Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Five-component trigonal nanoprism with six dynamic corners

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1. Synthesis

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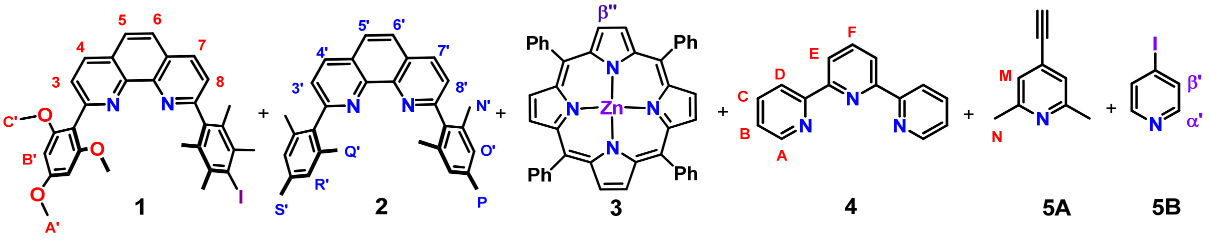
1.1 General information

All reagents were obtained from commercial suppliers and used without further purification. Technical grade solvents were distilled prior to use. Tetrahydrofuran (THF) was predried over basic alumina and then distilled over potassium. Dimethylformamide (DMF) and triethylamine (Et_3N) were distilled on calcium hydride. Diethyl ether (Et_2O) was predried over calcium hydride and then distilled over sodium.

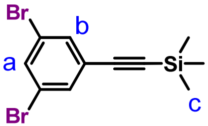
Melting points of compounds were measured using a Büchi SMP-11 instrument. ^1H, ^{13}C, and $^1H-^1H$ COSY NMR spectra were recorded on a Bruker Avance 400 at 298 K. DOSY NMR was recorded on Varian VNMR-S600 MHz. Chemical shifts refer to the residual protiated fraction of the NMR solvent ($CHCl_3$: $\delta_H = 7.26$ ppm, $\delta_C = 77.0$ ppm; $CHDCl_2$: $\delta_H = 5.32$ ppm, $\delta_C = 53.8$ ppm). Abbreviations were used in ^1H NMR assignments to describe splitting patterns (s: singlet, d: doublet, t: triplet, dd: doublet of doublet, ddd: doublet of doublet of doublet, bs: broad singlet, td: triplet of doublets, quint: quintet, m: multiplet), the value of coupling constant(s) is reported in hertz (Hz) and the number of protons are implied. Numbering of the carbon atoms is not in accordance with IUPAC nomenclature. UV-vis spectra were measured on Cary Win 50. Electrospray ionisation-mass spectra (ESI-MS) were recorded on a Thermo-Quest LCQ Deca instrument. Infrared spectra were recorded using a Perkin Elmer Spectrum-Two FT-IR spectrometer. Column chromatography was performed on silica gel 60 (60−230 mesh) or on neutral alumina (0.05−0.15 mm, Brockmann Activity 1). Thin layer chromatography (TLC) was performed using Merck silica gel (60 F254) or on neutral Al_2O_3 (150 F254) sheets. Size exclusion chromatography was performed on BioRads Biobeads-SX3 using toluene or THF as an eluents. Compounds **5A**,[1] **7**,[2] **10**,[3] **11**,[4] **13**,[5] **20**,[6] **21**[7] and **23**[8] were synthesised according to known protocols and in some cases modified procedures.



1 **2** **3** **4** **5A** **5B**

1.2 Synthesis of ligands

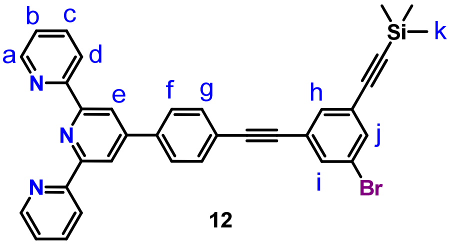
((3,5-Dibromophenyl)ethynyl)trimethylsilane (**10**)[3]



10

A mixture of 1,3,5-tribromobenzene (**9**, 5.00 g, 15.9 mmol), $PdCl_2(PPh_3)_2$ (600 mg, 860 µmol), and CuI (300 mg, 1.58 mmol) was placed in a tube. The tube was evacuated and filled with N_2 (3×), then freshly distilled Et_3N (60 mL) and benzene (20 mL) were added. Trimethylsilylacetylene (3.60 mL, 25.5 mmol) was added, and the reaction mixture was stirred at 55 °C for 36 h under inert atmosphere (TLC control). The mixture was cooled to 25 °C, and solvents were removed under reduced pressure. The residue was extracted in DCM (75 mL) and washed with deionised water (75 mL) and brine (30 mL). The organic layer was dried over anhydrous $MgSO_4$ and evaporated. The column chromatographic purification of crude product on silica gel (ϕ = 5 cm, l = 20 cm) using *n*-hexane (R_f = 0.40, SiO_2, *n*-hexane) afforded compound **10** as colourless oil (4.61 g, 12.2 mmol, 87%). IR (neat): 3073, 3056, 2958, 2897, 2108, 1761, 1761, 1736, 1577, 1554, 1540, 1418, 1359, 1262, 1102, 1078, 900, 843, 759, 669, 575 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.61 (t, ^4J = 1.8 Hz, 1H, a-H), 7.53 (d, ^4J = 1.8 Hz, 2H, b-H), 0.24 (s, 9H, c-H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 134.0, 133.9, 125.0, 121.6, 102.4, 96.6, –0.2 ppm.

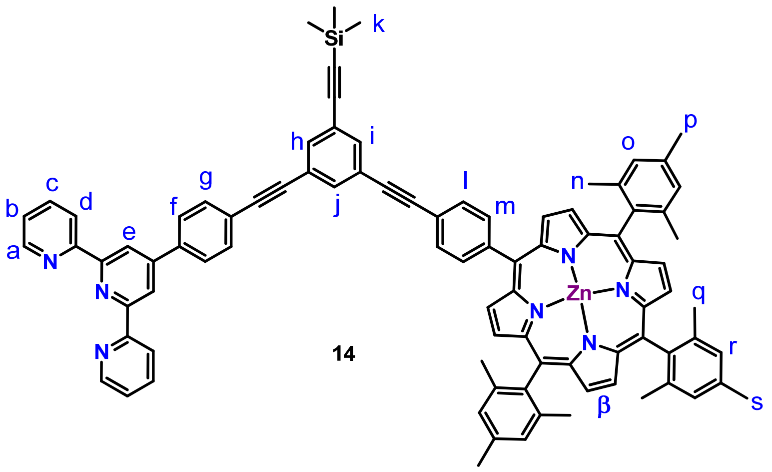
Compound **12**



12

A solution of 4'-(4-ethynylphenyl)-2,2':6',2''-terpyridine[4] (**11**, 350 mg, 1.05 mmol) and ((3,5-dibromophenyl)ethynyl)trimethylsilane[3] (**10**, 1.56 g, 4.70 mmol) in a mixture of distilled anhydrous DMF (20 mL) and Et_3N (40 mL) was subjected to freeze-pump-thaw cycles (3×). After addition of $Pd(PPh_3)_4$ (121 mg, 105 µmol), the reaction mixture was heated to 70 °C for 18 h (TLC). The reaction mixture was allowed to cool to 25 °C and the solvents were evaporated in *vacuo*. The crude product was extracted in DCM (50 mL) then washed with deionised water (60 mL × 2) and a saturated brine solution (30 mL). The organic layer was dried over anhydrous $MgSO_4$ and evaporated. The crude product was purified by column chromatography on silica gel (ϕ = 3.5 cm, l = 10 cm) using DCM as an eluent furnishing compound **12** as off white solid (599 mg, 1.02 mmol, 98%). Mp: 207 °C. IR (KBr): 3055, 3012, 2957, 2923, 2856, 2223, 2152, 1603, 1584, 1566, 1546, 1512, 1424, 1410, 1264, 1247, 1216, 1109, 1088, 1075, 1038, 989, 966, 895, 862, 840, 790 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.76 (s, 2H, e-H), 8.73 (ddd, ^3J = 4.7 Hz, ^4J = 1.8 Hz, ^5J = 1.0 Hz, 2H, a-H), 8.67 (ddd, ^3J = 7.6 Hz, ^4J = 1.2 Hz, ^5J = 1.0 Hz, 2H, d-H), 7.92 (d, ^3J = 8.4 Hz, 2H, f-H), 7.88 (td, ^3J = 7.6 Hz, ^4J = 1.8 Hz, 2H, c-H), 7.65 (d, ^3J = 8.4 Hz, 2H, g-H), 7.65 (t, ^4J = 1.4 Hz, 1H, i-H), 7.60 (t, ^4J = 1.4 Hz, 1H, h-H), 7.58 (t, ^4J = 1.4 Hz, 1H, j-H), 7.34 (ddd, ^3J = 7.6 Hz, ^3J = 4.7 Hz, ^4J = 1.2 Hz, 2H, b-H), 0.26 (s, 9H, k-H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 156.1, 149.2 (2C), 138.7, 136.9, 134.4, 134.1, 133.6, 132.3, 132.2, 127.3, 125.2, 125.1, 123.9, 123.2, 121.8, 121.4, 118.7, 102.4, 96.8, 90.9, 88.5, –0.2 ppm. ESI-MS: Calcd for $[C_{34}H_{26}BrN_3Si•H]^+$ = [**12**•H]$^+$, m/z = 586.1; Found: [**12**•H]$^+$, m/z (%) = 586.3 (100). Anal. calcd for $C_{34}H_{26}BrN_3Si$: C, 69.86; H, 4.48; N, 7.19. Found, C, 69.84; H, 4.61; N, 6.79.

Compound **14**

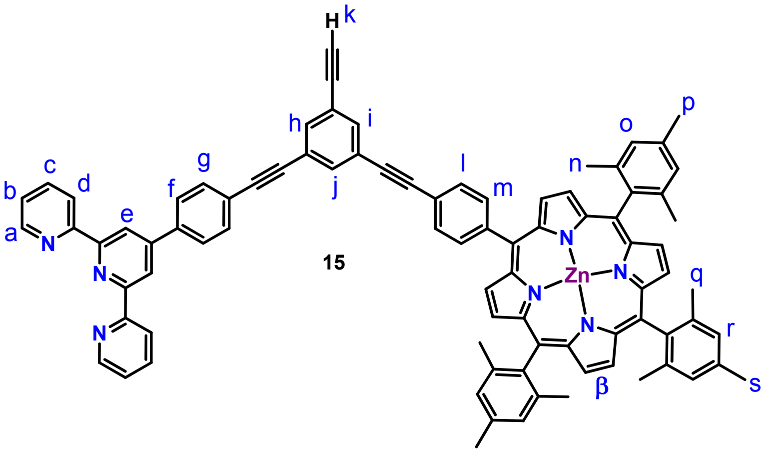


14

A solution of compounds **12** (150 mg, 257 μmol) and zinc(II)-5-(4-ethynylphenyl)-10,15,20-trimesitylporphyrin[5] (**13**, 425 mg, 513 μmol) in a mixture of freshly distilled anhydrous DMF (30 mL) and anhydrous Et_3N (20 mL) was degassed using freeze-pump-thaw cycles (3 ×). After addition of $Pd(PPh_3)_4$ (30.5 mg, 25.9 μmol), the resulting mixture was heated to 80 °C for 24 h

(TLC). Solvents were removed under reduced pressure. The crude product was extracted in DCM (20 mL) then washed successively with deionised water (30 mL × 2) and saturated brine solution (30 mL × 2). The organic layer was removed and the aqueous layer was re-extracted with DCM (30 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and evaporated in *vacuo*. The column chromatographic purification of crude product on silica gel (ϕ = 3.5 cm, l = 15 cm) using DCM provided compound **14** as purple solid (255 mg, 191 μmol, 75%). Mp > 250 °C. IR (KBr): 2955, 2915, 2854, 2204, 2152, 1806, 1605, 1582, 1567, 1523, 1510, 1477, 1465, 1440, 1385, 1334, 1249, 1203, 1062, 1038, 998, 975, 878, 850, 831, 811, 794, 739, 723, 681, 660, 619 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.89 (d, ^3J = 4.6 Hz, 2H, β-H), 8.81 (s, 2H, e-H), 8.76 (d, ^3J = 4.6 Hz, 2H, β-H), 8.74 (ddd, ^3J = 4.9 Hz, ^4J = 1.8 Hz, ^5J = 1.0 Hz, 2H, a-H), 8.71–8.73 (m, 6H, d-, β-H), 8.26 (d, ^3J = 8.2 Hz, 2H, l-H), 7.96 (d, ^3J = 8.2 Hz, 2H, m-H), 7.94 (d, ^3J = 8.4 Hz, 2H, f-H), 7.92 (td, ^3J = 7.6 Hz, ^4J = 1.8 Hz, 2H, c-H), 7.84 (t, ^4J = 1.5 Hz, 1H, j-H), 7.77 (d, ^3J = 8.4 Hz, 2H, g-H), 7.75 (t, ^4J = 1.5 Hz, 1H, h-H), 7.69 (t, ^4J = 1.5 Hz, 1H, i-H), 7.39 (ddd, ^3J = 7.6 Hz, ^3J = 4.9 Hz, ^4J = 1.0 Hz, 2H, b-H), 7.30 (s, 4H, o-H), 7.29 (s, 2H, r-H), 2.62 (2 s, 9H, p,s-H), 1.84 (s, 6H, q-H), 1.83 (s, 12H, n-H), 0.31 (s, 9H, k-H) ppm. ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 156.5, 156.3, 150.3 (2C), 150.1, 150.0, 149.5 (2C), 144.0, 139.6, 139.5 (2C), 139.3 (2C), 139.1, 137.9, 137.2, 134.9, 134.8, 134.7, 132.7, 132.2, 135.5, 131.4, 131.0, 130.3, 128.0 (2C), 127.7, 124.6, 124.5, 124.4, 124.3 (2C), 123.8, 122.1, 121.5, 119.5, 119.3, 119.2, 118.9, 103.4, 96.4, 91.1, 90.6, 89.4, 88.8, 21.8, 21.7 (2C), 21.5, –0.1 ppm. ESI-MS: Calcd for $[C_{89}H_{71}N_7SiZn\bullet H]^+$ = [**14**•H]$^+$, *m/z* = 1332.5; Found: [**14**•H]$^+$, *m/z* (%) = 1332.5 (100). Anal. calcd for $C_{89}H_{71}N_7SiZn$: C, 80.25; H, 5.37; N, 7.36. Found, C, 80.26; H, 5.30; N, 7.11.

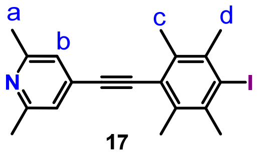
Compound **15**



15

To a solution of compound **14** (160 mg, 120 µmol) in THF–MeOH (v/v, 30 mL, 2:1) was added a solution of KOH (34.1 mg, 601 µmol in 5 mL of H_2O). The reaction mixture was stirred at 25 °C for 3 h. The solvent was evaporated in *vacuo*. The residue was extracted in DCM (20 mL) and washed with deionised water (20 mL × 3). The organic layer was dried over anhydrous $MgSO_4$. The evaporation of solvent yielded compound **15** as a purple solid (132 mg, 105 µmol, 87%). Mp > 200 °C. IR (KBr): 2956, 2914, 2853, 2731, 2222, 1689, 1605, 1581, 1566, 1478, 1466, 1441, 1410, 1383, 1333, 1298, 1263, 1226, 1062, 1038, 997, 878, 850, 810, 794, 739, 723, 680, 660, 621 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.89 (d, ^{3}J = 4.6 Hz, 2H, β-H), 8.81 (s, 2H, e-H), 8.76 (d, ^{3}J = 4.6 Hz, 2H, β-H), 8.73 (ddd, ^{3}J = 4.8 Hz, ^{4}J = 1.6 Hz, ^{5}J = 0.8 Hz, 2H, a-H), 8.69–8.72 (m, 6H, d-, β-H), 8.25 (d, ^{3}J = 8.2 Hz, 2H, l-H), 7.97 (d, ^{3}J = 8.2 Hz, 2H, m-H), 7.95 (d, ^{3}J = 8.4 Hz, 2H, f-H), 7.92 (td, ^{3}J = 7.6 Hz, ^{4}J = 1.6 Hz, 2H, c-H), 7.88 (t, ^{4}J = 1.5 Hz, 1H, j-H), 7.79 (d, ^{4}J = 1.5 Hz, 1H, h-H), 7.77 (d, ^{3}J = 8.4 Hz, 2H, g-H), 7.73 (t, ^{4}J = 1.5 Hz, 1H, i-H), 7.39 (ddd, ^{3}J = 7.6 Hz, ^{4}J = 4.8 Hz, ^{4}J = 1.0 Hz, 2H, b-H), 7.30 (s, 4H, o-H), 7.29 (s, 2H, r-H), 3.28, (s, 1H, k-H), 2.62 (2 s, 9H, p,s-H), 1.84 (s, 6H, q-H), 1.83 (s, 12H, n-H) ppm. ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 156.5, 156.3, 150.3 (2C), 150.1, 150.0, 149.6, 149.5 (2C), 144.0, 139.5 (2C), 139.3 (2C), 139.2, 137.9, 137.2, 135.1 (2C), 135.0, 134.9, 132.7, 132.2, 131.5, 131.4, 131.0, 130.3, 128.0 (2C), 127.7, 124.7, 124.5, 124.3, 123.8, 123.5, 122.0, 121.5, 119.5, 119.3, 119.2, 118.9, 91.3, 90.7, 89.3, 88.6, 82.2, 78.9, 21.8, 21.7 (2C), 21.5 ppm. ESI-MS: Calcd for $[C_{86}H_{63}N_7Zn{\bullet}H]^+$ = [**15**•H]$^+$, *m/z* = 1258.5; Found: [**15**•H]$^+$, *m/z* (%) = 1258.6 (100). Anal. calcd. for $C_{86}H_{63}N_7Zn$: C, 81.99; H, 5.04; N, 7.78. Found, C, 81.95; H, 4.93; N, 7.48.

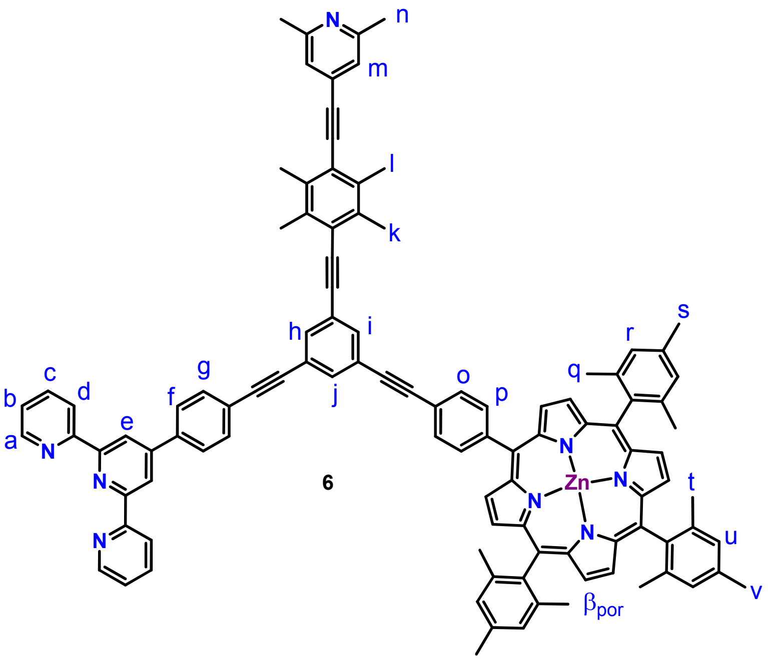
4-((4-Iodo-2,3,5,6-tetramethylphenyl)ethynyl)-2,6-dimethylpyridine (**17**)



17

A solution of 4-ethynyl-2,6-dimethylpyridine[1] (**5A,** 150 mg, 1.14 mmol) and 1,4-diiodo-2,3,5,6-tetramethylbenzene[9] (**16**, 2.20 g, 5.70 mmol) in a mixture of freshly distilled anhydrous DMF (20 mL), anhydrous C_6H_6 (20 mL) and Et_3N (20 mL) was degassed using freeze-pump-thaw cycles (3 ×). Catalyst $Pd(PPh_3)_4$ (66 mg, 57 µmol) was added and the reaction mixture was heated to 60 °C for 20 h (TLC). The reaction mixture was concentrated in *vacuo*. The residue was dissolved in DCM (30 mL), then successively washed with deionised water (30 mL × 2) and saturated brine solution (50 mL). The organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography on silica gel (ϕ = 2.5 cm, l = 25 cm) using 10% EtOAc in DCM. Compound **17** was afforded as a light gray solid (210 mg, 539 µmol, 47%). Mp: 213 °C. IR (KBr): 3049, 2990, 2922, 2861, 2735, 2401, 2232, 1699, 1594, 1543, 1524, 1446, 1411, 1343, 1225, 1213, 1155, 1013, 868, 854, 720, 605, 549 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.05 (s, 2H, b-H), 2.54 (s, 6H, c-H), 2.49 (s, 12H, a,d-H) ppm. ^{13}C NMR ($CDCl_3$:CD_2Cl_2 = 6:4, 100 MHz): δ 157.7, 137.6, 136.2, 131.8, 122.5, 121.5, 113.1, 95.3, 91.3, 27.4, 24.1, 20.0 ppm. ESI-MS: Calcd for $[C_{19}H_{20}IN\bullet H]^+$ = [**17**•H]$^+$, m/z = 390.1; Found: m/z (%) [**17**•H]$^+$ = 390.1 (100). Anal. calcd for $C_{19}H_{20}IN$: C, 58.62; H, 5.18; N, 3.60. Found: C, 58.55, H, 5.11, N, 3.52.

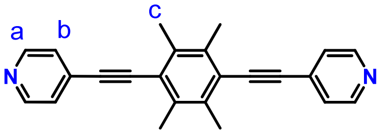
Compound **6**



6

A solution of compounds **15** (100 mg, 79.3 μmol) and 4-((4-iodo-2,3,5,6-tetramethylphenyl)ethynyl)-2,6-dimethylpyridine (**17**, 124 mg, 319 μmol) in a mixture of freshly distilled anhydrous DMF (25 mL) and anhydrous Et_3N (15 mL) was degassed using freeze-pump-thaw cycles (3 ×). Catalyst $Pd(PPh_3)_4$ (9.50 mg, 7.93 μmol) wad added under inert atmosphere, then the reaction mixture was heated to 80 °C for 24 h (TLC). The solvent was evaporated under reduced pressure. The residue was dissolved in DCM (25 mL), then subsequently washed with deionised water (30 mL × 2) and a saturated brine solution (15 mL × 2). The organic layer was dried over anhydrous $MgSO_4$ and evaporated in *vacuo*. The purple residue was purified by column chromatography on silica gel (ϕ = 3 cm, l = 15 cm) using 20% EtOAc in DCM to yield compound **6** as a purple solid. The crude product was further subjected to size-exclusion chromatography (ϕ = 2 cm, l = 55 cm) on Bio-beads-SX3 using toluene-DCM (v/v, 9:1) as an eluent. All fractions were analysed by ^{1}H NMR. Pure fractions were combined, and the solvent was evaporated in *vacuo* to furnish the title compound **6** as a purple solid. (39.0 mg, 25.6 μmol, 32%). Mp >250 °C. IR (KBr): 2942, 2916, 2872, 2214, 1601, 1581, 1566, 1550, 1521, 1477, 1466, 1440, 1410, 1383, 1332, 1202, 1015, 994, 871, 851, 830, 793, 738, 722 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.87 (d, ^3J = 4.6 Hz, 2H, β_{por}-H), 8.81 (s, 2H, e-H), 8.72–8.75 (m, 4H, a-, β_{por}-H), 8.69 (dt, ^3J = 7.5 Hz, ^4J = 1.2 Hz, 2H, d-H), 8.68 (s, 4H, β_{por}-H), 8.24 (d, ^3J = 8.2 Hz, 2H, p-H), 7.98 (d, ^{3}J = 8.2 Hz, 2H, o-H), 7.97 (d, ^{3}J = 8.5 Hz, 2H, f-H), 7.92 (td, ^{3}J = 7.5 Hz, ^{4}J = 1.2 Hz, 2H, c-H), 7.87 (2 t, ^{4}J = 1.2 Hz, 2H, j-, h-H), 7.81 (t, ^{4}J = 1.2 Hz, 1H, i-H), 7.79 (d, ^{3}J = 8.5 Hz, 2H, g-H), 7.39 (ddd, ^{3}J = 7.5 Hz, ^{3}J = 4.8 Hz, ^{4}J = 1.2 Hz, 2H, b-H), 7.29 (s, 4H, r-H), 7.28 (s, 2H, u-H), 7.11 (s, 2H, m-H), 2.62 (9H, s-,v-H), 2.59 (s, 6H, l-H), 2.54 (s, 6H, k-H), 2.50 (s, 6H, n-H), 1.83 (s, 6H, t-H), 1.82 (s, 12H, q-H) ppm. ^{13}C NMR ($CDCl_3$:CD_2Cl_2 = 4:6, 100 MHz): δ 157.7, 155.9, 155.8, 149.7, 149.6, 149.5, 149.3, 149.0 (2C), 143.5, 138.9 (3C), 138.8 (2C), 138.5, 137.3, 136.7, 136.0, 135.9, 134.3, 133.9, 133.8, 133.7, 132.1, 131.7, 131.5, 130.9, 130.7, 130.4, 129.7, 127.4 (2C), 127.2, 124.5, 124.1, 123.9, 123.8, 123.3 (2C), 122.6, 121.5, 121.4, 121.0, 118.7, 118.6, 118.4 (2C), 96.6, 95.8, 91.6, 90.7, 90.1, 89.6, 89.0, 88.4, 24.0, 21.4, 21.3 (2C), 21.1, 18.2, 18.1 ppm. ESI-MS: Calcd for $[C_{105}H_{82}N_8Zn\bullet H]^+$ = $[\mathbf{6}\bullet H]^+$, *m/z* = 1521.7; Found: $[\mathbf{6}\bullet H]^+$, *m/z* (%) = 1521.6 (100). Calcd for $[C_{105}H_{82}N_8Zn\bullet 2H]^{2+}$ = $[\mathbf{6}\bullet 2H]^{2+}$, *m/z* = 761.8; Found: $[\mathbf{6}\bullet 2H]^{2+}$, *m/z* (%) = 761.7 (32). Anal. calcd. for $C_{105}H_{82}N_8Zn\bullet 1/2CH_2Cl_2$: Found, C, 81.03; H, 5.35; N, 7.17; Zn, 4.18. Found: C, 81.30; H, 5.45; N, 7.30.

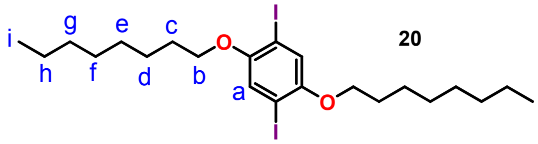
Compound **7**[2]



7

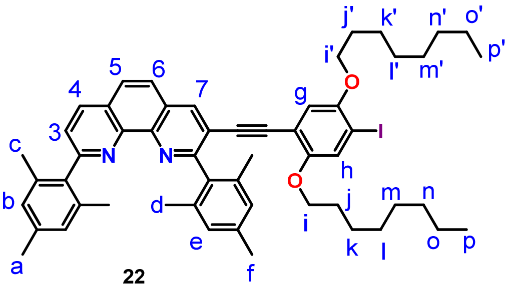
1,4-Diiodo-2,3,5,6-tetramethylbenzene (**16**, 500 mg, 1.30 mmol), $PdCl_2(PPh_3)_2$ (45.0 mg, 389 µmol) and CuI (75.0 mg, 394 µmol) were placed in a Schlenk tube. The tube was evacuated and filled with N_2 (3×). Then a pre-degassed solution of 4-ethynylpyridine hydrochloride (**18**, 900 mg, 6.50 mmol) in a mixture of anhydrous C_6H_6 (40 mL) and anhydrous Et_2NH (40 mL) was added under N_2. The reaction mixture was heated to 80 °C for 18 h (TLC). After evaporation of solvents, the greenish brown residue was extracted in DCM (30 mL). The organic layer was subsequently washed with deionised water (25 mL × 2) and saturated brine solution (50 mL). The combined organic layers were removed and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the crude product was subjected to chromatographic purification on silica gel (ϕ = 3.5 cm, l = 15 cm) using 10% EtOAc in DCM yielding **7** as yellow solid (228 mg, 550 µmol, 89%). Mp: 239 °C. IR (KBr): 3069, 3025, 2924, 2863, 2214, 2190, 1954, 1688, 1586, 1532, 1491, 1417, 1407, 1377, 1320, 1263, 1218, 1204, 1078, 1012, 987, 856, 819, 713, 665, 648, 557, 540 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.62 (d, ^3J = 4.4 Hz, 4H, a-H), 7.40 (d, ^3J = 4.4 Hz, 4H, b-H), 2.50 (s, 12H, c-H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz, 298 K): δ 149.8, 136.3, 131.7, 125.3, 123.1, 95.6, 92.9, 18.4 ppm.

1,4-Diiodo-2,5-bis(octyloxy)benzene (**20**)[6]



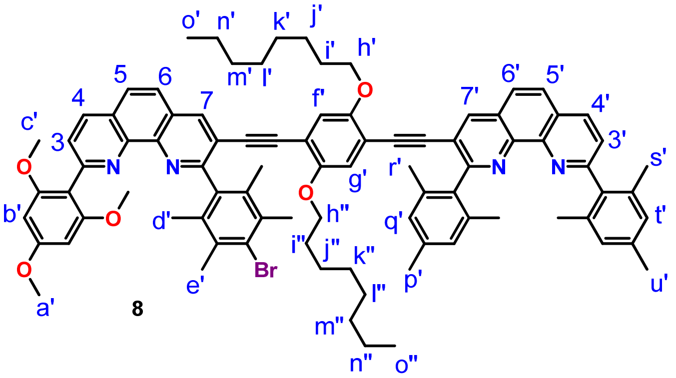
ICl (7.96 g, 49.0 mmol) was added dropwise to 100 mL of precooled MeOH (< 10 °C). Thereafter, 1,4-bis(octyloxy)benzene[6] (**19**, 4.10 g, 12.3 mmol) was added below 10 °C and the reaction mixture was heated to reflux for 3 h (TLC). The resultant mixture was allowed to cool to 25 °C and filtered. The solid was washed with cold methanol (25 mL × 4) and dried under vacuum to furnish **20** as a white powder (6.25 g, 10.7 mmol, 87%). Mp: 57 °C. IR (KBr): 2939, 2918, 2862, 2847, 1672, 1486, 1464, 1446, 1388, 1351, 1263, 1234, 1143, 1068, 1050, 1018, 1012, 997, 909, 900, 846, 834, 786, 746, 721 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.17 (s, 2H, a-H), 3.92 (t, ^3J = 6.4 Hz, 4H, b-H), 1.79 (tt, ^3J = 6.4 Hz, ^3J = 6.8 Hz, 4H, c-H), 1.49 (quint, ^3J = 6.8 Hz, 4H, d-H), 1.32 (m, 16H, e-, f-, g-, h-H), 0.89 (t, ^3J = 6.9 Hz, 6H, i-H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 152.9, 122.8, 86.3, 70.4, 31.8, 29.2 (2C), 29.1, 26.0, 22.7, 14.1 ppm.

3-((4-Iodo-2,5-bis(octyloxy)phenyl)ethynyl)-2,9-dimesityl-1,10-phenanthroline (**22**)



3-Ethynyl-2,9-dimesityl-1,10-phenanthroline[7] (**21**, 300 mg, 681 µmol) and 1,4-diiodo-2,5-bis(octyloxy)benzene[6] (**20**, 798 mg, 1.36 mmol) were placed in a Schlenk tube. Freshly distilled anhydrous DMF (30 mL) and Et$_3$N (10 mL) were added and the mixture was subjected to freeze-pump-thaw cycles (3×). After addition of Pd(PPh$_3$)$_4$ (79.0 mg, 68.1 µmol), the reaction mixture was heated to 70 °C for 16 h. The solvents were removed under reduced pressure and the residue was extracted in DCM. The crude product was purified by column chromatography on silica gel using 7% EtOAc in *n*-hexane affording compound **22** as light yellow solid (475 mg, 528 μmol, 77%). Mp: 140 °C. IR (KBr): 2924, 2853, 2202, 1614, 1579, 1536, 1485, 1461, 1410, 1377, 1355, 1266, 1211, 1106, 1065, 1027, 964, 925, 887, 860, 847, 775, 719, 635, 615 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.47 (s, 1H, 7-H), 8.32 (d, ^{3}J = 8.2 Hz, 1H, 4-H), 7.91 (d, ^{3}J = 8.8 Hz, 1H, 5-H), 7.86 (d, ^{3}J = 8.8 Hz, 1H, 6-H), 7.56 (d, ^{3}J = 8.2 Hz, 1H, 3-H), 7.28 (s, 1H, g-H), 6.97 (s, 2H, e-H), 6.95 (s, 2H, b-H), 6.33 (s, 1H, h-H), 3.92 (t, ^{3}J = 6.8 Hz, 2H, i-H), 3.85 (t, ^{3}J = 6.4 Hz, 2H, i'-H), 2.34 (s, 3H, f-H), 2.34 (s, 3H, a-H), 2.05 (s, 6H, d-H), 2.04 (s, 6H, c-H), 1.78 (2 x quint, ^{3}J = 6.8 Hz, ^{3}J = 6.4 Hz, 4H, j-, j'-H), 1.51 (2 x quint, ^{3}J = 6.8 Hz, ^{3}J = 6.4 Hz, 4H, k-, k'-H), 1.29–1.42 (m, 16H, l-, l'-, m-, m'-, n-, n'-, o-, o'-H), 0.90 (t, ^{3}J = 7.0 Hz, 3H, p-H), 0.86 (t, ^{3}J = 7.2 Hz, 3H, p'-H) ppm. ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 161.8, 160.9, 154.2, 152.1, 146.4, 145.4, 138.8, 138.4, 137.8, 137.6 (2C), 136.4 (2C), 136.1, 128.6 (2C), 128.2, 127.9, 127.3 (2C), 126.0, 125.1, 124.3, 120.1, 116.5, 113.3, 91.6, 88.3, 70.3, 70.2, 32.2 (2C), 29.8 (2C), 29.7, 29.6 (2C), 29.5, 26.4, 26.5, 23.1, 21.4, 21.2, 20.4 (2C), 20.1, 14.3, 14.2 ppm. ESI-MS: Calcd for $[C_{54}H_{63}IN_2O_2\bullet H]^+$ = [**22**•H]$^+$, *m/z* = 899.4; Found: [**22**•H]$^+$, *m/z* (%) = 899.4 (100). Anal. calcd for $C_{54}H_{63}IN_2O_2$: C, 72.14; H, 7.06; N, 3.12. Found, C, 72.38; H, 6.97; N, 3.07.

2-(4-Bromo-2,3,5,6-tetramethylphenyl)-3-((4-((2,9-dimesityl-1,10-phenanthrolin-3 yl)ethynyl)-2,5-bis(octyloxy)phenyl)ethynyl)-9-(2,4,6-trimethoxyphenyl)-1,10-phenanthroline (**8**)

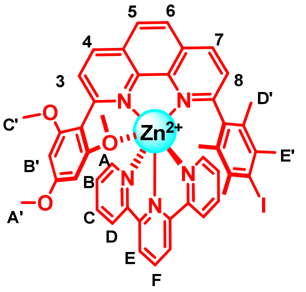


8

2-(4-Bromo-2,3,5,6-tetramethylphenyl)-3-ethynyl-9-(2,4,6-trimethoxyphenyl)-[1,10]-phenanthroline[8] (**23**, 101 mg, 112 μmol) and 3-((4-iodo-2,5-bis(octyloxy)phenyl)ethynyl)-2,9-dimesityl-1,10-phenanthroline (**22**, 50.0 mg, 85.9 μmol) in a mixture of anhydrous Et_3N (30 mL) and anhydrous DMF (30 mL) were degassed using freeze-pump-thaw cycles (3 ×). Pd(PPh$_3$)$_4$ (10.0 mg, 8.60 μmol) was added and the reaction mixture was stirred at 55 °C for 19 h (TLC). The solvent was evaporated in *vacuo* and purified by column chromatography on silica gel (ϕ = 2.5 cm, l = 15 cm) using 20% EtOAc in DCM. The pure fractions were combined and evaporated to furnish the title compound **8** as yellow solid (131 mg, 96.8 μmol, 86%). Mp: 249 °C. IR (KBr): 2923, 2854, 2208, 1609, 1584, 1500, 1457, 1411, 1383, 1355, 1334, 1274, 1213, 1205, 1154, 1127, 1104, 1061, 1026, 989, 948, 885, 865, 809, 825, 636, 610 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.46 (2 s, 2H, 7,7'-H), 8.32 (d, ^3J = 8.2 Hz, 1H, 4'-H), 8.27 (d, ^3J = 8.2 Hz, 1H, 4-H), 7.92 (d, ^3J = 8.8 Hz, 1H, 6'-H), 7.90 (d, ^3J = 8.8 Hz, 1H, 6-H), 7.86 (d, ^3J = 8.8 Hz, 1H, 5'-H), 7.85 (d, ^3J = 8.8 Hz, 1H, 5-H), 7.58 (d, ^3J = 8.2 Hz, 1H, 3'-H), 7.56 (d, ^3J = 8.1 Hz, 1H, 3-H), 6.97 (s, 2H, q'-H), 6.95 (s, 2H, t'-H), 6.37 (s, 1H, g'-H), 6.25 (s, 2H, b'-H), 6.19 (s, 1H, f'-H), 3.87 (s, 3H, a'-H), 3.85 (t, ^3J = 6.8 Hz, 2H, h''-H), 3.82 (t, ^3J = 6.8 Hz, 2H, h'-H), 3.69 (s, 6H, c'-H), 2.47 (s, 6H, d'-H), 2.35 (s, 3H, p'-H), 2.33 (s, 3H, u'-H), 2.04 (2 s, 12H, r',s'-H), 2.00 (s, 6H, e'-H), 1.76–1.87 (2 x quint, ^3J = 6.8 Hz, ^3J = 6.8 Hz, 4H, i'-, i''-H), 1.51–1.61 (m, 4H, j'-, j''-H), 1.26–1.48 (m, 16H, k'-, l'-, m'-, n'-, k''-, l''-, m''-, n''-H), 0.88 (t, ^3J = 6.8 Hz, 3H, o''-H), 0.87 (t, ^3J = 6.8 Hz, 3H, o'-H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 162.5, 162.0 161.9, 160.9, 159.3, 156.1, 153.5, 153.3, 146.4, 146.3, 145.4, 139.9, 138.8, 138.7, 138.4, 137.8, 137.6, 136.4 (2C), 136.1, 135.8, 134.1, 133.9, 129.0, 128.6, 128.3, 128.2, 127.9, 127.6, 127.3 (2C), 127.0, 126.0, 125.9, 125.1, 120.2, 120.1, 117.6, 117.0, 114.1, 114.0, 113.0, 92.6, 92.5, 92.2, 91.9, 91.2, 69.7, 56.3, 55.8, 32.3 (2C), 29.8 (4C), 29.6, 26.6, 26.5, 23.1, 21.4, 21.2, 21.1 (2C), 20.4 (2C), 20.1 (2C), 18.6, 14.3 ppm. ESI-MS: Calcd for [$C_{87}H_{91}BrN_4O_5$•H]$^+$ = [**8**•H]$^+$, *m/z* = 1353.6; Found [**8**•H]$^+$, *m/z* (%) = 1353.6 (28). Calcd for [$C_{87}H_{91}BrN_4O_5$•2H]$^+$ = [**8**•2H]$^{2+}$, *m/z* = 677.8; Found: [**8**•2H]$^{2+}$, *m/z* (%) = 677.8 (100). Anal. calcd for $C_{87}H_{91}BrN_4O_5$: C, 77.25; H, 6.78; N, 4.14. Found: C, 77.33; H, 6.76; N, 4.04.

1.3 Synthesis of metal complexes

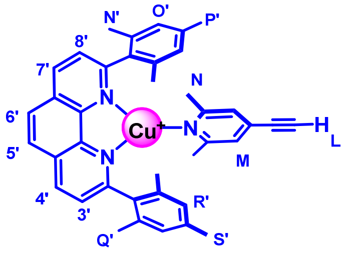
Synthesis of complex **C1** = [Zn(**1**)(**4**)]$(OTf)_2$



C1 = [Zn(**1**)(**4**)]$(OTf)_2$

$Zn(OTf)_2$ (910 µg, 2.50 µmol) was added to solution of 2-(4-iodo-2,3,5,6-tetramethylphenyl)-9-(2,4,6-trimethoxyphenyl)-1,10-phenanthroline (**1**, 1.51 mg, 2.50 µmol) in a mixture of CD_2Cl_2:CD_3CN (9:1) that was sonicated at 40 °C for 5 min. Thereafter, 2,2′:6′,2″-terpyridine (**4**, 583 µg, 2.50 µmol) was added. The ^1H NMR was measured without further purification. Yield: Quantitative. Mp: 163 °C. IR (KBr): 3077, 2942, 1605, 1583, 1454, 1417, 1341, 1275, 1224, 1206, 1156, 1128, 1029, 871, 779, 637, 572, 516 cm^{-1}. ^1H NMR (CD_2Cl_2:CD_3CN = 9:1, 400 MHz): δ 9.00 (d, ^3J = 8.3 Hz, 1H, 7-H), 8.96 (d, ^3J = 8.4 Hz, 1H, 4-H), 8.63 (t, ^3J = 7.4 Hz, 1H, F-H), 8.46–8.54 (m, 6H, D-, E-, 5-, 6-H), 8.22 (td, ^3J = 7.6 Hz, ^4J = 1.5 Hz, 2H, C-H), 8.10 (d, ^3J = 8.3 Hz, 1H, 8-H), 7.88 (d, ^3J = 8.4 Hz, 1H, 3-H), 7.67 (ddd, ^3J = 5.2 Hz, ^4J = 1.5 Hz, ^5J = 0.9 Hz, 2H, A-H), 7.55 (ddd, ^3J = 7.6 Hz, ^3J = 5.2 Hz, ^4J = 0.9 Hz, 2H, B-H), 5.61 (s, 2H, B'-H), 3.52 (s, 3H, A'-H), 2.95 (s, 6H, C'-H), 1.97 (s, 6H, D'-H), 0.83 (s, 6H, E'-H) ppm. ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 164.0, 161.1, 158.4, 157.5, 149.0, 147.3, 146.8, 145.6, 142.9, 142.7, 141.9, 141.3, 141.0, 138.6, 137.9, 131.5, 130.9, 129.3 (2C), 128.5, 128.3, 128.1, 127.5, 123.3, 123.2, 114.5, 107.7, 90.7, 56.0, 55.6, 27.2, 18.7 ppm. ESI-MS: Calcd for [Zn(**1**)(**4**)–OTf]$^+$ m/z = 1050.1 and [Zn(**1**)(**4**)–2OTf]$^+$ m/z = 450.6. Found: [Zn(**1**)(**4**)–OTf]$^+$ m/z (%) = 1049.8 (100) and [Zn(**1**)(**4**)–2OTf]$^{2+}$ m/z (%) = 450.9 (22). Anal. calcd for $C_{48}H_{40}F_6IN_5O_9S_2Zn{\bullet}1/10\ CH_2Cl_2$: C, 47.75; H, 3.35; N, 5.79, S, 5.30. Found: C, 47.46; H, 3.02; N, 5.57, S, 5.30.

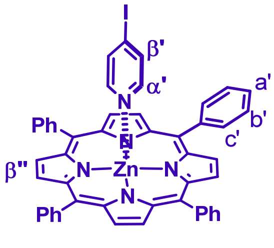
Synthesis of complex **C2** = [Cu(**2**)(**5A**)]B(C_6F_5)$_4$



C2 =[Cu(**2**)(**5A**)]B(C_6F_5)$_4$

2,9-Dimesityl-1,10-phenanthroline (**2**, 538 µg, 1.29 µmol), 4-ethynyl-2,6-dimethylpyridine (**5A**, 169 µg, 1.29 µmol) and [Cu(CH_3CN)$_4$]B(C_6F_5)$_4$ (1.17 mg, 1.29 µmol) were placed in an NMR tube and dissolved in CD_2Cl_2. The resultant complex **C2** was analysed by ^{1}H NMR spectroscopy. Yield: Quantitative. Mp: 219 °C. IR (KBr): 2919, 2859, 2116, 1615, 1584, 1552, 1509, 1481, 1439, 1379, 1362, 1146, 1026, 869, 840, 557 cm^{-1}. ^{1}H NMR (CD_2Cl_2 : CD_3CN = 9:1, 400 MHz): δ 8.60 (d, ^3J = 8.3 Hz, 2H, 4'-, 7'-H), 8.08 (s, 2H, 5'-, 6'-H), 7.81 (d, ^3J = 8.3 Hz, 2H, 3'-, 8'-H), 7.01 (s, 2H, M-H), 6.95 (s, 4H, O'-, R'-H), 3.31 (s, 1H, L-H), 2.40 (s, 6H, S'-, P'-H), 2.32 (s, 6H, N-H), 1.94 (s, 12H, N'-, Q'-H) ppm. ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 161.2, 156.7, 141.4, 139.9, 139.7, 136.8, 135.4, 131.9, 128.5, 128.3, 127.5, 127.2, 124.3, 116.9 ($CH_3\underline{CN}$), 84.1, 80.4, 25.9, 21.1, 20.5, 2.1 ($\underline{CH_3}CN$) ppm. ESI-MS: Calcd for [Cu(**2**)(**5A**)–B(C_6F_5)$_4$]$^+$ *m/z* = 610.2; Found: [Cu(**2**)(**5A**)–B(C_6F_5)$_4$]$^+$, *m/z* (%) = 610.4 (100). Anal. calcd for $C_{63}H_{37}BCuF_{20}N_3$•2/5CH_2Cl_2: C, 59.89; H, 4.82; N, 5.32. Found: C, 60.15; H, 4.52; N, 5.41.

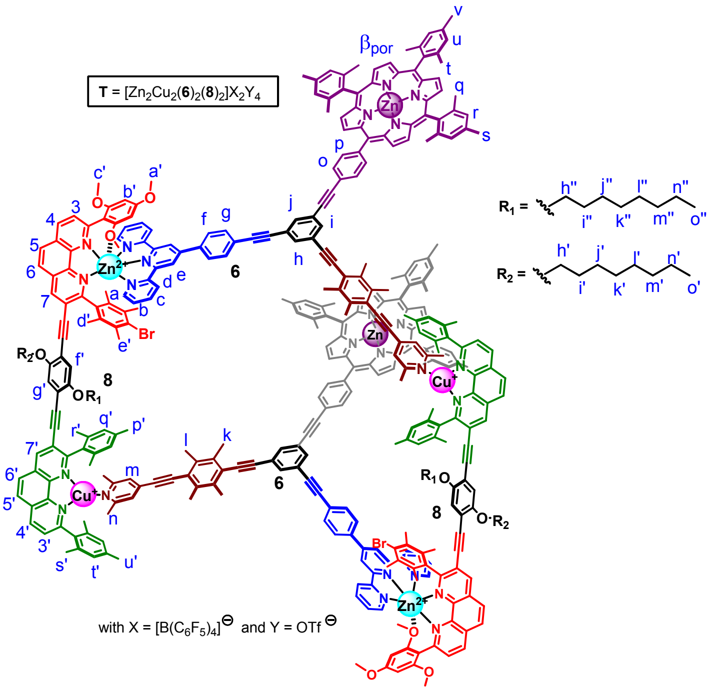
Synthesis of complex **C3** = [(**3**)(**5B**)]



C3 = [(**3**)(**5B**)]

Zinc(II)-5,10,15,20-tetraphenylporphyrin (**3**, 873 µg, 1.29 µmol) and 4-iodopyridine (**5B**, 264 µg, 1.29 µmol) were placed in an NMR tube and dissolved in CD_2Cl_2. The resultant complex **C3** was directly analysed by ^{1}H NMR spectroscopy. Yield: Quantitative. Mp: 190 °C (decomposition). IR (KBr): 3065, 2998, 1593, 1575, 1483, 1476, 1406, 1336, 1215, 1173, 1065, 1000, 992, 797, 746, 717, 701, 659, 673 cm^{-1}. ^{1}H NMR (CD_2Cl_2 : CD_3CN = 9:1, 400 MHz): δ 8.84 (s, 8H, β''-H), 8.16–8.18 (m, 8H, c'-H), 7.76–7.70 (m, 12H, a'-, b'-H), 6.64 (bs, 2H, β'-H), 4.52 (bs, 2H, α'-H) ppm. ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 150.4, 145.0, 143.6, 134.9, 132.5, 132.1, 127.7, 126.8, 121.2, 106.1 ppm. Anal. calcd for $C_{49}H_{32}IN_5Zn$:C, 66.64; H, 3.65; N, 7.93. Found: C, 66.83; H, 3.49; N, 7.62.

Synthesis of tweezer complex **T**

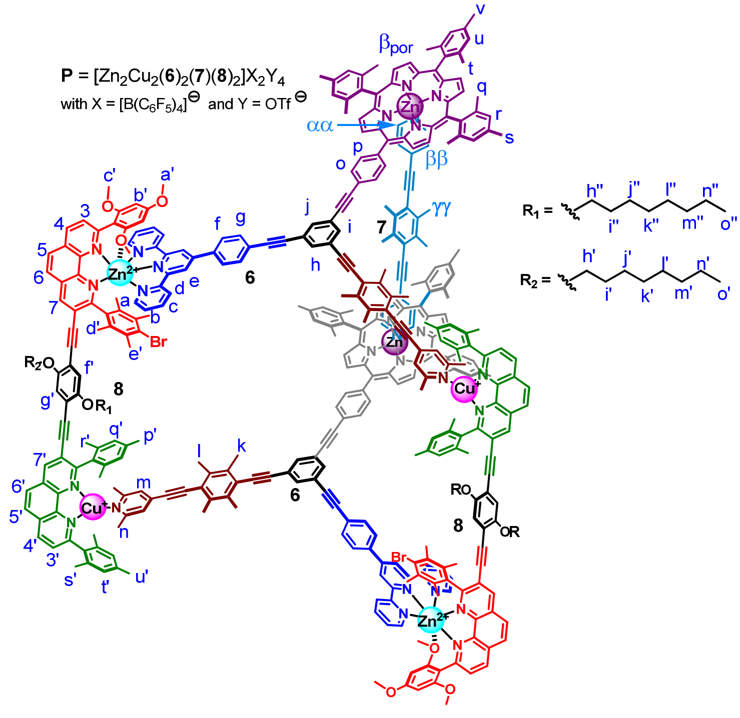


In an oven-dried 50 mL flask, 2-(4-bromo-2,3,5,6-tetramethylphenyl)-3-((4-((2,9-dimesityl-1,10-phenanthrolin-3yl)ethynyl)-2,5-bis(octyloxy)phenyl)ethynyl)-9-(2,4,6-trimethoxyphenyl)-1,10 phenanthroline (**8**, 1.38 mg, 1.02 µmol), ligand **6** (1.55 mg, 1.02 µmol), $Zn(OTf)_2$ (370 µg, 1.02 µmol) and $[Cu(CH_3CN)_4B(C_6F_5)_4]$ (924 µg, 1.02 µmol) were refluxed in a mixture of CH_3CN-CH_2Cl_2 (3:1, v/v, 20 mL) for 3.5 h. The reaction was cooled to 25 °C and evaporated under reduced pressure. The resultant complex **T** was subjected to characterisation without further purification. Yield: 95%.

^{1}H NMR (CD_2Cl_2:CD_3CN = 9:1, 400 MHz): δ 8.96 (s, 2H, 7-H), 8.94 (d, ^{3}J = 8.5 Hz, 2H, 4-H), 8.78–8.85 (m, 8H, d-, β$_{Por}$-H), 8.76 (s, 4H, e-H), 8.70 (d, ^{3}J = 4.6 Hz, 4H, β$_{Por}$-H), 8.66 (s, 2H, 7'-

H), 8.63 (s, 8H, β_{Por}-H), 8.59 (d, ^{3}J = 8.4 Hz, 2H, 4'-H), 8.43 (d, ^{3}J = 9.1 Hz, 4H, p-H), 8.35 (d, ^{3}J = 9.1 Hz, 4H, o-H), 8.32 (td, ^{3}J = 7.6 Hz, ^{4}J = 1.5 Hz, 4H, c-H), 8.27 (d, ^{3}J = 8.8 Hz, 4H, f-H), 8.20 (d, ^{3}J = 8.8 Hz, 2H, 5/6-H), 8.07 (d, ^{3}J = 8.8 Hz, 2H, 5'/6'-H), 8.07 (d, ^{3}J = 8.5 Hz, 2H, 3-H), 8.00 (d, ^{3}J = 8.8 Hz, 2H, 6'/5'-H), 7.95 (d, ^{3}J = 8.8 Hz, 4H, g-H), 7.93 (d, ^{3}J = 8.8 Hz, 2H, 6/5-H), 7.88 (2t, ^{3}J = 1.5 Hz, ^{3}J = 1.5 Hz, 4H, h-, j-H), 7.90 (t, ^{3}J = 1.5 Hz, 2H, i-H), 7.81 (d, ^{3}J = 8.4 Hz, 2H, 3'-H), 7.66 (ddd, ^{3}J = 5.3 Hz, ^{4}J = 1.5 Hz, 4H, a-H), 7.52 (ddd, ^{3}J = 7.6 Hz, ^{3}J = 5.3 Hz, ^{4}J = 0.8 Hz, 4H, b-H), 7.25 (2s, 12H, r-, u-H), 7.14 (s, 4H, m-H), 6.87 (s, 4H, q'-H), 6.80 (s, 4H, t'-H), 6.26 (s, 2H, g'-H), 6.24 (s, 2H, f'-H), 5.60 (s, 4H, b'-H), 3.64 (t, ^{3}J = 6.3 Hz, 4H, h''-H), 3.58 (t, ^{3}J = 6.7 Hz, 4H, h'-H), 3.46 (s, 6H, a'-H), 2.93 (s, 12H, c'-H), 2.59 (s, 6H, v-H), 2.58 (s, 12H, s-H), 2.52 (s, 12H, k-H), 2.42 (s, 12H, l-H), 2.41 (s, 12H, n-H), 2.24 (s, 6H, p'-H), 2.21 (s, 6H, u'-H), 1.92 (s, 12H, e'-H), 1.91 (2s, 24H, r'-, s'-H), 1.77–1.81 (2s, 36H, q-, t-H), 1.63–1.66 (m, 4H, i'-H), 1.35–1.45 (m, 20H, i''-, j''-, k'-, j'-, k''-H), 1.20–1.27 (m, 24H, l'-, m'-, n'-, l''-, m''-, n''-H), 0.94 (s, 12H, d'-H), 0.78–0.85 (m, 12H, o'-, o''-H) ppm. ESI-MS: Calcd for $[ZnCu(\mathbf{6})(\mathbf{8})]^{3+}$ *m/z* = 1001.4; Found: $[ZnCu(\mathbf{6})(\mathbf{8})]^{3+}$ *m/z* (%) = 1001.6 (97). Calcd for $[Zn_2Cu_2(\mathbf{6})_2(\mathbf{8})_2(OTf)]^{5+}$ *m/z* = 1231.2; Found; $[Zn_2Cu_2(\mathbf{6})_2(\mathbf{8})_2(OTf)]^{5+}$ *m/z* (%) = 1231.3 (100). Calcd for $[Zn_2Cu_2(\mathbf{6})_2(\mathbf{8})_2(OTf)_2]^{4+}$ *m/z* = 1576.3; Found: $[Zn_2Cu_2(\mathbf{6})_2(\mathbf{8})_2(OTf)_2]^{4+}$ *m/z* (%) = 1576.2 (45).

Synthesis of complex prism **P**



In an oven-dried 50 mL flask, 2-(4-bromo-2,3,5,6-tetramethylphenyl)-3-((4-((2,9-dimesityl-1,10-phenanthrolin-3yl)ethynyl)-2,5-bis(octyloxy)phenyl)ethynyl)-9-(2,4,6-trimethoxyphenyl)-1,10 phenanthroline (**8**, 863 μg, 0.639 μmol), tri-substituted ligand **6** (971 μg, 0.639 μmol), $Zn(OTf)_2$ (232 μg, 0.639 μmol), $[Cu(CH_3CN)_4B(C_6F_5)_4]$ (579 μg, 0.639 μmol) and bipyridine ligand **7** (107 μg, 0.319 μmol) were refluxed in a mixture of CH_3CN-CH_2Cl_2 (3:1, v/v, 20 mL). The reaction was cooled to 25 °C and evaporated under reduced pressure. The resultant complex **P** was subjected to characterisation without further purification. Yield: 95%. IR (KBr): 2922, 2854, 2201, 1641, 1604, 1512, 1463, 1375, 1336, 1275, 1257, 1223, 1205, 1158, 1084, 1030, 995, 851, 637 cm^{-1}. ^{1}H NMR (CD_2Cl_2:CD_3CN = 9:1, 400 MHz): δ 9.00 (s, 2H, 7-H), 8.98 (d, ^{3}J = 8.4 Hz, 2H, 4-H), 8.74–8.84 (m, 8H, d-, β_{Por}-H), 8.76 (s, 4H, e-H), 8.68 (d, ^{3}J = 4.6 Hz, 4H, β_{Por}-H), 8.64 (s, 2H, 7'-H), 8.62 (s, 8H, β_{Por}-H), 8.52 (d, ^{3}J = 8.2 Hz, 2H, 4'-H), 8.48 (d, ^{3}J = 9.0 Hz, 4H, p-H), 8.38 (d, ^{3}J = 9.0 Hz, 4H, o-H), 8.32 (td, ^{3}J = 7.6 Hz, ^{4}J = 1.6 Hz, 4H, c-H), 8.23–8.28 (m, 6H, 5/6-, f-H), 8.09 (d, ^{3}J = 8.4 Hz, 2H, 3-H), 8.08 (d, ^{3}J = 8.8 Hz, 2H, 5'/6'-H), 8.00 (d, ^{3}J = 8.8 Hz, 2H, 6'/5'-H), 7.93–7.95 (m, 6H, 6/5-, g-H), 7.90 (t, ^{3}J = 1.6 Hz, 2H, h-H), 7.89 (t, ^{3}J = 1.6 Hz, 2H, j-H), 7.84 (t, ^{3}J = 1.6 Hz, 2H, i-H), 7.80 (d, ^{3}J = 8.2 Hz, 2H, 3'-H), 7.67 (ddd, ^{3}J = 5.3 Hz, ^{4}J = 1.6 Hz, 4H, a-H), 7.53 (ddd, ^{3}J = 7.6 Hz, ^{3}J = 5.3 Hz, ^{4}J = 0.8 Hz, 4H, b-H), 7.27 (s, 8H, r-H), 7.27 (s, 4H, u-H), 7.11 (s, 4H, m-H), 6.90 (s, 4H, q'-H), 6.86 (s, 4H, t'-H), 6.31 (s, 2H, g'-H), 6.25 (s, 2H, f'-H), 6.14 (bs, 4H, ββ-H), 5.61 (s, 4H, b'-H), 3.67 (t, ^{3}J = 6.8 Hz, 4H, h''-H), 3.65 (bs, 4H, αα-H), 3.60 (t, ^{3}J = 6.8 Hz, 4H, h'-H), 3.48 (s, 6H, a'-H), 2.94 (s, 12H, c'-H), 2.595 (s, 6H, v-H), 2.591 (s, 12H, s-H), 2.586 (s, 12H, k-H), 2.53 (s, 12H, l-H), 2.47 (s, 12H, n-H), 2.29 (s, 6H, p'-H), 2.25 (s, 6H, u'-H), 2.05 (s, 12H, γγ-H), 1.91 (s, 12H, e'-H), 1.89 (2s, 24H, r'-, s'-H), 1.77–1.81 (m, 44H, i'-, i''-, q-, t-H), 1.63–1.76 (m, 8H, j'-, j''-H), 1.37–1.46 (m, 8H, k'-, k''-H), 1.22–1.35 (m, 24H, l'-, m'-, n'-, l''-, m''-, n''-H), 0.96 (s, 12H, d'-H), 0.79–0.84 (m, 12H, o'-, o''-H) ppm. ESI-MS: Calcd for $[ZnCu(\mathbf{6})(\mathbf{8})]^{3+}$, *m/z* = 1000.7; Found: $[ZnCu(\mathbf{6})(\mathbf{8})]^{3+}$, *m/z* (%) = 1000.2 (75). Calcd for $[Zn_2Cu_2(\mathbf{6})_2(\mathbf{8})_2(OTf)]^{5+}$, *m/z* = 1231.8; Found: *m/z* (%) = 1231.2 (100). Calcd for **P** = $[Zn_2Cu_2(\mathbf{6})_2(\mathbf{7})(\mathbf{8})_2(OTf)]^{5+}$: *m/z* =1298.1; Found: *m/z* (%) = 1298.3 (87).[10] Calcd for $[Zn_2Cu_2(\mathbf{6})_2(\mathbf{8})_2(OTf)_2]^{4+}$ *m/z* = 1575.8; Found: *m/z* (%) = 1575.5 (100). Calcd for $[ZnCu(\mathbf{6})(\mathbf{7})(\mathbf{8})(OTf)]^{2+}$ *m/z* = 1743.1; Found: *m/z* (%) = 1741.9 (66).[10] Anal. calcd. for $C_{460}H_{366}B_2Br_2Cu_2F_{52}N_{26}O_{22}S_4Zn_4$•$3CH_2Cl_2$: C, 65.03; H, 4.38; N, 4.26, S, 1.50. Found: C, 64.80; H, 4.13; N, 4.15, S, 1.23.

2. NMR spectra

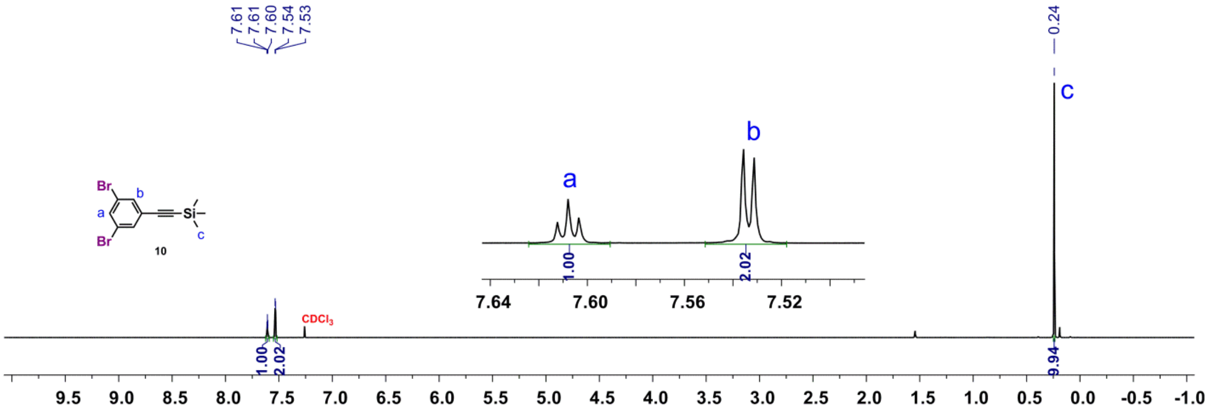


Figure S1. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **10**.

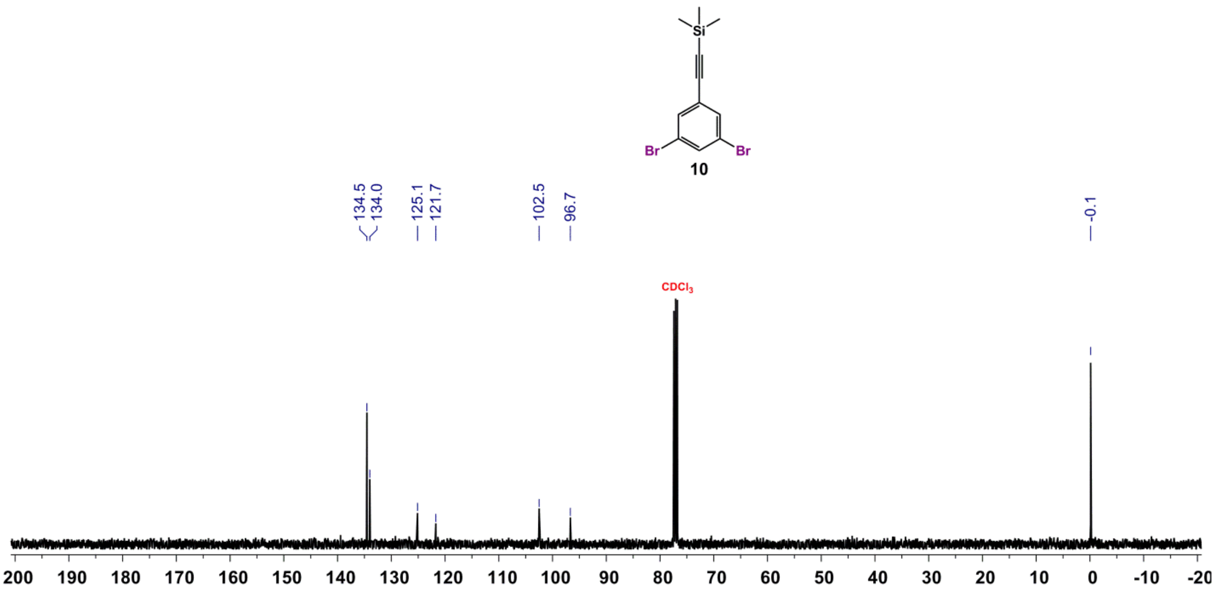


Figure S2. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of compound **10**.

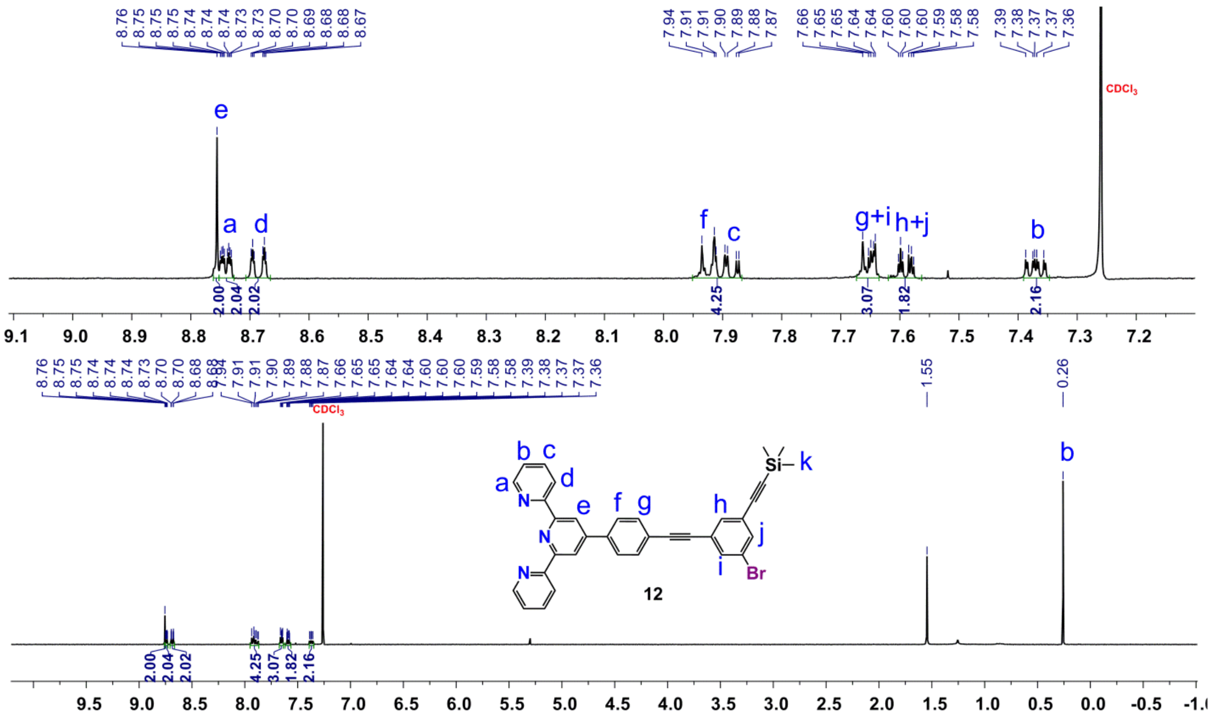


Figure S3. ^{1}H NMR spectrum (CDCl$_3$, 400 MHz) of compound **12**.

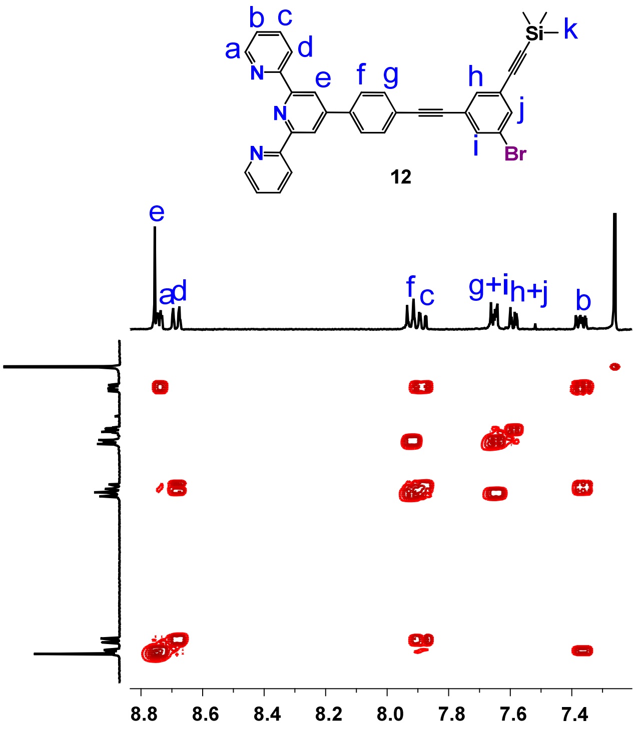


Figure S4. ^{1}H-^{1}H COSY NMR spectrum (CDCl$_3$, 400 MHz) of compound **12**.

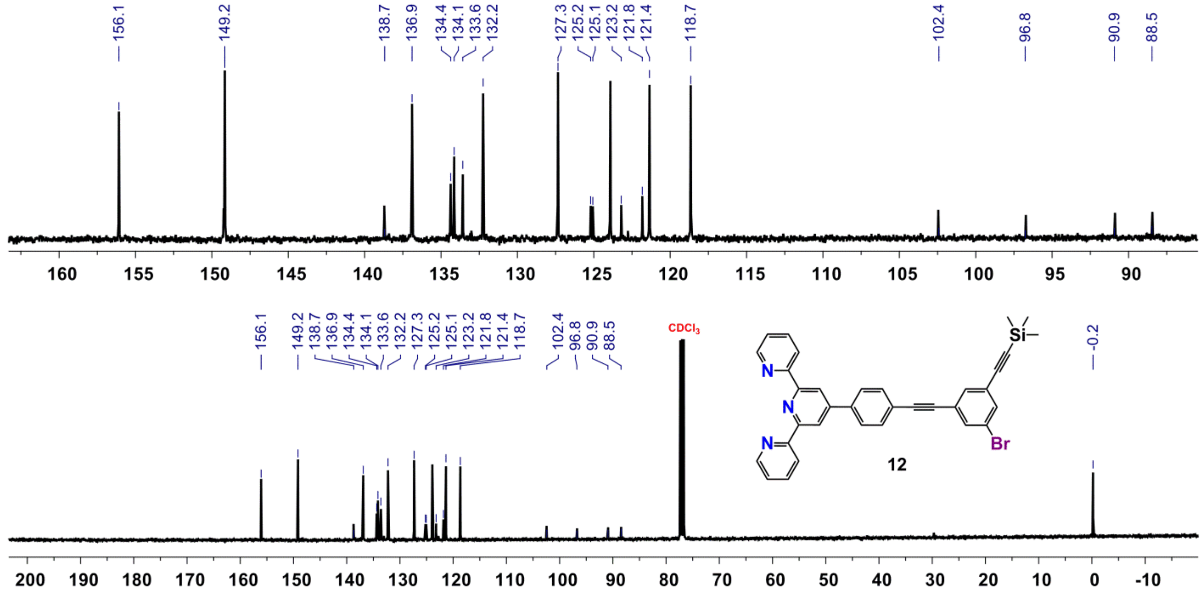


Figure S5. ^{13}C NMR spectrum (CDCl$_3$, 100 MHz) of compound **12**.

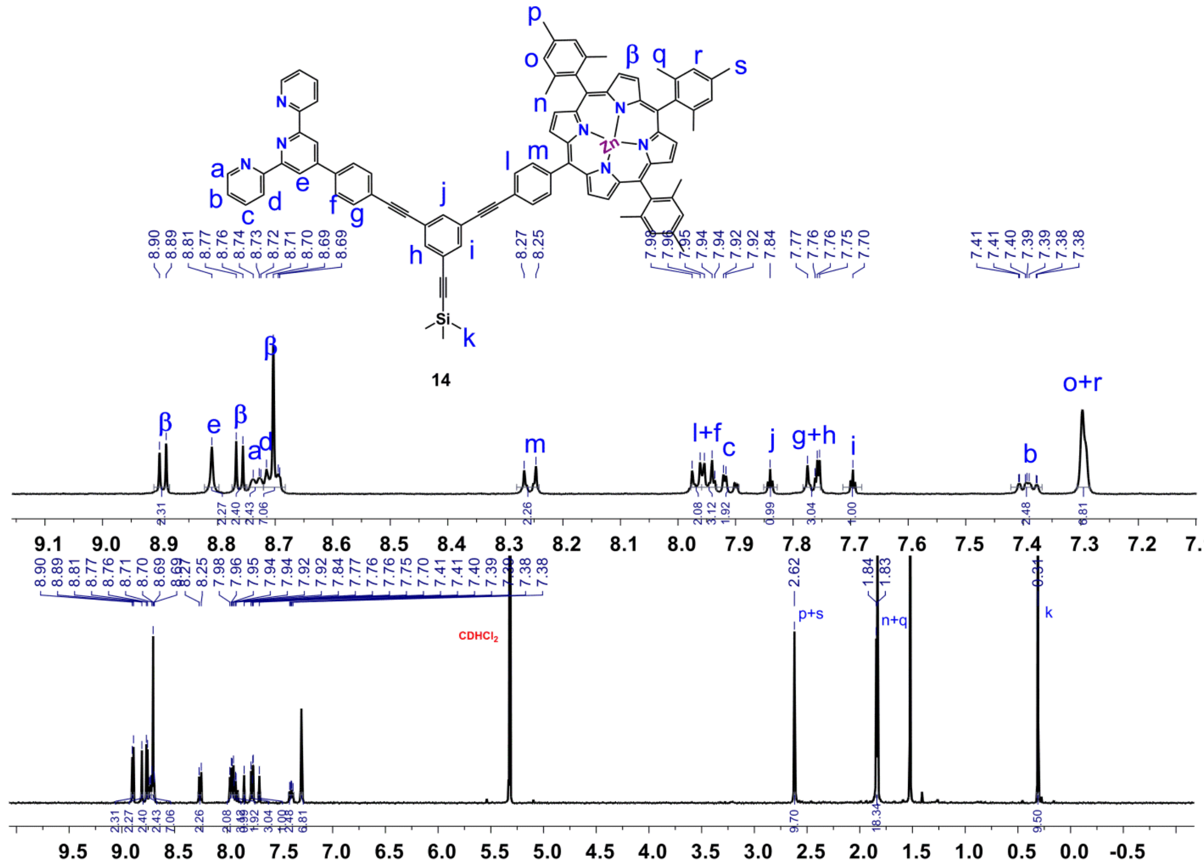


Figure S6. ^{1}H NMR spectrum (CD$_2$Cl$_2$, 400 MHz) of compound **14**.

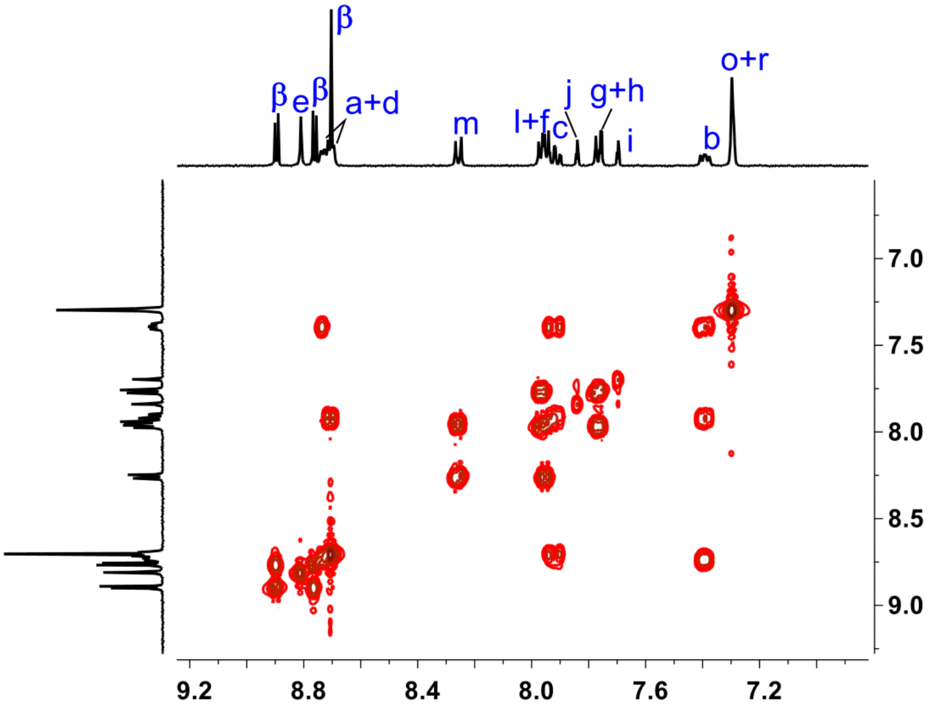


Figure S7. ^{1}H-^{1}H COSY NMR spectrum (CD_2Cl_2, 400 MHz) of compound **14**.

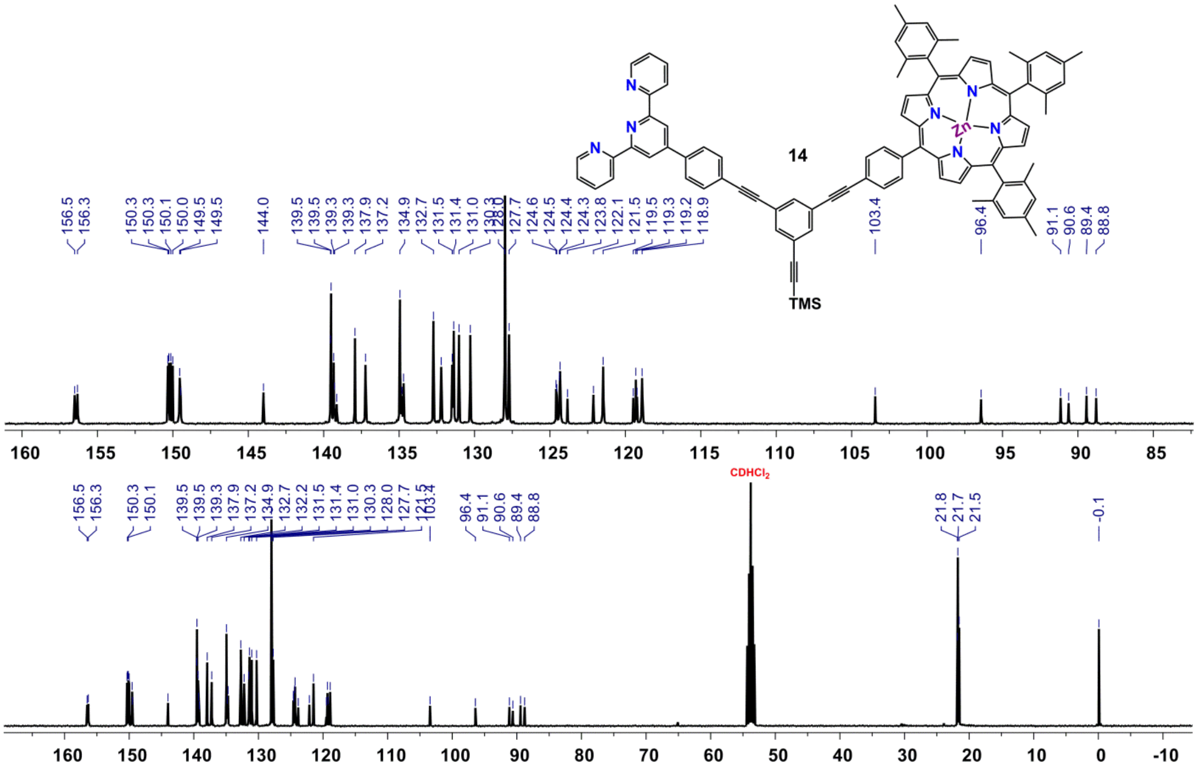


Figure S8. ^{13}C NMR spectrum (CD_2Cl_2, 100 MHz) of compound **14**.

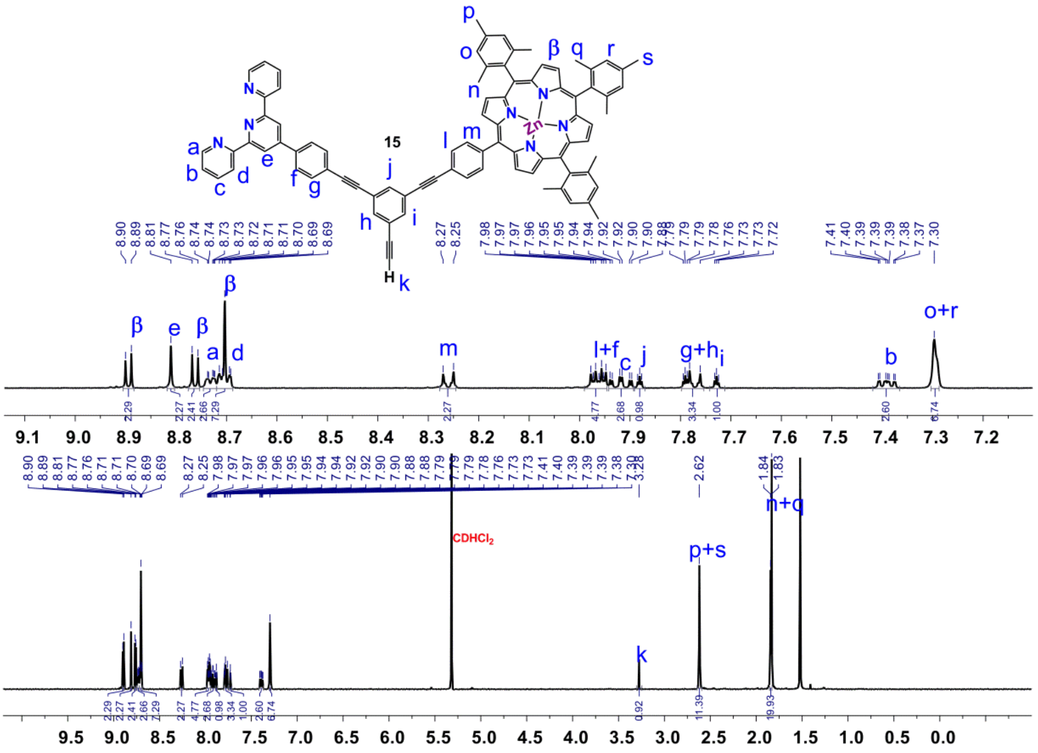


Figure S9. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz) of compound **15**.

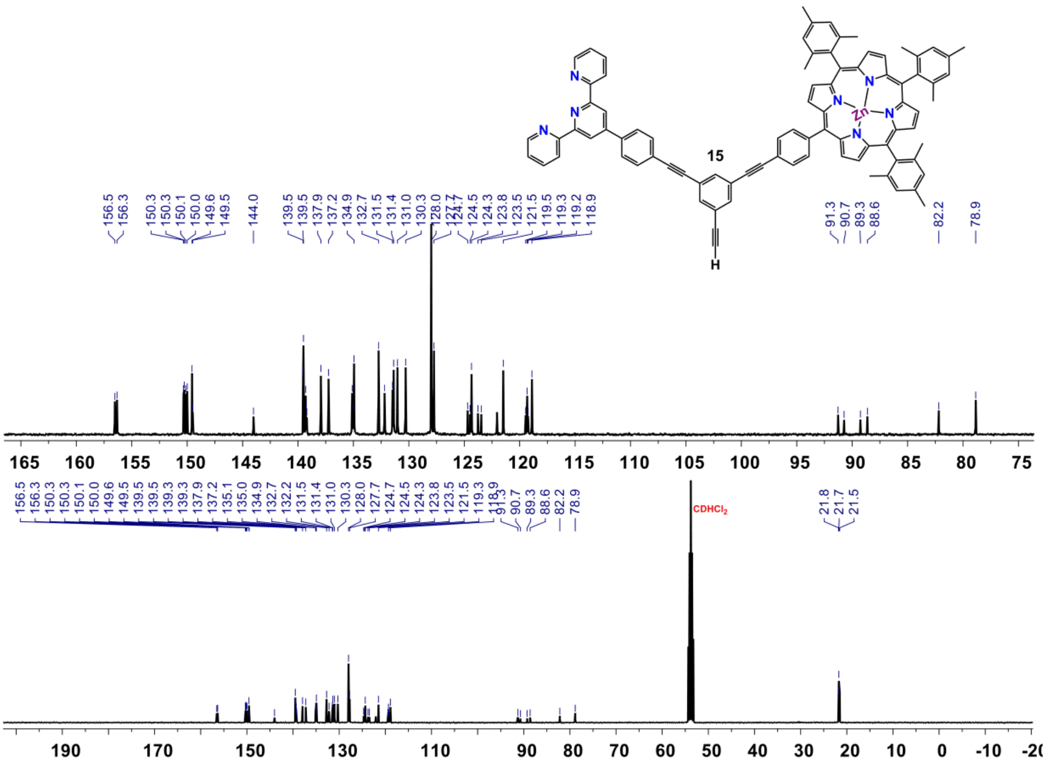


Figure S10. ^{13}C NMR spectrum (CD_2Cl_2, 100 MHz) of compound **15**.

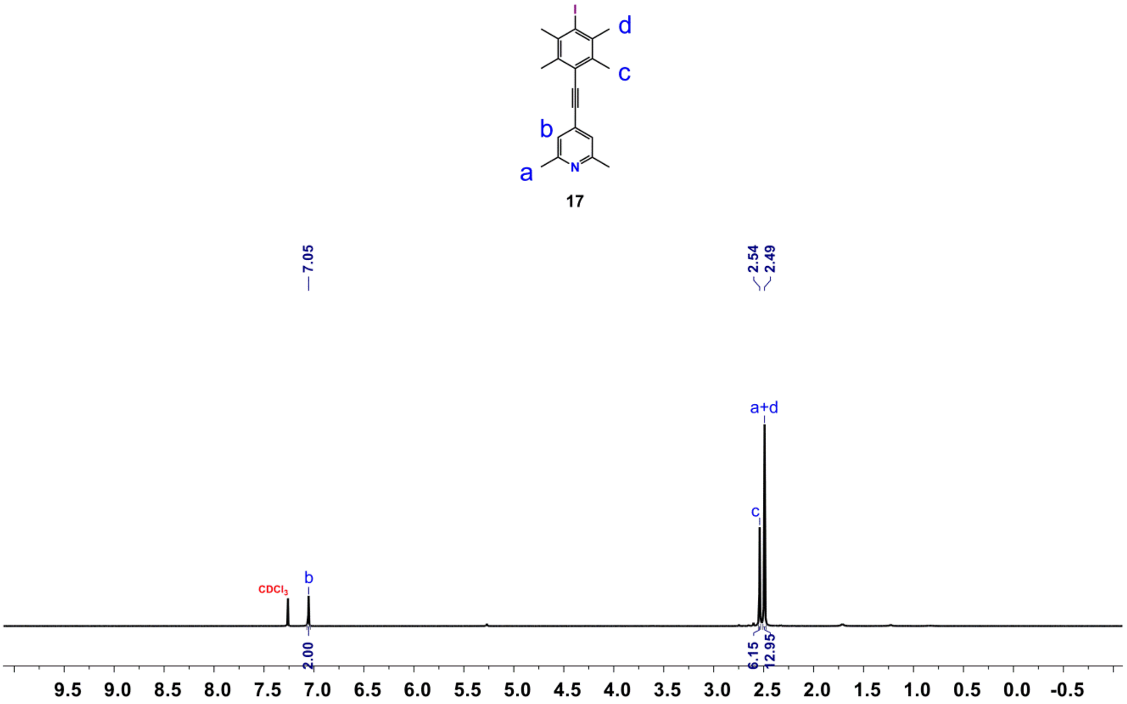


Figure S11. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz) of compound **17**.

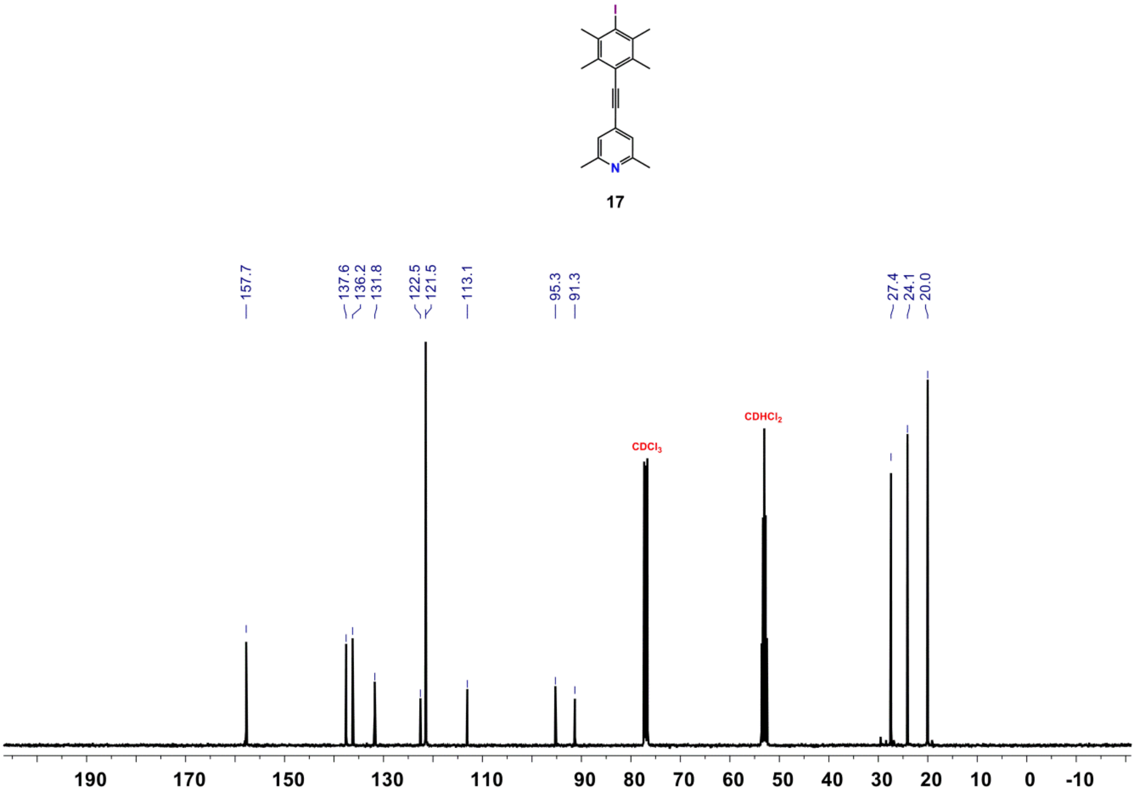
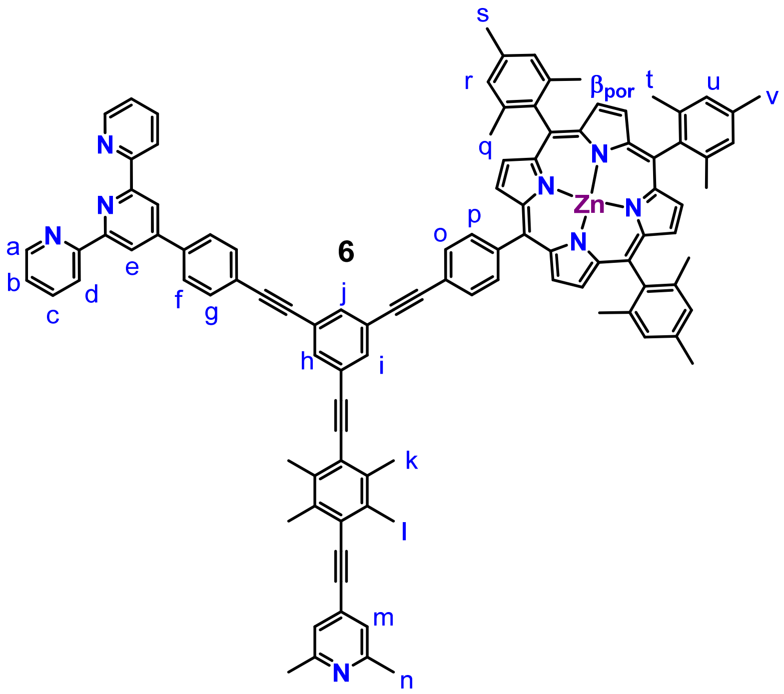


Figure S12. ^{13}C NMR spectrum ($CDCl_3$:CD_2Cl_2, 6:4, 100 MHz) of compound **17**.



6

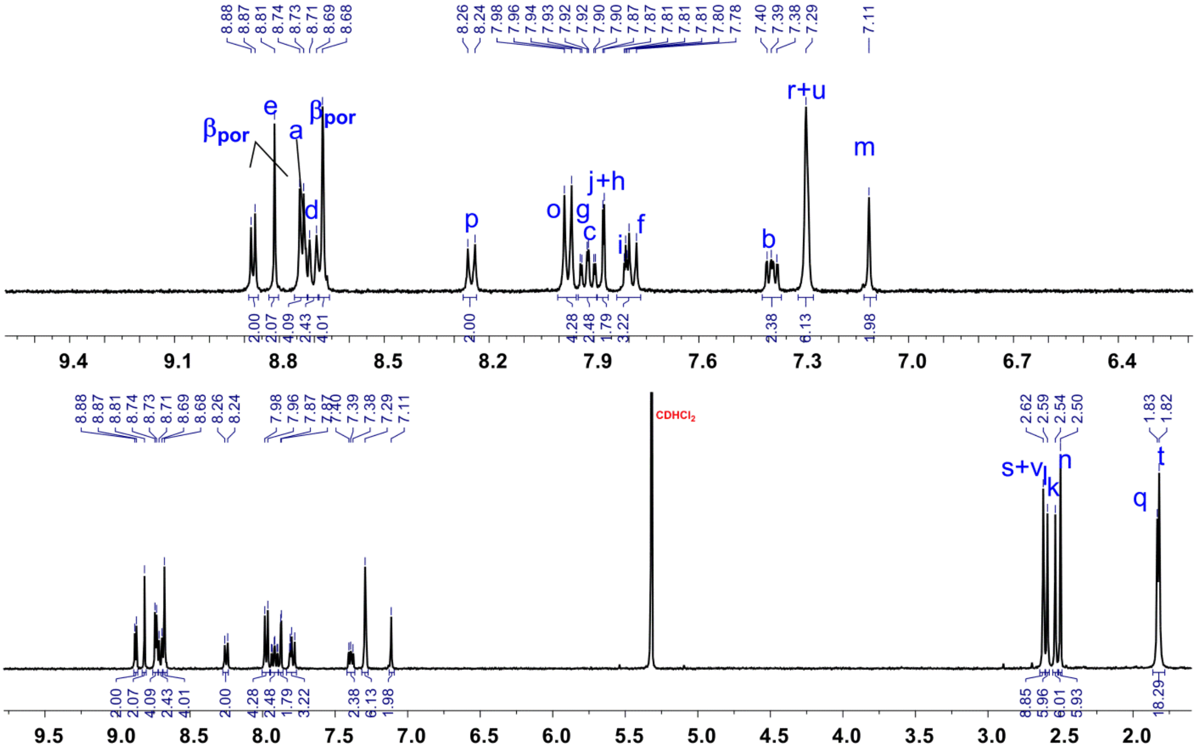


Figure S13. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz) of compound **6**.

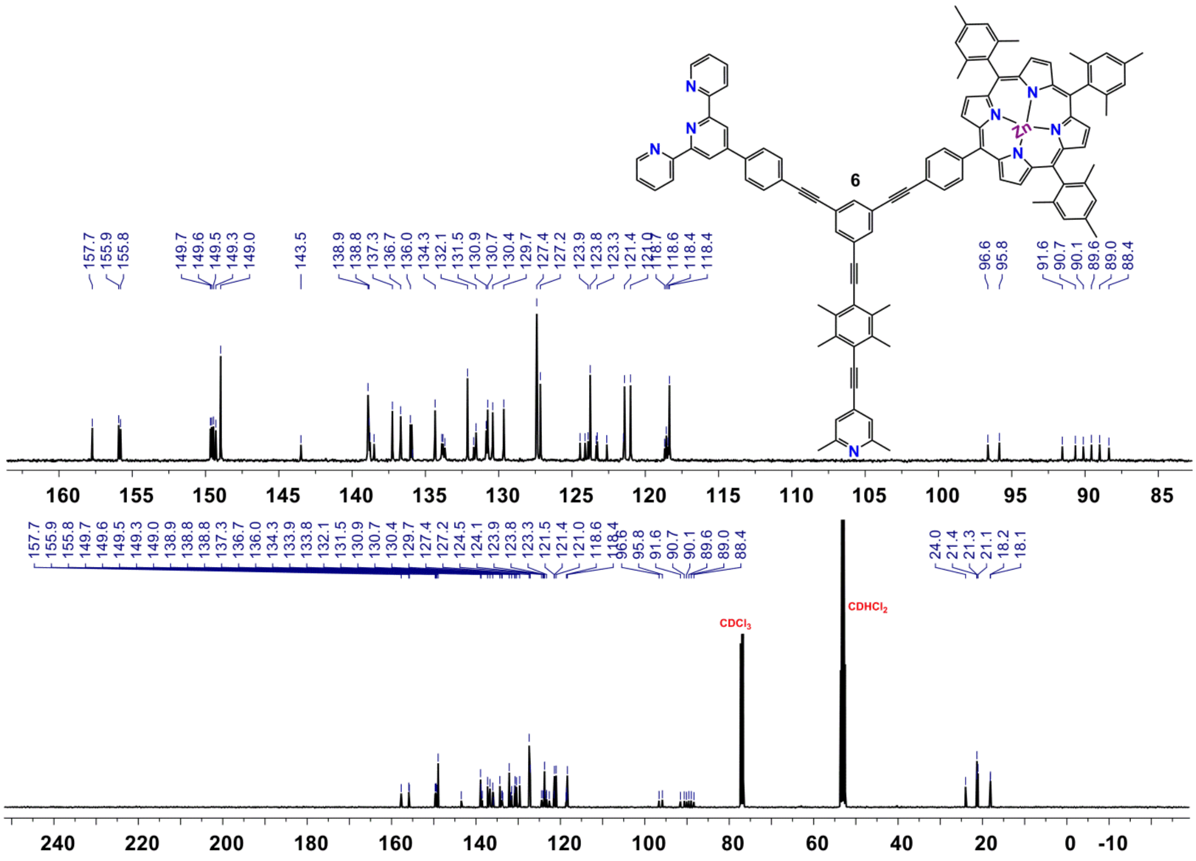


Figure S14. ^{13}C NMR spectrum ($CDCl_3$:CD_2Cl_2,4:6, 100 MHz) of compound **6**.

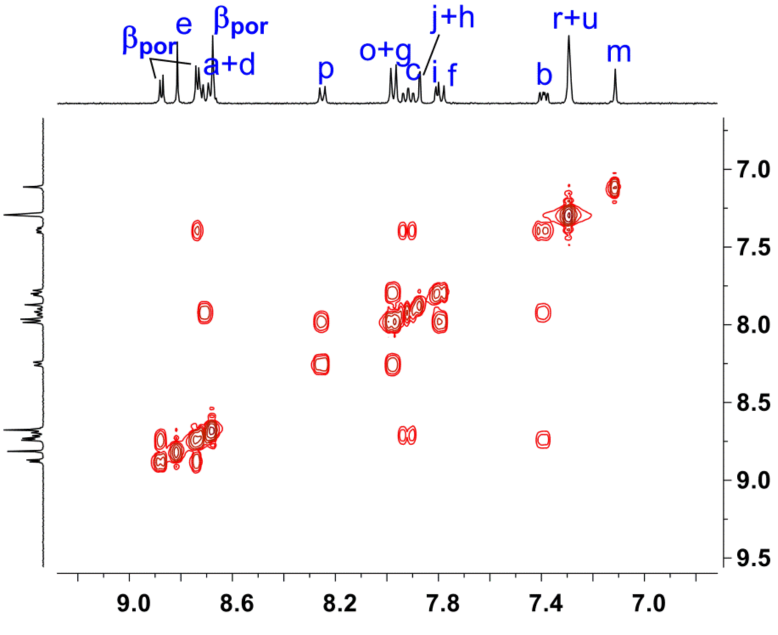


Figure S15. ^{1}H-^{1}H COSY NMR spectrum (CD_2Cl_2, 400 MHz) of compound **6**.

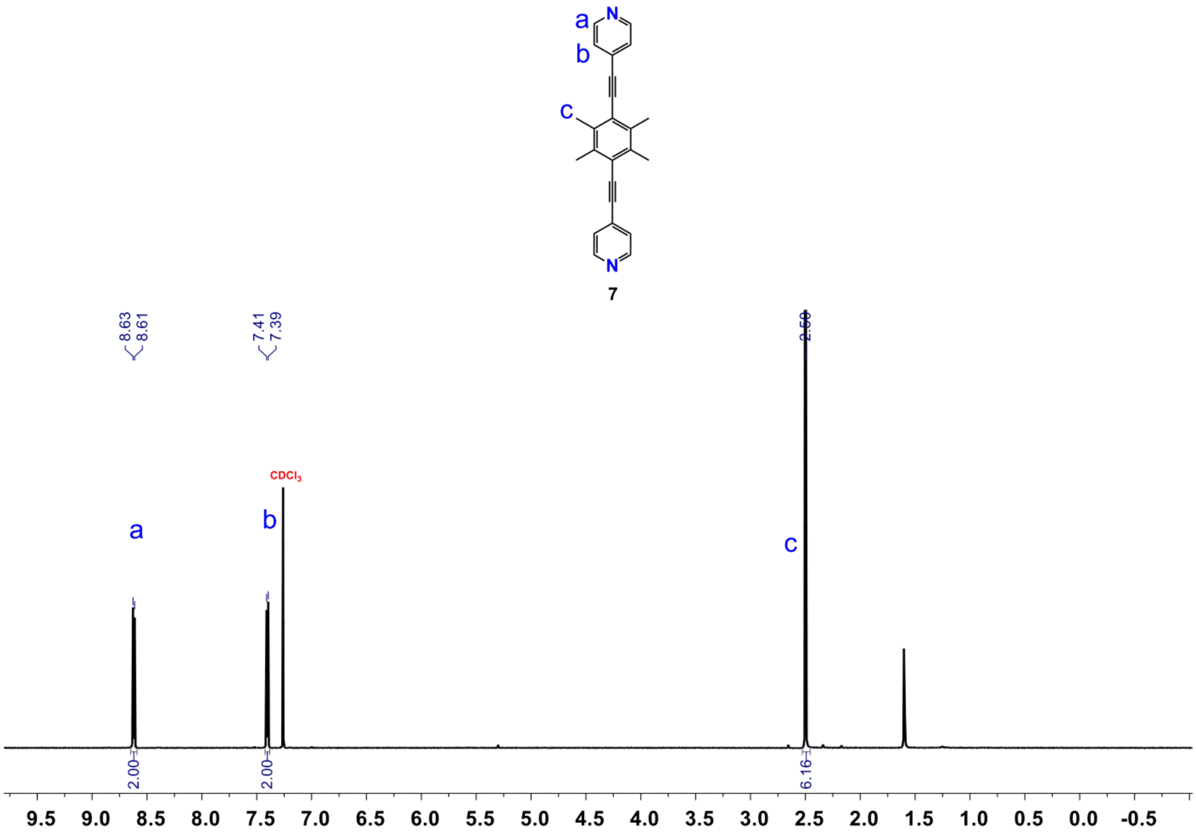


Figure S16. ^{1}H NMR spectrum (CDCl$_3$, 400 MHz) of compound **7**.

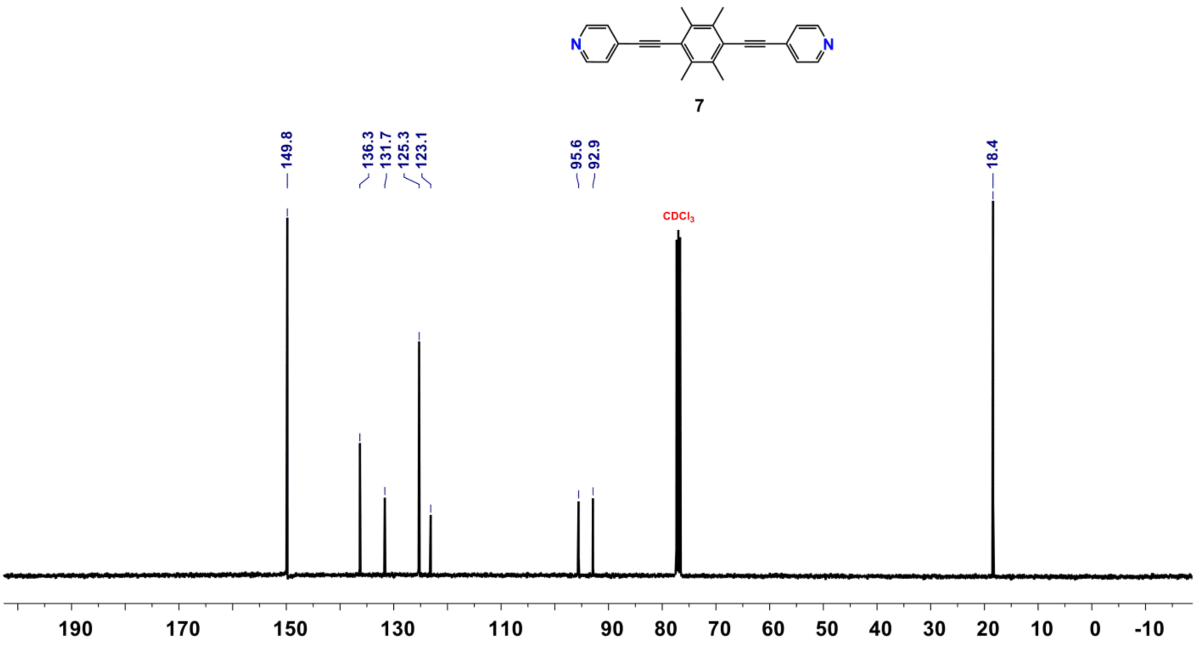


Figure S17. ^{13}C NMR spectrum (CDCl$_3$, 100 MHz) of compound **7**.

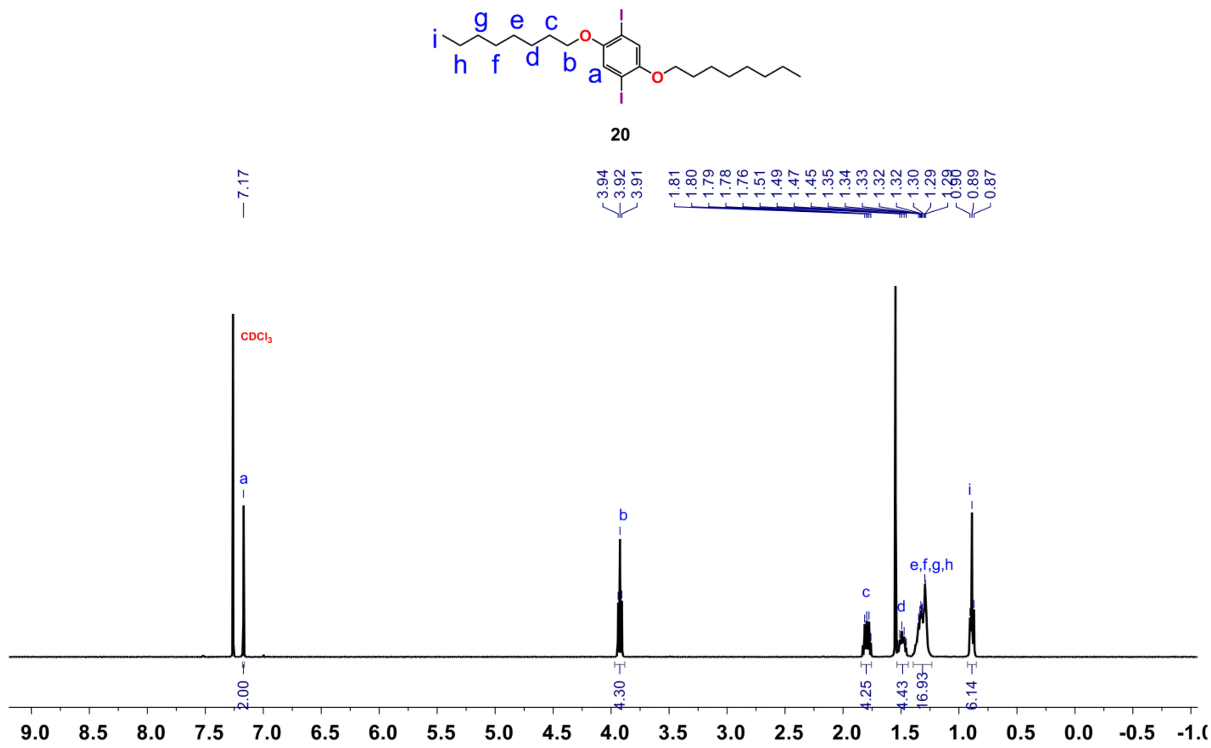

20

Figure S18. ^{1}H-^{1}H COSY NMR spectrum (CDCl$_3$, 400 MHz) of compound **20**.

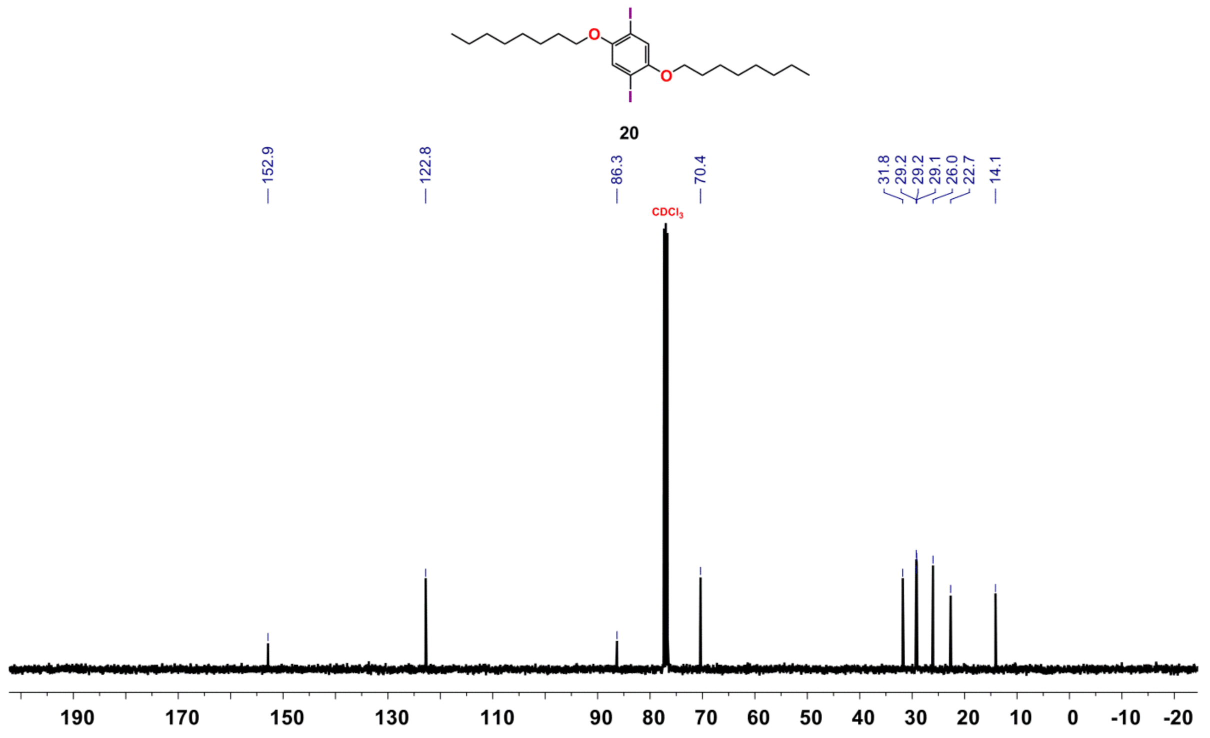

20

Figure S19. ^{13}C NMR spectrum (CDCl$_3$, 100 MHz) of compound **20**.

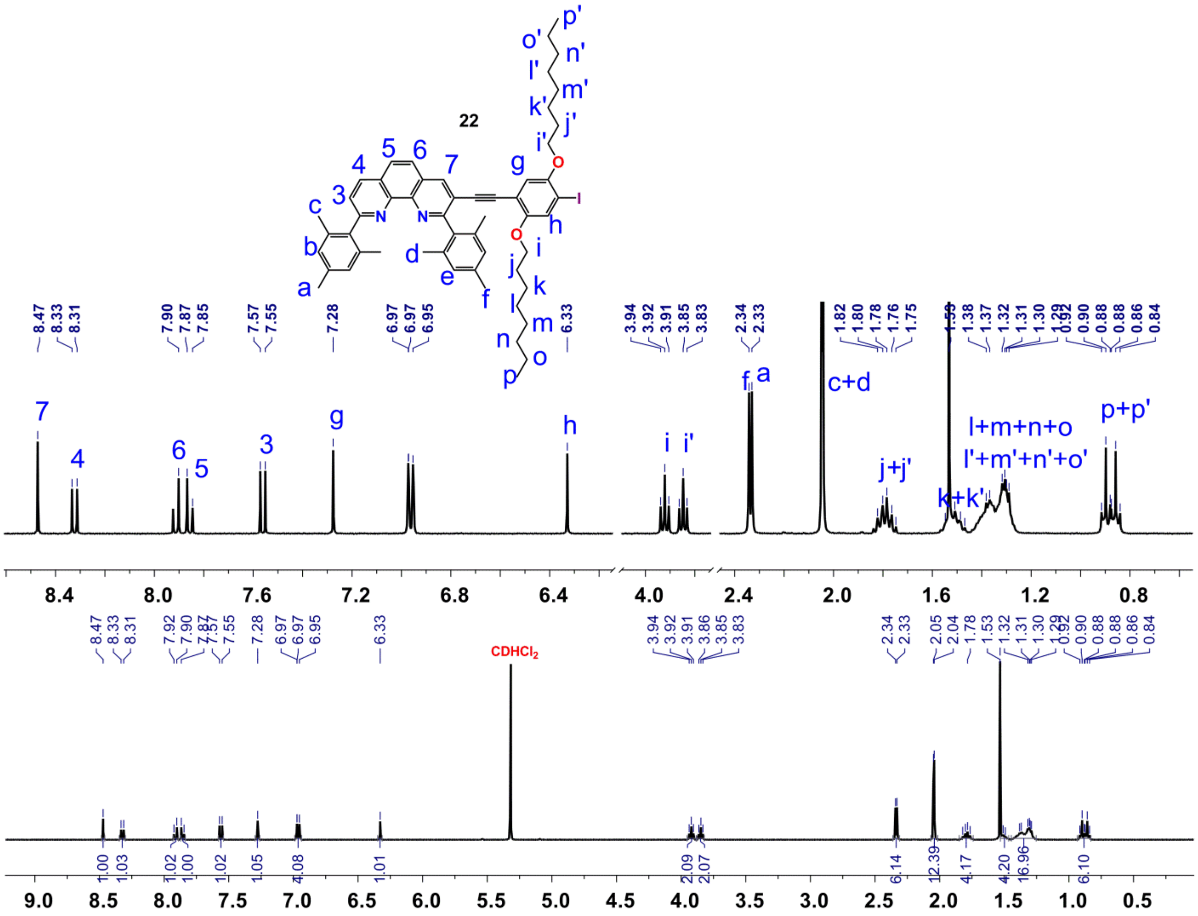


Figure S20. ^{1}H NMR spectrum (CD$_2$Cl$_2$, 400 MHz) of compound **22**.

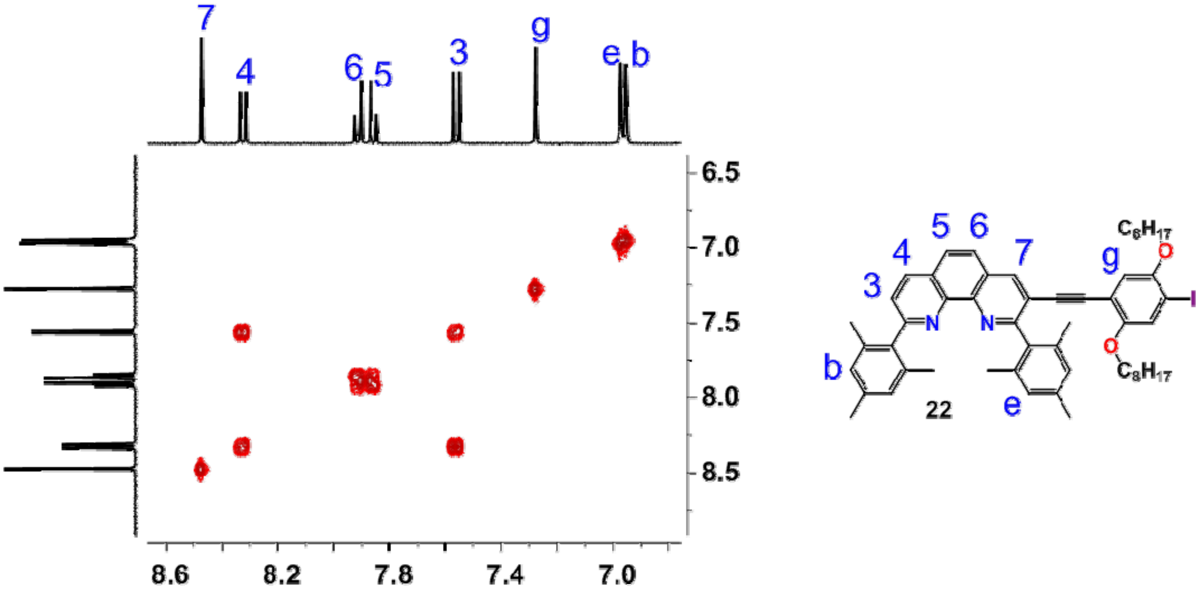


Figure S21. ^{1}H-^{1}H COSY NMR spectrum (CD$_2$Cl$_2$, 100 MHz) of compound **22**.

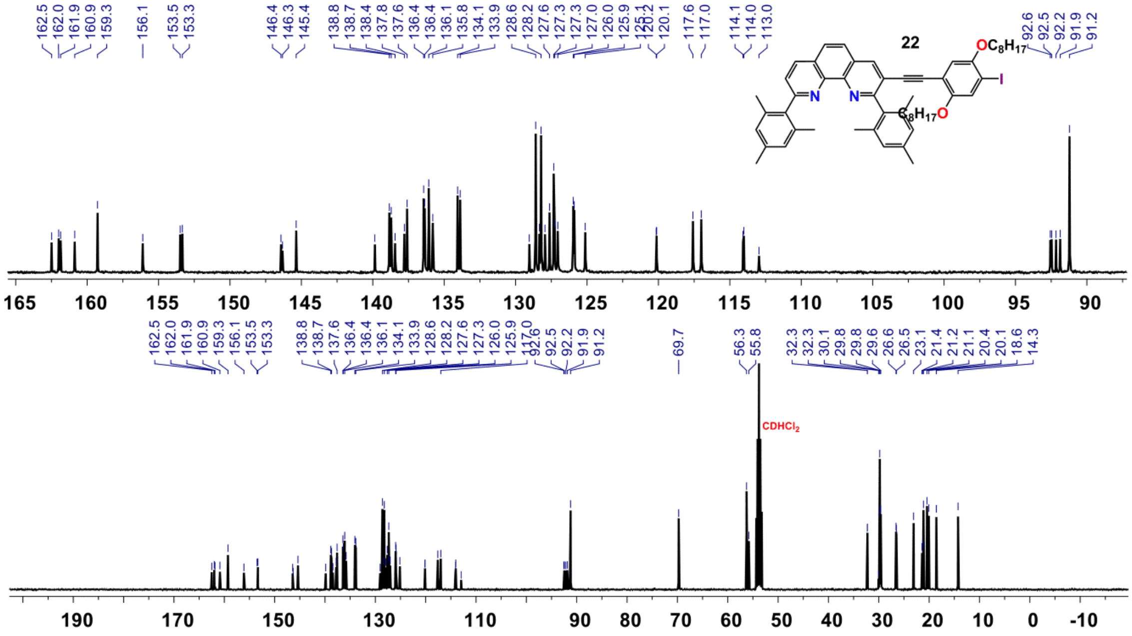


Figure S22. ^{13}C NMR spectrum (CD_2Cl_2, 100 MHz) of compound **22**.

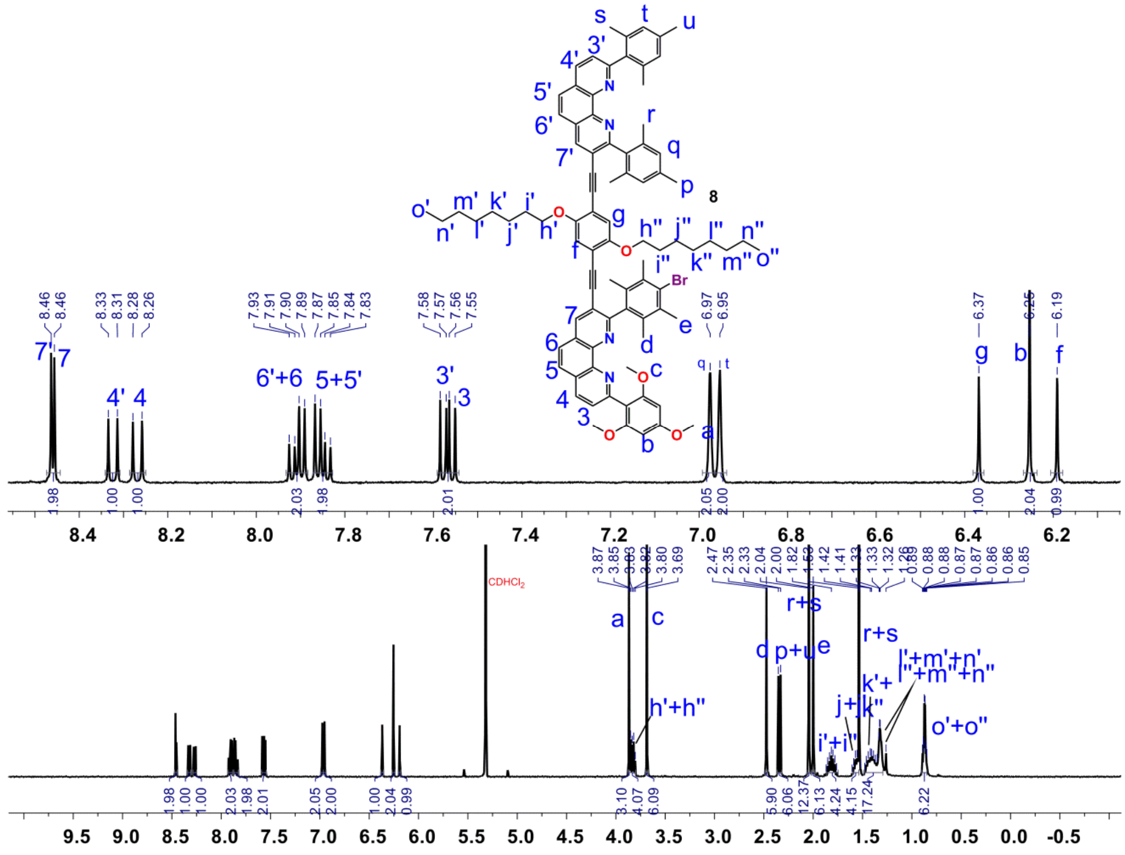


Figure S23. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz) of compound **8**.

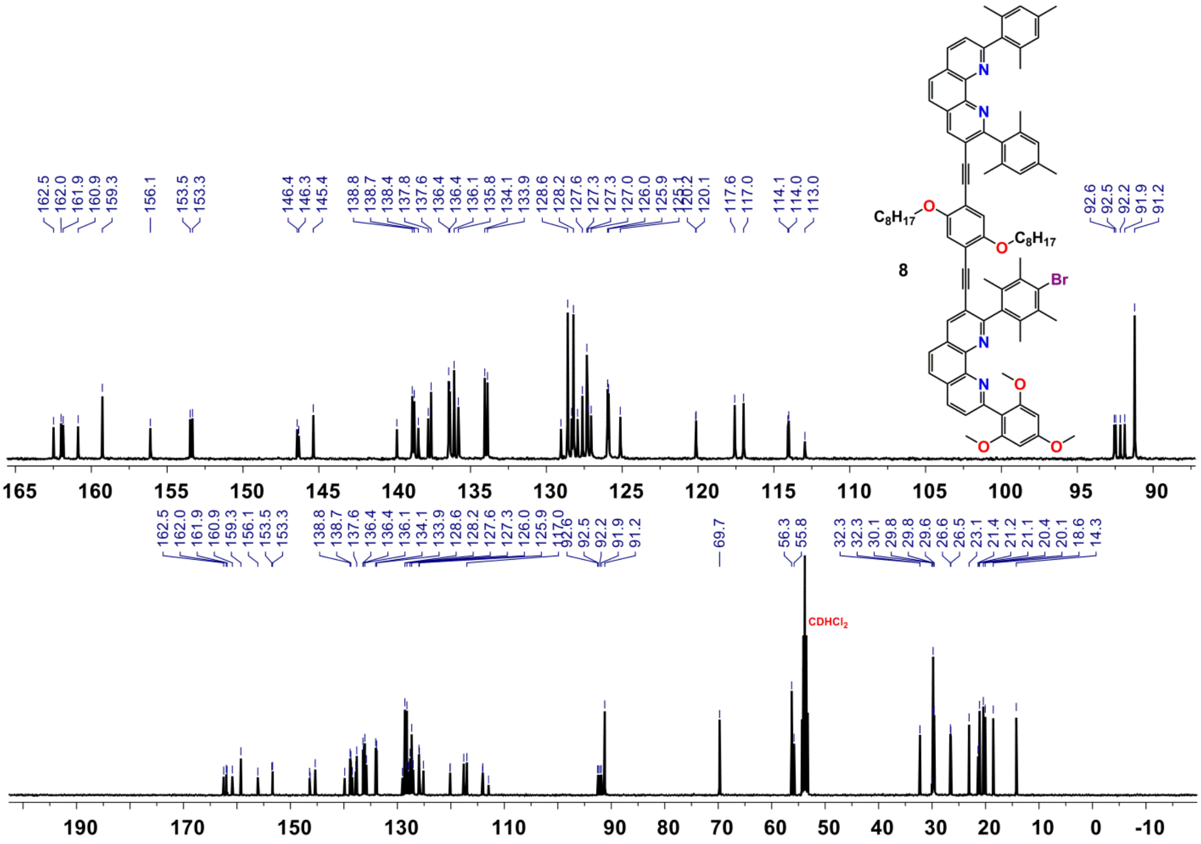


Figure S24. ^{13}C NMR spectrum (CD_2Cl_2, 100 MHz) of compound **8**.

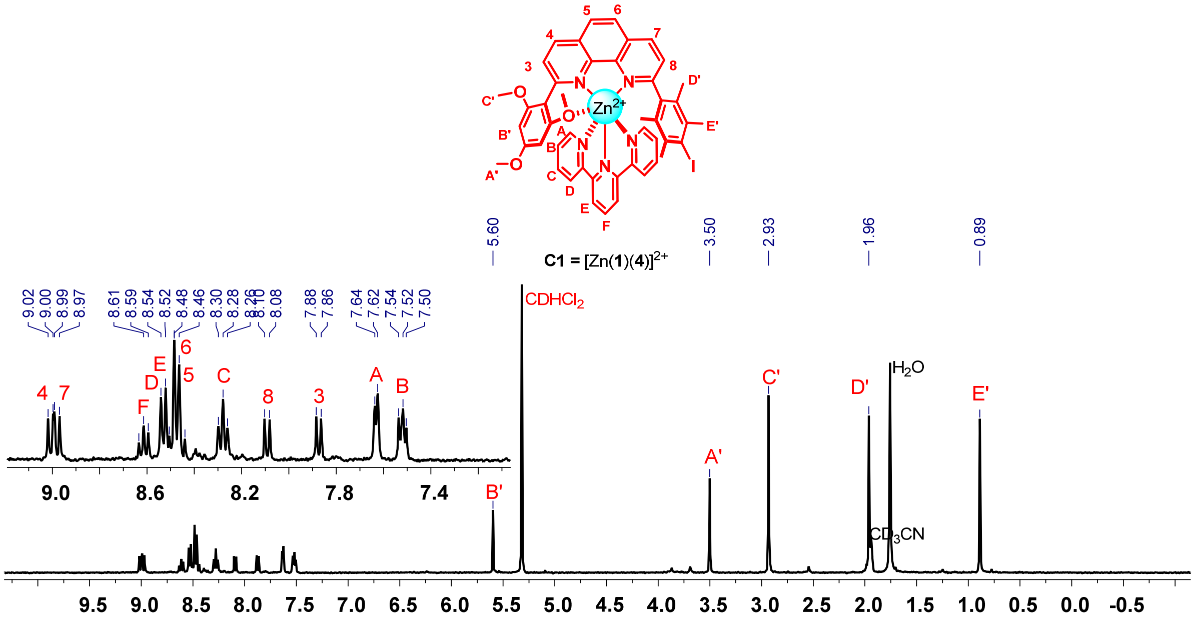


Figure S25. ^{1}H NMR spectrum (CD_2Cl_2:CD_3CN, 9:1, 400 MHz) of complex **C1** = [Zn(**1**)(**4**)]$(OTf)_2$.

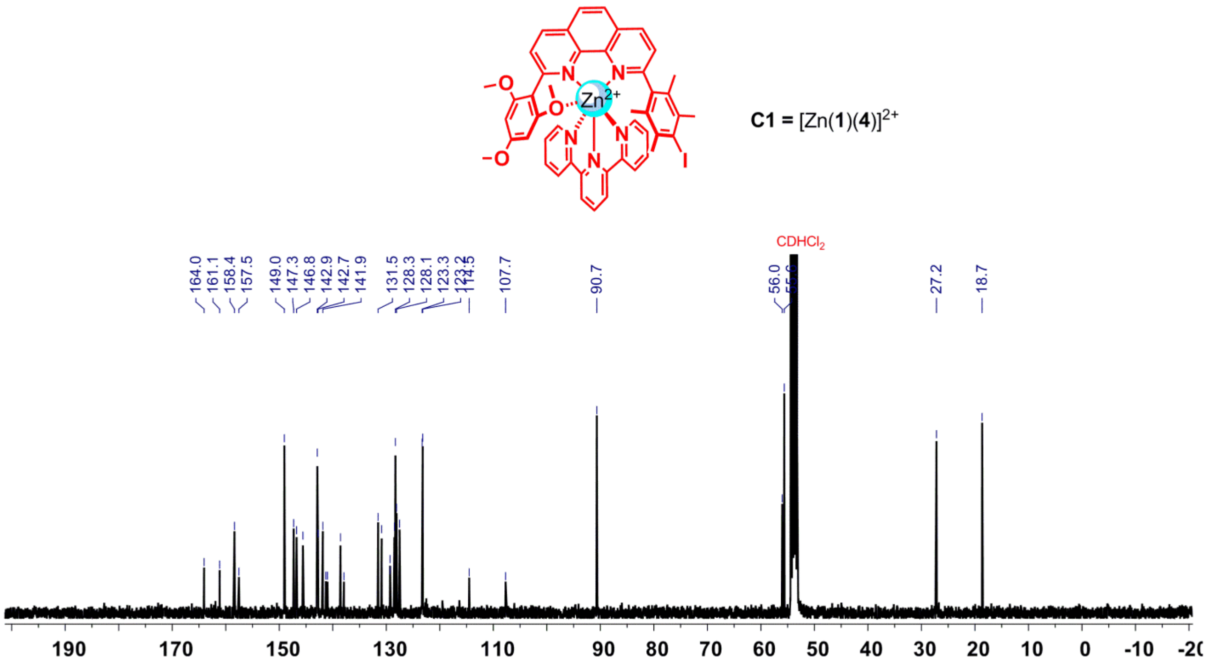


Figure S26. ^{13}C NMR spectrum (CD_2Cl_2, 100 MHz) of complex **C1** = [Zn(**1**)(**4**)](OTf)$_2$.

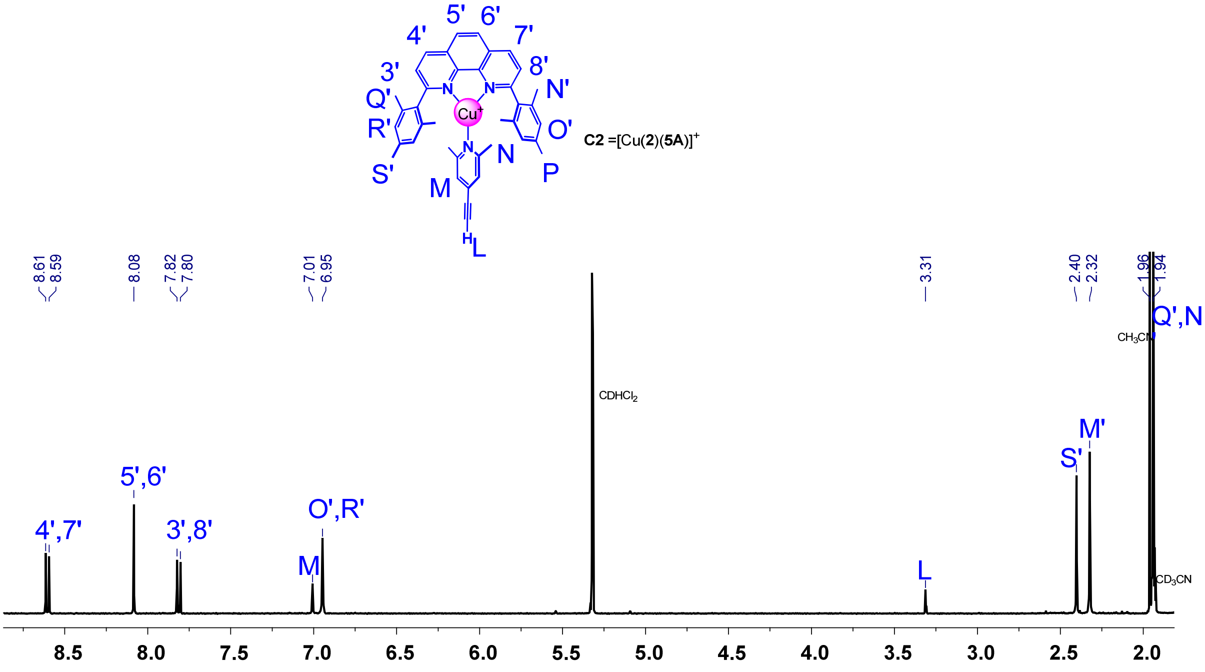


Figure S27. ^{1}H NMR spectrum (CD_2Cl_2:CD_3CN, 9:1, 400 MHz) of complex **C2** = [Cu(**2**)(**5A**)]B(C_6F_5)$_4$.

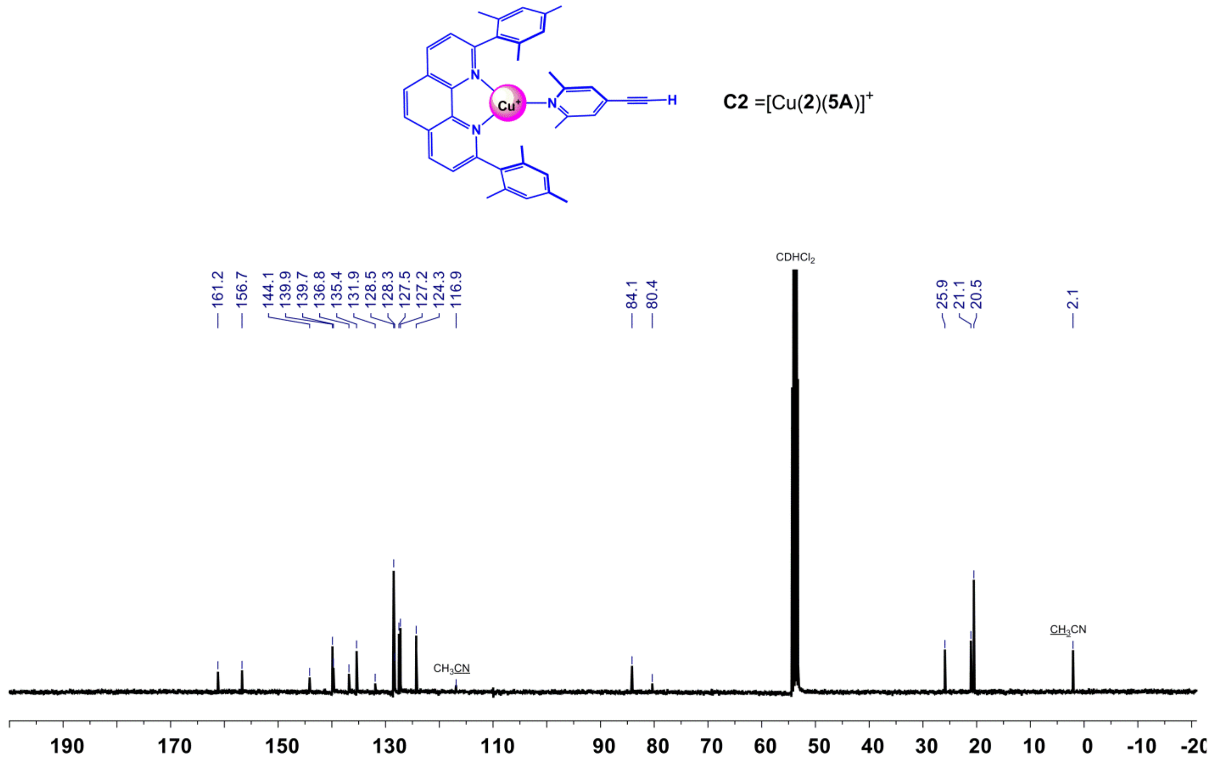


Figure S28. ^{13}C NMR spectrum (CD_2Cl_2, 100 MHz) of complex **C2** = [Cu(**2**)(**5A**)]B(C_6F_5)$_4$.

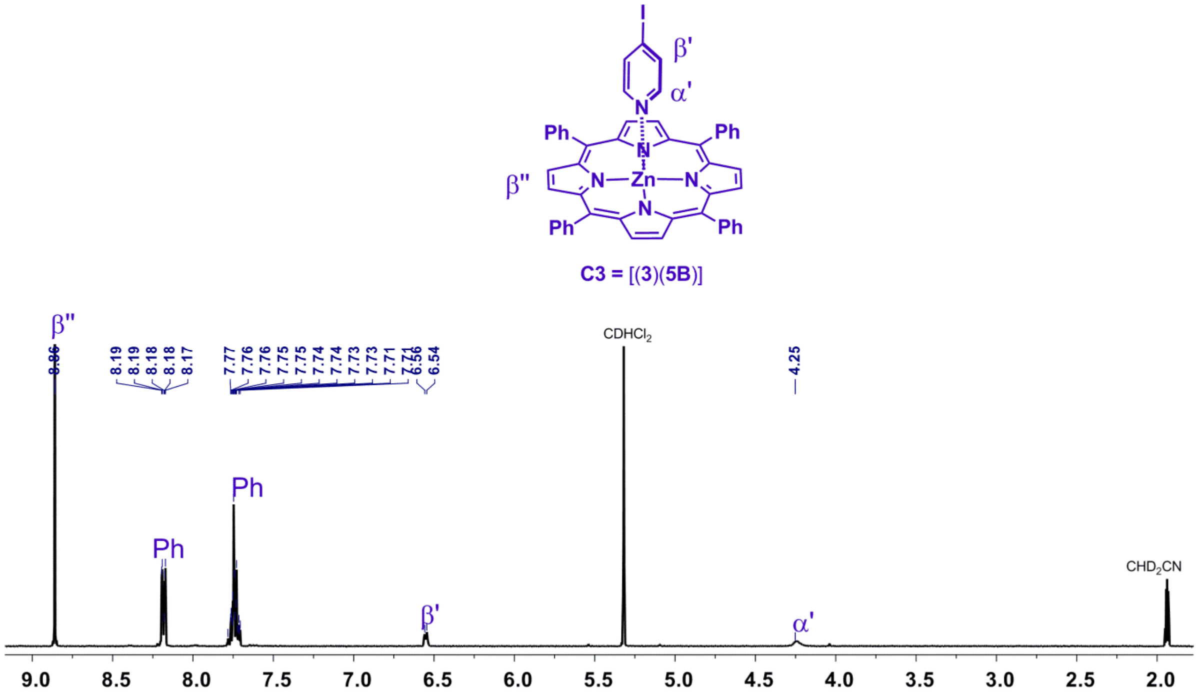


Figure S29. ^{1}H NMR spectrum (CD_2Cl_2:CD_3CN, 9:1, 400 MHz) of complex **C3** = [(**3**)(**5B**)].

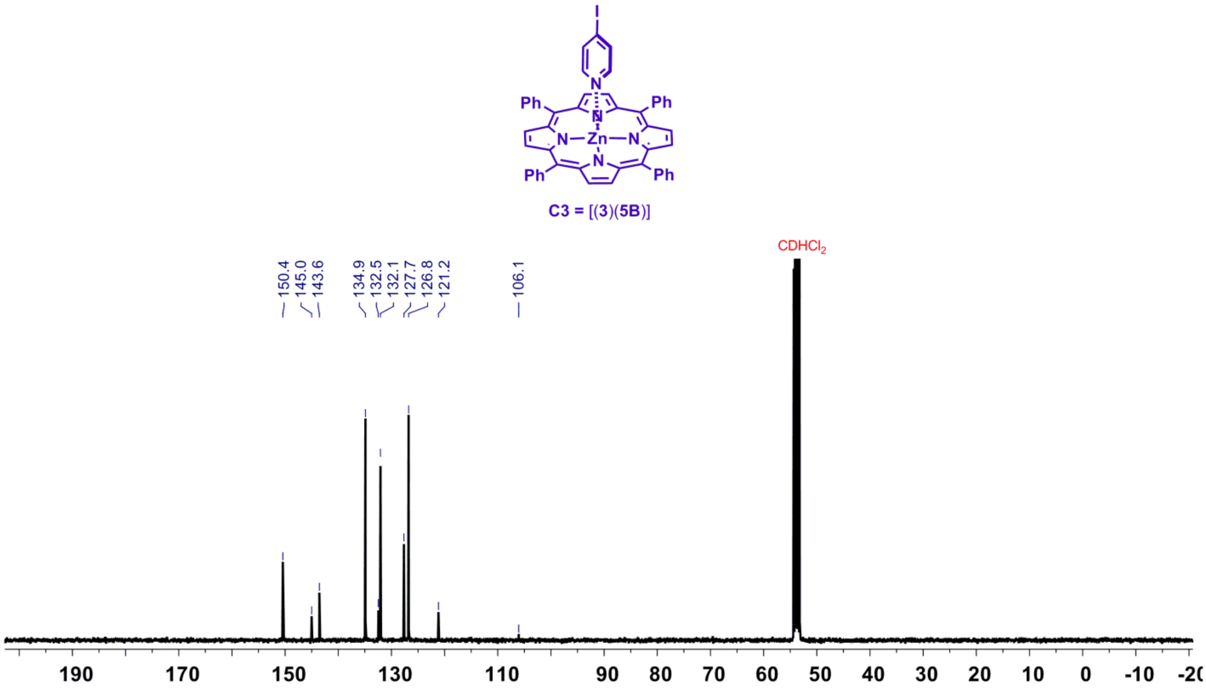


Figure S30. ^{13}C NMR spectrum (CD_2Cl_2, 100 MHz) of complex **C3** = [(**3**)(**5B**)].

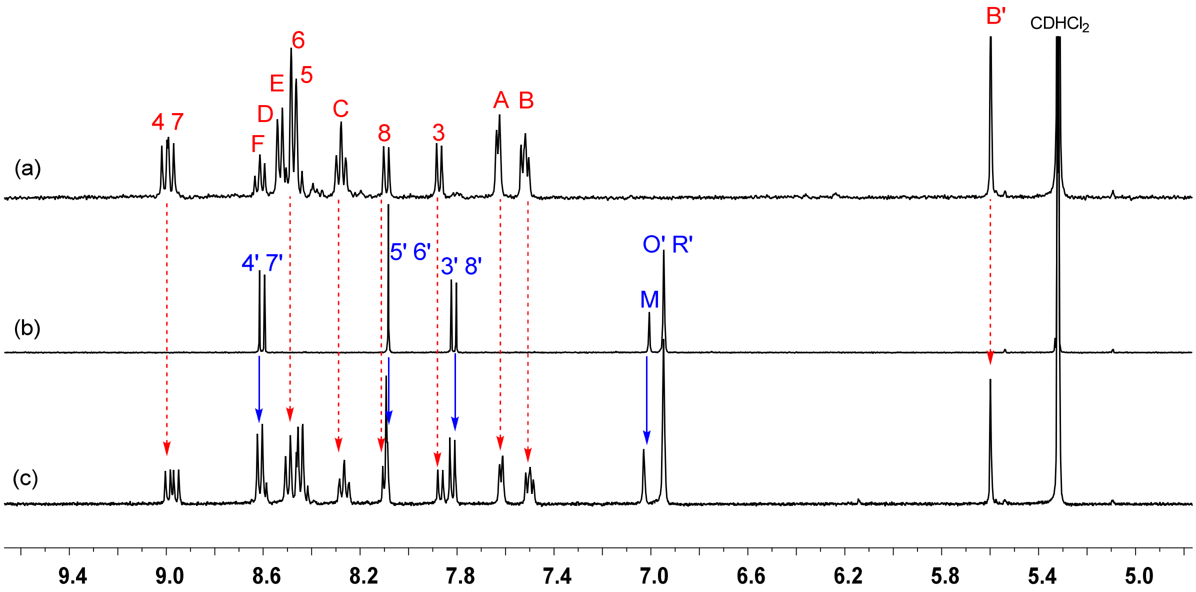


Figure S31. Comparison of partial ^{1}H NMR spectra (CD_2Cl_2:CD_3CN, 9:1, 400 MHz) of complex (a) **C1** = [Zn(**1**)(**4**)](OTf)$_2$, (b) **C2** = [Cu(**2**)(**5A**)]B(C_6F_5)$_4$ and (c) an equimolar mixture of **C1**, **2**, **5A** and [Cu(CH_3CN)$_4$B(C_6F_5)$_4$] after equilibration.

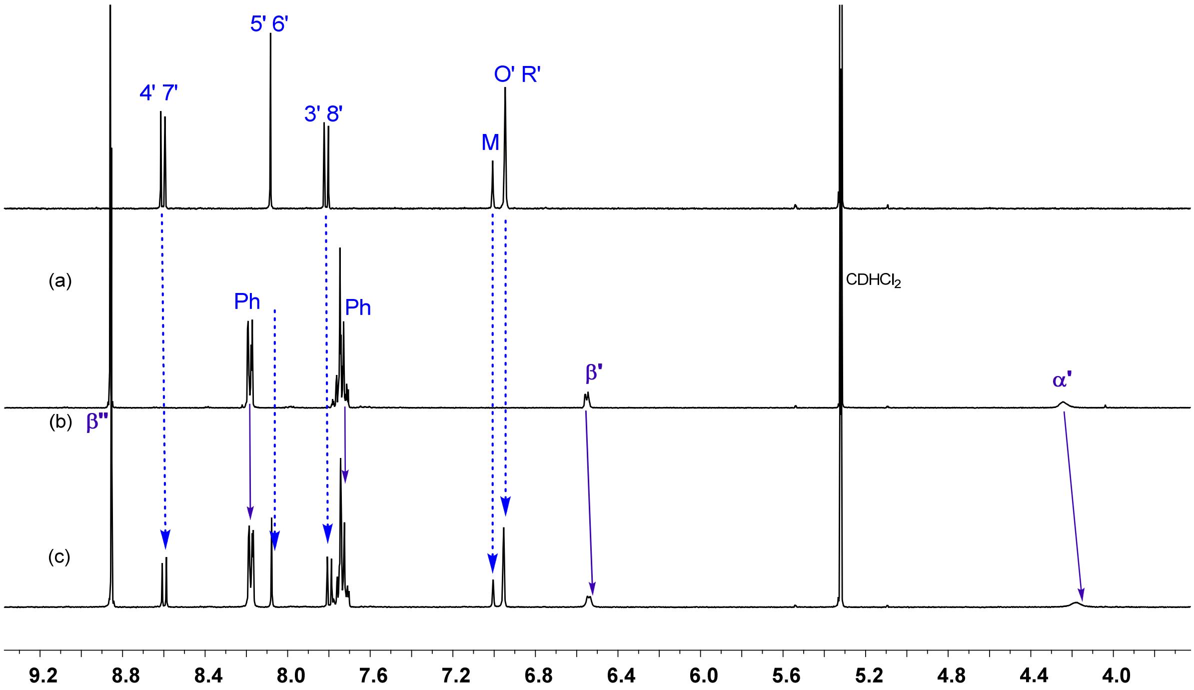


Figure S32. Comparison of partial ^{1}H NMR spectra (CD_2Cl_2:CD_3CN, 9:1, 400 MHz) of complex (a) **C2** = [Cu(**2**)(**5A**)]B(C_6F_5)$_4$, (b) **C3** = [(**3**)(**5B**)], and (c) an equimolar mixture of **C2**, **3**, **5B** after equilibration.

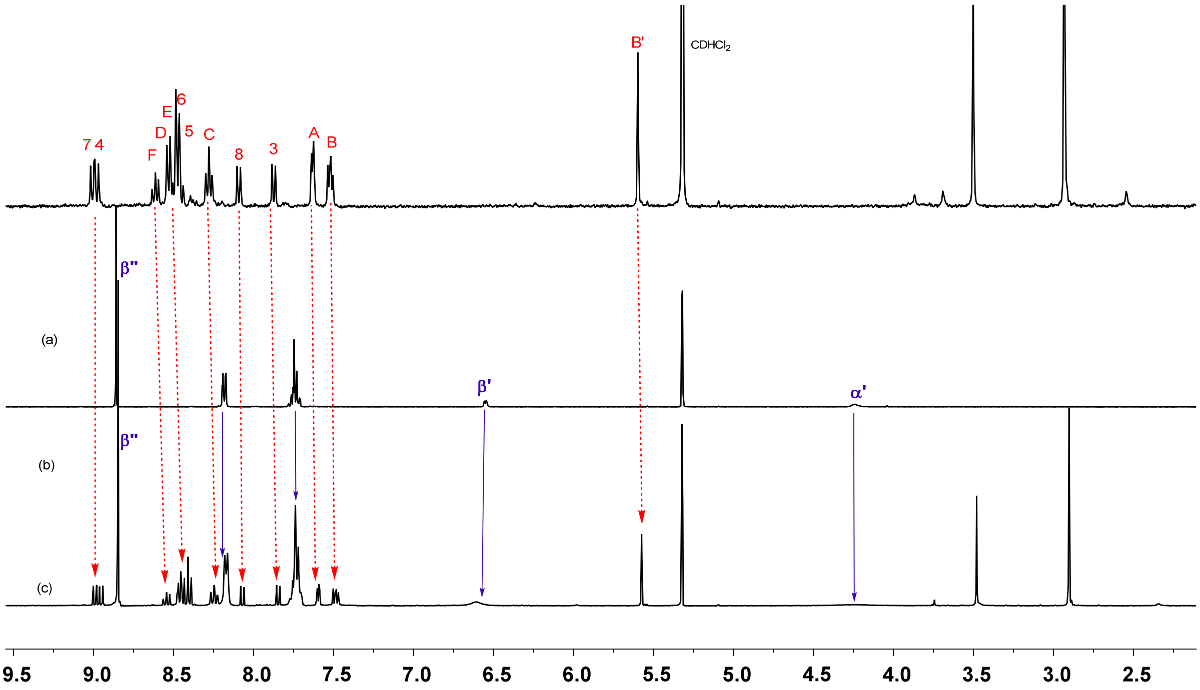


Figure S33. Comparison of partial ^{1}H NMR spectra (CD_2Cl_2:CD_3CN, 9:1, 400 MHz) of complex (a) **C1** = [Zn(**1**)(**4**)](OTf)$_2$, (b) **C3** = [(**3**)(**5B**)] and (c) an equimolar mixture of **C1**, **3**, and **5B** after equilibration.

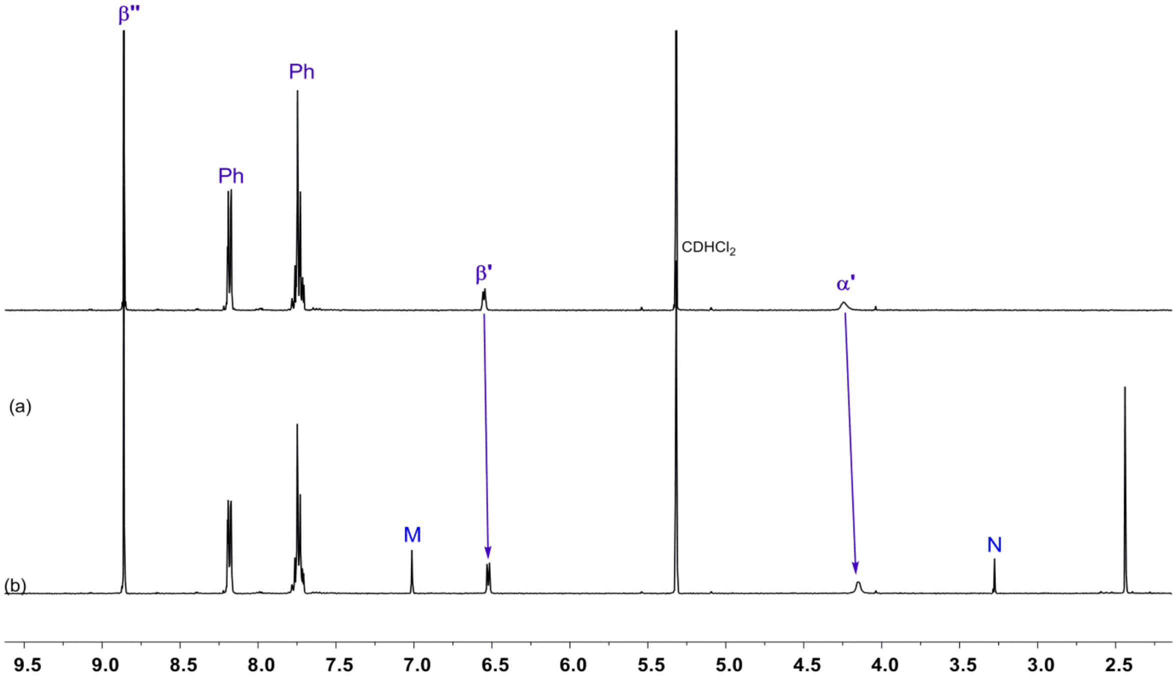


Figure S34. Comparison of partial ^{1}H NMR spectra (CD_2Cl_2:CD_3CN, 9:1, 400 MHz) of complex (a) **C3** = [(**3**)(**5B**)] and (b) an equimolar mixture of **C3** and **5A**.

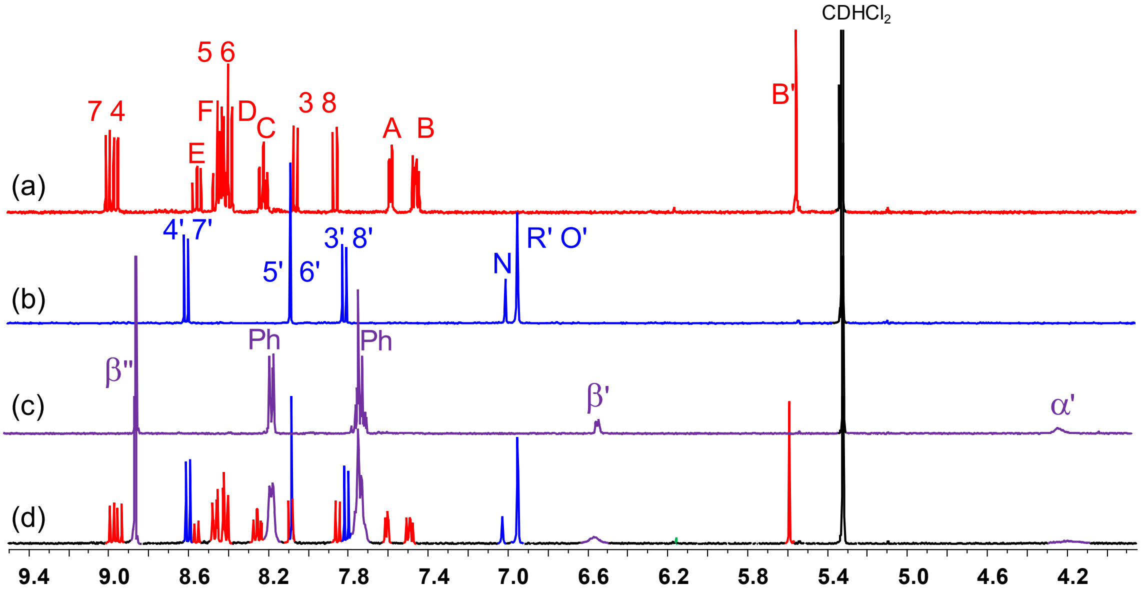


Figure S35. Comparison of partial ^{1}H NMR spectra (CD_2Cl_2:CD_3CN, 9:1, 400 MHz) of complex (a) **C1** = [Zn(**1**)(**4**)](OTf)$_2$, (b) **C2** = [Cu(**2**)(**5A**)]B(C_6F_5)$_4$, (c) **C3** = [(**3**)(**5B**)] and (d) an equimolar mixture of **1**, **2**, **3**, **4**, **5A**, **5B**, [Zn(OTf)$_2$] and [Cu(CH_3CN)$_4$B(C_6F_5)$_4$] after 3 h reflux in DCM-acetonitrile (1:3).

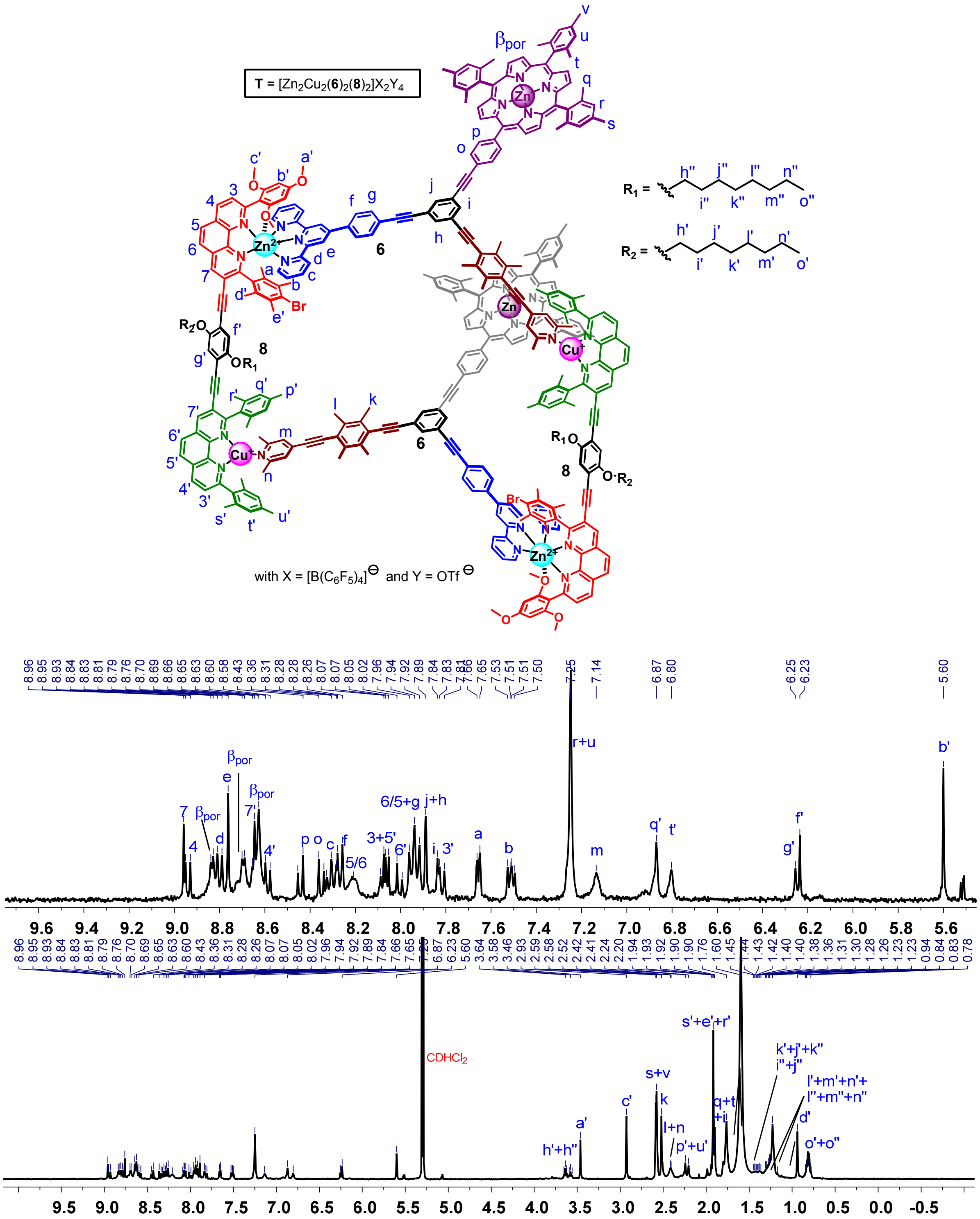


Figure S36. ^{1}H NMR spectrum (CD_2Cl_2:CD_3CN, 9:1, 400 MHz) of tweezer complex **T**.

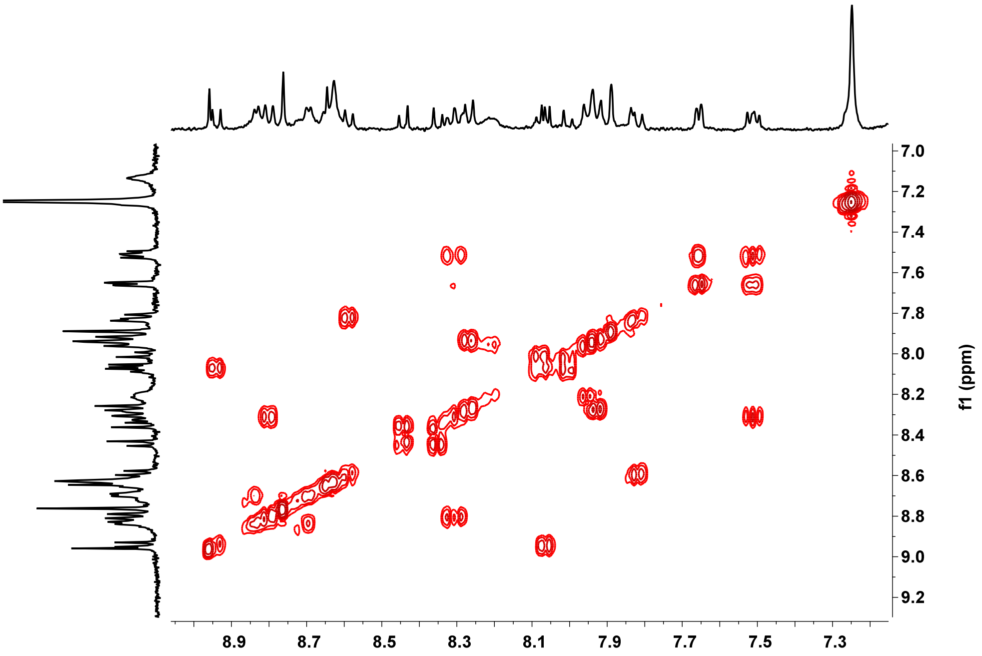
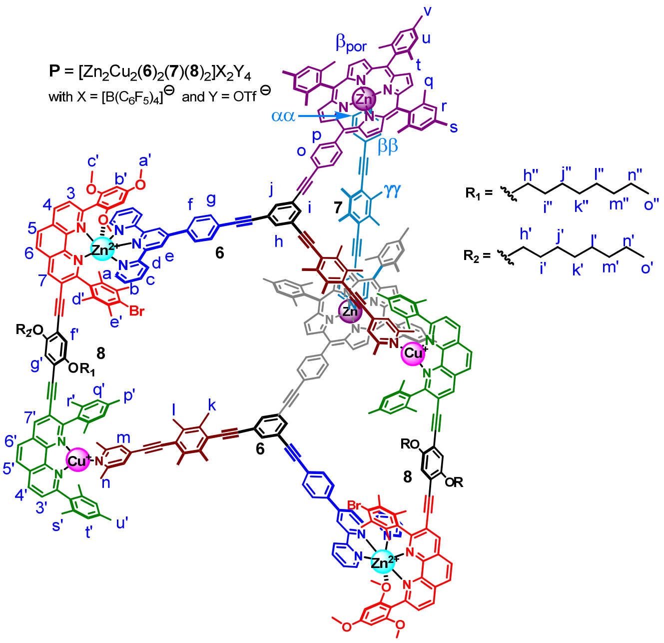


Figure S37. ^{1}H-^{1}H COSY NMR spectrum (CD_2Cl_2:CD_3CN, 9:1, 400 MHz) of tweezer **T**.



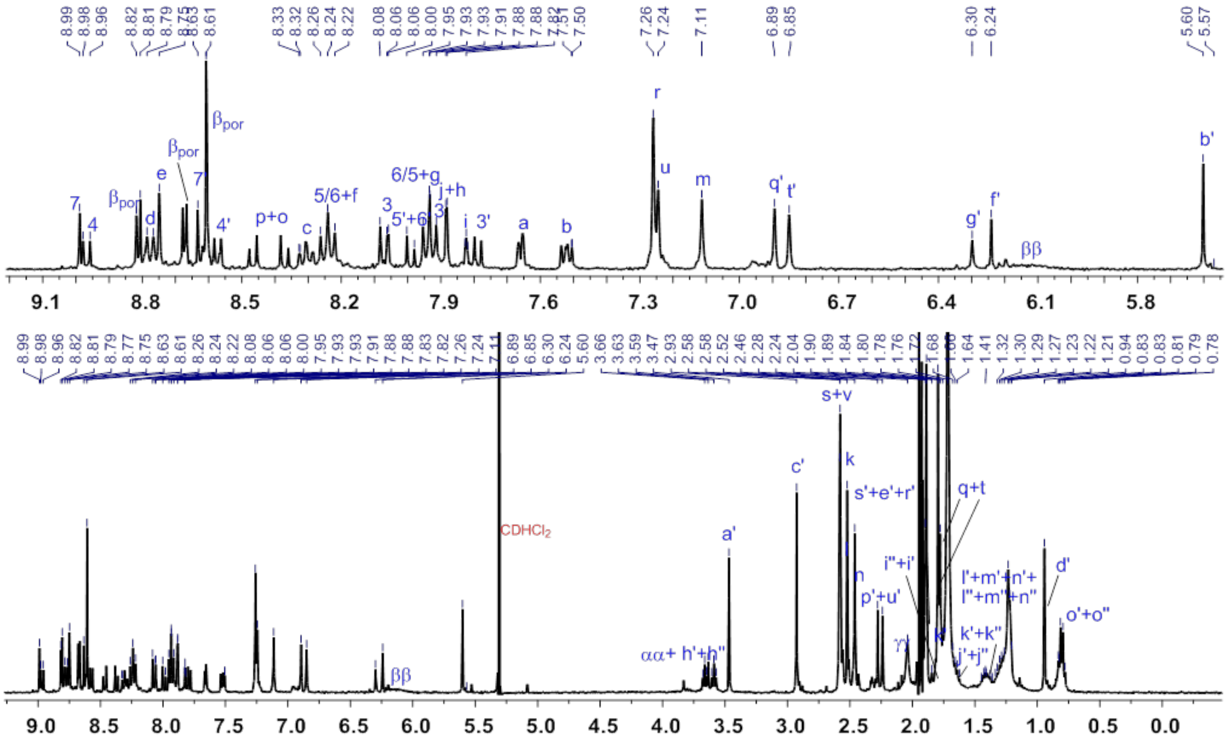
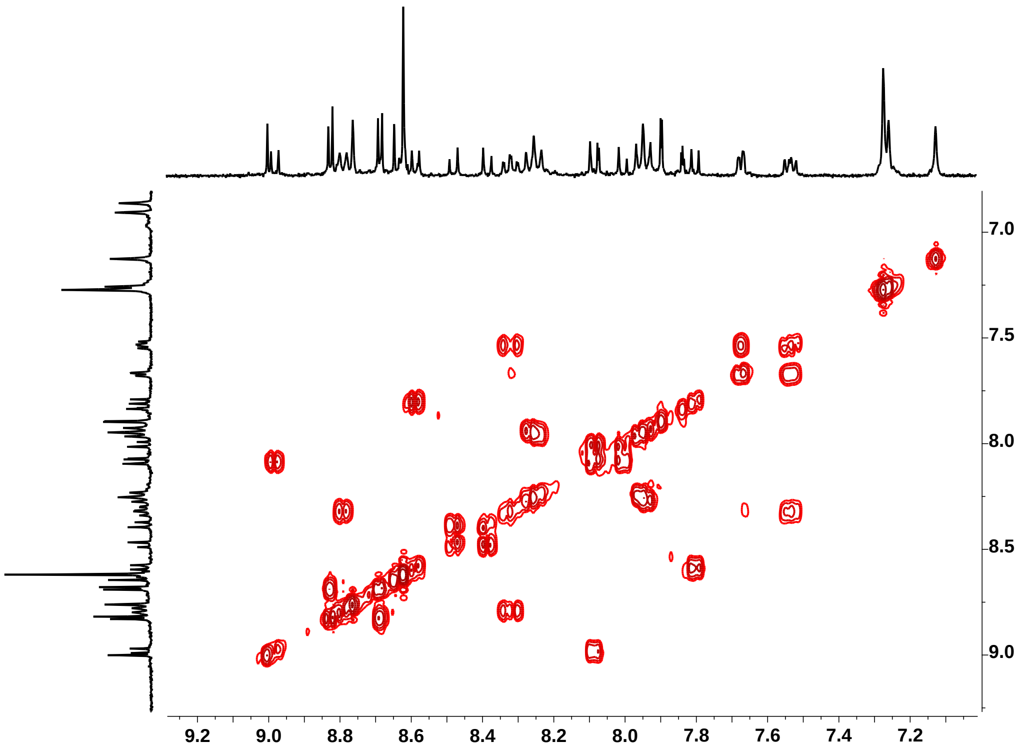


Figure S38. ^{1}H NMR spectrum (CD_2Cl_2:CD_3CN, 9:1, 400 MHz) of prism **P**.



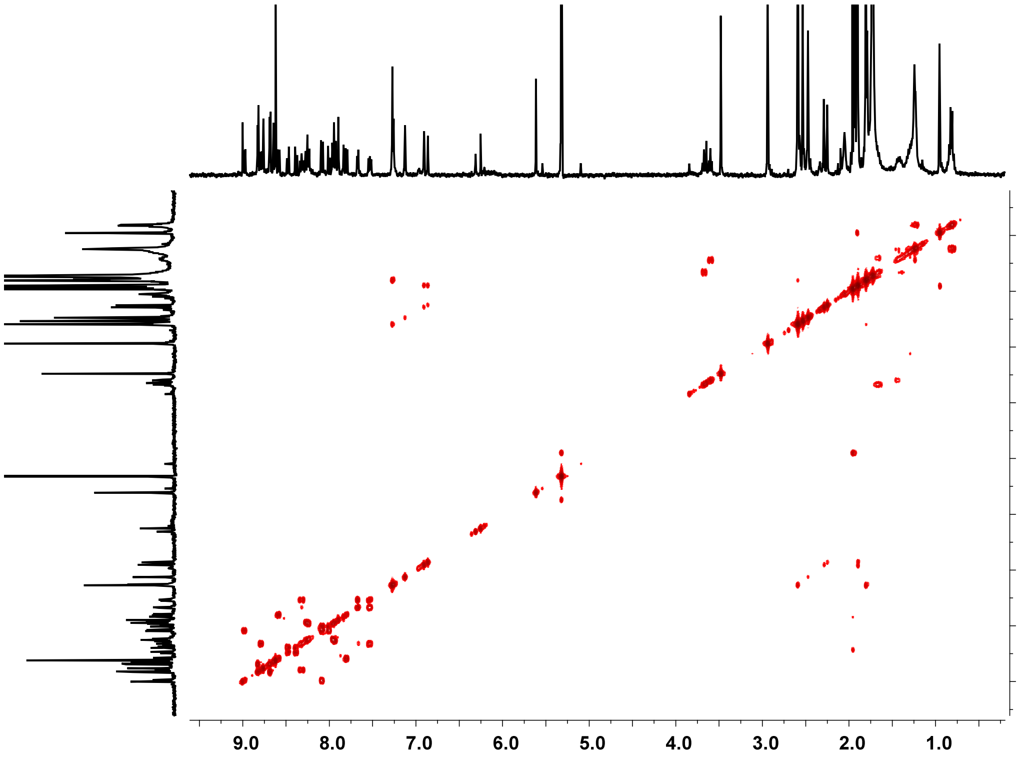


Figure S39. ^{1}H-^{1}H COSY NMR spectrum (CD_2Cl_2:CD_3CN, 9:1, 400 MHz) of prism **P**. Expanded parts of the aromatic region are shown at the top.

3. DOSY NMR spectrum of nanoprism P

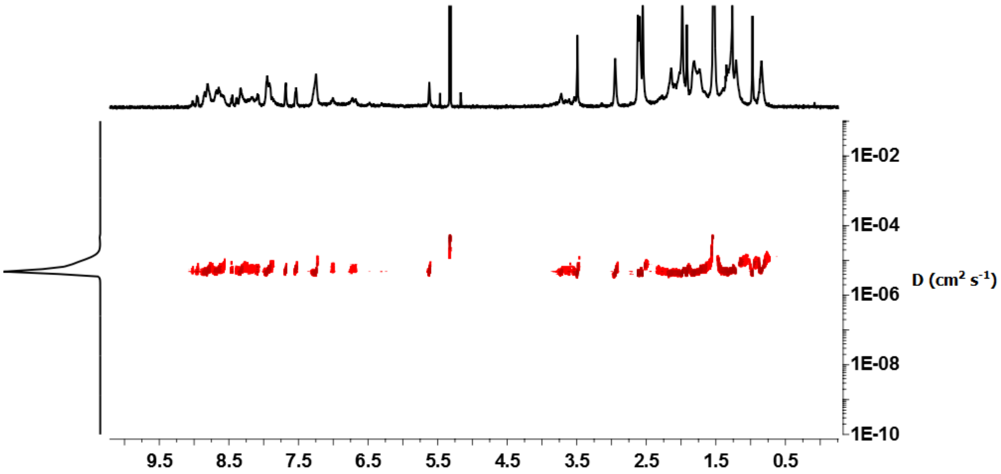


Figure S40. DOSY NMR spectrum (CD_2Cl_2, 600 MHz) of prism **P**.

4. **Energy minimised structure (MM$^+$ force field)**

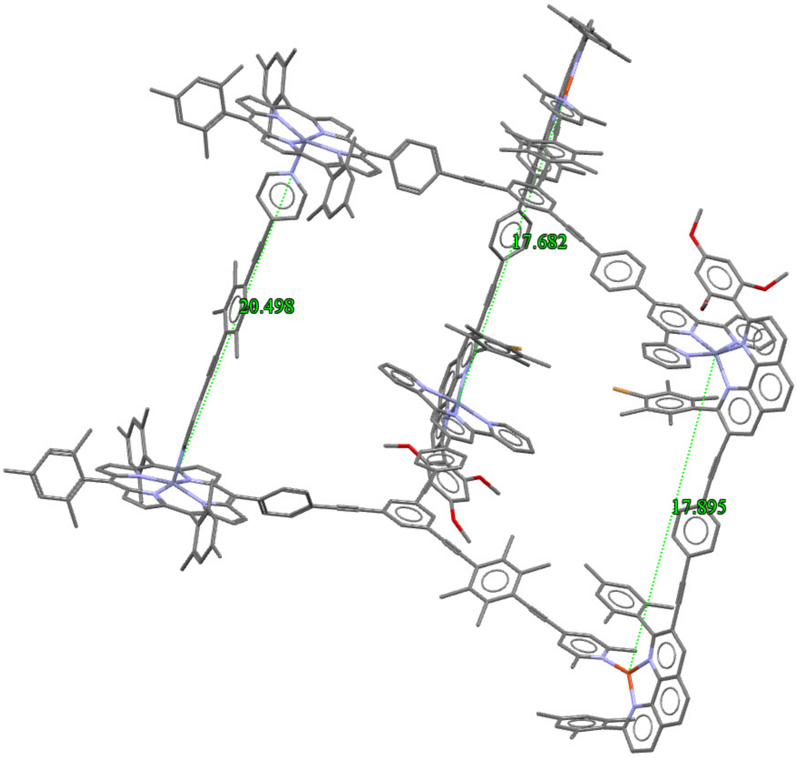


Figure S41. Energy minimised structure of the supramolecular nanoprism **P** (counteranions, hydrogens and alkyl chains are omitted for clarity).

5. ESI-MS spectra

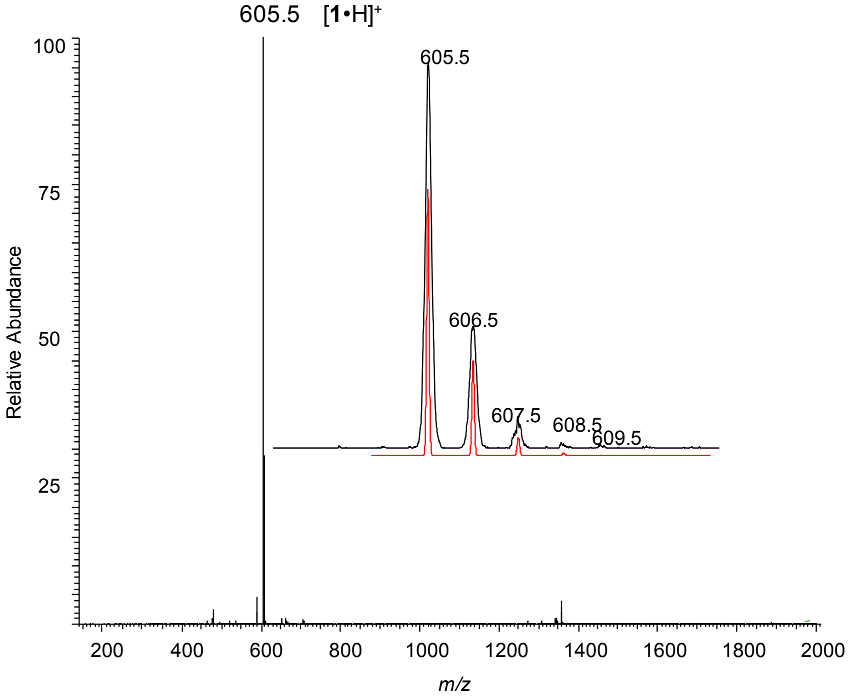


Figure S42. ESI-MS spectrum of compound **1** in DCM.

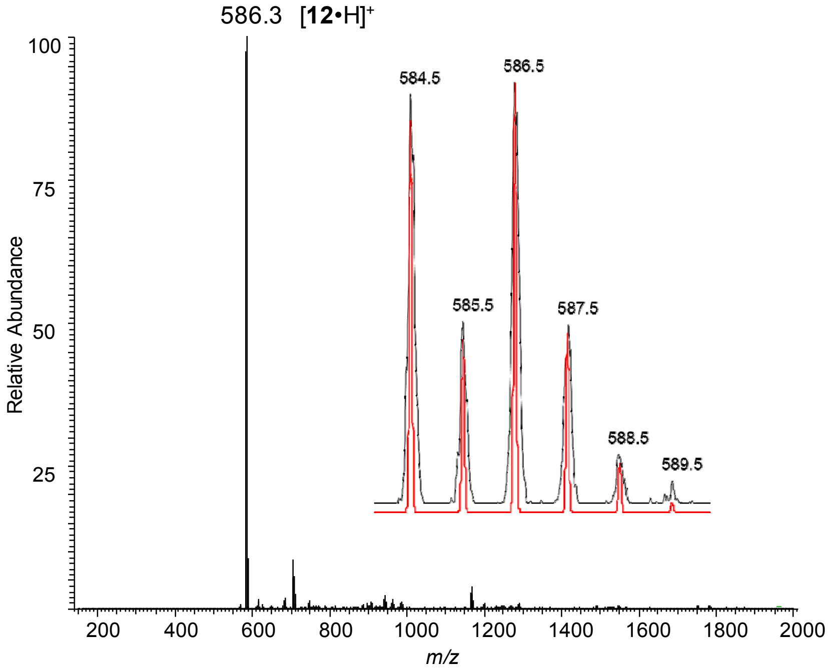


Figure S43. ESI-MS spectrum of compound **12** in DCM.

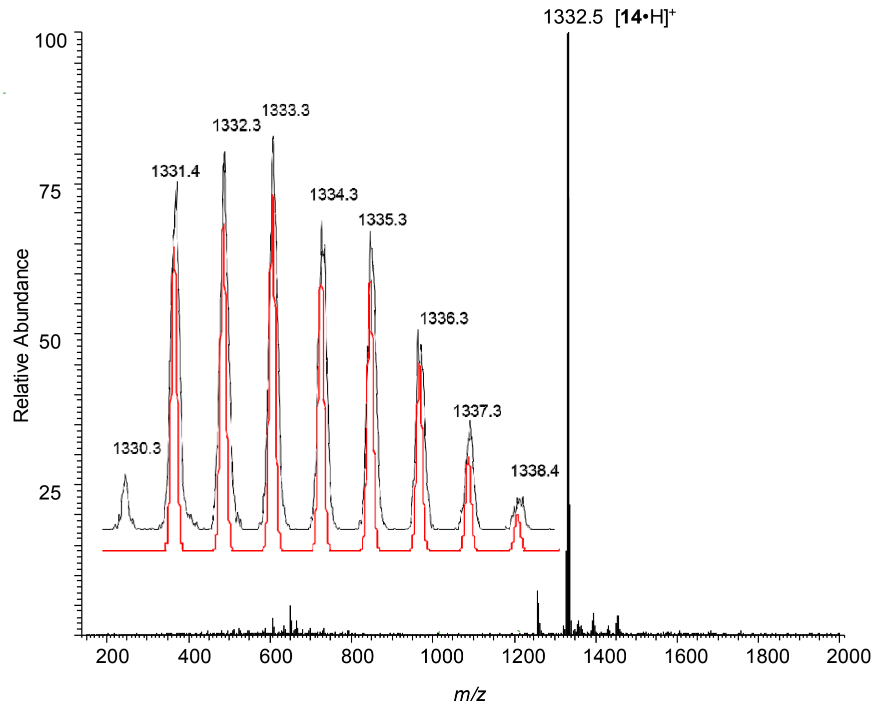


Figure S44. ESI-MS spectrum of compound **14** in DCM.

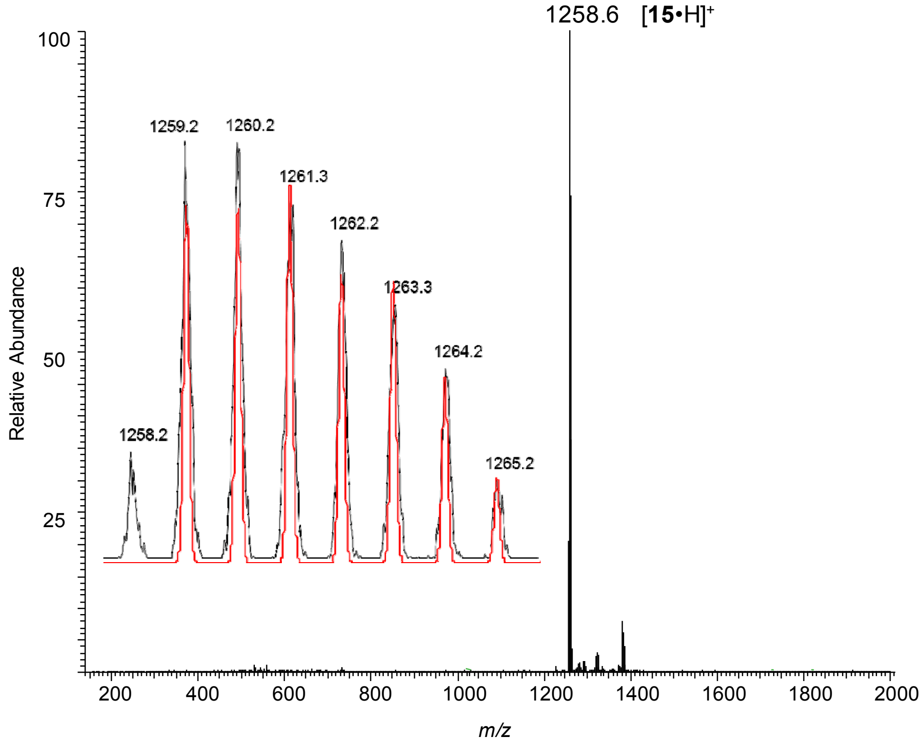


Figure S45. ESI-MS spectrum of compound **15** in DCM.

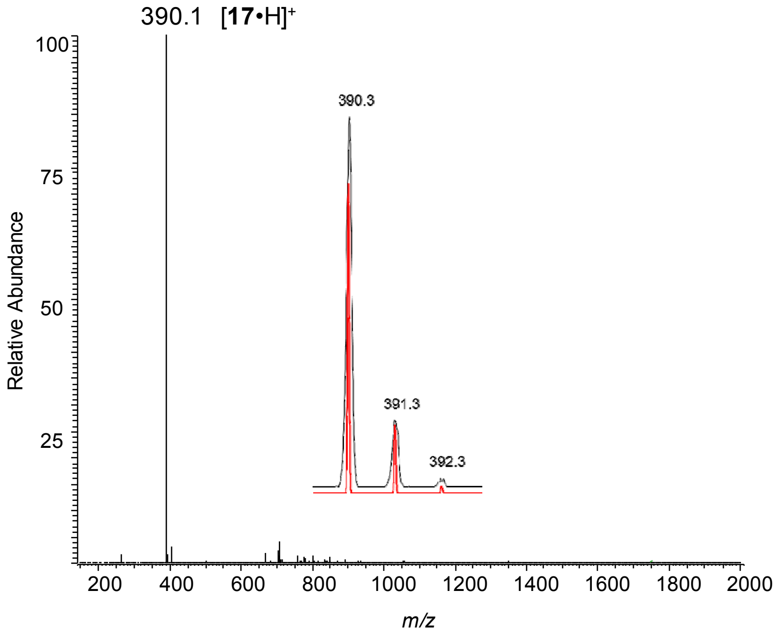


Figure S46. ESI-MS spectrum of compound **17** in DCM.

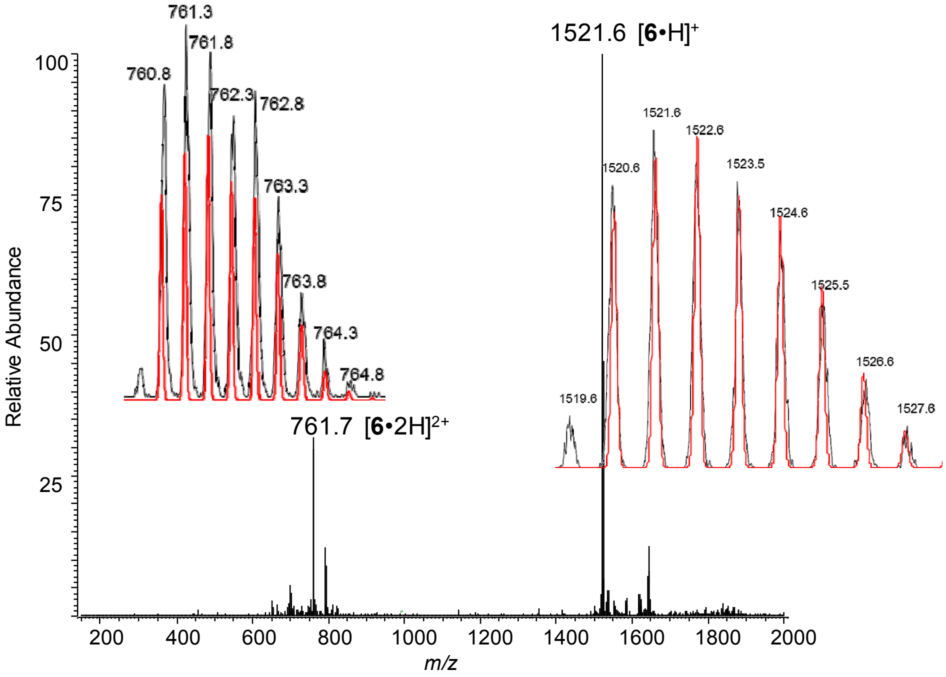


Figure S47. ESI-MS spectrum of compound **6** in DCM.

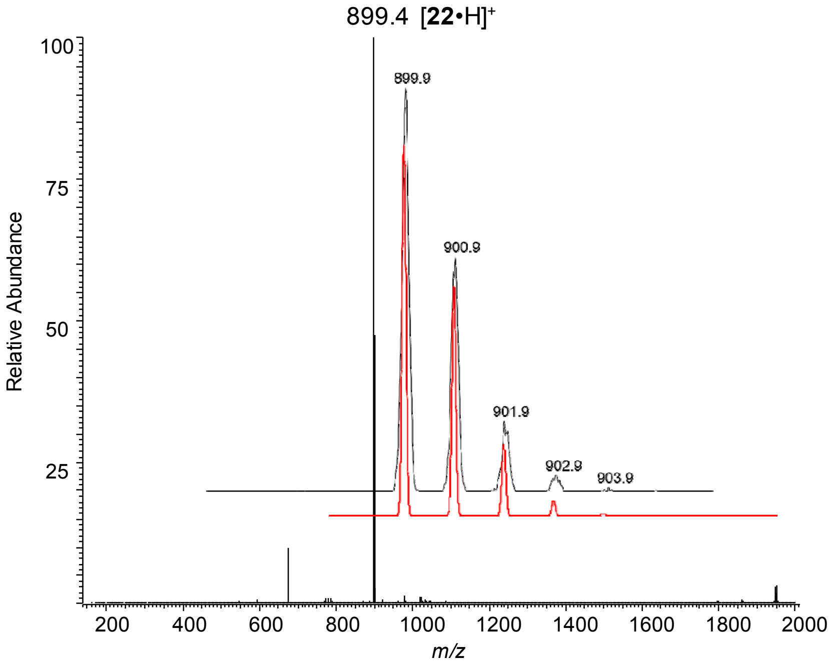


Figure S48. ESI-MS spectrum of compound **22** in DCM.

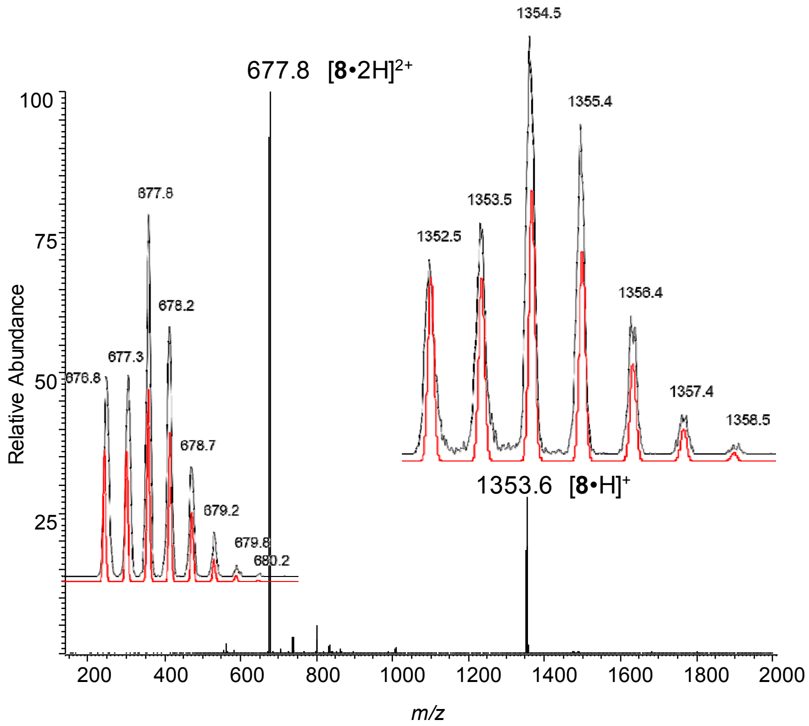


Figure S49. ESI-MS spectrum of compound **8** in DCM.

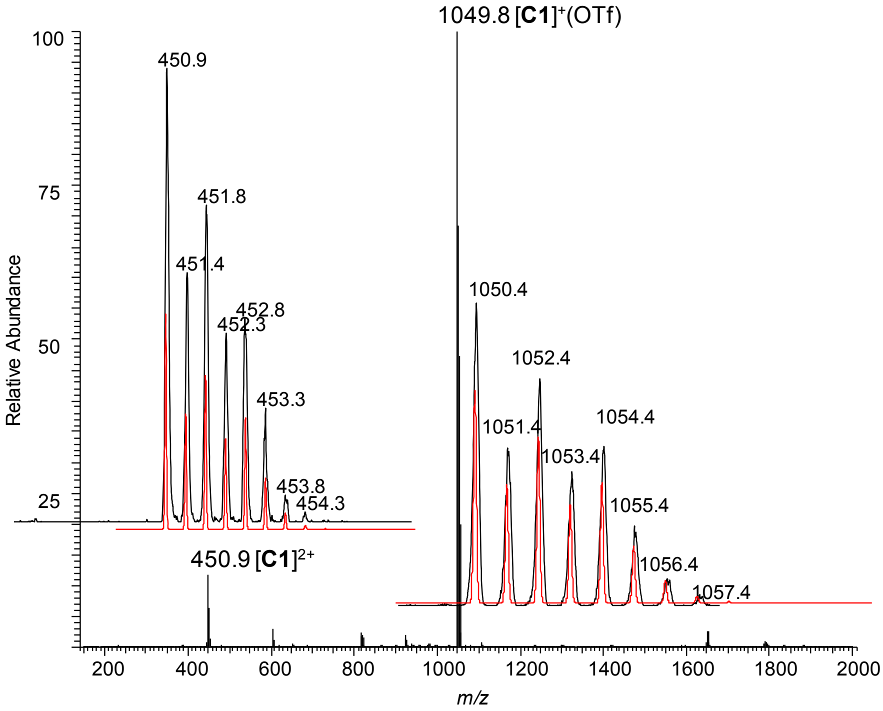


Figure S50. ESI-MS spectrum of compound **C1** = [Zn(**1**)(**4**)](OTf)$_2$ in DCM-CH$_3$CN.

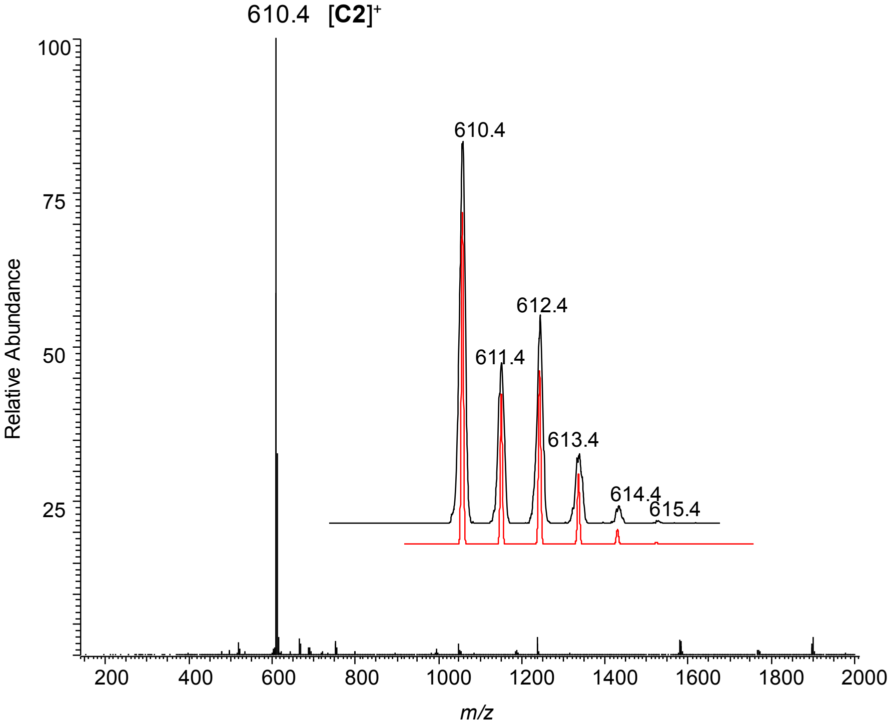


Figure S51. ESI-MS spectrum of compound **C2** = [Cu(**2**)(**5A**)]B(C$_6$F$_5$)$_4$ in DCM-CH$_3$CN.

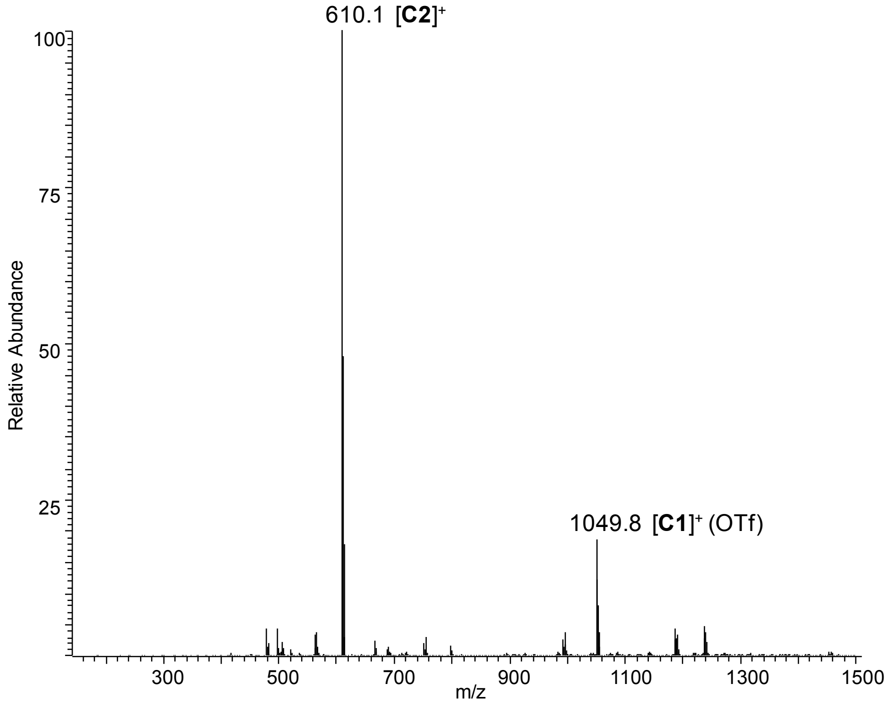


Figure S52. ESI-MS spectrum of equimolar mixture of **1**, **2**, **3**, **4**, **5A**, **5B**, $[Zn(OTf)_2]$ and $[Cu(CH_3CN)_4B(C_6F_5)_4]$ after 3 h reflux in DCM-acetonitrile (1:3).

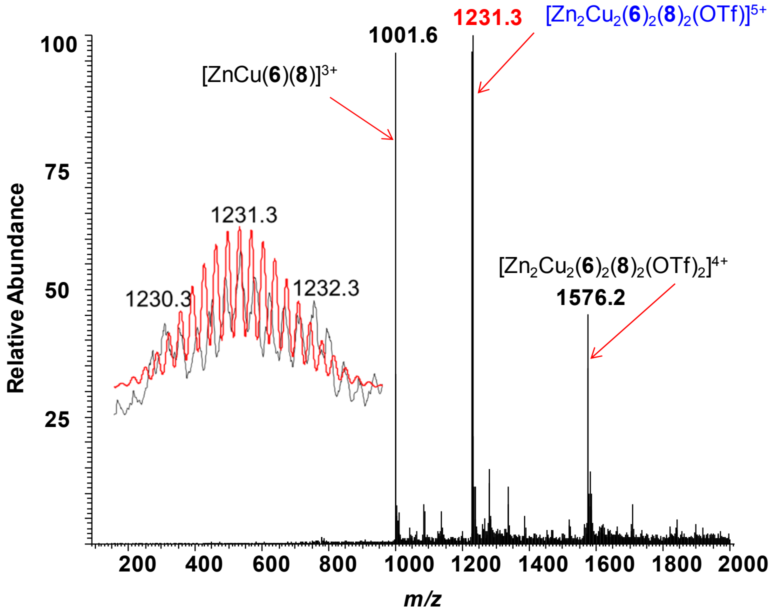


Figure S53. ESI-MS spectrum of tweezer **T** = $[Zn_2Cu_2(\mathbf{6})_2(\mathbf{8})_2](B(C_6F_5)_4)_2(OTf)_4$ in DCM: CH_3CN = 9:1.

6. UV-vis spectra

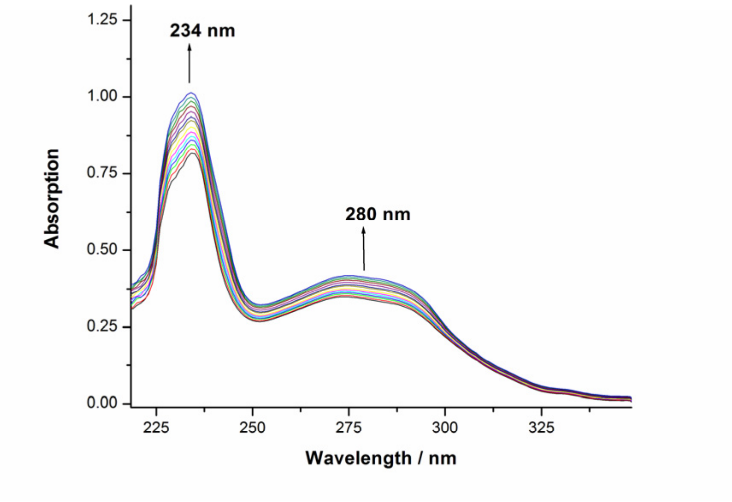


Figure S54. UV-vis titration of complex [Cu(**2**)]$^+$ (1.20 × 10^{-5} M) vs. ligand **5A** (8.38 × 10^{-5} M) in CH_2Cl_2 at 298 K. Wavelength region 220-350 nm was analysed using SPECFIT/32 global analysis system (Spectrum Software Associates, Marlborough, MA). Result: log K = 4.50 ± 0.21.

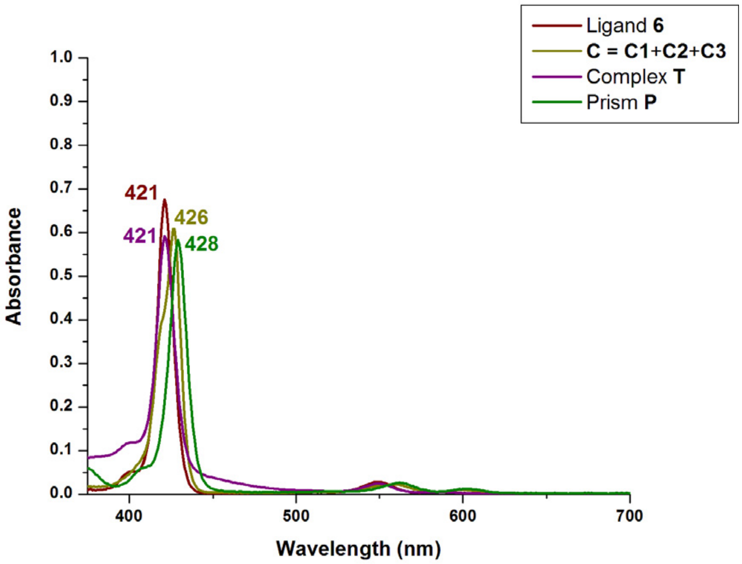


Figure S55. Comparison of UV-vis spectra of ligand **6**, **C** = **C1**+**C2**+**C3**, tweezer complex **T** and of nanoprism **P** in DCM (concentrations of ligand **6** and of complexes **C** ~10^{-6} M. Concentration of complex **T** and **P,** 0.50 × 10^{-6} M) at 298 K.

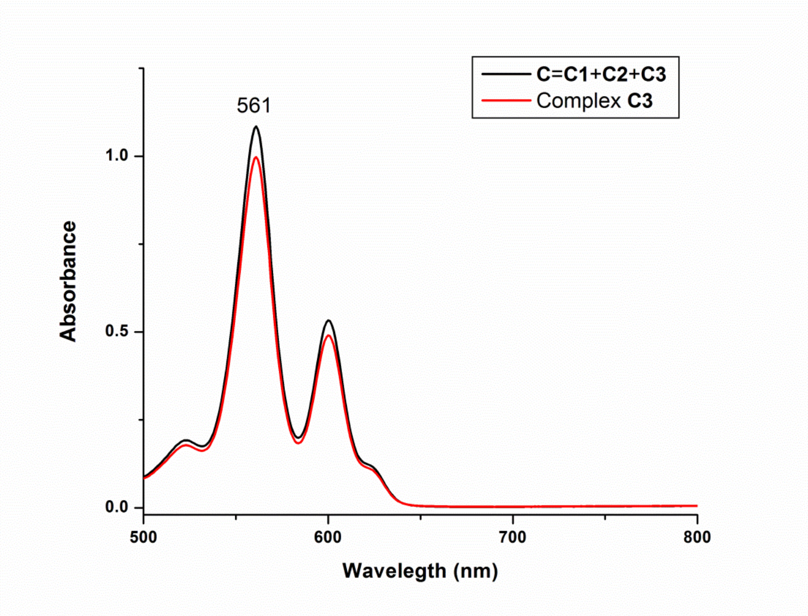


Figure S56. Comparison of UV-vis spectra of **C3** = [(**3**)(**5B**)] and of **C** = **C1**+**C2**+**C3** in DCM (both concentrations, *c* = 6 × 10^{-4} M) at 298 K.

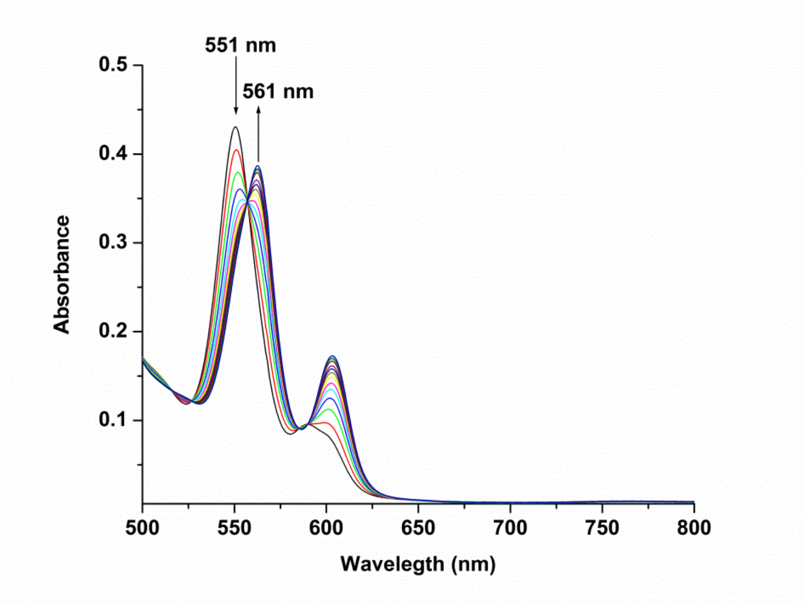


Figure S57. UV-vis titration of tweezer complex **T** (0.50 × 10^{-4} M) vs. ligand **7** (1.25 × 10^{-3} M) furnishing **P** (in CH_2Cl_2 at 298 K). The full wavelength region of 500-800 nm was analyzed using SPECFIT/32 global analysis system (Spectrum Software Associates, Marlborough, MA). Result: log *K* = 9.29 ± 0.04.

7. **References**

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