## Electronic Supplementary Information

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

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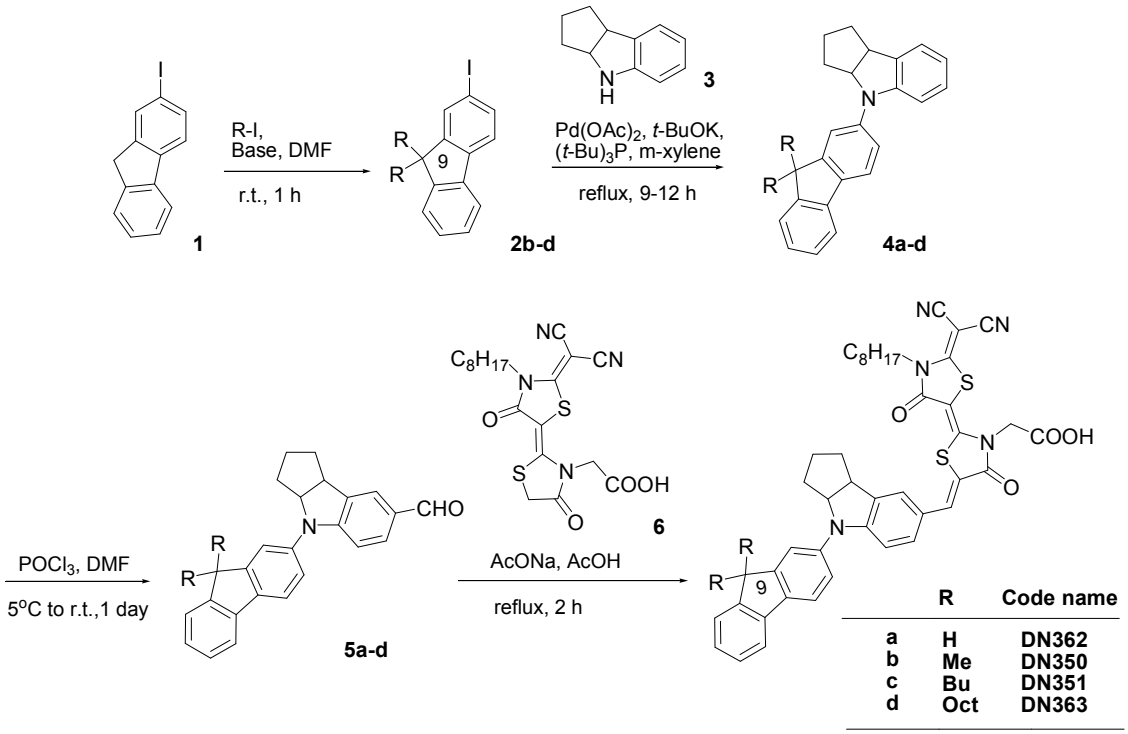


**Scheme 1** Synthesis of indoline dyes.

### 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. Compound **6** was synthesized as described in the previous paper.[a] Reagents and starting materials were purchased from Aldrich, Wako, Kanto Chemical, TCI and Merck.

Reference

a) S. Higashijima, H. Miura, T. Fujita, Y. Kubota, K. Funabiki, T. Yoshida and M. Matsui, *Tetrahedron.*, 2011, **67**, 6289.

**Synthesis of 2b**

To the DMF solution (400 ml) of 2-iodofluorene **1** (11.7 g, 40.0 mmol) and sodium methoxide (6.48 g, 120 mmol) was added methyl iodide (14.2 g, 100 mmol) at room temperature, then the mixture was stirred for 1 h. After the reaction was complete, water (350 ml) was added to the mixture. The product was extracted with chloroform (750 ml). The organic layer was washed with water (1000 ml) and dried over anhydrous sodium sulfate. After evaporating the extract under reduced pressure, the crude product was purified by column chlomatography ($SiO_2$, Hexane:AcOEt = 30:1) to give **2b** (8.45 g, 26.4 mmol, 66%) as a pale yellow oil: IR (liquid) $\nu$ = 2961, 2920, 2862, 1441, 735 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 1.44 (s, 6H), 7.30 (t, $J$ = 4.4 Hz, 1H), 7.32 (t, $J$ = 4.4 Hz, 1H), 7.38 (dt, $J$ = 5.2, 3.6 Hz, 1H), 7.43 (d, $J$ = 8.0 Hz, 1H), 7.63 (dd, $J$ = 8.0, 1.2 Hz, 1H), 7.66 (dt, $J$ = 5.6, 3.2 Hz, 1H), 7.75 (d, $J$ = 1.2 Hz, 1H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 26.9, 47.0, 92.5, 120.0, 121.7, 122.5, 127.1, 127.8, 132.0, 135.9, 138.1, 138.8, 152.9, 155.8; EI-MS (70 eV) *m/z* (rel intensity) 320 ($M^+$, 80), 178 (100); Anal. Found C, 55.99; H, 4.14%. Calcd. for $C_{15}H_{13}I$: C, 56.27; H, 4.09%.

**Synthesis of 2c**

To the DMF solution (400 ml) of 2-iodofluorene **1** (11.7 g, 40.0 mmol) and sodium methoxide (6.48 g, 120 mmol) was added butyl iodide (18.4 g, 100 mmol) at room temperature, then the mixture was stirred for 1 h. After the reaction was complete, water (350 ml) was added to the mixture. The product was extracted with chloroform (750 ml). The organic layer was washed with water (1000 ml) and dried over anhydrous sodium sulfate. After evaporating the extract under reduced pressure, the crude product was purified by column chlomatography ($SiO_2$, Hexane) to give **2c** (10.2 g, 25.3 mmol, 63%) as a pale yellow oil: IR (liquid) $\nu$ = 2949, 2924, 2857, 1439, 737 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 0.52-0.58 (m, 4H), 0.67 (t, $J$ = 7.6 Hz, 6H), 1.03-1.01 (m, 4H), 1.89-1.99 (m, 4H), 7.32-7.34 (m, 3H), 7.44 (d, $J$ = 7.6 Hz, 1H), 7.64-7.67 (m, 3H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 13.8 (2C), 23.0 (2C), 25.9 (2C), 40.1 (2C), 55.2, 92.4, 119.8, 121.4, 122.8, 126.9, 127.6, 132.0, 135.8, 140.1, 140.8, 150.1, 159.1; EI-MS (70 eV) *m/z* (rel intensity) 404 ($M^+$, 79), 220 (100); Anal. Found C, 62.27; H, 6.22%. Calcd. for $C_{21}H_{25}I$: C, 62.38; H, 6.23%.

**Synthesis of 2d**

To the DMF solution (400 ml) of 2-iodofluorene **1** (11.7 g, 40.0 mmol) and sodium *tert*.-butoxide (11.5 g, 120 mmol) was added octyl iodide (24.0 g, 100 mmol) at room temperature, then the mixture was stirred for 1 h. After the reaction was complete, water (350 ml) was added to the mixture. The product was extracted with chloroform (750 ml). The organic layer was washed with water (1000 ml) and dried over anhydrous sodium sulfate. After evaporating the extract under reduced pressure, the crude product was purified by column chlomatography ($SiO_2$, Hexane:AcOEt = 30:1) to give **2d** (19.0 g, 36.8 mmol, 92%) as a colorless oil: IR (liquid) $\nu$ = 2955, 2926, 2853, 1441, 739 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 0.54-0.64 (m, 4H), 0.82 (t, $J$ = 7.2 Hz, 6H), 0.99-1.15 (m, 16H), 1.20 (dt, $J$ = 14.4, 7.2 Hz, 4H), 1.92 (qt, $J$ = 12.0, 5.2 Hz, 4H), 7.29-7.33 (m,

3H), 7.43 (d, $J$ = 7.6 Hz, 1H), 7.62-7.66 (m, 3H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 14.1 (2C), 22.6 (2C), 23.6(2C), 29.1(2C), 29.2(2C), 29.9(2C), 31.8(2C), 40.2(2C), 55.3, 92.4, 119.7, 121.4, 122.8, 126.9, 127.6, 132.0, 135.7, 140.1, 140.7, 150.1, 153.1; EI-MS (70 eV) *m/z* (rel intensity) 516 ($M^+$, 57), 291 (44), 57 (100); Anal. Found C, 67.33; H,8.05%. Calcd. for $C_{29}H_{41}I$: C, 67.43; H, 8.00%.

**Synthesis of 4a**

To *m*-xylene (20 ml) were added indoline **3** (2.39 g, 15.0 mmol), **1a** (4.38 g, 15.0 mmol), potassium *tert.*-butoxide (2.52 g, 22.5 mmol), palladium acetate (33 mg, 0.15 mmol) and tri-*tert*.-butylphosphine (152 mg, 0.75 mmol). The mixture was refluxed for 12 hours under a nitrogen atmosphere. After the reaction was complete, the mixture was filtered. The filtrate was washed with 2N hydrochloric acid (25 ml) and dried over anhydrous sodium sulfate. After evaporating the extract under reduced pressure, the crude product was purified by column chlomatography ($SiO_2$, Hexane:AcOEt = 10:1) to give **4a** (2.86 g, 8.9 mmol, 59%) as a pale brown solid: mp 110-112°C; IR (KBr) $\nu$ = 3044, 2932, 1601, 1375, 729 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCL_3$) $\delta$ = 1.47-1.61 (m, 1H), 1.61-1.70 (m, 1H), 1.80-1.93 (m, 2H), 1.93-2.01 (m, 1H), 2.01-2.11 (m, 1H), 3.85 (dt, $J$ = 8.8, 2.4 Hz, 1H), 3.88 (s, 2H), 4.81 (ddd, $J$ = 8.8, 6.4, 2.4 Hz, 1H), 6.74 (dt, $J$ = 7.2, 1.6 Hz, 1H), 7.02 (d, $J$ = 7.2 Hz, 1H), 7.06 (t, $J$ = 8.0 Hz, 1H), 7.12 (d, $J$ = 7.2 Hz, 1H), 7.23 (dt, $J$ = 7.6, 0.8 Hz, 1H), 7.29 (dd, $J$ = 8.4, 2.0 Hz, 1H), 7.34 (t, $J$ = 7.6 Hz, 1H), 7.47 (s, 1H), 7.50 (d, $J$ = 7.2 Hz, 1H), 7.69 (d, $J$ = 7.2 Hz, 1H), 7.71 (d, $J$ = 8.0 Hz, 1H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 24.5, 34.1, 34.9, 37.0, 45.6, 69.0, 108.2, 115.9, 118.2, 118.6, 119.0, 120.3, 124.7, 124.8, 125.6, 126.7, 127.1, 135.0, 135.4, 141.8, 142.4, 142.8, 144.5, 147.5; EI-MS (70 eV) *m/z* (rel intensity) 323 ($M^+$, 92), 294 (100); Anal. Found C, 89.42; H, 6.71; N, 4.32%. Calcd. for $C_{24}H_{21}N$: C, 89.12; H, 6.54; N, 4.33%.

**Synthesis of 4b**

To *m*-xylene (20 ml) were added indoline **3** (3.12 g, 19.6 mmol), **2b** (6.30 g, 19.6 mmol), potassium *tert.*-butoxide (3.96 g, 35.3 mmol), palladium acetate (44 mg, 0.20 mmol) and tri-*tert*.-butylphosphine (198 mg, 0.98 mmol). The mixture was refluxed for 12 hours under a nitrogen atmosphere. After the reaction was complete, the mixture was filtered. The filtrate was washed with 2N hydrochloric acid (30 ml) and dried over anhydrous sodium sulfate. After evaporating the extract under reduced pressure, the crude product was purified by column chlomatography ($SiO_2$, Hexane:AcOEt = 30:1) to give **4b** (6.58 g, 18.7 mmol, 95%) as a pale pale yellow oil: IR (liquid) $\nu$ = 3019, 2955, 1601, 1373, 735 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 1.48 (s, 6H), 1.49-1.58 (m, 1H), 1.60-1.69 (m, 1H), 1.82-1.92 (m, 2H), 1.94-2.08 (m, 2H), 3.83 (m, 1H), 4.79 (m, 1H), 6.73 (dt, $J$ = 7.2, 2.0 Hz, 1H), 7.03 (d, $J$ = 8.0 Hz, 1H), 7.05 (d, $J$ = 6.8 Hz, 1H), 7.11 (d, $J$ = 7.2 Hz, 1H), 7.22 (dt, $J$ = 8.4, 1.6 Hz, 2H), 7.29 (dt, $J$ = 7.6, 1.2 Hz, 1H), 7.37 (s, 1H), 7.38 (d, $J$ = 8.0 Hz, 1H), 7.62 (d, $J$ = 7.2 Hz, 1H), 7.63 (d, $J$ = 8.4 Hz, 1H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 24.5, 27.2, 27.3, 34.0, 34.8, 45.5, 46.8, 69.0, 108.2, 113.2, 118.0, 118.6, 119.1, 120.5, 122.4, 124.7, 126.1, 126.9, 127.1, 132.6, 135.0, 139.2, 142.8, 147.3,

153.2, 154.9; EI-MS (70 eV) *m/z* (rel intensity) 351 ($M^+$, 98), 207 (100); Anal. Found C, 88.89; H, 7.34; N, 3.95%. Calcd. for $C_{26}H_{25}N$: C, 88.85; H, 7.17; N, 3.99%.

**Synthesis of 4c**

To *m*-xylene (20 ml) were added indoline **3** (2.39 g, 15.0 mmol), **2c** (6.06 g, 15.0 mmol), potassium *tert.*-butoxide (2.52 g, 22.5 mmol), palladium acetate (33 mg, 0.15 mmol) and tri-*tert*.-butylphosphine (152 mg, 0.75 mmol). The mixture was refluxed for 12 hours under a nitrogen atmosphere. After the reaction was complete, the mixture was filtered. The filtrate was washed with 2N hydrochloric acid (25 ml) and dried over anhydrous sodium sulfate. After evaporating the extract under reduced pressure, the crude product was purified by column chlomatography ($SiO_2$, Hexane:AcOEt = 10:1) to give **4c** (4.77 g, 11.0 mmol, 73%) as a pale yellow oil: IR (liquid) $\nu$ = 3019, 2953, 1601, 1385, 741 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 0.64-0.71 (m, 4H), 0.69 (t, *J* = 7.3 Hz, 3H), 0.71 (t, *J* = 7.3 Hz, 3H), 1.06-1.13 (m, 4H), 1.49-1.61 (m, 1H), 1.63-1.71 (m, 1H), 1.80-2.00 (m, 7H), 2.02-2.10 (m, 1H), 3.83-3.87 (m, 1H), 4.81-4.88 (m, 1H), 6.73 (t, *J* = 7.2 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 7.06 (t, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 7.1 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.25 (s, 1H), 7.30 (d, *J* = 7.1 Hz, 2H), 7.62 (dd, *J* = 6.2, 5.6 Hz, 2H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 13.8, 13.9, 23.0 (2C), 24.5, 26.0 (2C), 33.8, 34.9, 40.2 (2C), 45.6, 54.9, 69.0, 108.0, 113.9, 118.2, 118.5, 118.8, 120.1, 122.7, 124.7, 125.9, 126.7, 127.2, 134.8, 135.0, 141.2, 142.5, 147.6, 150.3, 151.9; EI-MS (70 eV) *m/z* (rel intensity) 435 ($M^+$, 100), 207 (96); Anal. Found C, 87.87; H, 8.83; N, 3.12%. Calcd. for $C_{32}H_{37}N$: C, 88.22; H, 8.56; N, 3.22%.

**Synthesis of 4d**

To *m*-xylene (30 ml) were added indoline **3** (4.70 g, 29.5 mmol), **2d** (16.2 g, 29.5 mmol), potassium *tert.*-butoxide (5.96 g, 53.2 mmol), palladium acetate (66 mg, 0.30 mmol) and tri-*tert*.-butylphosphine (298 mg, 1.48 mmol). The mixture was refluxed for 9 hours under a nitrogen atmosphere. After the reaction was complete, the mixture was filtered. The filtrate was washed with 2N hydrochloric acid (45 ml) and dried over anhydrous sodium sulfate. After evaporating the extract under reduced pressure, the crude product was purified by column chlomatography ($SiO_2$, Hexane:AcOEt = 30:1) to give **4d** (11.3 g, 20.7 mmol, 70%) as a pale yellow oil: IR (liquid) $\nu$ = 3019, 2953, 1601, 1385, 741 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 0.62-0.74 (m, 4H), 0.80 (t, *J* = 7.2 Hz, 3H), 0.81 (t, *J* = 7.2 Hz, 3H), 1.00-1.25 (m, 20H), 1.50-1.61 (m, 1H), 1.63-1.71 (m, 1H), 1.80-1.82 (m, 3H), 1.88-1.99 (m, 4H), 2.02-2.11 (m, 1H), 3.84-3.87 (m, 1H), 4.83-4.87 (m, 1H), 6.73 (t, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 7.06 (dd, *J* = 8.0, 7.2 Hz, 1H), 7.13 (d, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.25 (s, 1H), 7.28 (d, *J* = 6.0 Hz, 1H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.61 (d, *J* = 6.4 Hz, 1H), 7.63 (d, *J* = 6.8 Hz, 1H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 14.1 (2C), 22.6 (2C), 23.7, 23.8, 24.5, 29.2 (2C), 29.3 (2C), 30.0, 30.1, 31.8 (2C), 33.8, 34.9, 40.4, 40.5, 45.6, 55.0, 69.0, 107.9, 114.0, 118.3, 118.4, 118.8, 120.1, 122.7, 124.7, 125.9, 126.7, 127.1, 134.8, 135.0, 141.2, 142.5, 147.6, 150.3, 151.9; EI-MS (70 eV)

*m/z* (rel intensity) 547 ($M^+$, 100), 306 (23); Anal. Found C, 87.59; H, 9.82; N, 2.53%. Calcd. for $C_{40}H_{53}N$: C, 87.69; H, 9.75; N, 2.56%.

**Synthesis of 5a**

To DMF (7 ml) was added phosphoryl chloride (2.73 g, 17.8 mmol) at 5°C with stirring. To this mixture was added a DMF solution of **4a** (2.88 g, 8.9 mmol) at 5°C. The mixture was stirred for 1 h at 5°C. Then, the mixture was stirred for 1 day at room temperature. After the reaction was completed, to the mixture was added water (25 ml). The mixture was basified with 25% sodium hydroxide aqueous solution and extracted with chloroform (50 ml). The organic layer was washed with water (25 ml) and 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 **5a** (2.6 g, 7.5 mmol, 84%) as a orange solid: mp 69-71°C; IR (KBr) $\nu$ = 2949, 2862, 1670, 1597, 1491, 1456 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 1.48-1.61 (m, 1H), 1.67-1.81 (m, 2H), 1.88-1.97 (m, 2H), 2.03-2.13 (m, 1H), 3.87 (m, 1H), 3.92 (s, 2H), 4.99 (m, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 7.29 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.31 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.48 (s, 1H), 7.53 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.65 (s, 1H), 7.75 (d, *J* = 7.2 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 9.71 (s, 1H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 23.9, 32.9, 35.0, 36.6, 44.2, 69.7, 105.8, 118.3, 119.2, 120.2, 120.5, 124.6, 124.7, 126.1, 126.5, 127.7, 133.2, 135.4, 137.6, 139.3, 140.8, 142.6, 144.3, 153.4, 189.3; EI-MS (70 eV) *m/z* (rel intensity) 351 ($M^+$, 100), 322 (91); Anal. Found C, 85.22; H, 6.08; N, 3.91%. Calcd. for $C_{25}H_{21}NO$: C, 85.44; H, 6.02; N, 3.99%.

**Synthesis of 5b**

To DMF (15 ml) was added phosphoryl chloride (5.74 g, 37.4 mmol) at 5°C with stirring. To this mixture was added a DMF solution of **4b** (6.58 g, 18.7 mmol) at 5°C. The mixture was stirred for 1 h at 5°C. Then, the mixture was stirred for 1 day at room temperature. After the reaction was completed, to the mixture was added water (50 ml). The mixture was basified with 25% sodium hydroxide aqueous solution and extracted with chloroform (50 ml). The organic layer was washed with water (50 ml) and 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 **5b** (4.98 g, 13.1 mmol, 70%) as a pale green solid: mp 73-74°C; IR (KBr) $\nu$ = 2955, 2860, 1670, 1597, 1491, 1449 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 1.50 (s, 3H), 1.51 (s, 3H), 1.52-1.61 (m, 1H), 1.67-1.75 (m, 1H), 1.76-1.85 (m, 1H), 1.88-1.99 (m, 2H), 2.04-2.14 (m, 1H), 3.87 (m, 1H), 5.00 (m, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 7.27 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.31 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.33 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.36 (d, *J* = 2.0 Hz, 1H), 7.43 (d, *J* = 6.8 Hz, 1H), 7.54 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.66 (s, 1H), 7.68 (d, *J* = 6.8 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 9.71 (s, 1H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 24.3, 27.1, 27.3, 33.3, 35.3, 44.6, 46.9, 70.2, 106.1, 116.3, 119.6, 120.8, 121.0, 122.6, 125.0, 126.9, 127.1, 128.0, 133.7, 135.5, 135.7, 138.6, 140.2, 153.4, 153.9, 155.2, 189.8; EI-MS (70 eV) *m/z* (rel intensity) 379 ($M^+$, 51), 207 (100); Anal. Found C, 85.24; H, 6.74; N, 3.84%. Calcd. for $C_{27}H_{25}NO$: C, 85.45; H, 6.64; N, 3.69%.

**Synthesis of 5c**

To DMF (4 ml) was added phosphoryl chloride (1.51 g, 9.88 mmol) at 5°C with stirring. To this mixture was added a DMF solution of **4c** (2.15 g, 4.94 mmol) at 5°C. The mixture was stirred for 1 h at 5°C. Then, the mixture was stirred for 1 day at room temperature. After the reaction was completed, to the mixture was added water (20 ml). The mixture was basified with 25% sodium hydroxide aqueous solution and extracted with chloroform (20 ml). The organic layer was washed with water (20 ml) and dried over anhydrous sodium sulfate. After evaporating the extract *in vacuo*, the crude product was purified by column chlomatography ($SiO_2$, Hexane:AcOEt = 8:1) to give **5c** (1.84 g, 3.95 mmol, 80%) as a yellow solid: mp 138-139°C; IR (KBr) $\nu$ = 2924, 2855, 1674, 1595, 1493, 1452 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 0.59-0.73 (m, 4H), 0.68 (t, $J$ = 7.3 Hz, 3H), 0.72 (t, $J$ = 7.3 Hz, 3H), 1.05-1.12 (m, 4H), 1.50-1.59 (m, 1H), 1.69-1.81 (m, 2H), 1.90-1.98 (m, 6H), 2.05-2.14 (m, 1H), 3.87 (t, $J$ = 7.3 Hz, 1H), 5.02 (t, $J$ = 6.8 Hz, 1H), 6.83 (d, $J$ = 8.3 Hz, 1H), 7.25-7.35 (m, 5H), 7.54 (dd, $J$ = 8.3, 1.4 Hz, 1H), 7.66 (s, 1H), 7.67 (d, $J$ = 6.3 Hz, 1H), 7.70 (d, $J$ = 8.1 Hz, 1H), 9.71 (s, 1H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 13.7, 13.8, 23.0 (2C), 24.2, 25.9, 26.0, 33.1, 35.4, 40.0, 40.1, 44.6, 55.0, 70.2, 106.0, 116.7, 119.3, 120.4, 120.9, 122.8, 125.1, 126.7, 126.9, 127.9, 133.7, 135.7, 137.5, 139.9, 140.5, 150.5, 152.2, 153.9, 189.8; EI-MS (70 eV) *m/z* (rel intensity) 463 ($M^+$, 100), 334 (33); Anal. Found C, 85.20; H, 8.10; N, 3.23%. Calcd. for $C_{33}H_{37}NO$: C, 85.48; H, 8.04; N, 3.02%.

**Synthesis of 5d**

To DMF (15 ml) was added phosphoryl chloride (5.74 g, 37.4 mmol) at 5°C with stirring. To this mixture was added a DMF solution of **4d** (10.2 g, 18.7 mmol) at 5°C. The mixture was stirred for 1 h at 5°C. Then, the mixture was stirred for 1 day at room remperature. After the reaction was completed, to the mixture was added water (50 ml). The mixture was basified with 25% sodium hydroxide aqueous solution and extracted with chloroform (50 ml). The organic layer was washed with water (50 ml) and 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 **5d** (10.4 g, 18.0 mmol, 96%) as a yellow oil: IR (liquid) $\nu$ = 2926, 2855, 1678, 1599, 1495, 1454 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ =0.62-0.75 (m, 4H), 0.79 (t, $J$ = 7.6 Hz, 3H), 0.82 (t, $J$ = 6.8 Hz, 3H), 1.00-1.25 (m, 20H), 1.48-1.59 (m, 1H), 1.64-1.72 (m, 1H), 1.74-1.80 (m, 1H), 1.86-1.93 (m, 2H), 1.94-2.01 (m, 4H), 2.02-2.13 (m, 1H), 3.82-3.86 (m, 1H), 4.98-5.02 (m, 1H), 6.83 (d, $J$ = 8.4 Hz, 1H), 7.25-7.30 (m, 3H), 7.32 (t, $J$ = 7.2 Hz, 2H), 7.53 (dd, $J$ = 8.0, 1.2 Hz, 1H), 7.64 (d, $J$ = 8.4 Hz, 1H), 7.66 (d, $J$ = 0.8 Hz, 1H), 7.68 (d, $J$ = 8.0 Hz, 1H), 9.71 (s, 1H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 13.9, 14.0, 22.4, 22.5, 23.6, 23.7, 24.1, 28.9, 29.0 (2C), 29.1, 29.7, 29.8, 31.5, 31.6, 32.9, 35.2, 40.1, 40.2, 44.4, 55.0, 70.0, 105.9, 116.6, 119.2, 120.3, 120.7, 122.6, 124.9, 126.6, 126.7, 127.8, 133.5, 135.6, 137.4, 139.7, 140.4, 150.3, 152.1, 153.7, 189.5; EI-MS (70 eV) *m/z* (rel intensity) 575 ($M^+$, 100), 334 (18); Anal. Found C, 85.54; H, 9.37; N, 2.46%. Calcd. for $C_{41}H_{53}NO$: C, 85.51; H, 9.28; N, 2.43%.

**Synthesis of DN362**

To an acetic acid solution (4 ml) containing a **5a** (0.42 g, 1.2 mmol) and **6** (0.52 g, 1.2 mmol) was added ammonium acetate (4 mg). The mixture was refluxed for 2 h. After cooling, the resulting precipitate was filtered, washed with methanol (10 ml) and purified by column chlomatography ($SiO_2$, $CHCl_3$:MeOH=20:1) to give DN362 (0.44 g, 0.58 mmol, 48%) as a brown powder: mp 216°C (decompose); IR (KBr) $\nu$ = 2924, 2210, 1522, 1491, 1128 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 0.88 (t, $J$ = 6.4 Hz, 3H), 1.22-1.42 (m, 12H), 1.52-1.58 (m, 1H), 1.70-1.78 (m, 4H), 1.79-1.84 (m, 1H), 3.88-3.92 (m, 1H), 3.94 (s, 2H), 4.18 (t, $J$ = 7.8 Hz, 2H), 4.88 (s, 2H), 5.01-5.05 (m, 1H), 6.92 (d, $J$ = 9.0 Hz, 1H), 7.29-7.32 (m, 2H), 7.36-7.41 (m, 3H), 7.49 (s, 1H), 7.55 (d, $J$ = 7.3 Hz, 1H), 7.75-7.81 (m, 3H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 14.1, 22.6, 24.3, 26.0, 28.8, 29.1, 29.2, 31.7, 33.3, 35.6, 37.0, 44.9, 45.3, 45.7, 50.7, 70.3, 87.3, 107.7, 111.0, 113.0, 114.1, 118.6, 119.6, 120.7, 120.8, 123.4, 125.1, 126.5, 127.0, 127.9, 134.0, 136.6, 137.2, 138.2, 139.6, 141.2, 143.1, 144.8, 151.5, 151.8, 164.9 (2C), 165.6, 166.9; FABMS (NBA) *m/z* 768 ($MH^+$); Anal. Found C, 68.57; H, 5.35; N, 9.00%. Calcd. for $C_{44}H_{41}N_5O_4S_2$: C, 68.82; H, 5.38; N, 9.12%.

**Synthesis of DN350**

To an acetic acid solution (4 ml) containing a **5b** (0.46 g, 1.2 mmol) and **6** (0.52 g, 1.2 mmol) was added ammonium acetate (4 mg). The mixture was refluxed for 2 h. After cooling, the resulting precipitate was filtered, washed with methanol (10 ml) and purified by column chlomatography ($SiO_2$, $CHCl_3$:MeOH=20:1) to give DN350 (0.37 g, 0.46 mmol, 39%) as a brown powder: mp 254°C (decompose); IR (KBr) $\nu$ = 2924, 2212, 1522, 1491, 1126 $cm^{-1}$; $^1$H-NMR (400 MHz, DMSO-$d_6$) $\delta$ = 0.84 (t, $J$ = 7.2 Hz, 3H), 1.18-1.32 (m, 10H), 1.36-1.50 (m, 1H), 1.46 (s, 3H), 1.49 (s, 3H), 1.56-1.70 (m, 3H), 1.74-1.87 (m, 3H), 2.06-2.16 (m, 1H), 3.89-3.93 (m, 1H), 3.96-4.00 (m, 2H), 4.85 (s, 2H), 5.13-5.16 (m, 1H), 7.03 (d, $J$ = 8.4 Hz, 1H), 7.29 (t, $J$ = 7.6 Hz, 1H), 7.33 (t, $J$ = 6.0 Hz, 1H), 7.34 (d, $J$ = 8.0 Hz, 1H), 7.44 (d, $J$ = 8.8 Hz, 1H), 7.46 (s, 1H), 7.54 (d, $J$ = 6.8 Hz, 1H), 7.59 (d, $J$ = 1.6 Hz, 1H), 7.75 (s, 1H), 7.78 (d, $J$ = 7.2 Hz, 1H), 7.83 (d, $J$ = 8.4 Hz, 1H), 13.96 (brs, 1H); $^{13}$C-NMR (100 MHz, DMSO-$d_6$) $\delta$ = 13.9, 22.0, 23.9, 25.5, 26.7, 27.0, 27.9, 28.4, 28.5, 31.1, 32.7, 35.1, 44.0, 44.7, 45.8, 46.6, 49.3, 69.2, 87.5, 107.6, 111.0, 113.4, 114.4, 115.5, 119.7, 119.9, 121.0, 122.7, 123.0, 126.8, 127.1, 127.8, 133.2, 134.2, 135.5, 136.5, 138.2, 139.8, 149.8, 150.1, 153.2, 154.8, 165.0, 165.1, 166.0, 168.0; FABMS (NBA) *m/z* 796 ($MH^+$); Anal. Found C, 69.16; H, 5.66; N, 8.63%. Calcd. for $C_{46}H_{45}N_5O_4S_2$: C, 69.41; H, 5.70; N, 8.80%.

**Synthesis of DN351**

To an acetic acid solution (4 ml) containing a **5c** (0.56 g, 1.2 mmol) and **6** (0.52 g, 1.2 mmol) was added ammonium acetate (4 mg). The mixture was refluxed for 2 h. After cooling, the resulting precipitate was filtered, washed with methanol (10 ml) and purified by column chlomatography ($SiO_2$, $CHCl_3$:MeOH=20:1) to give DN351 (0.31 g, 0.35 mmol, 30%) as a brown powder: mp >300°C; IR (KBr) $\nu$ =2928, 2214, 1526, 1491, 1128 $cm^{-1}$; $^1$H-NMR (400 MHz, DMSO-$d_6$) $\delta$ = 0.47-0.58 (m, 4H), 0.62 (t, $J$ = 7.2 Hz, 3H), 0.67 (t, $J$ = 7.6 Hz,

3H), 0.84 (t, $J$ = 7.2 Hz, 3H), 1.06 (dq, $J$ = 15.6, 7.6 Hz, 4H), 1.17-1.33 (m, 10H), 1.35-1.48 (m, 1H), 1.56-1.69 (m, 3H), 1.71-1.84 (m, 3H), 1.90-2.06 (m, 4H), 2.06-2.17 (m, 1H), 3.88-3.93 (m, 1H), 3.96-4.02 (m, 2H), 4.85 (s, 2H), 5.15-5.20 (m, 1H), 6.98 (d, $J$ = 8.4 Hz, 1H), 7.28 (t, $J$ = 7.2 Hz, 1H), 7.32 (t, $J$ = 7.6 Hz, 1H), 7.36 (dd, $J$ = 8.0, 1.6 Hz, 1H), 7.42 (d, $J$ = 7.6 Hz, 1H), 7.43 (s, 1H), 7.44 (d, $J$ = 8.8 Hz, 1H), 7.46 (s, 1H), 7.75 (s, 1H), 7.76 (d, $J$ = 6.0 Hz, 1H), 7.80 (d, $J$ = 8.4 Hz, 1H), 13.95 (brs, 1H); $^{13}$C-NMR (100 MHz, DMSO-$d_6$) $\delta$ = 13.7, 13.8, 13.9, 22.0, 22.3 (2C), 23.8, 25.5, 25.8 (2C), 27.9, 28.4 (2C), 28.5 (2C), 31.1, 32.4, 35.2, 43.9, 44.7, 45.9, 49.3, 54.7, 69.3, 87.5, 107.3, 111.0, 113.4, 114.4, 115.9, 119.4, 120.0, 120.7, 122.7, 123.0, 126.7. 126.9, 127.5, 133.4, 135.5, 136.4, 136.6, 139.5, 140.2, 149.8, 150.0, 151.7, 165.1, 165.2, 166.0, 168.0; FABMS (NBA) *m/z* 880 ($MH^+$); Anal. Found C, 70.71; H, 6.48; N, 7.85%. Calcd. for $C_{52}H_{57}N_5O_4S_2$: C, 70.96; H, 6.53; N, 7.96%.

**Synthesis of DN363**

To an acetic acid solution (4 ml) containing a **5d** (0.40 g, 0.69 mmol) and **6** (0.30 g, 0.69 mmol) was added ammonium acetate (3 mg). The mixture was refluxed for 2 h. After cooling, the resulting precipitate was filtered, washed with methanol (10 ml) and purified by column chlomatography ($SiO_2$, $CHCl_3$:MeOH=20:1) to give DN363 (0.29 g, 0.29 mmol, 42%) as a brown powder: mp >300°C; IR (KBr) $\nu$ = 2924, 2214, 1526, 1491, 1128 cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ = 0.61-0.71 (m, 4H), 0.80 (t, $J$ = 7.1 Hz, 3H), 0.82 (t, $J$ = 6.8 Hz, 3H), 0.88 (t, $J$ = 6.8 Hz, 3H), 1.05-1.42 (m, 30H), 1.51-1.59 (m, 1H), 1.71-1.80 (m, 4H), 1.89-1.99 (m, 6H), 2.09-2.17 (m, 1H), 3.73 (brs, 1H), 3.88-3.93 (m, 1H), 4.19 (t, $J$ = 7.6 Hz, 2H), 4.97 (s 2H), 5.03-5.06 (m, 1H), 6.91 (d, $J$ = 8.3 Hz, 1H), 7.23-7.29 (m, 2H), 7.30-7.38 (m, 5H), 7.65-7.71 (m, 2H), 7.80 (s, 1H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ = 14.1 (2C), 14.8, 22.6 (3C), 23.8, 23.9, 24.3, 26.0, 28.8, 29.0, 29.1, 29.2 (3C), 29.3, 29.9, 30.0, 31.7, 31.8 (2C), 33.1, 35.6, 40.3, 40.4, 44.8, 45.3 (2C), 51.4, 55.2, 70.3, 87.3, 107.7, 110.5, 112.8, 113.9, 116.3, 119.4, 120.5, 120.6, 122.9, 123.2, 126.8, 126.9, 127.7, 134.4, 136.7, 137.5, 137.6, 139.6, 140.5, 150.6 (2C), 151.5, 152.4, 164.5 (2C), 165.6, 166.9; FABMS (NBA) *m/z* 993 ($MH^+$); Anal. Found C, 72.77; H, 7.36; N, 6.90%. Calcd. for $C_{60}H_{73}N_5O_4S_2$: C, 72.62; H, 7.41; N, 7.06%.

**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$^{-1}$.

**Photoelectrochemical measurements**

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

**Fabrication of DSSCs**

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-*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. Plutinum (6 μm thick) sputtered FTO glass plates were used as the counter electrode. The dye-adsorbed zinc oxide electrode and plutinum 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.