Electronic supporting information (ESI)

for

Seven–component metallosupramolecular quadrilateral with four different orthogonal complexation vertices

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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: δ_H = 5.32 ppm and δ_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 doublets, 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. Cyclic voltammetry (CV) was measured on a Parstat 2273 in dry DCM. Energy minimised structures were obtained using the MM^{+} forced field as implemented in Hyperchem® 8.0. Model complexes **C1**,[1] **C2**,[2] **C3**,[3] **C4**,[4] **C5**,[1] as well as ligands **1**,[5] **2**,[2] **11**,[4] **15**,[6] **16**,[2] (precursors for **10**), **17**,[2] **20**,[5] **21**[7] (precursors for **12** and **13**), were synthesised according to known procedures.

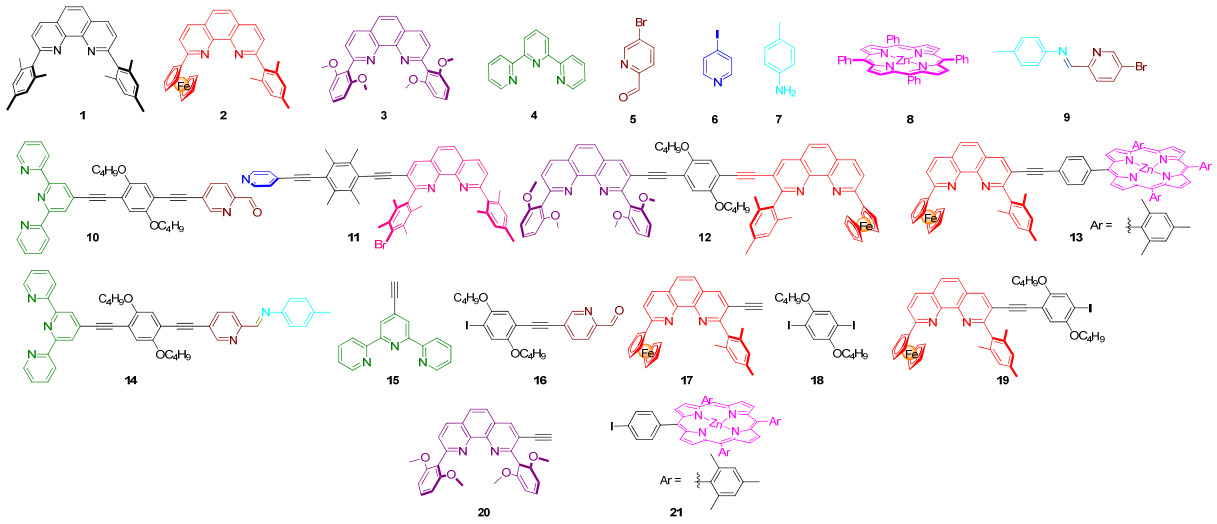
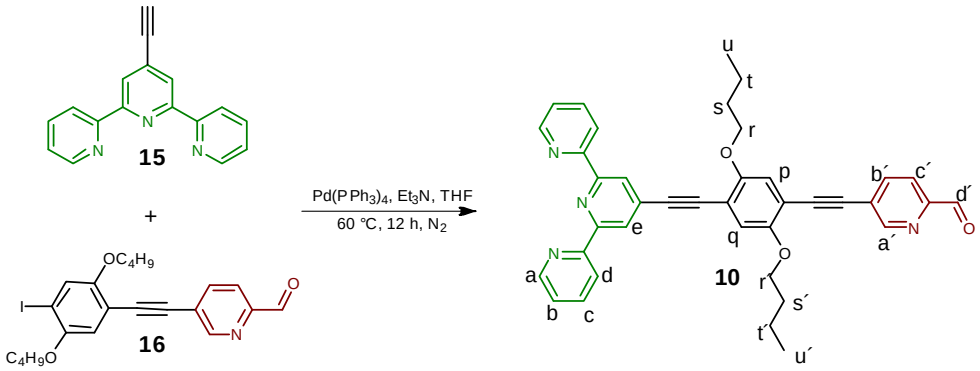


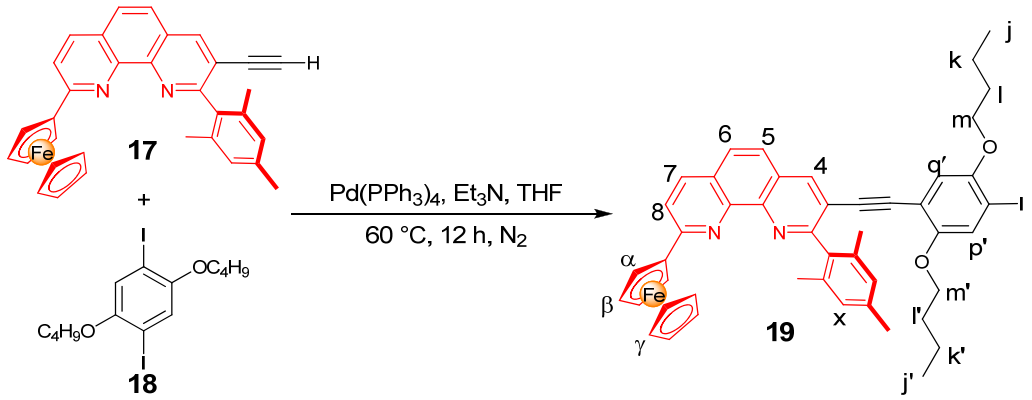
Chart 1: Chemical structures of compounds **1**–**21**.

5-((4-([2,2':6',2''-Terpyridin]-4'-ylethynyl)-2,5-dibutoxyphenyl)ethynyl)picolinaldehyde (10)



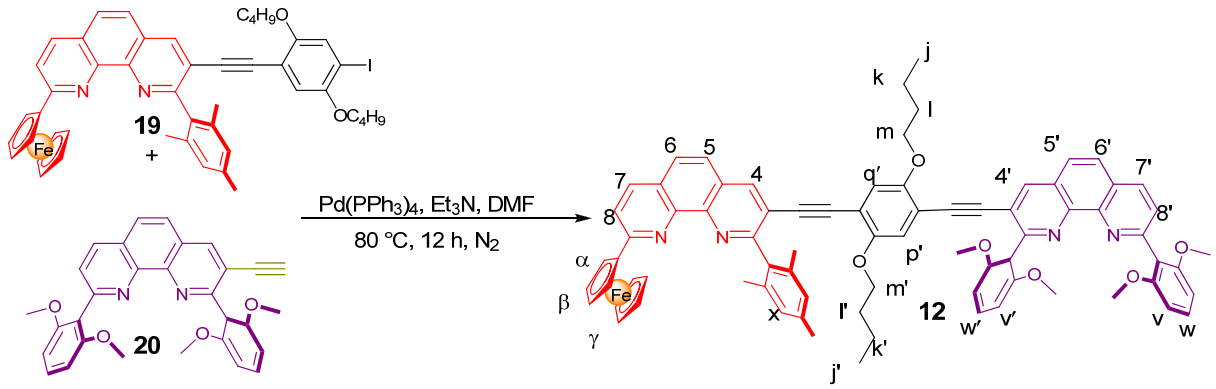
5-((2,5-Dibutoxy-4-iodophenyl)ethynyl)picolinaldehyde (**16**, 115 mg, 241 µmol), 4′-ethynyl-[(2,2′:6′,2″)-terpyridine] (**15**, 52.0 mg, 202 µmol), $Pd(PPh_3)_4$ (23.0 mg, 20.0 µmol), dry Et_3N (15 mL) and dry THF (20 mL) were placed in a 100 mL flask under nitrogen atmosphere and the mixture was heated to reflux for 12 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 =0.37 [SiO_2, EtOAC:DCM = 8:92]). Yield = 67 mg (55%); mp = 165 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 10.06 (d, ^5J = 0.8 Hz, 1 H, d′-H), 8.89 (dd, ^4J = 1.9 Hz, ^5J = 1.0 Hz, 1 H, a′-H), 8.71 (ddd, ^3J = 4.7 Hz, ^4J = 1.8 Hz, ^5J = 0.9 Hz, 2 H, a-H), 8.64 (dt, ^3J = 8.0 Hz, ^4J = 1.1 Hz, 2 H, d-H), 8.59 (s, 2 H, e-H), 7.98 (ddd, ^3J = 8.0 Hz, ^4J = 2.0 Hz, ^5J = 0.8 Hz, 1 H, b′-H), 7.94 (dd, ^3J = 8.0 Hz, ^5J = 0.8 Hz, 1 H, c′-H), 7.89 (td, ^3J = 7.6 Hz,^4J = 1.8 Hz, 2 H, c-H), 7.37 (ddd, ^3J = 7.6 Hz, ^3J = 4.8 Hz, ^4J = 1.2 Hz, 2 H, b-H), 7.13 (s, 1 H, [p/q]-H), 7.10 (s, 1 H, [q/p]-H), 4.10 (t, ^3J = 6.4 Hz, 2 H, [r/r′]-H, semicovered), 4.07 (t, ^3J = 6.4 Hz, 2 H, [r′/r]-H, semicovered), 1.93-1.83 (m, 4 H, s, s′-H), 1.69-1.55 (m, 4 H, t, t′-H), 1.07 (t, ^3J = 7.2 Hz, 3 H, [u/u′]-H), 1.03 (t, ^3J = 7.2 Hz, 3 H, [u′/u]-H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 193.0, 156.1, 155.9, 154.4, 154.3, 152.7, 151.4, 149.6, 139.5, 137.3, 133.5, 125.3, 124.5, 122.9, 121.4, 121.3, 117.4, 117.3, 114.7, 113.7, 93.7, 93.1, 91.5, 90.4, 69.9, 69.7, 31.8, 31.7, 19.8, 19.7, 14.1, 14.1; IR (KBr) ν 3426, 3050, 3010, 2956, 2932, 2879, 2810, 2389, 2208, 1709, 1599, 1580, 1566, 1502, 1466, 1446, 1420, 1391, 1360, 1281, 1207, 1116, 1095, 1067, 980, 985, 888, 859, 793, 744, 563; ESI-MS: m/z (%) 607.4 (100) $[M+H]^+$; Anal. calcd. for $C_{39}H_{34}N_4O_3$: C, 77.21; H, 5.65; N, 9.23; found: C, 76.90; H, 5.51, N, 9.19.

3-((2,5-Dibutoxy-4-iodophenyl)ethynyl)-9-ferrocenyl-2-mesityl-1,10-phenanthroline (19)



1,4-Dibutoxy-2,5-diiodobenzene (**18**, 468 mg, 987 µmol), 3-ethynyl-9-ferrocenyl-2-mesityl-[1,10]-phenanthroline (**17**, 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 (25 mL) and Et_3N (25 mL), the mixture was refluxed at 60 °C for 12 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 (neutral Al_2O_3, *n*-hexane: ethyl acetate = 97:3) to furnish an orange solid (R_f =0.45 [Al_2O_3, EtOAC: *n*-hexane = 3:97]). Yield = 40 mg (24%); mp = 85 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 8.45 (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), 7.81 (d, ^3J = 8.4 Hz, 1 H, 8-H), 7.78 (d, ^3J = 8.8 Hz, 1 H, 6-H), 7.29 (s, 1 H, [p′/q′]-H), 7.06 (s, 2 H, x-H), 6.37 (s, 1 H, [q′/p′]-H), 5.15 (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), 3.94 (t, ^3J = 6.4 Hz, 2 H, [m/m′]-H), 3.88 (t, ^3J = 6.4 Hz, 2 H, [m′/m]-H), 2.41 (s, 3 H, Me), 2.14 (s, 6 H, Me), 1.84-1.74 (m, 4 H, l, l′-H), 1.63-1.50 (m, 4 H, k, k′-H), 1.03 (t, ^3J = 7.2 Hz, 3 H, [j/j′]-H), 1.03 (t, ^3J = 7.2 Hz, 3 H, [j′/j]-H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 161.3, 160.3, 154.2, 152.1, 146.3, 145.0, 139.0, 137.8, 137.8, 136.7, 136.0, 128.4 (2C), 127.9, 127.6, 127.5, 125.0, 124.3, 121.5, 120.0, 116.5, 113.4, 91.7, 91.4, 88.3, 84.6, 70.8, 70.0, 69.9, 68.8, 31.7, 31.6, 21.4, 20.2, 19.8, 19.6, 14.1, 14.0; IR (KBr) *v* 3426, 3092, 2956, 2926, 2870, 2206, 1614, 1584, 1513, 1485, 1462, 1410, 1377, 1363, 1269, 1213, 1106, 1090, 1055, 1025, 1010, 975, 910, 874, 845, 819, 774, 723, 661, 620, 588, 543, 484; ESI-MS: *m/z* (%) 853.5 (100) $[M+H]^+$; Anal. calcd. for $C_{47}H_{45}FeIN_2O_2$•0.5 H_2O: C, 65.52; H, 5.38; N, 3.25; found: C, 65.33; H, 5.50, N, 3.04.

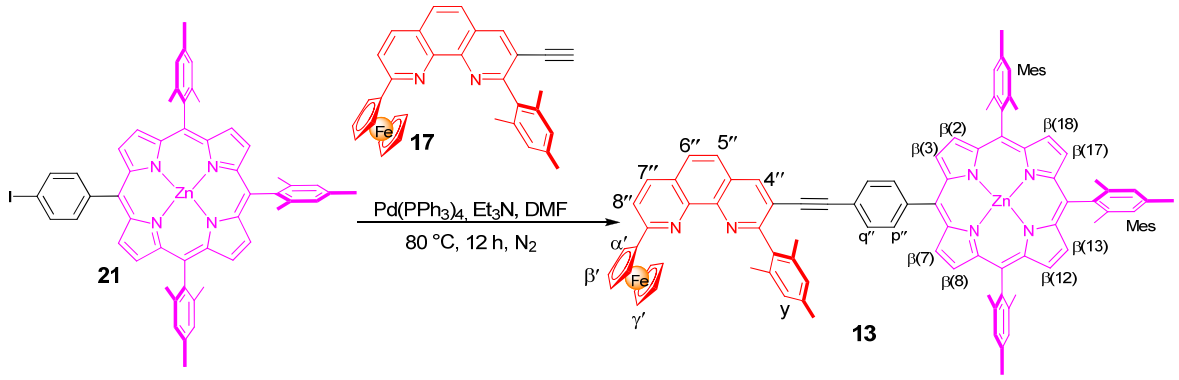
3-((2,5-Dibutoxy-4-((2,9- bis(2,6-dimethoxyphenyl)-1,10-phenanthrolin-3-yl)ethynyl)phenyl)ethynyl)-9- ferrocenyl-2-mesityl-1,10-phenanthroline (12)



3-((2,5-Dibutoxy-4-iodophenyl)ethynyl)-9-ferrocenyl-2-mesityl-1,10-phenanthroline (**19**, 100 mg, 117 µmol), 2,9-bis(2,6-dimethoxyphenyl)-3-ethynyl-[1,10]-phenanthroline (**20**, 46.5 mg, 97.7 µmol) and $Pd(PPh_3)_4$ (34.6 mg, 29.9 µmol) were placed in an oven-dried 100-mL flask under nitrogen atmosphere. After addition of dry DMF (25 mL) and Et_3N (25 mL), the solution was degassed thrice by freeze-pump-thaw cycles. Finally, the mixture was refluxed at 80 °C for 12 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, DCM: ethyl acetate = 95:5) to furnish an orange solid (R_f =0.37 [SiO_2, EtOAC:DCM = 8:92]). Yield = 50 mg (36%); mp > 160 °C (dec.); ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 8.45 (s, 1 H, 4′-H), 8.42 (s, 1 H, 4-H), 8.30 (d, ^3J = 8.4 Hz, 1 H, 7′-H), 8.17 (d, ^3J = 8.4 Hz, 1 H, 7-H), 7.89 (d, ^3J = 8.8 Hz, 1 H, 5′-H), 7.84 (d, ^3J = 8.8 Hz, 1 H, 6′-H), 7.82 (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), 7.58 (d, ^3J = 8.4 Hz, 1 H, 8′-H), 7.41 (t, ^3J = 8.4 Hz, 1 H, w-H), 7.38 (t, ^3J = 8.4 Hz, 1 H, w′-H), 7.07 (s, 2 H, x-H), 6.74 (d, ^3J = 8.8 Hz, 2 H, v-H), 6.70 (d, ^3J = 8.8 Hz, 2 H, v′-H), 6.43 (s, 1 H, [q′/p′]-H), 6.30 (s, 1 H, [p′/q′]-H), 5.15 (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), 3.90 (t, ^3J = 6.4 Hz, 2 H, [m/m′]-H), 3.87 (t, ^3J = 6.4 Hz, 2 H, [m′/m]-H), 3.72 (s, 6 H, OMe), 3.71 (s, 6 H, OMe), 2.42 (s, 3 H, Me), 2.14 (s, 6 H, Me), 1.86-1.77 (m, 4 H, l, l′-H), 1.66-1.55 (m, 4 H, k, k′-H), 1.09 (t, ^3J = 7.6 Hz, 6 H, j/j′-H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 161.3, 160.3, 158.8, 158.5, 157.3, 156.1, 153.3 (2C), 146.4, 146.3, 145.3, 145.0, 139.0, 138.3, 137.8, 137.8, 136.7, 136.1, 136.0, 130.1, 130.1, 128.4 (2C), 128.3, 127.9, 127.5, 127.5, 127.4, 126.1 (2C), 125.0, 121.5, 121.1, 120.0, 119.8, 118.9, 117.7, 117.6, 114.3, 113.9, 104.2, 104.1, 92.8, 92.5, 91.7, 91.6, 84.6, 70.8, 70.0, 69.7, 69.5, 68.8, 56.4, 56.3, 31.7, 31.6,

21.4, 20.2, 19.7, 19.7, 14.2(2C) ; IR (KBr) *v* 3430, 2955, 2932, 2871, 2205, 1598, 1536, 1499, 1473, 1431, 1278, 1250, 1210, 1111, 1061, 1026, 909, 875, 846, 781, 733, 495; ESI-MS: *m/z* (%) 1202.6 (100) $[M + H]^+$; Anal. calcd. for $C_{77}H_{68}FeN_4O_6$•0.5 CH_2Cl_2: C, 74.72; H, 5.74; N, 4.50; found: C, 74.93; H, 5.32, N, 4.47.

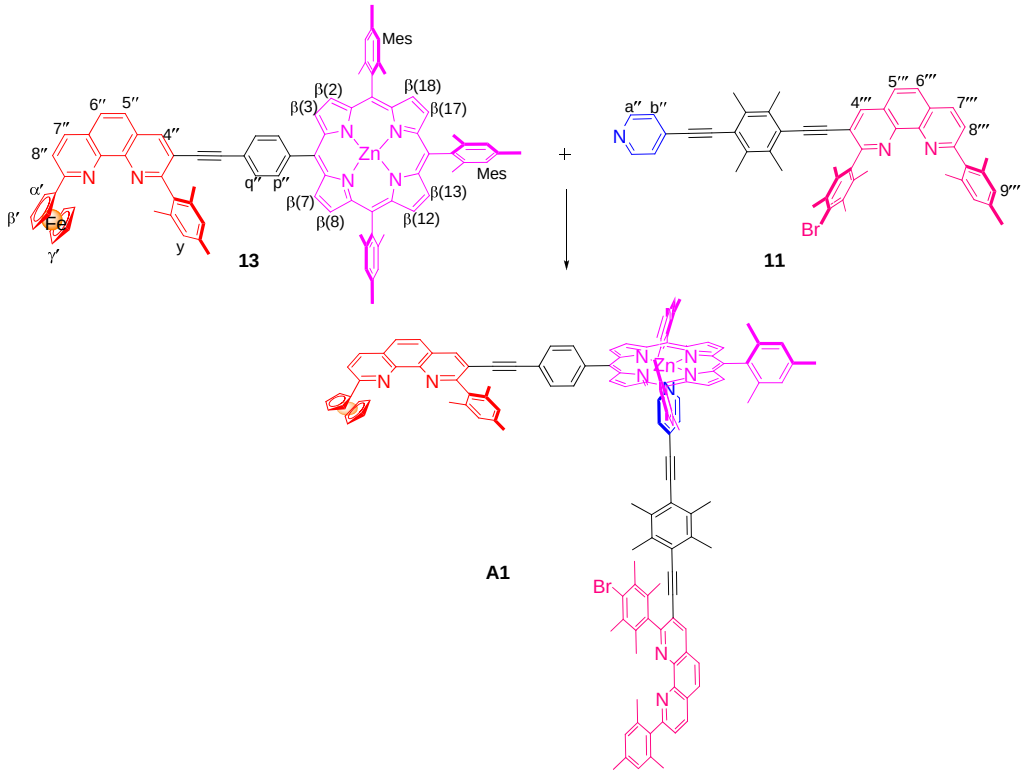
Zinc(II)-5-(4-(9-ferrocenyl-2-mesityl-[1,10]-phenanthrolin-3-yl)ethynyl)phenyl-10,15,20-trimesitylporphyrin (13)



3-Ethynyl-9-ferrocenyl-2-mesityl-[1,10]-phenanthroline (**17**, 110 mg, 118 µmol), zinc(II)-5-(4-iodophenyl)-10,15,20-trimesitylporphyrin (**21**, 50 mg, 98.7 µmol) and $Pd(PPh_3)_4$ (11.3 mg, 9.87 µmol) were placed in an oven-dried 100-mL flask under nitrogen atmosphere. After addition of dry DMF (25 mL) and Et_3N (25 mL), the solution was degassed thrice by freeze-pump-thaw cycles. Finally, the mixture was refluxed at 80 °C for 12 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 = 85:15) to furnish a violet solid (R_f =0.26 [SiO_2, *n*-hexane: ethyl acetate = 85:15]). Yield = 77 mg (60%); mp > 250 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 8.84 (d, ^3J = 4.8 Hz, 2 H, [$\beta_{(2,8)}$/ [$\beta_{(3,7)}$]-H), 8.74 (d, ^3J =4.8 Hz, 2 H, [$\beta_{(3,7)}$/ [$\beta_{(2,8)}$]-H), 8.70 (s, 4 H, $\beta_{(12,13,17,18)}$-H), 8.63 (s, 1 H, 4″-H), 8.21 (d, ^3J = 8.4 Hz, 1 H, 7″-H), 8.17 (d, ^3J = 8.4 Hz, 2 H, [p″/q″]-H), 7.87 (s, 2 H, 5″,6″-H), 7.85 (d, ^3J = 8.4 Hz, 1 H, 8″-H), 7.58 (d, ^3J = 8.4 Hz, 2 H, [q″/p″]-H), 7.30 (s, 6 H, Mes-H), 7.18 (s, 2 H, y-H), 5.18 (t, ^3J = 2.0 Hz, 2 H, α′-H), 4.50 (t, ^3J = 2.0 Hz, 2 H, β′-H), 4.09 (s, 5 H, γ′-H), 2.62 (s, 9 H, Me), 2.45 (s, 3 H, Me), 2.27 (s, 6 H, Me), 1.84 (s, 6 H, Me), 1.83 (s, 12 H, Me); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 161.7, 160.4, 150.3, 150.3, 150.1, 150.0, 146.3, 145.1, 143.9, 139.5, 139.5, 139.3, 139.3, 139.1, 138.2, 137.9, 137.8, 136.7, 136.0, 134.8, 132.1, 131.5, 131.4, 131.0, 130.1, 128.5, 128.0 (3C), 127.9, 127.6, 127.6, 125.1, 122.2, 121.6, 120.1, 119.4, 119.3, 119.2, 95.2, 88.1, 84.7, 70.8, 70.1, 68.8, 30.1, 21.8,

21.7, 21.5, 21.4, 20.3; IR (KBr) *v* 3428, 2916, 2853, 1656, 1612, 1583, 1515, 1456, 1436, 1378, 1336, 1203, 1104, 1061, 996, 851, 830, 797, 722, 485, 412; ESI-MS: *m/z* (%) 1307.4 (100) $[M + H]^+$; Anal. calcd. for $C_{86}H_{70}N_6FeZn•CH_2Cl_2$: C, 74.98; H, 5.21; N, 6.03; found: C, 75.09; H, 5.46, N, 5.66.

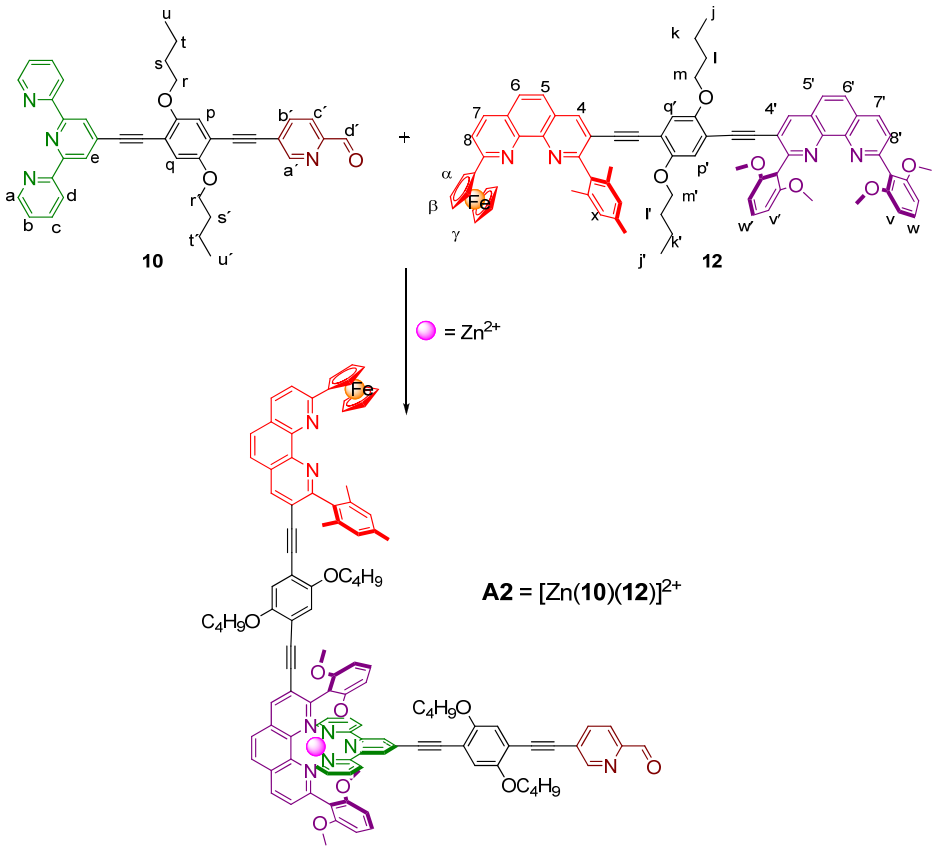
Metalloligand A1 = [(11)(13)]



2-(4-Bromo-2,3,5,6-tetramethylphenyl)-9-mesityl-3-((2,3,5,6-tetramethyl-4-(pyridin-4-yl-ethynyl)phenyl)ethynyl)-1,10-phenanthroline (**11**, 2.95 mg, 3.85 µmol) and zinc(II)-5-(4-(9-ferrocenyl-2-mesityl-[1,10]-phenanthrolin-3-yl)ethynyl)phenyl-10,15,20-trimesitylporphyrin (**13**, 5.04 mg, 3.85 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): δ = 8.80 (d, 2 H, ^3J = 4.8 Hz, [$\beta_{(2,8)}$/ [$\beta_{(3,7)}$]-H), 8.70 (d, 2 H, ^3J = 4.8 Hz, [$\beta_{(3,7)}$/ [$\beta_{(2,8)}$]-H), 8.65 (s, 4 H, $\beta_{(12,13,17,18)}$-H), 8.62 (s, 1 H, 4″-H), 8.49 (s, 1 H, 4‴-H), 8.31 (d, ^3J = 8.4 Hz, 1 H, 7‴-H), 8.21 (d, ^3J = 8.8 Hz, 1 H, 7″-H), 8.16 (d, ^3J = 8.0 Hz, 2 H, [p″/q″]-H), 7.90 (d, ^3J = 8.8 Hz, 1 H, [5‴/6‴]-H), 7.87 (s, 2 H, 5″,6″-H), 7.85 (d, ^3J = 8.8 Hz, 1 H, 8″-H), 7.84 (d, ^3J = 8.8 Hz, 1 H, [6‴/5‴]-H), 7.56 (d, ^3J = 8.0 Hz, 2 H, [q″/p″]-H), 7.55 (d, ^3J = 8.4 Hz, 1 H, 8‴-H), 7.29 (s, 4 H, Mes-H), 7.27 (s, 2 H, Mes-H), 7.17 (s, 2 H, y-H), 6.94 (s, 2 H, 9‴-H), 5.96 (br, 2 H, b″-H), 5.19 (t, 2 H, ^3J = 2.0 Hz, α′-H), 4.50 (t, 2 H, ^3J = 2.0 Hz, β′-H), 4.09 (s, 5 H, γ′-H), 3.07 (bs, 2 H, a″-H) 2.61 (s, 6 H, Me), 2.60 (s, 3 H, Me), 2.45 (s, 3 H, Me), 2.38 (s, 6 H, Me), 2.32 (s, 3 H, Me), 2.27 (s, 6 H,

Me), 2.06 (s, 6 H, Me), 2.01 (s, 6 H, Me), 1.95 (s, 6 H, Me), 1.92 (s, 6 H, Me), 1.82 (s, 12 H, Me), 1.80 (s, 6 H, Me); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 162.0, 161.7, 160.9, 160.4, 150.1, 150.0, 150.0, 149.9, 146.3, 145.3, 145.1, 144.4, 143.7, 139.8, 139.8, 139.8, 139.8, 139.5, 139.2, 139.1, 138.3, 138.2, 138.2, 138.0, 137.9, 137.8, 137.7, 137.7, 137.7, 136.7, 136.5, 136.4, 136.0, 135.0, 134.4, 133.4, 132.2, 131.9, 131.2, 131.1, 130.7, 129.9, 129.2, 128.6, 128.5, 128.0, 127.9 (2C), 127.7, 127.6, 127.5, 127.3, 125.8, 125.2, 125.2, 125.1, 124.3, 124.0, 122.0, 121.9, 121.6, 120.3, 120.1, 119.0, 118.8, 118.7, 95.9, 95.3, 94.6, 94.0, 93.9, 88.0, 84.7, 70.8, 70.1, 68.8, 30.1, 21.8 (2C), 21.5, 21.4, 21.2, 20.9, 20.4, 20.3, 18.3, 18.1, 17.5; IR (KBr) ν 3426, 2918, 2853, 2390, 2204, 1603, 1536, 1515, 1458, 1438, 1377, 1335, 1281, 1203, 1145, 1106, 1061, 996, 911, 849, 829, 798, 770, 722 ; UV-vis (CH_2Cl_2) : λ_{max} = 429 nm (Soret band, ε = 2.26 x 10^5 $M^{-1}cm^{-1}$) and 562 nm (Q band); Anal calcd for $C_{136}H_{114}BrFeN_9Zn$•1.75 CH_2Cl_2: C, 74.38; H, 5.32; N, 5.67; found: C, 74.43; H, 5.57; N, 5.29.

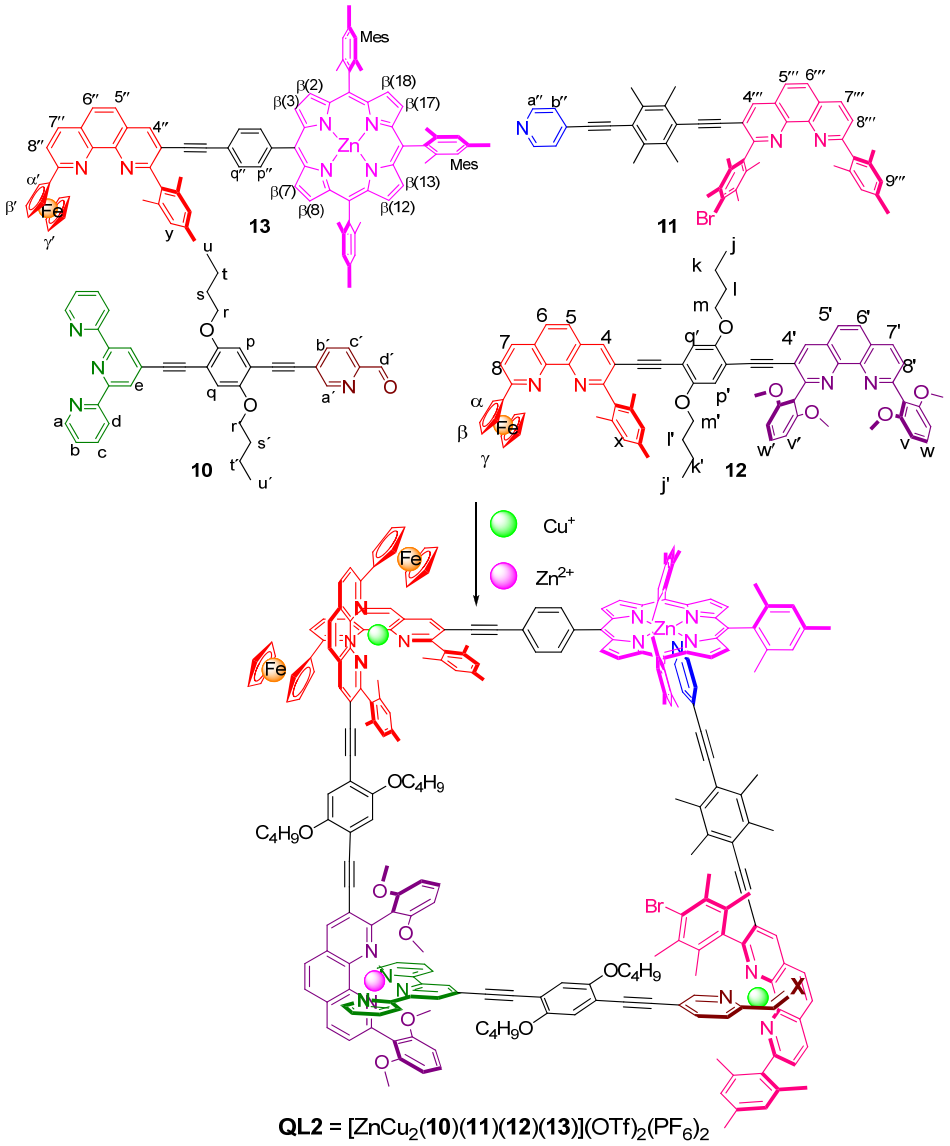
Metalloligand A2 = [Zn(10)(12)](OTf)$_2$



In an oven-dried 25-mL flask, the terpyridine-picolinaldehyde hybrid **10** (2.33 mg, 3.84 μmol), bisphenanthroline **12** (4.61 mg, 3.84 μmol) and $Zn(OTf)_2$ (1.40 mg, 3.84 μmol) were refluxed in 20 mL of CH_2Cl_2/CH_3CN (1:1) for 2 h. The reaction mixture was then cooled down to room temperature, and solvents were removed under reduced pressure. The resultant crude mixture was subjected to analytical characterisation without any further purification.

Yield quantitative; mp > 250 °C; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 10.08 (s, 1 H, d′-H), 8.96 (d, ^{3}J = 8.4 Hz, 1 H, 7′-H), 8.94 (s, 1 H, 4′-H), 8.93 (dd, ^{4}J = 2.0 Hz, ^{5}J = 0.8 Hz, 1 H, a′-H), 8.56 (d, ^{3}J = 8.0 Hz, 2 H, d-H), 8.53 (s, 2 H, e-H), 8.47 (d, ^{3}J = 9.2 Hz, 1 H, 5′-H), 8.42 (s, 1 H, 4-H), 8.39 (d, ^{3}J = 9.2 Hz, 1 H, 6′-H), 8.32 (td, ^{3}J = 8.0 Hz, ^{4}J = 1.6 Hz, 2 H, c-H), 8.16 (d, ^{3}J = 8.4 Hz, 1 H, 7-H), 8.02 (d, ^{3}J = 8.4 Hz, 1 H, 8′-H), 8.01 (dd, ^{3}J = 8.0 Hz, ^{5}J = 0.8 Hz, 1 H, c′-H), 8.93 (dd, ^{3}J = 8.0 Hz, ^{4}J = 2.0 Hz, 1 H, b′-H), 7.81 (d, ^{3}J = 8.8 Hz, 1 H, 5-H), 7.81 (d, ^{3}J = 8.4 Hz, 1 H, 8-H), 7.76 (d, ^{3}J = 8.8 Hz, 1 H, 6-H), 7.60 (ddd, ^{3}J = 5.2 Hz, ^{4}J = 1.6 Hz, ^{5}J = 0.8 Hz, 2 H, a-H), 7.54 (ddd, ^{3}J = 8.0 Hz, ^{3}J = 5.2 Hz, ^{4}J = 0.8 Hz, 2 H, b-H), 7.50 (s, 1 H, [p/q]-H), 7.18 (s, 1 H, [q/p]-H), 7.04 (t, ^{3}J = 8.8 Hz, 1 H, w′-H), 7.02 (s, 2 H, x-H), 7.01 (t, ^{3}J = 8.8 Hz, 1 H, w-H), 6.38 (s, 1 H, [p'/q']-H), 6.23 (s, 1 H, [q'/p']-H), 6.10 (d, ^{3}J = 8.8 Hz, 2 H, v′-H), 6.08 (d, ^{3}J = 8.4 Hz, 2 H, v-H), 5.14 (t, ^{3}J = 2.0 Hz, 2 H, α-H), 4.47 (t, ^{3}J = 2.0 Hz, 2 H, β-H), 4.22-4.18 (m, 4 H, j,j′-H), 4.05 (s, 5 H, γ′-H),3.80 (t, ^{3}J = 6.4 Hz, 2 H, [r/r′]-H), 3.82 (t, ^{3}J = 6.4 Hz, 2 H, [r′/r]-H), 2.93 (s, 6 H, OC$\underline{H}_3$), 2.90 (s, 6 H, OC$\underline{H}_3$), 2.38 (s, 3 H, Me), 2.09 (s, 6 H, Me), 2.02-1.94 (m, 2 H, [k/k′]-H), 1.93-1.86 (m, 2 H, [k′/k]-H), 1.76-1.61 (m, 8 H, l, l′, s, s′-H), 1.51-1.43 (m, 4 H, t, t′-H), 1.13 (t, ^{3}J = 7.2 Hz, 3 H, [m/m′]-H), 1.06 (t, ^{3}J = 7.2 Hz, 3 H, [m′/m]-H), 1.01 (t, ^{3}J = 7.2 Hz, 3 H, [u/u′]-H), 0.98 (t, ^{3}J = 7.2 Hz, 3 H, [u′/u]-H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 192.9, 161.2, 160.3, 158.5, 157.7, 157.4, 157.0, 154.7, 153.8, 153.2, 152.8, 151.5, 148.7, 147.7, 147.7, 146.5, 145.0, 142.7, 142.6, 141.9, 141.0, 140.6, 139.6, 139.2, 139.1, 137.8, 136.7, 136.1, 133.2, 133.2, 129.9, 129.2, 129.1, 128.9, 128.8, 128.3, 128.0, 127.9, 127.6, 127.5, 125.7, 125.1, 124.9, 124.8, 123.3, 121.6, 121.3, 119.8, 119.7, 118.3, 118.2, 117.5, 117.4, 117.0, 115.5, 115.5, 114.8, 114.3, 112.7, 112.3, 103.9, 103.8, 99.0, 95.5, 93.2, 92.8, 92.3, 91.3, 91.2, 89.6, 71.2, 70.9, 70.0, 69.8, 69.8, 69.6, 69.3, 68.7, 55.6, 55.6, 31.7, 31.6, 31.6, 31.4, 30.0, 21.4, 20.1, 19.7, 19.7, 19.6, 14.2, 14.1, 14.0, 14.0; IR (KBr) *v* 3459, 3071, 2929, 2870, 2207, 1708, 1601, 1501, 1475, 1430, 1257, 1222, 1153, 1111, 1030, 851, 791, 729, 637, 572, 517; ESI-MS: *m*/*z* (%) 936.4 (100) [Zn(**10**)(**12**)]$^{2+}$; Anal. calcd. for $C_{118}H_{102}F_6FeN_8O_{15}S_2Zn$•1.5 CH_2Cl_2: C, 62.43; H, 4.60; N, 4.87; S, 2.79; found: C, 62.72; H, 4.65; N, 4.58; S, 2.96.

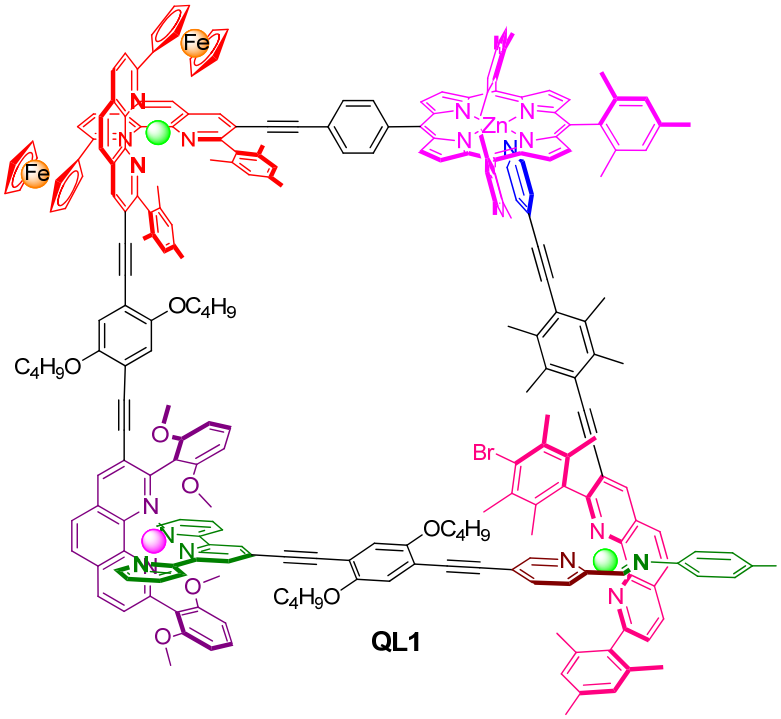
Six-component quadrilateral QL2 = $[ZnCu_2(10)(11)(12)(13)](OTf)_2(PF_6)_2$



In an oven-dried 25-mL round bottom flask, the ditopic terpyridine-picolinaldehyde hybrid **10** (182 µg, 0.300 µmol), bisphenanthroline **12** (360 µg, 0.300 µmol) and $Zn(OTf)_2$ (133 µg, 0.300 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 the phenanthroline-porphyrin hybrid **13** (392 µg, 0.300 µmol), phenanthroline-pyridine ligand **11** (230 µg, 0.300 µmol) and $[Cu(MeCN)_4]PF_6$ (224 µg, 0.600 µmol) in 15 mL of CH_2Cl_2 the resultant mixture was refluxed for 2 h.[8] It was 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 (600 MHz, 298 K, CD_2Cl_2) of two diastereomers in ratio of 23:27 δ = 9.55 (s, 0.46 H, d′-H), 9.51 (s, 0.54 H, d′-H), 8.97 (d, ^3J = 8.4 Hz, 0.46 H, 7′-H), 8.97 (d, ^3J = 8.4 Hz,

0.54 H, 7′-H), 8.90 (s, 1 H, 4′-H), 8.72 (s, 1 H, 4‴-H), 8.70 (d, ^3J = 4.8 Hz, 2 H, [$\beta_{(2,8)}$/ [$\beta_{(3,7)}$]-H), 8.69 (d, ^3J = 8.4 Hz, 1 H, 7‴-H), 8.67 (d, ^3J = 4.8 Hz, 2 H, [$\beta_{(3,7)}$/ [$\beta_{(2,8)}$]-H), 8.66 (s, 1.84 H, β(7)-H), 8.66 (s, 2.16 H, $\beta_{(12,13,17,18)}$-H), 8.65(s, 0.46 H, [4/4″]-H), 8.63(s, 0.54 H, [4/4″]-H), 8.62(s, 1 H, [4″/4]-H), 8.54-8.44 (m, 5 H, d, e, 5′-H), 8.38 (d, ^3J = 8.4 Hz, 0.46 H, 6′-H), 8.38 (d, ^3J = 8.4 Hz, 0.54 H, 6′-H), 8.33 (d, ^3J = 8.4 Hz, 1H, [7/7″] -H), 8.32-8.28 (m, 4 H, c, a′, [7″/7] -H), 8.15 (br, 2 H, [p″/q″]-H), 8.06 (d, ^3J = 9.6 Hz, 1 H, [5/5″]-H), 8.05 (d, ^3J = 9.6 Hz, 1 H, [5″/5]-H), 8.04 (d, ^3J = 8.4 Hz, 2 H, 8&8″-H), 8.04 (br, 1 H, b′-H), 8.03 (d, ^3J = 8.4 Hz, 0.46 H, 8′-H),8.02 (d, ^3J = 9.6 Hz, 2 H, 6&6″-H), 8.00 (d, ^3J = 8.4 Hz, 1 H, 5‴-H), 7.99 (d, ^3J = 8.4 Hz, 0.54 H, 8′-H), 7.95 (d, ^3J = 8.4 Hz, 1 H, 6‴-H), 7.92 (d, ^3J = 8.4 Hz, 1 H, 8‴-H), 7.57 (m, 4 H, [q″/p″], a-H), 7.51 (m, 3 H, [p/q], b-H), 7.28 (s, 4H, Mes-H), 7.25 (s, 2H, Mes-H), 7.21(d, ^3J = 7.2 Hz, 1 H, c′-H), 7.17 (s, 1H, [q/p]-H), 7.00-6.96 (m, 2 H, w&w′-H), 6.64 (s, 2 H, 9‴-H), 6.64 (s, 0.46 H, [x/x′]-H), 6.58 (s, 0.54 H, [x/x′]-H), 6.48 (s, 0.46 H, [y/y′]-H), 6.43 (s, 0.54 H, [y/y′]-H), 6.10-6.03 (m, 6 H, p′,q′, 9,9′-H), 5.92 (br, 2 H, b″-H), 5.85 (s, 0.54H, [x′/x]-H), 5.77 (s, 0.46H, [x′/x]-H), 5.72 (br, 0.46 H, [α/α′]-H), 5.64 (br, 1.54 H, [y′/y],α&α′-H), 5.58 (br, 1 H, [y′/y]&[α′/α]-H), 5.12 (br, 0.46 H, [α/α′]-H), 5.07 (br, 0.54 H, [α/α′]-H), 5.05 (br, 0.46 H, [α′/α]-H), 5.01 (br, 0.54 H, [α′/α]-H), 4.66 (br, 0.46 H, [β/β′]-H), 4.62 (br, 0.54 H, [β/β′]-H), 4.60 (br, 0.46 H, [β′/β]-H), 4.56 (br, 0.54 H, [β′/β]-H), 4.39 (br, 0.46 H, [β/β′]-H), 4.35 (br, 0.54 H, [β/β′]-H), 4.32 (br, 0.46 H, [β′/β]-H), 4.30 (br, 0.56 H, [β′/β]-H), 4.30 (s, 5 H, [γ/γ′]-H), 4.27-4.19 (m, 9 H, [γ′/γ], m, m′-H), 3.63-3.56 (m, 4 H, r,r′-H), 2.95 (br, 2 H, a″), 2.92 (s, 2.76 H, O$C\underline{H}_3$), 2.90 (s, 3.24 H, O$C\underline{H}_3$), 2.84 (s, 2.76 H, O$C\underline{H}_3$), 2.82 (s, 3.24 H, O$C\underline{H}_3$), 2.61 (s, 6 H, Me-Por), 2.60 (s, 3 H, Me-por), 2.19 (s, 3 H, Me), 2.15 (s, 3 H, Me), 2.11 (s, 6 H, Me), 2.09(s, 6 H, Me), 2.01-1.92 (m, 12 H, Me), 1.80 (s, 12 H, Me-por), 1.77 (s, 6 H, Me-por), 1.69-1.65 (m, 2 H, [k/k′]-H), 1.62-1.53 (m, 8 H, l, l′,s ,s′-H), 1.41-1.34 (m, 2 H, [k′/k]-H), 1.30-1.23(m, 13 H, Me,t,t′), 0.98-0.82 (m, 21 H, Me, u,u′, j,j′-H), 0.77 (s, 1.38 H, Me), 0.77 (s, 1.62 H, Me); IR (KBr) *v* 3436, 2959, 2919, 2869, 2204, 1709 (C=O), 1601, 1500, 1475, 1431, 1258, 1153, 1109, 1030, 996, 914, 841, 721, 638, 557, 517, 493; ESI-MS: *m*/*z* (%) 1018.2 () $[M-OTf]^{4+}$ and 1407.5 (100) $[M-OTf]^{3+}$; Anal calcd for $C_{254}H_{216}BrCu_2F_{18}Fe_2N_{17}O_{15}P_2S_2Zn_2 \cdot 1.5CH_2Cl_2$: C, 64.05; H, 4.61; N, 4.97; S, 1.34; found: C, 63.95; H, 4.66; N, 4.80; S, 1.08.

Seven-component quadrilateral QL1 = [$ZnCu_2$(11)(12)(13)(14)]$(OTf)_2(PF_6)_2$



QL1

An oven-dried 25-mL flask was charged with $[Cu(CH_3CN)]PF_6$ (924 mg, 2.48 μmol) and the metalloligands **A1** = [(**11**)(**13**)] (2.57 mg, 1.24 μmol) and **A2** = [Zn(**14**)(**12**)]$(OTf)_2$ (2.80 mg, 1.24 μmol). After addition of *p*-toludine (**6**, 0.133 mg, 1.24 μmol) and CH_2Cl_2 (20 mL), the mixture was refluxed for 1 h. Following the removal of the 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) *ν* 3437, 2923, 2871, 2361, 2207, 1602 (C=N), 1504, 1475, 1433, 1279, 1256, 1154, 1112, 1031, 997, 842, 797, 728, 638, 558; ESI-MS: *m/z* (%) 1040.5 $[M-OTf]^{4+}$and 1437.6 (100) $[M-OTf]^{3+}$; Anal calcd for $C_{261}H_{223}BrCu_2F_{18}Fe_2N_{18}O_{14}P_2S_2Zn_2$•$4CH_2Cl_2$•$C_4H_8O_2$: C, 62.36; H, 4.65; N, 4.87; S, 1.24; found: C, 62.19; H, 4.94; N, 4.46; S, 1.17. The ^{1}H-NMR of **QL1** is complicated due to the existence of three possible diastereomers. Diagnostically, in the ^{1}H NMR spectrum of **QL1**, the resonance of the aldehyde (*d*-H) protons (δ = 9.55 and 9.51 ppm for **QL2**) was absent, suggesting the complete formation of iminopyridine units of **14** = [(**10**)(**7**)-H_2O] in **QL1**. The observed broadness of ^{1}H signals obstructed our further analysis of the spectra. The DOSY NMR (Figure S34) of the quadrilateral shows all possible diastereomers to have basically identical diffusion constant (*ca.* $D = 2.8 \times 10^{-10}$ m^2s^{-1}).

Table S1: Selected characteristics of the individual corners in QL1 or QL2

	Cornerstones or Ligands			
	10 in **C5/C1** ^{1}H NMR (*d*'-H)	**C2** Cyclic Voltammetry	**12** in **C3** ^{1}H NMR (-OMe)	**C4** UV-Vis (Soret)
in	Ligand **10**: δ = 10.06	Model complex **C2**: $E_{1/2}$ = 0.61 & 0.72 V_{SCE}	Ligand **12**: δ = 3.71 and 3.72	Ligand **13**: 422 nm
				A1: 429 nm
			A2: δ =2.93, 2.90	
	QL2: δ = 9.55 & 9.51	**QL2**: $E_{1/2}$ = 0.61 & 0.70 V_{SCE}	**QL2**: δ = 2.92, 2.90, 2.84, 2.82	**QL2**: 429 nm
	QL1: disappeared	**QL1**: $E_{1/2}$ = 0.61 & 0.70 V_{SCE}		**QL1**: 429 nm

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

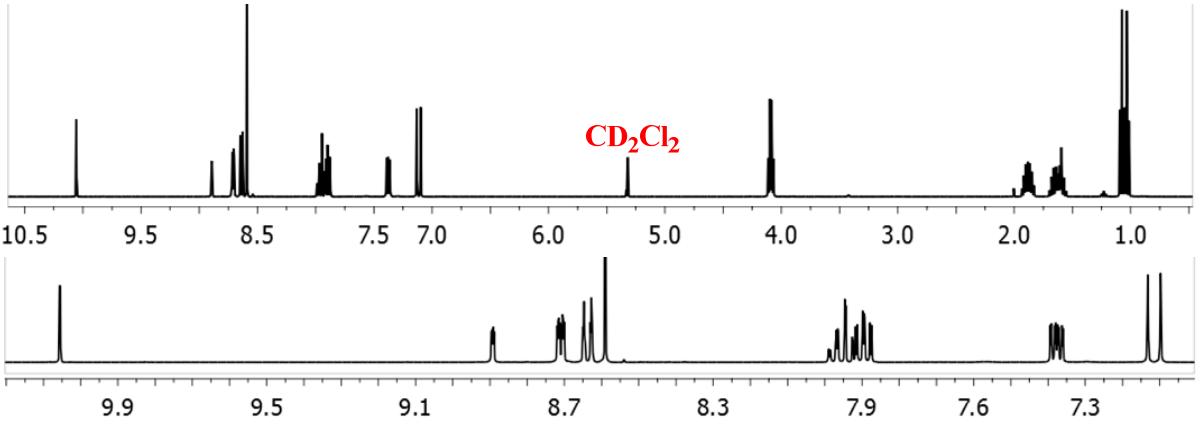


Figure S1: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of ligand **10**. An expanded part of the aromatic region is shown at the bottom.

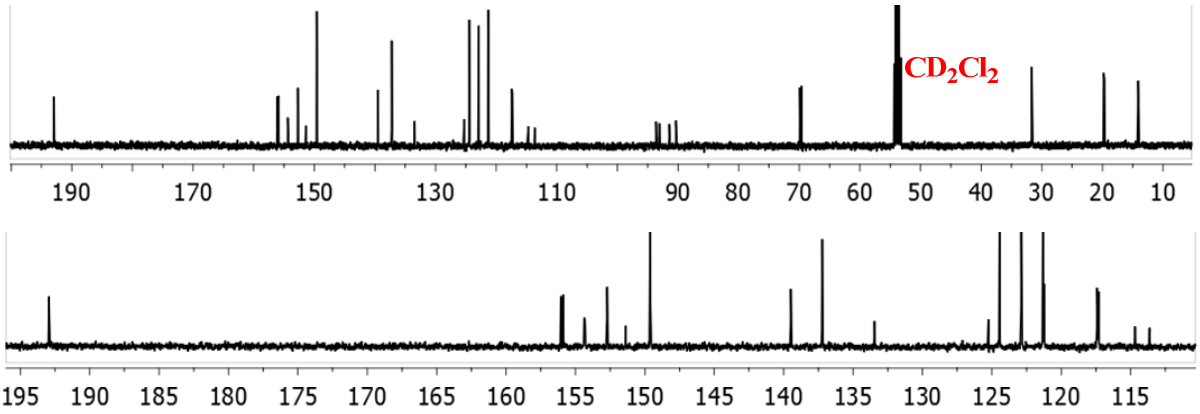


Figure S2: ^{13}C NMR spectrum (100 MHz, CD_2Cl_2, 298 K) of ligand **10**. An expanded part of the aromatic region is shown at the bottom.

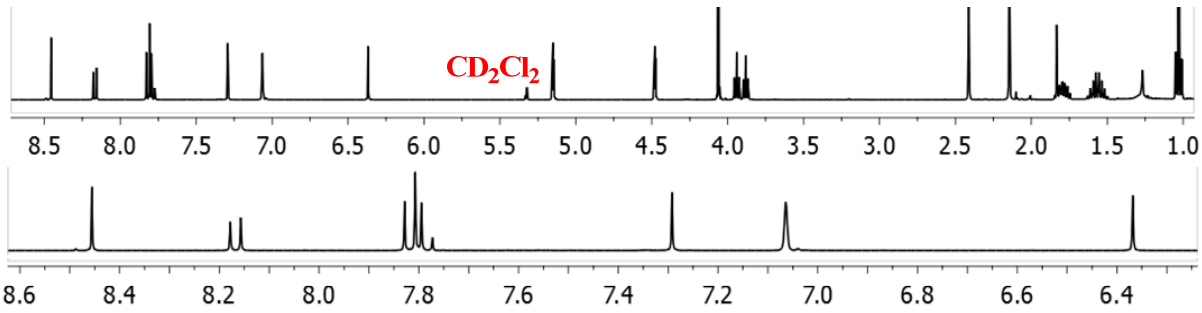


Figure S3: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of **19**. An expanded part of the aromatic region is shown at the bottom.

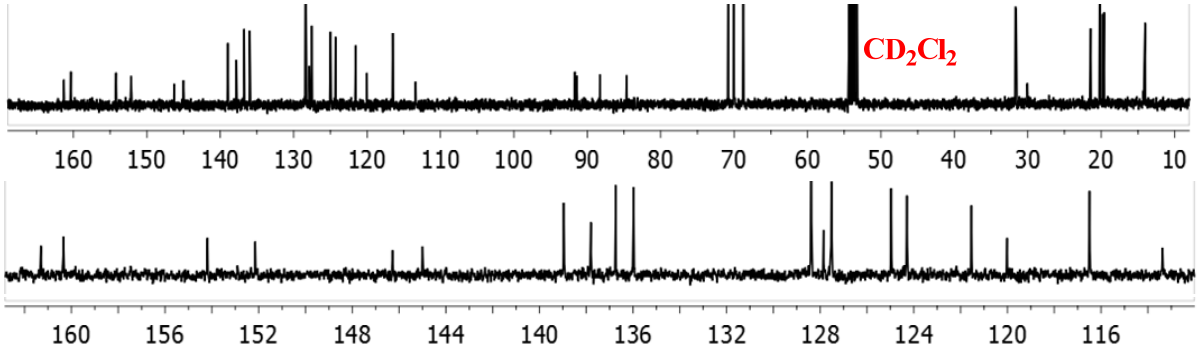


Figure S4: ^{13}C NMR spectrum (100 MHz, CD_2Cl_2, 298 K) of **19**. An expanded part of the aromatic region is shown at the bottom.

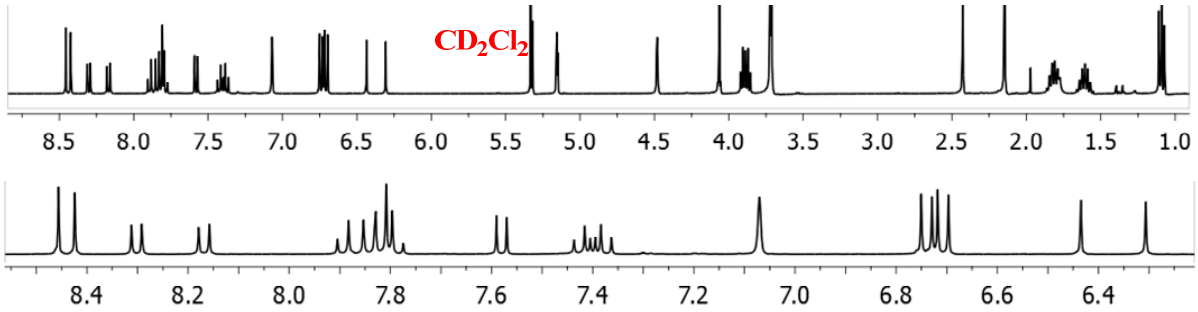


Figure S5: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of **12**. An expanded part of the aromatic region is shown at the bottom.

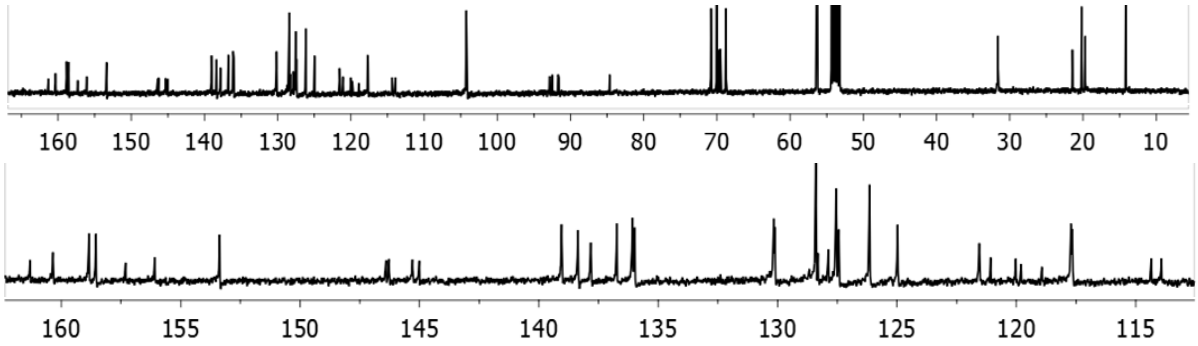


Figure S6: ^{13}C NMR spectrum (100 MHz, CD_2Cl_2, 298 K) of **12**. An expanded part of the aromatic region is shown at the bottom.

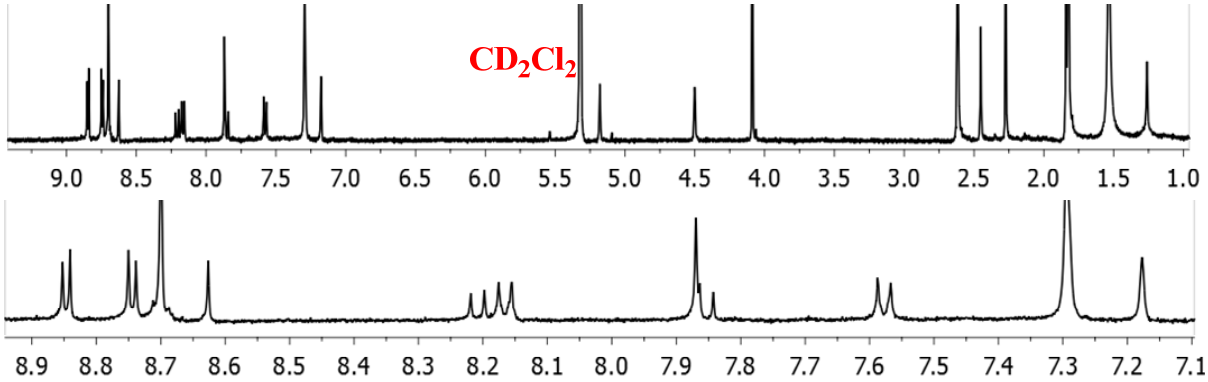


Figure S7: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of **13**. An expanded part of the aromatic region is shown at the bottom.

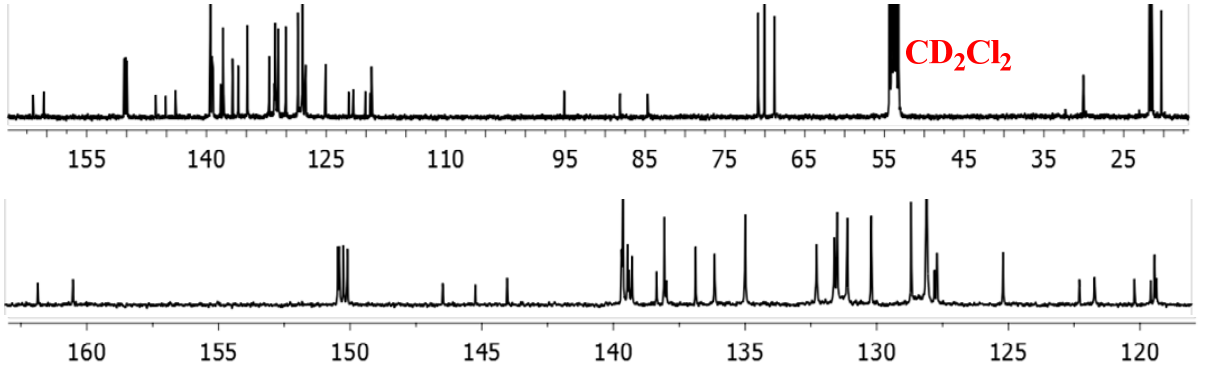


Figure S8: ^{13}C NMR spectrum (100 MHz, CD_2Cl_2, 298 K) of **13**. Expanded parts of the aromatic region are shown at the bottom.

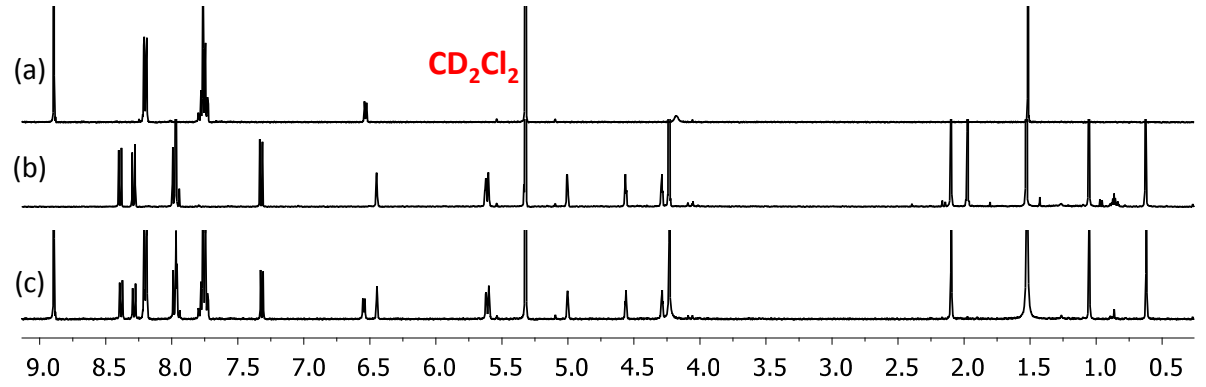


Figure S9: Partial ^{1}H NMR spectra for comparison (400 MHz, CD_2Cl_2, 298 K) of (a) **C4** = [(**6**)(**8**)], (b) **C2** = [Cu(**2**)$_2$]PF_6, and (c) an equimolar mixture of **C2**, ligand **6** and ligand **8** after equilibration.

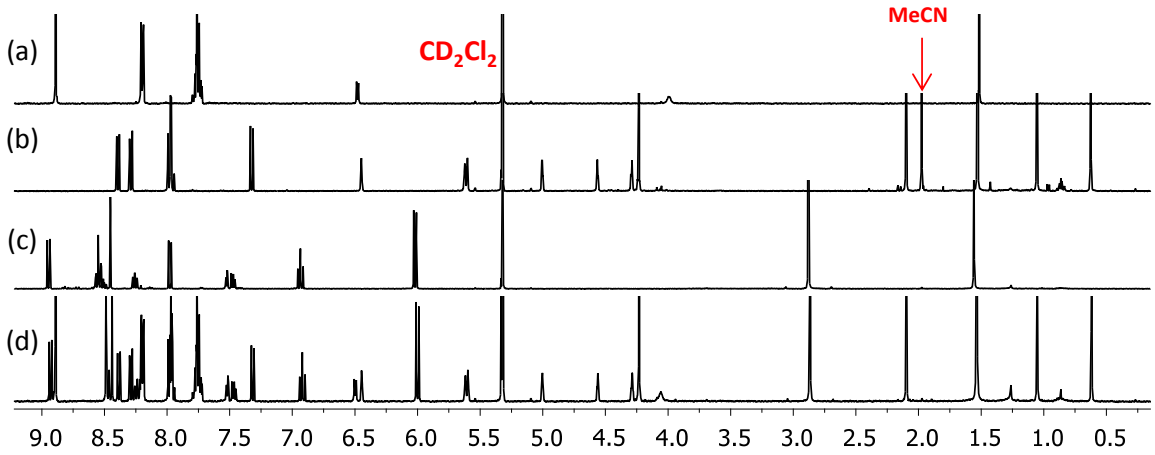


Figure S10: Partial ^{1}H NMR spectra for comparison (400 MHz, CD_2Cl_2, 298 K) of (a) **C4** = [(**6**)(**8**)], (b) **C2** = [Cu(**2**)$_2$]PF_6, (c) **C3** = [Zn(**3**)(**4**)]$(OTf)_2$, and (d) an equimolar mixture of **C2**, **C3**, ligand **6** and ligand **8** after equilibration.

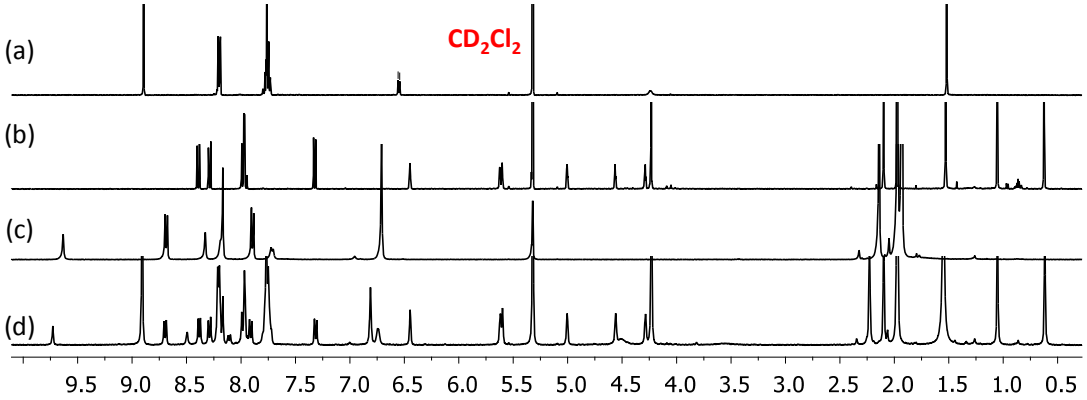


Figure S11: Partial ^{1}H NMR spectra for comparison (400 MHz, CD_2Cl_2, 298 K) of (a) **C4** = [(**6**)(**8**)], (b) **C2** = [Cu(**2**)$_2$]PF_6, (c) **C5** = [Cu(**1**)(**5**)]PF_6, and(d) an equimolar mixture of **C2**, **C5**, ligand **6** and ligand **8** after equilibration.

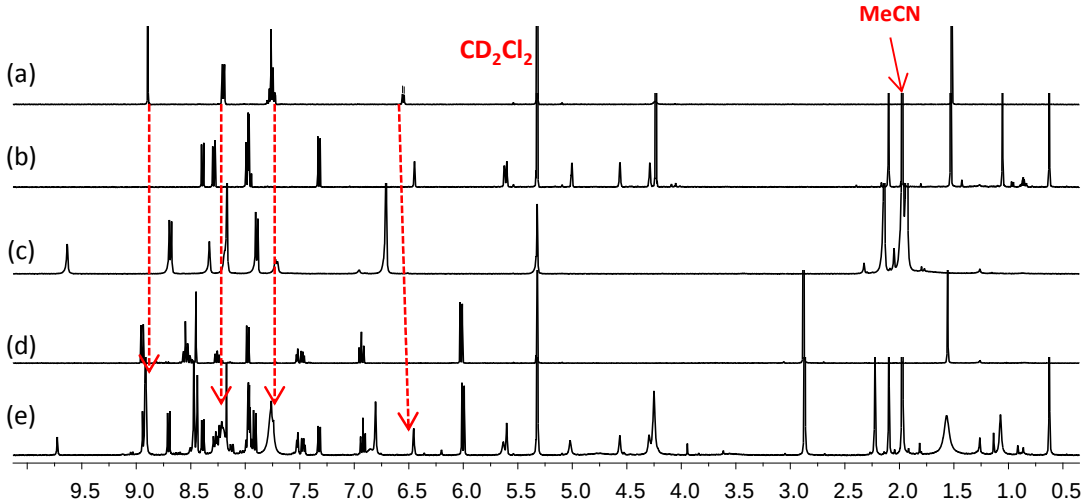


Figure S12: Partial ^{1}H NMR spectra for comparison (400 MHz, CD_2Cl_2, 298 K) of (a) **C4** = [(**6**)(**8**)], (b) **C2** = [Cu(**2**)$_2$]PF_6, (c) **C5** = [Cu(**1**)(**5**)]$(OTf)_2$, (d) **C3** = [Zn(**3**)(**4**)]$(OTf)_2$ and (e) an equimolar mixture of **C2**, **C5**, **C3,** ligand **6** and ligand **8** after equilibration.

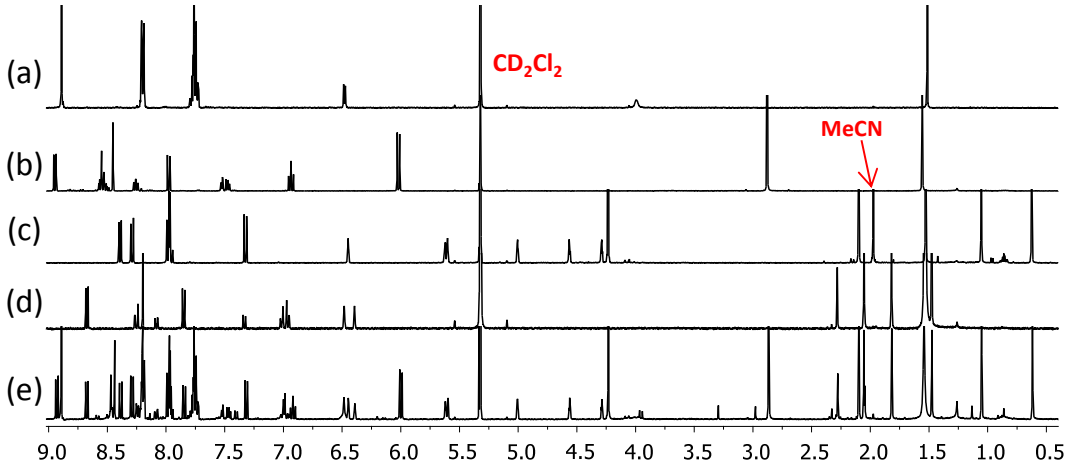


Figure S13: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of (a) **C4** = [(**6**)(**8**)], (b) **C3** = [Zn(**3**)(**4**)](OTf)$_2$, (c) **C2** = [Cu(**2**)$_2$]PF_6, (d) **C1** = [Cu(**1**)(**9**)]PF_6 and (e) an equimolar mixture of **C1**–**C4** after 1 h reflux in DCM.

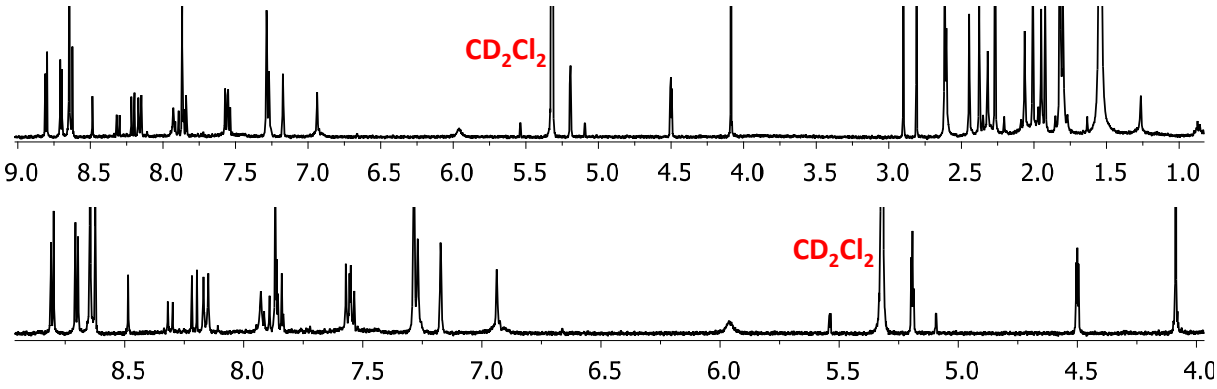


Figure S14: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of metalloligand **A1** = [(**11**)(**13**)]. An expanded part of the spectrum is shown at the bottom.

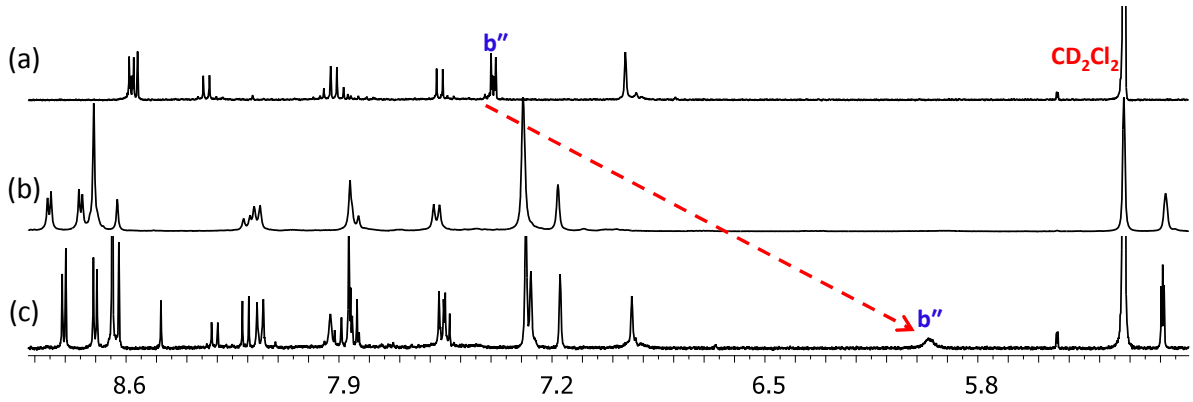


Figure S15: Partial ^{1}H NMR spectra for comparison (400 MHz, CD_2Cl_2, 298 K) of (a) ligand **11**, (b) ligand **13** and (c) the metalloligand **A1** = [(**11**)(**13**)].

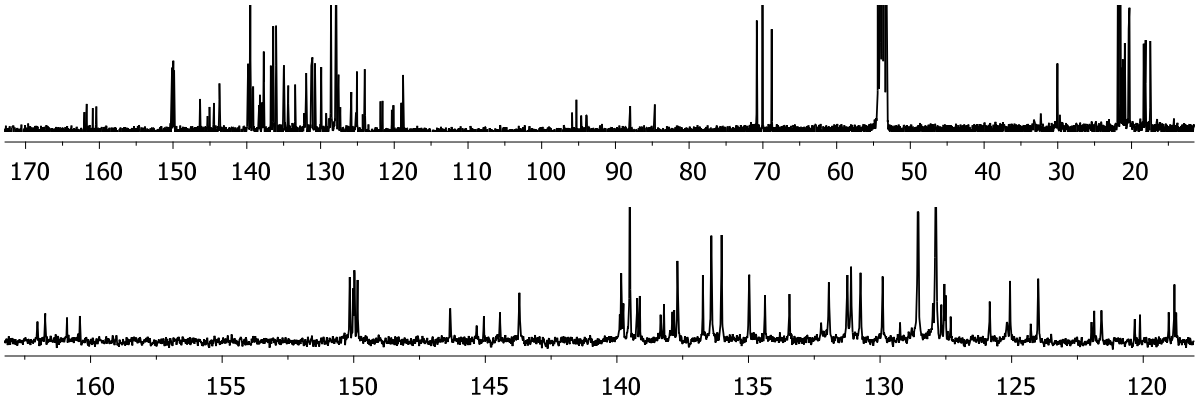


Figure S16: ^{13}C NMR spectrum (100 MHz, CD_2Cl_2, 298 K) of **A1** = [(**11**)(**13**)]. An expanded part of the aromatic region is shown at the bottom.

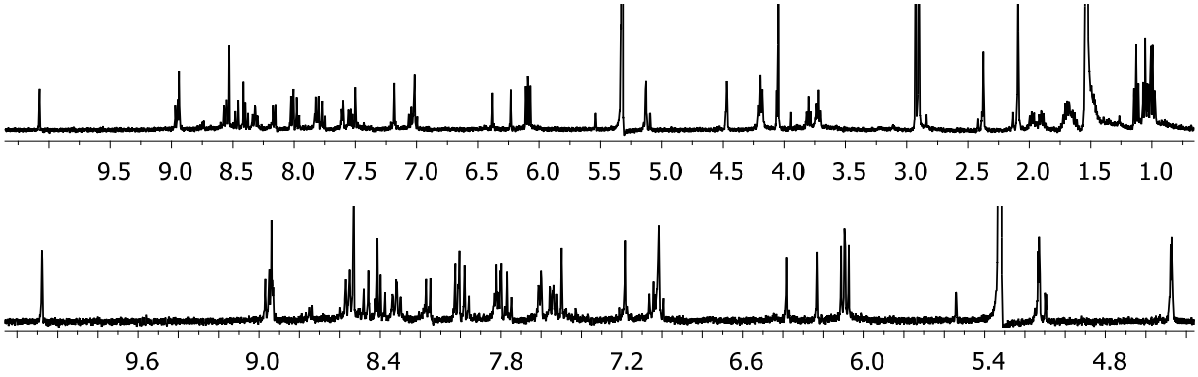


Figure S17: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of metalloligand **A2** = [Zn(**10**)(**12**)](OTf)$_2$. An expanded part of the spectrum is shown at the bottom.

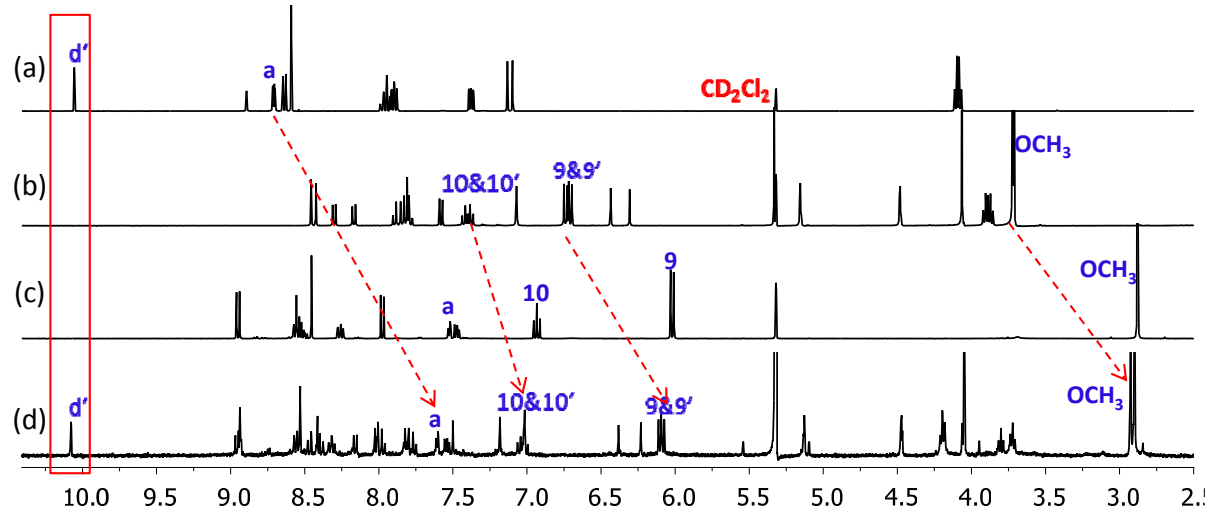


Figure S18: Partial ^{1}H NMR spectrum for comparison (400 MHz, CD_2Cl_2, 298 K) of (a) ligand **10**, (b) ligand **12**, (c) the archetypical complex **C3** = [Zn(**3**)(**4**)](OTf)$_2$ and (d) the metalloligand **A2** = [Zn(**10**)(**12**)](OTf)$_2$.

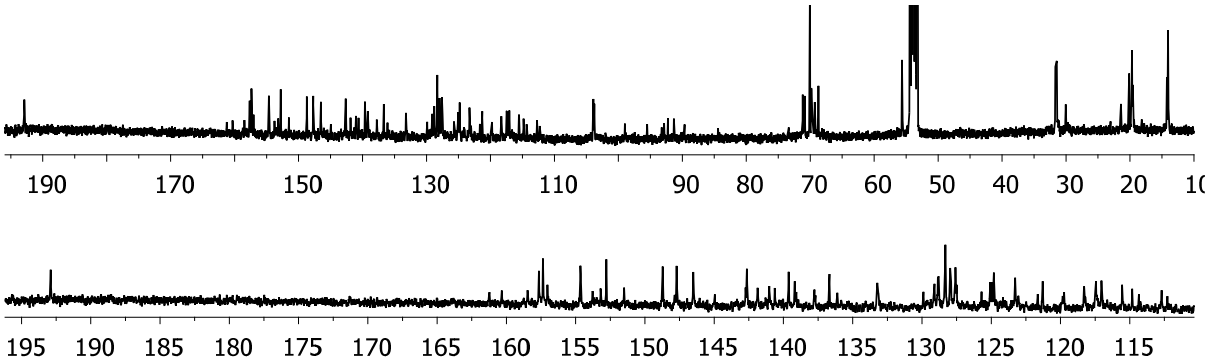


Figure S19: ^{13}C NMR spectrum (100 MHz, CD_2Cl_2, 298 K) of the metalloligand **A2** = [Zn(**10**)(**12**)]$(OTf)_2$.An expanded part of the spectrum is shown at the bottom.

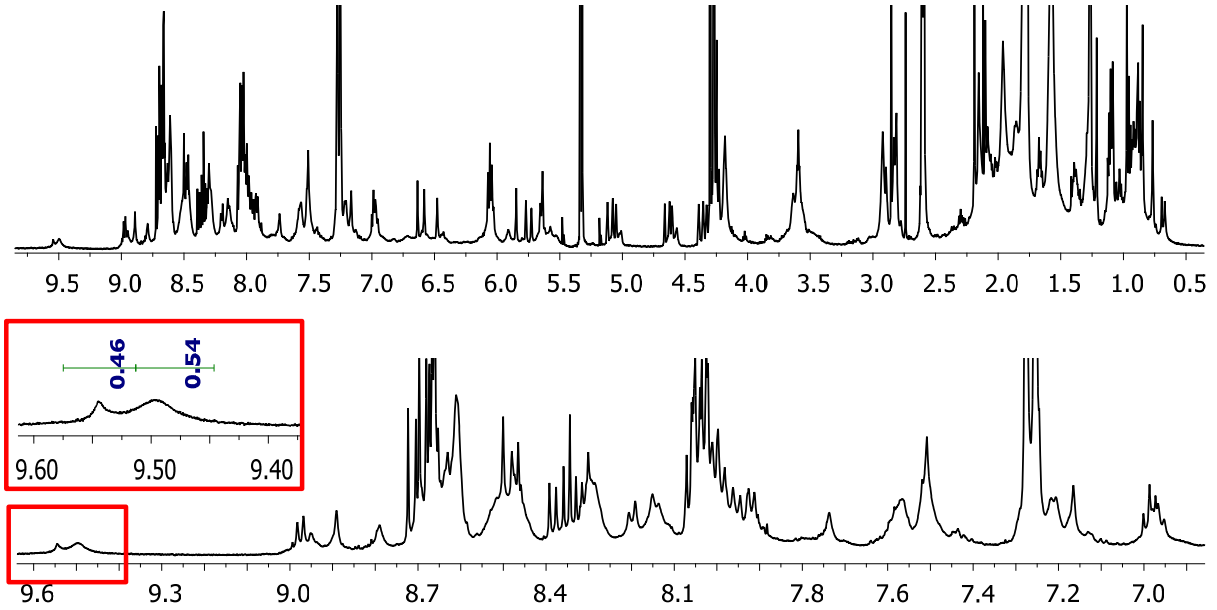


Figure S20: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of quadrilateral **QL2** = [$ZnCu_2$(**10**)(**11**)(**12**)(**13**)]$(OTf)_2(PF_6)_2$. An expanded part of the spectrum is shown at the bottom.

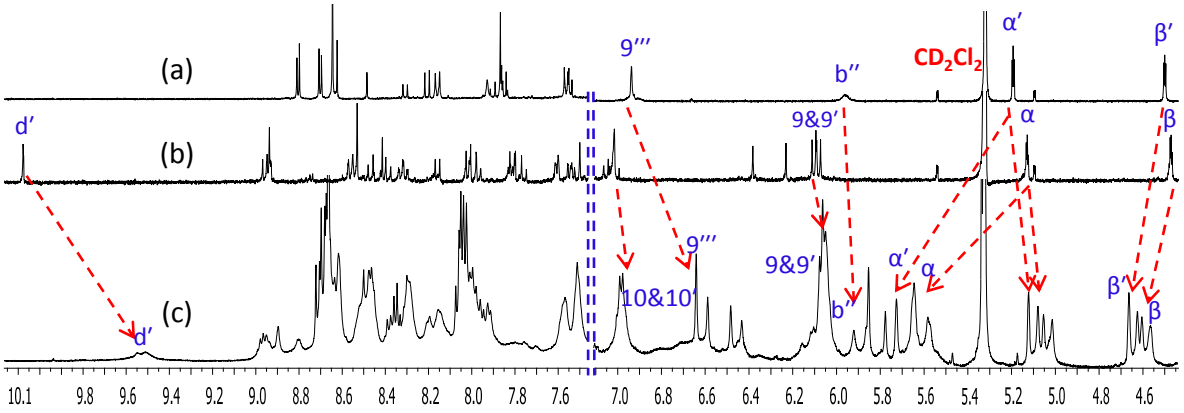


Figure S21: Partial ^{1}H NMR spectra for comparison (600 MHz, CD_2Cl_2, 298 K) of (a) the metalloligand **A1** = [(**11**)(**13**)], (b) the metalloligand **A2** = [Zn(**10**)(**12**)](OTf)$_2$, and (c) the quadrilateral **QL2** = [$ZnCu_2$(**10**)(**11**)(**12**)(**13**)](OTf)$_2$(PF_6)$_2$.

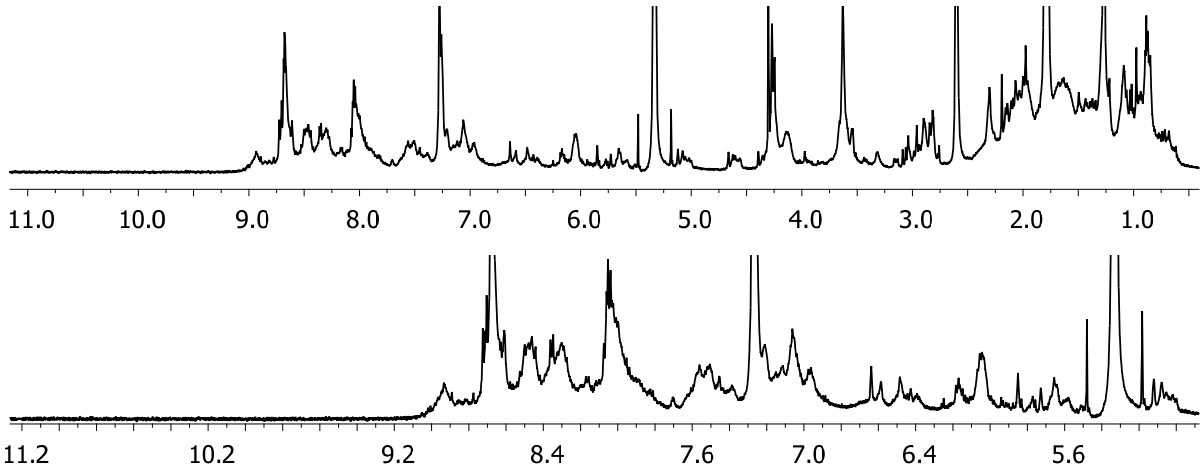


Figure S22: (a) ^{1}H NMR spectrum (600 MHz, CD_2Cl_2, 298 K) of pentagon **QL1** = [$ZnCu_2$(**11**)(**12**)(**13**)(**14**)](OTf)$_2$(PF_6)$_2$ prepared via the post–self–assembly modification approach, i.e. **QL2** + **7** → **QL1** (**QL2**:**7** = 1:1). An expanded part of the spectrum is shown at the bottom.

DOSY NMR

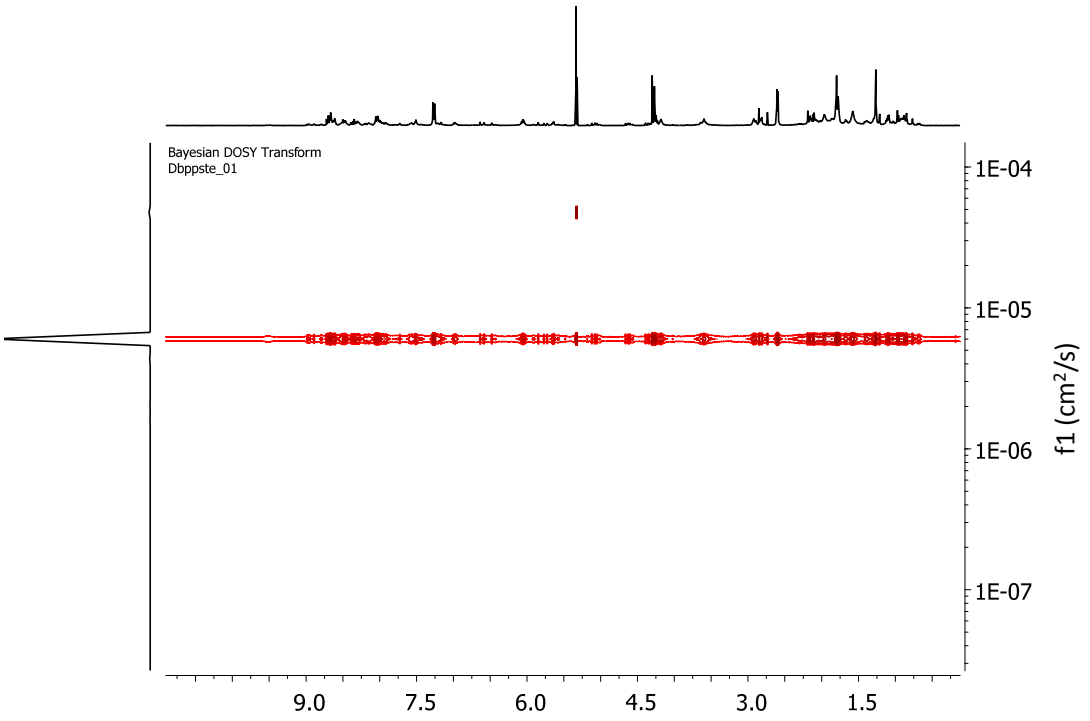


Figure S23: DOSY NMR spectrum (600 MHz, CD_2Cl_2, 298 K) of quadrilateral **QL2** = [$ZnCu_2$(**10**)(**11**)(**12**)(**13**)]$(OTf)_2(PF_6)_2$.

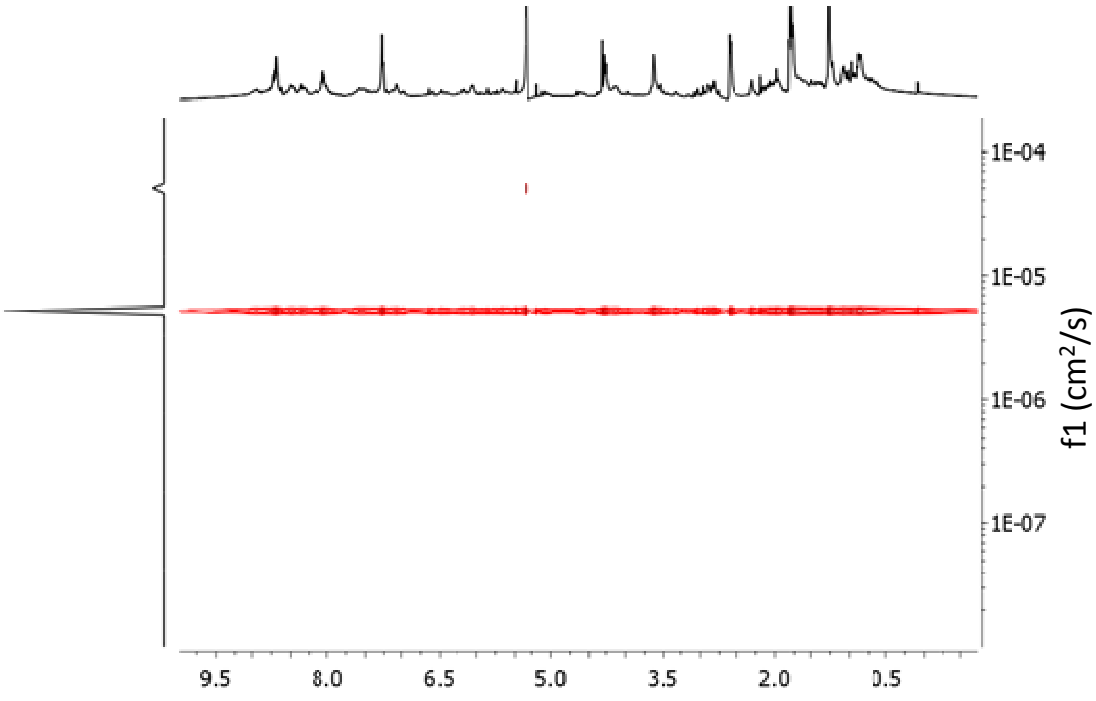


Figure S24: DOSY NMR spectrum (600 MHz, CD_2Cl_2, 298 K) of quadrilateral **QL1** = [$ZnCu_2$(**11**)(**12**)(**13**)(**14**)]$(OTf)_2(PF_6)_2$. Ligand **14** = (**10**)(**7**)–H_2O.

ESI-MS spectra

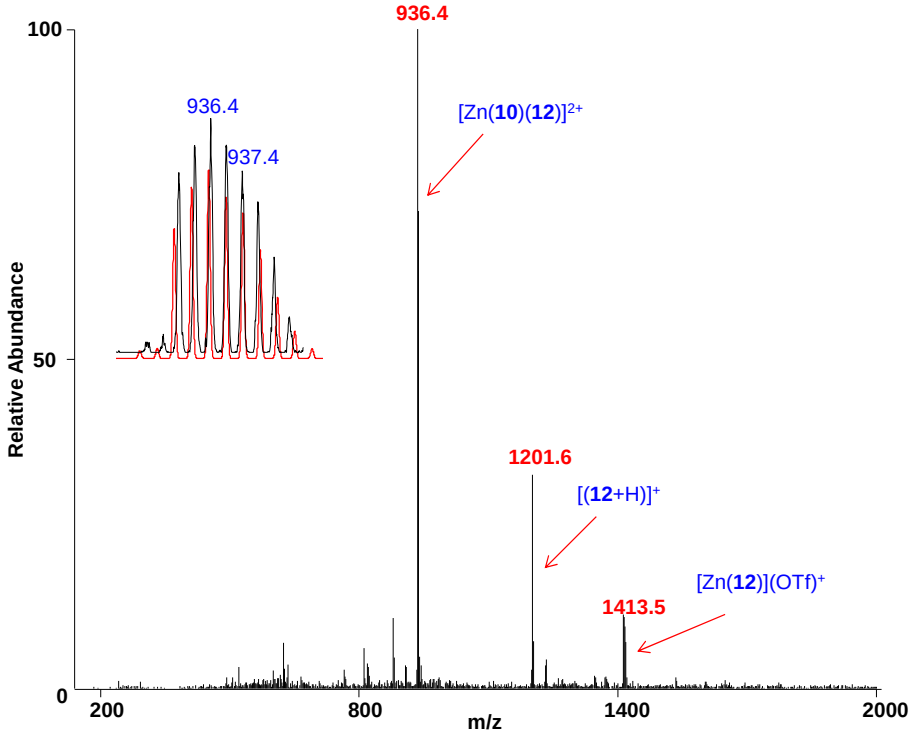


Figure S25: ESI-MS spectrum of **A2** = [Zn(**10**)(**12**)](OTf)$_2$ (in DCM) as well as experimental (black) and calculated isotopic distributions (red) for the species [Zn(1**0**)(**12**)]$^{2+}$.

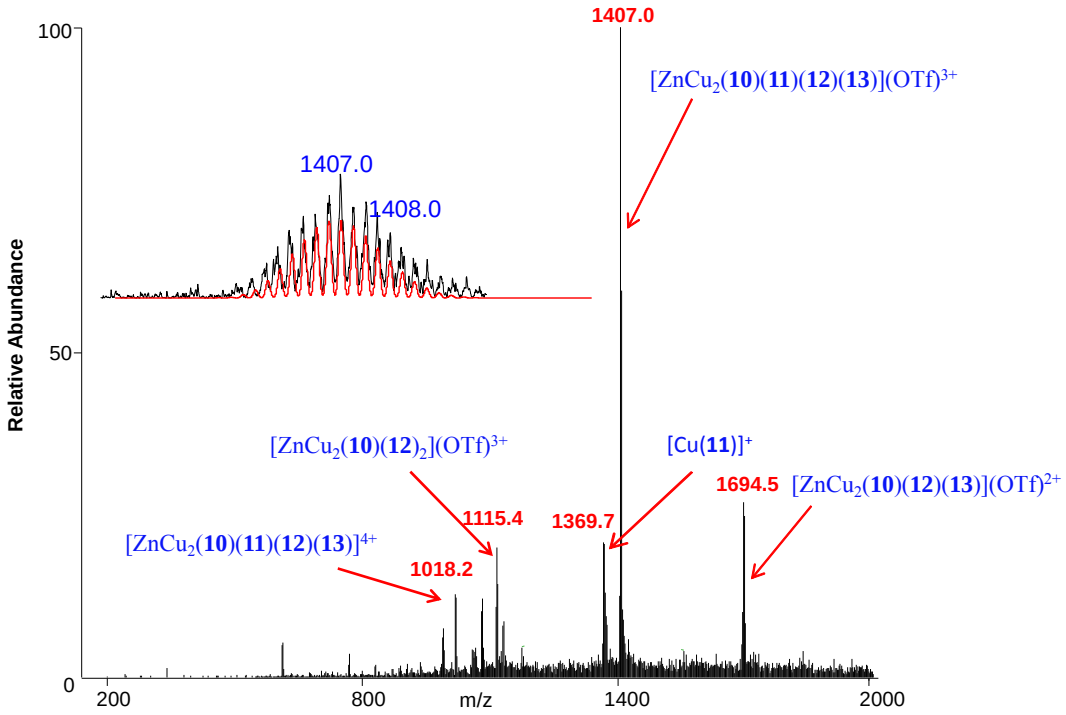


Figure S26: ESI-MS spectrum of **QL2** = [ZnCu$_2$(**11**)(**12**)(**13**)(**10**)](OTf)$_2$(PF$_6$)$_2$ (in DCM) along with experimental (black) and calculated isotopic distributions (red) for the species [ZnCu$_2$(**11**)(**12**)(**13**)(**10**)](OTf)$^{3+}$.

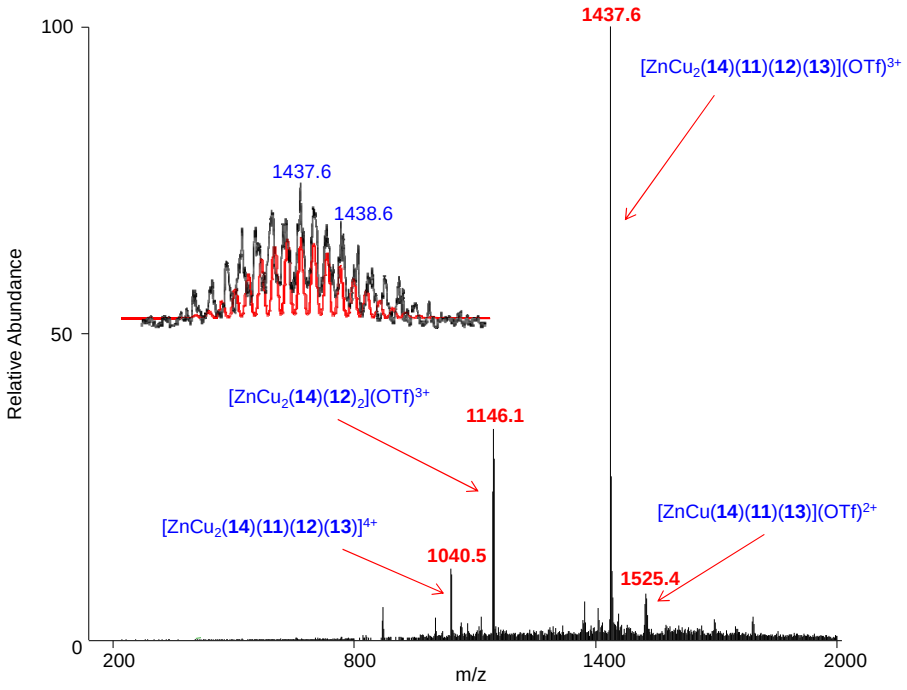


Figure S27: ESI-MS spectrum of **QL1** = $[ZnCu_2(\mathbf{11})(\mathbf{12})(\mathbf{13})(\mathbf{14})](OTf)_2(PF_6)_2$ (in DCM) along with experimental (black) and calculated isotopic distributions (red) for the species $[ZnCu_2(\mathbf{11})(\mathbf{12})(\mathbf{13})(\mathbf{14})](OTf)^{3+}$. (Ligand **14** = [(**10**)(**7**)-H_2O]).

UV-Vis Spectra

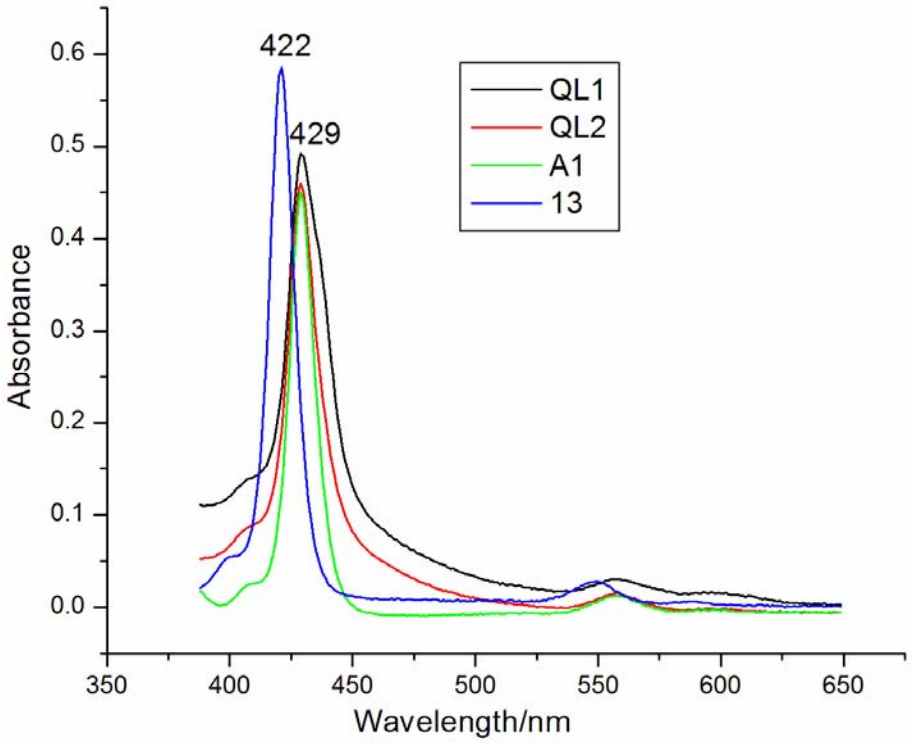


Figure S28: Comparison of UV-Vis spectra of ligand **13**, **A1**, **QL2** and **QL1** at 298 K.

Cyclic voltammetry (CV) experiments

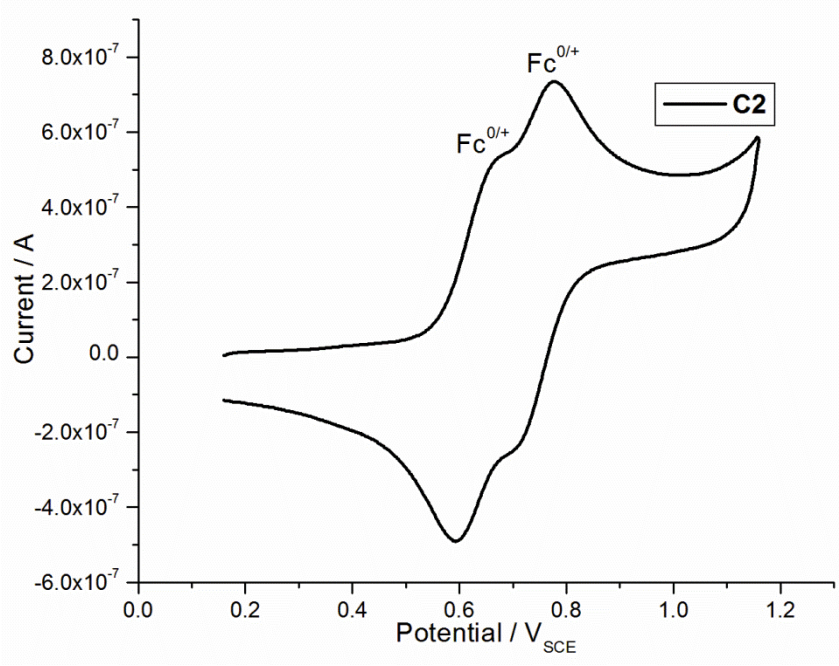


Figure S29: CV of complex **C2** in dry DCM with 0.1 M *n*-Bu_4NPF_6 as electrolyte against a Ag wire as pseudo-reference electrode and decamethylferrocene (dmfc) as internal reference.

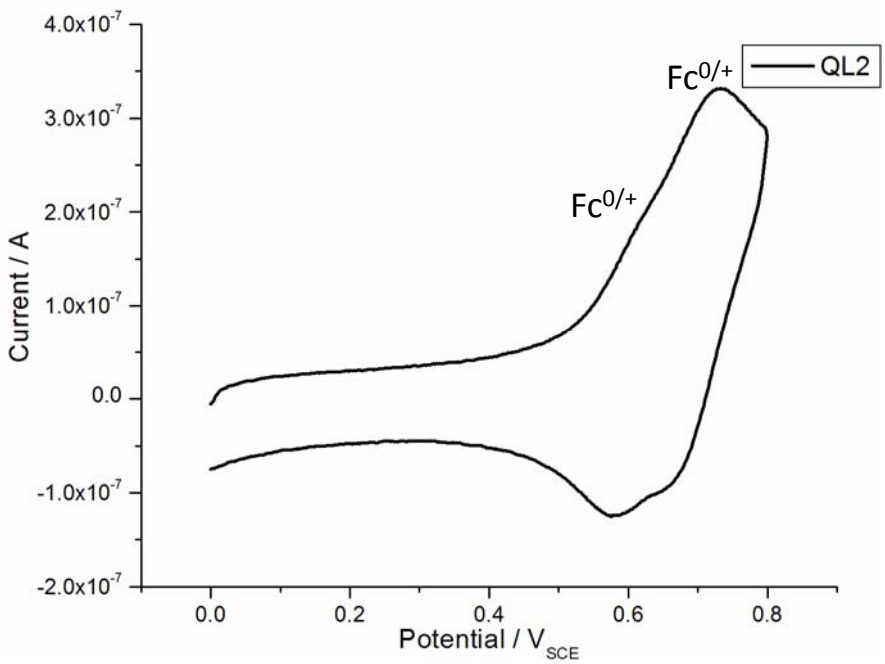


Figure S30: CV of complex **QL2** in dry DCM with 0.1 M *n*-Bu_4NPF_6 as electrolyte against a Ag wire as pseudo-reference electrode and decamethylferrocene (dmfc) as internal reference.

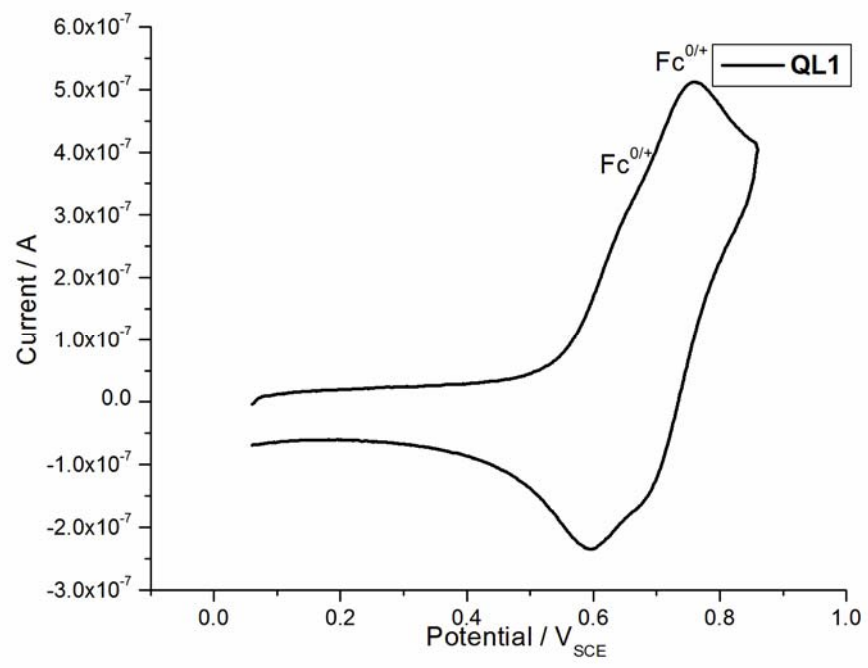


Figure S31: CV of complex **QL1** in dry DCM with 0.1 M *n*-Bu_4NPF_6 as electrolyte against a Ag wire as pseudo-reference electrode and decamethylferrocene (dmfc) as internal reference

Energy minimised structures from MM^+ force field computations

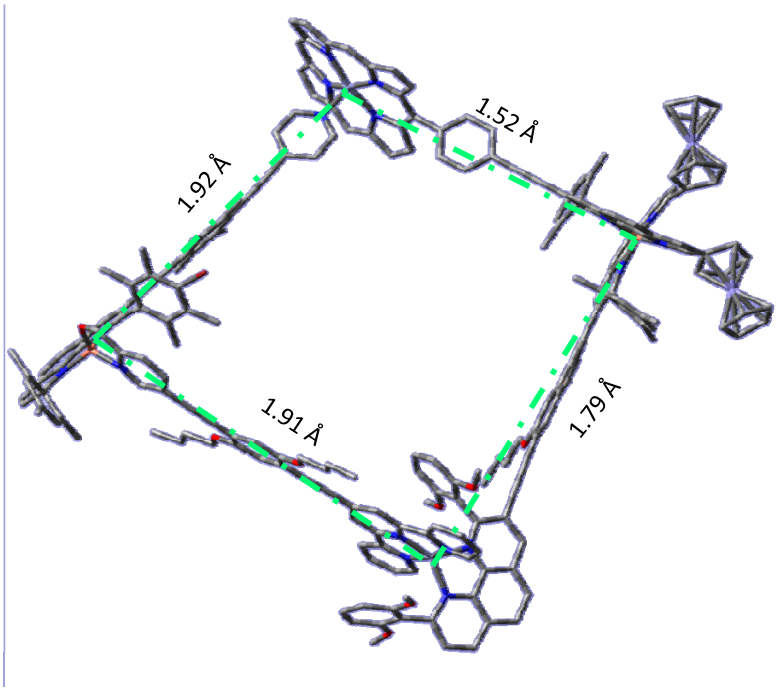


Figure S32: Energy minimised structure of the supramolecular pentagon **QL2**. Counter anions and hydrogens are omitted for clarity.

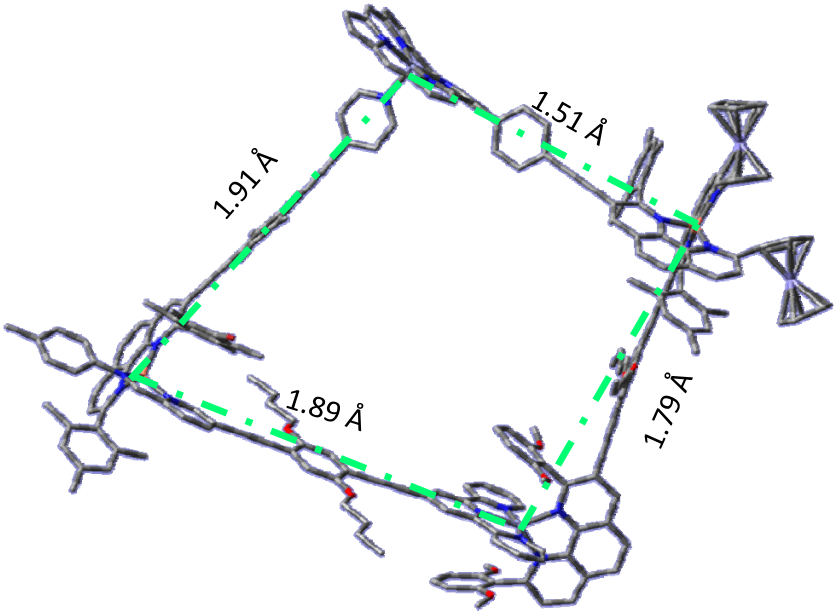


Figure S33: Energy minimised structure of the supramolecular pentagon **QL1**. Counter anions and Hydrogens are omitted for clarity.

References

(1) M. Schmittel, M. L. Saha and J. Fan, *Org. Lett.*, 2011, **13**, 3916.
(2) M. L. Saha, N. Mittal, J. W. Bats, and M. Schmitel, *Chem. Commun*., 2014, **50**, 12189.
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(5) M. Schmittel, C. Michel, A. Wiegrefe and V. Kalsani, *Synthesis*, 2001, 1561.
(6) V. Grosshenny, F. M. Romero, R. Ziessel, *J. Org. Chem*. 1997, **62**, 1491.
(7) W. Wagner, T. E. Johnson, and J. S. Lindsey, *J. Am. Chem. Soc.* 1996, **118**, 11166.
(8) Based on prior experience we realised that the formation of the metallosupramolecular structures would require heat because any error-correction (constitutional dynamics) is slow under ambient conditions.