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Application of novel *N*-(*p*-phenylene)-dicyanovinylidene double rhodanine indoline dye for zinc oxide dye-sensitized solar cell

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1. Introduction

Indoline dyes are known as one of the highly efficient organic sensitizers in dye-sensitized solar cells. D149 in which a double rhodanine ring is attached through a methine linkage at the 7position on the indoline ring has been reported to show excellent conversion efficiency 9.0% on titanium oxide [1,2]. The double rhodanine indoline dyes having two anchoring carboxyl groups [3], an octyl group at the terminal rhodanine ring [4], a thiophene spacer(s) [5], and dicyanovinylidene group [6,7] have been also designed, synthesized, and evaluated as the sensitizers. Furthermore, indoline dyes of mono rhodanine [8], triple rhodanine [9], cyanoacrylic acid acceptors [10-12], benzoindoline derivatives [13], and naphthalimides attached with two indoline moieties [14] have been reported. We suppose that the characteristic feature of indoline dyes is a cyclopentane moiety which can depress aggregates formation on semiconductors [15]. We have reported that when a double rhodanine ring is used as the acceptor, the energy

ABSTRACT

A new indoline dye in which a double rhodanine acceptor is attached to the indoline moiety by a *p*-phenylene spacer on the indoline—nitrogen, has been examined for its performance as a sensitizer for zinc oxide dye-sensitized solar cells. In the presence of cholic acid, chenodeoxycholic acid, or lithocholic acid; the performance was greatest for lithocholic acid as this showed the greatest reduction in dye H-aggregate formation.

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gap between the oxidation potential (E_{ox}) of the indoline dye and I^-/I_3^- redox level is small compared with that between the reduction potential of the indoline dye and the conduction level of zinc oxide [16]. Therefore, the positive shift of E_{ox} is desirable to obtain a high incident-photon-to-current conversion efficiency (IPCE). On the basis of these points, we have designed a new double rhodanine indoline dye GU104, in which a double rhodanine acceptor is attached to the indoline moiety by way of a *p*-phenylene spacer on the indoline–nitrogen and whose HOMO level was predicted to be more stable (-5.35 eV) than D149 (-5.07) by the DFT calculations. We report herein the application of novel indoline dye, GU104, to zinc oxide dye-sensitized solar cell.

2. Results and discussion

2.1. Synthesis

A new indoline dye GU104 was synthesized as shown in Scheme 1. An indoline **1** was allowed to react with 4-bromobenzaldehyde (**2**) to give a formyl derivative **3** followed by the reaction with a dicyanovinylidene double rhodanine acetic acid **4** to provide GU104.

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Scheme 1. Reagents and conditions: i) 1 (1.0 equiv), 2 (1.2 equiv), t-BuONa (1.4 equiv), Pd(OAc)₂ (5 mol%), SPhos (10 mol%), toluene, reflux, overnight, ii) 3 (1.0 equiv), 4 (1.0 equiv), piperidine (1.0 equiv), BuOH, 120 °C, 4 h.

2.2. UV-vis absorption and fluorescence spectra

The UV–vis absorption and fluorescence spectra of GU104 in chloroform are indicated in Fig. 1. The results are also listed in Table 1. The first absorption maximum (λ_{max}) of GU104 was observed at 541 nm with molar absorption coefficient (ε) 34,600 dm³ mol⁻¹ cm⁻¹. Though no remarkable difference in the λ_{max} was observed between GU104 and D149 (542 nm), the ε value of GU104 was significantly smaller than that of D149 (66,000). The fluorescence maximum (F_{max}) of GU104 was observed at 642 nm.

2.3. DFT calculations

The structure of GU104 was optimized by the B3LYP/3-21G level. The results are shown in Fig. 2 and Table 1. Fig. 2a indicates that the double bond at the 4-position on the *p*-phenylene ring adopts the Z-conformation in order to minimize repulsion between the orthophenyl hydrogen atom and the carbonyl oxygen of the inner rhodanine carbonyl group. The double bond between the two rhodanine moieties adopts the E-conformation as this avoids steric repulsion between the N-carboxymethyl group of the inner rhodanine ring and the carbonyl group of the terminal rhodanine ring. The dihedral angles θ^1 and θ^2 are calculated to be 16.2 and 1.1°, respectively. A large θ^1 could be attributed to repulsion between the hydrogen atom at the 3a-position in the indoline moiety and 6hydrogen atom on the p-phenylene ring. D149 ethyl ester has been reported to be almost planar through indoline-nitrogen to double rhodanine acceptor [15]. Thus, a smaller ε value (34,600) of GU104 in the first absorption band, compared with that of D149 (66,000), could come from the less planarity of GU104. Fig. 2b shows that the HOMO and LUMO levels of GU104 were calculated to be -5.35 and -2.60 eV, respectively. Those of D149 were calculated to be -5.07 and -2.37 eV, respectively [12]. Thus, the HOMO level of GU104 was more stable than that of D149. The isodensity surface plots of GU104 in the HOMO and LUMO levels



Fig. 1. UV–vis absorption and fluorescence spectra ($\lambda_{ex}=540\,$ nm) of GU104 (1.0 \times 10 $^{-5}$ mol dm $^{-3})$ in chloroform at 25 $^\circ C.$

indicate that GU104 consists of an intramolecular charge-transfer chromophoric system from indoline to rhodanine moiety as shown in Fig. 2c.

2.4. Electrochemical measurements

Fig. 3 shows the cyclic voltammogram of GU104 vs Ag quasi reference electrode (QRE) in DMF in the presence of ferrocene as an internal standard. The oxidative wave at +0.70 and 1.14 V correspond to the oxidation of ferrocene and GU104, respectively. Therefore, the oxidation potential (E_{ox}) of GU104 is estimated to be 0.44 V vs Fc/Fc⁺. That of D149 was estimated to be 0.40 V vs Fc/Fc⁺. Thus, the E_{ox} level of GU104 was more positive than that of D149. The result is consistent with the DFT calculations that the HOMO level of GU104 (-5.35) is more stable than that of D149 (-5.07). The I^-/I_3^- redox level was estimated to be -0.05 V vs Fc/Fc⁺. As no reduction potential peak was observed for GU104, the $E_{ox} - E_{0-1}$ 0 level was calculated as described in our previous paper [12]. The $E_{\rm ox} - E_{\rm 0-0}$ level of GU104 was calculated to be -1.67 V vs Fc/Fc⁺. This level is slightly more positive than that of D149 $(-1.70 \text{ V vs Fc/Fc}^+)$ [12]. The conduction band level of zinc oxide is -0.95 V vs Fc/Fc⁺. Therefore, GU104 can thermodynamically sensitize zinc oxide and the oxidized GU104 can accept electrons from I⁻.

2.5. Photoelectrochemical properties

The UV-vis absorption spectra on zinc oxide, IPCE action spectra, and *I*–*V* curve of GU104 in the presence of cholic acid (CA), chenodeoxycholic acid (CDCA), and lithocholic acid (LCA) are shown in Fig. 4 and Table 2. The conversion efficiency (η) of GU104 was higher in the order of the cholic acids: LCA (3.93) > CDCA(3.67) > CA (3.35). No remarkable differences in open-circuit photovoltage (V_{oc}) and fill factor (ff) were observed among the cholic acids. The η value mainly depends on the short-circuit photocurrent density (J_{sc}) . Fig. 4a depicts that the absorbance values were in the range of 1.95-2.11, indicating that similar amount of dyes were adsorbed on zinc oxide. Actually, the amounts of adsorbed GU104 were in the range of 2.81- $3.22\,\times\,10^{-6}$ mol cm^-2. Therefore, the ratio of aggregated GU104 on zinc oxide could affect the Jsc value. The normalized UV-vis absorption spectra of GU104, depicted in Fig. 4b, significantly show that the shoulder peak at around 470 nm comes from Haggregates and was broadened in the order of cholic acids: CA > CDCA > LCA. The IPCE spectra clearly show that the sensitization of GU104 was larger in the order of cholic acids: LCA > CDCA > CA as shown in Fig. 4c. Thus, LCA could most effectively prevent H-aggregate formation of GU104 on zinc oxide to show the best performance.

Table 1 Properties of GU104.

Compd	$\lambda_{\max} (\varepsilon)^a nm$	F _{max} ^a nm	$E_{\rm ox}^{\rm b} V$	$E_{\rm ox} - E_{0-0}{}^{\rm c} {\rm V}$	HOMO ^d eV	LUMO ^d eV	f ^e
GU104	392 (15,100), 541 (34,600)	642	+0.44	-1.67	-5.35	-2.60	1.02

 a Measured on 1.0 \times 10 $^{-5}$ mol dm $^{-3}$ of substrate in chloroform at 25 $^{\circ}\text{C}.$

^b vs Fc/Fc⁺ in DMF.

^c Calculated on the basis of E_{ox} and λ_{int} .

^d Calculated by the B3LYP/6-31G(d,p)//B3LYP/3-21G level.

^e Oscillator strength calculated by the INDO/S method.

3. Conclusion

We have made a molecular design, synthesis, and evaluation of a new indoline dye GU104 in which dicyanovinylidene rhodanine moiety is attached to the indoline moiety through an *p*-phenylene spacer on the indoline—nitrogen atom. GU104 could have more positive E_{ox} level than D149. Cell performance in the presence of CA, CDCA, or LDA was greatest for LCA as this showed the greatest reduction in dye H-aggregate formation.

4. Experimental

4.1. Instruments

Melting points were measured with a Yanaco MP-S2 micromelting-point apparatus. NMR spectra were taken with a JEOL JNM-ECX 400P spectrometer. Mass spectra were taken on a JEOL MStation 700 spectrometer. Elemental analysis was performed with a Yanaco MT-6 CHN corder. UV—vis absorption and fluorescence spectra were taken on Hitachi U-3500 and F-4500 spectrophotometers, respectively. Electrochemical measurement was carried out using an EG&G Princeton Applied Research Potentiostat/Galvanostat (Model 263A) driven by the M270 software package.

4.2. Materials

Compounds 1 and 4 were supplied from Chemicrea Co., Ltd.

4.3. Synthesis of 10-(4-formylphenyl)-6b,7,8,9,9a,10-hexahydro[g] cyclopenta[b]indole (**3**)

To toluene (300 mL) were added 1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (**1**, 3.986 g, 25.0 mmol), 4-bromobenzaldehyde (**2**, 6.547 g, 30.0 mmol), sodium *t*-butoxide (3.360 g, 35.0 mmol), palladium diacetate (0.281 g, 1.25 mmol), and 2-dicyclohexylphosphyno-2',6'-dimethoxybiphenyl (SPhos, 1.000 g, 2.44 mmol). The mixture was refluxed overnight. After the reaction was completed, the mixture was poured into water (300 mL). The product was extracted with chloroform (100 mL \times 3). The extract was washed with water (100 mL \times 3) and dried over anhydrous sodium sulfate. The product was purified by column chromatography (SiO₂, CHCl₃:C₆H₁₄ = 1:1) to give pale yellow liquid. Yield 31%; ¹H NMR (CDCl₃) $\delta = 0.85 - 0.99$ (m, 1H), 1.24 - 1.32 (m, 1H), 1.38 - 1.52 (m, 1H), 1.63-1.75 (m, 1H), 1.89-2.12 (m, 2H), 3.87-3.94 (m, 1H), 4.58–4.74 (m, 1H), 6.89 (t, J = 7.8 Hz, 1H), 7.14 (t, J = 7.8 Hz, 1H), 7.18 (d, J = 7.8 Hz, 1H), 7.27 (d, J = 7.8 Hz, 1H), 7.34 (d, J = 8.7 Hz, 2H), 7.81 $(d, J = 8.7 \text{ Hz}, 2\text{H}), 9.82 (s, 1\text{H}); {}^{13}\text{C} \text{ NMR} (\text{CDCl}_3) \delta = 24.7, 34.1 (2\text{C}),$ 45.5, 68.5, 110.7, 115.9 (2C), 121.2, 125.0, 127.1, 128.3, 131.5 (2C), 136.0, 144.7, 148.7, 190.3; IR (KBr) 2928, 2855, 1744, 1686, 1589, 1481, 1381 cm⁻¹; EIMS (70 eV) m/z (rel intensity) 263 (M⁺, 52), 234 (100), 104 (14); Anal. Found: 82.43; H, 6.90; N, 5.71%. Calcd for C₁₈H₁₇NO: C, 82.10, H, 6.51; N, 5.32%.

4.4. Synthesis of GU104

To 1-butanol (10 mL) were added 3 (200 mg, 0.76 mmol), a dicyanovinylidene double rhodanine acetic acid 4 (341 mg, 0.76 mmol). The mixture was heated to 120 °C. Then, to the mixture was added piperidine (65 mg, 0.76 mmol). The mixture was refluxed for 4 h. After the reaction was completed, the solvent was removed in vacuo. The product was purified by column chromatography (SiO₂, CHCl₃:MeOH = 20:1). The ¹³C NMR spectrum was not measured due to low solubility. Yield 69%; mp 242–243 °C; ¹H NMR (DMSO- d_6) $\delta = 0.85$ (t, J = 6.6 Hz, 3H), 1.17–1.36 (m, 11H), 1.55-1.68 (m, 3H), 1.71-1.87 (m, 2H), 1.98-2.11 (m, 2H), 3.85-3.93 (m, 1H), 3.97 (s, 2H), 4.54 (s, 2H), 4.75-4.83 (m, 1H), 6.88 (t, J = 7.7 Hz, 1H), 7.13 (t, J = 7.7 Hz, 1H), 7.23 (d, J = 7.7 Hz, 1H), 7.32 (d, J = 7.7 Hz, 1H), 7.46 (d, J = 8.5 Hz, 2H), 7.67 (d, J = 8.5 Hz, 2H), 7.76 (s, 1H); IR (KBr) 2928, 2195, 1655, 1578, 1543, 1508 cm⁻¹; FABMS (NBA) *m*/*z* 680 (MH⁺); Anal. Found: C, 65.07; H, 5.63; N, 10.39%. Calcd for C₃₇H₃₇N₅O₄S₂: C, 65.37; H, 5.49; N, 10.30%.



Fig. 2. DFT calculations (B3LYP/6-31G(d,p)//B3LYP/3-21G) of GU104. (a) optimized structure, (b) HOMO and LUMO levels, and (c) isodensity surface plots.



Fig. 3. Cyclic voltammogram of GU104 in the presence of ferrocene. Measured in DMF vs AgQRE at scan rate 100 mV s⁻¹.

4.5. Electrochemical measurements

The oxidation potential was measured by using small-size three electrodes. Ag *quasi* reference electrode (AgQRE) was used as a reference. Platinum wire was used as the working and counter electrodes. All electrode potentials were calibrated with respect to ferrocene (Fc)/ferrocenium (Fc⁺) redox couple. A DMF solution (2 mL) of dye containing tetrabutylammonium perchlorate (0.1 mol dm⁻³) and ferrocene (*ca*. 1 mmol dm⁻³) was prepared. The electrochemical measurement was performed at the scan rate of 100 mV s⁻¹.

4.6. Film preparation

The electrodes were formed by the screen printing of zinc oxide (0.28 cm^2) films on F-doped tin-oxide-coated (FTO) glass plates (Nippon Sheet Glass, Solar, 4 mm thick) with zinc oxide pastes

Photovoltaic properties of Gu104 on zinc oxide.

Run	Additives ^a	Adsorbed GU104 mol dm^{-3}	$J_{\rm sc}{}^{\rm b}{\rm mA}~{\rm cm}^{-2}$	$V_{\rm oc}$ V	∬ ^b	$\eta^{\mathbf{b}\%}$
1	CA	$3.22 imes 10^{-6}$	7.67	0.62	0.71	3.35
2	CDCA	3.81×10^{-6}	8.09	0.64	0.71	3.67
3	LCA	3.21×10^{-6}	8.53	0.64	0.72	3.93

^a Two molar amounts of cholic acids for GU104.

^b AM 1.5 irradiation (100 mW cm⁻²).

prepared from nanoparticle ZnO-410 (Sumitomo Osaka Cement Co., Ltd). The thickness of zinc oxide layer was 12 µm. An acetonitriletert-butyl alcohol (v/v, 1:1) mixed solution of dye (0.5 mM) containing a cholic acid (1.0 mM) was prepared. The zinc oxide electrodes were immersed into the solution and kept at room temperature for 90 min. Platinum (6 µm thick) sputtered FTO glass plates were used as the counter electrode. The dve-adsorbed zinc oxide electrode and platinum counter electrode were assembled into a sealed sandwich-type cell by heating with a hot melt type ionomer film (HIMILAN, 35 µm thick, DuPont), which is served as a spacer between the electrodes. A drop of the electrolyte solution was placed on a drilled hole in the counter electrode of the assembled cell, and was driven into the cell by means of vacuum backfilling method. The electrolyte composed of 1.0 M tetrapropylammonium iodide and 0.1 M iodine in acetonitrile-ethylene carbonate (v/v, 1:4) mixture. Finally, the hole was sealed using additional HIMILAN and a cover glass.

4.7. Photoelectrochemical measurements

An action spectrum was obtained under monochromatic light with a constant photon number $(0.5 \times 10^{16} \text{ photon cm}^{-2} \text{ s}^{-1})$. *I–V* characteristics were measured under illumination with AM 1.5 simulated sun light (100 mW cm⁻²) through a shading mast (5.0 mm × 4.0 mm) by using a Bunko-Keiki CEP-2000 system.



Fig. 4. Photoelectrochemical properties of GU104 in the presence of cholic acids LCA, CDCA, and CA. (a) UV-vis absorption spectra on zinc oxide, (b) normalized UV-vis absorption spectra, (c) IPCE spectra, and (d) *I*-*V* curve.

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