Tetrahedron 67 (2011) 6289–6293

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Highly efficient new indoline dye having strong electron-withdrawing group for zinc oxide dye-sensitized solar cell

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ARTICLE INFO

Article history:
Received 16 May 2011
Received in revised form 5 June 2011
Accepted 7 June 2011
Available online 14 June 2011

Keywords:
Indoline dyes
Dye-sensitized solar cell
Electron-withdrawing group
Zinc oxide

ABSTRACT

New indoline dye (DN319) having strong electron-withdrawing dicyanovinylidene moiety and octyl group in the terminal rhodanine ring gave higher efficiency than D205, which was known as an excellent organic dye sensitizer. This result is attributed to the bathochromic shift in the UV–vis absorption band and positive shift in the E_{ox} level of DN319.

1. Introduction

Dye-sensitized solar cells (DSSCs) have been extensively investigated as potential candidates for renewable-energy systems.[1] The highest conversion efficiency (η) of 11.2% was achieved by N719 on nanocrystalline-titanium oxide.[2] On the other hand, costly and environmentally friend metal-free organic dyes, such as oligothiophenes,[3a] coumarins,[3b] oligo(phenylenevinylene) derivatives[3c] and indolines[3d] have been also developed for the DSSC applications. In particular, indoline dye D205, indicated in Scheme 1, is known as the most efficient organic dye sensitizer on titanium oxide showing η of 9.5%.[4] Zinc oxide is a versatile semiconductor having similar band gap energy to titanium oxide and can be tailored to various nanostructures.[5] D205 also shows high performance on zinc oxide.[6]

We have previously reported that the positive shift of oxidation potential (E_{ox}) in indoline dyes can improve the incident photon-to-electron conversion efficiency (IPCE) to increase short-circuit photocurrent density (J_{sc}).[7] The E_{ox} level should be more positive than ca. 0.2 V versus Fc/Fc$^+$ to show high IPCE, corresponding to HOMO level more stable than 4.9 eV by the density functional theory (DFT) calculations. To achieve both the stabilization of HOMO energy level and strong push–pull system of the sensitizer, an electron-withdrawing group should be introduced into the acceptor moiety. Moreover, D205 in which the terminal amido moiety is substituted with octyl group has been reported to show improved open-circuit voltage (V_{oc}).[4] On the basis of these considerations, new indoline dyes DN317 and DN319 were synthesized. We report herein their photoelectrochemical properties.

2. Results and discussion

Scheme 1 shows the synthesis of DN317 and DN319. Known double rhodanine ethyl acetate **1** was oxidized by hydrogen peroxide in the presence of thionyl chloride to afford **2**, whose ester moiety was hydrolyzed to give **3**.[8] Malononitrile **5** was allowed to react with octyl isothiocyanate and ethyl bromoacetate in the presence of DBU to provide **6**, which was again allowed to react with ethyl isothiocyanatoacetate and ethyl bromoacetate in the presence of DBU to give **7**. Compound **7** was hydrolyzed to produce the corresponding acetic acid **8**. A carbaldehyde **4** was allowed to react with **3** and **8** to give DN317 and DN319, respectively.

The procedure for the fabrication of DSSC is as follows: 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 prepared from nanoparticle ZnO-410 (Sumitomo Osaka Cement Co., Ltd). The thickness of zinc oxide layer was 12 μm. An acetonitrile-

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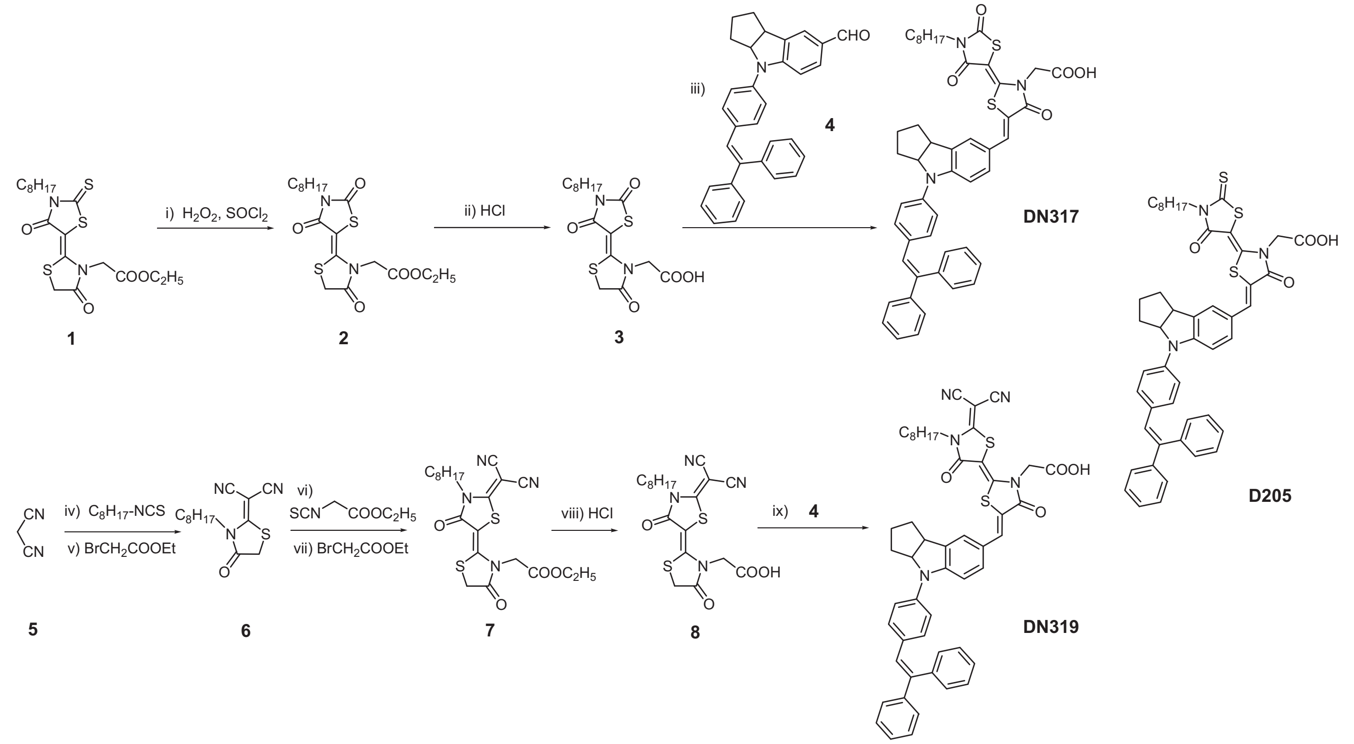
doi:10.1016/j.tet.2011.06.016



Scheme 1. Reagents and conditions: (i) **1** (1.0 equiv), 35% H_2O_2 (10 equiv), $SOCl_2$ (5.0 equiv), EtOH, 1 h, 50 °C, (ii) **2** (1.0 equiv), concd HCl, AcOH, reflux, 3 h, (iii) **3** (1.0 equiv), **4** (1.0 equiv), $AcONH_4$ (0.04 equiv), AcOH, reflux, 2 h, (iv) **5** (1.0 equiv), $C_8H_{17}NCS$ (1.1 equiv), DBU (1.0 equiv), MeCN, rt, 30 min, (v) $BrCH_2COOEt$ (1.7 equiv), rt to reflux, 3 h, (vi) **6** (1.0 equiv), $SCNCH_2COOEt$ (1.05 equiv), DBU (1.0 equiv), MeCN, rt, 30 min, (vii) $BrCH_2COOEt$ (1.7 equiv), rt to reflux, 3 h, (viii) **7** (1.0 equiv), concd HCl, AcOH, reflux, 3 h, (ix) **8** (1.0 equiv), **4** (1.0 equiv), $AcONH_4$ (0.04 equiv), AcOH, reflux, 2 h.

tert-butyl alcohol (v/v, 1:1) mixed solution of dye (0.5 mM) containing 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 dye-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.

Fig. 1a shows the normalized UV–vis absorption and fluorescence spectra of D205, DN317 and DN319 in chloroform, showing the absorption maxima (λ_{max}) at 554, 521 and 566 nm, respectively. As expected, the λ_{max} of DN319 was the most bathochromic due to strong electron-withdrawing dicyanovinylidene group. The results are also listed in Table 1. No marked difference in molar absorption coefficient (ε) was observed. Fig. 1b depicts the UV–vis absorption spectra of indoline dyes on zinc oxide. DN319 showed the most bathochromic absorption band on zinc oxide followed by D205 and DN317. The order of bathochromicity of these dyes on zinc oxide was same as that in chloroform. The λ_{max} of DN319 on zinc oxide was slightly hypsochromic compared to that in chloroform. The absorption band on zinc oxide was broad due to aggregates formation.[6]

The oxidation potentials of these dyes were measured in DMF as reported in our previous paper.[7] The E_{ox} of DN319 was estimated to be +0.37 V versus Fc/Fc$^+$. The I/I_3 redox level was estimated at 0.05 V versus Fc/Fc$^+$. As the reduction peaks of these dyes were not observed by the electrochemical measurement, the $E_{ox}-E_{0-0}$ levels,

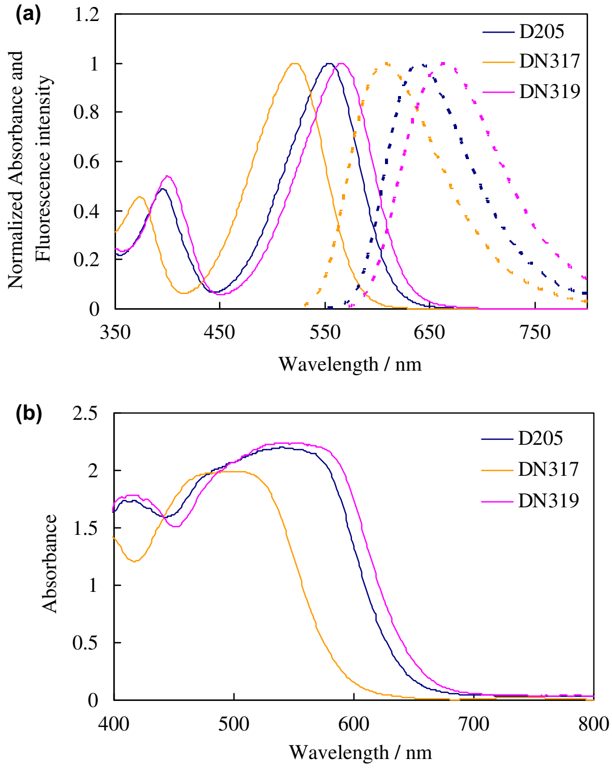


Fig. 1. (a) Normalized UV–vis absorption (solid line) and fluorescence (dotted line) spectra of indoline dyes in chloroform and (b) UV–vis absorption spectra of indoline dyes on zinc oxide.

Table 1
Physical properties of indoline dyes

Dye	λ_{max} (ε)[a]/nm	λ_{max} on ZnO/nm	F_{max}[a]/nm	E_{ox}[b]/V	$E_{ox}E_{0-0}$[c]/V	HOMO[d]/eV	LUMO[d]/eV
D205	395 (38,100), 554 (74,700)	540	641	+0.35	1.73	5.06	2.36
DN317	373 (28,200), 521 (61,900)	505	608	+0.35	1.85	4.99	2.15
DN319	400 (36,700), 566 (68,000)	542	662	+0.37	1.66	5.18	2.53

[a] Measured on 1.0×10^{5} mol dm^{3} of substrate in chloroform at 25 °C.
[b] Versus 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.

where E_{0-0} represents the intersection of normalized absorption and the fluorescence spectra in chloroform, were calculated.[9] These results are indicated in Table 1. As expected, the E_{ox} of DN319 was the most positive among D205, DN317 and DN319.

The DFT calculation was performed to confirm the molecular design of these dyes. The structures of indoline dyes were optimized by the B3LYP/3-21G level, and then the HOMO and LUMO levels were calculated by the B3LYP/6-31G (d,p) level. The results indicated that the HOMO level of DN319 was more stable than D205 followed by DN317 as shown in Table 1. The order is inconsistent with that of E_{ox} level. The HOMO level of DN319 was calculated to be 5.18 eV, being sufficiently stable to show high IPCE.[7]

The IPCE action spectra of D205, DN317 and DN319 are shown in Fig. 2. The spectra indicate that no significant differences in the maximum IPCE value between D205 and DN319 are observed. However, in comparison with D205, DN319 showed additional sensitization of zinc oxide at around 650 nm. DN317 could sensitize zinc oxide in hypsochromic region with less IPCE value.

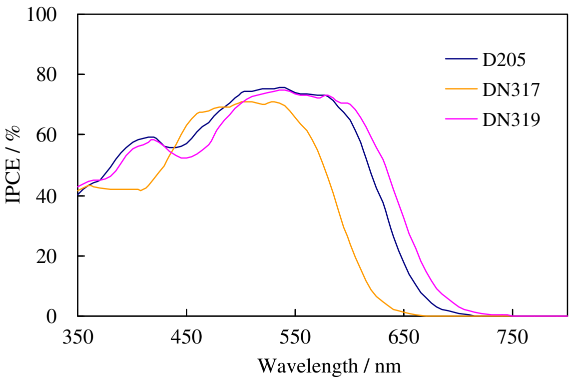


Fig. 2. IPCE action spectra of indoline dyes.

Fig. 3 shows the photovoltaic characteristics of DSSCs of D205, DN317 and DN319 under AM1.5 simulated sunlight (100 mW cm^{2}) illumination. Table 2 summarizes the results. The V_{oc} values of three indoline dyes were same. No significant differences in fill factor (FF) were observed among these dyes. In contrast, the J_{sc} values of these dyes are different. DN319 showed the highest J_{sc} value 11.82 mA cm^{2}, which is 0.79 mA cm^{2} higher than that of D205. In contrast, DN317 showed 3.08 mA cm^{2} lower J_{sc} value than D205. These results come from the most bathochromic UV–vis absorption band and positive E_{ox} level of DN319.

In summary, we have made a molecular design, synthesis and evaluation of novel indoline dyes. DN319, whose terminal group is attached with electron-withdrawing dicyanovinylidene group, exhibited higher conversion efficiency than D205, which is known as one of the best sensitizers in DSSC. This result is attributed to the bathochromic shift in the UV–vis absorption band and positive shift in the E_{ox} level.

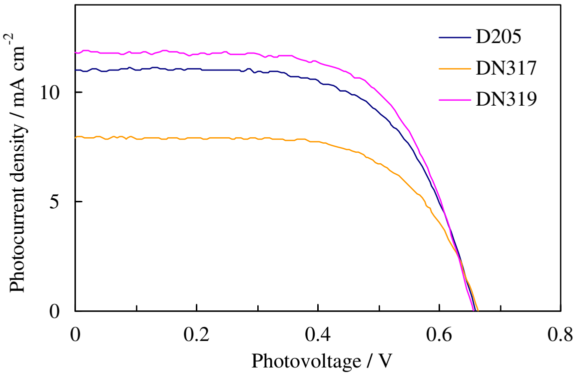


Fig. 3. Current density versus voltage characteristics for DSSC with indoline dyes as sensitizers under AM1.5 simulated sunlight (100 mW cm^{2}) illumination.

Table 2
Photovoltaic characteristics of indoline dyes

Dye	J_{sc}/mA cm^{2}	V_{oc}/V	FF	η/%
D205	11.03	0.66	0.63	4.59
DN317	7.95	0.66	0.64	3.38
DN319	11.82	0.66	0.65	5.01

3. Experimental

3.1. General procedure

Melting points were measured with a METTLER FP62 instrument. NMR spectra were obtained by a JEOL JNM-AL400 spectrometer. MS spectra were recorded on a JEOL MStation 700 spectrometer. 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. The solvents were distilled and dried, if necessary, by standard methods. Double rhodanine **1**, carbaldehyde **4** and indoline dye D205 were synthesized as described in the previous paper.[4] Reagents and starting materials were purchased from Aldrich, Wako, Kanto Chemical, TCI and Merck.

3.2. Synthesis

*3.2.1. Synthesis of **2**.* To an ethanol solution (24 ml) of double rhodanine **1** (2.60 g, 6.10 mmol) and 35% hydrogen peroxide (6.00 g, 61.0 mmol) was added thionyl chloride (3.65 g, 30.5 mmol) at 50 °C. The mixture was stirred for 1 h. After cooling, water (200 ml) was added to the mixture. The product was extracted with chloroform (200 ml). The organic layer was dried over anhydrous sodium sulfate. After evaporating the extract in vacuo, the crude product was purified by column chlomatography (SiO_2, $CHCl_3$) to give **2** (0.15 g, 0.36 mmol, 6%) as a pale yellow solid: mp 93–95 °C; IR (KBr) ν=1767, 1736, 1663, 1545, 1354 cm^1; ^{1}H NMR (400 MHz, $CDCl_3$) δ=0.88 (t, *J*=6.8 Hz, 3H), 1.26–1.35 (m, 13H), 1.59–1.63 (m, 2H), 3.69 (t, *J*=7.2 Hz, 2H), 3.88 (s, 2H), 4.29 (q, *J*=7.2 Hz, 2H), 4.69 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=14.0, 14.1, 22.6, 26.7, 27.7, 29.0, 29.1, 31.3, 31.7, 42.1, 45.2, 62.7, 91.9, 149.9, 165.9, 166.2, 166.3, 172.7; EIMS (70 eV) *m*/*z* (rel intensity) 414 (M^+, 41), 231 (100); Anal. Calcd for $C_{18}H_{26}N_2O_5S_2$: C, 52.15; H, 6.32; N, 6.76. Found C, 52.55; H, 6.22; N, 6.81.

*3.2.2. Synthesis of **3**.* To an acetic acid solution (1 ml) of **2** (149 mg, 0.359 mmol) was added concd hydrochloric acid (0.5 ml). The mixture was refluxed for 3 h. After cooling, water (50 ml) was added. The product was extracted with chloroform (50 ml×2). The combined organic layer was dried over anhydrous sodium sulfate. After evaporating the extract under reduced pressure, the crude product was washed with hexane (30 ml) to afford **3** (46.7 mg, 0.121 mmol, 34%) as a pale yellow solid: mp 152–153 °C; IR (KBr) ν=3254, 2922, 1719, 1655, 1134, 866 cm^1; ^{1}H NMR (400 MHz, DMSO-d_6) δ=0.853 (t, *J*=6.8 Hz, 3H), 1.24 (m, 10H), 1.53 (m, 2H), 3.59 (t, *J*=7.2 Hz, 2H), 4.12 (s, 2H), 4.59 (s, 2H), 13.7 (br s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ=13.9, 22.0, 26.1, 27.0, 28.4, 28.5, 30.7, 31.1, 41.2, 45.3, 89.5, 152.0, 165.0, 166.1, 168.2, 173.3; FABMS (NBA) *m*/*z* 387 (MH^+).

*3.2.3. Synthesis of **6**.* To an acetonitrile solution (166 ml) of malononitrile **5** (3.65 g, 55.3 mmol) and octyl isothiocyanate (9.95 g, 59.0 mmol) was added DBU (8.42 g, 55.3 mmol) at room temperature. The mixture was stirred for 30 min. Then, to the mixture was added ethyl bromoacetate (15.7 g, 94.0 mmol). The mixture was stirred for 1 h and then refluxed for 3 h. After the reaction was completed, the mixture was concentrated, acidified with aqueous 2 N hydrochloric acid (150 ml) and extracted with chloroform (150 ml×2). The combined organic layer was dried over anhydrous sodium sulfate. The extract was concentrated in vacuo. The crude product was washed with hexane (200 ml) to give **6** (14.0 g, 50.5 mmol, 91%) as a pale yellow solid: mp 73–74 °C; IR (KBr) ν=2220, 2203, 1736, 1537, 1460 cm^1; ^{1}H NMR (400 MHz, $CDCl_3$) δ=0.88 (t, *J*=6.6 Hz, 3H), 1.27–1.37 (m, 10H), 1.65–1.72 (m, 2H), 4.00 (s, 2H), 4.08 (t, *J*=8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=14.0, 22.6, 25.9, 28.5, 29.0, 31.6, 32.3, 45.3, 56.7, 111.6, 112.8, 171.5, 171.6; EIMS (70 eV) *m*/*z* (rel intensity) 277 (M^+, 13), 212 (100); Anal. Calcd for $C_{14}H_{19}N_3OS$: C, 60.62; H, 6.90; N, 15.15. Found C, 60.60; H, 6.77; N, 15.23.

*3.2.4. Synthesis of **7**.* To an acetonitrile solution (200 ml) of **6** (11.1 g, 40.0 mmol) and ethyl isothiocyanatoacetate (6.08 g, 42.0 mmol) was added DBU (6.08 g, 40.0 mmol) at room temperature. The mixture was stirred for 30 min. Then, to the mixture was added ethyl bromoacetate (11.4 g, 68.0 mmol). The mixture was stirred for 1 h and then refluxed for 3 h. After the reaction was completed, the mixture was concentrated, acidified with aqueous 2 N hydrochloric acid (150 ml). The product was extracted with chloroform (150 ml×2). The combined organic layer was dried over anhydrous sodium sulfate. The extract was concentrated in vacuo. The crude product was purified by column chromatography (SiO_2, $CHCl_3$) to give **7** (3.80 g, 8.21 mmol, 21%) as a pale yellow solid: mp 133–135 °C; IR (KBr) ν=2214, 2205, 1744, 1684, 1522 cm^1; ^{1}H NMR (400 MHz, $CDCl_3$) δ=0.88 (t, *J*=6.8 Hz, 3H), 1.27–1.31 (m, 10H), 1.38 (t, *J*=7.2 Hz, 3H), 1.68–1.75 (m, 2H), 3.93 (s, 2H), 4.15 (t, *J*=8.0 Hz, 2H), 4.33 (q, *J*=7.2 Hz, 2H), 4.73 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=14.0, 14.1, 22.6, 25.9, 28.7, 29.0, 29.1, 31.2, 31.7, 45.2, 45.5, 52.0, 63.3, 88.8, 112.5, 113.5, 155.3, 164.5, 165.9, 166.1, 172.3; EIMS (70 eV) *m*/*z* (rel intensity) 462 (M^+, 71), 397 (100); Anal. Calcd for $C_{21}H_{26}N_4O_4S_2$: C, 54.52; H, 5.67; N, 12.11. Found C, 54.85; H, 5.61; N, 12.21.

*3.2.5. Synthesis of **8**.* To an acetic acid solution (12 ml) of **7** (1.90 g, 4.11 mmol) was added concd hydrochloric acid (6 ml). The mixture was refluxed for 3 h. After cooling, water (50 ml) was added. The product was extracted with chloroform (50 ml×2). The combined organic layer was dried over anhydrous sodium sulfate. The extract was concentrated in vacuo. The crude product was washed with hexane (30 ml) to provide **8** (1.39 g, 3.20 mmol, 78%) as an orange solid: mp 164–167 °C; IR (KBr) ν=2205, 1740, 1684, 1541, 1279 cm^1; ^{1}H NMR (400 MHz, DMSO-d_6) δ=0.86 (t, *J*=6.4 Hz, 3H), 1.25–1.28 (m, 10H), 1.62 (m, 2H), 4.01 (t, *J*=7.6 Hz, 2H), 4.22 (s, 2H), 4.70 (s, 2H), 13.9 (br s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ=13.9, 22.0, 25.3, 25.4, 27.8, 28.4, 31.1, 31.2, 44.5, 45.6, 48.7, 87.1, 113.5, 114.5, 157.5, 165.5, 165.6, 167.9, 173.3; FABMS (NBA) *m*/*z* 435 (MH^+).

3.2.6. Synthesis of indoline dye DN317. To an acetic acid solution (1 ml) containing **3** (46.7 mg, 0.121 mmol) and carbaldehyde **4** (53.4 mg, 0.121 mmol) was added ammonium acetate (0.2 mg). The mixture was refluxed for 2 h. After cooling, the resulting precipitate was filtered, washed with methanol (2 ml) and purified by column chlomatography (SiO_2, $CHCl_3$/MeOH=20:1) to give DN317 (61.6 mg, 0.076 mmol, 63%) as a brown powder: mp 231–232 °C; IR (KBr) ν=2924, 2855, 1719, 1485, 1387, 1128 cm^1; ^{1}H NMR (400 MHz, DMSO-d_6) δ=0.85 (t, *J*=4.8 Hz, 3H), 1.18–1.34 (m, 11H), 1.50–1.72 (m, 4H), 1.73–1.84 (m, 2H), 2.00–2.12 (m, 1H), 3.61 (t, *J*=6.8 Hz, 2H), 3.85–3.89 (m, 2H), 4.75 (s, 2H), 4.94–4.98 (m, 1H), 7.02–7.04 (m, 3H), 7.09 (s, 1H), 7.15 (d, *J*=8.8 Hz, 2H), 7.20 (d, *J*=6.8 Hz, 2H), 7.29–7.37 (m, 5H), 7.39–7.48 (m, 5H), 7.65 (s, 1H), 13.8 (br s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ=13.9, 22.0, 23.8, 26.1, 27.0, 28.4, 28.5, 31.1, 32.8, 34.8, 37.5, 41.4, 44.0, 68.4, 90.1, 108.1, 113.2, 119.2 (2C), 123.8, 126.8 (3C), 127.1, 127.3, 127.6, 128.3 (3C), 129.1 (2C), 129.7 (2C), 130.3 (2C), 131.2, 133.4, 136.5, 139.4, 140.1, 140.2, 142.6, 144.9, 148.6, 164.8, 166.0, 166.3, 168.2; FABMS (NBA) *m*/*z* 810 (MH^+); Anal. Calcd for $C_{48}H_{47}N_3O_5S_2$: C, 71.17; H, 5.85; N, 5.19. Found C, 71.46; H, 5.84; N, 5.19.

3.2.7. Synthesis of indoline dye DN319. To an acetic acid solution (13 ml) containing **7** (1.00 g, 2.30 mmol) and aldehyde **4** (1.02 g, 2.30 mmol) was added ammonium acetate (7.0 mg). The mixture was refluxed for 2 h. After cooling, the resulting precipitate was filtered, washed with methanol (20 ml) and then purified by column chlomatography (SiO_2, $CHCl_3$/MeOH=20:1) to obtain DN319 (0.66 g, 0.77 mmol, 33%) as a brown powder: mp >250 °C; IR (KBr) ν=2214, 1522, 1485, 1387, 1128 cm^1; ^{1}H NMR (400 MHz, DMSO-d_6) δ=0.86 (t, *J*=6.4 Hz, 3H), 1.19–1.37 (m, 12H), 1.57–1.69 (m, 3H), 1.74–1.82 (m, 2H), 2.02–2.12 (m, 1H), 3.84–3.88 (m, 1H), 4.96–4.04 (m, 2H), 4.70 (br s, 2H), 4.94–5.00 (m, 1H), 7.01–7.05 (m, 3H), 7.09, (s, 1H), 7.15 (d, *J*=8.8 Hz, 2H), 7.18–7.22 (m, 2H), 7.27–7.37 (m, 5H), 7.40–7.49 (m, 5H), 7.72 (s, 1H); ^{13}C NMR (100 MHz, THF-d_8) δ=14.5, 23.5, 24.6, 24.7, 25.9, 26.0, 26.9, 29.4, 30.1, 32.7, 34.2, 36.0, 45.7, 70.1, 79.7, 88.7, 109.2, 113.8, 114.0, 114.7, 120.3 (2C), 125.4, 128.0, 128.1 (2C), 128.2, 128.3, 128.4, 128.9 (2C), 129.7 (2C), 131.1 (2C), 131.4 (2C), 133.1, 133.7, 135.8, 137.7, 140.8, 141.8, 142.2, 144.4, 150.4, 151.3, 165.9, 166.0, 166.5, 167.3; HRFABMS *m*/*z* 858.3186 (MH^+), Calcd for $C_{51}H_{48}N_5O_4S_2$: 858.3148.

3.3. Electrochemical measurements

Electrochemical measurement of indoline dyes was performed in DMF. The oxidation potential (E_{ox}) was measured by using small-size three electrodes. Ag quasi reference electrode (QRE) 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 dyes 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}.

3.4. Photoelectrochemical measurements

An action spectrum was measured under monochromatic light with a constant photon number (0.5×10^{16} photon cm^2 s^{-1}). I–V characteristics were measured under illumination with AM1.5 simulated sunlight (100 mW cm^2) through a shading mask (5.0 mm×4.0 mm) by using a Bunko-Keiki CEP-2000 system.

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