Allosteric Regulation of Rotational, Optical and Catalytic Properties within Multicomponent Machinery

Supporting Information

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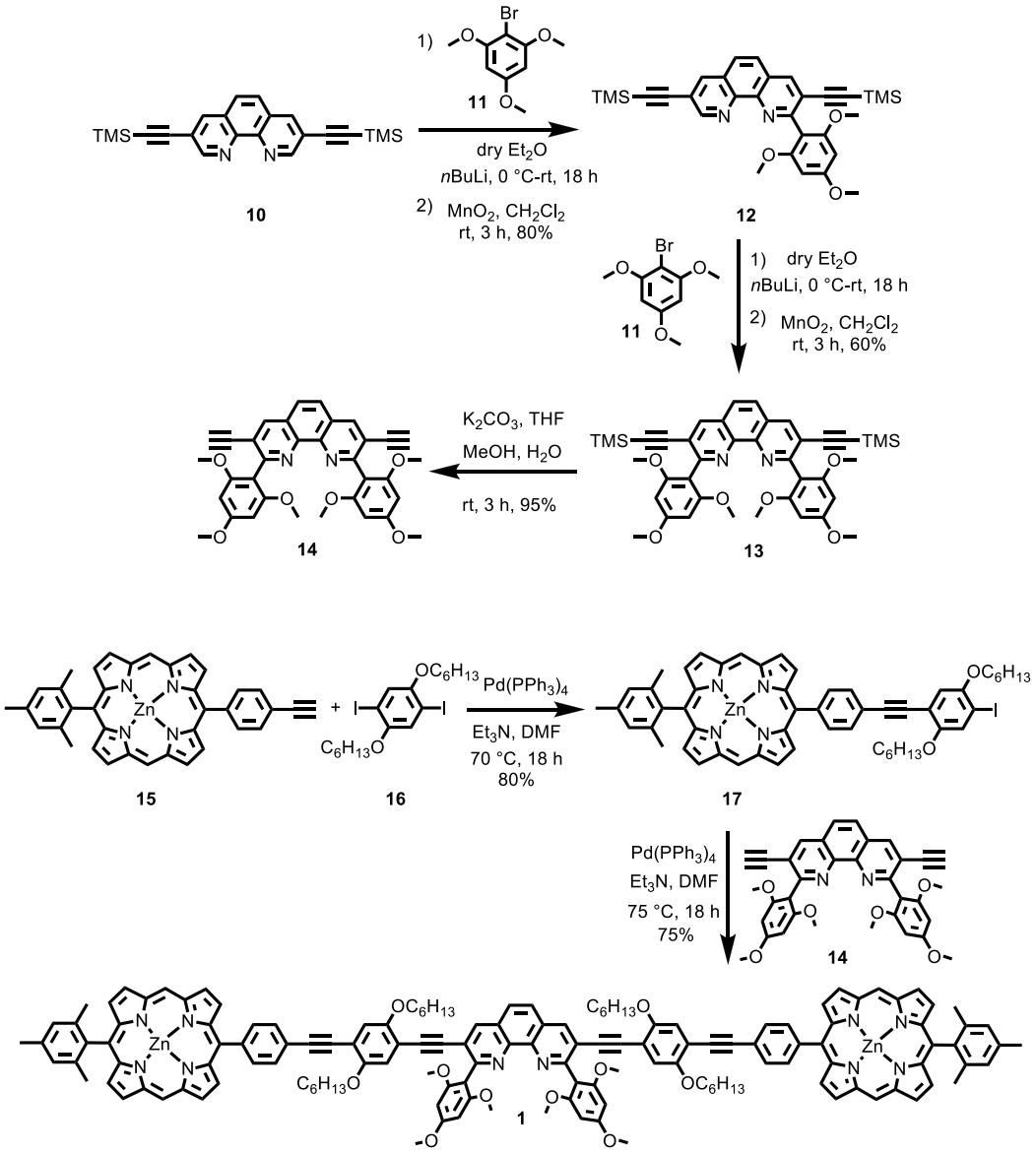
1. Synthesis

1.1 General information

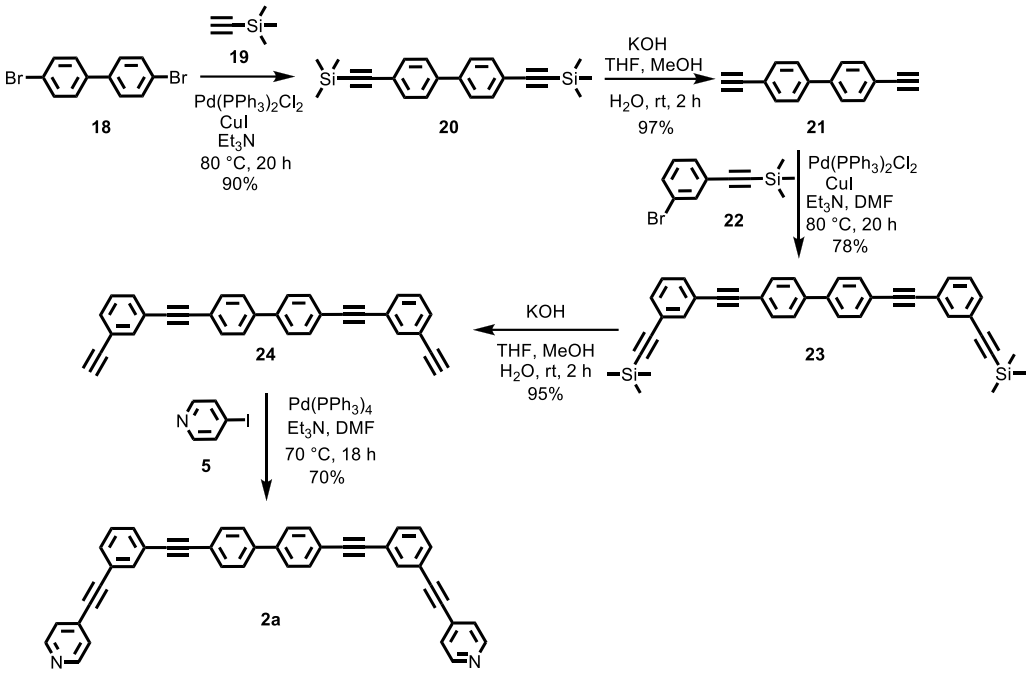
All solvents were dried by distillation prior to use while commercial reagents were used without any further purification. Brucker Avance (400 MHz), Jeol ECZ (500 MHz) and Varian (600 MHz) spectrometers were used to measure ^{1}H and ^{13}C NMR spectra using a deuterated solvent as the lock and residual protiated solvent as internal reference ($CDCl_3$: δ_H 7.26 ppm, δ_C 77.0 ppm; CD_2Cl_2: δ_H 5.32 ppm, δ_C 53.8 ppm, DMSO-d_6: δ_H 2.50 ppm, δ_C 39.52 ppm). The following abbreviations were used to define NMR peak pattern: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, bs = broad signal, m = multiplet. The coupling constant values are given in Hertz (Hz) and, wherever possible, assignments of protons are done. The numbering of different carbons in different molecular skeletons was not necessarily done following the IUPAC nomenclature rules; it is exclusively done for assigning NMR signals. All electrospray ionization (ESI-MS) spectra were recorded on a Thermo-Quest LCQ deca and the theoretical isotopic distributions of the mass signals were calculated (https://omics.pnl.gov/software/molecular-weight-calculator) using molecular weight calculator software. Melting points of compounds were measured on a BÜCHI 510 instrument and are not corrected. Infrared spectra were recorded on a Perkin Elmer Spectrum-Two FT-IR spectrometer. Elemental analysis was performed using the EA-3000 CHNS analyzer. UV-vis spectra were recorded on a Varian Cary 100 BioUV/Vis spectrometer. Column chromatography was performed either on silica gel (60-400 mesh) or neutral alumina (Fluka, 0.05-0.15 mm, Brockmann Activity 1). Merck silica gel (60 F254) or neutral alumina (150 F254) sheets were used for thin layer chromatography (TLC). All complex preparations were performed directly in the NMR tube using CD_2Cl_2 as solvent.

1.2 Syntheses and characterizations of ligands

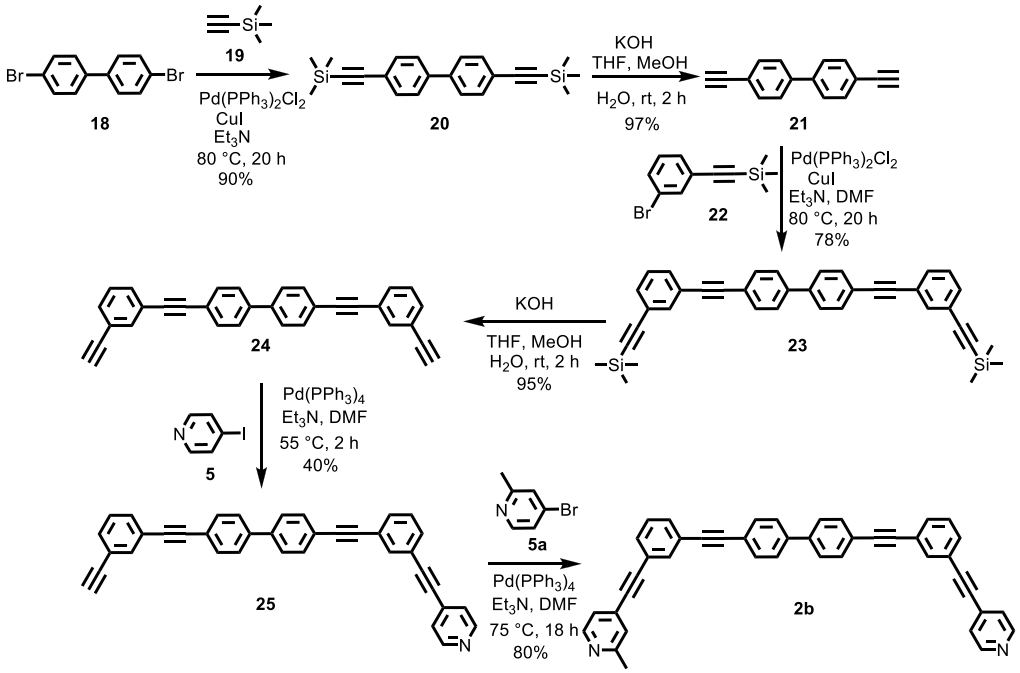


Scheme S1. Reaction scheme to prepare stator **1**.

Synthesis of **10**,[1] **15**[2] and **16**[3] was done following literature-known procedures.

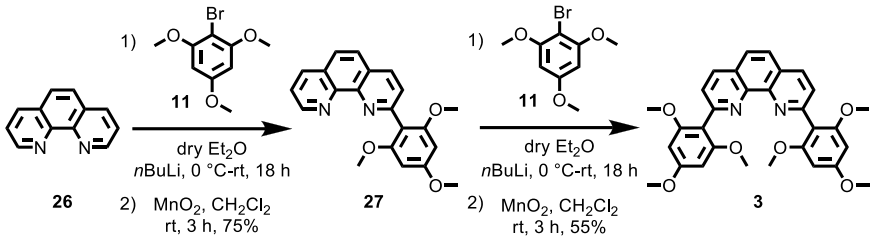


Scheme S2. Reaction scheme to prepare symmetric arm **2a**.



Scheme S3. Reaction scheme to prepare dissymmetric arm **2b**.

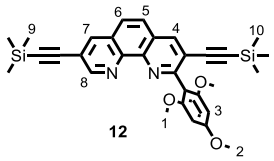
Synthesis of **20**,[4] **21**[4] and **22**[5] was done following literature known procedures.



Scheme S4. Reaction scheme to prepare model compound **3**.

Synthesis of model porphyrin **4** was accomplished by a literature known procedure.2

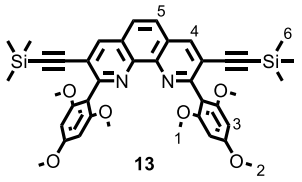
Synthesis of **12**



Under N_2 atmosphere, a solution of 1.6 M *n*-BuLi in *n*-hexane (1.00 mL, 1.60 mmol) was added slowly at 0 °C to a solution of 1-bromo-2,4,6-trimethoxybenzene (**11**, 398 mg, 1.61 mmol) in diethyl ether (30 mL) over a period of 10 min. Then it was warmed up to rt and stirred for 6 h, 3,8-bis((trimethylsilyl)ethynyl)-1,10-phenanthroline (**10**, 200 mg, 0.537 mmol) was added to the mixture under N_2 atmosphere. The resulting violet solution was stirred at room temp. for 12 h and then quenched with H_2O. The layers were separated and the aqueous layer was extracted with DCM. After oxidation with MnO_2 (185 mg, 2.13 mmol) at room temp. for 3 h the combined organic layers were filtered through a pad of celite and the solvents removed under reduced pressure to furnish an yellow residue. The compound was purified by column chromatography (SiO_2) using 30% EtOAc in hexane as eluent to afford a pale yellow solid (233 mg, 80%). $\boldsymbol{R_f}$ **=** 0.3 (SiO_2, 30% EtOAc in hexane). **mp:** >250 °C. **IR (KBr):** ν = 647.5, 700.3, 759.6, 841.0, 861.4, 1126.8, 1156.8, 1228.6, 1204.4, 1248.3, 1378.5, 1405.6, 1468.6, 1585.5, 1610.4, 2146.5,

2957.8 cm^{-1}.**^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 0.07 (s, 9H, 9/10-H), 0.31 (s, 9H, 10/9-H), 3.67 (s, 6H, 1-H), 3.87 (s, 3H, 2-H), 6.21 (s, 2H, 3-H), 7.70 (d, ^3J = 8.8 Hz, 1H, 6-H), 7.76 (d, ^3J = 8.8 Hz, 1H, 5-H), 8.28 (d, ^4J = 2.2 Hz, 1H, 7-H), 8.32 (s, 1H, 4-H), 9.17 (d, ^4J = 2.2 Hz, 1H, 8-H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = –0.28, –0.14, 55.5, 55.9, 90.8, 99.2, 99.8, 102.0, 102.6, 112.2, 119.0, 121.7, 126.1, 126.8, 127.1, 128.0, 138.5, 138.6, 144.6, 144.9, 152.5, 158.5, 159.2, 161.7 ppm. **Elemental analysis:** Anal. Calcd for $C_{31}H_{34}N_2O_3Si_2$: C, 69.11; H, 6.36; N, 5.20. Found: C, 68.83; H, 6.04; N, 5.26. **ESI-MS:** *m/z* (%) 539.2 (100) $[(H)(\mathbf{12})]^+$.

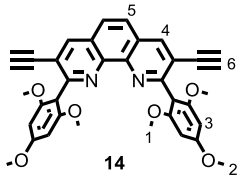
Synthesis of **13**



Under N_2 atmosphere a solution of 1.6 M *n*-BuLi in *n*-hexane (0.522 μL, 836 μmol) was added slowly at 0 °C to a solution of 1-bromo-2,4,6-trimethoxybenzene (**11**, 206 mg, 836 μmol) in diethyl ether (30 mL) over a period of 10 min. Then it was warmed up to rt and stirred for 6 h, compound **12** (150 mg, 278 μmol) was added to the mixture under N_2 atmosphere. The resulting violet solution was further stirred at room temperature for 12 h and then quenched with H_2O. The layers were separated and the aqueous layer was extracted with DCM. After oxidation with MnO_2 (185 mg, 2.13 mmol) at room temperature for 3 h the combined organic layers were filtered through a pad of celite and the solvents removed under reduced pressure to furnish an yellow residue. The compound was purified by column chromatography (SiO_2) using 60% EtOAc in hexane as eluent to afford a pale yellow solid (118 mg, 60%). $\boldsymbol{R_f}$ = 0.3 (SiO_2, 70%

EtOAc in hexane). **mp:** >250 °C. **IR (KBr):** ν = 545.0, 588.5, 626.2, 647.3, 698.6, 729.5, 759.8, 782.4, 916.5, 947.7, 994.4, 1037.4, 1059.4, 1130.7, 1154.4, 1204.0, 1223.3, 1336.9, 1394.4, 1406.2, 1468.4, 1589.1, 1613.7, 2149.6, 2837.2, 2899.5, 2954.9, 2999.7 cm^{-1}. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 0.07 (s, 18H, 6-H), 3.67 (s, 12H, 1-H), 3.83 (s, 6H, 2-H), 6.19 (s, 4H, 3-H), 7.71 (s, 2H, 5-H), 8.30 (s, 2H, 4-H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = –0.25, 55.4, 56.0, 91.2, 99.1, 102.8, 112.3, 121.2, 126.2, 127.2, 138.6, 144.6, 157.6, 159.1, 161.7 ppm. **Elemental analysis:** Anal. Calcd for $C_{40}H_{44}N_2O_6Si_2$: C, 68.15; H, 6.29; N, 3.97. Found: C, 68.18; H, 5.95; N, 3.75. **ESI-MS:** *m/z* (%) 705.3 (100) [(H)(**13**)]$^+$.

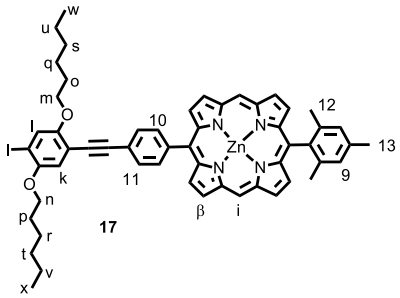
Synthesis of **14**



Compound **13** (100 mg, 142 μmol) and K_2CO_3 (196 mg, 1.42 mmol) were stirred in THF (30 mL), MeOH (20 mL) and H_2O (10 mL) at room temperature. After completion of the reaction as confirmed by TLC, the organic solvents were evaporated and the resultant suspension was extracted with DCM (150 mL). Finally DCM was evaporated under reduced pressure to obtain **14** as pale yellow solid (76.0 mg, 95%). ***R*$_f$ =** 0.3 (SiO_2, 75% EtOAc in hexane). **mp:** >250 °C. **IR (KBr):** ν = 638.3, 784.1, 811.2, 921.2, 987.9, 1032.5, 1058.1, 1154.7, 1205.3, 1226.2, 1338.3, 1410.4, 1466.1, 1508.9, 1589.4, 1612.3, 2150.2, 2839.8, 2940.8, 3282.5 cm^{-1}. **^{1}H NMR (DMSO-*d*$_6$, 400 MHz):** δ = 3.61 (s, 12H, 1-H), 3.83 (s, 6H, 2-H), 4.21 (s, 2H, 6-H), 6.33 (s, 4H, 3-H), 8.01 (s, 2H, 5-H), 8.64 (s, 2H, 4-H) ppm. **^{13}C NMR (DMSO-*d*$_6$, 100 MHz):** δ = 55.4, 55.6,

81.0, 85.1, 90.9, 110.7, 120.2, 126.4, 127.0, 139.7, 143.8, 156.8, 158.4, 161.3 ppm. **Elemental analysis:** Anal. Calcd for $C_{34}H_{28}N_2O_6 \bullet H_2O$: C, 70.58; H, 5.23; N, 4.84. Found: C, 70.41; H, 4.89; N, 4.75. **ESI-MS:** *m/z* (%) 561.2 (100) $[(H)(\mathbf{14})]^+$.

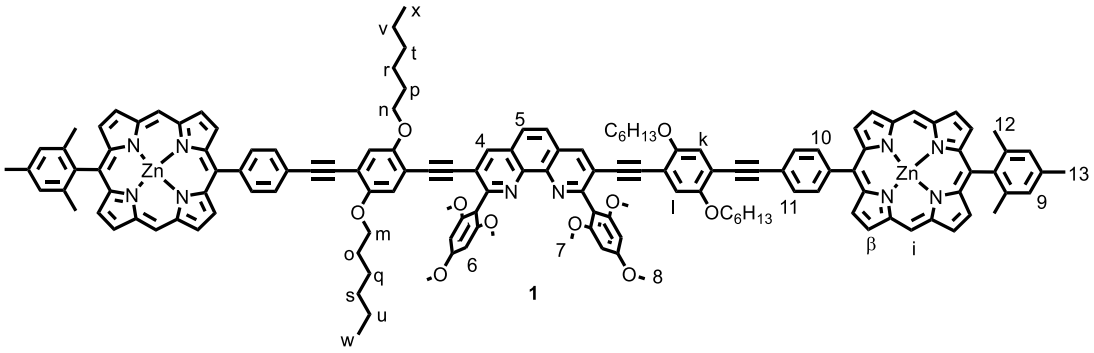
Synthesis of **17**



Compound **15** (500 mg, 845 μmol) and **16** (4.48 g, 8.45 mmol) were dissolved in dry DMF (20 mL) and dry Et_3N (20 mL) in a sealed tube under N_2 atmosphere. The mixture was degassed by using two freeze-pump-thaw cycles. Then $Pd(PPh_3)_4$ (50.0 mg, 43.3 μmol) was added under N_2 atmosphere. After degassing again by freeze-pump-thaw cycles, the reaction mixture was stirred at 70 ºC for 18 h. The solvent was evaporated under reduced pressure and the residue worked up with ice cold water to remove DMF. The organic part was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4 and concentrated. The compound was purified by column chromatography (SiO_2) using 20% DCM in hexane as eluent to afford a violet solid (670 mg, 80%). $\boldsymbol{R_f}$ **=** 0.3 (SiO_2, 20% DCM in hexane). **mp:** 183 ºC. **IR (KBr):** ν = 698.2, 782.1, 811.4, 848.9, 1057.9, 1211.5, 1392.4, 1463.6, 1612.5, 2205.1, 2854.3, 2925.5 cm^{-1}. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 0.94-0.98 (m, 6H, w+x-H), 1.39-1.41 (m, 4H, u+v-H), 1.42-1.46 (m, 4H, s+t-H), 1.54-1.61 (m, 2H, r-H), 1.62-1.69 (m, 2H, q-H), 1.85 (s, 6H, 12-H), 1.87-1.91 (m, 2H, p-H), 1.92-1.98 (m, 2H, o-H), 2.68 (s, 3H, l3-H), 4.06 (t, ^3J = 6.4 Hz, 2H, n-H), 4.09 (t, ^3J = 6.4 Hz, 2H, m-H), 7.08 (s,

1H, l-H), 7.34 (s, 2H, 9-H), 7.38 (s, 1H, k-H), 7.97 (d, ^3J = 8.2 Hz, 2H, 11-H), 8.23 (d, ^3J = 8.2 Hz, 2H, 10-H), 9.00 (d, ^3J = 4.4 Hz, 2H, β-H), 9.12 (d, ^3J = 4.4 Hz, 2H, β-H), 9.41 (d, ^3J = 4.4 Hz, 2H, β-H), 9.42 (d, ^3J = 4.4 Hz, 2H, β-H), 10.28 (s, 2H, i-H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 14.1 (2C), 21.5, 21.7, 22.6, 22.7, 25.8 (2C), 29.2, 29.4, 31.5, 31.7, 70.1, 70.2, 86.6, 87.7, 94.4, 106.0, 113.8, 116.1, 118.6, 119.1, 122.6, 124.0, 127.7, 129.8, 131.5, 131.8, 132.1, 132.3, 134.6, 137.6, 138.7, 139.3, 142.8, 149.4, 149.6, 149.7, 150.0, 151.9, 154.5 ppm. **Elemental analysis:** Anal. Calcd for $C_{55}H_{53}N_4IO_2Zn$: C, 66.43; H, 5.37; N, 5.63. Found: C, 66.61; H, 5.21; N, 5.52.

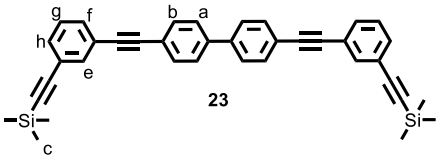
Synthesis of stator **1**



Compound **14** (60.0 mg, 107 μmol) and **17** (638 g, 642 μmol) were dissolved in dry DMF (20 mL) and dry Et_3N (20 mL) in a sealed tube under N_2 atmosphere. The mixture was degassed using two freeze-pump-thaw cycles. Then $Pd(PPh_3)_4$ (24.7 mg, 21.4 μmol) was added under N_2 atmosphere. After degassing again by freeze-pump-thaw cycles, the reaction mixture was stirred at 75 ºC for 18 h. The solvent was evaporated under reduced pressure and the residue worked up with ice cold water to remove DMF. The organic part was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4 and concentrated. The compound was purified by column chromategraphy (SiO_2) using 10% EtOAc in DCM as eluent to afford a violet solid (184 mg, 75%). $\boldsymbol{R_f}$ = 0.3

(SiO_2, 10% EtOAc in DCM). **mp:** > 250 ºC. **IR (KBr):** ν = 783.0, 993.2, 1056.8, 1127.3, 1204.1, 1391.7, 1609.7, 2206.5, 2854.8, 2927.9 cm^{-1}. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 0.96-1.02 (m, 12H, w+x-H), 1.46-1.50 (m, 16H, s+t+u+v-H), 1.59-1.62 (m, 4H, q/r-H, partially merged with H_2O signal), 1.70-1.78 (m, 4H, r/q-H), 1.83 (s, 12H, 12-H), 1.88-1.95 (m, 4H, p/o-H), 1.96-2.03 (m, 4H, o/p-H), 2.67 (s, 6H, 13-H), 3.74 (s, 12H, 7-H), 3.90 (s, 6H, 8-H), 4.05 (t, ^3J = 6.4 Hz, 4H, m/n-H), 4.11 (t, ^3J = 6.4 Hz, 4H, n/m-H), 6.31 (s, 4H, 6-H), 6.60 (s, 2H, l-H), 7.15 (s, 2H, k-H), 7.33 (s, 4H, 9-H), 7.83 (s, 2H, 5-H), 7.97 (d, ^3J = 8.2 Hz, 4H, 11-H), 8.26 (d, ^3J = 8.2 Hz, 4H, 10-H), 8.43 (s, 2H, 4-H), 8.99 (d, ^3J = 4.6 Hz, 4H, β-H), 9.15 (d, ^3J = 4.6 Hz, 4H, β-H), 9.41 (d, ^3J = 4.6 Hz, 4H, β-H), 9.46 (d, ^3J = 4.6 Hz, 4H, β-H), 10.30 (s, 4H, i-H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 14.2 (2C), 21.5, 21.7, 22.8 (2C), 25.8, 26.0, 29.3, 29.5, 31.7, 31.8, 55.4, 56.2, 69.5, 69.9, 87.1, 91.2, 93.4, 95.2, 106.0, 112.7, 114.1, 114.3, 117.3, 117.5, 118.6, 119.1, 121.6, 122.7, 126.4, 127.5, 127.7, 129.9, 131.5, 131.9, 132.1, 132.3, 134.6, 137.6, 138.0, 138.7, 139.3, 142.8, 144.7, 149.4, 149.6, 149.8, 150.0, 153.2, 153.8, 157.2, 159.6 (2C), 161.7 ppm. **Elemental analysis:** Anal. Calcd for $C_{145}H_{134}N_{10}Cl_2O_{10}Zn_2$•$CH_2Cl_2$: C, 73.22; H, 5.68; N, 5.89. Found: C, 72.84; H, 5.28; N, 5.91. **ESI-MS:** *m/z* (%) 1147.4 (100) $[(H)_2(\mathbf{1})]^{2+}$.

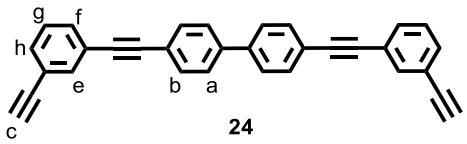
Synthesis of **23**



Compound **21** (300 mg, 1.48 mmol) and **22** (1.88 mg, 7.42 mmol) were dissolved in dry Et_3N (25 mL) in a sealed tube under N_2 atmosphere. The mixture was degassed by purging N_2 for 20 min. Then $Pd(PPh_3)_2Cl_2$ (104 mg, 0.148 mmol) and CuI (28.0 mg, 0.148 mmol) were added

under N_2 atmosphere. The reaction mixture was stirred at 80 ºC for 20 h. The solvent was evaporated under reduced pressure and the residue worked up with water. The organic part was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4 and concentrated. The compound was purified by column chromatography (SiO_2) using 3% EtOAc in hexane as eluent to afford a pale yellow solid (630 mg, 78%). $\boldsymbol{R_f}$ **=** 0.3 (SiO_2, 3% EtOAc in hexane). **mp:** > 250 ºC. **IR (KBr):** ν = 531.3, 646.4, 686.3, 699.6, 759.5, 793.4, 823.8, 840.1, 857.7, 893.8, 939.9, 1002.6, 1130.5, 1211.2, 1249.3, 1384.2, 1405.7, 1472.9, 1496.1, 1567.8, 1591.6, 2168.6, 2853.4, 2923.8, 2958.4 cm^{-1}. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 0.26 (s, 18H, c-H), 7.30 (t, ^3J = 7.8 Hz, 2H, g-H), 7.43 (dt, ^3J = 7.8 Hz, ^4J = 1.2 Hz, 2H, h/f-H), 7.48 (dt, ^3J = 7.8 Hz, ^4J = 1.2 Hz, 2H, f/h-H), 7.60 (s, 8H, a+b-H), 7.68 (t, ^4J = 1.2 Hz, 2H, e-H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = –0.12, 89.5, 89.7, 95.0, 104.1, 122.3, 123.4, 123.5, 126.9, 128.4, 131.5, 131.6, 132.1, 135.0, 140.2 ppm. **Elemental analysis:** Anal. Calcd for $C_{38}H_{34}Si_2$: C, 83.46; H, 6.27. Found: C, 83.38; H, 5.92.

Synthesis of **24**

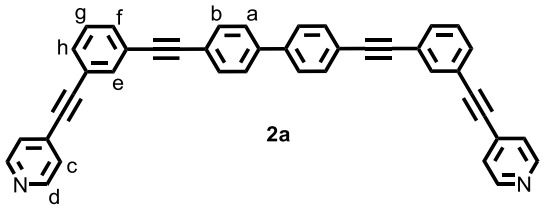


24

Compound **23** (500 mg, 914 μmol) and KOH (510 mg, 9.14 mmol) were stirred in THF (15 mL), MeOH (15 mL) and H_2O (5 mL) at room temperature. After completion of the reaction as confirmed by TLC, the organic solvents were evaporated and the resultant suspension was extracted with DCM (150 mL). Finally DCM was evaporated under reduced pressure to furnish **24** as yellow solid (350 mg, 95%). $\boldsymbol{R_f}$ **=** 0.3 (SiO_2, 5% EtOAc in hexane). **mp:** 197 ºC. **IR (KBr):** ν = 528.8, 599.6, 613.2, 689.3, 804.5, 823.0, 907.1, 999.6, 1114.0, 1247.9, 1322.7, 1384.3,

1405.5, 1472.4, 1496.9, 1590.9, 1638.0, 2169.7, 2859.4, 2923.1, 2961.8, 3294.5 cm^{-1}. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 3.11 (s, 2H, c-H), 7.33 (td, ^3J = 7.8 Hz, ^5J = 0.4 Hz, 2H, g-H), 7.46 (dt, ^3J = 7.8, ^4J = 1.4, 2H, h/f-H), 7.53 (dt, ^3J = 7.8, ^4J = 1.4, 2H, f/h-H), 7.61 (s, 8H, a+b-H), 7.69 (td, ^4J = 1.4 Hz, ^5J = 0.4 Hz, 2H, e-H), ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 77.8, 82.8, 89.3, 89.9, 122.3, 122.5, 123.6, 126.9, 128.5, 131.8(2C), 132.2, 135.1, 140.2 ppm. **Elemental analysis:** Anal. Calcd for $C_{32}H_{18}$: C, 95.49; H, 4.51. Found: C, 95.50; H, 4.58.

Synthesis of **2a**

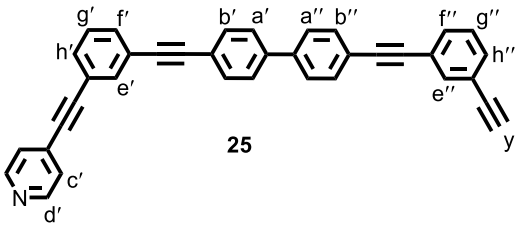


2a

Compound **24** (100 mg, 248 μmol) and **5** (306 mg, 1.49 mmol) were dissolved in dry DMF (15 mL) and dry Et_3N (15 mL) in a sealed tube under N_2 atmosphere. The mixture was degassed by using two freeze-pump-thaw cycles. Then $Pd(PPh_3)_4$ (28.0 mg, 24.8 μmol) was added under N_2 atmosphere. After degassing again by freeze-pump-thaw cycles, the reaction mixture was stirred at 70 ºC for 18 h. The solvent was evaporated under reduced pressure and the residue worked up with ice cold water to remove DMF. The organic part was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4 and concentrated. The compound was purified by column chromatography (SiO_2) using 2% MeOH in dichloromethane as eluent to afford a yellow solid (96.5 mg, 70%). $\boldsymbol{R_f}$ **=** 0.5 (SiO_2, 4% MeOH in DCM). **mp:** > 250 ºC. **IR (KBr):** ν = 527.8, 545.0, 686.9, 735.6, 802.2, 821.1, 905.2, 936.0, 988.8, 1116.2, 1214.3, 1384.4, 1406.8, 1496.3, 1537.4, 1571.0, 1594.8, 2213.8, 2855.4, 2923.2, 3041.8, 3076.0 cm^{-1}. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.387

(t, ^3J = 7.8 Hz, 2H, g-H), 7.390 (d, ^3J = 6.0 Hz, 4H, c-H), 7.52 (dt, ^3J = 7.8 Hz, ^4J = 1.2 Hz, 2H, h/f-H), 7.57 (dt, ^3J = 7.8 Hz, ^4J = 1.2 Hz, 2H, f/h-H), 7.63 (s, 8H, a+b-H), 7.76 (t, ^4J = 1.2 Hz, 2H, e-H), 8.62 (d, ^3J = 6.0 Hz, 4H, d-H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 87.2, 89.2, 90.1, 93.0, 122.2, 122.5, 123.8, 125.5, 126.9, 128.7, 131.2, 131.5, 132.2 (2C), 134.8, 140.3, 149.8 ppm. **Elemental analysis:** Anal. Calcd for $C_{42}H_{24}N_2 \bullet H_2O$: C, 87.78; H, 4.56; N, 4.87. Found: C, 88.11; H, 4.23; N, 4.72. **ESI-MS:** *m/z* (%) 557.8 (100) $[(H)(\mathbf{2a})]^+$.

Synthesis of **25**

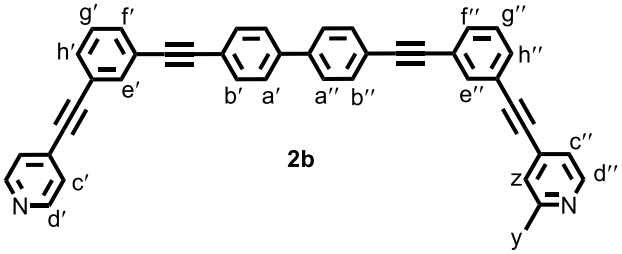


25

Compound **24** (200 mg, 497 μmol) and **5** (102 mg, 497 μmol) were dissolved in dry DMF (15 mL) and dry Et_3N (25 mL) in a sealed tube under N_2 atmosphere. The mixture was degassed by using two freeze-pump-thaw cycles. Then $Pd(PPh_3)_4$ (57.5 mg, 49.7 μmol) was added under N_2 atmosphere. After degassing again by freeze-pump-thaw cycles, the reaction mixture was stirred at 55 ºC for 2 h. The solvent was evaporated under reduced pressure and the residue worked up with ice cold water to remove DMF. The organic part was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4 and concentrated. The compound was purified by column chromatography (SiO_2) using 2% MeOH in dichloromethane as eluent to afford a pale yellow solid (95.0 mg, 40%). $\boldsymbol{R_f}$ **=** 0.6 (SiO_2, 4% MeOH in DCM). **mp:** > 250 ºC. **IR (KBr):** ν = 530.3, 543.9, 685.6, 800.6, 820.6, 905.3, 935.9, 991.6, 1002.7, 1084.4, 1116.3, 1213.5, 1404.9, 1474.1, 1495.6, 1538.0, 1568.2, 1593.1, 1661.6, 2095.7, 2210.9, 3040.7, 3161.4, 3292. cm^{-1}. **^{1}H NMR ($CDCl_3$,**

400 MHz): δ = 3.11 (s, 1H, y-H), 7.32 (t, ^3J = 7.8, 1H, g''-H), 7.38 (t, ^3J = 7.8 Hz, 1H, g'-H), 7.39 (d, ^3J = 6.0 Hz, 2H, c'-H), 7.46 (dt, ^3J = 7.8, ^4J = 1.6, 1H, h''-H), 7.51-7-54 (m, 2H, f'+f''-H), 7.56 (dt, ^3J = 7.8, ^4J = 1.6 Hz, 1H, h'-H), 7.61 (s, 4H, a''+b''-H), 7.62 (s, 4H, a'+b'-H), 7.69 (t, ^4J = 1.6 Hz, 1H, e''-H), 7.76 (t, ^4J = 1.6, 1H, e'-H), 8.62 (d, ^3J = 6.0 Hz, 2H, d'-H), ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 77.8, 82.8, 87.2, 89.2, 89.4, 89.9, 90.2, 93.0, 122.2, 122.3, 122.5 (2C), 123.6, 123.8, 125.6 (2C), 126.9, 127.0, 128.5, 128.7, 131.2, 131.5, 131.8, 131.9, 132.2 (2C), 134.9, 135.1, 140.2, 140.3, 149.8 ppm. **Elemental analysis:** Anal. Calcd for $C_{37}H_{21}N$: C, 92.67; H, 4.41; N, 2.92. Found: C, 92.77; H, 4.07; N, 2.61. **ESI-MS:** *m/z* (%) 480.3 (100) [**25** + H]$^+$.

Synthesis of **2b**

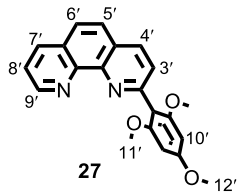


2b

Compound **25** (90.0 mg, 188 μmol) and **5a** (130 mg, 751 μmol) were dissolved in dry DMF (15 mL) and dry Et_3N (15 mL) in a sealed tube under N_2 atmosphere. The mixture was degassed by using two freeze-pump-thaw cycles. Then $Pd(PPh_3)_4$ (22.0 mg, 18.8 μmol) was added under N_2 atmosphere. After degassing again by freeze-pump-thaw cycles, the reaction mixture was stirred at 75 ºC for 18 h. The solvent was evaporated under reduced pressure and the residue worked up with ice cold water to remove DMF. The organic part was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4 and concentrated. The compound was purified by column chromatography (SiO_2) using 2% MeOH in dichloromethane as eluent to afford a pale yellow solid (85.5 mg,

80%). $\boldsymbol{R_f}$ **=** 0.5 (SiO_2, 4% MeOH in DCM). **mp:** > 250 ºC. **IR (KBr):** ν = 527.4, 545.0, 566.7, 586.9, 686.3, 716.1, 731.0, 801.9, 820.6, 891.6, 904.9, 937.0, 952.8, 989.1, 1003.2, 1034.0, 1086.7, 1116.0, 1215.6, 1285.4, 1406.1, 1436.8, 1495.5, 1536.6, 1567.8, 1595.8, 1706.8, 1916.6, 2213.1, 3037.1 cm^{-1}. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 2.58 (s, 3H, y-H), 7.20 (dd, ^3J = 5.2, ^4J = 1.4 Hz, 1H, c"-H), 7.26-7.30 (m, 1H, z-H), 7.35-7.43 (m, 2H, g'+g"-H), 7.39 (d, ^3J = 6.0 Hz, 2H, c'-H), 7.49-7.53 (m, 2H, f'+f"-H), 7.54-7.59 (m, 2H, h'+h"-H), 7.63 (s, 8H, a'+b'+a"+b"-H), 7.75 (td, ^4J = 1.6, ^5J = 0.6 Hz, 1H, e"-H), 7.76 (td, ^4J = 1.6, ^5J = 0.6 Hz, 1H, e'-H), 8.50 (dd, ^3J = 5.2, ^5J = 0.6 Hz, 1H, d"-H), 8.62 (d, ^3J = 6.0 Hz, 2H, d'-H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 24.4, 87.2, 87.5, 89.2, 89.3, 90.0(8), 90.1(3), 92.4, 93.0, 122.2, 122.3, 122.5, 122.5(9) (2C), 122.6(4), 123.7(8), 123.8(2), 125.1, 125.5 (2C), 126.9 (2C), 128.6, 128.7, 131.2, 131.3, 131.5, 132.1, 132.2 (2C), 134.8 (2C), 140.2, 140.3, 149.2, 149.8, 158.6 ppm. **Elemental analysis:** Anal. Calcd for $C_{43}H_{26}N_2$•0.5 H_2O: C, 89.09; H, 4.69; N, 4.83. Found: C, 88.87; H, 4.83; N, 4.80. **ESI-MS:** *m/z* (%) 571.8 (100) [(H)(**2b**)]$^+$.

Synthesis of **27**

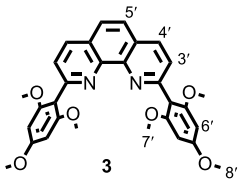


27

Under N_2 atmosphere a solution of 1.6 M *n*-BuLi in *n*-hexane (3.50 mL, 5.60 mmol) was added slowly at 0 °C to a solution of 1-bromo-2,4,6-trimethoxybenzene (**11**, 1.38 g, 5.60 mmol) in diethyl ether (30 mL) over a period of 10 min. Then it was warmed up to rt and stirred for 6 h, 1,10-phenanthroline (**26**, 500 mg, 2.78 mmol) was added to the mixture under N_2 atmosphere. The resulting violet solution was further stirred at room temp. for 12 h and then quenched with

H_2O. The layers were separated and the aqueous layer was extracted with DCM. After oxidation with MnO_2 (550 mg, 6.32 mmol) at room temp. for 3 h the combined organic layers were filtered through a pad of celite and the solvents removed under reduced pressure to furnish an yellow residue. The compound was purified by column chromatography (SiO_2) using 50% EtOAc in hexane as eluent to afford a colorless solid (722 mg, 75%). $\boldsymbol{R_f}$ **=** 0.3 (SiO_2, 50% EtOAc in hexane). **mp:** >250 °C. **IR (KBr):** ν = 632.6, 698.1, 737.4, 762.4, 795.1, 816.0, 846.5, 874.0, 918.6, 948.5, 968.9, 1023.9, 1065.6, 1083.6, 1120.0, 1160.1, 1190.6, 1208.6, 1234.6, 1274.9, 1331.6, 1387.5, 1417.4, 1436.8, 1550.9, 1588.0, 1608.4, 1705.5, 1734.8, 1796.2, 1899.3, 1941.1, 2010.8, 2250.5, 2837.7, 2941.7, 2989.7, 3038.1 cm^{-1}. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 3.69 (s, 6H, 11'-H), 3.88 (s, 3H, 12'-H), 6.23 (s, 2H, 10'-H), 7.57 (dd, ^3J = 8.0 Hz, ^3J = 4.4 Hz, 1H, 8'-H), 7.62 (d, ^3J = 8.0 Hz, 1H, 3'-H), 7.76 (d, ^3J = 8.8 Hz, 1H, 6'-H), 7.82 (d, ^3J = 8.8 Hz, 1H, 5'-H), 8.22 (dd, ^3J = 8.0 Hz, ^4J = 1.6 Hz, 1H, 7'-H), 8.23 (d, ^3J = 8.0 Hz, 1H, 4'-H), 9.19 (dd, ^3J = 4.4 Hz, ^4J = 1.6 Hz, 1H, 9'-H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 55.4, 55.9, 90.9, 113.4, 122.5, 125.9, 126.5(0), 126.5(2), 127.2, 128.6, 135.3, 135.7, 146.2, 146.4, 150.0, 155.5, 159.2, 161.4 ppm. **Elemental analysis:** Anal. Calcd for $C_{21}H_{18}N_2O_3$: C, 72.82; H, 5.24; N, 8.09. Found: C, 72.51; H, 5.03; N, 7.72. **ESI-MS:** *m/z* (%) 347.5 (100) $[(H)(\mathbf{27})]^+$.

Synthesis of **3**



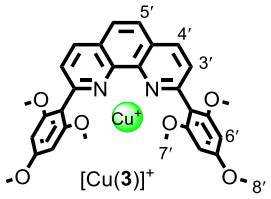
3

Under N_2 atmosphere a solution of 1.6 M *n*-BuLi in *n*-hexane (1.80 mL, 2.88 mmol) was added slowly at 0 °C to a solution of 1-bromo-2,4,6-trimethoxy benzene (**11**, 713 mg, 2.88 mmol) in diethyl ether (30 mL) over a period of 10 min. Then it was warmed up to rt and stirred for 6 h, compound **27** (500 mg, 1.44 mmol) was added to the mixture under N_2 atmosphere. The resulting violet solution was further stirred at room temperature for 12 h and then quenched with H_2O. The layers were separated and the aqueous layer was extracted with DCM. After oxidation with MnO_2 (376 mg, 4.32 mmol) at room temperature for 3 h the combined organic layers were filtered through a pad of celite and the solvents removed under reduced pressure to furnish an yellow residue. The compound was purified by column chromatography (SiO_2) using 5% EtOAc in DCM as eluent to afford a colorless solid (406 mg, 55%). $\boldsymbol{R_f}$ **=** 0.3 (SiO_2, 5% EtOAc in DCM). **mp:** >250 °C. **IR (KBr):** ν = 598.0, 637.9, 664.4, 721.3, 771.8, 813.2, 854.1, 889.9, 921.1, 949.7, 1031.0, 1065.4, 1125.9, 1156.1, 1204.4, 1224.4, 1279.4, 1297.9, 1334.4, 1352.6, 1413.7, 1438.8, 1466.5, 1484.4, 1510.3, 1541.9, 1586.4, 1608.5, 2837.9, 2939.1, 2996.7 cm^{-1}. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 3.72 (s, 12H, 7'-H), 3.84 (s, 6H, 8'-H), 6.23 (s, 4H, 6'-H), 7.61 (d, ^3J = 8.0 Hz, 2H, 3'-H), 7.78 (s, 2H, 5'-H), 8.20 (d, ^3J = 8.0 Hz, 2H, 4'-H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 55.4, 56.4, 91.7, 114.0, 126.1, 126.3, 127.3, 135.2, 146.3, 154.8, 159.2, 161.4 ppm. **Elemental analysis:** Anal. Calcd for $C_{30}H_{30}N_2O_7$•0.5 H_2O: C, 67.91; H, 5.70; N, 5.28. Found: C, 68.06; H, 4.95; N, 4.90. **ESI-MS:** *m/z* (%) 513.4 (100) $[(H)(\mathbf{3})]^+$.

1.3 Syntheses and characterizations of complexes

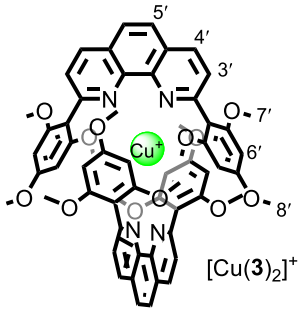
Model complexes

Synthesis of complex [Cu(**3**)]$^+$



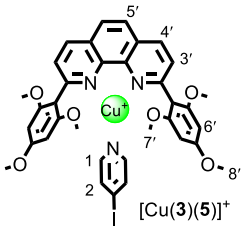
In an NMR tube compound **3** (440 µg, 0.858 µmol) and [Cu(CH$_3$CN)$_4$]PF$_6$ (320 µg, 0.858 µmol) were dissolved in 550 µL of CD_2Cl_2 to quantitatively furnish complex [Cu(**3**)]$^+$. **^{1}H NMR (CD_2Cl_2, 400 MHz):** δ = 3.74 (s, 12H, 7'-H), 3.91 (s, 6H, 8'-H), 6.30 (s, 4H, 6'-H), 7.91 (d, ^3J = 8.2 Hz, 2H, 3'-H), 8.00 (s, 2H, 5'-H), 8.49 (d, ^3J = 8.2 Hz, 2H, 4'-H) ppm. **ESI-MS:** *m/z* (%) 574.9 (100) [Cu(**3**)]$^+$.

Synthesis of complex [Cu(**3**)$_2$]$^+$



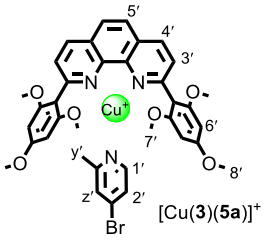
In an NMR tube compound **3** (880 µg, 1.72 µmol) and [Cu(CH$_3$CN)$_4$]PF$_6$ (320 µg, 0.858 µmol) were dissolved in 550 µL of CD_2Cl_2 to quantitatively furnish complex [Cu(**3**)$_2$]$^+$. **^{1}H NMR (CD_2Cl_2, 400 MHz):** δ = 3.04 (s, 24H, 7'-H), 3.75 (s, 12H, 8'-H), 5.43 (s, 8H, 6'-H), 7.47 (d, ^3J = 8.2 Hz, 4H, 3'-H), 7.87 (s, 4H, 5'-H), 8.23 (d, ^3J = 8.2 Hz, 4H, 4'-H) ppm. **ESI-MS:** *m/z* (%) 1087.1 (100) [Cu(**3**)$_2$]$^+$.

Synthesis of HETPYP-I complex [Cu(**3**)(**5**)]$^+$



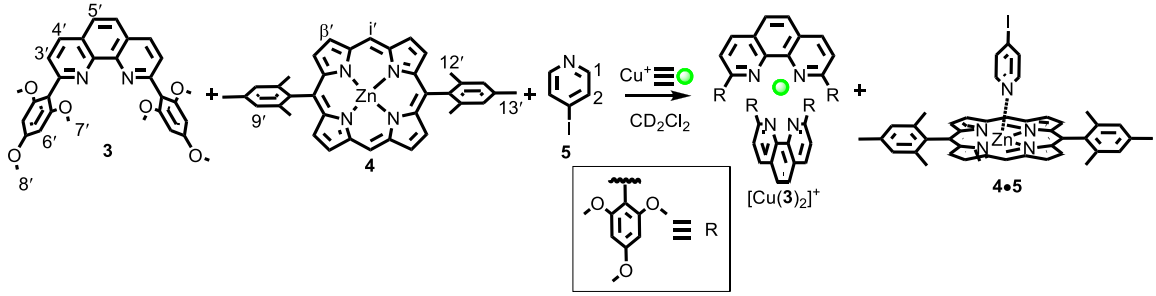
In an NMR tube compound **3** (418 µg, 0.815 µmol), 4-iodopyridine (**5**, 167 µg, 0.815 µmol) and $[Cu(CH_3CN)_4]PF_6$ (304 µg, 0.815 µmol) were dissolved in 550 µL of CD_2Cl_2 to quantitatively furnish complex [Cu(**3**)(**5**)]$^+$. **^{1}H NMR (CD_2Cl_2, 400 MHz):** δ = 3.63 (s, 12H, 7'-H), 3.84 (s, 6H, 8'-H), 6.12 (s, 4H, 6'-H), 7.44-7.70 (m, 4H, 1+2-H), 7.91 (d, ^3J = 8.2 Hz, 2H, 3'-H), 8.04 (s, 2H, 5'-H), 8.53 (d, ^3J = 8.2 Hz, 2H, 4'-H) ppm. **ESI-MS:** *m/z* (%) 780.8 (100) [Cu(**3**)(**5**)]$^+$.

Synthesis of HETPYP-I complex [Cu(**3**)(**5a**)]$^+$



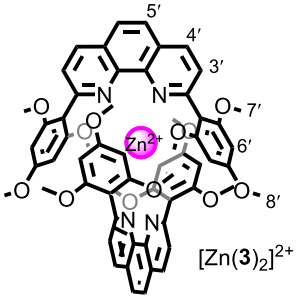
In an NMR tube compound **3** (450 µg, 877 nmol), 4-bromopicoline (**5a**, 149 µg, 877 nmol) as a standard solution in $CDCl_3$ and $[Cu(CH_3CN)_4]PF_6$ (327 µg, 877 nmol) were dissolved in 550 µL of CD_2Cl_2 to quantitatively furnish complex [Cu(**3**)(**5a**)]$^+$. **^{1}H NMR (CD_2Cl_2, 400 MHz):** δ = 2.28 (s, 3H, y'-H), 3.60 (s, 12H, 7'-H), 3.77 (s, 6H, 8'-H), 5.99 (s, 4H, 6'-H), 7.26 (bs, 1H, 2'-H), 7.38 (bs, 1H, z'-H), 7.89 (d, ^3J = 8.2 Hz, 2H, 3'-H), 7.95 (bs, 1H, 1'-H), 8.06 (s, 2H, 5'-H), 8.54 (d, ^3J = 8.2 Hz, 2H, 4'-H) ppm. **ESI-MS:** *m/z* (%) 748.0 (100) [Cu(**3**)(**5a**)]$^+$.

Synthesis of orthogonal complexes $[Cu(\mathbf{3})_2]^+$ + **4•5**



In an NMR tube compound **3** (880 µg, 1.72 µmol), **4** (524 µg, 858 nmol), **5** (176 µg, 858 nmol) and $[Cu(CH_3CN)_4]PF_6$ (320 µg, 858 nmol) were dissolved in 550 µL of CD_2Cl_2 to furnish the two complexes $[Cu(\mathbf{3})_2]^+$ + **4•5**. **^{1}H NMR (CD_2Cl_2, 400 MHz):** δ = 1.80 (s, 12H, 12'-H), 2.66 (s, 6H, 13'-H), 3.04 (s, 24H, 7'-H), 3.75 (s, 12H, 8'-H), 3.92 (bs, 2H, 1-H), 5.43 (s, 8H, 6'-H), 6.39 (bs, 2H, 2-H), 7.34 (s, 4H, 9'-H), 7.47 (d, ^3J = 8.2 Hz, 4H, 3'-H), 7.87 (s, 4H, 5'-H), 8.23 (d, ^3J = 8.2 Hz, 4H, 4'-H), 8.87 (d, ^3J = 4.4 Hz, 4H, β'-H), 9.34 (d, ^3J = 4.4 Hz, 4H, β'-H), 10.15 (s, 2H, i'-H) ppm. **ESI-MS:** *m/z* (%) 1087.1 (100) $[Cu(\mathbf{3})_2]^+$.

Synthesis of complex $[Zn(\mathbf{3})_2]^{2+}$

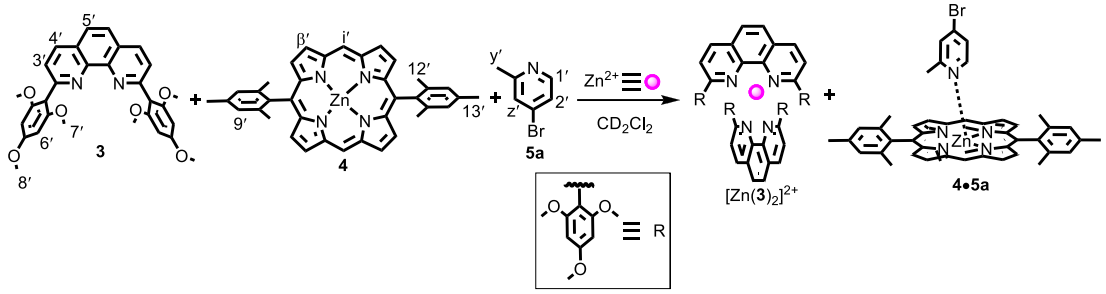


Proton signals 7'- and 6'-H are diagnostically split in four singlets (1:1:1:1) denoted as 7", 7"', 7"", 7""" and 6", 6"', 6"", 6""" respectively.

In an NMR tube compound **3** (592 µg, 1.15 µmol) and $Zn(OTf)_2$ (209 µg, 575 nmol: as a standard solution in CD_3CN) were mixed in 550 µL of CD_2Cl_2 to quantitatively furnish complex $[Zn(\mathbf{3})_2]^{2+}$. **^{1}H NMR (CD_2Cl_2:CD_3CN (30:1), 400 MHz):** δ = 2.90 (bs, 12H, 7"+7"'-H), 3.44 (bs,

6H, 7""-H), 3.80 (s, 12H, 8'-H), 3.89 (bs, 6H, 7"""-H), 5.45 (bs, 4H, 6"+6'"-H), 5.63 (bs, 2H, 6""-H), 6.33 (bs, 2H, 6"""-H), 7.84 (bs, 4H, 3'-H), 8.16 (s, 4H, 5'-H), 8.66 (d, ^3J = 8.2 Hz, 4H, 4'-H) ppm. **ESI-MS:** *m/z* (%) 1236.2 (100) [Zn(**3**)(OTf)]$^+$.

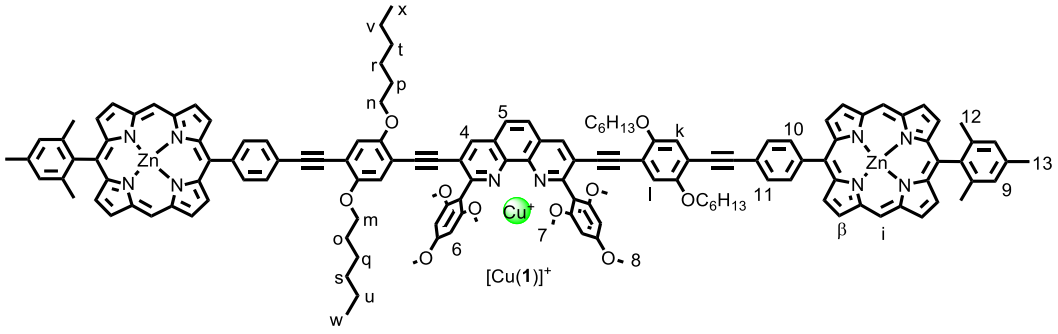
Synthesis of orthogonal complexes [Zn(**3**)$_2$]$^{2+}$ + **4•5a**



Proton signals 7'- and 6'-H are diagnostically split in four singlets (1:1:1:1) denoted as 7", 7'", 7"", 7""" and 6", 6'", 6"", 6""" respectively. Signals 7""" and 6"""-H became very broad and merged in the base line.

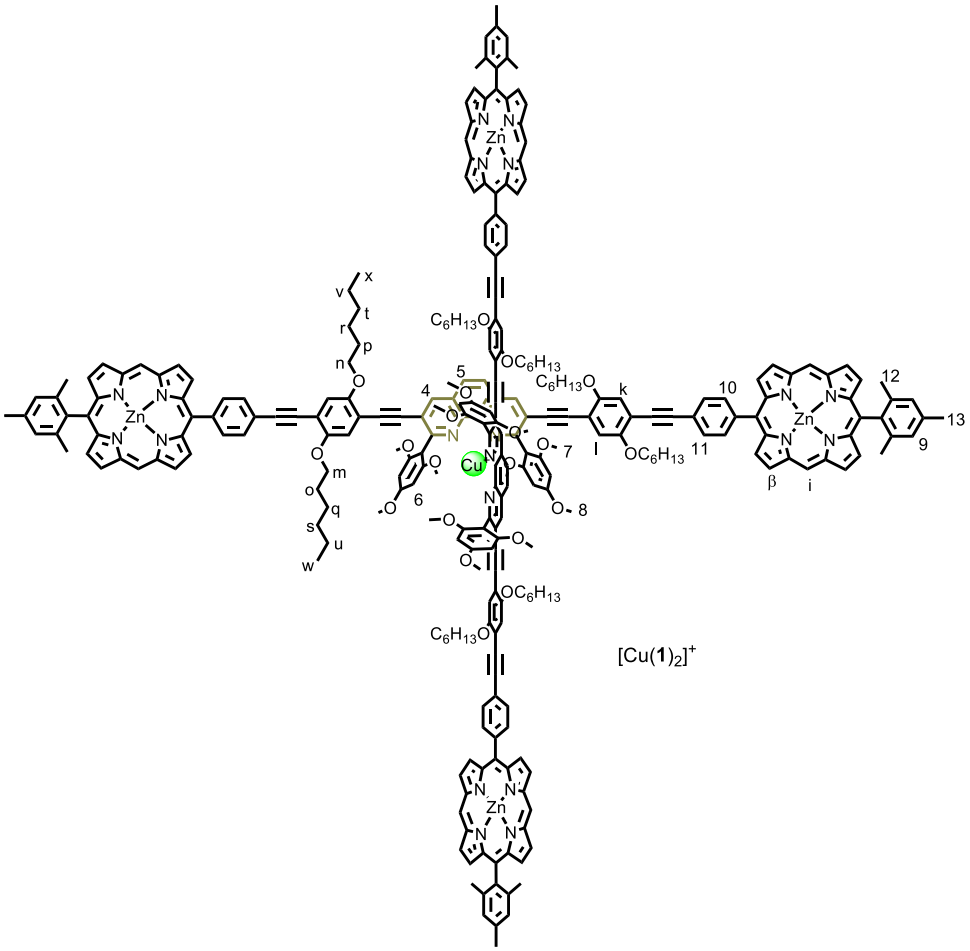
In an NMR tube compound **3** (1.53 mg, 2.99 µmol), **4** (911 µg, 1.49 µmol), **5a** (254 µg, 1.49 µmol) and Zn(OTf)$_2$ (543 µg, 1.49 µmol: as a standard solution in CD_3CN) were mixed in CD_2Cl_2. After sonication for 15 min the solvent was removed, as CD_3CN hampers the weak N_{pic}→ZnPor binding. It was again dissolved in 550 µL of CD_2Cl_2. It furnished orthogonal complexes [Zn(**3**)$_2$]$^{2+}$ + **4•5a**. **^{1}H NMR (CD_2Cl_2, 400 MHz):** δ = 0.86 (bs, 3H, y'-H), 1.80 (s, 12H, 12'-H), 2.66 (s, 6H, 13'-H), 2.91 (bs, 12H, 7"+7'"-H), 3.46 (bs, 6H, 7""-H), 3.80 (s, 12H, 8'-H), 5.45 (bs, 4H, 6"+6'"-H), 5.65 (bs, 2H, 6""-H), 6.84-6.94 (m, 2H, 1'+z'-H), 7.01 (bs, 1H, 2'-H), 7.34 (s, 4H, 9'-H), 7.85 (bs, 4H, 3'-H), 8.18 (s, 4H, 5'-H), 8.67 (d, ^3J = 8.2 Hz, 4H, 4'-H), 8.91 (d, ^3J = 4.4 Hz, 4H, β'-H), 9.39 (d, ^3J = 4.4 Hz, 4H, β'-H), 10.22 (s, 2H, i'-H) ppm. **ESI-MS:** *m/z* (%)1236.2 (100) [Zn(**3**)(OTf)]$^+$.

Synthesis of Cu^+ complex $[Cu(\mathbf{1})]^+$



In an NMR tube, compound **1** (1.40 mg, 610 nmol) and $[Cu(CH_3CN)_4]PF_6$ (228 µg, 610 nmol) were dissolved in 600 µL of CD_2Cl_2 to furnish the complex $[Cu(\mathbf{1})]^+$ in quantitative yield. **mp:** > 200 ºC. **^{1}H NMR (CD_2Cl_2, 400 MHz):** δ = 0.96-1.00 (m, 12H, w+x-H), 1.44-1.53 (m, merged with H_2O peak, 16H, s+t+u+v-H), 1.57-1.64 (m, 4H, r/q-H), 1.70-1.78 (m, 4H, q/r-H), 1.82 (s, 12H, 12-H), 1.86-1.93 (m, 4H, p/o-H), 1.98-2.02 (m, merged with CH_3CN peak coming from $[Cu(CH_3CN)_4]PF_6$ salt, 4H, o/p-H), 2.67 (s, 6H, 13-H), 3.82 (s, 12H, 7-H), 3.98 (s, 6H, 8-H), 4.07 (t, ^3J = 6.6 Hz, 4H, n/m-H), 4.12 (t, ^3J = 6.6 Hz, 4H, m/n-H), 6.40 (s, 4H, 6-H), 6.70 (s, 2H, l-H), 7.21 (s, 2H, k-H), 7.36 (s, 4H, 9-H), 7.99 (d, ^3J = 8.2 Hz, 4H, 11-H), 8.04 (s, 2H, 5-H), 8.31 (d, ^3J = 8.2 Hz, 4H, 10-H), 8.69 (s, 2H, 4-H), 8.98 (d, ^3J = 4.6 Hz, 4H, β-H), 9.17 (d, ^3J = 4.6 Hz, 4H, β-H), 9.45 (d, ^3J = 4.6 Hz, 4H, β-H), 9.51 (d, ^3J = 4.6 Hz, 4H, β-H), 10.34 (s, 4H, i-H) ppm. UV-vis (CH_2Cl_2): λ_{max} = 537 nm (Q band). **Elemental analysis:** Anal. Calcd for $CuZn_2C_{144}H_{132}N_{10}O_{10}PF_6$: C, 69.13; H, 5.32; N, 5.60. Found: C, 69.39; H, 4.97; N, 5.26. **ESI-MS:** *m/z* (%) 1178.2 (100) $[(Cu)(H)(\mathbf{1})]^{2+}$.

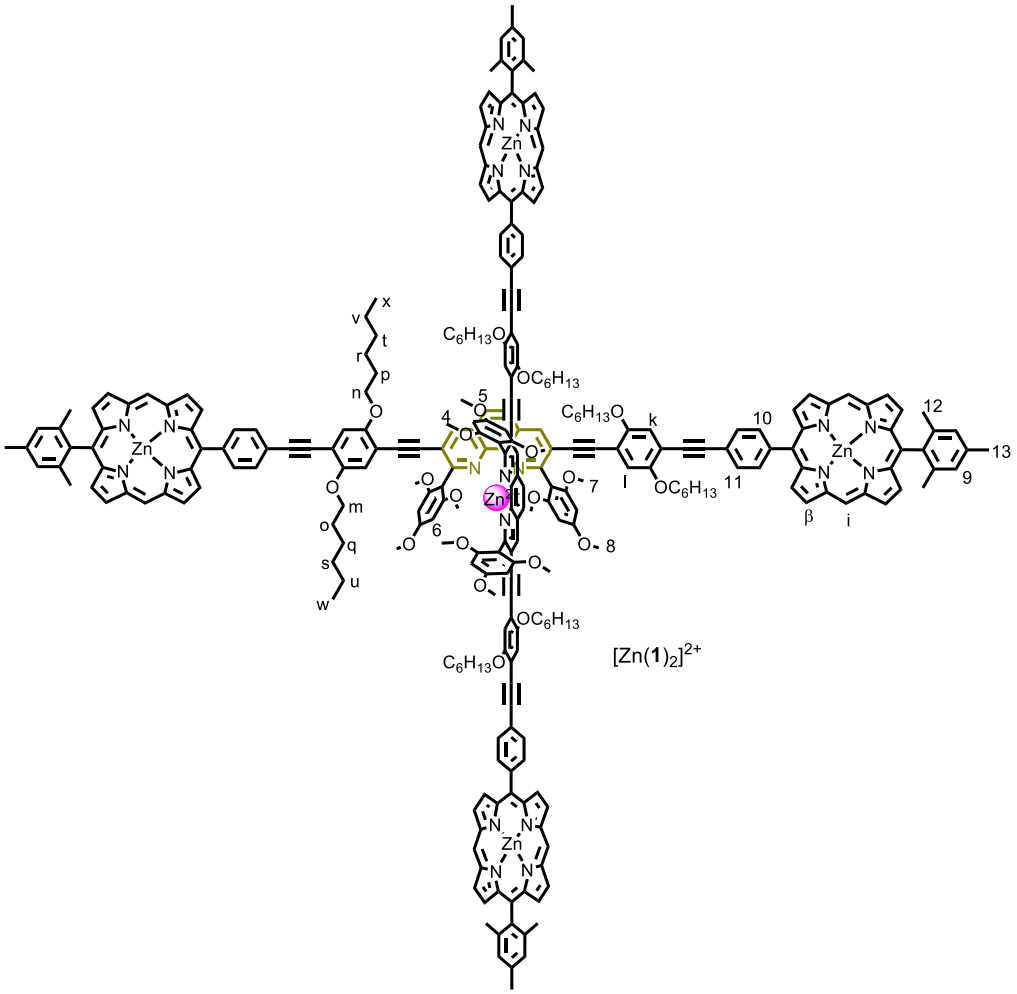
Synthesis of complex $[Cu(\mathbf{1})_2]^+$



In an NMR tube, compound **1** (1.40 mg, 610 nmol) and $[Cu(CH_3CN)_4]PF_6$ (114 mg, 305 nmol) were dissolved in 600 µL of CD_2Cl_2 to furnish $[Cu(\mathbf{1})_2]^+$ in quantitative yield. **mp:** > 200 ºC. **^{1}H NMR (CD_2Cl_2, 400 MHz):** δ = 1.00 (t, ^3J = 5.6 Hz, 12H, x/w-H), 1.03 (t, ^3J = 5.6 Hz, 12H, w/x-H), 1.48-1.54 (m, merged with H_2O peak, 32H, s+t+u+v-H), 1.61-1.66 (m, 8H, r/q-H), 1.71-1.79 (m, 8H, q/r-H), 1.82 (s, 24H, 12-H), 1.85-1.95 (m, 8H, p/o-H), 1.96-2.04 (m, merged with CH_3CN peak coming from $[Cu(CH_3CN)_4]PF_6$ salt, 8H, o/p-H), 2.67 (s, 12H, 13-H), 3.28 (s, 24H, 7-H), 3.94 (s, 12H, 8-H), 3.98 (t, ^3J = 6.4 Hz, 8H, n/m-H), 4.11 (t, ^3J = 6.4 Hz, 8H, m/n-H), 5.71 (s, 8H, 6-H), 6.43 (s, 4H, l-H), 7.18 (s, 4H, k-H), 7.35 (s, 8H, 9-H), 7.98 (d, ^3J = 8.2 Hz, 8H, 11-H), 8.00 (s, 4H, 5-H), 8.30 (d, ^3J = 8.2 Hz, 8H, 10-H), 8.50 (s, 4H, 4-H), 8.97 (d, ^3J = 4.6 Hz, 8H, β-H), 9.16 (d, ^3J = 4.6 Hz, 8H, β-H), 9.45 (d, ^3J = 4.6 Hz, 8H, β-H), 9.50 (d, ^3J = 4.6 Hz, 8H, β-H), 10.34 (s, 8H, i-H) ppm. UV-vis (CH_2Cl_2): λ_{max} = 537 nm (Q band). **Elemental analysis:**

Anal. Calcd for $CuZn_4C_{288}H_{264}N_{20}O_{20}PF_6 \bullet 2H_2O$: C, 71.60; H, 5.59; N, 5.80. Found: C, 71.93; H, 5.22; N, 5.85. **ESI-MS:** *m/z* (%) 1550.4 (100) $[Cu(H)_2(\mathbf{1})_2]^{3+}$, 2324.1 (58) $[Cu(H)(\mathbf{1})_2]^{2+}$.

Synthesis of complex $[Zn(\mathbf{1})_2]^{2+}$

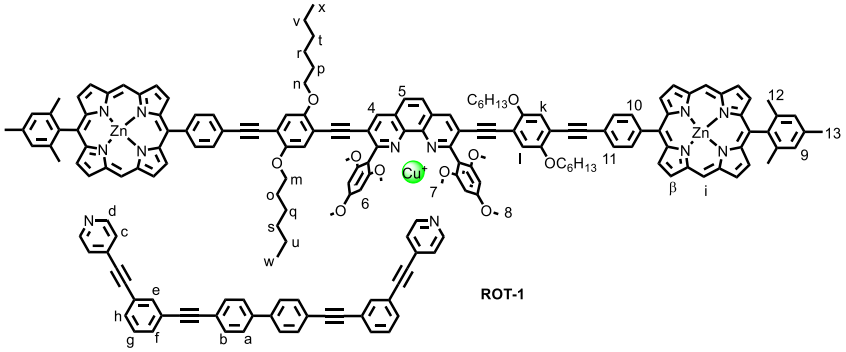


(7- and 6-H are split in four singlets (1:1:1:1) denoted as 7', 7", 7"', 7"" and 6', 6", 6"', 6"", respectively. Proton signals l- and k-H are split in two singlets (1:1) denoted as l', l" and k', k", respectively.)

In an NMR tube, compound **1** (1.40 mg, 610 nmol) and $Zn(OTf)_2$ (110 µg, 305 nmol: as a standard solution in CD_3CN) were mixed in 600 µL of CD_2Cl_2 to furnish $[Zn(\mathbf{1})]^{2+}$ in quantitative yield. **mp:** > 200 ºC. **^{1}H NMR (CD_2Cl_2:CD_3CN (60:1), 400 MHz):** δ = 0.96-1.04 (m, 24H, w+x-H), 1.41-1.53 (m, 32H, merged with H_2O peak, s+t+u+v-H), 1.70-1.79 (m, 16H, q+r-H), 1.82 (s, 24H, 12-H), 1.84-1.88 (m, 8H, p/o-H), 1.98-2.04 (m, 8H, o/p-H), 2.67 (s, 12H, 13-

H), 3.00 (s, 6H, 7'-H), 3.26 (s, 6H, 7''-H), 3.41 (s, 6H, 7'''-H), 3.94 (s, 12H, 8-H), 4.00 (s, 6H, 7''''-H), 4.05-4.14 (m, 16H, m+n-H), 5.45 (s, 2H, 6'-H), 5.69 (s, 2H, 6''-H), 5.89 (s, 2H, 6'''-H), 6.23 (s, 2H, 6''''-H), 6.37 (s, 2H, l'-H), 6.89 (s, 2H, l''-H), 7.16 (s, 2H, k'-H), 7.24 (s, 2H, k''-H), 7.35 (s, 8H, 9-H), 7.96-8.00 (m, 8H, 11-H), 8.30–8.38 (m, 12H, 5+10-H), 8.88 (s, 4H, 4-H), 8.96 (d, ^3J = 4.6 Hz, 8H, β-H), 9.15 (d, ^3J = 4.6 Hz, 8H, β-H), 9.44 (d, ^3J = 4.6 Hz, 8H, β-H), 9.49 (d, ^3J = 4.6 Hz, 8H, β-H), 10.33 (s, 8H, i-H) ppm. UV-vis (CH_2Cl_2): λ_{max} = 537 nm (Q band). **Elemental analysis:** Anal. Calcd for $Zn_5C_{290}H_{264}N_{20}O_{26}S_2F_6$•$3CH_2Cl_2$: C, 67.61; H, 5.23; N, 5.38. Found: C, 67.87; H, 4.88; N, 5.53. **ESI-MS:** *m/z* (%) 1550.7 (100) $[Zn(H)(\mathbf{1})_2]^{3+}$.

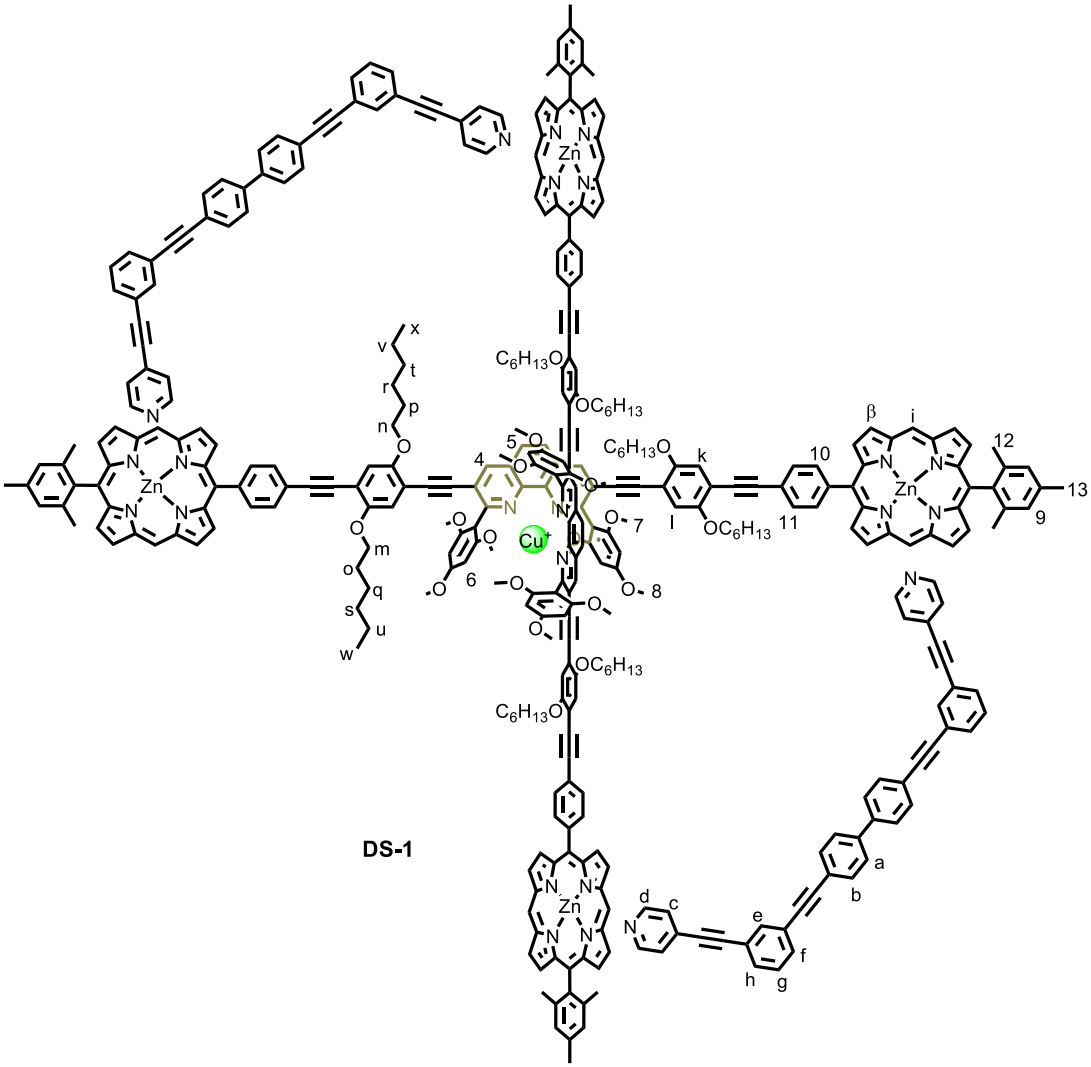
Synthesis of **ROT-1**



In an NMR tube, deck **1** (1.40 mg, 610 nmol), $[Cu(CH_3CN)_4]PF_6$ (228 µg, 610 nmol) and arm **2a** (340 µg, 610 nmol) were dissolved in 600 µL of CD_2Cl_2 to furnish **ROT-1** in quantitative yield. **mp:** > 200 ºC. **IR (KBr):** ν = 562.3, 672.6, 700.2, 735.7, 786.9, 822.3, 848.6, 995.4, 1057.3, 1130.8, 1213.7, 1384.1, 1466.4, 1495.8, 1606.2, 1653.7, 2213.2, 2854.5, 2925.2, 2954.0 cm^{-1}. **^{1}H NMR (CD_2Cl_2, 400 MHz):** δ = 0.97-1.01 (m, 12H, w+x-H), 1.47-1.53 (m, merged with H_2O peak, 16H, s+t+u+v-H), 1.59-1.64 (m, 4H, r/q-H), 1.71-1.77 (m, 4H, q/r-H), 1.83 (s, 12H, 12-H), 1.87-1.92 (m, 4H, p/o-H), 1.99-2.04 (m, merged with CH_3CN peak coming from $[Cu(CH_3CN)_4]PF_6$ salt, 4H, o/p-H), 2.67 (s, 6H, 13-H), 3.74 (s, 12H, 7-H), 3.96 (s, 6H, 8-H), 4.07 (t, ^3J = 6.6 Hz, 4H, n/m-H), 4.12 (t, ^3J = 6.6 Hz, 4H, m/n-H), 6.32 (s, 4H, 6-H), 6.64 (s, 2H, l-H), 7.21 (s, 2H, k-H), 7.24-7.32 (m, 4H, f+g-H), 7.36 (s, 4H, 9-H), 7.41-7.49 (m, 4H, e+h-H), 7.56 (d, ^3J = 8.8 Hz, 4H, b/a-H), 7.60 (d, ^3J = 8.8 Hz, 4H, a/b-H), 7.99 (d, ^3J = 7.8 Hz, 4H, 11-H), 8.06 (s, 2H, 5-H), 8.31 (d, ^3J = 7.8 Hz, 4H, 10-H), 8.70 (s, 2H, 4-H), 8.95 (d, ^3J = 4.2 Hz, 4H,

β-H), 9.14 (d, ^3J = 4.2 Hz, 4H, β-H), 9.41 (d, ^3J = 4.2 Hz, 4H, β-H), 9.47 (d, ^3J = 4.2 Hz, 4H, β-H), 10.28 (s, 4H, i-H) ppm. UV-vis (CH_2Cl_2): λ_{max} = 540 nm (Q band). **Elemental analysis:** Anal. Calcd for $CuZn_2C_{186}H_{156}N_{12}O_{10}PF_6 \bullet H_2O$: C, 72.61; H, 5.18; N, 5.46. Found: C, 72.61; H, 5.17; N, 5.12. **ESI-MS:** *m/z* (%) 1457.8 (100) [(Cu)(H)(**1**)(**2a**)]$^{2+}$.

Synthesis of **DS-1**



In an NMR tube, deck **1** (1.40 mg, 610 nmol), $[Cu(CH_3CN)_4]PF_6$ (114 µg, 305 nmol) and arm **2a** (340 µg, 610 nmol) were dissolved in 600 µL of CD_2Cl_2 to furnish **DS-1** in quantitative yield. **mp:** > 200 ºC. **IR (KBr):** ν = 558.4, 734.2, 783.9, 846.2, 995.4, 1057.2, 1132.0, 1157.3, 1214.7, 1280.0, 1384.4, 1467.1, 1496.5, 1515.8, 1607.0, 2209.2, 2855.3, 2926.9, 2954.0 cm^{-1}. **^{1}H NMR**

(CD_2Cl_2, 400 MHz): δ = 1.00-1.05 (m, 24H, w+x-H), 1.48-1.53 (m, merged with H_2O peak, 32H, s+t+u+v-H), 1.60-1.67 (m, 8H, r/q-H), 1.71-1.78 (m, 8H, q/r-H), 1.81 (s, 24H, 12-H), 1.87-1.95 (m, 8H, p/o-H), 1.96-2.02 (m, merged with CH_3CN peak coming from $[Cu(CH_3CN)_4]PF_6$ salt, 8H, o/p-H), 2.35 (bs, 8H, d-H), 2.67 (s, 12H, 13-H), 3.28 (s, 24H, 7-H), 3.94 (s, 12H, 8-H), 3.98 (t, ^3J = 6.6 Hz, 8H, n/m-H), 4.10 (t, ^3J = 6.6 Hz, 8H, m/n-H), 5.52 (bs, 8H, c-H), 5.72 (s, 8H, 6-H), 6.42 (s, 4H, l-H), 7.07 (d, ^3J = 7.8 Hz, 4H, f-H), 7.15 (t, ^3J = 7.8 Hz, 4H, g-H), 7.18 (s, 4H, k-H), 7.27 (s, 4H, e-H), 7.35 (s, 8H, 9-H), 7.38 (d, ^3J = 7.8 Hz, 4H, h-H), 7.47 (d, ^3J = 8.6 Hz, 8H, b/a-H), 7.52 (d, ^3J = 8.6 Hz, 8H, a/b-H), 7.96 (d, ^3J = 8.0 Hz, 8H, 11-H), 7.99 (s, 4H, 5-H), 8.32 (d, ^3J = 8.0 Hz, 8H, 10-H), 8.49 (s, 4H, 4-H), 8.90 (d, ^3J = 4.6 Hz, 8H, β-H), 9.11 (d, ^3J = 4.6 Hz, 8H, β-H), 9.37 (d, ^3J = 4.6 Hz, 8H, β-H), 9.44 (d, ^3J = 4.6 Hz, 8H, β-H), 10.22 (s, 8H, i-H) ppm. UV-vis (CH_2Cl_2): λ_{max} = 543 nm (Q band). **Elemental analysis:** Anal. Calcd. for $CuZn_4C_{372}H_{312}N_{24}O_{20}PF_6 \bullet 5CH_2Cl_2$: C, 71.49; H, 5.12; N, 5.31. Found: C, 71.68; H, 5.04; N, 5.53. **ESI-MS:** *m/z* (%) 2883.1 (100) $[Cu(H)(\mathbf{1})_2(\mathbf{2a})_2]^{2+}$.

Switching between **DS-1** and **ROT-1**

In an NMR tube, deck **1** (1.40 mg, 610 nmol), biped **2a** (340 µg, 610 nmol) and $[Cu(CH_3CN)_4]PF_6$ (114 µg, 305 nmol) were mixed in 600 µL of CD_2Cl_2 to furnish **DS-1**. Thereafter, to the same NMR tube, 0.5 equiv of $[Cu(CH_3CN)_4]PF_6$ (114 µg, 305 nmol) was added and sonicated for 10 min to furnish **ROT-1**.

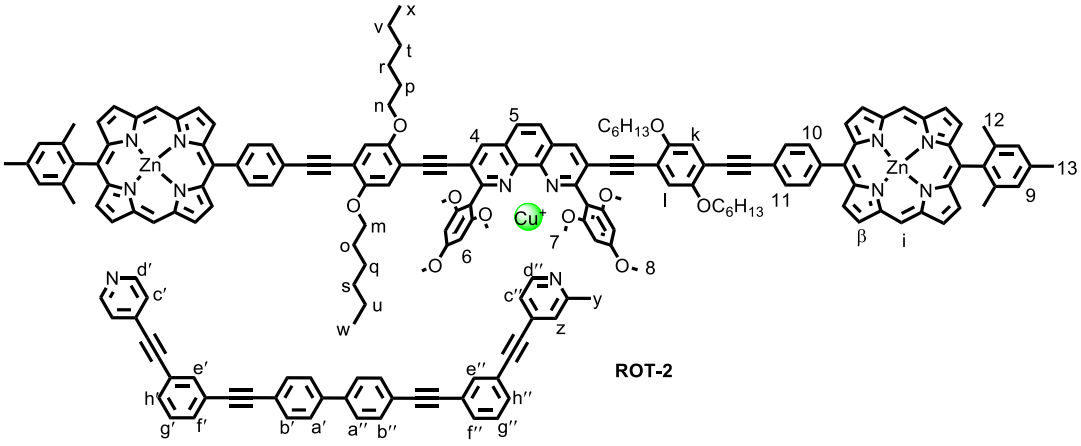
Now to refurnish **DS-1**, 0.5 equiv of cyclam (61.0 µg, 305 nmol) was added to the same NMR tube and sonicated for 10 min.

Half an equiv of $[Cu(CH_3CN)_4]PF_6$ (114 µg, 305 nmol) was added and sonicated for 10 min to furnish **ROT-1**.

Finally addition of 0.5 equiv of cyclam (61.0 µg, 305 nmol) to the mixture followed by 10 min of sonication completed the second cycle by regenerating **DS-1**.

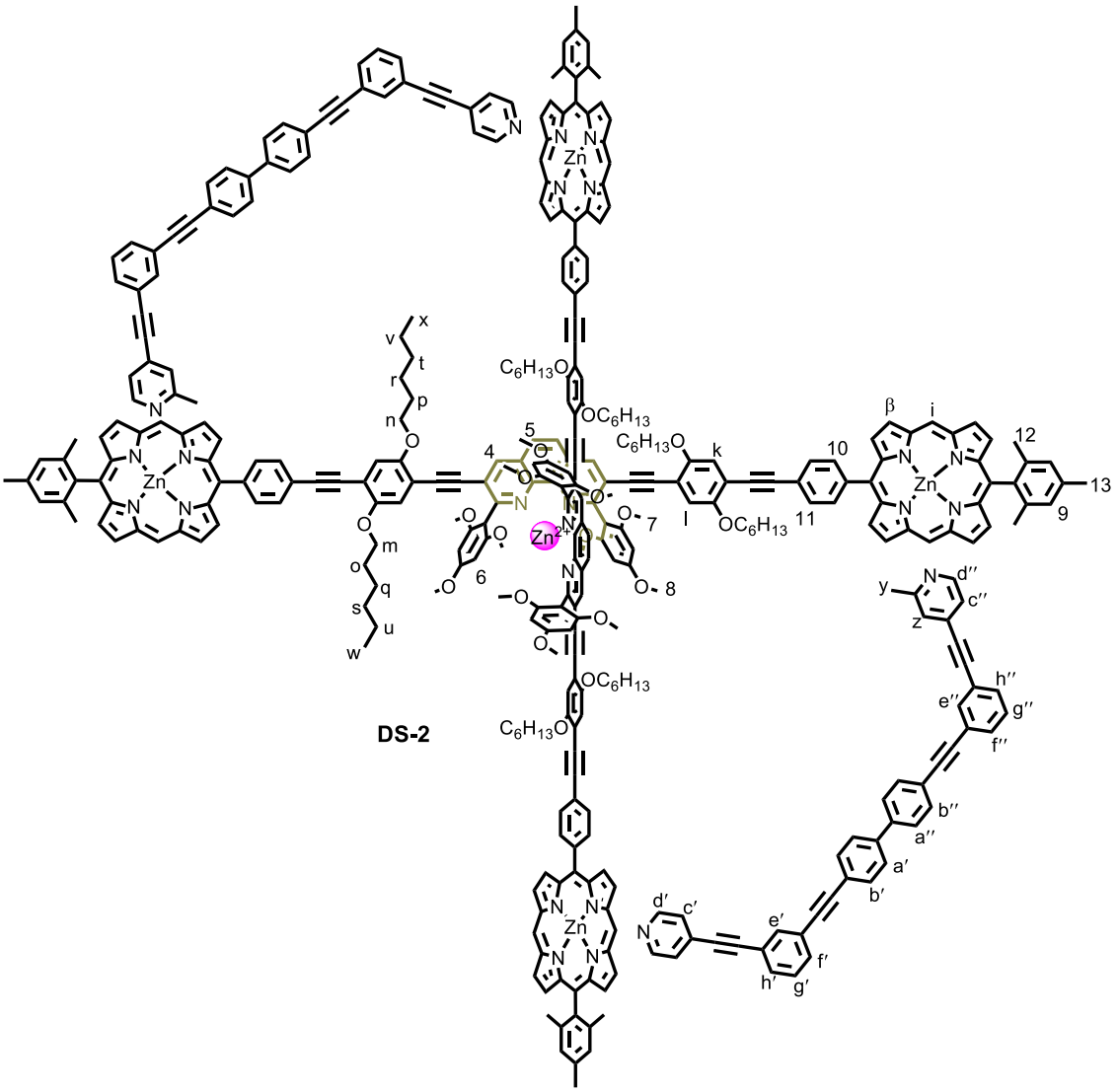
After each step ^1H NMR measurement was performed.

Synthesis of **ROT-2**



In an NMR tube, deck **1** (1.40 mg, 610 nmol), $[Cu(CH_3CN)_4]PF_6$ (228 µg, 610 nmol) and biped **2b** (348 µg, 610 nmol) were dissolved in 600 µL of CD_2Cl_2 to furnish **ROT-2** in quantitative yield. **mp:** > 200 ºC. **IR (KBr):** ν = 558.1, 701.8, 733.7, 784.2, 846.8, 995.3, 1057.3, 1129.5, 1156.8, 1207.0, 1280.8, 1338.7, 1393.1, 1466.6, 1496.1, 1607.8, 2209.8, 2856.7, 2926.0, 2957.9 cm^{-1}. **^{1}H NMR (CD_2Cl_2, 500 MHz):** δ = 0.97 (t, ^3J = 6.6 Hz, 6H, x/w-H), 0.99 (t, ^3J = 6.6 Hz, 6H, w/x-H), 1.42-1.53 (m, merged with H_2O peak, 16H, s+t+u+v-H), 1.57-1.64 (m, 4H, r/q-H), 1.69-1.76 (m, 4H, q/r-H), 1.83 (s, 12H, 12-H), 1.85-1.92 (m, 4H, p/o-H), 1.98-2.02 (m, 7H, merged with CH_3CN peak coming from $[Cu(CH_3CN)_4]PF_6$ salt, y+o/p-H), 2.42 (bs, 2H, d'-H), 2.67 (s, 6H, 13-H), 3.70 (s, 12H, 7-H), 3.87 (s, 6H, 8-H), 4.05 (t, ^3J = 6.6 Hz, 4H, n/m-H), 4.11 (t, ^3J = 6.6 Hz, 4H, m/n-H), 5.51 (bs, 2H, c'-H), 6.13 (s, 4H, 6-H), 6.64 (s, 2H, l-H), 7.03 (d, ^3J = 7.8 Hz, 1H, f''-H), 7.15 (t, ^3J = 7.8 Hz, 1H, g''-H), 7.21 (s, 2H, k-H), 7.28 (s, 1H, e''-H), 7.35 (d, ^3J = 7.8 Hz, 1H, h''-H), 7.36 (s, 4H, 9-H), 7.45 (d, ^3J = 7.8 Hz, 1H, f'-H), 7.50-7.54 (m, 3H, g'+c''+z-H), 7.58-7.61 (m, 2H, h'+e'-H), 7.63 (s, 8H, a'+b'+a''+b''-H), 7.77 (bs, 1H, d''-H), 7.98 (d, ^3J = 8.0 Hz, 4H, 11-H), 8.09 (s, 2H, 5-H), 8.31 (d, ^3J = 8.0 Hz, 4H, 10-H), 8.72 (s, 2H, 4-H), 8.93 (d, ^3J = 4.4 Hz, 4H, β-H), 9.13 (d, ^3J = 4.4 Hz, 4H, β-H), 9.39 (d, ^3J = 4.4 Hz, 4H, β-H), 9.44 (d, ^3J = 4.4 Hz, 4H, β-H), 10.26 (s, 4H, i-H) ppm. **Elemental analysis:** Anal. Calcd for $CuZn_2C_{187}H_{158}N_{12}O_{10}PF_6 \bullet H_2O$: C, 72.67; H, 5.22; N, 5.44. Found: C, 72.77; H, 5.06; N, 5.64. **ESI-MS:** *m/z* (%) 1464.1 (100) $[(Cu)(H)(\mathbf{1})(\mathbf{2b})]^{2+}$.

Synthesis of **DS-2**



(Proton signals 7- and 6-H are split in four singlets (1:1:1:1) denoted as 7', 7'', 7''', 7'''' and 6', 6'', 6''', 6'''', respectively. Proton signals l- and k-H are split in two singlets (1:1) denoted as l', l'' and k', k'', respectively.)

In an NMR tube, deck **1** (1.40 mg, 610 nmol), biped **2b** (348 µg, 610 nmol) and [Zn(OTf)$_2$ (110 µg, 305 nmol) as a standard solution in CD_3CN were dissolved in 600 µL of CD_2Cl_2 to furnish **DS-2** in quantitative yield. **mp:** > 200 ºC. **IR (KBr):** ν = 638.0, 701.6, 763.2, 784.1, 810.5, 814.5, 995.2, 1031.3, 1057.2, 1158.0, 1279.3, 1338.5, 1393.6, 1417.3, 1425.2, 1466.9, 1495.4, 1607.7, 1736.4, 2213.2, 2851.4, 2921.1, 2956.0 cm^{-1}. **^{1}H NMR (CD_2Cl_2:CD_3CN (60:1), 500**

MHz): δ = 0.05 (bs, 6H, y-H), 0.99-1.01 (m, 24H, w+x-H), 1.42-1.50 (m, merged with H_2O peak, 32H, s+t+u+v-H), 1.70-1.78 (m, 16H, q+r-H), 1.82 (s, 24H, 12-H), 1.84-1.88 (m, 8H, p/o-H), 1.97-2.04 (m, 8H, o/p-H), 2.66 (s, 12H, 13-H), 2.76 (bs, 4H, d'-H), 3.00 (s, 6H, 7'-H), 3.25 (s, 6H, 7"-H), 3.41 (s, 6H, 7"'-H), 3.94 (s, 12H, 8-H), 4.00 (s, 6H, 7""-H), 4.07-4.13 (m, 16H, m+n-H), 4.57 (bs, 2H, d"-H), 5.43 (s, 2H, 6'-H), 5.63 (bs, 4H, c'-H), 5.69 (s, 2H, 6"-H), 5.89 (s, 2H, 6"'-H), 6.15 (bs, 2H, c"-H), 6.23 (s, 4H, 6""+z-H), 6.38 (s, 2H, l'-H), 6.88 (s, 2H, l"-H), 7.08 (d, ^3J = 7.8 Hz, 2H, f"-H), 7.15-7.19 (m, 4H, k'+g"-H), 7.25-7.29 (m, 6H, e"+h"+k"-H), 7.34 (s, 8H, 9-H), 7.39 (d, ^3J = 7.8 Hz, 2H, f'-H), 7.44-7.47 (m, 6H, e'+g'+h'-H), 7.49-7.54 (m, 16H, a'+b'+a"+b"-H), 7.96-7.99 (m, 8H, 11-H), 8.30–8.36 (m, 12H, 5+10-H), 8.87 (s, 4H, 4-H), 8.91 (d, ^3J = 4.4 Hz, 8H, β-H), 9.11 (d, ^3J = 4.4 Hz, 8H, β-H), 9.38 (d, ^3J = 4.4 Hz, 8H, β-H), 9.44 (d, ^3J = 4.4 Hz, 8H, β-H), 10.24 (s, 8H, i-H) ppm. **Elemental analysis:** Anal. Calcd for $Zn_5C_{376}H_{316}N_{24}O_{26}S_2F_6$•$CH_3CN$: C, 74.03; H, 5.24; N, 5.71; S, 1.05. Found: C, 74.45; H, 5.23; N, 5.98; S, 1.18. **ESI-MS:** *m/z* (%) 1156.1 (100) $[Zn(H)_3(\mathbf{1})_2(\mathbf{2b})_2]^{5+}$.

Switching between **ROT-2** and **DS-2**

Deck **1** (1.40 mg, 610 nmol), biped **2b** (348 µg, 610 nmol) and $Zn(OTf)_2$ (110 µg, 305 nmol: as a standard solution in CD_3CN) were dissolved in 600 µL of CD_2Cl_2 to furnish **DS-2** quantitatively.

Now to the same NMR tube 0.5 equiv of hexacyclen (78.8 µg, 305 nmol) and 1.0 equiv $[Cu(CH_3CN)_4]PF_6$ (227 µg, 610 nmol) were added and sonicated for 2 h. Removal of CD_3CN quantitatively furnished **ROT-2**.

Now to refurnish **DS-2**, 1.0 equiv cyclam (122 µg, 610 nmol) and 0.5 equiv of $Zn(OTf)_2$ (110 µg, 305 nmol: as a standard solution in CD_3CN) were added and sonicated for 10 min.

Again, hexacyclen (78.8 µg, 305 nmol) and $[Cu(CH_3CN)_4]PF_6$ (227 µg, 610 nmol) were added to the same NMR tube and sonicated for 2 h. Removal of CD_3CN refurnished **ROT-2**.

Finally, addition of cyclam (122 µg, 610 nmol) and $Zn(OTf)_2$ (110 µg, 305 nmol: as a standard solution in CD_3CN) and sonication for 10 min completed the second cycle by regenerating **DS-2**.

After each step ^1H NMR measurement was performed.

2. NMR spectra: ^{1}H, ^{13}C, ^{1}H-^{1}H COSY

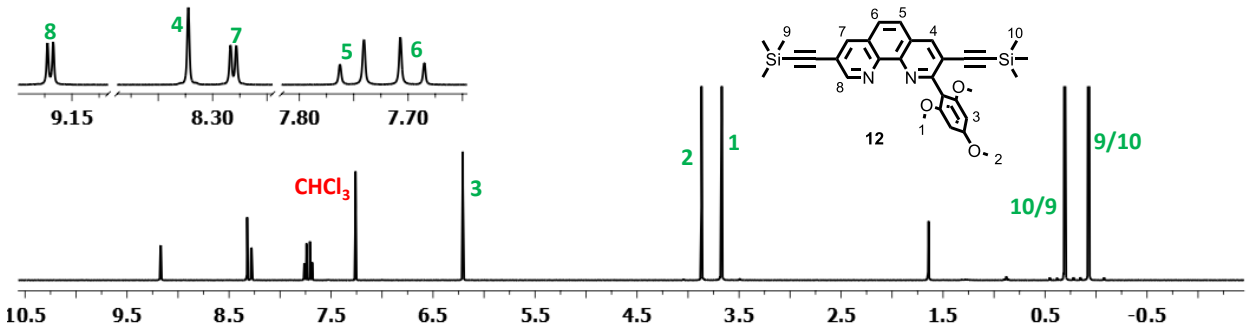


Figure S1. ^{1}H NMR of compound **12** in $CDCl_3$ (400 MHz, 295 K).

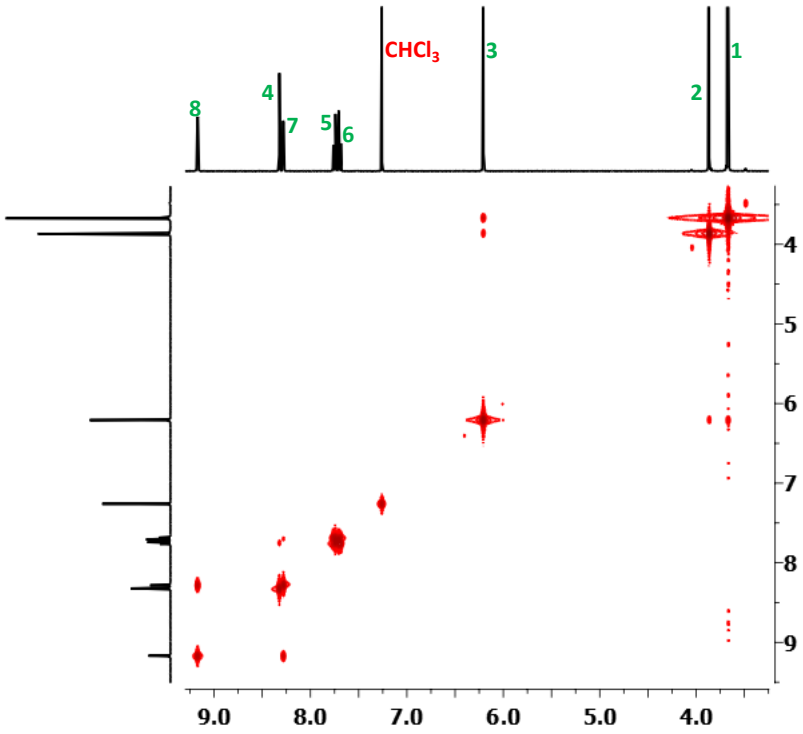


Figure S2. ^{1}H-^{1}H COSY NMR of compound **12** in $CDCl_3$ (400 MHz, 295 K).

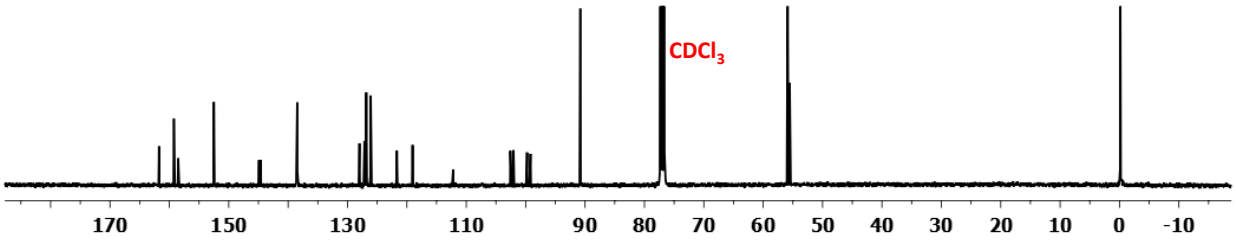


Figure S3. ^{13}C NMR of compound **12** in $CDCl_3$ (100 MHz, 295 K).

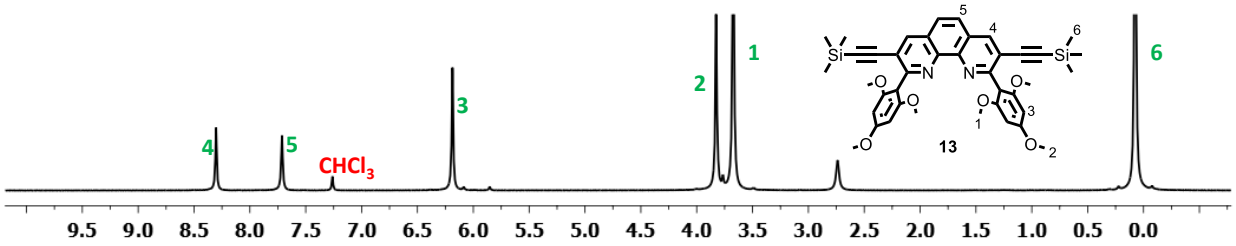


Figure S4. ^{1}H NMR of compound **13** in $CDCl_3$ (400 MHz, 295 K).

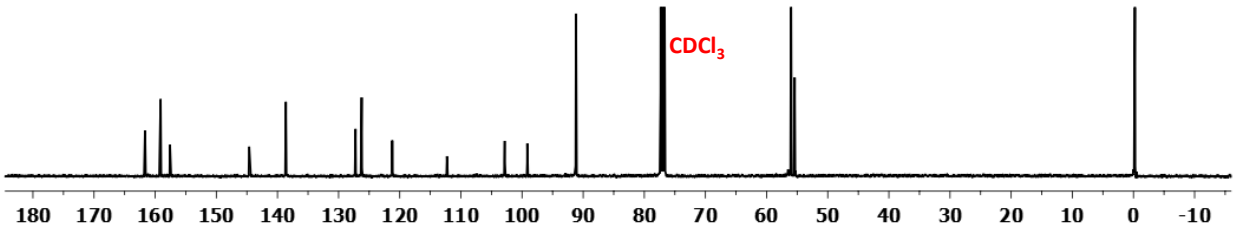


Figure S5. ^{13}C NMR of compound **13** in $CDCl_3$ (100 MHz, 295 K).

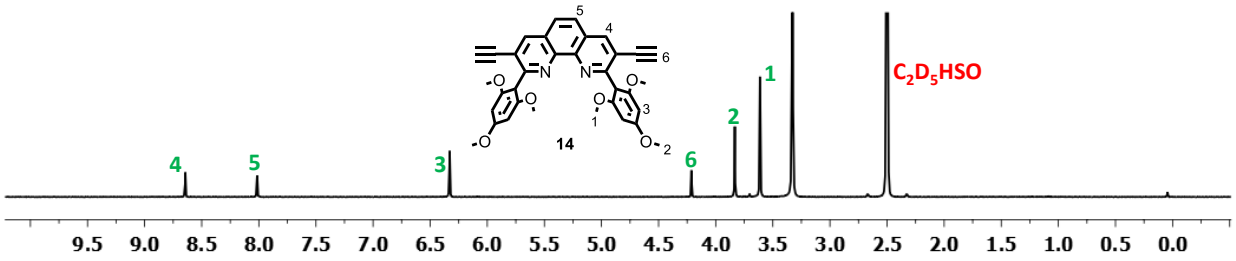


Figure S6. ^{1}H NMR of compound **14** in C_2D_6SO (400 MHz, 295 K).

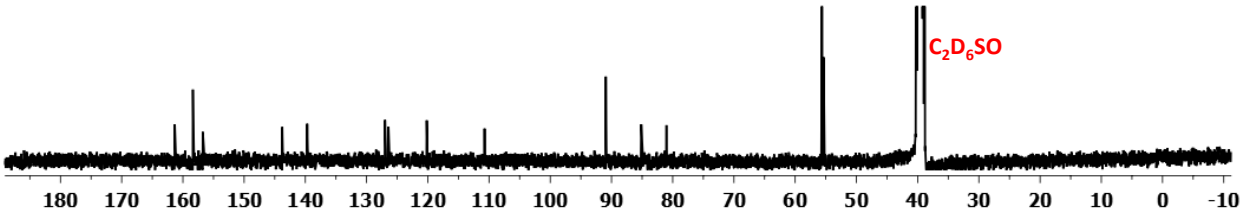


Figure S7. ^{13}C NMR of compound **14** in C_2D_6SO (100 MHz, 295 K).

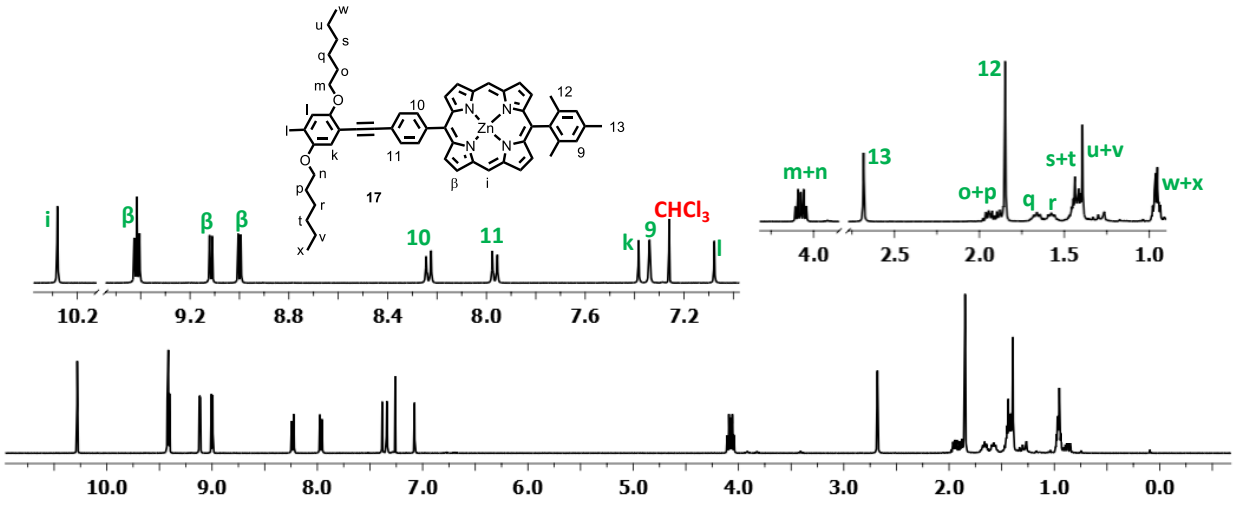


Figure S8. ^{1}H NMR of compound **17** in $CDCl_3$ (400 MHz, 295 K).

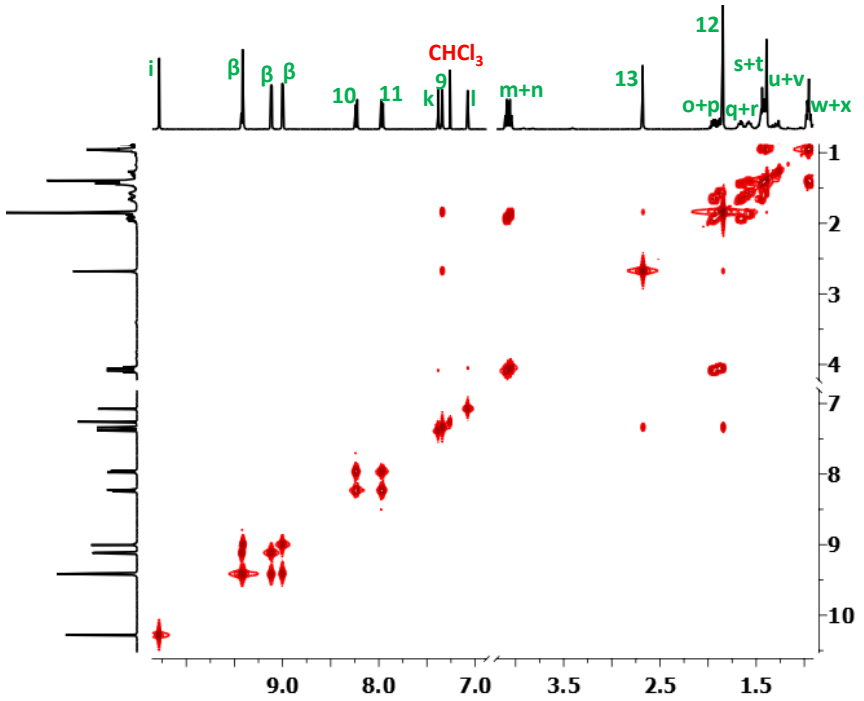


Figure S9. ^{1}H-^{1}H COSY NMR of compound **17** in $CDCl_3$ (400 MHz, 295 K).

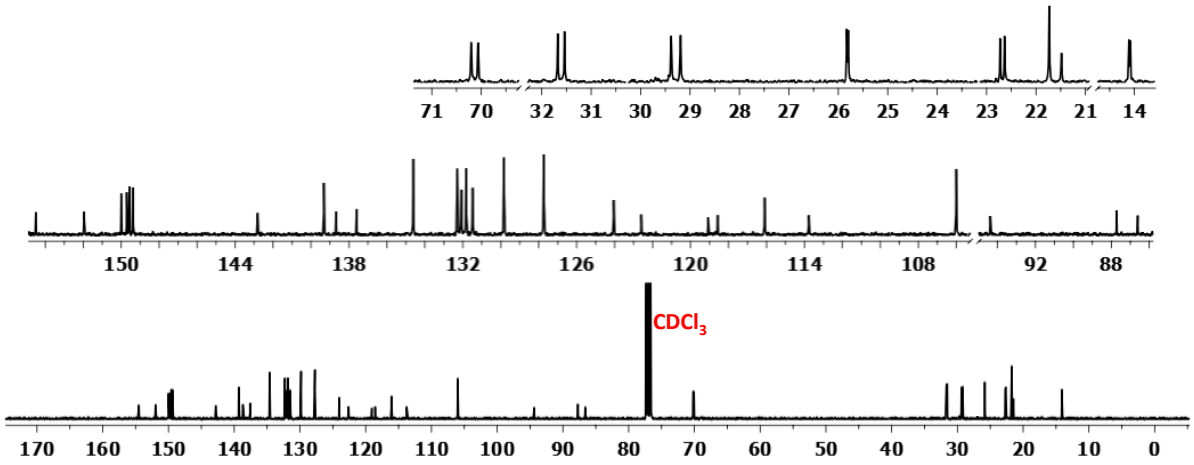


Figure S10. ^{13}C NMR of compound **17** in $CDCl_3$ (100 MHz, 295 K).

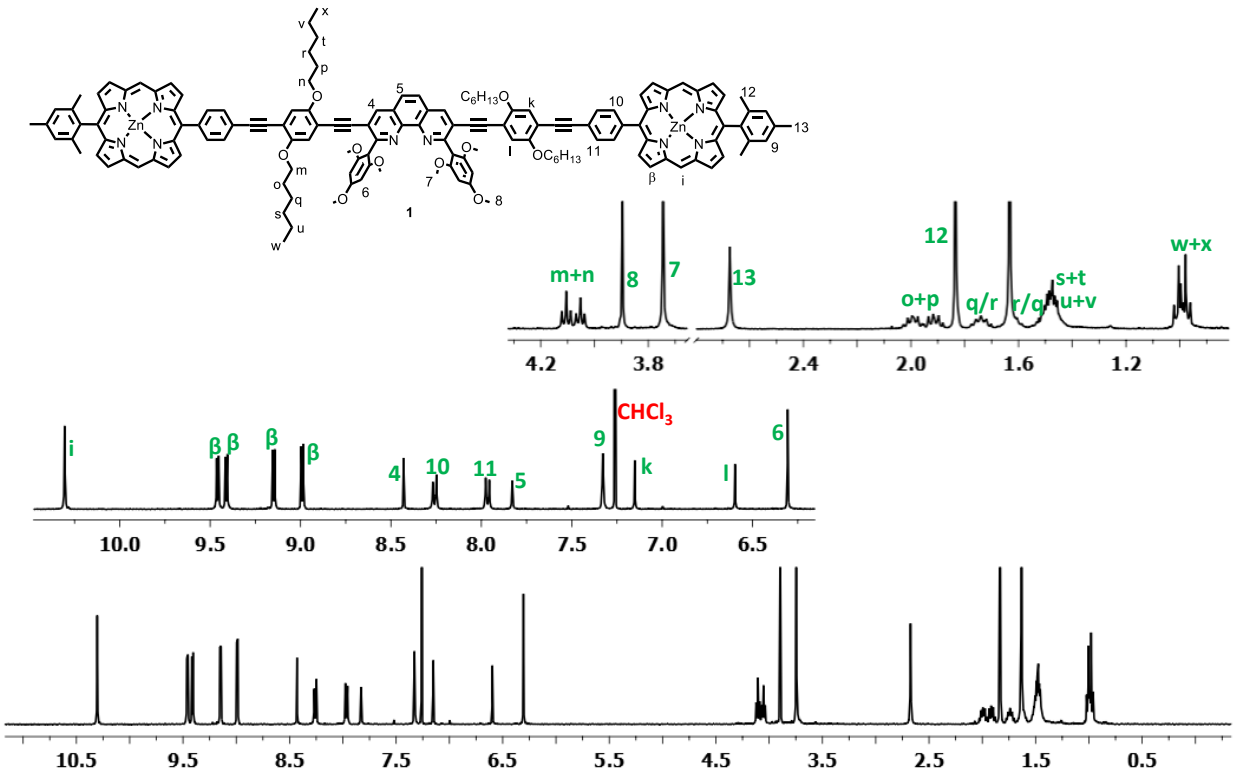


Figure S11. ^{1}H NMR of ligand **1** in $CDCl_3$ (400 MHz, 295 K).

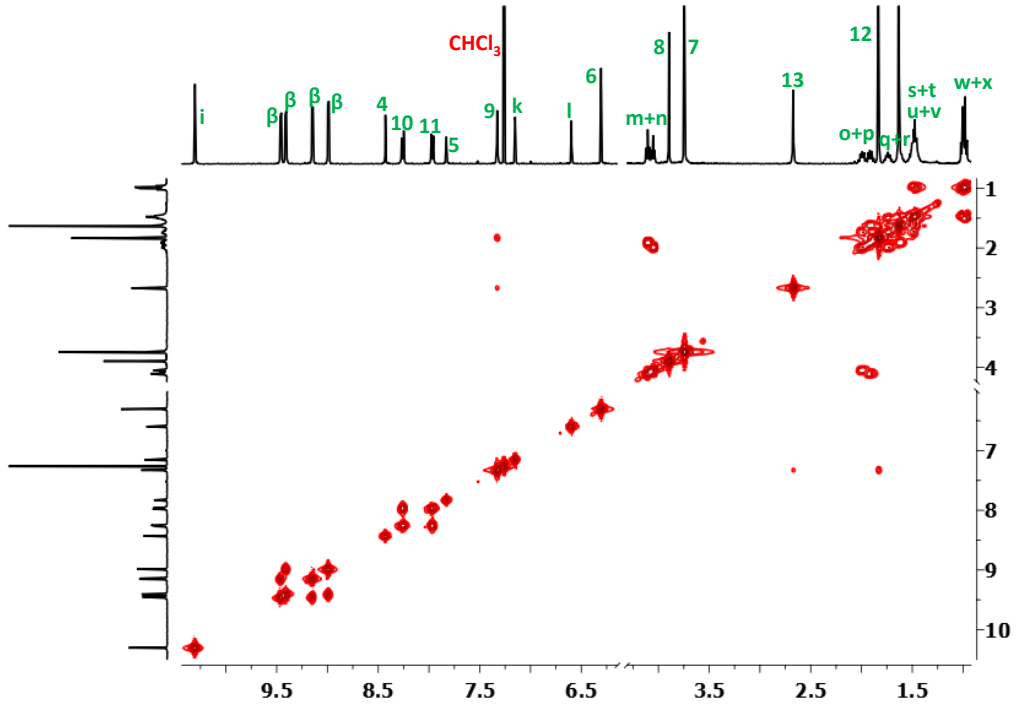


Figure S12. ^{1}H-^{1}H COSY NMR of ligand **1** in $CDCl_3$ (400 MHz, 295 K).

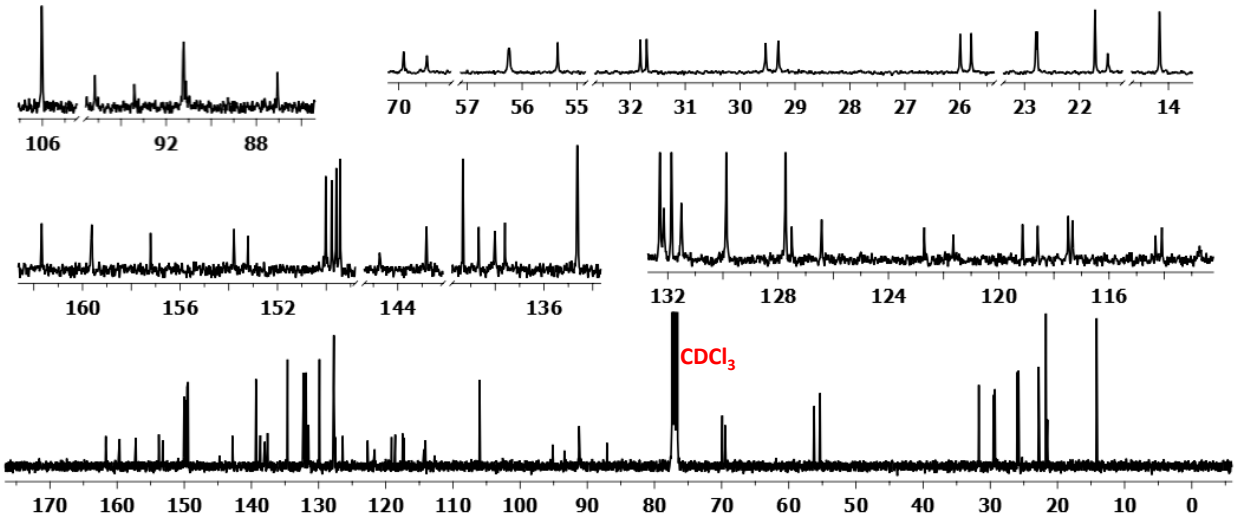


Figure S13. ^{13}C NMR of ligand **1** in $CDCl_3$ (100 MHz, 295 K).

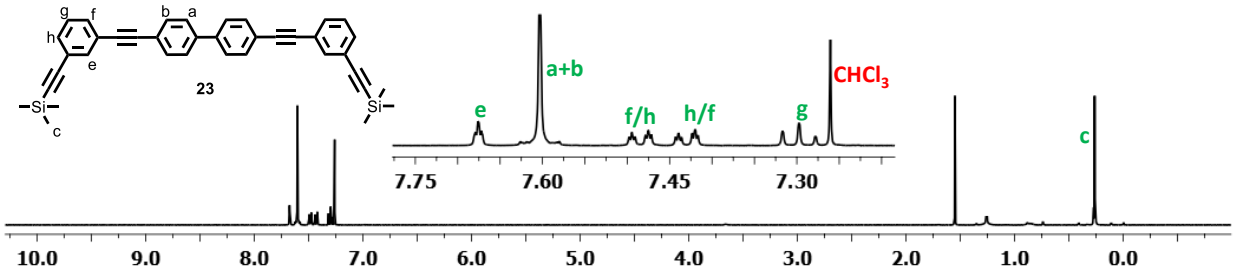


Figure S14. ^{1}H NMR of compound **23** in $CDCl_3$ (400 MHz, 295 K).

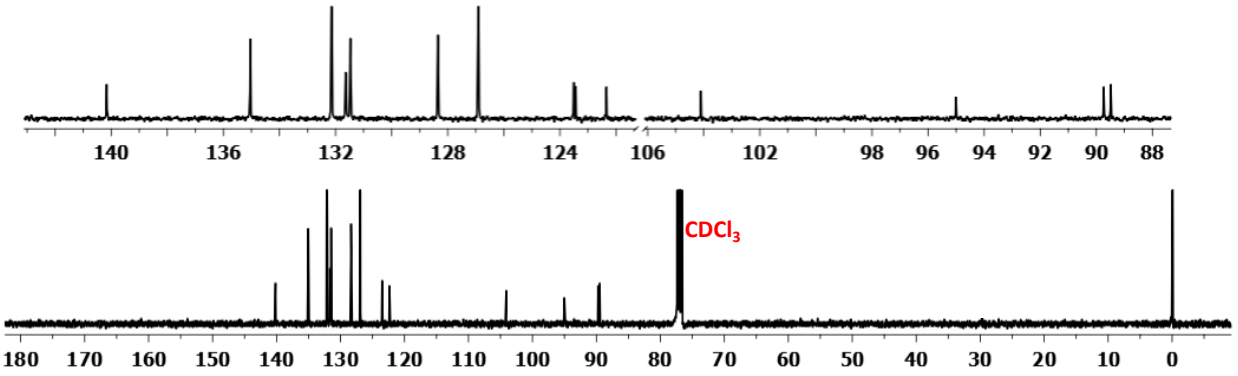


Figure S15. ^{13}C NMR of compound **23** in $CDCl_3$ (100 MHz, 295 K).

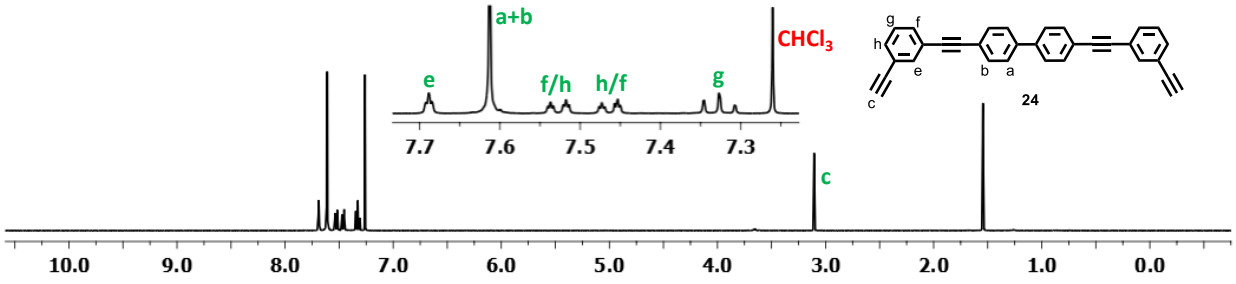


Figure S16. ^{1}H NMR of compound **24** in $CDCl_3$ (400 MHz, 295 K).

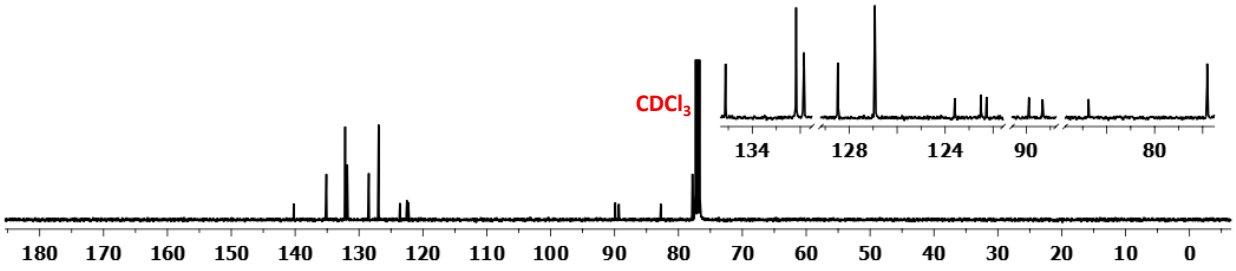


Figure S17. ^{13}C NMR of compound **24** in $CDCl_3$ (100 MHz, 295 K).

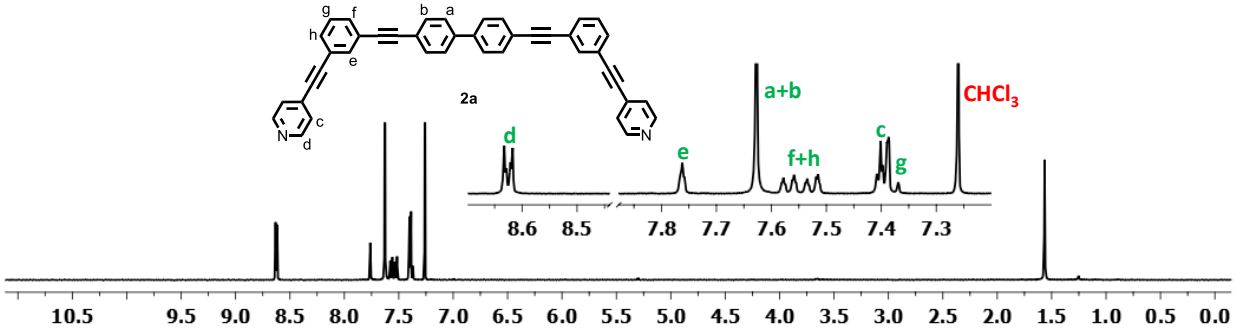


Figure S18. ^{1}H NMR of ligand **2a** in $CDCl_3$ (400 MHz, 295 K).

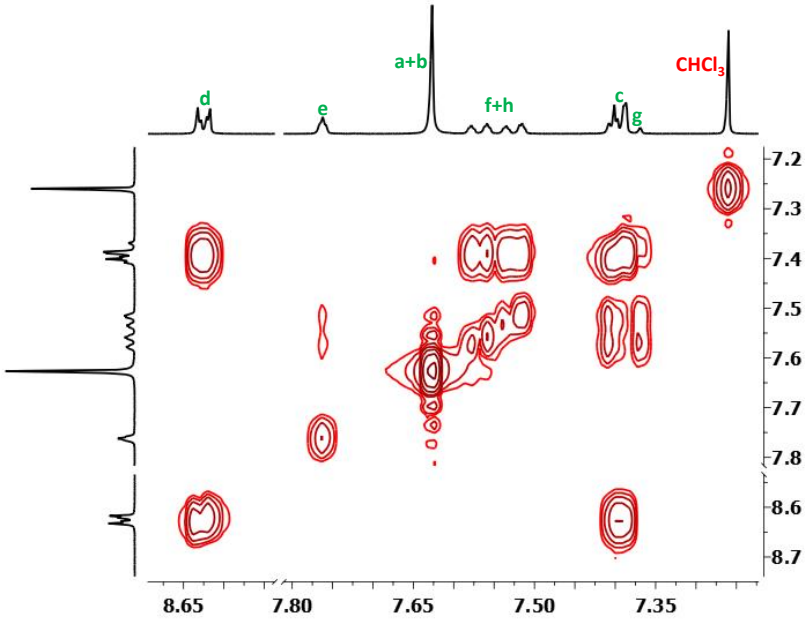


Figure S19. ^{1}H-^{1}H COSY NMR of ligand **2a** in $CDCl_3$ (400 MHz, 295 K).

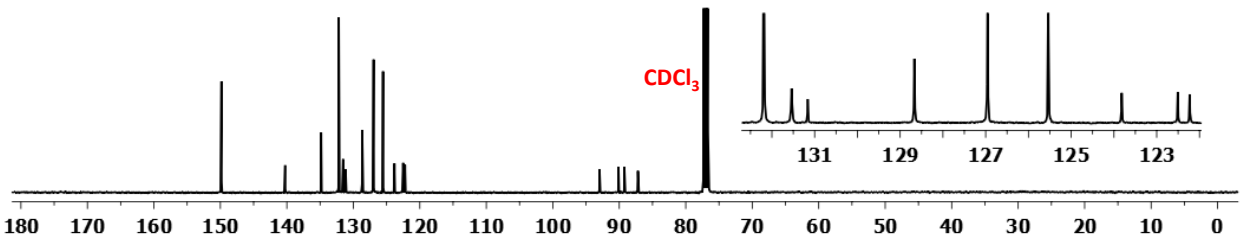


Figure S20. ^{13}C NMR of ligand **2a** in $CDCl_3$ (100 MHz, 295 K).

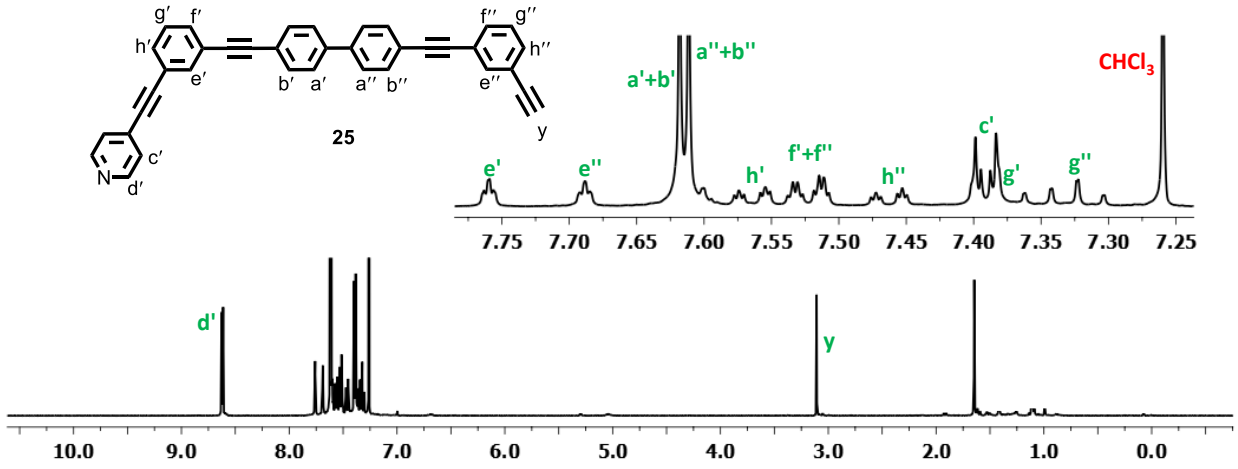


Figure S21. ^{1}H NMR of compound **25** in $CDCl_3$ (400 MHz, 295 K).

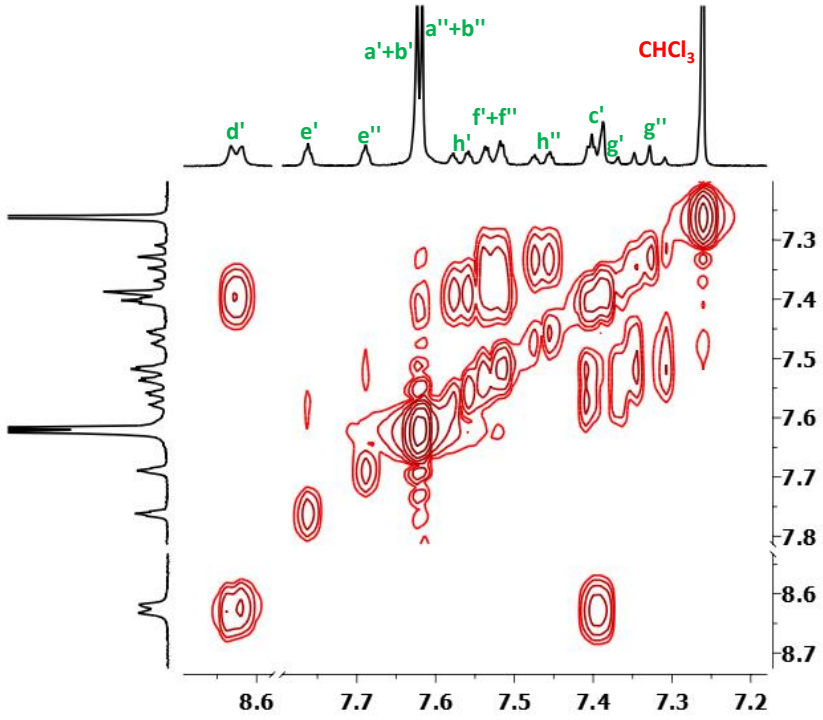


Figure S22. ^{1}H-^{1}H COSY NMR of compound **25** in $CDCl_3$ (400 MHz, 295 K).

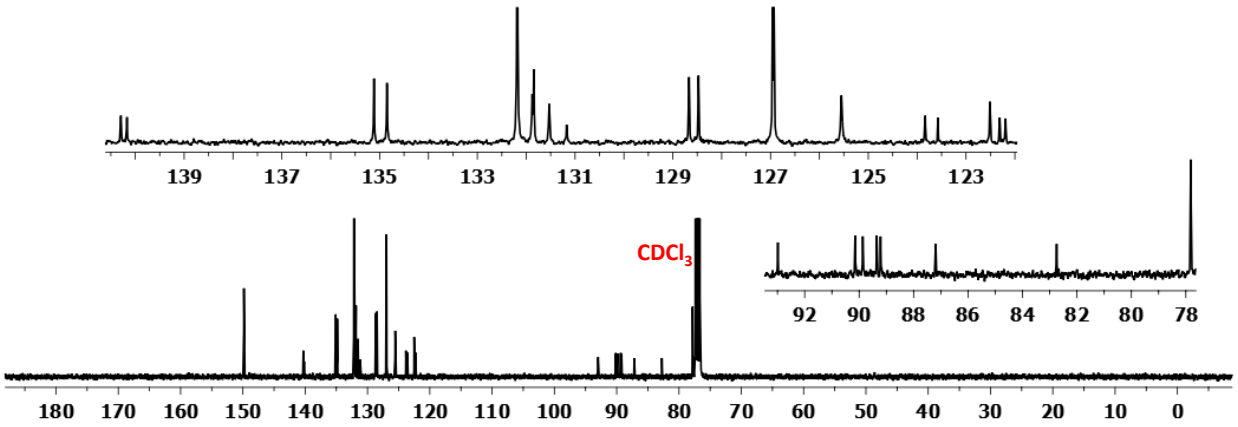


Figure S23. ^{13}C NMR of compound **25** in $CDCl_3$ (100 MHz, 295 K).

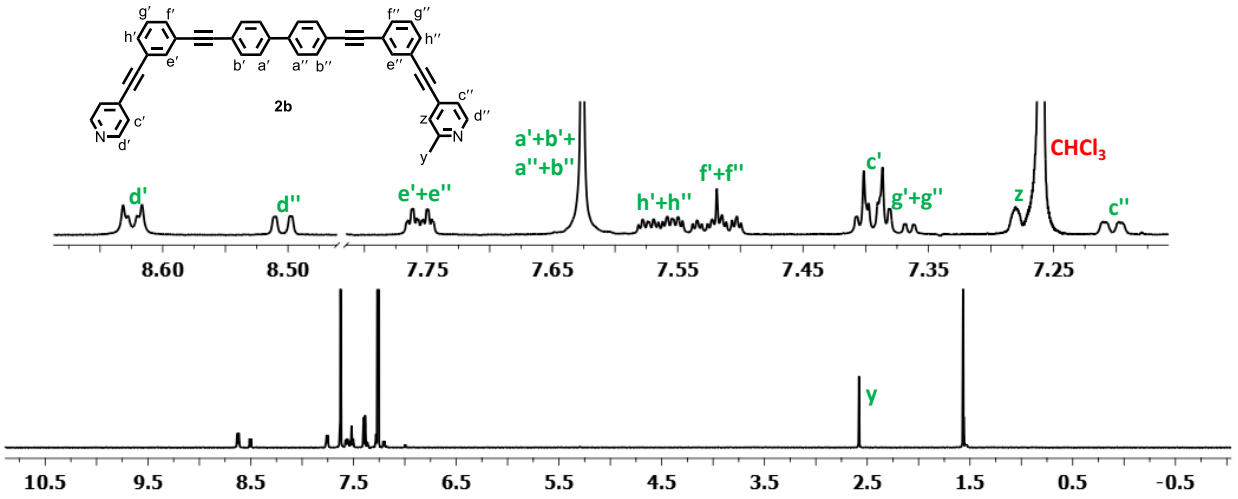


Figure S24. ^{1}H NMR of ligand **2b** in $CDCl_3$ (400 MHz, 295 K).

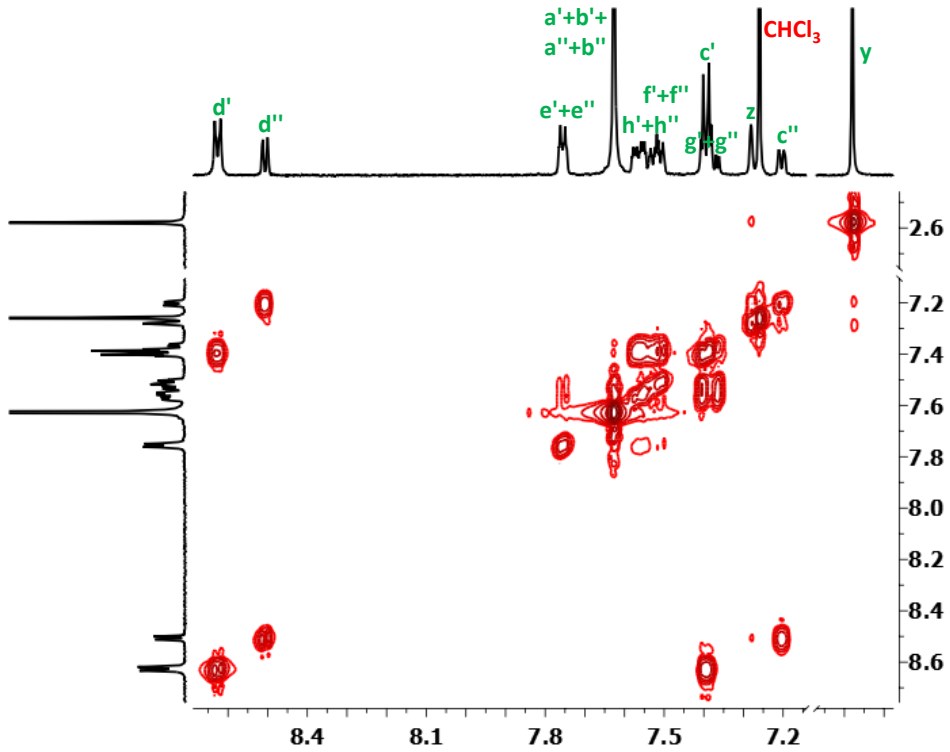


Figure S25. ^{1}H-^{1}H COSY NMR of ligand **2b** in $CDCl_3$ (400 MHz, 295 K).

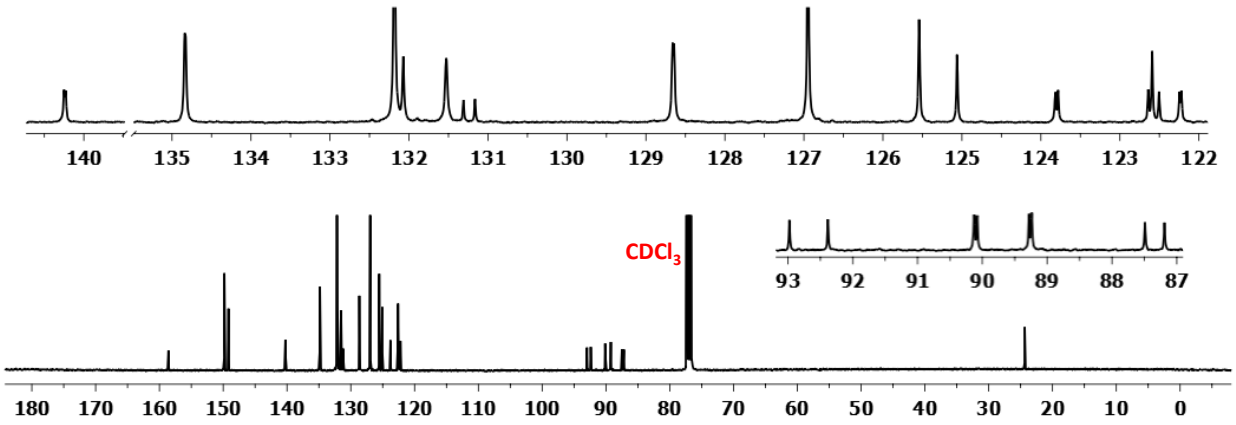


Figure S26. ^{13}C NMR of ligand **2b** in $CDCl_3$ (100 MHz, 295 K).

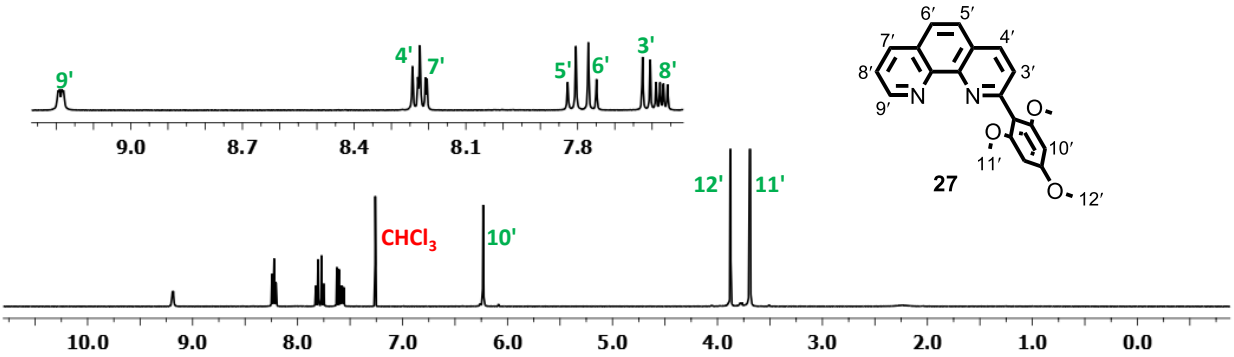


Figure S27. ^{1}H NMR of ligand **27** in $CDCl_3$ (400 MHz, 295 K).

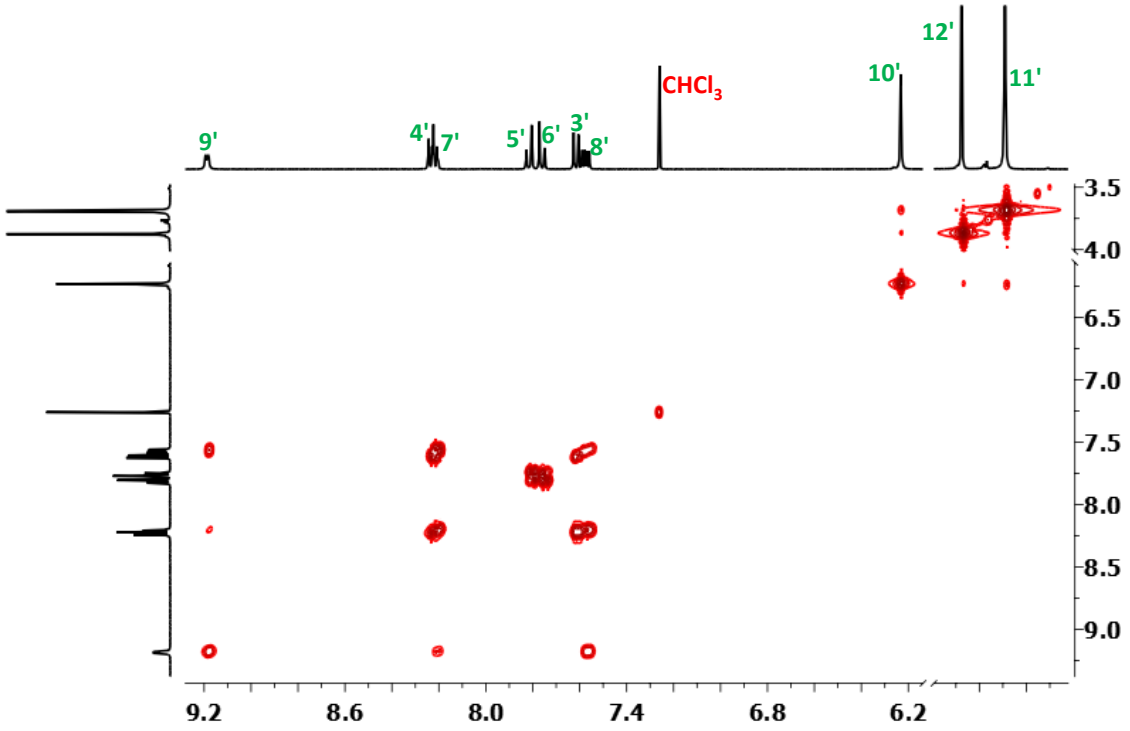


Figure S28. ^{1}H-^{1}H COSY NMR of ligand **27** in $CDCl_3$ (400 MHz, 295 K).

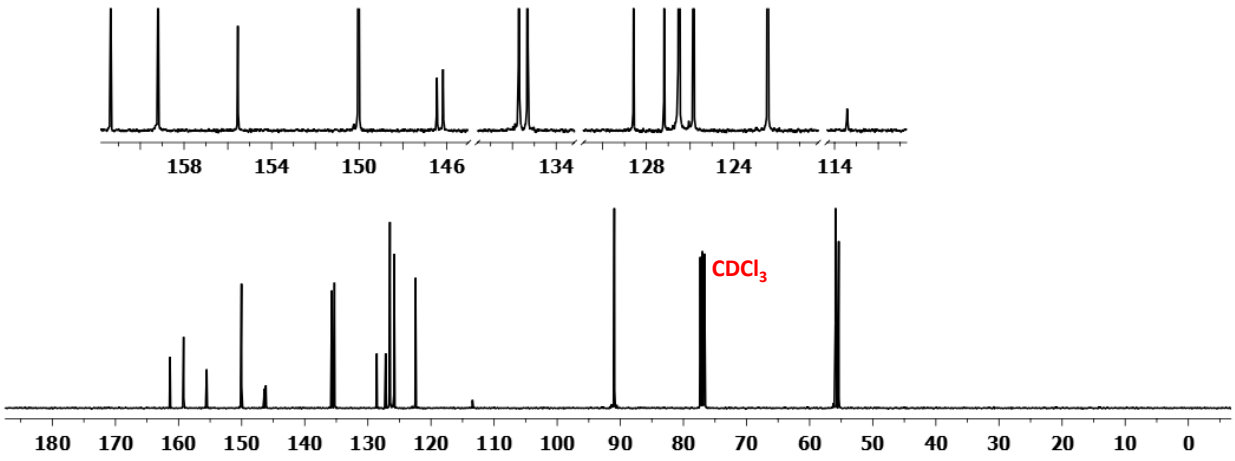


Figure S29. ^{13}C NMR of ligand **27** in $CDCl_3$ (100 MHz, 295 K).

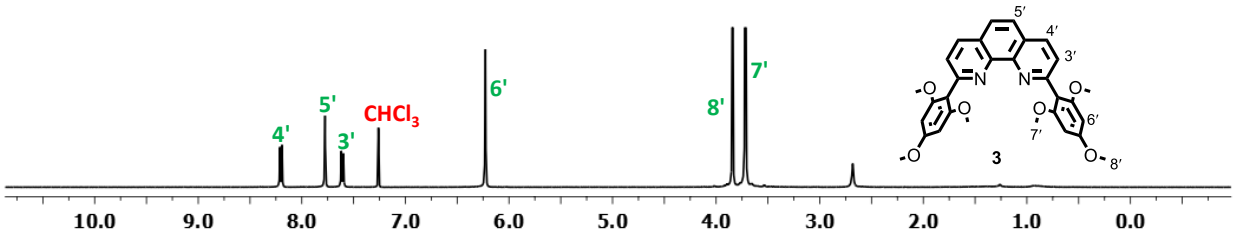


Figure S30. ^{1}H NMR of ligand **3** in $CDCl_3$ (400 MHz, 295 K).

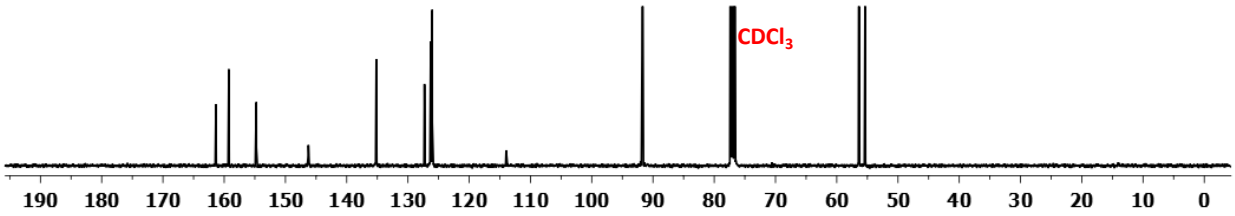


Figure S31. ^{13}C NMR of ligand **3** in $CDCl_3$ (100 MHz, 295 K).

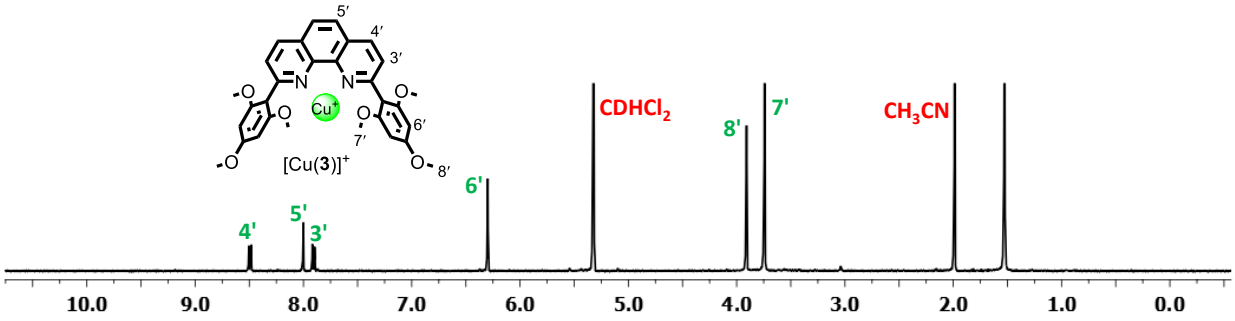


Figure S32. ^{1}H NMR of complex [Cu(**3**)]$^{+}$ in CD_2Cl_2 (400 MHz, 295 K).

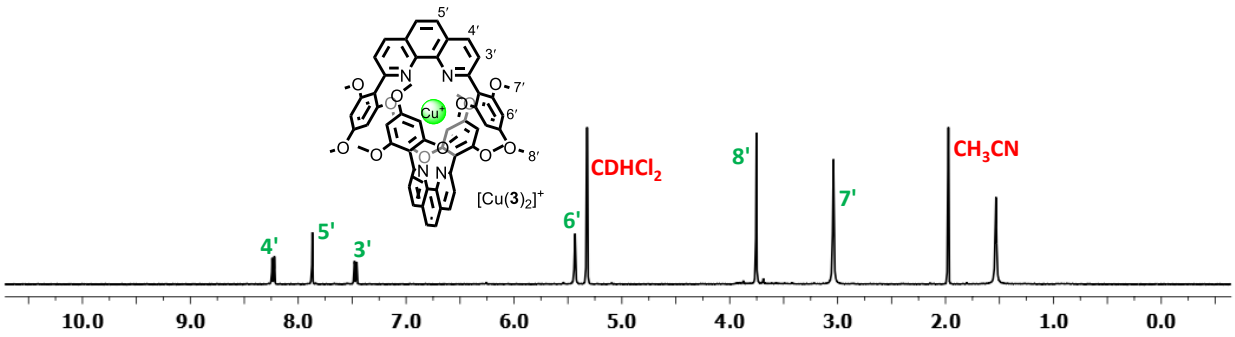


Figure S33. ^{1}H NMR of complex [Cu(**3**)$_2$]$^{+}$ in CD_2Cl_2 (400 MHz, 295 K).

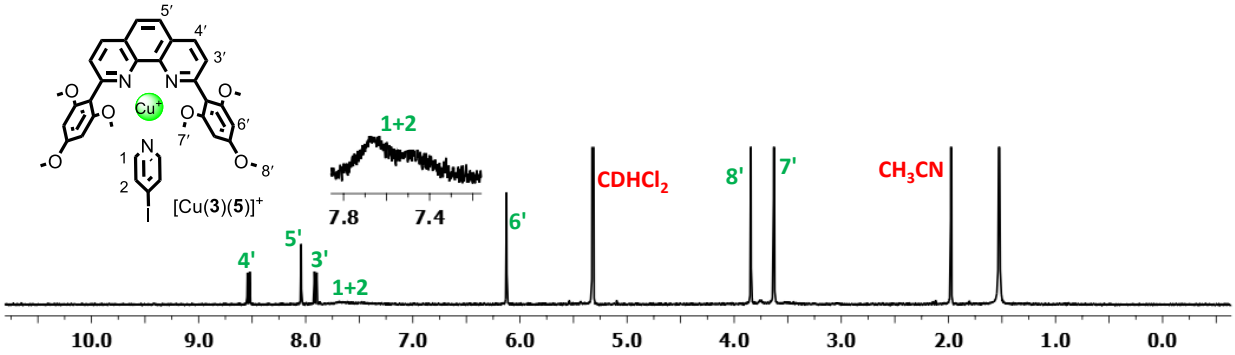


Figure S34. ^{1}H NMR of complex [Cu(**3**)(**5**)]$^{+}$ in CD_2Cl_2 (400 MHz, 295 K).

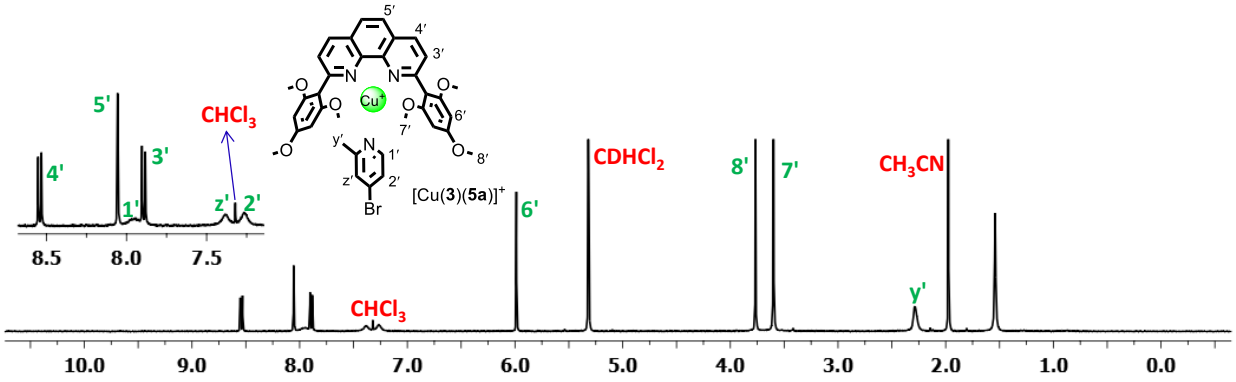


Figure S35. ^{1}H NMR of complex [Cu(**3**)(**5a**)]$^{+}$ in CD_2Cl_2 (400 MHz, 295 K).

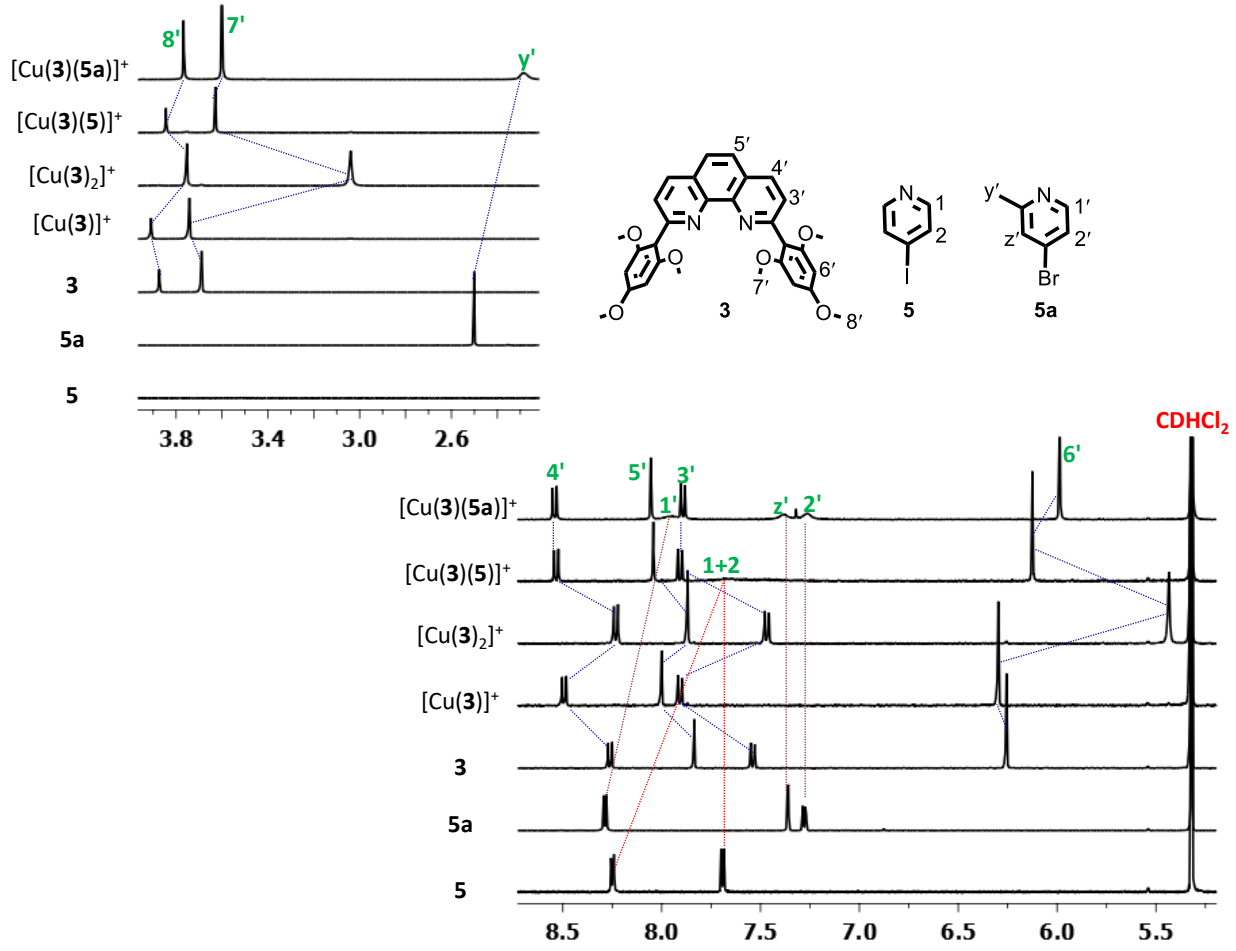


Figure S36. Comparison of ^{1}H NMR of compounds **5**, **5a**, **3**, complex [Cu(**3**)]$^{+}$, [Cu(**3**)$_2$]$^{+}$, [Cu(**3**)(**5**)]$^{+}$ and [Cu(**3**)(**5a**)]$^{+}$ in CD_2Cl_2 (400 MHz, 295 K).

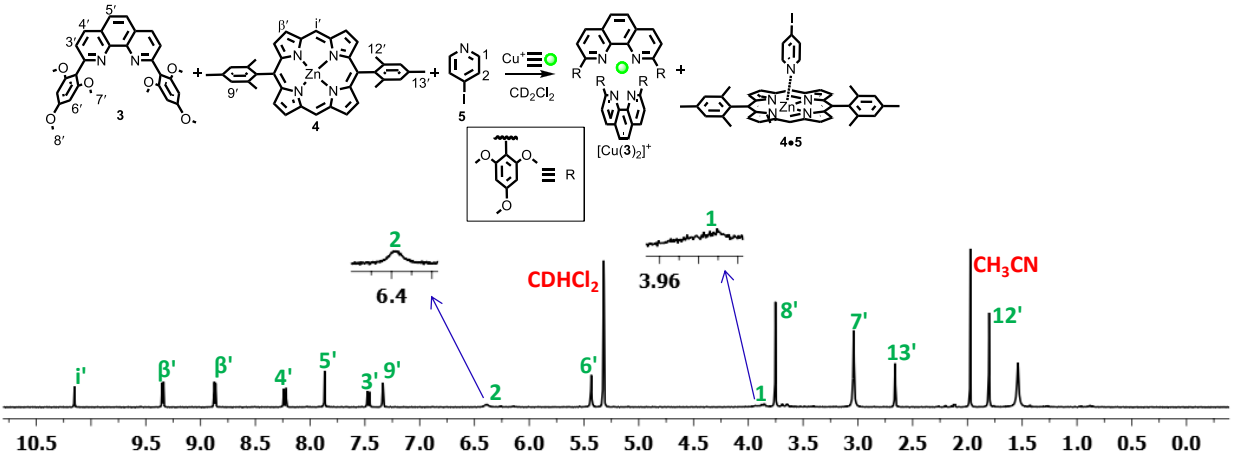


Figure S37: ^{1}H NMR of complex **4•5** + $[Cu(\mathbf{3})_2]^+$ in CD_2Cl_2 (400 MHz, 295 K).

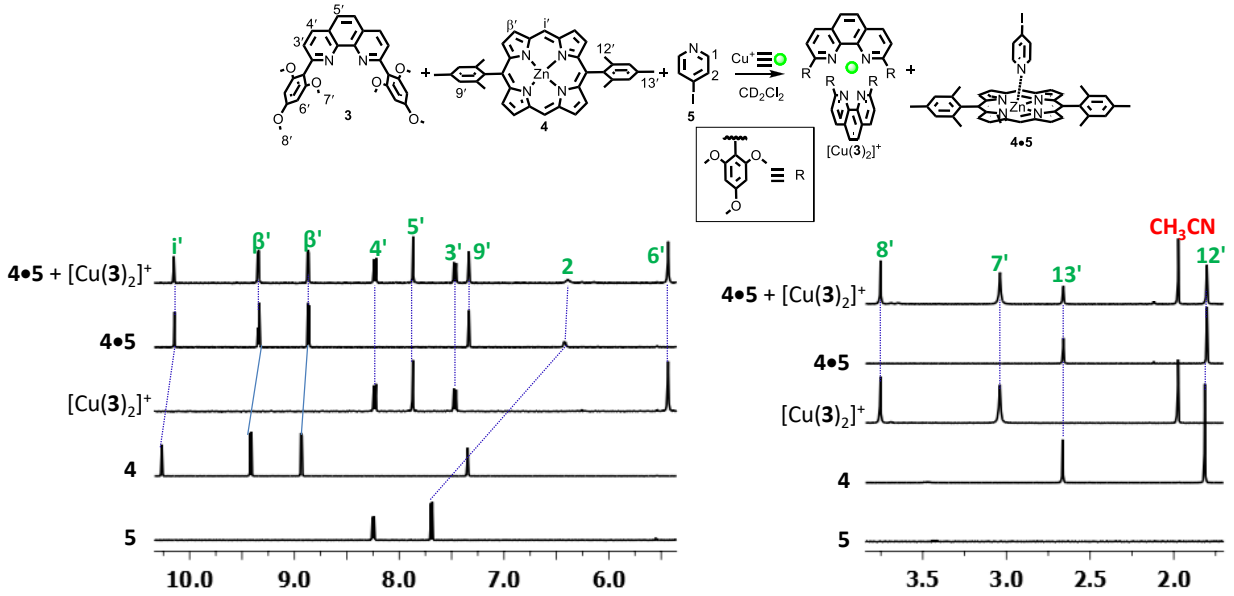


Figure S38. Comparison of ^{1}H NMR of compounds **5**, **4**, complex $[Cu(\mathbf{3})_2]^+$, **4•5** and **4•5** + $[Cu(\mathbf{3})_2]^+$ in CD_2Cl_2 (400 MHz, 295 K).

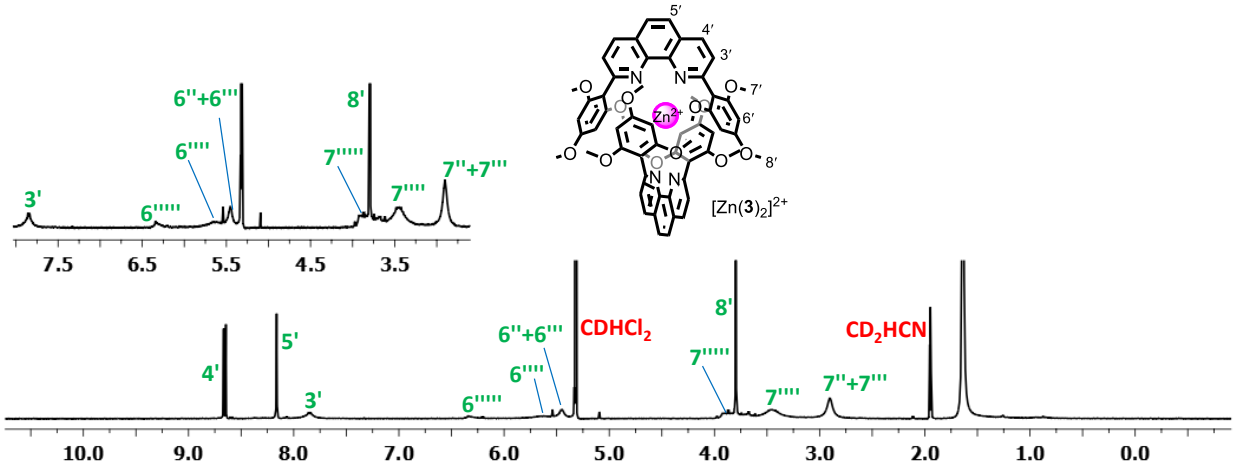


Figure S39. ^{1}H NMR of complex $[Zn(\mathbf{3})_2]^{2+}$ in CD_2Cl_2:CD_3CN (30:1) (400 MHz, 295 K). Proton signals of 7'- and 6'-H are diagnostically split in four singlets (1:1:1:1) denoted as 7'', 7''', 7'''', 7''''' and 6'', 6''', 6'''', 6''''', respectively.

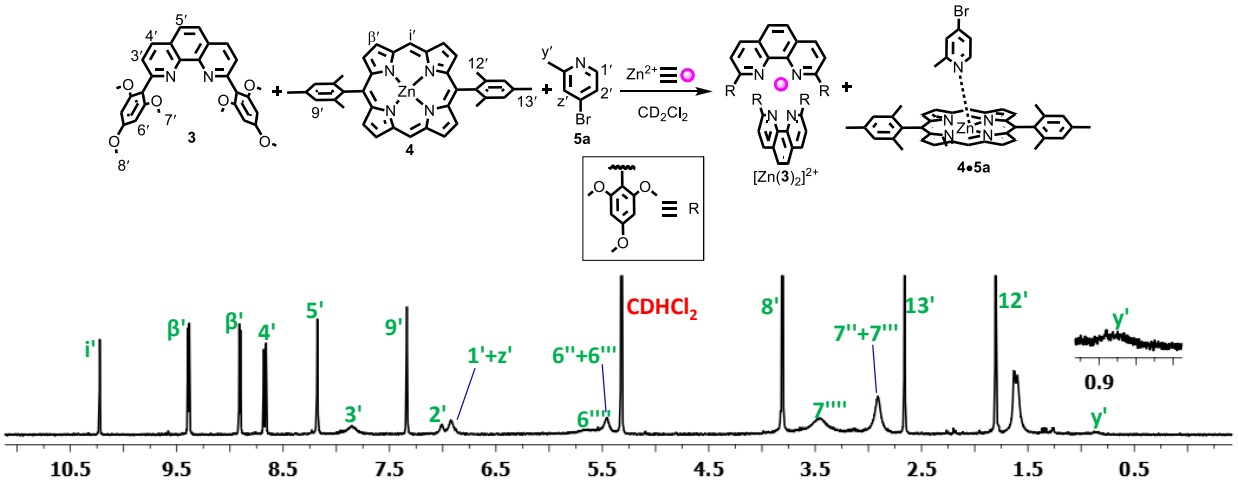


Figure S40. ^{1}H NMR of complex **4•5a** + $[Zn(\mathbf{3})_2]^{2+}$ in CD_2Cl_2 (400 MHz, 295 K). Proton signals of 7'- and 6'-H are diagnostically split in four singlets (1:1:1:1) denoted as 7'', 7''', 7'''', 7''''' and 6'', 6''', 6'''', 6''''', respectively. Signals 7''''' and 6'''''-H became very broad and merged with the base line.

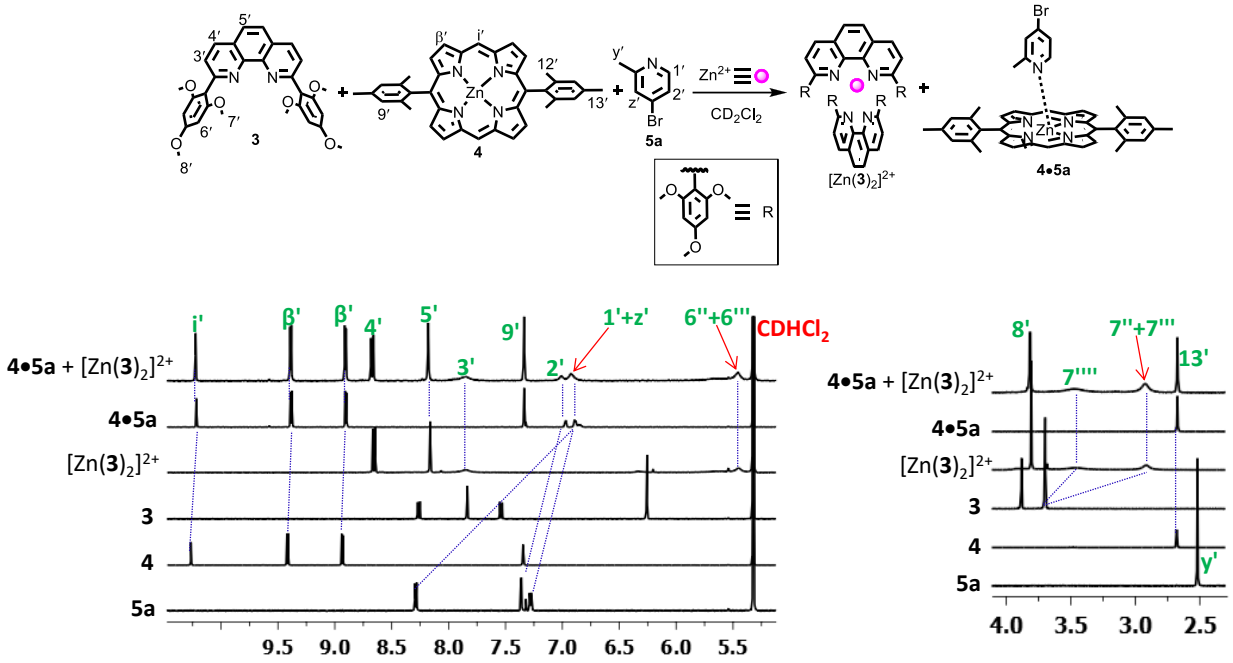


Figure S41. Comparison of ^{1}H NMR of compounds **5a**, **4**, **3**, complex $[Zn(\mathbf{3})_2]^{2+}$, **4•5a** and **4•5a** + $[Zn(\mathbf{3})_2]^{2+}$ in CD_2Cl_2 (400 MHz, 295 K). Proton signals of 7'- and 6'-H are diagnostically split in four singlets (1:1:1:1) denoted as 7'', 7''', 7'''', 7''''' and 6'', 6''', 6'''', 6''''' respectively. Signals 7''''' and 6''''-H became very broad and merged with the base line.

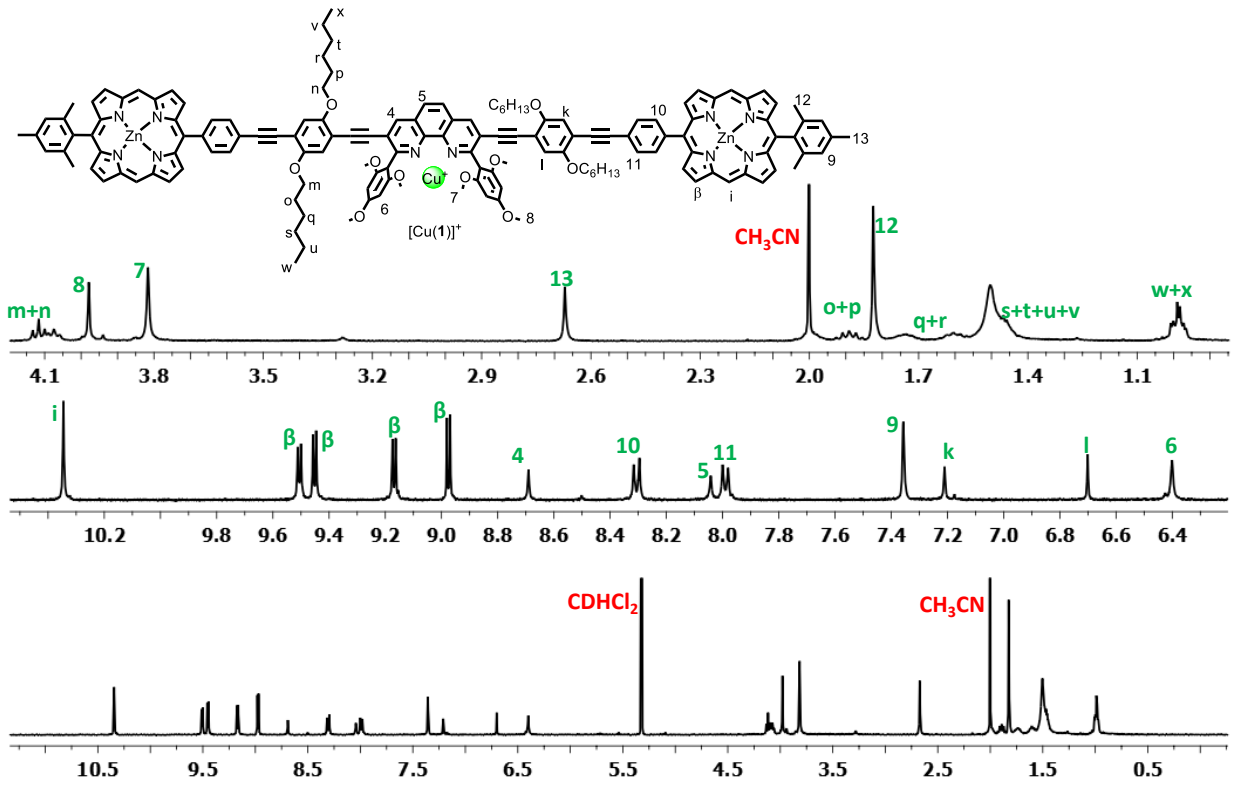


Figure S42. ^{1}H NMR of stator [Cu(**1**)]$^{+}$ in CD_2Cl_2 (400 MHz, 295 K).

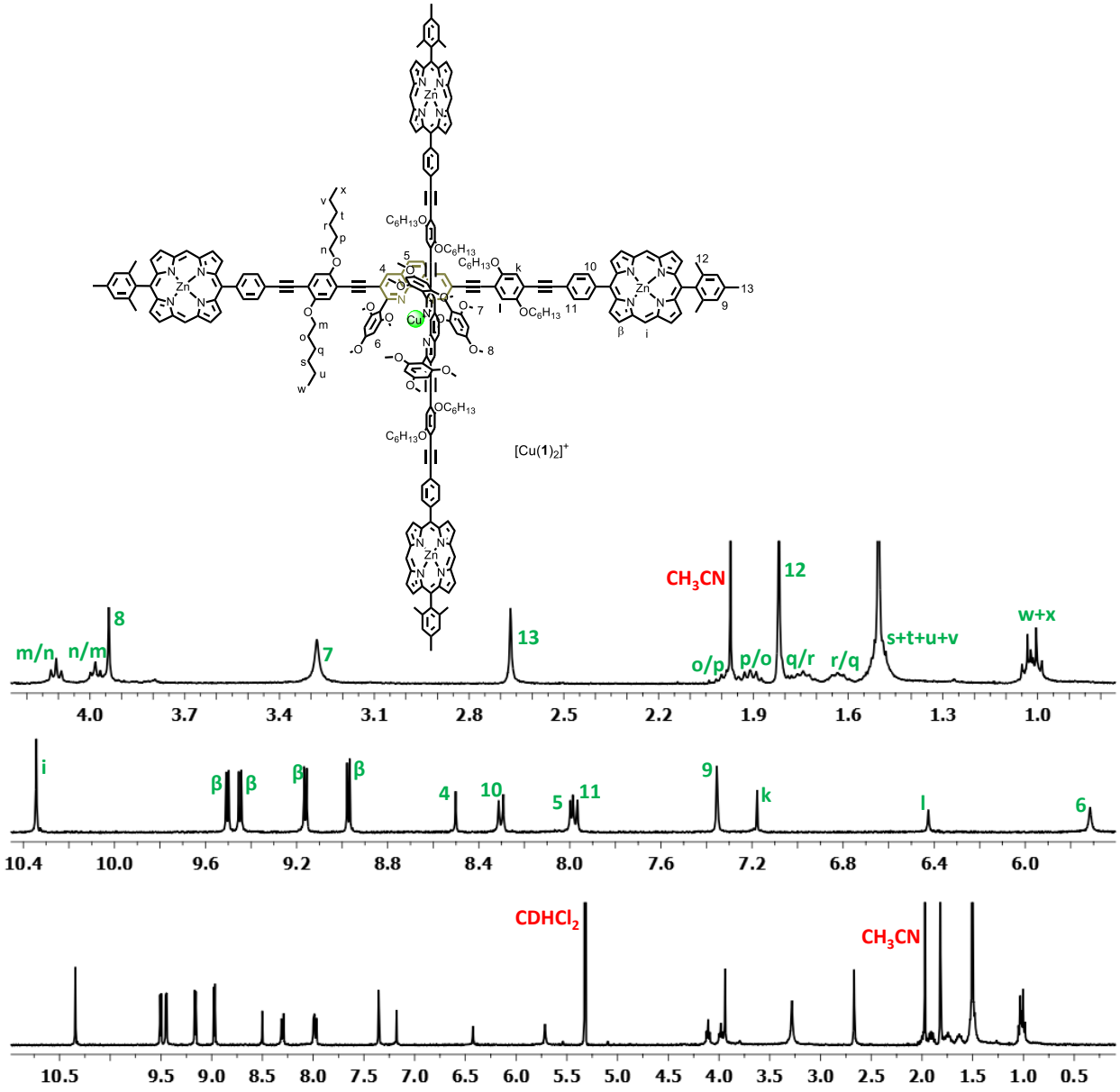


Figure S43. ^{1}H NMR of deck $[Cu(\mathbf{1})_2]^+$ in CD_2Cl_2 (400 MHz, 295 K).

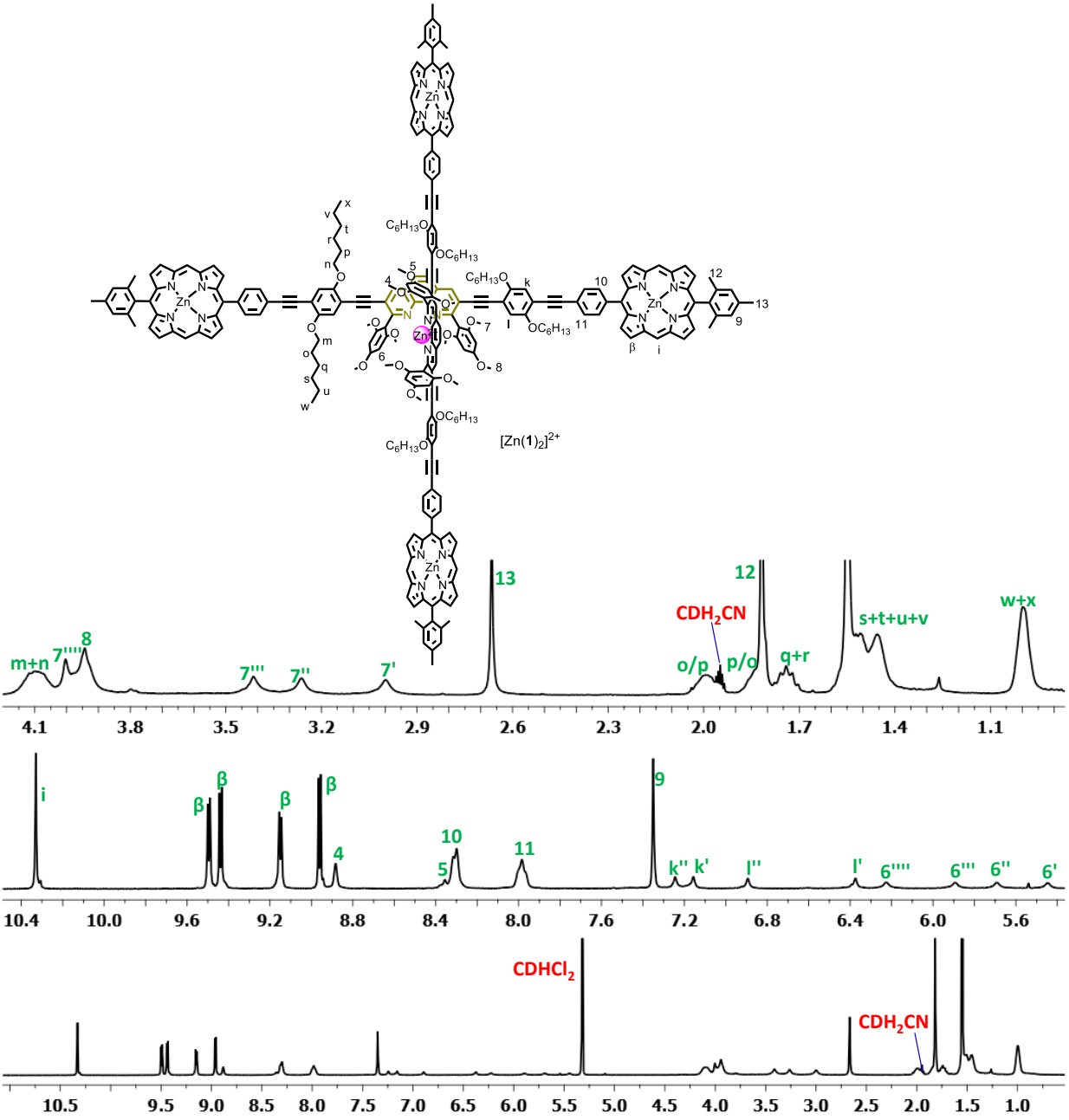


Figure S44. ^{1}H NMR (400 MHz, 295 K) of deck $[Zn(\mathbf{1})_2]^{2+}$ in CD_2Cl_2:CD_3CN (60:1). Proton signals of 7- and 6-H are split in four singlets (1:1:1:1) denoted as 7', 7'', 7''', 7'''' and 6', 6'', 6''', 6'''', respectively. Proton signals l- and k-H are split in two singlets (1:1) denoted as l', l'' and k', k'', respectively.

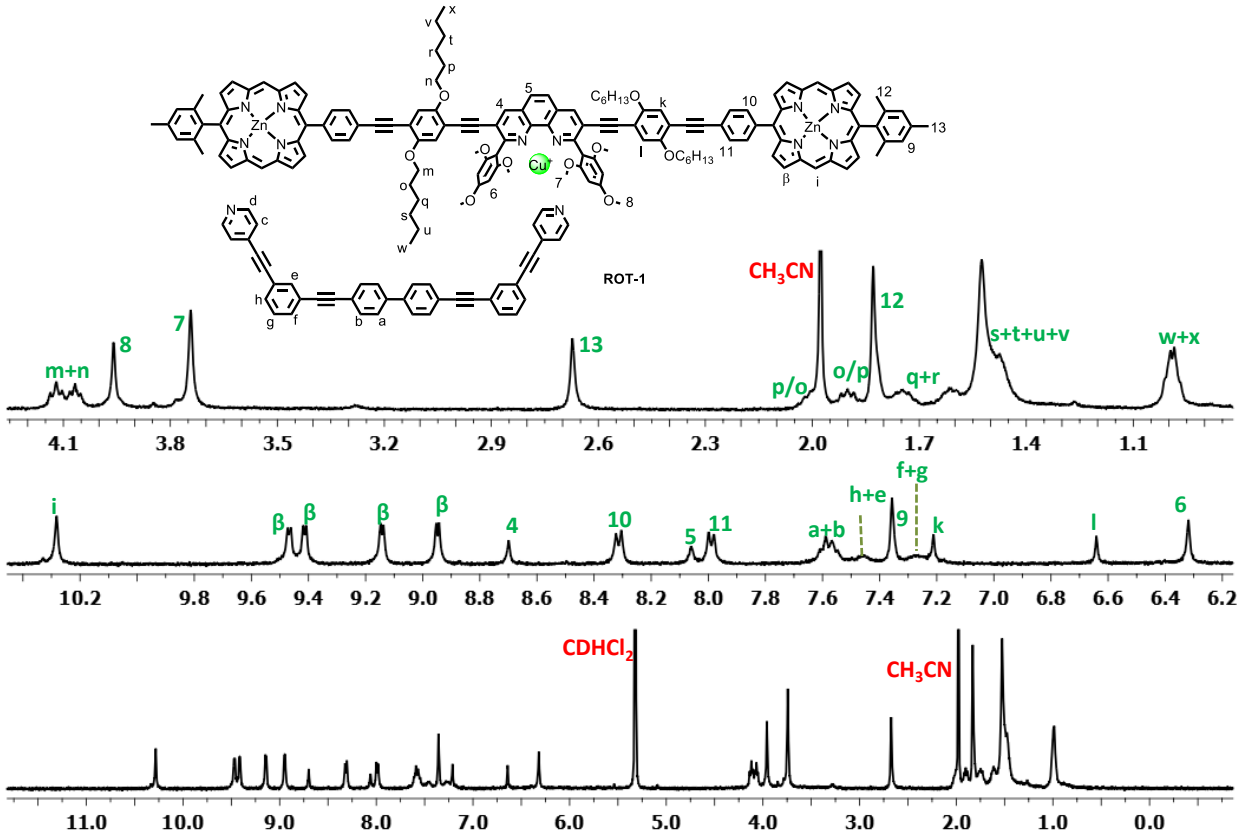


Figure S45. ^{1}H NMR of **ROT-1** in CD_2Cl_2 (400 MHz, 295 K).

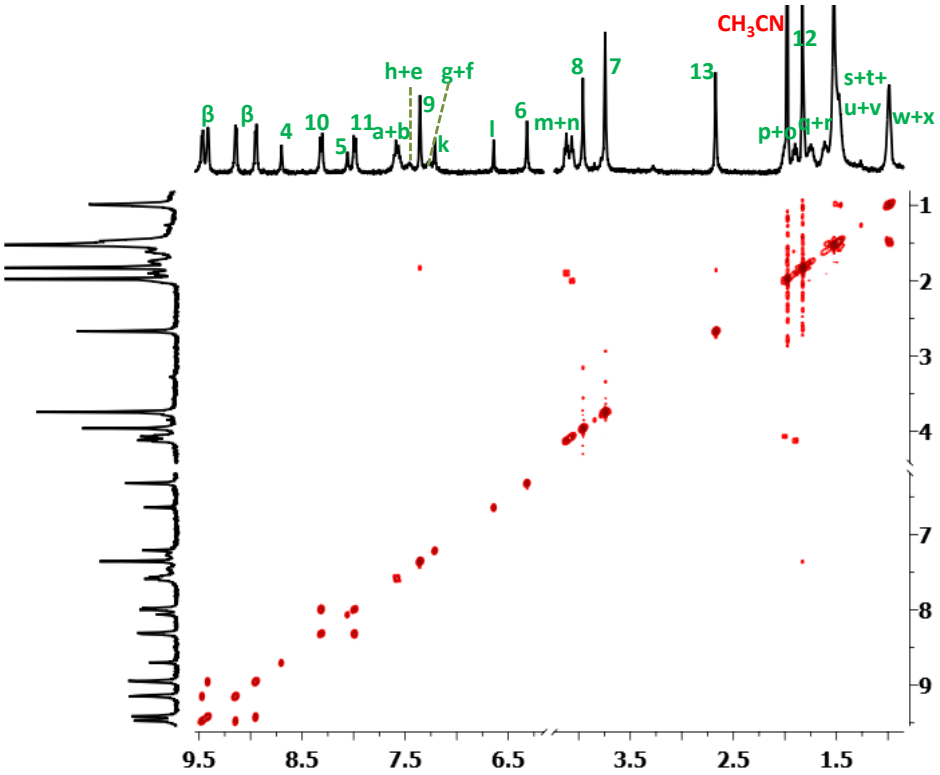


Figure S46. ^{1}H-^{1}H COSY NMR of **ROT-1** in CD_2Cl_2 (400 MHz, 295 K).

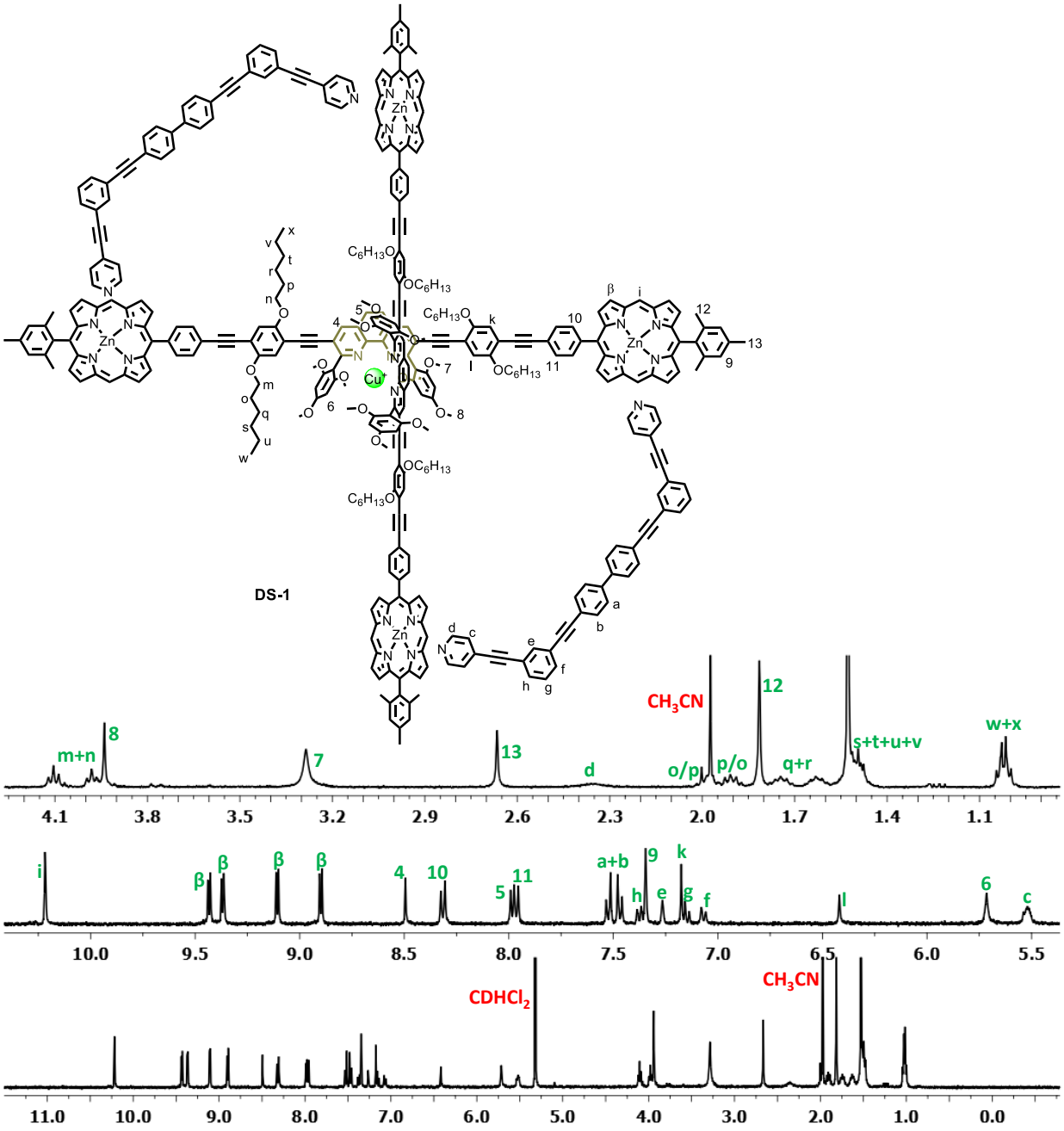


Figure S47. ^{1}H NMR of **DS-1** in CD_2Cl_2 (400 MHz, 295 K).

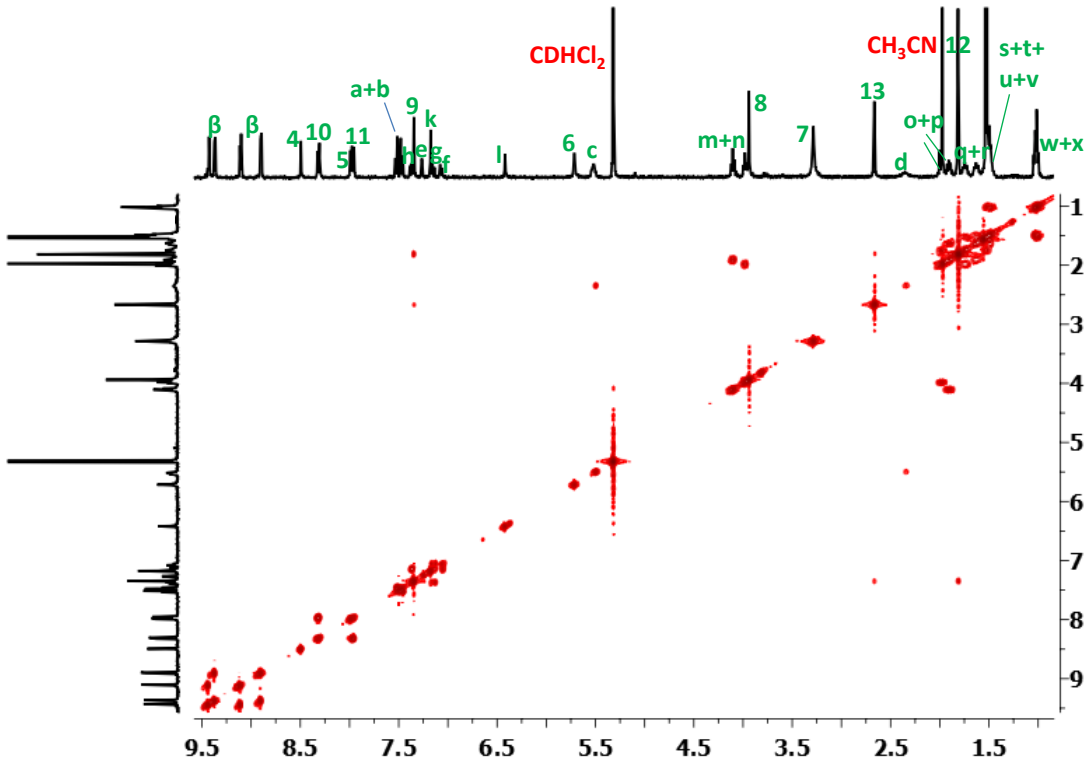


Figure S48. ^{1}H-^{1}H COSY NMR of **DS-1** in CD_2Cl_2 (400 MHz, 295 K).

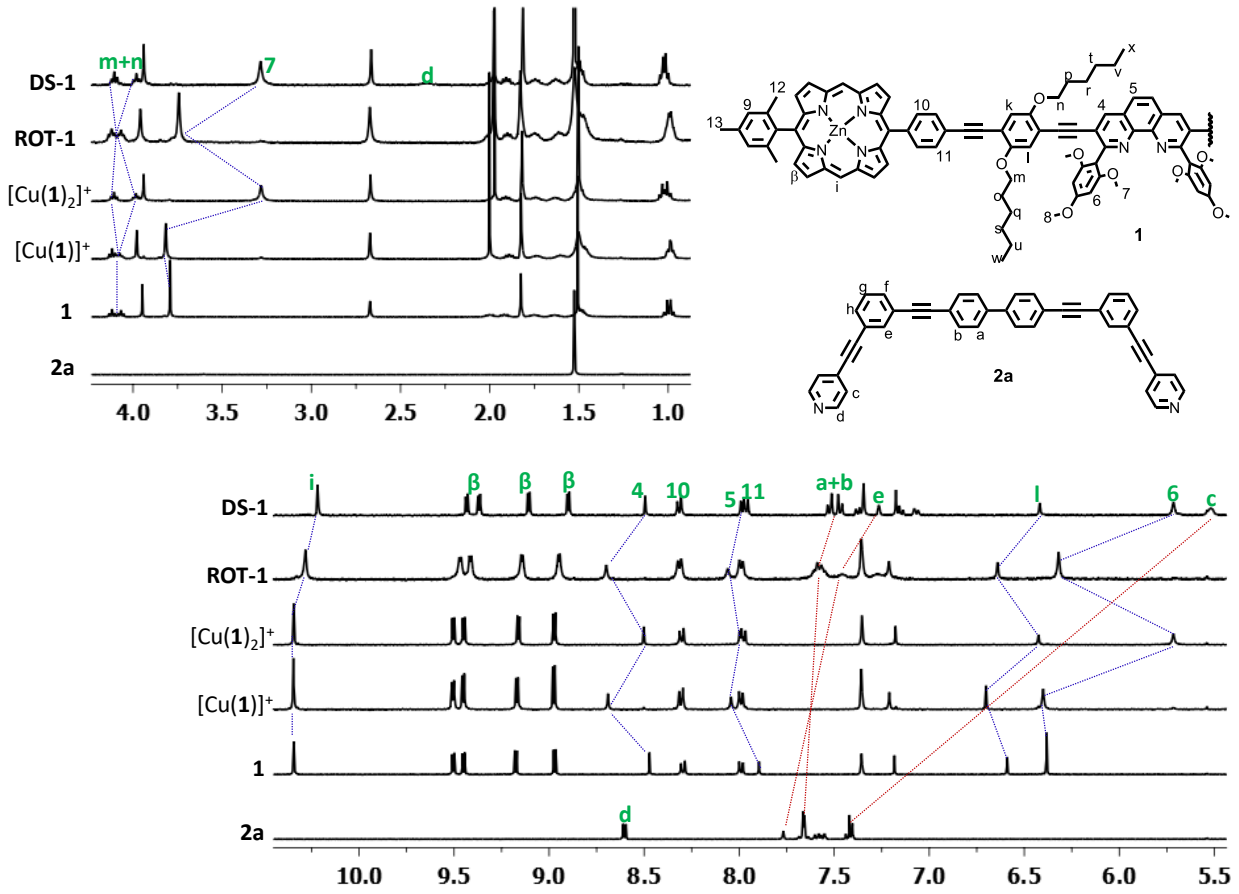


Figure S49. Comparison of ^{1}H NMR of ligand **2a**, **1**, complex [Cu(**1**)]$^{+}$, [Cu(**1**)$_2$]$^{+}$, **ROT-1** and **DS-1** in CD_2Cl_2 (400 MHz, 295 K).

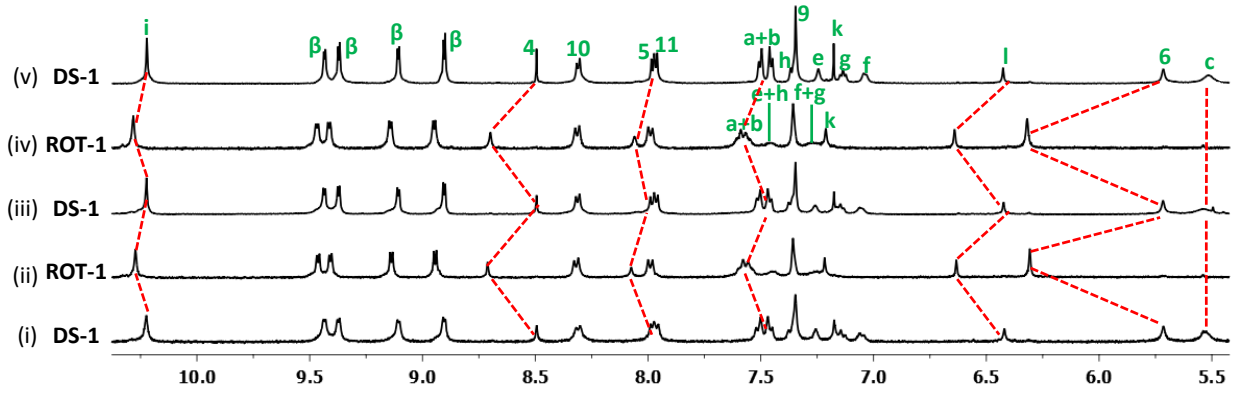


Figure S50. Partial ^{1}H NMR (400 MHz, 295 K) shows the reversible interconversion of **DS-1** and **ROT-1** over two full cycles in CD_2Cl_2. (i) **DS-1** was obtained by addition of **1**, Cu^{+} and **2a** (1:0.5:1) in CD_2Cl_2. (ii) After addition of 0.5 equiv. of Cu^{+} to **DS-1**. (iii) Addition of 0.5 equiv. of cyclam to **ROT-1**. (iv) Addition of 0.5 equiv. of Cu^{+} to (iii) regenerated **ROT-1**. (v) **DS-1** was regenerated from (iv) by addition of 0.5 equiv. of cyclam.

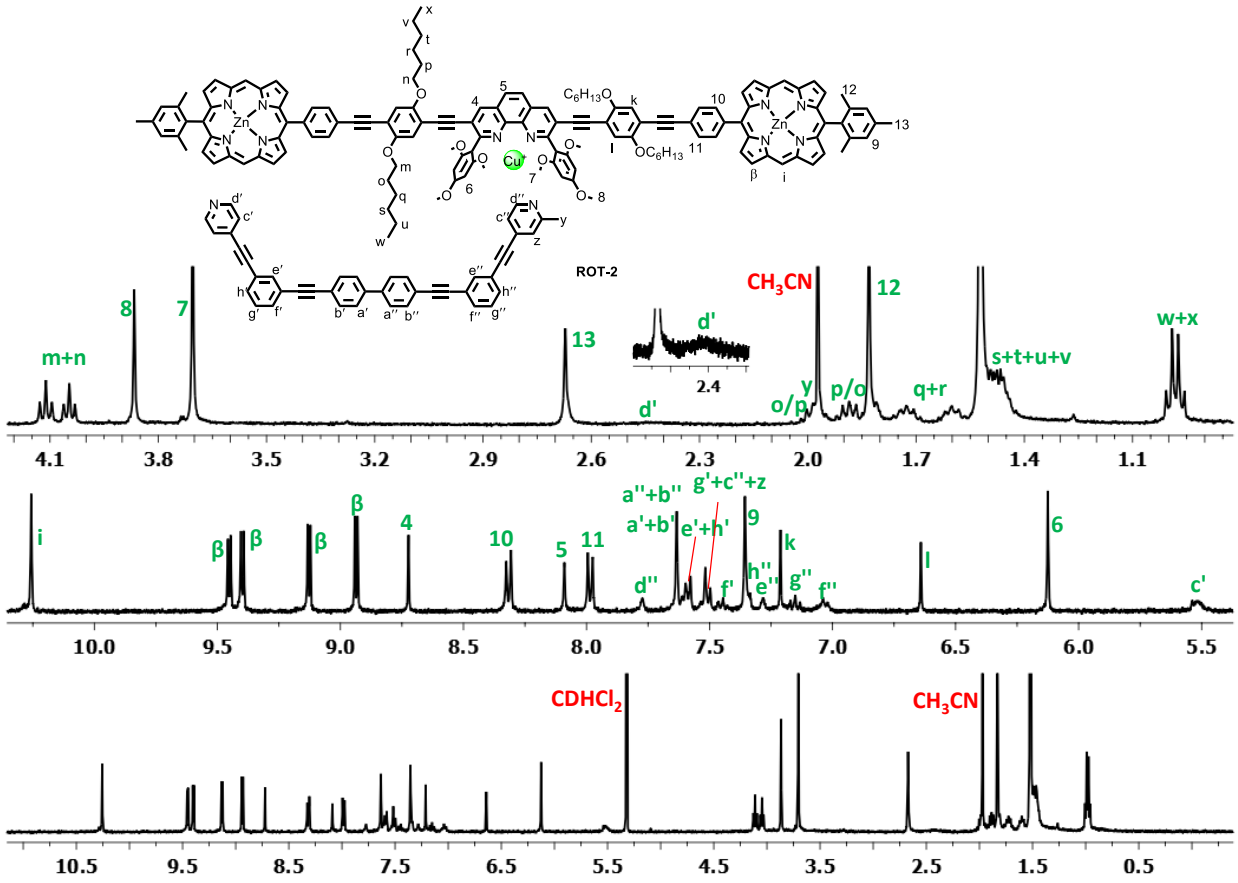


Figure S51. ^{1}H NMR of **ROT-2** in CD_2Cl_2 (500 MHz, 295 K).

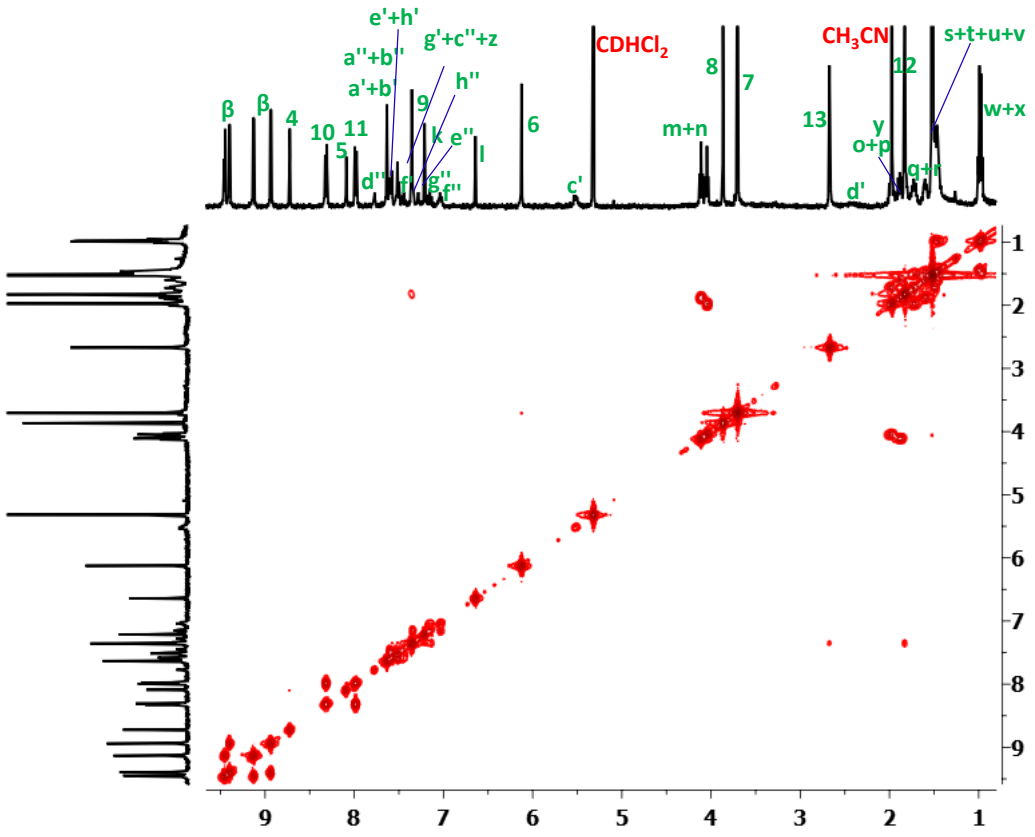


Figure S52. ^{1}H-^{1}H COSY NMR of **ROT-2** in CD_2Cl_2 (500 MHz, 295 K).

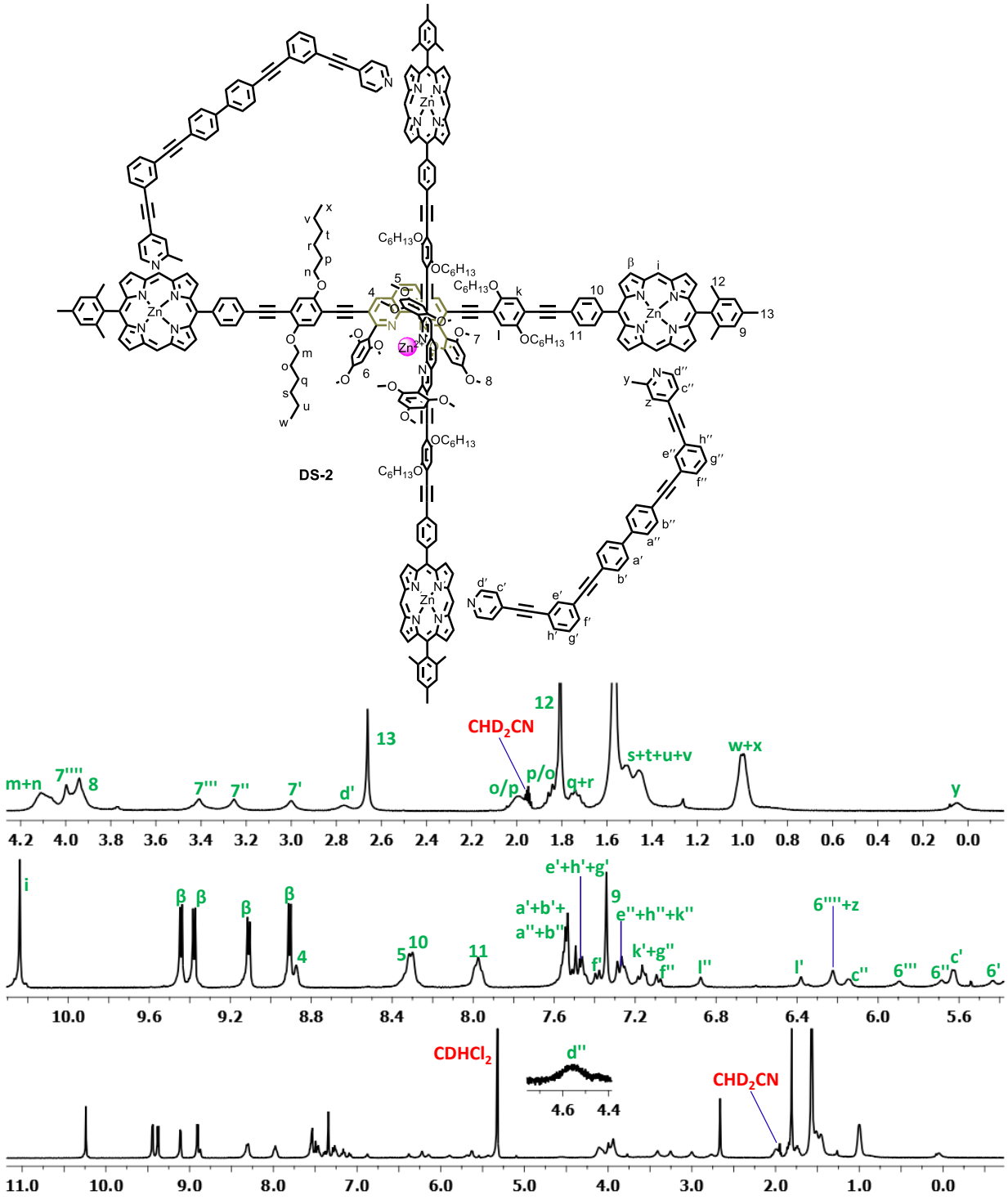


Figure S53. ^{1}H NMR (500 MHz, 295 K) of **DS-2** in CD_2Cl_2:CD_3CN (60:1). Proton signals of 7- and 6-H are split in four singlets (1:1:1:1) denoted as 7', 7'', 7''', 7'''' and 6', 6'', 6''', 6'''', respectively. Proton signals of l- and k-H are split in two singlets (1:1) denoted as l', l'' and k', k'', respectively.

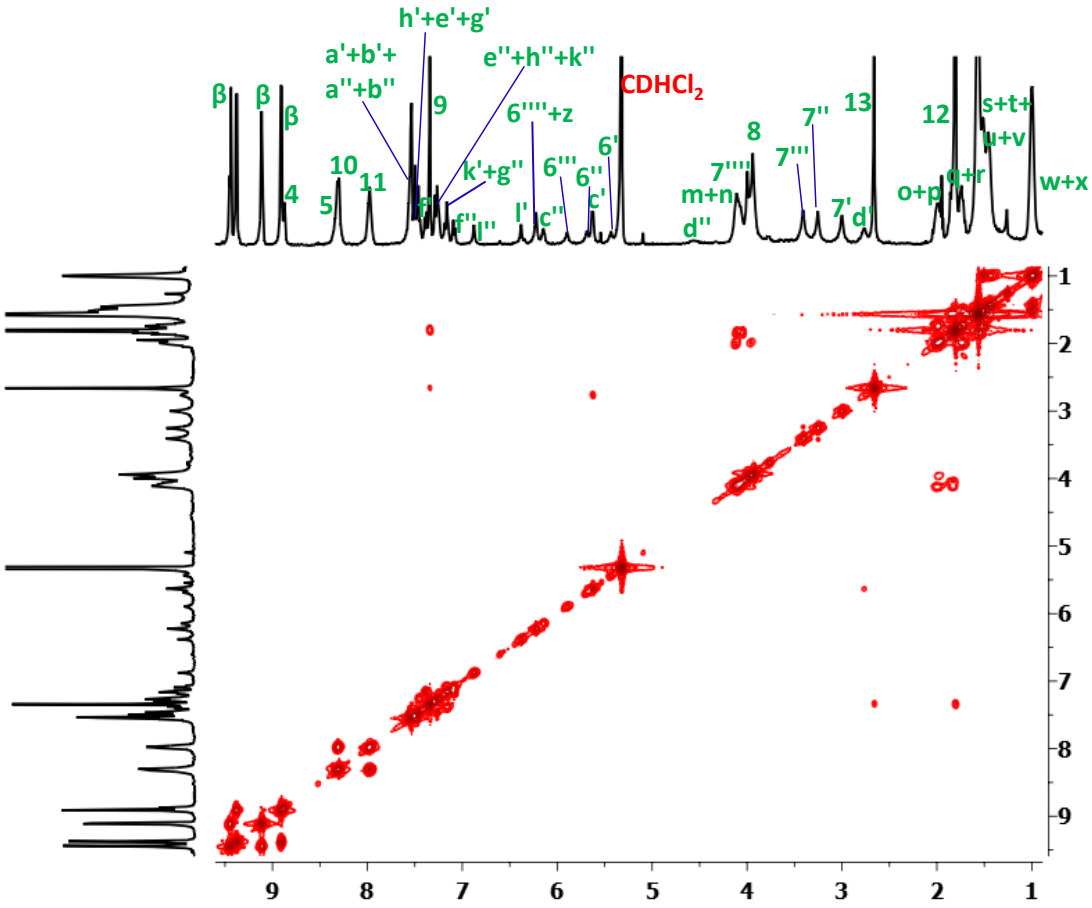


Figure S54. ^{1}H-^{1}H COSY NMR (500 MHz, 295 K) of **DS-2** in CD_2Cl_2:CD_3CN (60:1).

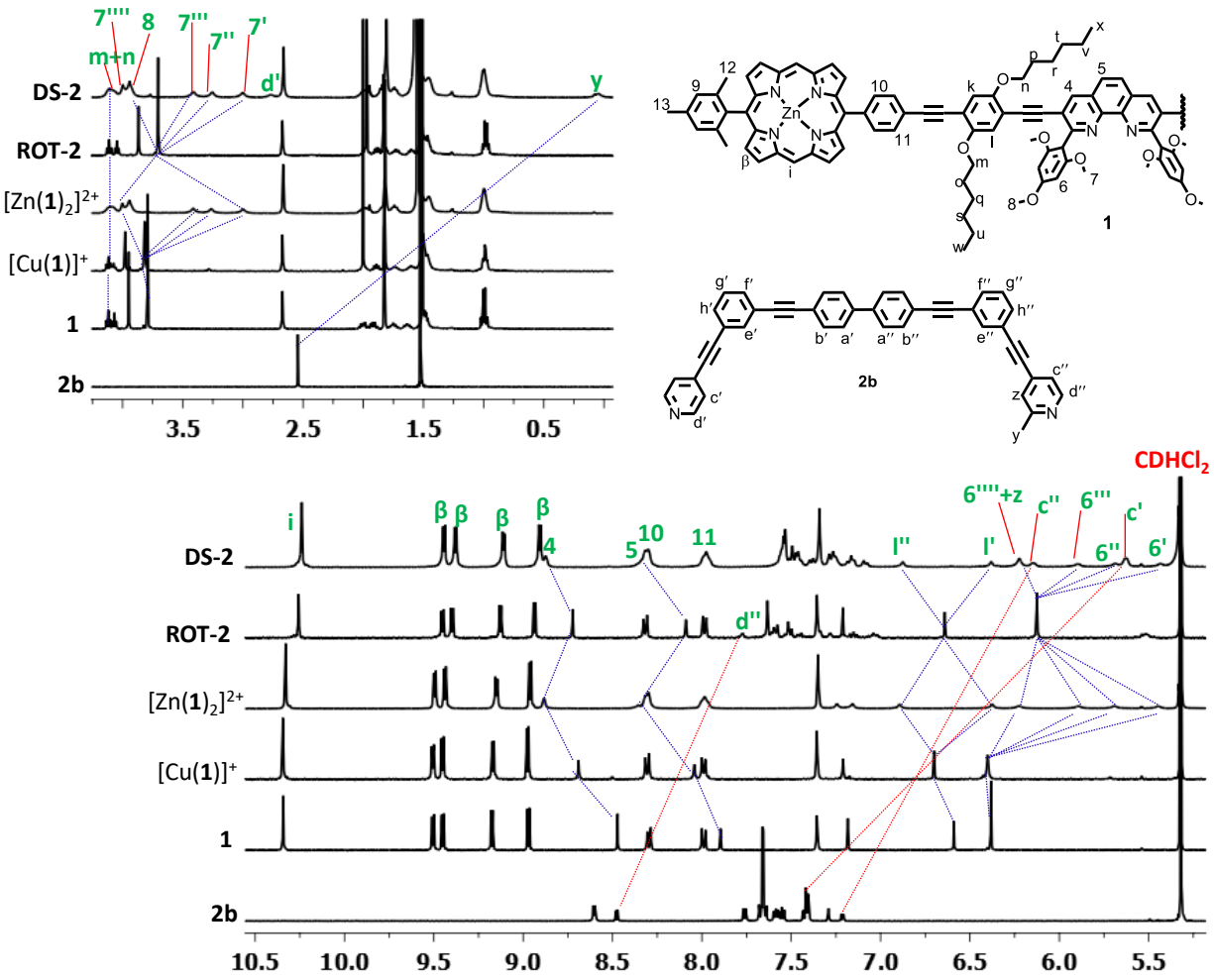


Figure S55. Comparison of ^{1}H NMR of ligand **2b**, **1**, complex [Cu(**1**)]$^{+}$, [Zn(**1**)$_2$]$^{2+}$, **ROT-2** and **DS-2** in CD_2Cl_2 (400 MHz, 295 K).

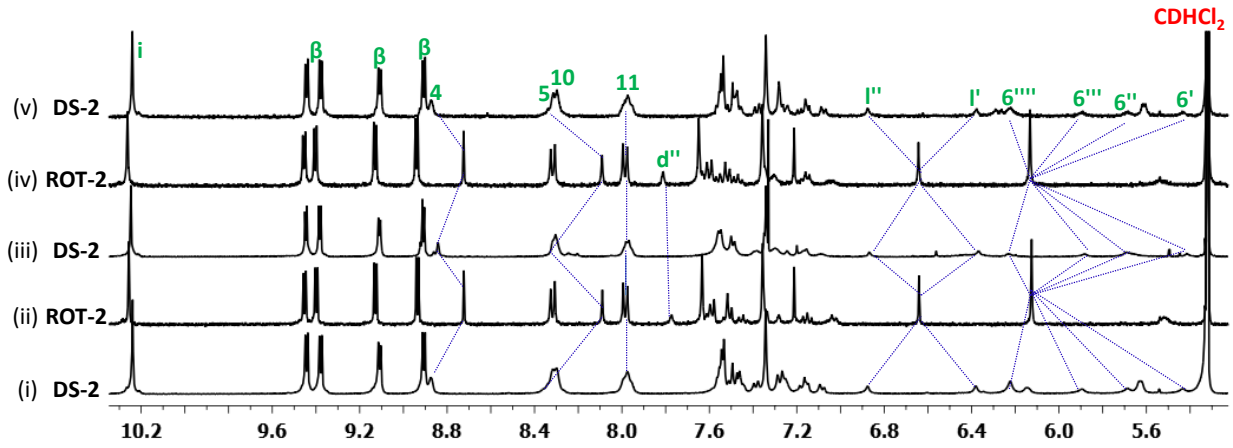


Figure S56. Partial ^{1}H NMR spectra (400 MHz, 295 K) show the reversible interconversion of **DS-2** and **ROT-2** over two full cycles in CD_2Cl_2. (i) **DS-2** was obtained by addition of **1**, Zn^{2+} and **2b** (1:0.5:1) in CD_2Cl_2. (ii) After addition of 0.5 equiv. of $[Cu_2(\text{hexacyclen})]^{2+}$ to **DS-1**. (iii) Addition of 0.5 equiv. of $[Zn(\text{cyclam})_2]^{2+}$ to **ROT-2**. (iv) Addition of 0.5 equiv. of $[Cu_2(\text{hexacyclen})]^{2+}$ to (iii) regenerated **ROT-2**. (v) **DS-2** was regenerated from (iv) by addition of 0.5 equiv. of $[Zn(\text{cyclam})_2]^{2+}$.

3. Variable temperature ^{1}H NMR spectra

The kinetics of rotational exchange at various temperatures was analyzed using the program WinDNMR through simulation of the experimental ^{1}H NMR spectra.[6] The spectra simulation was performed using the model of a 2-spin system undergoing mutual exchange and provided the rate constants. Activation parameters were determined from an Eyring plot.

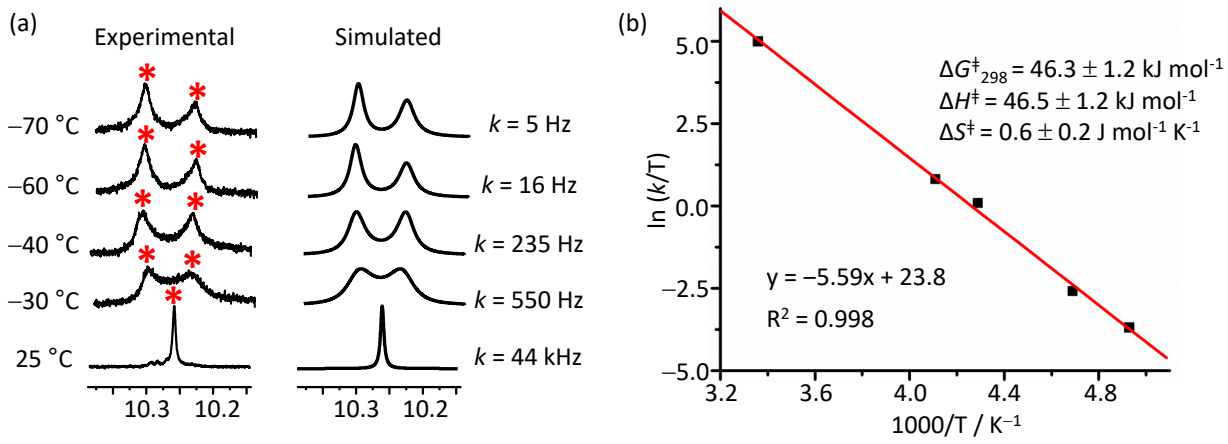


Figure S57. (a) VT ^{1}H NMR (600 MHz) of **ROT-1** in CD_2Cl_2 shows the splitting of proton signal i-H in 1:1 ratio at different temperatures. The corresponding rate constant at different temperatures was calculated from the simulation. (b) Eyring plot for exchange frequency in nanorotor **ROT-1**.

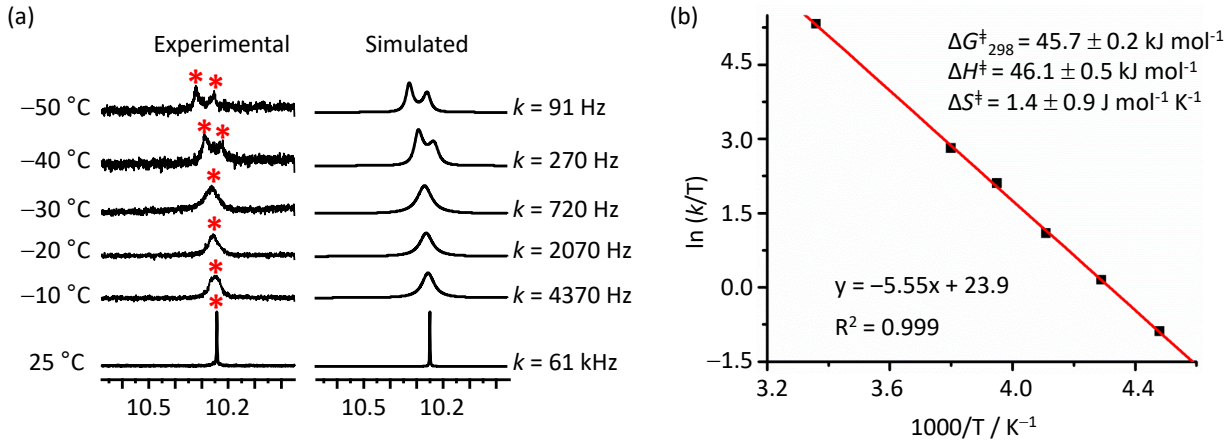


Figure S58. (a) VT ^{1}H NMR (600 MHz) of **ROT-2** in CD_2Cl_2 shows the splitting of proton signal i-H in 1:1 ratio at different temperatures. The corresponding rate constant at different temperatures was calculated from the simulation. (b) Eyring plot for exchange frequency in nanorotor **ROT-2**.

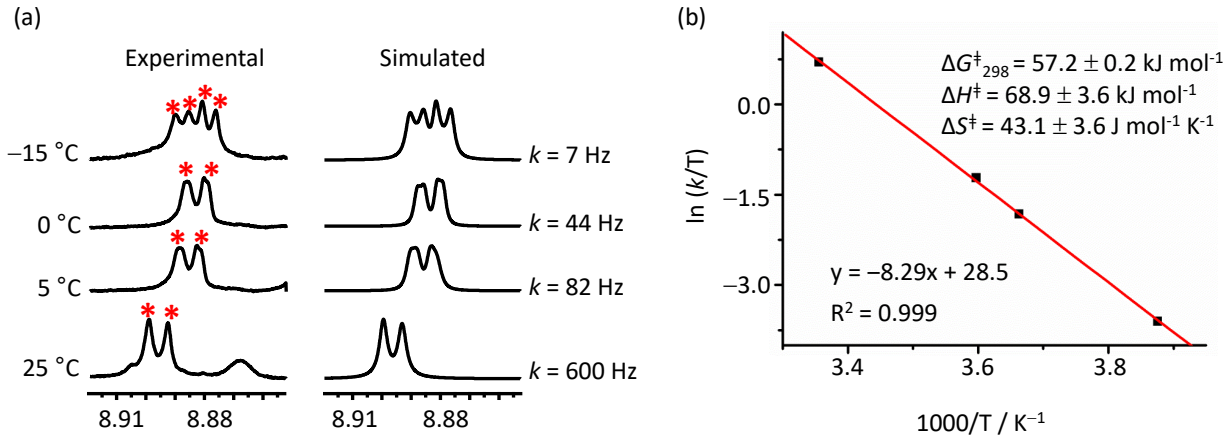


Figure S59. (a) VT ^{1}H NMR (600 MHz) of **DS-2** in CD_2Cl_2 shows the splitting of proton signals β-H in 1:1 ratio at different temperatures. The corresponding rate constant at different temperatures was calculated from the simulation. (b) Eyring plot for exchange frequency in **DS-2**.

4. DOSY NMR spectra

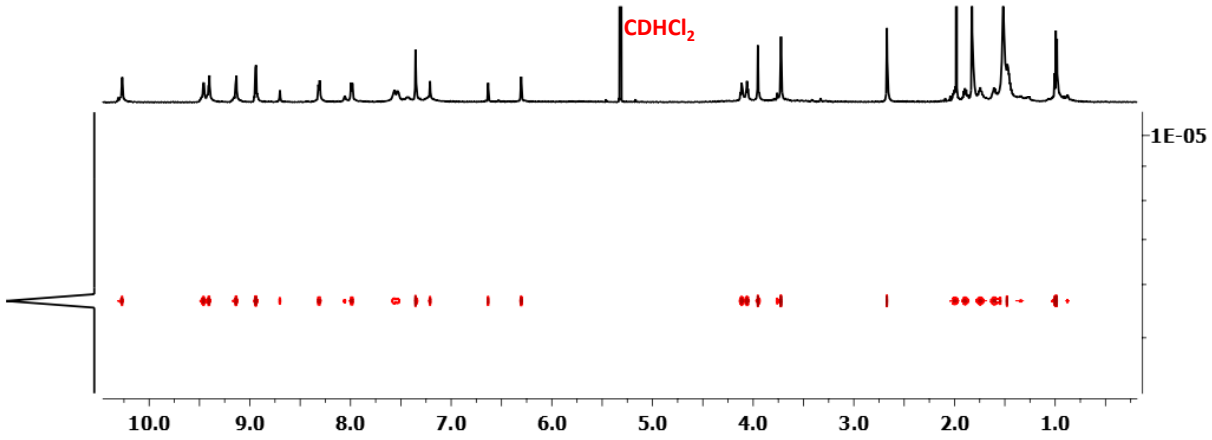


Figure S60. DOSY NMR of **ROT-1** in CD_2Cl_2 (600 MHz, 295 K) showing the single assembly in the solution.

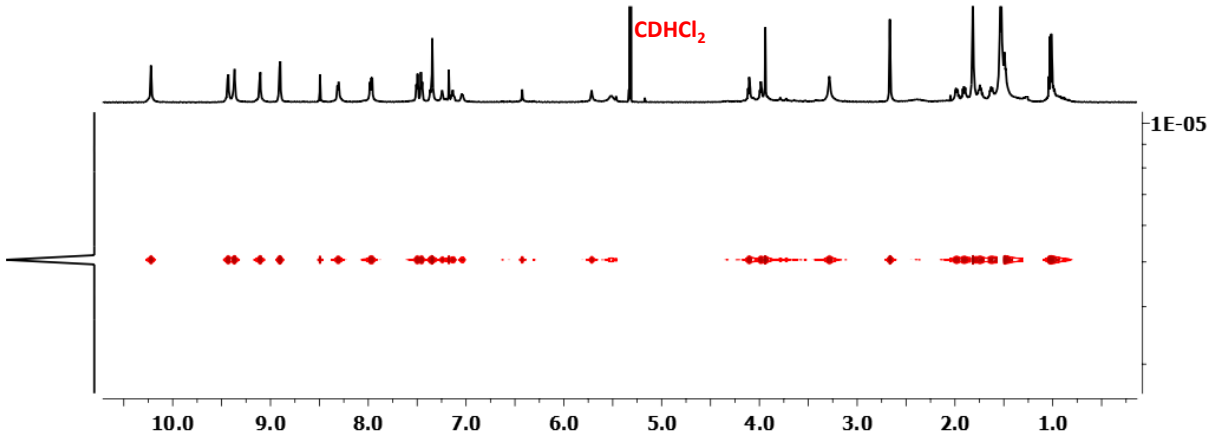


Figure S61. DOSY NMR of **DS-1** in CD_2Cl_2 (600 MHz, 295 K) showing the single assembly in the solution.

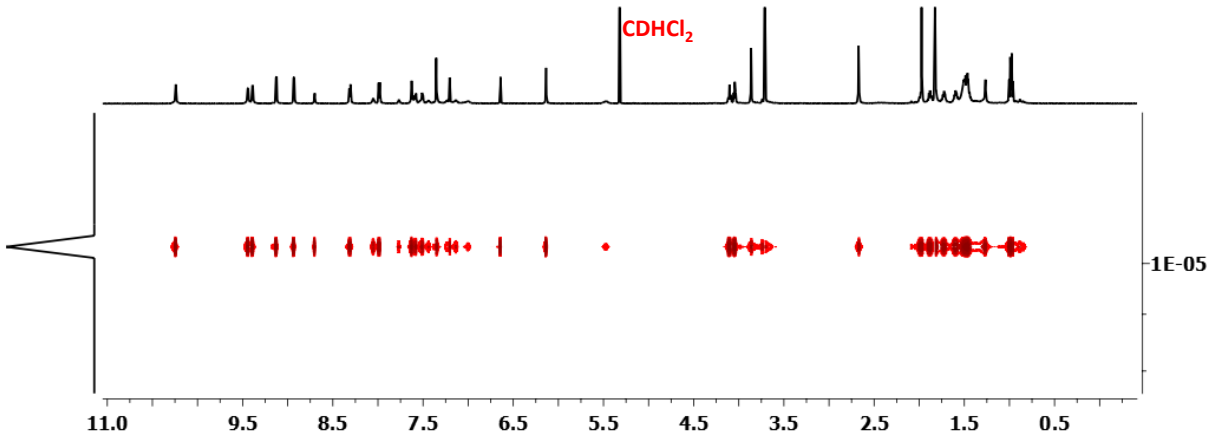


Figure S62. DOSY NMR of **ROT-2** in CD_2Cl_2 (600 MHz, 295 K) showing the single assembly in the solution.

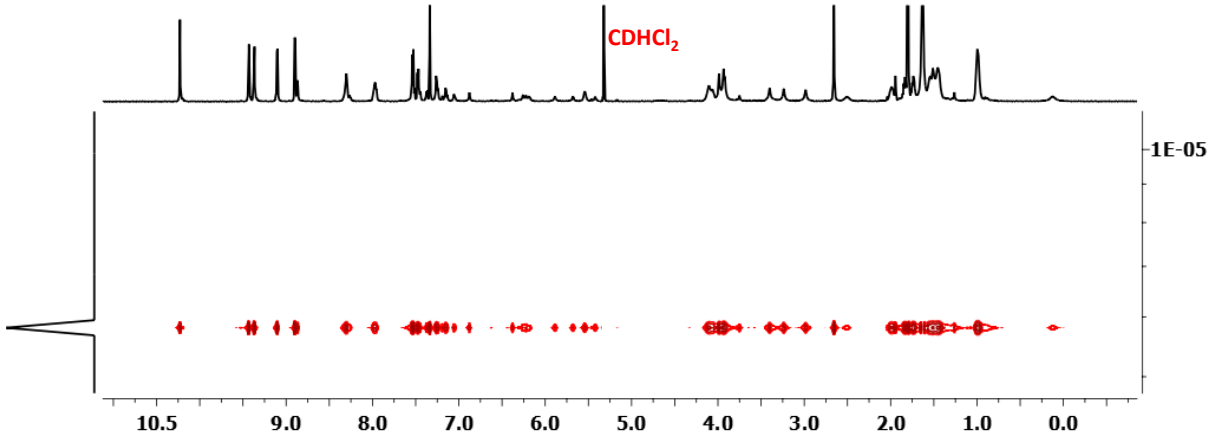


Figure S63. DOSY NMR of **DS-2** in CD_2Cl_2 (600 MHz, 295 K) showing the single assembly in the solution.

5. ESI-MS spectra

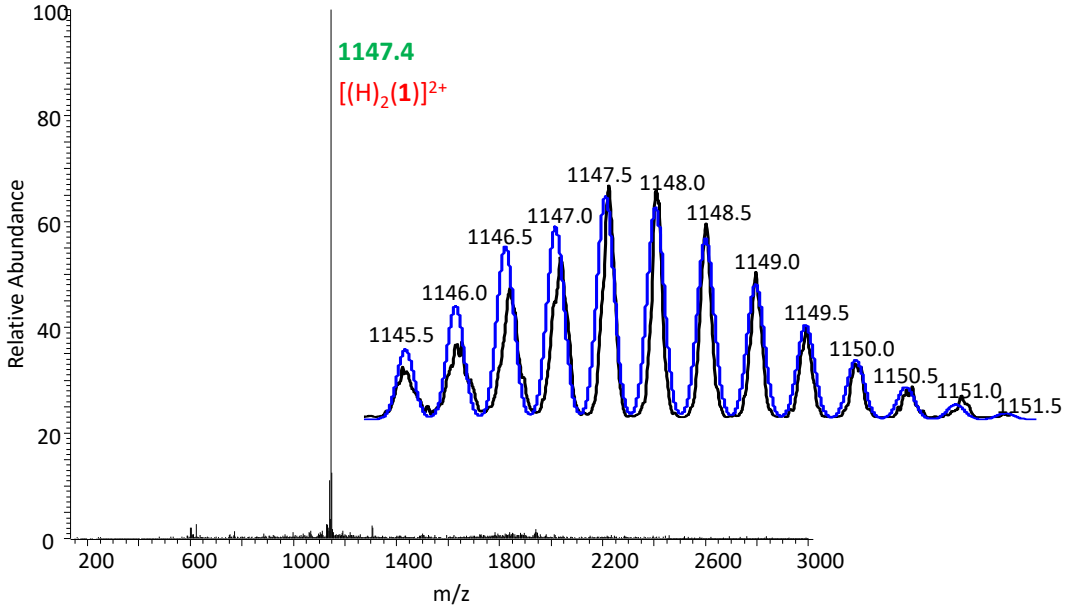


Figure S64. ESI-MS of $[(H)_2(\mathbf{1})]^{2+}$.

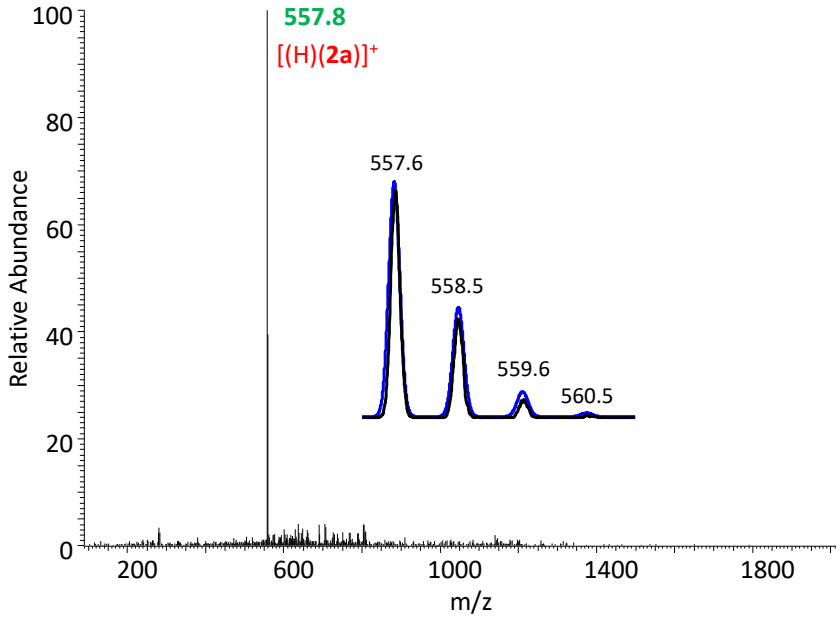


Figure S65. ESI-MS of $[(H)(\mathbf{2a})]^{+}$.

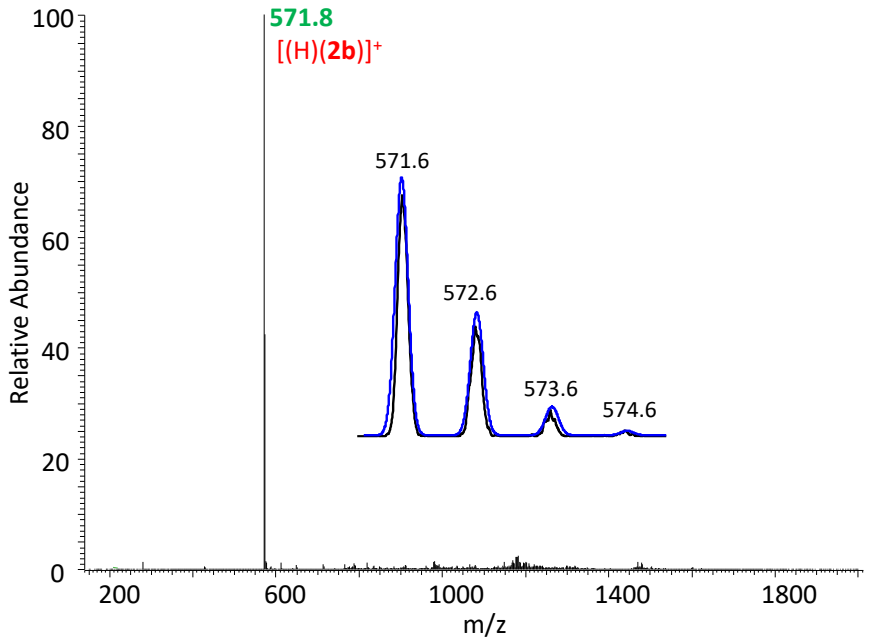


Figure S66. ESI-MS of $[(H)(\mathbf{2b})]^+$.

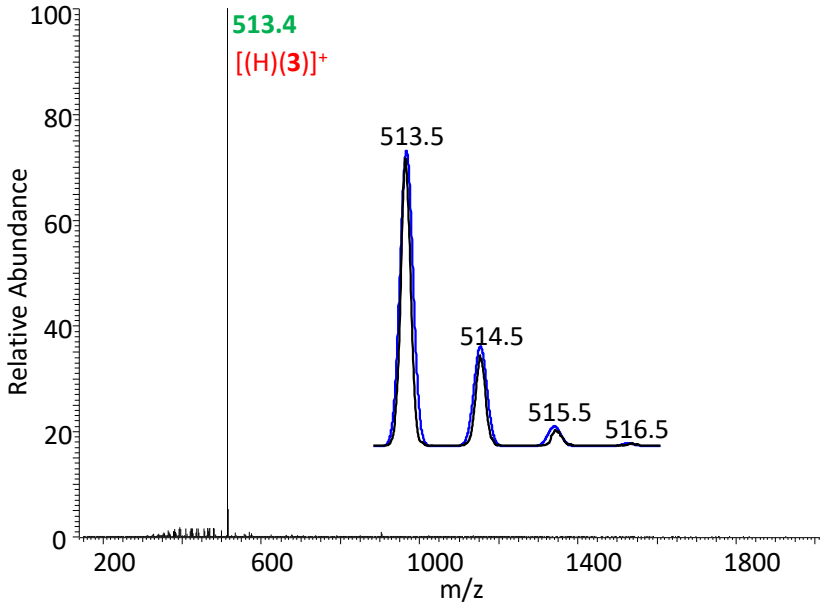


Figure S67. ESI-MS of $[(H)(\mathbf{3})]^+$.

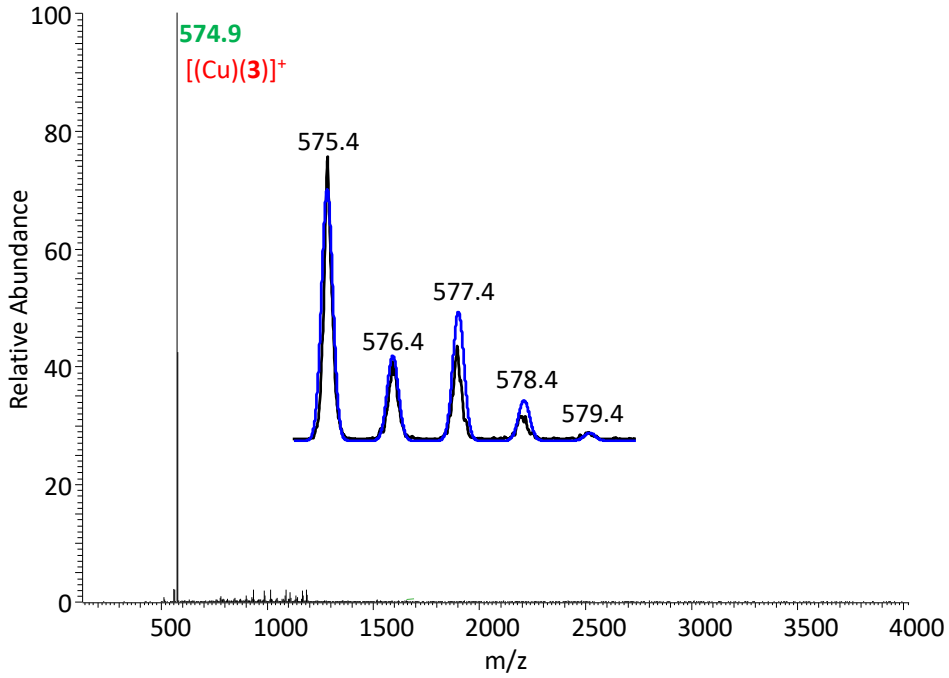


Figure S68. ESI-MS of $[(Cu)(\mathbf{3})]^+$.

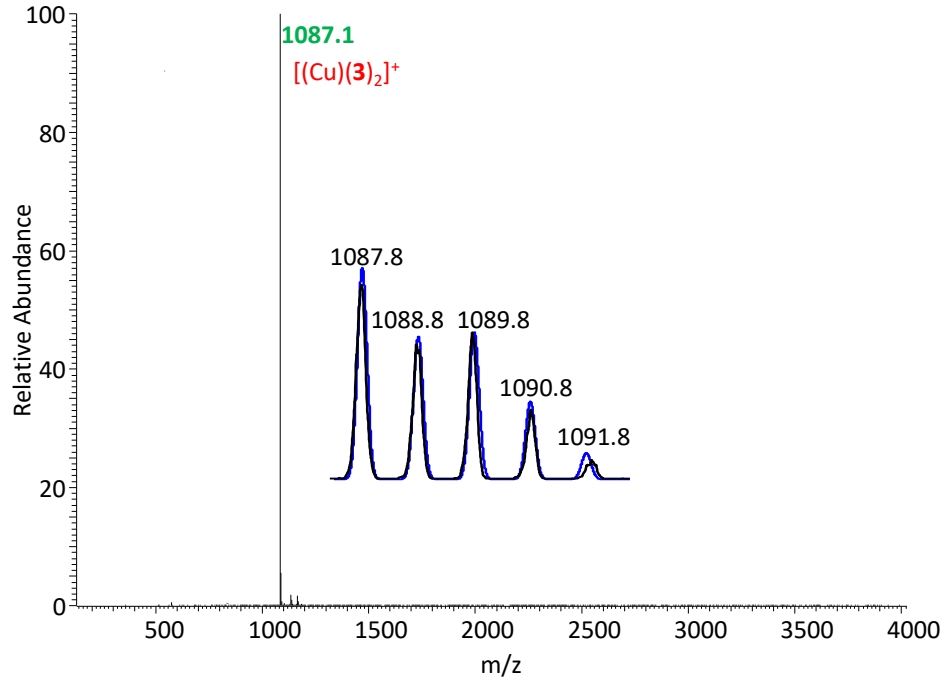


Figure S69. ESI-MS of $[(Cu)(\mathbf{3})_2]^+$.

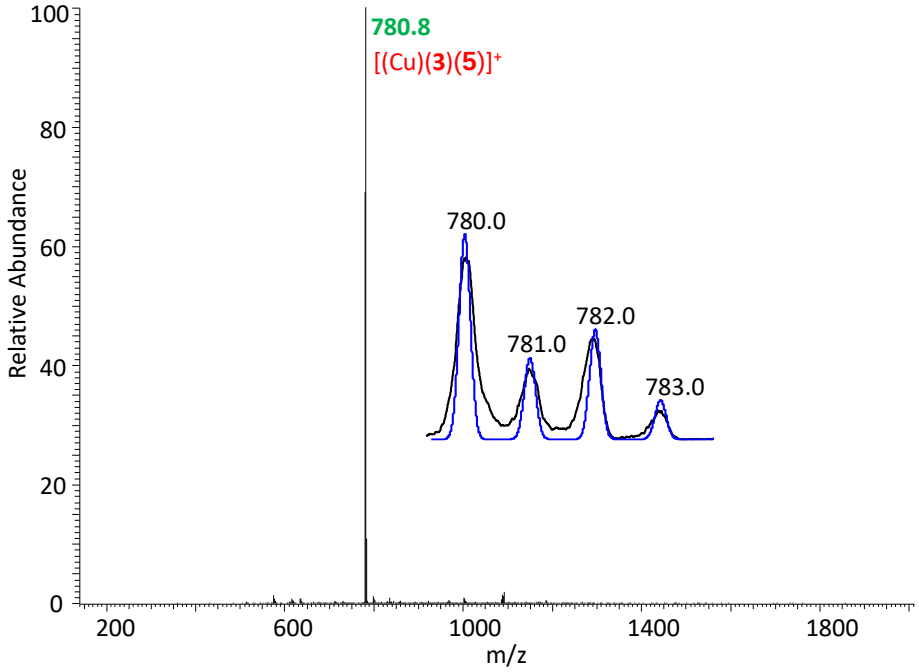


Figure S70. ESI-MS of $[(Cu)(\mathbf{3})(\mathbf{5})]^+$.

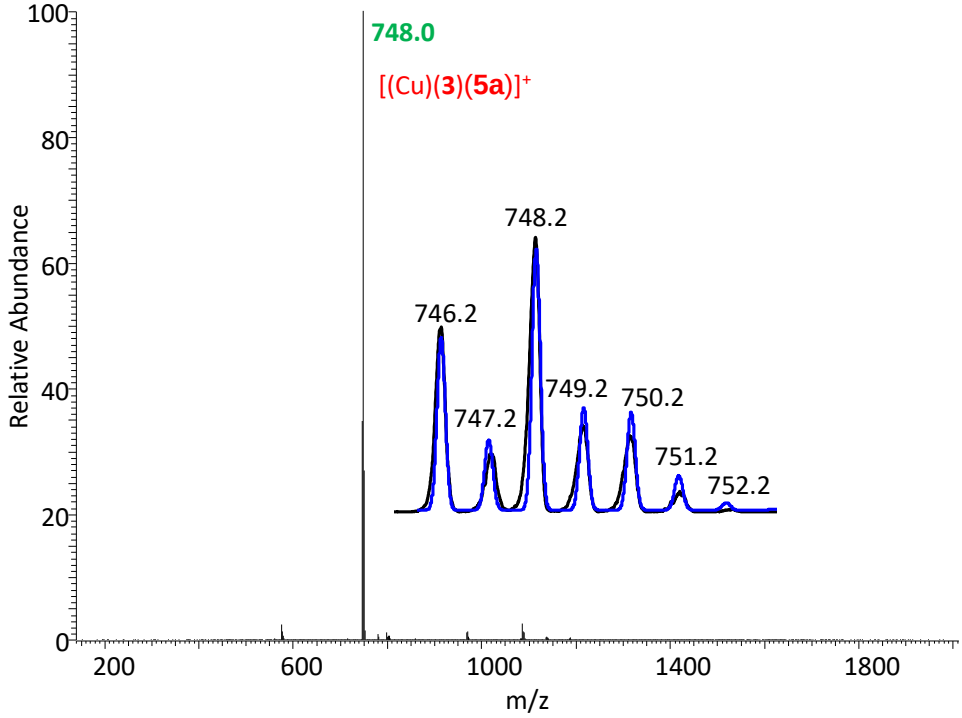


Figure S71. ESI-MS of $[(Cu)(\mathbf{3})(\mathbf{5a})]^+$.

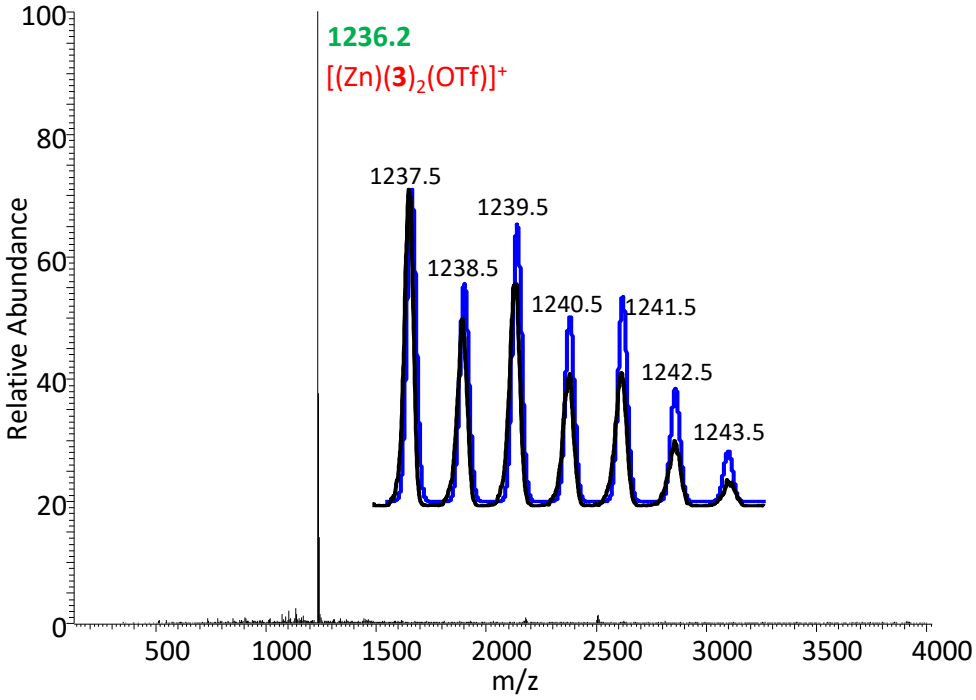


Figure S72. ESI-MS of $[(Zn)(\mathbf{3})_2(OTf)]^+$.

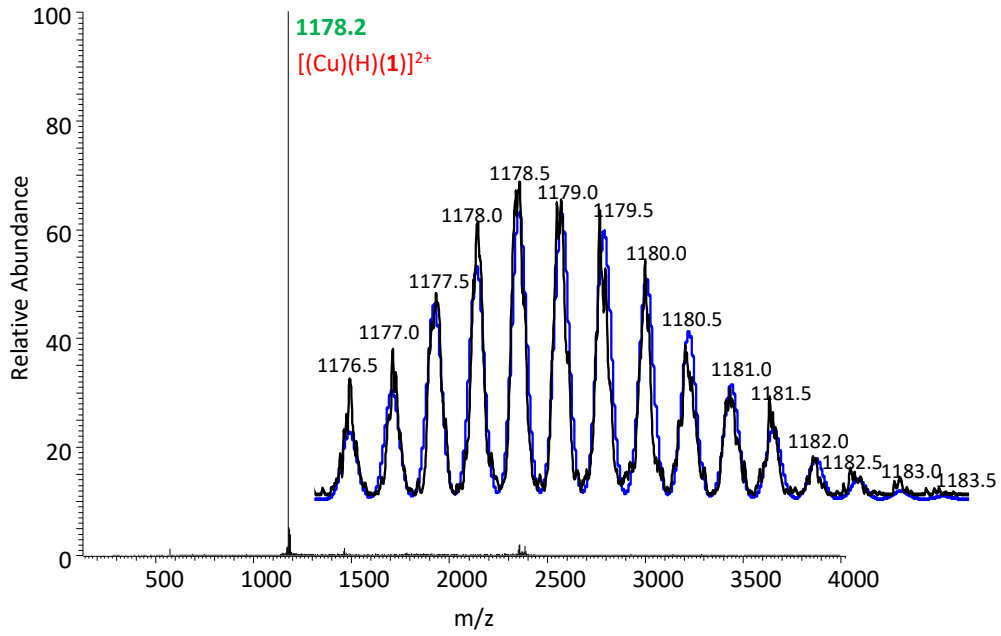


Figure S73. ESI-MS of $[(Cu)(H)(\mathbf{1})]^{2+}$.

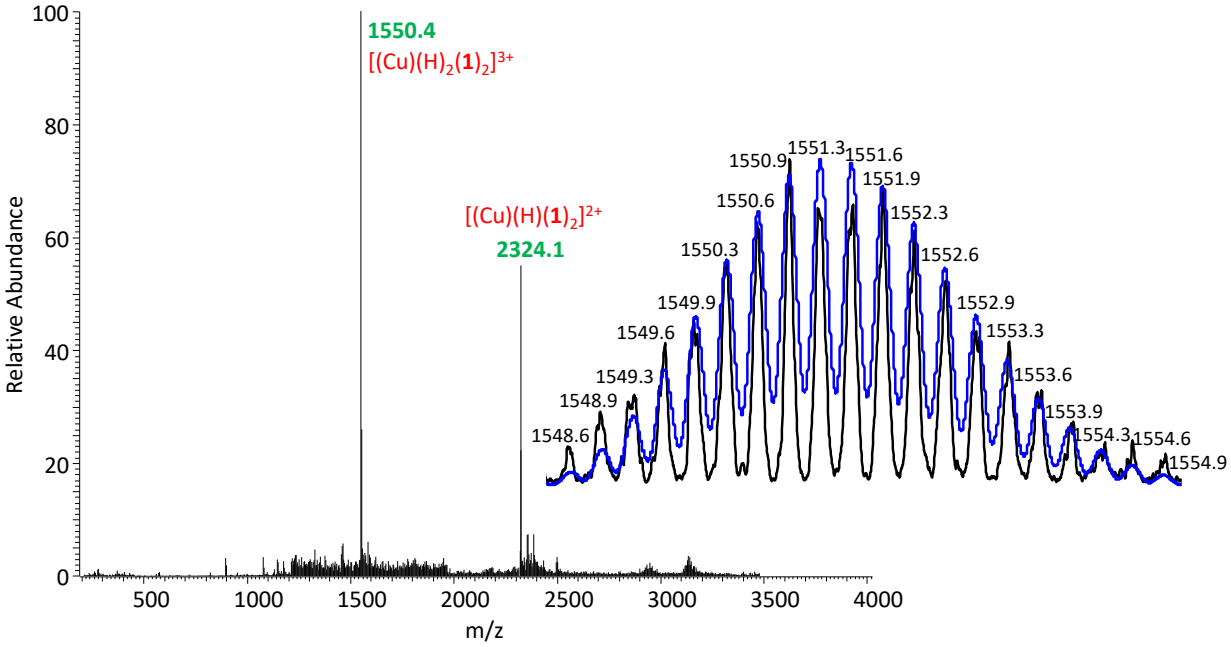


Figure S74. ESI-MS of $[(Cu)(H)(\mathbf{1})_2]^{2+}$.

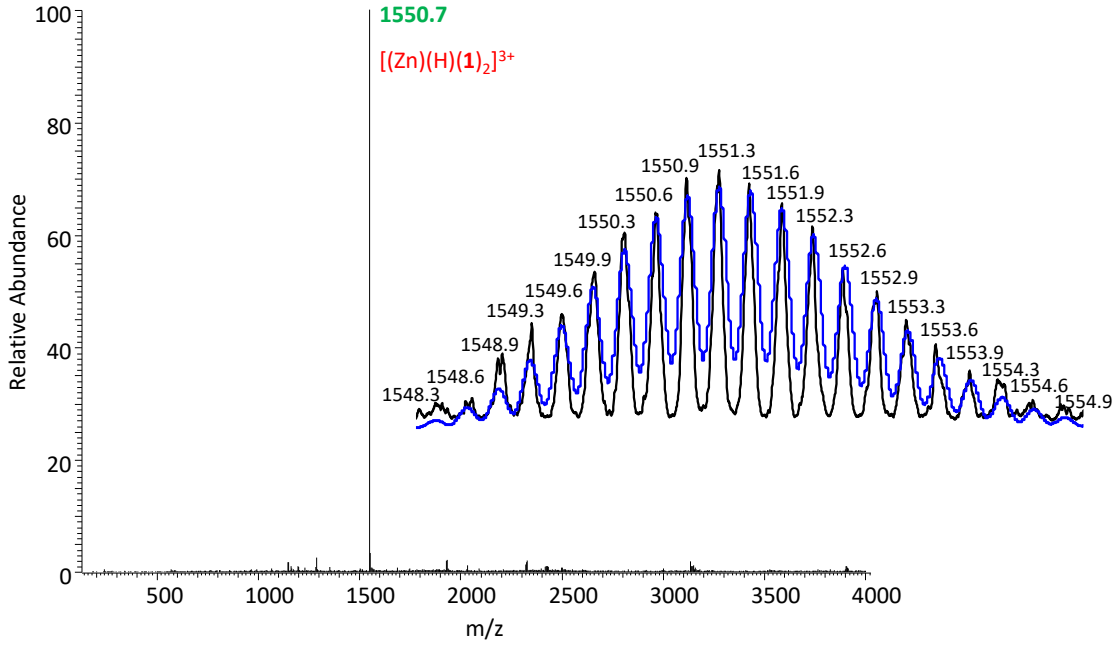


Figure S75. ESI-MS of $[(Zn)(H)(\mathbf{1})_2]^{3+}$.

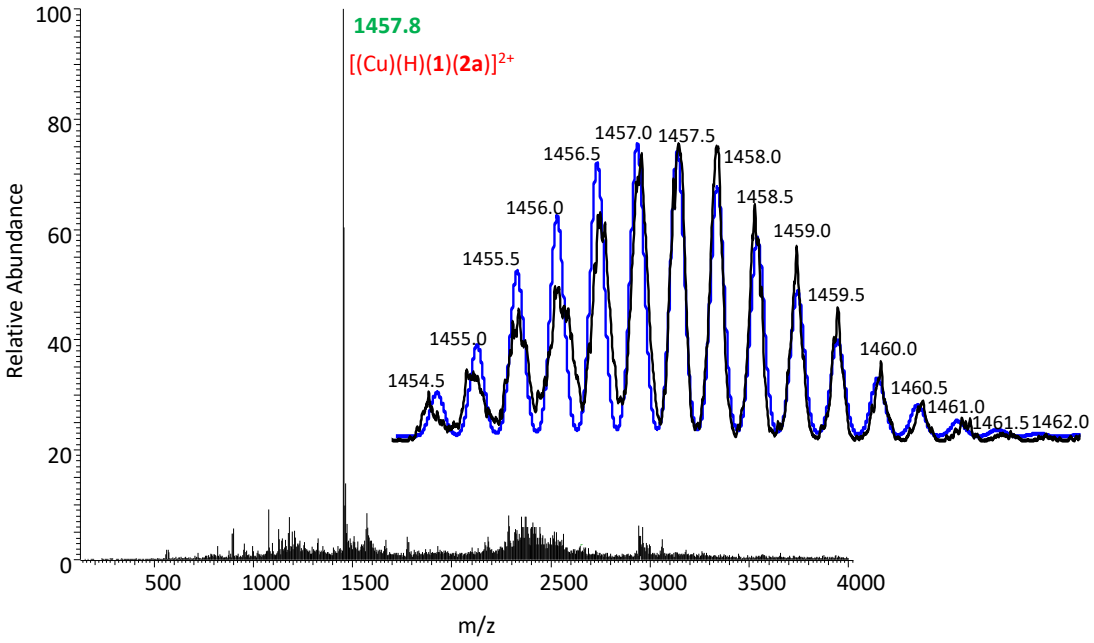


Figure S76. ESI-MS of $[(Cu)(H)(\mathbf{1})(\mathbf{2a})]^{2+}$.

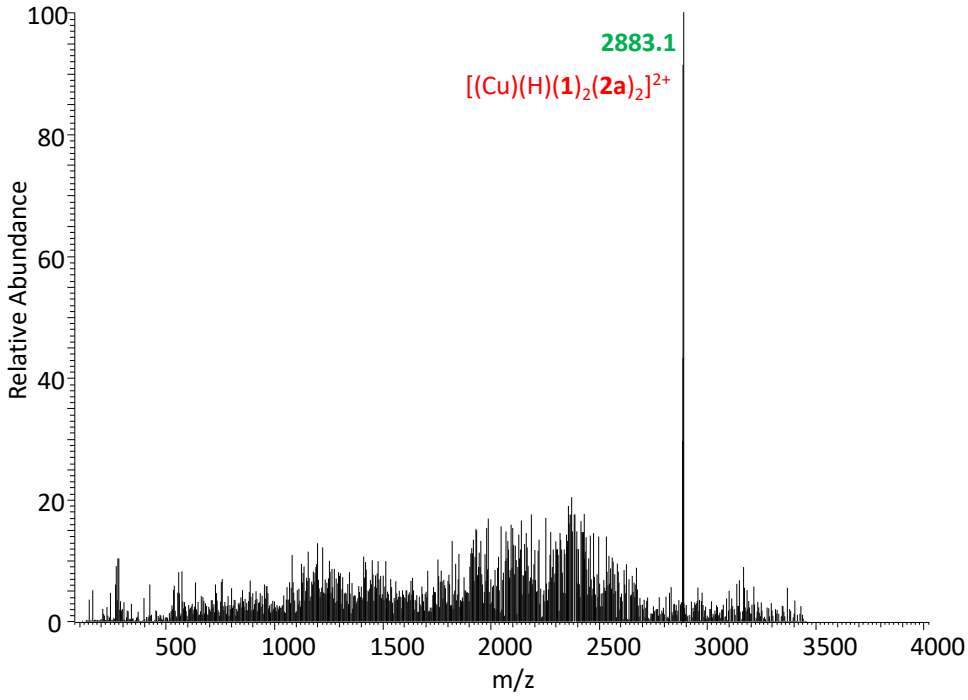


Figure S77. ESI-MS of $[(Cu)(H)(\mathbf{1})_2(\mathbf{2a})_2]^{2+}$.

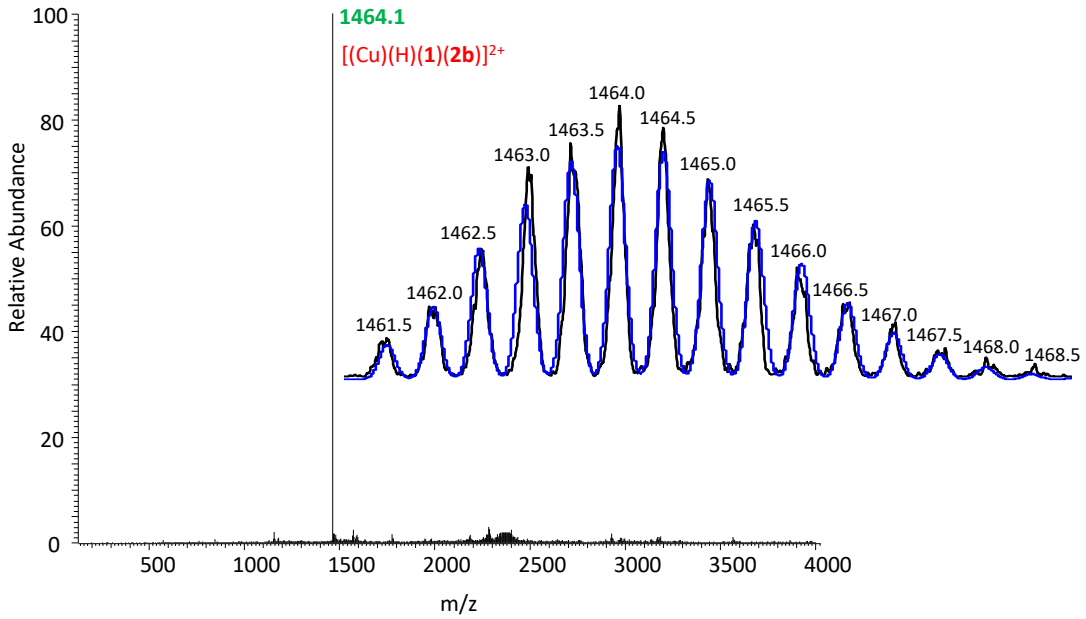


Figure S78. ESI-MS of $[(Cu)(H)(\mathbf{1})(\mathbf{2b})]^{2+}$.

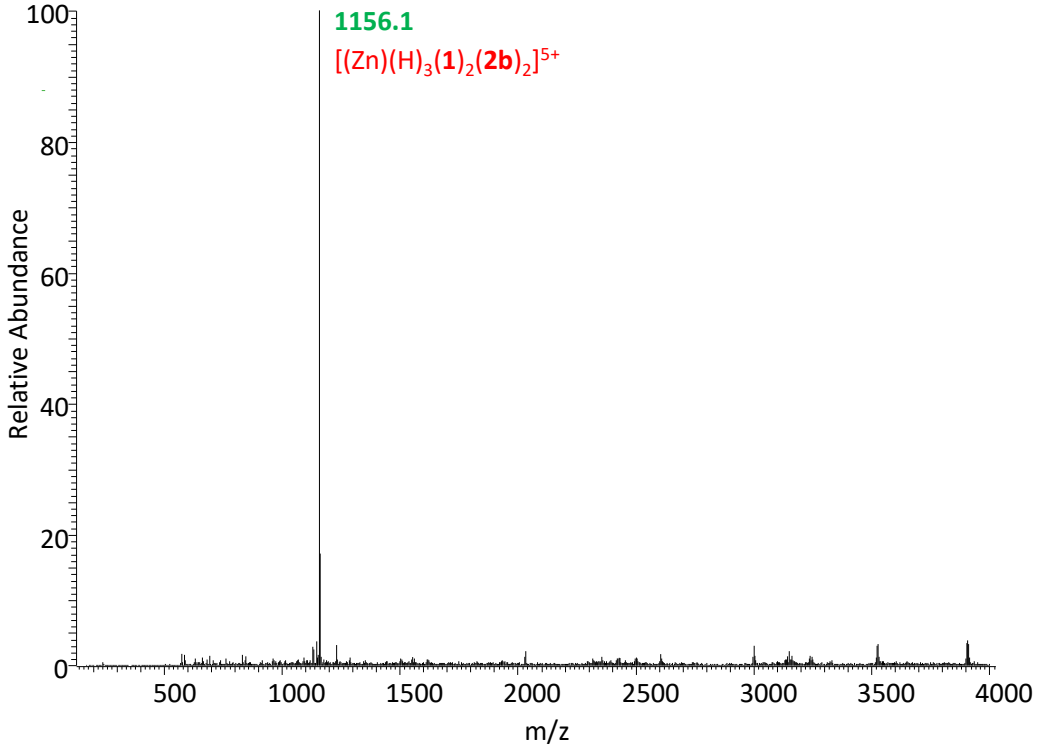


Figure S79. ESI-MS of $[(Zn)(H)_3(\mathbf{1})_2(\mathbf{2b})_2]^{5+}$.

6. UV-vis spectra

Measurement of binding constant. The UV-vis titration technique was used to measure binding constants of the complexes. The full data set of a selected wavelength region was analyzed using SPECFIT/32 global analysis system (Spectrum Software Associates, Marlborough, MA).

(a) Result: log *K* of $[Cu(\mathbf{3})]^+$ = 6.16 ± 0.08.

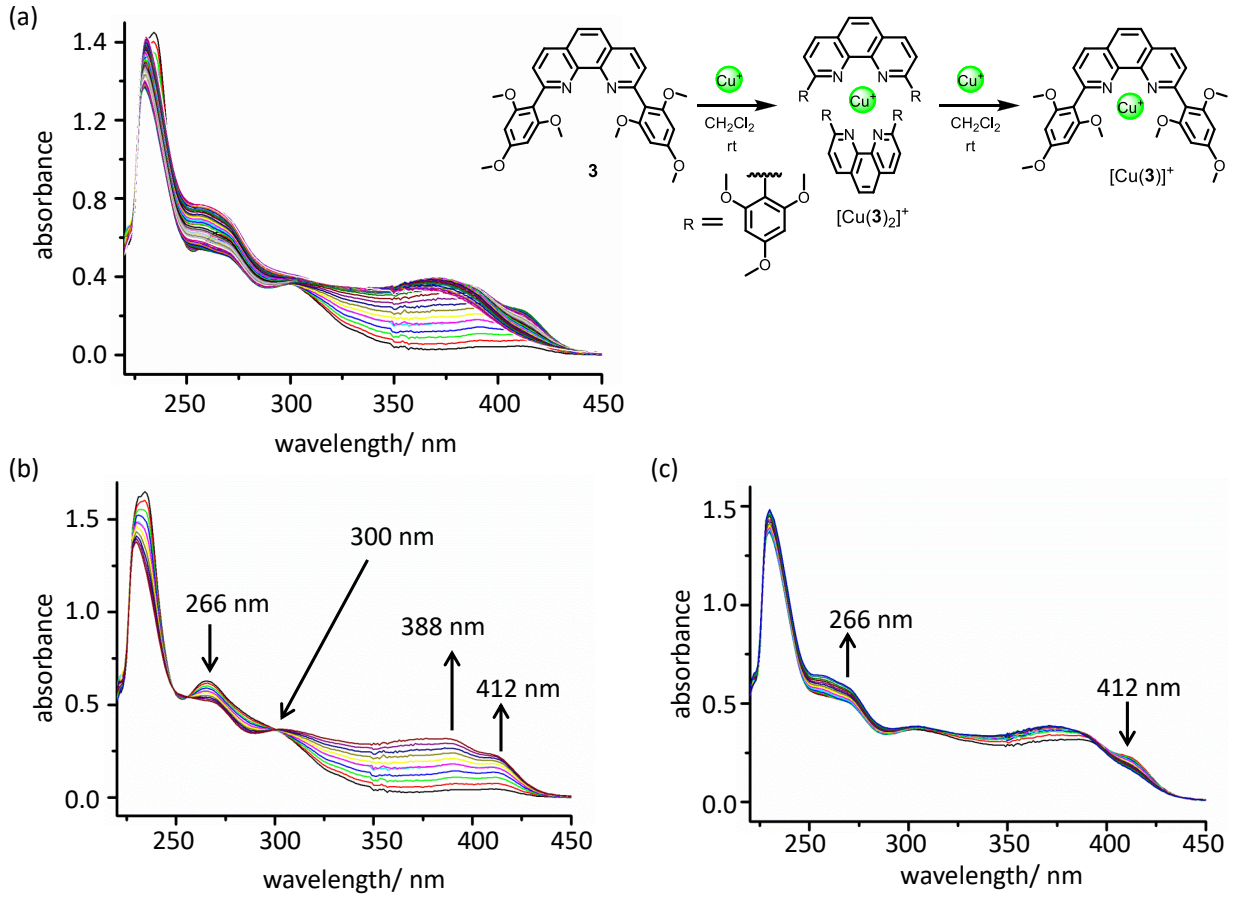


Figure S80. (a) UV-vis spectra of **3** (2.2 × 10^{-5} M) in CH_2Cl_2 (2 mL) upon addition of $[Cu(CH_3CN)_4]PF_6$ (4.3 ×10^{-4} M) at 298 K to afford the complex $[Cu(\mathbf{3})]^+$. The wavelength region 250-450 nm was analyzed. Result: log *K* of $[Cu(\mathbf{3})]^+$ = 6.16 ± 0.08. At first the broad peak (350 to 425 nm) appeared due to the MLCT transition of the homoleptic complex $[Cu(\mathbf{3})_2]^+$. After addition of more Cu^+ the MLCT band vanished due to the breaking up of $[Cu(\mathbf{3})_2]^+$. The peak at 266 nm appeared due to formation of $[Cu(\mathbf{3})]^+$. (b) UV-vis spectra of **3** (2.2 × 10^{-5} M) in CH_2Cl_2 (2 mL) upon addition of $[Cu(CH_3CN)_4]PF_6$ (4.3 ×10^{-4} M) at 298 K up to the formation of complex $[Cu(\mathbf{3})_2]^+$. (c) UV-vis spectra of **3** (2.2 × 10^{-5} M) in CH_2Cl_2 (2 mL) upon addition of $[Cu(CH_3CN)_4]PF_6$ (4.3 ×10^{-4} M) at 298 K after the formation of complex $[Cu(\mathbf{3})_2]^+$.

(b) Result : log K (**3** + [Cu(**3**)]$^{+}$) = 4.57 ± 0.88

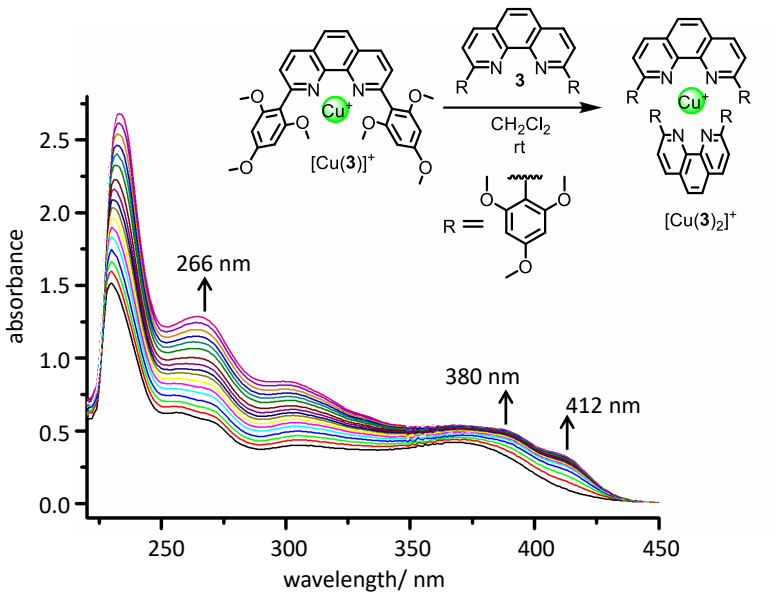


Figure S81. UV-vis spectra of [Cu(**3**)]$^{+}$ (2.4 × 10^{-5} M) in CH_2Cl_2 (2 mL) upon addition of **3** (4.7 ×10^{-4} M) at 298 K to afford complex [Cu(**3**)$_2$]$^{+}$. The wavelength region 250-450 nm was analyzed. The binding constant of **3** + [Cu(**3**)]$^{+}$ turned out to be log K = 4.57 ± 0.88. The broad peak from 350 nm to 425 nm appeared due to the MLCT transition of the homoleptic complex [Cu(**3**)$_2$]$^{+}$.

(c) Result : log *K* (**5** + [Cu(**3**)]$^+$) = 4.48 ± 0.55

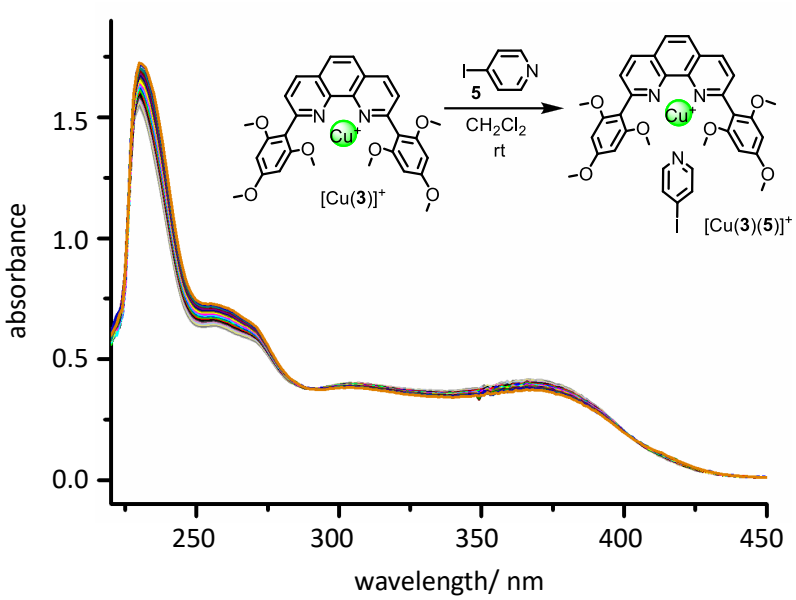


Figure S82. UV-vis spectra of [Cu(**3**)]$^+$ (2.4 × 10^{-5} M) in CH_2Cl_2 (2 mL) upon addition of **5** (4.7 ×10^{-4} M) at 298 K to afford complex [Cu(**3**)(**5**)]$^+$. The wavelength region 250-450 nm was analyzed. The binding constant of **5** + [Cu(**3**)]$^+$ turned out to be log *K* = 4.48 ± 0.55.

(d) Result : log *K* (**5a** + [Cu(**3**)]$^+$) = 5.86 ± 0.68

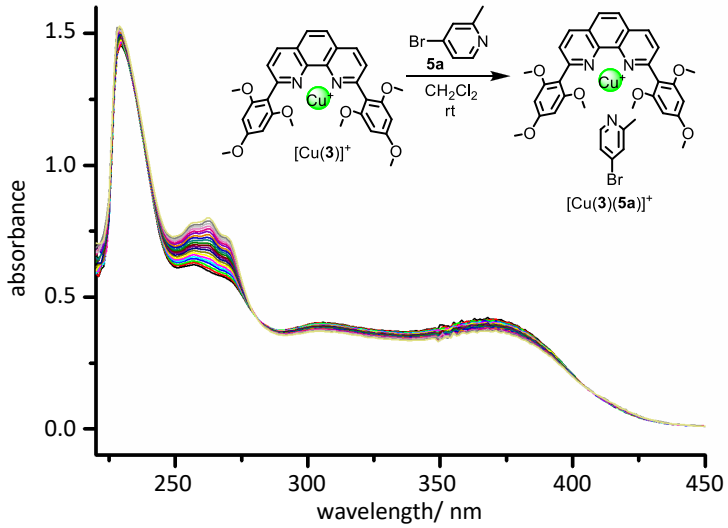


Figure S83. UV-vis spectra of [Cu(**3**)]$^+$ (2.4 × 10^{-5} M) in CH_2Cl_2 (2 mL) upon addition of **5a** (4.7 ×10^{-4} M) at 298 K to afford the complex [Cu(**3**)(**5a**)]$^+$. The wavelength region 250-450 nm was analyzed. The binding constant of **5a** + [Cu(**3**)]$^+$ turned out to be log *K* = 5.86 ± 0.68.

(e) Result : log K (**4** + **6**) = 4.90 ± 0.20

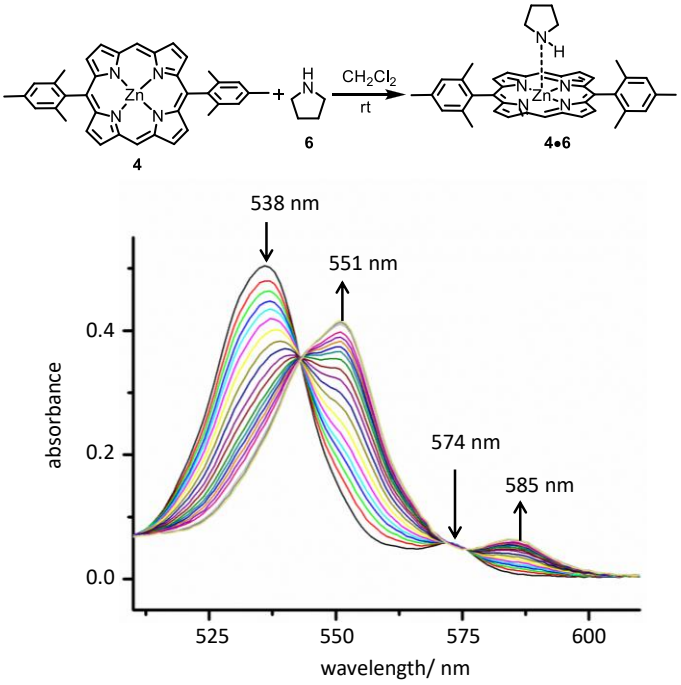


Figure S84. UV-vis spectra of **4** (2.7×10^{-5} M) in CH_2Cl_2 (2 mL) upon addition of **6** (5.5×10^{-4} M) at 298 K to afford the complex **4•6**. The wavelength region 500-600 nm was analyzed. The binding constant turned out to be log K = 4.90 ± 0.20.

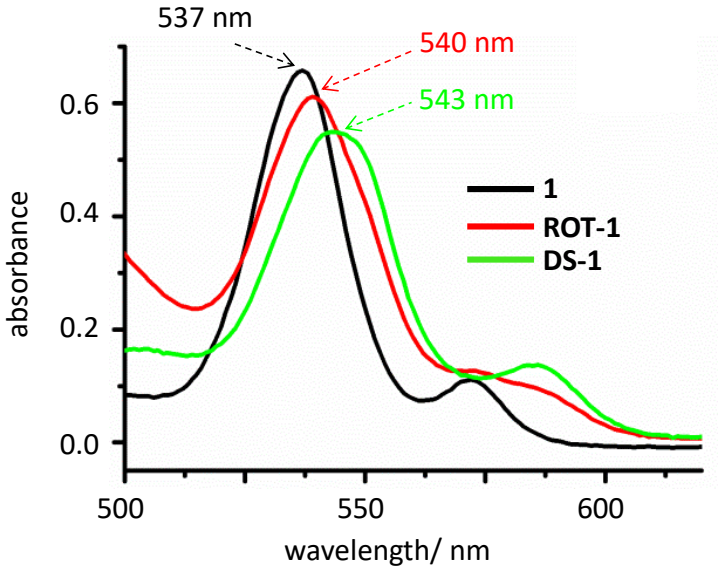


Figure S85. UV-vis spectra of **1**, **ROT-1** and **DS-1** in CH_2Cl_2 ($c = 10^{-5}$ M) at 298 K.

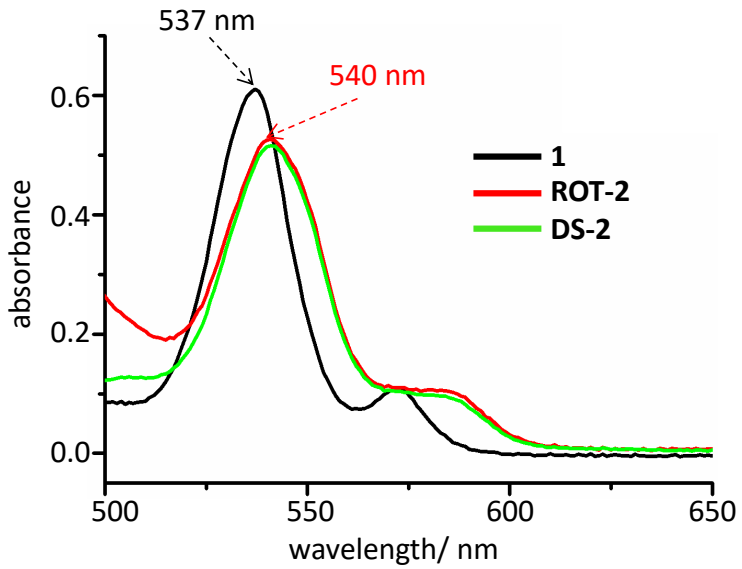


Figure S86. UV-vis spectra of **1**, **ROT-2** and **DS-2** in CH_2Cl_2 ($c = 10^{-5}$ M) at 298 K.

7. Kinetic studies and fluorescence spectra

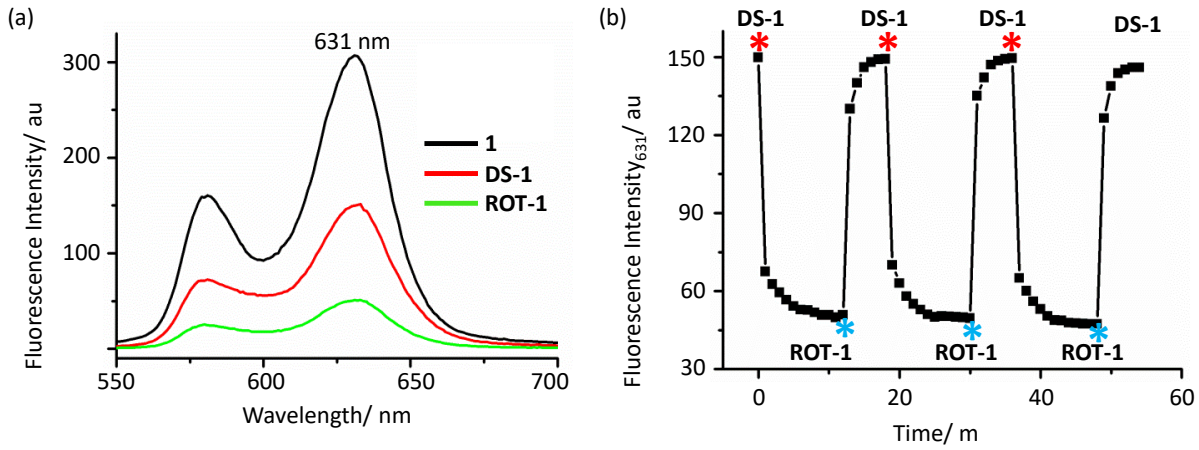


Figure S87. (a) Fluorescence spectra of **1**, **ROT-1**, **DS-1** in CH_2Cl_2 at 298 K (λ_{exc} = 540 nm, c = 10^{-5} M). (b) Fluorescence intensity changes at 631 nm vs. time over three cycles for interconversion between **DS-1→ROT-1** in CH_2Cl_2 at 298 K (λ_{exc} = 540 nm, c =10^{-5} M). Cu^{+} and cyclam addition is indicated by red and indigo asterisk, respectively. Transformation of **DS-1** → **ROT-1** took 12 min whereas **ROT-1** → **DS-1** took 6 min.

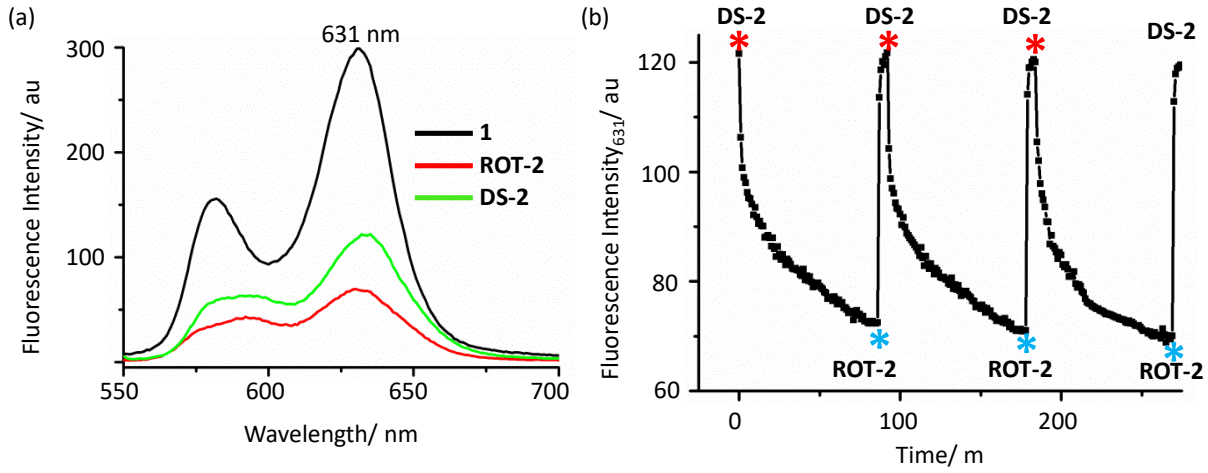


Figure S88. (a) Fluorescence spectra of **2**, **ROT-2**, **DS-2** in CH_2Cl_2 at 298 K (λ_{exc} = 540 nm, c = 10^{-5} M). (b) Fluorescence intensity changes at 631 nm vs. time over three cycles for interconversion between **DS-2→ROT-2** in CH_2Cl_2 at 298 K (λ_{exc} = 540 nm, c =10^{-5} M). $[Cu_2(hexacyclen)]^{2+}$ and $[Zn(cyclam)_2]^{2+}$ addition is indicated by red and blue asterisk, respectively. Transformation of **DS-2** → **ROT-2** took 85 min whereas **ROT-2** → **DS-2** took 6 min.

8. Catalytic experiments

General procedure

All catalytic reactions were performed in CD_2Cl_2:$CDCl_3$ (20:1) in an NMR tube. The mixture was heated at 50 °C for 4 h in a thermostat. Solids were transferred first, followed by addition of the solvent. Product yields were determined by using 1,3,5-trimethoxybenzene as an internal standard (6.07 ppm). All the catalytic reactions were performed three times and the errors of the yield are mentioned.

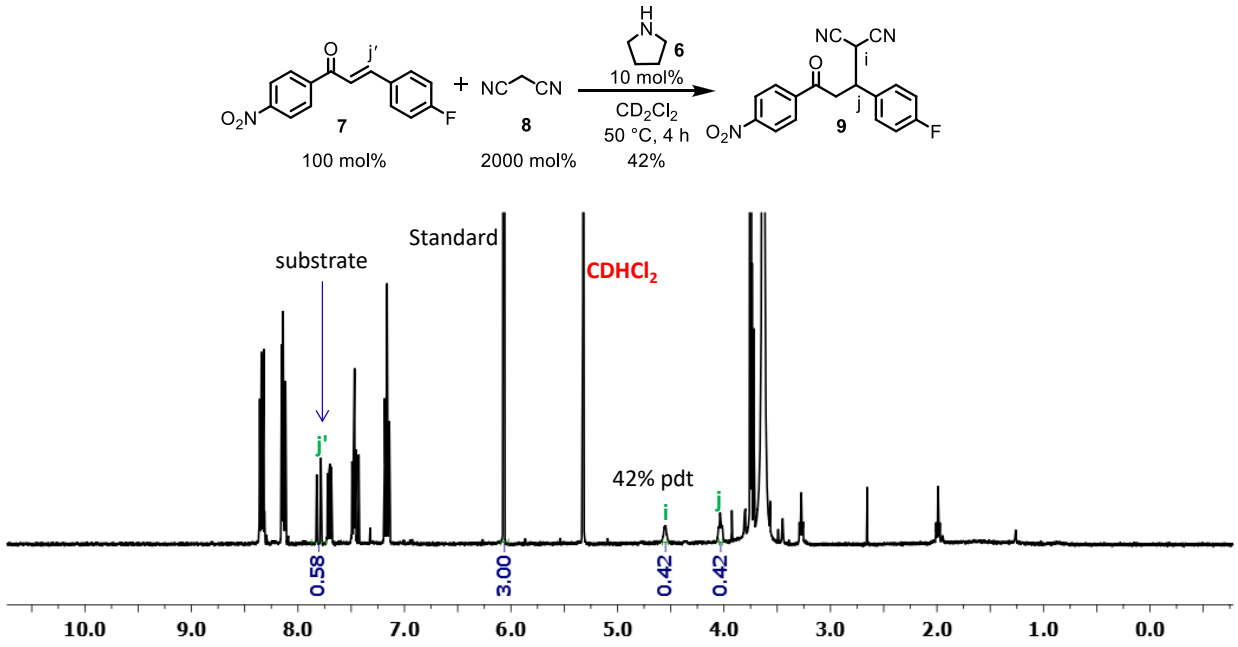


Figure S89. ^{1}H NMR (400 MHz, CD_2Cl_2:$CDCl_3$ (20:1), 295 K) spectrum obtained after heating the mixture of **6**, **7** (≈ 8.71 mM), **8**, and 1,3,5-trimethoxybenzene (1:10:200:10) at 50 °C for 4 h. Product **9** was formed in 42% yield according to ^{1}H NMR analysis.

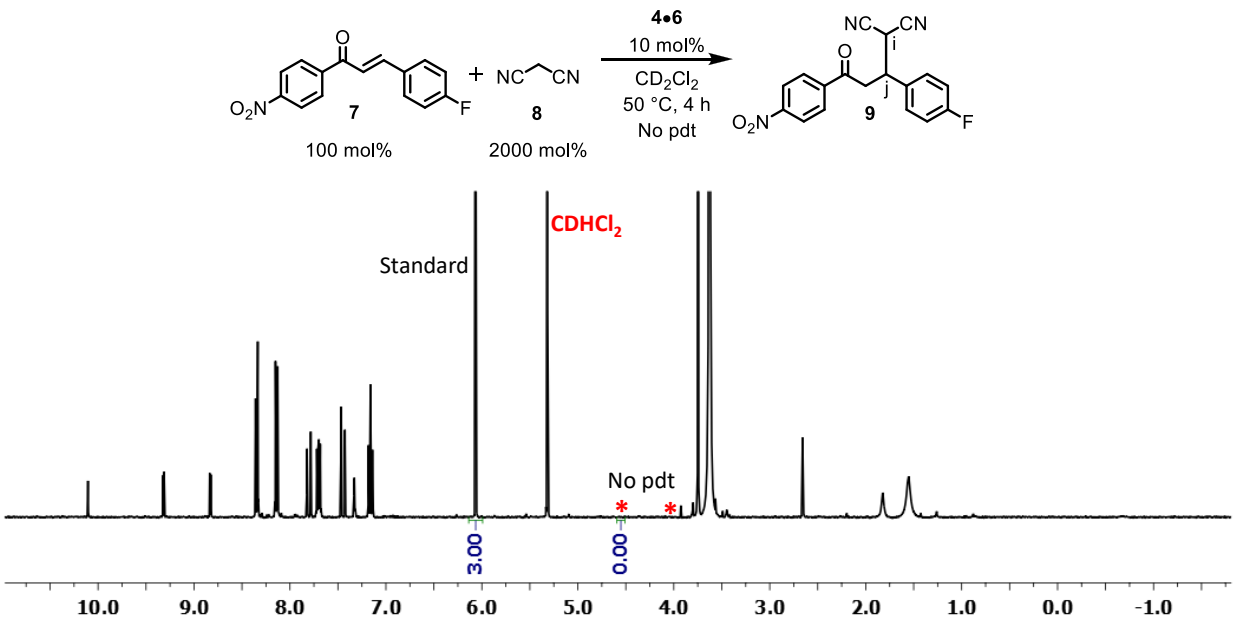


Figure S90. ^{1}H NMR (400 MHz, CD_2Cl_2:$CDCl_3$ (20:1), 295 K) spectrum obtained after heating the mixture of zinc(II) porphyrin **4**, **6**, **7** (≈ 8.71 mM), **8**, and 1,3,5-trimethoxybenzene (1:1:10:200:10) at 50 °C for 4 h. No product **9** was observed according to ^{1}H NMR analysis.

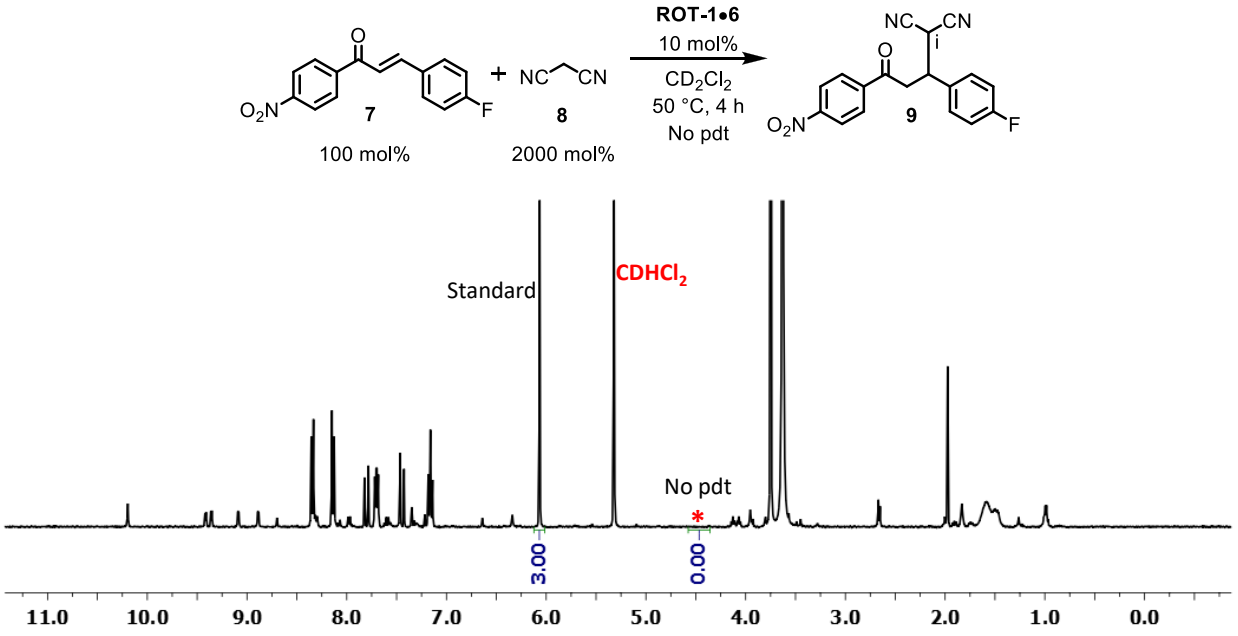


Figure S91. ^{1}H NMR (400 MHz, CD_2Cl_2:$CDCl_3$ (20:1), 295 K) spectrum obtained after heating the mixture of **ROT-1**, **6**, **7** (≈ 8.71 mM), **8**, and 1,3,5-trimethoxybenzene (1:1:10:200:10) at 50 °C for 4 h. No product **9** was observed according to ^{1}H NMR analysis.

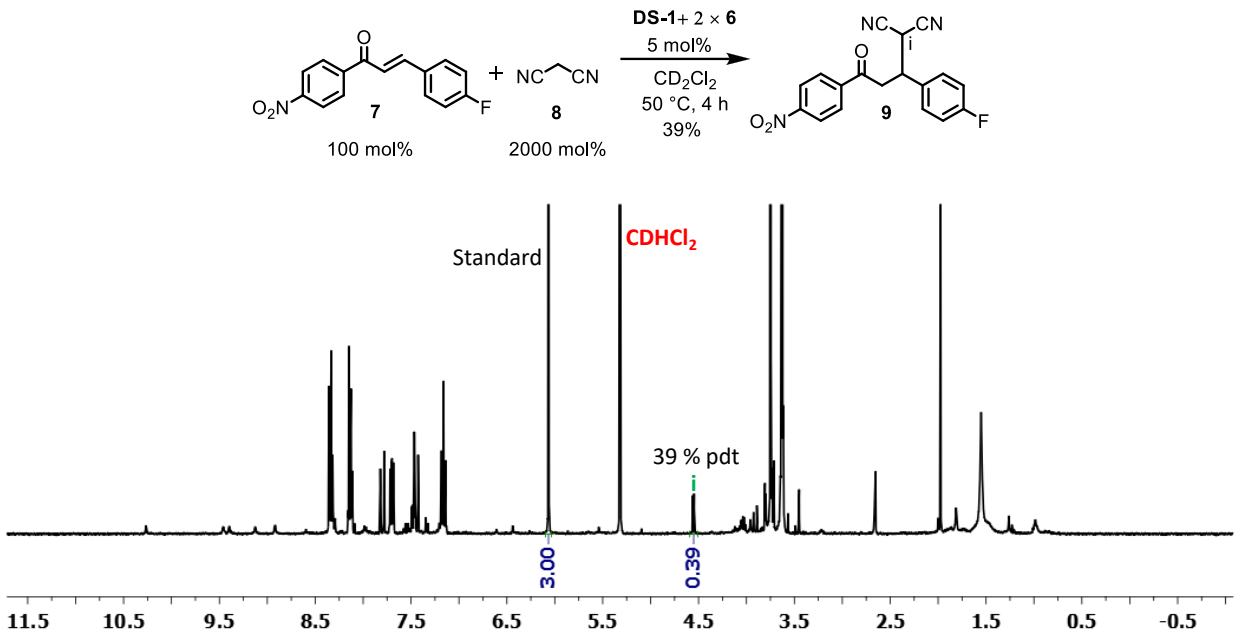


Figure S92. ^{1}H NMR (400 MHz, CD_2Cl_2:$CDCl_3$ (20:1), 295 K) spectrum obtained after heating the mixture of **DS-1**, **6**, **7** (≈ 8.71 mM), **8**, and 1,3,5-trimethoxybenzene (0.5:1:10:200:10) at 50 °C for 4 h. Product **9** was formed in 39% yield according to ^{1}H NMR analysis.

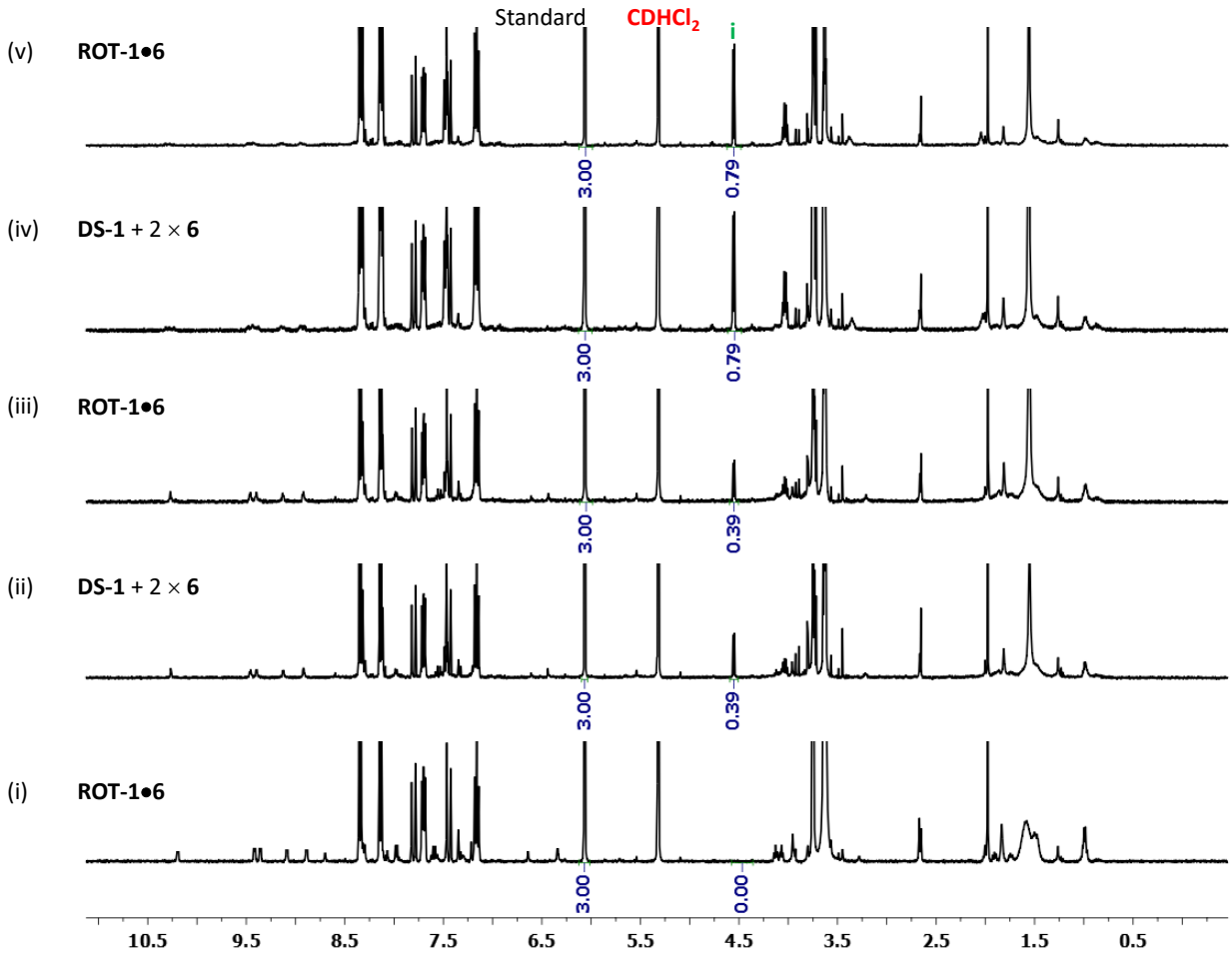


Figure S93. ^{1}H NMR (400 MHz, CD_2Cl_2:$CDCl_3$ (20:1), 295 K) spectrum obtained after heating the reaction mixture of (i) **ROT-1**, **6**, **7** (≈ 8.71 mM), **8**, and 1,3,5-trimethoxybenzene (1:1:10:200:10) at 50 °C for 4 h. No product **9** was observed in ^{1}H NMR. (ii) After addition of 0.5 equiv. of cyclam with respect to **ROT-1** and subsequent heating at 50 °C for 4 h. Product **9** was formed in 39% yield. (iii) After addition of 1.0 equiv. of $[Cu(CH_3CN)_4]PF_6$ with respect to **DS-1**, replacement of consumed substrates and subsequent heating at 50 °C for 4 h. No further product **9** was observed. (iv) After addition of 0.5 equiv. of cyclam with respect to **ROT-1** and subsequent heating at 50 °C for 4 h. Product **9** was formed in 40% yield (total product formed 79%). (v) After addition of 1.0 equiv. of $[Cu(CH_3CN)_4]PF_6$ with respect to **DS-1**, replacement of consumed substrates and subsequent heating at 50 °C for 4 h. No further product **9** was formed.

9. References

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