Electronic Supporting Information for

Porphyrins bearing a consolidated anthryl donor with dual functions for Efficient Dye-sensitized Solar Cells

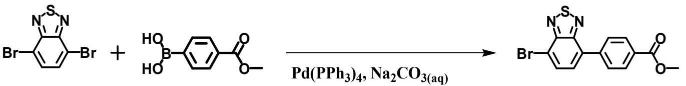
Chin-Li Wang,[a] Min Zhang,[b] Yu-Hsin Hsiao,[a] Chuan-Kai Tseng,[a] Chia-Lin Liu,[a] Mingfei Xu,[b] Peng Wang,*[,b] and Ching-Yao Lin*[,a]

[a] Department of Applied Chemistry, National Chi Nan University, Puli, Nantou Hsien 54561, Taiwan. Tel: +886-49-2910960 ext. 4152; fax: +886-49-2917956; E-mail: cyl@ncnu.edu.tw.

[b] State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, China. E-mail: peng.wang@ciac.ac.cn

Dye Synthesis and Characterization.

The syntheses of the LWP porphyrins are based on the Sonogashira cross-coupling methods.[S1-S2] The preparation procedures (shown below) are similar to our past publication.[S3-S4]



1 (55.3 %)

Chart S1. Synthetic route of compound1.

Compound 1: 4,7-dibromo-2,1,3-benzothiadiazole (300 mg, MW = 293.97 g/mol, 1.02 mmol), 4-methoxycarbonylphenylboronic acid (183 mg, MW = 179.97 g/mol, 1.02 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (118 mg, MW = 1156 g/mol, 10 mol %), aqueous Na_2CO_3 (1.0 M, 8 mL), THF (100 mL) and toluene (30 mL) were mixed in a flask. The mixture was degassed and refluxed for 14 h under N_2 purge. After being cooled, the solvent was evaporated under vacuum and the residue was dissolved in 100 mL EtOAc and washed with $NH_4Cl_{(aq)}$ .The organic phase was dried over Na_2SO_4 and filtered. After removing the solvent, the residue was then purified on a column chromatograph (silica gel) using THF/*n*-hexanes =1/5 as eluent to give 197 mg of **compound 1** (yellow solid, MW = 349.20 g/mol, yield = 55.3 %).

^{1}H-NMR ($CDCl_3$ at 7.26 ppm, 300 MHz): δ_H 8.19 (d, J = 8.5 Hz, 2H), 7.98 (d, J = 8.7 Hz, 2H), 7.95 (d, J = 7.7 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H), 3.97 (s, 3H). ^{13}C-NMR ($CDCl_3$ at 77.16 ppm, 300 MHz): δ_C 166.87, 154.00, 152.97, 141.05, 132.91, 132.31, 130.05, 129.28, 128.89, 125.65, 114.36, 52.43. Mass Spec.: *m/z* calc'd for $C_{14}H_9BrN_2O_2S$: 347.96; found: 347.64 (M^+).

Synthesis of LWP12:

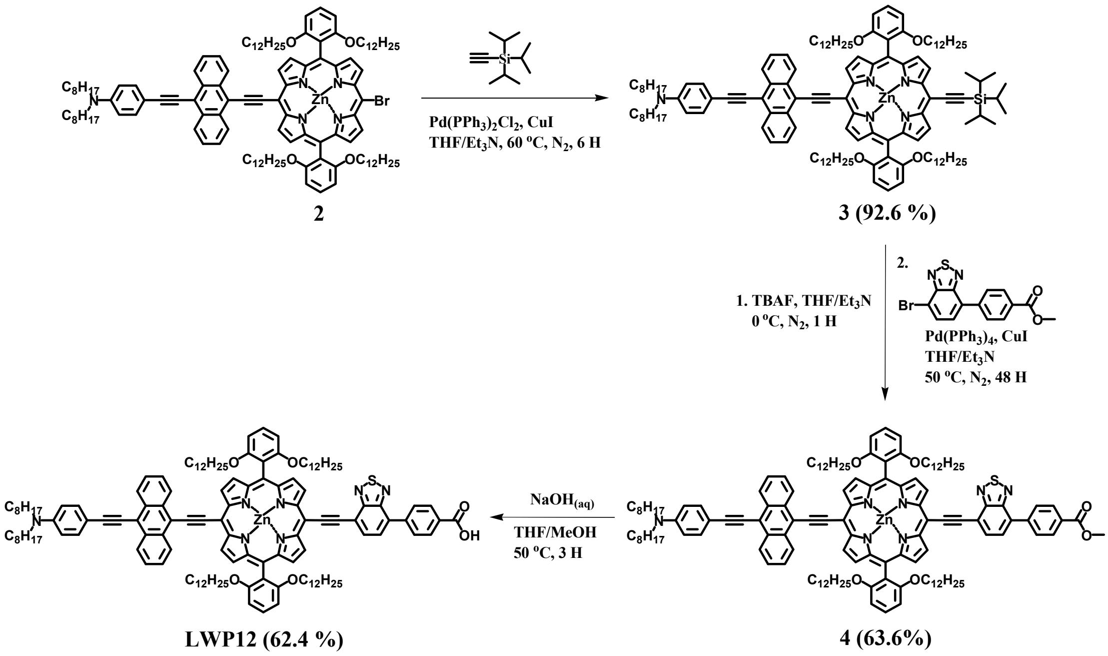


Chart 2. Synthetic route of LWP12.

Compound 3:100 mg of the **compound 2**^{S5} (MW = 1881.88 g/mol, 0.053 mmol) was mixed with 0.13 mL of (triisopropylsilyl)acetylene (MW = 182.38 g/mol, d = 0.813 g/mL, 0.58 mmol, 11 equiv) in 30 mL of THF and 5 mL of triethylamine. After 3 cycles of freeze−pump−thaw, 20 mol % of $Pd(PPh_3)_2Cl_2$ and CuI were added to the solution under an inert atmosphere in a glovebox. The reaction was stirred at 60 °C for 6 h. The completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residue was re-dissolved in CH_2Cl_2 for $NH_4Cl_{(aq)}$ washes. After dried over Na_2SO_4, the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using

THF/*n*-hexanes = 1/10 as eluent, followed by crystallization from CH_2Cl_2/MeOH to give 104 mg of **compound 3** (dark brown solid, MW = 1983.35 g/mol, yield = 99.0 %).

^{1}H-NMR (d_8-THF at 1.73 and 3.58 ppm, 300 MHz): δ_H 9.92 (d, *J* = 4.6 Hz, 2H), 9.58 (d, *J* = 4.6 Hz, 2H), 9.45 (d, *J* = 8.6 Hz, 2H), 8.88-8.86 (two overlapped doublets, 4H), 8.75 (d, *J* = 4.5 Hz, 2H), 7.88 (t, *J* = 7.4 Hz, 2H), 7.78-7.64 (m, overlapped, 6H), 7.09 (d, *J* = 8.5 Hz, 4H), 6.78 (d, *J* = 8.8 Hz, 2H), 3.90 (t, *J* = 5.7 Hz, 8H), 3.42 (t, *J* = 7.4 Hz, 4H), 1.65-1.25 (m, overlapped, 48H), 1.25-0.40 (m, overlapped, 114H). ^{13}C-NMR (d_8-THF at 25.3 and 67.4 ppm, 300 MHz): δ_C 161.03, 152.80, 152.30, 151.67, 151.45, 149.43, 133.86, 132.97, 132.69, 132.43, 130.97, 130.72, 130.62, 121.69, 120.39, 119.50, 116.47, 112.35, 109.93, 108.25, 106.18, 105.43, 100.61, 100.32, 97.36, 96.03, 93.85, 85.54, 69.10, 51.65, 32.86, 32.78, 30.54, 30.44, 30.36, 30.30, 30.18, 29.82, 29.75, 28.24, 28.03, 26.33, 23.59, 23.50, 19.63, 19.09, 18.88, 14.44, 12.98, 12.20, 11.97. Mass Spec.: *m/z* calc'd for $C_{131}H_{181}N_5O_4SiZn$: 1980.32; found: 1981.22 (MH^+).

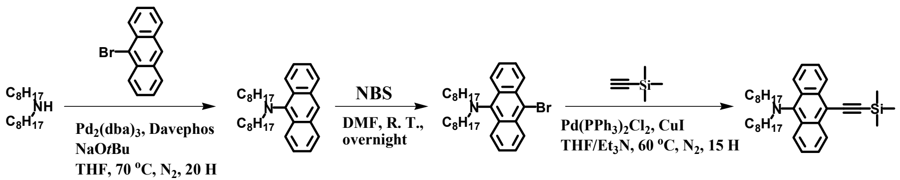
Compound 4: 104 mg of **compound 3** (MW = 1983.35 g/mol, 0.052 mmol) was mixed with 0.05 mL of tetrabutylammonium fluoride (1.0 M in THF, MW = 261.46 g/mol, 0.05 mmol, 1.0 equiv) in 20 mL of dry and de-gassed THF. The reaction was stirred in the dark at 0 °C for 1 h. Upon completion, the solvent was removed by rotary evaporation. The residue was re-dissolved in CH_2Cl_2 for $NH_4Cl_{(aq)}$ washes. After dried over Na_2SO_4, the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using THF/*n*-hexanes = 1/10 as eluent to give 86.9 mg of dark brown solid. The dark brown solid was immediately mixed with 14.9 mg of **compound 1** (MW = 349.20g/mol, 0.9 equiv) in 30 mL of THF and 5 mL of triethylamine. After 3 cycles of freeze−pump−thaw, 15 mol % of $Pd(PPh_3)_4$ and CuI were added to the solution under an inert atmosphere in a glovebox. The reaction was stirred at 50 °C for 48 h. The completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residue was re-dissolved in CH_2Cl_2 for $NH_4Cl_{(aq)}$ washes. After dried over Na_2SO_4, the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using THF/*n*-hexanes = 1/4 as eluent, followed by crystallization from CH_2Cl_2/MeOH to give 53.8 mg of **compound 4** (dark brown solid, MW = 2095.30 g/mol, yield = 49.4 %).

^{1}H-NMR (d_8-THF at 1.73 and 3.58 ppm, 300 MHz): δ_H 10.05 (d, *J* = 4.6 Hz, 2H), 9.93 (d, *J* = 4.5 Hz, 2H), 9.46 (d, *J* = 8.7 Hz, 2H), 8.92-8.83 (m, overlapped, 6H), 8.39 (d, *J* = 7.4 Hz, 1H), 8.33 (d, *J* = 8.5 Hz, 2H), 8.22 (d, *J* = 8.5 Hz, 2H), 8.14 (d, *J* = 7.4 Hz, 1H), 7.99 (d, *J* = 7.0 Hz, 2H), 7.79-7.72 (m, overlapped, 4H), 7.66 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 4H), 6.79 (d, *J* = 9.0 Hz, 2H), 3.97-3.92 (m, overlapped, 11H), 3.42 (t, *J* = 7.5 Hz, 4H), 1.51-1.20 (m, overlapped, 22H), 1.20-0.50 (m, overlapped, 100H). ^{13}C-NMR (d_8-THF at 25.3 and 67.4 ppm, 300 MHz): δ_C 166.81, 161.03, 157.26, 154.26, 152.87, 152.26, 151.74, 154.67, 149.45, 142.46, 133.87, 132.96, 132.71, 131.86, 131.40, 130.83, 130.70, 130.37, 130.08, 129.67, 128.62, 127.76, 127.37, 121.66, 120.50, 119.54, 119.42, 116.95, 112.35, 109.92, 108.21, 106.26, 105.49, 103.62, 101.30, 99.64, 94.07, 93.21, 85.56, 69.11, 68.22, 52.24, 51.65, 32.87, 32.96, 30.54, 30.43, 30.37, 30.28, 30.18, 29.90, 29.82, 28.25, 28.03, 26.42, 23.59, 23.48. Mass Spec.: *m/z* calc'd for $C_{136}H_{169}N_7O_6SZn$: 2092.22; found: 2093.26 (M^+).

LWP12:57.4 mg of the **compound 4** (MW = 2095.30 g/mol, 0.027 mmol) was dissolved in 50 mL of THF and 10 mL of MeOH. After adding 30 mL of 8.33 M $NaOH_{(aq)}$, the solution was stirred at 50 °C for 3 h. The completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residue was re-dissolved in CH_2Cl_2 for $NH_4Cl_{(aq)}$ washes. After dried over Na_2SO_4, the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using MeOH/ CH_2Cl_2 = 1/9 as eluent, followed by crystallization from CH_2Cl_2/MeOH to give 35.1 mg of **LWP12** (dark brown solid, MW = 2081.27 g/mol, yield = 62.5 %).

^{1}H-NMR ($CDCl_3$ at 7.26 ppm, 300 MHz, with trace amt. of d_5-pyridine): δ_H 9.93 (d, *J* = 4.4 Hz, 2H), 9.88 (d, *J* = 4.6 Hz, 2H), 9.34 (d, *J* = 8.5 Hz, 2H), 8.90 (d, *J* = 4.5 Hz, 4H), 8.82 (d, *J* = 8.5 Hz, 2H), 8.33 (d, *J*= 8.2 Hz, 2H), 8.25 (d, *J* = 7.3 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 7.2 Hz, 2H), 7.85-760 (m, overlapped, 8H), 7.03 (d, *J* = 8.4 Hz, 4H), 6.70 (d, *J* = 8.7 Hz, 2 H), 3.89 (t, *J* = 6.4 Hz, 8H), 3.35 (t, *J* = 7.5 Hz, 4H), 1.65 (s, 8H), 1.50-1.20 (m, overlapped, 28H), 1.20-0.65 (m, overlapped, 82H), 0.65-0.30 (m, overlapped, 26H). ^{13}C-NMR (d_8-THF at 25.3 and 67.4 ppm, 300 MHz): δ_C 161.03, 157.28, 154.33, 152.87, 152.26, 151.74, 151.66, 149.44, 142.11, 133.87, 133.12, 132.97, 132.72, 131.91, 131.42, 130.80, 130.67, 129.97, 129.59, 128.62, 127.75, 127.36, 121.67, 120.48, 119.43, 116.93, 112.35, 109.92, 108.22, 106.25, 105.48, 103.47, 101.25, 99.70, 94.04, 93.21, 85.56, 69.10, 51.65, 32.87, 32.76, 30.66, 30.54, 30.43, 30.37, 30.28, 30.18, 29.90, 29.82, 26.42, 23.59, 23.49, 14.48, 14.42. Elemental Anal.: calc'd for $C_{135}H_{167}N_7O_6SZn$: C 77.91 %, H 8.09 %, N 4.71 %; found: C 78.15 %, H 7.89 %, N 4.44 %. Mass Spec.: *m/z* calc'd for $C_{135}H_{167}N_7O_6SZn$: 2078.20; found: 2079.51 (MH$^+$).

Synthesis of electron-donating anthrylethynyl substituents.



5 (41.2 %) 6 (81.2 %) R$_1$ (96.6 %)

Chart S3. Synthetic route of R$_1$.

Compound 5: 1.0g of 9-bromoanthracene (MW = 257.13 g/mol, 3.889 mmol) was mixed with 10 mL of dioctylamine (MW = 241.456 g/mol, d = 0.799 g/mL, 33.1 mmol, 8.5 equiv) in 35 mL of THF. After 3 cycles of freeze−pump−thaw, 1.0 mol % of $Pd_2(dba)_3$, 6.0 mol % of Davephose and 2.8 equiv of NaO*t-Bu* were added to the solution under an inert atmosphere in a glovebox. The reaction was stirred at 70 ^{o}C for 20 h. The completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residue was re-dissolved in CH_2Cl_2 for $NH_4Cl_{(aq)}$ washes. After dried over Na_2SO_4, the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using *n*-hexanes as eluent to give 670 mg of **compound 5** (yellow oil, MW = 417.67 g/mol, yield = 41.2 %).

^{1}H-NMR ($CDCl_3$ at 7.26 ppm, 300 MHz): δ_H 8.44-8.40 (m, 2H), 8.29 (s, 1H), 8.02-7.99 (m, 2H), 7.49-7.41 (m, overlapped, 4H), 3.48 (t, *J* = 7.8 Hz, 4H), 1.56-1.47 (m, overlapped, 4H), 1.31-1.20 (m, overlapped, 20H), 0.85 (t, *J* = 6.8 Hz, 6H). ^{13}C-NMR (CDCl3 at 77.16 ppm, 300 MHz): δ_C 145.29, 132.75, 131.37, 128.98, 125.71, 125.07, 124.76, 124.41, 56.95, 31.94, 30.44, 29.65, 29.48, 27.53, 22.77, 14.24. Mass Spec.: *m/z* calc'd for $C_{30}H_{43}N$: 417.34; found: 417.99 (MH^+).

Compound 6: 314 mg of NBS (MW = 177.98 g/mol, 1.764 mmol, 1.1 equiv) was dissolved in 30 mL of DMF and added dropwise to 50 mL DMF containing 670 mg of the **compound 5** (MW = 417.67 g/mol, 1.60 mmol) at 0 ^{o}C. The reaction was stirred at room temperature for 12 h. The completion of the reaction was monitored by TLC. Upon completion, 10 mL of acetone was added to quench the reaction. The mixture was extracted with ether and $NH_4Cl_{(aq)}$. After dried over Na_2SO_4, the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using *n*-hexanes as eluent to give 645 mg of **compound 6** (yellow oil, MW = 496.57 g/mol, yield = 81.2 %).

^{1}H-NMR ($CDCl_3$ at 7.26 ppm, 300 MHz): δ_H 8.73 (d, *J* = 8.7 Hz, 2H), 8.43 (d, *J* = 8.6 Hz, 2H), 7.61-7.47 (m, overlapped, 4H), 3.47 (t, *J* = 7.8 Hz, 4H), 1.56-1.50 (m, overlapped, 4H), 1.33-1.20 (m, overlapped, 20H), 0.85 (t, *J* = 6.8 Hz, 6H). ^{13}C-NMR (CDCl3 at 77.16 ppm, 300 MHz): δ_C 145.88, 132.31, 131.43, 128.44, 126.96, 126.08, 125.11, 119.90, 57.03, 31.92, 30.33, 29.61, 29.45, 27.50, 22.76, 14.23. Mass Spec.: *m/z* calc'd for $C_{30}H_{42}BrN$: 495.25; found: 496.09 (MH^+).

R$_1$: 228 mg of the **compound 6** (MW = 496.57 g/mol, 0.459 mmol) was mixed with 1.0 mL of trimethylsilylacetylene (MW = 98.22 g/mol, d = 0.69 g/ml, 7.03 mmol, 15.3 equiv) in 30 mL of THF and 10 mL of diethylamine. After 3 cycles of freeze–pump–thaw, 5.0 mol % of $Pd(PPh_3)_4$ and 5.0 mol% of CuI were added to the solution under an inert atmosphere in a glovebox. The reaction was stirred at 70 °C for 18 h. The completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residue was re-dissolved in CH_2Cl_2 for $NH_4Cl_{(aq)}$ washes. After dried over Na_2SO_4, the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using *n*-hexanes as eluent to give 227.6 mg of **R1** (yellow oil, MW = 513.34 g/mol, yield = 96.6 %).

^{1}H-NMR ($CDCl_3$ at 7.26 ppm, 300 MHz): δ_H 8.60 (d, *J* = 8.6 Hz, 2H), 8.39 (d, *J* = 8.6 Hz, 2H), 7.59-7.46 (m, overlapped, 4H), 3.48 (t, *J* = 7.3 Hz, 4H), 1.56-1.45 (m, overlapped, 4H), 1.30-1.10 (m, overlapped, 20H), 0.84 (t, *J* = 6.8 Hz, 6H), 0.42 (s, 9H). ^{13}C-NMR ($CDCl_3$ at 77.16 ppm, 300 MHz): δ_C 146.90, 134.07, 130.94, 127.55, 126.43, 126.03, 125.04, 114.69, 105.70, 102.28, 56.84, 31.92, 30.18, 29.61, 29.44, 27.49, 22.76, 14.23, 0.48. Mass Spec.: *m/z* calc'd for $C_{35}H_{51}NSi$: 513.38; found: 513.12 (M^+).

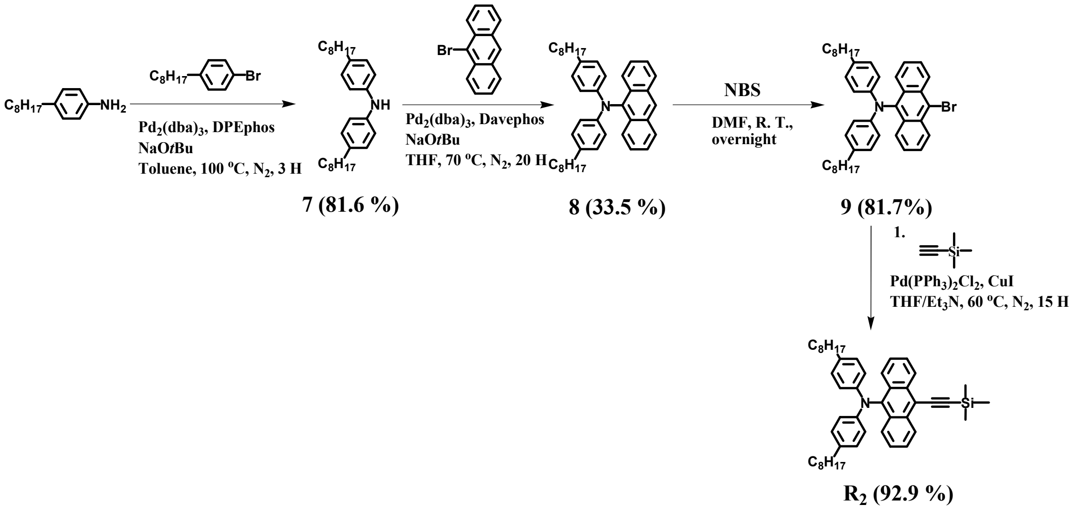


Chart S4. Synthetic route of R_2.

Compound 7: 683.8 mg of 1-bromo-4-octylbenzene (MW = 269.23 g/mol, 2.540 mmol) was mixed with 577.6 mg of 4-*n*-octylaniline (MW = 205.34 g/mol, 2.813 mmol, 1.11 equiv) in 65 mL of Toluene. After 3 cycles of freeze–pump–thaw, 3.0 mol % of $Pd_2(dba)_3$, 6.0 mol % of DPEphose and 1.4 equiv of NaO*t-Bu* were added to the solution under an inert atmosphere in a glovebox. The reaction was stirred at100 °C for 3 h. The completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residue was re-dissolved in CH_2Cl_2 for $NH_4Cl_{(aq)}$ washes. After dried over Na_2SO_4, the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using EA/*n*-hexanes = 1/10 as eluent to give 815.7 mg of **compound 7** (yellow solid, MW = 393.65 g/mol, yield = 81.6 %).

^{1}H-NMR ($CDCl_3$ at 7.26 ppm, 300 MHz): δ_H 7.06 (d, J = 7.9 Hz, 4H), 6.97 (d, J = 7.8 Hz, 4H), 5.54 (s, 1H), 2.54 (t, J = 7.5 Hz, 4H), 1.65-1.50 (m, overlapped, 4H), 1.42-1.16 (m, overlapped, 20H), 0.88 (t, J = 6.3 Hz, 6H) ^{13}C-NMR ($CDCl_3$ at 77.16 ppm, 300 MHz): δ_C 141.37, 135.52, 129.27, 117.91, 35.38, 32.06, 31.87, 29.67, 29.49, 29.45, 22.84, 14.27. Mass Spec.: *m/z* calc'd for $C_{28}H_{43}N$: 393.24; found: 392.97 (M^+).

Compound 8: 580 mg of 9-bromoanthracene (MW = 257.13 g/mol, 2.256 mmol) was mixed with 976 mg of **compound 7** (MW = 393.65 g/mol, 2.479 mmol, 1.10 equiv) in 35 mL of THF. After 3 cycles of freeze−pump−thaw, 1.0 mol % of $Pd_2(dba)_3$, 6.0 mol % of Davephose and 2.8 equiv of Na*Ot-Bu* were added to the solution under an inert atmosphere in a glovebox. The reaction was stirred at 70 °C for 20 h. The completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residue was re-dissolved in CH_2Cl_2 for $NH_4Cl_{(aq)}$ washes. After dried over Na_2SO_4, the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using *n*-hexanes as eluent to give 431.1 mg of **compound 8** (yellow oil, MW = 569.86 g/mol, yield = 33.5 %).

^{1}H-NMR ($CDCl_3$ at 7.26 ppm, 300 MHz): δ_H 8.49 (s, 1H), 8.15 (, *J* = 8.8 Hz, 2H), 8.05 (d, *J* = 8.0 Hz, 2H), 7.47-7.35 (m, overlapped, 4H), 7.00-6.93 (m, overlapped, 8H), 2.49 (t, *J* = 7.8 Hz, 4H), 1.63-1.48 (m, overlapped, 4H), 1.40-1.17 (m, overlapped, 20H), 0.88 (t, *J* = 6.7 Hz, 6H). ^{13}C-NMR ($CDCl_3$ at 77.16 ppm, 300 MHz): δ_C 145.80, 137.79, 135.48, 132.93, 130.92, 129.06, 128.93, 126.62, 125.54, 124.72, 120.08, 35.38, 32.03, 31.68, 29.63, 29.56, 24.41, 22.82, 14.27. Mass Spec.: *m/z* calc'd for $C_{42}H_{51}N$: 569.40; found: 569.97 (MH^+).

Compound 9: 93.8 mg of NBS (MW = 177.98 g/mol, 0.527 mmol, 1.2 equiv) was dissolved in 30 mL of DMF and added dropwise to 50 mL DMF containing 250.2 mg of the **compound 8** (MW = 569.86 g/mol, 0.439 mmol) at 0 °C. The reaction was stirred at room temperature for 12 h. The completion of the reaction was monitored by TLC. Upon completion, 10 mL of acetone was added to quench the reaction. The mixture was extracted with ether and $NH_4Cl_{(aq)}$. After dried over Na_2SO_4, the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using *n*-hexanes as eluent to give 232.6 mg of **compound 9** (yellow solid, MW = 648.76 g/mol, yield = 81.7 %).

^{1}H-NMR ($CDCl_3$ at 7.26 ppm, 300 MHz): δ_H 8.60 (d, J = 8.8 Hz, 2H), 8.20 (d, J = 8.7 Hz, 2H), 7.60-7.57 (m, 2H),7.44-7.39 (m, 2H) 6.95 (s, 8H), 2.48 (t, J = 7.8 Hz, 4H), 1.56-1.48 (m, overlapped, 4H), 1.38-1.16 (m, overlapped, 20H), 0.98 (t, J = 6.7 Hz, 6H). ^{13}C-NMR ($CDCl_3$ at 77.16 ppm, 300 MHz): δ_C 145.59, 138.39, 135.80, 131.78, 129.15, 128.50, 127.37, 126.97, 125.20, 122.35, 120.12, 25.36, 32.03, 31.65, 29.62, 29.54, 29.41, 22.82, 14.26. Mass Spec.: *m/z* calc'd for $C_{42}H_{50}BrN$: 647.31; found: 647.63 (MH^+).

R_2: 524 mg of the **compound 9** (MW = 648.76 g/mol, 0.8077 mmol) was mixed with 1.0 mL of trimethylsilylacetylene (MW = 98.22 g/mol, d = 0.69 g/ml, 7.03 mmol, 8.7 equiv) in 30 mL of THF and 10 mL of diethylamine. After 3 cycles of freeze−pump−thaw, 5.0 mol % of $Pd(PPh_3)_4$ and 5.0 mol% of CuI were added to the solution under an inert atmosphere in a glovebox. The reaction was stirred at 60 ^{o}C for 15 h. The completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residue was re-dissolved in CH_2Cl_2 for $NH_4Cl_{(aq)}$ washes. After dried over Na_2SO_4, the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using *n*-hexanes as eluent to give 500 mg of **R_2** (yellow solid, MW = 666.06 g/mol, yield = 92.9 %).

^{1}H-NMR ($CDCl_3$ at 7.26 ppm, 300 MHz): δ_H 8.63 (d, J = 8.6 Hz, 2H), 8.14 (d, J = 8.7 Hz, 2H), 7.6 (t, J = 7.6 Hz, 4H), 7.4 (t, J = 7.6 Hz, 4H), 6.94 (s, 8H), 2.48 (t, J = 7.3 Hz, 4H), 1.68-1.48 (m, overlapped, 4H), 1.40-1.16 (m, overlapped, 20H), 0.88 (t, J = 6.5 Hz, 6H), 0.45 (s, 9H). ^{13}C-NMR ($CDCl_3$ at 77.16 ppm, 300 MHz): δ_C 145.73, 139.08, 135.76, 134.23, 130.51, 129.12, 127.53, 126.85, 126.80, 125.15, 120.19, 117.28, 35.38, 32.04, 31.66, 29.63, 29.55, 29.42, 22.83, 14.27, 0.41. Mass Spec.: *m/z* calc'd for $C_{47}H_{59}NSi$: 665.44; found: 665.41 (M^+).

Synthesis of LWP13

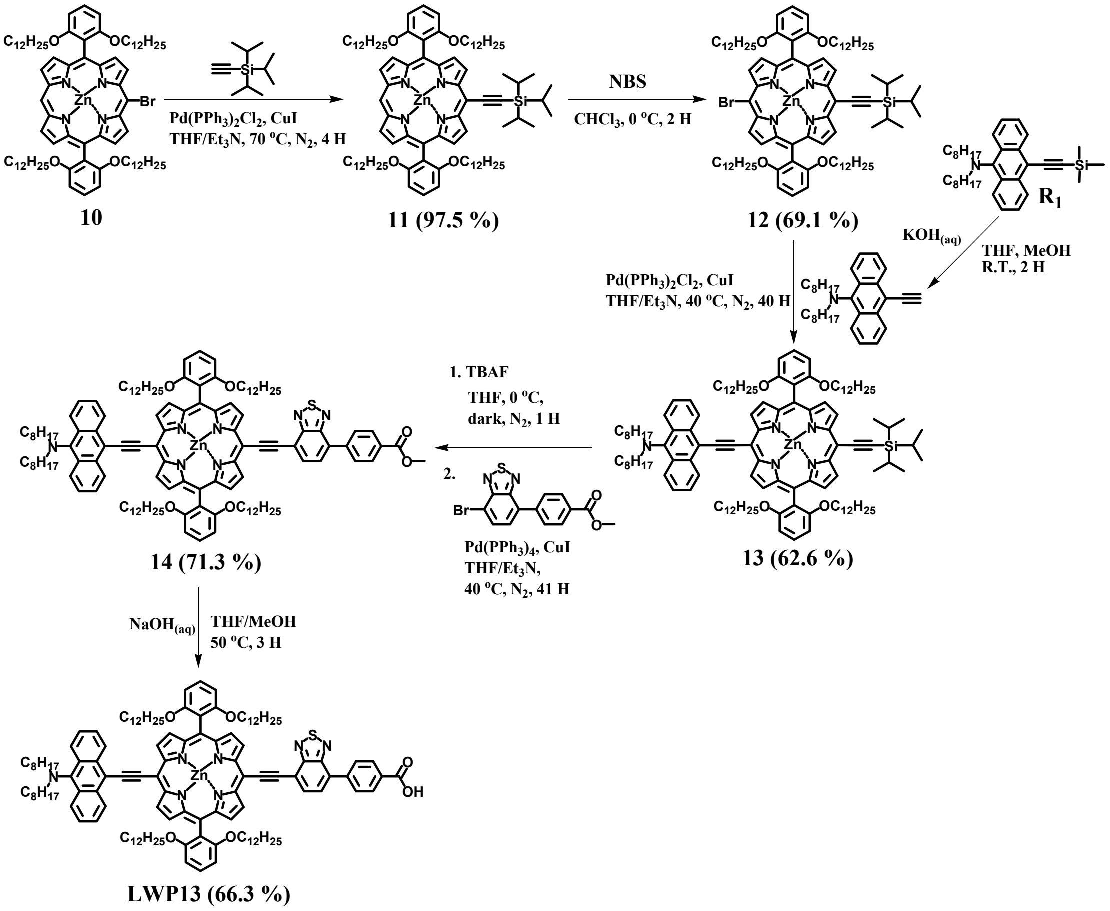


Chart S5. Synthetic route of LWP13.

Compound 11:496 mg of the **compound 10** (MW = 1342.09 g/mol, 0.369 mmol) was mixed with 0.81 mL of Triisopropylsilyl acetylene (MW = 182.38 g/mol, d = 0.831 g/mL, 3.69 mmol, 10 equiv) in 30 mL of THF and 5 mL of triethylamine. After 3 cycles of freeze−pump−thaw, 20 mol % of $Pd(PPh_3)_2Cl_2$ and CuI were added to the solution under an inert atmosphere in a glovebox. The reaction was stirred at 70 ^oC for 4 h. The completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residue was re-dissolved in CH_2Cl_2 for $NH_4Cl_{(aq)}$ washes. After dried over Na_2SO_4, the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using CH_2Cl_2/*n*-hexanes = 1/2 as eluent, followed by crystallization from CH_2Cl_2/MeOH to give 520 mg of **compound 11** (MW = 1443.55 g/mol, yield = 97.5 %).

^{1}H-NMR ($CDCl_3$ at 7.26 ppm, 300 MHz): δ_H 10.05 (s, 1H), 9.75 (d, *J* = 4.6 Hz, 2H), 9.23 (d, *J* = 4.5 Hz, 2H), 8.96 (two overlapped doublets, *J* = 4.7 Hz, 2H), 8.94 (two overlapped doublets, *J* = 4.6 Hz, 2H), 7.70 (t, *J* = 8.3 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 4H), 3.83 (t, *J* = 6.5 Hz, 8H), 1.30-1.02 (m, overlapped, 35H), 1.02-0.74 (m, overlapped, 42H), 0.72-0.58 (m, overlapped, 8H), 0.58-0.30 (m, overlapped, 28H). ^{13}C-NMR ($CDCl_3$ at 77.16 ppm, 300 MHz): δ_C 160.17, 152.17, 151.05, 150.42, 149.20, 132.07, 131.61, 131.47, 130.75, 129.81, 121.41, 113.81, 110.58, 106.39, 105.47, 99.01, 95.94, 94.90, 68.2, 65.53, 32.01, 29.60, 29.46, 29.40, 29.31, 29.12, 28.78, 28.73, 25.31, 23.86, 22.82, 19.29, 14.26, 12.13. Mass Spec.: *m/z* calc'd for $C_{91}H_{136}N_4O_4SiZn$: 1440.96; found: 1440.74 (M^+).

Compound 12: 498 mg of **compound 11** (MW = 1443.55 g/mol, 0.345 mmol) was mixed with 67.5 mg of NBS (MW = 177.98 g/mol, 1.1 equiv) in 80 mL of $CHCl_3$.The reaction was stirred at 0°C for 2 h. Upon completion, the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using CH_2Cl_2/*n*-hexanes = 1/2 as eluent to give 362.9 mg of **compound 12** (MW = 1522.45 g/mol, yield = 69.1 %)

^{1}H-NMR ($CDCl_3$ at 7.26 ppm, 300 MHz): δ_H 9.65 (d, *J* = 4.6 Hz, 2H), 9.58 (d, *J* = 4.7 Hz, 2H), 8.86 (d, *J* = 4.6 Hz, 2H), 8.83 (*J* = 4.7 Hz, 2H), 7.68 (t, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 4H), 3.83 (t, *J* = 6.5 Hz, 8H) 1.42 (m, overlapped, 8H), 1.32-1.01 (m, overlapped, 28H), 1.00-0.75 (m, overlapped, 41H), 0.74-0.32 (m, overlapped, 36H) ^{13}C-NMR ($CDCl_3$ at 77.16 ppm, 300 MHz): δ_C 160.09, 152.96, 151.49, 150.75, 148.94, 132.60, 132.47, 132.11, 131.07, 129.92, 121.09, 114.93, 110.29, 105.29, 99.35, 96.35, 90.37, 68.77, 65.44, 32.00, 29.61, 29.47, 29.40, 29.36, 29.17, 28.84, 28.76, 25.37, 23.78, 22.81, 19.26, 14.25, 12.07. Mass Spec.: *m/z* calc'd for $C_{91}H_{135}BrN_4O_4SiZn$: 1518.87; found: 1519.50 (MH^+).

Compound 13: 227.6 mg of the $\mathbf{R_1}$ (MW = 513.34 g/mol, 0.443 mmol) was mixed with 4 mL of 1.0 M $KOH_{(aq)}$ in 20 mL of MeOH and 80 mL of THF. The reaction was stirred in the dark at room temperature for 2 h. Upon completion, the solvent was removed by rotary evaporation. The residue was re-dissolved in CH_2Cl_2 for $NH_4Cl_{(aq)}$ washes. After dried over Na_2SO_4, the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using CH_2Cl_2/*n*-hexanes = 1/2 as eluent to give 194.4 mg of yellow oil. The yellow oil was immediately mixed with 674 mg of the **compound 12** (MW = 1522.45 g/mol, 0.443 mmol, 1 equiv) in 30 mL of THF and 5 mL of triethylamine. After 3 cycles of freeze−pump−thaw, 15 mol % of $Pd(PPh_3)_4$ and CuI were added to the solution under an inert atmosphere in a glovebox. The reaction was stirred at 40 ^{o}C for 40 h. The completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residue was re-dissolved in CH_2Cl_2 for $NH_4Cl_{(aq)}$ washes. After dried over Na_2SO_4, the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using CH_2Cl_2/*n*-hexanes = 1/3 as eluent, followed by crystallization from CH_2Cl_2/MeOH to give 522.3 mg of **compound 13**.(dark green solid, MW = 1883.23 g/mol, yield = 62.6 %).

^{1}H-NMR (d_8-THF at 1.73 and 3.58 ppm, 300 MHz): δ_H 9.89 (d, *J* = 4.5 Hz, 2H), 9.58 (d, *J* = 4.5 Hz, 2H), 9.42 (d, *J* = 8.6 Hz, 2H), 8.86 (d, *J* = 4.5 Hz, 2H), 8.75 (d, *J* = 4.5 Hz, 2H), 8.61 (d, *J* = 8.8 Hz, 2H), 7.80-7.61 (m, overlapped, 6H), 7.08 (d, *J* = 8.5 Hz, 4H), 3.90 (t, *J* = 6.5 Hz, 8H), 3.61 (t, *J* = 7.6 Hz, 4H), 1.50 (s, 18H), 1.49 (s, 3H), 1.40-1.22 (m, overlapped, 24H), 1.22-0.56 (m, overlapped, 108H). ^{13}C-NMR (d_8-THF at 25.3 and 67.4 ppm, 300 MHz): δ_C 161.05, 152.82, 152.58, 152.26, 151.59, 151.47, 146.72, 143.82, 142.51, 135.20, 132.55, 132.42, 132.33, 130.90, 130.82, 130.59, 128.94, 127.57, 127.17, 126.93, 126.05, 121.76, 117.67, 116.27, 112.80, 112.38, 106.19, 105.45, 101,08, 100.03, 95.89, 93.53, 69.12, 57.80, 49.99, 32.77, 31.21, 30.67, 30.51, 30.42, 30.32, 30.26, 30.16, 29.74, 28.42, 26.30, 23.50, 14.43, 12.99. Mass

Spec.: *m/z* calc'd for $C_{123}H_{177}N_5O_4SiZn$: 1880.29; found: 1880.86 (MH^+).

Compound 14: 166 mg of **compound 13** (MW = 1883.23, 0.088 mmol) was mixed with 0.09 mL of tetrabutylammonium fluoride (1.0 M in THF, MW = 261.46 g/mol, 0.09mmol, 1.02 equiv) in 20 mL of dry and de-gassed THF. The reaction was stirred in the dark at 0 °C for 1 h. Upon completion, the solvent was removed by rotary evaporation. The residue was re-dissolved in CH_2Cl_2 for $NH_4Cl_{(aq)}$ washes. After dried over Na_2SO_4, the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using THF/*n*-hexanes = 1/10 as eluent to give 150 mg of dark brown solid. The dark brown solid was immediately mixed with 29.05 mg of **compound 1** (MW = 349.20 g/mol, 0.95 equiv) in 30 mL of THF and 5 mL of triethylamine. After 3 cycles of freeze−pump−thaw, 15 mol % of $Pd(PPh_3)_4$ and CuI were added to the solution under an inert atmosphere in a glovebox. The reaction was stirred at 50 °C for 41 h. The completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residue was re-dissolved in CH_2Cl_2 for $NH_4Cl_{(aq)}$ washes. After dried over Na_2SO_4, the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using THF/*n*-hexanes = 1/4 as eluent, followed by crystallization from CH_2Cl_2/MeOH to give 118.4 mg of **compound 14** (dark brown solid, MW = 1995.18 g/mol, yield = 71.3 %).

^{1}H-NMR (d_8-THF at 1.73 and 3.58 ppm, 300 MHz): δ_H 10.04 (d, *J* = 4.6 Hz, 2H), 9.89 (d, *J* = 4.5 Hz, 2H), 9.42 (d, *J* = 8.6 Hz, 2H), 8.86 (two overlapped doublets, *J* = 4.5 Hz, 2H), 8.85 (two overlapped doublets, *J* = 4.5 Hz, 2H), 8.61 (d, *J* = 8.8 Hz, 2H), 8.39 (d, *J* = 7.4 Hz, 1H), 8.33 (d, *J* = 8.6 Hz, 2H), 8.22 (d, *J* = 8.6 Hz, 2H), 8.15 (d, *J* = 7.4 Hz, 1H), 7.81-7.71 (m, overlapped, 4H), 7.66-7.51 (m, 2H), 7.11 (d, *J* = 8.5 Hz, 4H), 3.94-3.91 (m, overlapped, 11H), 1.50-1.20 (m, overlapped, 22H), 1.20-0.54 (m, overlapped, 106H). ^{13}C-NMR (d_8-THF at 25.3 and 67.4 ppm, 300 MHz): δ_C 166.81, 161.04, 157.26, 154.27, 152.89, 152.23, 151.66, 146.83, 142.49, 135.24, 132.73, 132.55, 132.32, 131.81, 131.33, 130.89, 130.66, 130.37, 130.09, 129.68, 127.58, 127.21, 126.95, 126.06, 121.72, 119.60, 117.58, 116.76, 112.83, 106.16, 105.50, 103.69, 101.77, 99.33, 93.74, 93.11, 69.12, 68.22, 57.80, 52.23, 32.80, 32.75, 31.21, 30.51, 30.38, 30.33, 30.24, 30.16, 29.88, 29.80, 28.42, 26.39, 23.47, 14.41. Mass Spec.: *m/z* calc'd for $C_{128}H_{165}N_7O_6SZn$: 1992.18; found: 1993.16 (MH^+).

LWP13: 110 mg of the **compound 14** (MW = 1995.18 g/mol, 0.055 mmol) was dissolved in 50 mL of THF and 10 mL of MeOH. After adding 30 mL of 8.33 M $NaOH_{(aq)}$, the solution was stirred at 50 °C for 3 h. The completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residue was re-dissolved in CH_2Cl_2 for $NH_4Cl_{(aq)}$ washes. After dried over Na_2SO_4, the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using MeOH/ CH_2Cl_2 = 1/9 as eluent, followed by crystallization from CH_2Cl_2/MeOH to give 72.4 mg of **LWP13** (dark brown solid, MW = 1995.78 g/mol, yield = 66.3 %).

^{1}H-NMR (d_8-THF at 1.73 and 3.58 ppm, 300 MHz): δ_H 10.05 (d, *J* = 4.5 Hz, 2H), 9.89 (d, *J* = 4.5 Hz, 2H), 9.42 (d, *J* = 8.6 Hz, 2 H), 8.87 (two overlapped doublets, *J* = 4.3 Hz, 2H), 8.86 (two overlapped doublets, *J* = 4.2 Hz, 2H), 8.61 (d, *J*= 8.8 Hz, 2H), 8.40 (d, *J* = 7.4 Hz, 1H), 8.32 (d, *J* = 7.9 Hz, 2H), 8.26 (d, *J* = 7.6 Hz, 2H), 8.15 (d, *J* = 7.3 Hz, 1H), 7.81-7.71 (m, overlapped, 4H), 7.64 (t, *J*= 7.5 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 4H), 3.93 (t, *J* = 6.2 Hz, 8H), 3.67 (t, *J* = 7.7 Hz, 4H), 1.50-1.20 (m, overlapped, 26H), 1.20-0.50 (m, overlapped, 104H). ^{13}C-NMR (d_8-THF at 25.3 and 67.4 ppm, 300 MHz): δ_C 161.04, 157.29, 154.34, 152.89, 152.23, 151.66, 146.18, 142.08, 135.24, 133.11, 132.72, 132.55, 132.33, 131.87, 131.36, 130.90, 130.67, 129.95, 129.59, 128.95, 127.21, 126.95, 126.07, 121.73, 119.43, 117.60, 116.74, 106.18, 105.50, 103.52, 101.73, 99.42, 93.72, 93.14, 69.12, 57.80, 52.23, 32.80, 32.75, 31.21, 30.66, 30.39, 30.34, 30.24, 30.16, 29.88, 29.80, 28.42, 26.40, 23.48, 14.41. Elemental Anal calc'd for $C_{127}H_{163}N_7O_6SZn \cdot 2H_2O$: C 75.62 %, H 8.34 %, N 4.86 %. Found: C 75.87 %, H 8.27 %, N 4.68 %. Mass Spec.: *m/z* calc'd for $C_{127}H_{163}N_7O_6SZn$: 1978.17; found: 1979.20 (MH^+).

Synthesis of LWP14

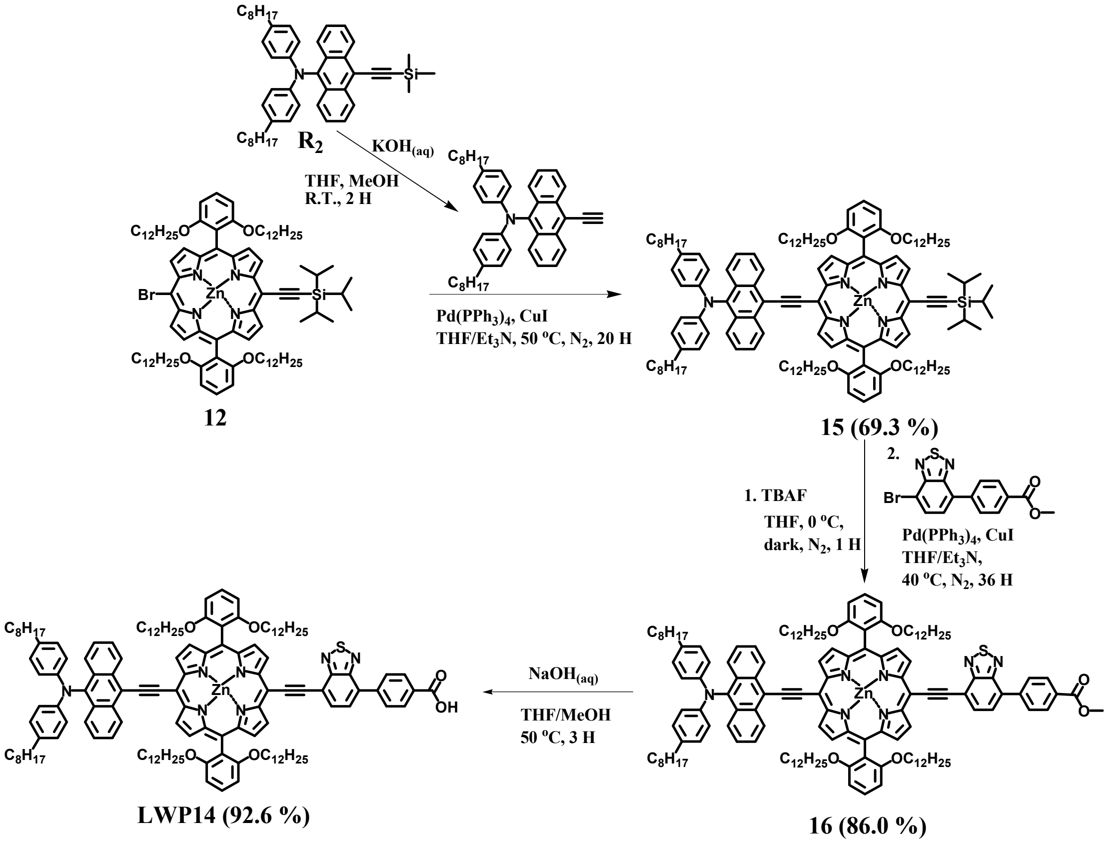


Chart S6.Synthetic route of LWP14.

Compound 15: 135 mg of $\mathbf{R_2}$ (MW = 666.06 g/mol, 0.203 mmol) was mixed with 4 mL of 1.0 M $KOH_{(aq)}$ in 20 mL of MeOH and 80 mL of THF. The reaction was stirred in the dark at room temperature for 2 h. Upon completion, the solvent was removed by rotary evaporation. The residue was re-dissolved in CH_2Cl_2 for $NH_4Cl_{(aq)}$ washes. After dried over Na_2SO_4, the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using *n*-hexanes as eluent to give 120 mg of yellow solid. The yellow solid was immediately mixed with 227 mg of the

compound 12 (MW = 1518.87 g/mol, 0.149 mmol) in 30 mL of THF and 5 mL of triethylamine. After 3 cycles of freeze–pump–thaw, 15 mol % of $Pd(PPh_3)_4$ and CuI were added to the solution under an inert atmosphere in a glovebox. The reaction was stirred at 50 °C for 20 h. The completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residue was re-dissolved in CH_2Cl_2 for $NH_4Cl_{(aq)}$ washes. After dried over Na_2SO_4, the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using CH_2Cl_2/*n*-hexanes = 1/3 as eluent, followed by crystallization from CH_2Cl_2/MeOH to give 190.0 mg of **compound 15** (dark green solid, MW = 2032.35 g/mol, yield = 69.3 %).

^{1}H-NMR (d_8-THF at 1.73 and 3.58 ppm, 300 MHz): δ_H 9.91 (d, J = 4.5, 2H), 9.59 (d, J = 4.5 Hz, 2H), 9.45 (d, J = 8.7 Hz, 2H), 8.87 (d, J = 4.5 Hz, 2H), 8.76 (d, J = 4.5 Hz, 2H), 8.31 (d, J = 8.7 Hz, 2H), 7.78-7.69 (m, overlapped, 4H), 7.54 (t, J = 7.7 Hz, 2H), 7.10-7.00 (m, overlapped, 12H), 3.88 (t, J = 6.6 Hz, 8H), 1.69-1.25 (m, overlapped, 46H), 1.25-0.55 (m, overlapped, 100H). ^{13}C-NMR (d_8-THF at 25.3 and 67.4 ppm, 300 MHz): δ_C 161.04, 152.80, 152.30, 151.69, 151.51, 146.93, 139.28, 136.28, 136.44, 135.32, 132.71, 132.45, 131.90, 130.99, 130.72, 130.63, 129.89, 128.87, 127.65, 127.53, 126.17, 121.69, 121.08, 120.06, 116.42, 112.30, 107.38, 105.46, 100.43, 100.33, 96.08, 93.11, 69.14, 68.22, 36.16, 32.88, 32.76, 30.49, 30.41, 30.40, 30.32, 30.26, 30.17, 30.14, 26.39, 26.31, 23.57, 23.49, 19.63, 14.43, 12.98. Mass Spec.: *m/z* calc'd for $C_{135}H_{185}N_5O_4SiZn$: 2032.35; found: 2033.36 (MH$^+$).

Compound 16: For the de-protection process, 186 mg of **compound 15** (MW = 2032.35 g/mol, 0.091 mmol) was mixed with 0.1 mL of tetrabutylammonium fluoride (1.0 M in THF, MW = 261.46 g/mol, 0.09 mmol, 1.1 equiv) in 20 mL of dry and de-gassed THF. The reaction was stirred in the dark at 0 °C for 1 h. Upon completion, the solvent was removed by rotary evaporation. The residue was re-dissolved in

CH_2Cl_2 for $NH_4Cl_{(aq)}$ washes. After dried over Na_2SO_4, the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using THF/*n*-hexanes = 1/10 as eluent to give 169 mg of dark brown solid. The dark brown solid was immediately mixed with 38.1 mg of **compound 1** (MW = 349.20 g/mol, 1.2 equiv) in 30 mL of THF and 5 mL of triethylamine. After 3 cycles of freeze−pump−thaw, 15 mol % of $Pd(PPh_3)_4$ and CuI were added to the solution under an inert atmosphere in a glovebox. The reaction was stirred at 50 ^oC for 36 h. The completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residue was re-dissolved in CH_2Cl_2 for $NH_4Cl_{(aq)}$ washes. After dried over Na_2SO_4, the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using THF/*n*-hexanes = 1/4 as eluent, followed by crystallization from CH_2Cl_2/MeOH to give 168.0 mg of **compound 16** (dark brown solid, MW = 2147.37 g/mol, yield = 86.0 %).

^{1}H-NMR (d_8-THF at 1.73 and 3.58 ppm, 300 MHz): δ_H 10.05 (d, *J* = 4.6, 2H), 9.91 (d, *J* = 4.6 Hz, 2H), 9.46 (d, *J* = 8.7 Hz, 2H), 8.88 (two overlapped doublets, *J* = 4.5 Hz, 2H), 8.87 (two overlapped doublets, *J* = 4.5 Hz, 2H), 8.40 (d, *J* = 7.4 Hz, 1H), 8.34 (two overlapped doublets, *J* = 8.5 Hz, 2H), 8.32 (two overlapped doublets, *J* = 8.4 Hz, 2H), 8.22 (d, *J* = 8.5 Hz, 2H), 8.15 (d, *J* = 7.4Hz, 1H), 7.81-7.72 (m, overlapped, 4H), 7.58-7.52 (m, 4H), 7.13-7.01 (m, overlapped, 12H), 3.96-3.92 (m, overlapped, 11H), 1.69-1.49 (m, 4H), 1.46-1.22 (m, overlapped, 24H), 1.17-0.55 (m, overlapped, 110). ^{13}C-NMR (d_8-THF at 25.3 and 67.4 ppm, 300 MHz): δ_C 166.82, 161.04, 154.27, 152.86, 152.27, 151.75, 146.93, 142.47, 139.37, 136.46, 135.36, 132.84, 132.74, 131.91, 131.43, 130.89, 130.83, 130.70, 130.37, 130.10, 129.90, 129.68, 128.88, 127.67, 127.57, 126.19, 121.67, 121.10, 119.98, 119.54, 116.90, 107.33, 105.51, 103.57, 101.57, 101.12, 99.64, 93.29, 93.19, 69.13, 68.21, 52.24, 36.16, 32.88, 32.74, 30.49, 30.38, 30.32, 30.25, 30.16, 29.88, 29.81, 26.40, 23.57, 23.47, 14.46, 14.41.

Mass Spec.: *m/z* calc'd for $C_{140}H_{173}N_7O_6SZn$: 2144.25; found: 2145.09 (MH^+).

LWP14: 140 mg of the **compound 16** (MW = 2147.37 g/mol, 0.065 mmol) was dissolved in 50 mL of THF and 20 mL of MeOH. After adding 30 mL of 8.33 M $NaOH_{(aq)}$, the solution was stirred at 50 °C for 3 h. The completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residue was re-dissolved in CH_2Cl_2 for $NH_4Cl_{(aq)}$ washes. After dried over Na_2SO_4, the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using MeOH/CH_2Cl_2 = 1/9 as eluent, followed by crystallization from CH_2Cl_2/MeOH to give 128.8 mg of **LWP14** (dark brown solid, MW =2133.34 g/mol, yield = 92.9 %).

^{1}H-NMR ($CDCl_3$ at 7.26 ppm, 300 MHz, trace amt. of d_5-pyridine): δ_H 9.94 (d, *J* = 4.5 Hz, 2H), 9.87 (d, *J* = 4.5 Hz, 2H), 9.37 (d, *J* = 8.7 Hz, 2 H), 8.90 (d, *J* = 4.4 Hz, 4H), 8.36 (d, *J* = 7.6 Hz, 2H), 8.25 (two overlapped doublets, 3H), 8.17 (d, *J* = 8.1 Hz, 2H), 7.95 (d, *J* = 7.4 Hz, 1H), 7.69 (t, *J* = 7.9 Hz, 4H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.15-6.90 (m, overlapped, 12H), 3.88 (t, *J* = 6.3 Hz, 8H), 2.50 (t, *J* = 7.6 Hz, 4H), 1.56 (t, *J* = 6.6 Hz, 4H), 1.45- 1.15 (m, overlapped, 24H), 1.15-0.30 (m, overlapped, 108H). ^{13}C-NMR (d_8-THF at 25.3 and 67.4 ppm, 300 MHz): δ_C 161.03, 157.29, 154.35, 152.86, 152.27, 151.74, 146.93, 141.98, 139.35, 136.45, 135.36, 132.21, 133.07, 132.72, 131.91, 131.45, 130.70, 129.90, 129.57, 128.87, 127.67, 127.65, 126.19, 121.68, 121.10, 119.99, 119.34, 116.87, 107.33, 107.35, 105.51, 103.39, 101.66, 99.73, 93.27, 93.22, 69.13, 36.16, 32.88, 32.74, 30.49, 30.38, 30.32, 30.26, 30.16, 29.88, 29.81, 26.40, 23.57, 23.47, 14.46, 14.41. Elemental Anal.: calc'd for $C_{139}H_{171}N_7O_6SZn \cdot 1.5\ H_2O$: C 77.28 %, H 8.12 %, N 4.54 %, found: C 77.03 %, H 7.98 %, N 4.48%. Mass Spec.: *m/z* calc'd for $C_{139}H_{171}N_7O_6SZn$: 2130.23; found: 2131.81 (MH^+).

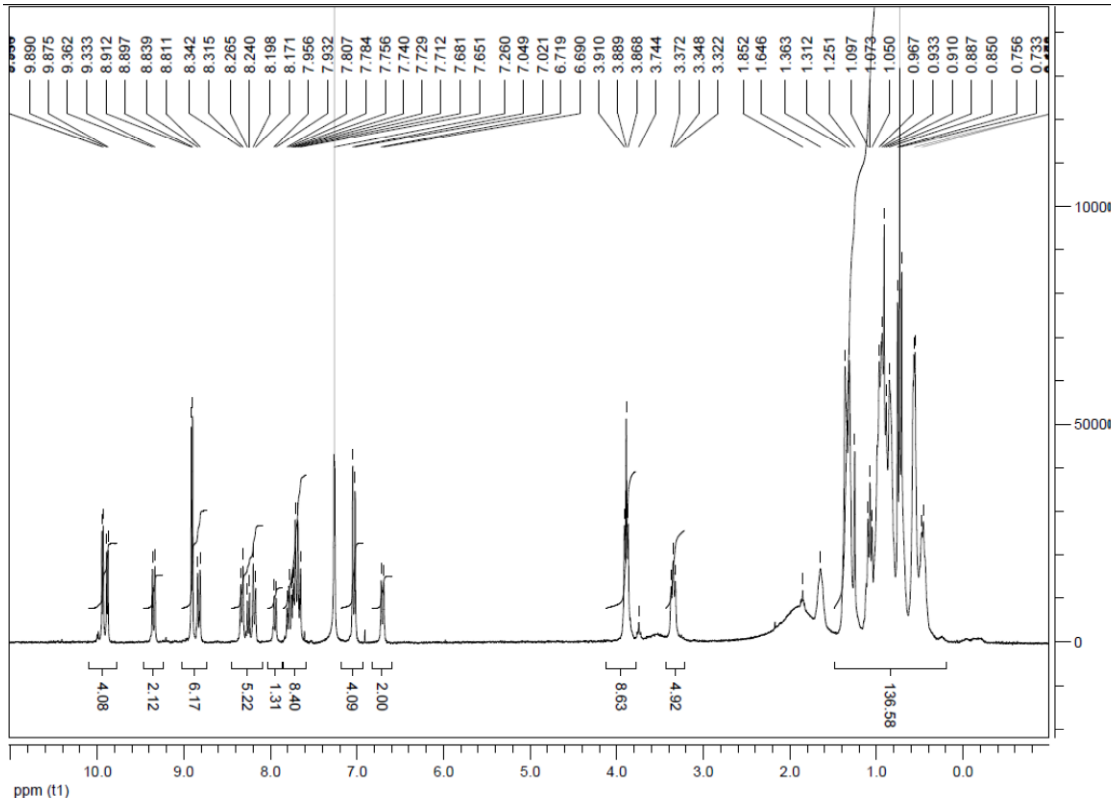


Fig. S1 ^{1}H-NMR spectrum of LWP12 dissolved in $CDCl_3$ with trace amount of d_5-pyridine.

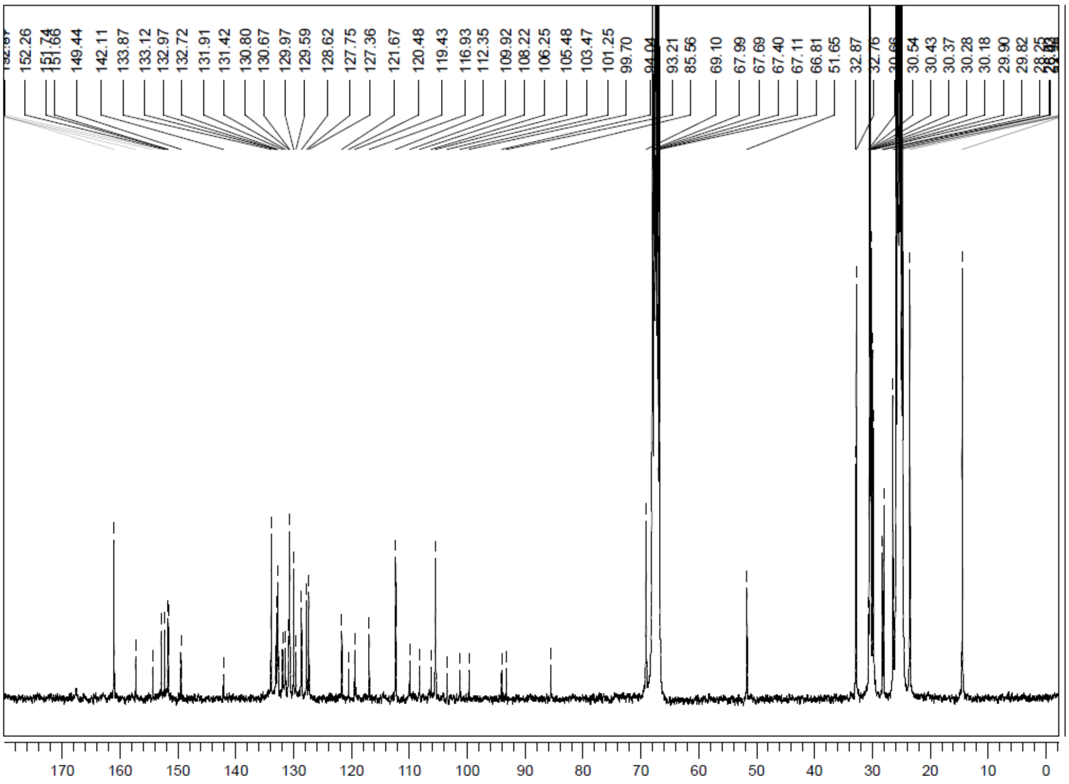


Fig. S2 ^{13}C-NMR spectrum of LWP12 dissolved in d_8-THF.

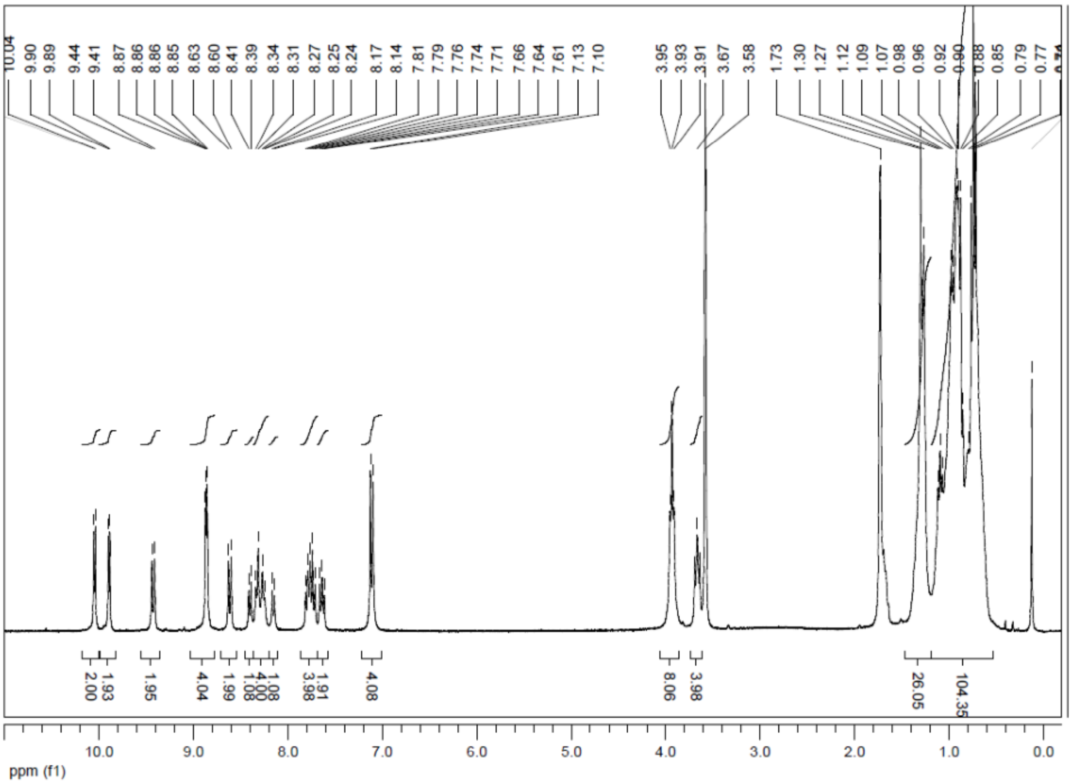


Fig. S3 ^{1}H-NMR spectrum of LWP13 dissolved in d_8-THF.

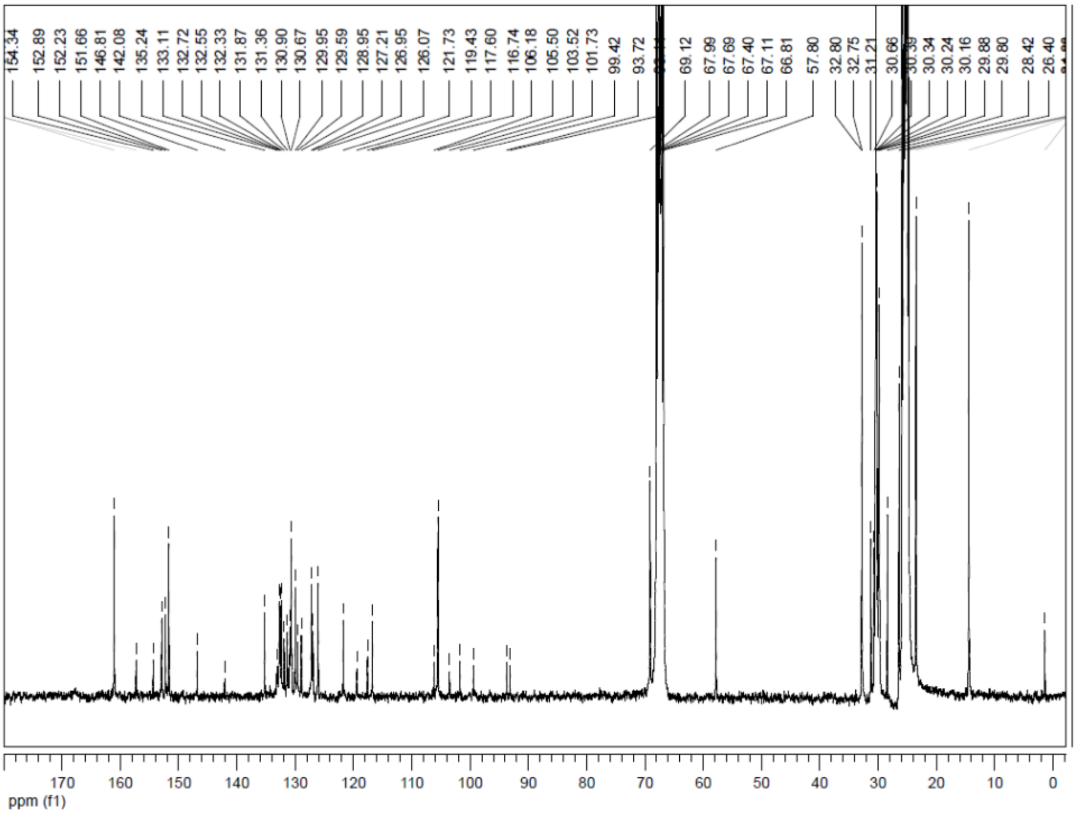


Fig. S4 ^{13}C-NMR spectrum of LWP13 dissolved in d_8-THF.

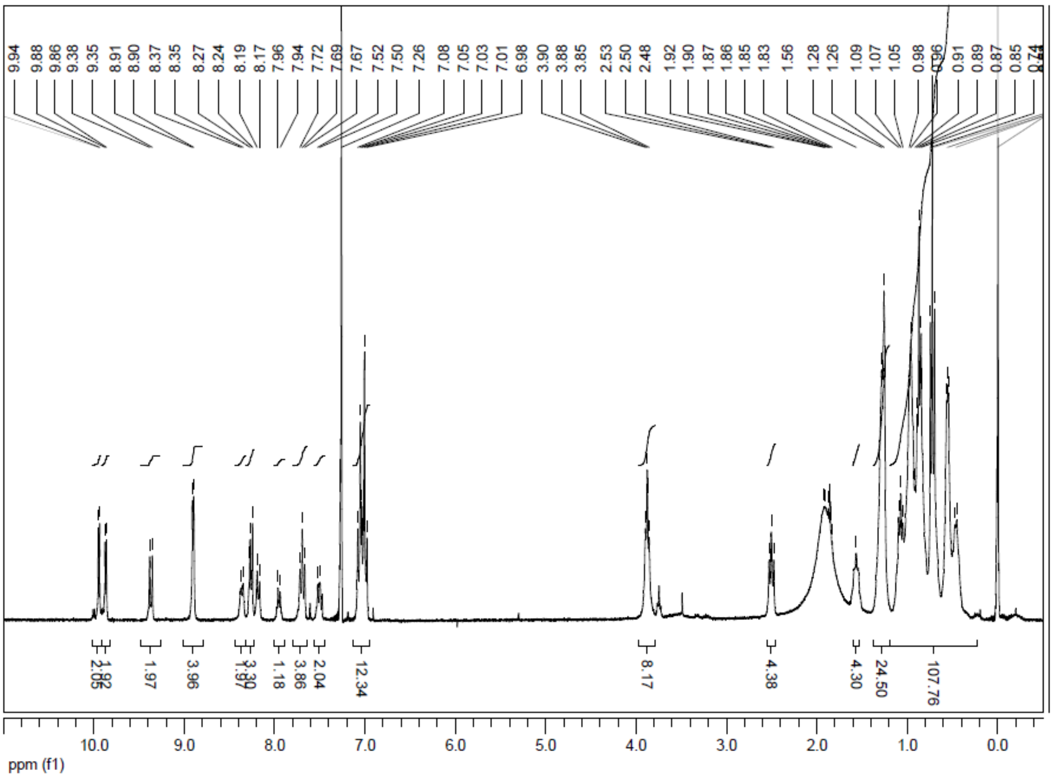


Fig. S5 ^{1}H-NMR spectrum of LWP14 dissolved in $CDCl_3$ with trace amount of d_5-pyridine.

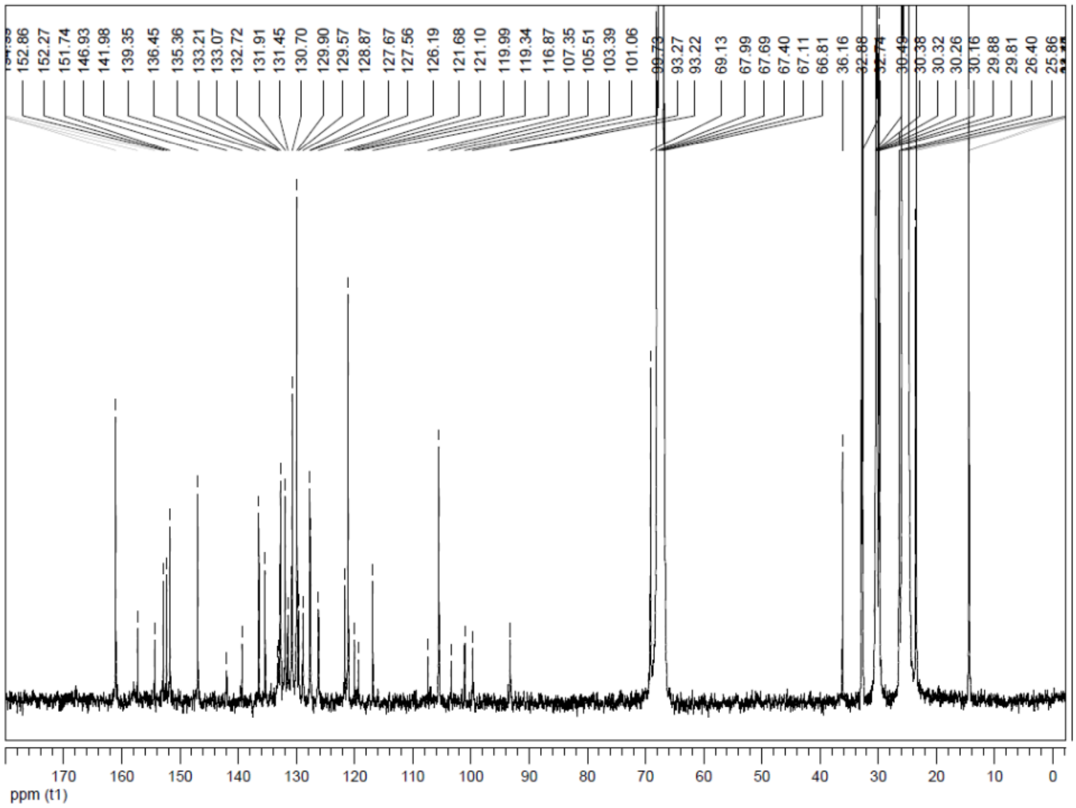


Fig. S6 ^{13}C-NMR spectrum of LWP14 dissolved in d_8-THF.

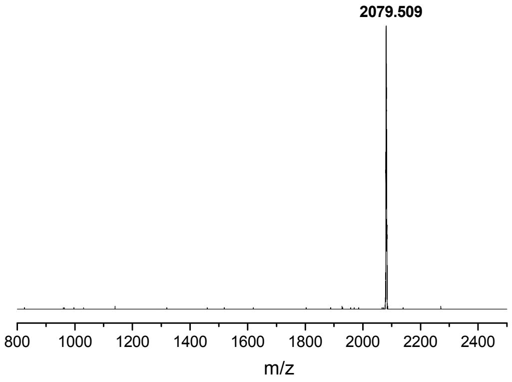


Fig. S7 Mass spectrum of LWP12.

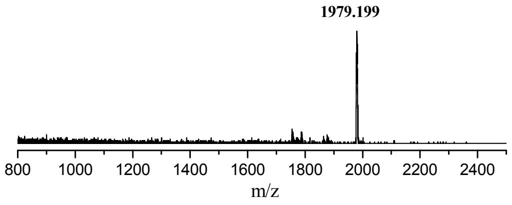


Fig. S8 Mass spectrum of LWP13.

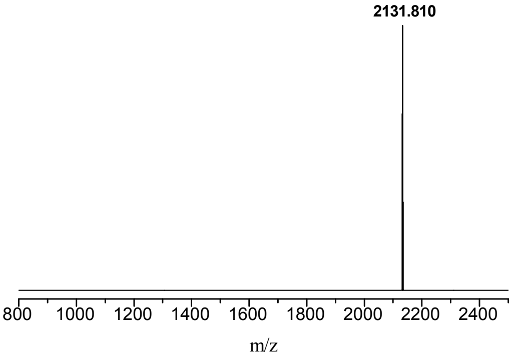


Fig. S9 Mass spectrum of LWP14.

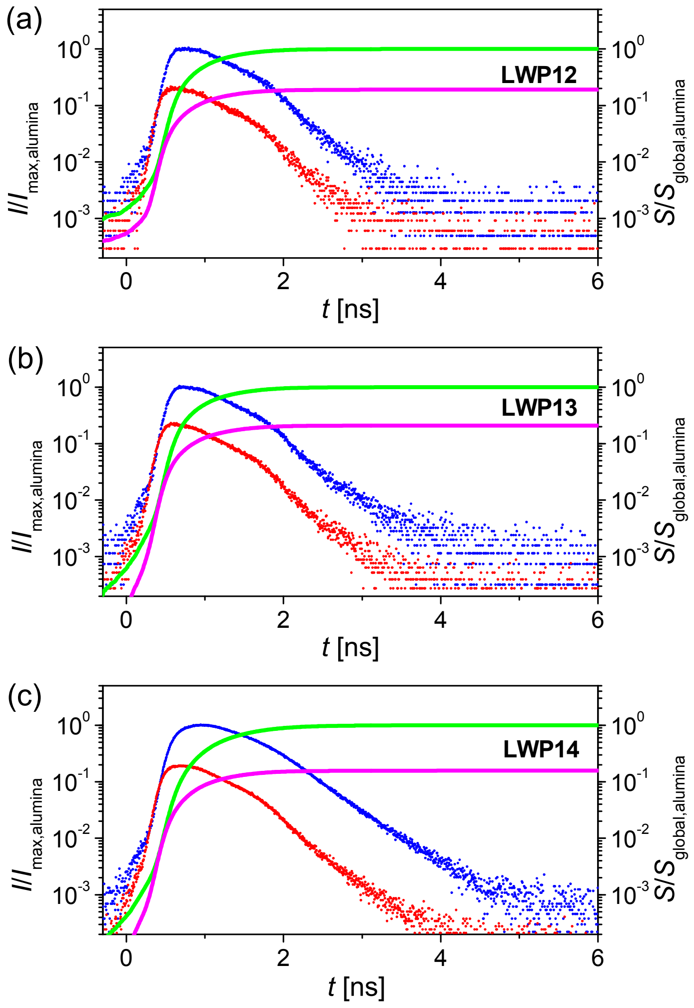


Fig. S10 PL transients of dye-grafted alumina (blue line) and titania (red line) films in combination with a cobalt electrolyte. Excitation wavelength: 482 nm; probe wavelength: 780 nm. The PL intensity (*I*) for all samples was corrected according to the absorbance at 482 nm. The *I* and PL integral areas (*S*) of the alumina (green line) and titania (magenta line) films were normalized with respect to the PL intensity ($I_{\mathrm{max,alumina}}$) and global PL integral area ($S_{\mathrm{global,alumina}}$) of a corresponding dye-grafted alumina film, respectively.

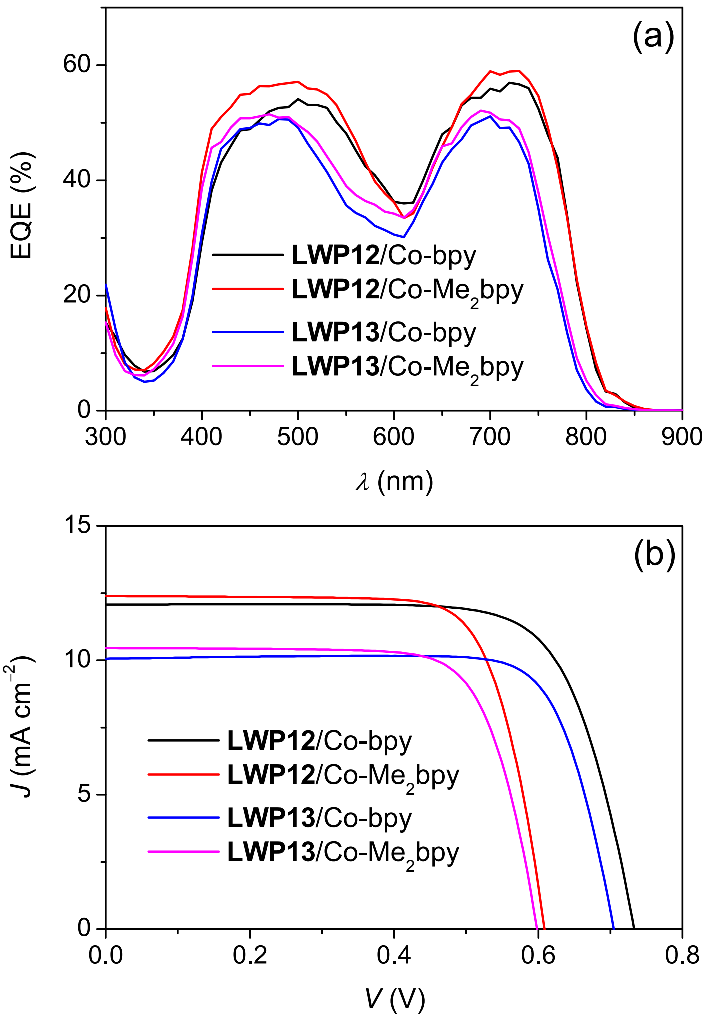


Fig. S11 (a) Plots of external quantum efficiency (EQE) as a function of wavelength (λ) of incident monochromatic light for LWP12 and LWP13 cells with Co-Me$_2$bpy electrolyte. The corresponding data with Co-bpy electrolyte are also included. (b) The J–V curves of LWP12 and LWP13 cells with Co-Me$_2$bpy electrolyte measured under an irradiance of 100 mW cm^{-2} simulated AM1.5G sunlight. The corresponding data with Co-bpy electrolyte are also included. The aperture area of the employed metal mask was 0.160 cm^{-2}.

Table S1 Photovoltaic parameters of LWP12 and LWP13 sensitized solar cells made from 4.0+5.0 μm thick bilayer titania films in combination with Co-bpy and Co-Me$_2$bpy electrolytes under irradiation of 100 mW cm^{-2} simulated AM1.5G sunlight.[a]

Dye	Electrolyte	J_{SC}^{EQE} (mA cm^{-2})	J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF (%)	η (%)
LWP12	Co-bpy	12.16	12.07	731	73.8	6.5
	Co-Me$_2$bpy	12.67	12.39	610	74.9	5.7
LWP13	Co-bpy	10.44	10.06	706	78.0	5.5
	Co-Me$_2$bpy	10.81	10.45	599	74.1	4.6

[a] J_{SC}^{EQE} is derived via wavelength integration of the product of the standard AM1.5 emission spectrum (ASTM G173-03) and the EQEs measured at the short-circuit. The validity of measured photovoltaic parameters is evaluated by comparing the calculated J_{SC}^{EQE} with the experimentally measured J_{SC}.

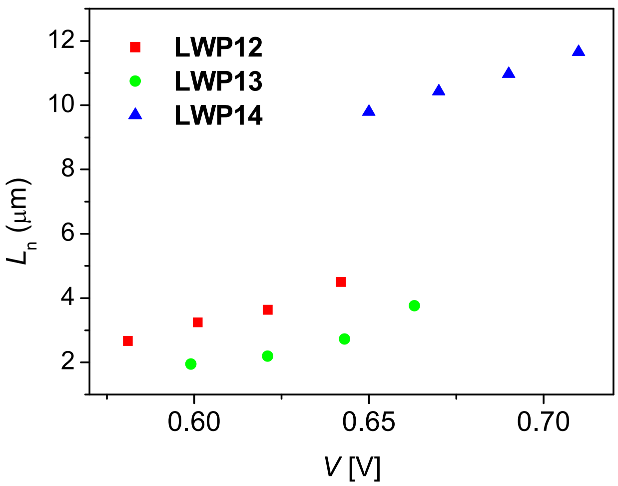


Fig. S12. Plots of electron diffusion length (L_n) *versus* potential bias (V). The data are derived from impedance spectroscopies.

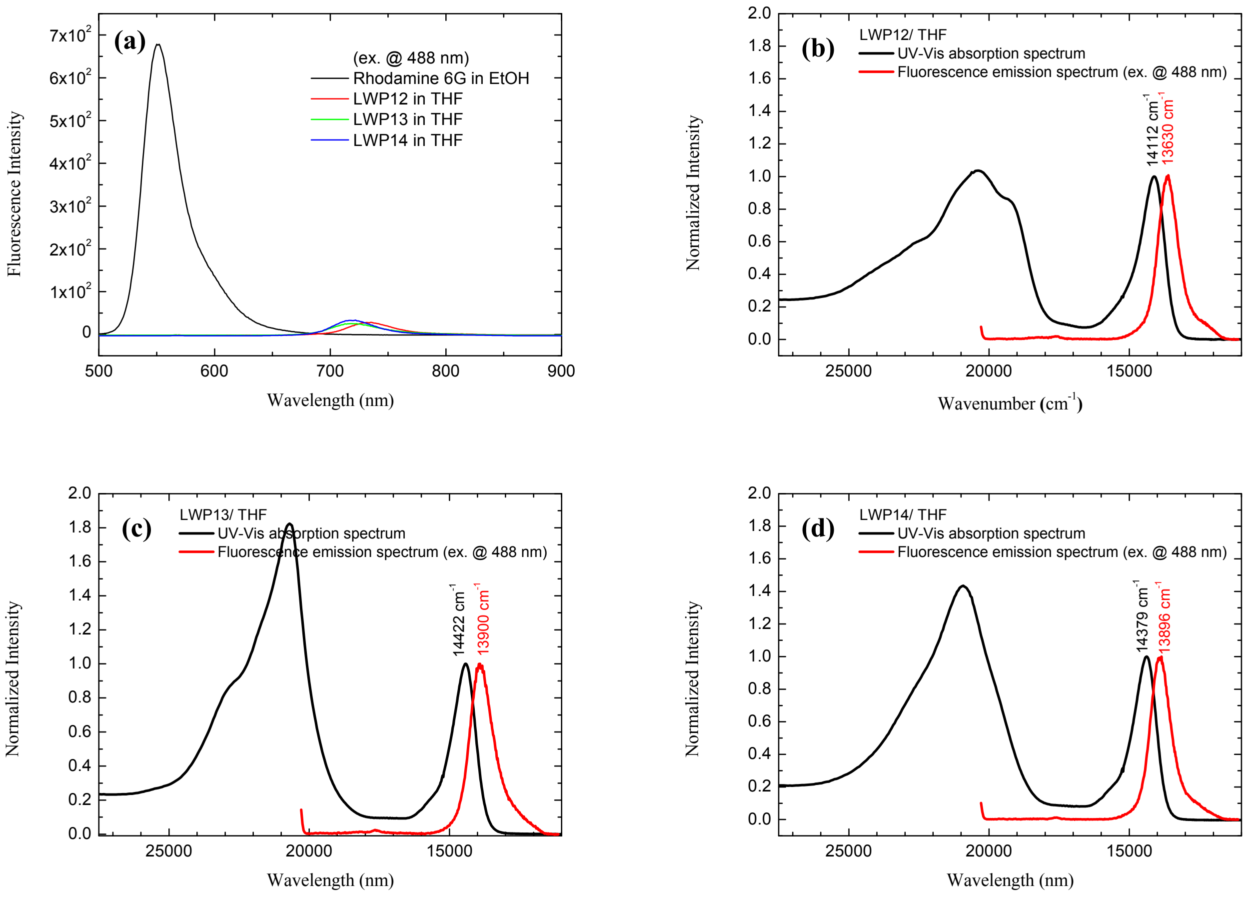


Fig. S13. (a) Fluorescence spectra of Rhodamine 6G and LWP porphyrins, and normalized UV-visible and fluorescence spectra of (b) LWP12, (c) LWP13, and (d) LWP14. (a) was used to estimate the quantum yields while (b)-(d) were used for the Stoke shifts. During the measurements, all samples were dissolved in de-gassed solvents and the absorption intensities were identical (0.025) at the excitation wavelength (488 nm). The integrated area in (a) were used to estimate the quantum yields. The quantum yields were estimated to be 3.3 %, 3.4 %, and 3.9 % for LWP12, LWP13, and LWP14, respectively, by comparing to that of Rhodamine 6G (94 %) according to the literature.[S6-S8] These values are comparable to that of a very common porphyrin, ZnTPP (3.3 %).[S9] The Stoke Shifts were determined to be 482, 522, and 483 cm^{-1} for LWP12, LWP13, and LWP14, respectively.

References

S1. K. Sonogashira, Y. Tohda, and N. Hagihara. A convenient synthesis of acetylenes: catalytic substitutions of acetylenic hydrogen with bromoalkenes, iodoarenes and bromopyridines. *Tet. Lett*. 1975, 4467-4470.

S2. S. Takahashi, Y. Kuroyama, and K. Sonogashira. A Convenient Synthesis of Ethynylarenes and Diethynylarenes. *Synthesis* 1980, 627-630.

S3. C.-F. Lo, S.-J. Hsu, C.-L. Wang, Y.-H. Cheng, H.-P. Lu, E. W.-G. Diau, and C.-Y. Lin. Tuning Spectral and Electrochemical Properties of Porphyrin-Sensitized Solar Cells. *J. Phys.Chem. C* 2010, **114**, 12018-12023.

S4. Y.-C. Chang, C.-L. Wang, T.-Y. Pan, S.-H. Hong, C.-M. Lan, H.-H. Kuo, C.-F. Lo, H.-Y. Hsu, C.-Y. Lin, and E. W.-G. Diau. A strategy to design highly efficient porphyrin sensitizers for dye-sensitized solar cells. *Chem. Commun*. 2011, **47**, 8910-8912.

S5. C.-L. Wang, J.-Y. Hu, C.-H. Wu, H.-H. Kuo, Y.-C. Chang, Z.-J. Lan, H.-P. Wu, E. W.-G. Diau, and C.-Y. Lin. Highly efficient porphyrin-sensitized solar cell with enhanced light harvesting ability beyond 800 nm and efficiency exceeding 10%. *Energy Environ. Sci.* 2014, **7**, 1392–1396.

S6. C. Würth, M. G. González, R. Niessner, U. Panne, C. Haisch, and U. R. Genger. Determination of the absolute fluorescence quantum yield of rhodamine 6G with optical and photoacoustic methods–Providing the basis for fluorescence quantum yield standards. *Talanta* 2012, **90**, 30-37.

S7. C. Würth, M. Grabolle, J. Pauli, M. Spieles, and U.R. Genger. Comparison of methods and achievable uncertainties for the relative and absolute measurement of photoluminescence quantum yields. *Anal. Chem*. 2011, **83**, 3431-3439.

S8. U. R. Genger and P. C. DeRose. Fluorescence standards: Classification, terminology, and recommendations on their selection, use, and production (IUPAC Technical Report). *Pure Appl. Chem.*, 2010, **82**, 2315-2335.

S9. S. Fery-Forgues and D. Lavabre. Are Fluorescence Quantum Yields So Tricky to Measure? A Demonstration Using Familiar Stationery Products. *J. Chem. Edu*. 1999, **76**, 1260-1264.