Supporting Information

Organic sensitizers featuring 9,10-diarylsubstituted anthracene unit

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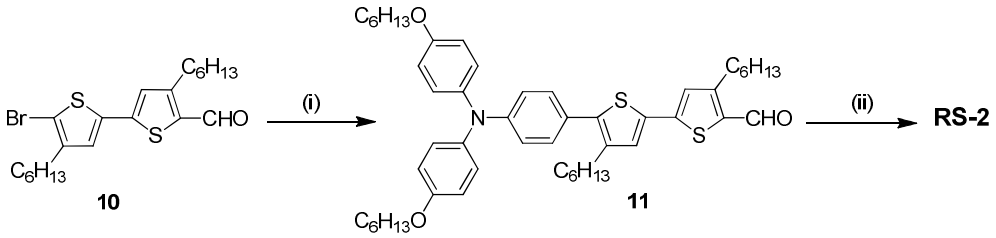

Scheme S1 (i) $2C_6H_{13}$OTPA-B, $Pd(PPh_3)_4$, THF/H_2O; (ii) cyanoacetic acid, ammonium acetate, acetic acid.

Synthesis

Coumpound **10** was prepared according to the literature.[1]

Synthesis of 2a. To a solution of 4-*t*-butylbromobenzene (6.39 g, 30.0 mmol) in anhydrous THF (150 mL) at -78 ^oC under an atmosphere of dry nitrogen, *n*-BuLi (2.0 M in hexane, 14.5 mL) was added dropwise. After addition of *n*-BuLi, the reaction mixture was stirred at -78 ^oC for 2 h before 2,6-dibromoanthraquinone (2.75 g, 7.5 mmol) was added. The mixture was stirred for 1 h at -78 ^oC, before it was allowed to warm up to room temperature and continued to be stirred overnight. The reaction was quenched by water and then extracted with ethyl acetate. The combined organic extracts were dried over anhydrous sodium sulfate. After the solvent was evaporated, the product was purified by column chromatography on silica gel (ethyl acetate/petroleum, 1/6) to obtain the white intermediate. The intermediate was dried in vacuum drying chamber overnight. Then a mixture of the intermediate (2.45 g, 3.86 mmol), sodium hypophosphite hydrate (5.30 g, 100.0 mmol), potassium iodide (2.49 g, 15.0 mmol) was dissolved in acetic acid (50 mL), and stirred vigorously under reflux until the reaction was complete as monitored by TLC. After cooling to room temperature, the precipitate was filtered, washed with water and recrystallized in a mixed solvent of dichloromethane and petroleum (v/v = 1/10) to give a light yellow solid (1.80 g, 39.4%). ^1H NMR ($CDCl_3$, 300MHz) δ (ppm): 7.86 (s, 2H, ArH), 7.63-7.55 (m, 6H, ArH), 7.38-7.33 (m, 6H, ArH), 1.48 (s, 18H, $-CH_3$). MS (EI, *m*/*z*): $[M]^+$ calcd for $C_{34}H_{32}Br_2$: 600.08. Found: 600.25.

Synthesis of 2b. The synthetic procedure was similar to that of **2a** as a light yellow solid (2.10 g, 56.2%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.87 (s, 2H, ArH), 7.59 (d, J = 9.3 Hz, 2H, ArH), 7.37 (d, J = 9.3 Hz, 2H, ArH), 7.32 (d, J = 8.7 Hz, 4H, ArH), 7.13 (d, J = 8.4 Hz, 4H, ArH), 4.12 (t, J = 6.6 Hz, 4H, -OCH_2-), 1.95-1.85 (m, 4H, -CH_2-), 1.59 (s, br, 4H, -CH_2-), 1.41 (s, br, 8H, -CH_2-), 0.95 (s, br, 6H, -CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 159.1, 136.7, 132.4, 131.4, 129.6, 129.3, 129.2, 129.1, 129.0, 120.2, 114.8, 68.3, 31.9, 29.6, 26.0, 22.9, 14.3. HRMS (ESI, m/z): $[M+1]^+$ calcd for $C_{38}H_{41}Br_2O_2$: 687.1473. Found: 687.1479.

Synthesis of 3a. To a solution of **2a** (800 mg, 1.32 mmol) suspended in toluene (30 mL) was added tributyl(4-hexylthiophen-2-yl)stannane (1.83 g, 4.00 mmol) and $Pd(PPh_3)_4$ (5% mmol) under an atmosphere of dry nitrogen. The reaction mixture was refluxed for 8 h. After cooling to room temperture, the solvent was evaporated under reduced pressure, and the product was purified by column chromatography (petroleum/chloroform, 2/1) on silica gel as an orange-yellow solid (690 mg, 67.4%). ^{1}H NMR ($CDCl_3$, 300MHz) δ (ppm): 7.86 (s, 2H, ArH), 7.74 (d, J = 9.3 Hz, 2H, ArH), 7.64 (d, J = 8.1 Hz, 4H, ArH), 7.56 (d, J = 9.0 Hz, 2H, ArH), 7.44 (d, J = 8.1 Hz, 4H, ArH), 7.07 (s, 2H, ArH), 6.83 (s, 2H, ArH), 2.57 (t, J = 7.5 Hz, 4H, -CH_2-), 1.60 (s, br, 4H, -CH_2-), 1.50 (s, 18H, -CH_3), 1.30 (s, br, 12H, -CH_2-), 0.88 (s, br, 6H, -CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 150.7, 144.6, 137.5, 135.7, 131.3, 131.1, 130.5, 129.96, 128.1, 125.6, 125.1, 124.3, 123.1, 120.1, 35.1, 32.0, 31.8, 30.9, 30.7, 29.3, 22.9, 14.4. HRMS (ESI, m/z): $[M+1]^+$ calcd for $C_{54}H_{63}S_2$: 775.4371. Found: 775.4373.

Synthesis of 3b. 3b was synthesized by the similar procedure of **3a** as a greenish yellow oil (563 mg, 74.8%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.91 (s, 2H, ArH), 7.73 (d, J = 9.0 Hz, 2H, ArH), 7.56 (d, J = 7.2 Hz, 2H, ArH), 7.40 (d, J = 8.4 Hz, 4H, ArH), 7.15 (d, J = 8.1 Hz, 4H, ArH), 7.10 (s, 2H, ArH), 6.84 (s, 2H, ArH), 4.13 (s, br, 4H, -OCH_2-), 2.58 (t, J = 7.2 Hz, 4H, -CH_2-), 1.91 (s, br, 4H, -CH_2-), 1.57 (s, br, 8H, -CH_2-), 1.42-1.30 (m, 20H, -CH_2-), 0.96 (s, br, 6H, -CH_3), 0.88 (s, br, 6H, -CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 158.8, 144.6, 144.4, 137.1, 132.6, 131.1, 130.6, 130.2, 127.9, 125.1, 124.1,

122.9, 120.0, 114.7, 68.4, 31.9, 30.8, 30.6, 29.6, 29.2, 26.1, 22.9, 22.8, 14.3. HRMS (ESI, *m/z*): $[M+1]^+$ calcd for $C_{58}H_{71}O_2S_2$: 863.4896. Found: 863.4896.

Synthesis of 4a. Dry DMF (2.0 equiv) was added to $POCl_3$ (1.2 equiv) at 0 ^oC in an ice water bath, and the mixture was continued to stir for 30 min, rendering its conversion into Vilsmeier reagent. Then a solution of **3a** (1.0 equiv) in 1,2-dichloroethane (15 mL) was added, the reaction solution was stirred at room temperature overnight, then poured into an aqueous solution of sodium carbonate and further stirred for 1 h. The crude product was extracted with dichloromethane, and the organic layer was washed with water, and dried over anhydrous sodium sulfate. After the solvent was evaporated under reduced pressure, the product was purified by column chromatography (petroleum/chloroform, 1/1) on silica gel as a yellow solid (300 mg, 57.9%). ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 9.98 (s, 1H, -CHO), 8.01 (s, 1H, ArH), 7.87 (s, 1H, ArH), 7.79 (d, J = 9.0 Hz, 1H, ArH), 7.73 (d, J = 9.0 Hz, 1H, ArH), 7.65-7.53 (m, 6H, ArH), 7.42 (d, J = 7.8 Hz, 4H, ArH), 7.12 (s, 1H, ArH), 7.08 (s, 1H, ArH), 6.84 (s, 1H, ArH), 2.92 (t, J = 7.5 Hz, 2H, $-CH_2-$), 2.57 (t, J = 7.5 Hz, 2H, $-CH_2-$), 1.66-1.60 (m, 4H, $-CH_2-$), 1.50 (s, 18H, $-CH_3$), 1.43-1.26 (m, 12H, $-CH_2-$), 0.88 (s, br, 6H, $-CH_3$). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 181.9, 154.2, 153.7, 150.9, 150.8, 144.6, 144.3, 138.3, 137.5, 136.8, 135.3, 135.2, 131.6, 131.2, 130.3, 130.1, 123.0, 129.4, 129.1, 128.5, 128.2, 126.8, 125.6, 125.3, 125.0, 124.5, 123.3, 123.0, 120.3, 106.2. 35.0, 34.5, 31.9, 31.8, 31.6, 30.8, 30.6, 29.9, 29.2, 28.8, 22.8, 14.4. MS (EI, *m/z*): $[M]^+$ calcd for $C_{55}H_{62}OS_2$: 802.42. Found:802.66.

Synthesis of 4b. 4b was synthesized by the similar procedure of **4a** as a yellow oil (350 mg, 64.4%). ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 9.99 (s, 1H, -CHO), 8.05 (s, 1H, ArH), 7.92 (s, 1H, ArH), 7.79-7.73 (m, 2H, ArH), 7.60-7.55 (m, 2H, ArH), 7.40 (d, J = 7.2 Hz, 4H, ArH), 7.18-7.12 (m, 6H, ArH), 6.86 (s, 1H, ArH), 4.16-4.12 (m, 4H, $-OCH_2-$), 2.94 (t, J = 7.5 Hz, 2H, $-CH_2-$), 2.59 (t, J = 7.5 Hz, 2H, $-CH_2-$), 1.92 (s, br, 2H, $-CH_2-$), 1.68-1.55 (m, 4H, $-CH_2-$), 1.42-1.31 (m, 26H, $-CH_2-$), 0.96-0.88 (m, 12H, $-CH_3$). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 182.2, 159.0, 154.5, 153.7, 144.7, 144.2, 138.1, 137.3, 136.7, 132.6, 131.7, 131.3, 130.6, 130.3, 129.5, 128.8, 128.5, 128.2, 126.9, 125.4, 125.1, 124.5, 123.3,

122.9, 120.3, 114.7, 68.4, 32.0, 31.8, 30.8, 30.7, 29.7, 29.3, 28.8, 26.1, 22.9, 14.4. HRMS (ESI, *m*/*z*): $[M+1]^+$ calcd for $C_{59}H_{71}O_3S_2$: 891.4845. Found: 891.4842.

Synthesis of 5a. To a solution of **4a** (300 mg, 0.37 mmol) in THF (15 mL) at 0 ^oC in an ice water bath was added *N*-bromosuccinimide (73 mg, 0.41 mmol) in batches under an atmosphere of dry nitrogen, and the mixture was further stirred at room temperature in the dark overnight. Then water (20 mL) was added into the mixture to quench the reaction, the crude product was extracted with dichloromethane, and the organic layer was dried over anhydrous sodium sulfate. After the solvent was evaporated under reduced pressure, the product was purified by column chromatography (petroleum/chloroform, 1/1) on silica gel as a yellow solid (300 mg, 90.9%). ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 9.98 (s, 1H, -CHO), 8.01 (s, 1H, ArH), 7.79-7.72 (m, 2H, ArH), 7.67-7.64 (m, 5H, ArH), 7.56 (d, J = 9.0 Hz, 1H, ArH), 7.50 (d, J = 8.7 Hz, 1H, ArH), 7.42 (d, J = 7.5 Hz, 4H, ArH), 7.13 (s, 1H, ArH), 6.94 (s, 1H, ArH), 2.92 (t, J = 7.2 Hz, 2H, $-CH_2-$), 2.53 (t, J = 7.5 Hz, 2H, $-CH_2-$), 1.67-1.63 (m, 2H, $-CH_2-$), 1.51 (s, 18H, $-CH_3$), 1.31 (s, br, 14H, $-CH_2-$), 0.88 (s, br, 6H, $-CH_3$). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 182.2, 154.4, 151.1, 144.0, 143.5, 138.4, 137.7, 136.8, 135.2, 131.2, 130.2, 129.7, 128.5, 126.9, 125.7, 125.1, 124.8, 123.8, 123.6, 122.9, 109.1, 35.1, 31.8, 29.9, 29.2, 28.9, 22.8, 14.4. HRMS (ESI, *m*/*z*): $[M+1]^+$ calcd for $C_{55}H_{62}BrOS_2$: 881.3425. Found: 881.3423.

Synthesis of 5b. 5b was synthesized by the similar procedure of **5a** as a yellow solid (268 mg, 94.6%). ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 9.99 (s, 1H, -CHO), 8.05 (s, 1H, ArH), 7.82 (s, 1H, ArH), 7.78-7.72 (m, 2H, ArH), 7.57 (d, J = 9.3 Hz, 1H, ArH), 7.50 (d, J = 8.7 Hz, 1H, ArH), 7.38 (d, J = 6.9 Hz, 4H, ArH), 7.17 (s, br, 6H, ArH), 6.98 (s, 1H, ArH), 4.15 (s, br, 4H, $-OCH_2-$), 2.93 (s, br, 2H, $-CH_2-$), 2.54 (s, br, 2H, $-CH_2-$), 1.92 (s, br, 4H, $-CH_2-$), 1.68-1.58 (m, 4H, $-CH_2-$), 1.42-1.25 (m, 24H, $-CH_2-$), 0.96-0.89 (m, 12H, $-CH_3$). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 182.1, 159.1, 154.4, 153.6, 143.9, 143.5, 138.1, 137.4, 136.8, 132.6, 131.2, 130.8, 130.4, 130.1, 129.9, 129.6, 128.5, 127.0, 125.0, 124.8, 123.6, 123.4, 122.9, 114.8, 109.1, 68.4, 32.0, 31.8, 29.9, 29.7, 29.2, 28.8, 26.1, 22.9, 14.4. HRMS (ESI, *m*/*z*): $[M+1]^+$ calcd for $C_{59}H_{70}BrO_3S_2$: 969.3950. Found: 969.3954.

Synthesis of 6. To a solution of **5a** (132 mg, 0.15 mmol) in THF and H_2O (4/1, v/v, 10 mL) was added **TPA-B** (67 mg, 0.18 mmol), potassium carbonate (83 mg, 0.60 mmol) and $Pd(PPh_3)_4$ (5% mmol) under an atmosphere of nitrogen. The reaction mixture was refluxed overnight. After cooling to room temperture, the mixture was poured into water and extracted with dichloromethane. Then the organic layer was washed with water and dried over anhydrous sodium sulfate. After the solvent was evaporated under reduced pressure, the product was purified by column chromatography (petroleum/chloroform, 1/1) on silica gel as an orange solid (160 mg, 85.5%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 9.98 (s, 1H, -CHO), 8.02 (s, 1H, ArH), 7.88 (s, 1H, ArH), 7.80-7.72 (m, 2H, ArH), 7.66-7.62 (m, 5H, ArH), 7.56 (d, J = 11.1 Hz, 1H, ArH), 7.44 (d, J = 8.1 Hz, 4H, ArH), 7.28-7.26 (m, 2H, ArH), 7.15-7.02 (m, 14H, ArH), 2.92 (t, J = 7.5 Hz, 2H, -CH_2-), 2.63 (t, J = 7.5 Hz, 2H, -CH_2-), 1.66-1.63 (m, 4H, -CH_2-), 1.51 (s, 9H, -CH_3), 1.50 (s, 9H, -CH_3), 1.31-1.25 (m, 12H, -CH_2-), 0.88-0.87 (m, 6H, -CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 182.0, 154.3, 153.7, 151.0, 150.8, 147.7, 147.3, 141.7, 139.6, 138.3, 138.3, 137.5, 136.7, 135.4, 135.2, 131.5, 131.2, 130.4, 130.1, 123.0, 129.6, 129.4, 128.6, 128.5, 128.2, 126.9, 126.6, 125.6, 125.0, 124.9, 124.4, 123.4, 123.2, 122.6, 35.1, 31.9, 31.8, 31.6, 31.1, 29.4, 29.2, 28.8, 22.8, 14.4. HRMS (ESI, m/z): $[M+1]^+$ calcd for $C_{73}H_{76}NOS_2$: 1046.5368. Found: 1046.5361.

Synthesis of 7. 7 was synthesized by the similar procedure of **6** as an orange solid (229 mg, 76.5%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 9.98 (s, 1H, -CHO), 8.02 (s, 1H, ArH), 7.87 (s, 1H, ArH), 7.78 (d, J = 8.7 Hz, 1H, ArH), 7.73 (d, J = 9.3 Hz, 1H, ArH), 7.64-7.61 (m, 5H, ArH), 7.56 (d, J = 10.5 Hz, 1H, ArH), 7.44 (d, J = 8.1 Hz, 4H, ArH), 7.20 (d, J = 8.7 Hz, 2H, ArH), 7.13-7.07 (m, 6H, ArH), 6.91 (d, J = 8.7 Hz, 2H, ArH), 6.84 (d, J = 9.0 Hz, 4H, ArH), 3.93 (t, J = 6.3 Hz, 4H, -OCH_2-), 2.92 (t, J = 7.8 Hz, 2H, -CH_2-), 2.61 (t, J = 7.5 Hz, 2H, -CH_2-), 1.80-1.73 (m, 4H, -CH_2-), 1.67-1.64 (m, 2H, -CH_2-), 1.51-1.48 (m, 20H, -CH_2- and -CH_3), 1.36-1.26 (m, 24H, -CH_2-), 0.91-0.87 (m, 12H, -CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 181.9, 155.8, 154.2, 153.6, 150.8, 150.7, 148.3, 141.2, 140.5, 139.2, 138.8, 138.2, 137.4, 136.7, 135.3, 135.2, 131.5, 131.2, 130.3, 130.0, 129.9, 129.7, 129.3, 128.5, 128.1, 127.0, 126.8, 126.5, 126.1, 125.5, 124.9, 124.4, 123.3, 122.4, 119.7, 115.4, 68.4, 35.0, 31.8, 31.8, 31.7, 31.5,

31.1, 29.5, 29.4, 29.1, 28.7, 25.9, 22.7, 14.3. HRMS (ESI, *m*/*z*): $[M+1]^+$ calcd for $C_{85}H_{100}NO_3S_2$: 1246.7145. Found: 1246.7146.

Synthesis of 8. 8 was synthesized by the similar procedure of **6** as an orange solid (114 mg, 72.8%). ^{1}H NMR ($CDCl_3$, 300MHz) δ (ppm): 9.99 (s, 1H, -CHO), 8.06 (s, 1H, ArH), 7.92 (s, 1H, ArH), 7.76-7.74 (m, 2H, ArH), 7.63-7.55 (m, 2H, ArH), 7.40 (d, J = 7.8 Hz, 4H, ArH), 7.31-7.26 (m, 4H, ArH), 7.16-7.05 (m, 16H, ArH), 4.16-4.13 (m, 4H, -OCH_2-), 2.94 (s, br, 2H, -CH_2-), 2.65 (s, br, 2H, -CH_2-), 1.92 (s, br, 4H, -CH_2-), 1.68-1.58 (m, 4H, -CH_2-), 1.42-1.30 (m, 24H, -CH_2-), 0.96-0.87 (m, 12H, -CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 182.0, 159.0, 158.9, 154.4, 153.7, 147.7, 147.3, 141.7, 139.6, 138.3, 138.0, 137.2, 136.7, 132.6, 132.5, 131.5, 131.3, 130.7, 130.3, 130.3, 130.2, 130.0, 129.5, 129.4, 128.4, 128.1, 126.9, 126.6, 125.0, 124.8, 124.2, 123.3, 123.2, 122.5, 114.7, 68.4, 31.9, 31.80, 31.2, 29.6, 29.4, 29.2, 29.1, 28.8, 26.1, 22.8, 14.3. HRMS (ESI, *m*/*z*): $[M+1]^+$ calcd for $C_{77}H_{84}NO_3S_2$: 1134.5893. Found: 1134.5894.

Synthesis of 9. 9 was synthesized by the similar procedure of **6** as an orange solid (120 mg, 58.8%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 9.99 (s, 1H, -CHO), 8.05 (s, 1H, ArH), 7.91 (s, 1H, ArH), 7.78-7.72 (m, 2H, ArH), 7.62-7.54 (m, 2H, ArH), 7.40 (d, J = 8.1 Hz, 4H, ArH), 7.19 (d, J = 10.5 Hz, 2H, ArH), 7.17-7.15 (m, 6H, ArH), 7.09 (d, J = 8.4 Hz, 4H, ArH), 6.92 (d, J = 8.7 Hz, 2H, ArH), 6.84 (d, J = 8.7 Hz, 4H, ArH), 4.18-4.12 (m, 4H, -OCH_2-), 3.94 (t, J = 6.3 Hz, 4H, -OCH_2-), 2.94 (t, J = 7.5 Hz, 2H, -CH_2-), 2.63 (t, J = 7.5 Hz, 2H, -CH_2-), 1.96-1.89 (m, 4H, -CH_2-), 1.81-1.74 (m, 4H, -CH_2-), 1.68-1.57 (m, 4H, -CH_2-), 1.43-1.27 (m, 36H, -CH_3), 0.96-0.87 (m, 18H, -CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 182.0, 159.0, 158.9, 155.8, 154.4, 153.7, 148.3, 141.3, 140.6, 139.3, 138.8, 138.0, 137.1, 136.6, 132.5, 131.6, 131.3, 130.6, 130.3, 130.1, 129.8, 129.3, 128.4, 128.0, 127.0, 126.8, 126.6, 126.1, 125.0, 124.2, 119.8, 115.4, 114.7, 68.4, 31.8, 31.2, 29.5, 29.1, 28.8, 25.9, 22.8, 14.3. HRMS (ESI, *m*/*z*): $[M+1]^+$ calcd for $C_{89}H_{108}NO_5S_2$: 1334.7669. Found: 1334.7666.

Synthesis of 11. 11 was synthesized by the similar procedure of **6** as an orange oil (864 mg, 78.1%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 9.97 (s, 1H, -CHO), 7.22-7.19 (m, 3H, ArH), 7.09 (d, J = 7.2 Hz,

4H, ArH), 7.02 (s, 1H, ArH), 6.92 (d, J = 9.3 Hz, 2H, ArH), 6.84 (d, J = 7.8 Hz, 4H, ArH), 3.94 (s, br, 4H, -OCH_2-), 2.91 (s, br, 2H, -CH_2-), 2.62 (s, br, 2H, -CH_2-), 1.79-1.58 (m, 8H, -CH_2-), 1.46-1.32 (m, 24H, -CH_2-), 0.91-0.89 (m, 12H, -CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 181.0, 155.8, 153.8, 148.5, 146.5, 140.4, 140.1, 139.0, 135.2, 132.9, 129.5, 128,5, 127.0, 125.7, 125.0, 119.3, 115.3, 68.1, 31.7, 31.3, 30.9, 29.4, 29.2, 29.0, 28.9, 28.5, 25.8, 22.7, 14.1. MS (ESI, m/z): $[M+1]^+$ calcd for $C_{51}H_{68}NO_3S_2$: 806.5. Found: 806.5.

Synthesis of RS-2. A mixture of **11** (486 mg, 0.60 mmol), ammonium acetate (100 mg) and cyanoacetic acid (77 mg, 0.90 mmol) were dissolved in acetic acid (10 mL) under an atmosphere of nitrogen. Then the reaction mixture was refluxed overnight. After cooling to room temperature, the mixture was poured into water (50 mL), extracted with dichloromethane (DCM), and dried over anhydrous sodium sulfate. After the solvent was evaporated under reduced pressure, the crude product was purified by column chromatography (chloroform/methanol from 100/1 to 20/1) as a dark red solid (376 mg, 71.4%).^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.42 (s, 1H, =CH-), 7.30 (s, 1H, ArH), 7.22 (d, J = 8.7 H, 2H, ArH), 7.11-7.07 (m, 5H, ArH), 6.92 (d, J = 8.7 Hz, 2H, ArH), 6.85 (d, J = 9.0 Hz, 4H, ArH), 3.94 (t, J = 6.6 Hz, 4H, -OCH_2-), 2.79 (s, br, 2H, -CH_2-), 2.63 (t, J = 7.2 Hz, 2H, -CH_2-), 1.81-1.75 (m, 4H, -CH_2-), 1.65 (s, br, 4H, -CH_2-), 1.47 (s, br, 4H, -CH_2-), 1.34 (s, br, 20H, -CH_2-), 0.90 (s, br, 12H, -CH_3). ^{13}C NMR (d_6-DMSO/$CDCl_3$ = 2/1, 75 MHz) δ (ppm): 164.4, 155.8, 148.5, 145.2, 142.8, 140.5, 139.6, 139.2, 132.2, 129.3, 128.2, 127.2, 125.6, 124.4, 118.7, 116.9, 115.4, 96.4, 67.9, 31.4, 30.9, 30.6, 29.1, 28.8, 25.6, 22.5, 14.2. MS (ESI, m/z): $[M+1]^+$ calcd for $C_{54}H_{69}N_2O_4S_2$: 873.5. Found: 873.4.

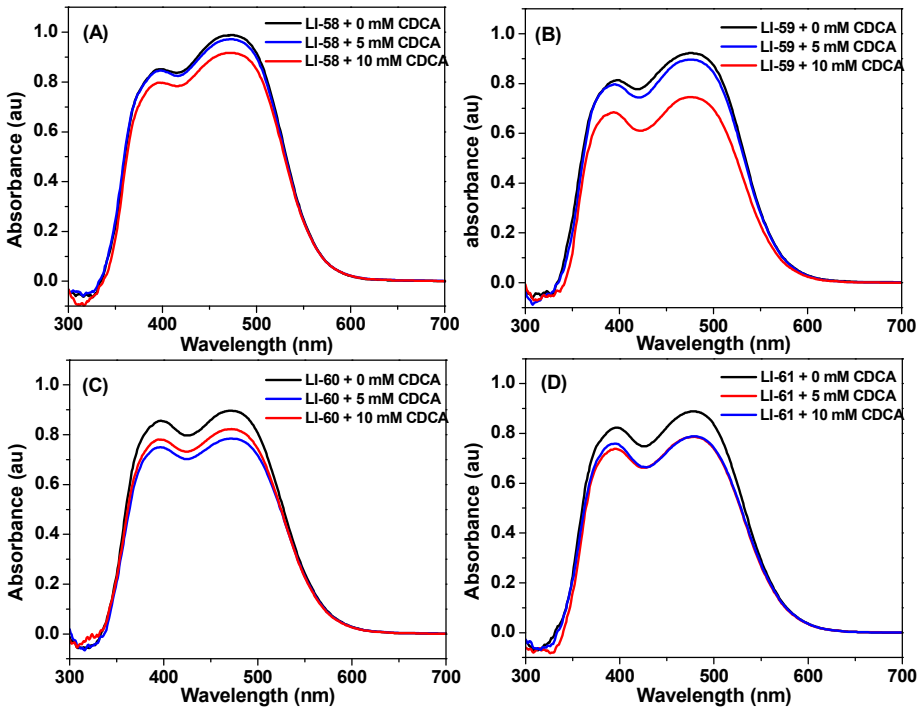

Figure S1 UV-vis spectra of the sensitizers on TiO_2 films (2 μm) with different concentrations of CDCA.

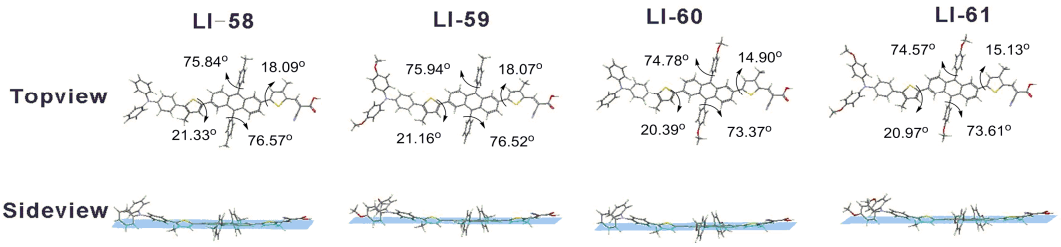

Figure S2 The optimized structures of the sensitizers.

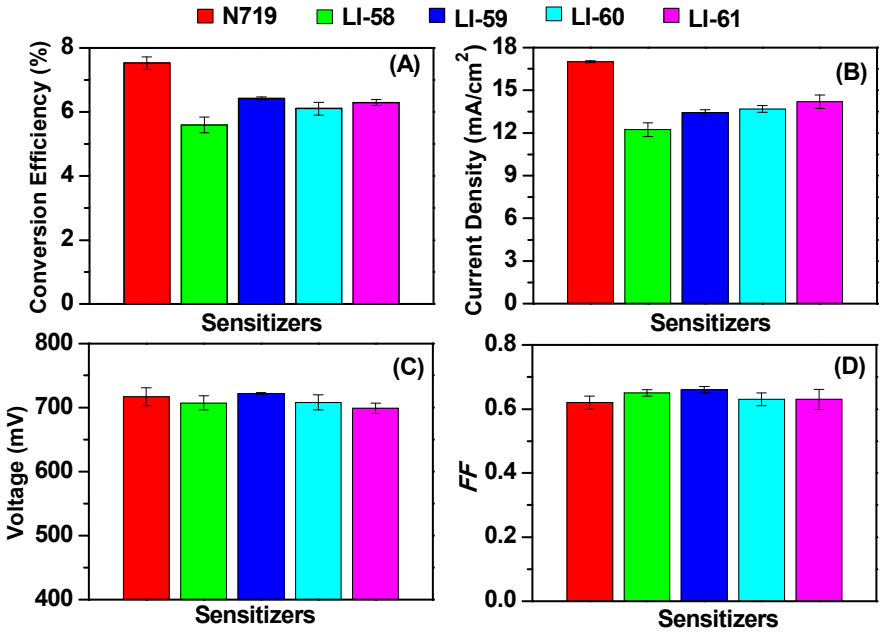

Figure S3 Photovoltaic performance parameters of DSCs based on the sensitizers.

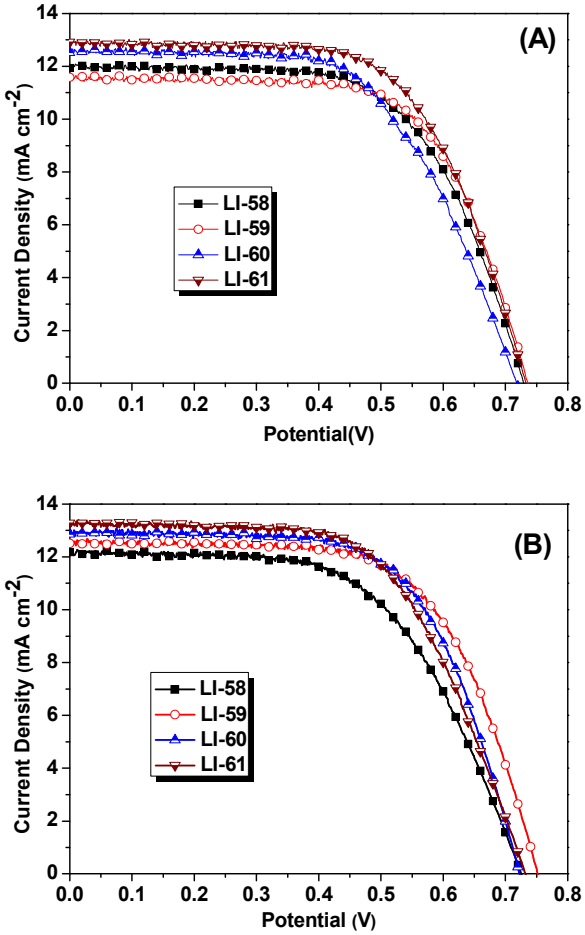

Figure S4 *J-V* characteristics of DSCs measured at simulated 100 mWcm^{-2} AM1.5 conditions. (A) The TiO_2 electrodes were pretreated with CDCA (5mM) for 6 h, then immersed into the dye solution (0.3 mM) in $CHCl_3$ for 24 h, (B) The TiO_2 electrodes were pretreated with CDCA (10 mM) for 6 h, then immersed into the dye solution (0.3 mM) in $CHCl_3$ for 24 h.

Table S1 The performance data of dye sensitized solar cells

sensitizer	CDCA (mM)	J_{sc} (mA cm^{-2})	V_{oc} (mV)	*FF*	η (%)	R_{rec} (ohm)	τ_n (ms)
LI-58	0	12.24±0.48	707±11	0.65±0.01	5.59±0.24	76.61	23.90
	5	11.93	728	0.63	5.47		
	10	12.18	725	0.58	5.13		
LI-59	0	13.42±0.22	722±1	0.66±0.01	6.42±0.04	91.86	24.76
	5	11.58	735	0.66	5.62		
	10	12.51	752	0.64	6.04		
LI-60	0	13.68±0.23	708±12	0.63±0.02	6.10±0.20	71.96	19.51
	5	12.53	719	0.60	5.40		
	10	12.86	722	0.65	6.00		
LI-61	0	14.20±0.47	699±8	0.63±0.02	6.29±0.10	53.96	13.49
	5	12.91	727	0.64	6.01		
	10	13.28	732	0.61	5.89		
N719	0	17.00±0.07	717±14	0.62±0.02	7.52±0.19		

References

(1) Hayashi, N.; Nishihara, T.; Matsukihira, T.; Nakashima, H.; Miyabayashi, K.; Miyake, M.; Higuchi, H. Orientation and Substituent Effects on the Properties of the Diacetylene-Group Connected Octaethylporphyrin-Dihexylbithiophene Derivatives (OEP-DHBTh-X) Carrying Electron-Withdrawing Groups. *Bull. Chem. Soc. Jpn.* **2007,** *80*, 371-386.