Electronic Supporting Information

Cation exchange reversibly switches rotor speed and is monitored by a networked fluorescent reporter

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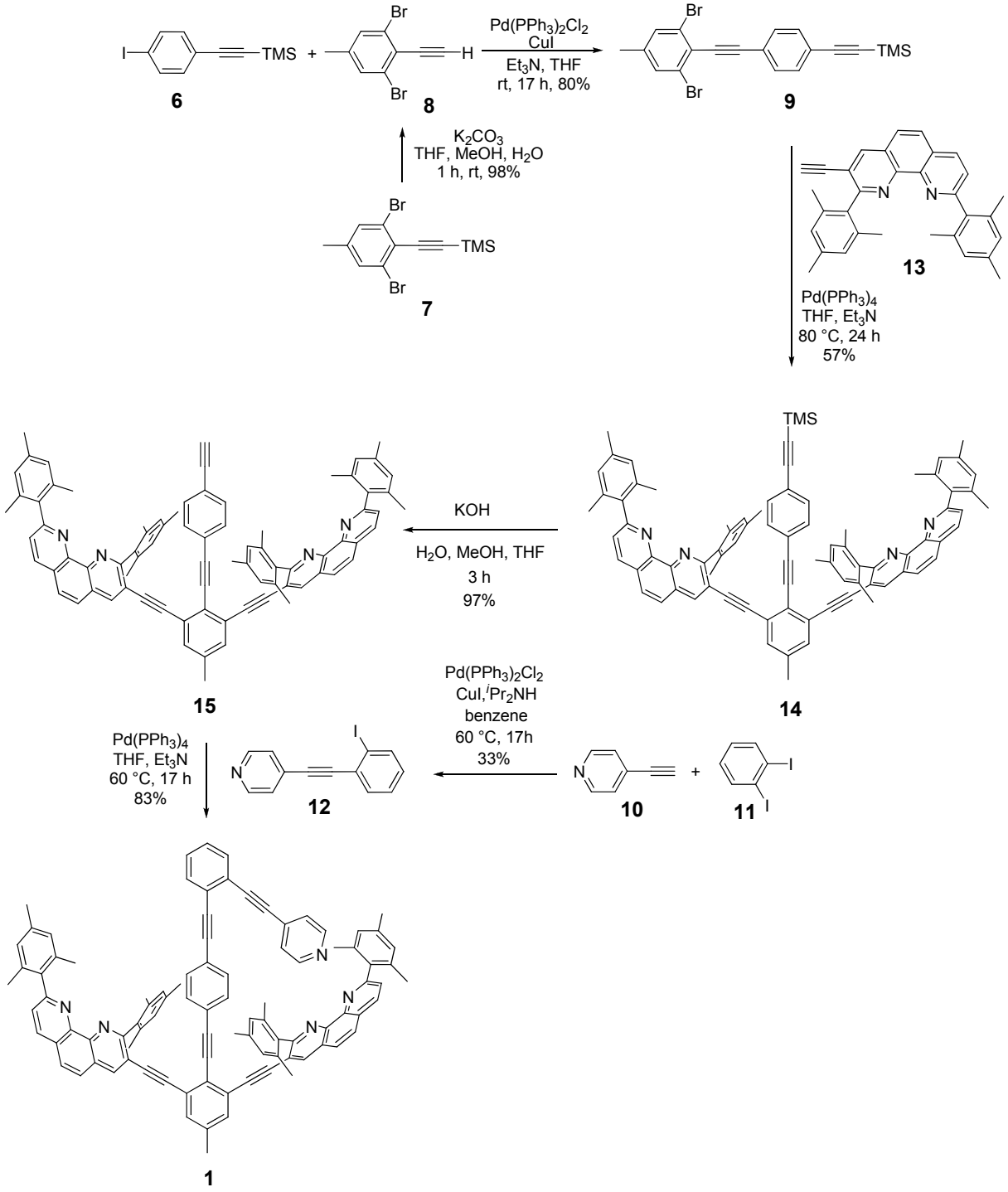
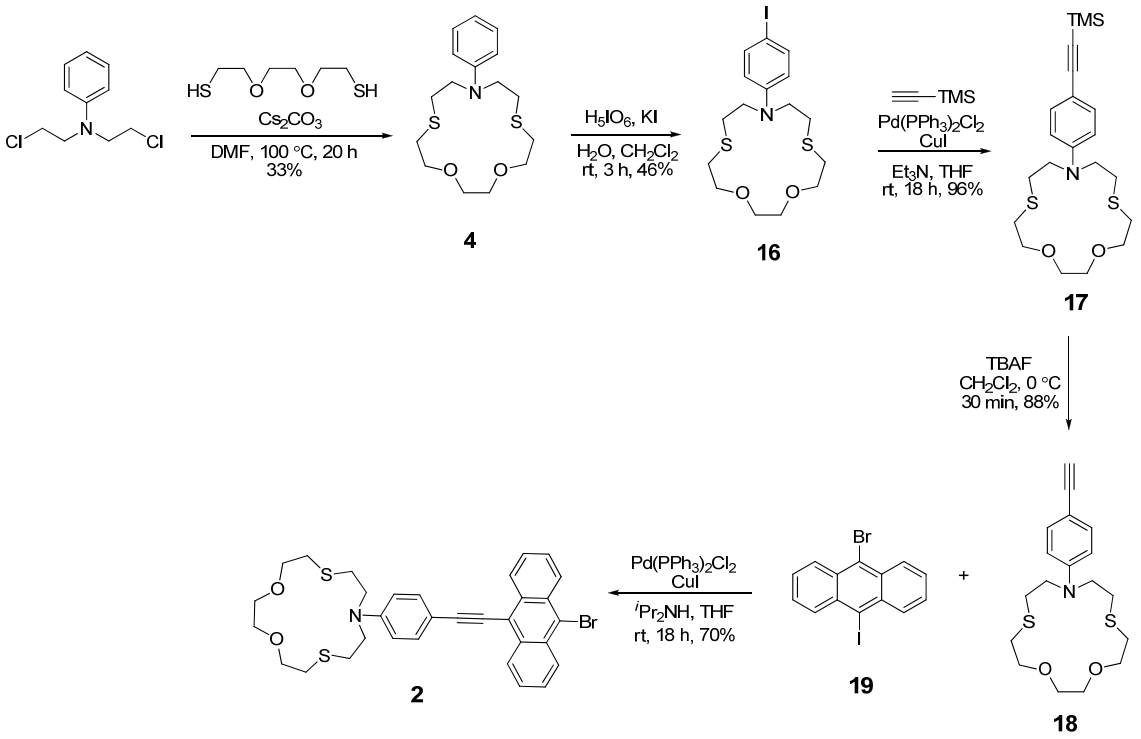
1. Synthesis

1.1. General section

^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance (400 MHz), Jeol ECZ (500 MHz) and Varian VNMR-S (600 MHz) spectrometers using a deuterated solvent as the lock and residual protiated solvent as internal reference. The following abbreviations were utilized to describe peak patterns: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, br = broad and m = multiplet. Electrospray-ionization (ESI) mass spectra were recorded on a Thermo-Quest LCQ deca. Melting points were measured on a Büchi SMP-20 and are uncorrected. Infrared spectra were recorded using a Perkin Elmer Spectrum-Two FT-IR spectrometer. Elemental analysis measurements were made using the EA 3000 CHNS. Energy minimized structures were obtained from DFT computations at the B3LYP/6-31G(d) level using the LanL2DZ basis set for metal ions. UV-vis spectra were recorded on a Cary Win 50 (298 K). Luminescence spectra were recorded on a Varian Cary Eclipse Fluorescence Spectrophotometer with excitation and emission slit widths set to 5 nm. Binding constants were determined through UV-vis titrations assuming a 1:1 binding scheme or with SPECFIT/32TM global analysis system by Spectrum Software Associates (Marlborough, MA). The numbering of the carbon skeleton in molecular formulae as shown in the manuscript does not comply with the IUPAC nomenclature rules; it is only used for assignments of NMR signals. Compounds **6**,[1] **7**,[2] **13**[3] and **19**[4] were synthesized according to literature known procedures.



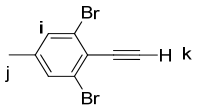
Scheme S1. Synthetic scheme used in the preparation of ligand **1**.



Scheme S2. Preparation of ligand **2**.

1.2. Synthesis of ligand 1

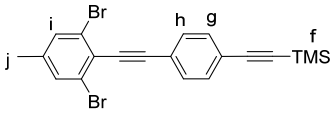
1,3-Dibromo-2-ethynyl-5-methylbenzene (8)



8

To a solution of compound **7** (2.80 g, 8.09 mmol) in THF (30 mL) and MeOH (30 mL), a solution of K_2CO_3 (5.59 g, 40.5 mmol) in H_2O (15 mL) was added and the resulting mixture was stirred for 1 h at rt. Thereafter, solvents were evaporated. The residue was extracted with DCM (3 x 25 mL) after addition 50 mL of water. After drying the organic layer over $MgSO_4$, DCM was evaporated to furnish a colorless solid (2.17 g, 7.93 mmol, 98%). Mp = 81 °C (DCM). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 0.5 Hz, 2H, i-H), 3.62 (s, 1H, k-H), 2.32 (s, 3H, j-H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 132.2, 126.4, 123.2, 85.8, 81.1, 21.0; IR (KBr) *v* 3280, 2957, 2924, 2110, 1723, 1579, 1446, 1380, 1364, 1268, 1249, 1189, 1055, 843, 742, 711, 669, 562 cm^{-1}; Anal. Calcd. for $C_9H_6Br_2$: C, 39.46; H, 2.21; found: C, 39.47; H, 2.10.

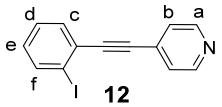
((4-((2,6-Dibromo-4-methylphenyl)ethynyl)phenyl)ethynyl)trimethylsilane (9)



9

Compounds **8** (1.12 g, 4.09 mmol) and **6** (1.35 g, 4.50 mmol), $PdCl_2(PPh_3)_2$ (144 mg, 205 µmol) as well as CuI (39.0 mg, 205 µmol) were dissolved in THF (10 mL) and Et_3N (10 mL). The resulting mixture was stirred at room temperature for 17 h. The solvents were evaporated and the residue was purified by column chromatography with hexane (R_f = 0.61) to furnish compound **9** as colorless solid (1.47 g, 3.29 mmol, 80%). Mp = 85 °C (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.51 (m, 2H, AA'BB' of g/h-H), 7.47 – 7.43 (m, 2H, AA'BB' of h/g-H), 7.40 (d, *J* = 0.6 Hz, 2H, i-H), 2.33 (s, 3H, j-H), 0.26 (s, 9H, f-H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 132.2, 132.0, 131.6, 126.1, 124.1, 123.6, 122.9, 104.7, 97.2, 96.7, 89.4, 21.1, 0.1; IR (KBr) *v* 2951, 2895, 2152, 1591, 1508, 1384, 1248, 1189, 865, 845, 832, 759, 742 cm^{-1}; Anal. Calcd. for $C_{20}H_{18}Br_2Si$: C, 53.83; H, 4.07; found: C, 54.12; H, 4.02.

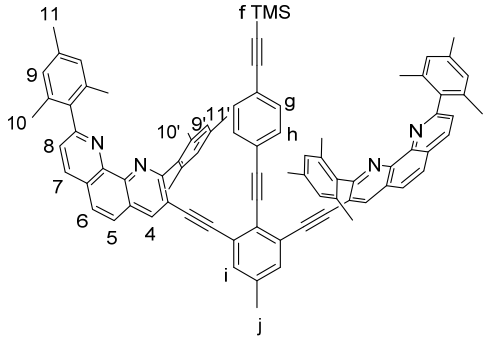
4-((2-Iodophenyl)ethynyl)pyridine (12)



12

4-Ethynylpyridine (**10**) as hydrochloride (500 mg, 4.85 mmol), 1,2-diiodobenzene (**11**) (480 mg, 14.6 mmol), $PdCl_2(PPh_3)_2$ (340 mg, 485 µmol) and CuI (92.0 mg, 485 µmol) were dissolved in benzene (30 mL) and diisopropylamine (20 mL). The resulting mixture was stirred under nitrogen at 60 °C for 17 h. After evaporation of the solvents, the residue was purified by column chromatography using 10% EtOAc in DCM (R_f = 0.33) to afford compound **12** (487 mg, 1.59 mmol, 33%) as a colorless solid. Mp = 60 °C (EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 6.0 Hz, 2H, a-H), 7.90 (dd, *J* = 8.0, 1.1 Hz, 1H, f-H), 7.55 (dd, *J* = 7.6, 1.7 Hz, 1H, c-H), 7.44 (d, *J* = 6.0 Hz, 2H, b-H), 7.36 (td, *J* = 7.6, 1.1 Hz, 1H, d-H), 7.08 (td, *J* = 8.0, 1.7 Hz, 1H, e-H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 139.0, 132.9, 131.1, 130.4, 128.7, 128.0, 125.5, 101.4, 95.9, 90.0; IR (KBr) *v* 3054, 2221, 1592, 1541, 1487, 1457, 1428, 1410, 1218, 1018, 991, 819, 752, 708, 543 cm^{-1}; Anal. Calcd. for $C_{13}H_8IN$: C, 51.17; H, 2.64; N, 4.59; found: C, 51.24; H, 2.52; N, 4.53; ESI-MS: *m/z* (%) 306.2 (100) $[M+H]^+$.

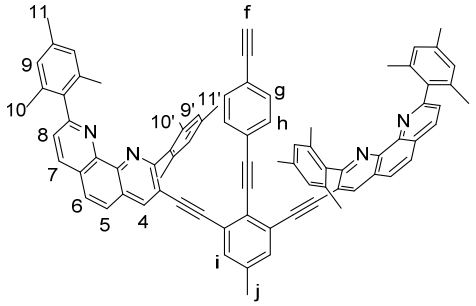
3,3'-((5-Methyl-2-((4-((trimethylsilyl)ethynyl)phenyl)ethynyl)-1,3-phenylene)bis(ethyne-2,1-diyl))bis(2,9-dimesityl-1,10-phenanthroline) (14)



14

Phenanthroline **13** (296 mg, 672 µmol) and compound **9** (100 mg, 224 µmol) were dissolved in THF (5 mL) and Et_3N (5 mL). The solution was degassed by freeze-thaw-pump cycles (three times). Then, $Pd(PPh_3)_4$ (50.8 mg, 44.0 µmol) was added and the mixture was heated at 80 °C for 2 d. After evaporation of the solvents, the product was purified by column chromatography on silica gel using 20% EtOAc in hexanes (R_f = 0.88, 10% EtOAc in hexanes on neutral alumina) to furnish a colorless solid (126 mg, 108 µmol, 48%). Mp > 230 °C (decomposition). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.42 (s, 2H, 4-H), 8.29 (d, *J* = 8.2 Hz, 2H, 7-H), 7.88 (d, *J* = 8.9 Hz, 2H, 5/6-H), 7.76 (d, *J* = 8.9 Hz, 2H, 6/5-H), 7.65 – 7.60 (m, 2H, g/h-H), 7.58 (d, *J* = 8.2 Hz, 2H, 8-H), 7.57 – 7.53 (m, 2H, h/g-H), 6.93 (s, 4H, 9/9'-H), 6.89 (s, 4H, 9'/9-H), 6.63 (d, *J* = 0.6 Hz, 2H, i-H), 2.32 (s, 6H, 11/11'-H), 2.31 (s, 6H, 11'/11-H), 2.20 (s, 3H, j-H), 2.12 (s, 12H, 10/10'-H), 2.08 (s, 12H, 10'/10-H), 0.31 (s, 9H, f-H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1, 160.6, 146.1, 145.2, 138.9, 138.1, 138.0, 137.7, 137.3, 137.1, 136.5, 136.3, 136.0, 133.5, 132.1, 131.6, 128.6, 128.1, 127.7, 127.1, 126.9, 125.8, 125.7, 125.3, 123.9, 123.6, 123.4, 119.9, 104.8, 96.8, 96.5, 93.5, 91.3, 89.4, 21.3, 21.2, 21.1, 20.7, 20.3, 0.1; IR (KBr) *v* 2964, 2919, 2853, 2159, 1612, 1585, 1505, 1457, 1252,1034, 844, 764 cm^{-1}; Anal. Calcd. for $C_{84}H_{72}N_4Si$: C, 86.56; H, 6.23; N, 4.81; found: C, 86.86; H, 5.95; N, 4.73; ESI-MS: *m/z* (%) 1165.9 (100) $[M+H]^+$ and 584.4 (100) $[M+2H]^{2+}$.

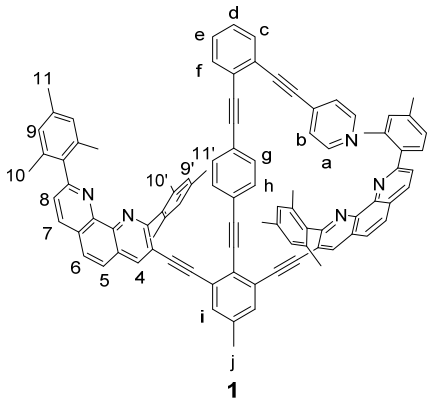
3,3'-(2-((4-Ethynylphenyl)ethynyl)-5-methyl-1,3-phenylene)bis(ethyne-2,1-diyl)bis(2,9-dimesityl-1,10-phenanthroline) (15)



15

Compound **14** (100 mg, 86.0 µmol) was dissolved in THF (2 mL) and MeOH (2 mL). Then KOH (24.0 mg, 427 µmol) in 1 mL H_2O was added and the mixture was stirred for 1 h. Water (10 mL) was added and the product was extracted with DCM (3 x 20 mL). After drying over $MgSO_4$, the extract was filtered and the solvent evaporated to furnish a colorless solid (91.0 mg, 83.0 µmol, 97%). Mp > 250 °C (DCM). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 2H, 4-H), 8.28 (d, *J* = 8.2 Hz, 2H, 7-H), 7.88 (d, *J* = 8.8 Hz, 2H, 5/6-H), 7.75 (d, *J* = 8.8 Hz, 2H, 6/5-H), 7.67 – 7.62 (m, 2H, g/h-H), 7.60 – 7.57 (m, 2H, h/g-H), 7.58 (d, *J* = 8.2 Hz, 2H, 8-H), 6.92 (s, 4H, 9/9'-H), 6.89 (s, 4H, 9'/9-H), 6.64 (d, *J* = 0.4 Hz, 2H, i-H), 3.26 (s, 1H, f-H), 2.32 (s, 6H, 11/11'-H), 2.31 (s, 6H, 11'/11-H), 2.20 (s, 3H, j-H), 2.12 (s, 12H, 10/10'-H), 2.08 (s, 6H, 10'/10-H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1, 160.6, 146.1, 145.2, 138.9, 138.2, 138.1, 137.7, 137.3, 137.1, 136.5, 136.3, 136.0, 133.5, 132.3, 131.7, 128.6 (2C), 128.1, 127.7, 127.1, 126.9, 125.8, 125.4, 124.3, 123.6, 122.4, 119.9, 96.3, 93.4, 91.3, 89.5, 83.4, 79.4, 21.3, 21.2, 21.1, 20.7, 20.3; IR (KBr) *v* 2924, 2859, 2120, 1619, 1513, 1460, 1443, 1382, 1300, 1039, 888, 847, 774, 639 cm^{-1}; Anal. Calcd. for $C_{81}H_{64}N_4$: C, 88.98; H, 5.90; N, 5.12; found: C, 88.62; H, 5.60; N, 5.19; ESI-MS: *m/z* (%) 1039.9 (100) $[M+H]^+$ and 548.1 (15) $[M+2H]^{2+}$.

Ligand 1

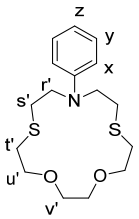


1

Compounds **15** (60 mg, 55 µmol) and **12** (60 mg, 82 µmol) were dissolved in THF (5 mL) and Et_3N (5 mL). The resultant solution was degassed by freeze-thaw-pump cycles. Then, $Pd(PPh_3)_4$ (60 mg, 11 µmol) was added to the reaction mixture which was stirred at 60 °C for 17 hours. After completion of the reaction, the solvents were evaporated. The crude product was purified by column chromatography on silica gel with 10% EtOAc in DCM (R_f = 0.79, 25% EtOAc in hexanes on neutral alumina) to furnish the desired product as a colorless solid (58 mg, 46 µmol, 83%). Mp > 220 °C (hexane, dec.). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.57 (d, *J* = 6.0 Hz, 2H, a-H), 8.49 (s, 2H, 4-H), 8.32 (d, *J* = 8.2 Hz, 2H, 7-H), 7.91 (d, *J* = 8.8 Hz, 2H, 5/6-H), 7.80 (d, *J* = 8.8 Hz, 2H, 6/5-H), 7.72 – 7.69 (m, 2H, g/h-H), 7.69 – 7.66 (m, 2H, h/g-H), 7.67 – 7.64 (m, 2H, [c + f] -H), 7.57 (d, *J* = 8.2 Hz, 2H, 8-H), 7.44 (d, *J* = 6.0 Hz, 2H, b-H), 7.48 – 7.40 (m, 2H, [d + e]-H), 6.97 (s, 4H, 9/9'-H), 6.96 (s, 4H, 9'/9-H), 6.68 (d, *J* = 0.6 Hz, 2H, i-H), 2.37 (s, 6H, 11/11'-H), 2.33 (s, 6H, 11'/11-H), 2.22 (s, 3H, j-H), 2.05 (s, 24H, [10 + 10']-H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 162.2, 161.1, 150.5, 146.6, 145.8, 139.4, 139.1, 138.6, 138.0, 137.6, 136.6, 136.6, 136.3, 134.0, 132.8, 132.6, 132.4, 132.3, 131.6, 129.7, 129.1, 128.8, 128.5, 128.2, 127.7, 127.4, 126.3, 126.1, 126.0, 125.9, 125.4, 125.1, 124.2, 123.87, 123.8, 120.0, 97.0, 94.0, 93.7, 92.8, 91.6, 91.3, 90.5, 89.7, 21.5, 21.4, 21.3, 20.6, 20.3; IR (KBr) *v* 2919, 2853, 2227, 1704, 1616, 1587, 1513, 1457, 1379, 1212, 1109, 1034, 848, 758, 638 cm^{-1}; Anal. Calcd. for $C_{94}H_{71}N_5$: C, 88.86; H, 5.63; N, 5.51 found: C, 88.67; H, 5.25; N, 5.33; ESI-MS: *m/z* (%) 1270.8 (100) $[M+H]^+$.

1.3. Synthesis of ligand 2

10-Phenyl-1,4-dioxa-7,13-dithia-10-azacyclopentadecane[5] (4)

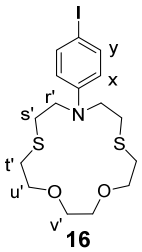


4

A mixture of *N*,*N*-bis(2-chloroethyl)aniline (5.37 g, 24.6 mmol) and 2,2'-(ethylenedioxy)diethanethiol (4.71 g, 24.6 mmol) in 75 mL of dry DMF was slowly added over 10 h to a well-stirred solution of $CsCO_3$ (8.82 g, 27.1 mmol) in 100 mL of dry DMF at 100 ˚C. The mixture was stirred for another 10 h at 100 ˚C and filtered. DMF was evaporated. The crude was purified by column chromatography in silica gel eluting with CH_2Cl_2 (R_f = 0.44) to afford a colorless solid (0.883 g, 2.70 mmol, 33%). Mp = 62 °C (DCM). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.18 (dd, *J* = 8.8, 7.3 Hz, 2H, y-H), 6.63 (dt, *J* = 7.3, 0.9 Hz, 1H, z-H), 6.62 (dd, *J* =

8.8, 0.9 Hz, 2H, x-H), 3.77 (t, *J* = 5.1 Hz, 4H, r'-H), 3.62 (s, 4-H, v'-H), 3.61 (t, *J* = 7.9 Hz, 4H, u'-H), 2.87 (t, *J* = 7.9 Hz, 4H, t'-H), 2.74 (t, *J* = 5.1 Hz, 4H, s'-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.0, 129.6, 116.3, 111.9, 74.4, 70.9, 51.9, 31.3, 29.6; IR (KBr) *v* 2963, 2924, 2867, 1597, 1504, 1352, 1282, 1189, 1138, 1102, 1035, 987, 744 cm^{-1}; Anal. Calcd. for $C_{16}H_{25}NO_2S_2$: C, 58.68; H, 7.69; N, 4.28; S, 19.58; found: C, 58.60; H, 7.68; N, 4.26; S, 19.62; ESI-MS: *m/z* (%) 328.5 (100) $[M+H]^+$.

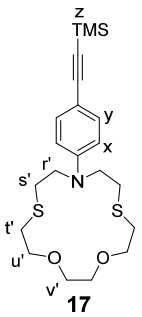
10-(4-Iodophenyl)-1,4-dioxa-7,13-dithia-10-azacyclopentadecane (16)



16

To a solution of crown **4** (582 mg, 1.78 mmol) in CH_2Cl_2 (15 mL) were added KI (354 mg, 2.13 mmol) and a solution of H_5IO_6 (485 mg, 2.13 mmol) in 15 mL of H_2O. The mixture was stirred vigorously at rt for 1 h. TLC indicated that starting material was still present. Further KI (354 mg, 2.13 mmol) and H_5IO_6 (485 mg, 2.13 mmol) were added, and the mixture was stirred for 3 more h. Then, TLC showed that the reactant was used up. The mixture was extracted with CH_2Cl_2 and the organic layer was washed with brine solution. After drying over $MgSO_4$, CH_2Cl_2 was evaporated. The crude product was purified by column chromatography on neutral alumina eluting with CH_2Cl_2:hexane (2:1) (R_f = 0.70 in CH_2Cl_2) to provide the product as a colorless solid (370 mg, 816 µmol, 46%). Mp = 85 °C (hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 9.1 Hz, 2H, y-H), 6.41 (d, *J* = 9.1 Hz, 2H, x-H), 3.80 (t, *J* = 5.0 Hz, 4H, r'-H), 3.64 (s, 4H, v'-H), 3.59 (t, *J* = 8.0 Hz, 4H, u'-H), 2.86 (t, *J* = 8.0 Hz, 4H, t'-H), 2.75 (t, *J* = 5.0 Hz, 4H, s'-H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 138.0, 114.2, 76.9, 74.4, 70.8, 51.9, 31.3, 29.4; IR (KBr) *v* 2948, 2912, 2883, 1586, 1491, 1388, 1353, 1280, 1191, 1136, 1102, 1039, 907, 801, 743 cm^{-1}; Anal. Calcd. for $C_{16}H_{24}INO_2S_2$: C, 42.39; H, 5.34; N, 3.09; S, 14.14; found: C, 42.50; H, 5.19; N, 3.05; S, 14.13; ESI-MS: *m/z* (%) 454.4 (100) $[M+H]^+$.

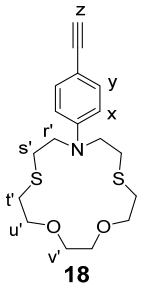
10-(4-((Trimethylsilyl)ethynyl)phenyl)-1,4-dioxa-7,13-dithia-10-azacyclopentadecane (17)



17

In a sealed tube, compound **16** (350 mg, 772 µmol), $PdCl_2(PPh_3)_2$ (54.0 mg, 77.0 µmol) and CuI (15.0 mg, 77.0 µmol) were dissolved in THF (5 mL) and Et_3N (5 mL) under nitrogen atmosphere. Then, trimethylsilylacetylene (550 µL, 3.86 mmol) was added. The sealed reaction mixture was stirred at room temperature for 18 h. Then solvents were evaporated and the crude mixture was purified by column chromategraphy on silica gel using CH_2Cl_2 (R_f = 0.48) to afford a colorless solid (315 mg, 743 µmol, 96%). Mp = 68 °C (DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 9.1 Hz, 2H, y-H), 6.52 (d, *J* = 9.1 Hz, 2H, x-H), 3.80 (t, *J* = 5.0 Hz, 4H, r'-H), 3.64 (s, 4H, v'-H), 3.63 (t, *J* = 8.0 Hz, 4H, u'-H), 2.87 (t, *J* = 8.0 Hz, 4H, t'-H), 2.75 (t, *J* = 5.0 Hz, 4H, s'-H), 0.22 (s, 9H, z-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.1, 133.7, 111.5, 110.2, 106.6, 91.5, 74.6, 71.0, 52.0, 31.5, 29.7, 0.5; IR (KBr) *v* 2951, 2916, 2865, 2141, 1605, 1518, 1353, 1287, 1246, 1183, 1091, 867, 842, 820 cm^{-1}; Anal. Calcd. for $C_{21}H_{33}NO_2S_2Si$: C, 59.53; H, 7.85; N, 3.31; S, 15.13; found: C, 59.37; H, 7.84; N, 3.21; S, 15.28; ESI-MS: *m/z* (%) 424.7 (100) $[M+H]^+$.

10-(4-Ethynylphenyl)-1,4-dioxa-7,13-dithia-10-azacyclopentadecane (18)

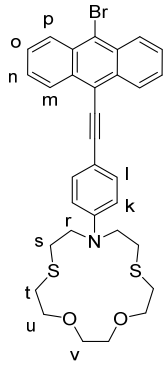


18

TBAF (537 mg, 2.05 mmol) in CH_2Cl_2 (5 mL) was added to a cold (0 ˚C) solution of **17** (290 mg, 684 µmol) in CH_2Cl_2 (10 mL). The reaction mixture was kept stirring at 0 ˚C for 30 min. Then the mixture was extracted with CH_2Cl_2 from water to furnish a colorless solid (212 mg, 603 µmol, 88%). Mp = 45 °C (DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 9.1 Hz, 2H, y-H), 6.55 (d, *J* = 9.1 Hz, 2H, x-H), 3.80 (t, *J* = 5.0 Hz,

4H, r'-H), 3.64 (s, 4H, v'-H), 3.64 (t, *J* = 8.0 Hz, 4H, u'-H), 2.96 (s, 1H, z-H), 2.88 (t, *J* = 8.0 Hz, 4H, t'-H), 2.75 (t, *J* = 5.0 Hz, 4H, s'-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.2, 133.7, 111.5, 108.9, 84.8, 75.0, 74.5, 70.9, 51.9, 31.4, 29.5; IR (KBr) *v* 2933, 2866, 2102, 1607, 1516, 1354, 1291, 1140, 1101, 950, 816 cm^{-1}; Anal. Calcd. for $C_{18}H_{25}NO_2S_2$: C, 61.50; H, 7.17; N, 3.98; S, 18.24; found: C, 61.53; H, 7.25; N, 3.73; S, 18.05.

10-(4-((10-Bromoanthracen-9-yl)ethynyl)phenyl)-1,4-dioxa-7,13-dithia-10-azacyclopentadecane (2)

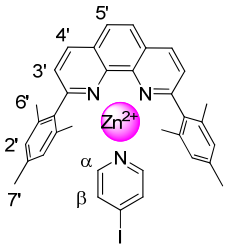


2

Crown ether **18** (100 mg, 0.284 mmol), anthracene **19**[4] (99.0 mg, 0.258 mmol), $PdCl_2(PPh_3)_2$ (18.0 mg, 26.0 µmol) and CuI (5.00 mg, 26.0 µmol) were dissolved in THF (3 mL) and $^{i}Pr_2NH$ (3 mL) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 18 h. The product was purified by column chromatography on silica gel with first CH_2Cl_2:hexane (1:1) and then with CH_2Cl_2 (R_f = 0.53) to afford a bright yellow solid (109 mg, 0.181 mmol,70%). Mp = 219 °C (hexane). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.75 – 8.67 (m, 2H, m/p-H), 8.58 – 8.53 (m, 2H, p/m-H), 7.69 – 7.62 (m, 4H, [n+o]-H), 7.63 (d, *J* = 9.0 Hz, 2H, l-H), 6.71 (d, *J* = 9.0 Hz, 2H, k-H), 3.79 (t, *J* = 5.0 Hz, 4H, r-H), 3.71 (t, *J* = 8.0 Hz, 4H, u-H), 3.63 (s, 4H, v-H), 2.93 (t, *J* = 8.0 Hz, 4H, t-H), 2.77 (t, 4H, *J* = 5.0 Hz, s-H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 148.0, 133.7, 133.1, 130.9, 128.5, 128.1, 128.0, 127.1, 123.1, 120.0, 112.2, 110.1, 104.4, 84.6, 74.8, 71.3, 52.5, 32.0, 30.0; IR (KBr) *v* 2908, 2866, 2185, 1604, 1518, 1347, 1283, 1187, 1158, 1140, 906, 813, 757, 622 cm^{-1}; Anal. Calcd. for $C_{32}H_{32}BrNO_2S_2$: C, 63.36; H, 5.32; N, 2.31; S, 10.57; found: C, 62.98; H, 4.95; N, 2.20; S, 10.71; ESI-MS: *m/z* (%) 607.1 (100) $[M+H]^+$.

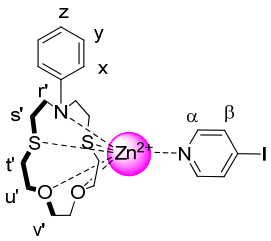
1.4. Preparation of model complexes

[Zn(3)(5)](OTf)$_2$



Shielded phenanthroline **3** (0.380 mg, 0.912 µmol) and 4-iodopyridine (**5**) (0.187 mg, 0.912 µmol) were dissolved in 550 µL of CD_2Cl_2, then $Zn(OTf)_2$ (0.331 mg, 0.912 µmol) was added as a standard solution in CD_3CN to give [Zn(**3**)(**5**)]$(OTf)_2$ quantitatively. ^{1}H NMR (400 MHz, CD_2Cl_2:CD_3CN, 98:2) δ 8.90 (d, *J* = 8.3 Hz, 2H, 4'-H), 8.30 (s, 2H, 5'-H), 7.99 (d, *J* = 8.3 Hz, 2H, 3'-H), 7.78 (d, *J* = 6.4 Hz, 2H, α-H), 7.75 (d, *J* = 6.4 Hz, 2H, β-H), 6.89 (s, 4H, 2'-H), 2.29 (s, 6H, 7'-H), 1.81 (s, 12H, 6'-H); IR (KBr) *v* 2929, 2858, 1659, 1599, 1564, 1283, 1263, 1227, 1164, 1029, 863, 641 cm^{-1}; ESI-MS: *m/z* (%) 833.6 (100) [M – OTf]$^+$.

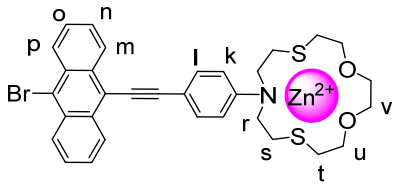
[Zn(4)(5)](OTf)$_2$



$Zn(OTf)_2$ (3.10 mg, 8.37 µmol) in 150 µL of CH_3CN was added to a solution of crown ether **4** (2.74 mg, 8.37 µmol) and 4-iodopyridine (**5**) (3.04 mg, 8.37 µmol) in 500 µL of CH_2Cl_2. Solvents were evaporated to quantitatively give [Zn(**4**)(**5**)]$(OTf)_2$. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.31 (d, *J* = 6.5 Hz, 2H, α-H), 8.03 (d, *J* = 6.5 Hz, 2H, β-H), 7.37 (dd, *J* = 8.0, 7.3 Hz, 2H, y-H), 7.06 (br s, 3H, [x + z]-H), 3.79 (t, *J* = 8.0 Hz, 4H, u'-H), 3.76 (t, *J* = 5.0 Hz, 4H, r'-H), 3.68 (s, 4H, v'-H), 2.83 (t, *J* = 8.0 Hz, 4H, t'-H), 2.78 (t, *J* = 5.0 Hz, 4H, s'-H); IR (KBr) *v* 2916, 2868, 1588, 1505, 1411, 1353, 1275, 1250, 1174, 1036, 817, 749, 654, 520 cm^{-1}; ESI-MS: *m/z* (%) 804.7 (100) [[Zn(**4**)(**5**)] + H_2O + CH_3CN – OTf]$^+$.

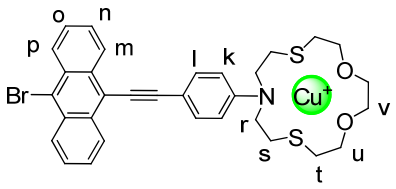
1.5. Preparation of rotor and receptor complexes

[Zn(2)](OTf)$_2$



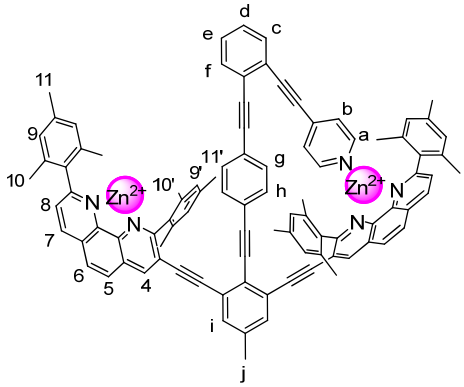
Addition of $Zn(OTf)_2$ (603 µg, 1.66 µmol) in 26 µL of CD_3CN to a solution of crown ether **2** (1.01 mg, 1.66 µmol) in 530 µL of CD_2Cl_2 quantitatively furnished [Zn(**2**)]OTf_2. ^{1}H NMR (400 MHz, CD_2Cl_2:CD_3CN, 98:2) δ 8.72 – 8.69 (m, 2H, m/p-H), 8.58 – 8.54 (m, 2H, p/m-H), 7.70 – 7.61 (m, 6H, [l+n+o]-H), 6.87 (br s, 2H, k-H), 3.74 (t, *J* = 5.0 Hz, 4H, r-H), 3.66 (br s, 4H, u-H), 3.65 (s, 4H, v-H), 2.99 (br s, 4H, t-H), 2.87 (br s, 4H, *J* = 5.0 Hz, s-H); IR (KBr) *v* 2928, 2864, 2187, 1633, 1605, 1519, 1261, 1184, 1034, 757, 645 cm^{-1}; Anal. Calcd. for $C_{34}H_{32}BrF_6NO_8S_4Zn \bullet 3CH_2Cl_2$: C, 36.28; H, 3.13; N, 1.14; S, 10.47; found: C, 36.50; H, 3.45; N, 1.22; S, 10.84; ESI-MS: *m/z* (%) 820.4 (100) [Zn(**2**)](OTf)]$^+$.

[Cu(2)]PF_6



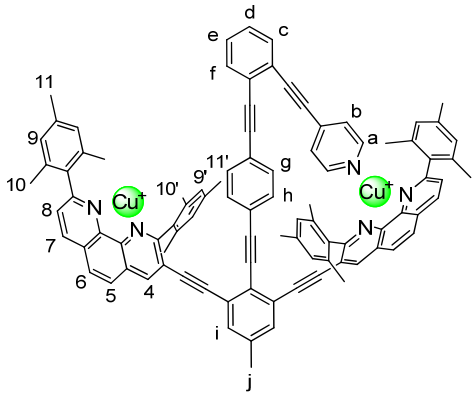
Ligand **2** (361 µg, 0.595 µmol) and $[Cu(CH_3CN)_4]PF_6$ (0.222 mg, 0.595 µmol) were dissolved in CD_2Cl_2 and sonicated in an NMR tube for 1 min to quantitatively furnish the complex. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.74 – 8.70 (m, 2H, m/p-H), 8.63 – 8.59 (m, 2H, p/m-H), 7.88 (d, *J* = 8.7 Hz, 2H, l-H), 7.74 – 7.65 (m, 4H, [n+o]-H), 7.55 (d, *J* = 8.7 Hz, 2H, k-H), 3.84 (s, 4H, v-H), 3.47 (t, *J* = 5.0 Hz, 4H, r-H), 3.28 (br s, 4H, u-H), 3.07 (br s, 4H, t-H), 2.94 (t, *J* = 5.0 Hz, 4H, s-H); IR (KBr) *v* 2982, 2872, 2195, 1636, 1605, 1513, 1462, 1343, 1288, 1133, 1034, 844, 753, 555; Anal. Calcd. for $C_{32}H_{32}BrCuF_6NO_2PS_2 \bullet 2H_2O$: C, 45.15; H, 4.26; N, 1.65; S, 7.52; found: C, 45.36; H, 3.91; N, 1.63; S, 7.13; ESI-MS: *m/z* (%) 670.4 (100) [Cu(**2**)]$^+$.

$[Zn_2(1)](OTf)_4$



Addition of $Zn(OTf)_2$ (446 µg, 1.23 µmol) in CD_3CN (20 µL) to ligand **1** (780 µg, 0.614 µmol) dissolved in 530 µL of CD_2Cl_2 quantitatively furnished $[Zn_2(\mathbf{1})](OTf)_4$. ^{1}H NMR (500 MHz, CD_2Cl_2:CD_3CN, 96:4) δ 8.94 (s, 2H, 4-H), 8.87 (d, *J* = 8.3 Hz, 2H, 7-H), 8.27 (d, *J* = 9.2 Hz, 2H, 5/6-H), 8.17 (d, *J* = 9.2 Hz, 2H, 6/5-H), 7.97 (d, *J* = 8.3 Hz, 2H, 8-H), 7.70 – 7.58 (m, 6H, [g + h]-H and [c + f]-H) 7.53 – 7.48 (m, 1H, e/d-H), 7.48 – 7.43 (m, 1H, d/e-H), 7.09 (br s, 2H, i-H), 7.01 (br s, 2H, b-H), 6.94 (br s, 8H, [9 + 9']-H), 6.56 (br s, 2H, a-H), 2.29 (s, 6H, 11/11'-H), 2.26 (s, 3H, j-H), 1.97 (s, 12H, 10/10'-H), 1.84 (br, 18H, 11'/11-H and 10'/10-H); IR (KBr) *v* 2923, 2853, 2219, 1613, 1509, 1466, 1384, 1259, 1171, 1033, 852, 641 cm^{-1}; Anal. Calcd. for $C_{98}H_{71}F_{12}N5O_{12}S_4Zn_2 \bullet 6CH_2Cl_2$: C, 49.82; H, 3.34; N, 2.79; S, 5.11; found: C, 49.88; H, 3.67; N, 2.70; S, 5.19; ESI-MS: *m/z* (%) 858.0 (100) $[M + H_2O - 2OTf]^{2+}$.

$[Cu_2(1)](PF_6)_2$



Ligand **1** (1.12 mg, 0.881 µmol) and $[Cu(CH_3CN)_4]PF_6$ (657 µg, 1.76 µmol) were dissolved in CD_2Cl_2 and sonicated in an NMR tube for 1 min to quantitatively furnish the complex. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.77 (s, 2H, 4-H), 8.66 (d, *J* = 8.3 Hz, 2H, 7-H), 8.13 (d, *J* = 8.9 Hz, 2H, 5/6-H), 8.06 (d, *J* = 8.9 Hz, 2H, 6/5-H), 7.90 (d, *J* = 8.3 Hz, 2H, 8-H), 7.68 – 7.53 (m, 6H, [g + h]-H and [c + f] -H), 7.52 – 7.47 (m, 1H, d/e-H), 7.47 – 7.42 (m, 1H, e/d-H), 7.10 (br s, 2H, b-H), 6.96 (s, 8H, [9 + 9']-H), 6.67 (br, 3H, i-H and a-H), 2.32 (s, 6H, 11/11'-H), 2.25 (s, 3H, j-H), 1.99 (s, 12H, 10/10'-H), 1.88 (br, 18H, 11'/11-H and 10'/10-H); IR (KBr) *v* 2933, 2855, 2223, 1655, 1606, 1513, 1460, 1378, 1284, 1035, 941, 770, 562 cm^{-1}; Anal. Calcd. for $C_{94}H_{71}Cu_2F_{12}N_5P_2 \bullet CH_2Cl_2$: C, 64.37; H, 4.15; N, 3.95 found: C, 64.11; H, 4.07; N, 3.67; ESI-MS: *m/z* (%) 719.5 (100) $[M - 2PF_6]^{2+}$.

2. NMR spectra

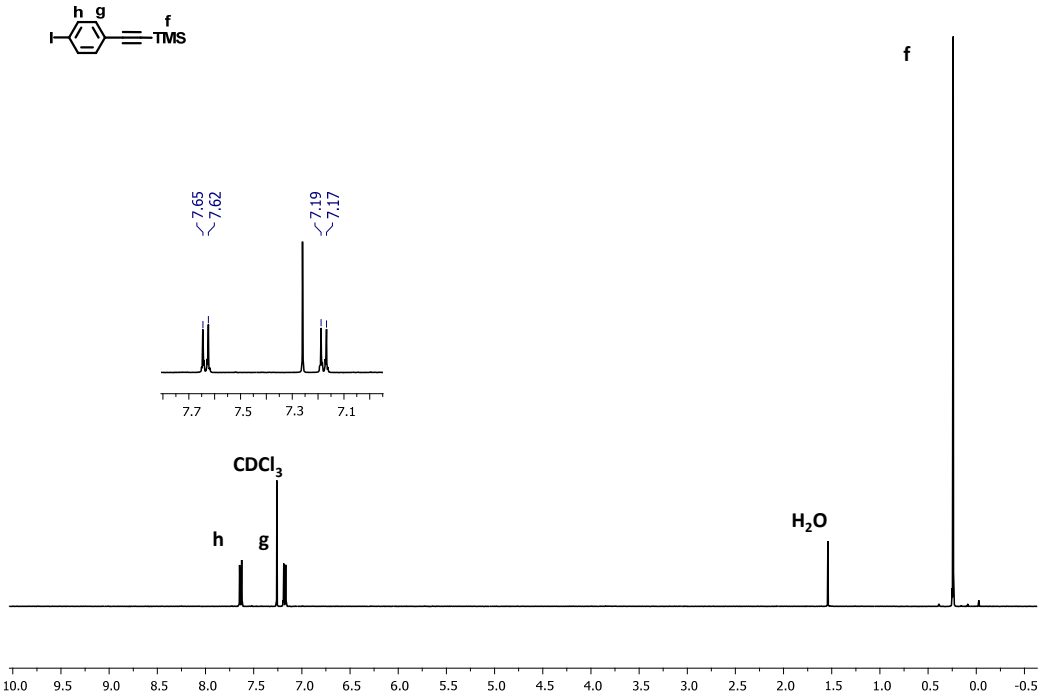


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **6**.

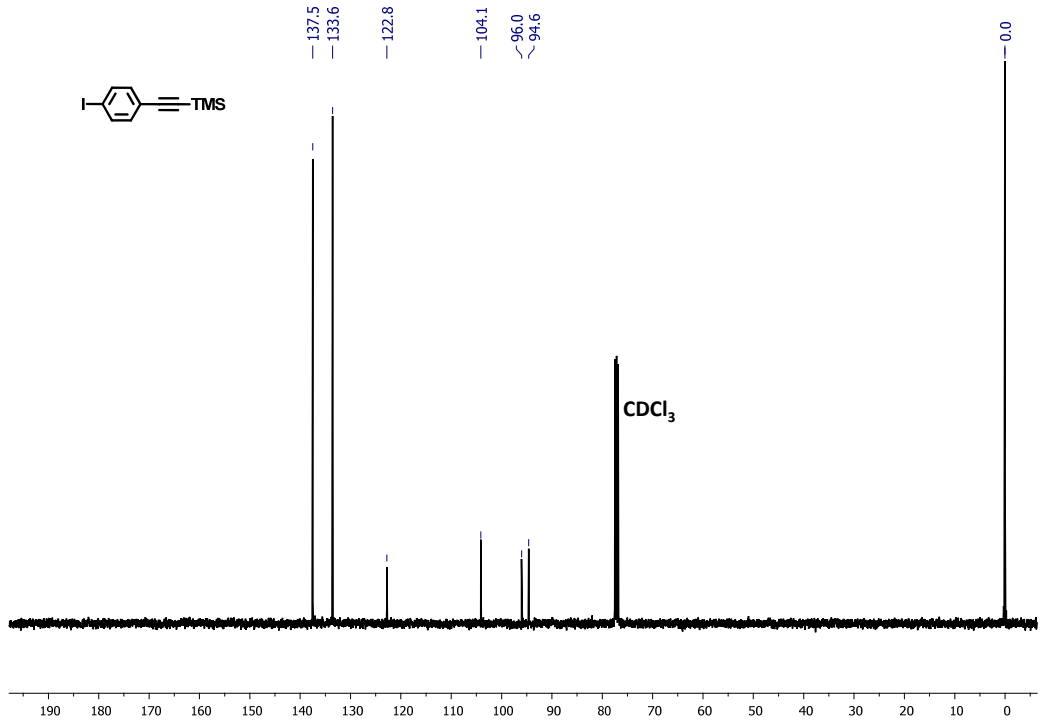


Figure S2. ^{13}C NMR (101 MHz, $CDCl_3$) of compound **6**.

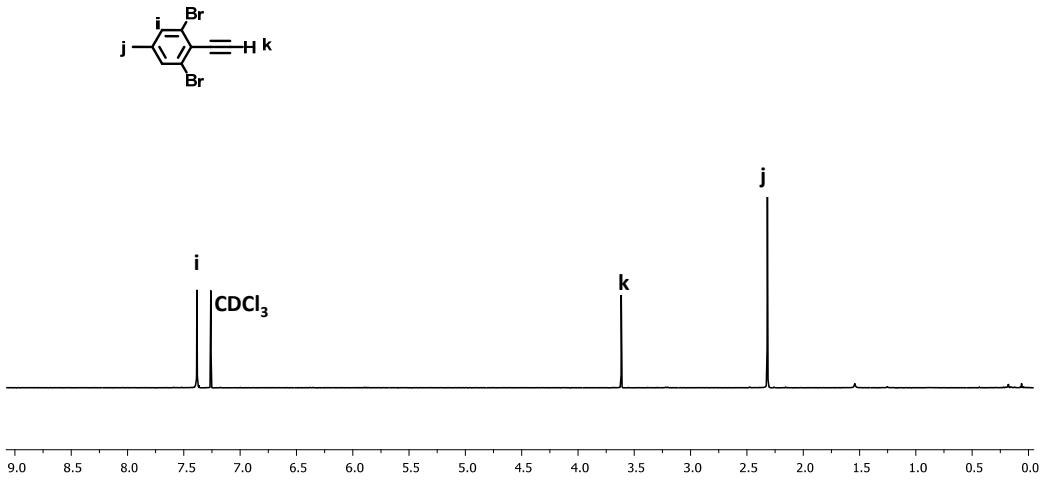


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **8**.

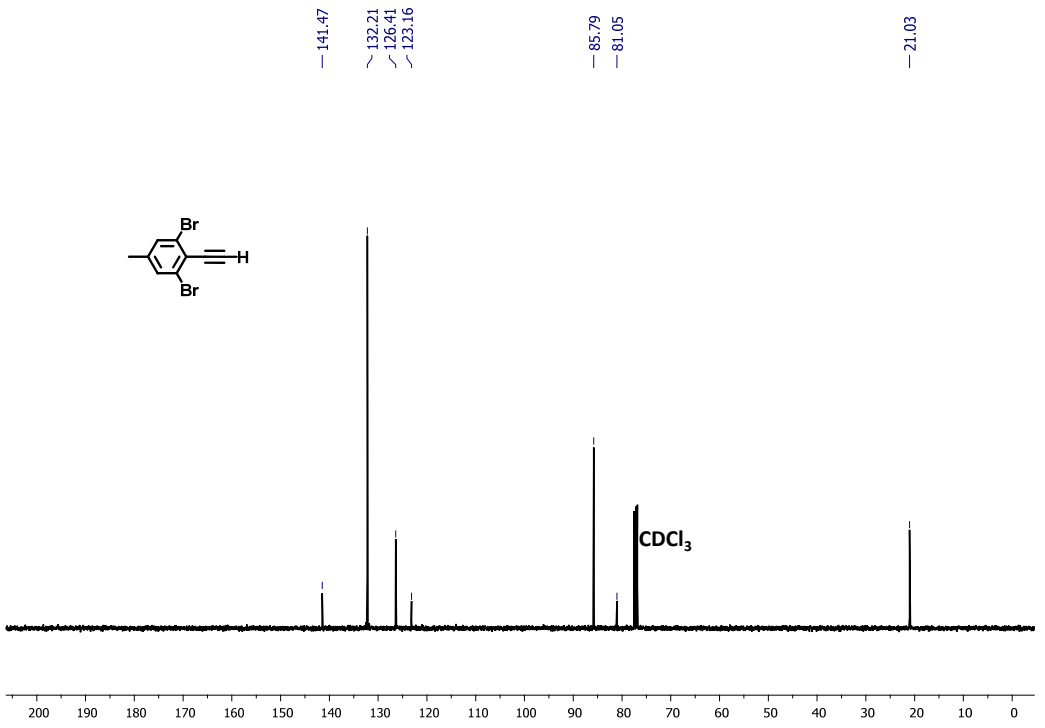


Figure S4. ^{13}C NMR (101 MHz, $CDCl_3$) of compound **8**.

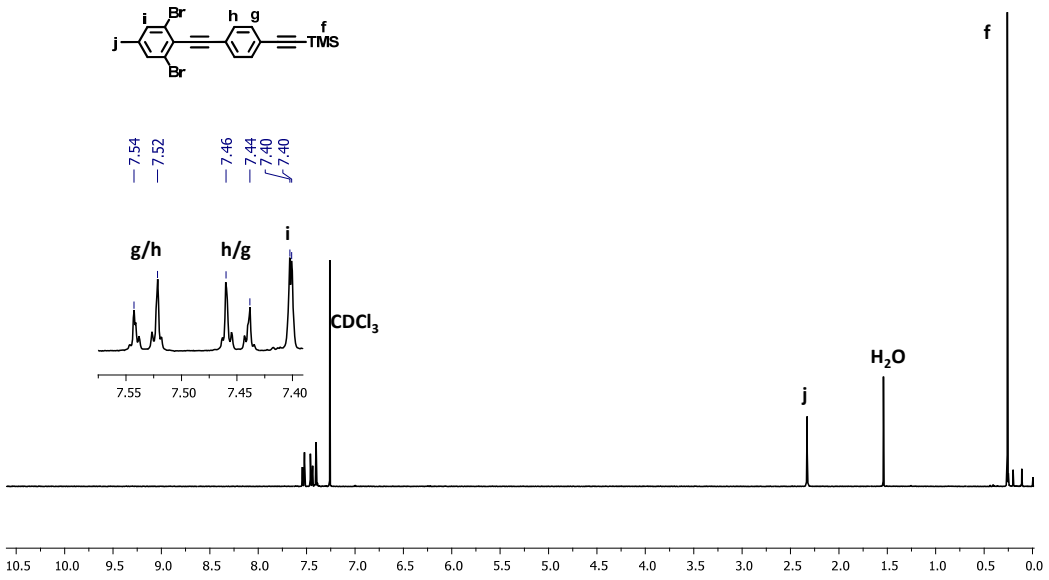


Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **9**.

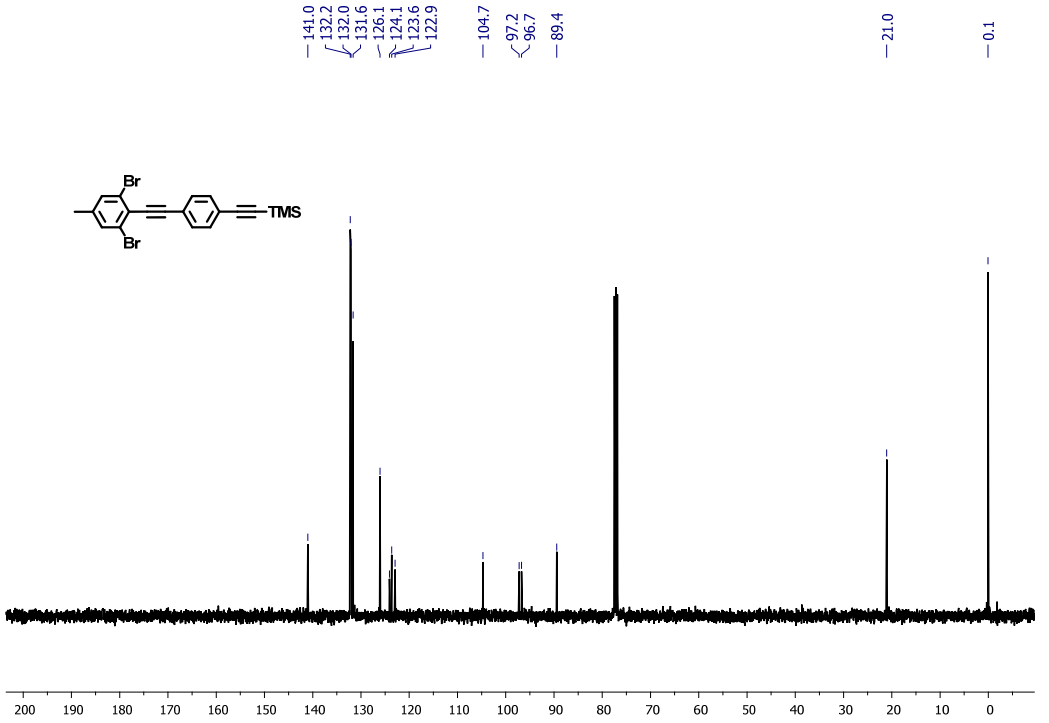


Figure S6. ^{13}C NMR (101 MHz, $CDCl_3$) of compound **9**.

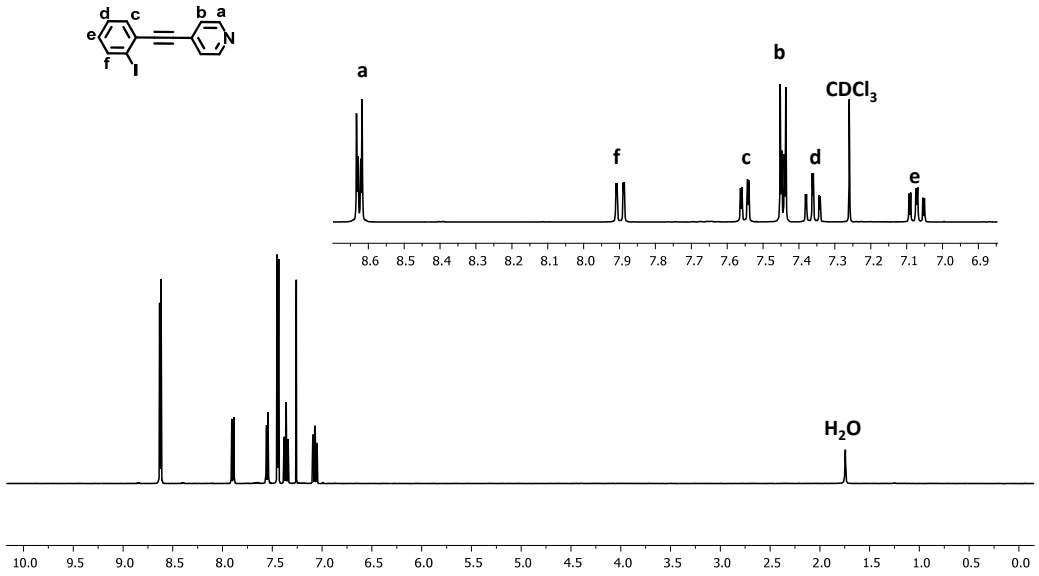


Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **12**.

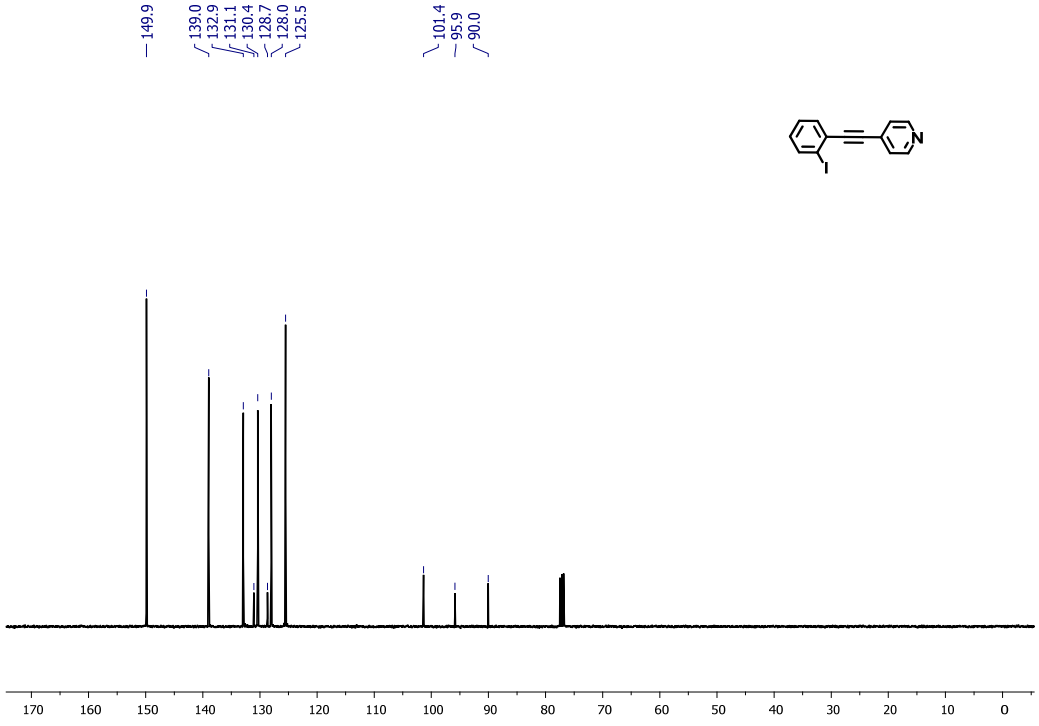


Figure S8. ^{13}C NMR (101 MHz, $CDCl_3$) of compound **12**.

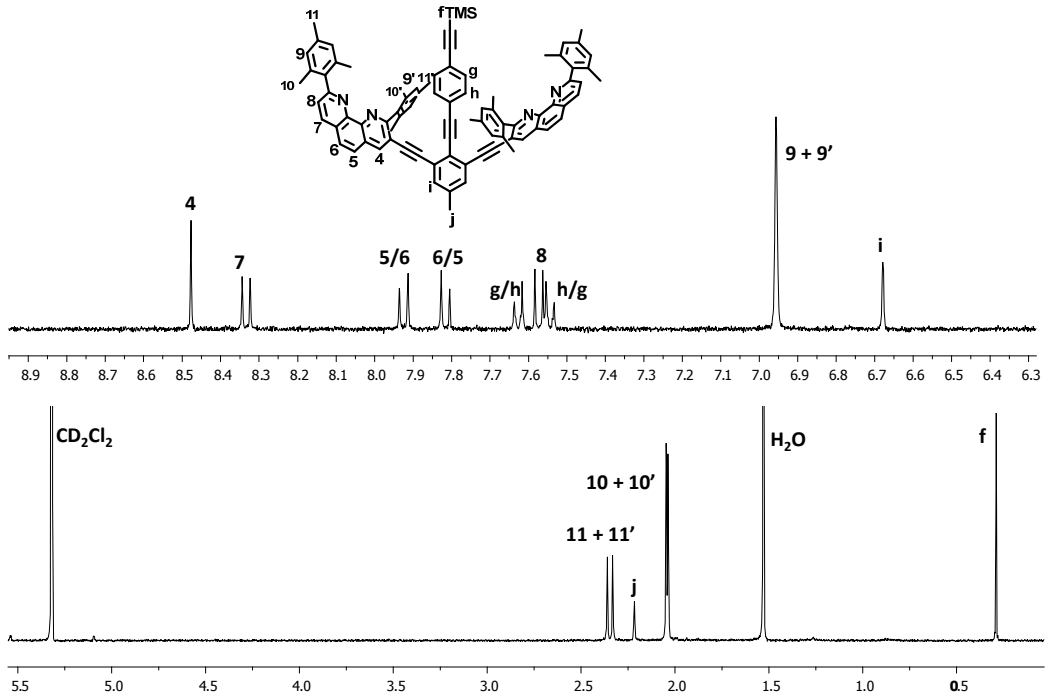


Figure S9. ^{1}H NMR (400 MHz, CD_2Cl_2) of compound **14**.

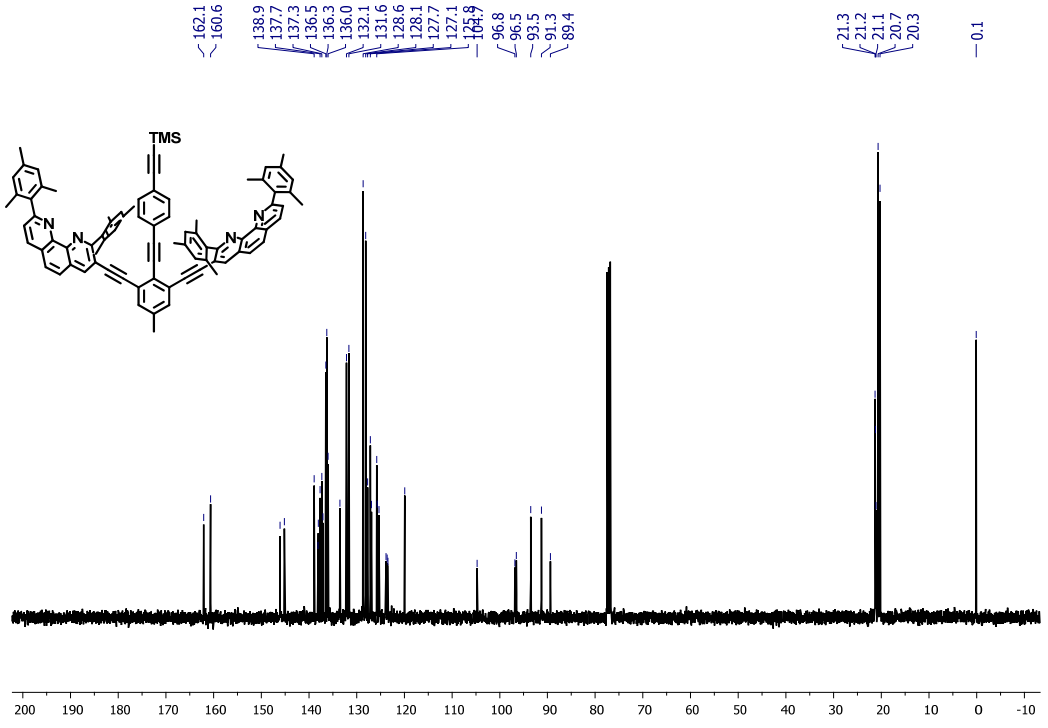


Figure S10. ^{13}C NMR (101 MHz, $CDCl_3$) of compound **14**.

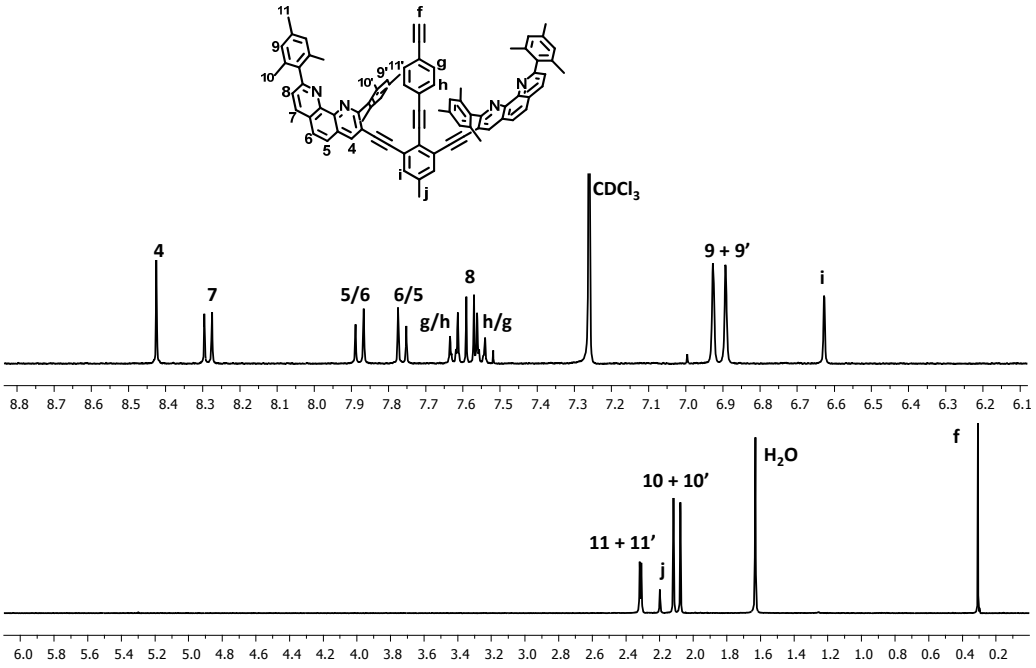


Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **15**.

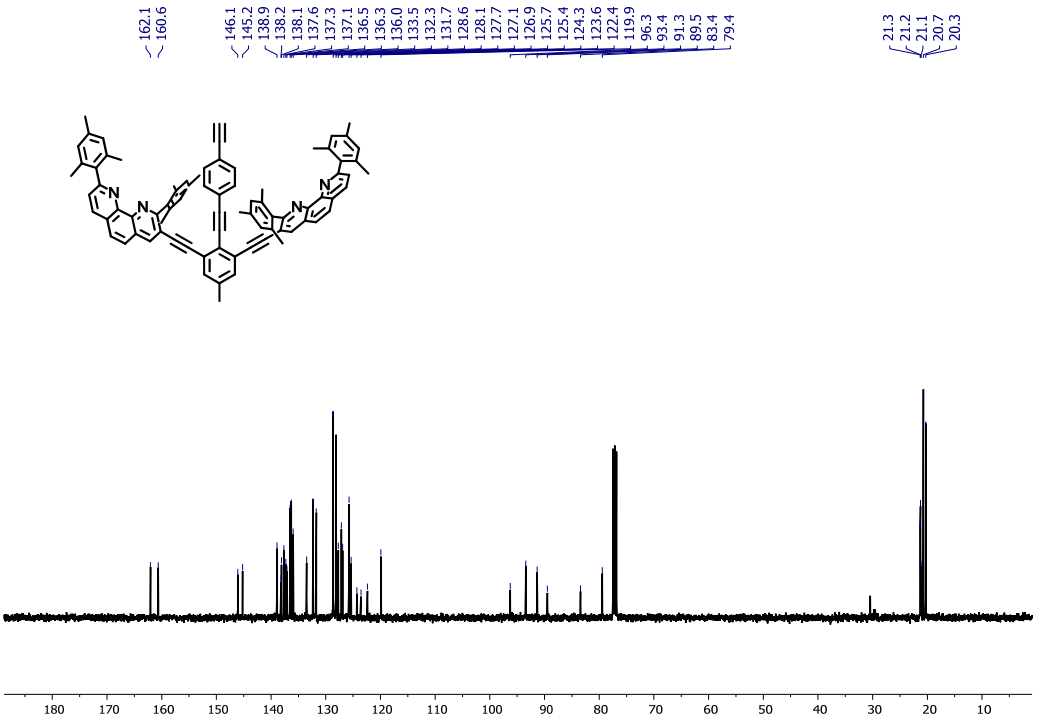


Figure S12. ^{13}C NMR (101 MHz, $CDCl_3$) of compound **15**.

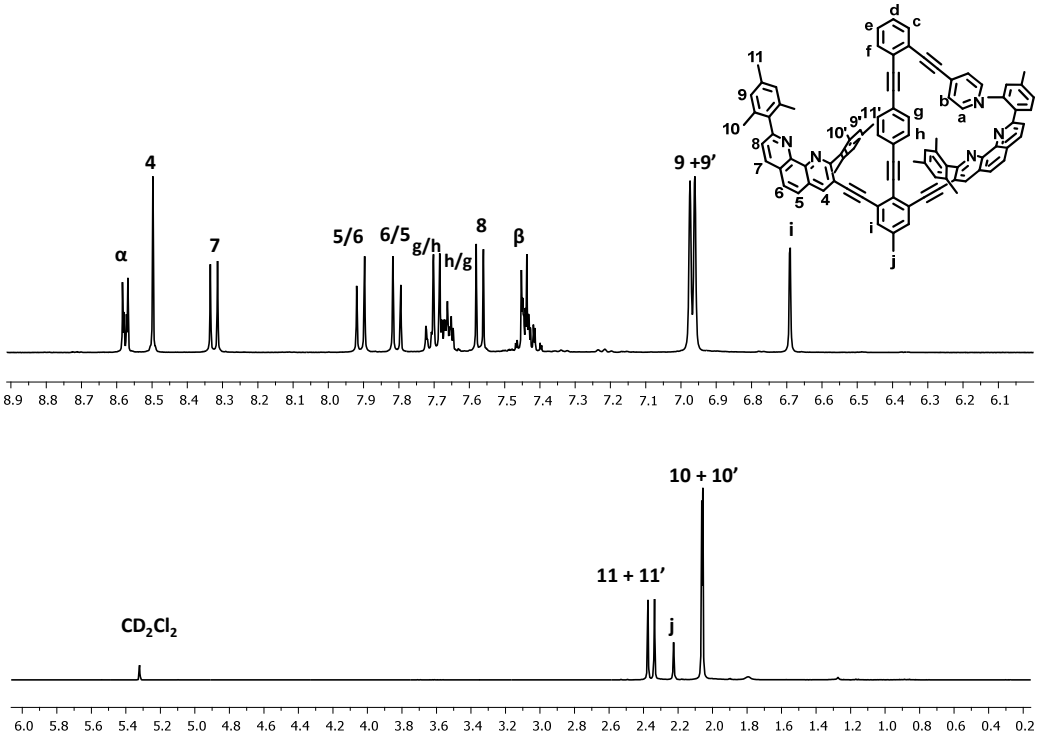


Figure S13. ^{1}H NMR (400 MHz, CD_2Cl_2) of compound **1**.

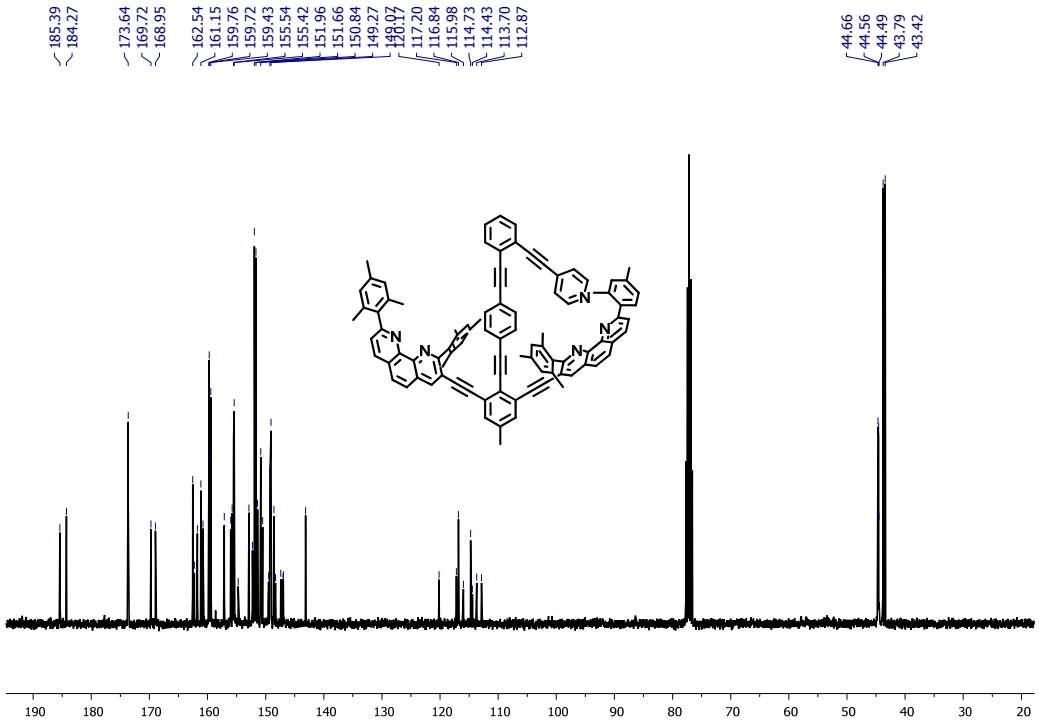


Figure S14. ^{13}C NMR (101 MHz, CD_2Cl_2) of compound **1**.

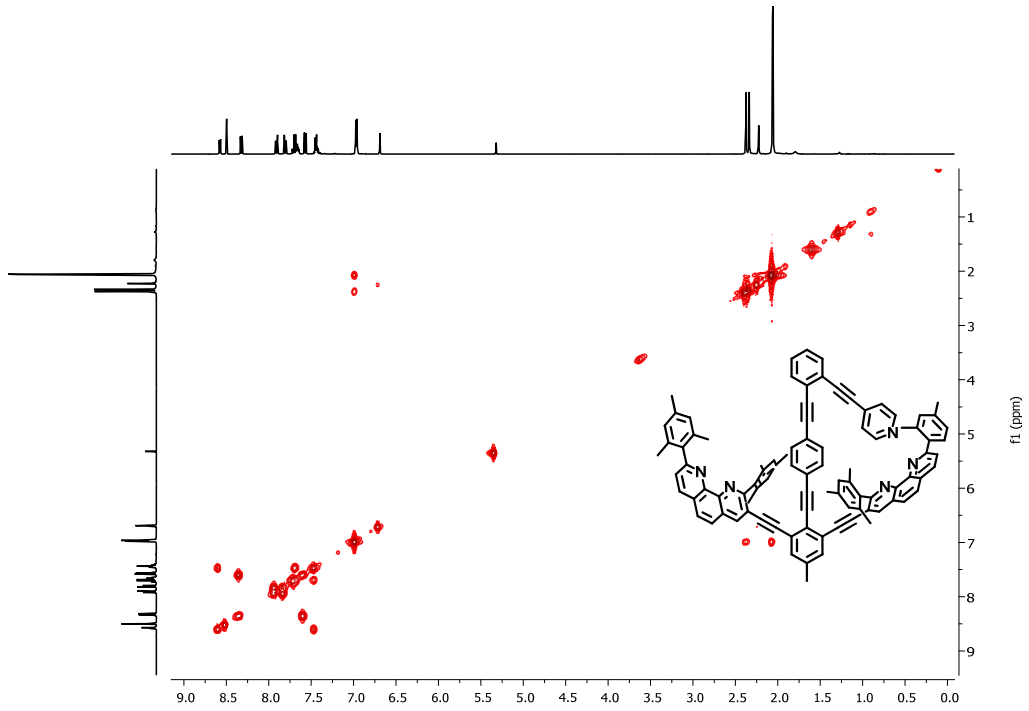


Figure S15. ^{1}H-^{1}H COSY (400 MHz, CD_2Cl_2) of compound **1**.

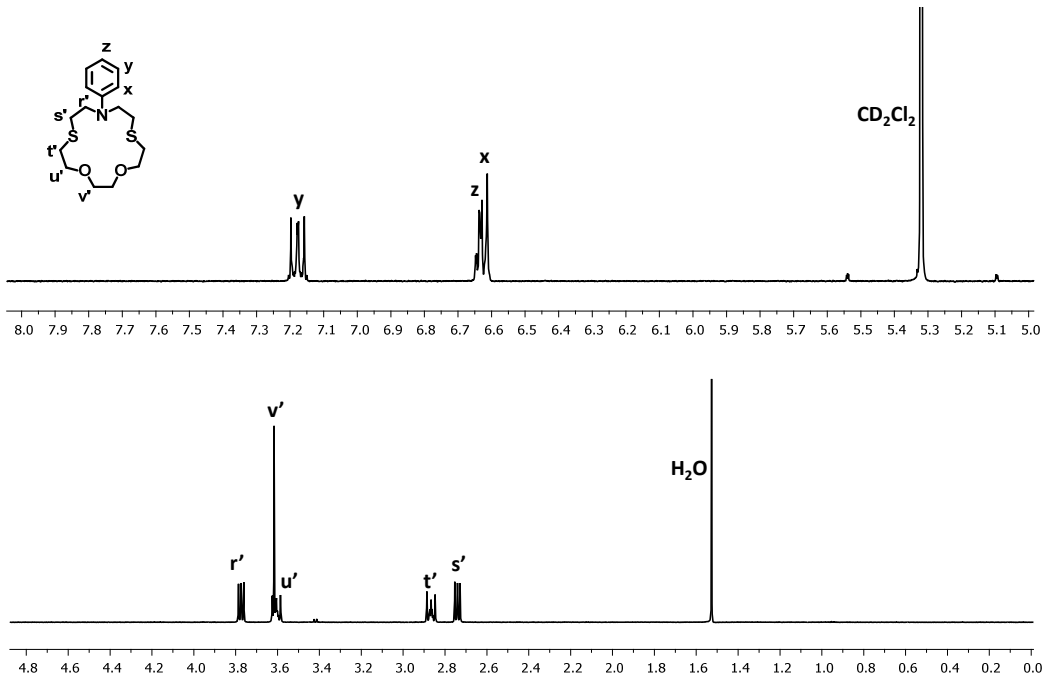


Figure S16. ^{1}H NMR (400 MHz, CD_2Cl_2) of compound **4**.

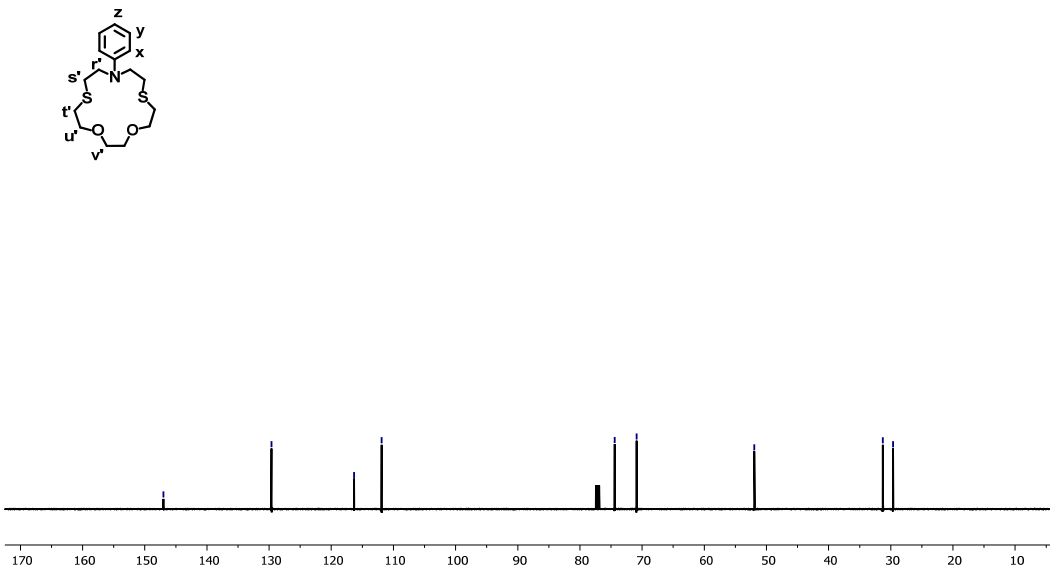


Figure S17. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **14**.

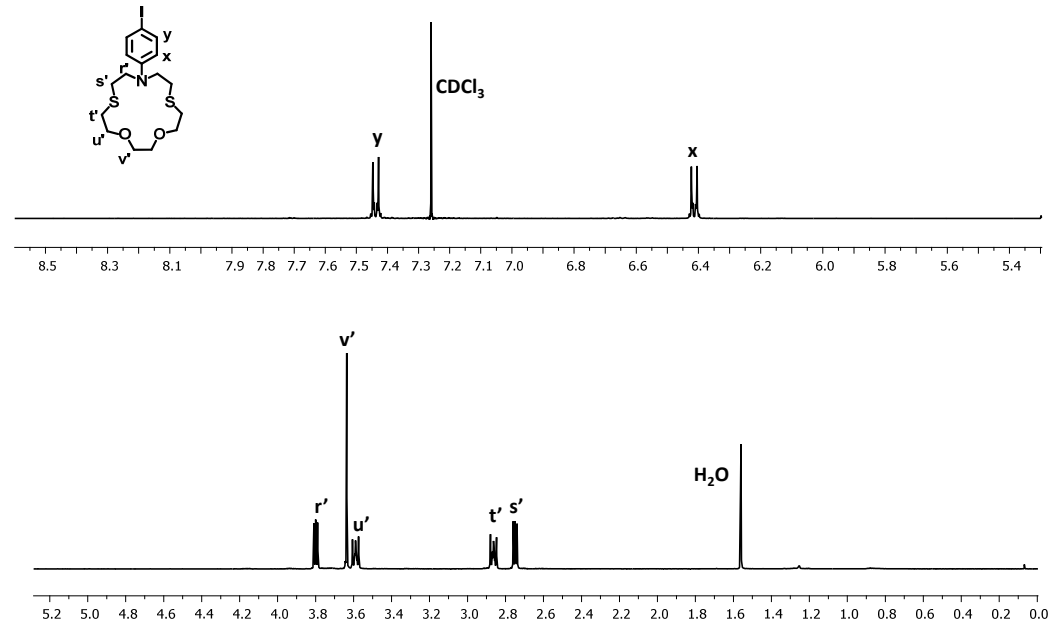


Figure S18. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **16**.

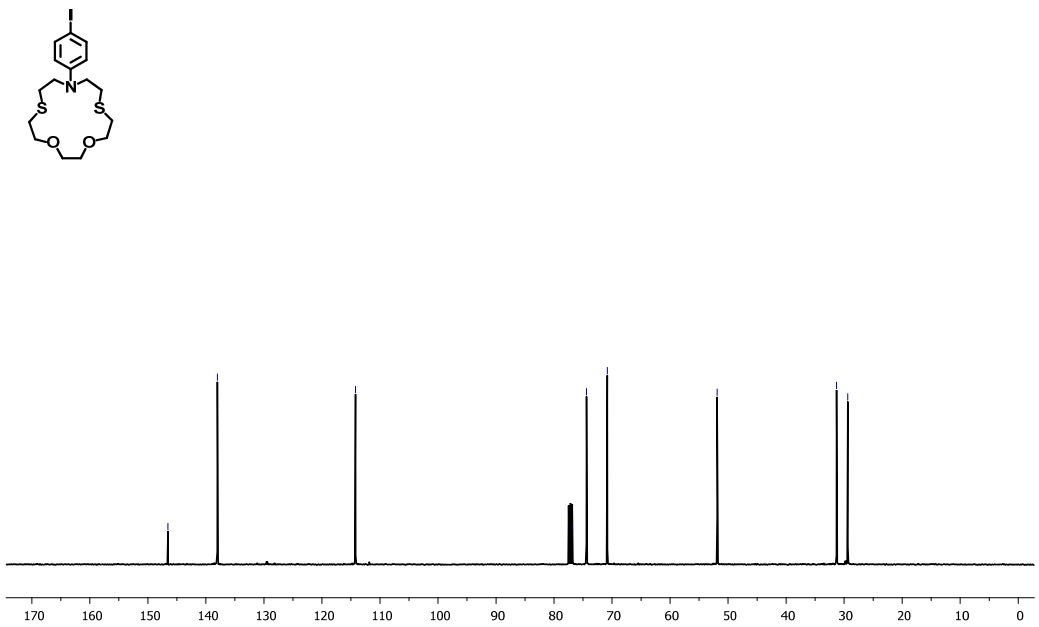


Figure S19. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **16**.

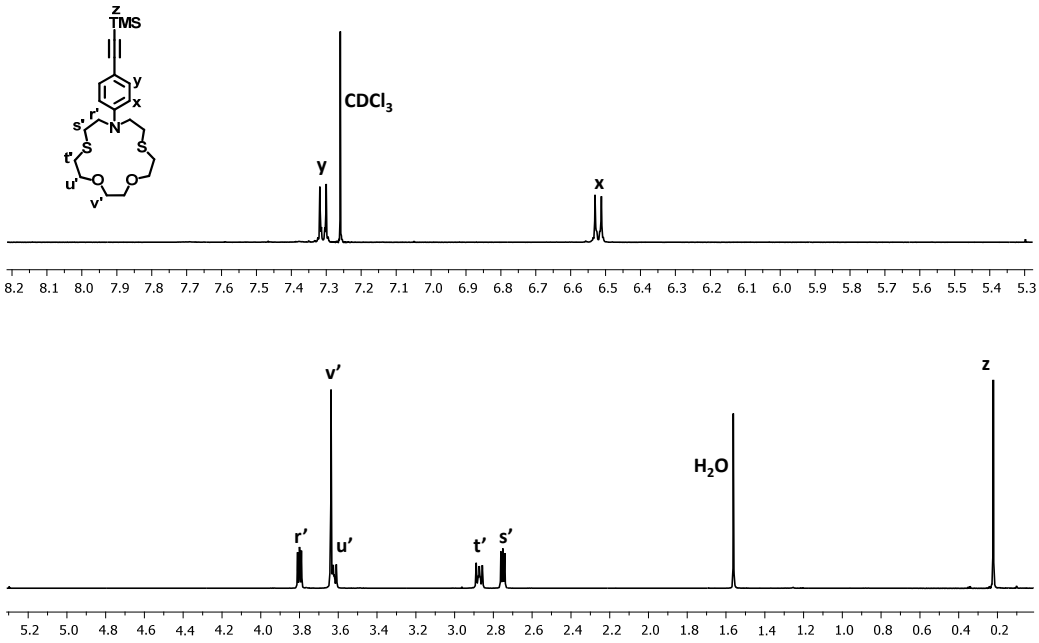


Figure S20. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **17**.

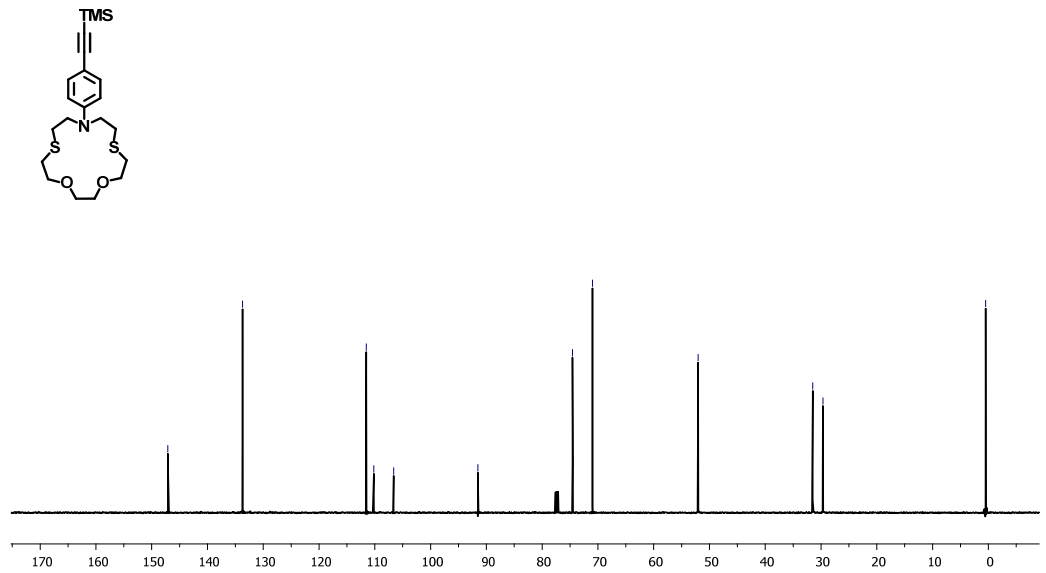


Figure S21. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **17**.

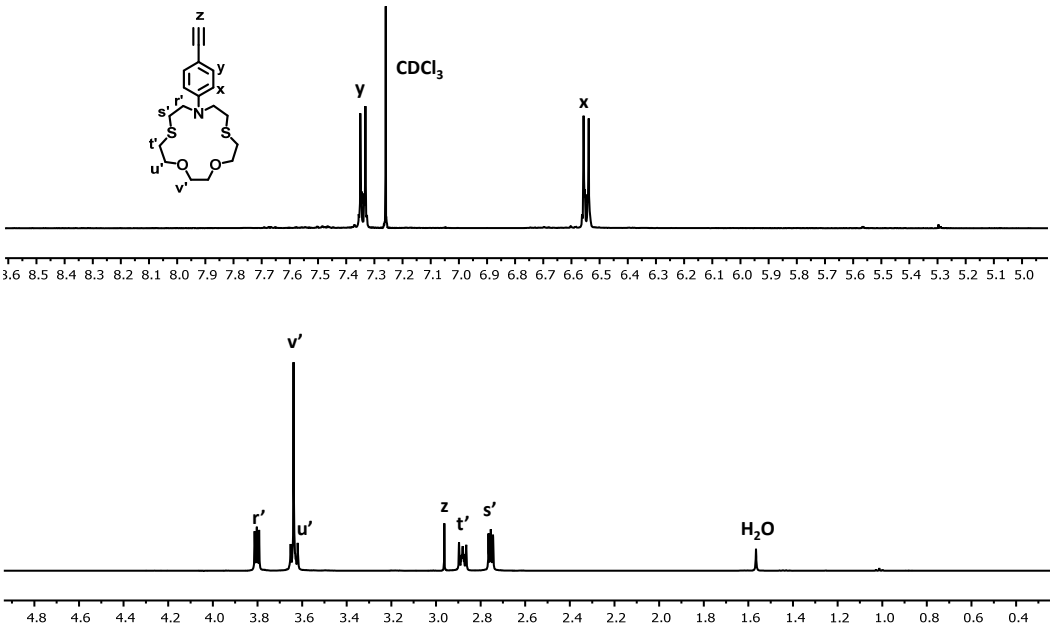


Figure S22. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **18**.

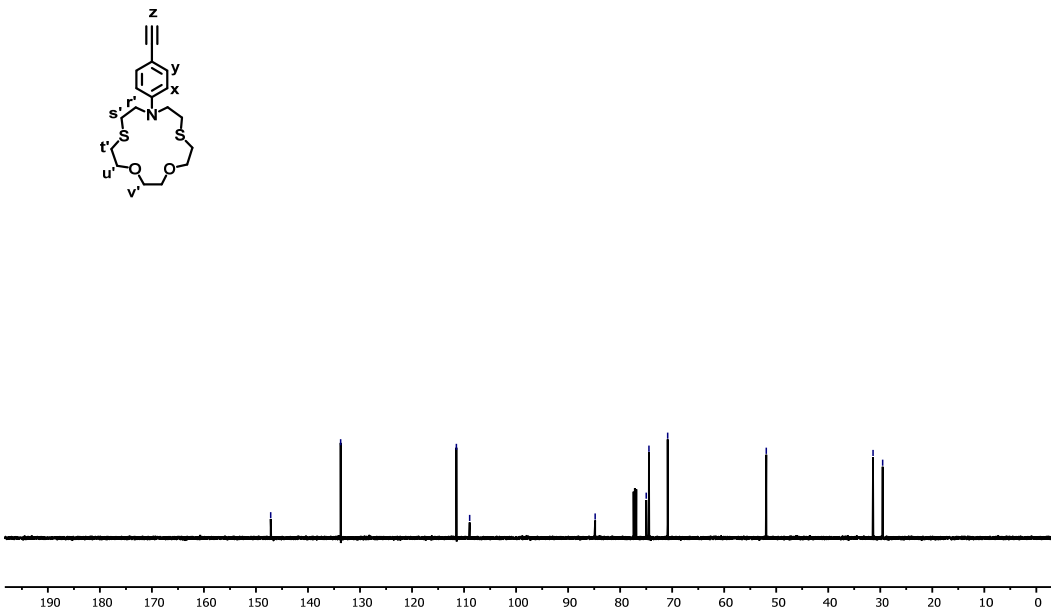


Figure S23. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **18**.

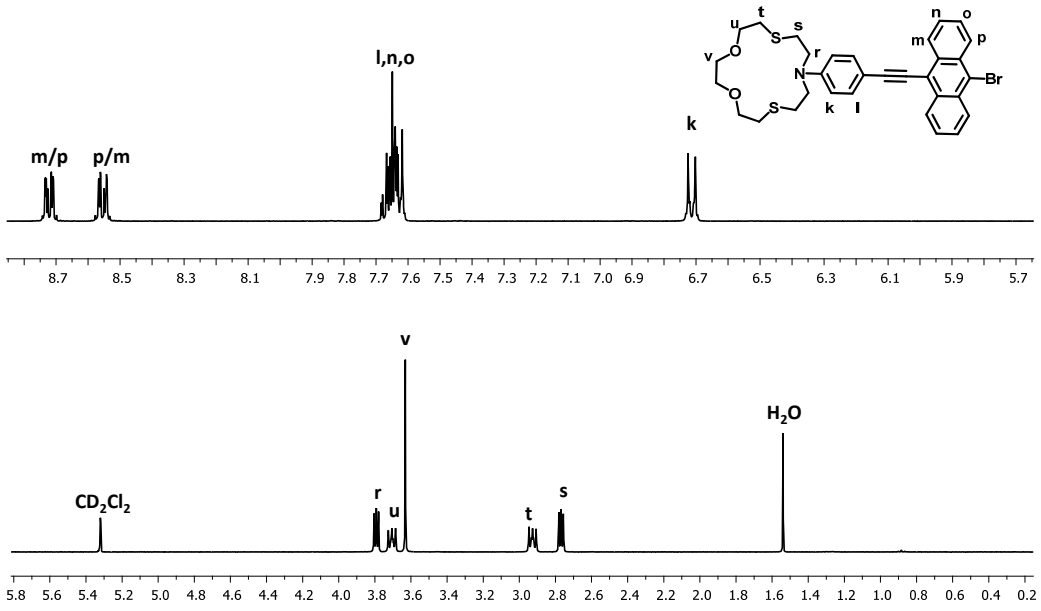


Figure S24. ^{1}H NMR (400 MHz, CD_2Cl_2) of compound **2**.

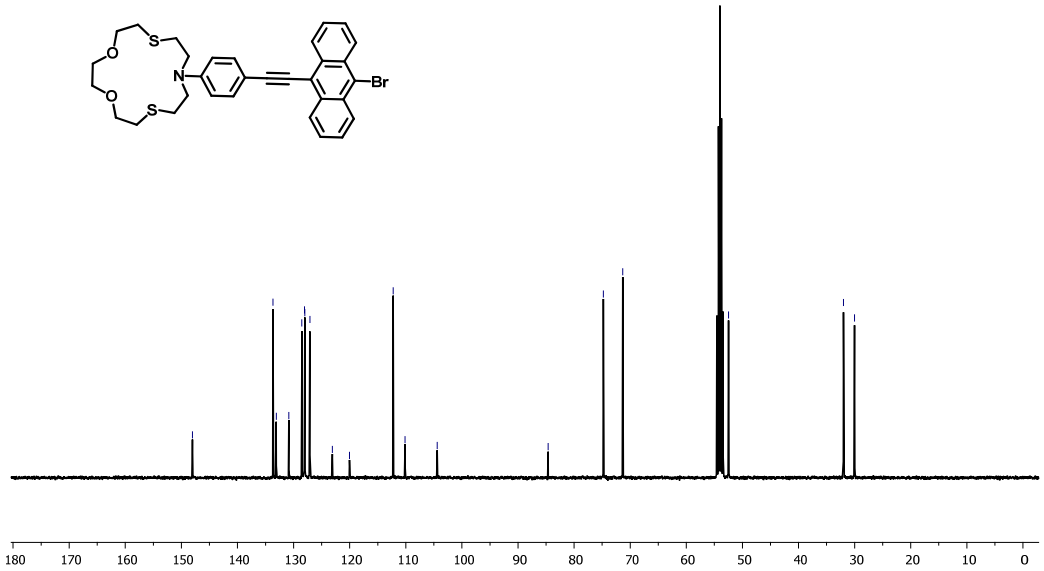


Figure S25. ^{13}C NMR (101 MHz, $CDCl_3$) of compound **2**.

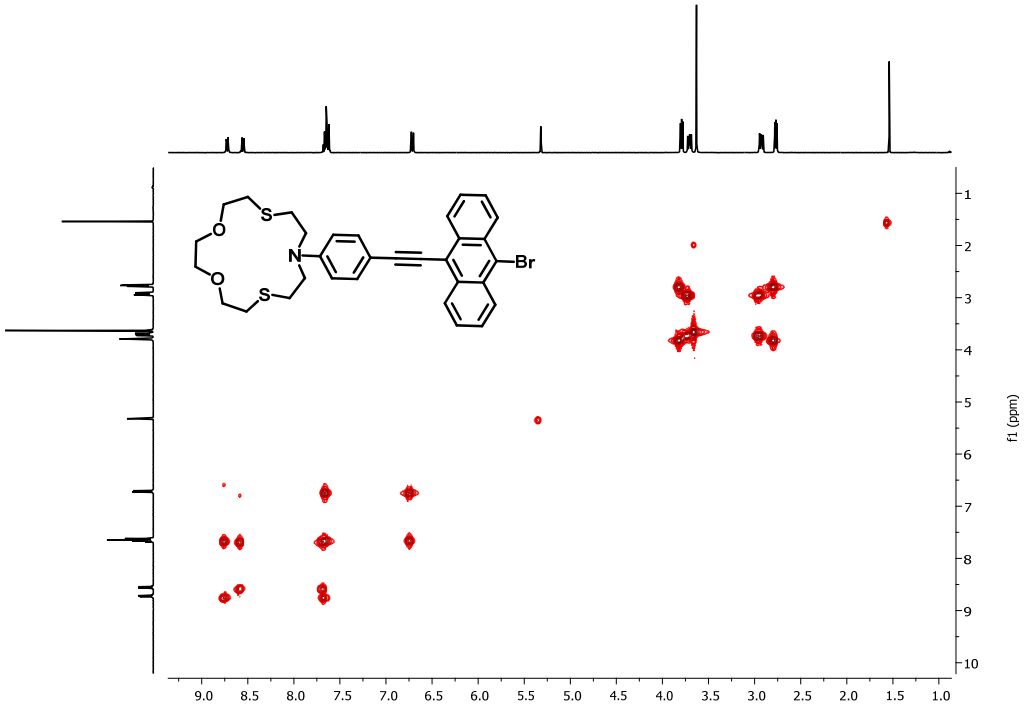


Figure S26. ^{1}H-^{1}H COSY (400 MHz, CD_2Cl_2) of compound **2**.

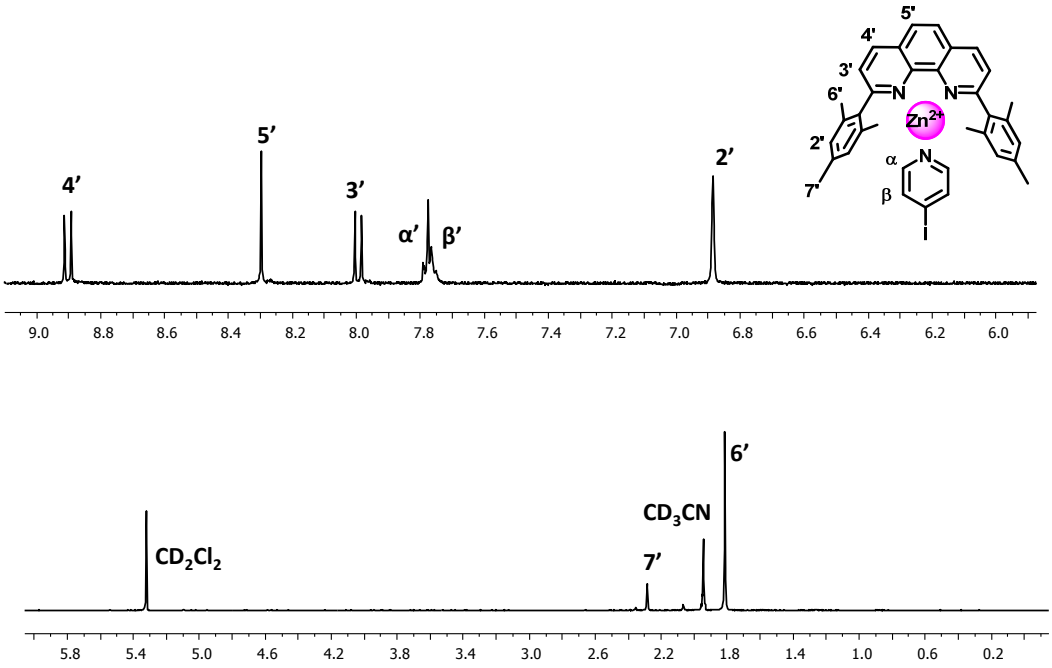


Figure S27. ^{1}H NMR (400 MHz, CD_2Cl_2:CD_3CN, 98:2) of complex [Zn(**3**)(**5**)](OTf)$_2$.

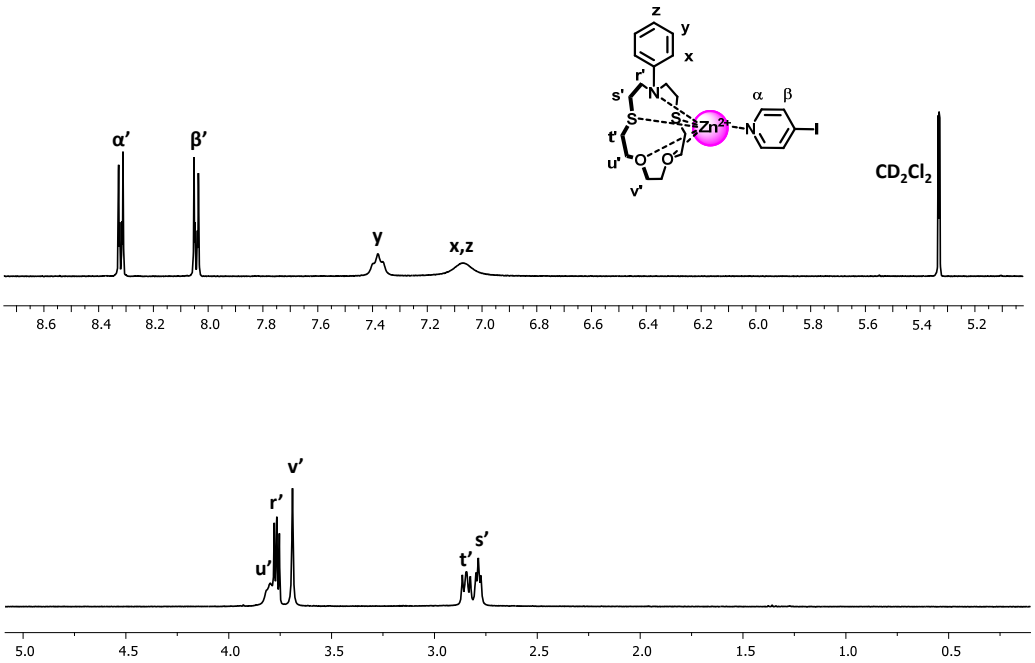


Figure S28. ^{1}H NMR (400 MHz, CD_2Cl_2) of complex [Zn(**4**)(**5**)](OTf)$_2$.

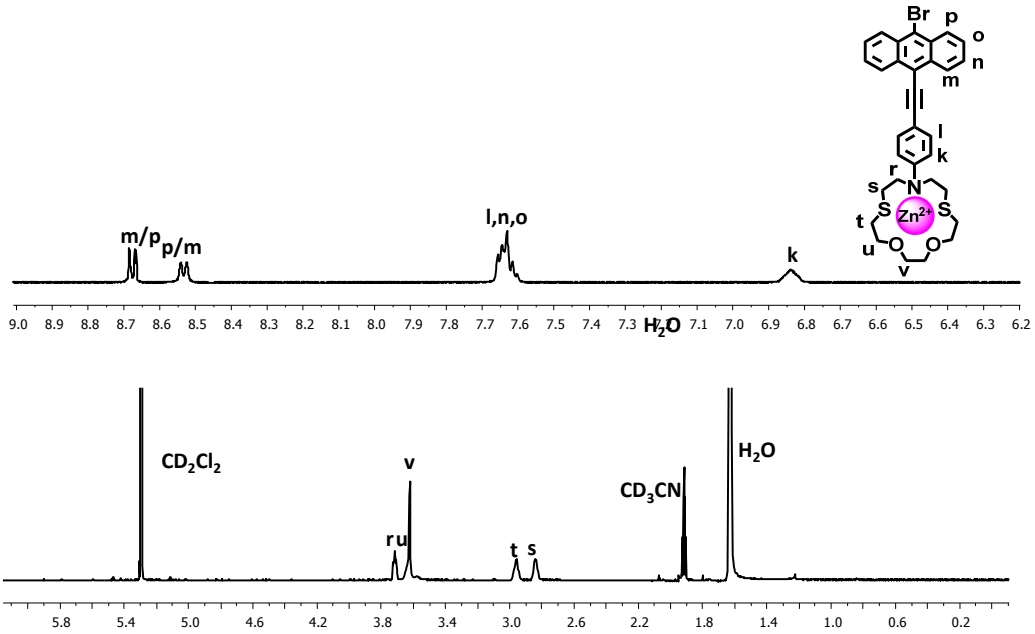


Figure S29. ^{1}H NMR (400 MHz, CD_2Cl_2:CD_3CN, 98:2) of complex [Zn(**2**)](OTf)$_2$.

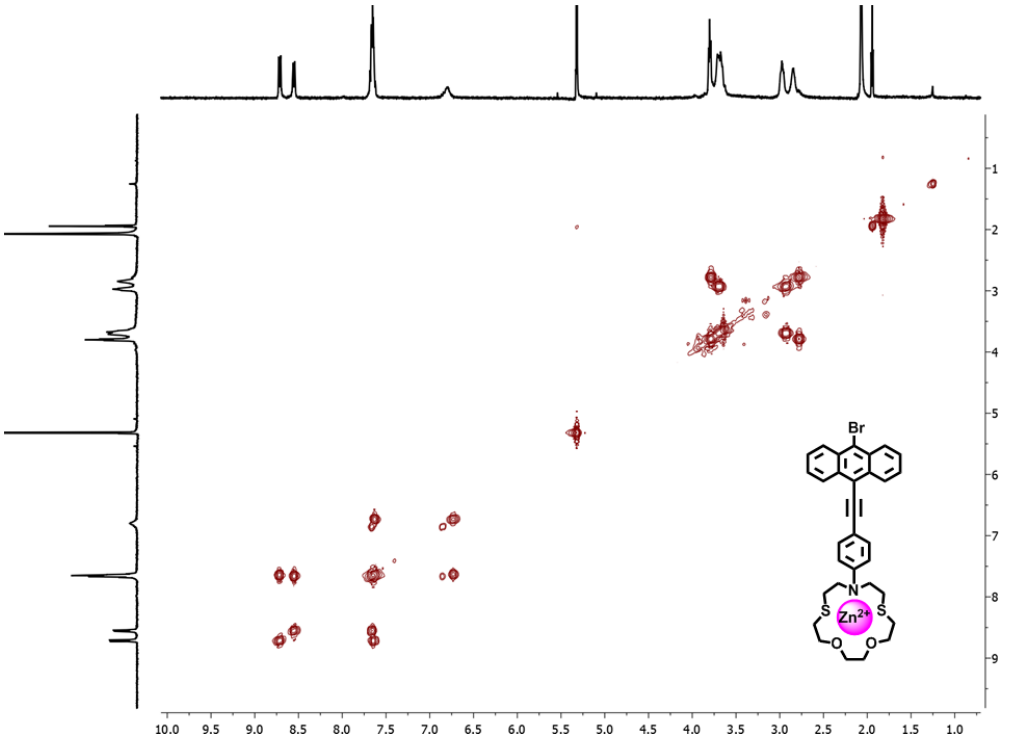


Figure S30. ^{1}H-^{1}H COSY (400 MHz, CD_2Cl_2:CD_3CN, 95:5) of complex [Zn(**2**)](OTf)$_2$.

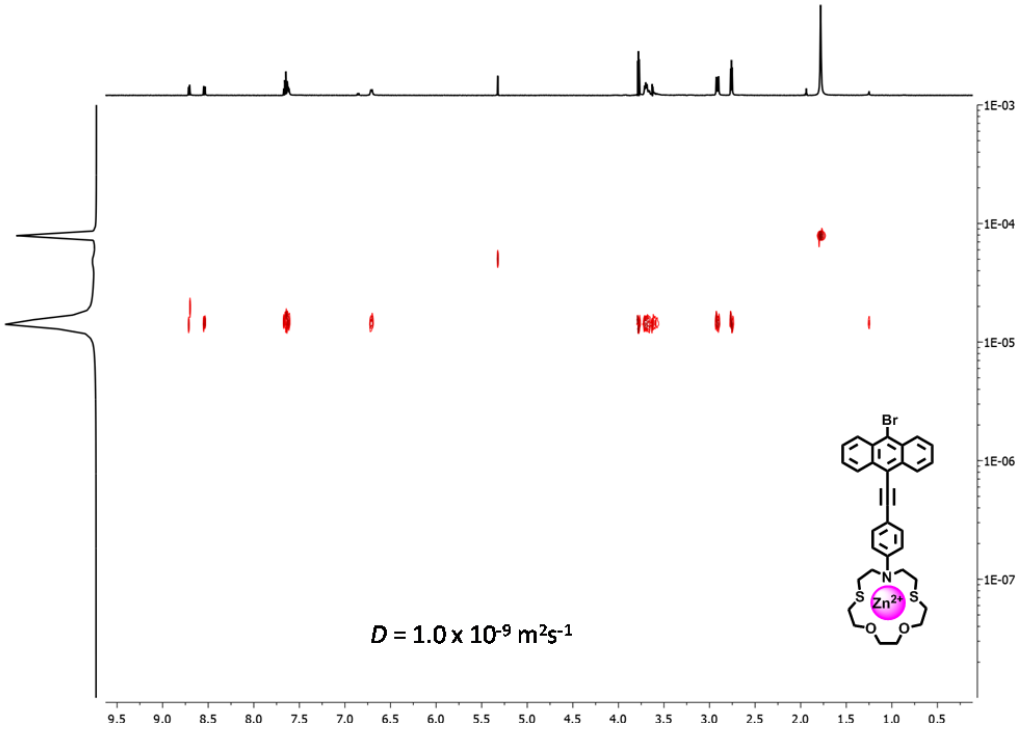


Figure S31. ^{1}H DOSY NMR (600 MHz, CD_2Cl_2:CD_3CN, 95:5) of complex [Zn(**2**)](OTf)$_2$.

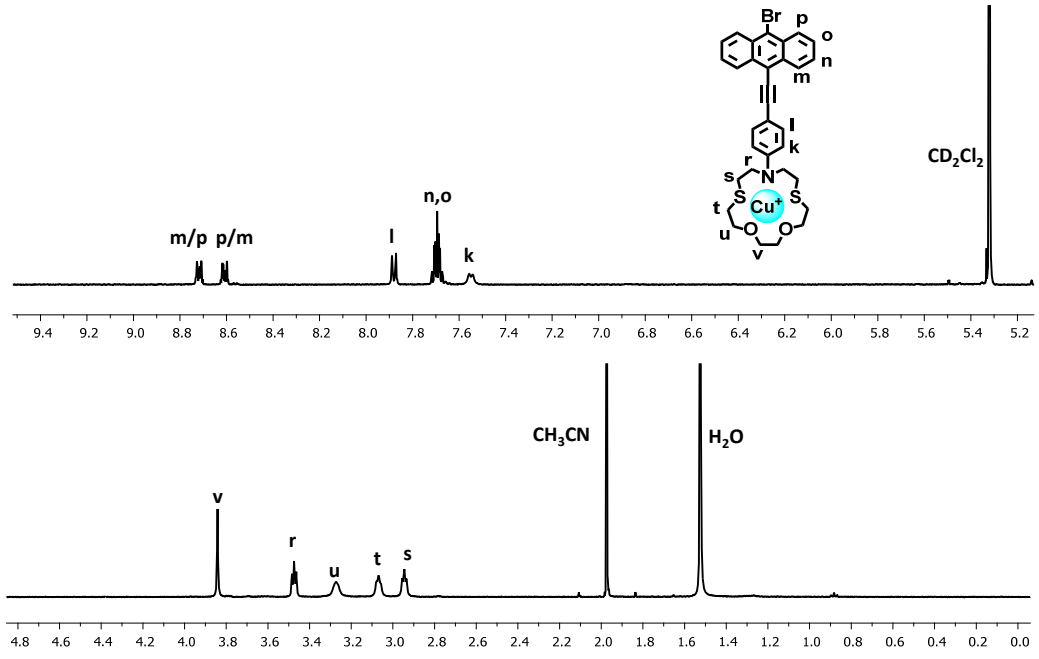


Figure S32. ^{1}H NMR (500 MHz, CD_2Cl_2) of complex [Cu(**2**)]PF_6.

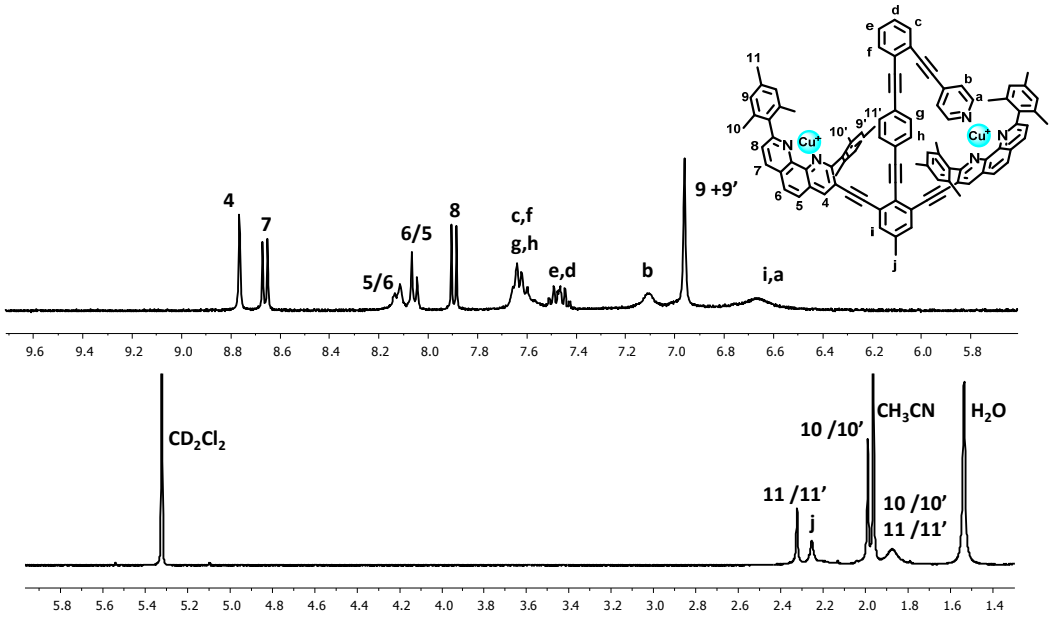


Figure S33. ^{1}H NMR (400 MHz, CD_2Cl_2) of complex $[Cu_2(\mathbf{1})](PF_6)_2$.

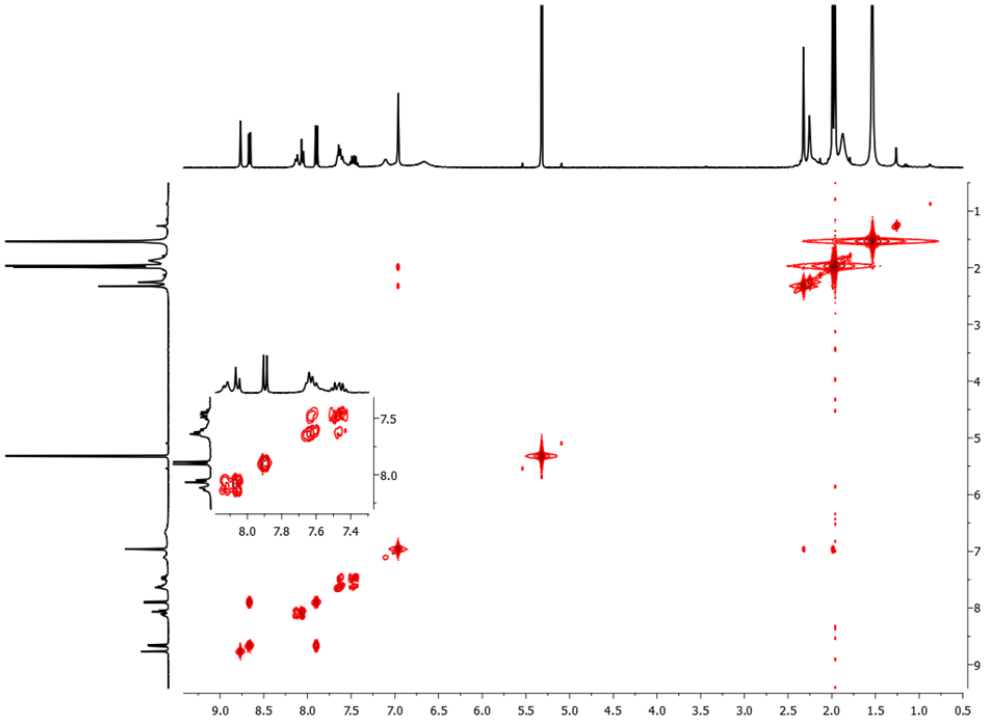


Figure S34. ^{1}H-^{1}H COSY (400 MHz, CD_2Cl_2) of complex $[Cu_2(\mathbf{1})](PF_6)_2$.

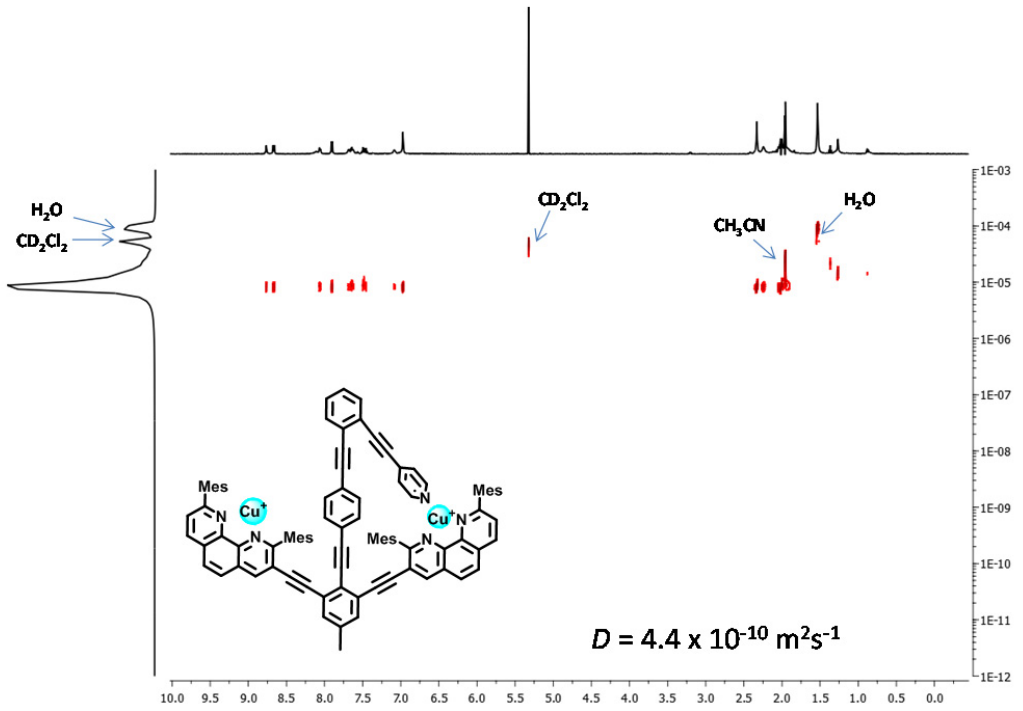


Figure S35. ^{1}H DOSY NMR (600 MHz, CD_2Cl_2) of complex $[Cu_2(\mathbf{1})](PF_6)_2$.

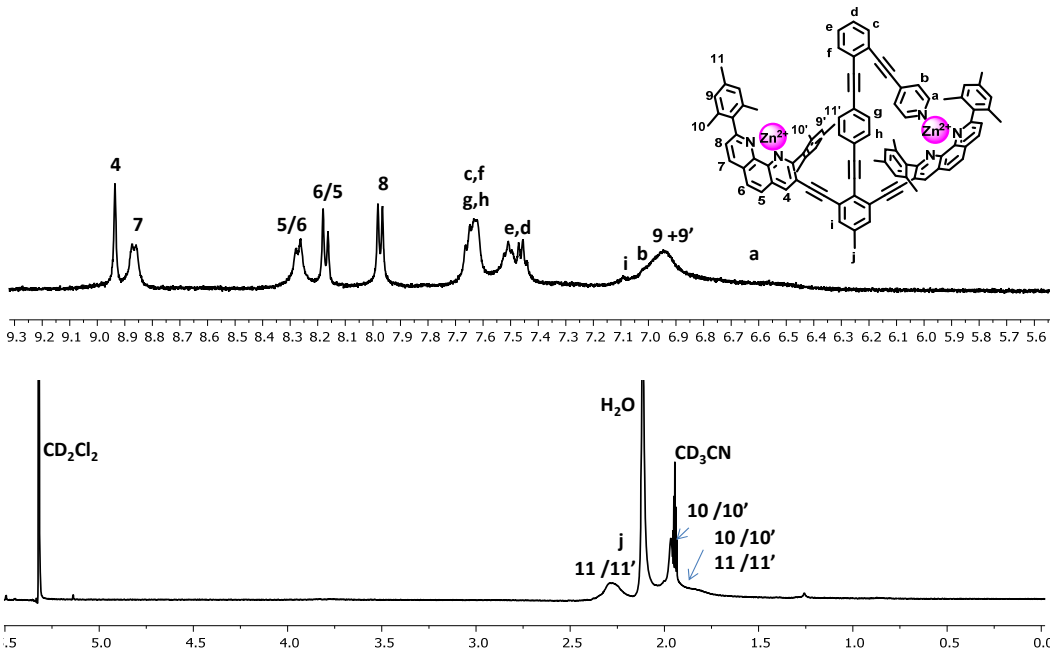


Figure S36. ^{1}H NMR (500 MHz, CD_2Cl_2:CD_3CN, 96:4) of complex $[Zn_2(\mathbf{1})](OTf)_4$.

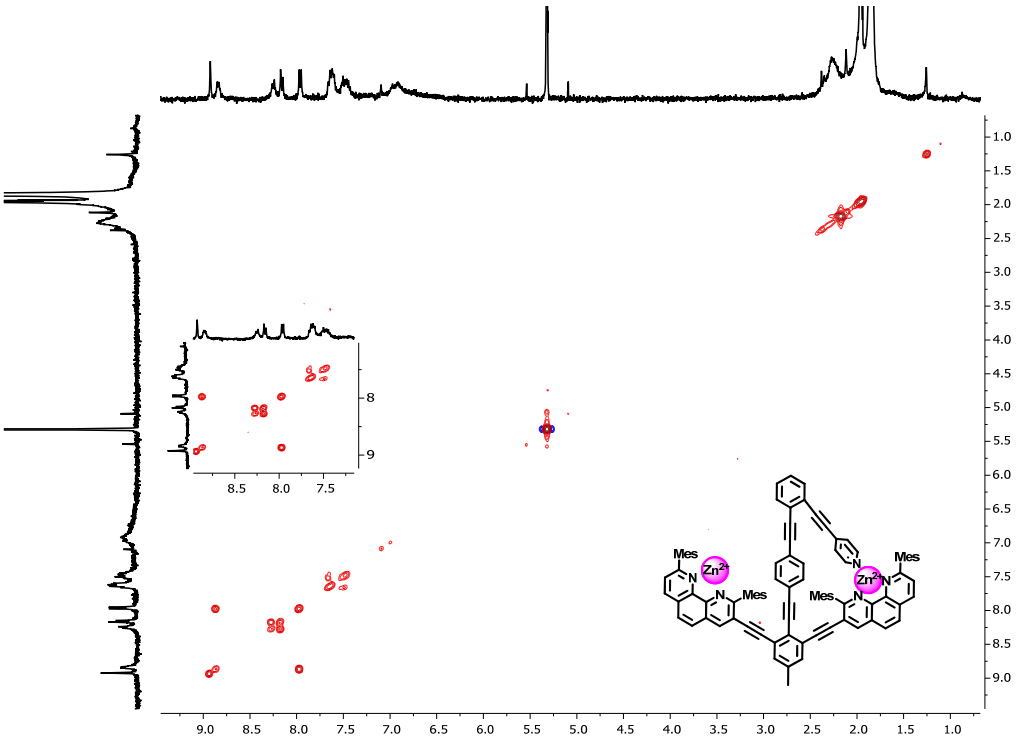


Figure S37. ^{1}H-^{1}H COSY (400 MHz, CD_2Cl_2:CD_3CN, 96:4) of complex [Zn_2(**1**)](OTf)$_4$.

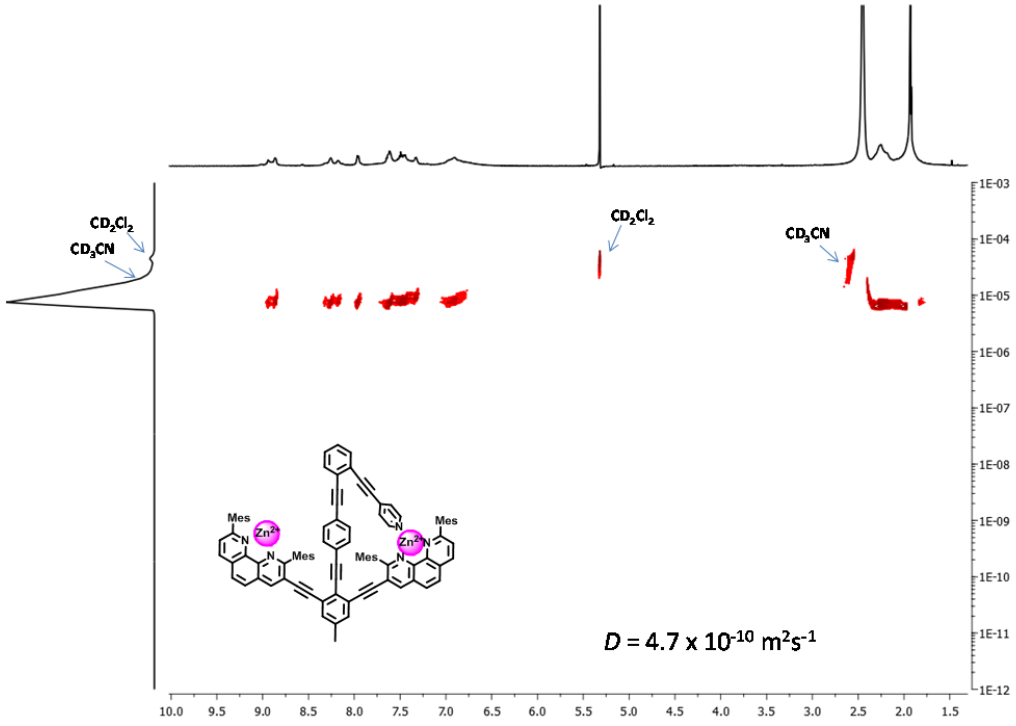


Figure S38. ^{1}H DOSY NMR (600 MHz, CD_2Cl_2:CD_3CN, 96:4) of complex [Zn_2(**1**)](OTf)$_4$.

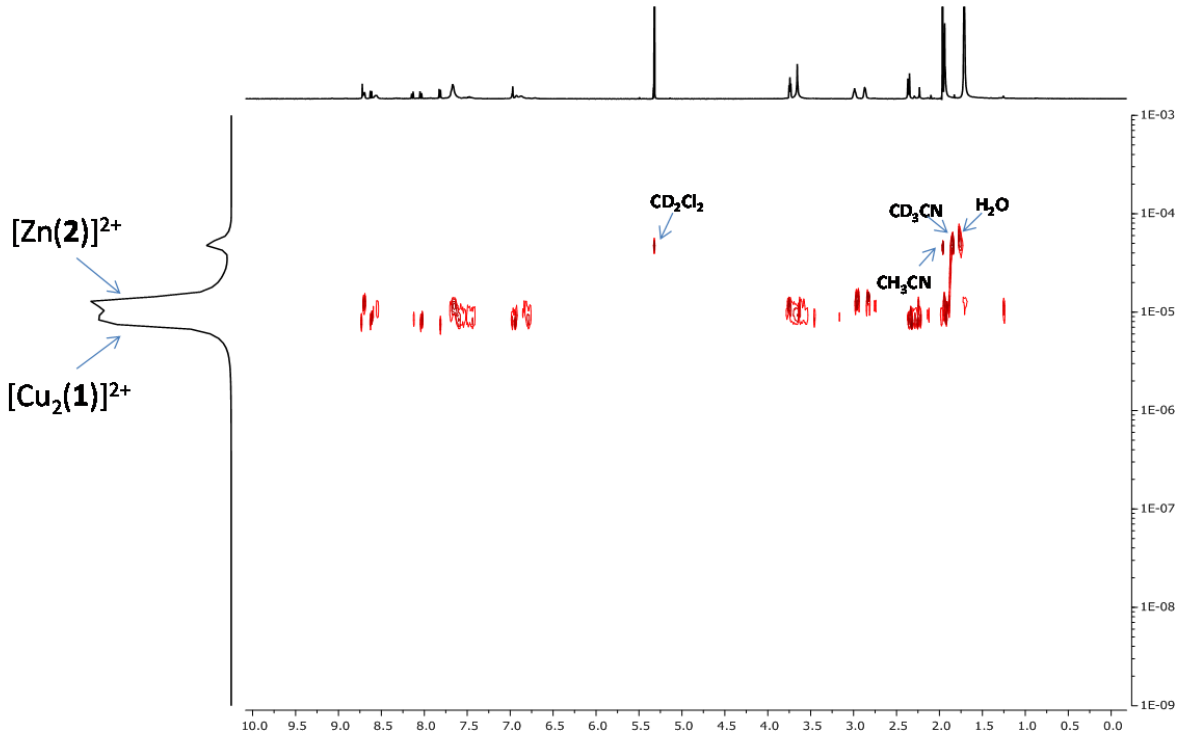


Figure S39. ^{1}H DOSY NMR (600 MHz, CD_2Cl_2:CD_3CN, 96:4) of complexes $[Cu_2(\mathbf{1})](PF_6)_2$ and $[Zn(\mathbf{2})](OTf)_2$.

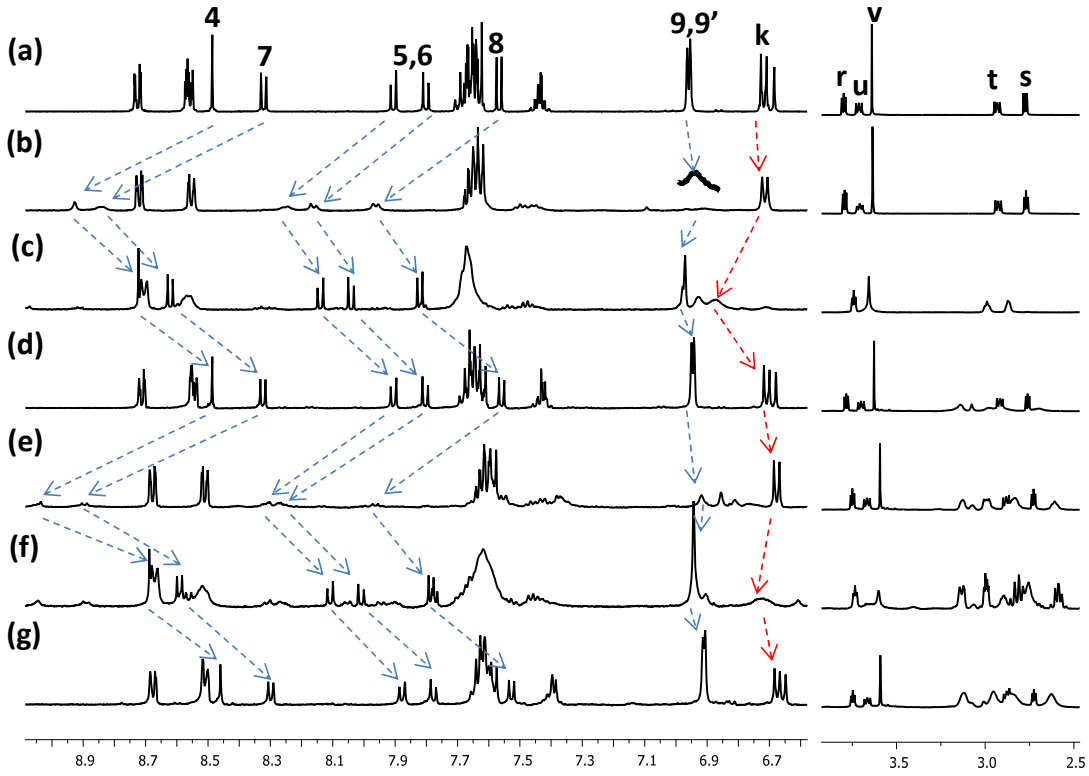


Figure S40. ^{1}H NMR (500 MHz, 298 K) showing the *in situ* network between rotor **1** and receptor **2** upon sequential addition of Zn^{2+} & Cu^{+} and removal of metal ions with cyclam. (a) Ligands **1** and **2** were mixed in 1:2 ratio in CD_2Cl_2; (b) addition of 2 equiv. of $Zn(OTf)_2$ in 20 µL of CD_3CN to ligands depicted in spectrum (a) furnished $[Zn_2(\mathbf{1})]^{4+}$ and **2** in CD_2Cl_2:CD_3CN (96:4); (c) addition of 2 equiv. of $[Cu(CH_3CN)_4]PF_6$ to the mixture depicted in spectrum (b) provided $[Cu_2(\mathbf{1})]^{2+}$ and $[Zn(\mathbf{2})]^{2+}$ in CD_2Cl_2:CD_3CN (96:4); (d) for removing Zn^{2+} & Cu^{+}, 4 equiv. of cyclam were added to the mixture depicted in (c) thus regenerating ligands **1** and **2** in CD_2Cl_2:CD_3CN (96:4); (e) addition of 2 equiv. of $Zn(OTf)_2$ in 20 µL of CD_3CN to ligands depicted in spectrum (d) afforded $[Zn_2(\mathbf{1})]^{4+}$ and **2** in CD_2Cl_2:CD_3CN (93:7); (f) addition of 2 equiv. of $[Cu(CH_3CN)_4]PF_6$ to mixture depicted in spectrum (e) afforded $[Cu_2(\mathbf{1})]^{2+}$ and $[Zn(\mathbf{2})]^{2+}$ in CD_2Cl_2:CD_3CN (93:7); (g) addition of 4 equiv. of cyclam to the mixture depicted in (f) furnished ligands **1** and **2** in CD_2Cl_2:CD_3CN (93:7).

3. Variable temperature ^{1}H NMR

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

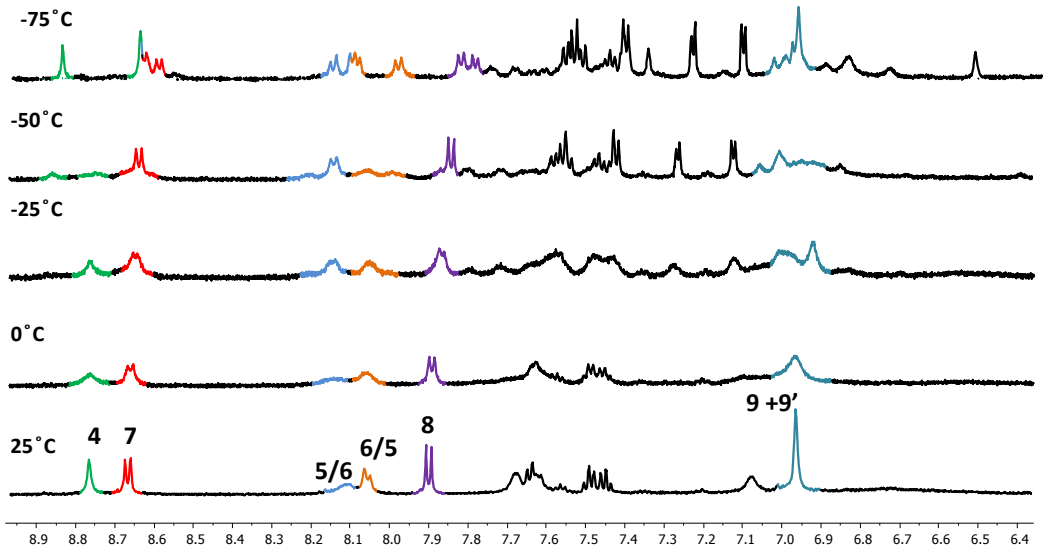


Figure S41. Partial ^{1}H VT-NMR (600 MHz, CD_2Cl_2) of $[Cu_2(\mathbf{1})](PF_6)_2$ shows splitting of protons 4, 5, 6, 7, 8 and 9-H.

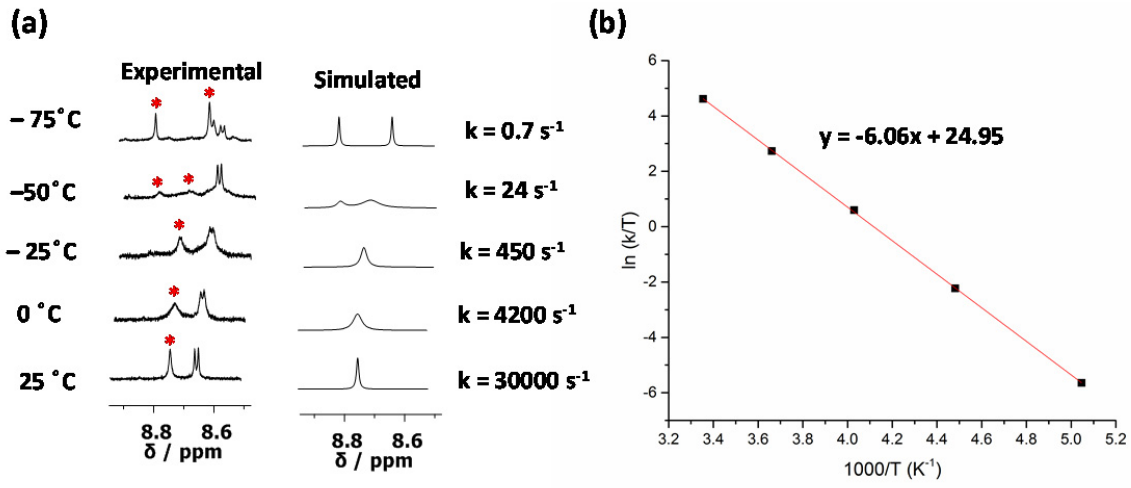


Figure S42. (a) Partial ^{1}H VT-NMR (600 MHz, CD_2Cl_2) of $[Cu_2(\mathbf{1})](PF_6)_2$ shows the splitting of proton 4-H (red asterisk marked). (b) Eyring plot for rotational dynamics in rotor $[Cu_2(\mathbf{1})](PF_6)_2$.

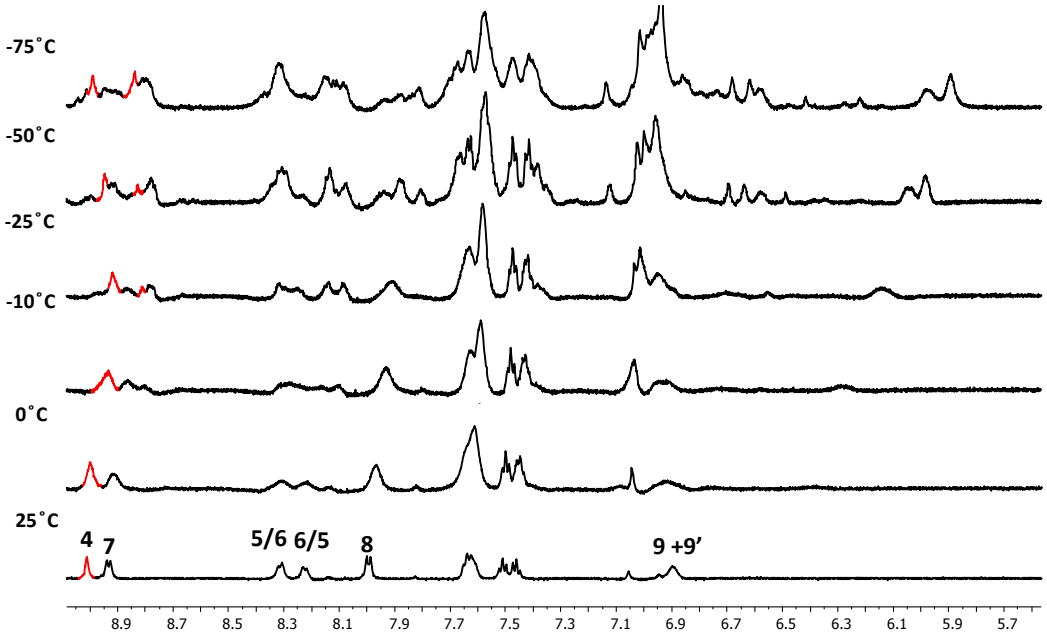


Figure S43. Partial ^{1}H VT-NMR (600 MHz, CD_2Cl_2:CD_3CN, 80:20) of $[Zn_2(\mathbf{1})](OTf)_4$ showing splitting of proton 4-H. Broadening and splitting of other aromatic protons are also observed.

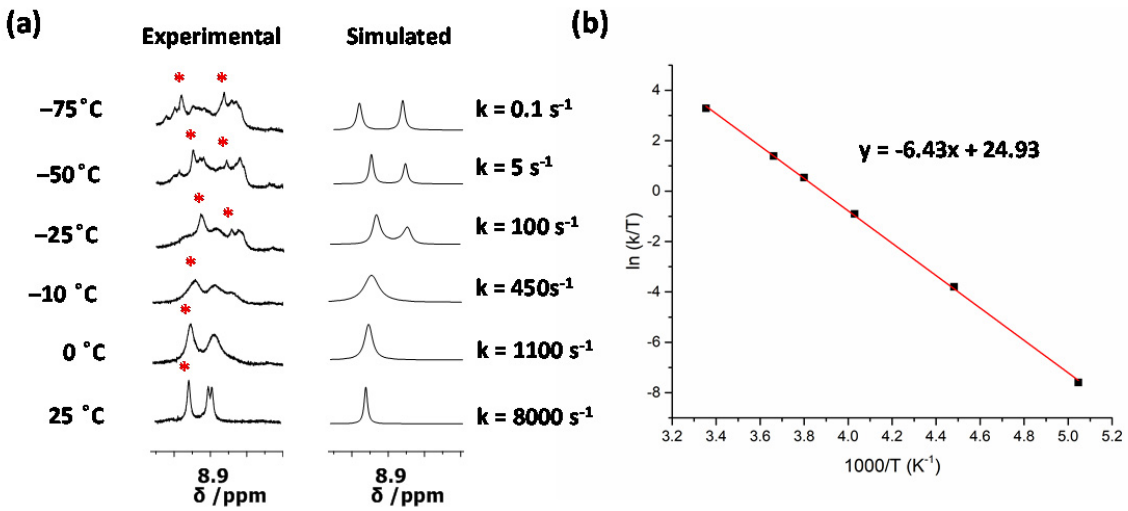


Figure S44. (a) Partial ^{1}H VT-NMR (600 MHz, CD_2Cl_2:CD_3CN, 80:20) of $[Zn_2(\mathbf{1})](OTf)_4$ shows the splitting of 4-H (red asterisk marked). (b) Eyring plot for rotational dynamics in rotor $[Zn_2(\mathbf{1})](OTf)_4$.

4. ESI-MS

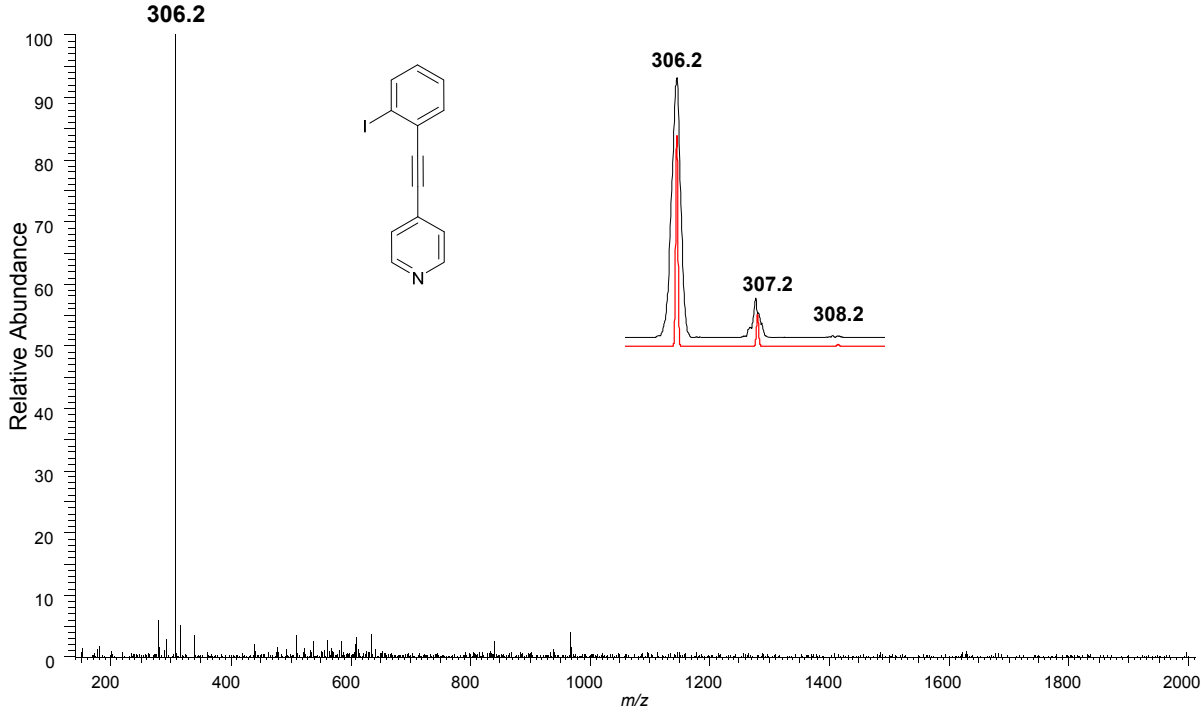


Figure S45. ESI-MS spectrum of [**12** + H]$^+$ in CH_2Cl_2 (protonation by CH_3CO_2H).

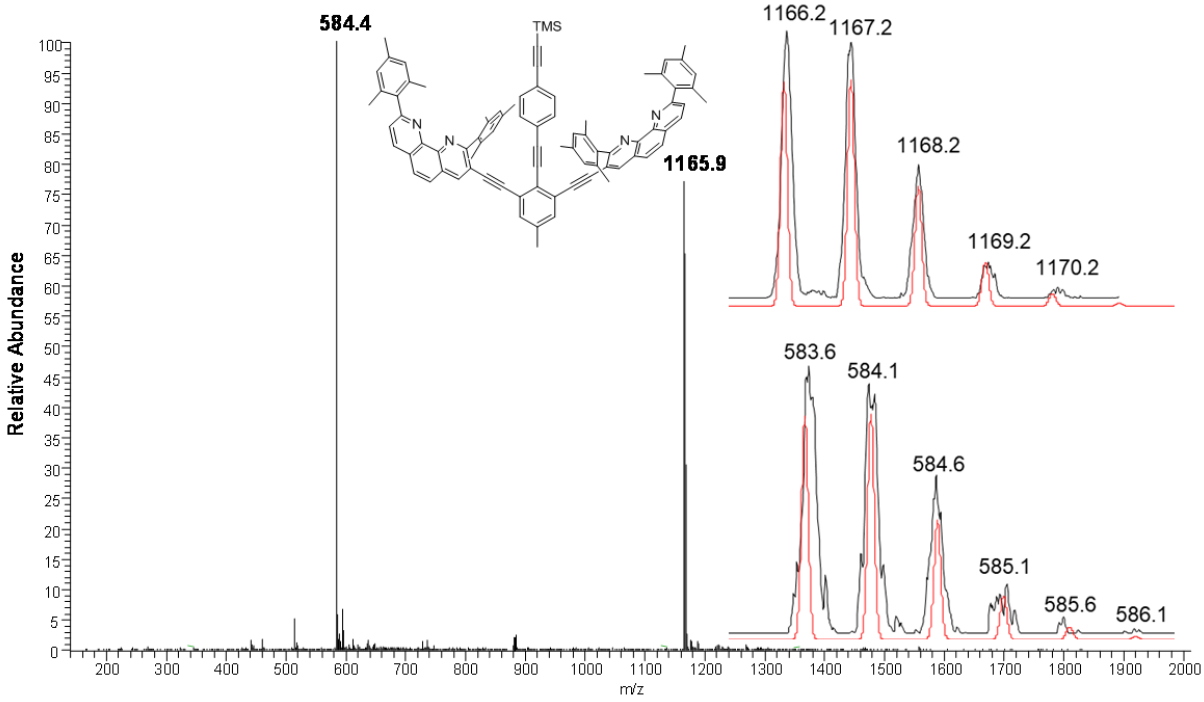


Figure S46. ESI-MS spectrum of [**14** + H]$^+$ and [**14** + 2H]$^{2+}$ in CH_2Cl_2 (protonation by CH_3CO_2H).

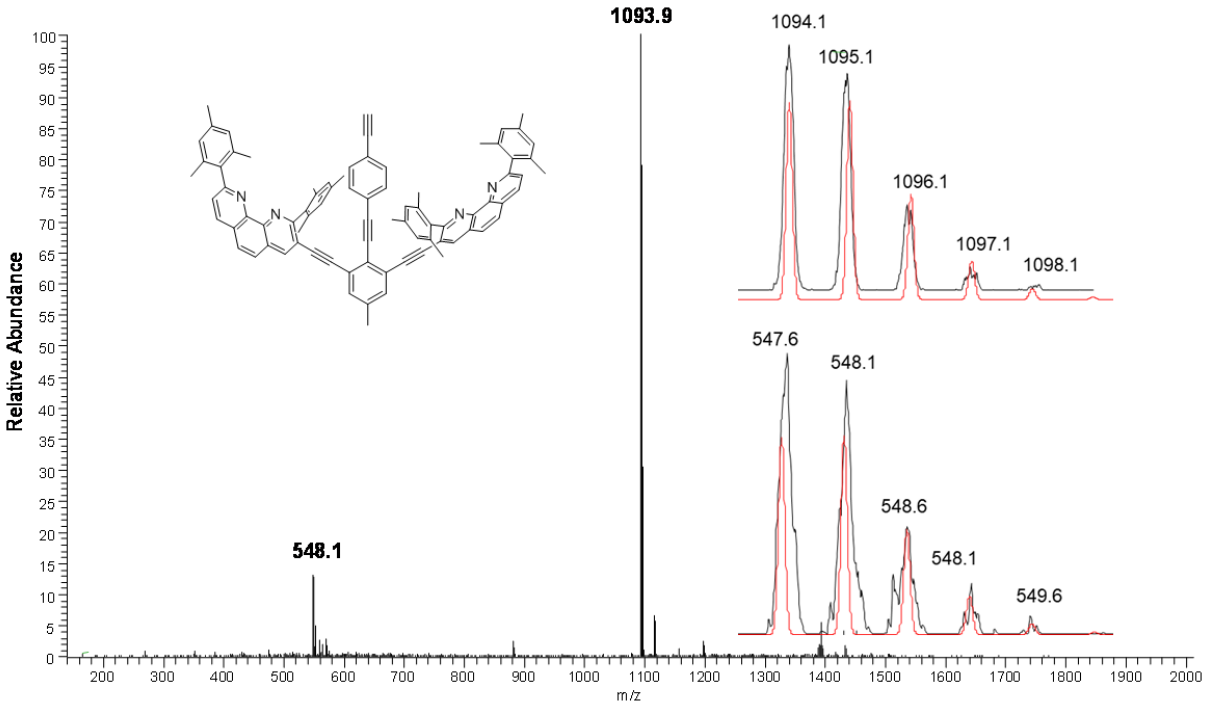


Figure S47. ESI-MS spectrum of [**15** + H]$^{+}$ and [**15** + 2H]$^{2+}$ in CH_2Cl_2 (protonation by CH_3CO_2H).

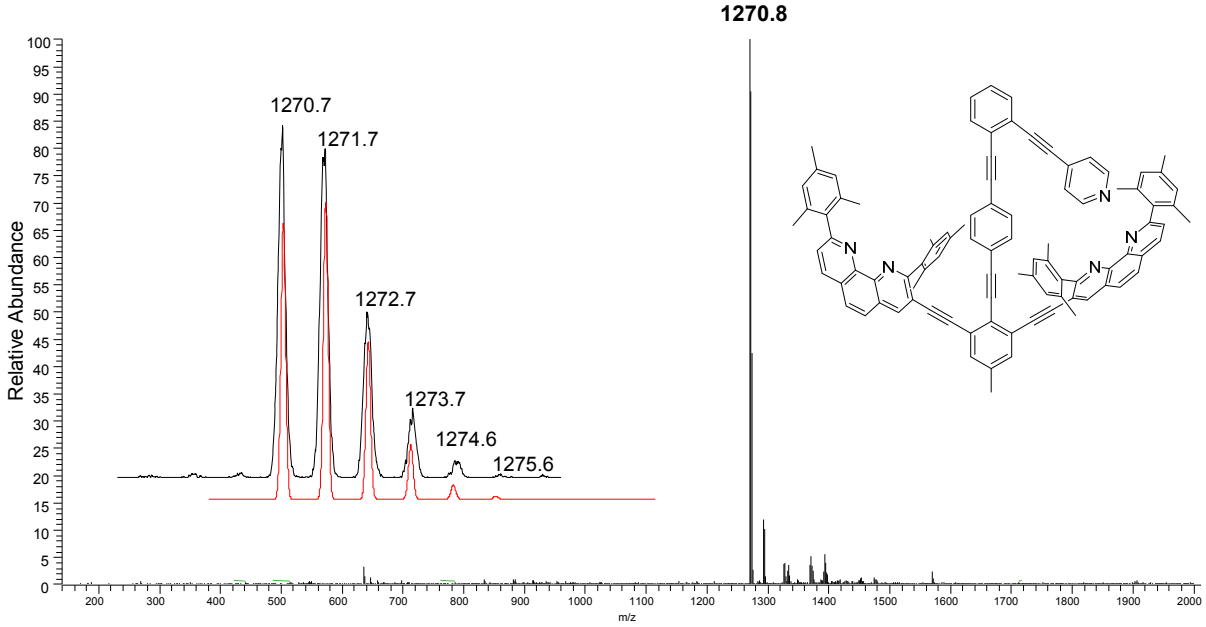


Figure S48. ESI-MS spectrum of [**1** + H]$^{+}$ in CH_2Cl_2 (protonation by CH_3CO_2H).

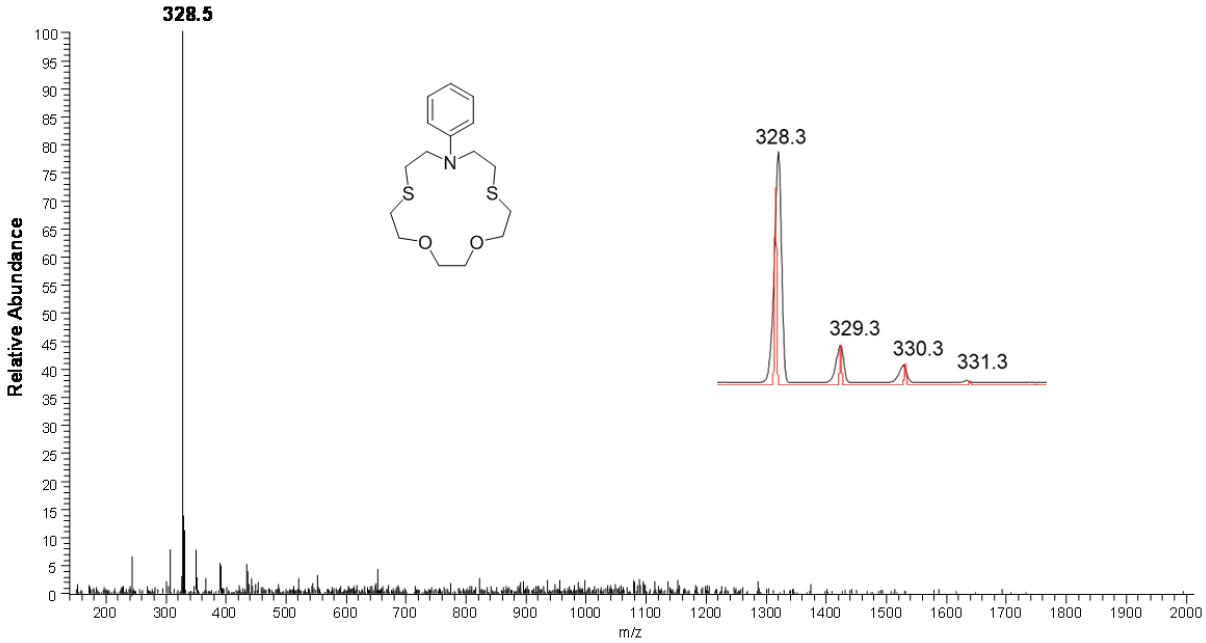


Figure S49. ESI-MS spectrum of [**4** + H]$^+$ in CH_3CN (protonation by CH_3CO_2H).

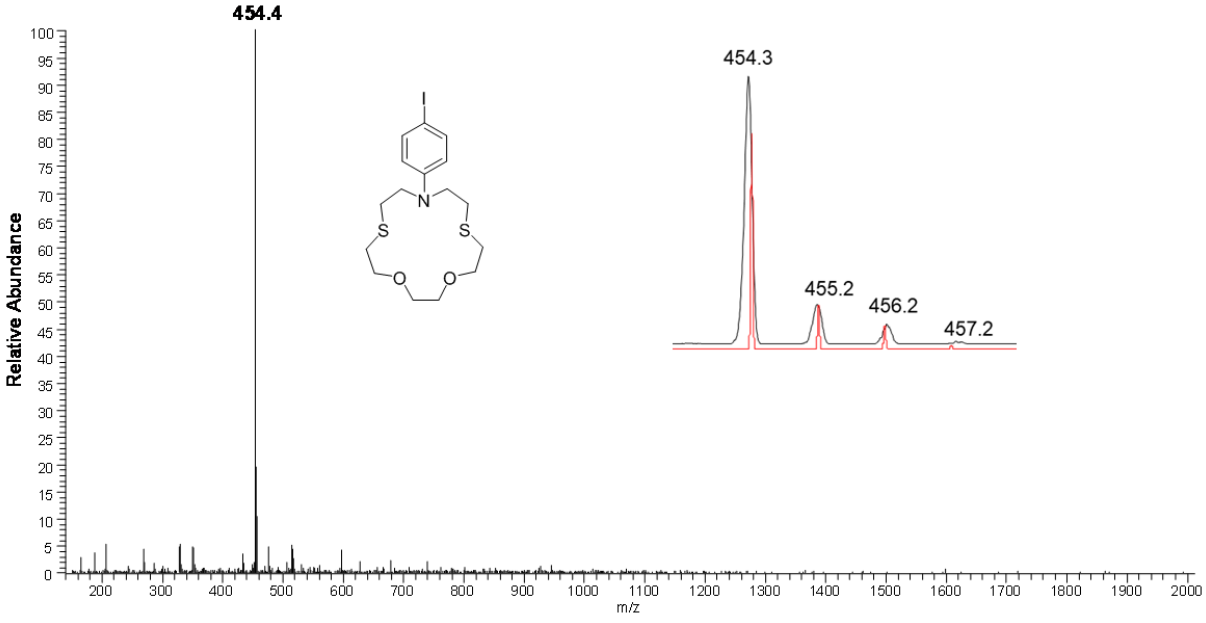


Figure S50. ESI-MS spectrum of [**16** + H]$^+$ in CH_3CN (protonation by CH_3CO_2H).

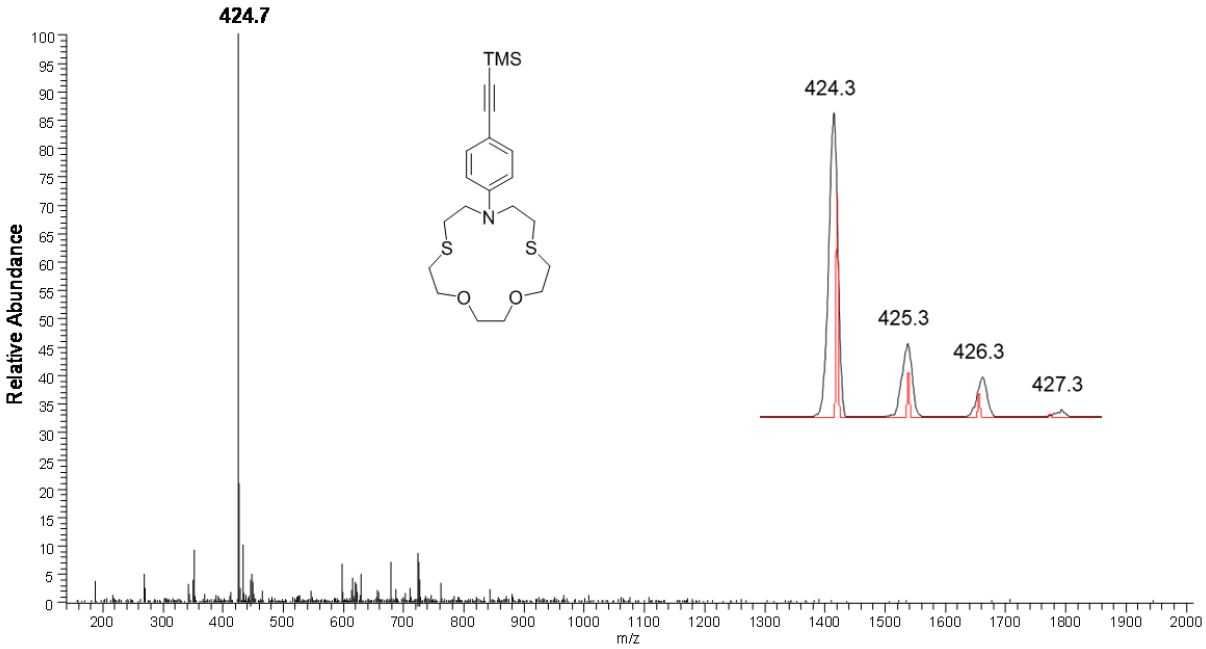


Figure S51. ESI-MS spectrum of [**17** + H]$^+$ in CH_3CN (protonation by CH_3CO_2H).

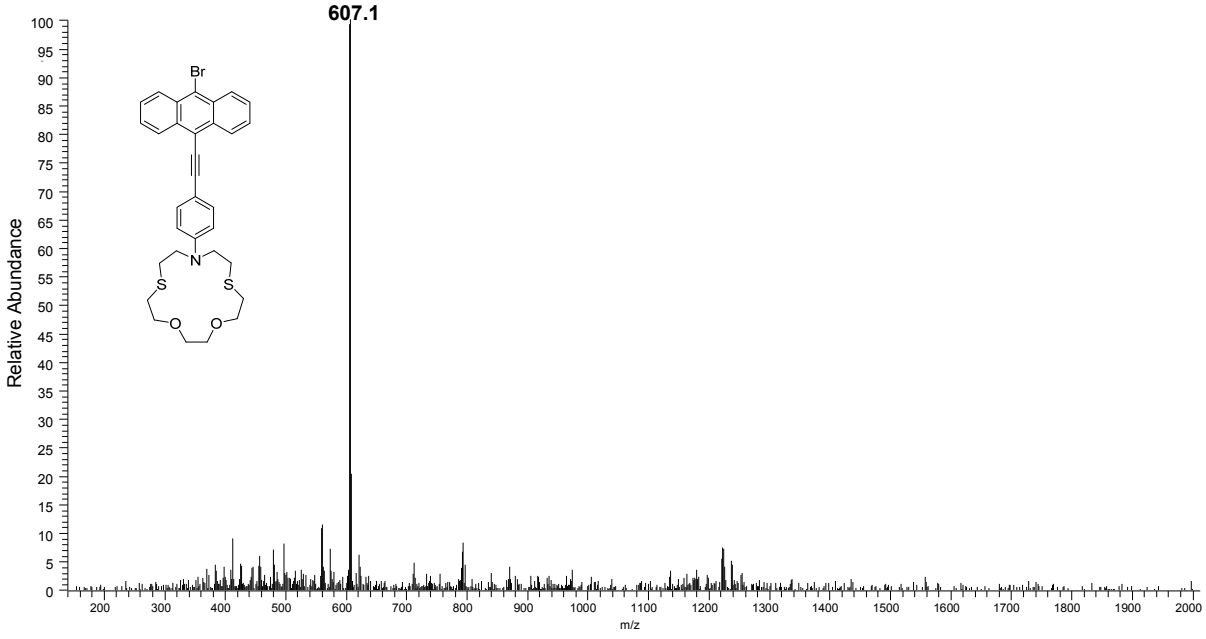


Figure S52. ESI-MS spectrum of [**2** + H]$^+$ in CH_2Cl_2 (protonation by CH_3CO_2H).

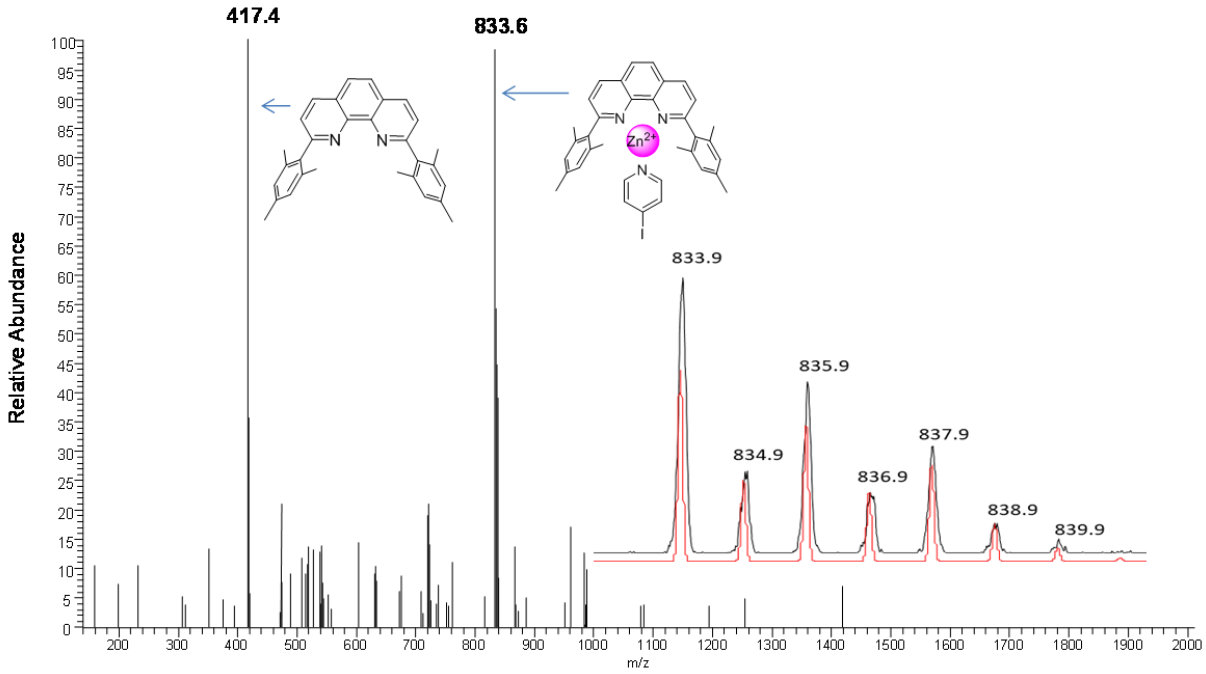


Figure S53. ESI-MS spectrum of complex [Zn(**3**)(**5**)](OTf)$_2$ in CH_2Cl_2 along with experimental (black) and calculated (red) isotopic distributions of [Zn(**3**)(**5**)]OTf$^+$.

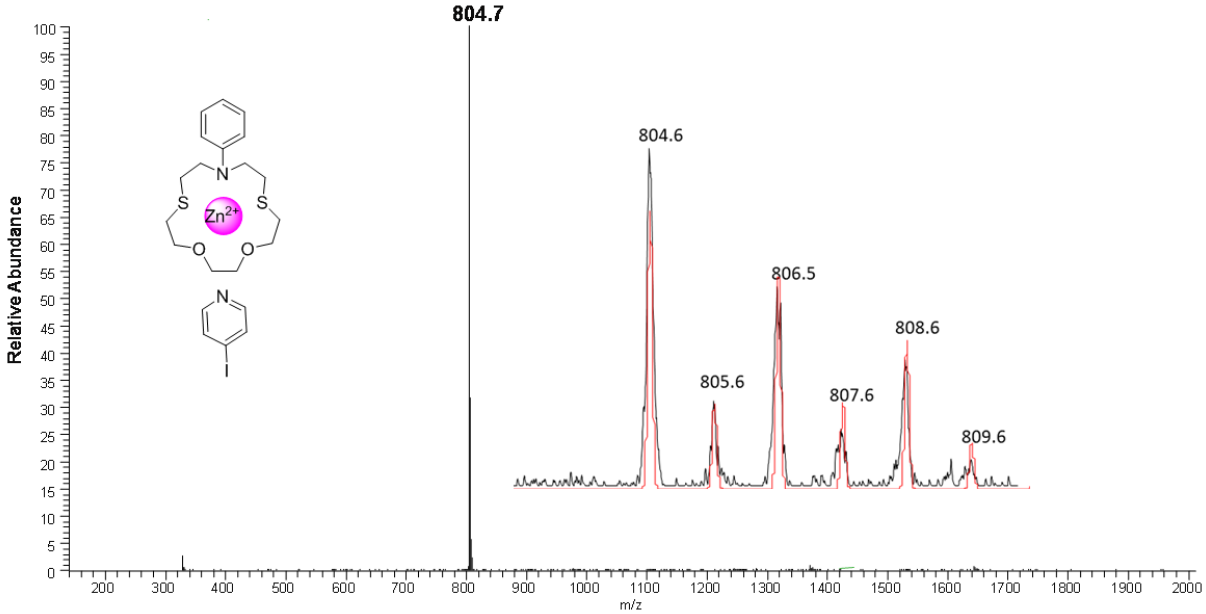


Figure S54. ESI-MS spectrum of complex [Zn(**4**)(**5**)](OTf)$_2$ in CH_2Cl_2 along with experimental (black) and calculated (red) isotopic distributions of [Zn(**4**)(**5**)(H_2O)(CH_3CN)]OTf$^+$.

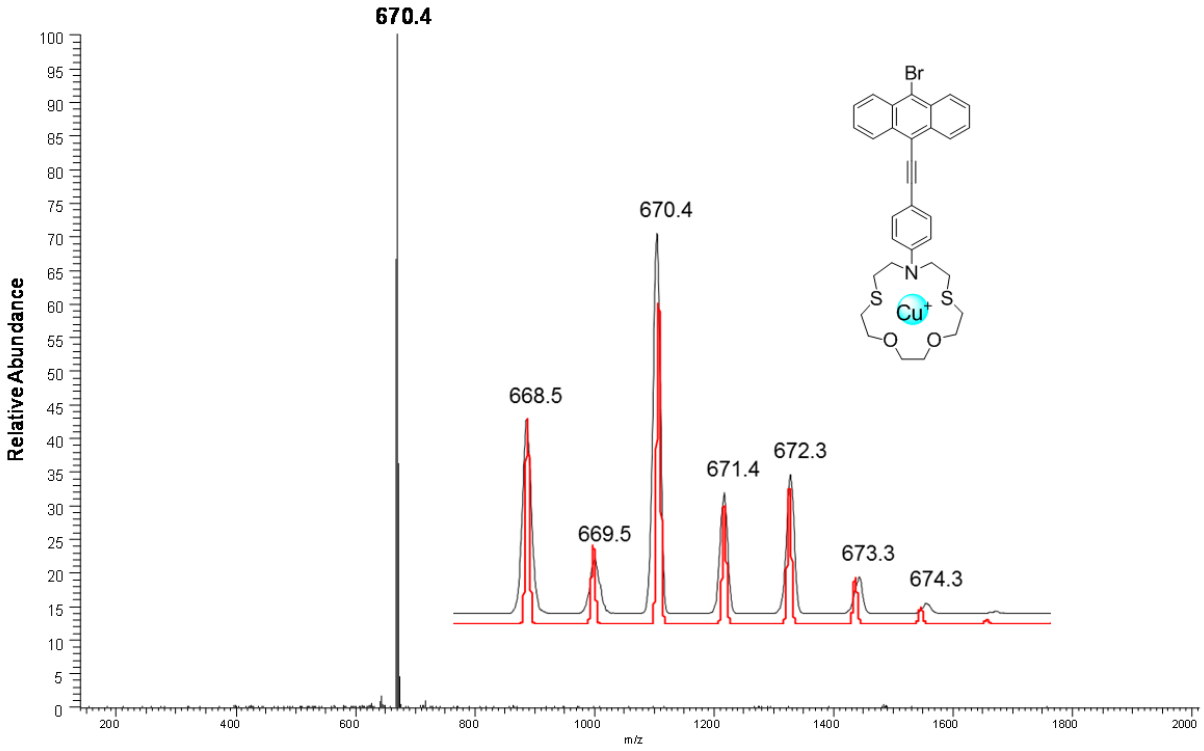


Figure S55. ESI-MS spectrum of complex [Cu(**2**)]PF_6 in CH_2Cl_2 along with experimental (black) and calculated (red) isotopic distributions of [Cu(**2**)]$^+$.

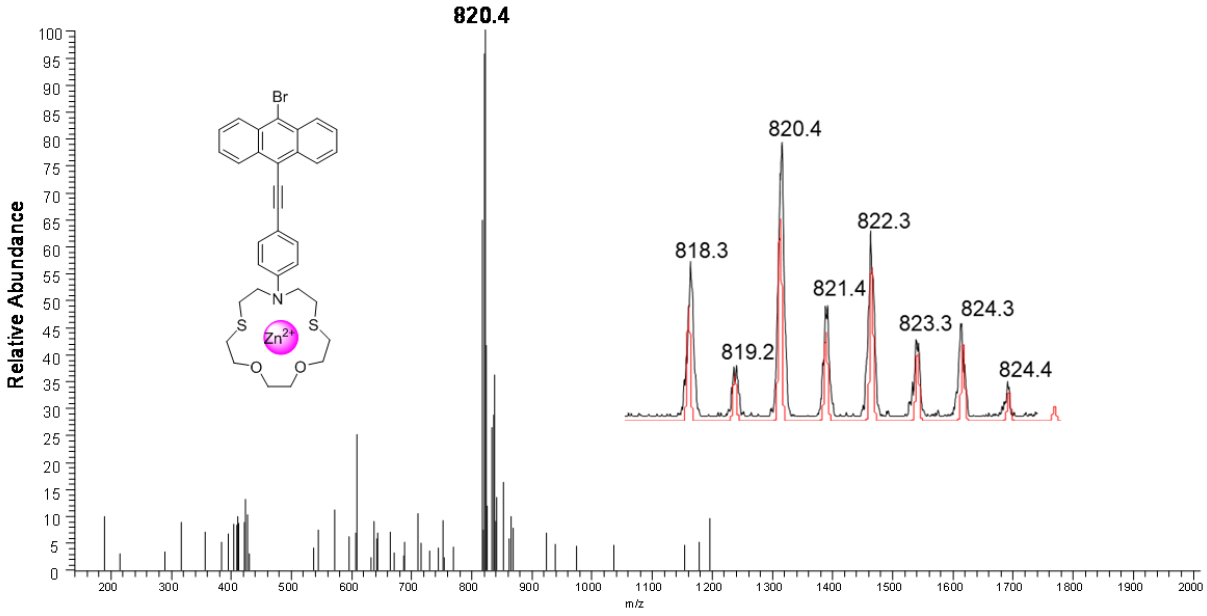


Figure S56. ESI-MS spectrum of complex [Zn(**2**)]$(OTf)_2$ in CH_2Cl_2 along with experimental (black) and calculated (red) isotopic distributions of [Zn(**2**)]OTf^+.

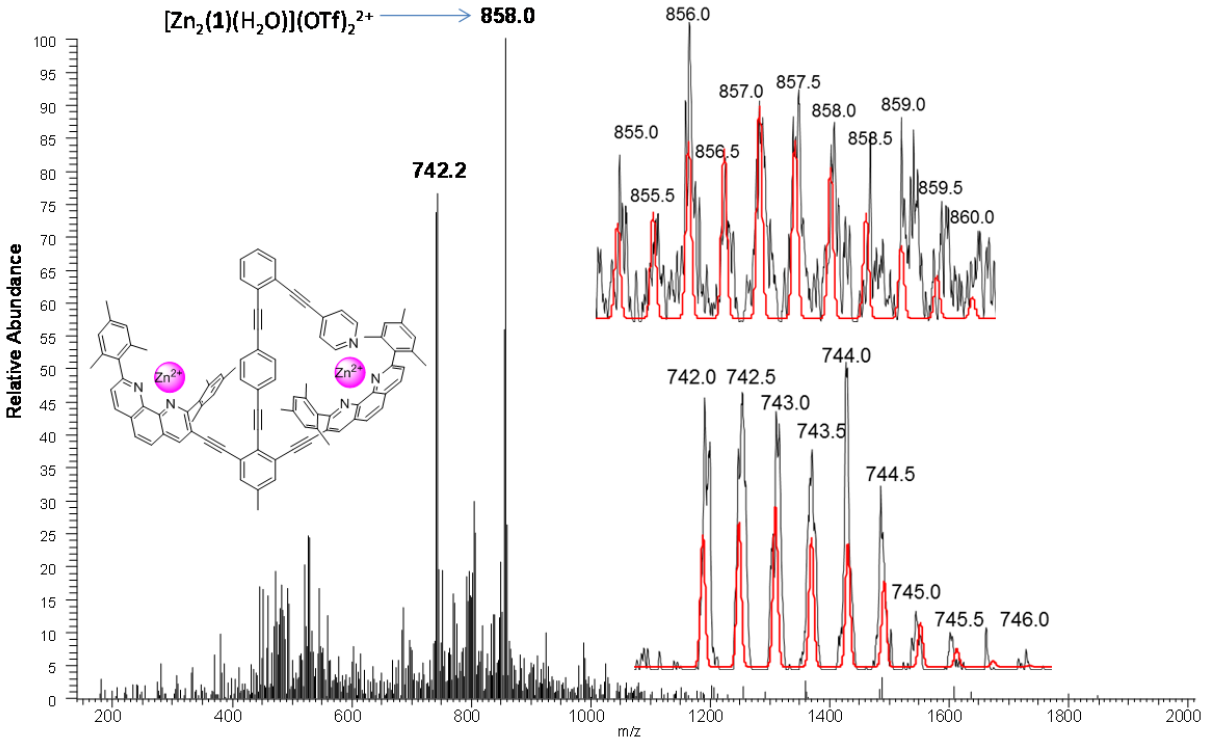


Figure S57. ESI-MS spectrum of complex $[Zn_2(\mathbf{1})](OTf)_4$ in CH_2Cl_2 along with experimental (black) and calculated (red) isotopic distributions of species $[Zn_2(\mathbf{1})(H_2O)](OTf)_2^{2+}$ and $[[Zn(\mathbf{1})](OTf) + H]^{2+}$.

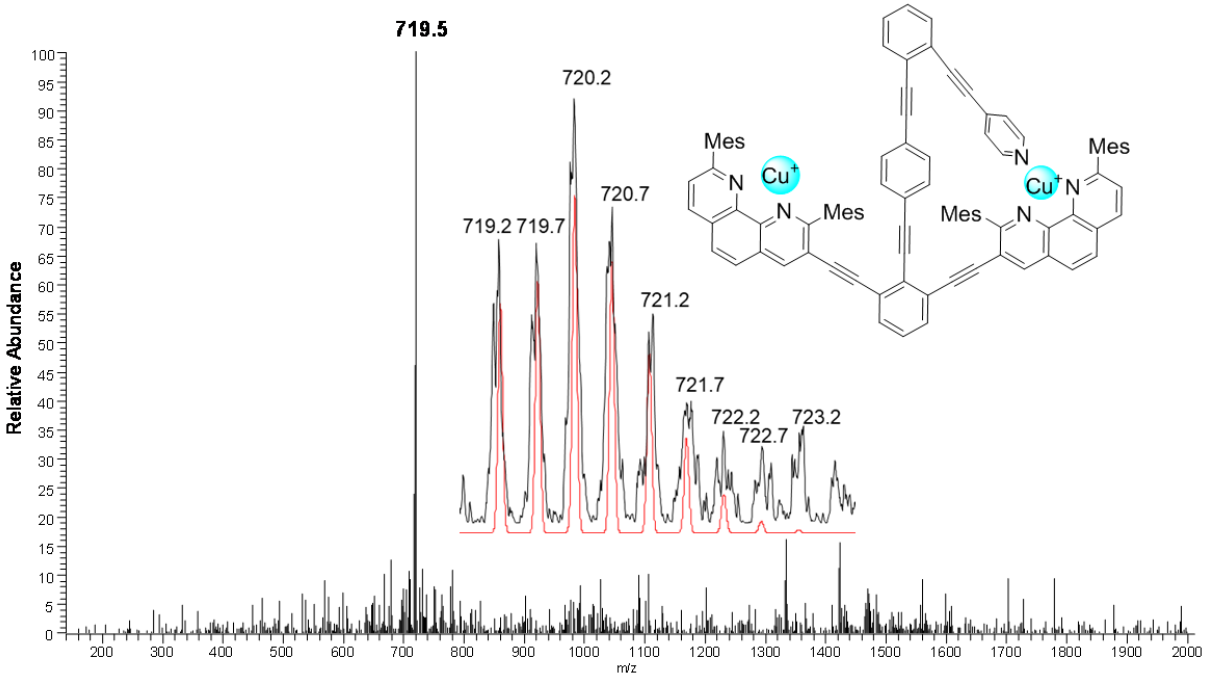


Figure S58. ESI-MS spectrum of complex $[Cu_2(\mathbf{1})](PF_6)_2$ in CH_2Cl_2 along with experimental (black) and calculated (red) isotopic distributions of $[Cu_2(\mathbf{1})(CH_3CN)]^{2+}$.

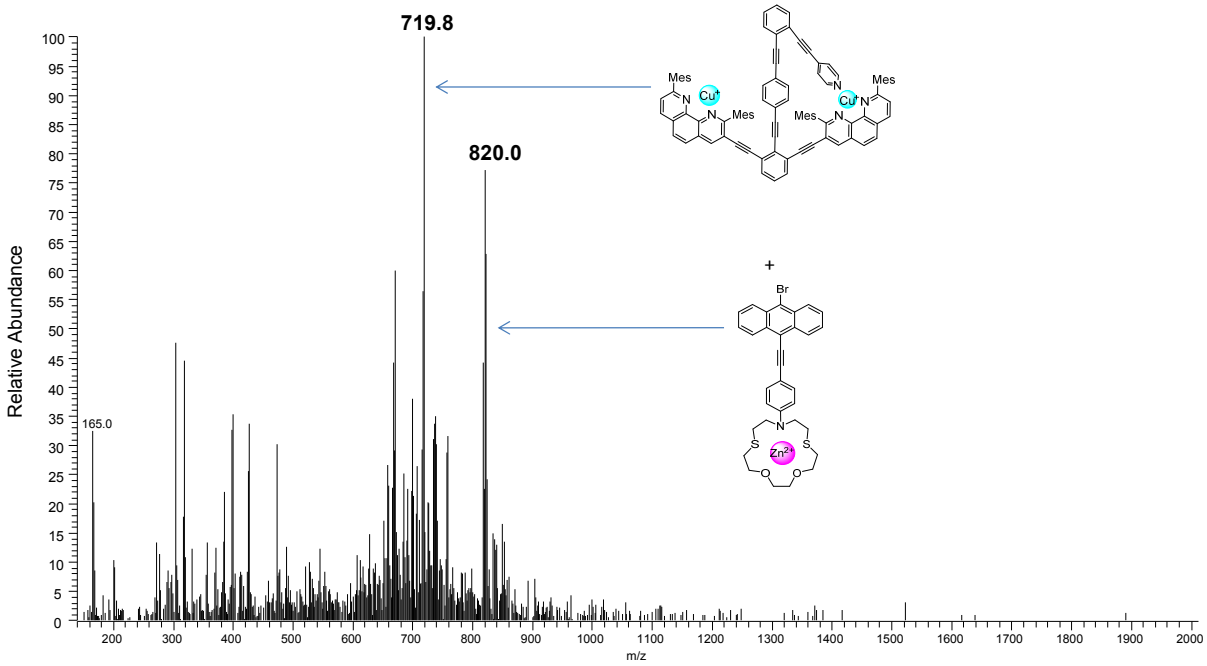


Figure S59. ESI-MS spectrum of complexes $[Cu_2(\mathbf{1})](PF_6)_2$ and $[Zn(\mathbf{2})](OTf)_2$ in the reaction mixture (in CH_2Cl_2) representing the species $[Cu_2(\mathbf{1})(CH_3CN)]^{2+}$ and $[Zn(\mathbf{2})]OTf^{+}$.

5. Emission spectra

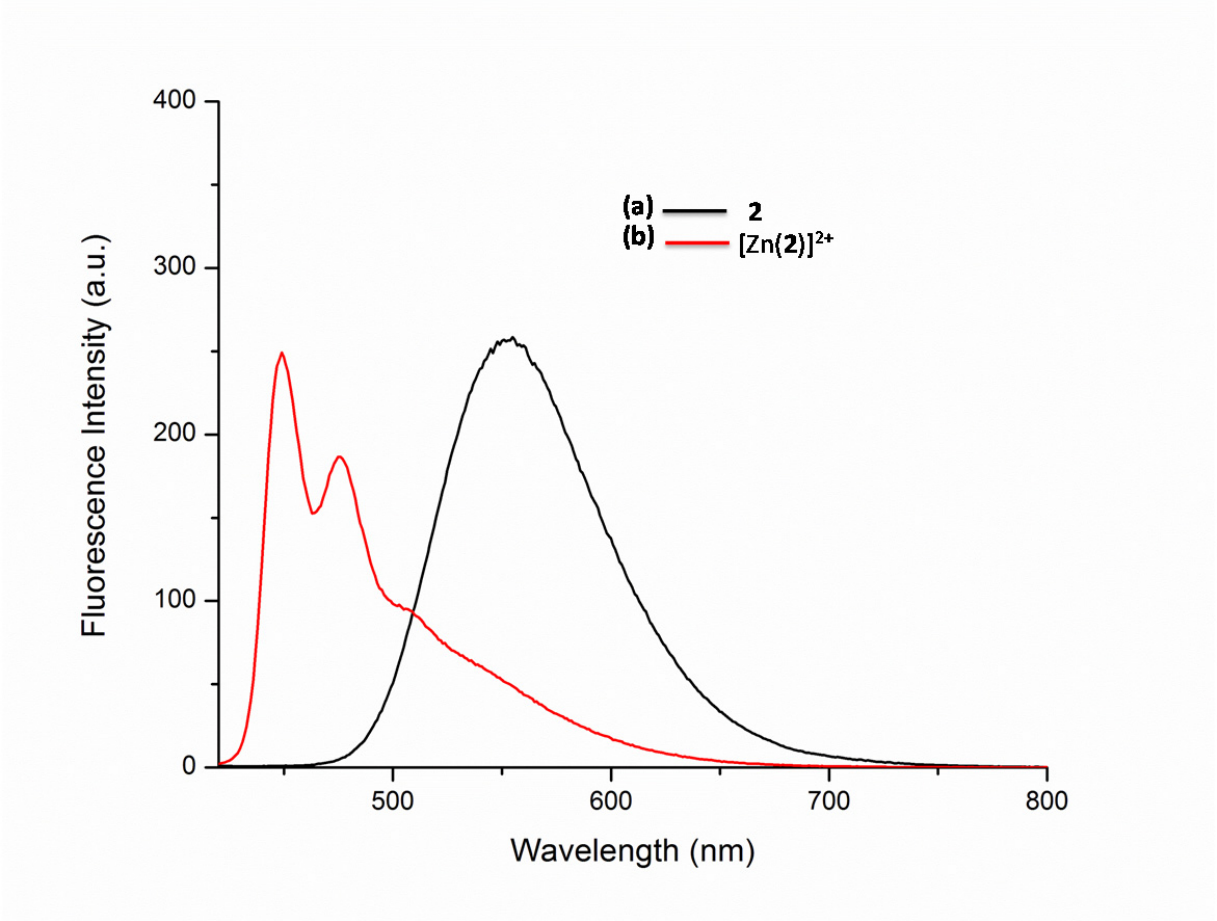


Figure S60. Emission spectra (λ_{exc} = 410 nm, 298 K) in 0.2% CH_3CN in CH_2Cl_2 at 1.25 µM (a) ligand 2; (b) $[Zn(\mathbf{2})]^{2+}$.

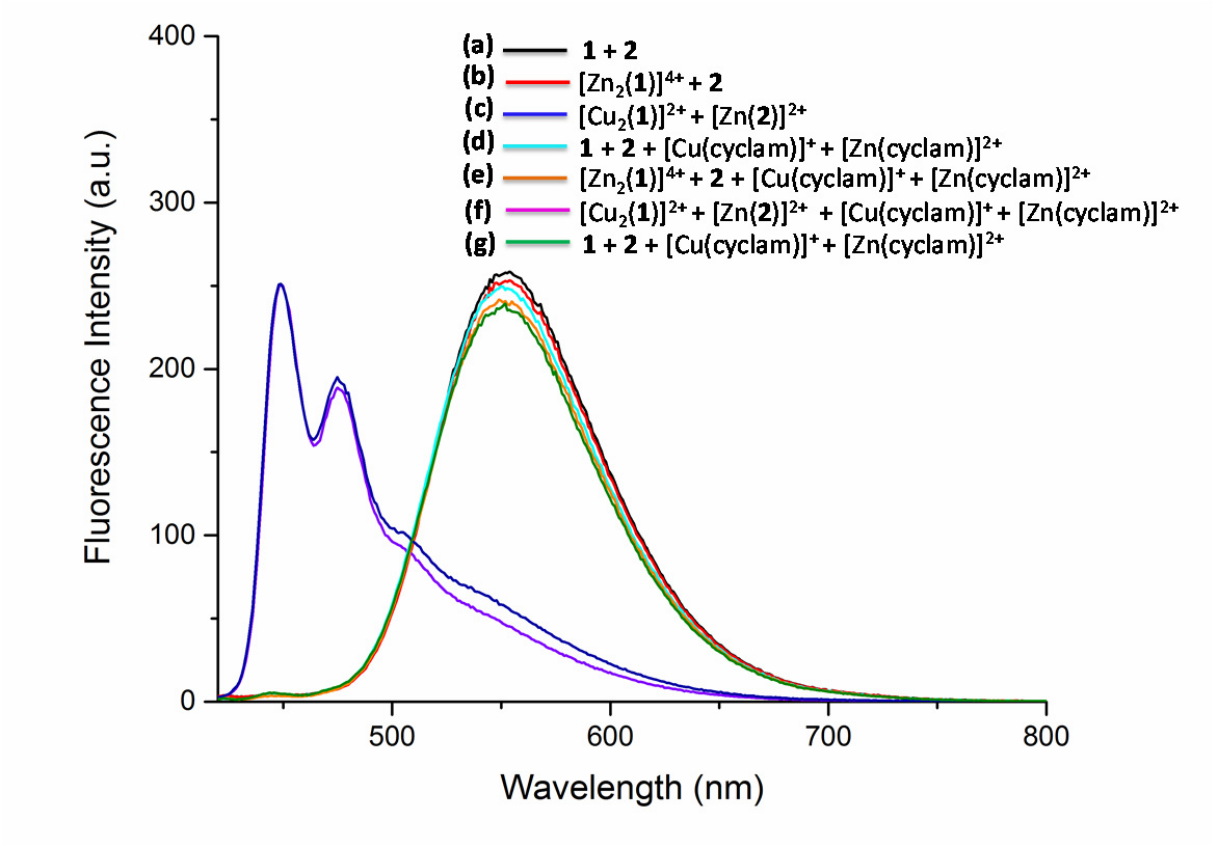


Figure S61. Emission spectra (λ_{exc} = 410 nm, 298 K) in 0.2% CH_3CN in CH_2Cl_2 showing the *in situ* network between rotor **1** (0.625 μM) and receptor **2** (1.25 μM) upon sequential addition of Zn^{2+} & Cu^{+} and removal of metal ions with cyclam. (a) Ligands **1** and **2** were mixed in 1:2 ratio; (b) addition of 2 equiv. of $Zn(OTf)_2$ to ligands depicted in spectrum (a) afforded $[Zn_2(\mathbf{1})]^{4+}$ and **2**; (c) addition of 2 equiv. of $[Cu(CH_3CN)_4]PF_6$ to mixture depicted in spectrum (b) generated $[Cu_2(\mathbf{1})]^{2+}$ and $[Zn(\mathbf{2})]^{2+}$; (d) addition of 4 equiv. of cyclam to the mixture depicted in (c) for removing the metal ions Zn^{2+} & Cu^{+} furnished ligands **1** and **2**; (e) addition of 2 equiv. of $Zn(OTf)_2$ to mixture depicted in spectrum (d) afforded $[Zn_2(\mathbf{1})]^{4+}$ and **2**; (f) addition of 2 equiv. of $[Cu(CH_3CN)_4]PF_6$ to mixture depicted in spectrum (e) furnished $[Cu_2(\mathbf{1})]^{2+}$ and $[Zn(\mathbf{2})]^{2+}$; (g) addition of 4 equiv. of cyclam to the mixture depicted in (f) for removing the metal ions Zn^{2+} & Cu^{+} regenerated ligands **1** and **2**.

6. Excitation Spectra

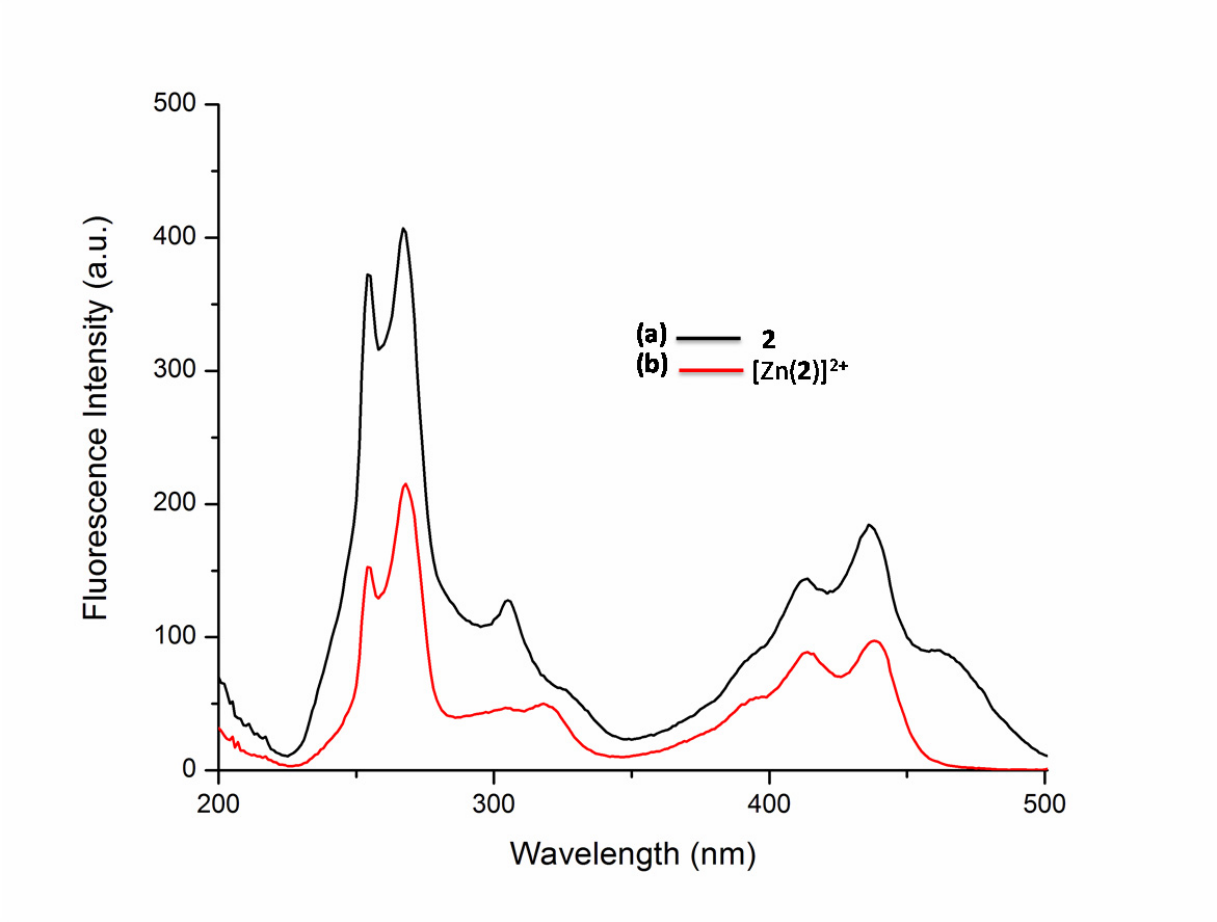


Figure S62. Excitation spectra (recorded based on emission wavelength λ = 509 nm = isoemission point of **2** and $[Zn(\mathbf{2})]^{2+}$) in 0.2% CH_3CN in CH_2Cl_2 at 1.25 µM at 298 K (a) ligand **2**; (b) $[Zn(\mathbf{2})]^{2+}$.

7. Measurement of binding constants

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

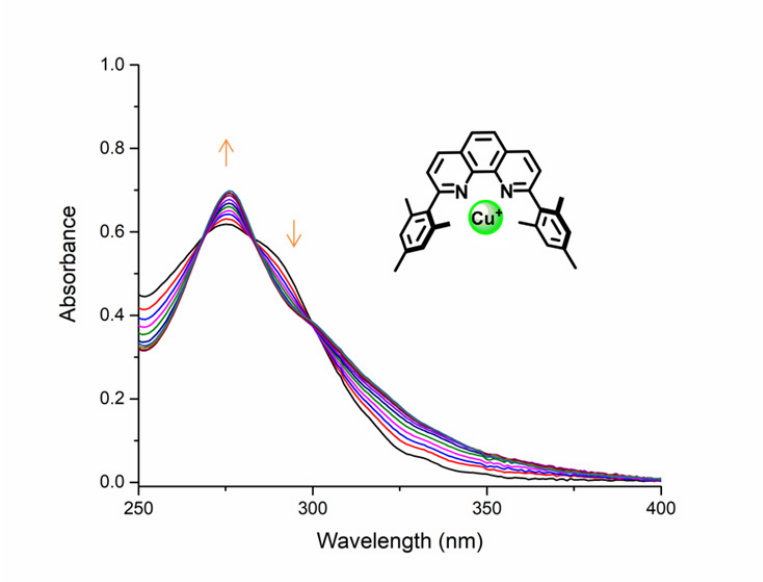


Figure S63. UV-vis spectra of **3** (2.00 x 10^{-5} M) in CH_2Cl_2 (2 mL) upon addition of $[Cu(CH_3CN)_4]PF_6$ (5.00 × 10^{-4} M) in CH_2Cl_2 at 298 K to afford complex [Cu(**3**)]PF_6. The wavelength region 250-400 nm was analyzed. Result: log *K* = 5.42 ± 0.10.

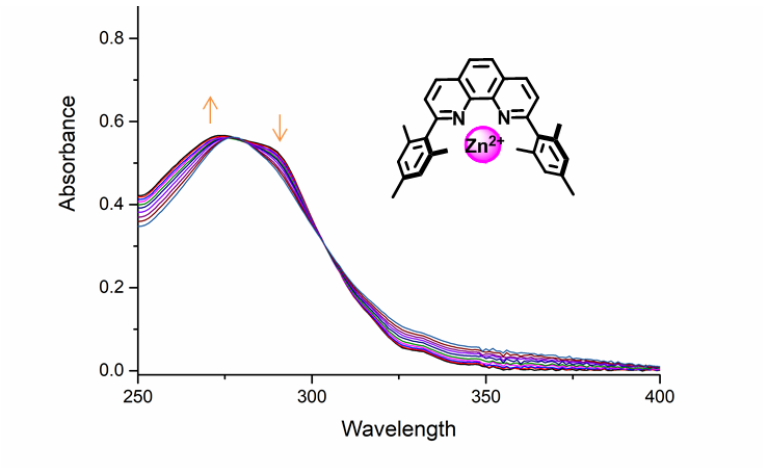


Figure S64. UV-vis spectra of **3** (2.00 x 10^{-5} M) in CH_2Cl_2 (2 mL) upon addition of $Zn(OTf)_2$ (5.00 × 10^{-4} M) in CH_2Cl_2:CH_3CN (98:2) at 298 K to afford the complex [Zn(**3**)]$(OTf)_2$. The wavelength region 250-400 nm was analyzed. Result: log *K* = 4.58 ± 0.58.

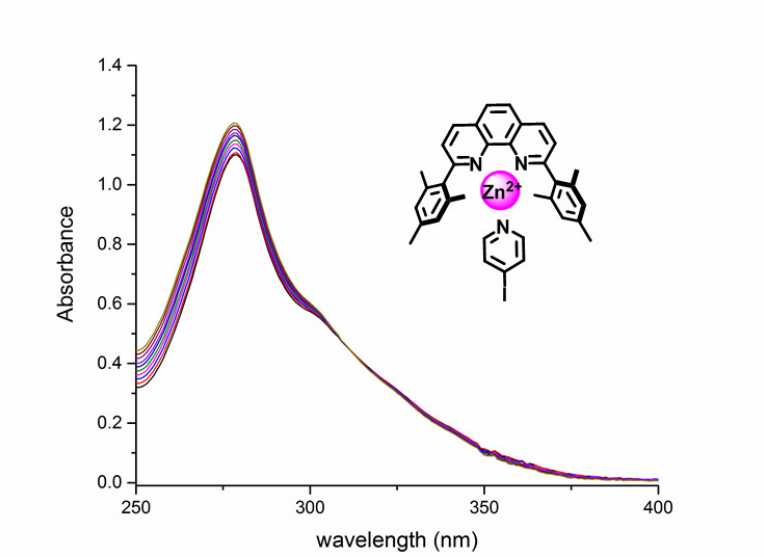


Figure S65. UV-vis spectra of [Zn(**3**)](OTf)$_2$ (7.45 x 10^{-5} M) in CH_2Cl_2 (2 mL) upon addition of Zn(OTf)$_2$ (1.18 × 10^{-3} M) in CH_2Cl_2:CH_3CN (99:1) at 298 K to afford the complex [Zn(**3**)(**5**)](OTf)$_2$. The wavelength region 250-400 nm was analyzed. Result: log *K* = 3.89 ± 0.12 which corresponds to 22.2 kJ mol^{-1}.

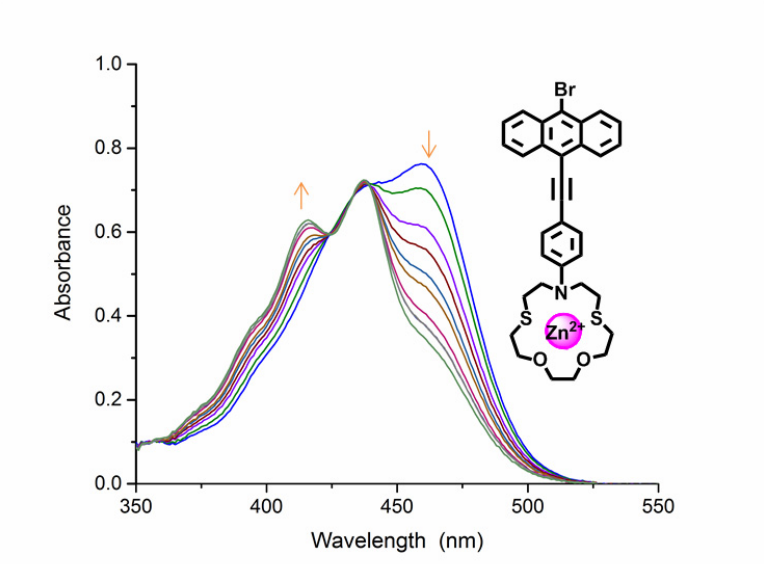


Figure S66. UV-vis spectra of **2** (1.47 x 10^{-4} M) in CH_2Cl_2 (2 mL) upon addition of Zn(OTf)$_2$ (2.27 × 10^{-2} M) in CH_3CN at 298 K to afford the complex [Zn(**2**)](OTf)$_2$. The wavelength region 350-550 nm was analyzed. Result: log *K* = 3.91 ± 0.41.

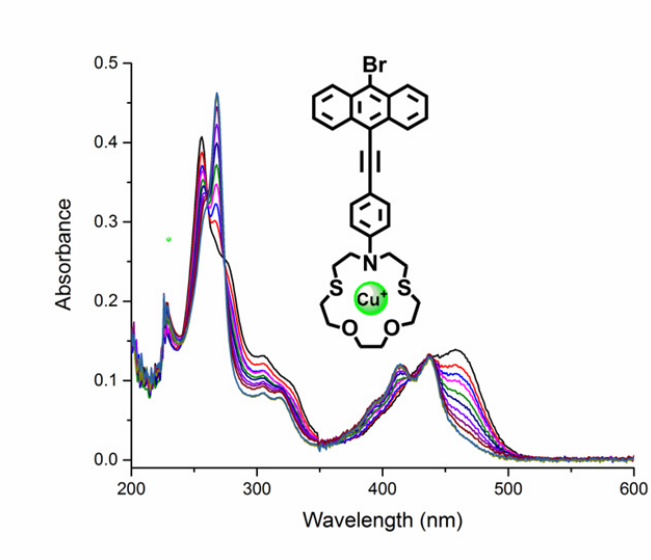


Figure S67. UV-vis spectra of **2** (5.00 x 10^{-6} M) in CH_2Cl_2 (2 mL) upon addition of $[Cu(CH_3CN)_4]PF_6$ (1.25 × 10^{-4} M) in CH_2Cl_2 at 298 K to afford complex [Cu(**2**)]PF_6. The wavelength region 200-600 nm was analyzed. Result: log K = 4.08 ± 0.18.

8. Kinetic analysis of Zn^{2+} translocation by UV-vis

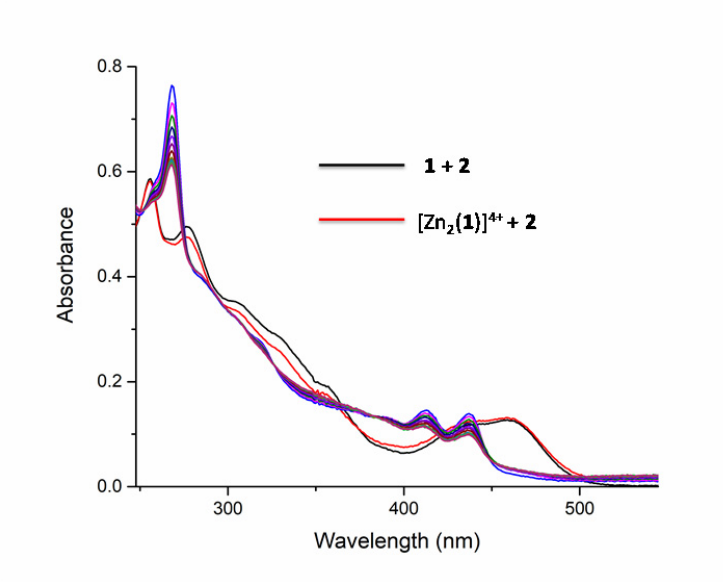


Figure S68. UV-vis spectra showing the changes during Zn^{2+} translocation from $[Zn_2(\mathbf{1})]^{4+}$ (3.60×10^{-6} M) to **2** (7.20×10^{-6} M) in 2mL of 0.2% CH_3CN in CH_2Cl_2 in 1 cm cuvette at 298 K. After addition of $[Cu(CH_3CN)_4]PF_6$, measurements were done at 5 min intervals. The kinetic trace was followed at 268 nm.

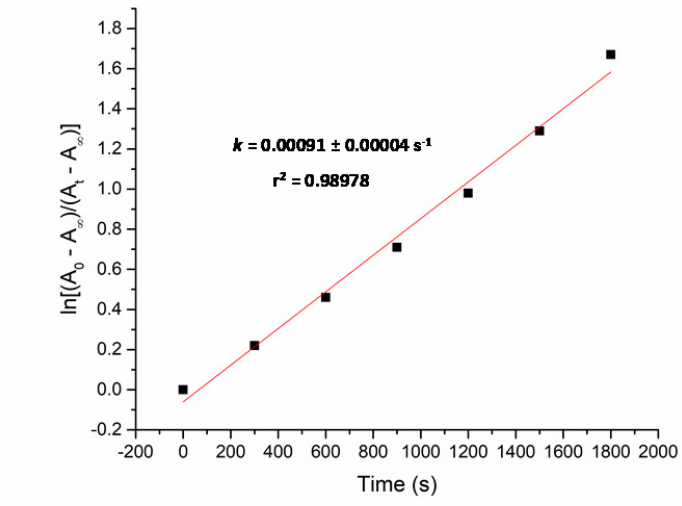


Figure S69. Zn^{2+} translocation from $[Zn_2(\mathbf{1})]^{4+}$ to **2** was monitored at 268 nm. The kinetic analysis furnishes a linear correlation over 2 half-life times indicative of a first-order process. The calculated $t_{1/2}$ is 762 s. The A_∞ value was determined 60 min after mixing.

9. Estimation of hydrodynamic radius and energy-minimized structures

Stokes-Einstein Equation; $D = kT/6\pi\eta r$

D = diffusion coefficient

k = Boltzmann constant

T = temperature

η = viscosity of the solution

r = hydrodynamic radius of the particle

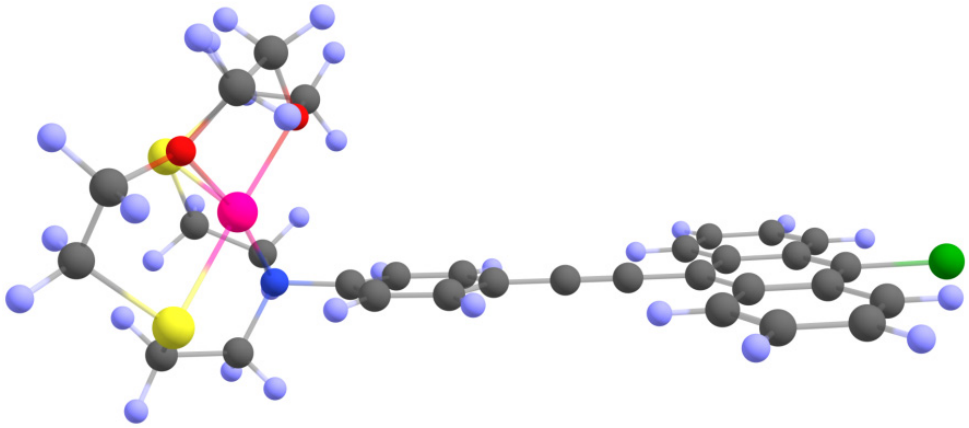


Figure S70. DFT optimized structure of $[Zn(\mathbf{2})]^{2+}$ using B3LYP/6-31G(d)) and separate the LanL2DZ basis set for Zn(II). Hydrogen atoms are shown in light purple; C, dark grey; N, blue; O, red; S, yellow; Br, green; Zn, pink. Counter anions are not included.

Experimental diffusion coefficient $D = 1.0 \times 10^{-9}$ m^2s^{-1}

Therefrom, the hydrodynamic radius was calculated as

$r_H = 5.3$ Å

From the energy minimized structure (DFT) the radius was calculated as

$r_H = 7.1$ Å

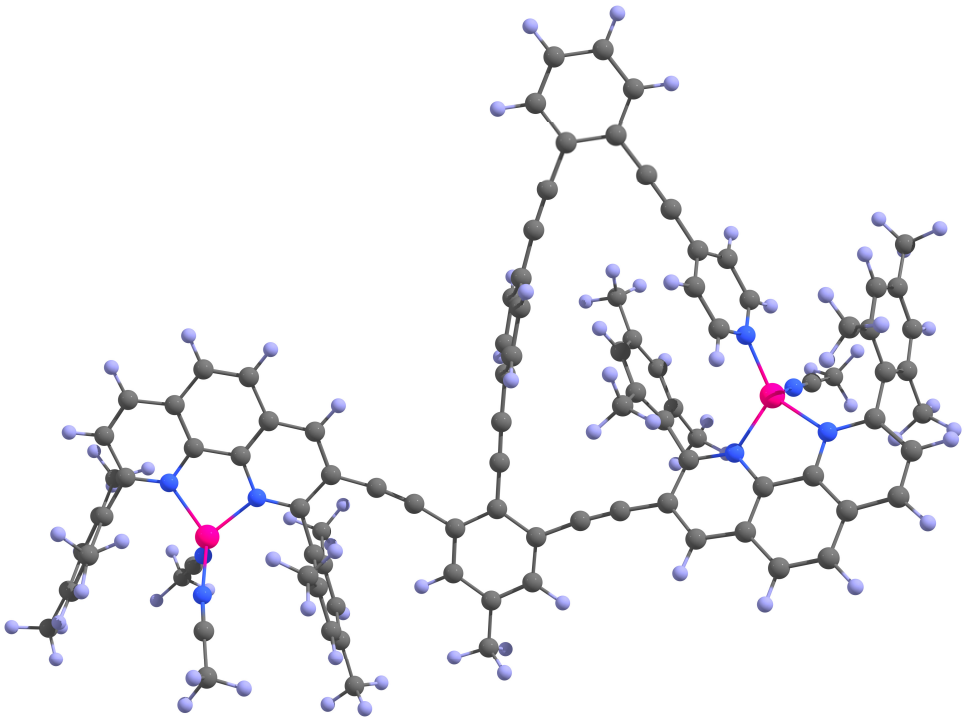


Figure S71. DFT optimized structure of $[Zn_2(\mathbf{1})](OTf)_4$ using B3LYP/6-31G(d)) and separate the LanL2DZ basis set for Zn(II). Hydrogen atoms are shown in purple; C, dark grey; N, blue; Zn, red. Acetonitrile ligands are added for the computation at the metal centers. Counter anions are not included.

Experimental diffusion coefficient $D = 4.7 \times 10^{-10}$ m^2s^{-1}

Therefrom, the hydrodynamic radius was calculated as

$r_H = 11$ Å

From the energy minimized structure (DFT) the radius was calculated as

$r_H = 9.6$ Å

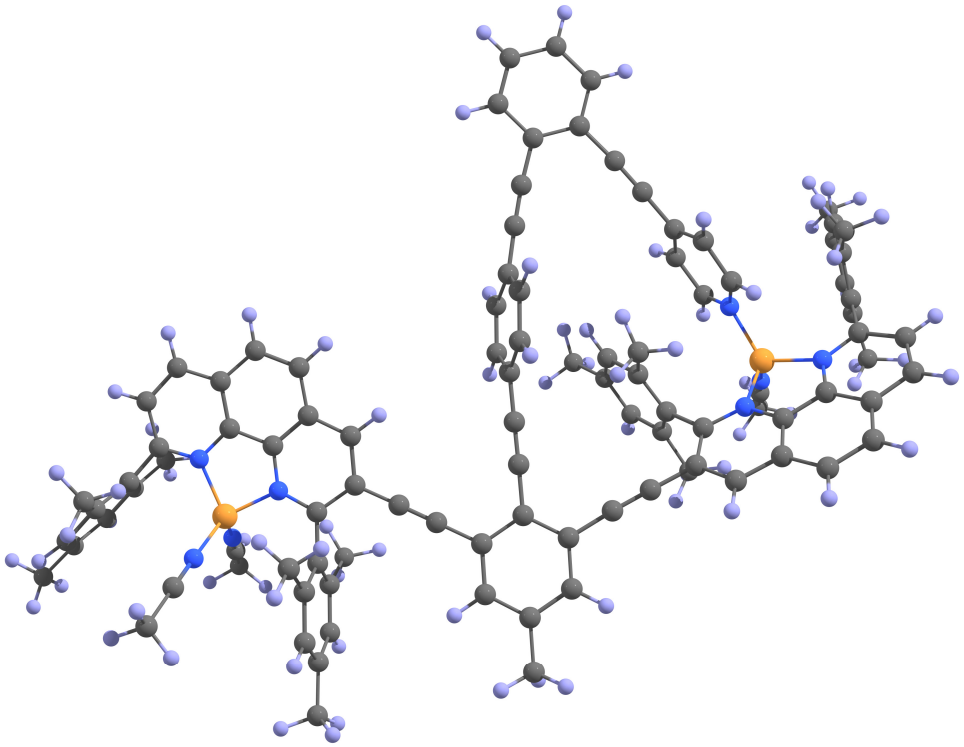


Figure S72. DFT optimized structure of $[Cu_2(\mathbf{1})](PF_6)_2$ using B3LYP/6-31G(d)) and separate LanL2DZ basis set for Cu(I). Hydrogen atoms are shown in purple; C, dark grey; N, blue; Cu, orange. Acetonitrile ligands are added for the computation at the metal centers. Counter anions are not included.

Experimental diffusion coefficient $D = 4.4 \times 10^{-10}$ m^2s^{-1}

Therefrom, the hydrodynamic radius was calculated as

$r_H =$ 12 Å

From the energy minimized structure (DFT) the radius was calculated as

$r_H = 9.6$ Å

10. References

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