SUPPORTING INFORMATION

Simultaneous generation of a [2×2] grid-like complex and a linear double helicate: a three-level self-sorting process

Jean-François Ayme,[†,‡] Jean-Marie Lehn,*[,†,‡] Corinne Bailly[§] and Lydia Karmazin[§]

[†]Institute of Nanotechnology, Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany

[‡]Laboratoire de Chimie Supramoléculaire, Institut de Science et d'Ingénierie Supramoléculaires, Université de Strasbourg ,8 allée Gaspard Monge, 67000 Strasbourg, France

[§]Service de Radiocristallographie, Fédération de chimie Le Bel FR2010, Université de Strasbourg, 1 rue Blaise Pascal, 67008 Strasbourg, France

Email : lehn@unistra.fr

Table des matières

1. General experimental section

1.1 General material

Unless stated otherwise, solvents and commercial reagents were used as received. Dry toluene was obtained by passing the solvent through an activated alumina on a Pure Solv solvent purification system. All reactions requiring anhydrous conditions were carried-out in oven-dried glassware and all reactions requiring inert gas atmosphere were performed under nitrogen using standard Schlenk techniques. All reactions not performed in a NMR tubes were agitated using magnetic stirrer bars. Room temperature is taken as 293 K. Flash column chromatography was carried out using silica gel (Geduran Si60, 40-63 µm, Merck) using eluents as specified. TLC was performed on precoated silica gel plates (Merck TLC silica gel 60 F254 aluminium plates) and product spots were visualized under UV light (λ_{max} = 280 nm or 365 nm) or by staining with $KMnO_4$. Celite® was obtained for Sigma-Aldrich and refers to diatomaceous earth. Brine refers to a saturated aqueous solution of NaCl. Ammonia in methanol was prepared by bubbling gaseous ammonia in methanol.

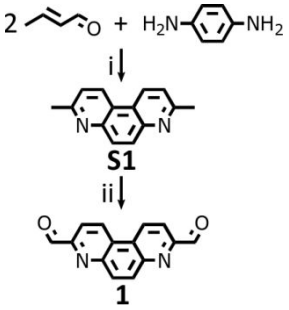
1.2 Characterization and analysis methods

NMR spectra were recorded on a Bruker Avance III 400 MHz, Bruker Avance III HD 400 MHz spectrometer or Bruker Avance Neo 500 MHz spectrometer. NMR spectra were digitally processed (phase and baseline corrections, integration, peak analysis) using MestReNova 10.0. Deuterated acetonitrile (CD_3CN) was obtained from Sigma-Aldrich and used without further purification. Deuterated chloroform ($CDCl_3$) was obtained from Sigma-Aldrich and was passed through a plug of sodium bicarbonate immediately before use to remove any acidic impurities. Chemical shifts are reported in parts per million (ppm) from low to high frequency using residual protonated solvent signals as reference (for ^{1}H NMR spectra $CDCl_3$ =7.26 ppm, CD_3CN = 1.94 ppm; for ^{13}C NMR spectra $CDCl_3$ =77.16 ppm, CD_3CN = 1.32 ppm). Coupling constants (*J*) are reported in hertz (Hz). The multiplicity of the 1H signals are indicated using the following standard abbreviations: s = singlet, d = doublet, t = triplet, dd = double doublet, q = quartet, m = multiplet, br = broad, ddd = doublet of double doublets. NMR signals are reported in terms of chemical shift (δ), multiplicity, coupling constants (*J*), relative integral, and assignment, in that order. All resonances are reported to the nearest 0.01 ppm. ^{1}H and ^{13}C NMR assignments were made using 2D-NMR methods (COSY, ROESY, TOCSY, HSQC, HMBC) and are unambiguous unless stated otherwise. High resolution ESI mass spectra were obtained in-house at the Institute of Science and Supramolecular Engineering (ISIS) by direct injection into a ThermoFisher Exactive Plus EMR Orbitrap mass spectrometer.

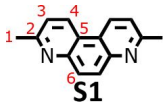
2. Synthesis

2.1 Synthesis of the ligands

2.1.1 Synthesis of dialdehyde 1



Scheme 1. Synthesis of dialdehyde **1**. Reagents and conditions: (i) HCl:AcOH 1:1, 90 °C, 3 h, 2%, (ii) I_2, TFA, DMSO, 150 °C, 2 h, 58%.



S1 was prepared by a modified literature procedure.[S1]

Benzene-1,4-diamine (10 g, 92.59 mmol, 1eq.) and crotonaldehyde (20 mL, 245.14 mmol, 2.5 eq.) were successively added to a mixture of HCl (50 mL) and AcOH (50 mL). The resulting mixture was heated to 90 °C for 3 h. After cooling to room temperature, the mixture was extracted with CH_2Cl_2 (3 x 200 mL). The dark organic layers were discarded and the combined aqueous layers were made basic using NaOH pellets. This solution was extracted with EtOAc (3 x 200 mL). The combined organic layers were washed with water (200 mL) and brine (200 mL), dried over with $MgSO_4$ and evaporated. Flash chromatography (SiO_2, EtOAc:petroleum ether 1:1 to EtOAc:petroleum ether:MeOH 47:47:6) afforded crude **S1** which was recrystallized from acetone to yield **S1** (342 mg, 1.64 mmol, 2%) as a brown solid.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 8.68 (d, J = 8.4 Hz, 2H, H^4), 8.12 (s, 2H, H^6), 7.42 (d, J = 8.4 Hz, 2H, H^3), 2.77 (s, 6H, H^1).

^{13}C-NMR (125.8 MHz, $CDCl_3$): δ (ppm) 158.98 (C^2), 147.04 (C^6), 131.69 (C^7), 130.73 (C^4), 122.63 (C^5), 122.33 (C^3), 25.16 (C^1).

HRMS (ESI+): *m/z* calcd. for [**S1**+H]$^+$ 209.1073 found 209.1082.

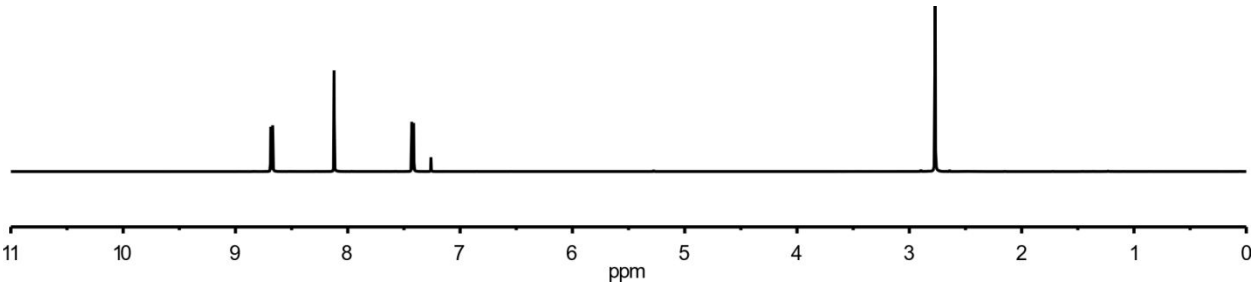


Figure S1. ^{1}H NMR (500 MHz, 297 K, $CDCl_3$) of compound **S1**.

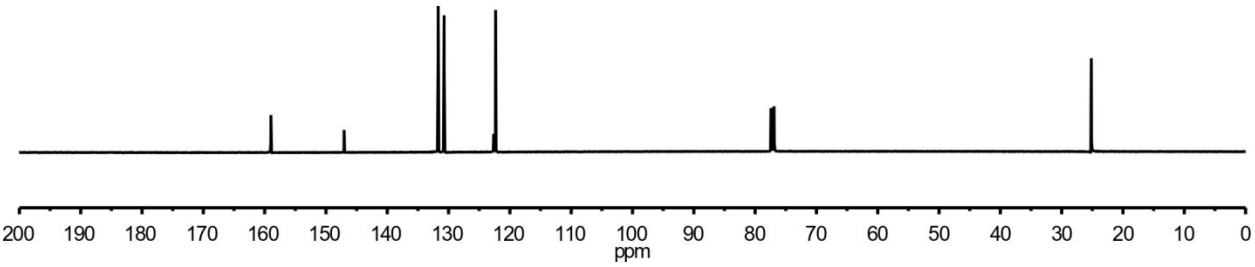
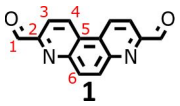


Figure S2. ^{13}C NMR (125 MHz, 297 K, $CDCl_3$) of compound **S1**.



1

1 was prepared by a modified literature procedure.[S2]

Iodine (939 mg, 3.71 mmol, 3.8 eq.), and trifluoroacetic acid (0.551 mL, 7.19 mmol, 7.5 eq.) were added to a degassed solution of **S1** (200 mg, 0.96 mmol, 1 eq.) in DMSO (7 mL). Then N_2 was bubbled through the solution for 10 min and the mixture was stirred at 150 °C for 2 h. After cooling to room temperature, the solution was treated with $Na_2S_2O_3.5H_2O$ (1.37 g, 8.64 mmol, 9 eq.) in water (5 mL), causing discharge of the I_2 color, and was made neutral with saturated $NaHCO_3$ solution. The mixture was extracted with CH_2Cl_2 (6 x 25 mL) and the organic layers were combined, dried ($MgSO_4$), and evaporated under reduced pressure. Flash chromatography (SiO_2, CH_2Cl_2:MeOH 98:2) afforded **1** as a brown solid (130 mg, 0.55 mmol, 58%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 10.32 (s, 2H, H^1), 9.14 (d, J = 8.4 Hz, 2H, H^4), 8.45 (s, 2H, H^7), 8.31 (d, J = 8.5 Hz, 2H, H^3).

^{13}C-NMR (125.8 MHz, $CDCl_3$): δ (ppm) 193.34 (C^1), 153.44 (C^2), 148.67 (C^6), 133.41 (C^7), 132.90 (C^4), 127.16 (C^5), 119.00 (C^3).

HRMS (ESI+): *m/z* calcd. for [**1**+H]$^+$ 237.0659 found 237.0656.

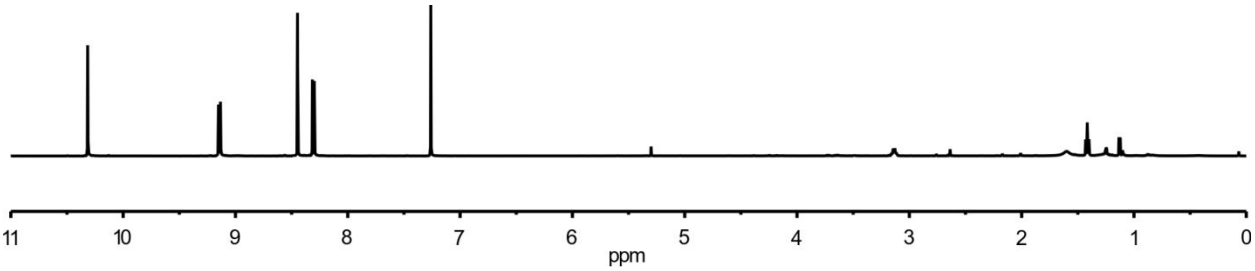


Figure S3. ^{1}H NMR (500 MHz, 297 K, $CDCl_3$) of compound **1**.

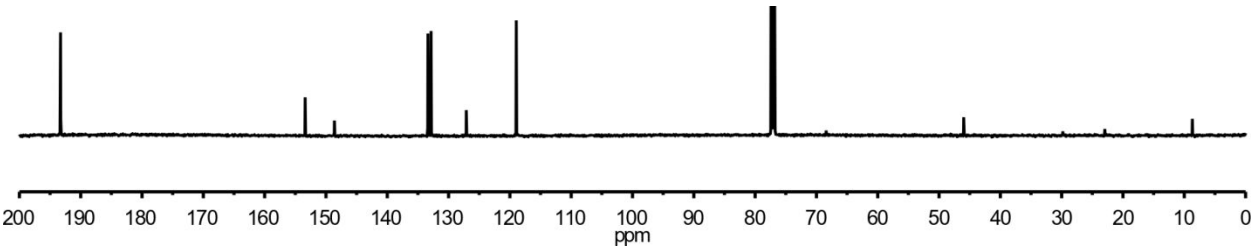
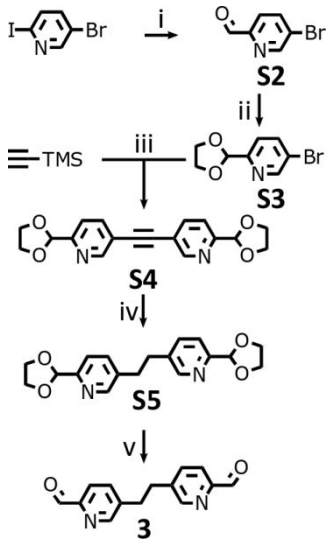
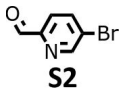


Figure S4. ^{13}C NMR (125 MHz, 297 K, $CDCl_3$) of compound **1**.

2.1.2 **Synthesis of dialdehyde 3**

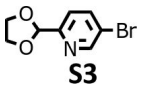


Scheme 2. Synthesis of dialdehyde **3**. Reagents and conditions: (i) a) *i*-PrMgCl, THF, -10 °C, 1 h, b) DMF, -10 °C, 1 h, 86%; (ii) ethylene glycol, *p*-TsOH, toluene, reflux, 44h, 91%; (iii) $PdCl_2(PPh_3)_2$, Cu(I), DBU, toluene, 60 °C, 15 h, 47%; (iv) H_2, Pd/C, THF/methanol 2:1, 24h; (v) 10% HCl, reflux, 1 h, 79% over two steps.



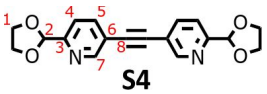
S2

S2 was synthesized as described in the literature. NMR and mass data were consistent with those previously reported.[S3]



S3

S3 was synthesized as described in the literature. NMR and mass data were consistent with those previously reported.[S3]



S4

S4 was prepared by a modified literature procedure.[S4]

$PdCl_2(PPh_3)_2$ (92 mg, 0.13 mmol, 0.1 eq.) and Cu(I) (50 mg, 0.26 mmol, 0.2 eq.) were added to a solution of **S3** (600 mg, 2.62 mmol, 2 eq.) in N_2 purged dry toluene (13 mL). Then 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 2.35 mL, 15.72 mmol, 6 eq.) was added to the mixture and N_2 bubbled through the solution for 5 min. Ice-cooled ethynyltrimethylsilane (181 µL, 1.31 mmol, 1 eq.) was added to the reaction mixture and the solution was stirred at 60 °C for 15 h. The solvent was removed under reduced pressure

and 1 N HCl (15 mL) was added to the residue. The resulting mixture was extracted with $CHCl_3$ (30 mL) and the organic layer was washed with brine (30 mL) and water (30 mL), dried ($MgSO_4$) and concentrated under reduced pressure. The resulting solid was purified by flash chromatography (SiO_2, CH_2Cl_2:acetone 5:1 then CH_2Cl_2:acetone:MeOH 80:16:4) to yield as an off-white solid (200 mg, 0.62 mmol, 47%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 8.77 (s, 2H, H^7), 7.87 (dd, J = 8.1, 1.8 Hz, 2H, H^5), 7.55 (d, J = 8.0 Hz, 2H, H^4), 5.87 (s, 2H, H^2), 4.24 – 4.00 (m, 8H, H^1).

^{13}C-NMR (125.8 MHz, $CDCl_3$): δ (ppm) 156.63 (C^3), 151.92 (C^7), 139.51 (C^5), 120.32 (C^4), 120.01 (C^6), 103.33 (C^2), 89.48 (C^8), 65.76 (C^1).

HRMS (ESI+): *m/z* calcd. for [**S4**+H]$^+$ 325.1183 found 325.1195.

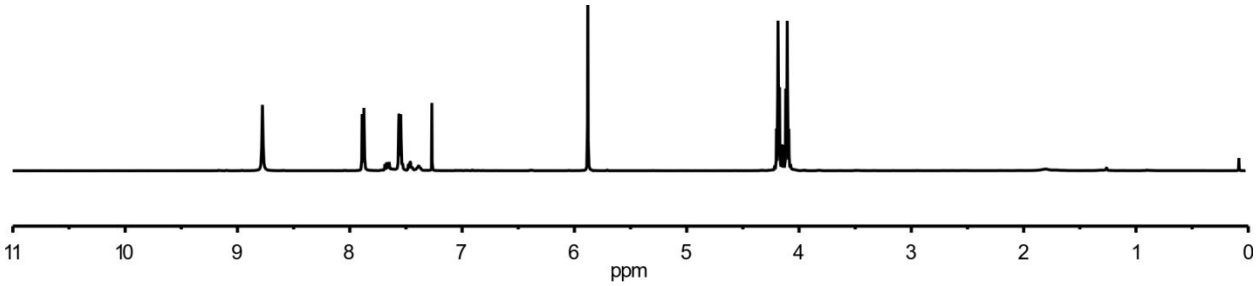


Figure S5. ^{1}H NMR (500 MHz, 297 K, $CDCl_3$) of compound **S4**.

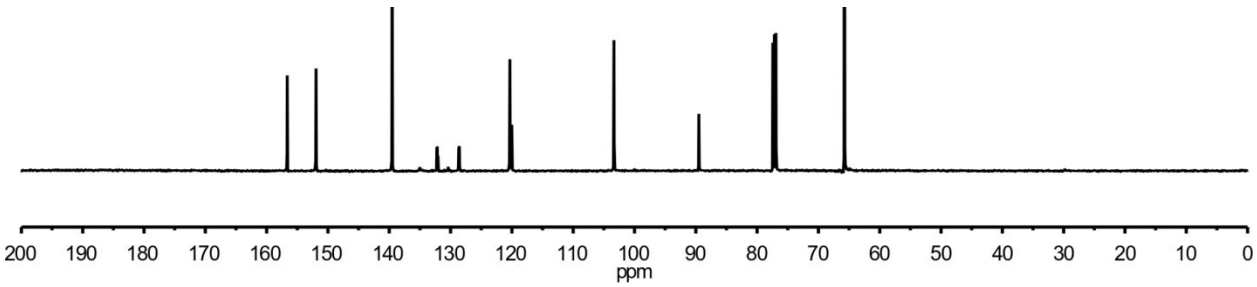
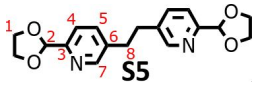


Figure S6. ^{13}C NMR (125 MHz, 297 K, $CDCl_3$) of compound **S4**.



S5 was prepared by a modified literature procedure.[S3]

S4 (100 mg, 0.309 mmol) was dissolved in THF:MeOH 2:1 (25 mL) and 10% w/w Pd/C (49 mg) was added. The mixture was stirred under H_2 for 24 hours. The mixture was filtered through Celite and the residue washed with CH_2Cl_2. The filtrate fractions were combined and the solvent removed under reduced pressure to give **S5** as an off-white solid which was used in the subsequent step without further purification.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 8.44 (d, J = 1.6 Hz, 2H, H^7), 7.47 (dd, J = 8.0, 2.1 Hz, 2H, H^5), 7.43 (d, J = 7.9 Hz, 2H, H^4), 5.82 (s, 2H, H^2), 4.21 – 4.02 (m, 8H, H^1), 2.93 (s, 4H, H^8).

^{13}C-NMR (125.8 MHz, $CDCl_3$): δ (ppm) 155.10 (C^3), 149.54 (C^7), 136.85 (C^5), 136.51 (C^6), 120.55 (C^4), 103.59 (C^2), 65.64 (C^1), 34.36 (C^8).

HRMS (ESI+): *m/z* calcd. for [**S5**+H]$^+$ 329.1496 found 329.1498.

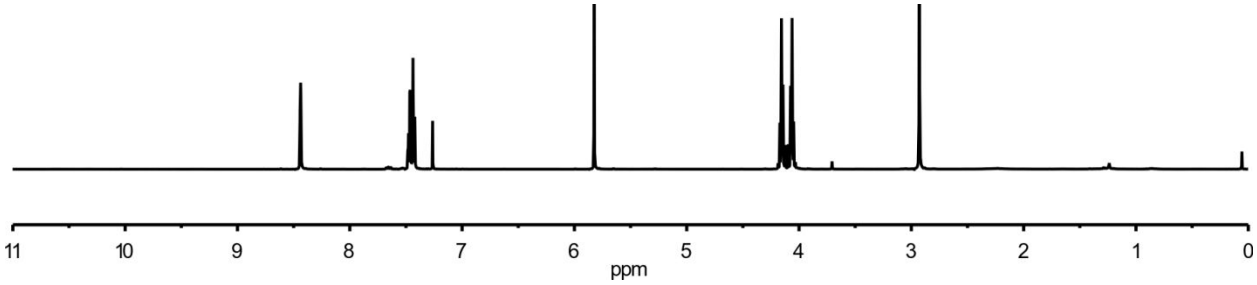


Figure S7. ^{1}H NMR (500 MHz, 297 K, $CDCl_3$) of compound **S5**.

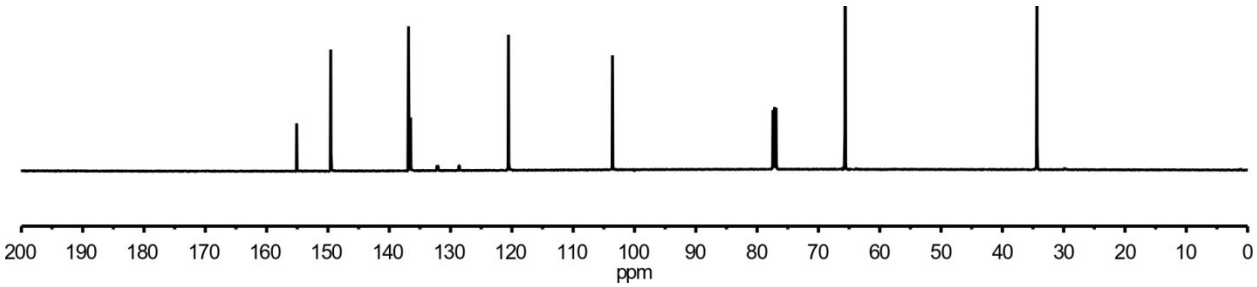
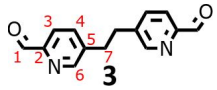


Figure S8. ^{13}C NMR (125 MHz, 297 K, $CDCl_3$) of compound **S5**.



3 was prepared by a modified literature procedure.[S3]

S5 was dissolved in 10% aqueous HCl (40 mL) and refluxed. After 1 h the reaction mixture was cooled to room temperature and neutralized by slow addition of solid $NaHCO_3$. The mixture was extracted with CH_2Cl_2 (50 mL) and the organic fraction was washed with brine (50 mL), dried over $MgSO_4$ and concentrated under reduced pressure. Flash chromatography (SiO_2, CH_2Cl_2 to CH_2Cl_2:MeOH :NEt_3 97:2:1) afforded **3** as a colorless solid (59 mg, 0.245 mmol, 79%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 10.05 (s, 2H, H^1), 8.57 (d, *J* = 1.8 Hz, 2H, H^6), 7.91 (d, *J* = 7.9 Hz, 2H, H^3), 7.64 (dd, *J* = 7.9, 1.9 Hz, 2H, H^4), 3.10 (s, 4H, H^7).

^{13}C-NMR (125.8 MHz, $CDCl_3$): δ (ppm) 193.34 (C^1), 151.90 (C^2), 150.73 (C^6), 140.89 (C^5), 137.31 (C^4), 122.05 (C^3), 34.64 (C^7).

HRMS (ESI+): *m/z* calcd. for [**3**+H]$^+$ 241.0972 found 241.0966.

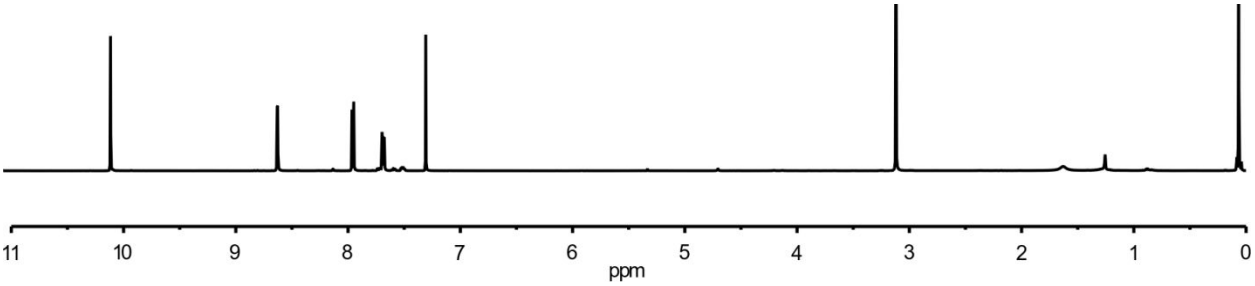


Figure S9. ^{1}H NMR (500 MHz, 297 K, $CDCl_3$) of compound **3**.

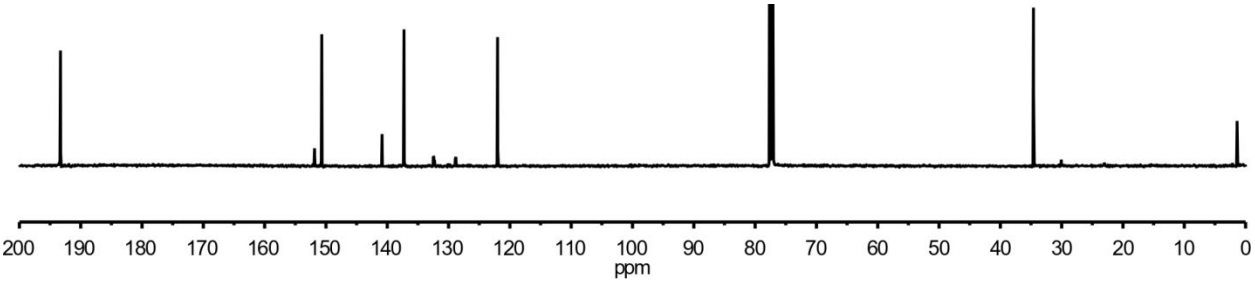
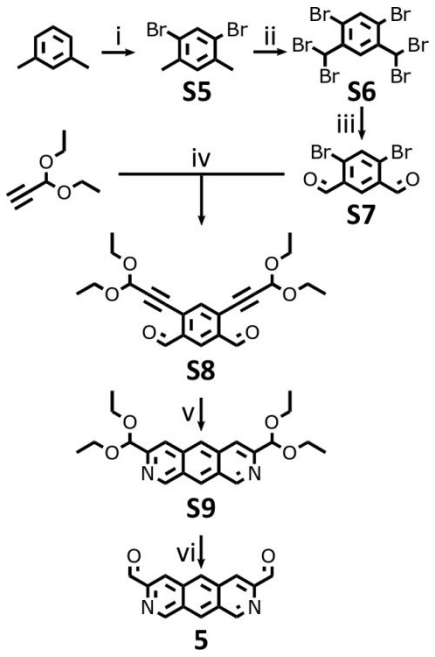
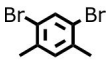


Figure S10. ^{13}C NMR (125 MHz, 297 K, $CDCl_3$) of compound **3**.

2.1.3 **Synthesis of dialdehyde 5**

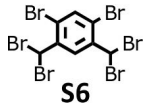


Scheme 3. Synthesis of dialdehyde **5**. Reagents and conditions: (i) Br_2, I_2, dark, 0 °C, 16 h, 47%; (ii) NBS, CCl_4, h*v*, reflux 9 h, 72%; (iii) $AgNO_3$, H_2O, EtOH, reflux 0.5 h, 91%; (iv) $Pd(PPh_3)_4$, Cu(I), diisopropylamine, toluene, r.t., 6 h, 36%; (v) methanolic ammonia, MW, 130°C, 15 min, 48%; (vi) 10% HCl, reflux, 1 h, 92%.



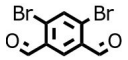
S5

S5 was synthesized as described in the literature. NMR and mass data were consistent with those previously reported.[S5]



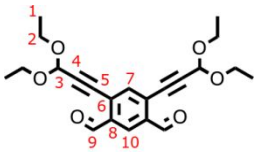
S6

S6 was synthesized as described in the literature. NMR and mass data were consistent with those previously reported.[S5]



S7

S7 was synthesized as described in the literature. NMR and mass data were consistent with those previously reported.[S5]



S8

S7 (453 mg, 1.57 mmol, 1 eq.) was suspended in a mixture of dry toluene (15 mL) and diisopropylamine (4.5 mL) and N_2 was bubbled through the solution for 5 min. Then propargylaldehyde diethyl acetal (422 mg, 3.30 mmol, 2.1 eq.), Cu(I) (60 mg, 0.32 mmol, 20%) and $Pd(PPh_3)_4$ (109 mg, 0.09 mmol, 6%) were added to the solution. The reaction mixture was stirred at r.t. for 6 h before being concentrated under reduced pressure. The residue was dissolved in a minimum of CH_2Cl_2 and absorbed onto SiO_2. Flash chromatography (SiO_2, cyclohexane:EtOAc 90:10 to 85:15) afforded **S8** as a yellow oil (220 mg, 0.57 mmol, 36%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 10.47 (s, 2H, H^9), 8.42 (s, 1H,), 7.83 (s, 1H, H), 5.54 (s, 2H, H^3), 3.75 (ddq, *J*=61.4, 9.4, 7.1, 8H, H^2), 1.29 (t, *J*=7.1, 12H, H^1).

^{13}C-NMR (125.8 MHz, $CDCl_3$): δ (ppm) 189.49 (C^9), 139.05(C^7), 135.95 (C^8), 129.43(C^6), 127.27(C^{10}), 95.73 (C^4), 91.70 (C^3), 79.34 (C^5), 61.61 (C^2), 15.24 (C^1).

HRMS (ESI+): *m/z* calcd. for [**S8**+Na]$^+$ 409.1627 found 409.1620.

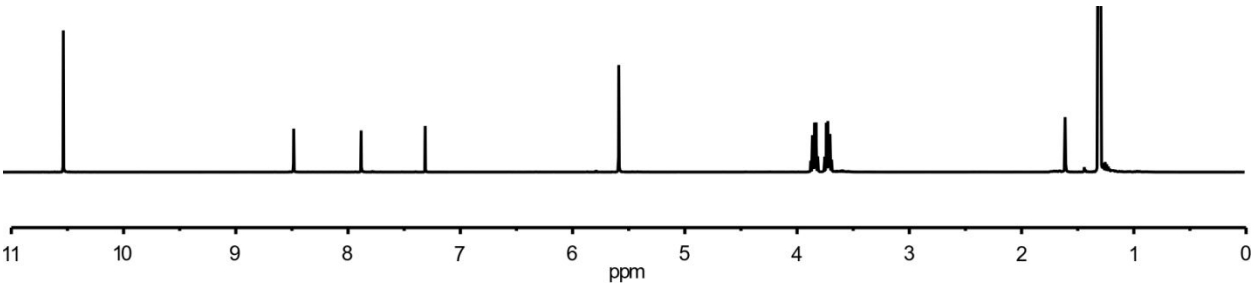


Figure S11. ^{1}H NMR (500 MHz, 297 K, $CDCl_3$) of compound **S8**.

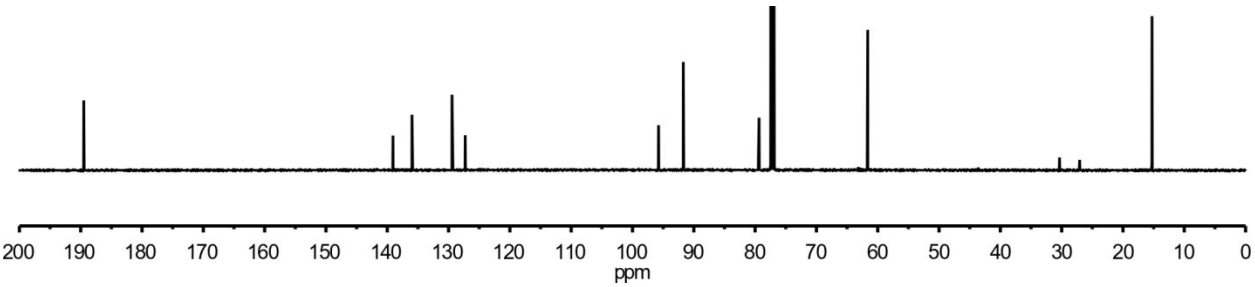
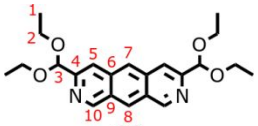


Figure S12. ^{13}C NMR (125 MHz, 297 K, $CDCl_3$) of compound **S8**.



S9

S9 was prepared by a modified literature procedure.[S6]

A stirred solution of **S8** (102 mg, 0.26 mmol) in dry ammonia in methanol (2 M, 2.6 mL) was heated at 130°C in a sealed tube for 15 min in a microwave oven. The solvent was removed under reduced pressure. The crude product was purified by flash chromatography (SiO_2, Et_2O to Et_2O:MeOH 96:4) yielded **S9** as a a brown solid (49 mg, 0.13 mmol, 48%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 9.57 (s, 2H, H^{10}), 8.80 (s, 1H, H^8), 8.43 (s, 1H, H^7), 8.09 (s, 2H, H^5), 5.73 (s, 2H, H^3), 3.84 – 3.65 (m, 8H, H^2), 1.32 (t, J=7.1, 12H, H^1).

^{13}C-NMR (125.8 MHz, $CDCl_3$): δ (ppm) 155.08 (C^{10}), 151.25 (C^4), 135.26 (C^9), 129.07 (C^8), 127.25 (C^6), 125.29 (C^7), 117.13 (C^5), 102.18 (C^3), 62.34 (C^2), 15.45 (C^1).

HRMS (ESI+): *m/z* calcd. for [**S9**+H]$^+$ 385.2122 found 385.2121.

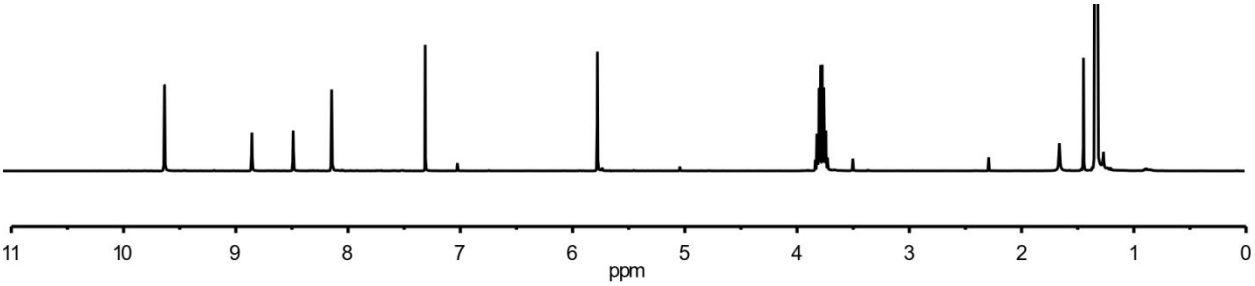


Figure S13. ^{1}H NMR (500 MHz, 297 K, $CDCl_3$) of compound **S9**.

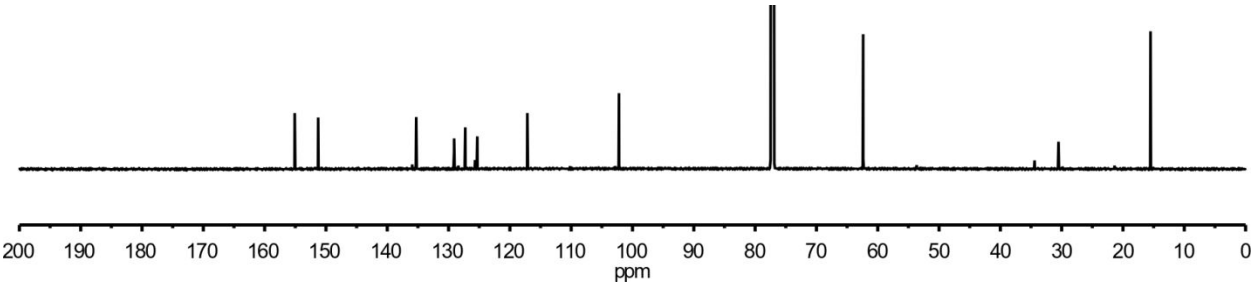
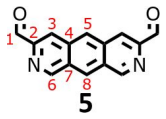


Figure S14. ^{13}C NMR (125 MHz, 297 K, $CDCl_3$) of compound **S9**.



5

5 was prepared by a modified literature procedure.[S3]

S9 (49 mg, 0.13 mmol) was dissolved in 10% aqueous HCl (15 mL) and refluxed. After 1 h the reaction mixture was cooled to room temperature and neutralized by slow addition of solid $NaHCO_3$. The mixture was extracted with CH_2Cl_2 (30 mL) and the organic fraction was washed with brine (30 mL), dried over $MgSO_4$ and concentrated under reduced pressure to afford **5** as a slightly yellow solid (27 mg, 0.12 mmol, 92%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 10.36 (s, 2H, H^1), 9.76 (d, J = 1.0 Hz, 2H, H^3), 9.00 (t, J = 1.1 Hz, 1H, H^5), 8.82 (m, 1H, H^4), 8.60 (q, J = 1.0 Hz, 2H, H^2).

^{13}C-NMR (125.8 MHz, $CDCl_3$): δ (ppm) 192.64 (C^1), 155.94 (C^6), 146.74 (C^2), 134.39 (C^4), 130.06 (C^5), 129.67 (C^8), 129.40 (C^7), 121.85 (C^3).

HRMS (ESI+): *m/z* calcd. for [**5**+H]$^+$ 237.0659 found 237.0655.

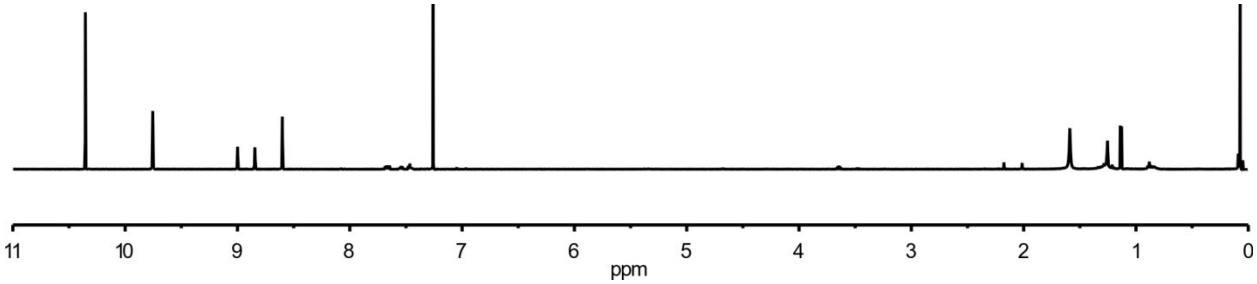


Figure S15. ^{1}H NMR (500 MHz, 297 K, $CDCl_3$) of compound **5**.

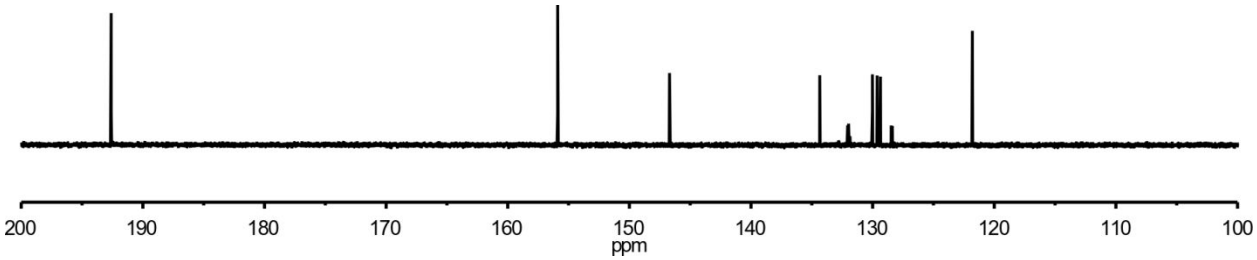
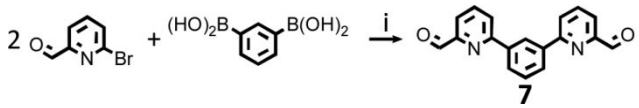


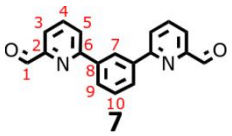
Figure S16. ^{13}C NMR (125 MHz, 297 K, $CDCl_3$) of compound **5**.

2.1.4 **Synthesis of dialdehyde 7**



7

Scheme 4. Synthesis of dialdehyde **7**. Reagents and conditions: (i) $Pd(PPh_3)_4$, Cs_2CO_3, dioxane/H_2O, 90°C, 18 h, 41%.



7

7 was prepared by a modified literature procedure.[S7]

6-Bromo-2-pyridinecarboxaldehyde (1 g, 5.37 mmol, 2 eq.) and 1,3-benzenediboronic acid (444 mg, 2.69 mmol, 1 eq.) were dissolved in dioxane (36 mL) and water (4 mL) and flushed with N_2. $Pd(PPh_3)_4$ (290 mg, 0.25 mmol, 9%) and Cs_2CO_3 (8.1 g, 25 mmol, 9 eq.) were added and the mixture was stirred at 90 °C overnight. CH_2Cl_2 (100 mL) and water (100 mL) were added, the organic phase isolated and the aqueous phase washed with CH_2Cl_2 (2 x 50 mL). The combined organic layers were washed with brine and the solvent removed under reduced pressure. Flash chromatography (SiO_2, CH_2Cl_2 to CH_2Cl_2:EtOH 9:1) afforded crude **7** which was further purified by flash chromatography (SiO_2, petroleum ether:CH_2Cl_2:EtOAc:NEt_3 98.9:0.5:0.5:0.1 to 96.8:2:2:0.2), to afford **7** as a slightly yellow solid (320 mg, 1.11 mmol, 41%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 10.22 (s, 2H, H^1), 8.83 (s, 1H, H^7), 8.20 (dd, J = 7.8, 1.8 Hz, 2H, H^9), 8.09 (dd, J = 7.7, 1.2 Hz, 2H, H^5), 8.04 – 7.97 (m, 2H, H^4), 7.95 (dd, J = 7.6, 1.2 Hz, 2H, H^3), 7.68 (t, J = 7.8 Hz, 1H, H^{10}).

^{13}C-NMR (125.8 MHz, $CDCl_3$): δ (ppm) 193.90 (C^1), 157.49 (C^6), 152.80 (C^2), 138.93 (C^8), 137.99 (C^4), 129.65 (C^{10}), 128.21 (C^9), 125.71 (C^7), 124.72 (C^5), 120.13 (C^3).

HRMS (ESI+): *m/z* calcd. for [**7**+H]$^+$ 289.0972 found 289.0966.

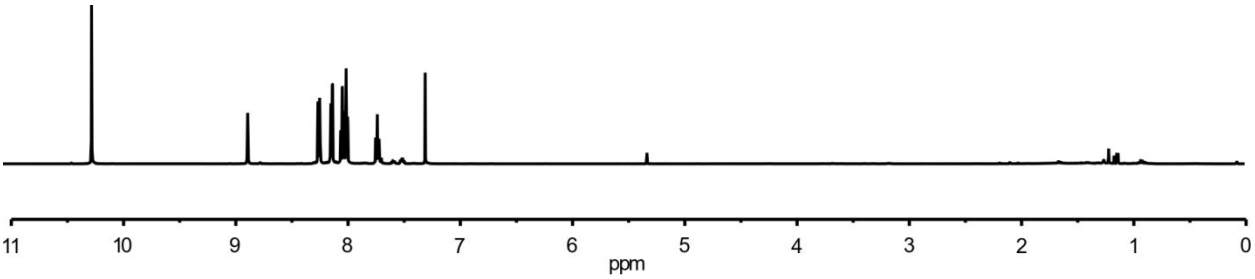


Figure S17. ^{1}H NMR (500 MHz, 297 K, $CDCl_3$) of compound **7**.

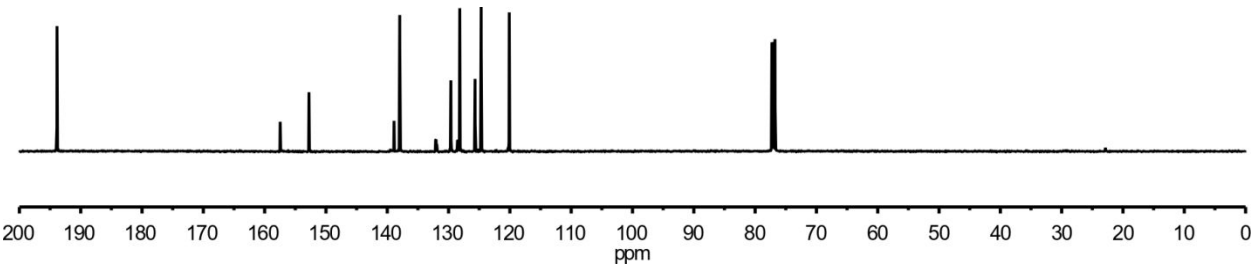


Figure S18. ^{13}C NMR (125 MHz, 297 K, $CDCl_3$) of compound **7**.

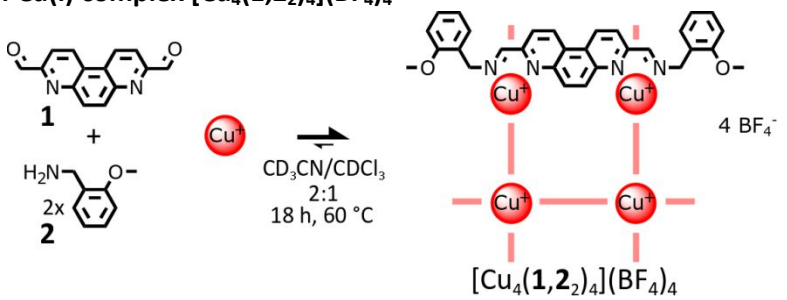
2.2 Synthesis of polynuclear metal complexes

2.2.1 General synthetic procedure

General synthetic procedure: A $CDCl_3$ solution of the dialdehyde containing component (100 µL of 160 mM, 16 µmol, 1 eq.) and a CD_3CN solution of the amine containing component (100 µL of 320 mM, 32

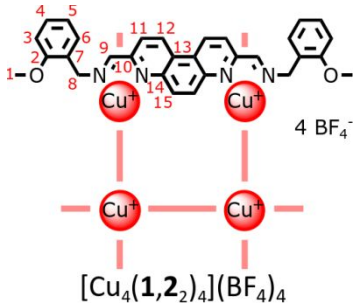
µmol, 2 eq.) were combined. The resulting mixture was either treated with a CD_3CN solution of $Fe(BF_4)_2 \cdot 6H_2O$ (100 µL of 160 mM, 16 µmol, 1 eq.) or a CD_3CN solution of $[Cu(CH_3CN)_4](BF_4)$ (100 µL of 160 mM, 16 µmol, 1 eq.) or a CD_3CN solution of $[Zn(C_2H_6OS)_6](BF_4)_2$ (100 µL of 160 mM, 16 µmol, 1 eq.) and heated at 60 °C for 18 h. After cooling to room temperature, diisopropyl ether (≈1 mL) was added. A fine suspension of material formed which was collected on Celite, washed with water, EtOH, diethylether. The resulting solid was dissolved in acetonitrile and concentrated under reduced pressure to give the desired complex. In all cases, the desired complex appeared pure by NMR spectroscopy.

2.2.2 Synthesis of Cu(I) complex $[Cu_4(1,2_2)_4](BF_4)_4$



Scheme 5. Synthesis of the Cu(I) complex $[Cu_4(\mathbf{1},\mathbf{2}_2)_4](BF_4)_4$.

$[Cu_4(\mathbf{1},\mathbf{2}_2)_4](BF_4)_4$ was synthesized using the general procedure described in section 2.2.1.·



^{1}H-NMR (500 MHz, CD_3CN:$CDCl_3$ 2:1): δ (ppm) 9.27 (d, J = 8.6 Hz, 8H, H^{12}), 8.85 (s, 8H, H^9), 8.15 (d, J = 8.6 Hz, 8H, H^{11}), 6.83 (s, 8H, H^{15}), 6.78 – 6.68 (m, 16H, H^{4+6}), 6.40 (t, J = 7.4 Hz, 8H, H^5), 6.29 (d, J = 8.1 Hz, 8H, H^3), 4.69 (d, J = 13.0 Hz, 9H, H^{8a}), 4.28 (d, J = 13.0 Hz, 8H, H^{8b}), 3.31 (s, 24H, H^1).

^{13}C-NMR (125.8 MHz, CD_3CN:$CDCl_3$ 2:1): δ (ppm) 160.64 (C^9), 158.15 (C^2), 151.98 (C^{10}), 145.36 (C^{14}), 134.67 (C^{12}), 131.75 (C^{15}), 131.60 (C^6), 130.20 (C^4), 127.38 (C^{13}), 125.36 (C^{11}), 125.23 (C^7), 120.57 (C^5), 110.76 (C^3), 58.92 (C^8), 55.38 (C^1).

HRMS (ESI+): *m/z* calcd. for $[[Cu_4(\mathbf{1},\mathbf{2}_2)_4](BF_4)_2]^{2+}$ 1162.7715 found 1162.7747.

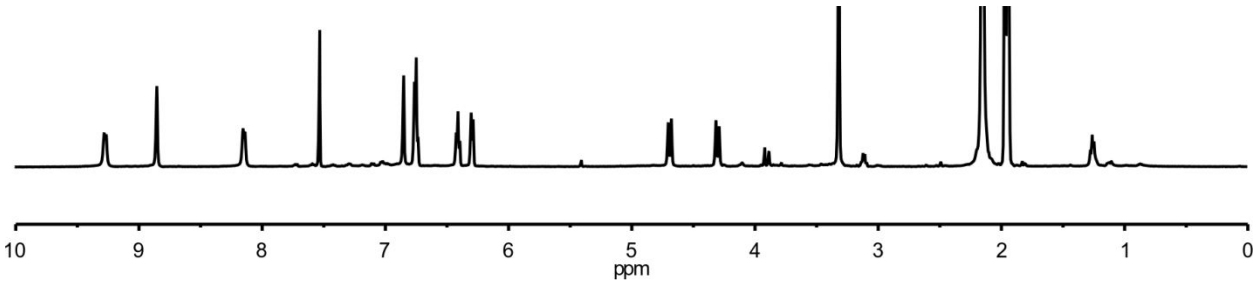


Figure S19. ^{1}H NMR (500 MHz, 297 K, CD_3CN:$CDCl_3$ 2:1) of Cu(I) complex $[Cu_4(\mathbf{1},\mathbf{2}_2)_4](BF_4)_4$.

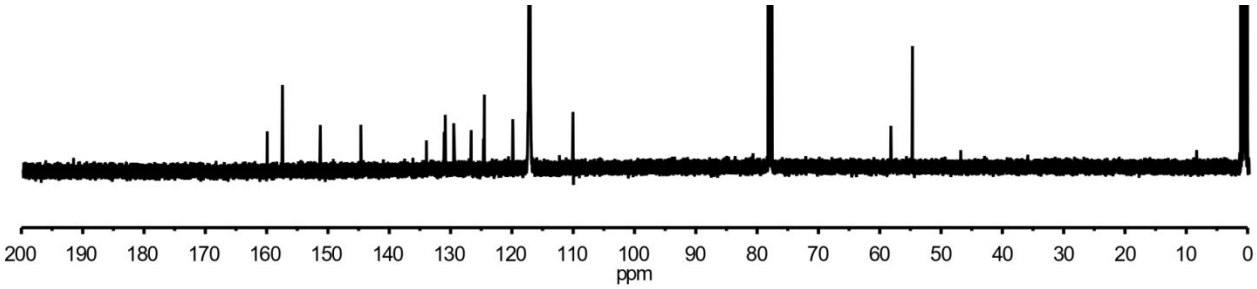
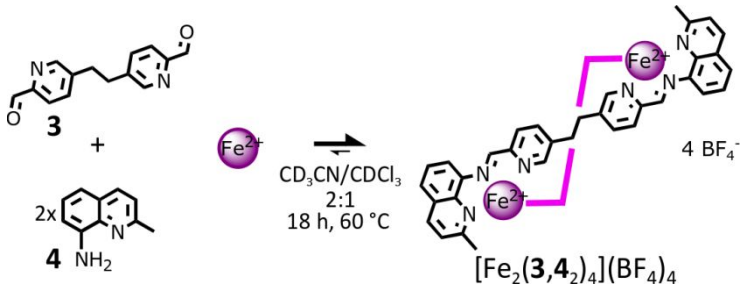


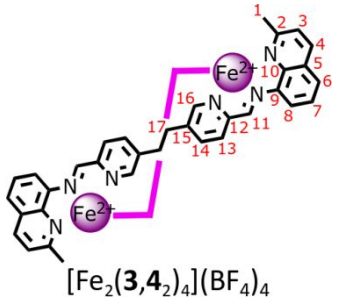
Figure S20. ^{13}C NMR (125 MHz, 297 K, CD_3CN:$CDCl_3$ 2:1) of Cu(I) complex $[Cu_4(\mathbf{1},\mathbf{2}_2)_4](BF_4)_4$.

2.2.3 Synthesis of Fe(II) complex $[Fe_2(\mathbf{3},\mathbf{4}_2)_2](BF_4)_4$



Scheme 6. Synthesis of the Fe(II) complex $[Fe_2(\mathbf{3},\mathbf{4}_2)_2](BF_4)_4$.

$[Fe_2(\mathbf{3},\mathbf{4}_2)_2](BF_4)_4$ was synthesized using the general procedure described in section 2.2.1.



^{1}H-NMR (500 MHz, 285 K, CD_3CN:$CDCl_3$ 2:1): δ (ppm) 11.87 (br s, 4H, H^{11}), 9.40 (d, J = 7.7 Hz, 4H, H^{8}), 8.47 (d, J = 8.0 Hz, 4H, H^{13}), 8.30 (d, J = 8.0 Hz, 4H, H^{6}), 8.19 (t, J = 7.9 Hz, 4H, H^{7}), 8.13 (d, J = 8.5 Hz, 4H, H^{4}), 7.91 (d, J = 8.0 Hz, 4H, H^{14}), 7.45 (br s, 4H, H^{16}), 7.29 (d, J = 8.3 Hz, 4H, H^{3}), 2.72 (d, J = 11.1 Hz, 2H, H^{17a}), 2.63 (d, J = 11.3 Hz, 2H, H^{17b}), 2.01 (br s, 12H, H^{1}).

^{13}C-NMR (125.8 MHz, 285 K, CD_3CN:$CDCl_3$ 2:1): δ (ppm) 174.21 (C^{2}), 160.20 (C^{11}), 155.69 (C^{12}), 152.52 (C^{16}), 148.48 (C^{10}), 143.80 (C^{15}), 142.37 (C^{5}), 139.15 (C^{4}), 137.56 (C^{14}), 132.74 (C^{6}), 131.53 (C^{13}), 129.78 (C^{3+9}), 129.01 (C^{7}), 121.15 (C^{8}), 30.91 (C^{17}), 26.39 (C^{1}).

HRMS (ESI+): *m/z* calcd. for $[[Fe_2(\mathbf{3},\mathbf{4}_2)_2](BF_4)_3]^+$ 1413.3563 found 1413.3539.

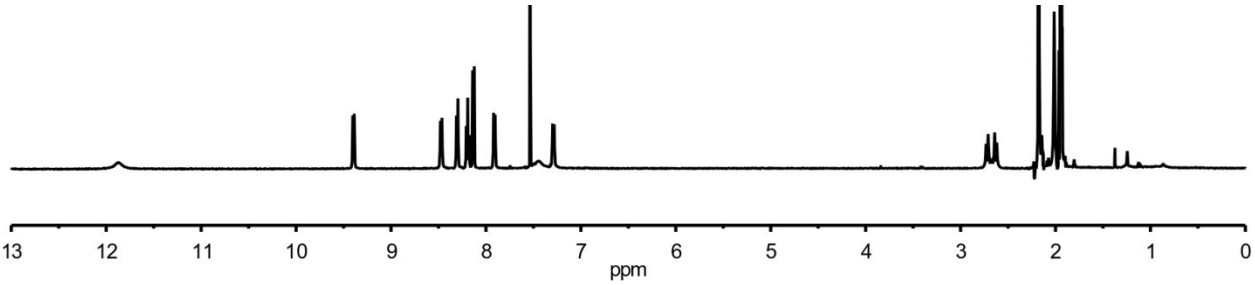


Figure S21. ^{1}H NMR (500 MHz, 285 K, CD_3CN:$CDCl_3$ 2:1) of Fe(II) complex $[Fe_2(\mathbf{3},\mathbf{4}_2)_2](BF_4)_4$.

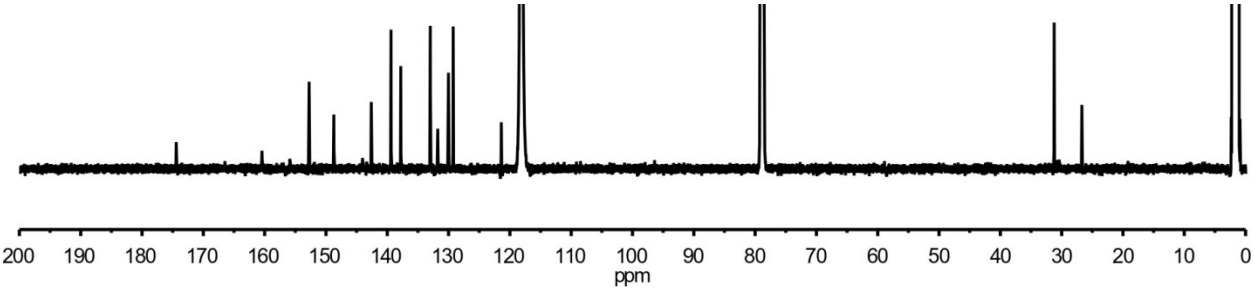


Figure S22. ^{13}C NMR (125 MHz, 285 K, CD_3CN:$CDCl_3$ 2:1) of Fe(II) complex $[Fe_2(\mathbf{3},\mathbf{4}_2)_2](BF_4)_4$.

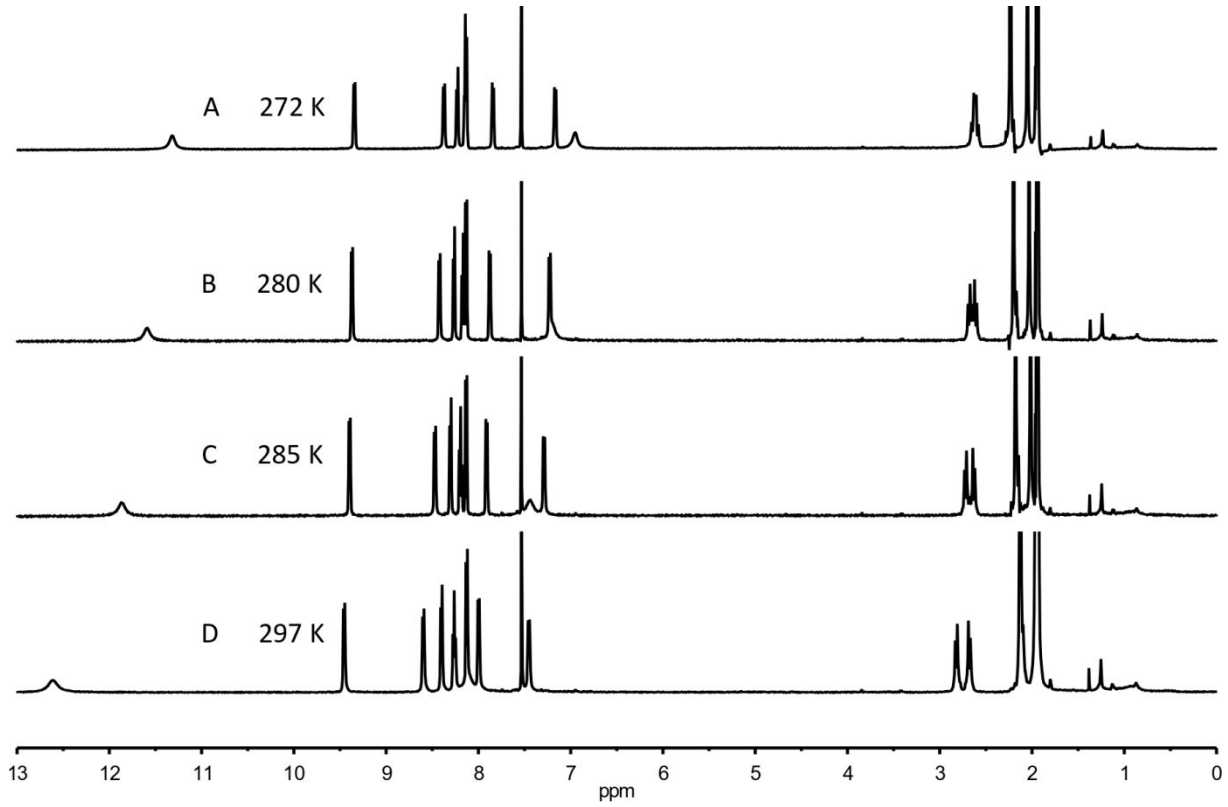
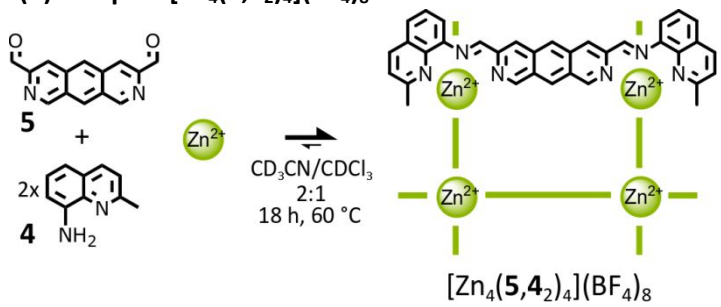


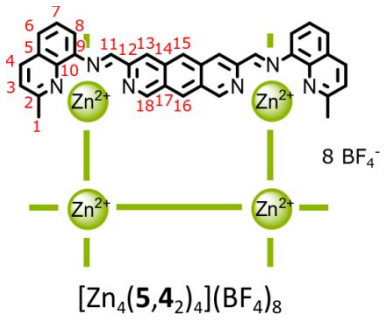
Figure S23. ^{1}H NMR spectra (500 MHz, CD_3CN) of the Fe(II) complex $[Fe_2(\mathbf{3},\mathbf{4}_2)_2](BF_4)_4$ at variable temperature from 272 K to 297 K. VT-NMR was performed from low to high temperature, starting from 272 K.

2.2.4 Synthesis of Zn(II) complex $[Zn_4(5,4_2)_4](BF_4)_8$



Scheme 7. Synthesis of the Zn(II) complex $[Zn_4(\mathbf{5},\mathbf{4}_2)_4](BF_4)_8$.

$[Zn_4(\mathbf{5},\mathbf{4}_2)_4](BF_4)_8$ was synthesized using the general procedure described in section 2.2.1.



^{1}H-NMR (500 MHz, 273 K, CD_3CN:$CDCl_3$ 2:1): δ (ppm) 9.87 (s, 8H, H^{11}), 8.78 (d, J = 9.0 Hz, 12H, H^{8+15}), 8.61 (s, 8H, H^{13}), 8.53 (s, 4H, H^{16}), 8.51 (s, 8H, H^{18}), 8.45 (d, J = 8.2 Hz, 8H, H^4), 8.25 (d, J = 8.2 Hz, 8H, H^6), 8.05 (t, J = 8.1 Hz, 8H, H^7), 7.40 (d, J = 7.9 Hz, 8H, H^3), 2.06 (s, 24H, H^1).

^{13}C-NMR (125.8 MHz, 273 K, CD_3CN:$CDCl_3$ 2:1): δ (ppm) 162.66 (C^2), 157.15 (C^{11}), 156.01 (C^{18}), 141.30 (C^{12}), 141.02 (C^4), 140.65 (C^{10}), 135.99 (C^{14}), 134.79 (C^{16}), 134.50 (C^9), 132.11 (C^6), 130.59 (C^{13}), 130.09 (C^{15}), 129.18 (C^{17}), 128.74 (C^5), 128.09 (C^7), 125.94 (C^3), 120.87 (C^8), 24.63 (C^1).

HRMS (ESI+): *m/z* calcd. for $[[Zn_4(\mathbf{5},\mathbf{4}_2)_4](BF_4)]^{7+}$ 344.9342 found 344.9334.

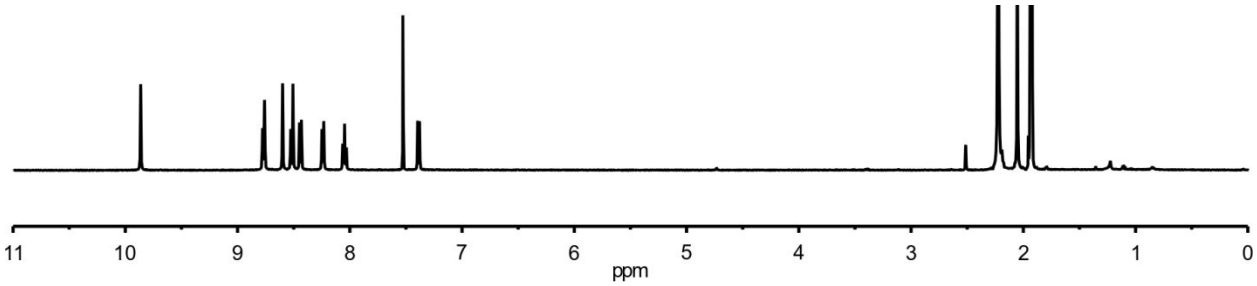


Figure S24. ^{1}H NMR (500 MHz, 273 K, CD_3CN:$CDCl_3$ 2:1) of Zn(II) complex $[Zn_4(\mathbf{5},\mathbf{4}_2)_4](BF_4)_8$.

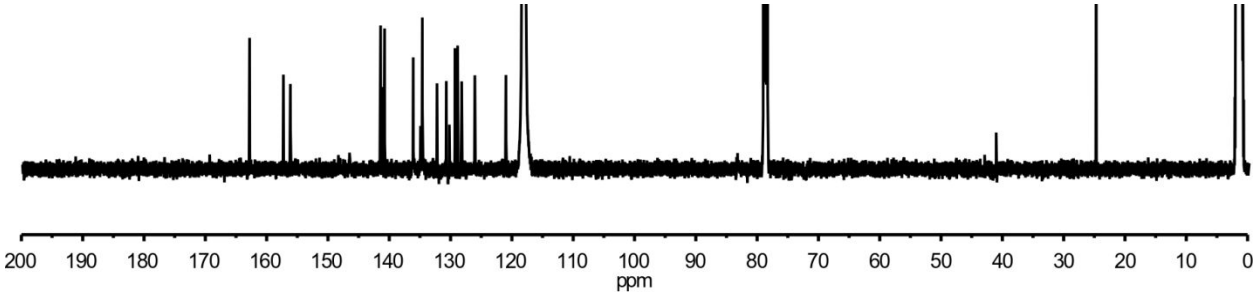


Figure S25. ^{13}C NMR (125 MHz, 273 K, CD_3CN:$CDCl_3$ 2:1) of Zn(II) complex $[Zn_4(\mathbf{5},\mathbf{4}_2)_4](BF_4)_8$.

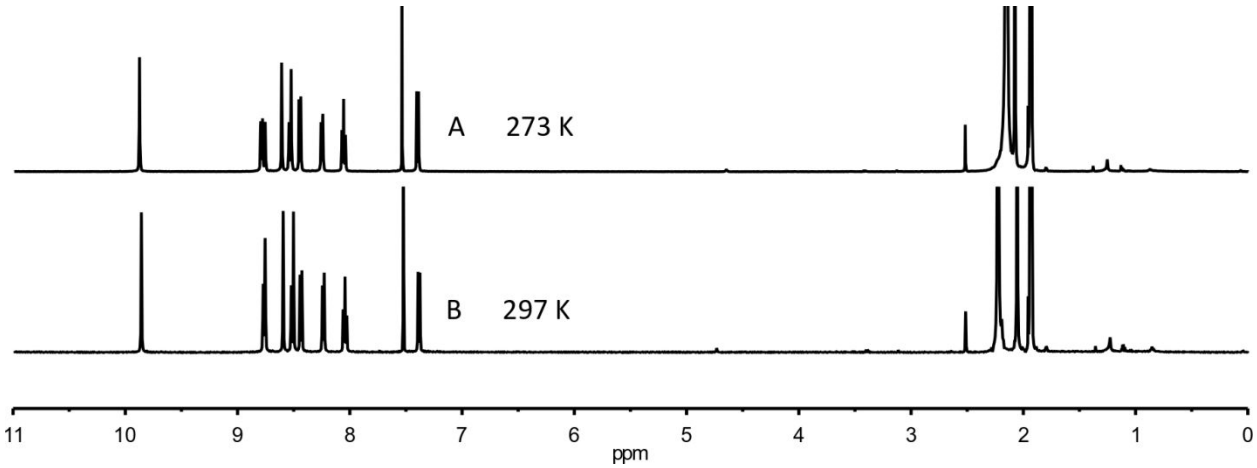
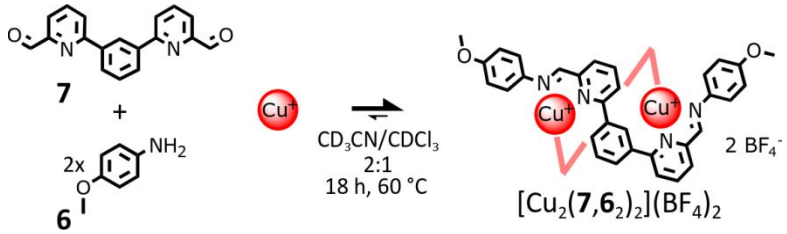


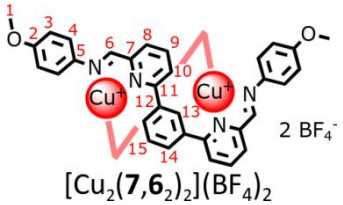
Figure S26. ^{1}H NMR spectra (500 MHz, CD_3CN) of Zn(II) complex $[Zn_4(\mathbf{5},\mathbf{4}_2)_4](BF_4)_8$ at 273 K and 297 K. VT-NMR was performed from low to high temperature, starting from 273 K.

2.2.5 Synthesis of Cu(I) complex $[Cu_2(\mathbf{7},\mathbf{6}_2)_2](BF_4)_2$



Scheme 8. Synthesis of the Cu(I) complex $[Cu_2(\mathbf{7},\mathbf{6}_2)_2](BF_4)_2$.

$[Cu_2(\mathbf{7},\mathbf{6}_2)_2](BF_4)_2$ was synthesized using the general procedure described in section 2.2.1.



^{1}H-NMR (500 MHz, 273 K, CD_3CN:$CDCl_3$ 2:1): δ (ppm) 9.39 (s, 2H, H^{13}), 8.43 (s, 4H, H^6), 7.94 (t, J = 7.7 Hz, 4H, H^9), 7.71 (d, J = 7.5 Hz, 4H, H^{10}), 7.50 (d, J = 7.4 Hz, 4H, H^8), 7.14 (d, J = 8.3 Hz, 4H, H^{14}), 7.11 – 7.04 (m, 2H, H^{15}), 6.63 (d, J = 9.0 Hz, 8H, H^4), 6.52 (d, J = 9.0 Hz, 8H, H^3), 3.70 (s, 12H, H^1).

^{13}C-NMR (125.8 MHz, 273 K, CD_3CN:$CDCl_3$ 2:1): δ (ppm) 161.20 (C^2), 155.93 (C^{11}), 155.40 (C^6), 151.57 (C^7), 140.08 (C^9), 139.44 (C^5), 138.35 (C^{12}), 129.91 (C^{15}), 128.56 (C^{13}), 128.05 (C^{14}), 127.15 (C^8), 126.53 (C^{10}), 124.54 (C^4), 114.76 (C^3), 56.23 (C^1).

HRMS (ESI+): *m/z* calcd. for $[Cu_2(\mathbf{7},\mathbf{6}_2)_2]^{2+}$ 562.1342 found 562.1327.

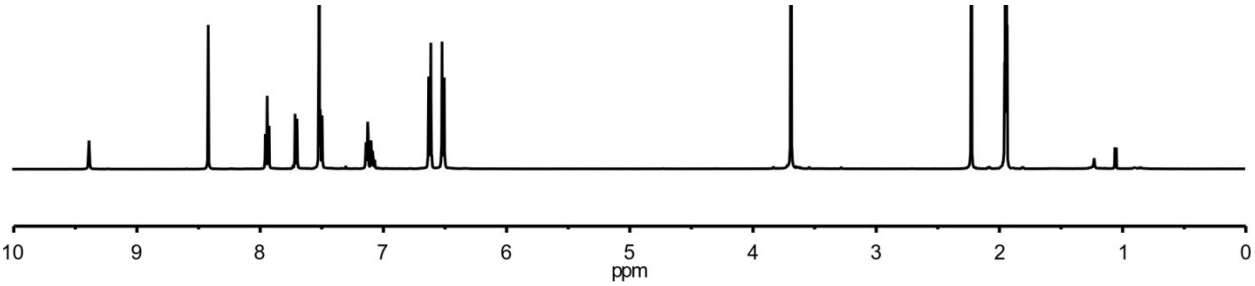


Figure S27. ^{1}H NMR (500 MHz, 273 K, CD_3CN:$CDCl_3$ 2:1) of Cu(I) complex $[Cu_2(\mathbf{7},\mathbf{6}_2)_2](BF_4)_2$.

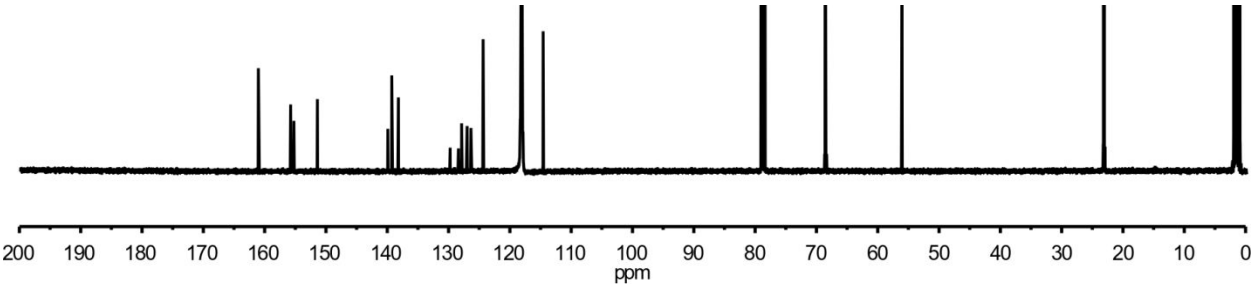


Figure S28. ^{13}C NMR (125 MHz, 273 K, CD_3CN:$CDCl_3$ 2:1) of Cu(I) complex $[Cu_2(\mathbf{7},\mathbf{6}_2)_2](BF_4)_2$.

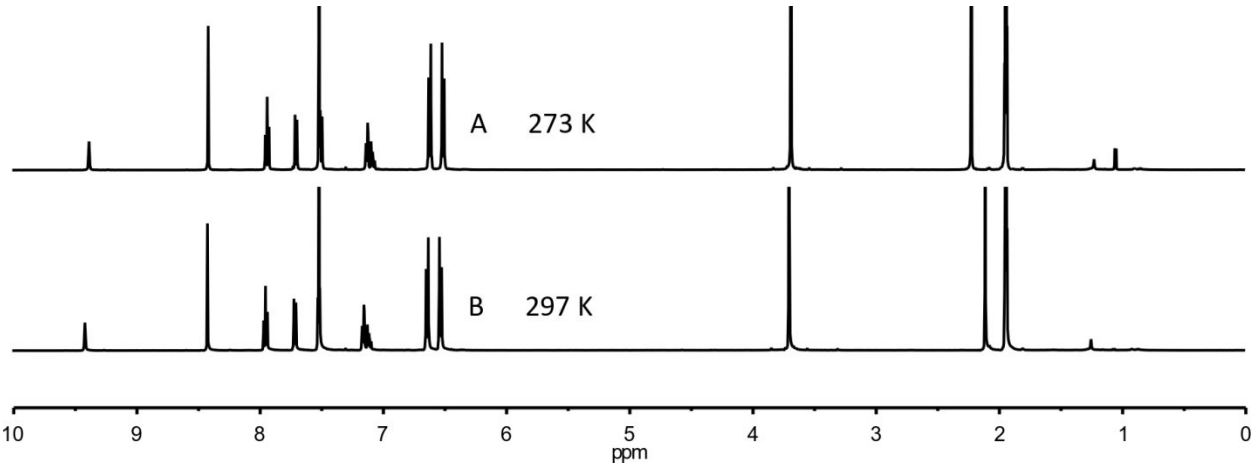
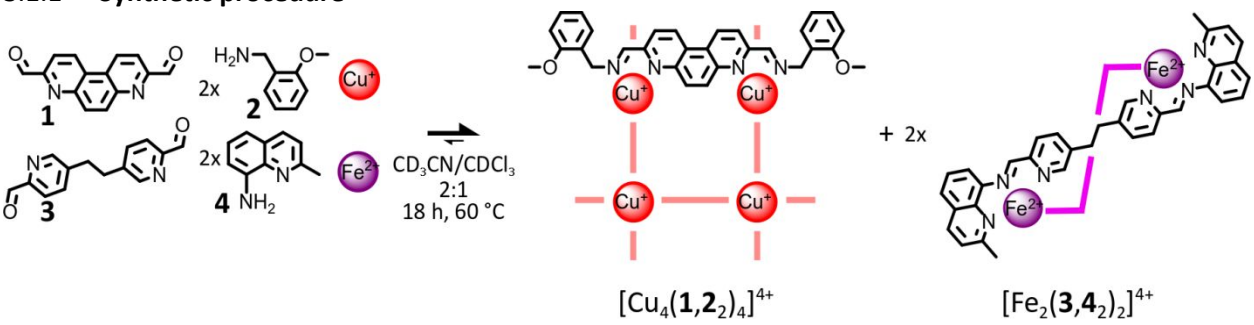


Figure S29. ^{1}H NMR spectra (500 MHz, CD_3CN) of Cu(I) complex $[Cu_2(\mathbf{7},\mathbf{6}_2)_2](BF_4)_2$ at 273 K and 297 K. VT-NMR was performed from low to high temperature, starting from 273 K.

3. Self-sorting reactions

3.1 Self-sorting of complexes $[Cu_4(1,2_2)_4]^{4+}$ and $[Fe_2(3,4_2)_2]^{4+}$

3.1.1 Synthetic procedure



Scheme 9. Synthesis of of complexes $[Cu_4(\mathbf{1},\mathbf{2}_2)_4]^{4+}$ and $[Fe_2(\mathbf{3},\mathbf{4}_2)_2]^{4+}$ through the self-sorting of their initial reactants.

$CDCl_3$ solutions of the dialdheydes **1** (100 µL of 16 mM, 1.6 µmol, 1 eq.) and **3** (100 µL of 16 mM, 1.6 µmol, 1 eq.) and CD_3CN solutions of the amine containing components **2** (100 µL of 32 mM, 3.2 µmol, 2 eq.) and **4** (100 µL of 32 mM, 3.2 µmol, 2 eq.) were combined. The resulting mixture was treated with CD_3CN solutions of $[Cu(CH_3CN)_4](BF_4)$ (100 µL of 16 mM, 1.6 µmol, 1 eq.) and $Fe(BF_4)_2{\cdot}6H_2O$ (100 µL of 16 mM, 1.6 µmol, 1 eq.) and heated at 60 °C for 18 h. The complexes were never isolated, all the present experiments and analysis were done on the crude reaction mixture.

3.1.2 Simultaneous generation of complexes $[Cu_4(1,2_2)_4]^{4+}$ and $[Fe_2(3,4_2)_2]^{4+}$

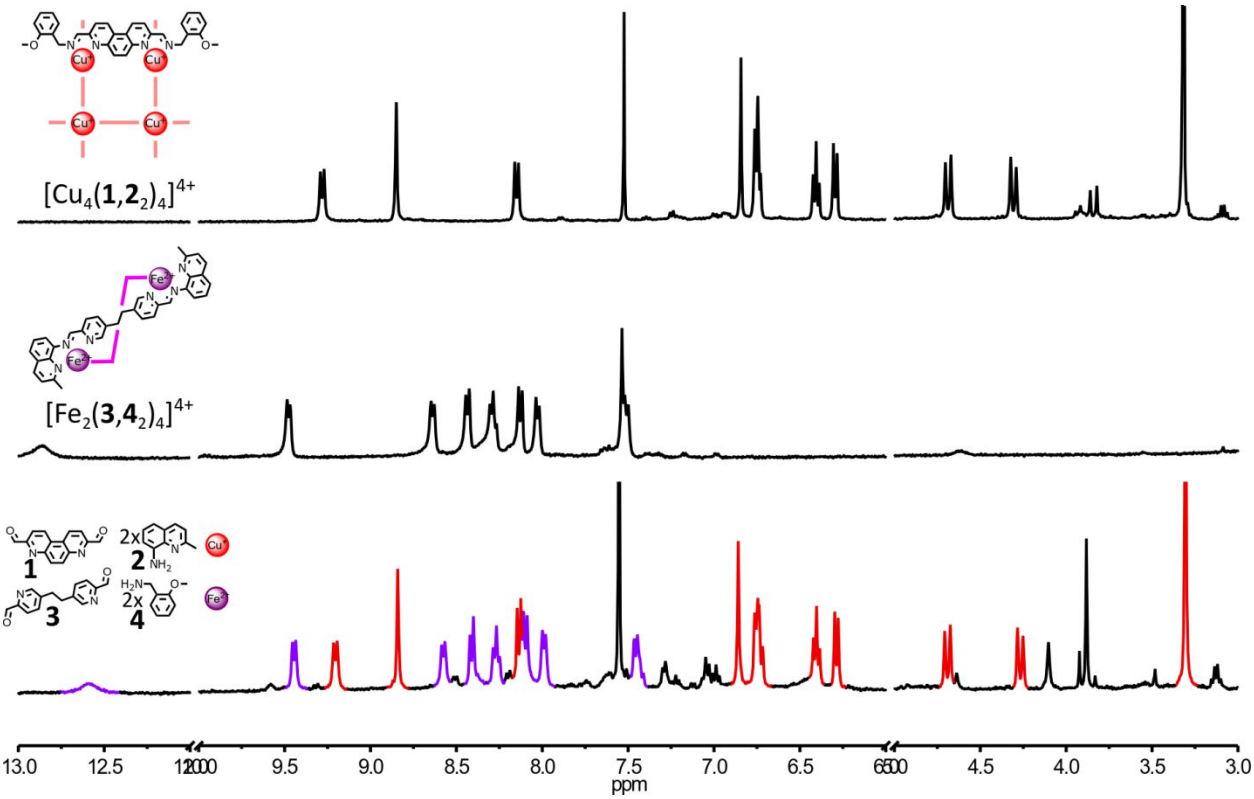


Figure S30. Partial ^{1}H NMR spectra (400 MHz, CD_3CN:$CDCl_3$ 2:1, 297 K) of: (top) complex $[Cu_4(\mathbf{1},\mathbf{2}_2)_4]^{4+}$, (middle) complex $[Fe_2(\mathbf{3},\mathbf{4}_2)_2]^{4+}$, (bottom) synthesis of complexes $[Cu_4(\mathbf{1},\mathbf{2}_2)_4]^{4+}$ and $[Fe_2(\mathbf{3},\mathbf{4}_2)_2]^{4+}$ through the self-sorting of their initial reactants. Reaction conditions: **1**:**2**:**3**:**4**:$Cu(BF_4)$:$Fe(BF_4)_2$ (2:2:1:1:1:1), CD_3CN:$CDCl_3$ 2:1, 60 °C, 18 h. The diagnostic signals of the complexes are colour coded, $[Cu_4(\mathbf{1},\mathbf{2}_2)_4]^{4+}$ in red and $[Fe_2(\mathbf{3},\mathbf{4}_2)_2]^{4+}$ in purple.

3.1.3 Probing the selectivity of the self-assembly of $[Cu_4(1,2_2)_4]^{4+}$ and $[Fe_2(3,4_2)_2]^{4+}$ from a mixture of components 1, 2, 3 and 4

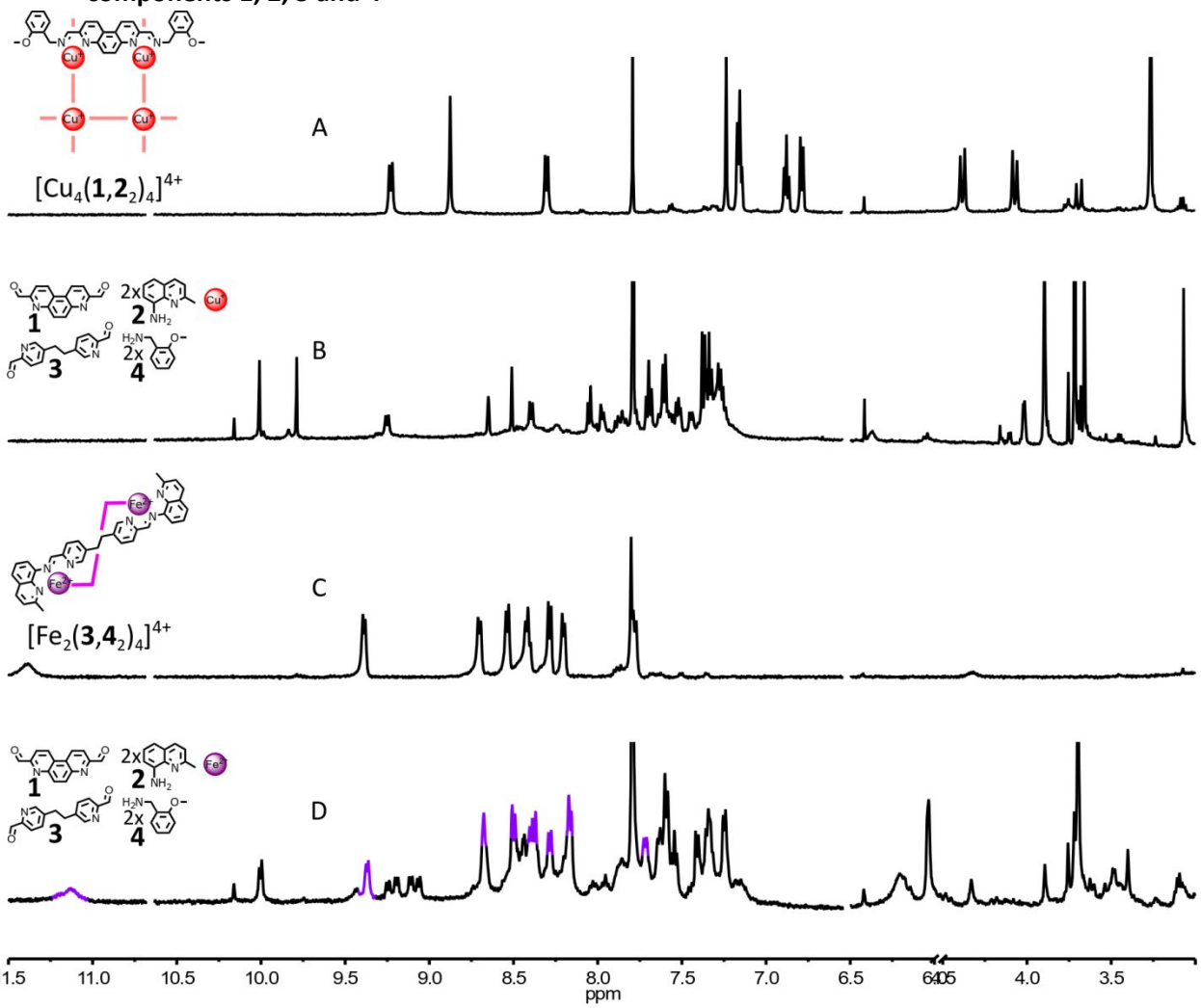
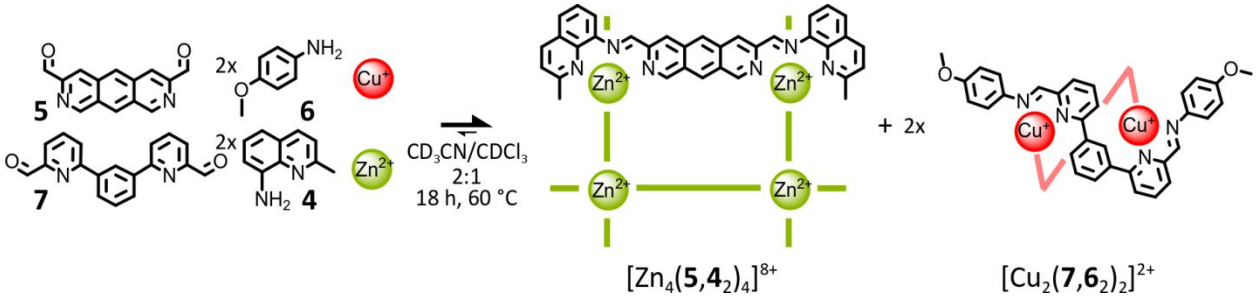


Figure S31. Partial ^{1}H NMR spectra (400 MHz, CD_3CN:$CDCl_3$ 2:1, 297 K) of: (A) complex $[Cu_4(\mathbf{1},\mathbf{2}_2)_4]^{4+}$, (B) the crude reaction mixture obtained by reacting components **1**, **2**, **3** and **4** with $Cu(BF_4)_2$ in the molar ratio 2:2:1:1:1 at 60 °C for 18 h, (C) complex $[Fe_2(\mathbf{3},\mathbf{4}_2)_2]^{4+}$ and (D) the crude reaction mixture obtained by reacting components **1**, **2**, **3** and **4** with $Fe(BF_4)_2$ in the molar ratio 2:2:1:1:1 at 60 °C for 18 h. Diagnostic signals of the complex $[Fe_2(\mathbf{3},\mathbf{4}_2)_2]^{4+}$ are colour coded in purple.

3.2 Self-sorting of complexes $[Cu_2(7,6_2)_2]^{2+}$ and $[Zn_4(5,4_2)_4]^{8+}$

3.2.1 Synthetic procedure



Scheme 10. Synthesis of of complexes $[Cu_2(\mathbf{7},\mathbf{6}_2)_2]^{2+}$ and $[Zn_4(\mathbf{5},\mathbf{4}_2)_4]^{8+}$ through the self-sorting of their initial reactants.

$CDCl_3$ solutions of the dialdheydes **5** (100 µL of 16 mM, 1.6 µmol, 1 eq.) and **7** (100 µL of 16 mM, 1.6 µmol, 1 eq.) and CD_3CN solutions of the amine containing components **4** (100 µL of 32 mM, 3.2 µmol, 2 eq.) and **6** (100 µL of 32 mM, 3.2 µmol, 2 eq.) were combined. The resulting mixture was treated with CD_3CN solutions of $[Cu(CH_3CN)_4](BF_4)$ (100 µL of 16 mM, 1.6 µmol, 1 eq.) and $[Zn(C_2H_6OS)_6](BF_4)_2$ (100 µL of 16 mM, 1.6 µmol, 1 eq.) and heated at 60 °C for 18 h. The complexes were never isolated, all the present experiments and analysis were done on the crude reaction mixture.

3.2.2 Simultaneous generation of complexes $[Cu_2(7,6_2)_2]^{2+}$ and $[Zn_4(5,4_2)_4]^{8+}$

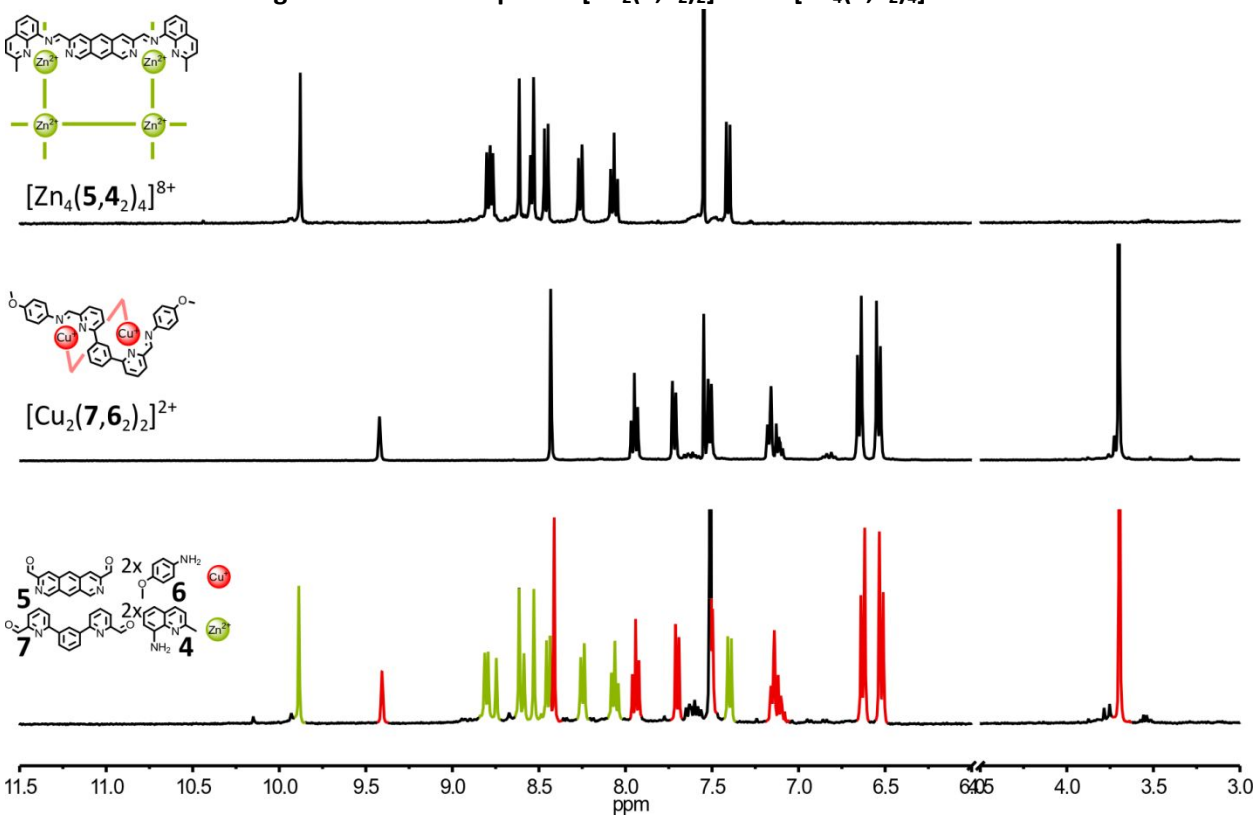


Figure S32. Partial ^{1}H NMR spectra (400 MHz, CD_3CN:$CDCl_3$ 2:1, 297 K) of: (top) complex $[Zn_4(\mathbf{5},\mathbf{4}_2)_4]^{8+}$, (middle) complex $[Cu_2(\mathbf{7},\mathbf{6}_2)_2]^{2+}$, (bottom) synthesis of complexes $[Cu_2(\mathbf{7},\mathbf{6}_2)_2]^{2+}$ and $[Zn_4(\mathbf{5},\mathbf{4}_2)_4]^{8+}$ through the self-sorting of their initial reactants. Reaction conditions: **4**:**5**:**6**:**7**:$Cu(BF_4)$:$Zn(BF_4)_2$ (2:2:1:1:1:1), CD_3CN:$CDCl_3$ 2:1, 60 °C, 18 h. The diagnostic signals of the complexes are colour coded, $[Cu_2(\mathbf{7},\mathbf{6}_2)_2]^{2+}$ in red and $[Zn_4(\mathbf{5},\mathbf{4}_2)_4]^{8+}$ in green.

3.2.3 Probing the selectivity of the self-assembly of $[Cu_2(7,6_2)_2]^{2+}$ and $[Zn_4(5,4_2)_4]^{8+}$ from a mixture of components 4, 5, 6 and 7

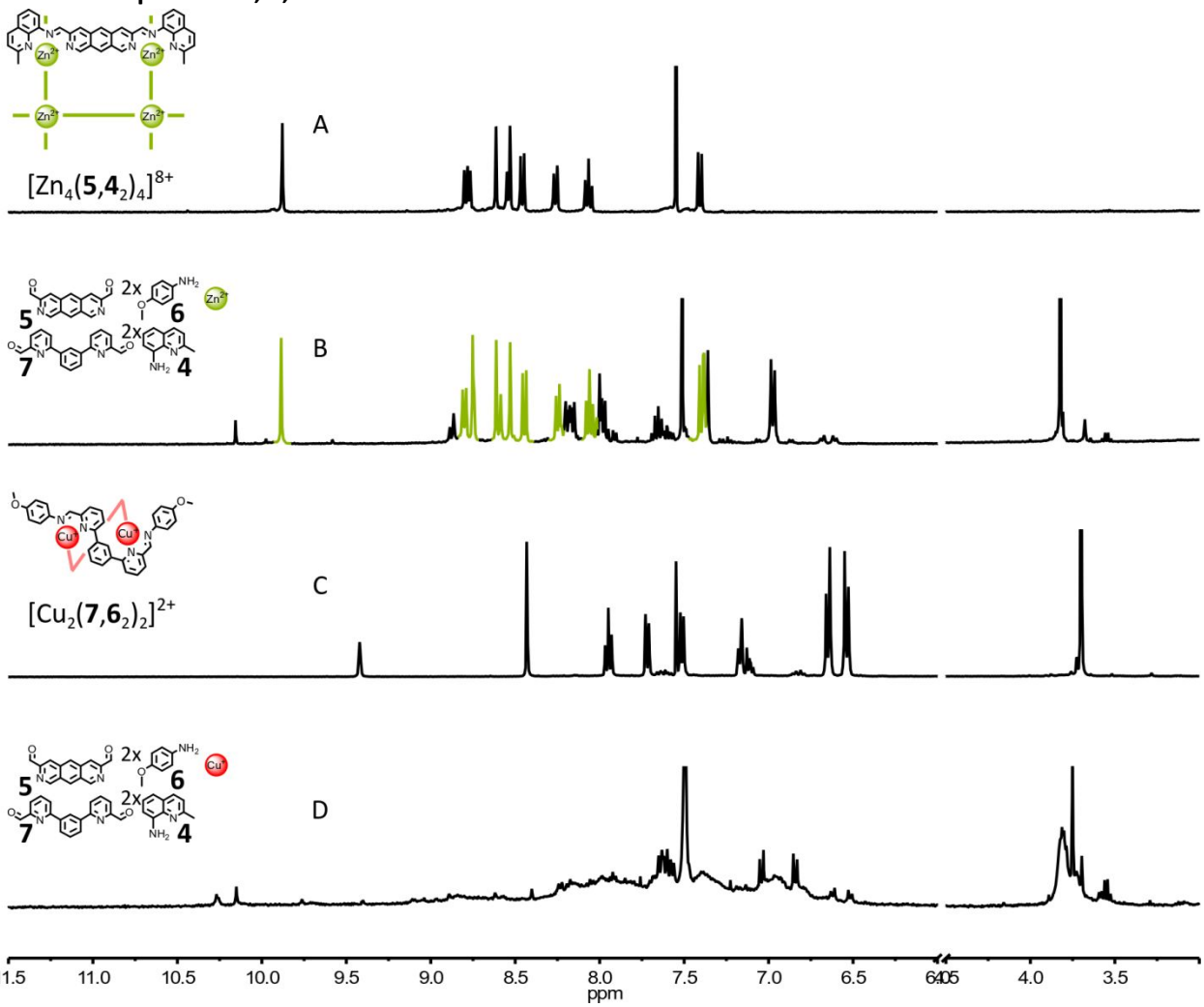


Figure S33. Partial ^{1}H NMR spectra (400 MHz, CD_3CN:$CDCl_3$ 2:1, 297 K) of: (A) complex $[Zn_4(5,4_2)_4]^{8+}$, (B) the crude reaction mixture obtained by reacting components **4**, **5**, **6** and **7** with $Zn(BF_4)_2$ in the molar ratio 2:2:1:1:1 at 60 °C for 18 h, (C) complex $[Cu_2(7,6_2)_2]^{2+}$ and (D) the crude reaction mixture obtained by reacting components **4**, **5**, **6** and **7** with $Cu(BF_4)_2$ in the molar ratio 2:2:1:1:1 at 60 °C for 18 h. Diagnostic signals of the complex $[Zn_4(5,4_2)_4]^{8+}$ are colour coded in green.

4. X-ray crystal structures

Single-crystal X-ray diffraction experiments were carried out by the service of the University of Strasbourg (Corinne Bailly and Dr. Lydia Karmazin). The crystals were placed in oil, and a single crystal was selected, mounted on a glass fibre and placed in a low-temperature N_2 stream.

CCDC-1947518 ($[Cu_2(7,6_2)_2](ClO_4)_2$·xSolvent), CCDC-1947519 ($[Fe_2(3,4_2)_4](PF_6)_4$·xSolvent), CCDC-1947520 ($[[Cu_4(1,2_2)_4]$·$C_6H_6](BPh_4)_4$·xSolvent) and CCDC-1947521 ($[Zn_4(5,4_2)_4](BF_4)_8$·xSolvent) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.1 X-ray crystal structure of $[Cu_2(7,6_2)_2](ClO_4)_2$·xSolvent

Single crystals of $[Cu_2(\mathbf{7},\mathbf{6}_2)_2](ClO_4)_2$ were grown by solvent diffusion of diisopropyl ether into an acetonitrile solution of $[Cu_2(\mathbf{7},\mathbf{6}_2)_2](BF_4)_2$ containing excess $KClO_4$.

X-ray diffraction data collection was carried out on a Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using Mo-Kα radiation (λ = 0.71073 Å). The crystal-detector distance was 38mm. The cell parameters were determined (APEX2 software)[S8] from reflections taken from three sets of 6 frames, each at 10s exposure. The structure was solved by Direct methods using the program SHELXS-2013.[S9] The refinement and all further calculations were carried out using SHELXL-2013.[S10] The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. A semi-empirical absorption correction was applied using SADABS in APEX2;[S8] transmission factors: T_{min}/T_{max} = 0.6421/0.7460.

4.2 X-ray crystal structure of $[[Cu_4(1,2)_2)_4]\cdot C_6H_6](BPh_4)_4$·xSolvent

X- Single crystals of $[[Cu_4(\mathbf{1},\mathbf{2}_2)_4]\cdot C_6H_6](BPh_4)_4$ were grown by solvent diffusion of benzene into an acetonitrile solution of $[Cu_4(\mathbf{1},\mathbf{2}_2)_4](BF_4)_4$ containing excess $KBPh_4$.

X-Ray diffraction data collection was carried out on a Bruker PHOTON-III DUO CPAD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using Cu-Kα radiation (λ = 1.54178 Å). The crystal-detector distance was 40 mm. The cell parameters were determined (APEX3 software)[S11] from reflections taken from two sets of 10 frames, each at 10s exposure. The structure was solved using the program SHELXT-2014.[S12] The refinement and all further calculations were carried out using SHELXL-2014.[S13] The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. A semi-empirical absorption correction was applied using SADABS in APEX3;[S11] transmission factors: T_{min}/T_{max} = 0.5257/0.7528

The SQUEEZE instruction in PLATON[S14] was applied. The residual electron density was assigned to half a molecule of the benzene solvent.

4.3 X-ray crystal structure of $[Fe_2(3,4_2)_4](PF_6)_4$·xSolvent

Single crystals of $[Fe_2(\mathbf{3},\mathbf{4}_2)_2](PF_6)_4$ were grown by solvent diffusion of diisopropyl ether into an acetonitrile solution of $[Fe_2(\mathbf{3},\mathbf{4}_2)_2](BF_4)_4$ containing excess KPF_6.

X-ray diffraction data collection was carried out on a Bruker PHOTON III DUO CPAD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using Cu-Kα radiation (λ = 1.54178 Å). The crystal-detector distance was 40mm. The cell parameters were determined (APEX3 software)[S11] from reflections taken from two sets of 10 frames, each at 10s exposure. The structure was solved using the program SHELXT-2014.[S12] The refinement and all further calculations were carried out using SHELXL-2014.[S13] The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. A semi-empirical absorption correction was applied using SADABS in APEX3;[S11] transmission factors: T_{min}/T_{max} = 0.4013/0.7528. The SQUEEZE instruction in PLATON[S14] was applied. The residual electron density was assigned to half a molecule of the acetonitrile solvent.

4.4 X-ray crystal structure of $[Zn_4(5,4_2)_4](BF_4)_8 \cdot x$Solvent

Slow diffusion of benzene into a solution of $[Zn_4(\mathbf{5},\mathbf{4}_2)_4](BF_4)_8$ in acetonitrile yellow crystals.

X-Ray diffraction data collection was carried out on a Bruker PHOTON-III DUO CPAD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using Cu-Kα radiation (λ = 1.54178 Å). The crystal-detector distance was 40 mm. The cell parameters were determined (APEX3 software)[S11] from reflections taken from two sets of 6 frames, each at 10s exposure. The structure was solved using the program SHELXT-2014.[S12] The refinement and all further calculations were carried out using SHELXL-2014.[S13] The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. A semi-empirical absorption correction was applied using SADABS in APEX3;[S11] transmission factors: T_{min}/T_{max} = 0.6255/0.7528.

The SQUEEZE instruction in PLATON[S14] was applied. The residual electron density was assigned to half a molecule of the tetrafluoroborate anion and three molecules of the acetonitrile solvent.

5. References

[S1] Choi, H. Y.; Srisook, E.; Jang, K. S.; Chi, D. Y. *J. Org. Chem.* **2005**, *70*, 1222–1226.

[S2] Cao, X.-Y.; Harrowfield, J.; Nitschke, J.; Ramírez, J.; Stadler, A.-M.; Kyritsakas-Gruber, N.; Madalan, A.; Rissanen, K.; Russo, L.; Vaughan, G.; Lehn, J.-M. *Eur. J. Inorg. Chem.* **2007**, 2944–2965.

[S3] Ayme, J.-F.; Beves, J. E.; Leigh, D. A.; McBurney, R. T.; Rissanen, K.; Schultz, D. *Nat. Chem.* **2012**, *4*, 15–20.

[S4] Bhalla, V.; Vij, V.; Dhir, A.; Kumar, M. *Chem. Eur. J.* **2012**, *18*, 3765–3772.

[S5] Bonifacio, M. C.; Robertson, C. R.; Jung, J.-Y.; King, B. T. *J. Org. Chem.* **2005**, *70*, 8522–8526.

[S6] Alfonsi, M. ; Dell'Acqua, M. ; Facoetti, D. ; Arcadi, A. ; Abbiati, G. ; Rossi, E. *Eur. J. Org. Chem.* **2009**, 2852–2862.

[S7] Campbell, C. J.; Leigh, D. A.; Vitorica-Yrezabal, I. J.; Woltering, I. J. *Angew. Chem. Int. Ed.* **2014**, *53*, 13771–13774.

[S8] "M86-E01078 APEX2 User Manual", Bruker AXS Inc., Madison, USA, 2006.

[S9] Sheldrick, G. M. *Acta Cryst.* **1990***,* A46, 467-473.

[S10] Sheldrick, G. M. *Acta Cryst.* **2008**, A64, 112-122.

[S11] "M86-EXX229V1 APEX3 User Manual", Bruker AXS Inc., Madison, USA, 2016.

[S12] Sheldrick, G. M. *Acta Cryst.* **2015***,* A71, 3-8.

[S13] Sheldrick, G. M. *Acta Cryst.* **2015**, C71, 3-8.

[S14] Spek, A.L. *J. Appl. Cryst.* **2003**, *36*, 7-13.