocenium (Fc/Fc$^+$) (Table 2). The corresponding reduction

<table>
<thead>
<tr>
<th>Dye</th>
<th>$E_{pa}$/V$^a$</th>
<th>$E_{pc}$/V$^a$</th>
<th>$E_{pa}^{1/2}$/V$^a$</th>
<th>HOMO/V$^b$</th>
<th>LUMO/V$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NI-6</td>
<td>0.37</td>
<td>0.30</td>
<td>0.34</td>
<td>0.97</td>
<td>-1.87</td>
</tr>
<tr>
<td>OUJ-1</td>
<td>0.42</td>
<td>0.35</td>
<td>0.39</td>
<td>1.11</td>
<td>-1.68</td>
</tr>
<tr>
<td>OUJ-1</td>
<td>0.45</td>
<td>0.37</td>
<td>0.41</td>
<td>1.13</td>
<td>-1.40</td>
</tr>
</tbody>
</table>

$^a$ Anodic ($E_{pa}$) and cathodic ($E_{pc}$) peak potentials, and half-wave potentials for oxidation ($E_{pa}^{1/2}$) vs. Fc/Fc$^+$ were recorded in CH$_2$Cl$_2$/Bu$_4$NClO$_4$ (0.1 M) solution for NI-6 and DMF/Bu$_4$NClO$_4$ (0.1 M) solution for OUJ-1 and OUJ-1, respectively. $^b$ vs. normal hydrogen electrode (NHE).
waves appeared at 0.30 V for NI-6, 0.35 V for OUK-1 and 0.37 V for OUJ-1, respectively, thus showing that the oxidized states of the three dyes are stable. The HOMO energy level vs. the normal hydrogen electrode (NHE) was evaluated from the half-wave potential for oxidation ($E_{1/2}^{ox}$ = 0.34 V for NI-6, 0.39 V for OUK-1 and 0.41 V for OUJ-1). The HOMO energy level was 0.97 V for NI-6, 1.11 V for OUK-1 and 1.13 V for OUJ-1, respectively, vs. NHE, thus indicating that the three dyes have comparable HOMO energy levels. This result shows that the HOMO energy levels are more positive than the $I_3^-/I^-_{0.5}$ redox potential (0.4 V), and thus this ensures an efficient regeneration of the oxidized dyes by electron transfer from the $I_3^-/I^-_{0.5}$ redox couple in the electrolyte. The LUMO energy level was estimated from the HOMO energy level and an intersection of absorption and fluorescence spectra (436 nm; 2.84 eV for NI-6, 445 nm; 2.79 eV for OUK-1, 491 nm; 2.52 eV for OUJ-1) in 1,4-dioxane, that is, the LUMO energy level was obtained through $E_{1/2}^{ox} - [E_{0-0} - $HOMO$]$, where $E_{0-0}$ transition energy is an intersection of absorption and fluorescence spectra corresponding to the energy gap between HOMO and LUMO, and HOMO vs. NHE was evaluated from the $E_{1/2}^{ox}$ value. The LUMO energy levels decrease in the order of NI-6 (1.87 V) > OUK-1 (1.68 V) > OUJ-1 (1.40 V), showing that the lowering of LUMO energy levels is dependent on the electron-withdrawing ability of azine ring. Consequently, it was revealed that the red-shift of the ICT absorption band for OUJ-1 relative to NI-6 and OUK-1 is attributed to stabilization of the LUMO level because of stronger electron-withdrawing ability of triazinyl group relative to pyridyl and pyrazyl groups, resulting in a decrease in the HOMO–LUMO band gap. Evidently, the LUMO energy levels of the three dyes are higher than the energy level ($E_{cb}$) of the CB of TiO2 (−0.5 V), suggesting that an electron injection to the CB of TiO2 is thermodynamically feasible.

### Theoretical calculations

In order to examine the electronic structures of NI-6, OUK-1 and OUJ-1, the molecular orbitals of the three dyes were calculated using density functional theory (DFT) at the B3LYP/6-31G(d, p) level. The DFT calculations indicate that for the three dyes the HOMOs were mostly localized on the (diphenylamino)carbazole containing a thiophene ring, and the LUMOs were mostly localized on the thienylpyridine for NI-6, thienylpyrazine for OUK-1 and thienyltriazine for OUJ-1, respectively (Fig. 3).

Accordingly, the DFT calculations reveal that dye excitations upon light irradiation induce a strong ICT from the (diphenylamino)carbazole to the azine ring.

### FTIR spectra

To elucidate the adsorption states of OUJ-1 on TiO2 nanoparticles, we measured the FTIR spectra of the dye powders and the dyes adsorbed on TiO2 nanoparticles (Fig. 4). In our previous study, it was found that the dye NI-6 was predominantly adsorbed on the TiO2 through coordinate bonding between the pyridyl group of the dye and the Lewis acid site (exposed Ti$^{4+}$ cations) on the TiO2 surface, and the dye OUK-1 was adsorbed on the TiO2 through both the formations of hydrogen bonding of pyrazyl group and pyrazinium ion at Bronsted acid sites (surface-bound hydroxyl groups, Ti–OH) on the TiO2 surface, where the adsorption amount of the dye adsorbed on TiO2 electrode is $3.1 \times 10^{16}$ and $3.0 \times 10^{16}$ molecules per cm$^2$ for NI-6 and OUK-1, respectively.$^{10-11}$ For the powders of OUJ-1, the C=N stretching band of trizaine ring was clearly observed at 1536 cm$^{-1}$. When the dye OUJ-1 was adsorbed on the TiO2 surface, where the adsorption amount of the dye adsorbed on TiO2 electrode is $2.5 \times 10^{16}$ molecules per cm$^2$, the band at 1536 cm$^{-1}$ disappeared completely and a new band appeared at around 1650 cm$^{-1}$, indicating that the dye OUJ-1 is adsorbed onto the TiO2 through the formation of trizainium ion at the Bronsted acid sites on TiO2 surface. These results suggest that the binding modes of D–π–A dye sensitizers with azine rings on TiO2 surface can be changed by control of the basicity and electron density of azine rings.

### Dye-sensitized solar cells

The DSSCs were fabricated by using the dye-adsorbed TiO2 electrode (9 μm), Pt-coated glass as a counter electrode, and an acetonitrile solution with iodine (0.05 M), lithium iodide (0.1 M), and 1,2-dimethyl-3-propylimidazolium iodide (0.6 M) as an electrolyte. The photocurrent–voltage (I-V) characteristics were measured under simulated solar light (AM 1.5, 100 mW cm$^{-2}$). The incident photon-to-current conversion efficiency (IPCE) spectra and the I-V curves are shown in Fig. 5. The photovoltaic performance parameters are collected in Table 3. The adsorption amount of dyes adsorbed on TiO2 is $3.0 \times 10^{16}$ and $2.5 \times 10^{17}$ molecules per cm$^2$ for OUK-1 and OUJ-1, respectively, when
6.9 ability onto TiO₂ surface among the three dyes may be associated with the basicity and electron density of azine rings, leading to changes of the binding modes of azine rings on TiO₂ surface. Consequently, this result indicates that the pyridyl unit is better anchoring group for achieving high dye loading than pyrazyl and triazyl group. When the adsorption amount of the dye is 2.5–3.1 × 10¹⁶ molecules per cm², the maximum IPCE value at around 420 nm increases in the order of OUK-1 (18%) < NI-6 (36%) = OUJ-1 (38%) (Fig. 5a). The short-circuit photocurrent density (\(J\)\(_{sc}\)) and solar energy-to-electricity conversion yield (\(\eta\)) also increase in the order of OUJ-1 (2.00 mA cm⁻², 0.54%) < NI-6 (2.96 mA cm⁻², 0.79%) = OUK-1 (2.99 mA cm⁻², 0.89%) (Fig. 5b and Table 2). The lower photovoltaic performances for DSCC based on OUJ-1 are attributed to low adsorption amount of the dyes on TiO₂ electrode. On the other hand, the DSCC based on NI-6-adsorbed TiO₂ electrode with 6.9 × 10¹⁶ molecules per cm² showed the \(J\)\(_{sc}\) (4.76 mA cm⁻²), \(\eta\) values (1.47%) and maximum IPCE value (64% at 420 nm), which are twice as high as those of low adsorption amount of the dye (3.1 × 10¹⁶ molecules cm⁻²) due to the enhancement of LHE with increasing dye loading on TiO₂ electrode. Moreover, the open-circuit photovoltage (\(V\)\(_{oc}\)) for DSCCs based on OUK-1 (448 mV) and OUJ-1 (444 mV) is lower than that of NI-6 (460 mV and 523 mV for 3.1 × 10¹⁶ and 6.9 × 10¹⁶ molecules per cm², respectively). Thus, electrochemical impedance spectroscopy (EIS) analysis was performed to study the electron recombination process in DSCCs in the dark under a forward bias of −0.45 V or −0.60 V with a frequency range of 10 mHz to 100 kHz. The large semicircle in the Nyquist plot (Fig. 6a), which corresponds to the midfrequency peaks in the Bode phase plots, represents the charge recombination between the injected electrons in TiO₂ and I₃⁻ ions in the electrolyte, that is, the charge-transfer resistances at the TiO₂/dye/electrolyte interface. The Nyquist plots show that the resistance value of the large semicircle for NI-6 (44 Ω and 50 Ω for 3.1 × 10¹⁶ and 6.9 × 10¹⁶ molecules per cm², respectively) is larger than those of OUK-1 (26 Ω) and OUJ-1 (20 Ω), indicating that the electron recombination resistance of NI-6 is higher than those of OUK-1 and OUJ-1. The electron recombination lifetimes (\(\tau\)\(_e\)) expressing the electron recombination between the injected electrons in TiO₂ and I₃⁻ ions in the electrolyte, extracted from the angular frequency (\(ω\)\(_{rec}\)) at the midfrequency peak in the Bode phase plot (Fig. 6b) using \(\tau\)\(_e\) = 1/\(ω\)\(_{rec}\), are 16 ms for both DSCCs based on NI-6-adsorbed TiO₂ electrode with 3.1 × 10¹⁶ and 6.9 × 10¹⁶ molecules per cm², which is larger than 10 ms and 8 ms for DSCCs based on OUK-1 and OUJ-1, respectively. Thus, this result revealed that the charge recombination between the injected electrons in TiO₂ and I₃⁻ ions in the electrolyte is not major reason for the difference in \(V\)\(_{oc}\) value between the three dyes, but the negative shift of the \(E\)\(_{cb}\) of TiO₂ by the formations of coordinate bonding between the pyridyl group of the dye and the Lewis acid site on the TiO₂ surface may result in a higher \(V\)\(_{oc}\) value for NI-6.⁶

**Table 3 DSCC performance parameters of NI-6, OUK-1 and OUJ-1**

<table>
<thead>
<tr>
<th>Dye</th>
<th>Molecules cm⁻²</th>
<th>(J)(_{sc}) mA cm⁻²</th>
<th>(V)(_{oc}) mV</th>
<th>FF (%)</th>
<th>(\eta) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NI-6</td>
<td>6.9 × 10¹⁶</td>
<td>4.76</td>
<td>523</td>
<td>0.59</td>
<td>1.47</td>
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<tr>
<td></td>
<td>3.1 × 10¹⁶</td>
<td>2.96</td>
<td>460</td>
<td>0.58</td>
<td>0.79</td>
</tr>
<tr>
<td>OUK-1</td>
<td>3.0 × 10¹⁶</td>
<td>2.99</td>
<td>448</td>
<td>0.67</td>
<td>0.89</td>
</tr>
<tr>
<td>OUJ-1</td>
<td>2.5 × 10¹⁶</td>
<td>2.00</td>
<td>444</td>
<td>0.61</td>
<td>0.54</td>
</tr>
</tbody>
</table>

⁶ The 9 μm thick TiO₂ electrode was immersed into dye solution in THF.

**Fig. 5** (a) IPCE spectra and (b) \(I–V\) curves and of DSSCs based on NI-6, OUK-1 and OUJ-1. The adsorption amount of the dye adsorbed on TiO₂ electrode is 3.1 × 10¹⁶ and 6.9 × 10¹⁶ molecules per cm² for NI-6, and 3.0 × 10¹⁶ and 2.5 × 10¹⁶ molecules per cm² for OUK-1 and OUJ-1, respectively.

**Conclusions**

We have designed and synthesized D-π-A fluorescent dye OUJ-1 with 1,3,5-triazine ring as electron-withdrawing anchoring group and (diphenylamino)carbazole containing a thiophene group, leading to changes of the binding modes of azine rings on TiO₂ surface. Consequently, this result indicates that the pyridyl unit is better anchoring group for achieving high dye loading than pyrazyl and triazyl group. When the adsorption amount of the dye is 2.5–3.1 × 10¹⁶ molecules per cm², the maximum IPCE value at around 420 nm increases in the order of OUK-1 (18%) < NI-6 (36%) = OUJ-1 (38%) (Fig. 5a). The short-circuit photocurrent density (\(J\)\(_{sc}\)) and solar energy-to-electricity conversion yield (\(\eta\)) also increase in the order of OUJ-1 (2.00 mA cm⁻², 0.54%) < NI-6 (2.96 mA cm⁻², 0.79%) = OUK-1 (2.99 mA cm⁻², 0.89%) (Fig. 5b and Table 2). The lower photovoltaic performances for DSCC based on OUJ-1 are attributed to low adsorption amount of the dyes on TiO₂ electrode. On the other hand, the DSCC based on NI-6-adsorbed TiO₂ electrode with 6.9 × 10¹⁶ molecules per cm² showed the \(J\)\(_{sc}\) (4.76 mA cm⁻²), \(\eta\) values (1.47%) and maximum IPCE value (64% at 420 nm), which are twice as high as those of low adsorption amount of the dye (3.1 × 10¹⁶ molecules cm⁻²) due to the enhancement of LHE with increasing dye loading on TiO₂ electrode. Moreover, the open-circuit photovoltage (\(V\)\(_{oc}\)) for DSCCs based on OUK-1 (448 mV) and OUJ-1 (444 mV) is lower than that of NI-6 (460 mV and 523 mV for 3.1 × 10¹⁶ and 6.9 × 10¹⁶ molecules per cm², respectively). Thus, electrochemical impedance spectroscopy (EIS) analysis was performed to study the electron recombination process in DSCCs in the dark under a forward bias of −0.45 V or −0.60 V with a frequency range of 10 mHz to 100 kHz. The large semicircle in the Nyquist plot (Fig. 6a), which corresponds to the midfrequency peaks in the Bode phase plots, represents the charge recombination between the injected electrons in TiO₂ and I₃⁻ ions in the electrolyte, that is, the charge-transfer resistances at the TiO₂/dye/electrolyte interface. The Nyquist plots show that the resistance value of the large semicircle for NI-6 (44 Ω and 50 Ω for 3.1 × 10¹⁶ and 6.9 × 10¹⁶ molecules per cm², respectively) is larger than those of OUK-1 (26 Ω) and OUJ-1 (20 Ω), indicating that the electron recombination resistance of NI-6 is higher than those of OUK-1 and OUJ-1. The electron recombination lifetimes (\(\tau\)\(_e\)) expressing the electron recombination between the injected electrons in TiO₂ and I₃⁻ ions in the electrolyte, extracted from the angular frequency (\(ω\)\(_{rec}\)) at the midfrequency peak in the Bode phase plot (Fig. 6b) using \(\tau\)\(_e\) = 1/\(ω\)\(_{rec}\), are 16 ms for both DSCCs based on NI-6-adsorbed TiO₂ electrode with 3.1 × 10¹⁶ and 6.9 × 10¹⁶ molecules per cm², which is larger than 10 ms and 8 ms for DSCCs based on OUK-1 and OUJ-1, respectively. Thus, this result revealed that the charge recombination between the injected electrons in TiO₂ and I₃⁻ ions in the electrolyte is not major reason for the difference in \(V\)\(_{oc}\) value between the three dyes, but the negative shift of the \(E\)\(_{cb}\) of TiO₂ by the formations of coordinate bonding between the pyridyl group of the dye and the Lewis acid site on the TiO₂ surface may result in a higher \(V\)\(_{oc}\) value for NI-6.⁶

**Fig. 6** (a) Nyquist plots and (b) Bode phase plots of DSSCs based on NI-6, OUK-1 and OUJ-1. The adsorption amount of the dye adsorbed on TiO₂ electrode is 3.1 × 10¹⁶ and 6.9 × 10¹⁶ molecules per cm² for NI-6, and 3.0 × 10¹⁶ and 2.5 × 10¹⁶ molecules per cm² for OUK-1 and OUJ-1, respectively.
ring as D–π moity. The dye OIJ-1 exhibits significant fluorescence solvatochromic properties due to change from the ICT excited state to the TICT excited state with increasing solvent polarity, compared with D–π–A dye NI-6 with a pyridyl group and D–π–A dye OUK-1 with a pyrazyl group. It was found the dye OIJ-1 is adsorbed onto the TiO₂ surface through the formation of triazinium ion at the Brønsted acid sites on TiO₂ surface, although the dye NI-6 was predominantly adsorbed on the TiO₂ through coordinate bonding between the pyridyl group of the dye and the Lewis acid site on the TiO₂ surface, and the dye OUK-1 was adsorbed on the TiO₂ surface through both the formations of hydrogen bonding of pyrazyl group and pyrazinium ion at Brønsted acid sites on the TiO₂ surface. The photovoltaic performance of DSSC based on OIJ-1 is lower than those of NI-6 and OUK-1 due to low dye loading of OIJ-1 on TiO₂ electrode. In addition, our results indicate that the pyridyl unit is better anchoring group for achieving high dye loading than pyrazyl and triazyl group. Consequently, this work suggests that the binding modes of D–π–A dye sensitizers with azine rings on TiO₂ surface can be changed by control of the basicity and electron density of azine rings. Further studies to ensure this conclusion are now in progress by estimating pKₐ values of D–π–A dye sensitizers with azine rings.

Experimental

General

Melting points were determined 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. High-resolution mass spectral data were acquired on a Thermo Fisher Scientific LTQ Orbitrap XL. ¹H NMR spectra were recorded on a Varian-400 (400 MHz) FT NMR spectrometer. Absorption spectra were observed with a Shimadzu UV-3150 spectrophotometer and fluorescence spectra were measured with a HORIBA FluoroMax-4 spectrofluorometer. The fluorescence quantum yields in solution were determined by a HORIBA FluoroMax-4 spectrofluorometer by using a calibrated integrating sphere. Cyclic voltammetry (CV) curves were recorded in CH₂Cl₂/MeCN (0.1 M) solution for NI-6 and DMF/MeCN (0.1 M) solution for OIJ-1 and OUK-1, respectively, 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 AMETEK Versa STAT 3. IR spectra were recorded on a PerkinElmer 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 HORIBA FluoroMax-4 spectrofluorometer. The fluorescence quantum yields in solution were determined by a HORIBA FluoroMax-4 spectrofluorometer by using a calibrated integrating sphere. Cyclic voltammetry (CV) curves were recorded in CH₂Cl₂/MeCN (0.1 M) solution for NI-6 and DMF/MeCN (0.1 M) solution for OIJ-1 and OUK-1, respectively, 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 AMETEK Versa STAT 4 potentiostat. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of NI-6, OUK-1 and OIJ-1 were evaluated from the spectral analyses and the CV data (the HOMO energy level was evaluated from the E⁻½ max). The LUMO energy level was estimated from the E⁺½ max and an intersection of absorption and fluorescence spectra (436 nm; 2.84 eV for NI-6, 445 nm; 2.79 eV for OUK-1, 491 nm; 2.52 eV for OIJ-1) in 1,4-dioxane, that is, the LUMO energy level was obtained through eqn [-E₀⁻½ max – HOMO], where E₀ transition energy is an intersection of absorption and fluorescence spectra corresponding to the energy gap between HOMO and LUMO, and HOMO vs. NHE was evaluated from the E⁺½ max value. Electrochemical impedance spectroscopy (EIS) for DSSCs in the dark under a forward bias of −0.60 V for NI-6 and OUK-1 and −0.45 V for OIJ-1 with a frequency range of 10 mHz to 100 kHz was measured with a AMETEK Versa STAT 3.

Synthesis

9-Butyl-7-(5-(4-chloro-1,3,5-triazin-2-yl)thiophen-2-yl)-N,N-diaryl-9H-carbazol-2-amine (OIJ-1). A solution of 1 (ref. 11) [0.34 g, 0.53 mmol], 2,4-dichloro-1,3,5-triazine (0.09 g, 0.58 mmol), and Pd(PPh₃)₄ (0.018 g, 0.016 mmol) in toluene (15 mL) was stirred for 3 h at 110 °C under an argon atmosphere. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane and washed with water. The dichloromethane extract were evaporated under reduced pressure. The residue was chromatographed on silica gel (ethyl acetate–hexane = 1 : 6 as eluent as eluent) to give OIJ-1 (0.13 g, yield 42%) as a yellow solid; m.p. 201–202 °C; IR (ATR): ν = 1586, 1536, 1488, 1444 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 0.88 (t, J = 7.4 Hz, 3H), 1.26–1.33 (m, 2H), 1.73–1.80 (m, 2H), 4.19 (t, J = 7.0 Hz, 2H), 6.95 (dd, J = 1.6 and 8.4 Hz, 1H), 7.02–7.06 (m, 2H), 7.12–7.16 (m, 5H), 7.25–7.30 (m, 4H), 7.56 (d, J = 4.0 Hz, 1H), 7.58 (dd, J = 1.6 and 8.1 Hz, 1H), 7.69 (d, J = 1.2 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 8.1 Hz, 1H), 8.24 (d, J = 4.0 Hz, 1H), 8.89 (s, 1H); HRMS (APCI): m/z (%): [M + H⁺] calcld for C₃₅H₂₉N₅Cl₂S, 586.18267; found 586.18292.

Preparation of DSSCs

The TiO₂ 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 TiO₂ electrode was immersed into 0.06 mM or 0.1 mM dye (NI-6) solution in THF or 1.0 mM dye (OK-1 and OIJ-1) solution in THF for 15 hours enough to adsorb the dye sensitizers. The DSSCs were fabricated by using the TiO₂ electrode (0.5 × 0.5 cm² in photoactive area) 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 dye-coated film for NI-6 and OUK-1 was immersed in a mixed solvent of THF–DMSO–NaOHaq. 1 M (5 : 4 : 1), which was used to determine the amount of dye molecules adsorbed onto the film by measuring the absorbance. The quantitative of dye was made based on the molar extinction coefficient for λmax of dye in the above solution. For OIJ-1, the amount of adsorbed dye on TiO₂ nanoparticles was determined form the calibration curve by absorption spectral measurement of the concentration change of the dye solution before and after adsorption, because the dye OIJ-1 is decomposed by the mixed solvent of THF–DMSO–NaOHaq. 1 M (5 : 4 : 1). Absorption spectra of the dyes adsorbed on TiO₂ nanoparticles were recorded on the dyes-adsorbed TiO₂ film in the transmission mode with a calibrated integrating sphere.
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Notes and references


