Electronic Supporting Information (ESI)

for

Spontaneous and Catalytic Fusion of Supramolecules

Manik Lal Saha, Susnata Pramanik, Michael Schmittel*

Center of Micro- and Nanochemistry and Engineering, Organische Chemie I, Universität Siegen, Adolf-Reichwein-Str. 2, D-57068 Siegen, Germany,
E-mail: **schmittel@chemie.uni-siegen.de**
Fax: (+49) 271-740-3270

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Synthesis

General

All commercial reagents were used without further purification. The 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 recorded on a Bruker Avance 400 MHz, whereas DOSY NMR, and all kinetics data were recorded on a Varian VNMR-S 600 MHz spectrometer, equipped with a 3 mm triple resonance inverse probe, using the deuterated solvent as the lock and residual solvent as the internal reference. The following abbreviations were utilised to describe peak patterns: s = singlet, d = doublet, t = triplet, dd = doublet of doublet, 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. All DOSY measurements were carried out without temperature regulation (room temperature was 295 K) using the 'Dbppste' pulse sequence from the Varian library. The gradient ramp was built in 32 steps for **T1** and in 64 steps for **R1** and **T2** with gradient strength from 0.16 G/cm to 40.8 G/cm and gradient length 2 millisecond. The diffusion delay has been 80 ms for **T1** and **R1** and 100 ms for **T2**. The DOSY data were processed according to mono exponential fitting[1] by VNMRJ 2.2C for **T1** and VNMRJ 3.2A for **R1** and **T2**. For **R1** and **T2** data were corrected for non-uniform gradient. Differential pulse voltammetry (DPV) was measured on a Parstat 2273 in dry acetonitrile. 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. The numbering of the compounds follows the scheme in the publication. Complexes **C3**, **C4**[2] and compounds **11**,[3] **12**[4] (precursors for **7**) as well as ligands **8**[5] and **9**[6] were synthesised according to known procedures. Energy minimised structures were obtained using the MM^{+} forced field as implemented in Hyperchem® 8.0.

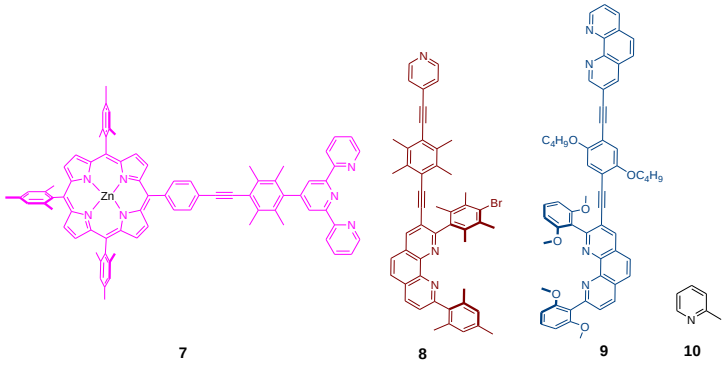
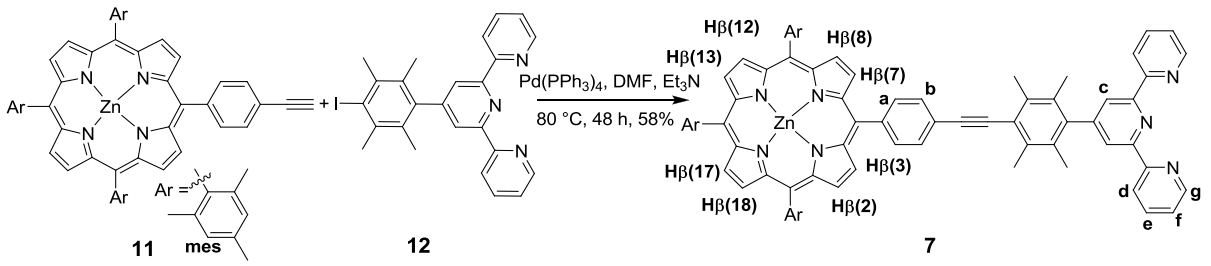


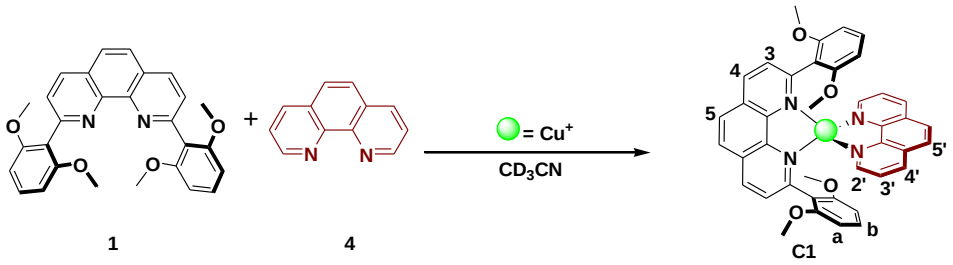
Chart 1: Ligands used in the present study.

Synthesis of zinc(II)-*meso*-5-{4-(2-[4-(2,2´:6´,2´´)terpyridine)duryl]ethynyl)}phenyl-10,15,20-trimesitylporphyrin (7).



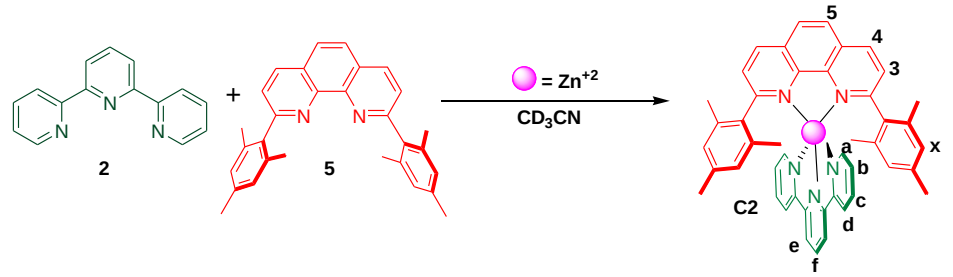
In an oven-dried 100 mL three-neck round-bottom flask, a mixture of zinc(II)-5-(4´-ethynyl)phenyl-10,15,20-trimesitylporphyrine (**11**, 337 mg, 407 μmol), 4´-(4-iodo-2,3,5,6-tetramethylphenyl)-(2,2´:6´,2´´)terpyridine (**12**, 100 mg, 204 μmol) and $Pd(PPh_3)_4$ (9.80 mg, 8.48 μmol) were stirred in dry DMF (20 mL) and triethylamine (10 mL) at 80 °C for 48 h under nitrogen atmosphere. The reaction mixture was then cooled down to room temperature and the solvents were removed under reduced pressure. The residue was dissolved in dichloromethane (200 mL) and washed with water (150 mL). After drying over Na_2SO_4, the organic solvent was evaporated to afford a pink residue. The crude product was purified using column chromatography (SiO_2). The first separation was effected with dichloromethane as eluent. Finally, the target compound was furnished by size exclusion chromatography (BioBeads SX-3, swollen in toluene/dichloromethane (9:1), run under gravity flow).Yield 58%; mp = 269 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.91 (d, ^3J = 4.8 Hz, 2 H, $\beta_{[3,7]}$-H), 8.78 (d, ^3J = 4.8 Hz, 2 H, $\beta_{[2,8]}$-H), 8.74 (dd, ^3J = 8.0 Hz, ^4J = 1.2 Hz, 2 H, d-H), 8.72-8.71 (m, 6 H, g-, $\beta_{[(18,12,\ 17,13)]}$-H), 8.35 (s, 2 H, c-H), 8.24 (d, ^3J = 8.4 Hz, 2 H, [a/b]-H), 7.97 (d, ^3J = 8.4 Hz, 2 H, [a/b]-H), 7.91 (dt, ^3J = 8.0 Hz, ^4J = 2.0 Hz, 2 H, e-H), 7.36 (ddd, ^3J = 8.0 Hz, ^3J = 4.8 Hz, ^4J = 1.2 Hz, 2 H, f-H), 7.29 (bs, 4 H, mes-H), 7.27 (bs, 2 H, mes-H), 2.70 (s, 6 H, Me), 2.64 (s, 6 H, Me), 2.63 (s, 3 H, Me), 2.08 (s, 6 H, Me), 1.86(s, 6 H, Me), 1.85 (s, 12 H, Me); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.3, 155.7, 152.9, 149.9, 149.9, 149.7, 149.7, 149.2 (2C), 142.8, 140.2, 139.3(2C), 139.1, 139.0, 137.4, 136.9, 136.2, 134.5, 131.9, 131.2, 131.1, 131.1 (2C), 130.7, 129.5, 127.6 (2C), 123.8, 123.1 121.9, 121.3, 119.3, 118.9, 118.7, 97.2, 89.7, 21.8, 21.7 (2C), 21.5, 18.7, 18.2; IR (KBr) ν 3434, 3104, 2916, 2855, 2730, 2354, 1808, 1582, 1467, 1385, 1382, 1263, 1203, 1115, 1063, 947, 833, 796, 725, 655, 511;ESI-MS *m*/*z* (%) 1190.5 (100) $[M + H]^+$; Anal. Calcd for $C_{80}H_{67}N_7Zn{\bullet}H_2O$: C, 79.42; H, 5.75; N, 8.10. Found: C, 79.78; H, 5.66; N, 8.08.

Synthesis of complex C1 = [Cu(1)(4)](PF$_6$)



2,9-Bis(2,6-dimethoxyphenyl)-1,10-phenanthroline (**1**, 10.2 mg, 22.5 µmol), 1,10-phenanthroline (**4**, 4.06 mg, 22.5 µmol), and [Cu(MeCN)$_4$]PF$_6$ (8.40 mg, 22.5 µmol) were loaded in an NMR tube and dissolved in CD_3CN. The resultant mixture was subjected to analytical characterisation without any further purification. Yield quantitative; mp >250 °C; ^{1}H NMR (400 MHz, CD_3CN): δ = 8.70 (d, ^3J = 8.4 Hz, 2 H, 4-H), 8.47-8.43 (m, 4 H, 2'-, 4'-H), 8.22 (s, 2 H, 5-H), 7.94 (s, 2 H, 5'-H),7.82 (d, ^3J = 8.4 Hz, 2 H, 3-H), 7.74 (dd, ^3J = 8.0 Hz, ^3J = 4.8 Hz, 2 H, 3'-H), 6.40 (t, ^3J = 8.4Hz, 2 H, b-H), 5.72 (d, ^3J = 8.4Hz, 4 H, a-H), 3.22 (s, 12 H, OMe); IR (KBr) ν 3665, 3581, 3432, 3114, 3002, 2942, 2840, 2187, 1932, 1590, 1511, 1474, 1427, 1357, 1253, 1176, 1110,1024, 945, 844, 725, 656, 557; ESI-MS: *m*/*z* (%) 695.1 (100) [M−PF$_6$]$^+$; Anal calcd for $C_{40}H_{32}CuF_6N_4O_4P•H_2O$: C, 55.91; H, 3.99; N, 6.52; found: C, 56.16; H, 3.91; N, 6.29.

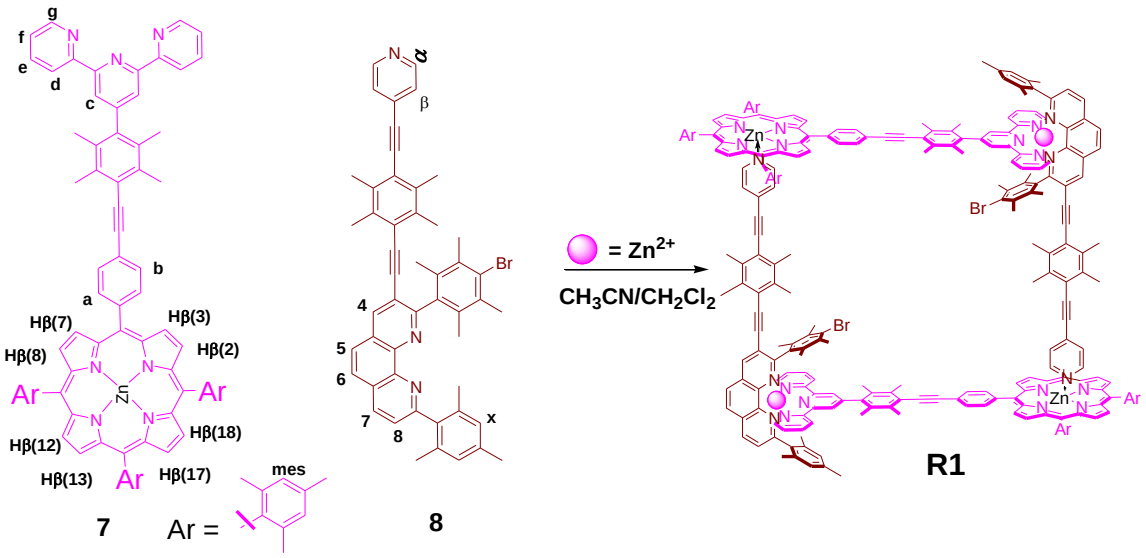
Synthesis of complex C2 = [Zn(2)(5)](OTf)$_2$



2,9-Dimesityl-1,10-phenanthroline (**5**, 5.46 mg, 13.1 µmol) and Zn(OTf)$_2$ (4.76 mg, 13.1 µmol) were loaded into a 25 mL round-bottom flask and dissolved in 5 mL of DCM/ CH_3CN (1:4) furnishing a light yellow solution. After addition of 2,2´:6´,2´´-terpyridine (**2**, 3.06 mg, 13.1 µmol), the mixture was placed in a ultrasonic bath at 60 °C temperature for 1 h. The reaction mixture was then cooled down to room temperature and the solvents were removed under reduced pressure. The resultant mixture was subjected to analytical characterisation without any further purification. Yield quantitative; ^{1}H NMR (400 MHz, CD_3CN): δ = 9.12 (d, ^3J = 8.4 Hz, 2 H, 4-H), 8.53 (s, 2 H, 5-H), 8.51-8.41(m, 5 H, d-, e-, f-H), 8.25 (dt, ^3J = 8.0 Hz, ^4J = 1.6 Hz, 2 H, c-H), 8.14 (d, ^3J = 8.4 Hz, 2 H, 3-H), 7.73 (ddd, ^3J = 5.2 Hz, ^4J = 1.6 Hz,

^5J = 1.0 Hz, 2 H, a-H), 7.46 (ddd, ^3J = 8.0 Hz, ^3J = 5.2 Hz, ^4J = 1.2 Hz, 2 H, b-H), 6.17 (s, 4 H, x-H), 1.76 (s, 6 H, Me), 1.10 (s, 12 H, Me); IR (KBr) *v* 3474, 3073, 2958, 2924, 2856, 1727, 1596, 1473, 1381, 1259, 1153, 1109, 1026, 843, 802, 727, 637, 563, 518; ESI-MS: *m*/*z* (%) 356.5 (5) $[M-2OTf]^{2+}$, 862.3 (100) $[M-OTf]^{+}$; Anal calcd for $C_{47}H_{39}F_6N_5O_6S_2Zn{\bullet}CH_2Cl_2$: C, 52.49; H, 3.76; N, 6.38; S, 5.84; found: C, 52. 50; H, 3.41; N, 6.09; S, 5.49.

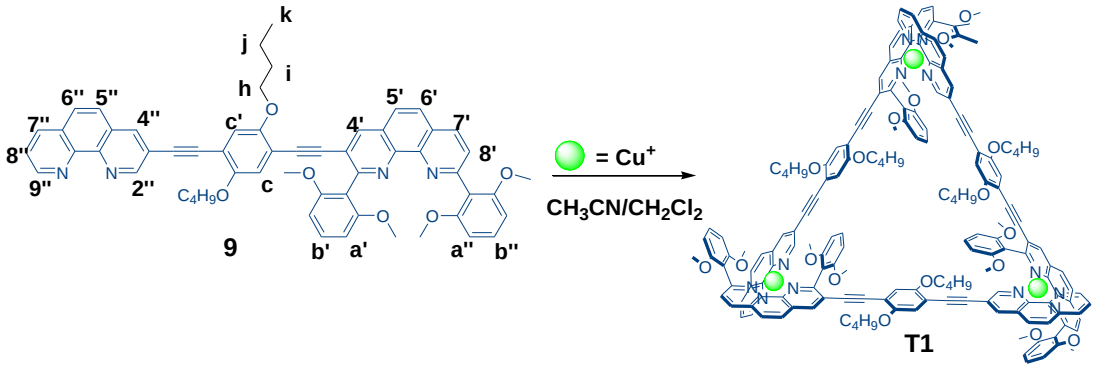
Synthesis of rectangle R1.



In an oven-dried 10 mL single-neck round-bottom flask, a mixture of **7** (1.25 mg, 1.05 μmol), **8** (0.80 mg, 1.05 μmol), and $Zn(OTf)_2$ (0.38 mg, 1.05 μmol) was refluxed in 5 mL of CH_2Cl_2/CH_3CN (8:1) for 1 h. The reaction mixture was then cooled down to room temperature and the 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 = 9.07 (s, 2 H, 4-H), 9.00 (d, ^3J = 8.4 Hz, 2 H, 7-H), 8.83 (d, ^3J = 4.8 Hz, 4 H, $\beta_{[3,7]}$-H), 8.68 (d, ^3J = 4.8 Hz, 4 H, $\beta_{[2,8]}$-H), 8.64 (d, ^3J = 4.8 Hz, 4 H, $\beta_{[12,18]}$-H), 8.62 (d, ^3J = 4.8 Hz, 4 H, $\beta_{[13,17]}$-H), 8.49 (d, ^3J = 9.6 Hz, 2 H, [5/6]-H), 8.44 (d, ^3J = 9.6 Hz, 2 H, [5/6]-H), 8.38 (d, ^3J = 8.0 Hz, 4 H, [a/b]-H), 8.30 (d, ^3J = 8.0 Hz, 2 H, [a/b]-H), 8.29 (t, ^3J = 8.0 Hz, 4 H, e-H), 8.19 (s, 4 H, c-H), 8.06 (d, ^3J = 4.8 Hz, 4 H, g-H), 7.98 (d, ^3J = 8.0 Hz, 4 H, d-H), 7.96 (d, ^3J = 8.4 Hz, 2 H, 8-H), 7.65 (dd, ^3J = 8.0 Hz, ^4J = 4.8 Hz, 4 H, f-H), 7.28 (bs, 8 H, mes-H), 7.27 (bs, 4 H, mes-H), 6.30 (s, 4 H, x-H), 5.62 (br, 4 H, β-H), 3.41 (bs, 4 H, α-H), 2.78 (s, 6 H, Me), 2.77(s, 6 H, Me), 2.61 (s, 6 H, Me), 2.61 (s, 12 H, Me), 2.20 (s, 6 H, Me), 2.10 (s, 6 H, Me), 1.96 (s, 6 H, Me), 1.91 (s, 12 H, Me), 1.83 (s, 6 H, Me), 1.83 (s, 12 H, Me), 1.79 (s, 30 H, Me), 1.74 (s, 12 H, Me), 1.25 (s, 12 H, Me),

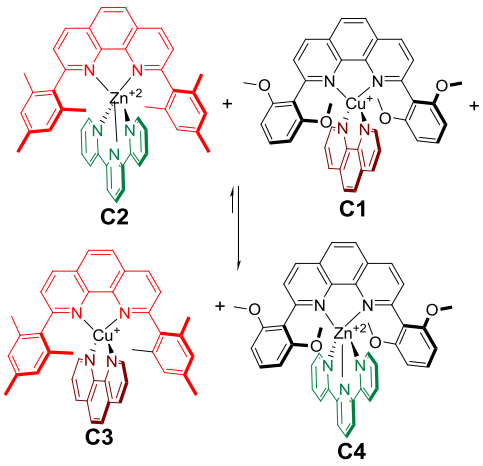
1.21 (s, 12 H, Me); IR (KBr) *v* 3436, 2923, 2855, 2732, 2491, 2360, 2344, 2204, 1625, 1607, 1462, 1427, 1383, 1261, 1162, 1105, 1029, 801, 724, 655, 641, 572; ESI-MS: *m*/*z* (%) 1011.7 (100) $[M-4OTf]^{4+}$, 1399.0 (30) $[M-3OTf]^{3+}$; Anal calcd for $C_{264}H_{222}Br_2F_{12}N_{20}O_{12}S_4Zn_4 \bullet 3CH_2Cl_2$: C, 65.46; H, 4.69; N, 5.72; S, 2.62; found: C, 65.37; H, 4.80; N, 5.46; S, 2.54.

Synthesis of equilateral triangle T1.



In an oven-dried 10-mL single-neck round-bottom flask, a mixture of the unsymmetrical bisphenanthroline **9** (6.26 mg, 6.96 μmol) and $[Cu(MeCN)_4]PF_6$ (2.59 mg, 6.96 μmol) were refluxed in 5 mL of CH_2Cl_2/CH_3CN (1:4) for 1 h. The reaction mixture was then cooled down to room temperature and the 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_3CN): δ = 8.83 (s, 1 H, 4'-H), 8.81 (s, 1 H, 4'-H), 8.78 (s, 1 H, 4'-H), 8.76 (s, 1 H, 4'-H), 8.74- 8.69 (m, 4 H, 7'-H), 8.54- 8.43 (m, 16 H, 2'', 4'', 7'', 9''-H), 8.28- 8.16 (m, 8 H, 5', 6'-H), 8.02- 7.74 (m, 16 H, 8', 5'', 6'', 8''-H), 7.05 (s, 2 H, [c'/c'']-H), 7.00 (s, 1 H, [c'/c'']-H), 6.98 (s, 1 H, [c'/c'']-H), 6.52- 6.38 (m, 8 H, b',b''-H), 6.33 (s, 1 H, [c'/c'']-H), 6.31 (s, 1 H, [c'/c'']-H), 6.30 (s, 1 H, [c'/c'']-H), 6.27 (s, 1 H, [c'/c'']-H),), 6.03- 5.89 (m, 6 H, [a'/a'']-H), 5.83- 5.79 (m, 2 H, [a'/a'']-H), 5.67- 5.54 (m, 8 H, [a'/a'']-H), 3.94- 3.88 (m, 4 H, h-H), 3.84- 3.70 (m, 12 H, h-H), 3.54 (s, 3 H, OMe), 3.53 (s, 9 H, OMe), 3.49 (s, 3 H, OMe), 3.44 (s, 3 H, OMe), 3.38 (s, 3 H, OMe), 3.36 (s, 3 H, OMe), 3.07 (s, 3 H, OMe), 3.03 (s, 3 H, OMe), 3.02 (s, 6 H, OMe), 2.94 (s, 3 H, OMe), 2.93 (s, 3 H, OMe), 2.92(s, 6 H, OMe), 1.65- 1.27 (m, 32 H, i, j-H), 0.99- 0.87 (m, 15 H, k-H), 0.74 (t, ^3J = 7.2 Hz, 3 H, k-H), 0.63 (t, ^3J = 7.2 Hz, 3 H, k-H), 0.37 (t, ^3J = 6.4 Hz, 3 H, k-H); IR (KBr) *v* 3436, 2930, 2866, 2207, 1821, 1665, 1593, 1471, 1428, 1252, 1210, 1110, 1024, 842, 783, 725, 655, 557; ESI-MS: 962.0 (100) $[M-3PF_6]^{3+}$, 1515.7 (10) $[M-2PF_6]^{2+}$; Anal calcd for $C_{174}H_{150}Cu_3F_{18}N_{12}O_{18}P_3 \bullet 2CH_2Cl_2$: C, 60.53; H, 4.44; N, 4.81; found: C, 60.85; H, 4.30; N, 4.79.

Synthesis of complex C3 = [Cu(5)(4)](PF$_6$) and C2 = [Zn(1)(2)](OTf)$_2$ starting from C1 and C2.



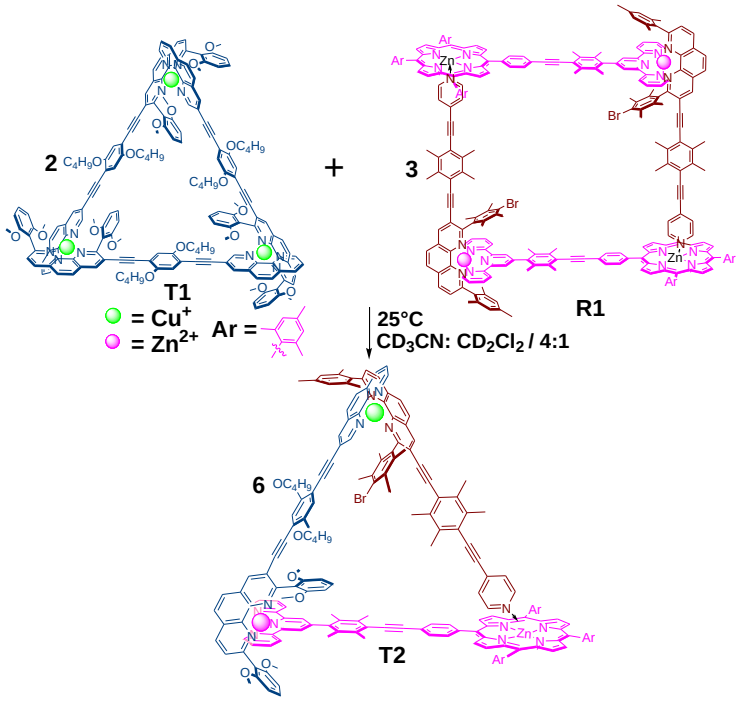
Preparation of standard CH_3NO_2 solution

In an oven-dried 5 mL single-neck round-bottom flask 200 µL of CD_3CN were added to CH_3NO_2 (1 µL) and the resultant solution was used as a stock solution.

Experimental Procedure

C1 (0.93 mg, 1.10 µmol) and **C2** (1.12 mg, 1.10 µmol) were loaded in an oven-dried 5-mL single-neck round-bottom flask, and 1265 µL of CD_3CN was added. To this solution 1µL of the freshly prepared standard CH_3NO_2/CD_3CN mixture was also added and a portion of the mixture was then kept in the NMR machine for 2 h at 25 °C.

Synthesis of scalene triangle T2 starting from T1 and R1.



Preparation of standard CH_3NO_2 solution

In an oven-dried 5 mL single-neck round-bottom flask 200 µL of CD_2Cl_2 was added to 1 µL of CH_3NO_2; the resultant solution was used as a stock solution.

*Preparation of standard 2-methylpyridine (**10**) solution*

In an oven-dried 10 mL single-neck round-bottom flask 5 mL CH_2Cl_2 was added to 5 µL of 2-methylpyridine (**10**) and the resultant solution was used as a stock solution for the following experiment.

Procedure a: Reaction performed without 2-methylpyridine

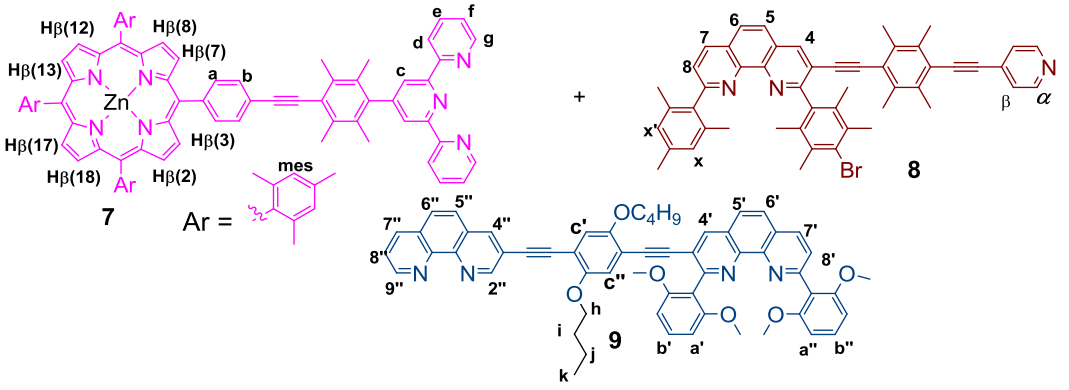
T1 (0.72 mg, 0.21 µmol) and **R1** (1.51 mg, 0.32 µmol) were loaded in an oven-dried 5 mL single-neck round-bottom flask, and 250 µL CD_2Cl_2/CD_3CN (1:4) mixture were added. To this solution 1 µL of the freshly prepared standard CH_3NO_2/CD_2Cl_2 mixture was added and a portion of the mixture was then kept in the NMR machine for 15 h at 25 °C.

Procedure b: Reaction performed with 2-methylpyridine

T1 (0.72 mg, 0.21 µmol) and **R1** (1.51 mg, 0.32 µmol) were loaded in an oven-dried 5-mL single-neck round-bottom flask, and 250 µL CD_2Cl_2/CD_3CN (1:4) mixture were added. To this solution 1 µL of the freshly prepared standard CH_3NO_2/CD_2Cl_2 mixture and 3.1 µL of the freshly prepared standard 2-methylpyridine (**10**) mixture were added and a portion of the mixture was then kept in the NMR machine for 2 h at 25°C.

Characterisation of the scalene triangle T2

For the convenience of data analysis, in the following procedure we prepared a fresh sample and recorded the ^{1}H-NMR, ^{1}H-^{1}H COSY, DOSY, DPV, elemental analysis, and ESI-MS data for **T2**.



T1 (1.98 mg, 0.59 µmol) and **R1** (4.15 mg, 0.89 µmol) were loaded in an oven-dried 5-mL single-neck round-bottom flask, and 500 µL CH_2Cl_2/CH_3CN (1:4) mixture were added. Then the mixture was placed in a HAAKE-N2 thermostat (temperature stability of ±0.1 °C) at 25 °C. After 17 h, the solvents were removed first in a flow of argon and then under reduced

pressure. The resultant mixture was subjected to analytical characterisation without any further purification. mp >250 °C; ^{1}H NMR (400 MHz, CD_3CN) δ = 9.08 (d, ^{3}J = 8.4 Hz, 1 H, 7-H), 9.07 (s, 1 H, 4-H), 8.90 (s, 1 H, 4′-H), 8.79 (d, ^{3}J = 4.4 Hz, 2 H, $\beta_{[3,7]}$-H), 8.75 (d, ^{3}J = 8.4 Hz, 1 H,7′-H), 8.58-8.52 (m, 8 H, 4″, 7″, $\beta_{[2, 8, 12, 13, 17, 18]}$-H), 8.49 (s, 2 H, c-H), 8.47-8.44 (m, 2 H, 2’’, 9’’-H), 8.36-8.32 (m, 2 H, d-H), 8.23 (d, ^{3}J = 8.4 Hz, 4 H, a, b-H), 8.19-8.11 (m, 4 H, e, 5, 5’-H), 8.08 (d, ^{3}J = 8.4 Hz, 1 H, 8-H), 7.92 (d, ^{3}J = 9.2 Hz, 2 H, 6, 6’-H), 7.92 (d, ^{3}J = 8.4 Hz, 1 H, [5’’/6’’]-H), 7.90 (d, ^{3}J = 8.4 Hz, 1 H, [5’’/6’’]-H), 7.85 (d, ^{3}J = 8.4 Hz, 1 H, 8′-H), 7.72 (dd, ^{3}J = 8.0 Hz, ^{3}J = 4.4 Hz, 1 H, 8″-H), 7.68 (d, ^{3}J = 4.8 Hz, 2 H, g-H), 7.50 (dd, ^{3}J = 8.4 Hz, ^{3}J = 4.8 Hz, 2 H, f-H), 7.28 (s, 1 H, [c’/c’’]-H), 7.24 (s, 2 H, mes-H), 7.18 (s, 4 H, mes-H), 7.02 (s, 1 H, [c’/c’’]-H), 6.96 (t, ^{3}J = 8.4 Hz, 1 H, [b’/b’’]-H), 6.90 (t, ^{3}J = 8.4 Hz, 1 H, [b’/b’’]-H), 6.15 (s, 1 H, [x/x′]-H), 6.09 (d, ^{3}J = 8.4 Hz, 2 H, [a’/a’’]-H), 6.05-6.02 (br, 2 H, [a’/a’’]-H), 5.97 (s, 1 H, [x/x′]-H), 5.88 (br, 2 H, β-H), 3.88 (t, ^{3}J = 6.8 Hz, 2 H, h-H), 3.67 (t, ^{3}J = 6.4 Hz, 2 H, h-H), 3.30 (br, 2 H, α-H), 2.83 (s, 3 H, OMe), 2.75 (s, 3 H, OMe), 2.74 (s, 3 H, OMe), 2.73 (s, 3 H, OMe), 2.65 (s, 3 H, Me), 2.56 (s, 3 H, Me), 2.54 (s, 3 H, Me), 2.49 (s, 6 H, Me), 2.05 (s, 3 H, Me), 1.87 (s, 3 H, Me), 1.73 (s, 15 H, Me), 1.69-16.5 (br, 21 H, Me), 1.58 (s, 3 H, Me), 1.53 (s, 3 H, Me), 1.48 (s, 3 H, Me), 1.43-1.24 (m, 14 H, i, j-H, Me), 0.92 (t, ^{3}J = 7.2 Hz, 3 H, k-H), 0.64 (t, ^{3}J = 7.2 Hz, 3 H, k-H); IR (KBr) ν 3441, 2923, 2856, 2537, 2387, 2284, 1747, 1598, 1472, 1425, 1379, 1258, 1158, 1109, 1030, 904, 843, 794, 725, 638, 558; ESI-MS: 995.7 (100) $[M-PF_6, 2OTf]^{3+}$, 1565.6 (10) $[M-2OTf]^{2+}$; Anal calcd for $C_{190}H_{161}BrCuF_{12}N_{14}O_{12}PS_2Zn_2 \bullet 2CH_2Cl_2$: C, 64.06; H, 4.62; N, 5.45; S, 1.78; found: C, 64.34; H, 4.66; N, 5.28; S, 1.69.

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

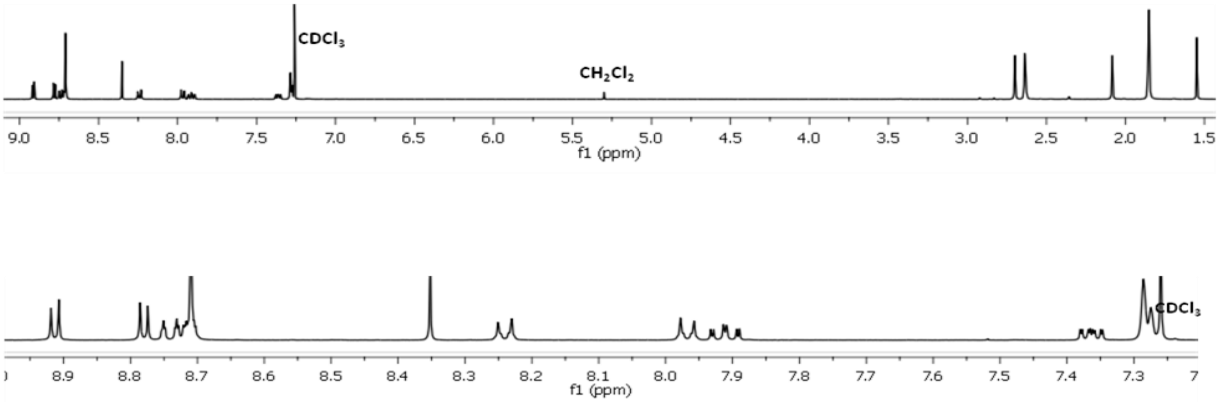


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **7**. An expanded aromatic part of the spectrum is shown at the bottom.

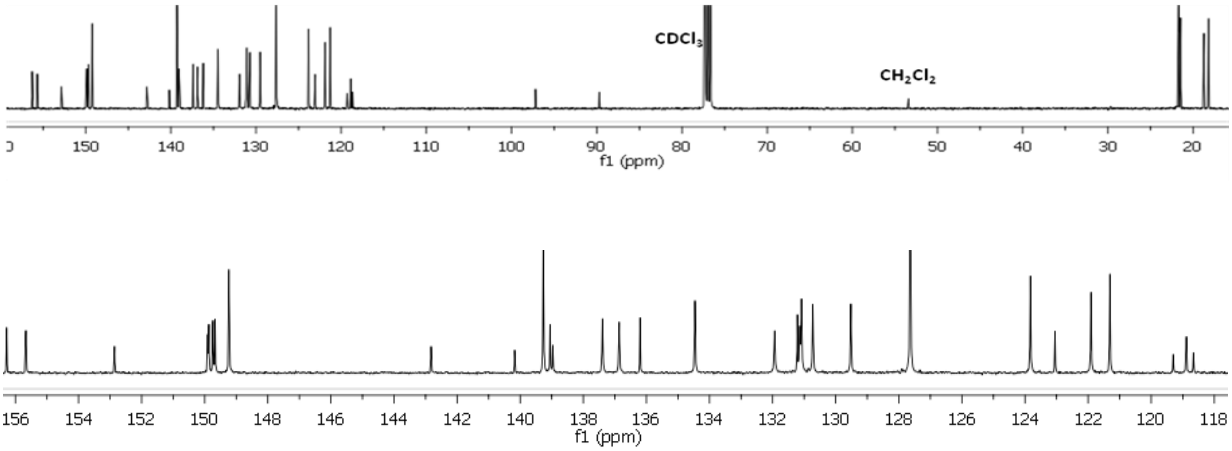


Figure S2. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **7**. An expanded aromatic part of the spectrum is shown at the bottom.

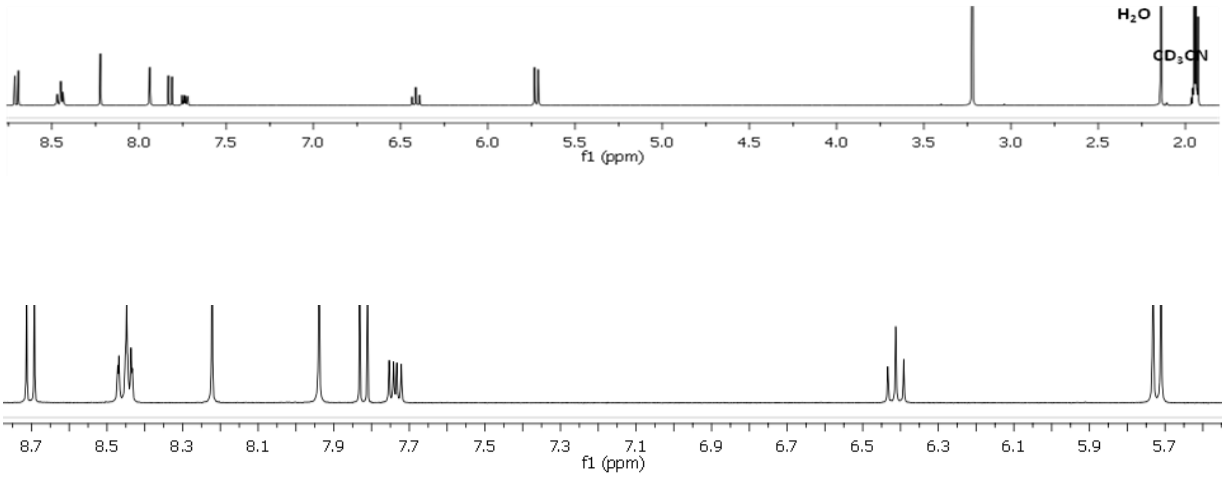


Figure S3. ^{1}H NMR spectrum (400 MHz, CD_3CN, 298 K) of **C1** = [Cu(**1**)(**4**)](PF_6). An expanded aromatic part of the spectrum is shown at the bottom.

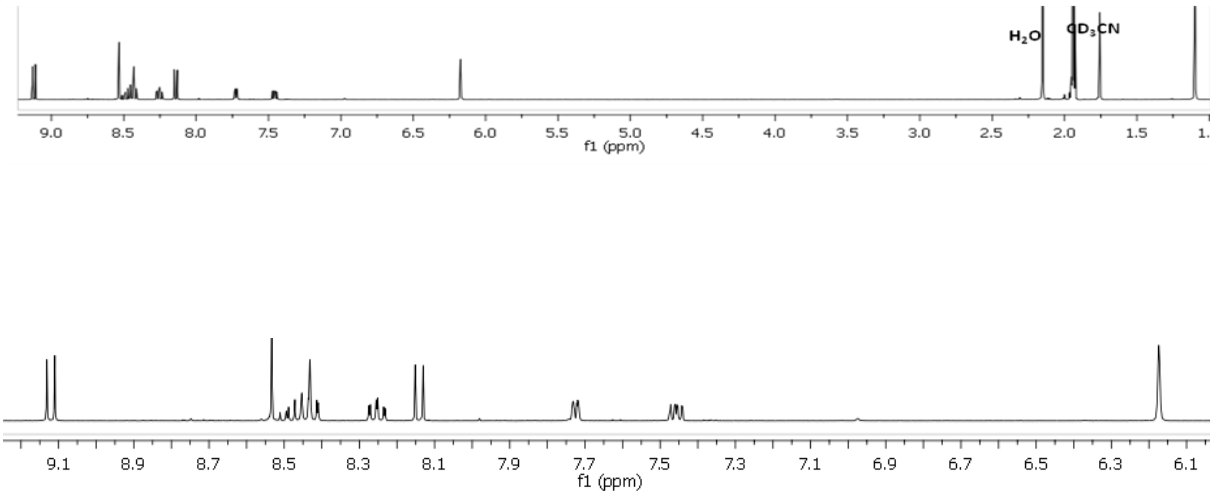


Figure S4. ^{1}H NMR spectrum (400 MHz, CD_3CN, 298 K) of **C2** = [Zn(**2**)(**5**)]($OTf)_2$. An expanded aromatic part of the spectrum is shown at the bottom.

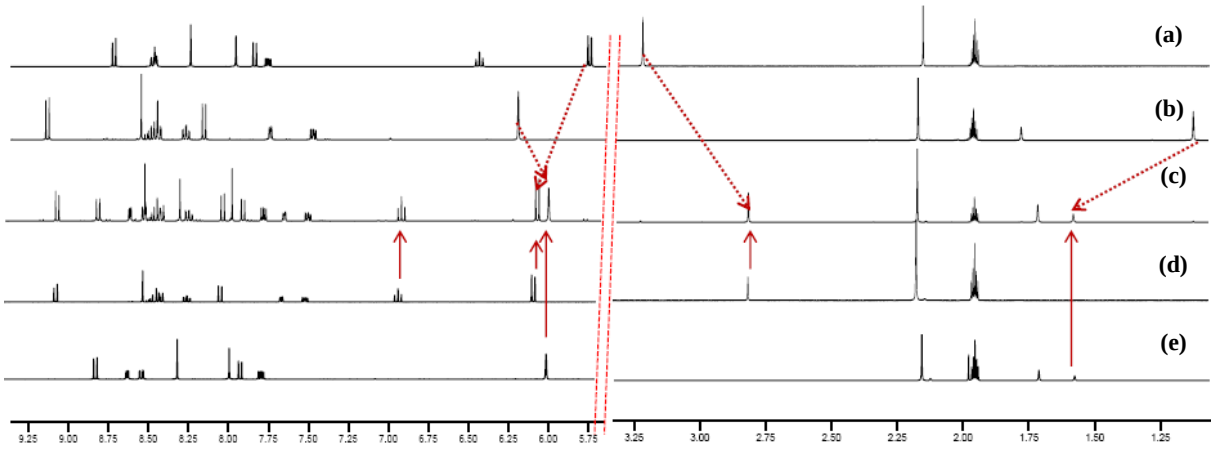


Figure S5. Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 298 K) of (a) **C1** = [Cu(**1**)(**4**)](PF_6); (b) **C2** = [Zn(**2**)(**5**)]$(OTf)_2$; (c) an equimolar mixture of **C1** and **C2** after 26 min at 25 °C; (d) **C3** = [Zn(**1**)(**2**)]$(OTf)_2$; (e) **C4** = [Cu(**4**)(**5**)](PF_6).

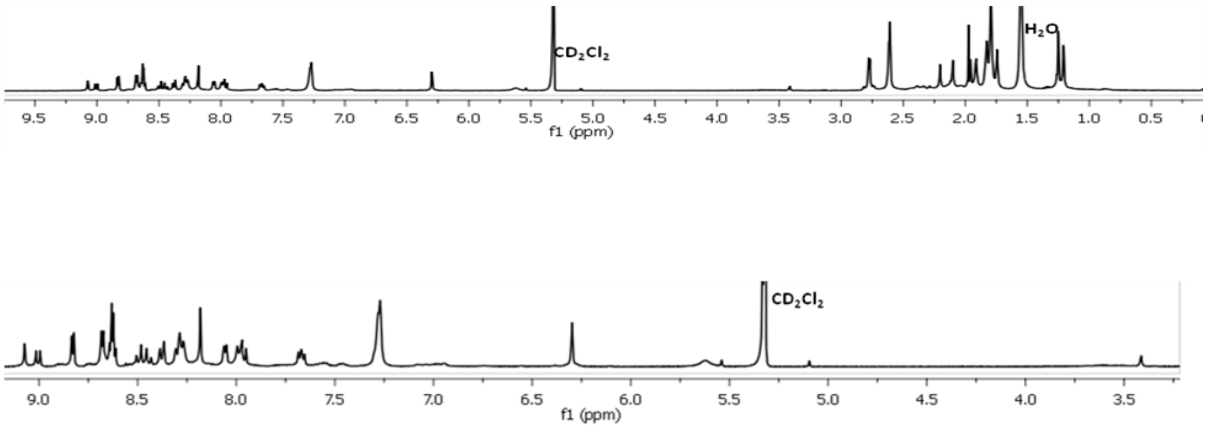


Figure S6. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of **R1** = $[Zn_2(\mathbf{7})_2(\mathbf{8})_2](OTf)_4$. An expanded part of the spectrum is shown at the bottom.

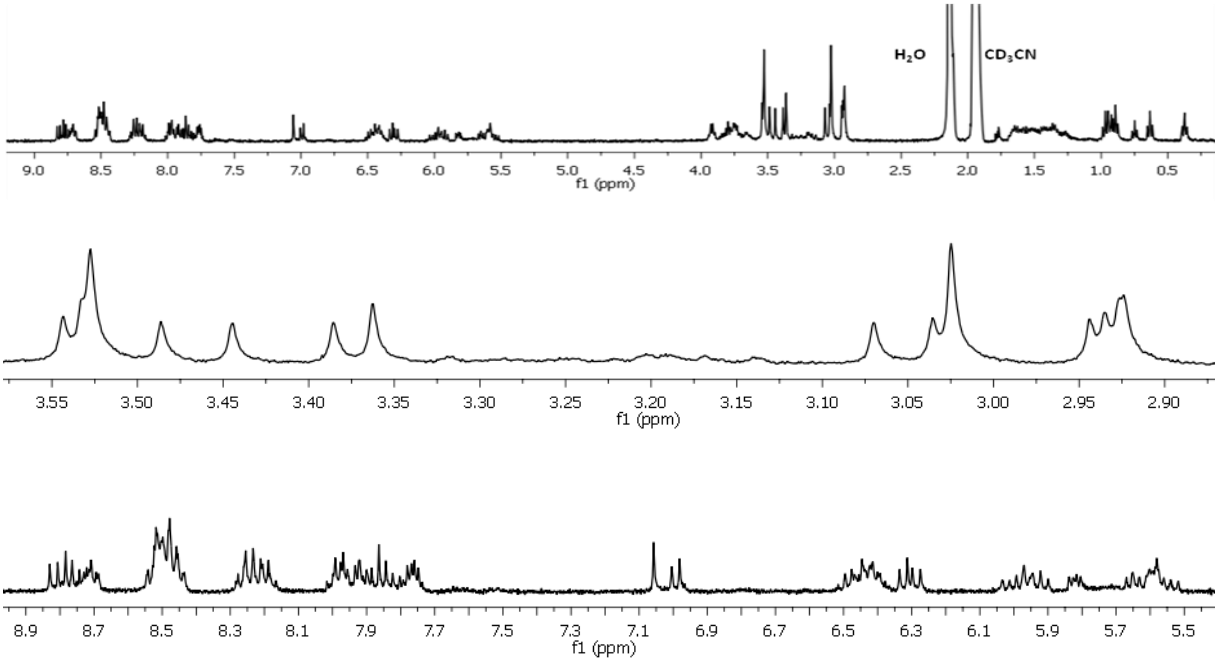


Figure S7. ^{1}H NMR spectrum (400 MHz, CD_3CN, 298 K) of **T1** = $[Cu_3(\mathbf{9})_3](PF_6)_3$. Expanded parts of the spectrum are shown at the bottom.

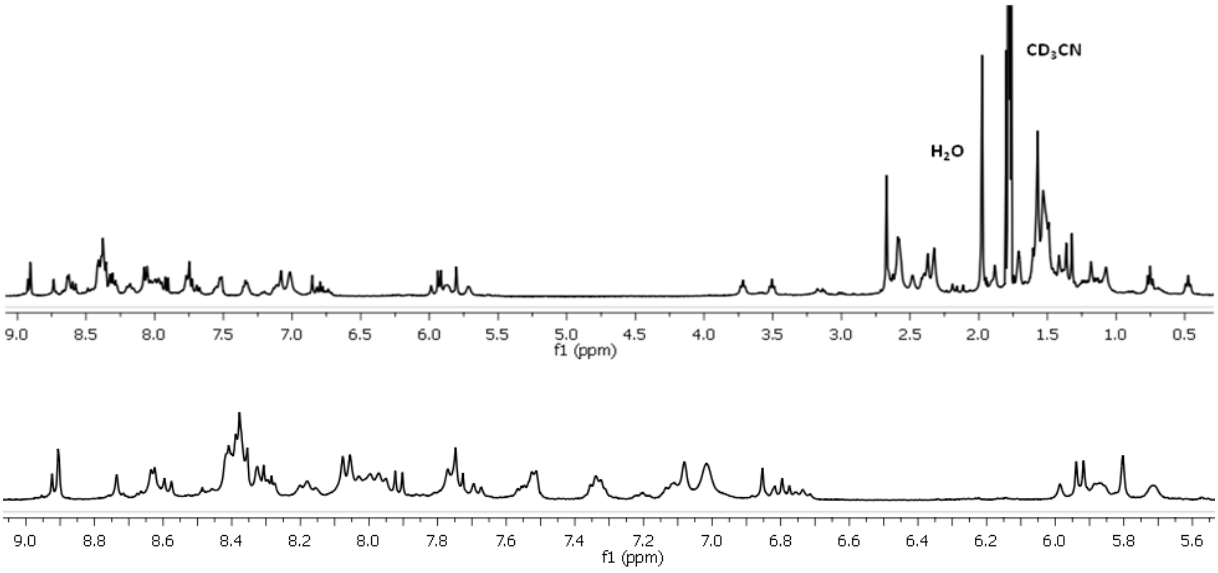


Figure S8. ^{1}H NMR spectrum (400 MHz, CD_3CN, 298 K) of **T2** = $[CuZn(\mathbf{7})(\mathbf{8})(\mathbf{9})](PF_6)(OTf)_2$. An expanded aromatic part of the spectrum is shown at the bottom.

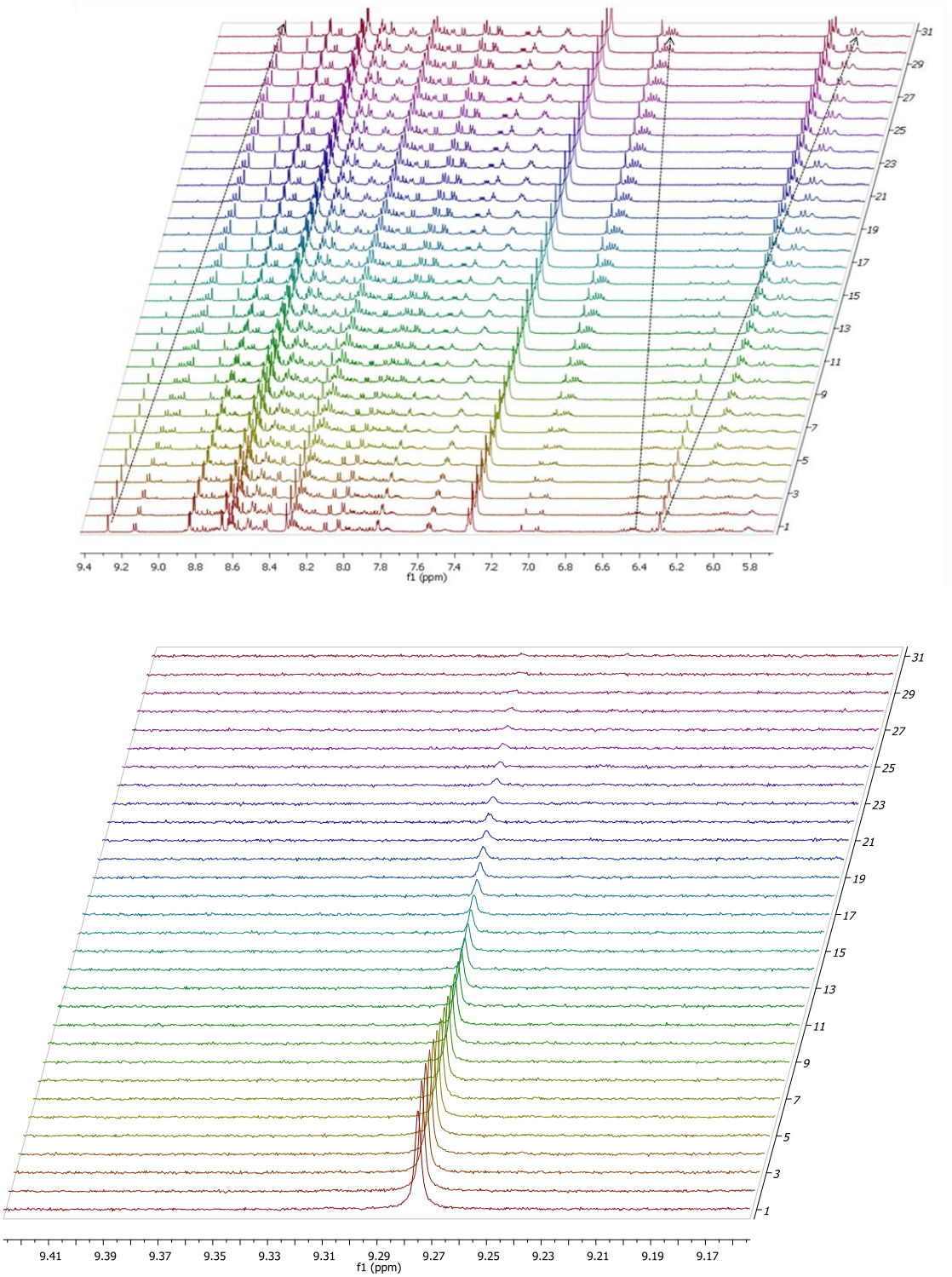


Figure S9. Stacked plot of partial ^{1}H NMR spectra (600 MHz, CD_3CN:CD_2Cl_2 (4:1), 298 K) of a mixture of **T1** and **R1** (2:3) over 15 h 9 min. Data were recorded in 30 min interval. The first data was acquired 9 minutes after the addition of solvents. CH_3NO_2 was used as an internal standard to calibrate the area of each resonance. A gradual decrease of the resonance at δ = 9.28 ppm is shown in the spectrum at bottom.

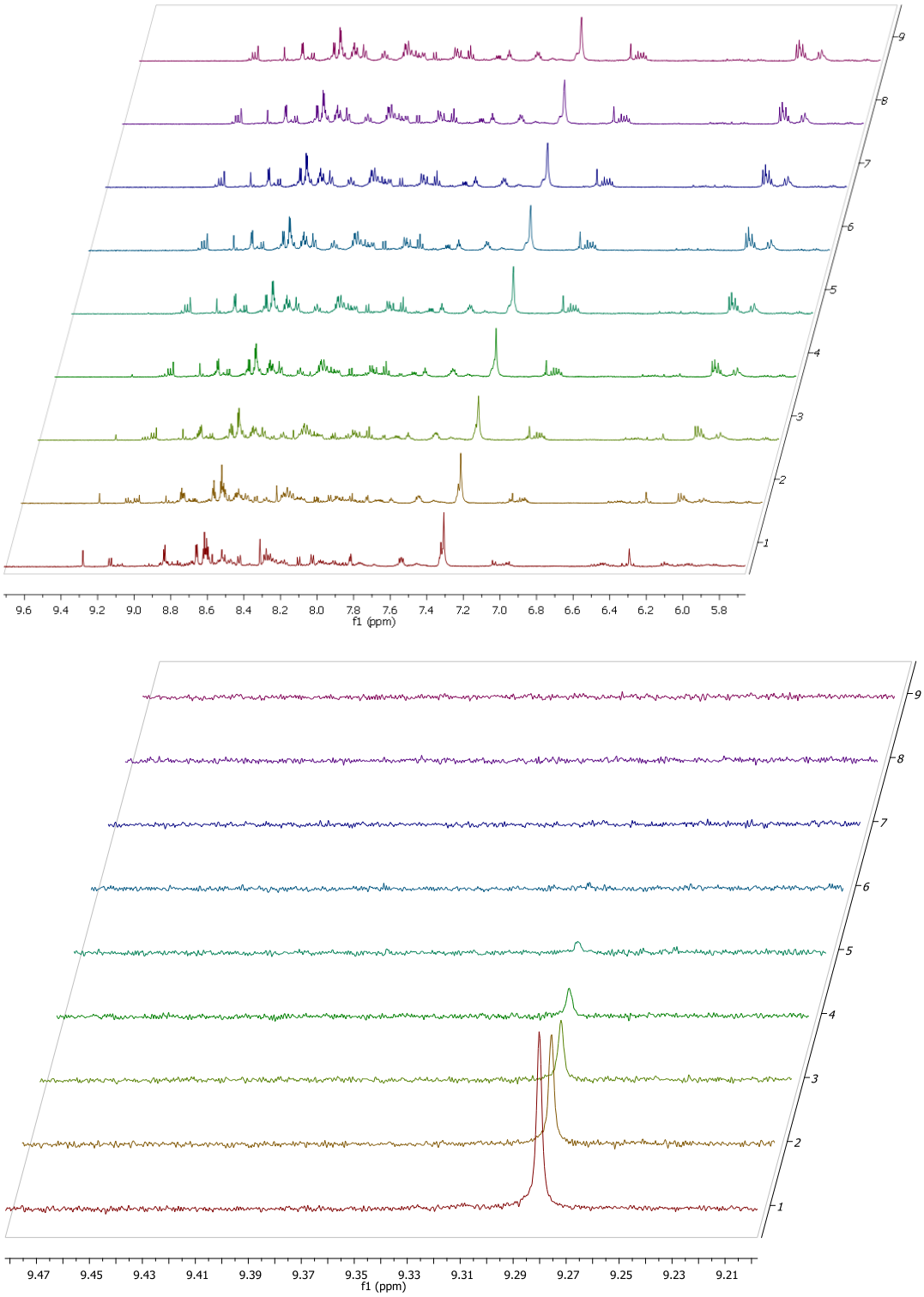


Figure S10. Stacked plot of partial ^{1}H NMR spectra (600 MHz, CD_3CN:CD_2Cl_2 (4:1), 298 K) of a mixture of **T1** and **R1** (2:3) upon addition of **10** (10 mol% with respect to **R1**) over 2 h and 7 min. Data were recorded in 15 min interval. The first data was acquired 7 minute after the addition of solvents. CH_3NO_2 was used as an internal standard to calibrate the area of each resonance. A gradual decrease of the resonance at δ = 9.28 ppm is shown in the spectrum at bottom.

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

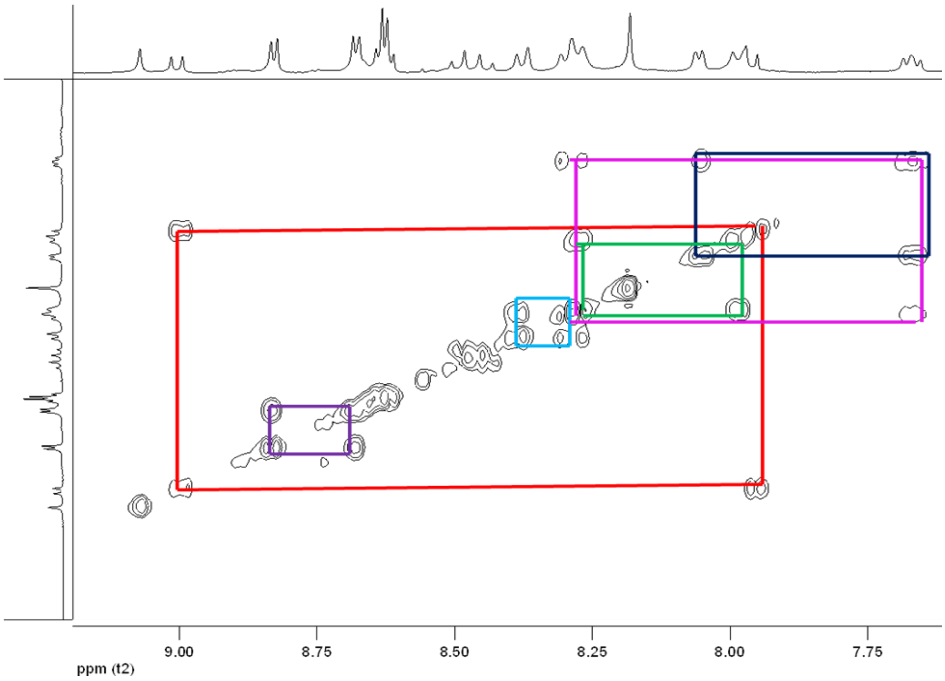


Figure S11. Partial ^{1}H-^{1}H COSY NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of **R1**.

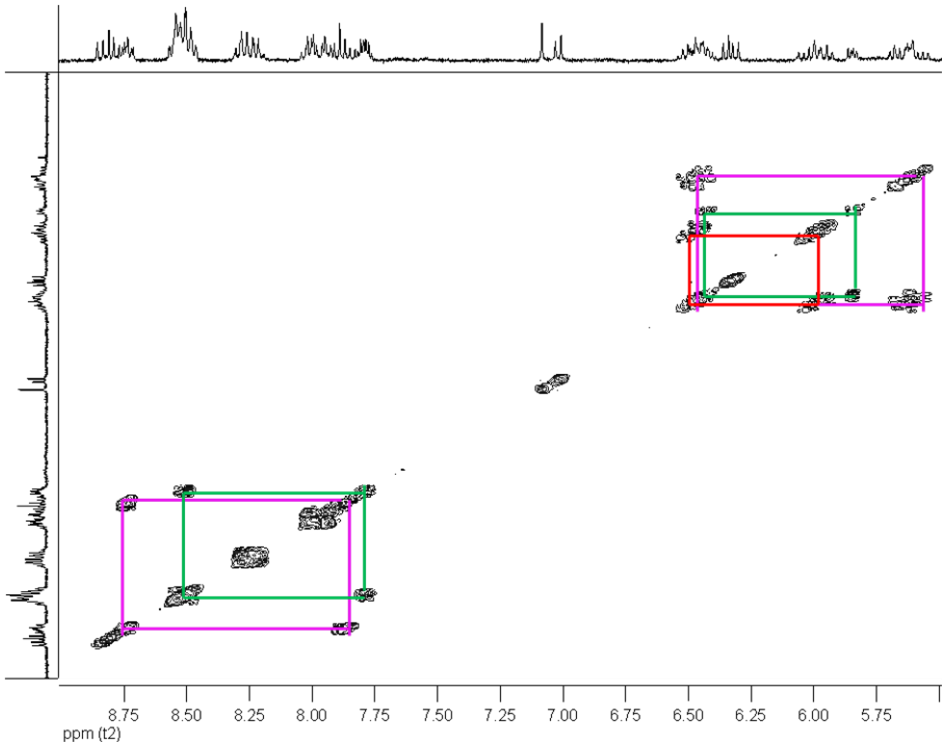


Figure S12. Partial ^{1}H-^{1}H COSY NMR spectrum (400 MHz, CD_3CN, 298 K) of **T1**.

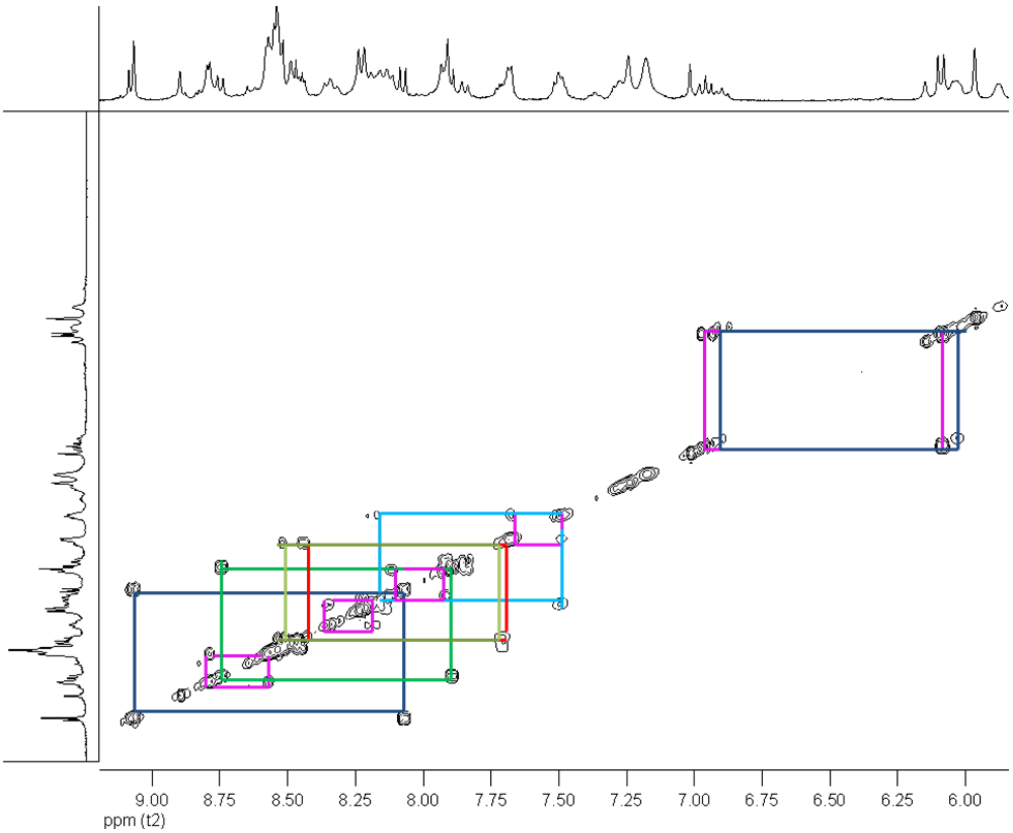


Figure S13. Partial ^{1}H-^{1}H COSY NMR spectrum (400 MHz, CD_3CN, 298 K) of **T2**.

DOSY NMR Spectra

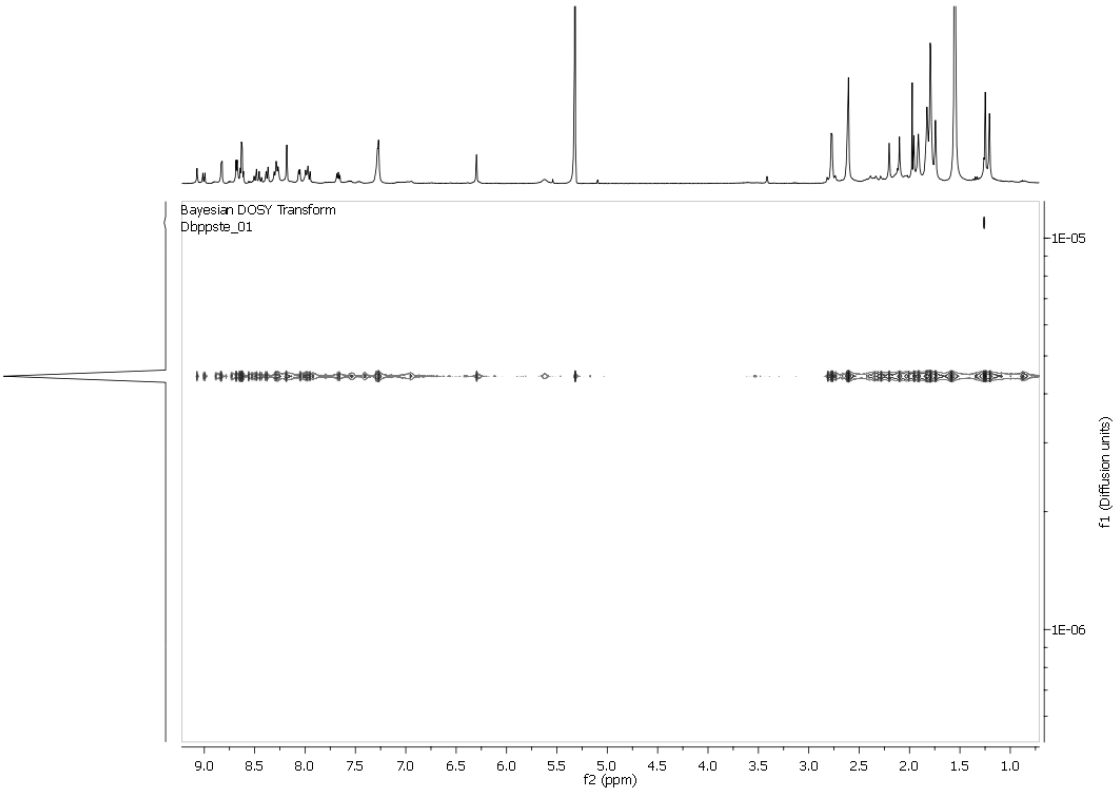


Figure S14. DOSY plot of rectangle **R1** = $[Zn_2(\mathbf{7})_2(\mathbf{8})_2](OTf)_4$ in CD_2Cl_2.

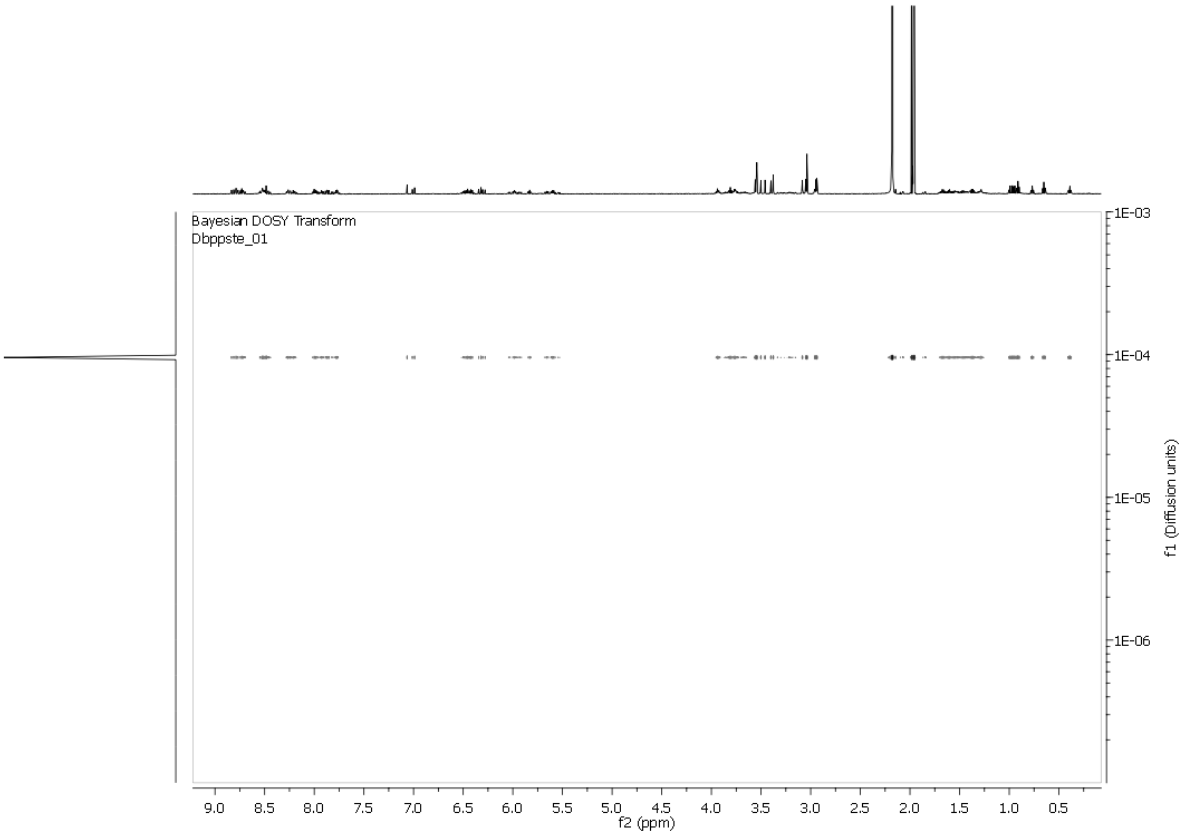


Figure S15. DOSY plot of triangle **T1** = $[Cu(\mathbf{9})_3](PF_6)_3$ in CD_3CN.

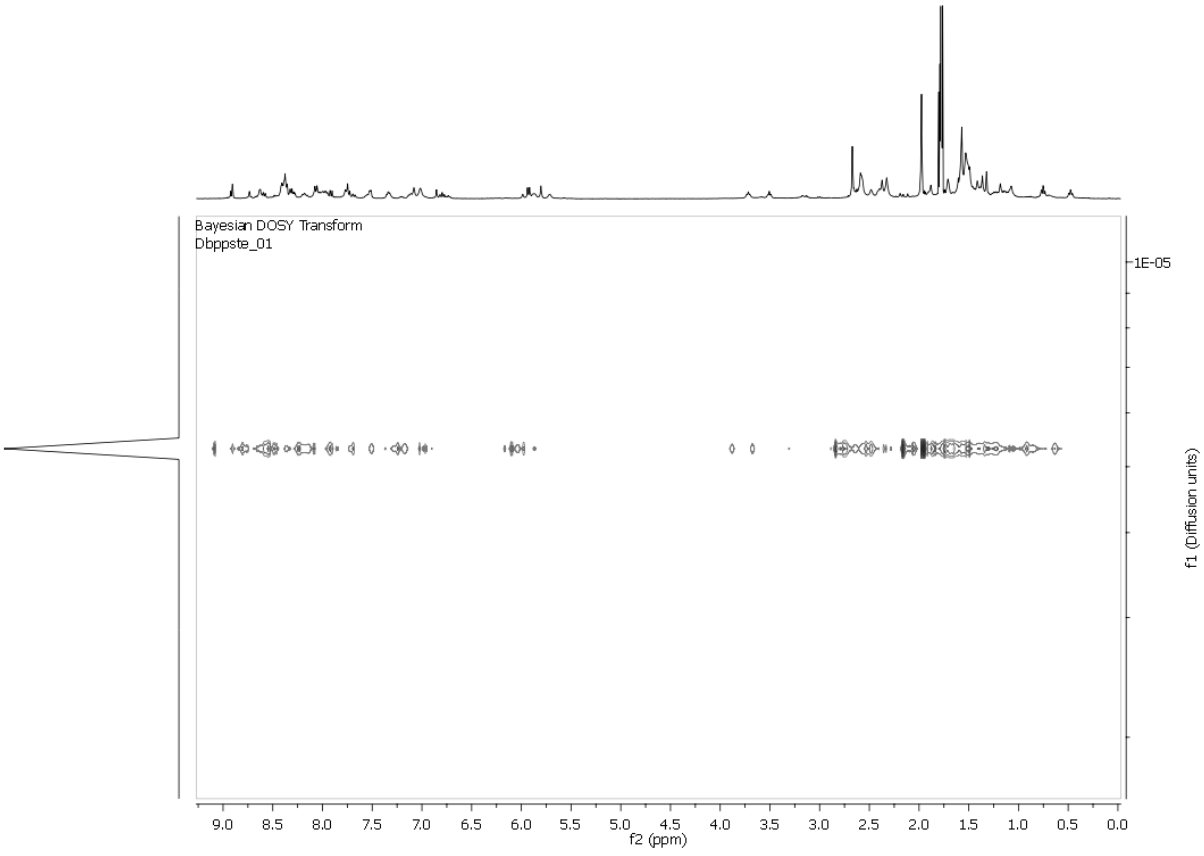


Figure S16. DOSY plot of triangle **T2** = $[CuZn(\mathbf{7})(\mathbf{8})(\mathbf{9})](OTf)_2(PF_6)$ in CD_3CN.

ESI-MS spectra

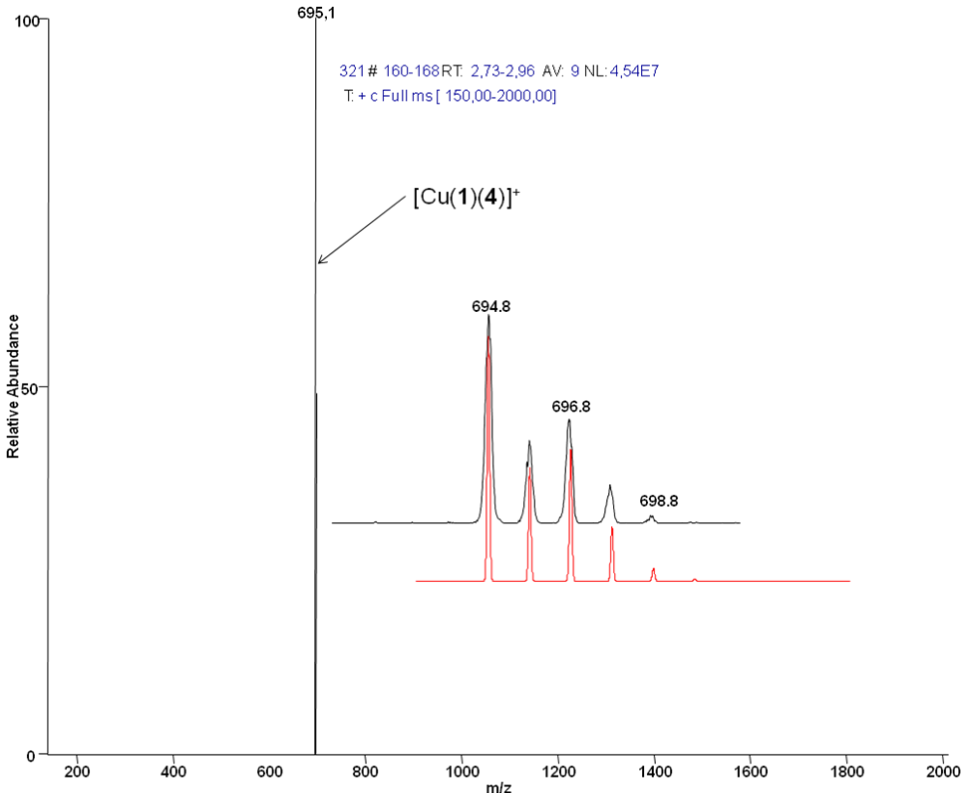


Figure S17. ESI-MS spectrum of **C1** = [Cu(**1**)(**4**)](PF_6) (in CH_3CN) and experimental isotopic distribution (black) along with calculated isotopic distribution (red) for [Cu(**1**)(**4**)]$^+$.

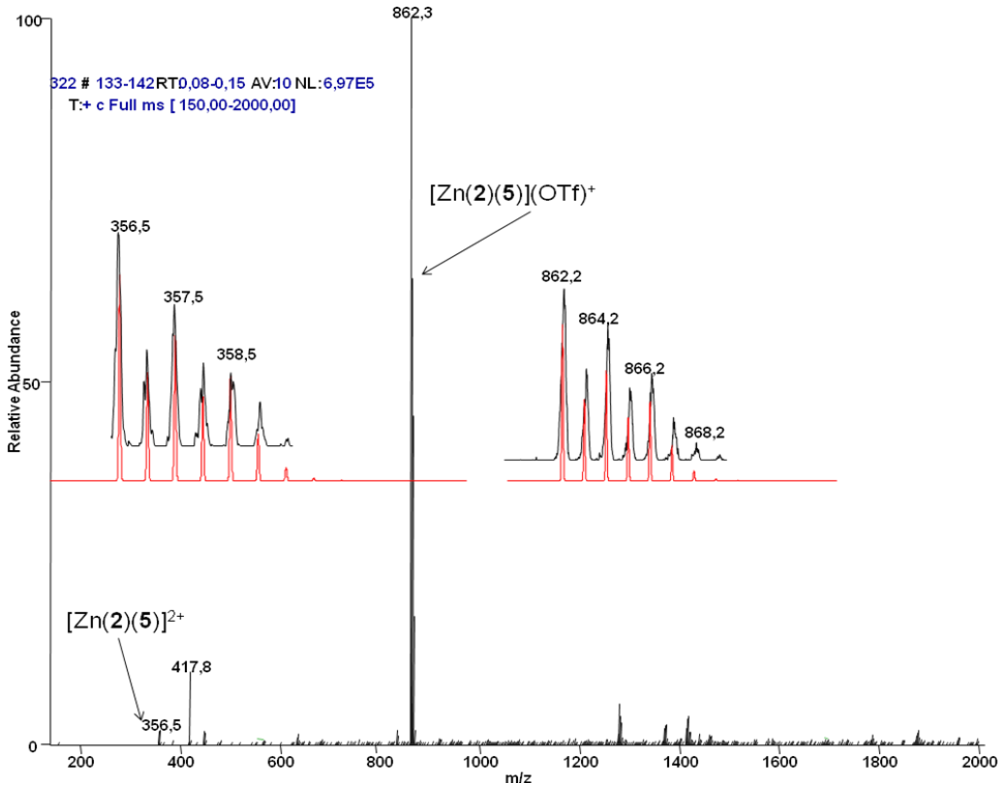


Figure S18. ESI-MS spectrum of **C2** = [Zn(**2**)(**5**)]($OTf)_2$ (in CH_3CN) and experimental isotopic distribution (black) along with calculated isotopic distribution (red) for [Zn(**2**)(**5**)]$^{2+}$ and [Zn(**2**)(**5**)](OTf)$^+$.

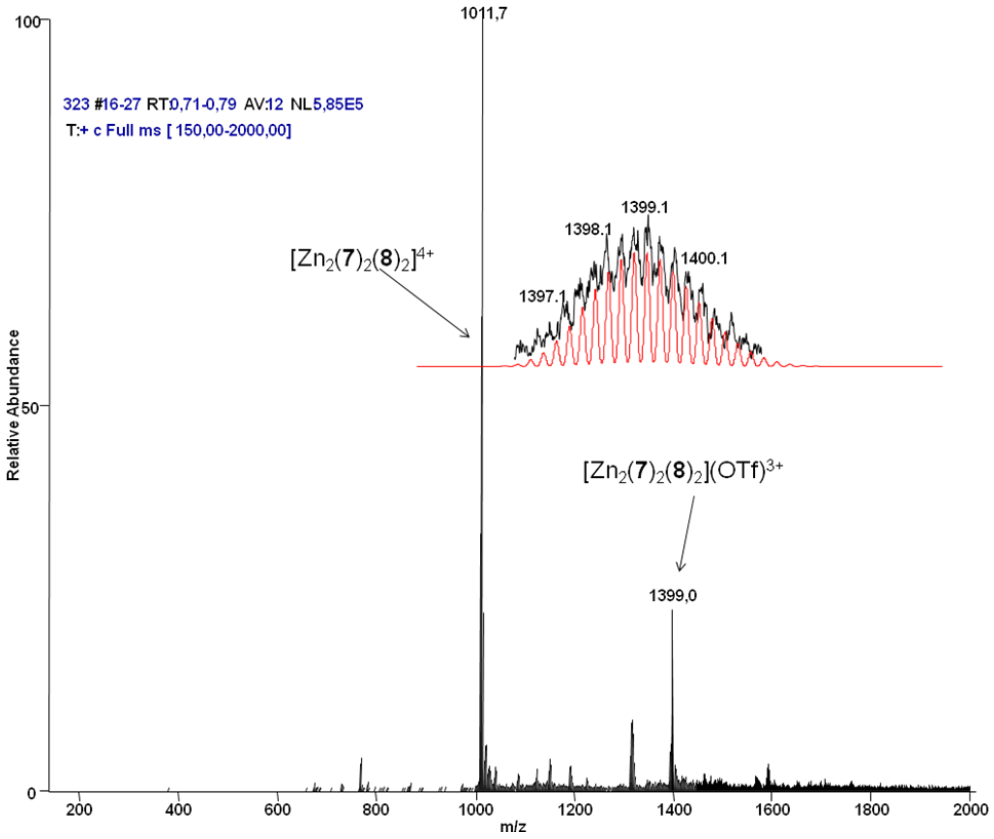


Figure S19. ESI-MS spectrum of **R1** = $[Zn_2(\mathbf{7})_2(\mathbf{8})_2](OTf)_4$ (in CH_2Cl_2) and experimental isotopic distribution (black) along with calculated isotopic distribution (red) for $[Zn_2(\mathbf{7})_2(\mathbf{8})_2](OTf)^{3+}$.

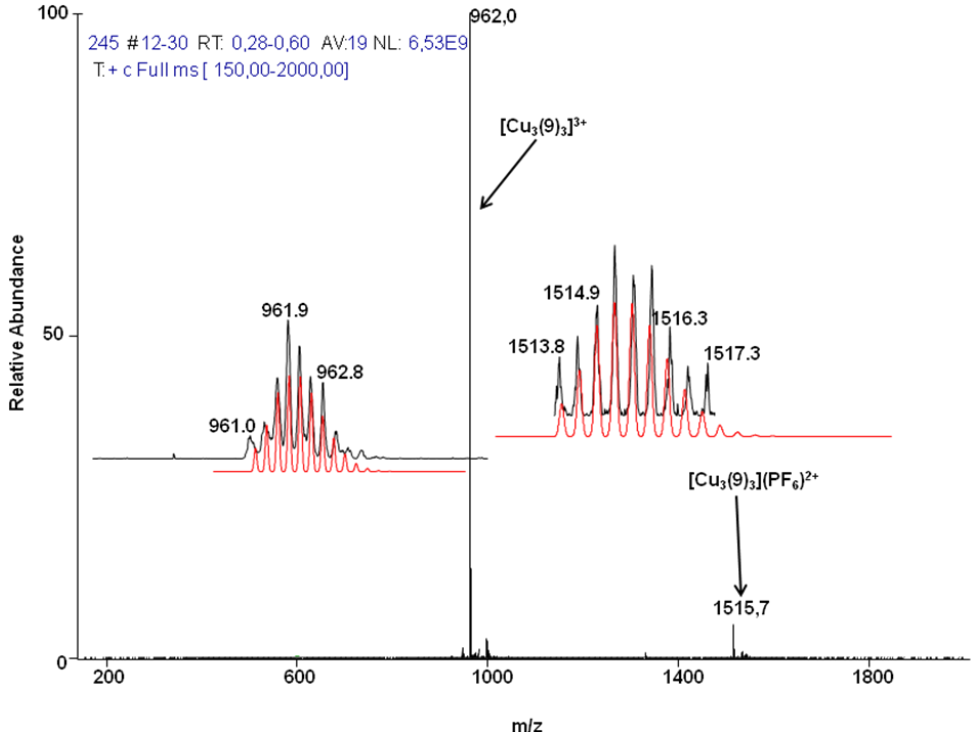


Figure S20. ESI-MS spectrum of **T1** = $[Cu(\mathbf{9})_3](PF_6)_3$ (in CH_3CN) and experimental isotopic distribution (black) along with calculated isotopic distribution (red) for $[Cu(\mathbf{9})_3]^{3+}$ and $[Cu(\mathbf{9})_3](PF_6)^{2+}$.

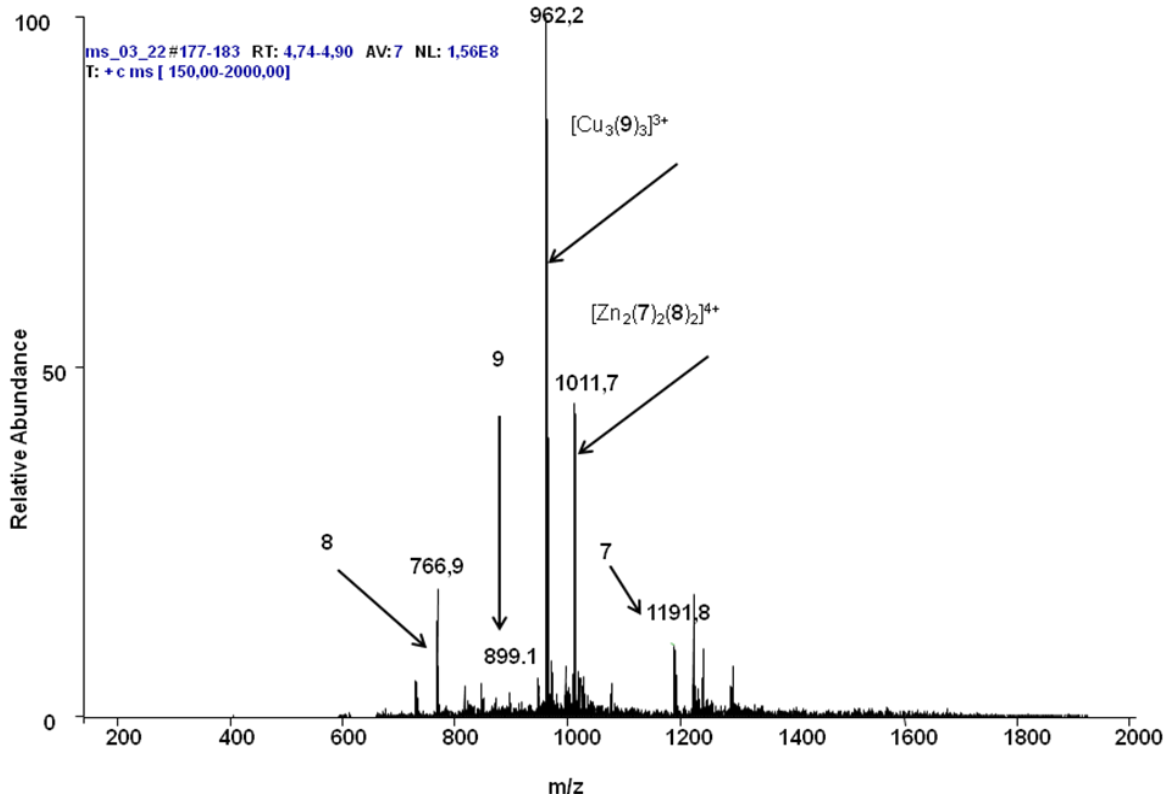


Figure S21. ESI-MS of a mixture **T1**:**R1** (2:3) after 20 min at 298 K.

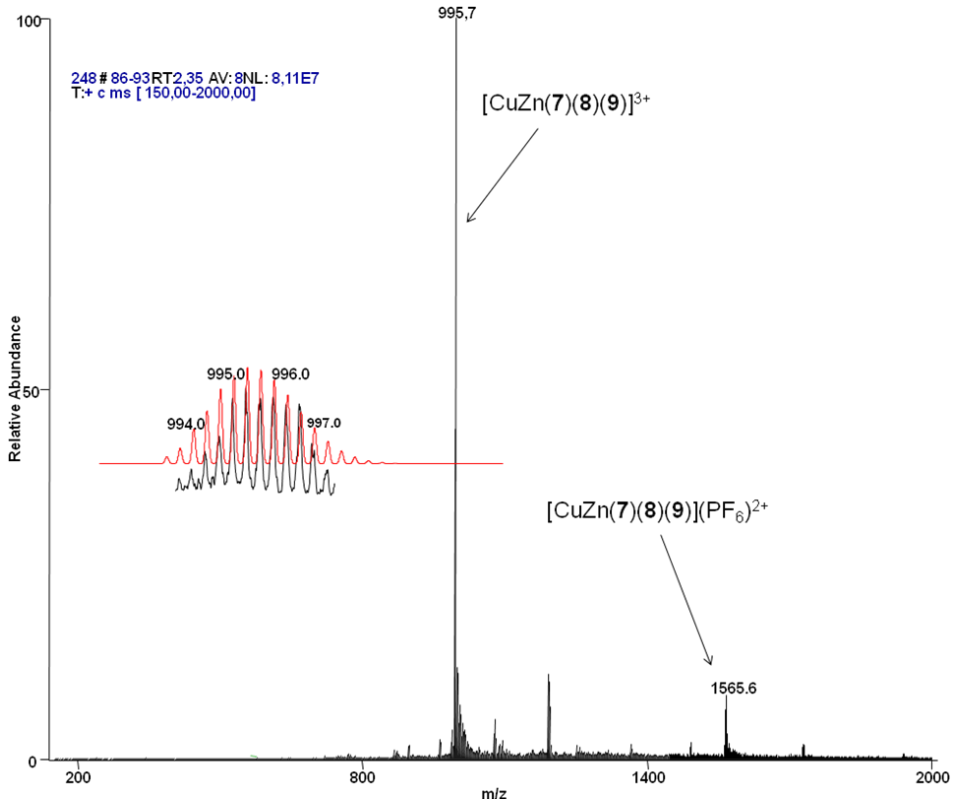


Figure S22: ESI-MS spectrum of **T2** = $[CuZn(\mathbf{7})(\mathbf{8})(\mathbf{9})](OTf)_2(PF_6)$ (in CH_3CN) and experimental isotopic distribution (black) along with calculated isotopic distribution (red) for the species $[CuZn(\mathbf{7})(\mathbf{8})(\mathbf{9})]^{3+}$. The ESI-MS experiment was carried out using the ^{1}H-NMR sample as depicted in Figure S8.

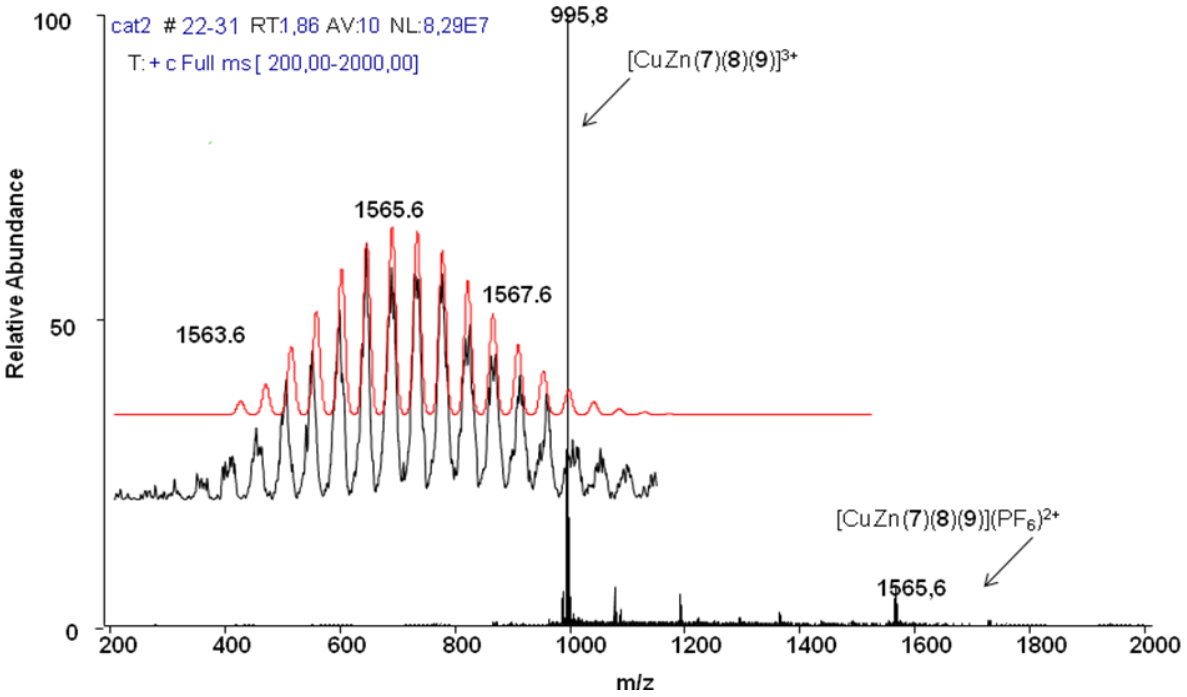


Figure S23: ESI-MS of a mixture **T1**:**R1** in presence of **10** (10 mol% with respect to **R1**) after 1.5 h at 298 K. Inset: Experimental (black) and calculated (red) isotopic distribution of [Zn Cu(**7**)(**8**)(**9**)]$(PF_6)^{2+}$.

Differential pulse voltammetry (DPV)

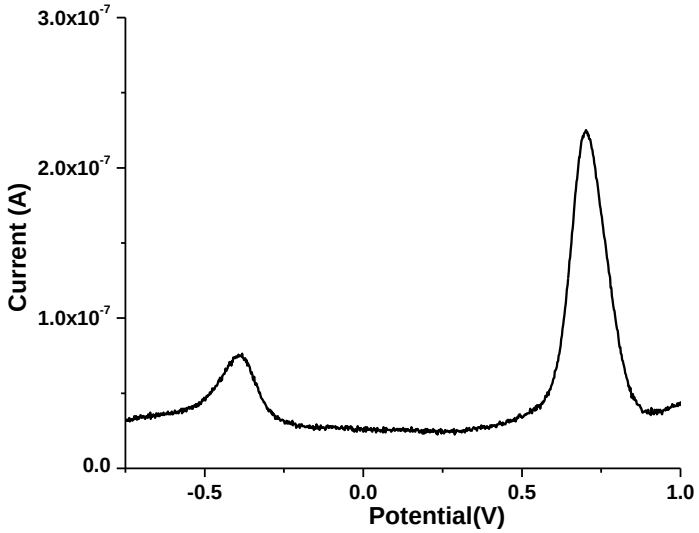


Figure S24. Differential pulse voltammetry (DPV) investigation of scalene triangle **T2** = [CuZn(**7**)(**8**)(**9**)]$(OTf)_2(PF_6)$. The experiment was carried out in dry acetonitrile with 0.1 M *n*-Bu_4NPF_6 as electrolyte against a Ag wire as a quasi-reference electrode and triphenylpyrylium tetrafluoroborate as internal standard (scan rate of 20 mVs^{-1} and a pulse height of 2 mV).

Energy minimised structures

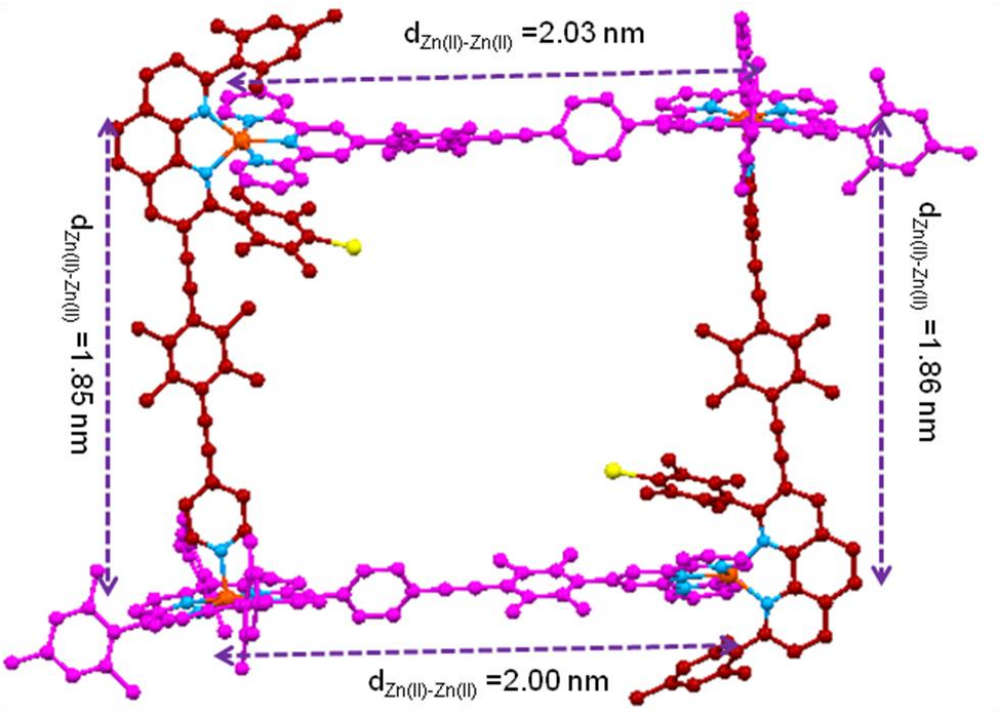


Figure S25. Energy minimised structure of the rectangle **R1**. Hydrogens are omitted for clarity.

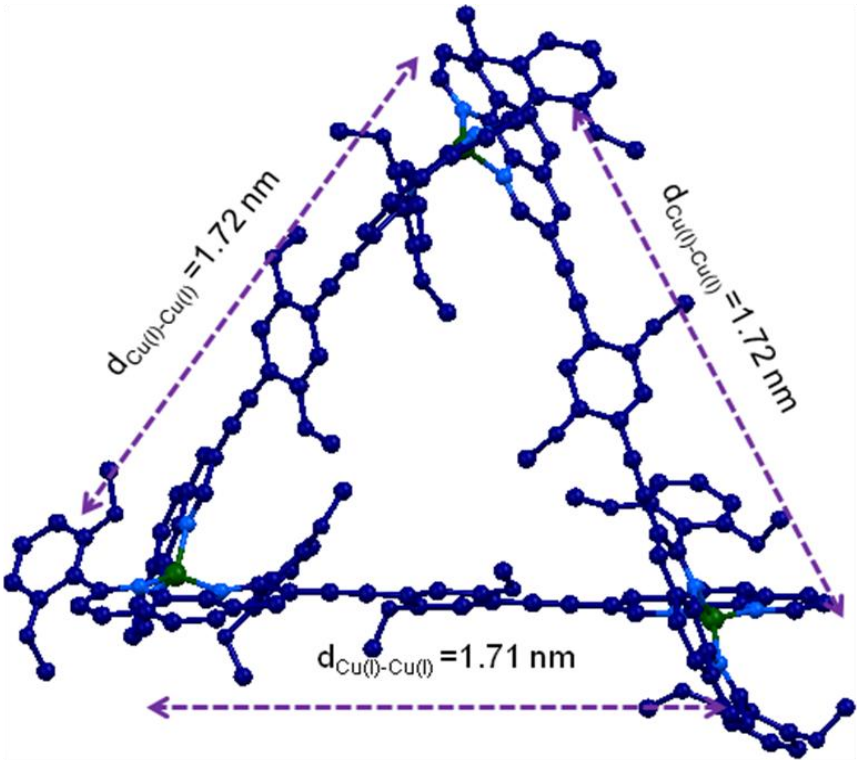


Figure S26. Energy minimised structure of the equilateral triangle **T1**. Counter anions and alkoxy chains are not included. Hydrogens are omitted for clarity.

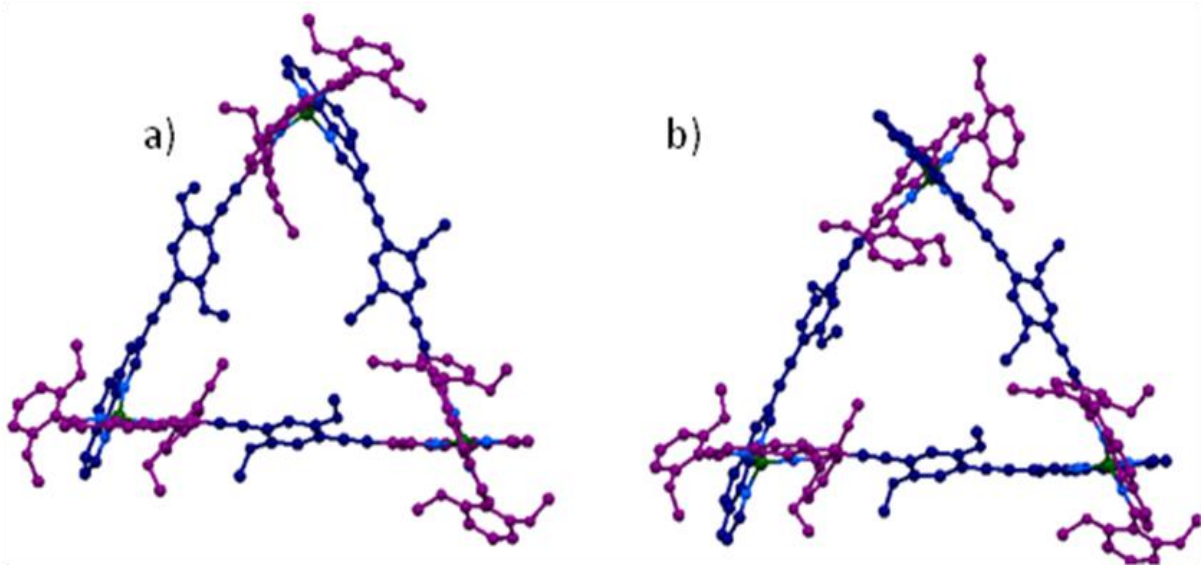


Figure S27. Energy minimised structure of (a) *M*(Cu), *M*(Cu), *M*(Cu) equilateral triangle **T1**; (b) *P*(Cu), *M*(Cu), *M*(Cu) equilateral triangle **T1**. Counter anions and alkoxy chains are not included. Hydrogens are omitted for clarity.

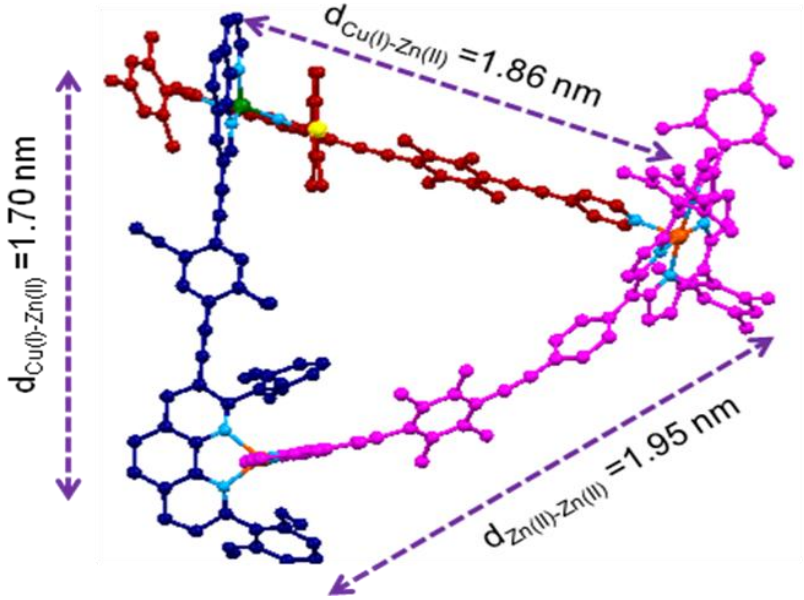


Figure S28. Energy minimised structure of the scalene triangle **T2**. Counter anions and alkoxy chains are not included. Hydrogens are omitted for clarity.

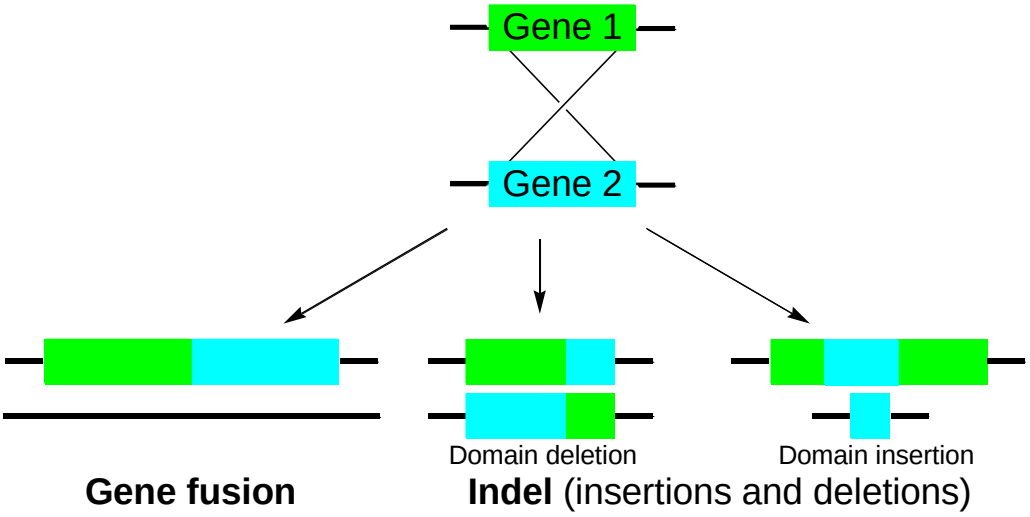


Figure S29. Gene shuffling and its main mechanistic facets.

References

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3 R. W. Wagner, T. E. Johnson, F. Li and J. S. Lindsey, *J. Org. Chem.* 1995, **60**, 5266.

4 M. Schmittel and B. He, *Chem. Commun*. 2008, 4723.

5 K. Mahata, M. L. Saha and M. Schmittel, *J. Am. Chem. Soc.* 2010, **132**, 15933.

6 M. Schmittel and K. Mahata, *Chem. Commun*. 2010, **46**, 4163.