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Indoline Dyes with Benzothiazole Unit for Dye-sensitized Solar Cells

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We report a new series of indoline dyes with a donor–aromatic–acceptor (D–π–A) structure. D–π–A metal-free organic dyes with indoline–benzothiazole–rhodanine units were synthesized and their photovoltaic performances were evaluated. The photoelectric conversion efficiency (η) of the indoline–benzothiazole–rhodanine dye is 3.7%, while that of the indoline–thiophene–rhodanine dye is 0.9% under the same conditions. The incident photon-to-current conversion efficiencies (IPCEs) of these dyes are 60% and 25%, respectively, at 500 nm. To understand their electronic structures, the geometries of the dyes were optimized by density functional theory (DFT) calculations at the 6-31G(d) level using a B3LYP exchange-correlation functional. As a result, the localized highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the indoline–benzothiazole–rhodanine dye were obtained and were compared with those of the indoline–thiophene–rhodanine dye.

Keywords: Dye-sensitized solar cell (DSSC) | Metal-free organic dye | Indoline

Dye-sensitized solar cells have attracted considerable attention as inexpensive next-generation power-generating devices.[1–3] These are the only solar cells capable of combining colorful designs, transparency, and flexibility. By exploiting these advantages, even from the standpoint of photovoltaic devices, the use of dye-sensitized solar cells will become widespread, and an industry that can actively support future energy levels will grow. However, the conversion efficiency and durability of dye-sensitized solar cells need to be further improved to suit more practical applications and to establish the industry. Thus, continuous development of new materials is essential. In particular, the refinement of dyes plays a crucial role in fulfilling this task. These dyes are classified into two groups: "metal complex dyes," such as ruthenium complexes, and "metal-free organic dyes," which do not contain metal ions. Metal-free dyes have unique features like high molecular absorption coefficients, vivid colors, and a wide variety of molecular designs. In particular, good photovoltaic performance has been reported for dyes containing indoline as the donor unit.[4–6] Perovskite solar cells have attracted considerable attention in recent years due to their excellent photovoltaic performances.[7–10] Although the energy conversion efficiencies of dye-sensitized solar cells are lower than perovskite solar cells, it has little load for environment.

It has recently been shown that to fabricate sensitized dyes with large wavelengths, an aromatic ring such as the thiophene derivative should be introduced between the donor and acceptor units.[11–13] The development of the NKX-2195 dye, with a rhodanine ring as the acceptor and a coumarin ring as the donor, has been reported.[14] This dye has oxidation potential values (E_{OX}) minus the 0–0 energy ($E_{0\text{–}0}$) that are more negative than approximately −0.7 V vs. NHE, and show high incident photon-to-current conversion efficiencies (IPCEs). For $E_{\mathrm{OX}} = -0.63$ V, the IPCE value of NKX-2195 at λ_{max} was 40%. In donor–aromatic–acceptor (D–π–A)-type dyes with a rhodanine ring, the absorption band of LMc with a 4-methine chain as the π unit was red-shifted compared to that of Mc with a 2-methine chain as the π unit, and the absorption thresholds in ethanol solution were 700 and 570 nm, respectively.[15] However, the photoelectric conversion efficiency (η) and short-circuit photocurrent density (J_{SC}) of the LMc were very low (η: 0.4%, J_{SC}: 2.62 mA cm^{-2}) compared to those of the Mc (η: 4.5%, J_{SC}: 11.4 mA cm^{-2}).[16] The low excitation energy, occurrence of cis–trans isomerization, and disorder of the alignment of chromophores in the J-like aggregate were used to explain these observations.

Molecular design of the dyes is thus necessary to prevent cis–trans isomerization and to obtain good energy matching to TiO_2 and I_2. We examined π units that would be effective for D–π–A type dyes with a rhodanine ring as the acceptor, and found that the benzothiazole ring has a molecular structure that would not allow cis–trans isomerization. Here, we report on a new type of organic dye, based on indoline with a benzothiazole unit.

The chemical structure of the indoline dyes (BT-1 and BT-2) are shown in Figure 1. T-1 and T-2, both of which have a thiophene unit, were synthesized for reference. Details of the conditions and route for the synthesis of BT-2, T-1, and T-2 are presented in the Supporting Information. Only the synthesis of BT-1 is described below.

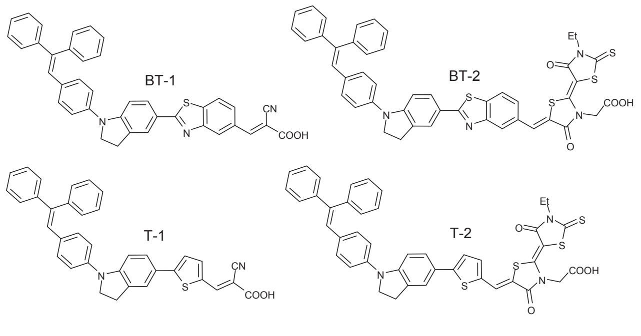

Figure 1. Chemical structure of indoline dyes.

BT-1 was produced by heating a mixture of 2-{1-[4-(2,2-diphenylvinyl)phenyl]indolin-5-yl}benzo[*d*]thiazole-5-carbaldehyde (0.50 g, 0.935 mmol), cyanoacetic acid (0.16 g, 1.88 mmol), piperidine (0.35 g, 4.11 mmol), and acetonitrile (20.0 mL) and chlorobenzene (3 mL) to 80 °C in a N_2 atmosphere. The reaction finished after 1.5 h, and the mixture was cooled to room temperature. It was then poured into water, and ethyl acetate and toluene were used to extract the reaction products. The organic layer was washed with water and separated, dried over magnesium sulfate, and was then subjected to vacuum concentration. The residue was purified using silica gel chromatography with a mixture of toluene and ethyl acetate as the solvent, and recrystallized from a mixture of toluene and hexane. The yield of the target product obtained thus was 0.53 g.

The experimental section is presented in the Supporting Information.

Recently, solid-state dye-sensitized solar cells have been reported.[17–19] These solid-state dye-sensitized solar cells are necessary for 2-µm TiO_2 thin films due to the use of high-resistance hole-transport materials. Then, a sensitizing dye with a high absorbance coefficient is required for effective light absorption. The absorption spectra of T-1 and BT-1 in dichloromethane are presented in the Supporting Information. The absorbance coefficients measured for BT-1 and BT-2 in dichloromethane were, respectively, 42700 $M^{-1}\,cm^{-1}$ at 410 nm and 41300 $M^{-1}\,cm^{-1}$ at 391 nm. In contrast, T-1 and T-2 show similar absorption maxima to that of BT-1, at 361 and 332 nm, respectively. The highest occupied molecular orbital (HOMO) was measured with a photoelectron spectrometer (AC-2, Riken Keiki Co., Ltd.); the band gap was determined from the edge of the UV–vis spectra; and the lowest unoccupied molecular orbital (LUMO) was calculated. The HOMOs and LUMOs of these dyes are presented in the Supporting Information. The band gap of the indoline dyes with the benzothiazole unit was larger than that of the thiophene unit. In terms of the red shift of the absorption spectra, the benzothiazole unit is less favorable than the thiophene unit.

The photovoltaic performances of the solar cells constructed from these dyes were measured. The measured open-circuit photovoltage (V_{OC}), short-circuit photocurrent density (J_{SC}), fill factor (ff), and solar-to-electric conversion efficiency (η) of these indoline dyes are listed in Table 1. Figure 2 shows the IPCE spectra of BT-2 and T-2, respectively. The IPCE spectra of T-1, BT-1, and these reference dyes are presented in the Supporting Information.

The photovoltaic performances of the indoline dyes containing cyanoacetic acid were compared. The η values of BT-1 and T-1 were almost the same. When CDCA was added as a coadsorbent to BT-1 and T-1 solutions, the efficiency of these dyes decreased because of the weak molecular interaction between the dye molecules on TiO_2. A decrease in the IPCE value was evident in the spectra of both BT-1 and T-1 with the coaddition of CDCA. On the other hand, the photovoltaic performance slightly increased with the addition of 0.05-mM tBP to the electrolyte. When the thiophene unit was changed to the benzothiazole unit, the IPCE increased slightly in the 400–500-nm region. However, a shift to shorter wavelength was obtained. In the dye with cyanoacetic acid as the acceptor, the edges of the absorption and IPCE spectra showed the same behavior, and T-1 was red-shifted with respect to BT-1. The large absorption peak at 410 nm of T-1 was not observed in the IPCE.

Table 1. Photovoltaic performance of indoline dyes

Dye	CDCA	tBP	V_{OC} /V	J_{SC} /mA cm^{-2}	ff	η /%
T-1	○	○	0.504	12.72	0.614	3.94
	○	—	0.459	15.21	0.375	2.62
	—	○	0.525	12.28	0.676	4.36
	—	—	0.462	15.7	0.527	3.82
BT-1	○	○	0.591	12.72	0.525	4.02
	○	—	0.543	12.02	0.457	2.98
	—	○	0.572	13.51	0.651	5.03
	—	—	0.529	13.87	0.556	4.09
T-2	○	○	0.442	5.42	0.591	1.42
	○	—	0.407	8.01	0.402	1.31
	—	○	0.403	3.56	0.633	0.91
	—	—	0.373	6.32	0.608	1.43
BT-2	○	○	0.508	9.88	0.58	2.91
	○	—	0.462	8.69	0.502	2.01
	—	○	0.51	10.89	0.668	3.71
	—	—	0.447	14.69	0.504	3.31

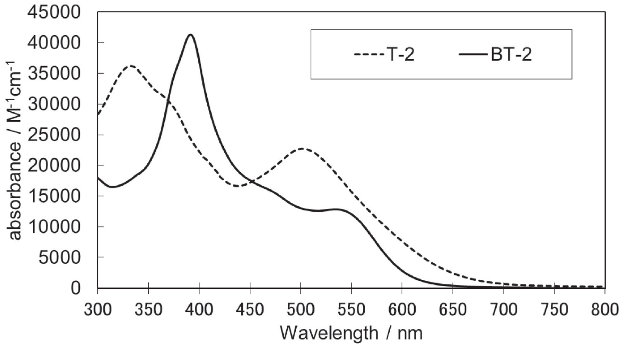

Figure 2. Absorption spectra of BT-2 and T-2.

Table 1 summarizes the photovoltaic performances of the indoline dyes with a double-rhodanine ring as the adsorption unit. The η value of BT-2 is slightly higher than that of T-2. This differed from the behavior observed when cyanoacetic acid was the adsorption unit, and T-2 showed an increase in J_{SC} when CDCA was used. However, BT-2 showed a decrease in J_{SC}. Figure 2 shows that the IPCE spectrum of BT-2 was higher than that of T-2. There is no example of a high IPCE value for a D–π–A-type sensitized dye containing a double-rhodanine unit. We found that the benzothiazole unit was useful for sensitized dyes. For the dye with a rhodanine ring as the acceptor, the edges of absorption and IPCE spectra also showed the same behavior, and T-2 was red-shifted in comparison to BT-2. The IPCE of BT-2 displayed a flat shape, and the IPCE of T-2 had a similar shape to that of the absorption spectrum. The energy levels of BT-2 and T-2 were almost equivalent. This result may arise from a difference in the efficiency of electronic injection from the dye cation to TiO_2. The thermogravimetry (TG) of the dyes with cyanoacetic acid, BT-1 and T-1, were 406 and 378 °C, respectively. The TG of the dye with double rhodanine ring, BT-2 and T-2 were 284 and 276 °C, respectively. It is apparent

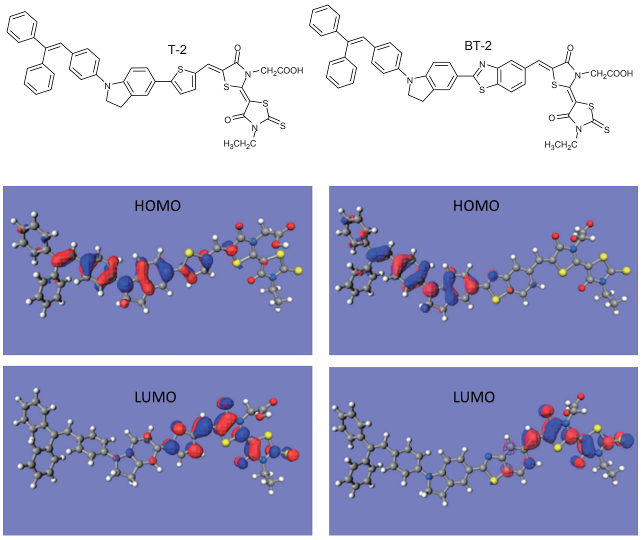

Figure 3. Graphical representation of the HOMOs and LUMOs of T-2 and BT-2 as determined at B3LYP/6-311+G(d,p) on B3LYP/6-31G(d) optimized geometries.

that heat durability of the dye with a benzothiazole ring is higher than a thiophene ring.

In order to understand the electronic structure of the dyes, their geometries were optimized by density functional theory (DFT) calculations at the 6-31G(d) level using a B3LYP exchange-correlation functional. Graphical representations of the HOMOs and LUMOs of T-1 and BT-1, as determined from DFT calculations, are presented in the Supporting Information. T-1 has a wide HOMO area between the cyanoacetic acid and the stylyl units. In addition, T-1 has a wide LUMO area between the cyanoacetic acid and indoline ring. Figure 3 shows a graphical representation of the HOMOs and LUMOs of T-2 and BT-2, as determined from DFT calculations. BT-1 has a localized HOMO area between the indoline ring and stylyl unit and a localized LUMO area between the cyanoacetic acid and benzothiazole unit. In general, the most efficient dye molecules show charge-transfer absorption when the acceptor unit is close to the TiO_2 surface and the donor unit is away from the TiO_2 surface.[16,20–23] The excited electron is close to the TiO_2 surface, and the hole is instead located further from the TiO_2 surface, which decreases the rate of charge-recombination of the electron in TiO_2 with the hole on the dye. Therefore, a dye with the D–π–A-type molecular structure shows efficient electron injection. We believe that the localized HOMO and LUMO performed better with the introduction of the benzothiazole unit.

In conclusion, we have synthesized new metal-free organic sensitizers based on indoline–benzothiazole–cyanoacetic acid (BT-1) and indoline–benzothiazole–rhodanine (BT-2) for application in dye-sensitized solar cells. For comparison, reference species with a thiophene unit (T-1 and T-2) were also synthesized. The values of photoelectric conversion efficiency (η) of the cells based on BT-1 and BT-2 are 5.03% and 3.71%, respectively, which are higher than the values of 4.36% and 0.91% for T-1 and T-2, respectively, under the same conditions. The IPCE of BT-2 with the benzothiazole unit is 60% at 500 nm, which is higher than the value of 25% at 500 nm for T-2 with the thiophene unit. The IPCE spectrum of BT-2 was flat in shape. DFT calculations showed that dyes with benzothiazole units have localized HOMO and LUMO. Therefore, we conclude that the benzothiazole unit allows effective electron injection from the dye cation to the TiO_2 surface.

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Supporting Information is available on http://dx.doi.org/10.1246/cl.160084.

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