Electronic Supporting Information (ESI)

for

Merging strong and weak coordination motifs in the integrative self-sorting of a 5-component trapezoid and scalene triangle

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Table of Contents

Synthesis

General. All commercial reagents were used without further purification. Solvents were dried with 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 measured at 298 K on a Bruker Avance 400 MHz spectrometer equipped with a 5 mm dual probe. Residual solvent signals are used as internal reference. 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, ddd = doublet of doublet of doublets, br = broad and m = multiplet. The numbering of carbon atoms in the molecular formulae is only used for assignment of NMR signals and thus is not necessarily in accordance with IUPAC nomenclature rules. DOSY NMR data were recorded on a Varian VNMR-S 600 MHz spectrometer equipped with a 3 mm triple resonance inverse probe. All DOSY measurements were carried out without temperature regulation (room temperature was 298 K) using the 'Dbppste' pulse sequence from the Varian library. 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] 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 measurements were done using the EA 3000 CHNS. X-ray single-crystal diffraction data for **C3** were collected on Siemens SMART 1K CCD area-detector diffractometer. The structure was 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 atom model. Non-hydrogen atoms were refined with anisotropic thermal parameters. An empirical absorption correction resulted in a correction range of 0.531 to 0.602. Further details are provided in the section of X-ray structure analysis. Energy minimised structures were obtained using the MM^{+} forced field as implemented in Hyperchem® 8.0. Complex **C1**, compounds **11** as well as **12** (precursors for **6**), **17** (precursors for **9**),[3] **18** (precursors for **10**) and **8**[4] were synthesised as described earlier.

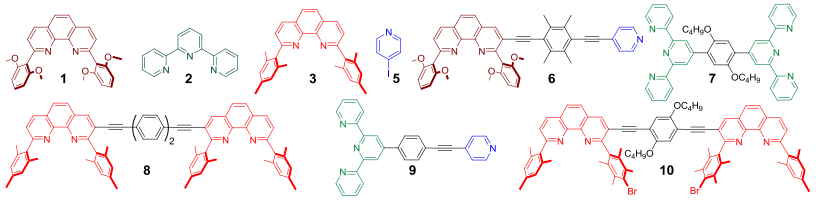
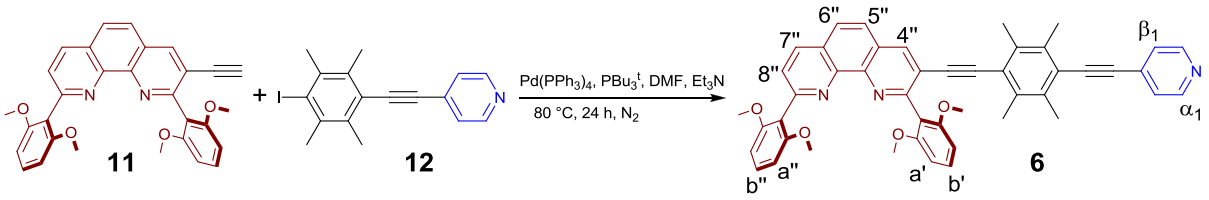


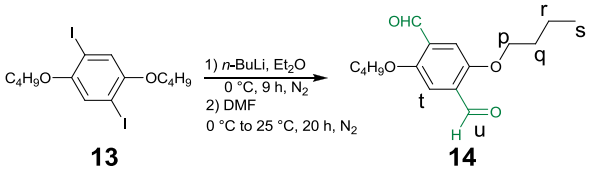
Chart 1: Ligands used in the present study.

Synthesis of 2,9-bis(2,6-dimethoxyphenyl)-3-((2,3,5,6-tetramethyl-4-(pyridin-4-ylethynyl)phenyl)ethynyl)-1,10-phenanthroline (6).



An oven-dried 100 mL three-neck round-bottom flask was charged with 2,9-bis(2,6-dimethoxyphenyl)-3-ethynyl-1,10-phenanthroline (**11**, 50.0 mg, 104 μmol), 4-((4-iodo-2,3,5,6-tetramethylphenyl)ethynyl)pyridine (**12**, 45.0 mg, 125 μmol) and $Pd(PPh_3)_4$ (35.0 mg, 30.3 μmol) under nitrogen atmosphere. After addition of dry DMF (20 mL) and triethylamine (20 mL), the solution was degassed thrice by freeze-pump-thaw cycles. Finally, tri-*tert*-butylphosphine (100 μL) was added to this mixture, which was refluxed at 80 °C for 24 h under nitrogen atmosphere. The mixture was then cooled down to room temperature and the solvents were removed under reduced pressure. The residue was dissolved in DCM (200 mL) and washed with water (150 mL). After drying over Na_2SO_4, the organic solvent was evaporated to afford a brown residue. The crude product was purified using column chromatography (SiO_2, DCM:EtOAC= 4:1 [R_f =0.45 [EtOAC:CH_2Cl_2, 1:1]). Yield 77%; mp >275 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.60 (d, ^3J = 6.0 Hz, 2 H, α_1-H), 8.46 (s, 1 H, 4''-H), 8.24 (d, ^3J = 8.4 Hz, 1 H, 7''-H), 7.83 (d, ^3J = 8.8 Hz, 1 H, [5''/6'']-H), 7.80 (d, ^3J = 8.8 Hz, 1 H, [5''/6'']-H), 7.65 (d, ^3J = 8.4 Hz, 1 H, 8''-H), 7.38 (d, ^3J = 6.0 Hz, 2 H, β_1-H), 7.30 (t, ^3J = 8.4 Hz, 1 H, [b''/b']-H), 7.30 (t, ^3J = 8.4 Hz, 1 H, [b''/b']-H), 6.65 (d, ^3J = 8.4 Hz, 2 H, [a''/a']-H), 6.63 (d, ^3J = 8.4 Hz, 2 H, [a''/a']-H), 3.73 (s, 6 H, OMe), 3.68 (s, 6 H, OMe), 2.42 (s, 6 H, Me), 2.17 (s, 6 H, Me); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 158.5, 156.7, 156.0, 150.0, 146.3, 145.2, 139.1, 136.5, 136.5, 136.2, 132.2, 132.1, 130.3, 130.2, 128.3, 127.5, 127.4, 126.1, 126.1, 125.5, 124.3, 122.6, 121.4, 119.6, 118.9, 104.4, 104.2, 96.5, 95.7, 93.4, 93.2, 56.3, 56.2, 18.5, 18.1; IR (KBr) ν 3427, 2933, 2833, 2204, 1591, 1468, 1433, 1249, 1182, 1109, 1027, 908, 847, 818, 783, 735, 650, 563; ESI-MS *m*/*z* (%) 710.9 (100) $[M + H]^+$; Anal. calcd for $C_{47}H_{39}N_3O_4$•2/3CH_2Cl_2: C, 74.70; H, 5.30; N, 5.48. Found: C, 74.41; H, 5.20; N, 5.58.

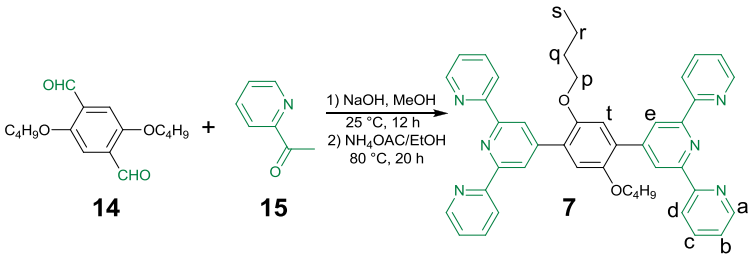
Synthesis of 2,5-dibutoxyterephthalaldehyde (14).



13 **14**

To a solution of 1,4-dibutoxy-2,5-diiodobenzene (**13**, 4.00 g, 8.43 mmol) in dry diethyl ether (100 mL), 2.5 M solution of *n*-BuLi in *n*-hexane (8.40 mL, 21.0 mmol) was added slowly at 0 °C under N_2 atmosphere over a period of 20 min. After 9 h, dry DMF (1.60 mL, 20.7 mmol) was added. The resulting solution was then stirred for further 20 h under nitrogen atmosphere while warming up from 0 °C to room temperature . The reaction was neutralised with saturated NH_4Cl and extracted with DCM (150 mL). The organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The remaining solution was kept at –32 ºC for 1 day for crystallisation. Yellow crystals were filtered off and washed with cold *n*-hexane and dried under vacuum to afford **14** as a pure product. Yield 50%; mp = 67 °C; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 10.5 (s, 2 H, u-H), 7.42 (s, 2 H, t-H), 4.10 (t, ^3J = 6.8 Hz, 4 H, p-H), 1.85-1.80 (m, 4 H, q-H), 1.56-1.47 (m, 4 H, r-H), 0.98 (t, ^3J = 7.6 Hz, 6 H, s-H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 189.5, 155.6, 129.7, 111.8, 69.4, 31.5, 19.6, 13.9; IR (KBr) ν 3351, 3052, 2951, 2873, 2759, 1982, 1681, 1486, 1427, 1371, 1282, 1213, 1121, 1065, 1023, 976, 887, 837, 741, 688, 507, 456; Anal calcd for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97; found: C, 69.07; H, 8.05.

Synthesis of 2''',5'''-bis-[4'-[(2,2':6',2'')terpyridyl]]-1''',4'''-dibutoxybenzene (7).

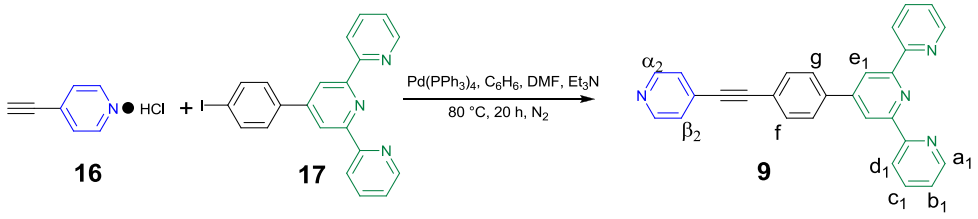


14 **15** **7**

Solid NaOH (1.92 g, 48.0 mmol) was added to a methanolic solution (75 mL) of 2,5-di-butoxyterephthalaldehyde (**14**, 672 mg, 2.41 mmol) and 1-(pyridin-2-yl)ethanone (**15**, 1.32 g, 10.9 mmol). The mixture was stirred for 12 h at room temperature. After removing the sol-vent, 100 mL of water was added and the product extracted with DCM (150 mL). The organic layer was subsequently dried over Na_2SO_4 and evapourated to dryness. The solid residue was treated with ammonium acetate (5.50 g, 71.3 mmol) in EtOH (100 mL) at 80 °C for 20 h. The solution was then cooled, reduced in volume, and water (100 ml) was added.

The mixture was extracted with DCM, and the organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The desired product **7** was finally purified by crystallisation; diethyl ether was diffused into a DCM solution of the crude mixture to afford the pure product as pale brown crystals. Yield: ≤10%; mp = 198 °C; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.79 (s, 4 H, e-H), 8.72 (ddd, ^3J = 4.8 Hz, ^4J = 2.0 Hz, ^5J = 1.0 Hz, 4 H, a-H), 8.70 (ddd, ^3J = 7.6 Hz, ^4J = 1.0 Hz, ^5J = 1.0 Hz, 4 H, d-H), 7.91 (td, ^3J = 7.6 Hz, ^4J = 2.0 Hz, 4 H, c-H), 7.37 (ddd, ^3J = 7.6 Hz, ^3J = 4.8 Hz, ^4J = 1.0 Hz, 4 H, b-H), 7.28 (s, 2 H, t-H), 4.09 (t, ^3J = 6.2 Hz, 4 H, p-H), 1.76-1.69 (m, 4 H, q-H), 1.52-1.42 (m, 4 H, r-H), 0.84 (t, ^3J = 7.2 Hz, 6 H, s-H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 156.7, 155.6, 151.1, 149.5, 148.2, 137.1, 130.0, 124.1, 121.9, 121.3, 115.9, 69.9, 31.8, 19.7, 13.9; IR (KBr) ν 3432, 3041, 3014, 2955, 2868, 1582, 1504, 1466, 1386, 1334, 1242, 1208, 1119, 1066, 1024, 962, 886, 792, 736, 677, 617, 514; ESI-MS: *m*/*z* (%) 685.4 (100) $[M + H]^+$; Anal calcd for $C_{44}H_{40}N_6O_2$•4/5CH_2Cl_2: C, 71.48; H, 5.57; N, 11.16; found: C, 71.15; H, 5.53; N, 10.96.

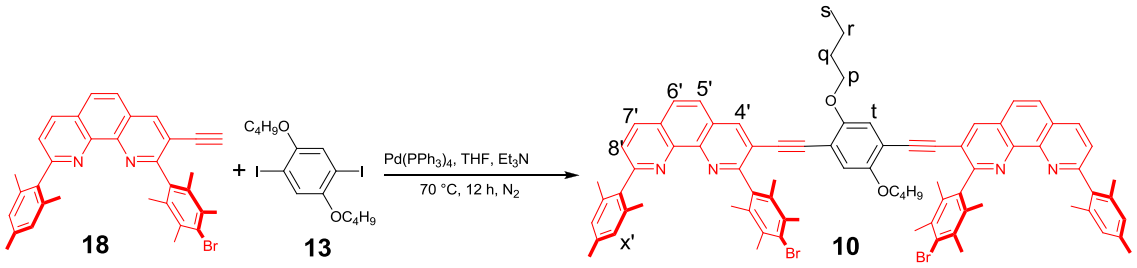
Synthesis of 4'-(4-pyridin-4-ylethynyl-phenyl)-[2,2';6',2'']terpyridine (9).



Under N_2 atmosphere 4-ethynylpyridine hydrochloride (**16**, 38.3 mg, 274 µmol), 4'-(4-iodophenyl)-[2,2';6',2'']terpyridine (**17**, 100 mg, 229 µmol) and $Pd(PPh_3)_4$ (25.0 mg, 21.6 µmol) were placed in an oven-dry 100-mL three-neck round-bottom flask. After addition of dry benzene (10 mL), dry Et_3N (10 mL) and dry DMF (5 mL), the reaction mixture was stirred at 80 °C for 20 h under N_2 atmosphere. The reaction mixture was then cooled down to room temperature and the solvents were removed under reduced pressure. The residue was dissolved in DCM (100 mL) and washed first with aqueous KOH (200 mL), then with water (200 mL). After drying over Na_2SO_4, the organic solvent was evaporated to afford a brown residue. The crude product was purified using column chromatography (SiO_2, DCM:EtOAC = 1:1 to DCM:MeOH= 99:1 [R_f =0.35 [EtOAC:CH_2Cl_2, 1:1]). Yield: 45%; mp = 156 °C; ^{1}H NMR (400 MHz, $CDCl_2$): δ = 8.77 (s, 2 H, e_1-H), 8.72 (d, ^3J = 4.4 Hz, 2 H, a_1-H), 8.68 (d, ^3J = 8.0 Hz, 2 H, d_1-H), 8.61 (d, ^3J = 6.0 Hz, 2 H, α_2-H), 7.93 (d, ^3J = 8.4 Hz, 2 H, [f/g]-H), 7.90 (td, ^3J = 8.0 Hz, ^4J = 2.0 Hz, 2 H, c_1-H), 7.73 (d, ^3J = 8.4 Hz, 2 H, [f/g]-H), 7.43 (d, ^3J = 6.0 Hz, 2 H, β_2-H), 7.40-7.36 (m, 2 H, b_1-H), ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.1, 156.0,

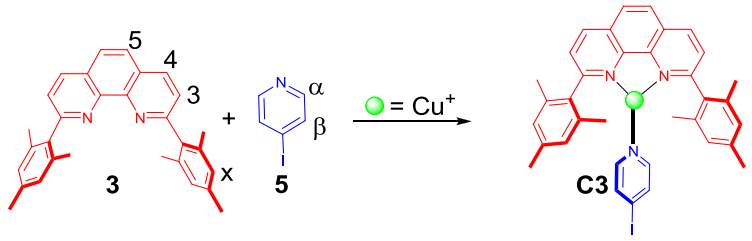
149.8, 149.1, 139.2, 136.9, 132.4, 131.3, 127.4, 126.0, 125.5, 124.0, 122.7, 121.4, 118.7, 93.6, 87.9; IR (KBr): ν =3422, 3035, 2360, 2218, 1664, 1587, 1468, 1388, 1263, 1217, 1079, 1037, 990, 893, 824, 789, 669, 620, 521; ESI-MS m/z (%): 411.4 (100) $[M + H]^+$; Anal calcd for $C_{28}H_{18}N_4 \bullet H_2O$: C, 78.49; H, 4.70; N, 13.08; found: C, 78.62; H, 4.35; N, 12.79.

Synthesis of 3,3'-(2,5-dibutoxy-1,4-phenylene)bis(ethyn-2,1-diyl)bis(2-(4-bromo-2,3,5,6-tetramethylphenyl)-9-mesityl-1,10-phenanthroline) (10).



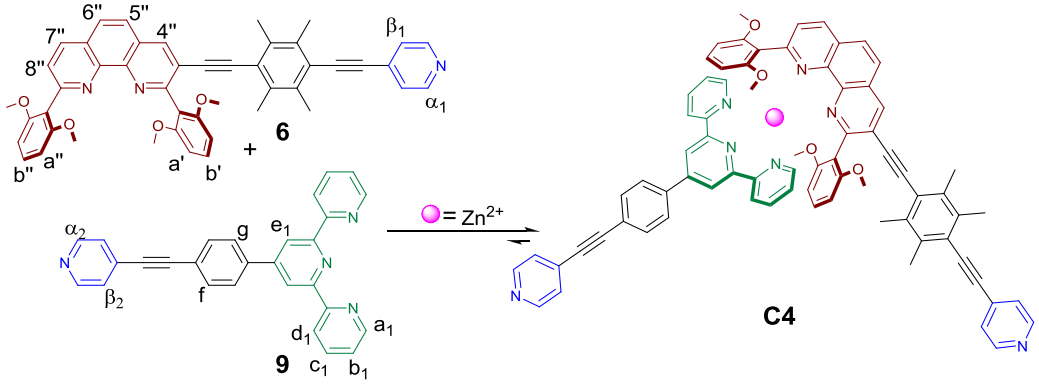
An oven-dry 100-mL three-neck round-bottom flask equipped with reflux condenser was charged with 2-(4-bromo-2,3,5,6-tetramethylphenyl)-3-ethynyl-9-mesityl-[1,10]-phenanthroline (**18**, 100 mg, 187 μmol), 1,4-dibutoxy-2,5-diiodobenzene (**13**, 44.4 mg, 93.7 μmol) and $Pd(PPh_3)_4$ (20.0 mg, 17.3 μmol) under N_2 atmosphere. After addition of dry Et_3N (10 mL) and dry THF (40 mL), the mixture was refluxed for 12 h under N_2 atmosphere. Following removal of solvents, the resulting solid was dissolved in DCM and washed with water. The organic layer was dried over Na_2SO_4, then the solvent was removed. The residue was purified by column chromatography using 5% ethyl acetate in *n*-hexane as eluent affording **10** as yellow solid [R_f =0.1 [*n*-pentane/CH_2Cl_2, 1:1]. Yield 55%; mp = 240 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.42 (s, 2 H, 4'-H), 8.29 (d, ^3J = 8.4 Hz, 2 H, 7'-H), 7.89 (d, ^3J = 8.8 Hz, 2 H, [5'/6']-H), 7.84 (d, ^3J = 8.8 Hz, 2 H, [5'/6']-H), 7.57 (d, ^3J = 8.4 Hz, 2 H, 8'-H), 6.92 (s, 4 H, x'-H), 6.14 (s, 2 H, t-H), 3.83 (t, ^3J = 6.2 Hz, 4 H, p-H), 2.43 (s, 12 H, Me), 2.30 (s, 6 H, Me), 2.10 (s, 12 H, Me), 2.00 (s, 12 H, Me), 1.87-1.80 (m, 4 H, q-H), 1.66-1.57 (m, 4 H, r-H), 1.07 (t, ^3J = 7.4 Hz, 6 H, s-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.4, 160.6, 153.0, 145.8, 144.6, 139.2, 138.2, 137.8, 137.6, 136.0, 136.0, 133.8, 133.4, 128.9, 128.5, 127.6, 127.1, 126.9, 125.7, 125.2, 120.3, 116.7, 113.7, 92.3, 92.1, 69.1, 31.3, 29.7, 21.1, 21.0, 20.5, 19.4, 18.5; IR (KBr) ν 3429, 2925, 2867, 2359, 2207, 1723, 1611, 1585, 1502, 1457, 1378, 1274, 1210, 1063, 986, 906, 849, 719, 638; ESI-MS: *m/z* (%) 1285.8 (100) $[M + H]^+$; Anal calcd for $C_{80}H_{76}Br_2N_4O_2 \bullet 1.6CH_2Cl_2$: C, 68.96; H, 5.62; N, 3.94; found: C, 68. 65; H, 5.27, N, 4.34.

Synthesis of complex C3 = [Cu(3)(5)](PF$_6$).



2,9-Dimesityl-1,10-phenanthroline (**3**, 6.32 mg, 15.2 μmol), 4-iodopyridine (**5**, 3.11 mg, 15.2 μmol), and [Cu(MeCN)$_4$]PF$_6$ (5.67 mg, 15.2 μmol) were added to 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 the slow diffusion of Et_2O into the above mixture. Yield quantitative; mp unknown (decomposition >176 °C); ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 8.73 (d, ^3J = 8.4 Hz, 2 H, 4-H), 8.19 (s, 2 H, 5-H), 7.93 (d, ^3J = 8.4 Hz, 2 H, 3-H), 7.44 (br, 2 H, β-H), 6.97 (s, 4 H, x-H), 6.42 (br, 2 H, α-H), 2.36 (s, 6 H, Me), 2.03 (s, 12 H, Me); ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 160.8, 150.0, 144.0, 139.9, 139.9, 137.3, 136.2 (2C), 129.2 (2C), 128.3, 127.6, 127.3, 21.2, 20.5; IR (KBr) ν 3435, 2914, 1614, 1579, 1479, 1371, 1298, 1219, 1147, 1112, 1047, 840, 652, 624, 555; ESI-MS: m/z (%) 684.3 (100) [M−PF$_6$]$^+$; Anal calcd for $C_{35}H_{32}CuF_6IN_3P$•1/5CH_2Cl_2: C, 49.91; H, 3.86; N, 4.96; found: C, 50. 01; H, 3.53; N, 5.33.

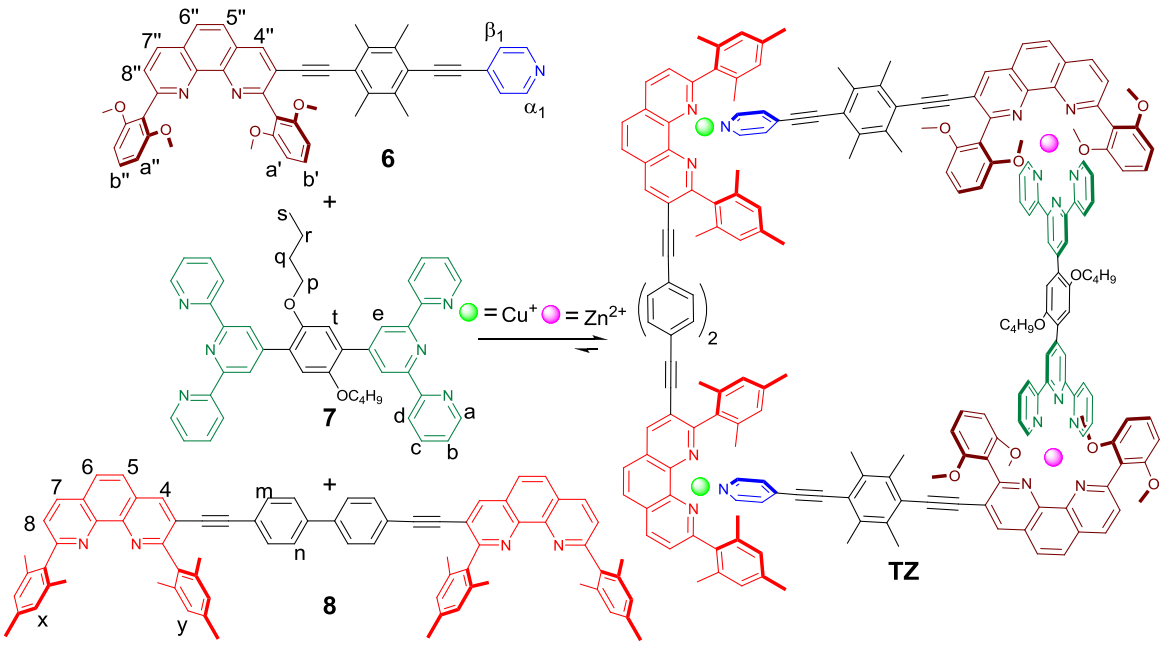
Synthesis of complex C4 = [Zn(6)(9)](OTf)$_2$.



In an oven-dried 25-mL single-neck round-bottom flask, a mixture of phenanthroline-pyridine hybrid **6** (1.20 mg, 1.69 μmol), terpyridine-pyridine hybrid **9** (0.70 mg, 1.69 μmol) and Zn(OTf)$_2$ (0.62 mg, 1.69 μmol) were refluxed in 15 mL of 1,2-dichloroethane/CH_3CN (1:4) 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) δ = 9.03 (s, 1 H, 4''-H), 8.95 (d, ^3J = 8.4 Hz, 1 H, 7''-H), 8.86 (ddd, ^3J = 8.4 Hz, ^4J = 0.8 Hz, ^5J = 0.8 Hz, 2 H, d_1-H), 8.83 (s, 2 H, e_1-H), 8.64 (d, ^3J = 6.0 Hz, 2 H, [α_1/ α_2]-H), 8.57 (d, ^3J = 6.0 Hz, 2 H, [α_1/ α_2]-H), 8.47 (d, ^3J = 9.2 Hz, 1 H, [5''/6'']-H), 8.41 (d, ^3J = 9.2 Hz, 1 H, [5''/6'']-H), 8.35-8.30 (m, 4 H, c_1, [f/g]-H), 8.01 (d, ^3J = 8.4 Hz, 1 H, 8''-H), 7.93 (d, ^3J = 8.8 Hz, 2 H, [f/g]-H), 7.60 (ddd, ^3J = 5.2 Hz, ^4J = 1.6 Hz, ^5J = 0.8 Hz, 2 H, a_1-H), 7.53 (d, ^3J = 6.0 Hz, 2 H, [β_1/ β_2]-H), 7.47 (ddd, ^3J = 8.4 Hz, ^3J = 5.2 Hz, ^4J = 0.8 Hz, 2 H, b_1-H), 7.41 (d, ^3J = 6.0 Hz, 2 H, [β_1/ β_2]-H), 6.94 (t, ^3J = 8.4 Hz, 1 H, [b''/b']-H), 6.92 (t, ^3J = 8.4 Hz, 1 H, [b''/b']-H), 6.08 (d, ^3J = 8.4 Hz, 4 H, a'', a'-H), 2.92 (s, 6 H, OMe), 2.88 (s, 6 H, OMe), 2.37 (s, 6 H, Me), 2.01 (s, 6 H, Me); ^{13}C NMR (100 MHz, CD_2Cl_2:CD_3CN/1:4): δ = 158.3, 158.0, 157.9, 157.4, 156.1, 150.8, 150.5, 149.8, 148.8, 147.3, 144.1, 142.8, 142.4, 141.9, 140.4, 137.6, 137.5, 137.4, 133.8, 133.5, 133.3, 132.6, 132.5, 132.1, 130.1, 130.0, 129.7, 129.4, 128.5, 128.1, 127.0, 126.6, 126.5, 125.7, 125.4, 124.0, 123.7, 121.8, 115.5, 114.9, 104.4, 104.3, 96.5, 96.5, 94.2, 94.1, 93.8, 89.7, 55.8 (2C), 18.4, 18.0; IR (KBr) ν 3436, 2925, 2868, 2358, 2208, 1619, 1499, 1463, 1382, 1272, 1213, 1154, 1113, 1022, 843, 637, 558; ESI-MS: m/z (%) 592.9 (100) $[M-2OTf]^{2+}$, 1334.2 (30) $[M-OTf]^+$. Anal calcd for $C_{77}H_{57}F_6N_7O_{10}S_2Zn$•9/4$C_2H_4Cl_2$: C, 57.36; H, 3.90; N, 5.75; S, 3.76; found: C, 57.37; H, 4.11; N, 5.81; S, 3.34.

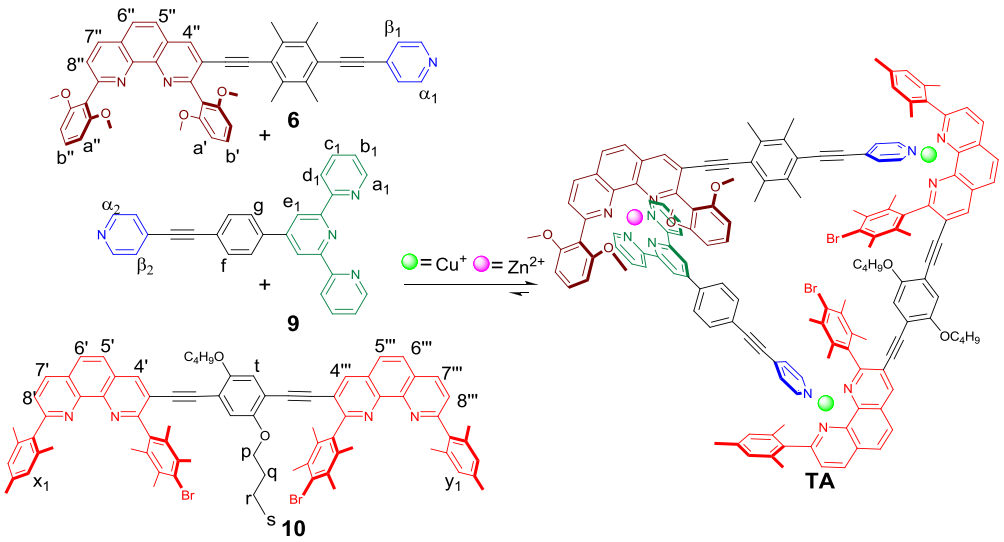
Synthesis of isosceles trapezoid TZ = $[Cu_2Zn_2(6)_2(7)(8)](PF_6)_2(OTf)_2$.



In an oven-dried 25-mL single-neck round-bottom flask, a mixture of phenanthroline-pyridine hybrid **6** (1.06 mg, 1.49 μmol), bisterpyridine **7** (0.51 mg, 0.75 μmol) and $Zn(OTf)_2$

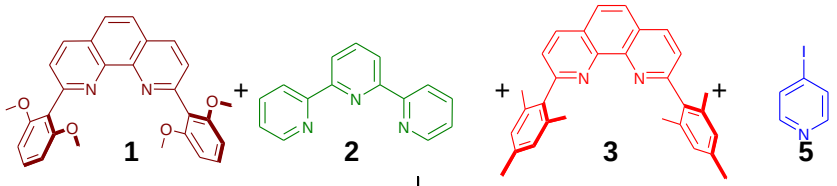
(0.54 mg, 1.49 μmol) was refluxed in 15 mL of CH_3CN for 2 h. The reaction mixture was then cooled down to room temperature, and solvents were removed at reduced pressure. After addition of solid $[Cu(MeCN)_4](PF_6)$ (0.56 mg, 1.49 μmol), bisphenanthroline **8** (0.77 mg, 0.75 μmol) and 15 mL of CH_2Cl_2 the resultant mixture was refluxed for 1 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, CD_2Cl_2): δ = 9.12 (s, 2 H, 4''-H), 9.01 (d, ^3J = 8.4 Hz, 2 H, 7''-H), 8.90 (s, 4 H, e-H), 8.84 (s, 2 H, 4-H), 8.72 (d, ^3J = 8.4 Hz, 2 H, 7-H), 8.70 (d, ^3J = 8.0 Hz, 4 H, d-H), 8.53 (d, ^3J = 9.2 Hz, 2 H, [5''/6'']-H), 8.49 (d, ^3J = 9.2 Hz, 2 H, [5''/6'']-H), 8.32 (td, ^3J = 8.0 Hz, ^4J = 1.6 Hz, 4 H, c-H), 8.20 (d, ^3J = 9.2 Hz, 2 H, [5/6]-H), 8.16 (d, ^3J = 9.2 Hz, 2 H, [5/6]-H), 8.05 (d, ^3J = 8.4 Hz, 2 H, 8''-H), 7.94 (d, ^3J = 8.4 Hz, 2 H, 8-H), 7.66 (d, ^3J = 5.2 Hz, 4 H, a-H), 7.65 (s, 2 H, t-H), 7.57-7.54 (m, 8 H, [m/n], b-H), 7.22 (d, ^3J = 8.4 Hz, 4 H, [m/n]-H), 7.05- 6.98 (m, 16 H, x, y, b', b'', β_1-H), 6.60 (br, 4 H, α_1-H), 6.13 (d, ^3J = 8.4 Hz, 4 H, a''-H), 6.11 (d, ^3J = 8.8 Hz, 4 H, a'-H), 4.54 (t, ^3J = 6.4 Hz, 4 H, p-H), 2.95 (s, 12 H, OMe), 2.91 (s, 12 H, OMe), 2.40 (s, 6 H, Me), 2.39 (s, 12 H, Me), 2.36 (s, 6 H, Me), 2.07 (s, 24 H, Me), 2.06 (s, 12 H, Me), 1.98-1.91(m, 4 H, q-H), 1.68-1.61 (m, 4 H, r-H), 1.03 (t, ^3J = 7.2 Hz, 6 H, s-H); IR (KBr) ν 3442, 3067, 2928, 2871, 2367, 2203, 1601, 1474, 1429, 1259, 1156, 1109, 1027, 842, 788, 730, 689, 636, 557; ESI-MS: m/z (%) 1992.4 (5) $[M-OTf, PF_6]^{2+}$, 1279.6 (40) $[M-OTf, 2PF_6]^{3+}$, 923.2 (100) $[M-2OTf, 2PF_6]^{4+}$, and 708.4 (10) $[M-3OTf, 2PF_6]^{5+}$; Anal calcd for $C_{218}H_{180}Cu_2F_{24}N_{16}O_{22}P_2S_4Zn_2$: C, 61.18; H, 4.24; N, 5.24; S, 3.00; found: C, 61.10; H, 4.51; N, 5.12; S, 2.62.

Synthesis of scalene triangle TA = $[Cu_2Zn(6)(9)(10)](PF_6)_2(OTf)_2$.



In an oven-dried 25-mL single-neck round-bottom flask, a mixture of phenanthroline-pyridine hybrid **6** (1.25 mg, 1.76 μmol), terpyridine-pyridine hybrid **9** (0.72 mg, 1.76 μmol) and $Zn(OTf)_2$ (0.64 mg, 1.76 μmol) was refluxed in 15 mL of CH_3CN (1:4) for 2 h. The reaction mixture was then cooled down to room temperature and solvents were removed at reduced pressure. After addition of solid $[Cu(MeCN)_4](PF_6)$ (1.31 mg, 3.52 μmol), bisphenanthroline **10** (2.26 mg, 1.76 μmol) and 15 mL of CH_2Cl_2 the resultant mixture was refluxed for 1 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, CD_2Cl_2): δ = 9.02 (d, ^3J = 8.4 Hz, 1 H, 7’’-H), 8.98 (s, 1 H, 4’’-H), 8.88 (d, ^3J = 8.4 Hz, 2 H, d_1-H), 8.84 (s, 2 H, 4’, 4’’’-H), 8.79 (s, 2 H, e_1-H), 8.71 (d, ^3J = 8.4 Hz, 2 H, 7’, 7’’’-H), 8.50 (d, ^3J = 8.8 Hz, 1 H, [5’’/6’’]-H), 8.42 (d, ^3J = 8.8 Hz, 1 H, [5’’/6’’]-H), 8.39 (d, ^3J = 8.8 Hz, 2 H, [f/g]-H), 8.30 (td, ^3J = 8.4 Hz, ^4J = 1.6 Hz, 2 H, c_1-H), 8.20 (d, ^3J = 8.8 Hz, 2 H, [5’/6’ or 5’’’/6’’’]-H), 8.15 (d, ^3J = 8.8 Hz, 2 H, [5’/6’ or 5’’’/6’’’]-H), 8.14 (d, ^3J = 8.4 Hz, 1 H, 8’’-H), 7.99 (d, ^3J = 8.8 Hz, 2 H, [f/g]-H), 7.94 (d, ^3J = 8.4 Hz, 2 H, 8’, 8’’’-H), 7.60 (d, ^3J = 4.0 Hz, 2 H, a_1-H), 7.47 (dd, ^3J = 8.4 Hz, ^3J = 4.0 Hz, 2 H, b_1-H), 7.28 (br, 2 H, β_2-H), 7.12 (br, 2 H, β_1-H), 7.04 (t, ^3J = 8.4 Hz, 1 H, b’’-H), 6.96 (br s, 8 H, α_1, α_2, x_1, y_1-H), 6.85 (t, ^3J = 8.4 Hz, 1 H, b’-H), 6.39 (s, 2 H, t-H), 6.17 (d, ^3J = 8.4 Hz, 2 H, a’’-H), 6.08 (d, ^3J = 8.4 Hz, 2 H, a’-H), 3.79 (t, ^3J = 6.4 Hz, 4 H, p-H), 3.03 (s, 6 H, OMe), 2.85 (s, 6 H, OMe), 2.36 (s, 6 H, Me), 2.35 (s, 12 H, Me), 2.32 (s, 6 H, Me), 2.03 (s, 12 H, Me), 1.95 (s, 18 H, Me), 1.69-1.61 (m, 4 H, q-H), 1.51-1.41 (m, 4 H, r-H), 0.98 (t, ^3J = 7.2 Hz, 6 H, s-H); IR (KBr) ν 3436, 2960, 2925, 2900, 2204, 1602, 1473, 1426, 1369, 1260, 1155, 1107, 1024, 840, 727, 634, 554; ESI-MS m/z (%) 1445.3 (25) $[M - PF_6, OTf]^{2+}$, 915.3 (100) $[M-2PF_6, OTf]^{3+}$, 649.4 (10) $[M-2PF_6, 2OTf]^{4+}$. Anal calcd for $C_{157}H_{133}Br_2Cu_2F_{18}N_{11}O_{12}P_2S_2Zn\bullet 4/3CH_2Cl_2$: C, 57.64; H, 4.14; N, 4.67; S, 1.94; found: C, 58.01; H, 4.29; N, 4.70; S, 1.54.

Calculation of Degree of self-sorting (*M*)[5]



$[Cu(\mathbf{1})_2]^+ + [Cu(\mathbf{1})(\mathbf{2})]^+ + [Cu(\mathbf{2})(\mathbf{5})]^+ + [Zn(\mathbf{3})_2]^{2+} + [Zn(\mathbf{1})(\mathbf{3})]^{2+} + [Zn(\mathbf{2})(\mathbf{5})]^{2+} + [Zn(\mathbf{3})(\mathbf{5})_4]^{2+} + [Zn(\mathbf{1})(\mathbf{2})(\mathbf{5})]^{2+}$

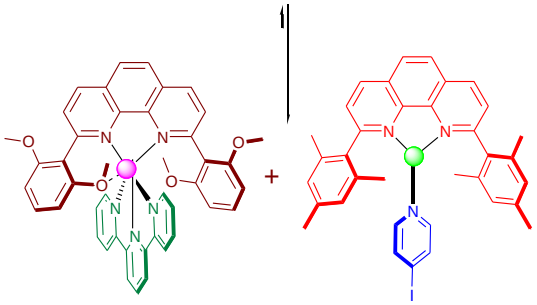
$[Cu(\mathbf{2})_2]^+ + [Cu(\mathbf{1})(\mathbf{3})]^+ + [Cu(\mathbf{3})(\mathbf{5})]^+ + [Zn(\mathbf{5})_4]^{2+} + [Zn(\mathbf{1})(\mathbf{5})_3]^{2+} + [Zn(\mathbf{2})(\mathbf{5})_2]^{2+} + [Zn(\mathbf{1})_2(\mathbf{5})]^{2+} + [Zn(\mathbf{1})(\mathbf{3})(\mathbf{5})]^{2+}$

$[Cu(\mathbf{3})_2]^+ + [Cu(\mathbf{1})(\mathbf{5})]^+ + [Cu(\mathbf{3})(\mathbf{5})_2]^+ + [Zn(\mathbf{5})_5]^{2+} + [Zn(\mathbf{1})(\mathbf{5})_4]^{2+} + [Zn(\mathbf{2})(\mathbf{5})_3]^{2+} + [Zn(\mathbf{1})_2(\mathbf{5})_2]^{2+} + [Zn(\mathbf{1})(\mathbf{3})(\mathbf{5})_2]^{2+}$

$[Cu(\mathbf{5})_3]^+ + [Cu(\mathbf{1})(\mathbf{5})_2]^+ + [Zn(\mathbf{1})_2]^{2+} + [Zn(\mathbf{5})_6]^{2+} + [Zn(\mathbf{1})(\mathbf{5})_5]^{2+} + [Zn(\mathbf{3})(\mathbf{5})_2]^{2+} + [Zn(\mathbf{3})_2(\mathbf{5})]^{2+} + [Zn(\mathbf{3})(\mathbf{2})(\mathbf{5})]^{2+}$

$[Cu(\mathbf{5})_4]^+ + [Cu(\mathbf{2})(\mathbf{3})]^+ + [Zn(\mathbf{2})_2]^{2+} + [Zn(\mathbf{1})(\mathbf{2})]^{2+} + [Zn(\mathbf{2})(\mathbf{3})]^{2+} + [Zn(\mathbf{3})(\mathbf{5})_3]^{2+} + [Zn(\mathbf{3})_2(\mathbf{5})_2]^{2+}$

Dynamic library



C1 = $[Zn(\mathbf{1})(\mathbf{2})]^{2+}$ **C3** = $[Cu(\mathbf{3})(\mathbf{5})]^+$

Degree of self-sorting (*M*) = P_0/P= 39/2=19.5

P_0 = the number of all possible aggregates

P = number of observed assemblies in the experiment

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

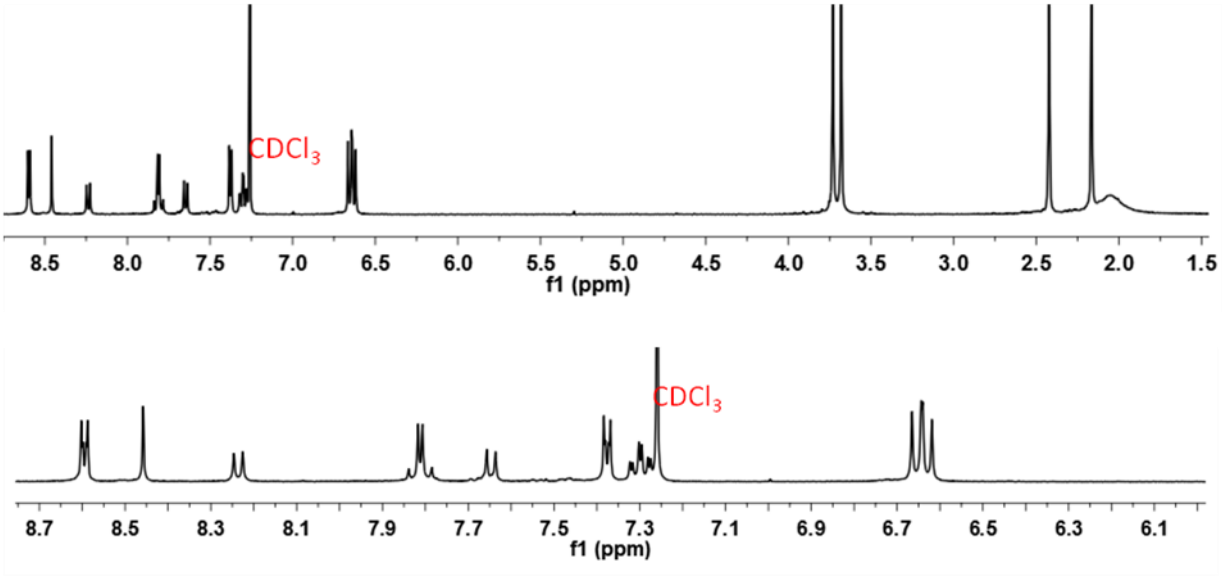


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **6**. An expanded aromatic part of the spectrum is shown at the bottom.

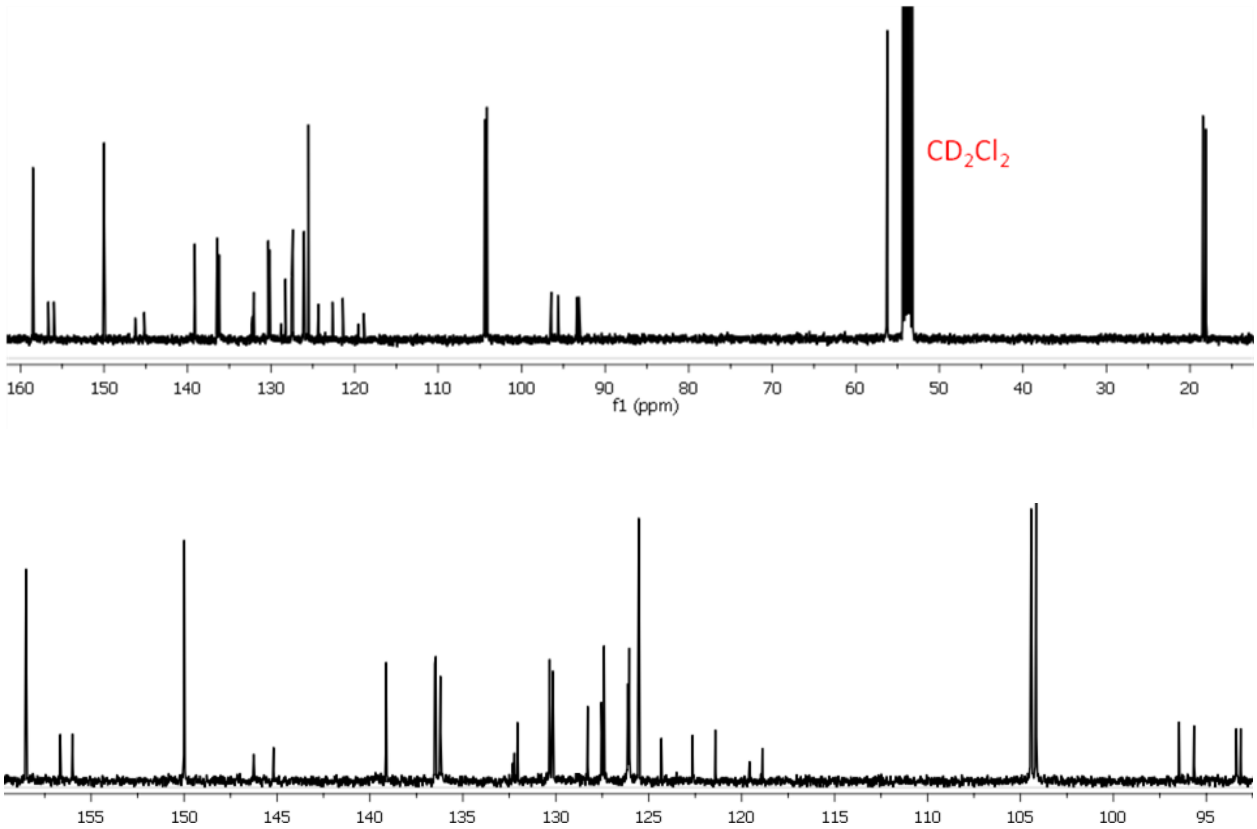


Figure S2. ^{13}C NMR spectrum (100 MHz, CD_2Cl_2, 298 K) of **6**. An expanded aromatic part of the spectrum is shown at the bottom.

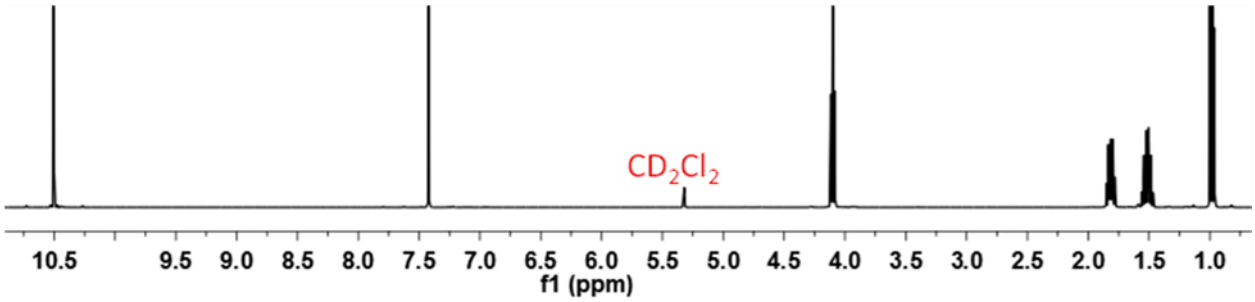


Figure S3. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of **14**.

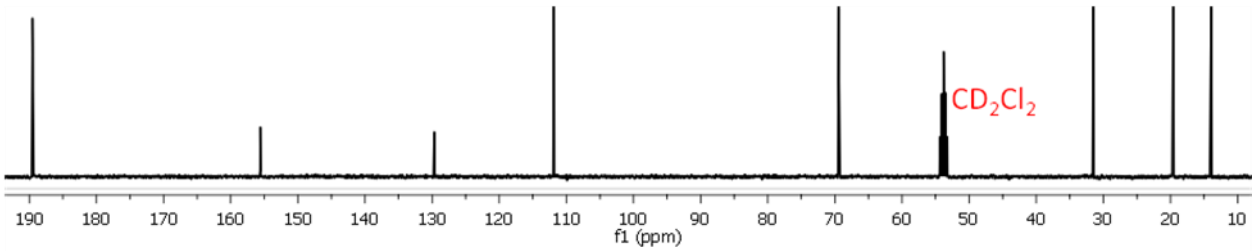


Figure S4. ^{13}C NMR spectrum (100 MHz, CD_2Cl_2, 298 K) of **14**.

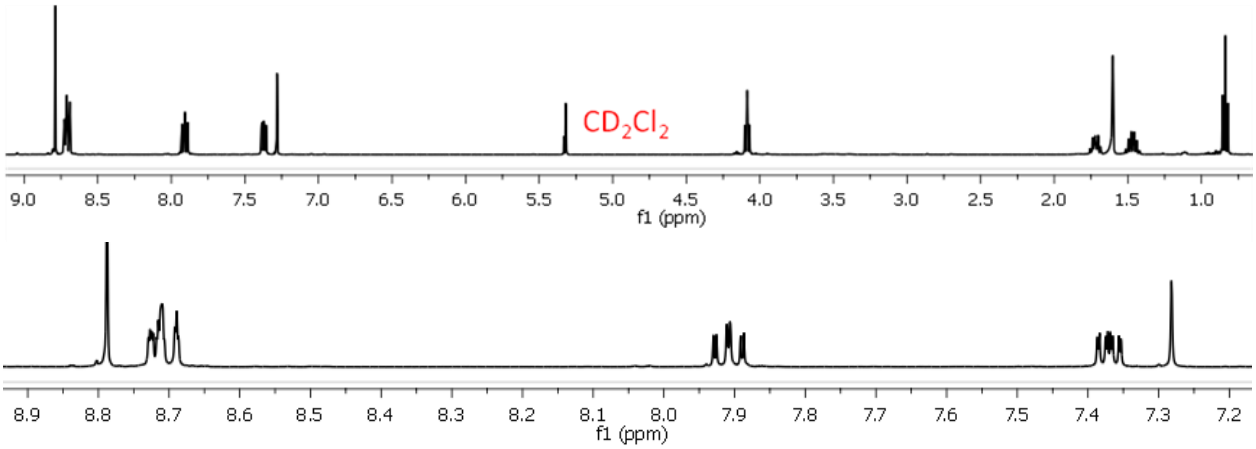


Figure S5. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of **7**. An expanded aromatic part of the spectrum is shown at the bottom.

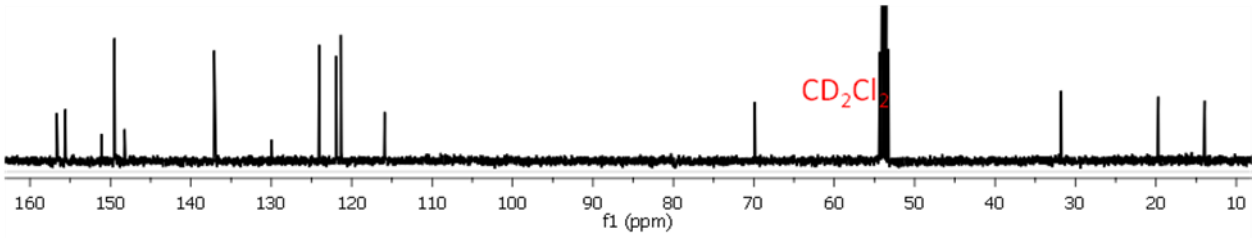


Figure S6. ^{13}C NMR spectrum (100 MHz, CD_2Cl_2, 298 K) of **7**.

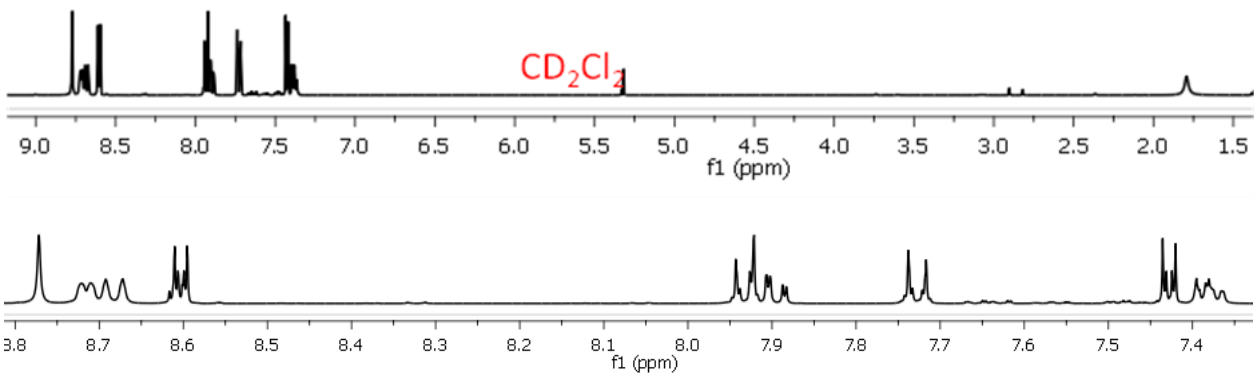


Figure S7. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of **9**. An expanded aromatic part of the spectrum is shown at the bottom.

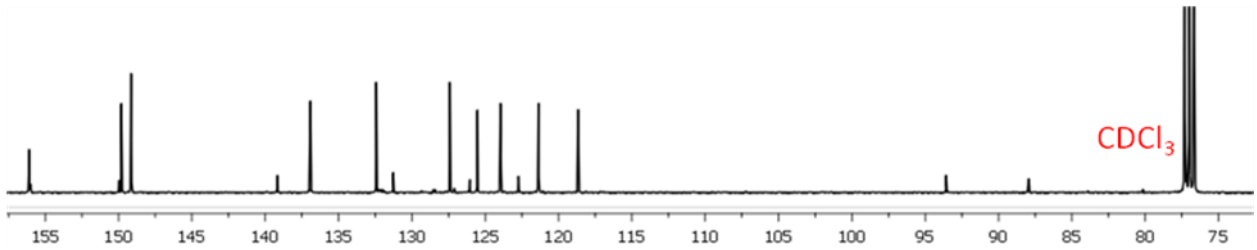


Figure S8. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **9**.

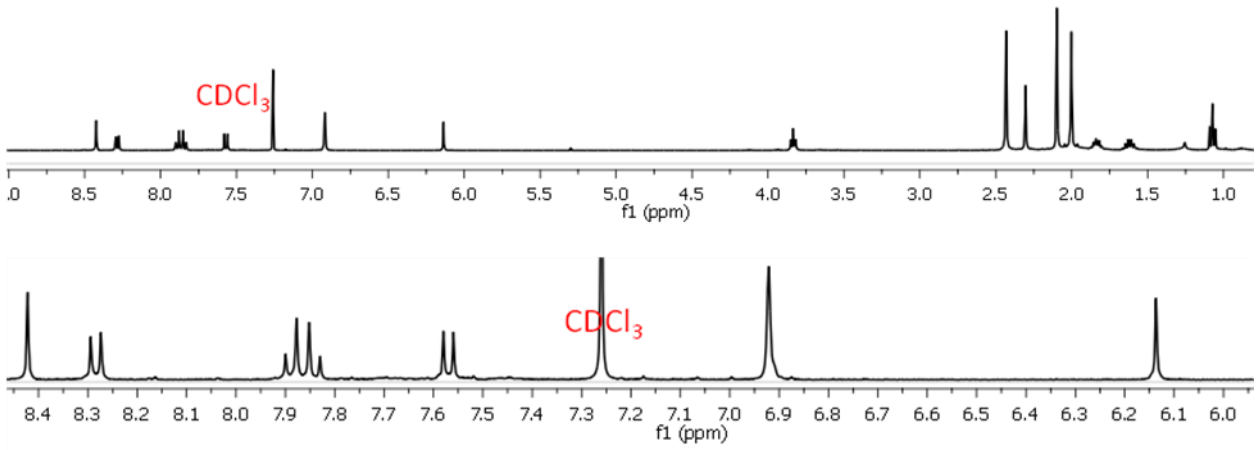


Figure S9. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **10**. An expanded aromatic part of the spectrum is shown at the bottom.

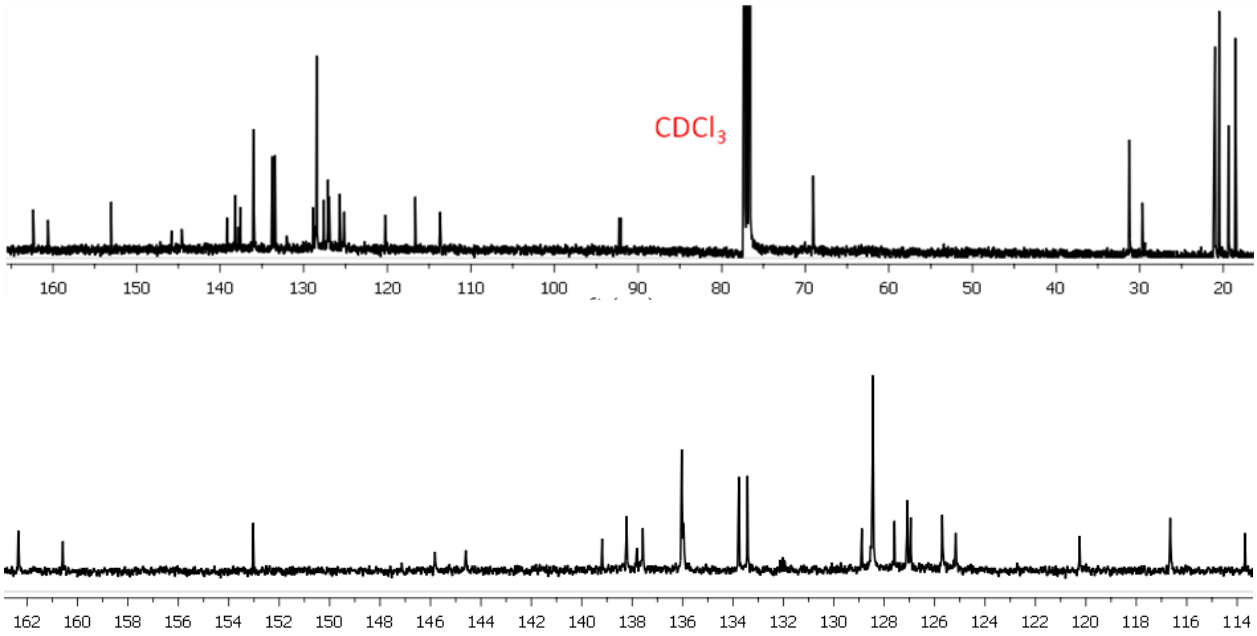


Figure S10. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **10**. An expanded aromatic part of the spectrum is shown at the bottom.

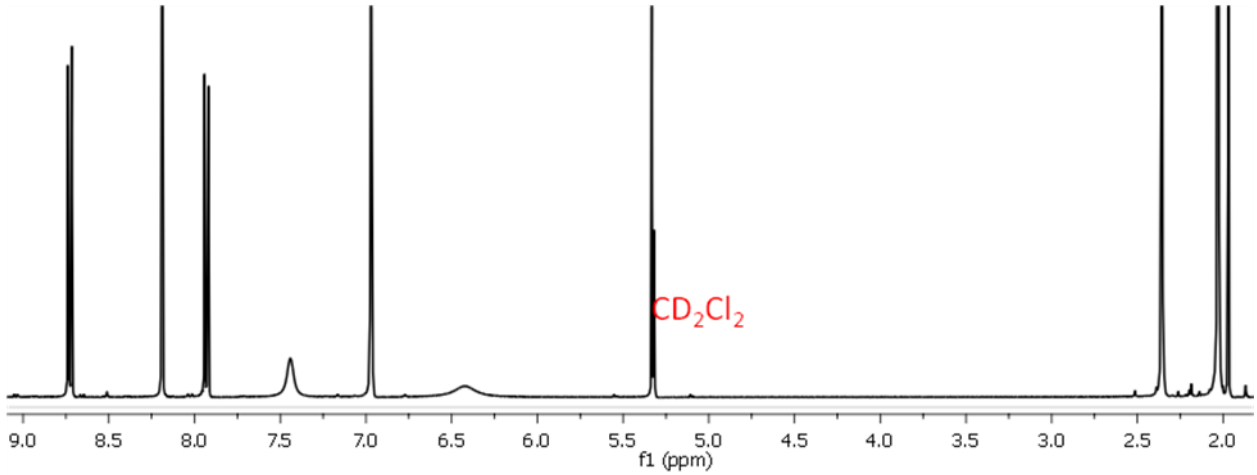


Figure S11. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of **C3** = [Cu(**3**)(**5**)](PF_6).

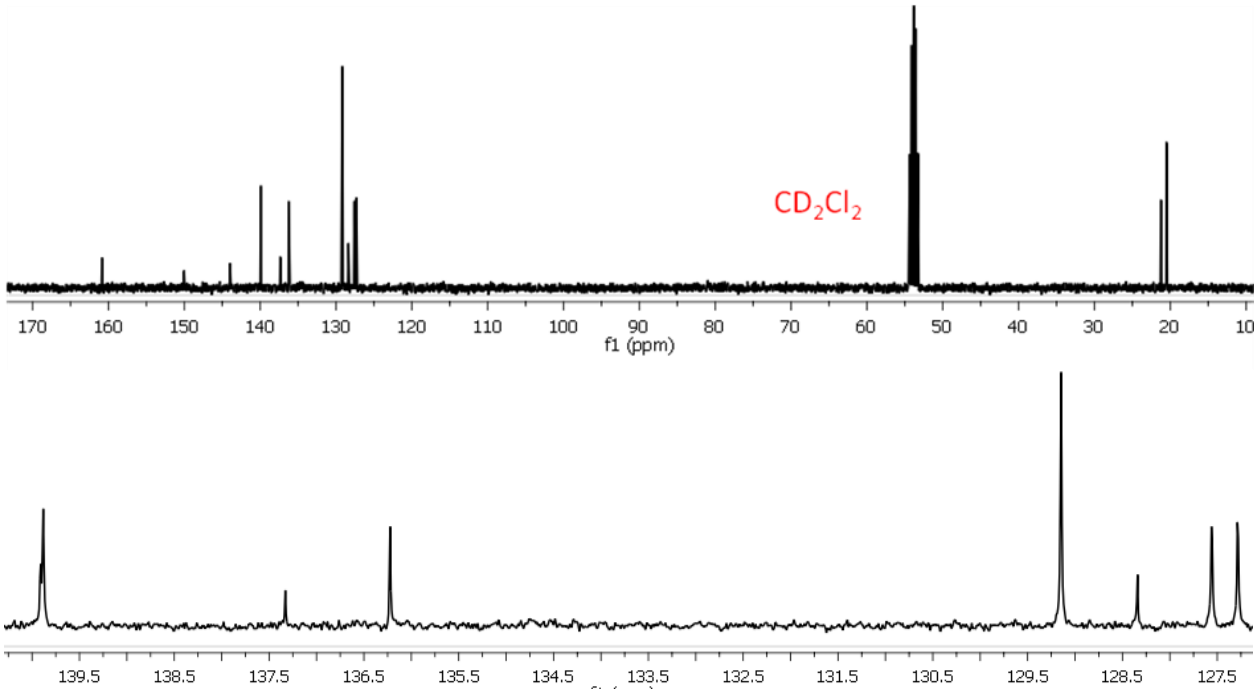


Figure S12. ^{13}C NMR spectrum (100 MHz, CD_2Cl_2, 298 K) of **C3** = [Cu(**3**)(**5**)](PF_6). An expanded aromatic part of the spectrum is shown at the bottom.

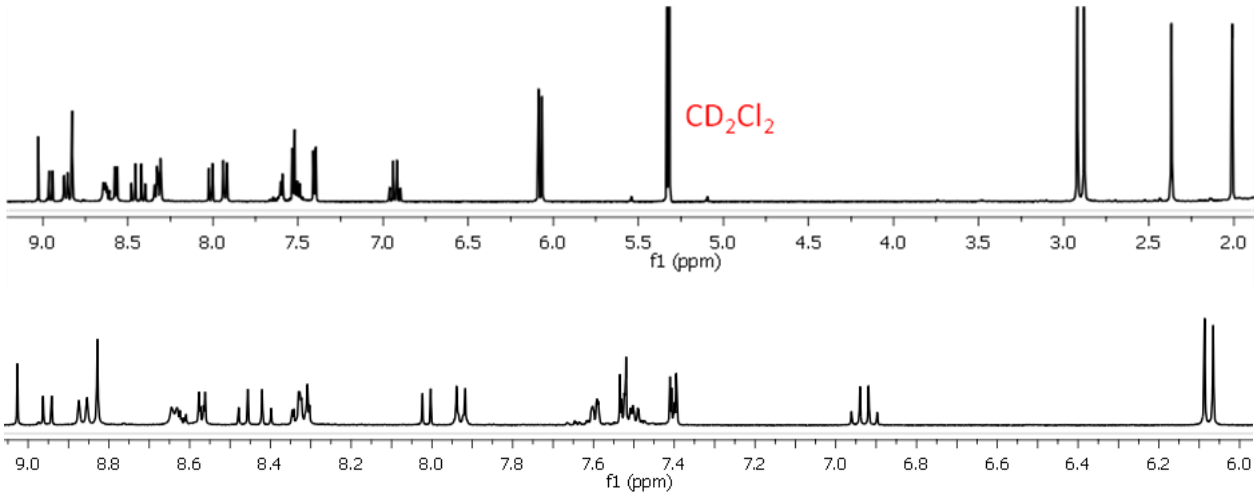


Figure S13. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of **C4** = [Zn(**6**)(**9**)]($OTf)_2$. An expanded aromatic part of the spectrum is shown at the bottom.

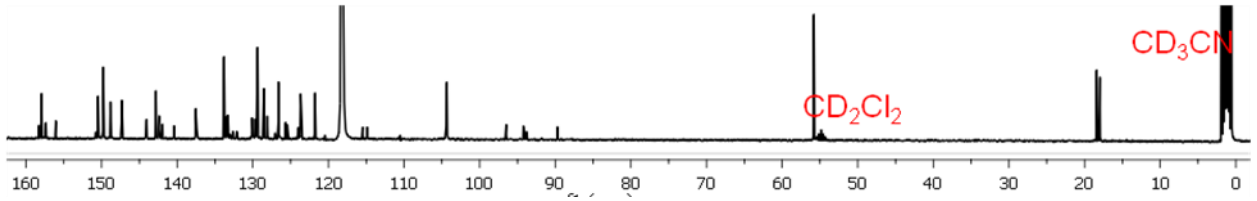


Figure S14. ^{13}C NMR spectrum (100 MHz, CD_2Cl_2:CD_3CN/1:4, 298 K) of **C4** = [Zn(**6**)(**9**)]($OTf)_2$.

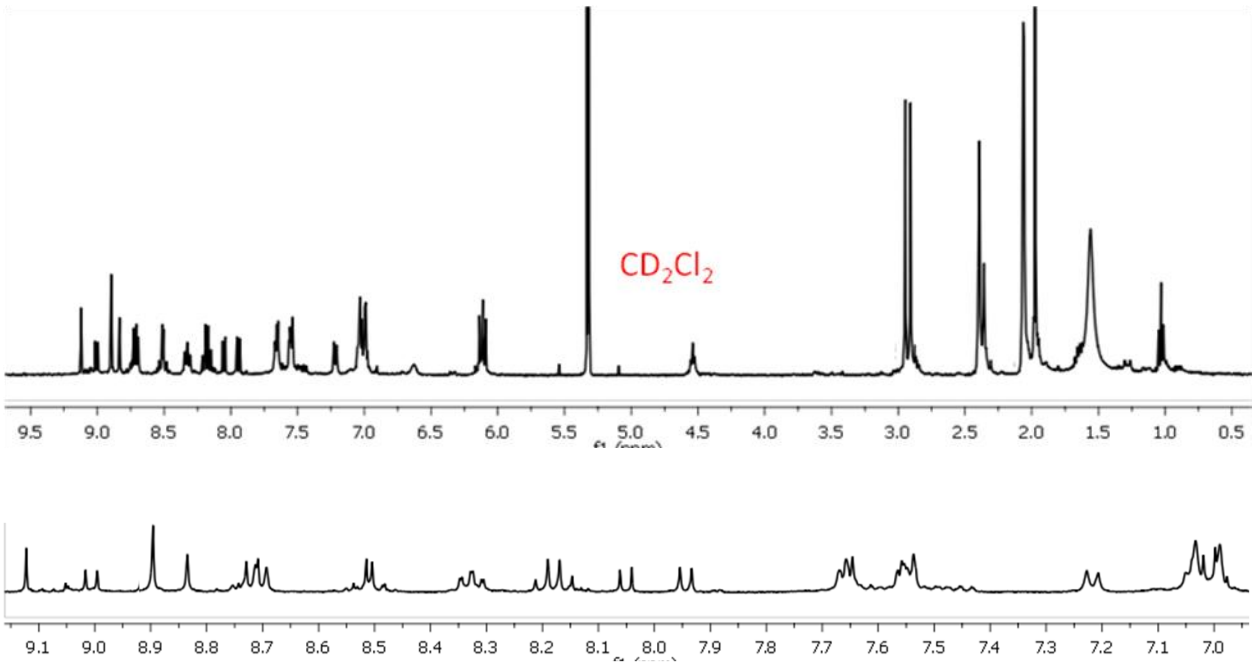


Figure S15. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of **TZ** = $[Cu_2Zn_2(\mathbf{6})_2(\mathbf{7})(\mathbf{8})](PF_6)_2(OTf)_2$. An expanded aromatic part of the spectrum is shown at the bottom.

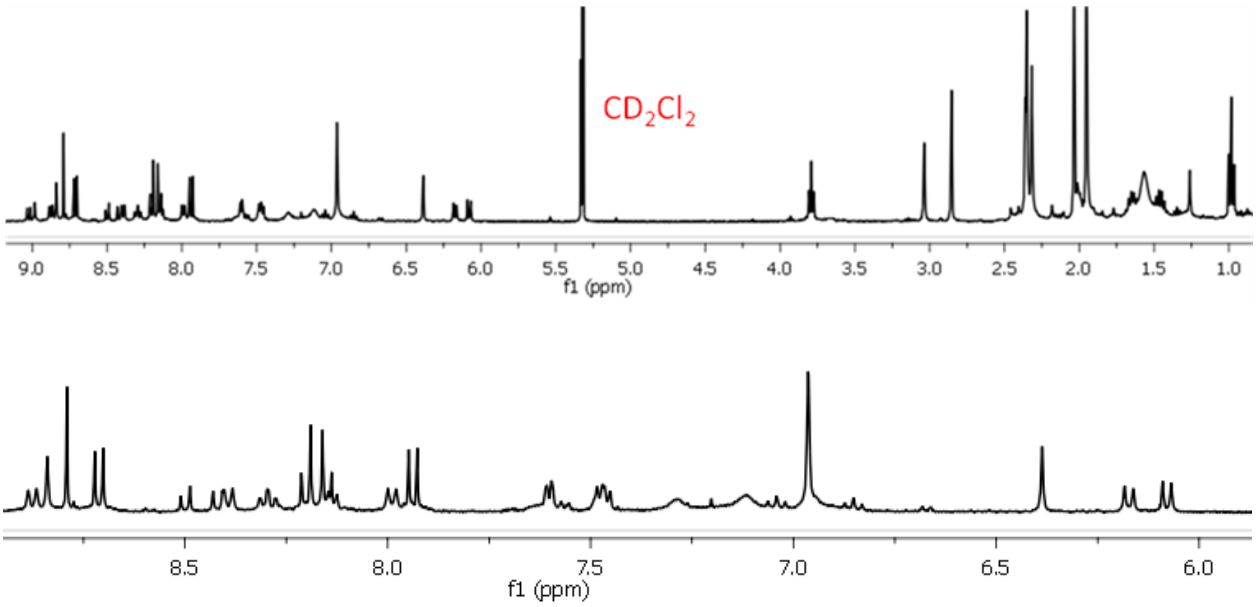


Figure S16. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of **TA** = $[Cu_2Zn(\mathbf{6})(\mathbf{9})(\mathbf{10})](PF_6)(OTf)_2$. An expanded aromatic part of the spectrum is shown at the bottom.

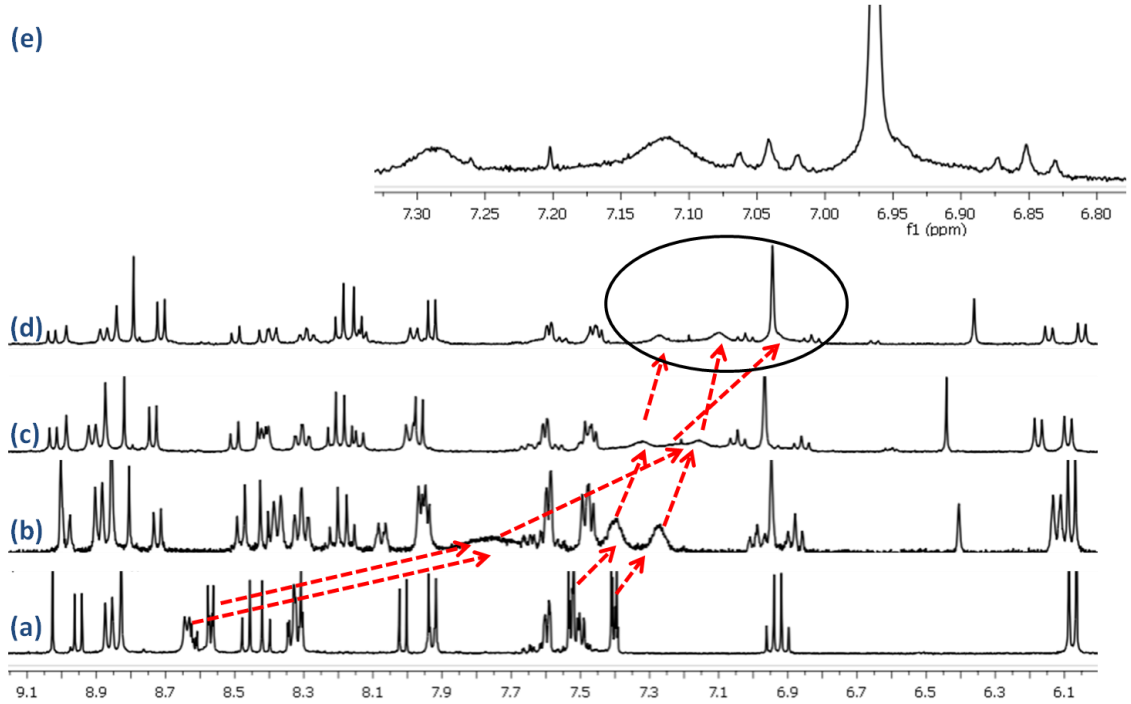


Figure S17. Partial ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of (a) **C4** = [Zn(**6**)(**9**)](OTf)$_2$; (b) after addition of 0.33 equiv of [Cu_2(**10**)](PF$_6$)$_2$ (related to the initial amount of **C4**; (c) after addition of 0.66 equiv of [Cu_2(**10**)](PF$_6$)$_2$ (related to the initial amount of **C4**; (d) after addition of 1.00 equiv of [Cu_2(**10**)](PF$_6$)$_2$ (related to the initial amount of **C4**, (e) zoom-in view of S14 (d) from 6.80 to 7.30 ppm.

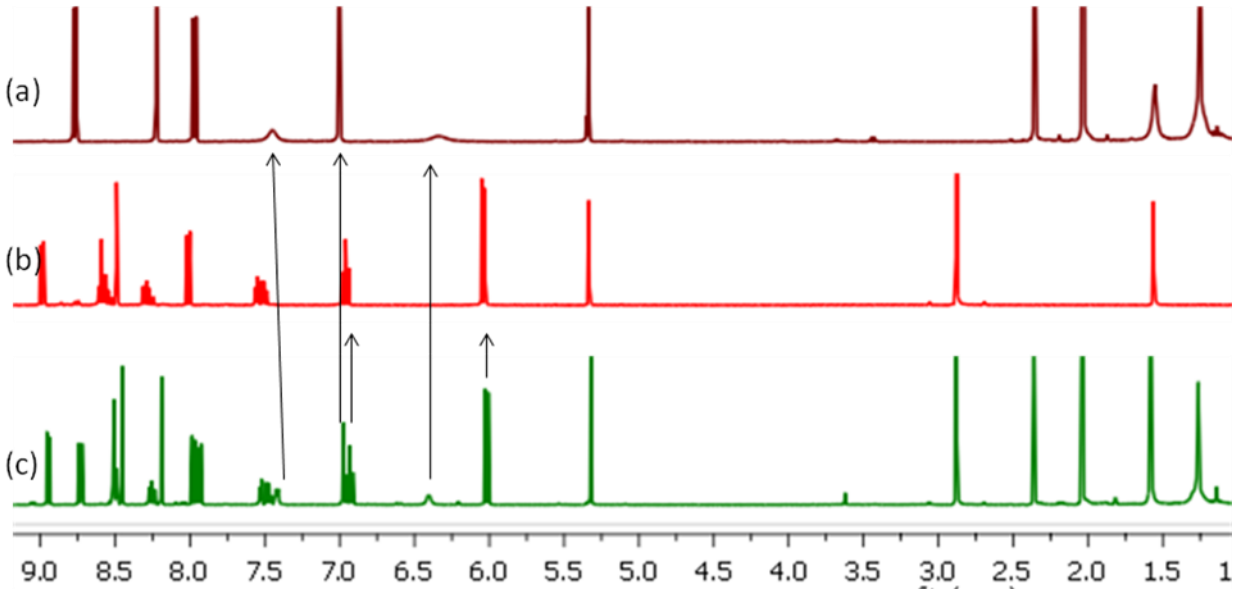


Figure S18. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of (a) **C1**; (b) **C3**; (c) an equimolar mixture of **1**, **2**, **3**, **5** in presence of Zn(OTf)$_2$ and [Cu(MeCN)$_4$]PF$_6$.

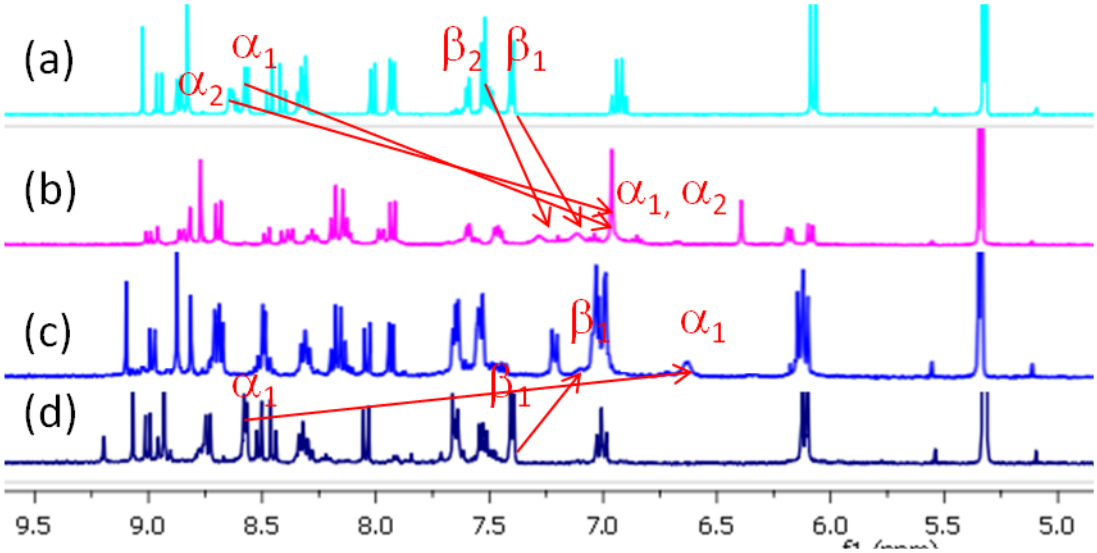


Figure S19. Partial ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of (a) **C4**; (b) **TA**.; (c) **TZ**; (d) $[Zn_2(\mathbf{6})_2(\mathbf{7})](OTf)_4$

^{1}H-^{1}H COSY NMR spectra

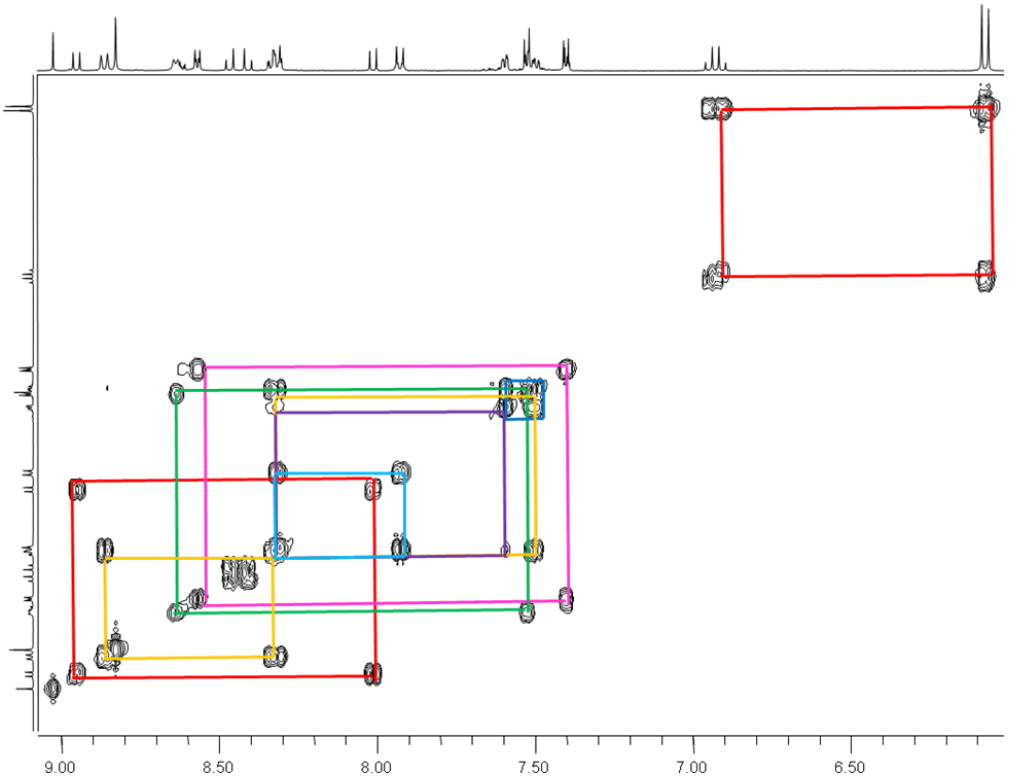


Figure S20. Partial ^{1}H-^{1}H COSY NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of **C4**.

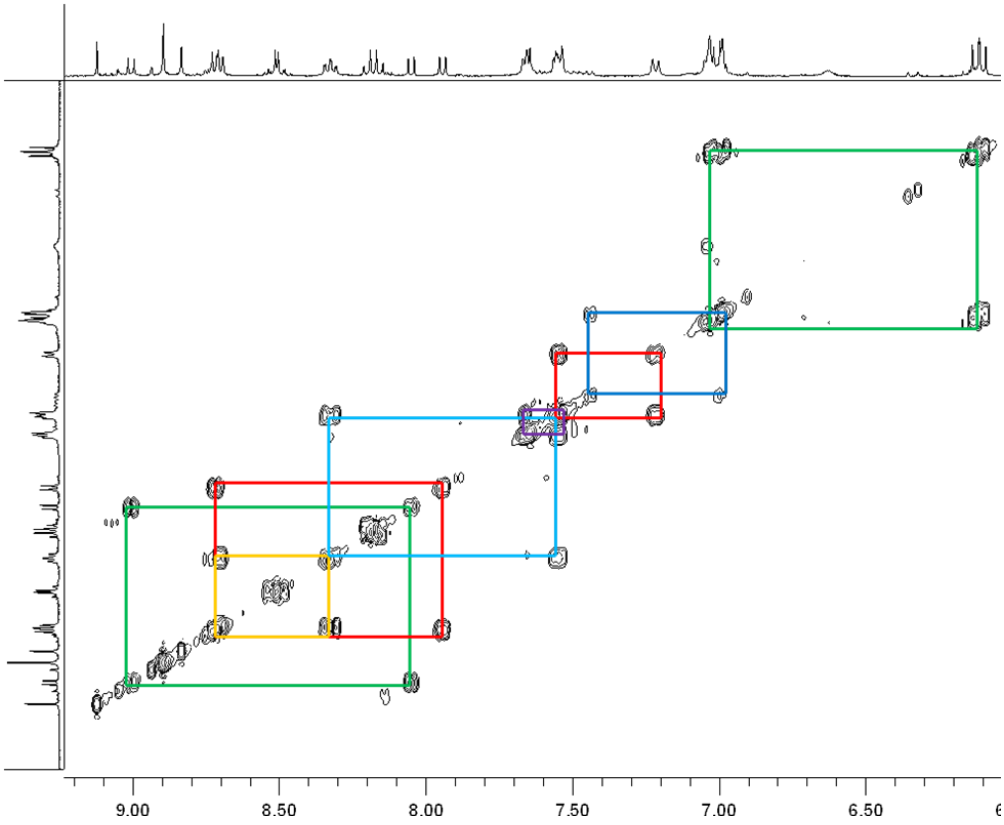


Figure S21. Partial ^{1}H-^{1}H COSY NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of **TZ**.

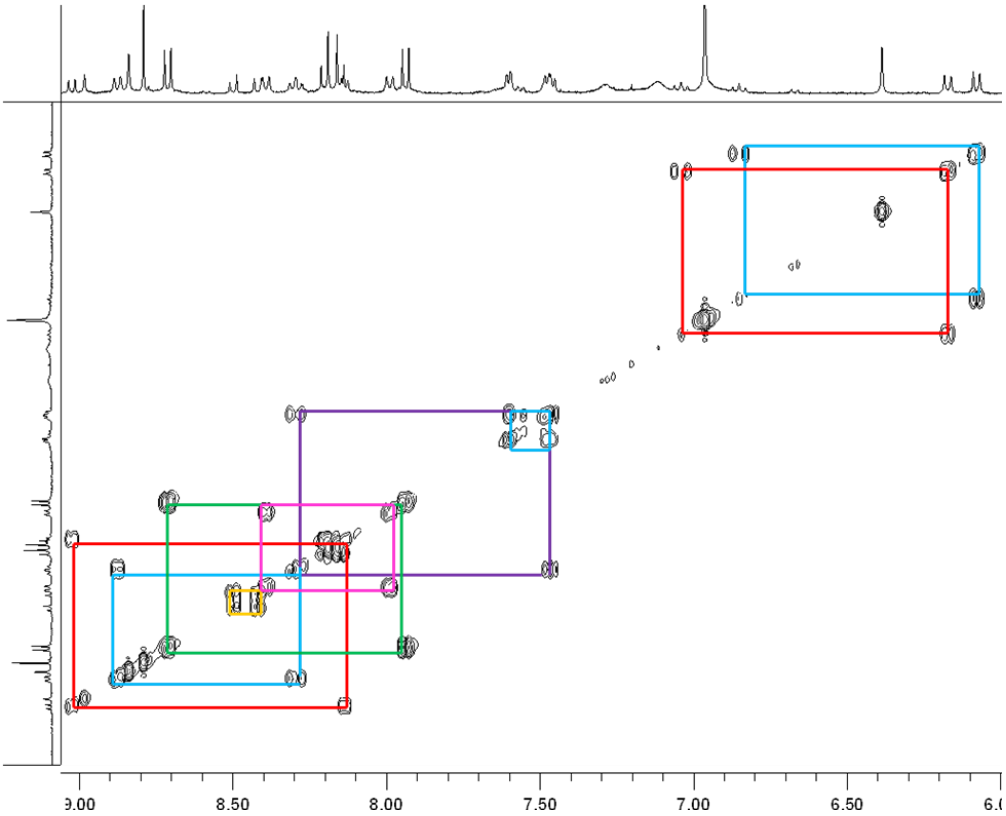


Figure S22. Partial ^{1}H-^{1}H COSY NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of **TA**.

DOSY NMR Spectra

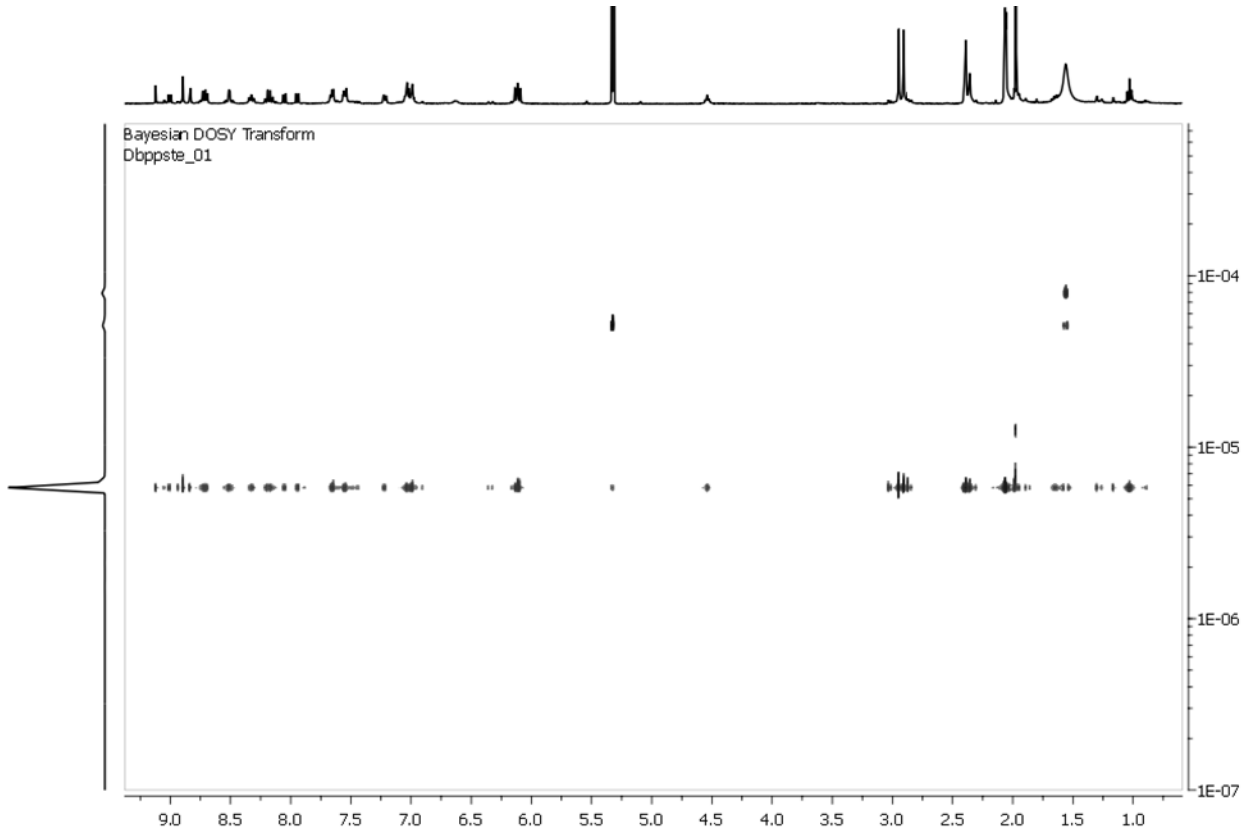


Figure S23. DOSY plot of isosceles trapezoid **TZ** = $[Zn_2Cu_2(\mathbf{8})(\mathbf{6})_2(\mathbf{7})](OTf)_4(PF_6)_2$ in CD_2Cl_2.

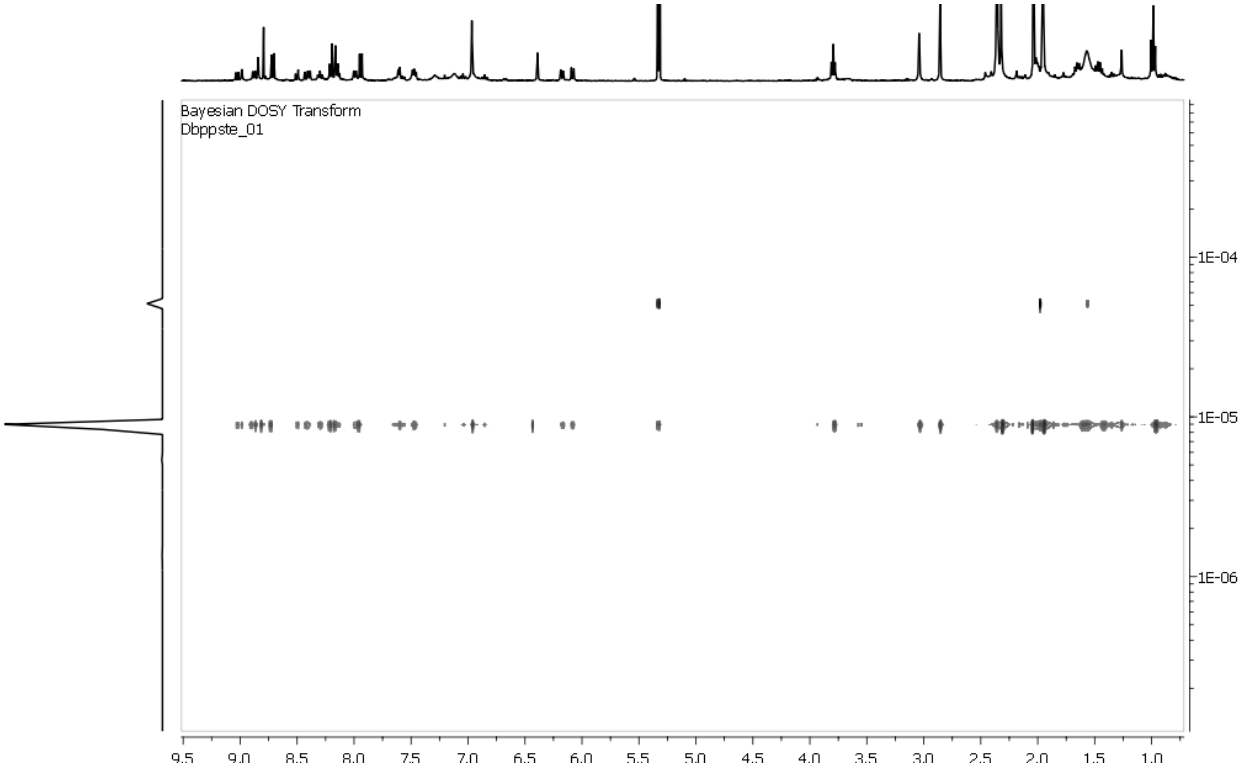


Figure S24. DOSY plot of scalene triangle **TA** = $[Cu_2Zn(\mathbf{6})(\mathbf{9})(\mathbf{10})](PF_6)_2(OTf)_2$ in CD_2Cl_2.

ESI-MS spectra

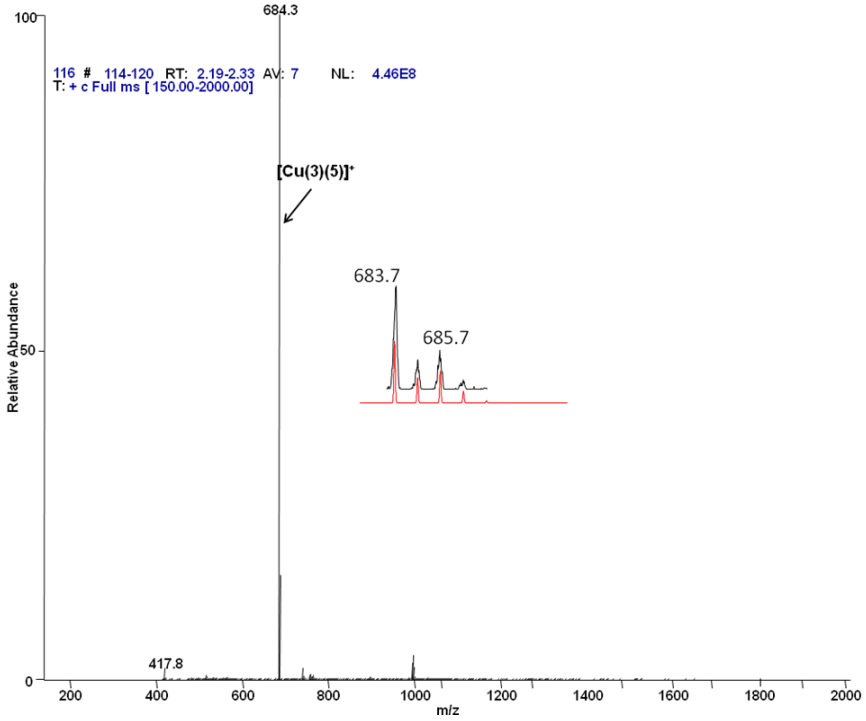


Figure S25. ESI-MS spectrum of **C3** = [Cu(**3**)(**5**)](PF_6) (in DCM) and experimental isotopic distribution (black) along with calculated isotopic distribution (red) for $[Cu(\mathbf{3})(\mathbf{5})]^+$.

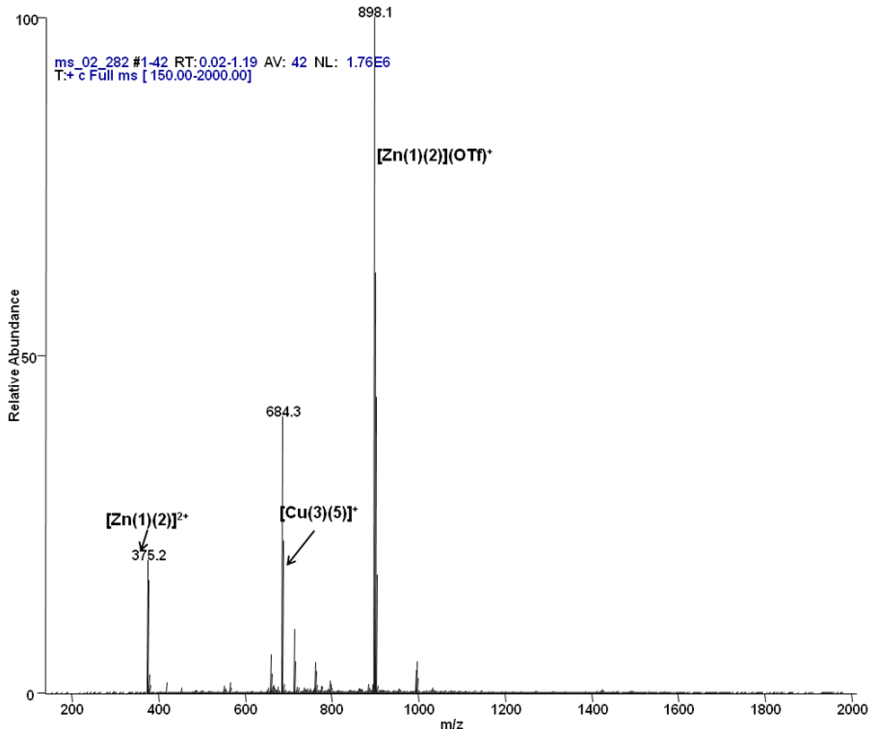


Figure S26. ESI-MS spectrum of an equimolar mixture of **1**, **2**, **3**, **5** in presence of $Zn(OTf)_2$ and $[Cu(MeCN)_4]PF_6$.

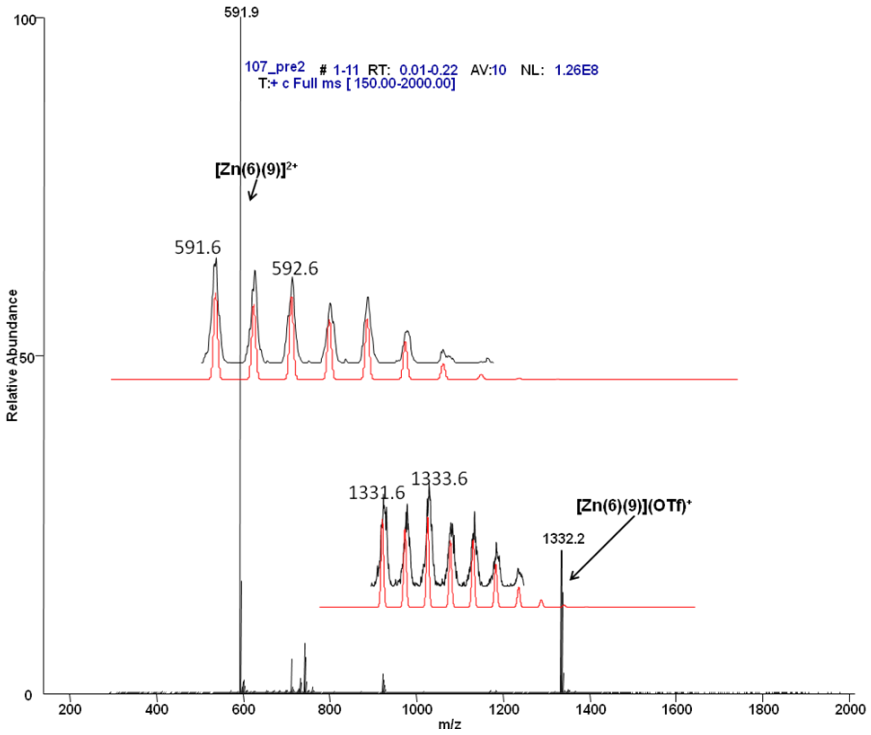


Figure S27. ESI-MS spectrum of **C4** = [Zn(**6**)(**9**)](OTf)$_2$ (in CH_2Cl_2) and experimental isotopic distribution (black) along with calculated isotopic distribution (red) for $[Zn_2(\mathbf{6})(\mathbf{9})]^{2+}$ and $[Zn_2(\mathbf{6})(\mathbf{9})](OTf)^{+}$.

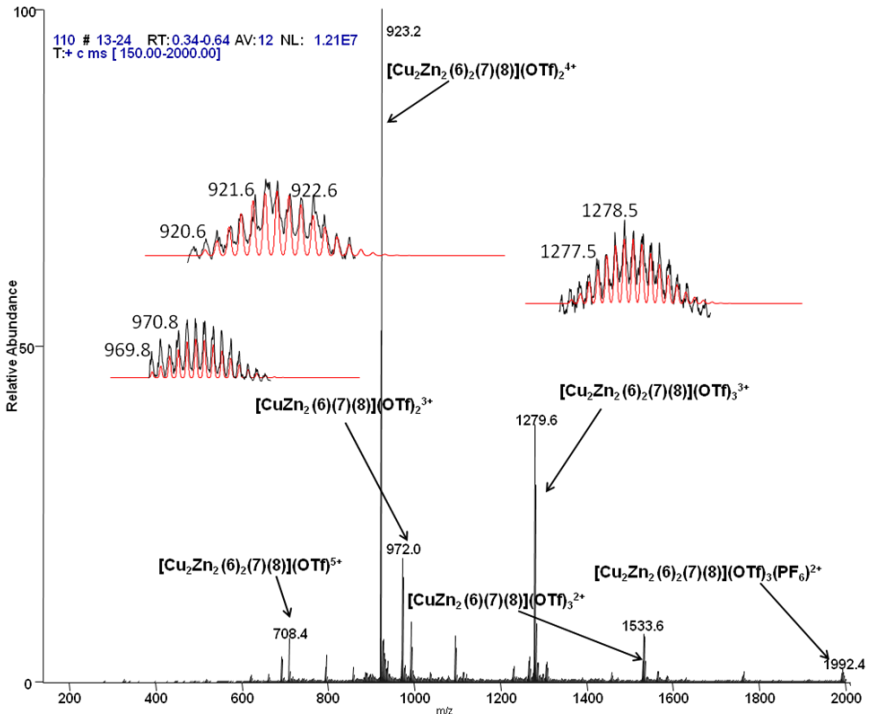


Figure S28. ESI-MS spectrum of **TZ** = $[Cu_2Zn_2(\mathbf{6})_2(\mathbf{7})(\mathbf{8})](PF_6)_2(OTf)_4$ in CH_2Cl_2 and experimental isotopic distributions (black lines) along with calculated isotopic distributions

(red lines) for peaks associate with $[Cu_2Zn_2(\mathbf{6})_2(\mathbf{7})(\mathbf{8})](OTf)_2^{4+}$, $[CuZn_2(\mathbf{6})(\mathbf{7})(\mathbf{8})](OTf)_2^{3+}$, and $[Cu_2Zn_2(\mathbf{6})_2(\mathbf{7})(\mathbf{8})](OTf)_3^{3+}$.

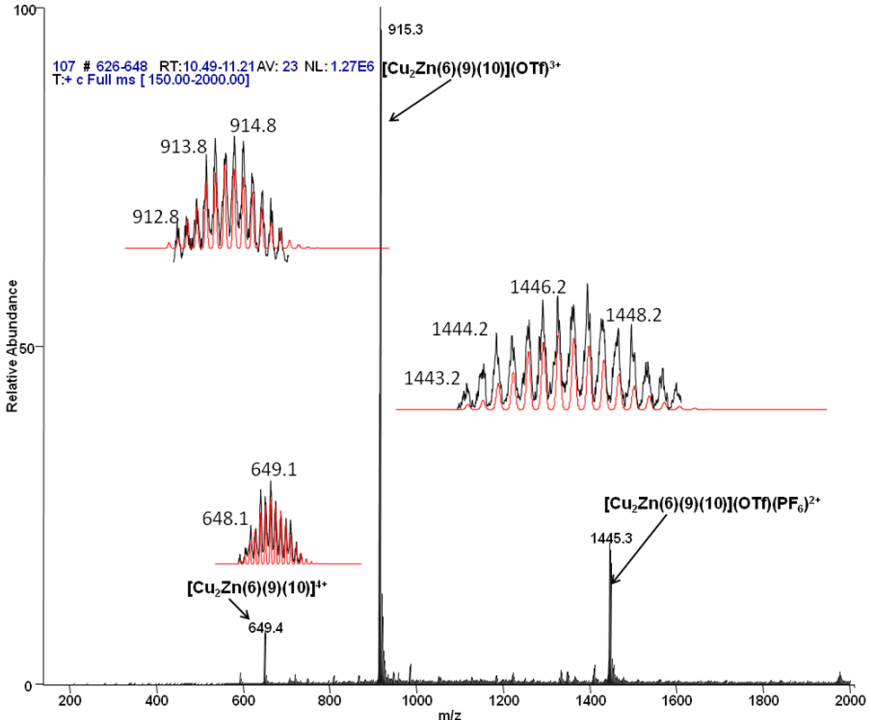


Figure S29: ESI-MS spectrum of **TA** = $[Cu_2Zn(\mathbf{6})(\mathbf{9})(\mathbf{10})](PF_6)_2(OTf)_2$ in CH_2Cl_2 and experimental isotopic distributions (black lines) along with calculated isotopic distributions (red lines) for the peaks associated with $[Cu_2Zn(\mathbf{6})(\mathbf{9})(\mathbf{10})]^{4+}$, $[Cu_2Zn(\mathbf{6})(\mathbf{9})(\mathbf{10})](OTf)^{3+}$ and $[Cu_2Zn(\mathbf{6})(\mathbf{9})(\mathbf{10})](PF_6)(OTf)^{2+}$.

Binding Constants

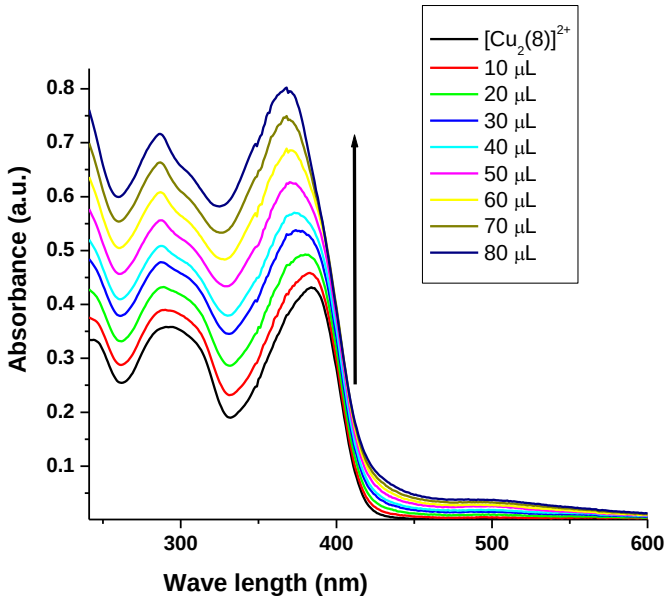


Figure S30. UV-Vis absorption of 0.50 $\times 10^{-5}$ M $[Cu_2(\mathbf{8})](PF_6)_2$ in CH_2Cl_2 (2 mL) upon addition of $[Zn_2(\mathbf{6})_2(\mathbf{7})](OTf)_4$ (1.26 $\times 10^{-4}$ M) at 25 °C. Result: log β = 6.32 ± 0.26. The data was analysed in the wavelength region 200-600 nm.

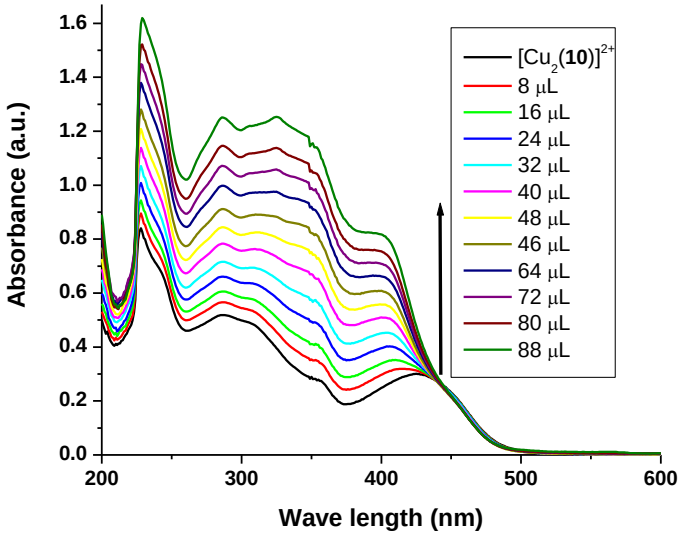
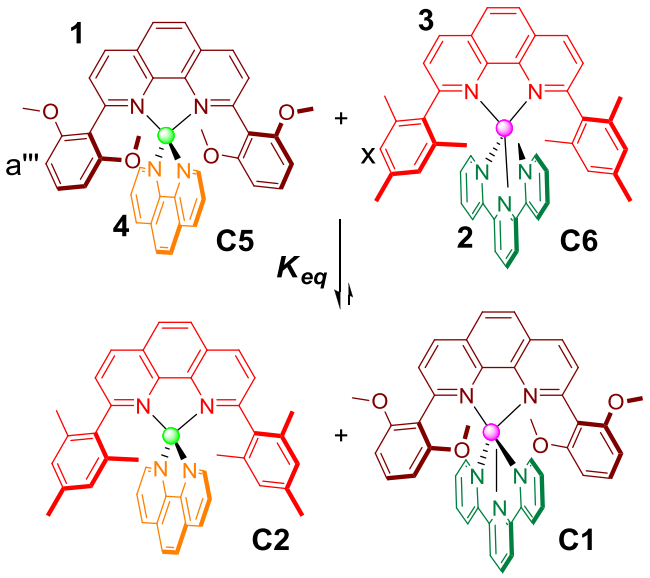


Figure S31. UV-Vis absorption of 0.98 $\times 10^{-5}$ M $[Cu_2(\mathbf{10})](PF_6)_2$ in CH_2Cl_2 (2 mL) upon addition of **C4** = $[Zn(\mathbf{6})(\mathbf{9})](OTf)_2$ (0.23 $\times 10^{-3}$ M) at 25 °C. Result: log β = 5.43 ± 0.26. The data was analysed in the wavelength region 200-600 nm.

Determination of relative binding constant for $[Zn(1)(2)]^{2+}$ -types of motifs

Unfortunately, direct determination of the overall binding constant for $[Zn(\mathbf{1})(\mathbf{2})]^{2+}$ motifs was impossible, because (i) $[Zn(\mathbf{1})]^{2+}$ motifs are always in equilibrium with $[Zn(\mathbf{1})_2]^{2+}$ even at a 1:1 ratio of Zn^{2+} and **1**, and (ii) upon addition of terpyridine **2** to a 1:1 mixture of Zn^{2+} and **1,** $[Zn(\mathbf{2})_2]^{2+}$ complex is produced as a kinetically controlled product that only dissociates with time to the thermodynamically more stable $[Zn(\mathbf{1})(\mathbf{2})]^{2+}$ complex. The kinetics of these complex pathways is too slow to get reliable spectroscopic data from UV Vis.

As a way out we determined the complexation constant for $[Zn(\mathbf{1})(2)]^{2+}$ motifs indirectly via a thermochemical cycle, as described in Scheme 1.[6] The ratio of (**C1**+**C2**) : (**C5**+**C6**) in full equilibrium was determined to 1:0.06 (Figure S31), as based on ^{1}H-NMR integration. The overall binding constant (log β) for **C2**, **C5**, and **C6** are 9.47, 10.27, and 12.40, respectively.[7]



Scheme S1: Reshuffling of components in a 6-component *completive* library.[6]

Using the thermochemical cycle, we derived log $\beta_{\mathbf{C1}}$ as:

$$\log \beta_{\mathbf{C1}} = \log(K_{eq}) - \log \beta_{\mathbf{C2}} + \log \beta_{\mathbf{C5}} + \log \beta_{\mathbf{C6}}$$

Implementing the experimental values into the above equation, we determined log $\beta_{\mathbf{C1}} \approx 14$

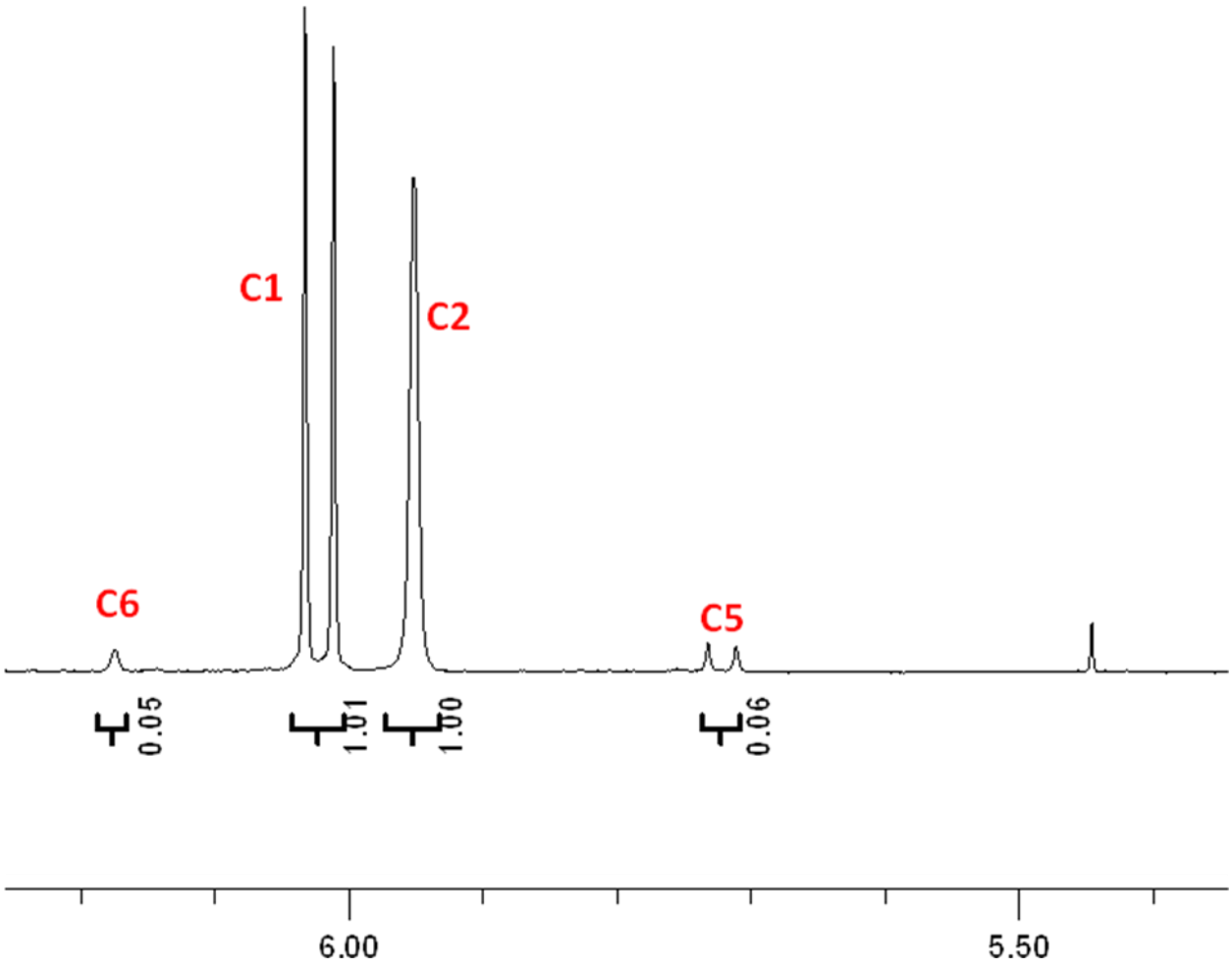


Figure S32. Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 298 K) of an equimolar mixture of **C5** and **C6** after full equilibration. The spectrum was recorded after 26 min of mixing at 298 K.[6] Integrals were measured by using MestRe-C software. Peaks at 5.72 ppm (**C5**, a'''-H), 6.02 ppm (**C1**, a'''-H), 5.95 ppm (**C2**, a'''-H) and 6.17 ppm (**C6**, a'''-H) were used.

X-ray structure analysis

Table S1. Crystal data for compound **C3** = [Cu(**3**)(**5**)]PF_6

Compound name	**C3** (CCDC 933109)
Empirical formula	$C_{35}H_{32}CuIN_3F_6P$
Formula weight	830.05
Temperature/ K	171(2)
Wavelength/ Å	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
a/ Å	11.8031(6)
b/ Å	12.1213(6)
c/ Å	14.0357(7)
α/ deg	91.4930(10)
β/ deg	113.8990(10)
γ/ deg	111.5580(10)
Volume/ $Å^3$	1670.95(14)
Z	2
Density (calculated) (g/cm^3)	1.650
Absorption coefficient ($mm^{-1)}$	1.689
F(000)	828
Reflections collected	20122
Independent reflections	8042 [*R*(int) = 0.0260]
Reflections with I > 2sigma(I)	6675
Absorption correction type	Multi-scan
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.027
Final R indices	[I>2sigma(I)] *R*1 = 0.0314, *wR*2 = 0.0710
R indices (all data)	*R*1 = 0.0431, *wR*2 = 0.0754

Table S2. Selected bond lengths (Å) and angles (deg) for **C3**

Cu1–N1	1.9948(18)	N1–Cu1–N2	81.25(7)
Cu1–N2	2.0997(17)	N1–Cu1–N3	150.04(7)
Cu1–N3	1.9135(18)	N2–Cu1–N3	128.66(7)

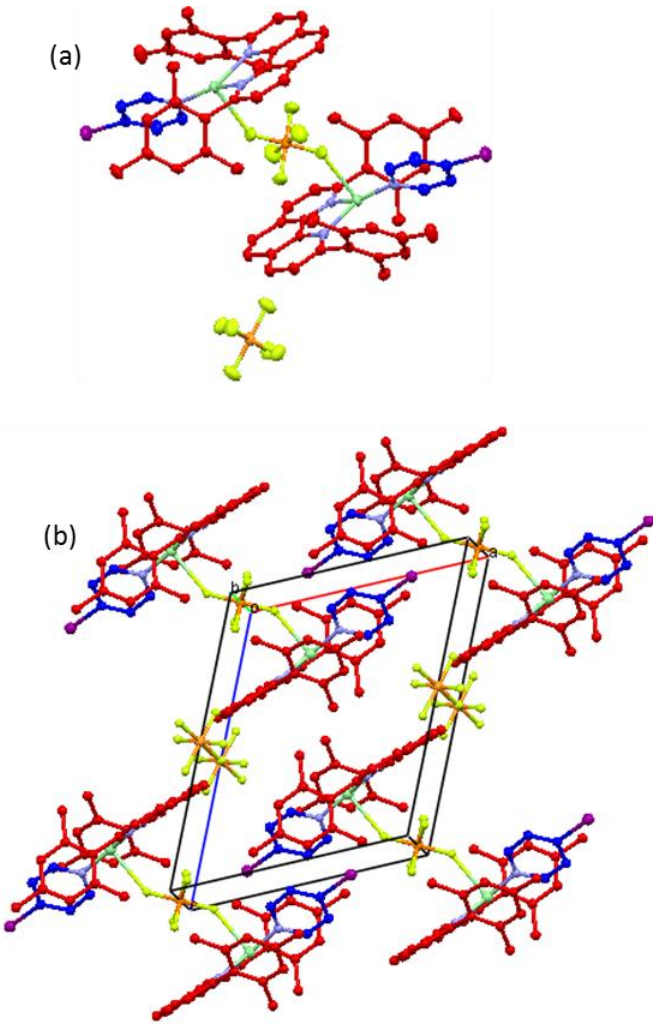


Figure S33: Solid state structure of (a) **C3** = [Cu(**3**)(**5**)]PF_6 (thermal ellipsoids were drawn at the 50% probability level) (b) Ball and stick representation of the packing diagram of **C3**. Hydrogen atoms are omitted for clarity.

Energy minimised structures using MM+ force field

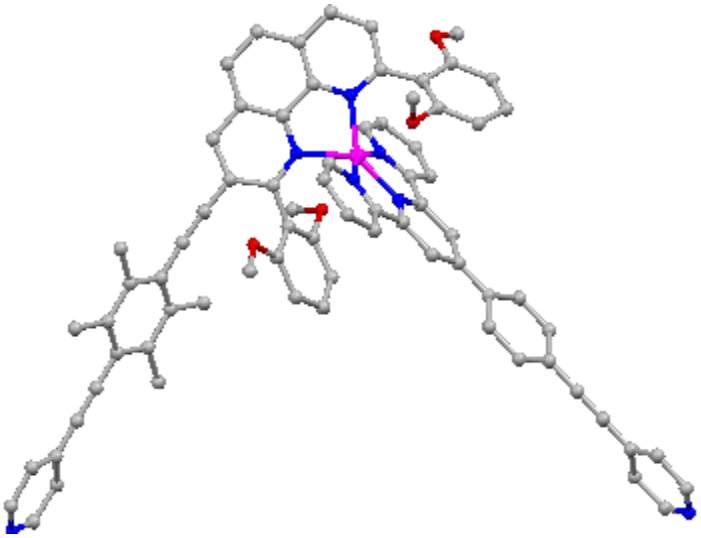


Figure S34. Energy minimised structure of the heteroleptic complex **C4**. Counter anions are not included. Hydrogens are omitted for clarity.

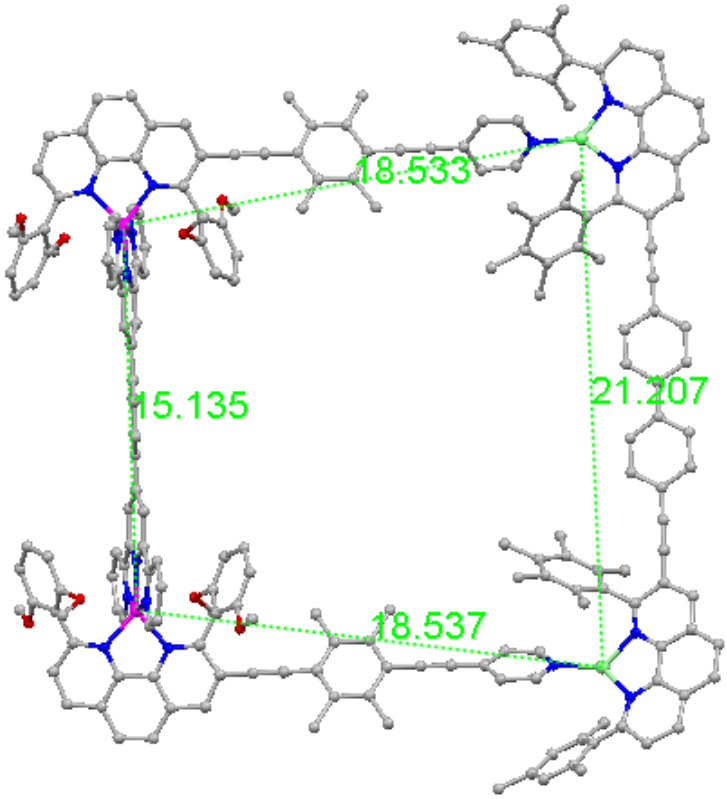


Figure S35. Energy minimised structure of the isosceles trapezoid **TZ**. Counter anions and alkoxy chains are not included. Hydrogens are omitted for clarity.

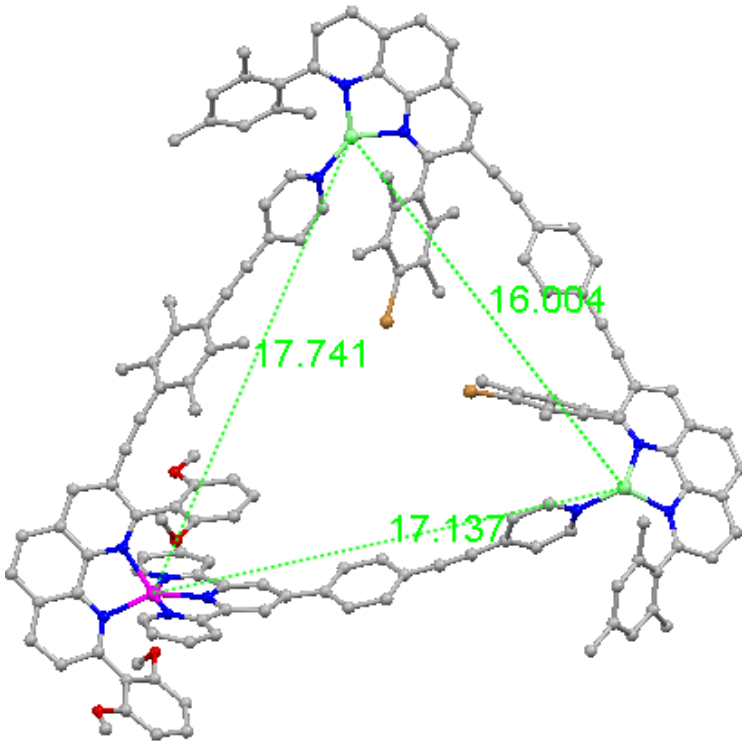


Figure S36. Energy minimised structure of the scalene triangle **TA**. Counter anions and alkoxy chains are not included. Hydrogens are omitted for clarity.

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.

(2) (a) G. M. Sheldrick, SHELXS97: *Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1997. (b) G. M. Sheldrick, *Program for Crystal Structural Refinement*; University of Göttingen: Göttingen, Germany, 1997. (c) G. M. Sheldrick, *Acta Cryst*., 2008, **A64**, 112.

(3) (a) K. Mahata and M. Schmittel, *J. Am. Chem. Soc*., 2009, **131**, 16544. (b) K. Mahata, M. L. Saha and M. Schmittel, *J. Am. Chem. Soc*., 2010, **132**, 15933.

(4) M. Schmittel and K. Mahata, *Inorg. Chem*., 2009, **48**, 822.

(5) M. L. Saha and M. Schmittel, *Org. Biomol. Chem*., 2012, **10**, 4651.

(6) M. L. Saha, S. Pramanik and M. Schmittel, *Chem. Commun.* 2012, **48**, 9459.

(7) (a) M. Schmittel, , R. S. K. Kishore, H. Cölfen and J. W. Bats, *J. Am. Chem. Soc*., 2005, **127**, 11544. (b) V. Kalsani, Dissertation, University of Siegen, 2005.