

Supplementary Information for

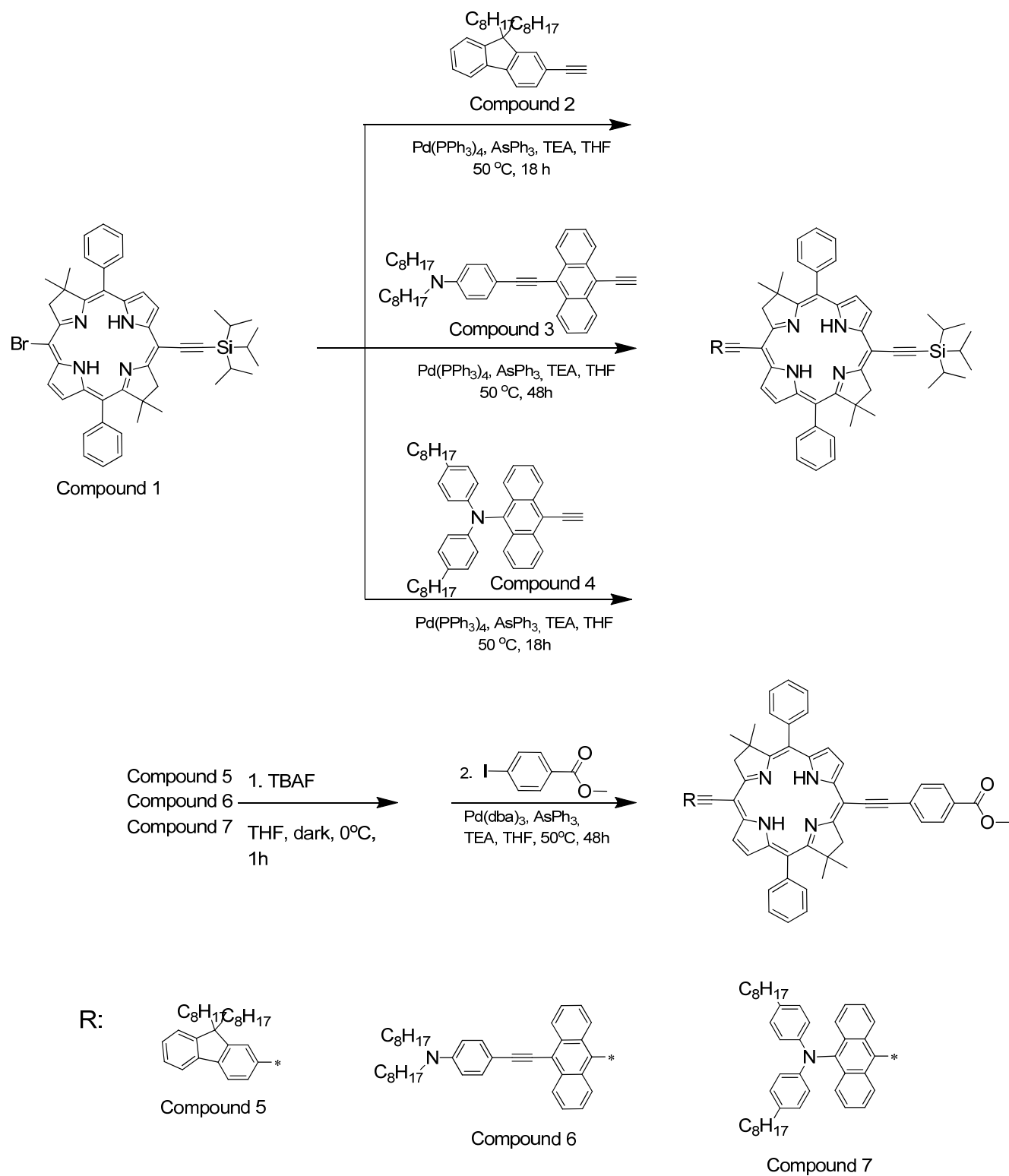
Synthesis, Properties and Photovoltaic Performance in Dye-Sensitized Solar Cell of Three *meso*- Diphenylbacteriochlorins Bearing a Dual-Functioned Electron-Donor

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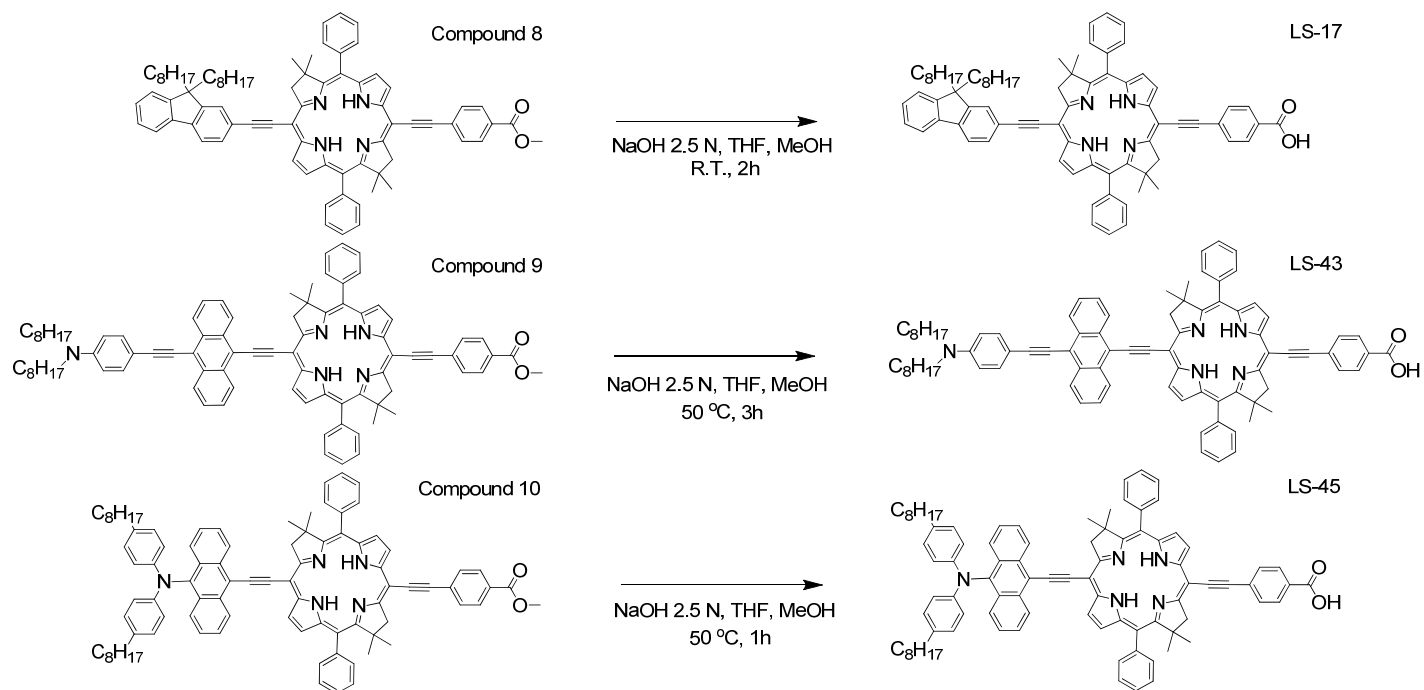
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Dye Synthesis and Characterization

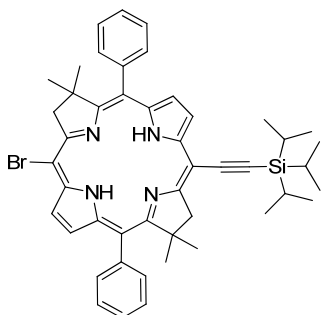


Scheme S1. Synthesis of the LS-17, LS-43, and LS-45 precursors.



Scheme S2. Base hydrolysis of the LS-17, LS-43, and LS-45 precursors.

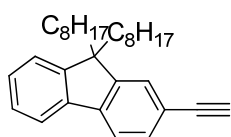
Compound 1



Synthesis of the Compound 1 is as the reported procedure,^{S1} except for the dihydrodipyrin. The final step in the synthesis of the dihydrodipyrin, the precursor to the bacteriochlorin, requires use of TiCl_3 . In this work, the procedure is adjusted (see next page) due to the change of TiCl_3 solution from 12 wt% (Sigma-Aldrich) to ~15 wt% in ~10% HCl (Merck). TiCl_3 solution is crucial to the reaction, therefore, it is important to adjust the experimental conditions according to its composition.^{S2}

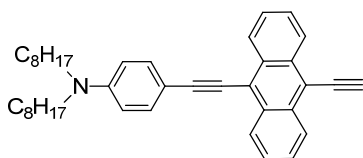
Also note that the weight of the product was mistyped in our previous report (p. S14 of the SI).^{S1} The correct weight of the yellow product should be 1.084 g, not 158 mg. Nonetheless, the yield was correctly reported.

Compound 2



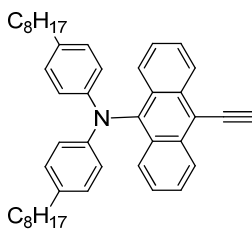
Synthesis of the Compound 2 is similar to that in the literature.^{S3}

Compound 3



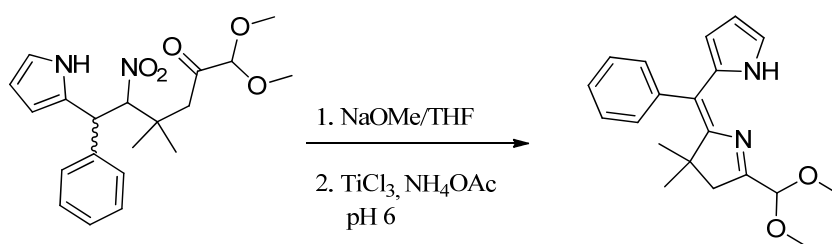
Synthesis of the Compound 3 has been reported previously.^{S4}

Compound 4



Synthesis of the Compound 3 has been reported previously.^{S5}

2-[(5-(dimethoxymethyl)-3,3-dimethyl-3,4-dihydro-2H-pyrrol-2-ylidene)(phenyl)methyl]-1H-pyrrole



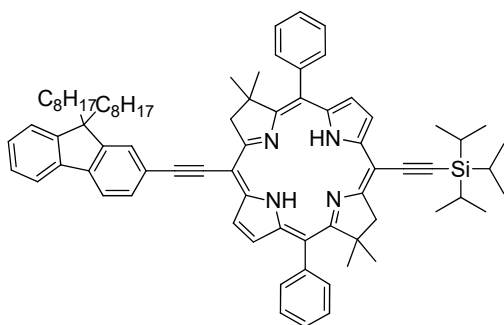
First flask: A solution of 1,1-dimethoxy-4,4-dimethyl-5-nitro-6-phenyl-6-(1H-pyrrol-2-yl)hexan-2-one (5.50 g, M.W.=374.43, 14.7 mmol.) in anhydrous THF (60 mL) under nitrogen was treated with NaOMe (2.16 g, M.W.=54.02, 40.0 mmol.) and the mixture was stirred for 1 h at room temperature.

Second flask: TiCl₃ (Merck, ~15 wt % TiCl₃ in ~10 wt % HCl, 69 mL) and D. D. H₂O (400 mL) were first combined and bubbled with N_{2(g)}. NH₄OAc (129 g, M.W. = 77.08, 1.67 mol.) was then added to buffer the solution to pH 6.0. After checking with a pH meter, 10 mL of THF was added.

The solution in the first flask containing the nitronate anion of 1,1-dimethoxy-4,4-dimethyl-5-nitro-6-phenyl-6-(1H-pyrrol-2-yl)hexan-2-one was transferred to the buffered TiCl₃ solution in the second flask *via* a cannula. The resulting mixture was stirred under nitrogen at room temperature for 18 hours. After stirring for 18 hours, the green mixture was neutralized with NaHCO₃ (caution: large amt. of CO₂). After neutralization, the solution turned blue and was diluted with 1 L of water for extraction with ethyl acetate in portions of 100 mL. Perform a secondary extraction of the blue aqueous solution with ethyl acetate if necessary. After extraction, the organic extracts were combined and dried over Na₂SO₄, followed by concentration under reduced pressure. The crude product was passed through a short column [alumina, hexanes/ethyl acetate (95:5)] to afford a light yellow solid (1.097g, M.W. = 324.42, 23.0 %).

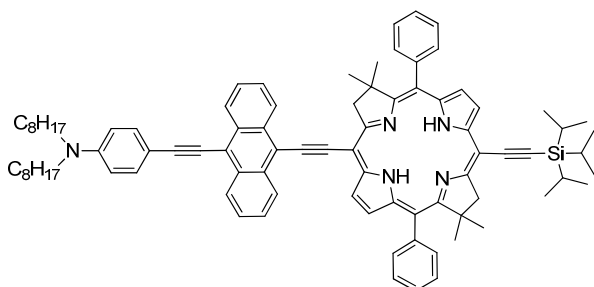
Characterization data are as those in reference S1.

Compound 5



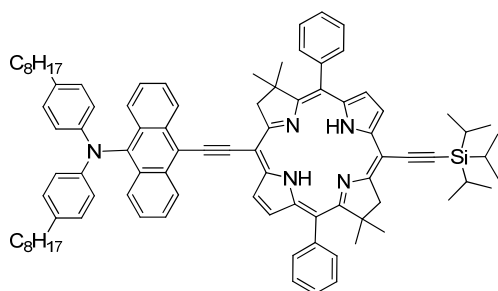
75 mg of compound 1 (M.W. = 781.94 g/mol, 0.10 mmol, 1.0 eq.) was mixed with 93 mg of compound 2 (M.W. = 414.67 g/mol, 0.22 mmol, 2.2 eq.) in 80 mL of dried THF and 5 mL of Et₃N. After 3 cycles of freeze–pump–thaw, 30 mol. % of Pd(PPh₃)₄ and 2.4eq AsPh₃ were added to the solution under an inert atmosphere. The reaction was stirred at 50 °C for 18 hours. Completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residues were re-dissolved in CH₂Cl₂. After NH₄Cl_(aq) washes, the organic layer was dried over Na₂SO₄. The solvent was removed by rotary evaporation. The residues were purified by column chromatography (silica gel, 230-400 mesh, eluent: CH₂Cl₂/*n*-hexanes = 1/9), followed by crystallization from CH₂Cl₂/MeOH to give Compound 5 (purple solids, 68mg, yield: 63%). ¹H NMR (CDCl₃ at 7.26 ppm, 300 MHz), δ_H(ppm): 9.08 (d, *J* = 4.8 Hz, 1H), 8.97 (d, *J* = 2.5 Hz, 1H), 8.08-7.52 (overlapped, 16H), 7.46-7.30 (overlapped, 3H), 4.70 (s, 2H), 4.42 (s, 2H), 2.19-1.95 (m, 4H), 1.60 (s, 6H), 1.55 (s, 6H), 1.41-0.99 (overlapped, 40H), 0.93-0.57 (overlapped, 11H), -0.93 (s, 1H), -0.98 (s, 1H). ¹³C NMR (CDCl₃ at 77.16 ppm, 75 MHz), δ_C (ppm): 167.50, 161.52, 160.98, 151.29, 141.51, 140.78, 140.67, 138.87, 137.51, 136.84, 33.99, 133.79, 130.63, 128.10, 127.92, 127.68, 127.12, 126.98, 126.88, 126.59, 125.67, 123.75, 123.49, 123.17, 122.77, 122.47, 122.21, 120.20, 120.04, 116.91, 116.85, 110.01, 97.43, 96.82, 96.73, 93.33, 56.48, 55.96, 55.47, 46.88, 46.73, 46.62, 40.65, 32.00, 30.89, 30.65, 30.28, 29.94, 29.47, 29.19, 29.04, 24.02, 22.80, 19.21, 14.28, 11.96, 1.25.

Compound 6



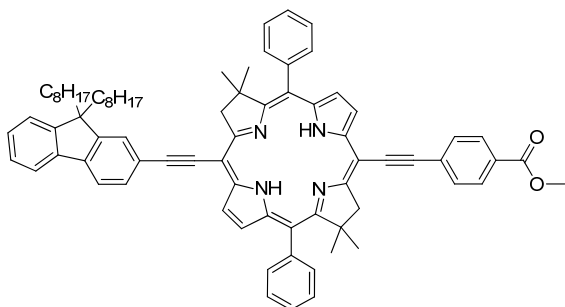
100 mg of compound 1 (M.W. = 781.94 g/mol, 0.13 mmol, 1.0 eq.) was mixed with 103 mg of compound 3 (M.W. = 541.81 g/mol, 0.19 mmol, 1.5 eq.) in 90 mL of dried THF and 10 mL of Et₃N. After 3 cycles of freeze–pump–thaw, 30 mol. % of Pd(PPh₃)₄ and 2.4eq AsPh₃ were added to the solution under an inert atmosphere. The reaction was stirred at 50 °C for 48 hours. Completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residues were re-dissolved in CH₂Cl₂. After NH₄Cl_(aq) washes, the organic layer was dried over Na₂SO₄. The solvent was removed by rotary evaporation. The residues were purified by column chromatography (silica gel, 230-400 mesh, eluent: CH₂Cl₂/*n*-hexanes = 1/4) to give Compound 6 (dark greenish blue solids, 138mg, yield: 86%). ¹H NMR (CDCl₃ at 7.26 ppm, 300 MHz), δ_H(ppm): 9.27 (d, *J* = 3.11 Hz, 1H), 9.09 (d, *J* = 7.94 Hz, 2H), 9.00 (d, *J* = 3.22 Hz, 1H), 8.78 (d, *J* = 8.10 Hz, 2H), 7.84-7.92 (m, 6H), 7.58-7.73 (m, 12H), 6.68 (d, *J* = 8.78 Hz, 2H), 4.80 (s, 2H), 4.51 (s, 2H), 3.33 (t, *J* = 7.36 Hz, 4H), 1.64 (s, 4H), 1.55 (t, *J* = 7.64 Hz, 6H), 1.32-1.35 (m, 47H), 0.92 (t, *J* = 6.87 Hz, 6H), -0.79 (s, 1H), -0.86 (s, 1H). ¹³C NMR (CDCl₃ at 77.16 ppm, 75 MHz), δ_C (ppm): 167.4, 167.3, 161.5, 160.8, 148.3, 140.6, 140.5, 138.9, 138.6, 137.4, 136.6, 133.8, 133.1, 132.5, 131.9, 127.8, 127.5, 126.8, 126.4, 123.7, 123.5, 122.4, 122.0, 119.7, 118.2, 116.9, 116.8, 111.4, 109.8, 108.9, 105.8, 104.9, 97.4, 97.0, 96.8, 94.0, 85.0, 56.6, 56.3, 51.1, 46.8, 46.5, 31.9, 30.5, 29.7, 29.5, 29.4, 27.2, 22.7, 19.0, 14.1, 11.8.

Compound 7



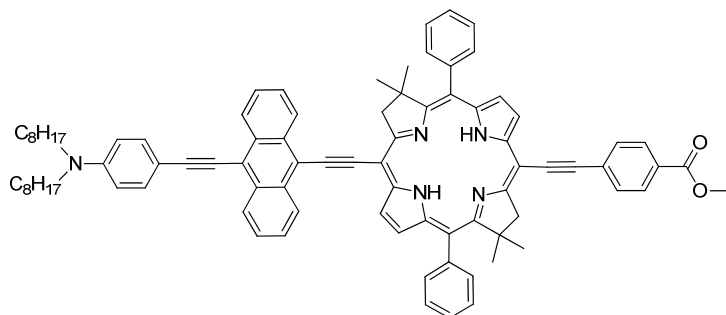
100 mg of compound 1 (M.W. = 781.94 g/mol, 0.13 mmol, 1.0 eq.) was mixed with 152 mg of compound 4 (M.W. = 593.88 g/mol, 0.26 mmol, 2.0 eq.) in 90 mL of dried THF and 10 mL of Et₃N. After 3 cycles of freeze–pump–thaw, 30 mol. % of Pd(PPh₃)₄ and 2.4eq AsPh₃ were added to the solution under an inert atmosphere. The reaction was stirred at 50 °C for 18 hours. Completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residues were re-dissolved in CH₂Cl₂. After NH₄Cl_(aq) washes, the organic layer was dried over Na₂SO₄. The solvent was removed by rotary evaporation. The residues were purified by column chromatography (silica gel, 230-400 mesh, eluent: CH₂Cl₂/*n*-hexanes = 1/4) to give Compound 7 (dark greenish blue solids, 133mg, yield: 80%). ¹H NMR (CDCl₃ at 7.26 ppm, 300 MHz), δ_H(ppm): 9.26 (d, *J* = 4.56 Hz, 1H), 9.15 (d, *J* = 8.57 Hz, 2H), 9.00 (d, *J* = 4.60 Hz, 1H), 8.24 (d, *J* = 8.74 Hz, 2H), 7.85-7.90 (m, 6H), 7.58-7.67 (m, 8H), 7.48 (t, *J* = 7.51 Hz, 2H), 7.01 (overlapped, *J* = 8.57, 17.02 Hz, 8H), 4.81 (s, 2H), 4.50 (s, 2H), 2.50 (t, *J* = 7.93 Hz, 4H), 1.56 (t, *J* = 9.58 Hz, 24H), 1.33-1.34 (m, 16H), 1.26-1.31 (m, 17H), 0.88 (t, *J* = 6.90 Hz, 6H), -0.80 (s, 1H), -0.87 (s, 1H). ¹³C NMR (CDCl₃ at 77.16 ppm, 75 MHz), δ_C (ppm): 167.5, 167.3, 161.5, 160.7, 145.7, 140.6, 140.5, 138.9, 138.6, 137.5, 136.6, 135.7, 134.1, 133.7, 130.8, 129.1, 127.8, 126.8, 126.7, 126.4, 125.3, 123.7, 123.5, 122.5, 121.9, 120.2, 118.7, 117.0, 116.8, 109.7, 105.0, 97.5, 96.8, 93.3, 56.6, 56.3, 46.8, 46.5, 35.3, 31.9, 31.5, 30.5, 29.5, 29.4, 29.3, 22.7, 19.0, 14.1, 11.8.

Compound 8



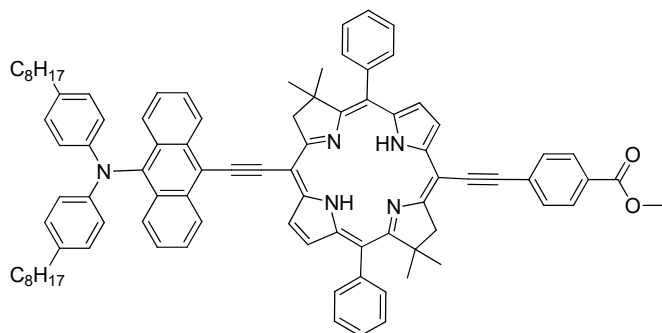
74 mg of compound 5 (M.W. = 1115.69 g/mol, 0.07 mmol, 1.0 eq.) was dissolved in 70 mL of THF and 0.1 mL TBAF solution (1M in THF) was added under dark with ice bath. The reaction was stirred at 0 °C for 1 hour. Completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residues were re-dissolved in CH₂Cl₂. After NH₄Cl_(aq) washes, the organic layer was dried over Na₂SO₄. The solvent was removed by rotary evaporation. The residue was directly go to next step without further purification. The residue was mixed with 35mg methyl 4-iodobenzoate (M.W. = 262.04 g/mol, 0.13 mmol, 1.9 eq.) in 60 mL of dried THF and 6 mL of Et₃N. After 3 cycles of freeze–pump–thaw, 30 mol. % of Pd(PPh₃)₄ and 2.4eq AsPh₃ were added to the solution under an inert atmosphere. The reaction was stirred at 50 °C for 18 hours. Completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residues were re-dissolved in CH₂Cl₂. After NH₄Cl_(aq) washes, the organic layer was dried over Na₂SO₄. The solvent was removed by rotary evaporation. The residues were purified by column chromatography (silica gel, 230-400 mesh, eluent: CH₂Cl₂/*n*-hexanes = 2/3), followed by crystallization from CH₂Cl₂/MeOH to give Compound 8 (blue solids, 34mg, yield: 47%). ¹H NMR (CDCl₃ at 7.26 ppm, 300 MHz), δ_H(ppm): 9.10 (d, *J* = 3.9 Hz, 1H), 8.99 (d, *J* = 3.4 Hz, 1H), 8.14 (d, *J* = 8.1 Hz, 2H), 7.92-7.57 (overlapped, 18H), 7.40-7.33 (overlapped, 3H), 4.61 (s, 2H), 4.56 (s, 2H), 3.98 (s, 3H), 2.06 (s, 4H), 1.58 (s, 6H), 1.55 (s, 6H), 1.49-0.42 (overlapped, 30H), -0.85 (s, 2H). ¹³C NMR (CDCl₃ at 77.16 ppm, 75 MHz), δ_C (ppm): 167.87, 166.95, , 161.28, 161.11, 151.31, 141.61, 140.76, 140.64, 139.19, 137.08, 136.86, 133.98, 131.32, 130.66, 129.99, 129.30, 128.02, 127.73, 127.14, 126.65, 125.70, 123.79, 123.70, 123.19, 122.67, 121.87, 120.23, 120.07, 117.41, 116.92, 97.67, 97.24, 96.67, 95.68, 95.51, 93.23, 77.66, 77.24, 76.82, 56.02, 55.93.

Compound 9



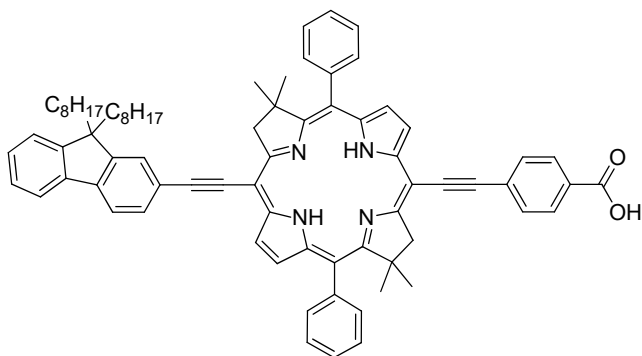
114 mg of compound 6 (M.W. = 1242.84 g/mol, 0.09 mmol, 1.0 eq.) was dissolved in 100 mL of THF and 0.10 mL TBAF solution (1M in THF) was added under dark with ice bath. The reaction was stirred at 0 °C for 1 hour. Completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residues were re-dissolved in CH₂Cl₂. After NH₄Cl_(aq) washes, the organic layer was dried over Na₂SO₄. The solvent was removed by rotary evaporation. The residue was directly go to next step without further purification. The residue was mixed with 48 mg methyl 4-iodobenzoate (M.W. = 262.04 g/mol, 0.18 mmol, 2.0 eq.) in 90 mL of dried THF and 10 mL of Et₃N. After 3 cycles of freeze–pump–thaw, 30 mol. % of Pd(dba)₃ and 2.4eq AsPh₃ were added to the solution under an inert atmosphere. The reaction was stirred at 50 °C for 48 hours. Completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residues were re-dissolved in CH₂Cl₂. After NH₄Cl_(aq) washes, the organic layer was dried over Na₂SO₄. The solvent was removed by rotary evaporation. The residues were purified by column chromatography (silica gel, 230-400 mesh, eluent: CH₂Cl₂/*n*-hexanes = 3/2) to give Compound 9 (dark greenish blue solids, 105mg, yield: 93%). ¹H NMR (CDCl₃ at 7.26 ppm, 300 MHz), δ_H(ppm): 9.25 (d, *J* = 2.95 Hz, 1H), 8.98-9.03 (m, 3H), 8.72 (d, *J* = 8.54 Hz, 2H), 8.09 (d, *J* = 8.35 Hz, 2H), 7.81-7.90 (m, 8H), 7.61-7.70 (m, 12H), 6.66 (d, *J* = 8.88 Hz, 2H), 4.78 (s, 2H), 4.46 (s, 2H), 3.97 (s, 3H), 3.32 (t, *J* = 7.32 Hz, 4H), 1.55-1.63 (m, 16H), 1.26-1.35 (m, 20H), 0.91 (t, *J* = 6.83 Hz, 6H), -0.78 (s, 1H), -0.81 (s, 1H). ¹³C NMR (CDCl₃ at 77.16 ppm, 75 MHz), δ_C(ppm): 167.8, 167.5, 166.9, 161.3, 148.5, 140.7, 139.1, 138.9, 137.1, 137.0, 134.0, 133.3, 132.6, 132.1, 131.3, 129.9, 128.0, 127.0, 126.7, 126.5, 124.0, 123.8, 122.6, 122.0, 118.3, 117.5, 117.2, 111.6, 109.1, 105.9, 105.2, 97.6, 96.7, 95.9, 95.6, 94.4, 85.1, 56.9, 55.9, 52.5, 51.3, 46.9, 32.1, 30.7, 29.7, 29.6, 27.4, 22.9, 14.4.

Compound 10



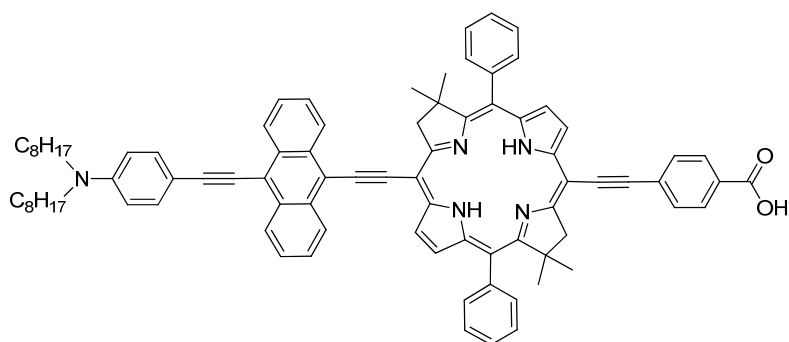
103 mg of compound 7 (M.W. = 1294.91 g/mol, 0.08 mmol, 1.0 eq.) was dissolved in 70 mL of THF and 0.1 mL TBAF solution was added under dark with ice bath. The reaction was stirred at 0 °C for 1 hour. Completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residues were re-dissolved in CH₂Cl₂. After NH₄Cl_(aq) washes, the organic layer was dried over Na₂SO₄. The solvent was removed by rotary evaporation. The residue was directly go to next step without further purification. The residue was mixed with 39mg methyl 4-iodobenzoate (M.W. = 262.04 g/mol, 0.15 mmol, 1.9 eq.) in 60 mL of dried THF and 6 mL of Et₃N. After 3 cycles of freeze–pump–thaw, 30 mol. % of Pd(PPh₃)₄ and 2.4eq AsPh₃ were added to the solution under an inert atmosphere. The reaction was stirred at 50 °C for 18 hours. Completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residues were re-dissolved in CH₂Cl₂. After NH₄Cl_(aq) washes, the organic layer was dried over Na₂SO₄. The solvent was removed by rotary evaporation. The residues were purified by column chromatography (silica gel, 230-400 mesh, eluent: CH₂Cl₂/*n*-hexanes = 3/2) to give Compound 10 (dark greenish blue solids, 73mg, yield: 73%). ¹H NMR (CDCl₃ at 7.26 ppm, 300 MHz), δ_H(ppm): 9.29 (d, *J* = 4.42 Hz, 1H), 9.16 (d, *J* = 8.63 Hz, 2H), 9.02 (d, *J* = 4.50 Hz, 1H), 8.26 (d, *J* = 8.72 Hz, 2H), 8.17 (d, *J* = 8.30 Hz, 2H), 7.86-7.94 (m, 6H), 7.62-7.70 (m, 10H), 7.50 (d, *J* = 8.00 Hz, 2H), 7.03 (overlapped, *J* = 8.58, 16.35 Hz, 8H), 4.84 (s, 2H), 4.60 (s, 2H), 4.00 (s, 3H), 2.52 (t, *J* = 8.05 Hz, 4H), 1.62 (s, 6H), 1.55 (s, 6H), 1.29 (d, *J* = 6.62 Hz, 24H), 0.88 (t, *J* = 6.92 Hz, 6H), -0.71 (s, 1H), -0.74 (s, 1H). ¹³C NMR (CDCl₃ at 77.16 ppm, 75 MHz), δ_C (ppm): 167.9, 167.7, 167.0, 161.4, 161.3, 146.0, 140.7, 139.1, 138.9, 137.1, 136.0, 134.3, 134.0, 131.4, 131.0, 130.0, 129.3, 128.1, 127.1, 127.0, 126.7, 125.6, 124.0, 122.5, 122.2, 120.4, 118.9, 117.5, 105.1, 97.4, 96.6, 96.0, 95.7, 93.7, 56.9, 56.0, 52.5, 47.1, 35.5, 32.1, 31.8, 30.7, 29.7, 29.7, 29.5, 22.9, 14.4.

LS-17



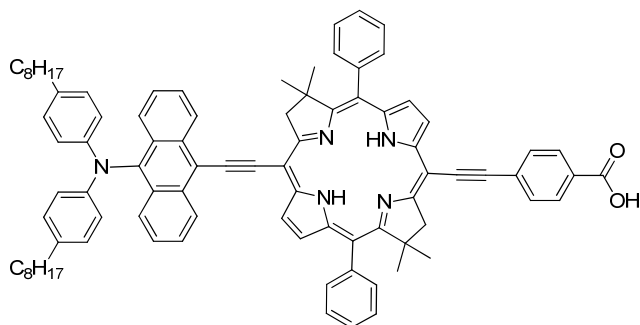
34 mg of compound 8 (M.W. = 1093.48 g/mol, 0.03 mmol, 1.0 eq.) was dissolved in 10 mL of THF and 5 mL MeOH. And then the 3 mL 2.5N NaOH_(aq) was added to the solution. The reaction was stirred at R.T. for 1.5 hour. Completion of the reaction was monitored by TLC. Upon completion, conc. HCl_(aq) was add to neutralize the solution. The solvent was removed by rotary evaporation. The precipitation was collected by filtration, then purified by column chromatography (silica gel, 230-400 mesh, eluent: CH₂Cl₂/MeOH = 9/1), followed by crystallization from THF/MeOH to give Compound LS-17 (blue purple solids, 26 mg, yield: 78%). ¹H NMR (CDCl₃ at 7.26 ppm, 300 MHz), δ_H(ppm): 9.11 (d, *J* = 3.6 Hz, 1H), 9.04 (d, *J* = 4.4 Hz, 1H), 8.15 (d, *J* = 8.1 Hz, 2H), 8.03-7.75 (overlapped, 12H), 7.73-7.55 (overlapped, 6H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.39-7.25 (m, 2H), 4.63 (s, 2H), 4.61 (s, 2H), 2.13 (s, 4H), 1.60 (s, 6H), 1.55 (s, 6H), 1.39-0.99 (overlapped, 22H), 0.98-0.50 (overlapped, 8H), -0.85 (s, 2H). ¹³C NMR (CDCl₃ at 77.16 ppm, 75 MHz), δ_C (ppm): 168.55, 168.20, 161.93, 161.87, 152.08, 151.98, 142.72, 141.83, 141.70, 139.97, 139.68, 137.82, 137.72, 134.85, 131.97, 131.62, 130.90, 129.61, 128.87, 128.56, 128.00, 127.48, 126.42, 124.31, 123.88, 123.25, 122.72, 121.11, 120.91, 118.33, 117.93, 98.62, 98.06, 96.67, 93.85, 68.17, 67.87, 67.58, 67.29, 66.99, 56.80, 56.30, 47.70, 41.39, 32.93, 31.16, 30.84, 30.38, 26.03, 25.76, 25.50, 25.23, 24.96, 23.63, 14.57. MALDI-TOF: *m/z* calc'd for C₇₆H₇₈N₄O₂ 1078.61; found 1078.70 [M]⁺. Elemental Analysis: calc'd for C₇₆H₇₈N₄O₂·1H₂O: C, 83.17 %; H, 7.35 %; N, 5.11 % found C, 83.21 %; H, 7.34 %; N, 5.27 %.

LS-43



80 mg of compound 9 (M.W. = 1220.63 g/mol, 0.06 mmol, 1.0 eq.) was dissolved in 83 mL of THF and 17 mL MeOH. And then the 10 mL 2.5N NaOH_(aq) was added to the solution. The reaction was stirred at 50°C for 3 hours. Completion of the reaction was monitored by TLC. Upon completion, 1N HCl_(aq) was add to neutralize the solution. The solvent was removed by rotary evaporation. The precipitation was collected by filtration, then the residue was re-dissolved in THF dried over Na₂SO₄, and concentrated. The residue was purified by column chromatography (silica gel, 230-400 mesh, eluent: CH₂Cl₂/MeOH = 9/1), followed by crystallization from THF/MeOH to give Compound LS-43 (dark green solids, 60 mg, yield: 76%). ¹H NMR (d₈-THF at 3.58, 1.73ppm, 600 MHz), δ_H(ppm): 9.06-9.39 (overlapped, 4H), 8.79 (s, 2H), 7.62-8.15 (m, 22H), 6.77 (d, *J* = 6.38 Hz, 2H), 4.87 (s, 1H), 4.60 (m, 2H), 4.46 (s, 1H), 3.40 (s, 4H), 1.56 (overlapped, 12H), 1.29-1.34 (overlapped, 33H), 0.92 (m, 12H), -0.71 (s, 2H). Note that the total number of hydrogens in LS-43 should be 83. However, the total number of hydrogens of LS-43 is still greater than 83 in Figure S3. We suspect that this discrepancy originates from the overly integrated values around 0.92 and 1.29 ppm. According to literature report (*Organometallics* **2010**, 29, 2176–2179), n-hexane gives rise to NMR signals at 0.89 and 1.29 ppm in d₈-THF. Possibly due to the low solubility of LS-43 in organic solvents, interference from hexane residual signals may be more severe. ¹³C NMR spectrum of LS-43 is not available due to lower solubility of the compound in organic solvent. MALDI-TOF: *m/z* calc'd for C₈₅H₈₃N₅O₂ 1205.65; found 1205.56 [M]⁺. Elemental Analysis: calc'd for C₈₅H₈₃N₅O₂·2H₂O: C, 82.16 %; H, 7.06 %; N, 5.64 % found C, 82.39 %; H, 7.00 %; N, 5.77 %.

LS-45



220 mg of compound 10 (M.W. = 1272.70 g/mol, 0.17 mmol, 1.0 eq.) was dissolved in 83 mL of THF and 17 mL MeOH. And then the 10 mL 2.5N NaOH_(aq) was added to the solution. The reaction was stirred at 50°C for 1 hour. Completion of the reaction was monitored by TLC. Upon completion, 1N HCl_(aq) was added to neutralize the solution. The solvent was removed by rotary evaporation. The precipitation was collected by filtration, then the residue was re-dissolved in THF dried over Na₂SO₄, and concentrated. The residue was purified by column chromatography (silica gel, 230-400 mesh, eluent: CH₂Cl₂/MeOH = 9/1), followed by crystallization from THF/MeOH to give Compound LS-45 (dark green solids, 202 mg, yield: 93%). ¹H NMR (d₈-THF at 3.58, 1.73 ppm, 600 MHz), δ_H(ppm): 9.32 (d, *J* = 3.85 Hz, 1H), 9.19 (d, *J* = 8.75 Hz, 2H), 9.09 (d, *J* = 2.60 Hz, 1H), 8.28 (d, *J* = 8.61 Hz, 2H), 8.17 (d, *J* = 7.04 Hz, 2H), 7.91-7.96 (m, 8H), 7.68 (d, *J* = 3.06 Hz, 8H), 7.50 (t, *J* = 6.83 Hz, 2H), 7.03 (m, 8H), 4.89 (s, 2H), 4.66 (s, 2H), 2.51 (t, *J* = 7.43 Hz, 4H), 1.59 (overlapped, 16H), 1.32 (overlapped, 20H), 0.89 (t, *J* = 6.56 Hz, 6H), -0.69 (s, 1H), -0.74 (s, 1H). ¹³C NMR (d₈-THF at 67.21, 25.13 ppm, 150 MHz), δ_C (ppm): 168.4, 162.0, 161.8, 146.8, 141.4, 141.4, 139.7, 137.7, 137.6, 136.5, 135.0, 134.6, 134.6, 131.8, 131.7, 130.8, 129.9, 128.7, 128.4, 127.7, 127.4, 126.1, 124.4, 122.8, 122.7, 121.0, 119.2, 118.2, 118.2, 105.6, 97.7, 96.8, 96.6, 96.2, 94.1, 57.4, 56.6, 47.7, 47.5, 36.1, 32.8, 32.7, 30.7, 30.6, 30.5, 30.3, 30.2, 23.5, 14.4. MALDI-TOF: *m/z* calc'd for C₈₉H₈₇N₅O₂ 1257.69; found 1257.85 [M]⁺. Elemental Analysis: calc'd for C₈₉H₈₇N₅O₂·1.5H₂O: C, 83.14%; H, 7.06%; N, 5.45%; O, 4.36%, found C, 83.30%; H, 7.14%; N, 5.37%.

Materials and methods

Device fabrication. Each DSC device was fabricated with a titania working electrode and a Pt-coated counter electrode in a sandwich fashion. The TiO₂ bi-layer film of the working electrode consists a 8- μ m translucent layer of small particles (15-20 nm, Ti-2105A, Eternal Materials Co.,Ltd.) and a 5- μ m light-scattering layer of large TiO₂ particles (\sim 300 nm, Ti-2325, Eternal Materials Co.,Ltd.). The active size of the TiO₂ film was 0.5 \times 0.5 cm². The post sintering procedures of the working and the counter electrodes are as those in our previous work.^{S1} The dye-uptake procedures involve soaking the anodes in a THF solution containing 0.20 mM (1eq.) LS-11 with 4.0 eq. chenodeoxycholic acid (CDCA), or 0.20 mM LS-17 with 0.5 eq. CDCA, or 0.20 mM LS-43 with 0.5 eq. CDCA, or LS-45 with 0.20 mM with 0.5 eq. CDCA in at 25 °C for 2 hours. The counter electrode was made with repetitive screen-printing of Pt paste (Pt-201, Everlight Chemical Industrial Corp., Taiwan) onto a FTO glass substrate through a typical procedure of thermal decomposition. The two electrodes were assembled (hot-pressed, 125°C) into a sandwich cell and sealed with a spacer of thickness 35 μ m Surlyn film. Different composition of the electrolytes were used in order to achieve a better overall efficiency for each dye. For LS-11, I₂ (0.05 M), LiI (0.40 M), PMII (0.60 M), 4-*t*-butylpyridine (0.30 M) in a mixed solvent containing 85% of acetonitrile and 15% of valeronitrile. For LS-17, LS-43 and LS-45, I₂ (0.05 M), LiI (0.40 M), BMII (1.00 M), 4-*t*-butylpyridine (1.00 M), GuSCN (1.00 M). The injection holes were sealed with another layer of Surlyn film (100 μ m) and a microslide glass.

Instrument. NMR spectra (Bruker Avance II 300 MHz NMR Spectrometer at National Chi Nan University or Varian Inova 600 NMR Spectrometer at the MOST Instrumentation Center in National Chung Hsing University), UV-visible (Agilent 8454), fluorescence (Varian Cary Eclipse), elemental analyses (Elementar Vario EL III at the MOST Instrumentation Center in National Taiwan University), mass spectra (Microflex MALDI-TOF MS, Bruker Daltonics) were recorded with the indicated instruments. Electrochemical properties were performed with a CH Instruments, Inc. Workstation 611A in a three-electrode electrochemical cell with a platinum working electrode, a platinum wire counter electrode, and an SCE reference electrode. Oxidation potentials of monomers (0.5 mM) were measured in anhydrous THF containing TBAP (0.1 M) as a supporting electrolyte. EIS/IMVS/IMPS measurement were carried out by a photo-electrochemical workstation (Zahner IM6/PP201, Germany) with CIMPS system, the setting parameters of EIS contains using frequency range was from 100 kHz to 0.1 Hz and an ac amplitude was 5 mV. The current-voltage (J-V) characteristics of the DSSC devices covered with a black mask (aperture area = 0.4 \times 0.4 cm²) were collected with a solar simulator (AM 1.5G, SS50 AAA-EM, PET) and a source meter (Keithley 2400). The measurement of the incident photon-to-current conversion efficiency (IPCE, scanning range = 300-900 nm, interval = 10 nm, delay

time = 2 s, pick times = 5) was performed by the 7-SCSpec system (Sofn Instruments Co., Ltd., Beijing, China) with a source meter (Keithley 2000).

Materials. A glovebox (MBraun Uni-Lab), a vacuum line and standard Schlenk glassware were employed to process all materials sensitive to air. Solvents for the synthesis (ACS grade) were CH₂Cl₂ (Mallinckrodt Baker), hexanes (Haltermann, Hamburg, Germany), THF (Merck, Darmstadt, Germany) and Acetonitrile (Merck, Darmstadt Germany). These solvents were used as received unless otherwise stated. Other chemicals were obtained commercially (Acros Organics, NJ, USA). THF for cross-coupling reactions was purified and dried with a solvent purification system (Asiawong SD-500, Taipei, Taiwan). The Pd(PPh₃)₄ catalyst (Strem, MA, USA) and Pd₂(dba)₃ (Acros Organics, NJ, USA) were used as received. For electrochemical measurements, THF was distilled over sodium under N₂. For chromatographic purification, we used silica gel P60 (40-63µm, 230–400 mesh, Silicycle, Canada).

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NMR Spectra:

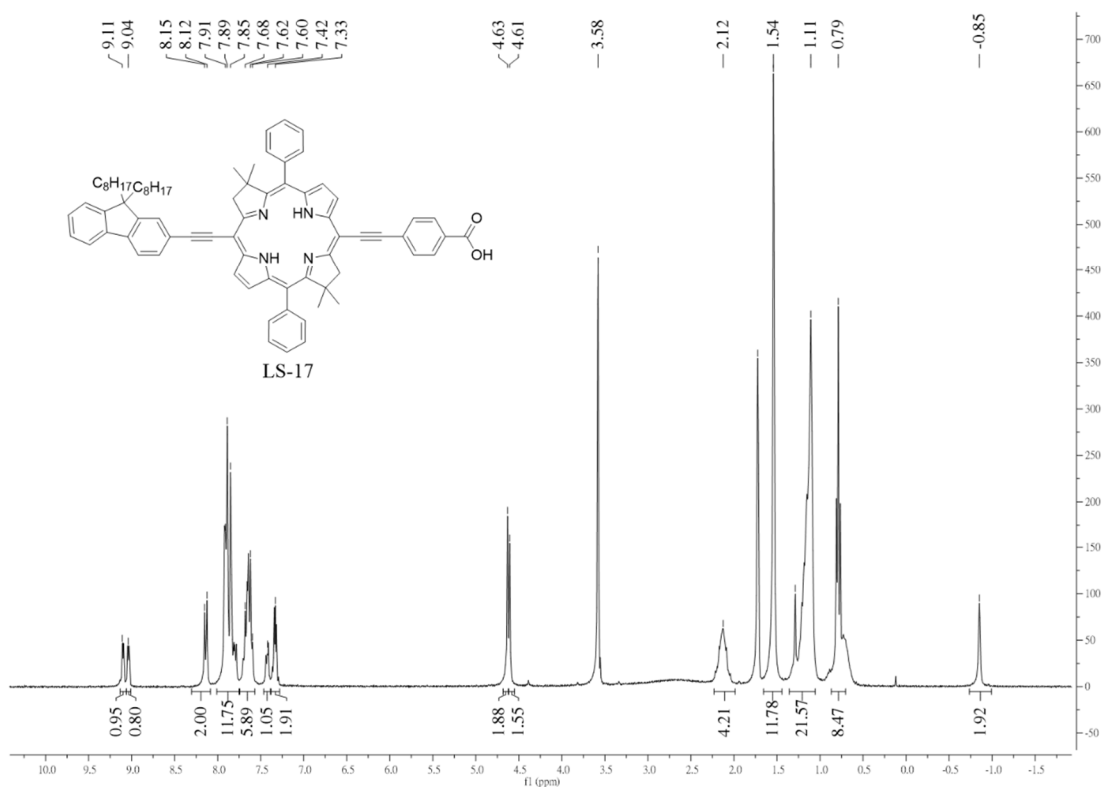


Figure S1. ¹H-NMR of LS-17

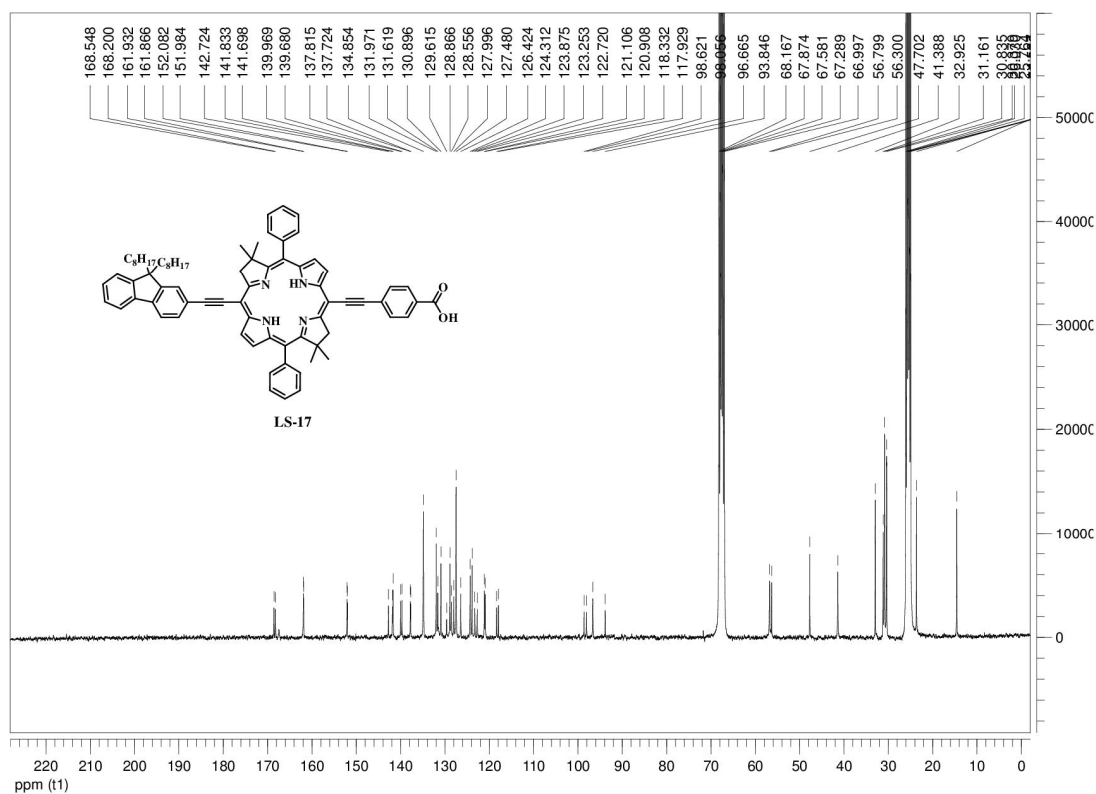


Figure S2. ¹³C-NMR of LS-17

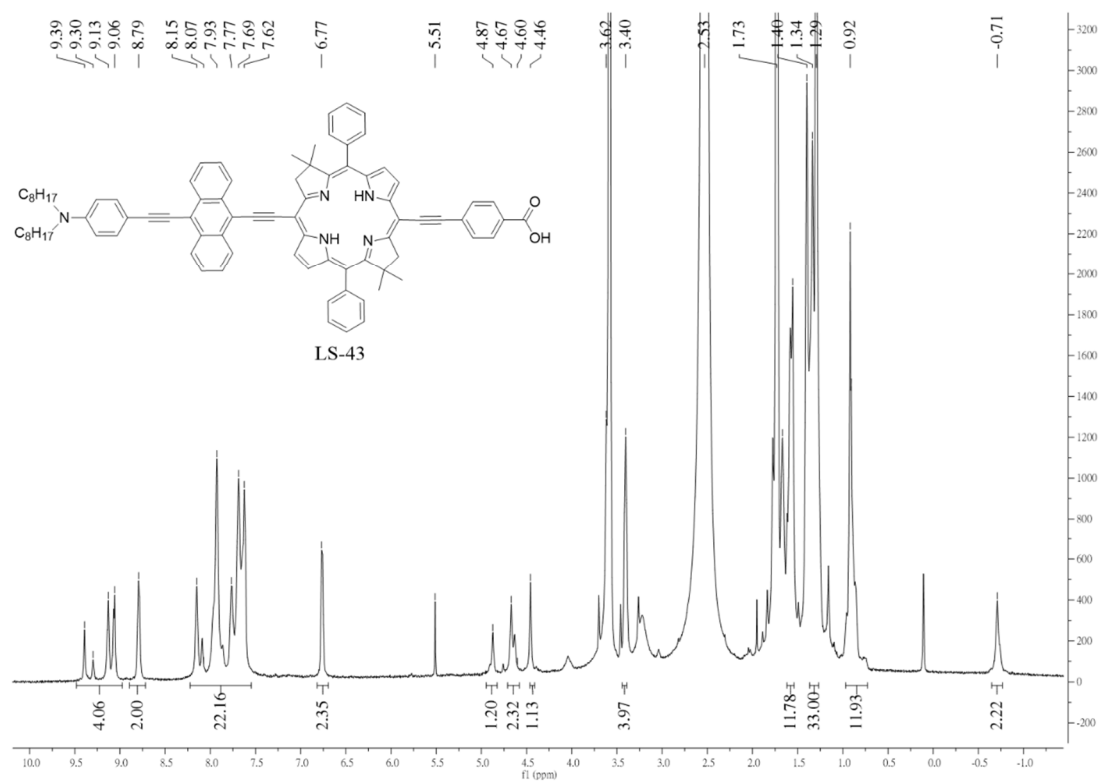


Figure S3. $^1\text{H-NMR}$ of LS-43

($^{13}\text{C-NMR}$ of LS-43 is not available due to the lower solubility in organic solvents)

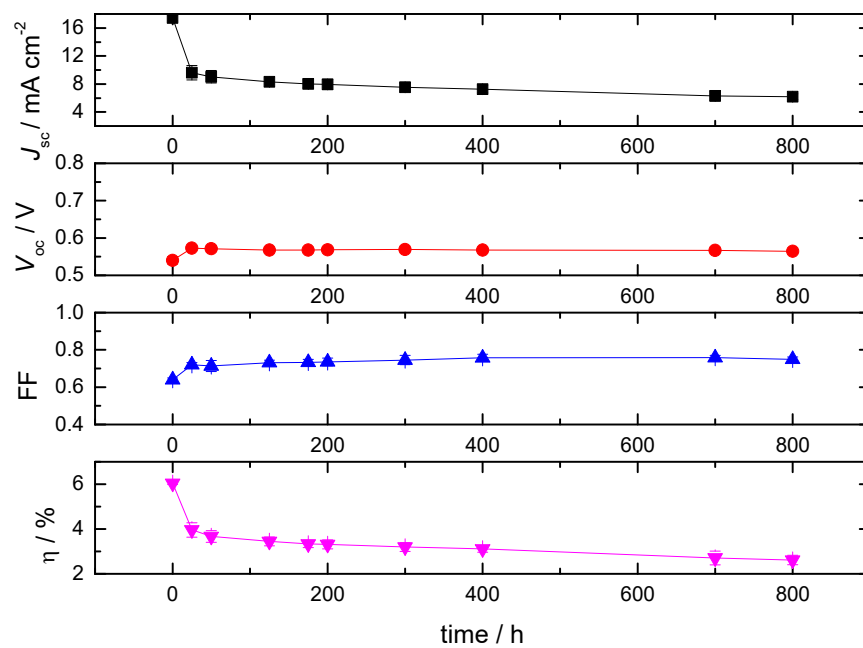


Figure S6. Stability test of the LS-45 DSC under ambient condition.

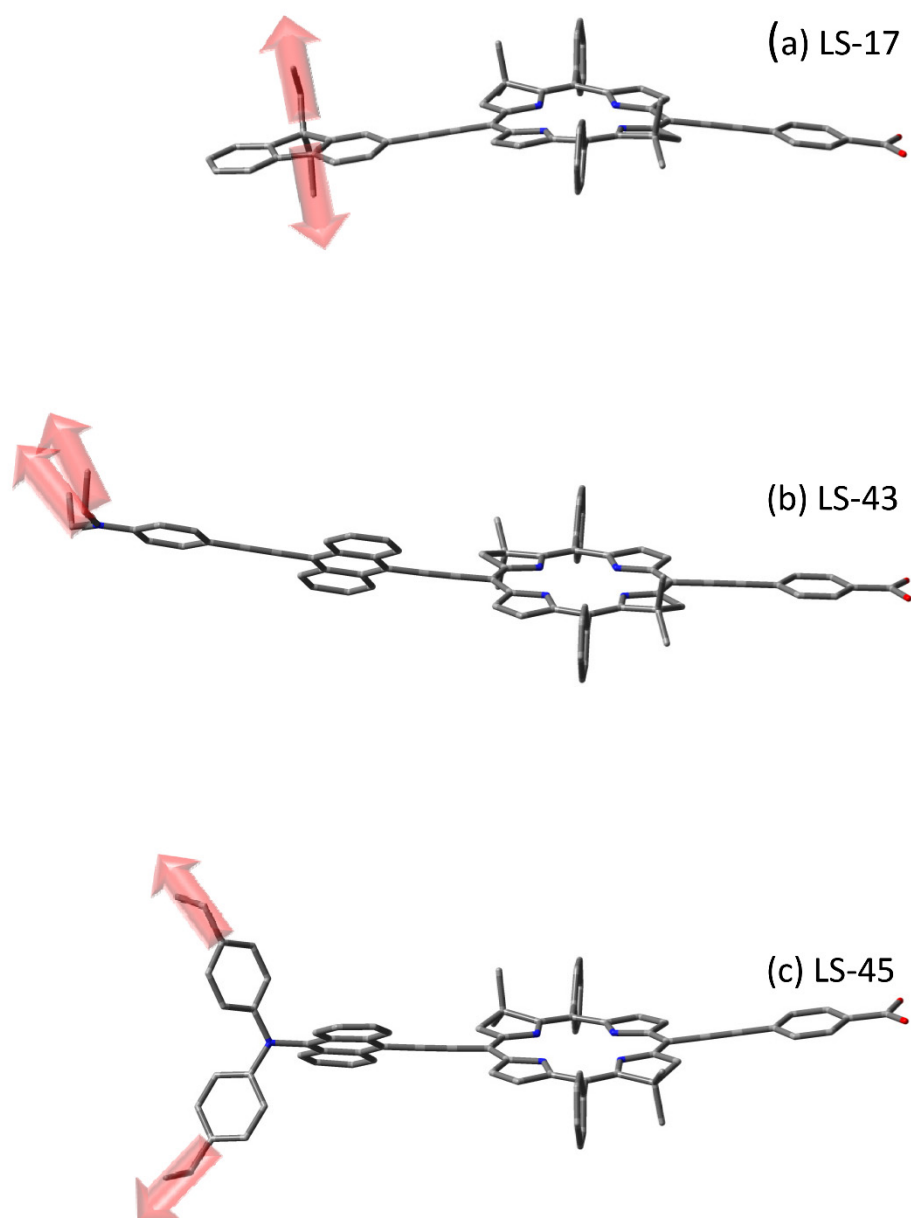


Figure S7. Optimized Geometry of the (a) LS-17, (b) LS-43, and (c) LS-45, calculated by DFT at B3LYP/6-31(d,p). For clarity, the hydrogen atoms are omitted in the figure. To simplify the calculations, the octyl chains were represented by ethyl groups. The red arrows are to emphasize orientations of the alkyl groups.