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# A six–component metallosupramolecular pentagon via self-sorting

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DCM: dichloromethane

## Synthesis

### General

All commercial reagents were used without further purification. Solvents were dried with the appropriate desiccants and distilled prior to use. Silica gel (60-230 mesh) was used for column chromatography. $^{1}$H NMR and $^{13}$C NMR were recorded on a Bruker Avance 400 MHz using the deuterated solvent as the lock and residual protiated solvent as the internal reference ($CD_2Cl_2$: $\delta_H$ = 5.32 ppm and $\delta_C$ = 53.8 ppm). DOSY NMR was recorded on Varian VNMR-S 600 MHz. The following abbreviations were utilised to describe peak patterns: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, td = triplet of doublet, dt = doublet of triplets, br = broad, brs = broad singlet and m = multiplet. The numbering of the carbon atoms in the molecular formulae (*vide infra*) is only used for the assignments of the NMR signals and is not in accordance with IUPAC nomenclature rules. Electrospray ionisation mass spectra (ESI-MS) were recorded on a Thermo-Quest LCQ Deca. Melting points were measured on a Büchi SMP-20 instrument. Infrared spectra were recorded using a Varian 1000 FT-IR instrument. Elemental analysis was done on the EA 3000 CHNS. UV-Vis spectra were recorded on a Varian Cary 100 BioUV/Visible spectrometer. Binding constants were determined using the SPECFIT/32 global analysis system by Spectrum Software Associates (Marlborough,MA).[1] Single-crystal X-ray diffraction data for for **C2** were collected on a Siemens SMART 1K CCD area-detector diffractometer. The structures were solved using SHELXS-97 and refined by full-matrix least-squares analysis.[2] Hydrogen atoms were generated theoretically onto the specific atoms and refined using a riding model. The non-hydrogen atoms were refined with aniosotropic thermal parameters. Further details are provided in the X-ray structure analysis section. Energy minimised structures were obtained using the MM$^{+}$ forced field as implemented in Hyperchem® 8.0. Model complexes **C1**,[3] **C3**,[4] **C5**[3] as well as ligands **1**,[5] **3**,[5] **9**,[4] **17**[6] (precursors for **8**), **18**,[3] **21**[5] (precursors for **10**), were synthesised according to known procedures.

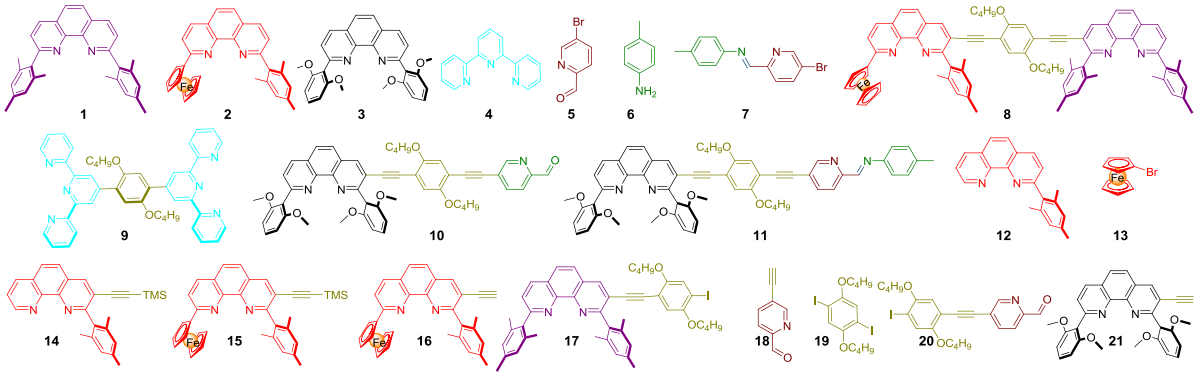
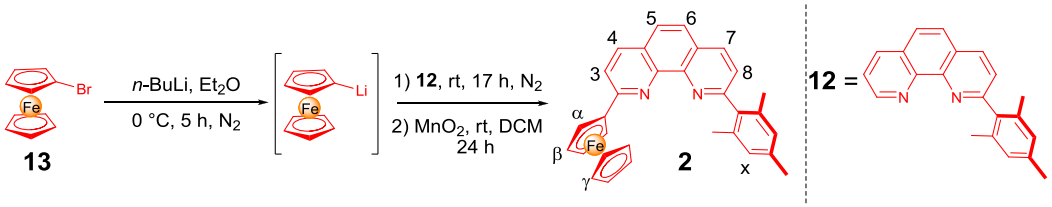


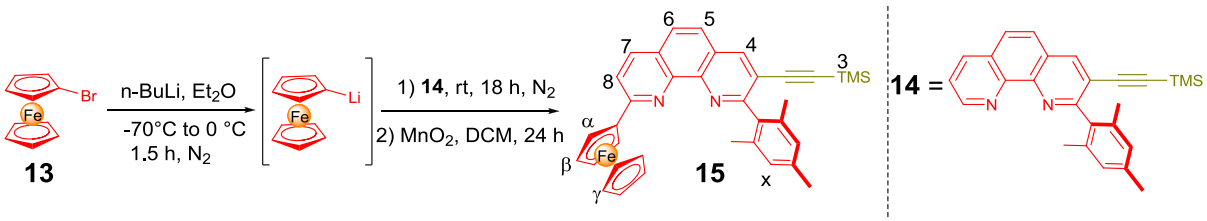

**Chart 1**: Chemical structures of compounds **1**–**21**.

**2-Ferrocenyl-9-mesityl-1,10-phenanthroline (2)**




Under $N_2$ atmosphere a solution of 2.5 M *n*-BuLi in *n*-hexane (900 µL, 2.25 mmol) was added slowly at 0 °C to a solution of bromoferrocene (**13**, 795 mg, 3.00 mmol) in diethyl ether (30 mL) over a period of 10 min. After stirring at 0 °C for 5 h, 2-mesityl-1,10-phenanthroline (**12**, 500 mg, 1.68 mmol) was added to the mixture under $N_2$ atmosphere. The resulting black solution was further stirred at room temperature for 17 h and then neutralised with $H_2O$. The layers were separated and the aqueous layer was extracted with DCM. After oxidation with $MnO_2$ (3.00 g, 34.5 mmol) at room temperature for 24 h the combined organic layers were filtered through a pad of celite and the solvents removed under reduced pressure to furnish an orange residue. The crude product was purified by column chromatography ($SiO_2$, $R_f$ =0.30 [$SiO_2$, EtOAC: *n*-hexane = 1:9] ) using a mixture of 8% of ethyl acetate in *n*-hexane affording an orange solid. Yield = 250 mg (31%); mp 120 °C; $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 8.31 (d, $^3J$ = 8.4 Hz, 1 H, 7-H), 8.17 (d, $^3J$ = 8.4 Hz, 1 H, 4-H), 7.81 (d, $^3J$ = 8.8 Hz, 1 H, 5-H), 7.80 (d, $^3J$ = 8.4 Hz, 1 H, 3-H), 7.79 (d, $^3J$ = 8.8 Hz, 1 H, 6-H), 7.56 (d, $^3J$ = 8.4 Hz, 1 H, 8-H), 7.06 (s, 2 H, x-H), 5.19 (t, $^3J$ = 2.0 Hz, 2 H, α-H), 4.48 (t, $^3J$ = 2.0 Hz, 2 H, β-H), 4.06 (s, 5 H, γ-H), 2.41 (s, 3 H, Me), 2.17 (s, 6 H, Me); $^{13}$C NMR (100 MHz, $CD_2Cl_2$): $\delta$ = 159.9, 159.9, 146.4, 146.1, 138.5, 137.9, 136.3, 136.3, 135.9, 128.8, 127.8, 127.4, 126.7, 125.4, 124.8, 121.1, 84.6, 70.7, 69.9, 68.6, 21.2, 20.6; IR (KBr) $\nu$ 3401, 3092, 2917, 1611, 1602, 1509, 1388, 1282, 1105, 1007, 862, 738, 633, 617, 490; ESI-MS: *m*/*z* (%) 483.3 (100) $[M+H]^+$; Anal. calcd. for $C_{31}H_{26}N_2Fe$•0.75 $C_4H_8O_2$: C, 74.45; H, 5.88; N, 5.11; found: C, 74.73; H, 5.57; N, 4.99.

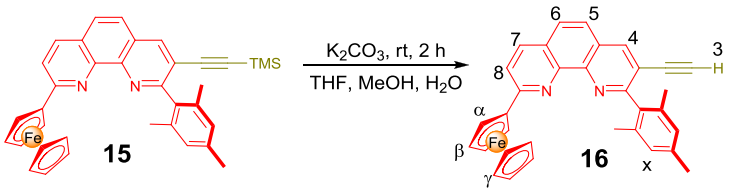
**9-Ferrocenyl-2-mesityl-3-((trimethylsilyl)ethynyl)-1,10-phenanthroline (15)**




Under $N_2$ atmosphere and at –70 °C, *n*-BuLi (2.5 M) in *n*-hexane (800 µL, 2.00 mmol) was added slowly over a period of 15 min to a solution of bromoferrocene (**13**, 600 mg, 2.26

mmol) in dry diethyl ether (30 mL). Subsequently, the reaction mixture was allowed to warm to 0 °C.[7] After 1.5 h, 2-mesityl-3-((trimethylsilyl)ethynyl)-1,10-phenanthroline (**14**, 450 mg, 1.14 mmol) was added and the resultant mixture was allowed to warm to room temperature. Finally, 100 mL of $H_2O$ was added to the mixture after 18 h. The layers were separated and the aqueous layer was extracted with DCM. The combined organic layers were treated with $MnO_2$ (3.50 g, 40.3 mmol) for 24 h at room temperature. Subsequently, $MnO_2$ was filtered out through a pad of celite and the resultant orange solution was evaporated to dryness. Finally the desired compound **15** was purified from the residue *via* column chromatography by using a mixture of *n*-hexane and ethyl acetate (14:1) as eluent ($R_f$ =0.26 [$SiO_2$, EtOAC:*n*-hexane = 1:9]). Yield = 462 mg (70 %); mp 106 °C; $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 8.39 (s, 1 H, 4-H), 8.16 (d, $^3J$ = 8.4 Hz, 1 H, 7-H), 7.81 (d, $^3J$ = 8.4 Hz, 1 H, 8-H), 7.80 (d, $^3J$ = 8.8 Hz, 1 H, 5-H), 7.75 (d, $^3J$ = 8.8 Hz, 1 H, 6-H), 7.02 (s, 2 H, x-H), 5.18 (t, $^3J$ = 2.0 Hz, 2 H, α-H), 4.47 (t, $^3J$ = 2.0 Hz, 2 H, β-H), 4.05 (s, 5 H, γ-H), 2.39 (s, 3 H, Me), 2.07 (s, 6 H, Me), 0.04 (s, 9 H, 3-H); $^{13}$C NMR (100 MHz, $CD_2Cl_2$): $\delta$ = 162.1, 160.4, 146.1, 144.8, 139.3, 137.9, 137.4, 136.2, 136.0, 128.3, 127.8, 127.4, 127.3, 124.9, 121.5, 119.9, 102.3, 101.0, 84.4, 70.8, 70.0, 68.7, 21.2, 19.9, –0.5; IR (KBr) *v* 3420, 3292, 3092, 2954, 2919, 2857, 2416, 1711, 1610, 1512, 1456, 1367, 1281, 1248, 1182, 1105, 1005, 856, 763, 648; ESI-MS: *m*/*z* (%) 579.4 (100) $[M+H]^+$; Anal. calcd. for $C_{36}H_{34}N_2FeSi$•0.25 $C_4H_8O_2$: C, 73.99; H, 6.04; N, 4.66; found: C, 74.23; H, 5.95; N, 4.29.

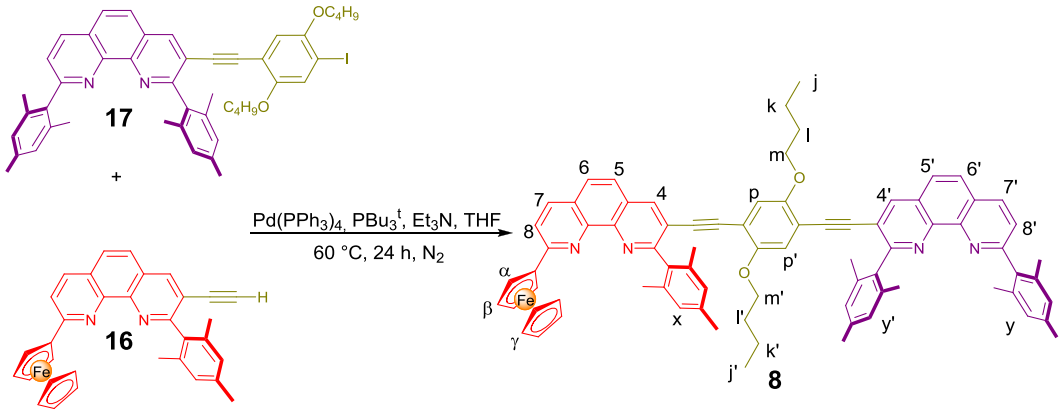
**3-Ethynyl-9-ferrocenyl-2-mesityl-1,10-phenanthroline (16)**




9-Ferrocenyl-2-mesityl-3-((trimethylsilyl)ethynyl)-1,10-phenanthroline (**15**, 450 mg, 0.78 mmol) and $K_2CO_3$ (216 mg, 1.56 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 **16** as orange solid. Yield = 370 mg (94%); mp (decomposition above 230 °C); $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 8.50 (s,1 H, 4-H), 8.17 (d, $^3J$ = 8.4 Hz, 1 H, 7-H), 7.82 (d, $^3J$ = 8.8 Hz, 1 H, 5-H), 7.82 (d, $^3J$ = 8.4 Hz, 1 H, 8-H),7.77 (d, $^3J$ = 8.8 Hz, 1 H, 6-H), 7.04 (s, 2 H, x-H), 5.18 (t, $^3J$ = 2.0 Hz, 2 H, α-

H), 4.47 (t, $^3J$ = 2.0 Hz, 2 H, β-H), 4.05 (s, 5 H, γ-H), 3.20 (s, 1 H, 3-H), 2.41 (s, 3 H, Me), 2.09 (s, 6 H, Me); $^{13}$C NMR (100 MHz, $CD_2Cl_2$): $\delta$ = 161.4, 160.6, 146.1, 145.3, 141.0, 138.2, 137.3, 136.5, 136.0, 128.5, 128.0, 127.7, 127.4, 124.7, 121.8, 118.7, 84.4, 82.3, 80.9, 70.9, 70.0, 68.8, 21.3, 20.0; IR (KBr) $\nu$ 3281, 3089, 2916, 2359, 1609, 1592, 1516, 1456, 1387, 1279, 1107, 1003, 911, 841, 643; ESI-MS: *m/z* (%) 507.3 (100) $[M+H]^+$; Anal. calcd. for $C_{33}H_{26}N_2Fe$•0.25 $C_4H_8O_2$: C, 77.28; H, 5.34; N, 5.30; found: C, 77.58; H, 5.39; N, 5.04.

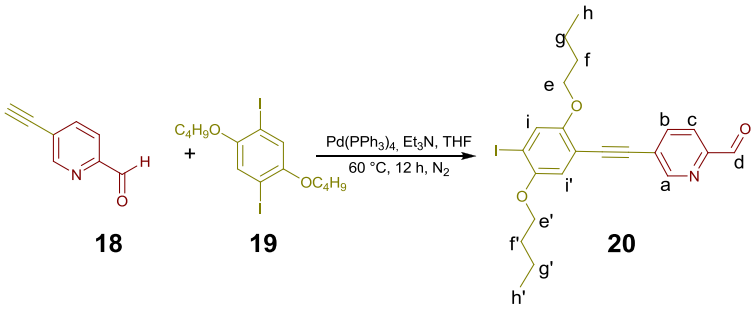
**3-((2,5-Dibutoxy-4-((2,9-dimesityl-1,10-phenanthrolin-3-yl)ethynyl)phenyl)ethynyl)-9-ferrocenyl-2-mesityl-1,10-phenanthroline (8)**




3-((2,5-Dibutoxy-4-iodophenyl)ethynyl)-2,9-dimesityl-1,10-phenanthroline (**17**,[6] 160 mg, 203 µmol), 3-ethynyl-9-ferrocenyl-2-mesityl-[1,10]-phenanthroline (**16**, 100 mg, 197 µmol) and $Pd(PPh_3)_4$ (46.0 mg, 39.8 µmol) were placed in an oven-dried 100-mL flask under nitrogen atmosphere. After addition of dry THF (40 mL) and $Et_3N$ (40 mL), the solution was degassed thrice by freeze-pump-thaw cycles. Finally, after addition of tri-*tert*-butylphosphine (200 µL), the mixture was refluxed at 60 °C for 24 h under nitrogen atmosphere. Then it was cooled down to room temperature and the solvents were removed under reduced pressure. The residue was dissolved in DCM and washed with water (200 mL). After drying over $Na_2SO_4$, the solvent was evaporated to furnish the crude product. The crude product was first purified using column chromatography ($SiO_2$, *n*-hexane: ethyl acetate = 88:12) to furnish an orange solid ($R_f$ =0.26 [$SiO_2$, EtOAC: *n*-hexane = 16:84]). Yield = 24 mg (10%); mp > 250 °C; $^1$H NMR (400 MHz, $CD_2Cl_2$) $\delta$ = 8.48 (s, 1 H, 4′-H), 8.45 (s, 1 H, 4-H), 8.33 (d, $^3J$ = 8.4 Hz, 1 H, 7′-H), 8.17 (d, $^3J$ = 8.4 Hz, 1 H, 7-H), 7.92 (d, $^3J$ = 8.8 Hz, 1 H, 5′-H), 7.87 (d, $^3J$ = 8.8 Hz, 1 H, 6′-H), 7.83 (d, $^3J$ = 8.8 Hz, 1 H, 5-H), 7.82 (d, $^3J$ = 8.4 Hz, 1 H, 8-H), 7.79 (d, $^3J$ = 8.8 Hz, 1 H, 6-H), 7.57 (d, $^3J$ = 8.4 Hz, 1 H, 8′-H), 7.06 (s, 2 H, x-H), 6.98 (s, 2 H, y-H), 6.96 (s, 2 H, y′-H), 6.41 (s, 1 H, [p/p′]-H), 6.40 (s, 1 H, [p/p′]-H), 5.18 (t, $^3J$ = 2.0 Hz, 2 H, α-H), 4.48 (t, $^3J$

= 2.0 Hz, 2 H, β-H), 4.06 (s, 5 H, γ-H), 3.88 (t, $^{3}J$ = 6.4 Hz, 2 H, [m/m′]-H), 3.87 (t, $^{3}J$ = 6.4 Hz, 2 H, [m/m′]-H), 2.42 (s, 3 H, Me), 2.36 (s, 3 H, Me), 2.33 (s, 3 H, Me), 2.13 (s, 6 H, Me), 2.05 (s, 6 H, Me), 2.05 (s, 6 H, Me), 1.84-1.76 (m, 4 H, l, l′-H), 1.62-1.56 (m, 4 H, k, k′-H), 1.07 (t, $^{3}J$ = 7.2 Hz, 3 H, [j/j′]-H), 1.07 (t, $^{3}J$ = 7.2 Hz, 3 H, [j/j′]-H); $^{13}$C NMR (100 MHz, $CD_2Cl_2$): $\delta$ = 161.8, 161.3, 160.8, 160.4, 153.4, 153.3, 146.3, 146.1, 145.2, 144.8, 139.1, 138.9, 138.3, 137.9, 137.8, 137.6, 137.5, 136.7, 136.4 (2C), 136.0, 136.0, 135.2, 130.2, 128.6, 128.4, 128.2, 127.9, 127.8, 127.6, 127.5, 127.3, 127.2, 126.0, 125.1, 124.9, 121.6, 120.1, 120.0, 117.5 (2C), 114.0, 92.4, 91.8, 91.8, 84.4, 70.8, 70.0, 69.4, 68.8, 31.7 (2C), 21.4, 21.4, 21.2, 20.4 (2C), 20.1, 20.0 (2C), 19.7 (2C), 14.1 (2C); IR (KBr) $\nu$ 3429, 2953, 2920, 2865, 2205, 1714, 1611, 1582, 1503, 1464, 1381, 1208, 1106, 1063, 1023, 846, 720, 638, 608, 484; ESI-MS: *m*/*z* (%) 1165.8 (100) $[M + H]^{+}$; Anal. calcd. for $C_{79}H_{72}N_4O_2Fe$: C, 81.43; H, 6.23; N, 4.81; found: C, 81.29; H, 5.98, N, 4.50.

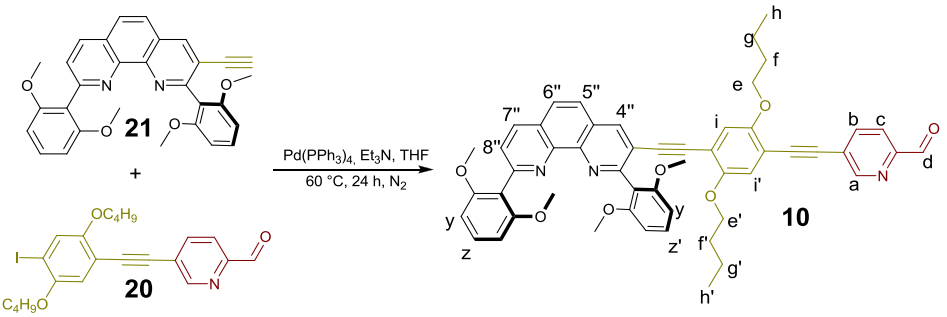
**5-((2,5-Dibutoxy-4-iodophenyl)ethynyl)picolinaldehyde (20)**




Under $N_2$ atmosphere an oven-dry 100-mL flask was charged with 5-ethynylpicolinaldehyde (**18**,[3] 140 mg, 1.07 mmol), 1,4-dibutoxy-2,5-diiodobenzene (**19**, 2.17 mg, 4.58 mmol) and $Pd(PPh_3)_4$ (30.0 mg, 26.0 μmol). After addition of dry $Et_3N$ (15 mL) and dry THF (30 mL), the mixture was refluxed for 12 h under $N_2$ atmosphere. Following removal of all solvents, the resulting solid was dissolved in DCM and washed with water. The residue was purified by column chromatography using DCM as eluent affording **20** as yellow solid ($R_f$ =0.25 [$SiO_2$, DCM:*n*-hexane = 6:4]. Yield = 240 mg (47%); mp = 93 °C; $^{1}$H NMR (400 MHz, $CD_2Cl_2$) $\delta$ = 10.04 (d, $^{5}J$ = 0.4 Hz, 1 H, d-H), 8.87 (dd, $^{4}J$ = 2.0 Hz, $^{5}J$ = 1.2 Hz, 1 H, a-H), 7.96 (ddd, $^{3}J$ = 8.4 Hz, $^{4}J$ = 2.0 Hz, $^{5}J$ = 0.4 Hz, 1 H, b-H), 7.92 (dd, $^{3}J$ = 8.4 Hz, $^{5}J$ = 1.2 Hz, 1 H, c-H), 7.38 (s, 1 H, i′-H), 6.96 (s, 1 H, i-H), 4.01 (t, $^{3}J$ = 6.4 Hz, 2 H, [e/e′]-H), 3.99 (t, $^{3}J$ = 6.4 Hz, 2 H, [e/e′]-H), 1.85-1.77 (m, 4 H, f, f′-H), 1.61-1.51 (m, 4 H, g, g′-H), 1.00 (t, $^{3}J$ = 7.4 Hz, 3 H, [h/h′]-H), 0.99 (t, $^{3}J$ = 7.4 Hz, 3 H, [h/h′]-H); $^{13}$C NMR (100 MHz, $CD_2Cl_2$): $\delta$ = 192.9, 155.0, 152.7, 152.3, 151.4, 139.4, 125.3, 124.2, 121.2, 116.1, 112.4, 92.8, 90.5, 89.6, 70.2, 69.9,

31.6, 31.6, 19.7, 19.6, 14.0, 14.0; IR (KBr) *v* 3425, 2935, 2206, 1706, 1588, 1470, 1430, 1250,1207, 1114, 1025, 848, 779, 733; Anal. calcd. for $C_{22}H_{24}INO_3$•1/2 $H_2O$: C, 54.33; H, 5.18; N, 2.88; found: C, 54.01; H, 5.01, N, 2.96.

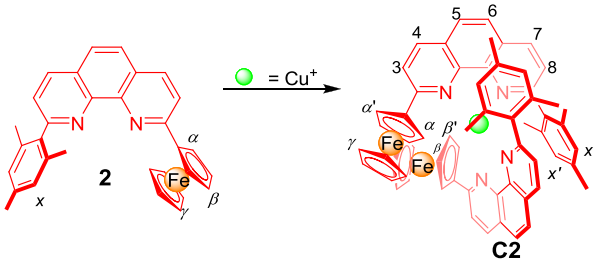
**5-((4-((2,9-Bis(2,6-dimethoxyphenyl)-1,10-phenanthrolin-3-yl)ethynyl)-2,5-dibutoxyphenyl)ethynyl)picolinaldehyde (10)**




5-((2,5-Dibutoxy-4-iodophenyl)ethynyl)picolinaldehyde (**20**, 78.0 mg, 163 μmol), 2,9-bis(2,6-dimethoxyphenyl)-3-ethynyl-[1,10]-phenanthroline (**21**,[5] 65.0 mg, 136 μmol), $Pd(PPh_3)_4$ (30.0 mg, 26.0 μmol), dry $NEt_3$ (10 mL) and dry THF (20 mL) were placed in a 100 mL flask under nitrogen atmosphere and the mixture was heated to reflux for 24 h. After removal of all solvents, the resulting solid was dissolved in DCM and washed with water. The organic layer was dried over $Na_2SO_4$ and then purified by column chromatography ($SiO_2$) starting with DCM as eluent, later switching to 5% EtOAc in DCM to afford **10** as a pale yellow solid ($R_f$ =0.20 [$SiO_2$, EtOAC:DCM = 8:92]. Yield = 67 mg (58%); mp = 227 °C; $^1$H NMR (400 MHz, $CD_2Cl_2$) $\delta$ = 10.05 (d, $^5J$ = 0.8 Hz, 1 H, d-H), 8.87 (dd, $^4J$ = 2.0 Hz, $^5J$ = 1.2 Hz, 1 H, a-H), 8.45 (s, 1 H, 4″-H), 8.31 (d, $^3J$ = 8.4 Hz, 1 H, 7″-H), 7.95 (ddd, $^3J$ = 8.4 Hz, $^4J$ = 2.0 Hz, $^5J$ = 0.8 Hz, 1 H, b-H), 7.93 (dd, $^3J$ = 8.4 Hz, $^5J$ = 1.2 Hz, 1 H, c-H), 7.90 (d, $^3J$ = 8.8 Hz, 1 H, 5″-H), 7.85 (d, $^3J$ = 8.8 Hz, 1 H, 6″-H), 7.59 (d, $^3J$ = 8.4 Hz, 1 H, 8″-H), 7.42 (t, $^3J$ = 8.4 Hz, 1 H, z′-H), 7.38 (t, $^3J$ = 8.4 Hz, 1 H, z-H), 7.01 (s, 1 H, i-H), 6.75 (d, $^3J$ = 8.4 Hz, 2 H, y′-H), 6.71 (d, $^3J$ = 8.4 Hz, 2 H, y-H), 6.39 (s, 1 H, i′-H), 4.00 (t, $^3J$ = 6.8 Hz, 2 H, [e/e′]-H), 3.94 (t, $^3J$ = 6.8 Hz, 2 H, [e/e′]-H), 3.73 (s, 6 H, OMe), 3.71 (s, 6 H, OMe), 1.89-1.78 (m, 4 H, f, f′-H), 1.64-1.53 (m, 4 H, g, g′-H), 1.06 (t, $^3J$ = 7.2 Hz, 6 H, h, h′-H); $^{13}$C NMR (100 MHz, $CD_2Cl_2$): $\delta$ = 192.9, 158.8, 158.5, 157.3, 156.1, 154.2, 153.4, 152.7, 151.3, 146.3, 145.2, 139.4, 138.5, 136.2, 130.2, 130.2, 128.4, 127.6, 127.5, 126.3, 126.2, 125.3, 121.2, 121.0, 119.6, 118.9, 117.5, 117.4, 115.4, 112.9, 104.2, 104.2, 93.2, 93.1, 91.4, 91.2, 69.9, 69.6, 56.4, 56.3, 31.6, 31.6, 19.7, 19.6, 14.1, 14.1; IR (KBr) *v* 3874, 3750, 3680, 3427, 3060, 2942, 2869, 2837, 2361, 2206, 1707, 1588, 1469, 1429, 1281, 1250, 1207, 1115, 1023, 912, 848, 780, 733, 562;

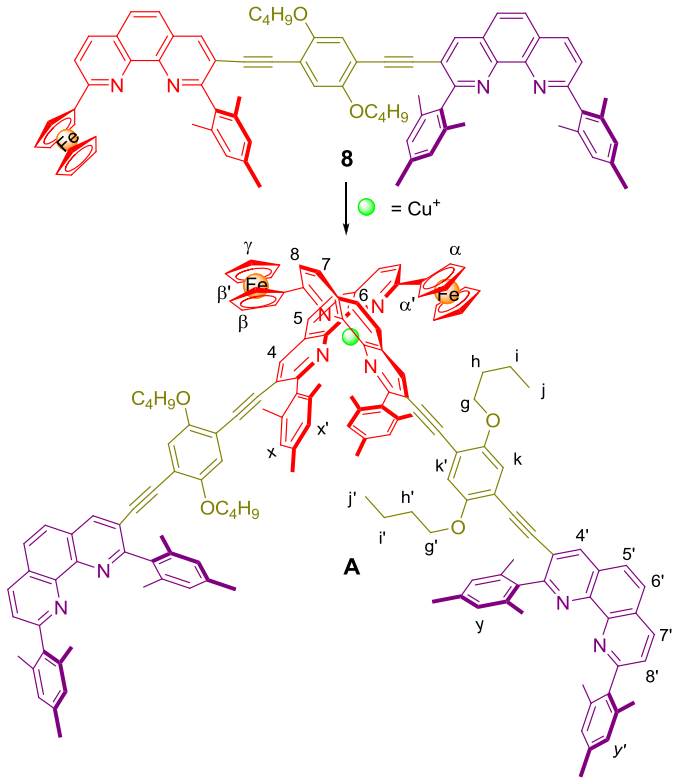
ESI-MS: *m/z* (%) 826.7 (100) $[M+H]^+$; Anal. calcd. for $C_{52}H_{47}N_3O_7$•0.5 $H_2O$: C, 74.80; H, 5.79; N, 5.03; found: C, 74.83; H, 5.57, N, 4.99.

**Model complex C2 = $[Cu(2)_2](PF_6)$**




2-Ferrocenyl-9-mesityl-[1,10]-phenanthroline (**2**, 8.43 mg, 17.5 µmol) and $[Cu(MeCN)_4]PF_6$ (3.26 mg, 8.75 µmol) were loaded in an NMR tube and dissolved in $CD_2Cl_2$. The resultant mixture was subjected to analytical characterisation without any further purification. Single crystals suitable for X-ray analysis were obtained by slow diffusion of $Et_2O$ into the above mixture. Yield quantitative; mp (with decomposition) > 180 °C; $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 8.39 (d, $^3J$ = 8.0 Hz, 2 H, 7-H), 8.29 (d, $^3J$ = 8.4 Hz, 2 H, 4-H), 7.99 (d, $^3J$ = 8.4 Hz, 4 H, 3-H, 5-H), 7.96 (d, $^3J$ = 8.4 Hz, 2 H, 6-H), 7.32 (d, $^3J$ = 8.0 Hz, 2 H, 8-H), 6.45 (s, 2 H, [x/x′]-H), 5.62 (dt, $^3J$ = 2.4 Hz, $^4J$ = 1.2 Hz, 2 H, [α/α′]-H), 5.60 (s, 2 H, [x/x′]-H), 5.01 (dt, $^3J$ = 2.4 Hz, $^4J$ = 1.2 Hz, 2 H, [α/α′]-H), 4.56 (dt, $^3J$ = 2.4 Hz, $^4J$ = 1.2 Hz, 2 H, [β/β′]-H), 4.29 (dt, $^3J$ = 2.4 Hz, $^4J$ = 1.2 Hz, 2 H, [β/β′]-H), 4.23 (s, 10 H, γ-H), 2.10 (s, 6 H, Me), 1.06 (s, 6 H, Me), 0.63 (s, 6 H, Me); $^{13}$C NMR (100 MHz, $CD_2Cl_2$): $\delta$ = 159.8, 159.4, 144.4, 144.0, 137.8, 137.7, 136.0, 135.8, 134.9, 133.3, 128.6, 128.5, 128.3, 127.2, 126.8, 126.6, 125.9, 109.9, 83.1, 73.9, 71.9, 71.4, 71.1, 68.8, 21.2, 20.7, 19.3; IR (KBr) *v* 3447, 3088, 2917, 2857, 2373, 1614, 1583, 1511, 1355, 1280, 1108, 847, 556, 490; ESI-MS: *m/z* (%) 1027.3(100) $[M-PF_6]^+$; Anal. calcd. for $C_{62}H_{52}CuF_6Fe_2N_4P$•1.25 $CH_2Cl_2$: C, 59.37; H, 4.29; N, 4.38; found: C, 59.37; H, 4.17; N, 4.32.

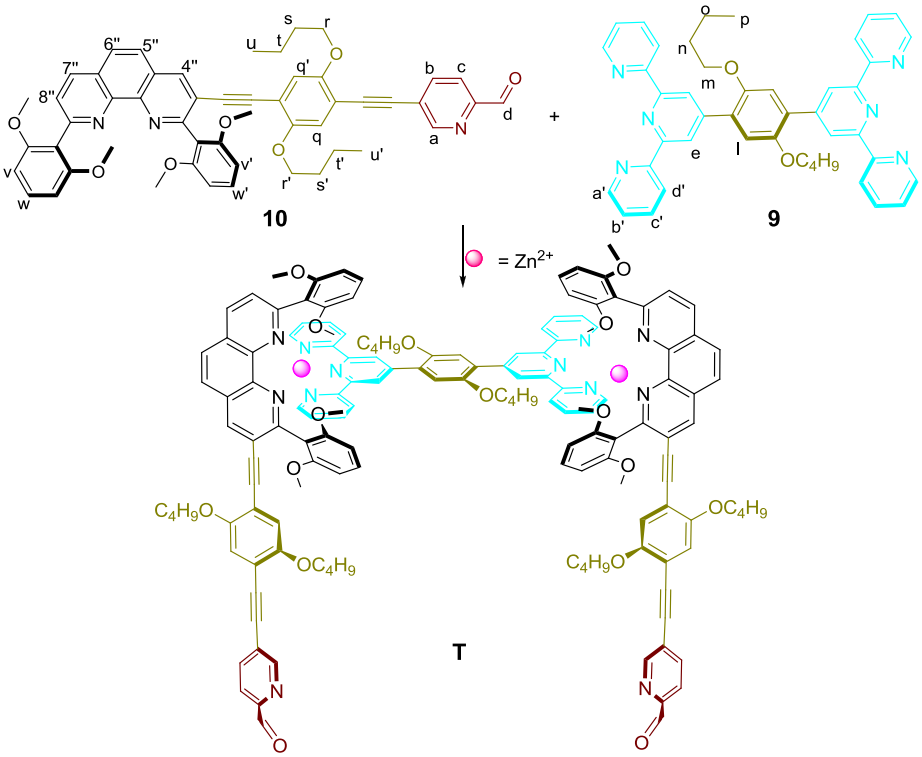
**Metalloligand A = [Cu(8)$_2$](PF$_6$)**




[Cu(MeCN)$_4$]PF$_6$ (673 µg, 1.81 µmol) and 9-(ferrocenyl)-3-((2,5-dibutoxy-4-((2,9-dimesityl-1,10-phenanthrolin-3-yl)ethynyl)phenyl)ethynyl)-2-mesityl-1,10-phenanthroline (**8**, 4.21 mg, 3.61 µmol) were loaded in an NMR tube and dissolved in $CD_2Cl_2$. The resultant mixture was subjected to analytical characterisation without any further purification. Yield quantitative; mp > 250 °C; $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 8.50 (s, 2 H, 4-H), 8.42 (s, 2 H, 4'-H), 8.32 (d, $^3J$ = 8.2 Hz, 2 H, 7-H), 8.30 (d, $^3J$ = 8.4 Hz, 2 H, 7'-H), 8.00 (d, $^3J$ = 8.2 Hz, 2 H, 8-H), 7.99 (d, $^3J$ = 8.8 Hz, 2 H, 5-H), 7.96 (d, $^3J$ = 8.8 Hz, 2 H, 6-H), 7.91 (d, $^3J$ = 8.8 Hz, 2 H, 5'-H), 7.84 (d, $^3J$ = 8.8 Hz, 2 H, 6'-H), 7.56 (d, $^3J$ = 8.4 Hz, 2 H, 8'-H), 6.94 (s, 4 H, [y/y']-H), 6.92 (s, 4 H, [y/y']-H), 6.48 (s, 2 H, [x/x′]-H), 6.29 (s, 2 H, [k/k′]-H), 5.90 (s, 2 H, [k/k′]-H), 5.65(s, 2 H, [x/x′]-H), 5.61 (br, 2 H, [α/α′]-H), 5.03 (br, 2 H, [α/α′]-H), 4.60 (br, 2 H, [β/β′]-H), 4.33 (br, 2 H, [β/β′]-H), 4.26 (s, 10 H, γ-H), 3.74 (t, $^3J$ = 6.0 Hz, 4 H, [g/g′]-H), 3.65 (t, $^3J$ = 6.0 Hz, 4 H, [g/g′]-H), 2.32 (s, 6 H, Me), 2.30 (s, 6 H, Me), 2.12 (s, 6 H, Me), 2.03 (s, 12 H, Me), 2.00 (s, 12 H, Me), 1.74-1.65 (m, 8 H, h, h′-H), 1.53-1.51 (m, 8 H, i, i′-H), 1.10 (s, 6 H, Me),1.02 (t, $^3J$ = 7.2 Hz, 6 H, [j/j′]-H), 0.99 (t, $^3J$ = 7.2 Hz, 6 H, [j/j′]-H), 0.75 (s, 6 H, Me); $^{13}$C NMR (100 MHz, $CD_2Cl_2$): δ = 161.8, 161.2, 160.9, 160.0, 153.4, 153.1, 146.4, 145.4, 144.0, 142.7, 139.5, 138.9, 138.4, 137.8, 137.6, 137.5, 136.4 (2C), 136.3, 136.1, 135.0, 134.9, 134.1, 128.7, 128.6 (2C), 128.4, 128.2, 128.2, 128.0, 127.4, 127.2, 126.3, 125.9, 125.6, 125.2, 122.7, 119.9, 117.4, 117.3, 114.8, 112.7, 93.6, 92.9, 91.4, 90.2, 83.1, 74.2, 72.1, 71.6, 71.2,

69.3, 69.2, 68.7, 31.5, 31.5, 21.5, 21.3, 21.2, 20.4, 20.3, 20.0, 20.0, 19.7, 19.7, 19.6, 19.3, 14.1, 14.1; IR (KBr) *v* 3905, 3867, 3752, 3681, 3445, 2925, 2370, 2206, 1620, 1461, 1272, 1207, 1105, 1026, 847, 720, 555, 491; ESI-MS: *m*/*z* (%) 2392.2 (100) $[M-PF_6]^+$. Anal calcd for $C_{158}H_{144}CuF_6Fe_2N_8O_4P{\bullet}H_2O$: C, 74.21; H, 5.75; N, 4.38; found: C, 74.27; H, 5.97; N, 4.27.

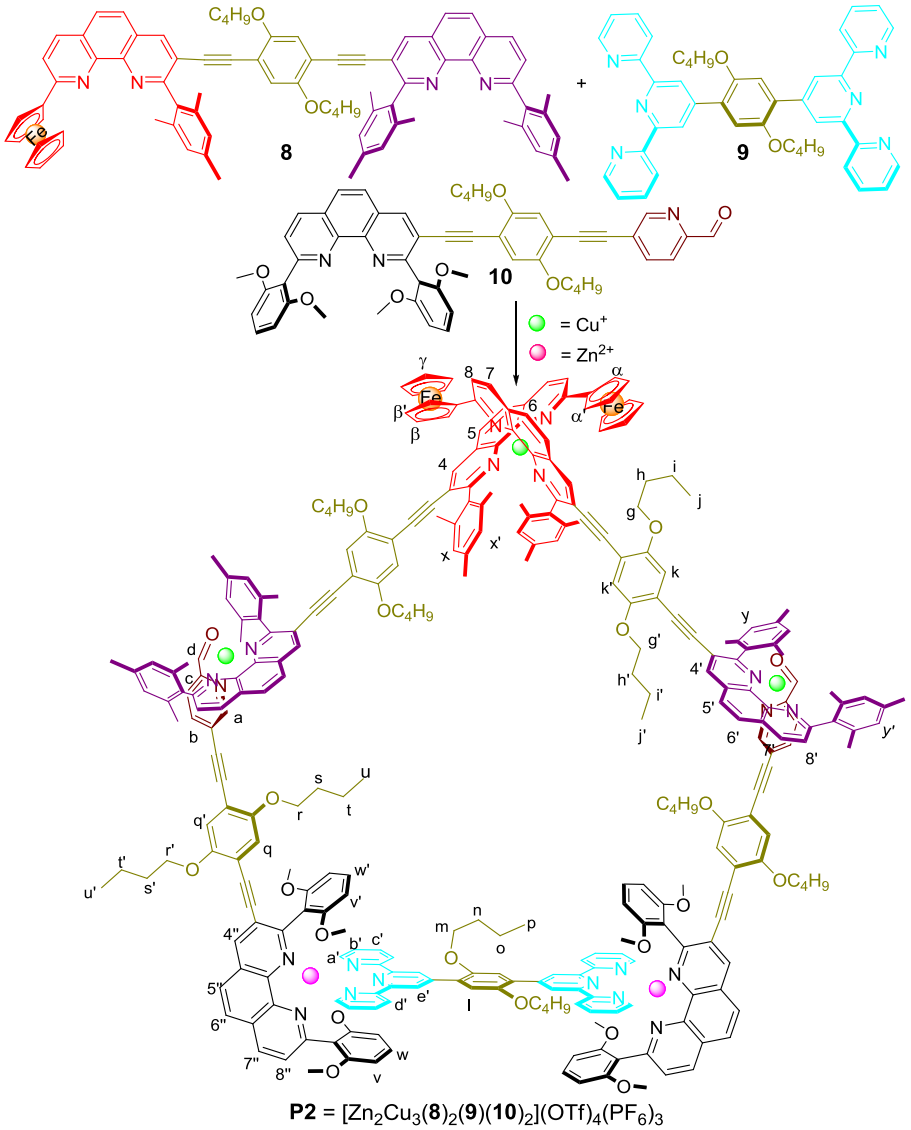
**Metalloligand T = $[Zn_2(10)(9)](OTf)_4$**




In an oven-dried 10-mL flask, the phenanthroline-picolinaldehyde hybrid **10** (2.09 mg, 2.53 μmol), bisterpyridine **9** (866 μg, 1.27 μmol) and $Zn(OTf)_2$ (919 μg, 2.53 μmol) were refluxed in 15 mL of $CH_2Cl_2/CH_3CN$ (4:1) for 2 h. The reaction mixture was then cooled down to room temperature, and solvents were removed under reduced pressure. The resultant mixture was subjected to analytical characterisation without any further purification. Yield quantitative; mp > 250 °C; $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 10.02 (s, 2 H, d-H), 9.00 (s, 2 H, 4″-H), 8.99 (d, $^3J$ = 8.4 Hz, 2 H, 7″-H), 8.95 (s, 4 H, e-H), 8.83 (dd, $^4J$ = 1.6 Hz, $^5J$ = 1.2 Hz, 2 H, a-H), 8.74 (d, $^3J$ = 8.4 Hz, 4 H, d'-H), 8.50 (d, $^3J$ = 8.8 Hz, 2 H, 5″-H), 8.43 (d, $^3J$ = 8.8 Hz, 2 H, 6″-H), 8.31 (td, $^3J$ = 8.4 Hz, $^4J$ = 1.6 Hz, 4 H, c'-H), 8.05 (d, $^3J$ = 8.4 Hz, 2 H, 8″-H), 7.93-7.91 (m, 4 H, b, c-H), 7.66 (s, 2 H, l-H), 7.63 (dd, $^3J$ = 4.4 Hz, $^4J$ = 1.6 Hz, 4 H, a'-H), 7.65 (dd, $^3J$ = 8.4 Hz, $^4J$ = 4.4 Hz, 4 H, b'-H), 7.04 (t, $^3J$ = 8.4 Hz, 2 H, w′-H), 7.01 (t, $^3J$ = 8.4 Hz, 2 H, w-H), 6.97 (s, 2 H, [q/q']-H), 6.38 (s, 2 H, [q/q']-H), 6.15 (d, $^3J$ = 8.4 Hz, 4 H, v′-H), 6.13 (d, $^3J$ = 8.4 Hz, 4 H, v-H), 4.55 (t, $^3J$ = 6.0 Hz, 4 H, m-H), 3.91 (t, $^3J$ = 6.4 Hz, 4 H, [r/r′]-H),

3.82 (t, $^3J$ = 6.4 Hz, 4 H, [r/r′]-H), 2.97 (s, 12 H, OC$\underline{H}_3$), 2.95 (s, 12 H, OC$\underline{H}_3$), 1.97-1.90 (m, 4 H, n-H), 1.79-1.71 (m, 4 H, o-H), 1.70-1.60 (m, 8 H, s, s′-H), 1.54-1.43 (m, 8 H, t, t′-H), 1.00 (t, $^3J$ = 7.2 Hz, 6 H, [u/u′]-H), 0.99 (t, $^3J$ = 7.2 Hz, 6 H, [u/u′]-H), 0.98 (t, $^3J$ = 6.8 Hz, 6 H, p-H); $^{13}$C NMR (100 MHz, $CD_2Cl_2$): 192.8, 158.6, 157.7, 157.4, 157.2, 155.0, 154.0, 153.9, 152.7, 151.5, 151.3, 148.6, 147.4, 147.4, 142.9, 142.5, 141.8, 141.1, 139.5, 139.2, 133.2, 130.0, 129.1, 128.9, 128.8, 128.0, 127.6, 127.5, 125.7, 124.9, 124.2, 123.4, 123.0, 121.2, 117.3, 117.2, 115.7, 114.8, 114.5, 114.3, 113.3, 103.9, 103.8, 95.2, 92.5, 91.9, 90.0, 69.6, 69.6, 55.7, 55.6, 54.3, 32.2, 31.5, 31.4, 20.1, 19.6, 19.5, 14.3, 14.0, 14.0; IR (KBr) *v* 3445, 3074, 2935, 2366, 2208, 1713, 1599, 1474, 1427, 1263, 1158, 1109, 1027, 858, 789, 637, 517; ESI-MS: *m/z* (%) 872.5 (35) $[M-3OTf]^{3+}$, 1382.8 (100) $[M-2OTf]^{2+}$; Anal. calcd. for $C_{152}H_{134}F_{12}N_{12}O_{28}S_4Zn_2$•1.25 $CH_2Cl_2$: C, 58.06; H, 4.34; N, 5.30; S, 4.05; found: C, 57.93; H, 4.19; N, 5.05; S, 3.82.

**Five-component pentagon P2 = $[Zn_2Cu_3(8)_2(9)(10)_2](OTf)_4(PF_6)_3$**



In an oven-dried 25-mL flask, phenanthroline-picolinaldehyde hybrid **10** (306 μg, 0.370 μmol), bisterpyridine **9** (127 μg, 0.185 μmol) and $Zn(OTf)_2$ (135 μg, 0.371 μmol) were refluxed in 15 mL of $CH_2Cl_2/CH_3CN$ (4:1) for 2 h. The reaction mixture was then cooled down to room temperature, and solvents were removed under reduced pressure. After addition of solid $[Cu(MeCN)_4]PF_6$ (207 μg, 0.555 μmol) and bisphenanthroline **8** (432 μg, 0.371 μmol) and 15 mL of $CH_2Cl_2$ the resultant mixture was refluxed for 2 h. It was then cooled down to room temperature, then $CH_2Cl_2$ was removed at reduced pressure. The residue was subjected to analytical characterisation without any further purification. Yield quantitative; mp > 250 °C. $^1$H NMR (400 MHz, 298 K, $CD_2Cl_2$) of two diastereomers in ratio of 19:1 $\delta$ = 9.47 (s, 1.9 H, d-H), 9.45 (s, 0.1 H, d-H), 9.02 (s, 1.9 H, 4″-H), 8.98 (d, $^3J$ = 8.4 Hz, 2 H, 7″-H), 8.85 (s, 0.1 H, 4″-H), 8.84 (s, 0.2 H, e′-H), 8.82 (s, 3.8 H, e′-H), 8.71 (s, 2 H, 4′-H), 8.67 (d, $^3J$ = 8.4 Hz, 2 H, 7′-H), 8.65 (d, $^3J$ = 8.4 Hz, 4 H, d'-H), 8.50 (d, $^3J$ = 9.2 Hz, 2 H, 5″-H), 8.47 (s, 2 H, 4-H), 8.45 (d, $^3J$ = 9.2 Hz, 2 H, 6″-H), 8.33-8.29 (m, 8 H, a, c', 7-H), 8.17 (d, $^3J$ = 9.2 Hz, 2 H, 5-H), 8.11 (d, $^3J$ = 9.2 Hz, 2 H, 6-H), 8.08 (dd, $^3J$ = 8.0 Hz, $^4J$ = 1.6 Hz, 2 H, b-H), 8.06 (d, $^3J$ = 8.4 Hz, 2 H, 8″-H), 8.00 (d, $^3J$ = 8.4 Hz, 2 H, 8-H), 7.98 (d, $^3J$ = 8.8 Hz, 2 H, 5′-H), 7.94 (d, $^3J$ = 8.8 Hz, 2 H, 6′-H), 7.88 (d, $^3J$ = 8.4 Hz, 2 H, 8′-H), 7.72 (d, $^3J$ = 8.0 Hz, 2 H, c-H), 7.63 (d, $^3J$ = 4.4 Hz, 4 H, a'-H), 7.61 (s, 1 H, l-H), 7.55-7.51 (m, 4 H, b'-H), 7.28 (br, 3H, [q/q'], l-H), 7.04 (t, $^3J$ = 8.4 Hz, 2 H, w′-H), 7.03 (t, $^3J$ = 8.4 Hz, 2 H, w-H), 6.98 (s, 2 H, [q/q']-H), 6.58 (br, 4 H, [y/y']-H), 6.50 (br, 4 H, [y/y']-H), 6.43 (s, 2 H, [x/x′]-H), 6.38 (s, 2 H, [k/k']-H), 6.16 (d, $^3J$ = 8.4 Hz, 4 H, v′-H), 6.12 (d, $^3J$ = 8.4 Hz, 4 H, v-H), 5.89 (s, 2 H, [k/k′]-H), 5.59 (s, 2 H, [x/x′]-H), 5.57 (br, 2 H, [α/α′]-H), 5.01 (br, 2 H, [α/α′]-H), 4.58 (br, 2 H, [β/β′]-H), 4.50 (t, $^3J$ = 6.0 Hz, 4 H, m-H), 4.32 (br, 2 H, [β/β′]-H), 4.24 (s, 10 H, γ-H), 3.91 (t, $^3J$ = 6.4 Hz, 4 H, [r/r′]-H), 3.82 (t, $^3J$ = 6.4 Hz, 4 H, [r/r′]-H), 3.68-3.54 (m, 8 H, g, g′]-H), 2.97 (s, 11.4 H, OC$\underline{H}_3$), 2.93 (s, 11.4 H, OC$\underline{H}_3$), 2.92 (s, 0.6 H, OC$\underline{H}_3$), 2.91 (s, 0.6 H, OC$\underline{H}_3$), 2.06 (s, 6 H, Me), 2.03 (s, 6 H, Me), 1.97 (s, 6 H, Me), 1.89 (s, 12 H, Me), 1.87 (s, 12 H, Me), 1.74-1.34 (m, 40 H, h, h′, i, i′, s, s′, t, t′, n, o-H), 1.10 (s, 6 H, Me), 0.98 (t, $^3J$ = 7.2 Hz, 6 H, p-H), 0.92-0.82 (m, 24 H, j, j′, u, u′-H), 0.69 (s, 6 H, Me); IR (KBr) *v* 3446, 2929, 2866, 2345, 2291, 2209, 1708 (C=O), 1605, 1472, 1261, 1157, 1111, 1030, 844, 791, 639, 559; ESI-MS: *m*/*z* (%) 1057.6 (100) $[M-3PF_6, 2OTf]^{5+}$, 1358.5 (60) $[M-3PF_6, OTf]^{4+}$, 1861.2 (20) $[M-3PF_6]^{3+}$; Anal calcd for $C_{310}H_{278}Cu_3F_{30}Fe_2N_{20}O_{32}P_3S_4Zn_2 \bullet CH_2Cl_2$: C, 61.19; H, 4.62; N, 4.59; S, 2.10; found: C, 61.10; H, 4.51; N, 4.32; S, 2.38.

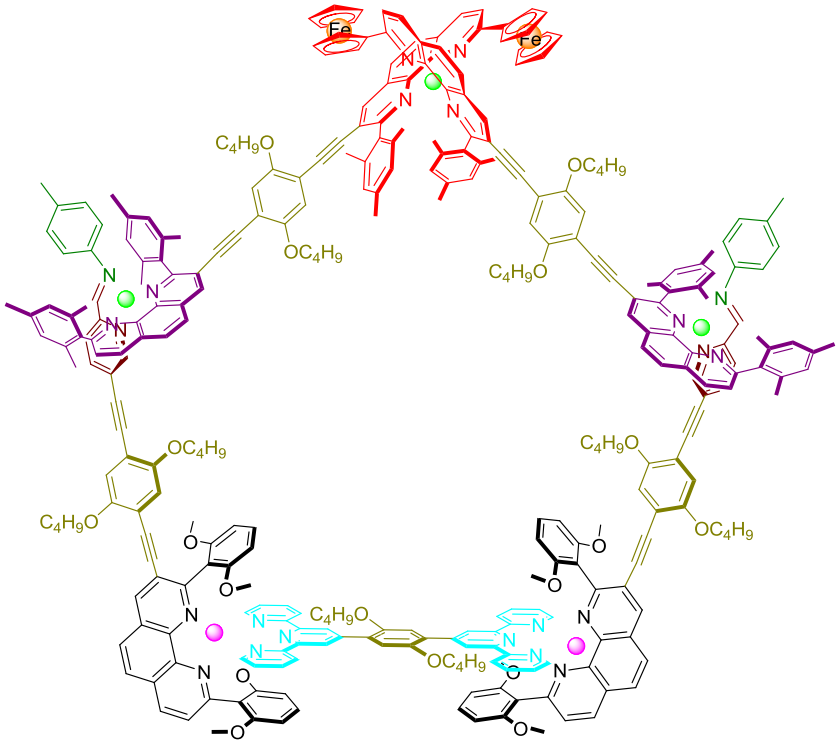
The following table summarises some diagnostic shifts indicating that in **P2** the complexation motifs of **C2**, **C3** and **C5** are well realised.

**Table S1: Selected chemical shifts (400 MHz, $CD_2Cl_2$, 298 K) in different complexes**

| Compounds | d-H | x-H + x'-H | y-H + y'-H | a'-H | OMe | a-H + a'-H |
|---|---|---|---|---|---|---|
| **8** | ..... | 7.06 | 6.96 & 6.98 | ..... | ..... | 5.18 |
| **9** | ..... | ..... | ..... | | ..... | ..... |
| **10** | 10.05 | ..... | ..... | ..... | 3.71 & 3.73 | ..... |
| **C2** | ..... | 5.60 & 6.45 | ..... | ..... | ..... | 5.01 & 5.62 |
| **C3** | ..... | ..... | ..... | 7.52 | 2.88 | ..... |
| **C5**[a,3] | 9.63 | ..... | 6.71 | ..... | ..... | ..... |
| **A** | ..... | 5.65 & 6.48 | 6.92 & 6.94 | ..... | ..... | 5.03 & 5.61 |
| **T** | 10.02 | ..... | ..... | 7.63 | 2.95 & 2.97 | ..... |
| **P2** | 9.47 & 9.45 | 5.59 & 6.43 | 6.50 & 6.58 | 7.63 | 2.97 – 2.91 | 5.01 & 5.57 |

[a] **C5** = [Cu(**1**)(**5**)]$PF_6$

**Six-component pentagon P1 = $[Zn_2Cu_3(8)_2(9)(11)_2](OTf)_4(PF_6)_3$**




**P1** = $[Zn_2Cu_3(\mathbf{8})_2(\mathbf{9})(\mathbf{11})_2](OTf)_4(PF_6)_3$
**11** = [(**10**)(**6**)-$H_2O$]

An oven-dried 25-mL flask was charged with metalloligands **A** = [Cu(**8**)$_2$]($PF_6$) (853 μg, 0.336 μmol), **T** = [$Zn_2$(**10**)(**9**)](OTf)$_4$ (1.03 mg, 0.336 μmol). After addition of 1.12 (M) *p*-toludine in (**6**, 300 μL) and $CH_2Cl_2$ (20 mL), the mixture was refluxed for 1 h. Following the

removal of all solvent, the resulting solid was dissolved in $CD_2Cl_2$ and subjected to analytical characterisation without any further purification. Yield quantitative; mp > 250 °C; IR (KBr) *v* 34447, 2930, 2372, 2208, 1618 (C=N), 1472, 1432, 1261, 1156, 1111, 1029, 844, 730, 639, 556; ESI-MS: *m*/*z* (%) 1093.2 (40) $[M-3PF_6, 2OTf]^{5+}$, 1403.1 (100) $[M-3PF_6, OTf]^{4+}$, 1920.6 (20) $[M-3PF_6]^{3+}$; The $^1$H-NMR of **P1** is complicated due to the existence of three possible diastereomers. Diagnostically, in the $^1$H NMR spectrum of **P1**, the resonance of the aldehyde (*d*-H) protons ($\delta$ = 9.47 and 9.45 ppm for **P2**) was absent, suggesting the complete formation of iminopyridine units of **11** = [(**10**)(**6**)-$H_2O$] in **P1**. The observed broadness of $^1$H signals obstructed our further analysis of the spectra. The DOSY NMR (Figure S34) of the pentagon shows all possible diastereomers to have approximately identical diffusion constant (*ca.* $D$ = $3.2 \times 10^{-10}$ $m^2s^{-1}$).

## $^{1}$H and $^{13}$C NMR Spectra

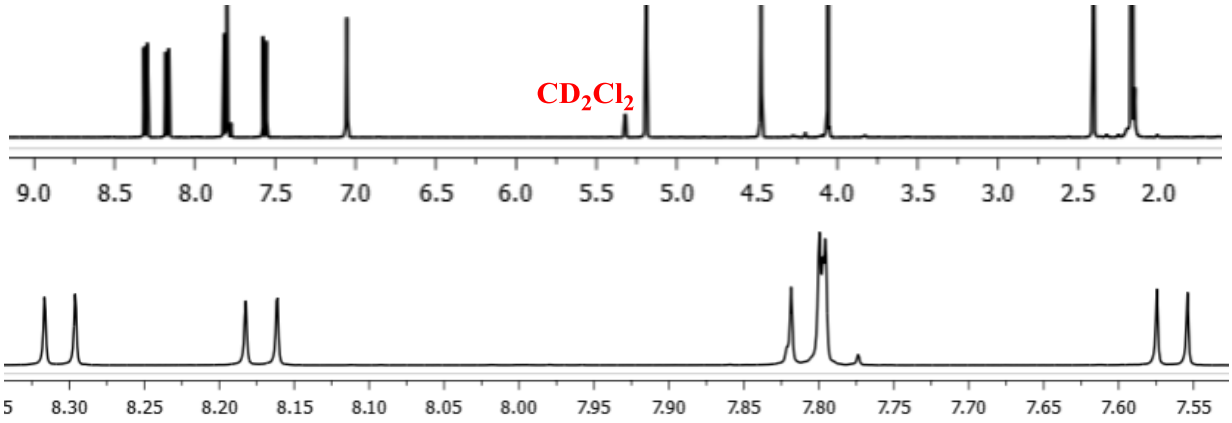



**Figure S1:** $^{1}$H NMR spectrum (400 MHz, $CD_2Cl_2$, 298 K) of ligand **2**. An expanded part of the aromatic region is shown at the bottom.

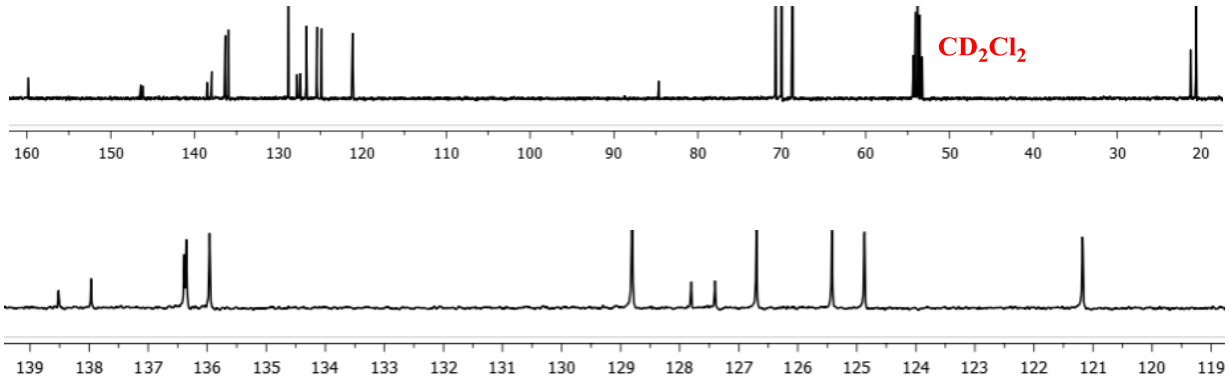



**Figure S2:** $^{13}$C NMR spectrum (100 MHz, $CD_2Cl_2$, 298 K) of ligand **2**. An expanded part of the aromatic region is shown at the bottom.

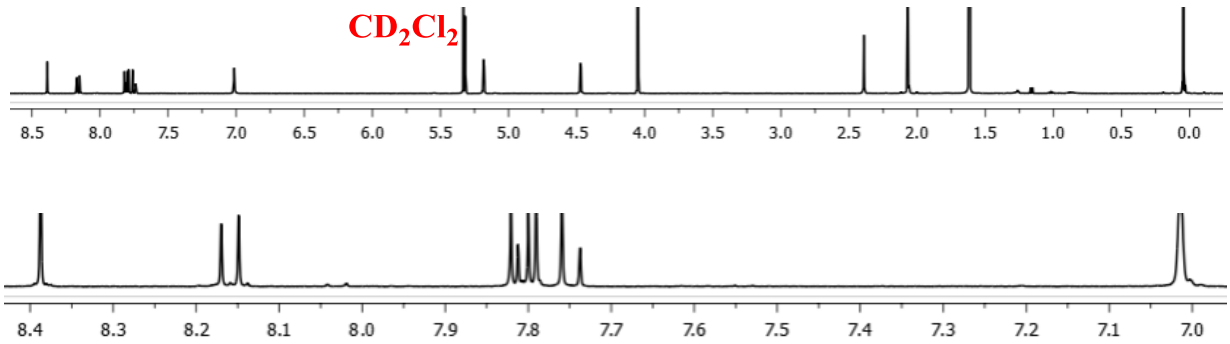



**Figure S3:** $^{1}$H NMR spectrum (400 MHz, $CD_2Cl_2$, 298 K) of **15**. An expanded part of the aromatic region is shown at the bottom.

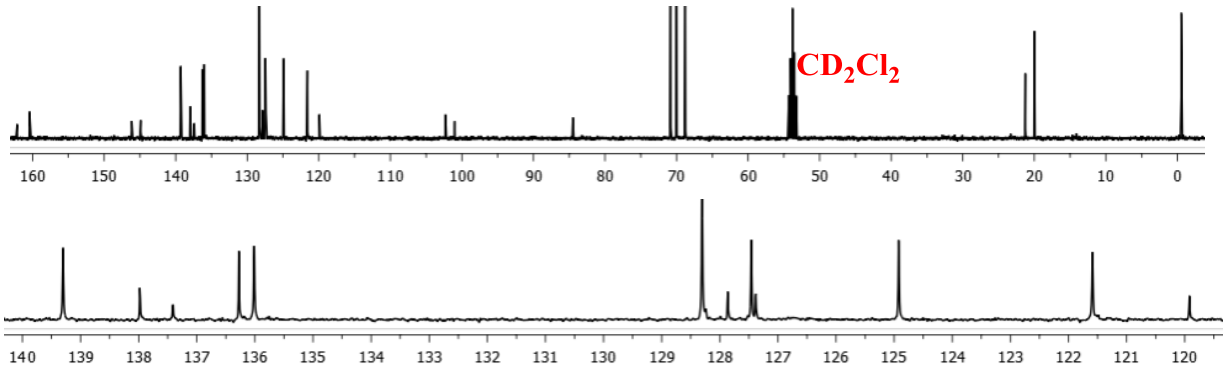



**Figure S4:** $^{13}C$ NMR spectrum (100 MHz, $CD_2Cl_2$, 298 K) of **15**. An expanded part of the aromatic region is shown at the bottom.

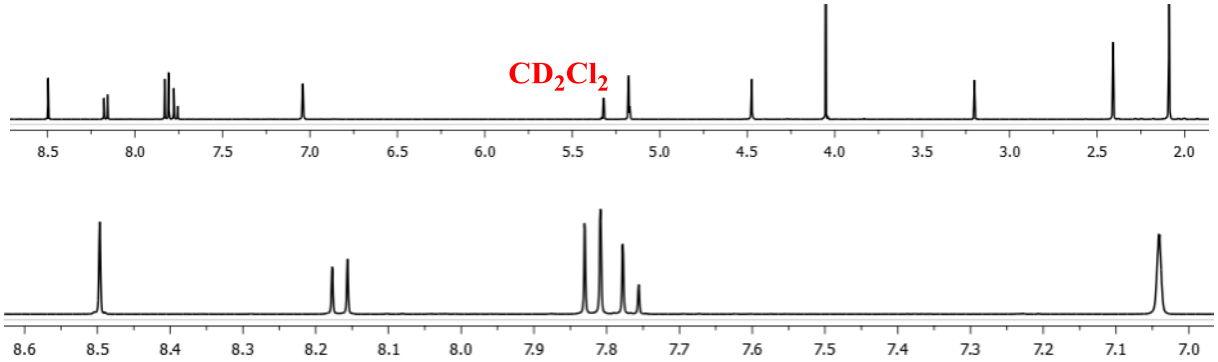



**Figure S5:** $^{1}H$ NMR spectrum (400 MHz, $CD_2Cl_2$, 298 K) of **16**. An expanded part of the aromatic region is shown at the bottom.

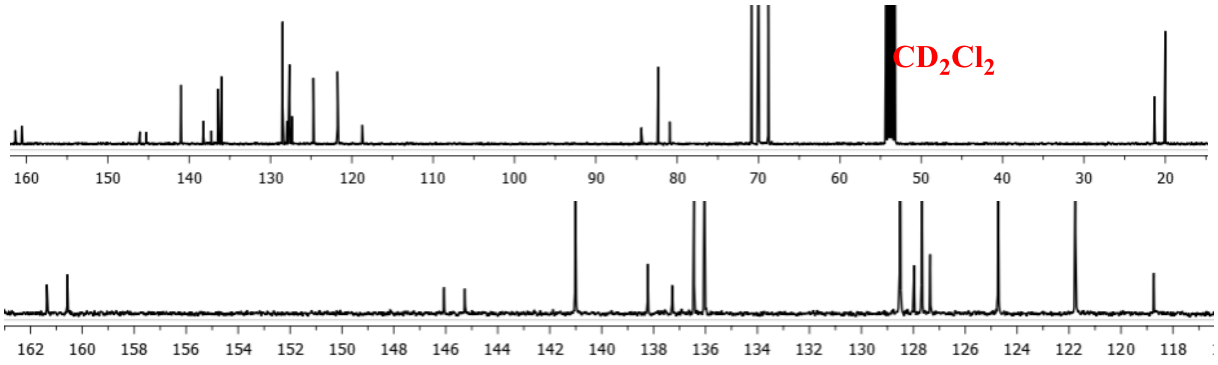



**Figure S6:** $^{13}C$ NMR spectrum (100 MHz, $CD_2Cl_2$, 298 K) of **16**. An expanded part of the aromatic region is shown at the bottom.

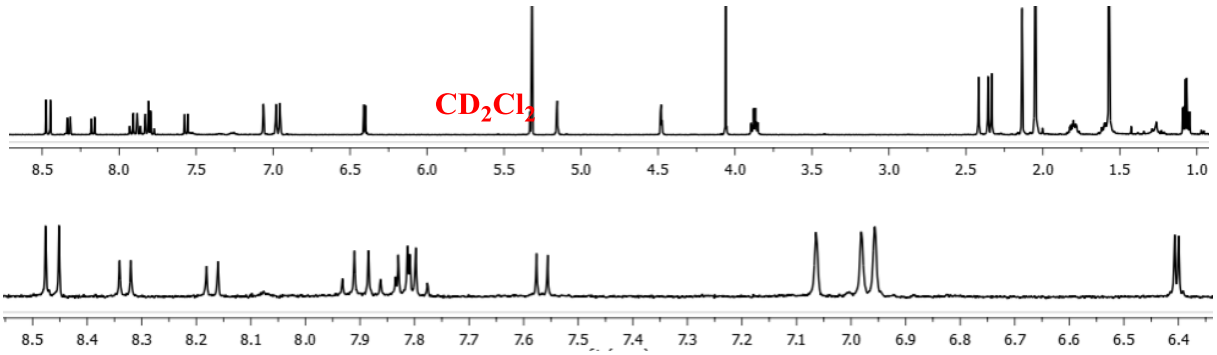



**Figure S7:** $^{1}$H NMR spectrum (400 MHz, $CD_2Cl_2$, 298 K) of **8**. An expanded part of the aromatic region is shown at the bottom.

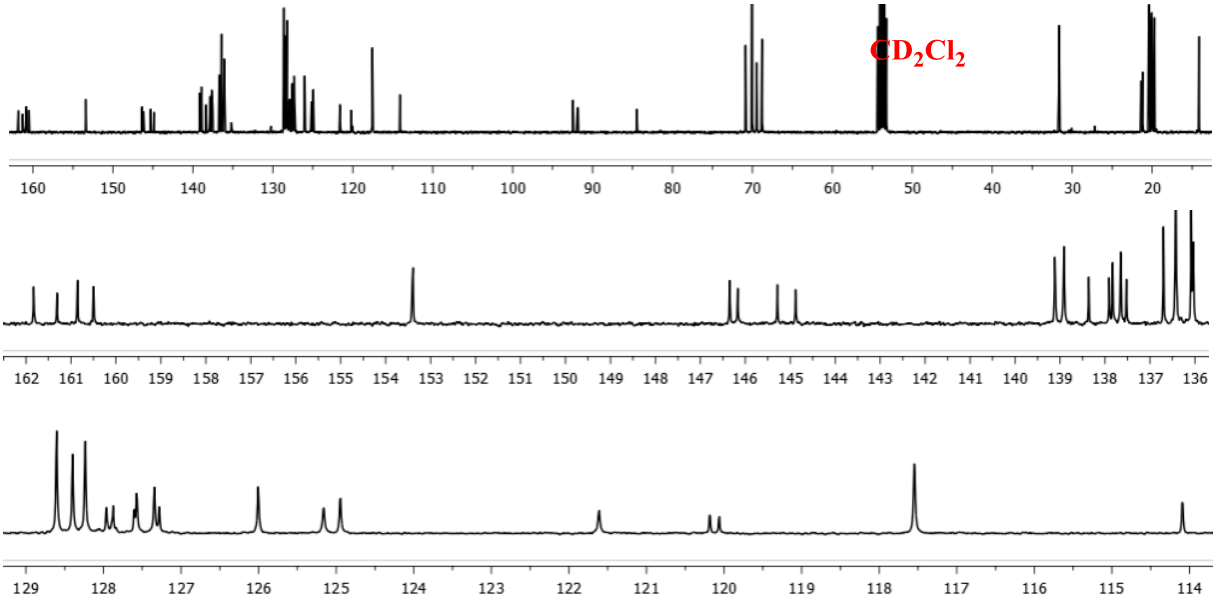



**Figure S8:** $^{13}$C NMR spectrum (100 MHz, $CD_2Cl_2$, 298 K) of **8**. Expanded parts of the aromatic region are shown at the bottom.

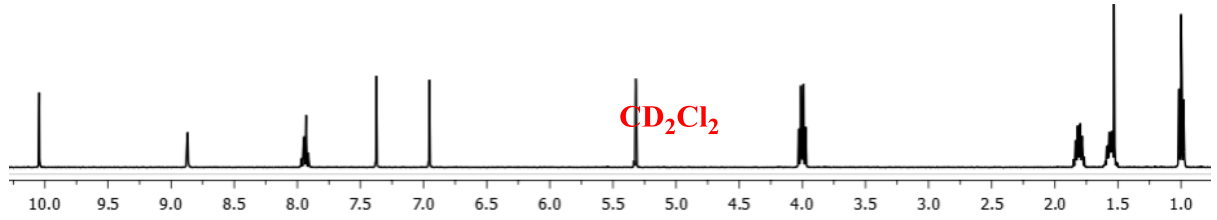



**Figure S9:** $^{1}$H NMR spectrum (400 MHz, $CD_2Cl_2$, 298 K) of **20**.

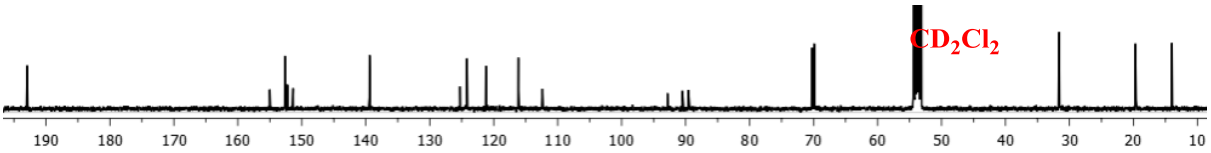



**Figure S10:** $^{13}$C NMR spectrum (100 MHz, $CD_2Cl_2$, 298 K) of **20**.

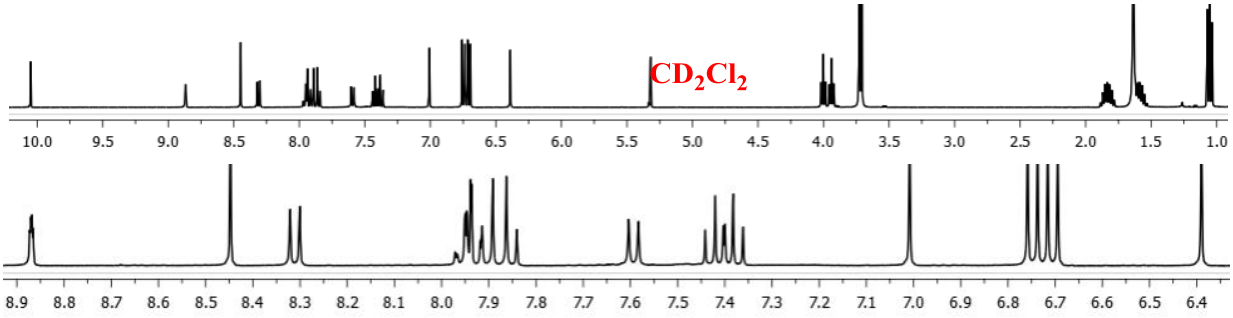



**Figure S11:** $^{1}$H NMR spectrum (400 MHz, $CD_2Cl_2$, 298 K) of **10**. An expanded part of the aromatic region is shown at the bottom.

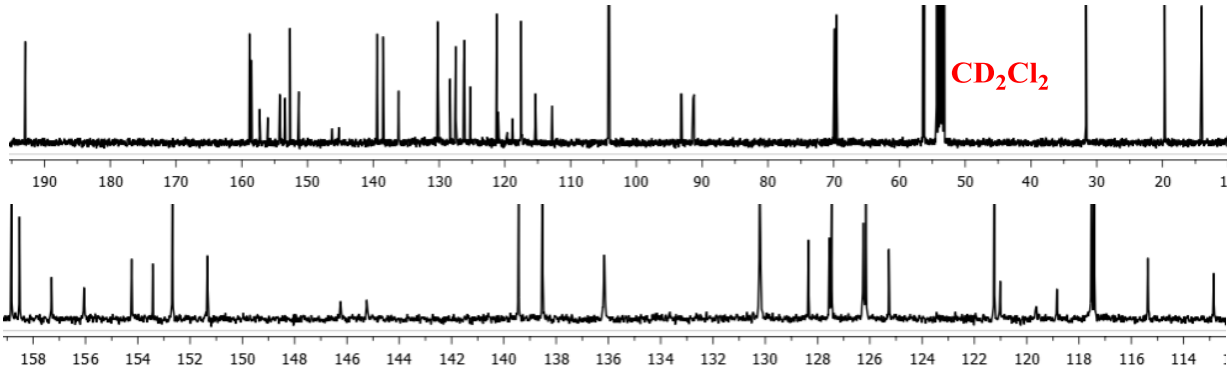



**Figure S12:** $^{13}$C NMR spectrum (100 MHz, $CD_2Cl_2$, 298 K) of **10**. An expanded part of the aromatic region is shown at the bottom.

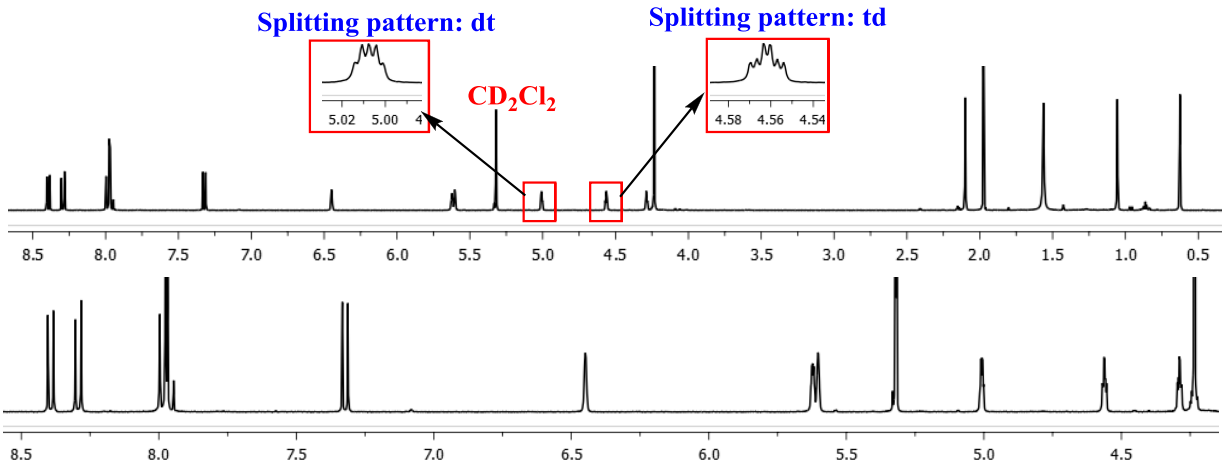



**Figure S13:** $^{1}$H NMR spectrum (400 MHz, $CD_2Cl_2$, 298 K) of **C2** = [Cu(**2**)$_2$]$PF_6$. An expanded part of the spectrum is shown at the bottom.

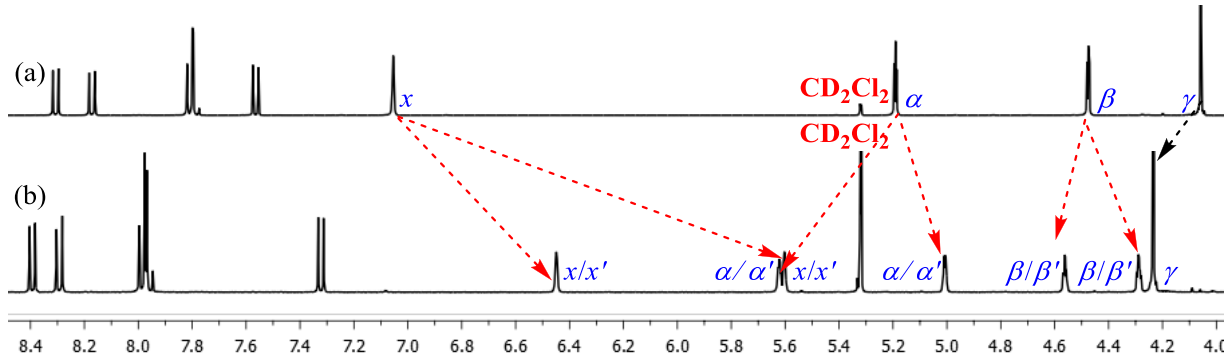



**Figure S14:** Partial $^{1}$H NMR spectrum for comparison (400 MHz, $CD_2Cl_2$, 298 K) of (a) ligand **2** and (b) complex **C2** = [Cu(**2**)$_2$]$PF_6$.

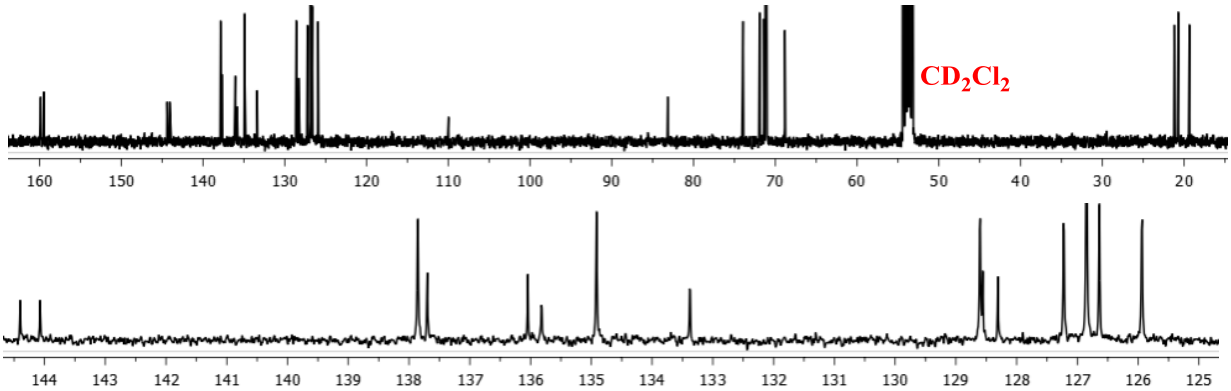



**Figure S15:** $^{13}$C NMR spectrum (100 MHz, $CD_2Cl_2$, 298 K) of **C2** = [Cu(**2**)$_2$]$PF_6$. An expanded part of the aromatic region is shown at the bottom.

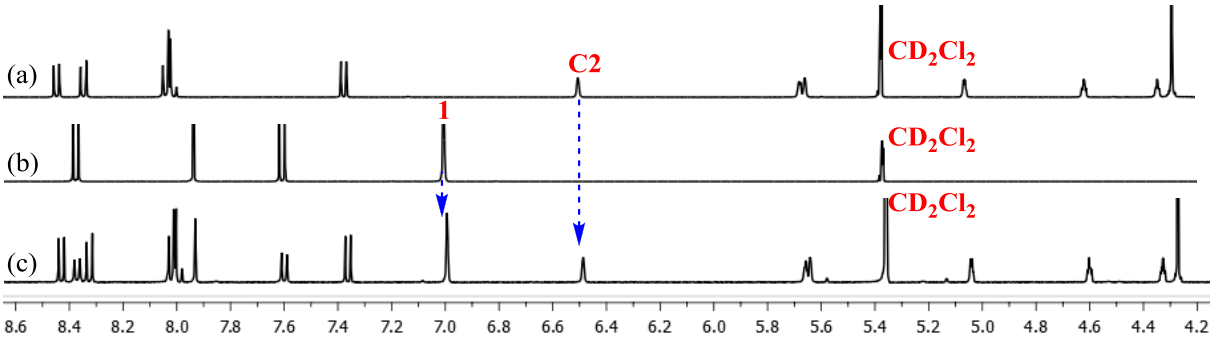



**Figure S16:** Partial $^{1}$H NMR spectra for comparison (400 MHz, $CD_2Cl_2$, 298 K) of (a) **C2** = $[Cu(\mathbf{2})_2]PF_6$, (b) ligand **1** and (c) 2:1:1 mixture of ligands **2**, **1** and $[Cu(CH_3CN)_4]PF_6$ after equilibration.

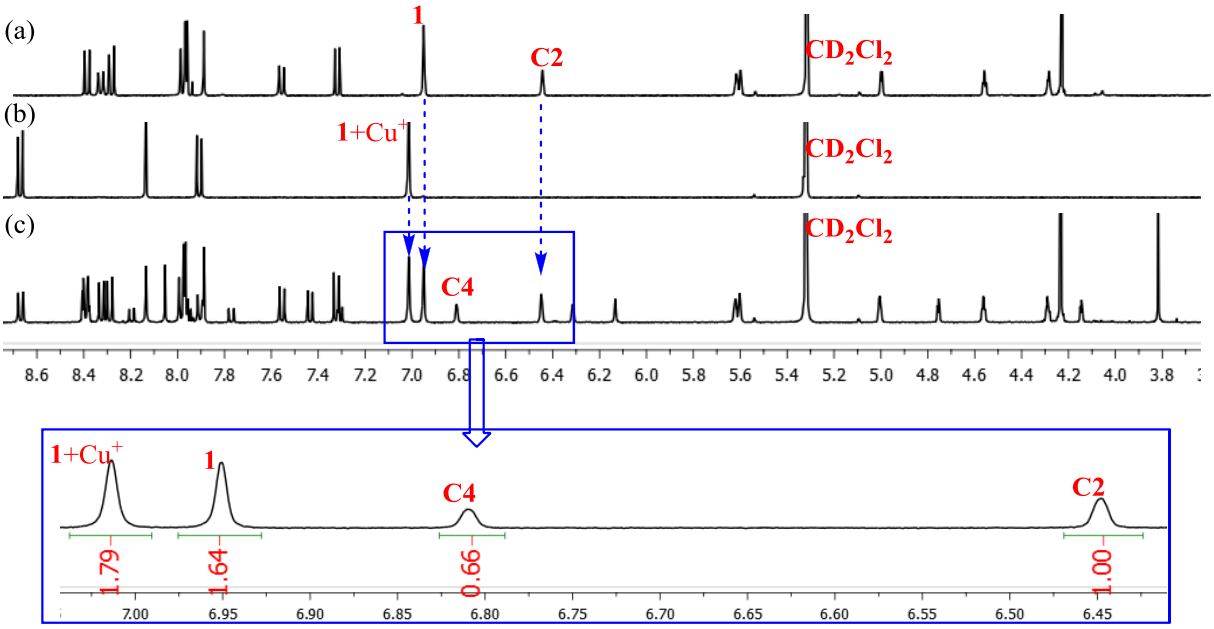



**Figure S17:** Partial $^{1}$H NMR spectra for comparison (400 MHz, $CD_2Cl_2$, 298 K) of (a) **C2** = $[Cu(\mathbf{2})_2]PF_6$ + ligand **1** (1:1), (b) 1:1 mix of ligand **1** and $[Cu(CH_3CN)_4]PF_6$ after equilibration, (c) an equimolar mixture of ligands **2**, **1** and $[Cu(CH_3CN)_4]PF_6$ after equilibration. (**C4** = $[Cu(\mathbf{1})(\mathbf{2})]PF_6$)).

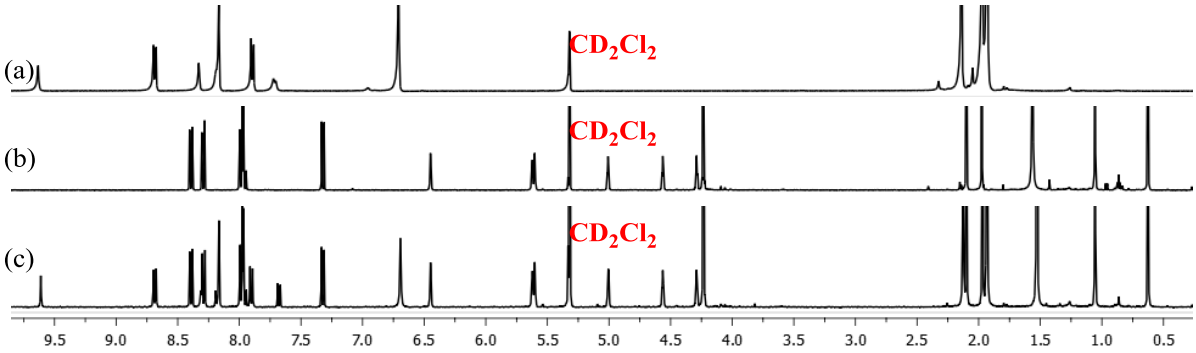



**Figure S18:** Partial $^{1}$H NMR spectra for comparison (400 MHz, $CD_2Cl_2$, 298 K) of (a) **C5** = [Cu(**1**)(**5**)]$PF_6$,[3] (b) **C2** = [Cu(**2**)$_2$]$PF_6$, and (c) an equimolar mixture of **C2**, ligand **1**, ligand **5** and [Cu($CH_3CN$)$_4$]$PF_6$ after equilibration.

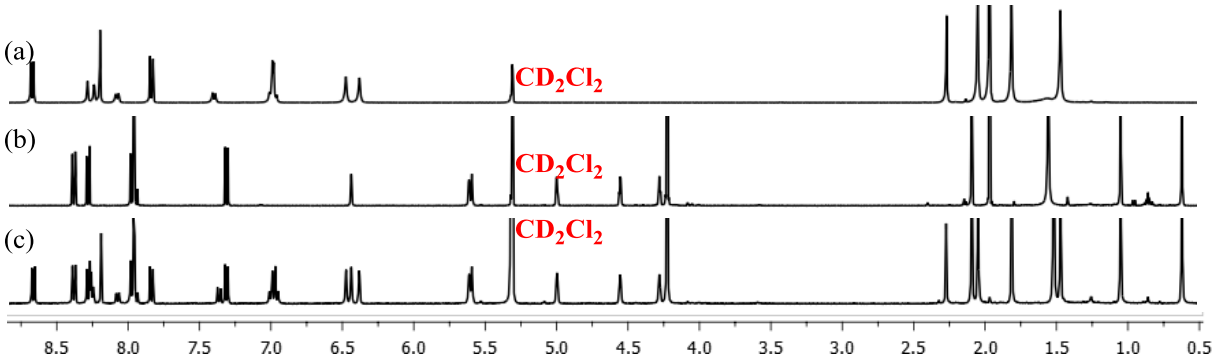



**Figure S19:** Partial $^{1}$H NMR spectrum for comparison (400 MHz, $CD_2Cl_2$, 298 K) of (a) **C1** = [Cu(**1**)(**7**)]$PF_6$ (ligand **7** = [(**5**)(**6**)–$H_2O$]),[3] (b) **C2** = [Cu(**2**)$_2$]$PF_6$, and (c) an equimolar mixture of **C2**, **C5** = [Cu(**1**)(**5**)]$PF_6$ and ligand **6** after equilibration.

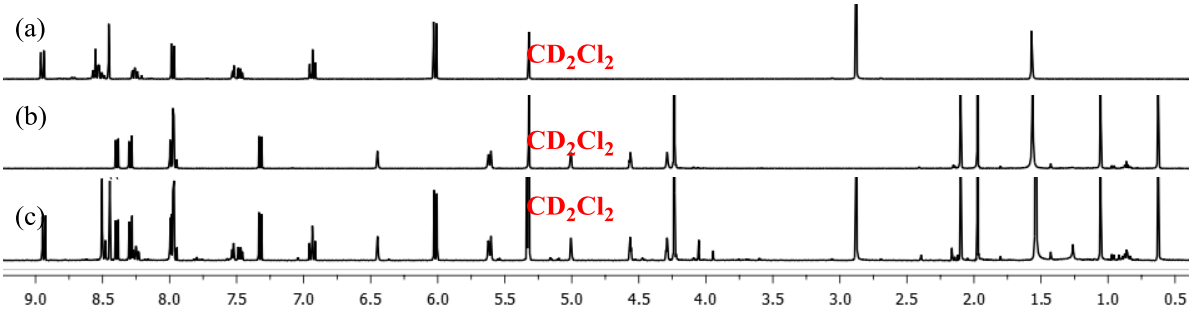



**Figure S20:** Partial $^{1}$H NMR spectrum for comparison (400 MHz, $CD_2Cl_2$, 298 K) of (a) **C3** = [Zn(**3**)(**4**)]$(OTf)_2$,[4] (b) **C2** = [Cu(**2**)$_2$]$PF_6$, and (c) an equimolar mixture of **C2**, ligand **3**, ligand **4** and $Zn(OTf)_2$ after equilibration.

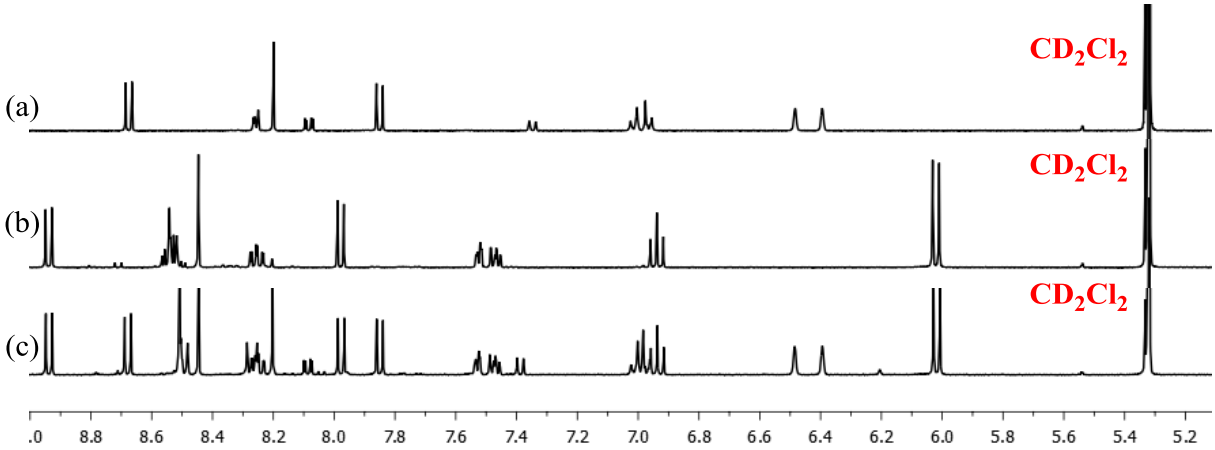



**Figure S21:** Partial $^{1}$H NMR spectrum for comparison (400 MHz, $CD_2Cl_2$, 298 K) of (a) **C1** = [Cu(**1**)(**7**)]$PF_6$, (b) **C3** = [Zn(**3**)(**4**)]$(OTf)_2$,[4] (c) an equimolar mixture of **C1** and **C3** after equilibration.

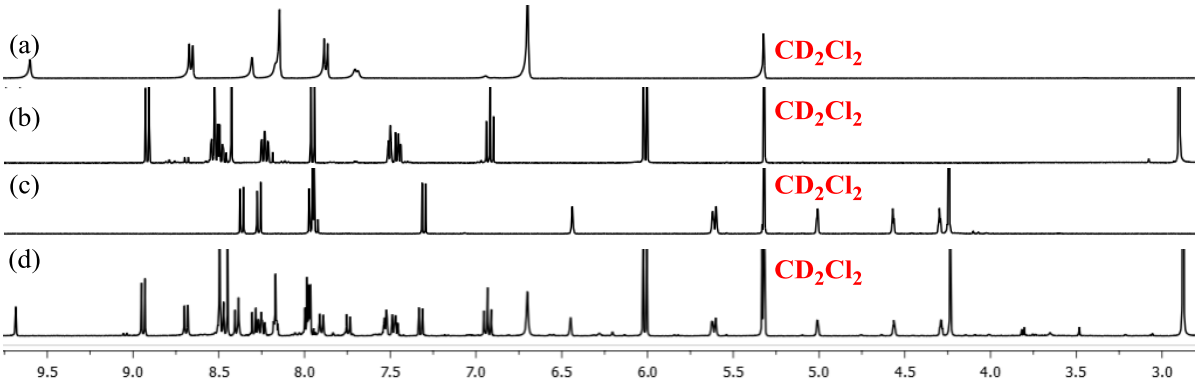



**Figure S22:** Partial $^{1}$H NMR spectra for comparison (400 MHz, $CD_2Cl_2$, 298 K) of (a) **C5** = [Cu(**1**)(**5**)]$PF_6$, (b) **C3** = [Zn(**3**)(**4**)]$(OTf)_2$, (c) **C2** = [Cu(**2**)$_2$]$PF_6$, and (d) an equimolar mixture of **C2**, **C3** and **C5** after 1 h reflux in DCM.

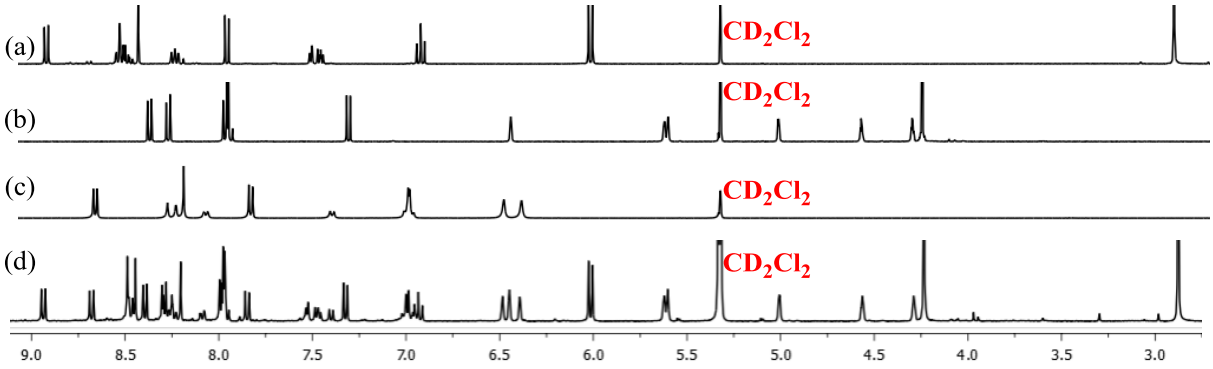



**Figure S23:** Partial $^{1}$H NMR spectra for comparison (400 MHz, $CD_2Cl_2$, 298 K) of (a) **C3** = [Zn(**3**)(**4**)](OTf)$_2$,[4] (b) **C2** = [Cu(**2**)$_2$]$PF_6$, (c) **C1** = [Cu(**1**)(**7**)]$PF_6$, and (d) an equimolar mixture of **C1**–**C3** after 1 h reflux in DCM.

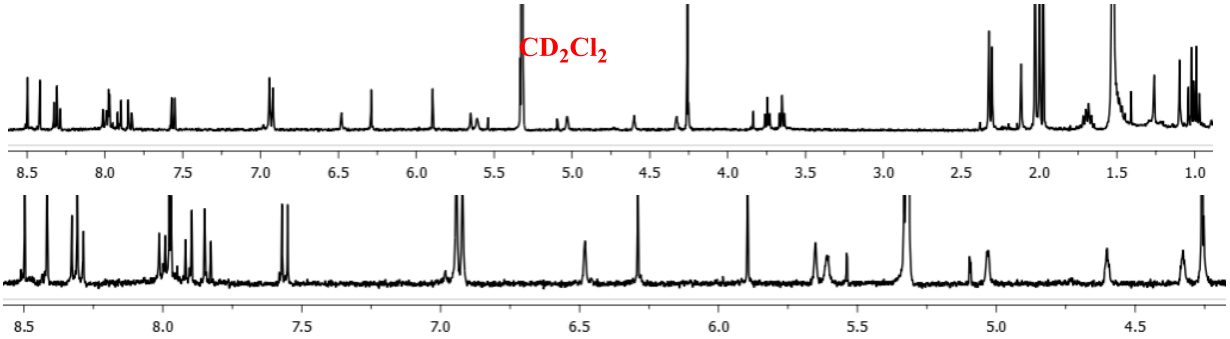



**Figure S24:** $^{1}$H NMR spectrum (400 MHz, $CD_2Cl_2$, 298 K) of metalloligand **A** = [Cu(**8**)$_2$]$PF_6$. An expanded part of the spectrum is shown at the bottom.

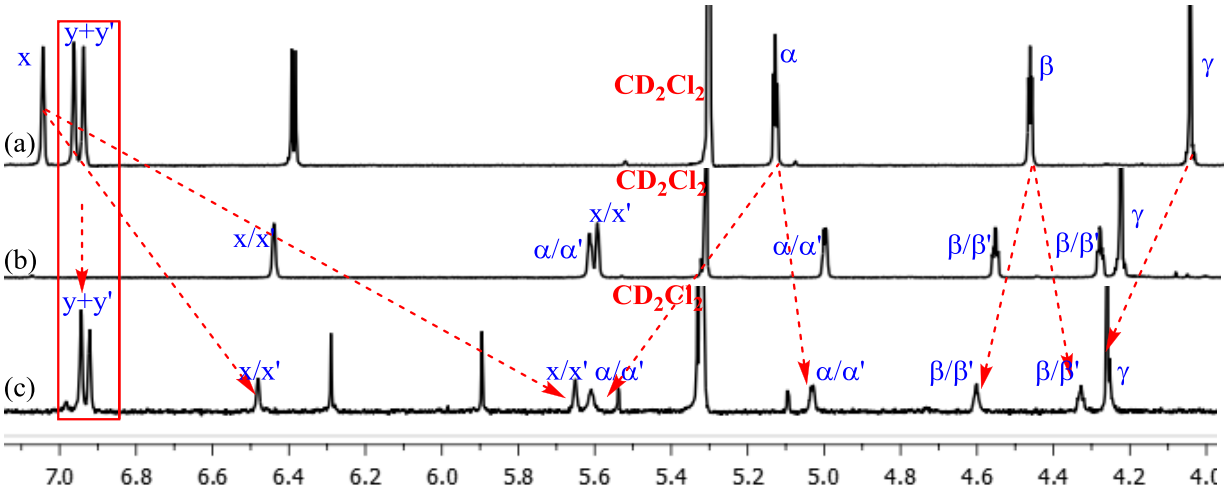



**Figure S25:** Partial $^{1}$H NMR spectra for comparison (400 MHz, $CD_2Cl_2$, 298 K) of (a) ligand **8**, (b) the archetypical complex **C2** = [Cu(**2**)$_2$]$PF_6$ and (c) the metalloligand **A** = [Cu(**8**)$_2$]$PF_6$.

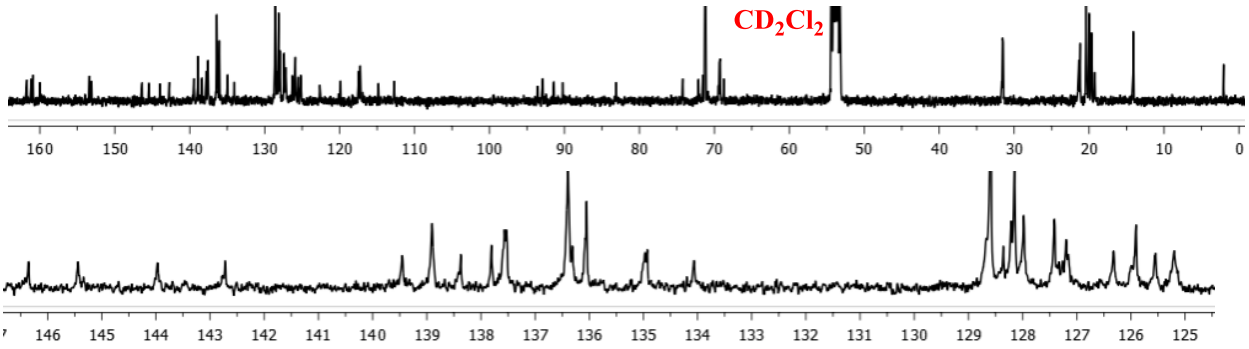



**Figure S26:** $^{13}$C NMR spectrum (100 MHz, $CD_2Cl_2$, 298 K) of **A** = [Cu(**8**)$_2$]$PF_6$. An expanded part of the aromatic region is shown at the bottom.

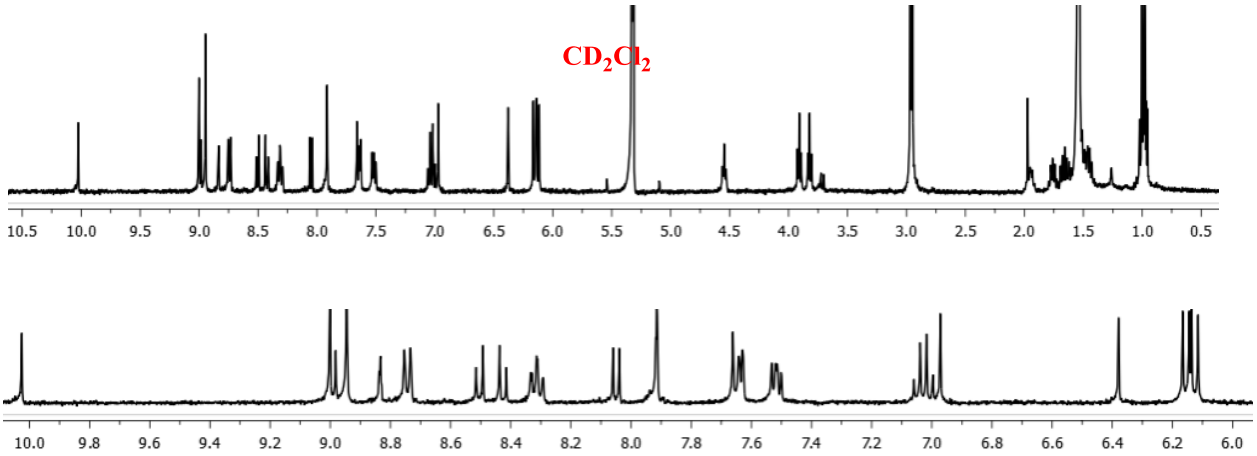



**Figure S27:** $^{1}$H NMR spectrum (400 MHz, $CD_2Cl_2$, 298 K) of metalloligand **T** = [$Zn_2$(**10**)(**9**)](OTf)$_2$. An expanded part of the spectrum is shown at the bottom.

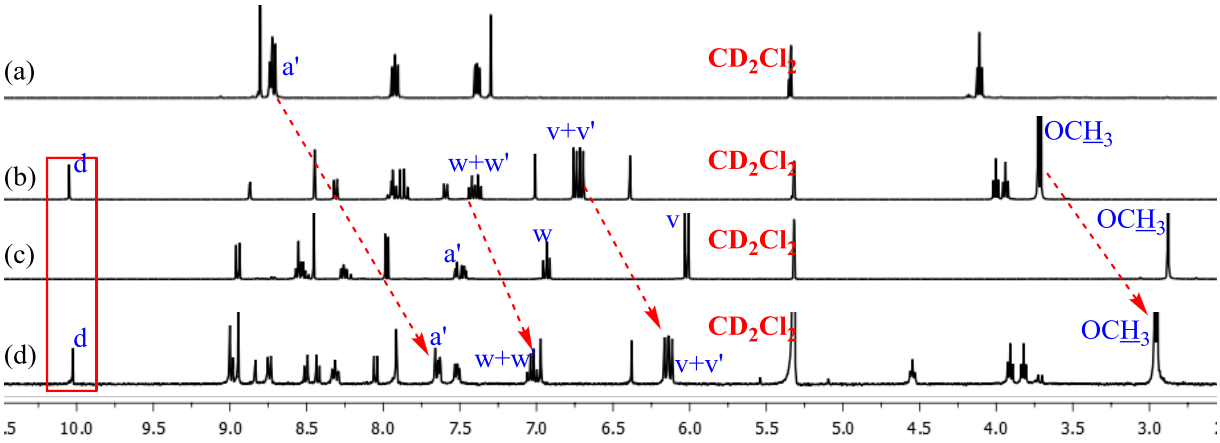



**Figure S28:** Partial $^{1}$H NMR spectrum for comparison (400 MHz, $CD_2Cl_2$, 298 K) of (a) ligand **9**, (b) ligand **10**, (c) the archetypical complex **C3** = [Zn(**3**)(**4**)](OTf)$_2$ and (d) the metalloligand **T** = [$Zn_2$(**10**)(**9**)](OTf)$_2$.

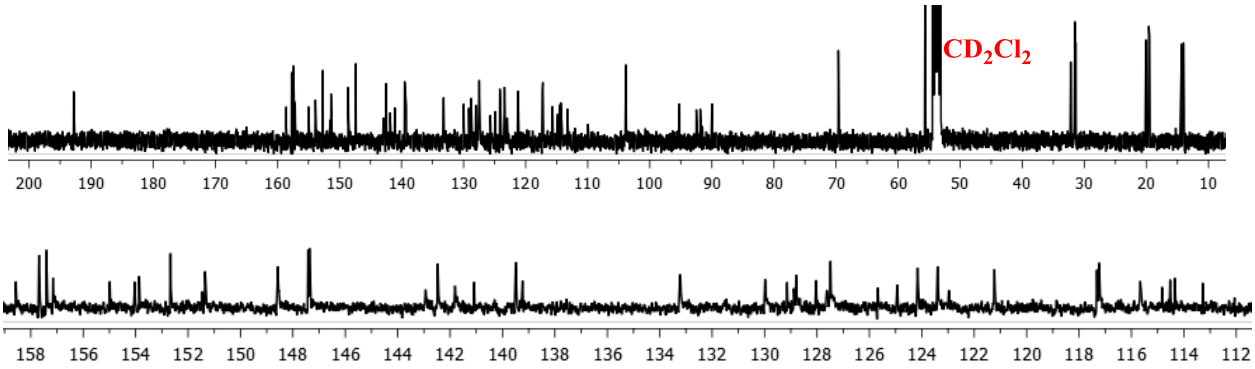



**Figure S29:** $^{13}$C NMR spectrum (100 MHz, $CD_2Cl_2$, 298 K) of the metalloligand **T** = $[Zn_2(\mathbf{10})(\mathbf{9})](OTf)_2$. An expanded part of the spectrum is shown at the bottom.

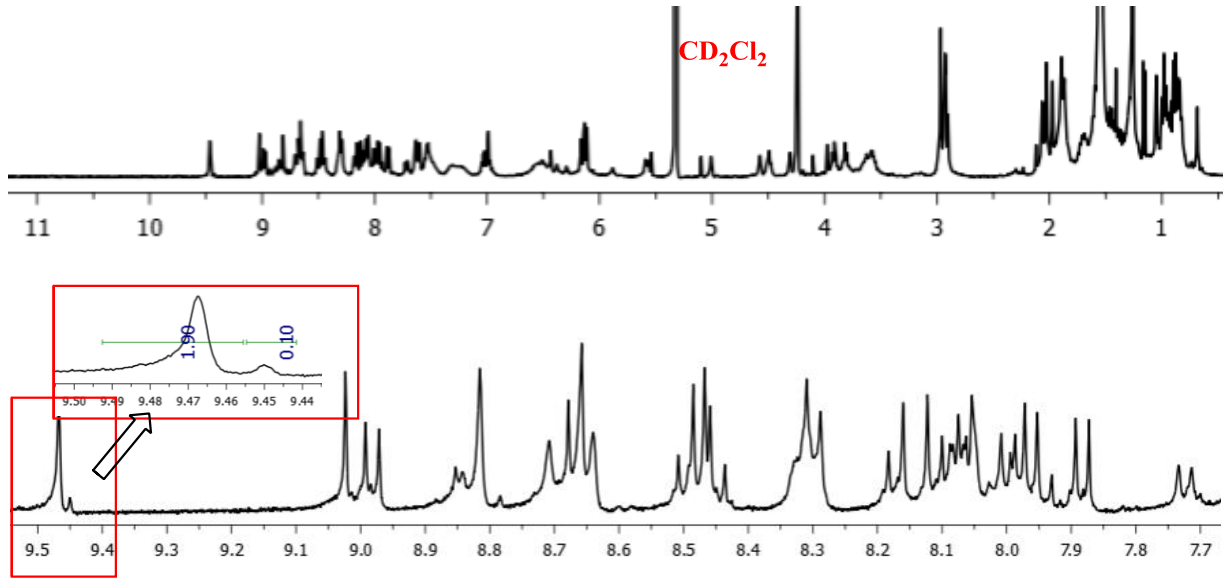



**Figure S30:** $^{1}$H NMR spectrum (400 MHz, $CD_2Cl_2$, 298 K) of pentagon **P2** = $[Zn_2Cu_3(\mathbf{8})_2(\mathbf{9})(\mathbf{10})_2](OTf)_4(PF_6)_3$. An expanded part of the spectrum is shown at the bottom.

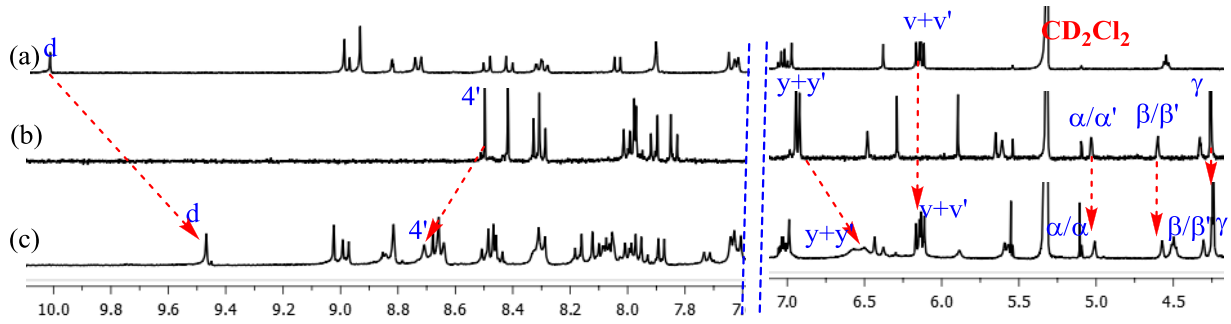



**Figure S31:** Partial $^{1}$H NMR spectra for comparison (400 MHz, $CD_2Cl_2$, 298 K) of (a) the metalloligand **T** = $[Zn_2(\mathbf{10})(\mathbf{9})](OTf)_2$, (b) the metalloligand **A** = $[Cu(\mathbf{8})_2]PF_6$, and (c) the pentagon **P2** = $[Zn_2Cu_3(\mathbf{8})_2(\mathbf{9})(\mathbf{10})_2](OTf)_4(PF_6)_3$. See also Table S1.

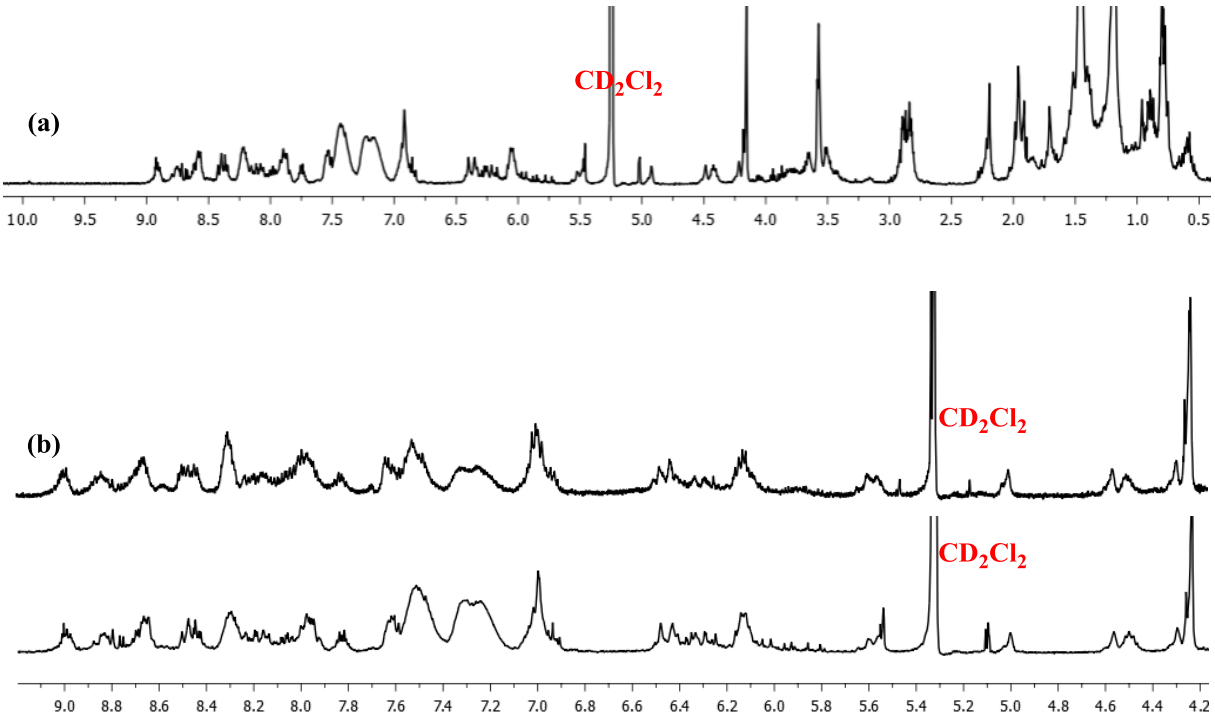



**Figure S32:** (a) $^{1}$H NMR spectrum (400 MHz, $CD_2Cl_2$, 298 K) of pentagon **P1** = $[Zn_2Cu_3(\mathbf{8})_2(\mathbf{9})(\mathbf{11})_2](OTf)_4(PF_6)_3$ prepared via the post–self–assembly modification approach, i.e. **P2**+ **6** → **P1** (**P2**:**6** = 1:2). (b) Partial $^{1}$H NMR spectra (400 MHz, $CD_2Cl_2$, 298 K) of pentagon **P1** prepared from its precursor ligands and metal ions [**6**:**8**:**9**:**10**:$Cu^{+}$:$Zn^{2+}$ = 2:2:1:2:3:2] (upper spectrum) and prepared from the post–self–assembly modification approach, i.e. **P1**+ **6** → **P1** (**P1**:**6** = 1:2) (lower spectrum).

## DOSY NMR

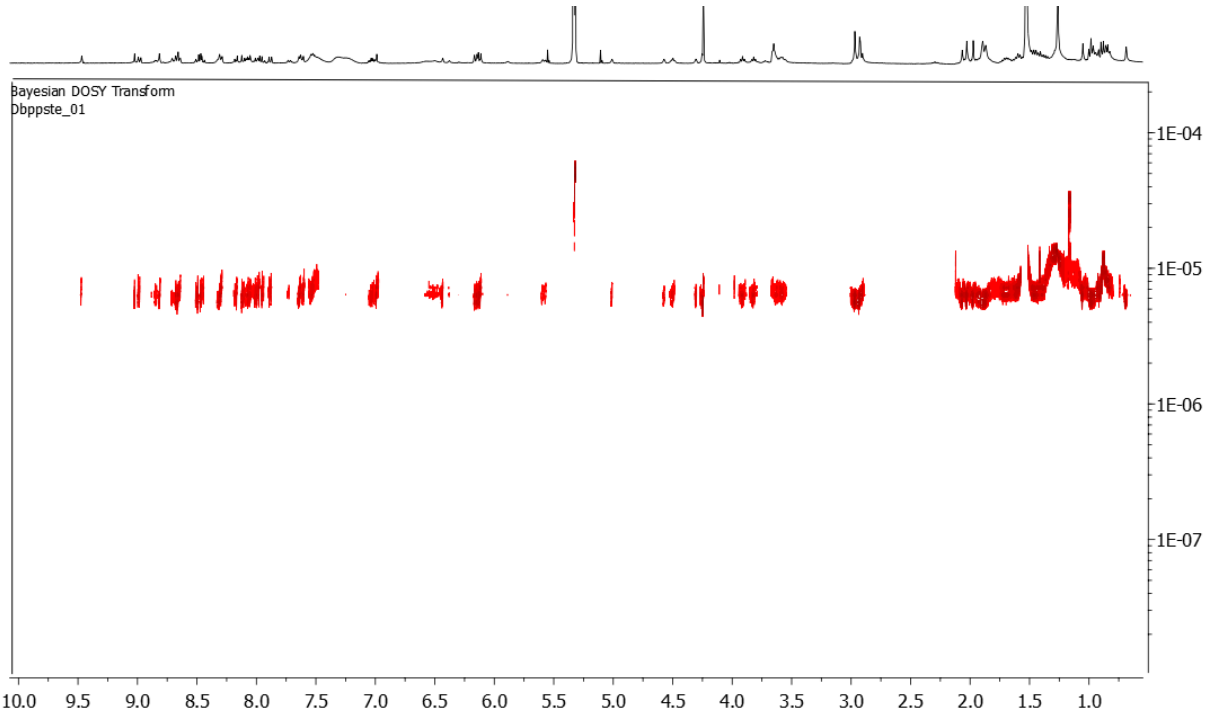



**Figure S33**: DOSY NMR spectrum (600 MHz, $CD_2Cl_2$, 298 K) of pentagon **P2** = $[Zn_2Cu_3(\mathbf{8})_2(\mathbf{9})(\mathbf{10})_2](OTf)_4(PF_\mathbf{6})_3$.

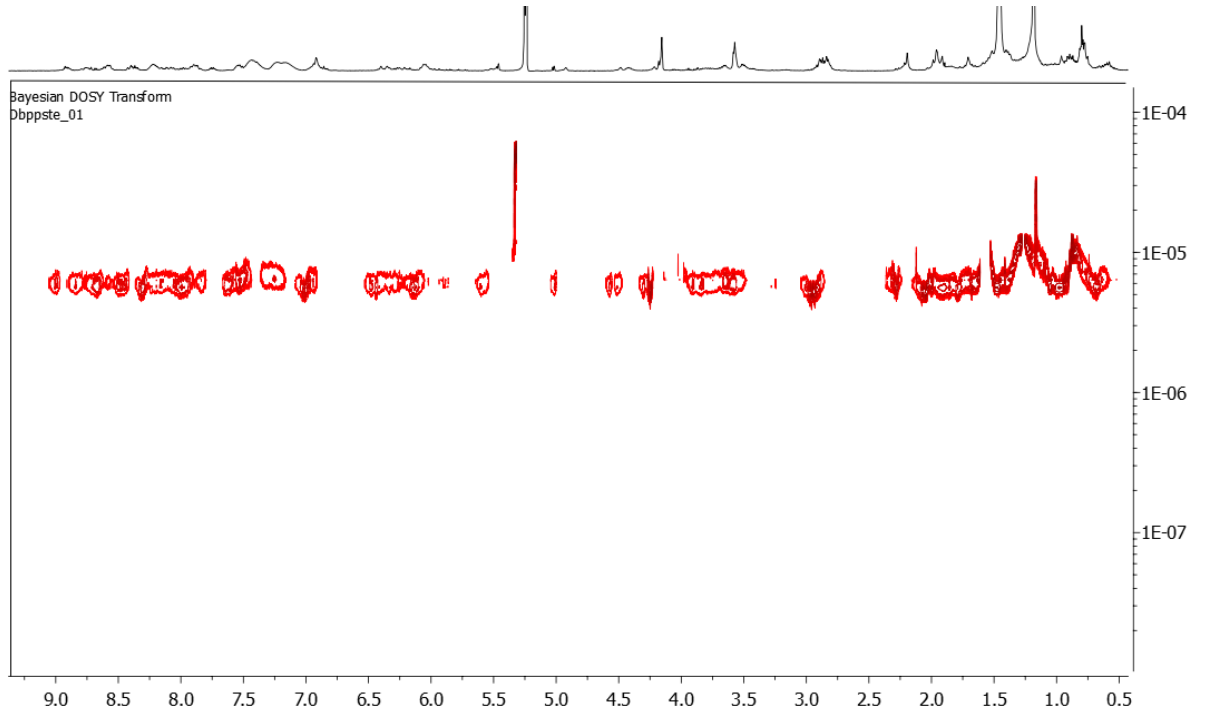



**Figure S34**: DOSY NMR spectrum (600 MHz, $CD_2Cl_2$, 298 K) of pentagon **P1** = $[Zn_2Cu_3(\mathbf{8})_2(\mathbf{9})(\mathbf{11})_2](OTf)_4(PF_6)_3$.

## ESI-MS spectra

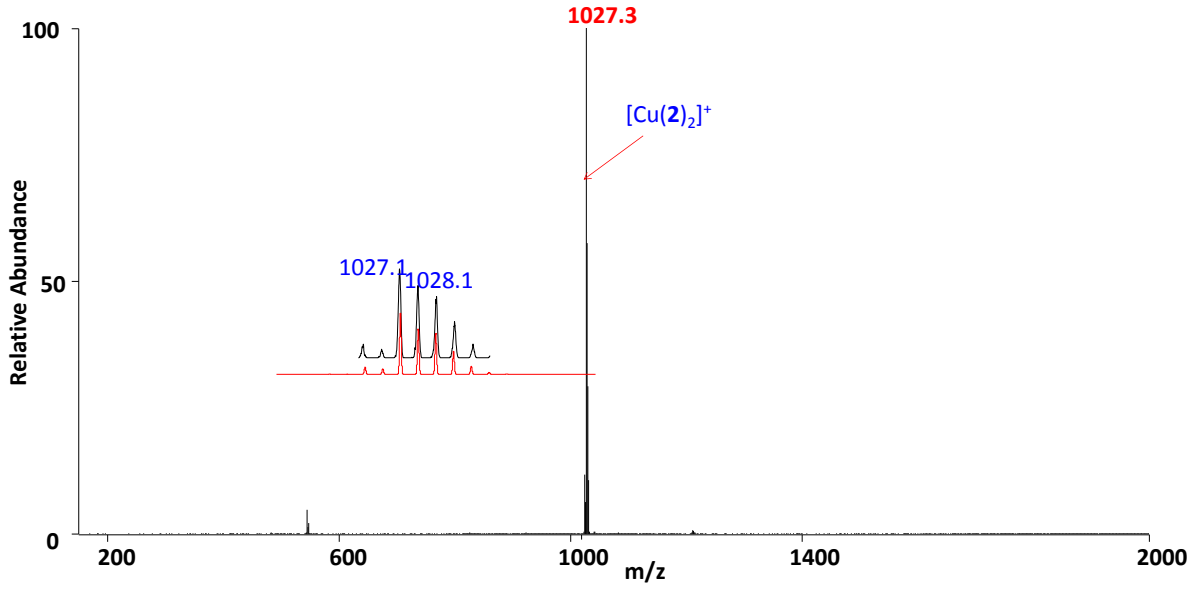



**Figure S35:** ESI-MS spectrum of **C2** = $[Cu(\mathbf{2})_2]PF_6$ (in DCM) as well as experimental (black) and calculated isotopic distributions (red) for the species $[Cu(\mathbf{2})_2]^+$.

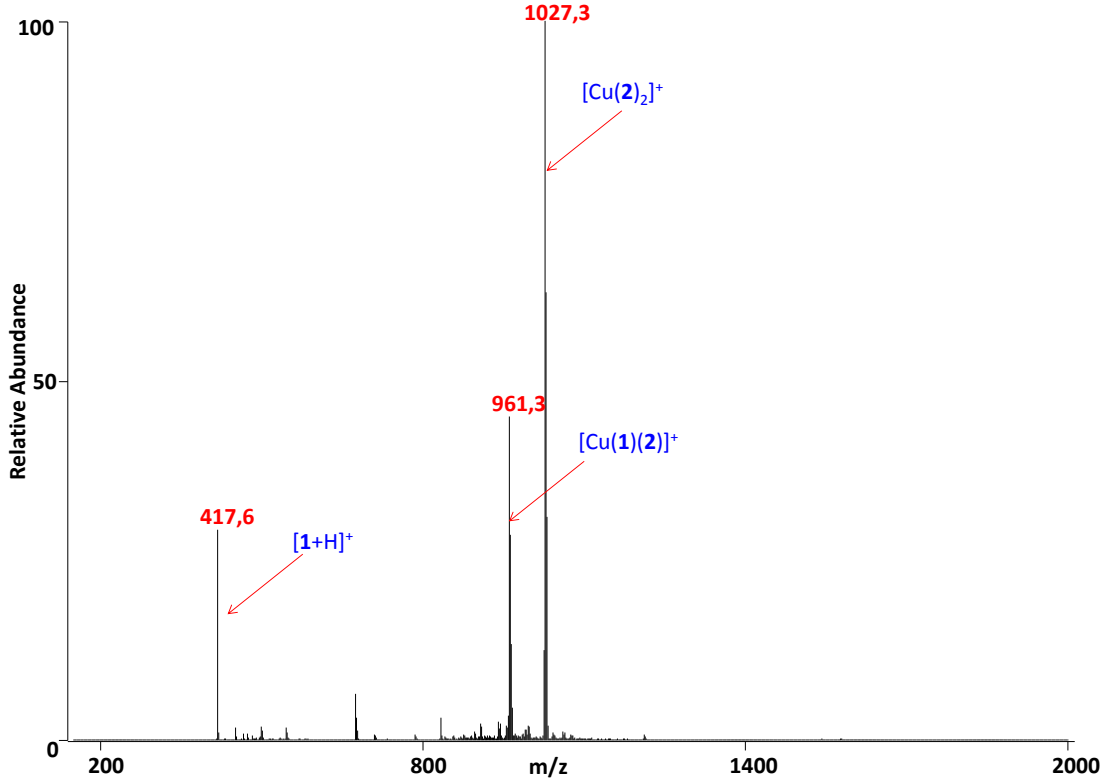



**Figure S36:** ESI-MS spectrum (in DCM) of an equimolar mixture of ligands **1**, **2** and $[Cu(CH_3CN)_4]PF_6$ after equilibration. (**C4** = $[Cu(\mathbf{1})(\mathbf{2})]PF_6$ and **C2** = $[Cu(\mathbf{2})_2]PF_6$).

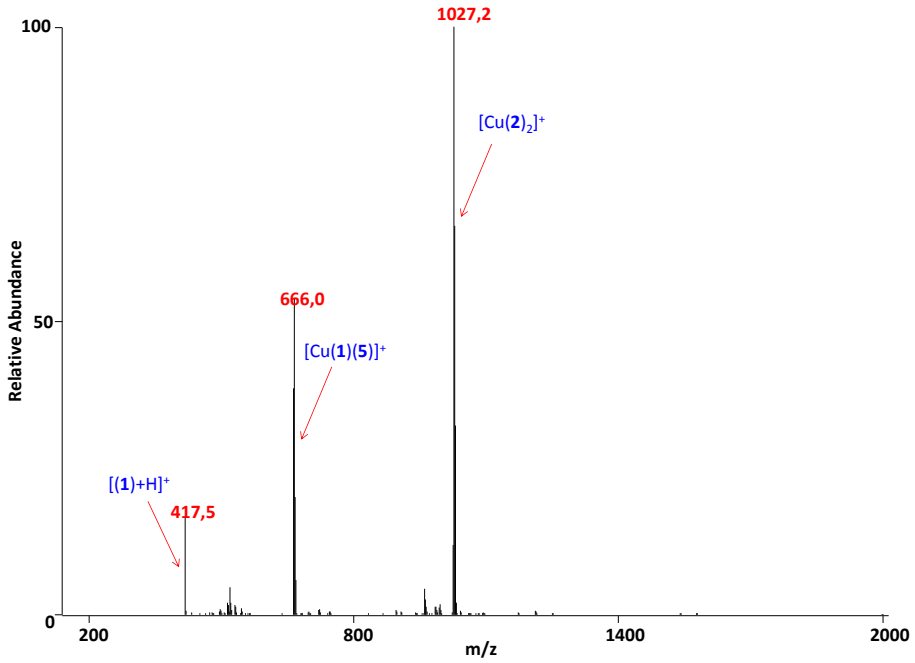



**Figure S37:** ESI-MS spectrum (in DCM) of an equimolar mixture of complex **C2** = $[Cu(\mathbf{2})_2]PF_6$, ligand **1**, ligand **5** and $[Cu(CH_3CN)_4]PF_6$ after equilibration. (**C5** = $[Cu(\mathbf{1})(\mathbf{5})]PF_6$).

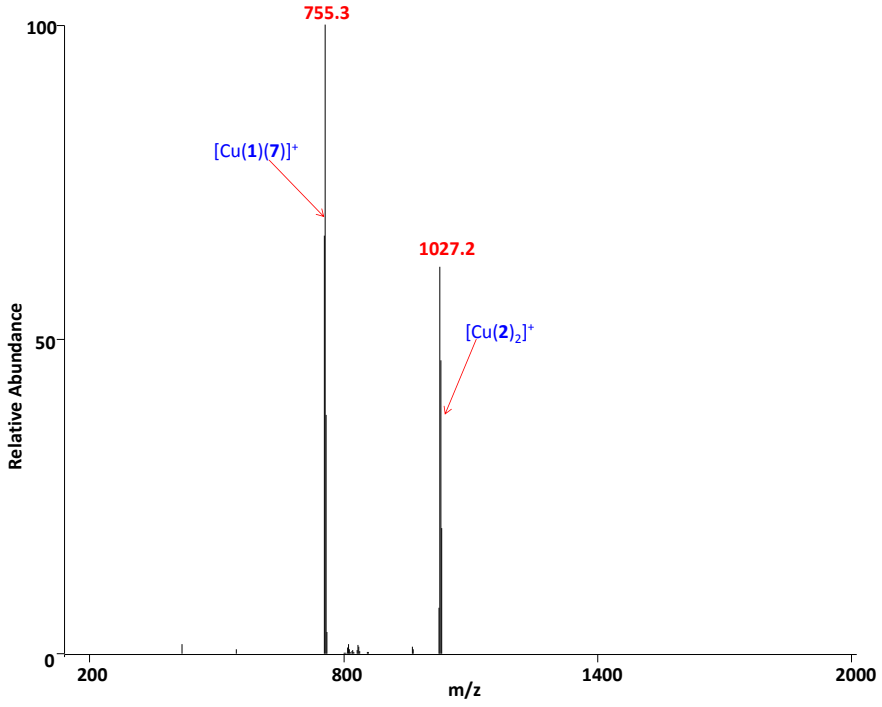



**Figure S38:** ESI-MS spectrum (in DCM) of an equimolar mixture of **C2** = $[Cu(\mathbf{2})_2]PF_6$, **C5** = $[Cu(\mathbf{1})(\mathbf{5})]PF_6$ and ligand **6** after equilibration. (**C1** = $[Cu(\mathbf{1})(\mathbf{7})]PF_6$ and ligand **7** = $[(\mathbf{5})(\mathbf{6})\text{-}H_2O]$).

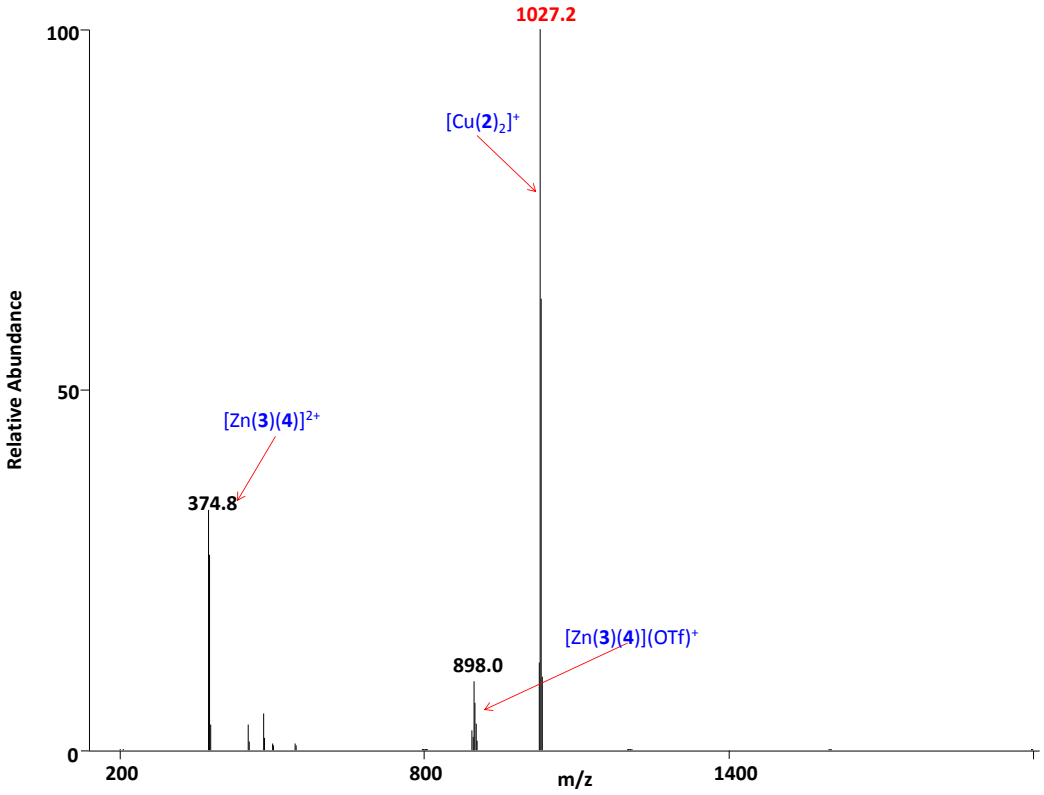



**Figure S39:** ESI-MS spectrum (in DCM) of an equimolar mixture of **C2** = $[Cu(\mathbf{2})_2]PF_6$, ligand **3**, ligand **4** and $Zn(OTf)_2$ after equilibration. (**C3** = $[Zn(\mathbf{3})(\mathbf{4})](OTf)_2$).

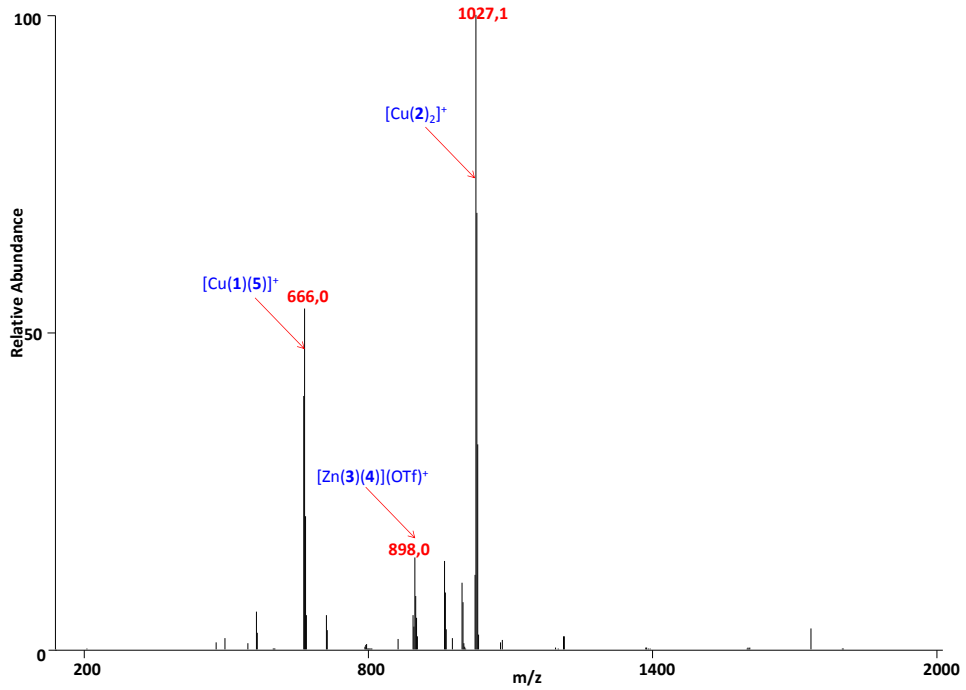



**Figure S40:** ESI-MS spectrum of an equimolar mixture of **C2**, **C3** and **C5** after 1 h reflux in DCM. (**C2** = $[Cu(\mathbf{2})_2]PF_6$, **C3** = $[Zn(\mathbf{3})(\mathbf{4})](OTf)_2$, **C5** = $[Cu(\mathbf{1})(\mathbf{5})]PF_6$).

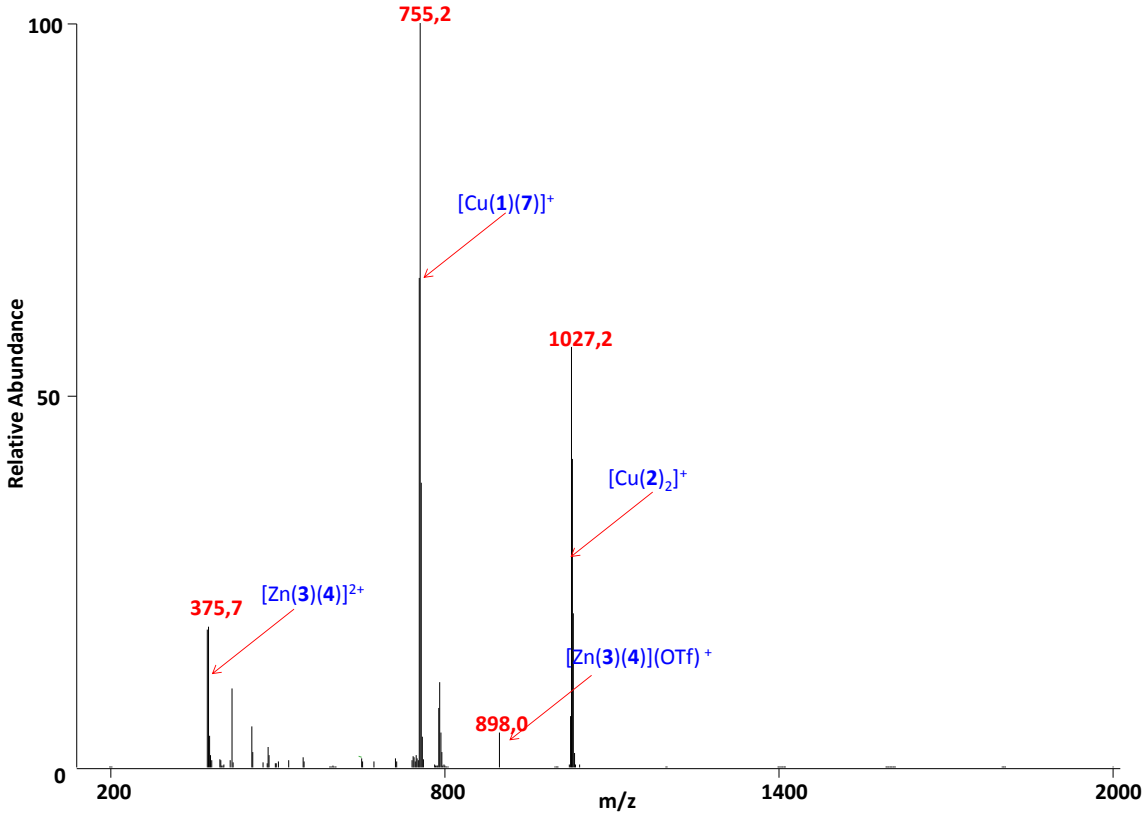



**Figure S41:** ESI-MS spectrum of an equimolar mixture of **C1**–**C3** after 1 h reflux in DCM. (**C1** = [Cu(**1**)(**7**)]$PF_6$), **C2** = [Cu(**2**)$_2$]$PF_6$, **C3** = [Zn(**3**)(**4**)]$(OTf)_2$).

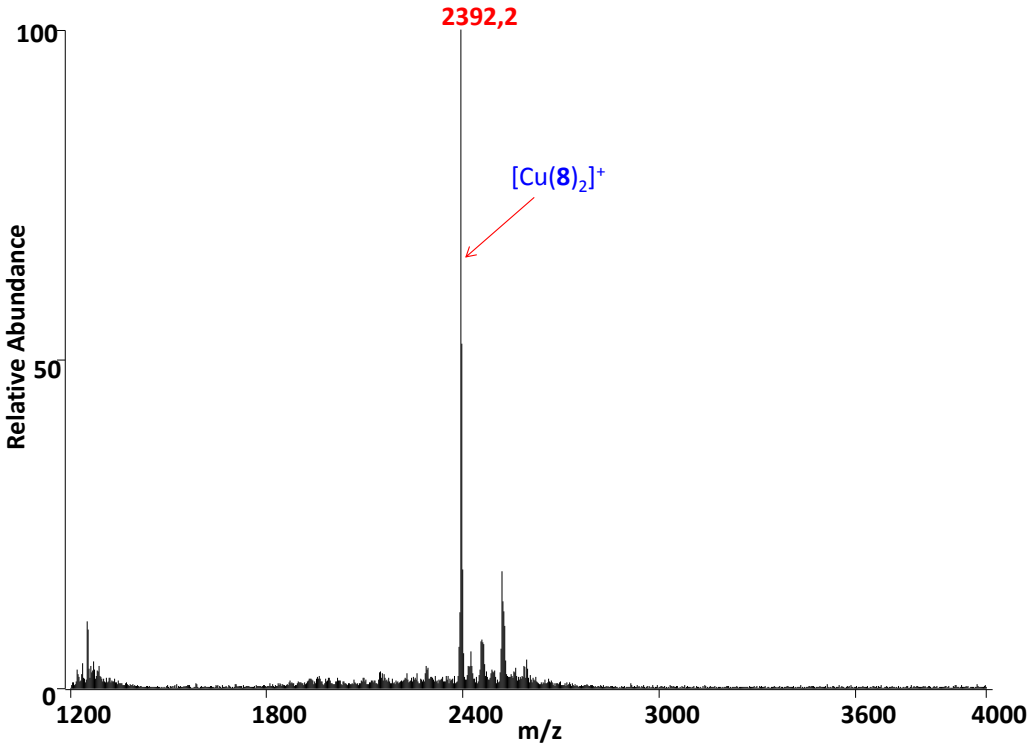



**Figure S42:** ESI-MS spectrum of the metalloligand **A** = [Cu(**8**)$_2$]$PF_6$ (in DCM). No isotopic splitting was available in the mass range > 2000 Da.

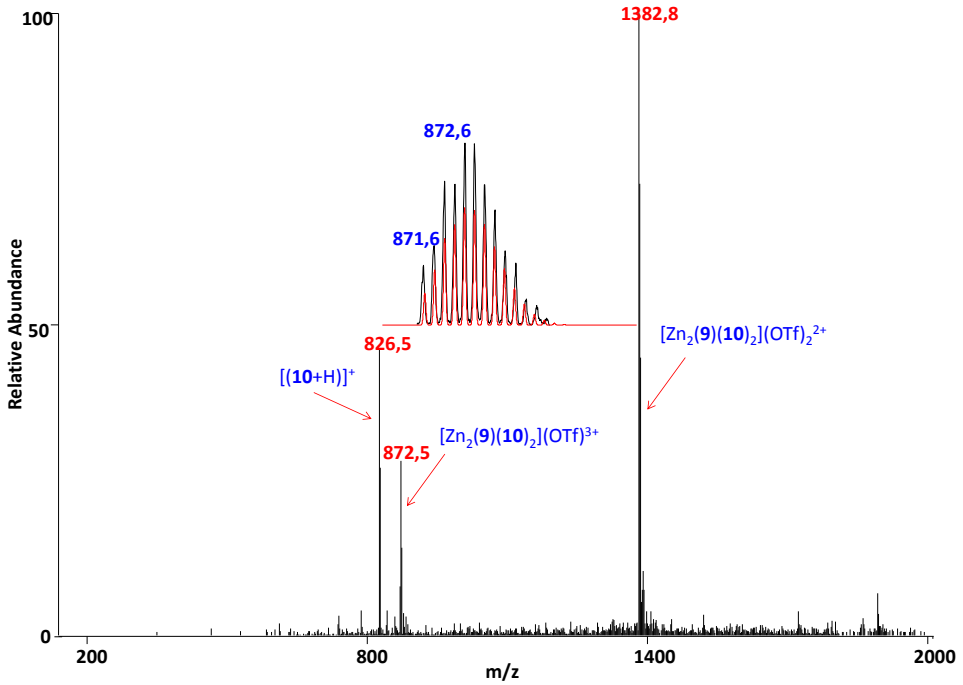



**Figure S43:** ESI-MS spectrum of the metalloligand **T** = $[Zn_2(\mathbf{9})(\mathbf{10})_2](OTf)_4$ (in DCM) along with experimental (black) and calculated isotopic distributions (red) for the species $[Zn_2(\mathbf{9})(\mathbf{10})_2](OTf)^{3+}$ and $[Zn_2(\mathbf{9})(\mathbf{10})_2](OTf)_2{}^{2+}$.

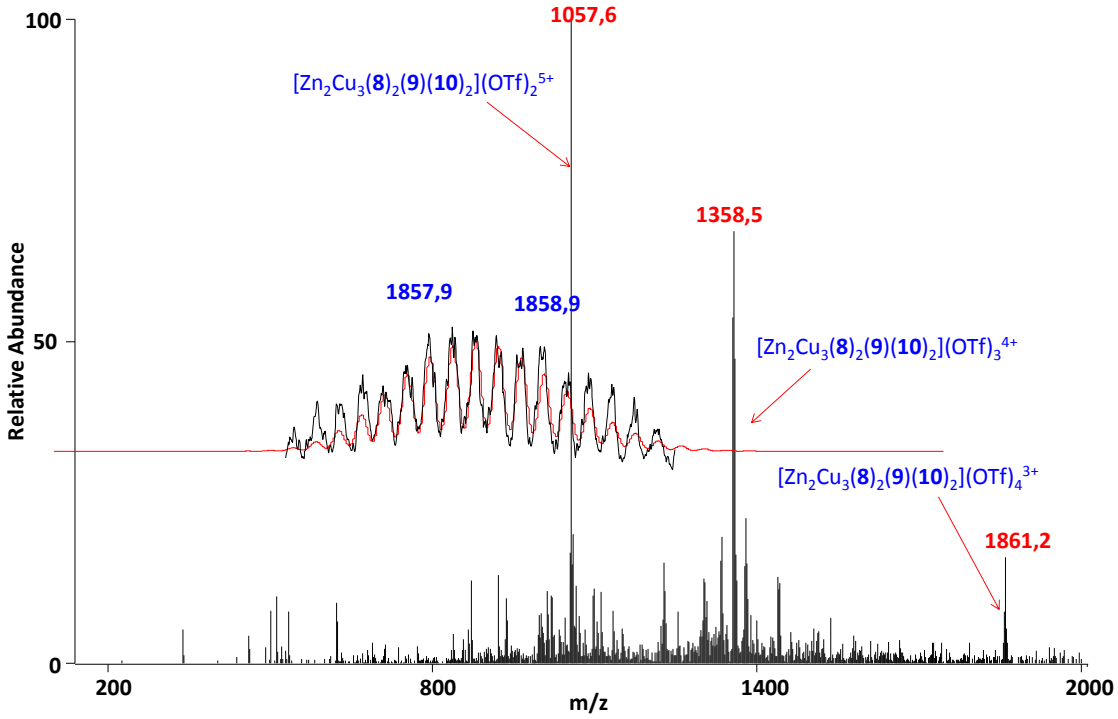



**Figure S44:** ESI-MS spectrum of **P2** = $[Zn_2Cu_3(\mathbf{8})_2(\mathbf{9})(\mathbf{10})_2](OTf)_4(PF_6)_3$ (in DCM) along with experimental (black) and calculated isotopic distributions (red) for the species $[Zn_2Cu_3(\mathbf{8})_2(\mathbf{9})(\mathbf{10})_2](OTf)_4{}^{3+}$.

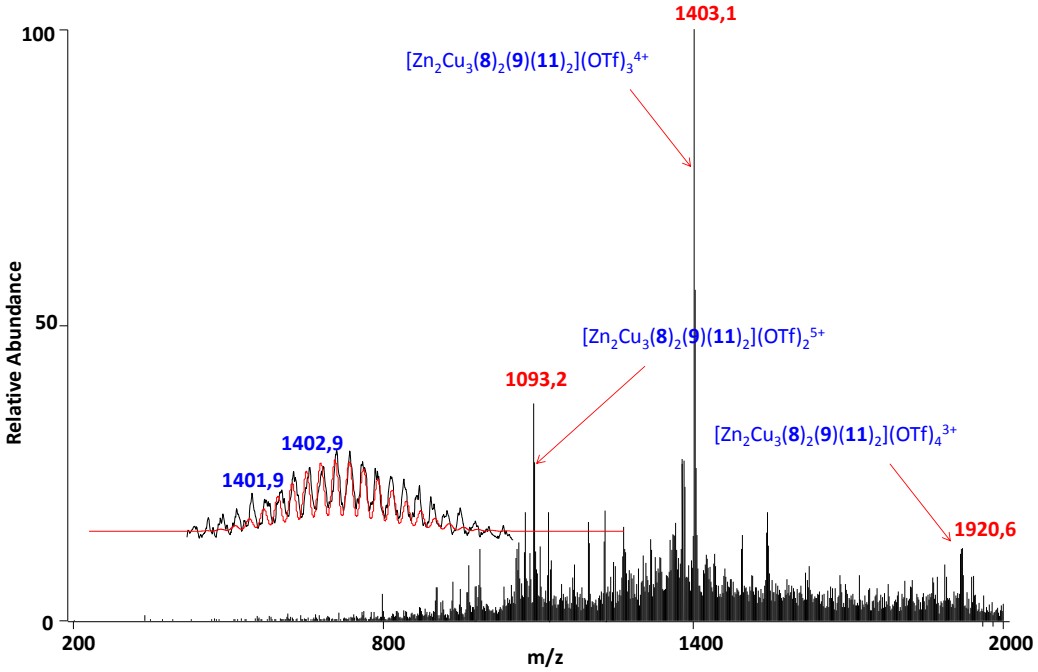



**Figure S45:** ESI-MS spectrum of **P1** = $[Zn_2Cu_3(\mathbf{8})_2(\mathbf{9})(\mathbf{11})_2](OTf)_4(PF_6)_3$ (in DCM) along with experimental (black) and calculated isotopic distributions (red) for the species $[Zn_2Cu_3(\mathbf{8})_2(\mathbf{9})(\mathbf{11})_2](OTf)_3^{4+}$. (Ligand **11** = [(**10**)(**6**)-$H_2O$]).

## UV-Vis spectra

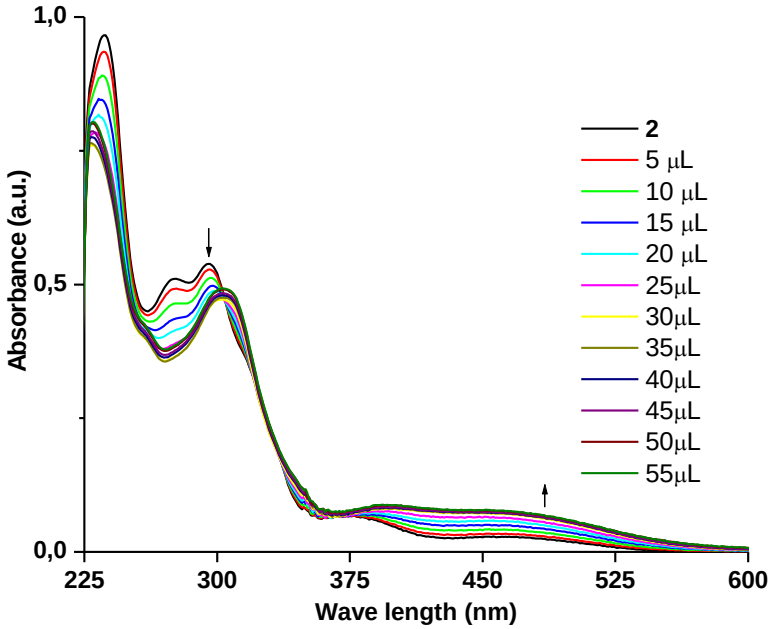



**Figure S46:** Partial UV-Vis absorption spectrum of ligand **2** (2.01 ×$10^{-5}$ M) in $CH_2Cl_2$ (2 mL) upon addition of $[Cu(CH_3CN)_4](PF_6)$ (9.87 ×$10^{-4}$ M) at 25 °C. The full data (wavelength region 200-650 nm) was analysed using the SPECFIT/32 global analysis system (Spectrum Software Associates, Marlborough, MA). Result: log $K_{[(2)Cu]}^{+}$ = 5.28 ± 0.33 and log $\beta_{[(2)Cu(2)]}^{+}$ = 11.0 ± 0.35.

## X-ray structure analysis for C2

**Table S2.** Single crystal data for compounds **C2**= $[Cu(\mathbf{2})_2]PF_6$

| | |
|---|---|
| Compound name | **C2** (CCDC 1013251) |
| Empirical formula | $2(C_{62}H_{52}CuFe_2N_4^+)\ 2(PF_6^-) \bullet 2\ CH_2Cl_2 \bullet C_4H_{10}O$ |
| Formula weight | 2590.54 |
| Temperature/ K | 192(2) |
| Wavelength/ Å | 0.71073 |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| *a*/ Å | 13.3060(11) |
| *b*/ Å | 15.0432(12) |
| *c*/ Å | 16.3418(14) |
| $\alpha$/ deg | 105.9300(10) |
| $\beta$/ deg | 93.4090(10) |
| $\gamma$/ deg | 112.2700(10) |
| Volume/ $Å^3$ | 2861.3(4) |
| Z | 1 |
| Density (calculated) ($g/cm^3$) | 1.503 |
| Absorption coefficient ($mm^{-1)}$ | 1.056 |
| F(000) | 1330 |
| Reflections collected | 20754 |
| Independent reflections | 10490 [R(int) = 0.0948] |
| Reflections with I > 2sigma(I) | 5077 |
| Absorption correction type | Semi-empirical |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Goodness-of-fit on $F^2$ | 1.036 |
| Final R indices [>2sigma(I)] | R1 = 0.0986, *wR2* = 0.1800 |
| R indices (all data) | R1 = 0.2006, *wR2* = 0.2221 |

**Table S3.** Selected bond lengths (Å) and angles (deg) for **C2** = [Cu(**2**)$_2$]PF$_6$

| | | | |
|---|---|---|---|
| Cu1–N1 | 2.051(6) | N1–Cu1–N2 | 83.8(2) |
| | | N1–Cu1–N3 | 146.0(2) |
| Cu1–N2 | 2.063(6) | N1–Cu1–N4 | 115.3(2) |
| Cu1–N3 | 2.051(5) | N2–Cu1–N3 | 114.4(2) |
| Cu1–N4 | 2.052(6) | N2–Cu1–N4 | 116.2(2) |
| | | N3–Cu1–N4 | 83.5(2) |

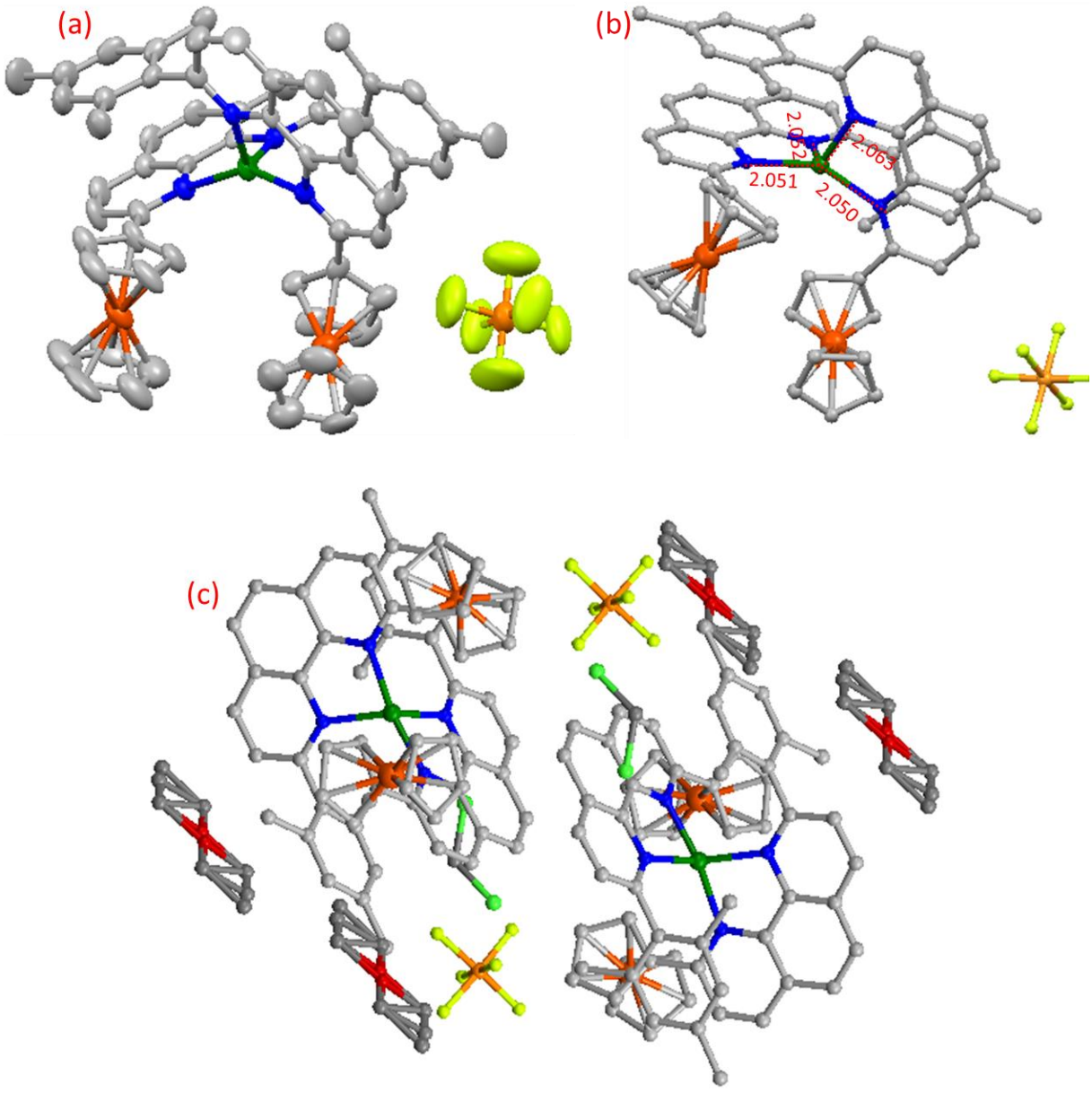



**Figure S47:** Solid state structure of (a) **C2**= [Cu(**2**)$_2$](PF$_6$) (thermal ellipsoids are drawn at the 50% probability level). (b) Ball and stick representation of **C2** showing important Cu–N distances. (c) The packing diagram of **C2**. The diethyl ether solvate molecules are statistically distributed over two symmetry-equivalent orientations. Hydrogen atoms are omitted for clarity.

Calculation of distortion in **C2** = $[Cu(\mathbf{2})_2]PF_6$ along angle $\theta_z$[8]

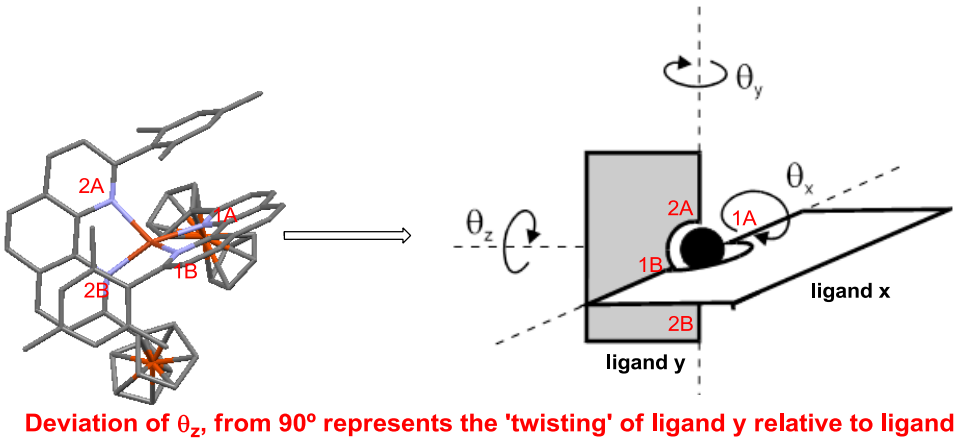



**Figure S48:** Cartoon representation of distortion angles $\theta_x$, $\theta_y$ and $\theta_z$ in complex **C2**.

The angle $\theta_z$ derived from the following equations:

$$\cos\theta_z = \frac{n_1 l_2 - l_1 n_2}{[(m_1 n_2 - n_1 m_2)^2 + (n_1 l_2 - l_1 n_2)^2 + (l_1 m_2 - m_1 l_2)^2]^{1/2}} \quad (1)$$

In addition,

$$n_1 = \frac{\cos\beta + \cos\rho}{2\cos\alpha/2} \qquad n_2 = \frac{\cos\gamma + \cos\sigma}{2\cos\alpha/2}$$

$$l_1 = \frac{\cos\beta - \cos\rho}{2\sin\alpha/2} \qquad l_2 = \frac{\cos\gamma - \cos\sigma}{2\sin\alpha/2}$$

$$m_1 = \sqrt{1 - l_1^2 - n_1^2} \qquad m_2 = -\sqrt{1 - l_2^2 - n_2^2}$$

α = N(1A)–Cu–N(1B) β = N(1A)–Cu–N(2A)

γ = N(1A)–Cu–N(2B) ρ = N(1B)–Cu–N(2A)

σ = N(1B)–Cu–N(2B) ω = N(2A)–Cu–N(2B)

From the crystal structure of **C2** we calculated

| α | β | γ | ρ | σ | ω |
|---|---|---|---|---|---|
| 83.44 | 114.33 | 146.05 | 116.25 | 115.30 | 83.76 |

Implementing those values of α–ω into equation 1 the distortion angle $\theta_z$ translates to 78.86º.

## Energy minimised structures using $MM^+$ force field

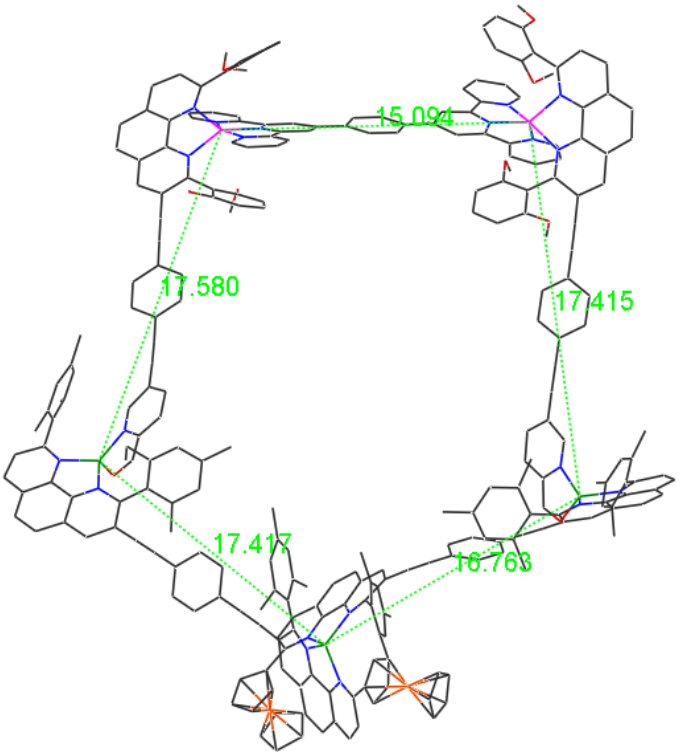



**Figure S49:** Energy minimised structure of the supramolecular pentagon **P2**. Counter anions and alkoxy chains are not included. Hydrogens are omitted for clarity.

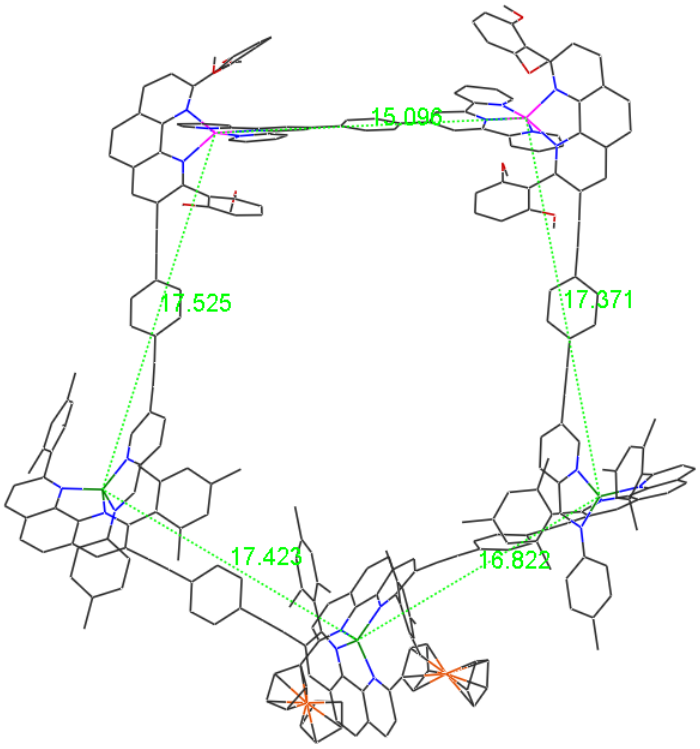



**Figure S50:** Energy minimised structure of the supramolecular pentagon **P1**. Counter anions and alkoxy chains are not included. Hydrogens are omitted for clarity.

## References


(1) UV-Vis titrations were analysed by fitting the whole series of spectra at 0.5 nm intervals using the software SPECFIT. The SPECFIT program analyses equilibrium data sets using singular value decomposition and linear regression modeling by the Levenberg-Marquardt method to determine cumulative binding constant. (a) H. Gampp, M. Maeder, C. J. Meyer, A. D. Zuberbühler, *Talanta* 1986, **33**, 943.

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