Supporting Information for:

Reversible anion templated self-assembly of [2+2] and [3+3] metallomacrocycles containing a new dicopper(I) motif

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1 Experimental

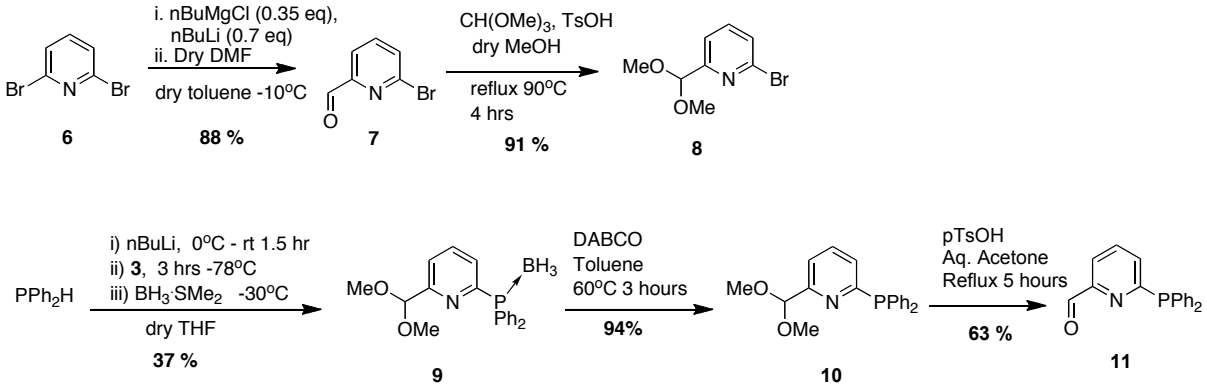
1.1 General

All synthetic procedures were carried out with freshly distilled solvents and under strict anhydrous conditions with a nitrogen over pressure. Where solvents are described as deoxygenated, this was achieved either by sparging the solvent with nitrogen flow for at least 20 minutes, or three vacuum-pump-thaw cycles. With the following exceptions, all reagents were purchased from Alfa Aesar or Aldrich and used without further purification. DMF was distilled over calcium hydride under high vacuum (90°C) directly into a pre-dried storage flask containing molecular sieves activated in a microwave oven for 90 seconds. N-butyllithium was purchased from Acros Organics, and its concentration calculated by titration with diphenylacetic acid in dry THF under a nitrogen atmosphere.[S1] $Cu(CH_3CN)_4BF_4$ was prepared according to literature procedures.[S2]

Self-assembly reactions were undertaken in degassed, deuterated solvents purchased from Euriso-top. NMR spectra were recorded on Avance BB500-ATM, Bruker DPX 400, Bruker DRX 400, Avance 500 Cryo and Avance III 400 QNP Cryo spectrometers. Chemical shifts are reported in ppm and are referenced to residual acetonitrile (1.94 ppm for ^{1}H NMR, 1.32 ppm for ^{13}C) or benzene (7.16 ppm for ^{1}H NMR, 128.06 ppm for ^{13}C). All coupling constants are reported in Hz. ^{31}P NMR spectra were referenced to 85 % H_3PO_4 at 0 ppm in $CDCl_3$. Low resolution electrospray ionisation mass spectra (ESI-MS) were obtained on a Perkin Elmer Turbomass. High resolution ESI were measured on either a Walters LCT or Bruker Daltonics FTICR Bioapex II.

Molecular modelling was done at the MM2 level using CAChe Workspace, WorkSystem Pro Version 7.5.0.85.[S3]

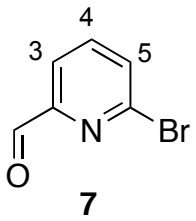
1.2 Synthesis of 6-(diphenylphosphino)picolinaldehyde



6 **7** **8** **9** **10** **11**

Scheme S 1 Synthesis of **11**

6-bromopicolinaldehyde 7[S4]

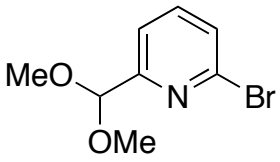


7

A solution of *n*-butyl lithium (69.4 mL, 1.6 M in hexanes, 111 mmol) in dry toluene (53 mL) was cooled to -10 °C. *n*-Butyl magnesium chloride (28.0 mL, 2 M in THF, 55.5 mmol) was added slowly over 30 minutes and the mixture stirred at -10 °C for a further 30 minutes. A solution of 2,6-dibromopyridine (35.0 g, 148 mmol) in dry toluene (280 mL) was canulated into a dropping funnel attached to the main reaction vessel, and then added dropwise over 70 minutes. The reaction was then stirred between -8 °C and -10 °C monitored by an internal thermometer for 30 minutes. The solution was canulated into a cooled (-10 °C) solution of dry DMF (15.0 mL) in dry toluene (50 mL) over 45 minutes, and then stirred for a further 30 minutes. The reaction was quenched by canulation onto a cooled (-10 °C) aqueous solution of citric acid (57.8 g). After stirring below 20 °C for 20 minutes, the organic layer was separated off in two batches. The organic layers were washed with water, Na_2CO_3 and brine. The aqueous layers were back extracted with toluene, and the combined organic layers were dried ($NaSO_4$) and concentrated *in vacuo* to yield a white crystalline solid (24.2 g, 88 %). If required, purification was effected by sublimation under high vacuum at 50 °C. ^{1}H NMR (400 MHz; 298 K; C_6D_6): δ 6.43 (1H, t, $J_{H\text{-}H}$ = 8.0 Hz, 4-pyridine), 6.79 (1H, d, $J_{H\text{-}H}$ = 8.0

Hz, 5-pyridine), 7.28 (1H, d, J_{H-H} = 8.0 Hz, 3-pyridine), 9.75 (1H, s, C*H*O). ^{13}C NMR (101 MHz; 298 K; C_6D_6): δ 120.2, 132.6, 139.3, 143.0, 154.3, 191.6. HRMS (ESI) calculated for C_6H_4NOBr $[MNa]^+$ *m/z*: 207.9368; found *m/z*: 207.9375.

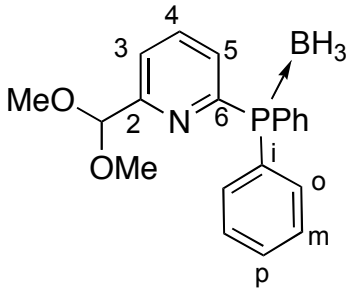
2-bromo-6-(dimethoxymethyl)pyridine 8[S5]



8

A flask was charged with **7** (24.0 g, 130 mmol), *p*-toluenesulphonic acid (490 mg, cat.) and trimethylorthoformate (60 mL) and sparged with nitrogen. Dry methanol (240 ml) was added *via* canula. The reaction was refluxed at 67 ^{o}C for 4 hours. The mixture was diluted with dichloromethane and washed with sat. Na_2CO_3 and water. The aqueous layers were back extracted with dichloromethane, and the combined organic layers were washed with brine, dried ($MgSO_4$) and evaporated to dryness to yield a yellow oil which solidified on placing in freezer (27.4 g, 91 %). ^{1}H NMR (400 MHz; 298 K; C_6D_6): δ 3.11 (6H, s, -O*Me*), 5.20 (1H, s, C*H*$(OMe)_2$), 6.71 (1H, t, J_{H-H} = 7.8 Hz, 4-pyridine), 6.90 (1H, d, J_{H-H} = 7.8 Hz, 5-pyridine), 7.31 (1H, d, J_{H-H} = 7.8Hz, 3-pyridine). ^{13}C NMR (101 MHz; 298 K; C_6D_6): δ 54.3, 104.7, 120.6, 139.2, 142.2, 160.2. HRMS (ESI) calculated for $C_8H_{10}NO_2Br$ $[MH]^+$ *m/z*: 231.9973; found *m/z*: 231.9975.

2-(dimethoxymethyl)-6-(diphenylphosphino)pyridine-Borane adduct 9[S6, 7]

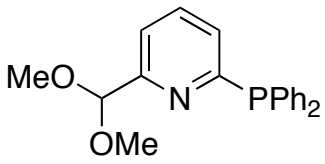


9

A solution of diphenylphosphine (17.5 mL, 101 mmol) in dry THF (115 mL) was cooled to 0 ºC, and *n*-butyl lithium (72 mL, 1.4 M in hexanes, 101 mmol) was added dropwise over 40 minutes yielding a bright orange solution. The solution was allowed to warm to room

temperature and stirred for 3.5 hours. A solution of **8** (23.4 g, 101 mmol) in dry THF (115 ml) was prepared and both flasks cooled to -78 ºC. The solution of **8** was canulated slowly into the PPh_2Li solution, resulting in a deep brown colour. The reaction mixture was allowed to warm to room temperature overnight. The reaction was then cooled to -30 ºC and an excess of $BH_3{\cdot}SMe_2$ (>3 eq) was slowly added. The reaction was stirred at -30 ºC for 40 minutes, then at room temperature for 2 hours. The reaction was quenched by careful addition of saturated ammonium chloride solution until cessation of effervescence. Water and ether were added and the organic layer separated in batches. The aqueous layers were back-extracted with ether, and the organic layers washed with brine. The combined ether solutions were dried ($MgSO_4$) and evaporated to yield an orange oil (28.3 g, 80 % crude). Purification by flash column chromatography in two batches (isocratic solvent: 15% ethyl acetate/ hexane; 900 mL silica gel; loaded via adsorption onto 50 mL silica) gave a pure white crystalline solid (14.1 g, 37 %). ^{1}H NMR (400 MHz; 298 K; C_6D_6): δ 2.23 (3H, br q, $J_{H\text{-}B}$ = 117.3 Hz, -B*H*$_3$), 3.06 (6H, s, -O*Me*), 5.15 (1H, s, C*H*(OMe)$_2$), 7.02 (7H, m, *m,p*-Ph_2, 5-pyridine), 7.41 (1H, d, $J_{H\text{-}H}$ = 7.9 Hz, 3-pyridine), 8.00 (4H, m, *o*- Ph_2), 8.14 (1H, t, $J_{H\text{-}H}$ = 6.7 4-pyridine). ^{13}C NMR (101 MHz; 298 K; C_6D_6): δ 54.1 (s, O*C*H$_3$), 104.9 (s, -*C*H(OMe)$_2$), 123.3 (d, $J_{C\text{-}P}$ = 2.2 Hz, 3-pyridine), 129.2 (d, $J_{C\text{-}P}$ = 10.8 Hz, *m*-Ph), 130.5 (d, $J_{C\text{-}P}$ = 7.7 Hz, 5-pyridine), 130.8 (d, $J_{C\text{-}P}$ = 23.5 Hz, *i*-Ph), 131.7 (d, $J_{C\text{-}P}$ = 2.2 Hz, *p*-Ph), 134.5 (d, $J_{C\text{-}P}$ = 9.7 Hz, *o*-Ph), 137.5 (d, $J_{C\text{-}P}$ = 10.0 Hz, 4-pyridine), 154.5 (d, $J_{C\text{-}P}$ = 73.8 Hz, 6-pyridyl carbon), 159.7 (d, $J_{C\text{-}P}$ = 11.8 Hz, 2-pyridine). ^{31}P NMR (202.5 MHz; 298K; C_6D_6): δ 18.5 (br d, 53.4 Hz). ^{11}B NMR (160 MHz; 298K; C_6D_6): δ -37.73 (br m). HRMS (ESI) calculated for $C_{20}H_{23}BNO_2P$ $[MH]^+$ *m/z*: 352.1645; found *m/z*: 352.1638. Elemental analysis calcd (%) for $C_{20}H_{23}NO_2P$: C 68.40, H 6.6, N 3.44; found C 68.18, H 6.56, N 4.01.

2-(dimethoxymethyl)-6-(diphenylphosphino)pyridine 10[S7]

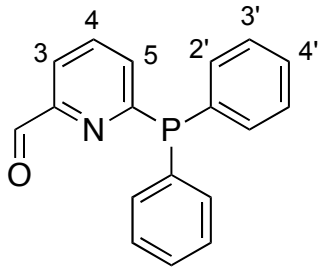


10

A flask was charged with diazabicycloundecane (2.41 g, 21.4 mmol, 2.2 eq), **9** (3.711 g, 9.76 mmol), and sparged with nitrogen. Dry, deoxygenated toluene (50 mL) was added and the mixture heated at 60 ºC for 90 minutes. An aqueous workup was performed with

deoxygenated solvents; the reaction mixture was washed with 3N HCl, water and brine, dried ($NaSO_4$) and evaporated to a clear oil (3.4 g, 94 %). ^{1}H NMR (400 MHz; 298 K; C_6D_6): δ 3.17 (6H, s, O*Me*), 5.30 (1H, s, C*H*$(OMe)_2$), 6.99 (2H, m, 3,5-pyridine), 7.06 (6H, m, *m,p*-Ph_2), 7.46 (1H, t, J_{H-H} = 4.5 Hz, 4-pyridine), 7.50 (4H, td, J_{H-H} = 7.7 Hz, J_{H-P} = 1.8 Hz, *o*- Ph_2). ^{13}C NMR (100.6 MHz; 298K; C_6D_6): δ 54.0, 105.4, 119.8, 128.8 (d, J_{C-P} = 7.2 Hz), 129.1, 134.7 (d, J_{C-P} = 19.8 Hz), 136.22 (d, J_{C-P} = 2.7 Hz), 137.5 (d, J_{C-P} = 11.8 Hz), 159.12 (d, J_{C-P} = 11.7 Hz), 163.3 (d, J_{C-P} = 2.5 Hz). ^{31}P NMR (202.5 MHz; 298K; C_6D_6): δ -3.31 (s, pyr-*P*Ph_2).

6-(diphenylphosphino)picolinaldehyde 11

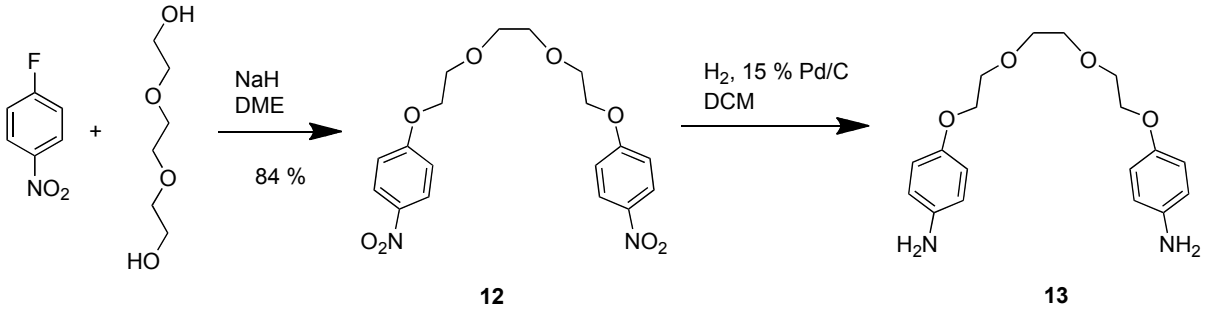


11

Acetone (40 mL) and water (6 mL) were combined and sparged with nitrogen for 50 minutes, and then added to a deoxygenated flask containing **10** (3.10 g, 9.2 mmol) and *p*-toluenesulphonic acid (241 mg, 0.13 eq). A condenser was fitted under positive nitrogen pressure, and the mixture heated under nitrogen to reflux (60ºC) for 5 hours. The solvents were removed under high vacuum on a manifold, and the reaction quenched by addition of deoxygenated sat. $NaHCO_3$. Deoxygenated dichloromethane was added, and the mixture transferred to a large degassed Schlenk flask. The aqueous layer was removed and the organic layer dried in situ ($NaSO_4$). The organic layer was transferred to a new Schlenk flask, and the solvent removed by dynamic vacuum to yield a yellow oil. The residue was rinsed to the bottom of the flask with ether (2-3 ml) where immediately some solid formed. The ether was allowed to slowly evaporate under a flow of nitrogen from the side arm of the flask, leaving behind yellow crystals. The crystals were triturated with small amounts of ethanol (>10 x 0.5 ml) until the colour of the washings had faded and then dried to yield a yellow crystalline solid (1.679 g, 63 %). IR (neat) ν = 1706 cm^{-1}. ^{1}H NMR (400 MHz; 298 K; C_6D_6): δ 6.77 (1H, t, J_{H-H} = 7.6 Hz, 4-pyridine), 7.01 (1H, d, J_{H-H} = 7.6Hz, 5-pyridine), 7.07 (6H, m, *m,p*-Ph_2), 7.45 (5H, m, *o*-Ph_2, 3-pyridine), 9.93 (1H, s, C*H*O). ^{13}C NMR (101 MHz; 298 K;

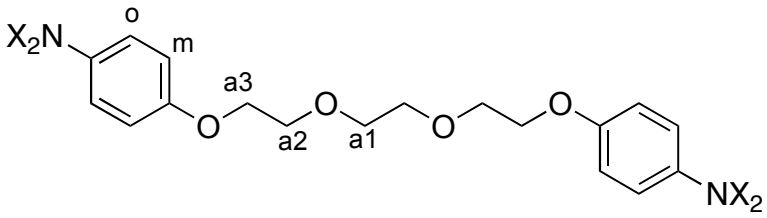
C_6D_6): δ 119.4 (s, 3-pyridine), 129.0 (d, J_{C-P} = 7.3 Hz, *m*-Ph), 129.4 (s, *p*-Ph), 131.4 (d, J_{C-P} = 18.2 Hz, 5-pyridine), 134.7 (d, J_{C-P} = 20.2 Hz, *o*-Ph), 136.4 (d, J_{C-P} = 2.8 Hz, 4-pyridine), 136.7 (d, J_{C-P} = 11.5 Hz, *i*-Ph), 153.8 (d, J_{C-P} = 9.9 Hz, 6-pyridine), 165.3 (d, J_{C-P} = 2.0 Hz, 2-pyridine), 193.0 (s, *C*HO). ^{31}P NMR (202.5 MHz, 298 K, C_6D_6) : δ -2.71. HRMS (ESI) calculated for $C_{18}H_{14}NOP$ $[MH]^+$ *m/z*: 292.0891; found *m/z*: 292.0880. Elemental analysis calcd (%) for $C_{18}H_{14}NOP\cdot{}^1/_2(H_2O)$: C 71.99, H 5.03, N 4.66, P 10.31; found C 71.72, H 4.92, N 4.70, P 10.06.

1.3 Synthesis of triethyleneglycol bis(*p*-aminophenyl)ether



12 **13**

Scheme S2 Synthesis of triethyleneglycol bis(*p*-aminophenyl)ether, **13**[S8]



12/13

Triethyleneglycol bis(*p*-nitrophenyl)ether 12[S8]

Into a deoxygenated two-necked flask sodium hydride (0.523 g 60 % by wt, 12.5 mmol), triethylene glycol (0.67 mL, 5 mmol) and dimethoxyethane (DME) (30 mL) were added. The solution was stirred at room temperature until no further gas evolved. 4-fluoronitrobenzene (1.06 mL, 10 mmol) was then added resulting in a red/white colour. The reaction was stirred at room temperature overnight after which the colour had become very dark red. The reaction mixture was concentrated *in vacuo* and the product was then dissolved in dichloromethane, washed twice with water and finally dried to yield a yellow solid (1.603 g, 84 %). ^{1}H NMR

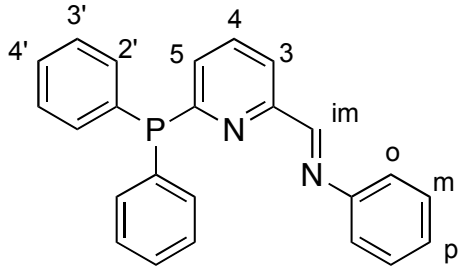
(400 MHz; 300 K; $CDCl_3$): δ 8.18 (4H, d, J = 8.6 Hz, o-H), 6.96 (4H, d, J = 8.6 Hz, m-H), 4.21 (4H, m, a^3-CH_2), 3.89 (4H, m, a^3-CH_2), 3.74 (4 H, s, a^1-CH_2).

Triethyleneglycol bis(*p*-aminophenyl)ether 13[S8]

Into a two-necked flask 12 (2.00 g, 5.1 mmol), palladium on carbon (300 mg, 15% wt) and dichloromethane (100 mL) were added. The flask was sealed and the atmosphere purged of dioxygen with three vacuum/hydrogen cycles using a hydrogen balloon. The reaction mixture was stirred at room temperature under a hydrogen atmosphere overnight. The solution was filtered and dichloromethane evaporated to yield a black oily solid (1.31 g, 77 %) that was used without further purification. ^{1}H NMR (400 MHz; 300 K; CD_3CN): δ 6.69 (4H, d, J = 8.8 Hz, o-H), 6.56 (4H, d, J = 8.6 Hz, m-H), 3.97 (4H, m, a^3-CH_2), 3.71 (4H, m, a^3-CH_2), 3.79 (4H, br s, NH_2), 3.62 (4 H, s, a^1-CH_2). ^{13}C NMR (100 MHz; 300K; CD_3CN): δ = 152.07, 142.85, 118.32, 116.58, 71.33, 70.56, 69.01. HRMS (ESI) calculated for $C_{18}H_{24}N_2O_4$ $[MH]^+$ *m/z*: 332.17; found *m/z*: 333.4.

1.4 Synthesis of copper(I) complexes and metallomacrocycles

1.4.1 $[Cu_2L^1{}_2MeCN_2]\cdot 2BF_4$ 1



L^1

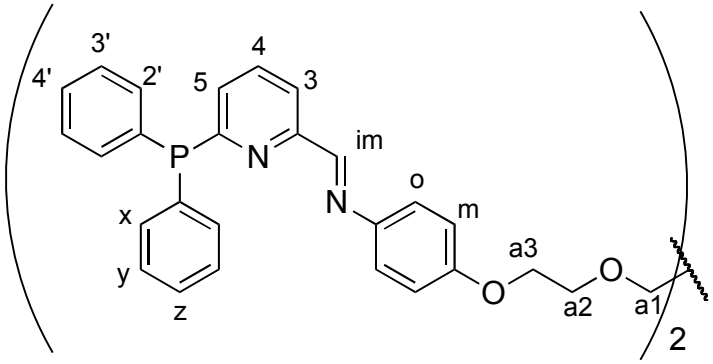
Into a dry and deoxygenated Schlenk flask with a teflon screw top, **11** (613.4 mg, 2.106 mmol), aniline (192 μl, 2.106 mmol) and acetonitrile (48 mL) were added. The solution was purged of dioxygen with three vacuum/nitrogen cycles. $Cu(CH_3CN)_4BF_4$ (662.8 mg, 2.106 mmol) was then added and the Schlenk flask deoxygenated a further time. The reaction mixture was stirred at 50 °C overnight and then solvent removed under dynamic vacuum until the product was only just soluble (about half). The teflon tap was then sealed and the reaction mixture heated to 70 °C to ensure all product was dissolved. The flask was then

allowed to cool slowly in the oil bath and left at room temperature for several days before being moved to fridge and then freezer to encourage slow crystallisation. Bright red crystals (544.5 mg, 46%) were obtained by decanting off the mother liquor (which was subsequently reset up for crystallisation by the same method) and rinsing from the Schlenk flask with ethanol. ^{1}H NMR (400 MHz; 298 K; CD_3CN): δ 7.00 (8H, apt t, J = 10.2 Hz, *2'*-P*Ph*$_2$), 7.09 (4H, m, *m*-aniline), 7.20 (6H, m, *o,p*-aniline), 7.30 (2H, dt, $^{3}J_{H\text{-}H}$ = 6.4 Hz, $^{4}J_{H\text{-}H}$ = 2.3 Hz, 5-pyridine), 7.35 (8H, td, $^{3}J_{H\text{-}H}$ = 7.7 Hz, $^{4}J_{H\text{-}P}$ = 1.6 Hz, 3'-P*Ph*$_2$), 7.47 (4H, td, $^{3}J_{H\text{-}H}$ = 7.7 Hz, $^{4}J_{H\text{-}H}$ = 1.2 Hz, 4'-*PPh*$_2$), 8.09 (4H, m, 3- & 4-pyridine), 8.68 (2H, s, imine). ^{13}C NMR (101 MHz; 298 K; CD_3CN): δ 122.7 (s, *m*-aniline), 129.3 (s, *p*-aniline), 130.1 (s, *o*-aniline), 130.2 (d, $J_{C\text{-}P}$ = 9.8 Hz, *3'*-P*Ph*$_2$), 130.6 (s, 4-pyridine), 130.9 (s, *i*-aniline), 132.0 (s, 4'-P*Ph*$_2$), 133.8 (5-pyridine), 134.0 (d, $J_{C\text{-}P}$ = 14.6 Hz, 2'-P*Ph*$_2$), 140.5 (s, 3-pyridine), 147.9 (s, 2-pyridine), 152.91 (d, $J_{C\text{-}P}$ = 13.2 Hz, 6-pyridine, 159.3 (s, imine), 160.2 (d, $J_{C\text{-}P}$ = 50.2 Hz, 1'-P*Ph*$_2$). ^{31}P NMR (202.5 MHz, 298 K) δ 6.21 (br s). ESI-MS *m/z*: 429.12 $[Cu_2\mathbf{L}^{1}{}_2]^{2+}$, 945.12 $[Cu_2\mathbf{L}^{1}{}_2BF_4]^{+}$; elemental analysis calcd (%) for $C_{52}H_{44}B_2Cu_2F_8N_6P_2$: C 55.98, H 3.98, N 7.53, P 5.55; found C 55.91, H 3.99, N 7.55, P 5.54.

Preparation of crystals for crystal structure in Fig 1:

1 (2.09 mg, 1.87 μmol) and TBA HSO_4 (2.73 mg, 8.04 μmol) were dissolved in CD_3CN (1ml). The solution was left to crystallise at room temperature for 2 weeks.

1.4.2 Synthesis of [1+1] metallomacrocycle $[Cu_2L^3]\cdot 2BF_4$, 3



L^3

Into a Schlenk flask was added **11** (62.4 mg, 0.21 mmol), **13** (35.5 mg, 0.11 mmol) and deoxygenated acetonitrile (2.5 mL). The flask was purged of dioxygen by three vacuum-nitrogen cycles and then $Cu(CH_3CN)_4BF_4$ (67.5 mg, 0.21mmol) was added. The reaction mixture was deoxygenated once more and then stirred at 50 °C overnight. **3** was purified by

layering of deoxygenated diethylether onto the acetonitrile solution. Once diffusion of the non-solvent through the acetonitrile layer was complete, the mother liquor was decanted off and the product was dried under high vacuum to yield an orange solid (107.2 mg, 79%). ^{1}H NMR (400 MHz; 298 K; CD_3CN) δ 3.65 (4H, s, a1-peg chain), 3.77 (4H, t, $J_{H\text{-}H}$ = 4.5 Hz, a2-peg chain), 4.07 (4H, t, $J_{H\text{-}H}$ = 4.5 Hz, a3-peg chain), 6.73 (4H, d, $J_{H\text{-}H}$ = 8.8 Hz, m-anisidine), 7.01 (8H, ap t, $J_{H\text{-}H}$ = 8.2 Hz, 2'-P*Ph*$_2$), 7.15 (4H, d, $J_{H\text{-}H}$ = 8.8 Hz, o-anisidine) 7.27 (2H, d, $J_{H\text{-}H}$ = 7.2 Hz, 5-pyridine), 7.37 (8H, t, $J_{H\text{-}H}$ = 7.4 Hz, 3'-P*Ph*$_2$), 7.46 (4H, t, $J_{H\text{-}H}$ = 7.3 Hz, 4'-P*Ph*$_2$), 8.06 (4H, m, 3 & 4-pyridine), 8.64 (2H, s, imine). ^{13}C NMR (126 MHz; 300 K; CD_3CN): δ 68.8, 70.15, 71.34, 115.8, 124.7, 130.2 (d, $J_{C\text{-}P}$ = 9.5 Hz), 134.7, 131.1, 132.0, 133.5, 133.9 (d, $J_{C\text{-}P}$ = 14.3 Hz), 140.3, 140.9, 153.3 (d, $J_{C\text{-}P}$ = 13.4 Hz), 156.3, 159.8, 160.3. ^{31}P NMR (162 MHz; 300 K; CD_3CN) δ 6.91 (br s). ESI-MS *m/z*: 522.64 $[Cu_2\mathbf{L}^{3}\cdot MeCN]^{2+}$. Elemental analysis calcd (%) for $C_{53}H_{46}Cu_2N_4O_4P_2\cdot 2(BF_4)\cdot MeCN\cdot 3(H_2O)$: C 52.40, H 4.40, N 5.56; found C 52.68, H 4.30, N 5.86.

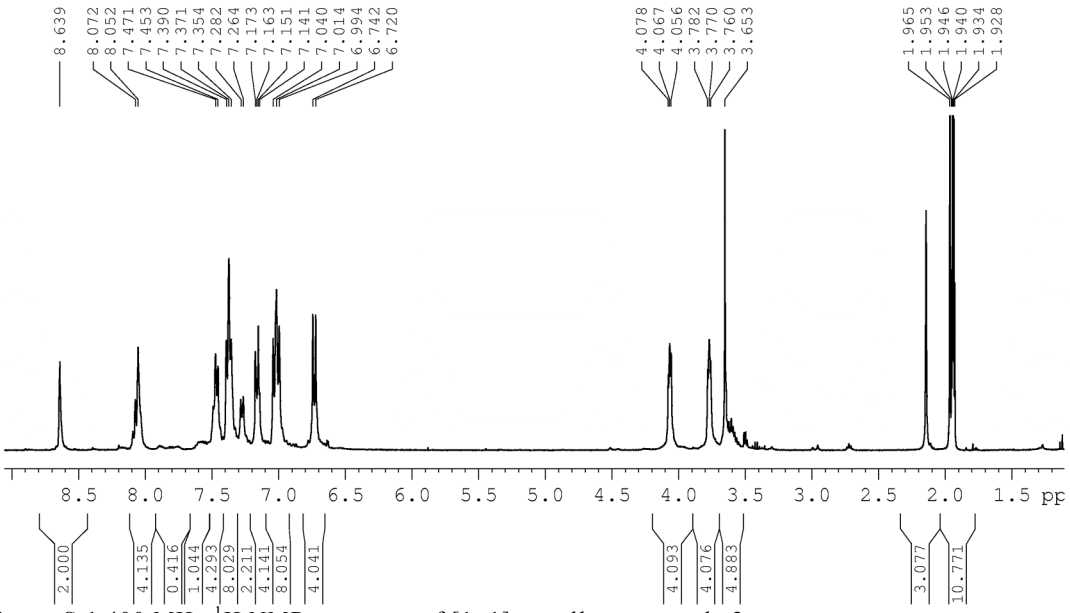


Figure S 1 400 MHz ^{1}H NMR spectrum of [1+1] metallomacrocycle **3**.

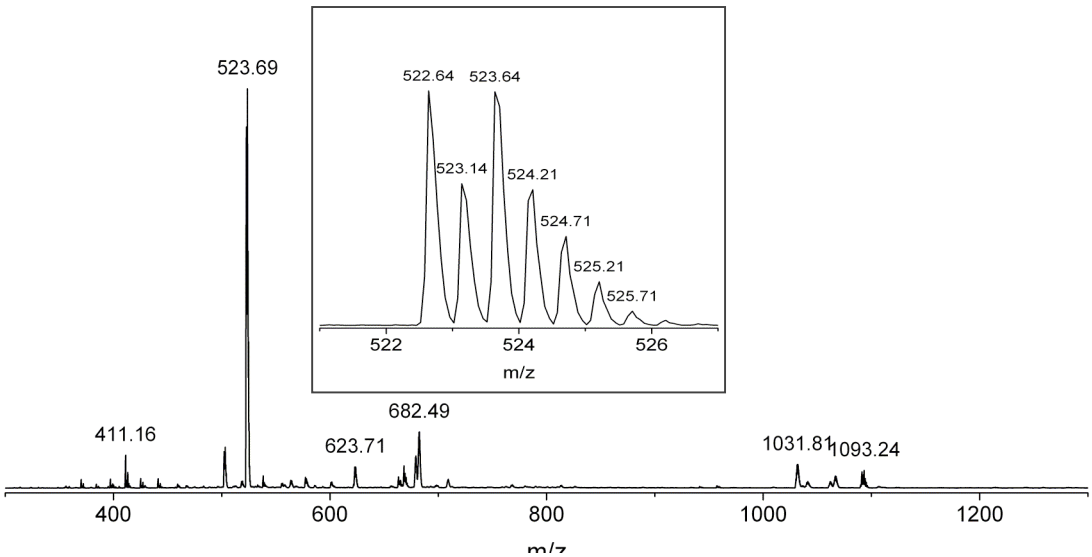
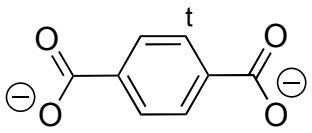


Figure S 2 ESI-MS of [1+1] metallomacrocycle **3** including zoom in on M^{2+} peak

1.4.3 Synthesis of [2+2] metallomacrocycle $[Cu_4L^2L^3_2]\cdot 2BF_4$ 4



L^2

Into an NMR tube with a teflon screw cap, **11** (7.15 mg, 25 μmol), **13** (4.05 mg, 12 μmol), $Cu(CH_3CN)_4BF_4$ (8.9 mg, 28 μmol) and CD_3CN (0.5 mL) were added. The tube was sealed and deoxygenated with three freeze-pump-thaw cycles. The tube was sonicated for 10 minutes to ensure dissolution of subcomponents and then heated at 50 °C for at least 20 hours. **3** was purified from excess subcomponents by layering of diethyl ether. Once redissolved, it was found that a library of oligomers persisted after recrystallisation. ESI-MS showed the presence of both the [1+1] macrocycle and a [2+2] macrocycle. To this reaction, disodium terephthalate (1.5 mg, 6.1 μmol) was added, and D_2O (0.05 mL) to solubilise. The reaction was followed by NMR analysis and it was found that a new set of peaks were obtained, although broad. **4** was crystallised in situ and analysed by X-ray diffraction. Redissolution of the crystals yielded the NMR spectrum shown in Figure S 3. 2D COSY and ROESY confirmed the presence of two isomers of the [2+2] templated metallomacrocycle (Figure S 4 and Figure S 5). Heating the solution to 70 °C did not change the ratio of these species as observed by ^{1}H NMR. After recrystallisation only crystals corresponding to *meso* **4**

were obtained and upon disolution both the *meso* and *rac* forms were observed in the same ratio observed previously. These observations show that although no exchange correlations were observed in the ROESY experiment, these species are interconverting and the interconversion between them is not affected by a kinetic barrier.

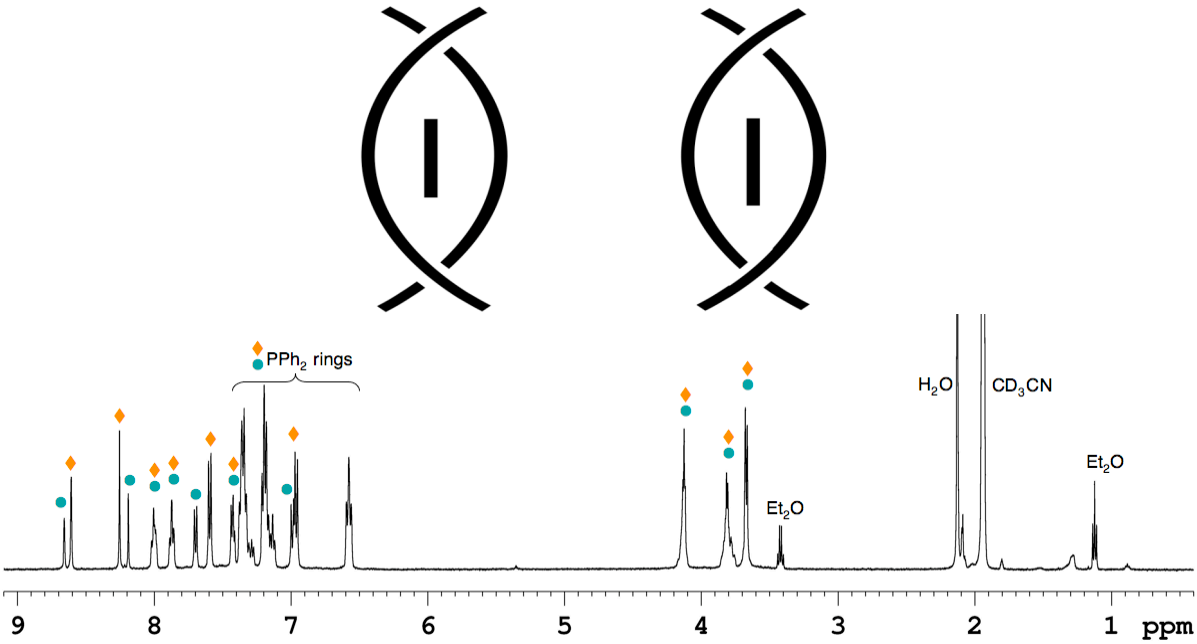


Figure S 3 500 MHz ^{1}H NMR spectrum of **4** in CD_3CN solution showing two isomers of the metallomacrocycle. Above are schematic representations of the two isomers, the achiral *meso* (left) and helical *rac* (right).

Characterisation: Isomers denoted as follows: T = minority species (34 %) (teal dots). O = majority species (66 %) (orange diamonds). ^{1}H NMR (500 MHz; 300 K; CD_3CN) δ 3.66 (8H, s, a1-peg chain (T)), 3.68 (8H, s, a1-peg chain (O)), 3.80 (8H, m, a2-peg chain (TO)), 4.13 (8H, m, a3-peg chain (TO)), 6.58 (8H, t, $J_{H\text{-}H}$ = 8.6 Hz, 2'-P*Ph*$_2$ (TO)), 6.96 (8H, d, $J_{H\text{-}H}$ = 8.6 Hz, m-anisidine (O)), 6.99 (8H, d, $J_{H\text{-}H}$ = 8.7 Hz, m-anisidine (T)), 7.15 (16H, m, P*Ph*$_2$ (TO)), 7.31 (20H, m, 5-pyridine & P*Ph*$_2$ (TO)), 7.60 (4H, d, $J_{H\text{-}H}$ = 8.7 Hz, o-anisidine (O)), 7.70 (4H, d, $J_{H\text{-}H}$ = 8.4 Hz, o-anisidine (T)), 7.87 (4H, t, $J_{H\text{-}H}$ = 7 Hz, 4-pyridine (TO)), 8.01 ((4H, m, 3-pyridine (TO)), 8.19 (4H, s, terphthalate (T)), 8.26 (4H, s, terphthalate (O)), 8.61 (4H, s, imine (O)), 8.66 (4H, s, imine (T)). ^{13}C NMR (126 MHz; 300 K; CD_3CN): δ 69.3 (O), 69.4 (T), 70.5 (O), 70.6 (T), 71.8 (O), 72.0 (T), 116.4 (CH, O), 118.9 (CH, T), 125.4 (CH, O), 125.5 (CH, T), 130.1 (CH, O), 130.2 (CH, T), 130.5 (CH, d, $J_{C\text{-}P}$ = 17.6 Hz), 130.6 (CH, m), 131.2 (CH, T), 131.4 (CH, O), 132.8 (CH), 132.9 (CH), 133.0 (CH), 135.0 (CH, d, $J_{C\text{-}P}$ = 16.1 Hz, T), 135.3 (CH, d, $J_{C\text{-}P}$ = 16.2 Hz, O), 140.4 (CH, OT), 142.7 (C, OT), 152.9 (C, d, OT), 156.5 (CH, OT), 159.7 (C), 160.1 (C), 160.7 (C, O), 160.8 (C, T). ^{31}P NMR (202.5

MHz, 298 K, CD_3CN): δ 7.01 (br s). ESI-MS *m/z*: 1086.24 $[Cu_4\mathbf{L}^2\mathbf{L}^3{}_2]^{2+}$. Elemental analysis calcd (%) for $C_{116}H_{100}Cu_4N_8O_{12}P_4{\cdot}2(BF_4){\cdot}5(H_2O)$: C 57.10, H 4.54, N 4.59; found C 57.23, H 4.21, N 4.25.

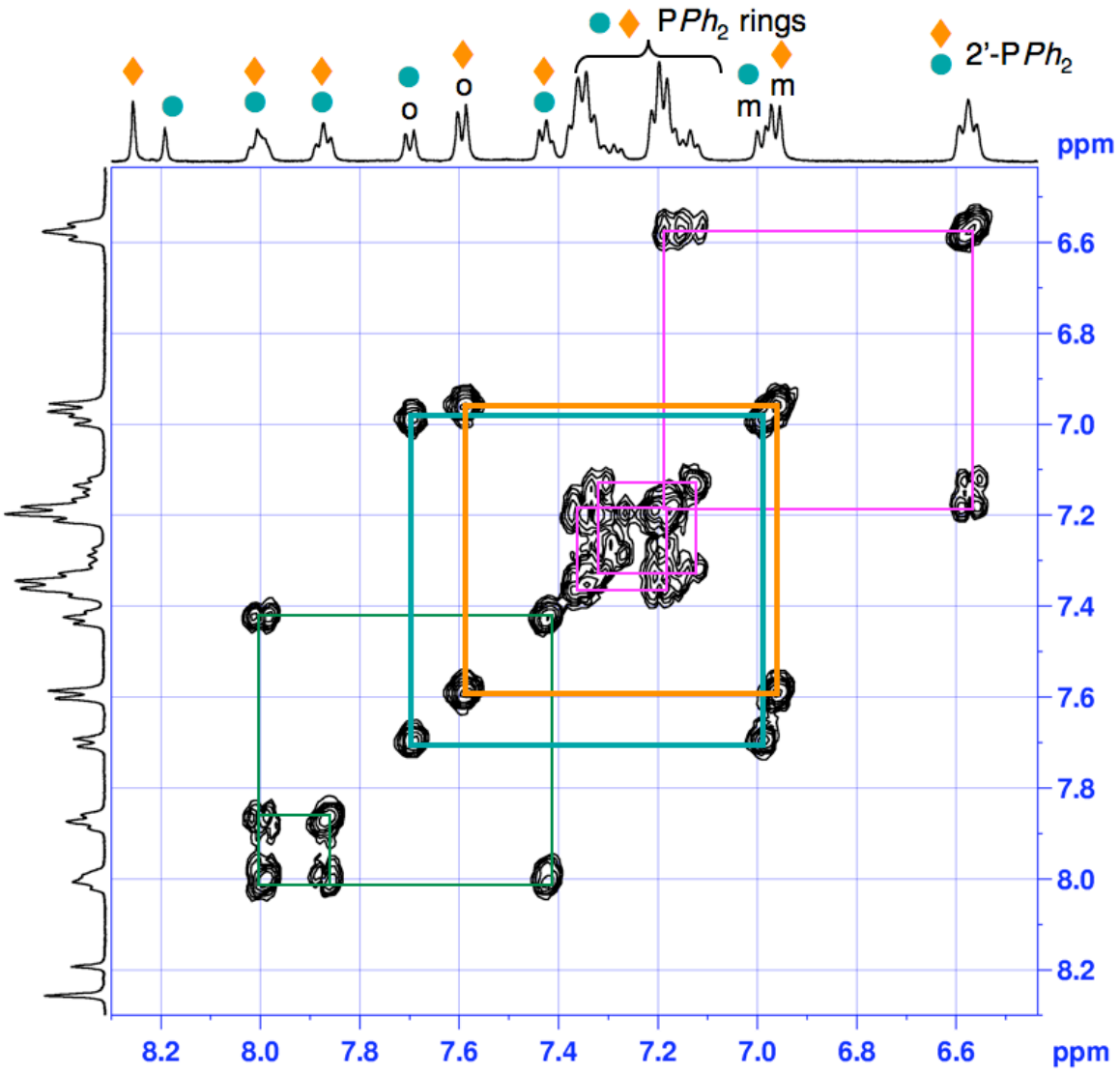


Figure S 4 ^{1}H-^{1}H COSY spectrum of **4**. Teal and orange squares show two sets of aniline protons coupling in two pairs confirming the presence of two distinct isomers. Pink and green squares show phenyl and pyridyl peak sets respectively.

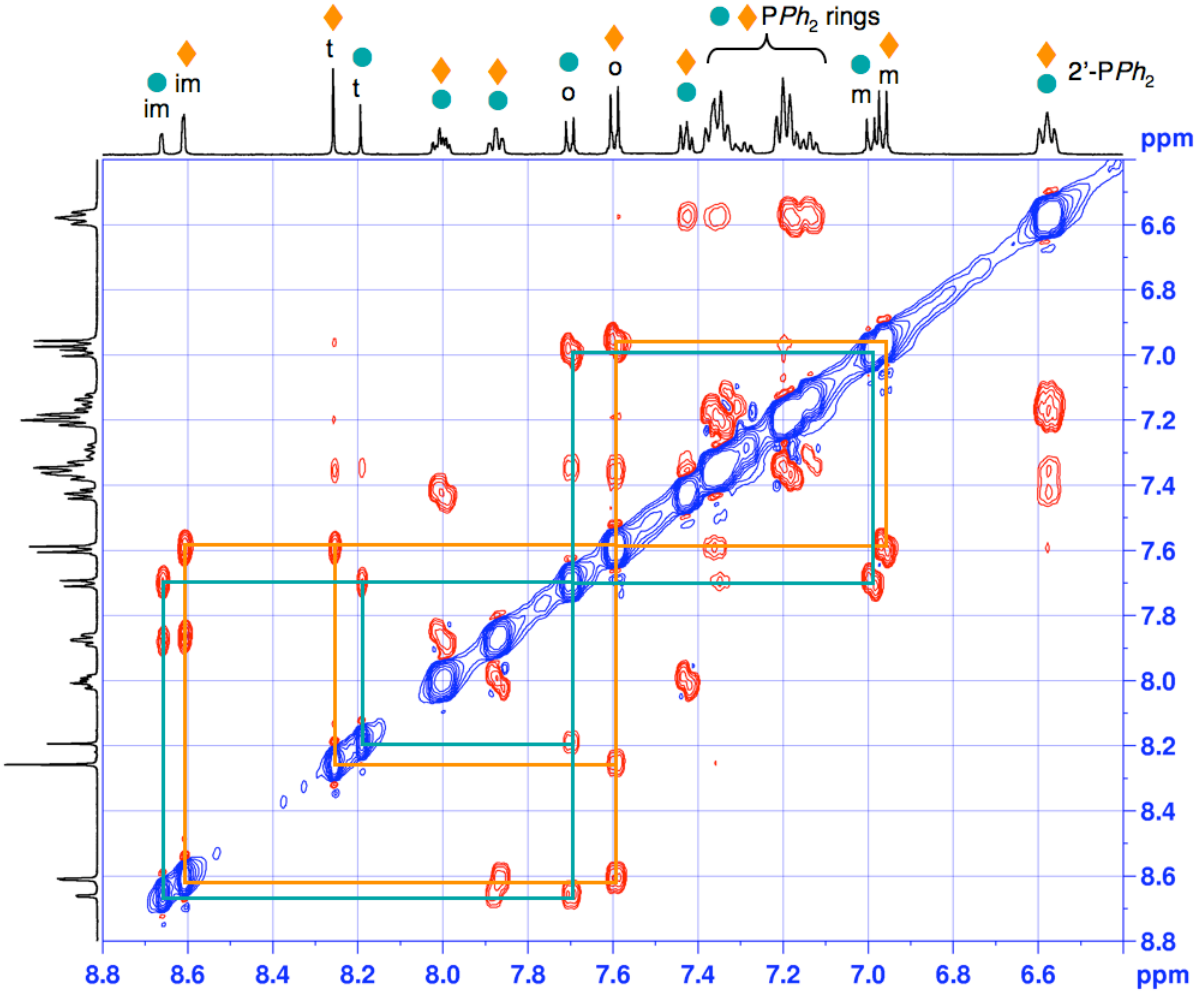


Figure S 5 ^{1}H-^{1}H ROESY spectrum of **4**. Red cross peaks denote NOE correlations: teal and orange squares show two sets of NOE correlations between protons within the *meso* and *rac* isomers. The absence of blue cross peaks shows that the isomers are interconverting slowly on the NMR timescale (0.5 s).

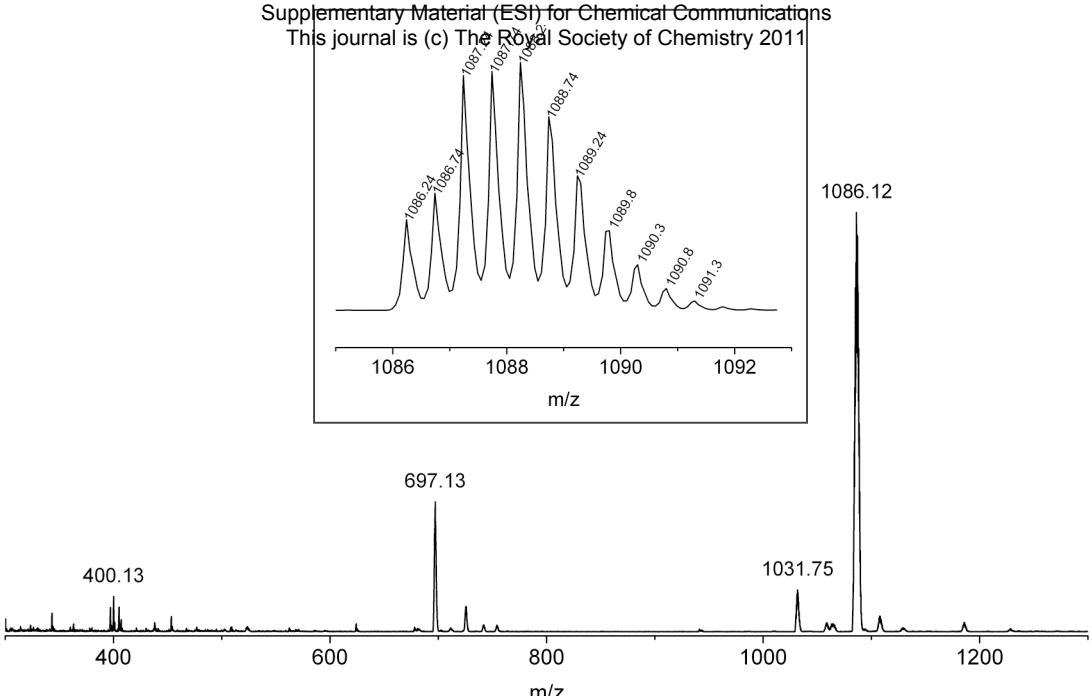


Figure S 6 ESI-MS of [2+2] metallomacrocycle **4** including zoom in on M^{2+} peak

1.4.4 Synthesis of $[(Cu_2L^1)_2L^2]\cdot 2BF_4$ 2 and transformation to [2+2] metallomacrocycle 4

Into an NMR tube with a teflon screw cap, **1** (4.72 mg, 4 μmol), disodium terephthalate (0.58 mg, 2 μmol), CD_3CN (0.45 mL) and D_2O (0.05 mL) were added. Purification by slow diffusion with diethyl ether led to the growth of crystals of **2** which were analysed by X-ray diffraction. Redissolution of crystals led to protonation of $\mathbf{L^2}$ and thus disassembly of **2**. A second experiment was carried out without a purification step, and to this reaction **13** (1.44 mg, 2 μmol) was added. Heating to 40 °C for 3 days led to quantitative conversion of **2** to **4**. ^{1}H NMR of complex assembly **2** (400 MHz; 298 K; CD_3CN) δ 6.92 (8H, br s, 2'-P*Ph*$_2$), 7.19 (16H, m, P*Ph*$_2$), 7.25 (20H, m, 5-pyridine, P*Ph*$_2$), 7.34 (8H, m, P*Ph*$_2$), 7.93 (4H, br s, terphthalate), 7.98 – 8.05 (8H, m, 3 & 4-pyridine), 8.67 (4H, s, imine).

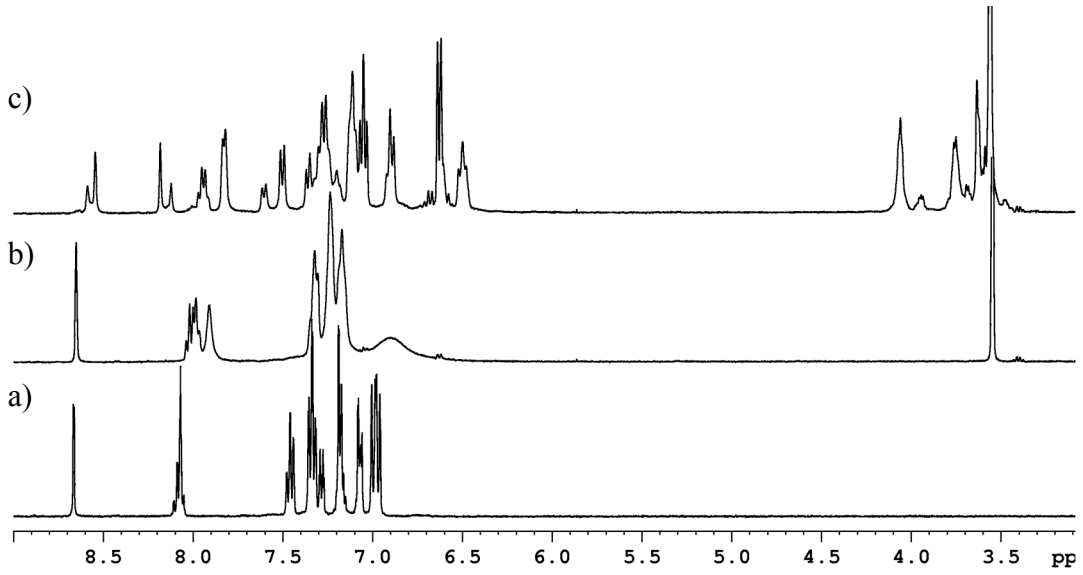
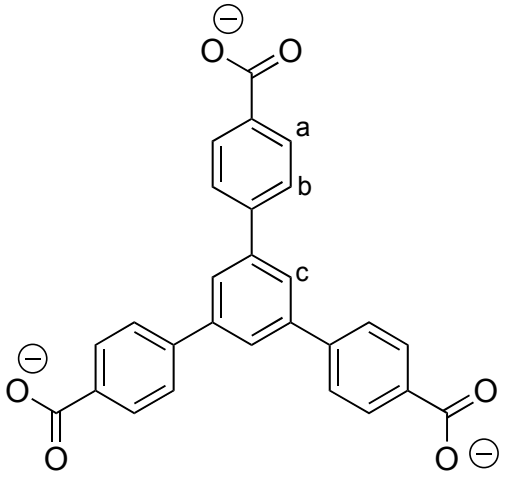


Figure S 7 ^{1}H NMR stackplot of transformation of **2** into **4**. a) **1**, b) **2**, c) **4** obtained quantitatively after reaction of **13** with **2** for 3 days at 40°C.

1.4.5 Synthesis of [3+3] metallomacrocycle $[Cu_6L^3{}_3L^4]\cdot 3BF_4$ 5



L^4

Into a Schlenk flask 1,3,5-tris(4-carboxyphenyl)benzene (5.8 mg, 0.01 mmol), 1,8-diazabicycloundec-7-ene (DBU) (4.8µl, 0.03 mmol), deoxygenated acetonitrile (2.7 mL) and H_2O (0.3 mL) were added. The Schlenk flask was purged of dioxygen by 3 vacuum/nitrogen cycles and the reagents stirred until dissolved. Finally **3** (40.2 mg, 0.03 mmol) was added, the reaction mixture deoxygenated once more and then stirred at 40 °C overnight yielding a deep red solution. **5** was purified by layering diisopropyl ether onto the acetonitrile/water solution. Once diffusion of the non-solvent through the acetonitrile/water layer was complete, the mother liquor was decanted off and the product was dried under high vacuum to yield a red

solid. ^{1}H NMR (500 MHz; 300 K; CD_3CN): δ 3.65 (12H, s, a1-peg chain), 3.81 (12H, m, a2-peg chain), 4.14 (12H, t, J_{H-H} = 4.5 Hz, a3-peg chain), 6.54 (12H, t, J_{H-H} = 8.8 Hz, 2'-PPh_2), 6.90 (12H, d, J_{H-H} = 8.9 Hz, m-anisidine), 7.17 (24H, m, PPh_2), 7.33 (24H, m, PPh_2), 7.40 (6H, d, J_{H-H} = 7.6 Hz, 5-pyridine), 7.49 (12H, d, J_{H-H} = 8.8 Hz, o-anisidine), 7.90 (6H, dd, J_{H-H} = 7.7 Hz, J_{H-P} = 1.3 Hz, 3-pyridine), 8.00 (12H, t and m superimposed, J_{H-H} = 7.7 Hz, 4-pyridine, b-triacetate), 8.1 (3H, s, c-triacetate), 8.30 (6H, d, J_{H-H} = 8.1 Hz, a-triacetate), 8.62 (6H, s, imine). ^{13}C NMR (126 MHz; 300 K; CD_3CN): δ 69.2, 70.2, 71.1, 124.9, 128.1, 129.7, 129.1 (d, J_{C-P} = 8.4 Hz), 131.0, 131.3, 131.6, 131.9, 132.4 (d, J_{C-P} = 13.3 Hz), 132.9 (d, J_{C-P} = 7 Hz), 134.8 (d, J_{C-P} = 16.2 Hz), 137.0, 141.1, 142.4, 143.8, 152.2 (d, J_{C-P} = 15.3 Hz), 156.4, 159.2, 159.6, 160.0. ^{31}P NMR (202.5 MHz, 298 K, CD_3CN): δ 6.91 (br s). ESI-MS *m/z*: 1149.64 $[Cu_6\mathbf{L^3}_3\mathbf{L^4}]^{3+}$. Elemental analysis calcd (%) for $C_{189}H_{159}Cu_6N_{12}O_{18}P_6{\cdot}3(BF_4){\cdot}8(H_2O)$: C 58.83, H 4.57, N 4.36; found C 58.95, H 4.41, N 4.31.

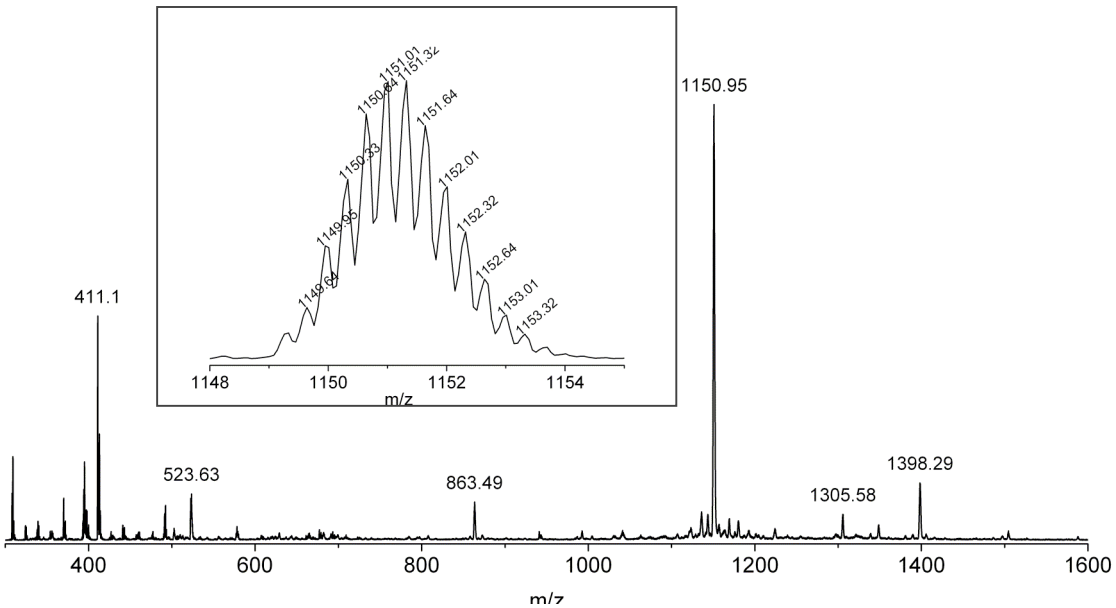


Figure S 8 ESI-MS of [3+3] metallomacrocycle **5** including zoom in on M^{3+} peak

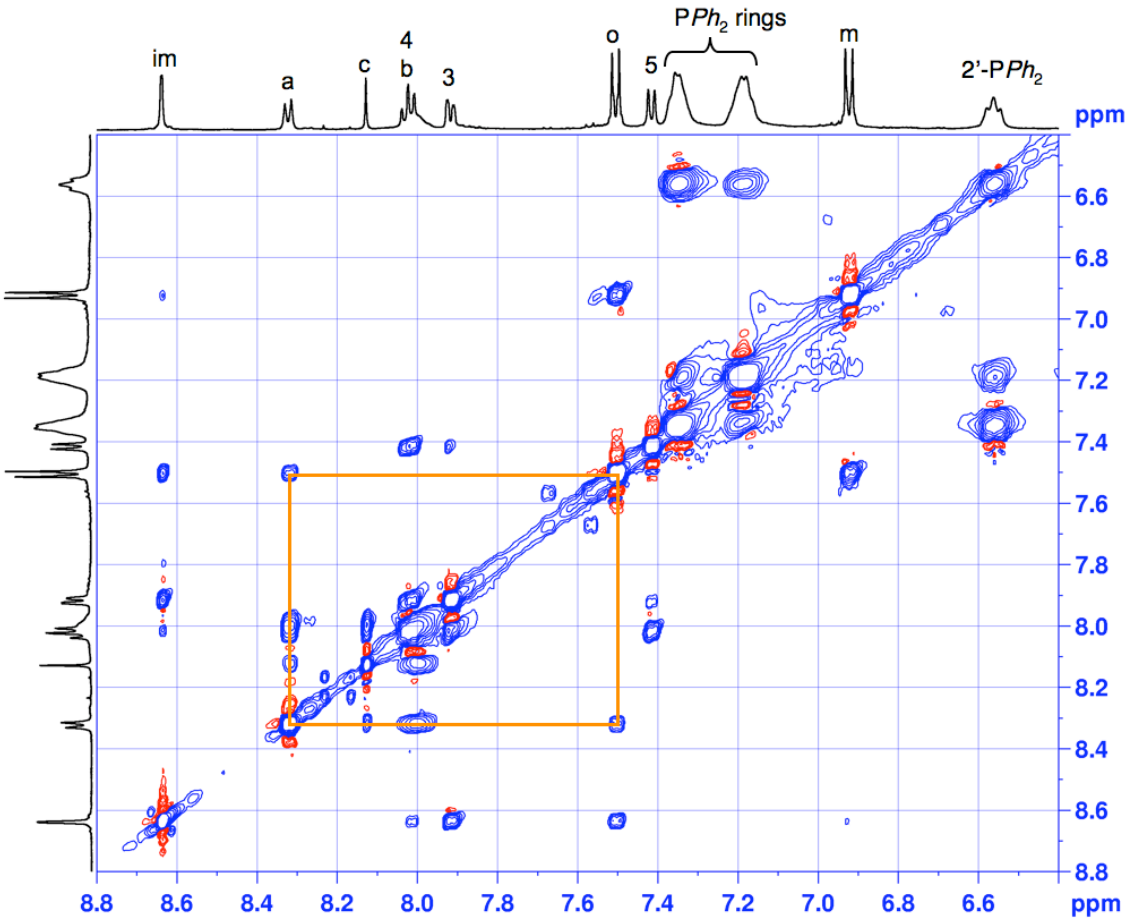


Figure S 9 ^{1}H-^{1}H NOESY spectrum of **5**. The orange square shows an NOE correlation between the proton *ortho* to the carboxylate of $\mathbf{L}^{4}$ (a) and the proton *ortho* to the nitrogen of $\mathbf{L}^{3}$ (o), confirming the presence of a $\mathbf{L}^{4}$ templated metallomacrocycle.

1.5 Reversible destruction and retemplation of templated metallomacrocycles by acid and base respectively

[2+2] metallomacrocycle 4

Into an NMR tube with a teflon screw cap, **3** (4.82 mg, 3.8 μmol), disodium terephthalate (0.49 mg, 2.3 μmol), CD_3CN (0.45 mL) and D_2O (0.05 mL) were added. The tube was sealed and deoxygenated by three vacuum-pump-thaw cycles, and the tube heated at 50 °C overnight, yielding **4** in quantitative yield as confirmed by ^{1}H NMR and ESI-MS. HBF_4 was added to the tube (0.6μl of a 50% wt solution, 4.7 μmol), the tube purged of dioxygen by three vacuum/nitrogen cycles and heated at 50 °C overnight. This procedure was repeated as only part disassembly of **4** was observed by ^{1}H NMR, and ESI-MS confirmed the persistence of **4**. After a second addition of HBF_4, the ^{1}H NMR and ESI-MS matched that of the library containing untemplated macrocycle **3**. It is reasoned that presence of ether chains in **4**

become protonated, requiring more acid for full protonation of $\mathbf{L^2}$. To the reaction mixture DBU (1.4μl , 9.3 μmol) was then added, and the tube purged of dioxygen once again. The quantitative reemergence of **4** was clear by ^{1}H NMR and ESI-MS, and once again, crystals of **4** formed in situ. Layering of diethylether on the solution purified **4** and redissolution of the precipitate returned the original ^{1}H NMR spectrum.

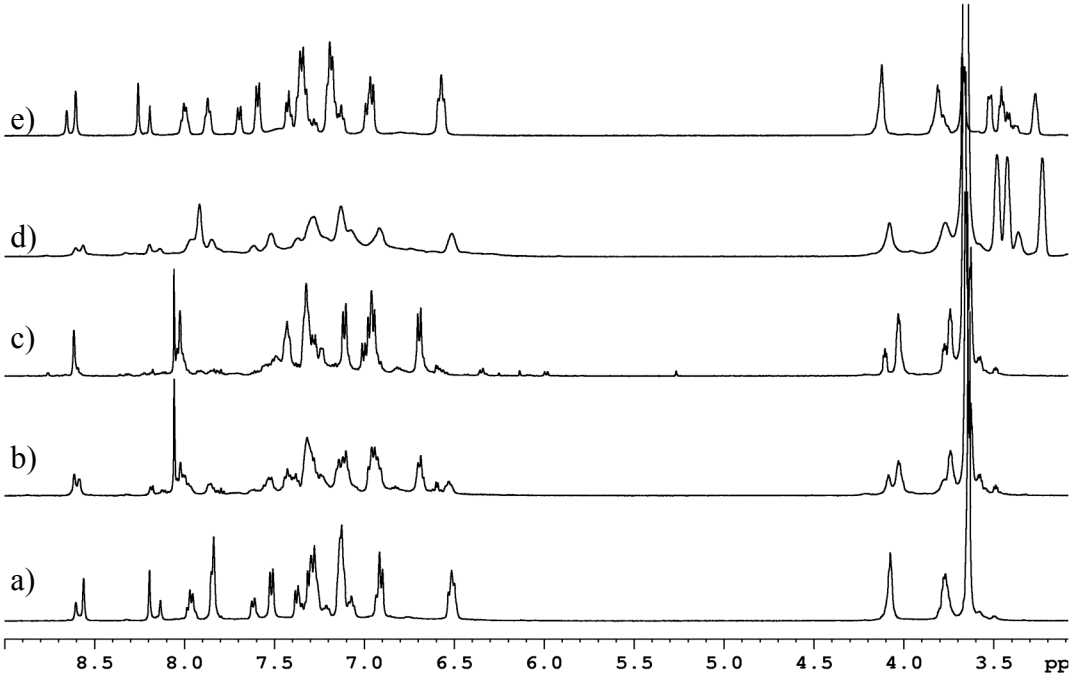


Figure S 10 ^{1}H NMR stack plot for destruction and reformation of [2+2] metallomacrocycle **4**. a) **4**, b) 2 eq HBF_4, c) 4 eq HBF_4 yielding **3**, d) 4 eq HBF_4 and 4 eq DBU – **4** reformed, e) **4** post recrystallisation

[3+3] metallomacrocycle 5

Due to the limited solubility of **5**, a saturated solution of **5** in deoxygenated CD_3CN containing 0.67mM 2,3,4,5-terfluoroxylene was filtered through a glass wool plug. 400μl was measured into an NMR tube with a teflon screw cap, and the concentration of **5** was measured by ^{1}H NMR integration (without deoxygenation of the tube) and found to be 1.05 mM (0.42 μmol). HBF_4 was added to the tube (3.2μl of a 5% stock solution, 2.5 μmol), the tube was then purged of dioxygen by three vacuum/nitrogen cycles and heated at 40 °C for 2 days resulting in a pale yellow solution with white precipitate (triacid). ^{1}H NMR and ESI-MS matched that of the library containing untemplated macrocycle **3**, and no peak at *m/z* 1149 were observed. To the reaction mixture D_2O (0.1 mL) and DBU (0.4μl , 2.5 μmol) was then added, and the tube purged of dioxygen once again. The quantitative conversion of **3** to **5** was

clear by ^{1}H NMR and ESI-MS. Layering of diisopropylether onto the reaction mixture facilitated purification of **5**.

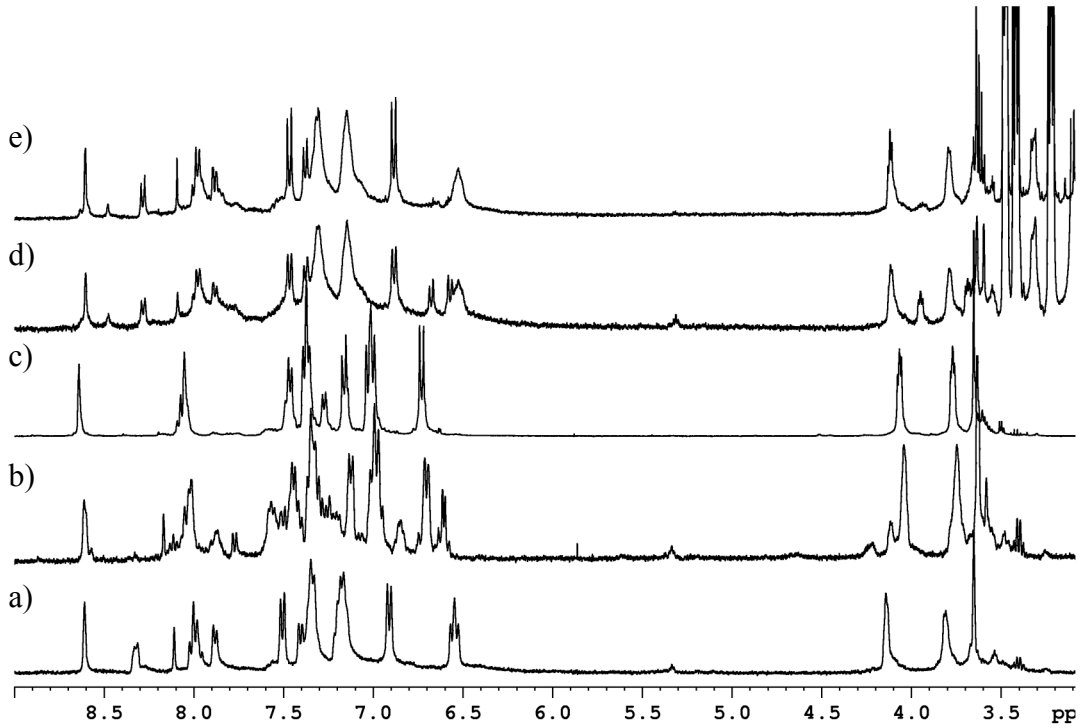


Figure S 11 ^{1}H NMR stack plot for destruction and reformation of [3+3] metallomacrocycle **5**. a) **5**, b) 6 eq HBF_4, yielding **3** c) ^{1}H NMR of **3** for comparison d) DBU added – **5** reformed. e) **5** post recrystallisation

1.6 One-pot competition between [2+2] and [3+3] macrocycles

Into an NMR tube with a teflon screw cap, **3** (8.22 mg, 6.8 μmol), disodium terephthalate (0.73 mg, 3.5 μmol), 1,3,5-tris(4-carboxyphenyl)benzene (1.24 mg, 2.36 μmol), CD_3CN (0.45 mL) and D_2O (0.05 mL) were added. 1,8-diazabicycloundec-7-ene (DBU) (1 μl, 6.8 μmol) was then added and the tube sonicated to dissolve the triacid. The tube was then sealed and deoxygenated by three vacuum-pump-thaw cycles, and then heated to 40 °C overnight. Significant precipitation occurred and the supernatant was analysed by both ^{1}H NMR and ESI-MS. Both techniques showed the presence of both the [2+2] and [3+3] metallomacrocycle. Overlapping peaks in the ^{1}H NMR spectrum prevented us from quantifying the proportion of each metallomacrocycle in the supernatant. Although the ^{1}H NMR indicated a strong preference for the [2+2] metallomacrocycle, due to the lower solubility of the [3+3] macrocycle it is likely that the precipitate is predominantly [3+3] macrocycle. Thus we cannot give any estimation of the preference of this system for one macroycle over another.

2 X-ray

Data were collected on a Nonius Kappa FR590 diffractometer employing graphite-monochromated Mo-K_α radiation generated from a sealed tube (0.71073 Å) with ω and ψ scans at 180(2) K.[S9] Data integration and reduction were undertaken with HKL Denzo and Scalepack.[S10] Subsequent computations were carried out using the WinGX-32 graphical user interface.[S11] Structure were solved using SIR97[S12] . Multi-scan empirical absorption corrections were applied to the data set using the program SORTAV.[S13] Data were refined and extended with SHELXL-97.[S14] In general, non-hydrogen atoms with occupancies of greater than 0.5 were refined anisotropically, Carbon-bound hydrogen atoms were included in idealised positions and refined using a riding model. Water hydrogen atoms were first located in the difference Fourier map before refinement. Where these hydrogen atoms could not be located, they were not modelled. Disorder was modelled using standard crystallographic methods including constraints, restraints and rigid bodies where necessary. Crystal data and specific details regarding the refinement are detailed below

1·2HSO$_4$·2MeCN

Formula $C_{56}H_{52}Cu_2N_8O_8P_2S_2$, M 1218.20, triclinic, space group $P\bar{1}$(#2), a 12.360(3), b 14.495(3), c 16.258(3) Å, α 95.16(3), β 91.69(3), γ 105.61(3)º, V 2789.5(10) Å^3, D_c 1.450 g cm^{-3}, Z 2, crystal size 0.32 by 0.07 by 0.02 mm, colour red, habit needle, temperature 180(2) Kelvin, λ(MoKα) 0.71073 Å, μ(MoKα) 0.956 mm^{-1}, T(SORTAV)$_{min,max}$ 0.812, 1.007, $2\theta_{max}$ 54.84, *hkl* range -15 15, -18 18, -20 21, N 60657, N_{ind} 12532(R_{merge} 0.1261), N_{obs} 7020(I > 2σ(I)), N_{var} 696, residuals* $R1(F)$ 0.0829, $wR2(F^2)$ 0.2499, GoF(all) 1.032, $\Delta\rho_{min,max}$ -0.705, 1.441 e$^-$ Å^{-3}.

*$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_c^2)^2)^{1/2}$ all reflections

$w=1/[\sigma^2(F_o^2)+(0.1173P)^2+7.9628P]$ where $P=(F_o^2+2F_c^2)/3$

Specific details:

One of the bisulfate anions is disordered and was modelled in two equal occupancy positions. The acetonitrile solvent molecules are also disordered over two positions, the N(7) containing molecule included in two equal occupancy positions, while the N(8) was modelling over two positions corresponding to 0.75 and 0.25 occupancy. Each of the disordered species was modelled with identical thermal parameters and a number of constraints and restraints were applied to facilitate a realistic model. There are a number of intra-molecular offset face-to-face π-π interactions present in molecule, acting to assist its stabilisation, while adjacent molecules pack closely together in the lattice interacting via a number of edge-to-face π-π interactions forming an infinite 3D array with small pockets in which the solvent molecules and anions reside. The anions are involved in hydrogen bonding interactions forming a discrete tetrameric arrangement (Fig S1 and Table S1).

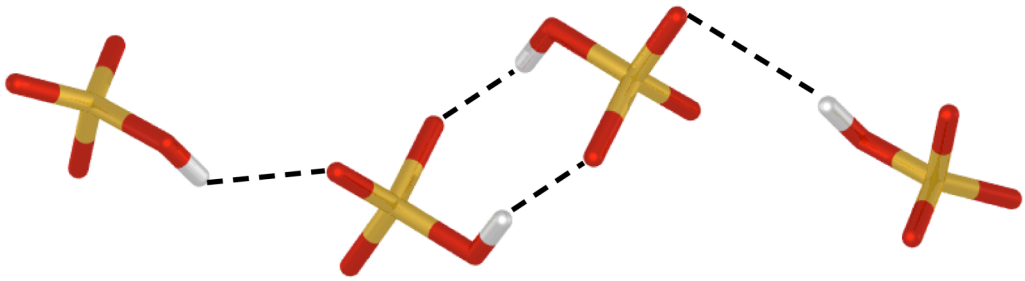


Figure S1. Schematic representation of one of the tetrameric anion clusters in **1**·2HSO_4·2MeCN. Dashed lines indicate hydrogen bonds. Disorder removed for clarity.

Table S1. Hydrogen Bond Geometry

Donor	Hydrogen	Acceptor	D-H(Å)	H-A(Å)	D-A(Å)	DHA Angle(º)
O(1)	H(1)	O(3)^{i}	0.84	1.82	2.628(9)	160.5
O(1)	H(1)	S(1)^{i}	0.84	2.83	3.517(7)	140.6

O(6)	H(6A)	O(4)	0.84	2.05	2.69(2)	132.5
O(6A)	H(6A1)	O(4)	0.84	1.94	2.70(2)	150.1

Symmetry Operator

[i] –x+1, -y, -z+1

2·2BF_4·1.5H_2O·2$C_4H_{10}O$·MeCN

Formula $C_{114}H_{106}B_2Cu_4F_8N_9O_{7.50}P_4$, *M* 2273.74, orthorhombic, space group pbam(#55), *a* 12.147(2), *b* 18.712(4), *c* 23.253(5) Å, *V* 5285.3(18) $Å^3$, D_c 1.429 g cm^{-3}, *Z* 2, crystal size 0.28 by 0.23 by 0.10 mm, colour red, habit plate, temperature 180(2) Kelvin, λ(MoKα) 0.71073 Å, μ(MoKα) 0.930 mm^{-1}, $T(\text{SORTAV})_{\text{min,max}}$ 0.775, 0.906, $2\theta_{\text{max}}$ 56.54, *hkl* range -15 16, -24 24, -30 30, *N* 51480, N_{ind} 6686(R_{merge} 0.0377), N_{obs} 6023(I > 2σ(I)), N_{var} 368, residuals* *R*1(*F*) 0.0372, *wR*2(F^2) 0.0967, GoF(all) 1.119, $\Delta\rho_{\text{min,max}}$ -0.731, 0.870 e^- $Å^{-3}$.

*$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_c^2)^2)^{1/2}$ all reflections

$w=1/[\sigma^2(F_o^2)+(0.0337P)^2+6.5054P]$ where $P=(F_o^2+2F_c^2)/3$

Specific details:

The water molecules are disordered across three equal occupancy positions. Their hydrogen atoms could not be located in the difference Fourier map and they were not included in the model. There are a number of weak intra and inter-molecular π-π interactions present as well as weak informal $CH_{(phenylene)}$-anion hydrogen bonds throughout the lattice.

4·2BF$_4$·4MeCN

Formula $C_{124}H_{112}B_2Cu_4F_8N_{12}O_{12}P_4$, M 2513.92, triclinic, space group $P\bar{1}$(#2), a 11.583(2), b 16.843(3), c 19.661(4) Å, α 66.03(3), β 78.91(3), γ 88.69(3)º, V 3433.1(14) Å^3, D_c 1.216 g cm^{-3}, Z 1, crystal size 0.28 by 0.23 by 0.10 mm, colour red, habit needle, temperature 180(2) Kelvin, λ(MoKα) 0.71073 Å, μ(MoKα) 0.725 mm^{-1}, T(SORTAV)$_{min,max}$ 0.698, 0.935, $2\theta_{max}$ 50.06, *hkl* range -13 13, -20 20, -23 23, N 61240, N_{ind} 12082(R_{merge} 0.0748), N_{obs} 8932(I > 2σ(I)), N_{var} 727, residuals* $R1(F)$ 0.0812, $wR2(F^2)$ 0.2437, GoF(all) 1.063, $\Delta\rho_{min,max}$ -0.568, 1.306 e$^-$ Å^{-3}.

*$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_c^2)^2)^{1/2}$ all reflections

$w=1/[\sigma^2(F_o^2)+(0.1399P)^2+5.7730P]$ where $P=(F_o^2+2F_c^2)/3$

Specific details:

The O(1) – C(28) part of the ethylene glycol chain is disordered and was modelled over two equal occupancy positions as are the fluorine atoms of the tetrafluoroborate counter ion. These were modelled with identical thermal ellipsoids and a number of constraints and restraints were required. There is a large void present in the structure which is filled with

smeared electron density. The SQUEEZE function of PLATON was employed[S15] to remove this contribution from the model and it was included in the formula weight calculations as two acetonitrile solvent molecules. Once again there are a variety of π-π interactions between molecules in the lattice as well as informal $CH_{(phenylene)}$-anion and $CH_{(phenylene)}$-oxygen hydrogen bonds present.

3 References

S1. W. Kofron and L. Baclawski, *J. Org. Chem.*, 1976, **41**, 1879-1880.
S2. T. Ogura, *Transition Met.Chem.*, 1976, **1**, 179-182.
S3. CAChe WorkSystem Pro, Fujitsu Limited, Version 7.5.0.85, 2000-2006
S4. T. Iida, T. Wada, K. Tomimoto and T. Mase, *Tetrahedron Letters*, 2001, **42**, 4841-4844.
S5. R. G. Hicks, B. D. Koivisto and M. T. Lemaire, *Organic Letters*, 2004, **6**, 1887-1890.
S6. S. L. Darling, E. Stulz, N. Feeder, N. Bampos and J. K. M. Sanders, *New J. Chem.*, 2000, **24**, 261-264; L. P. Spencer, R. Altwer, P. R. Wei, L. Gelmini, J. Gauld and D. W. Stephan, *Organometallics*, 2003, **22**, 3841-3854; J. S. Field, R. J. Haines, E. I. Lakoba and M. H. Sosabowski, *J. Chem. Soc.-Perkin Trans. 1*, 2001, 3352-3360; D. B. Grotjahn and D. A. Lev, *J. Am. Chem. Soc.*, 2004, **126**, 12232-12233.
S7. H. Fernández-Pérez, M. Pericàs and A. Vidal-Ferran, *Adv. Synth. Cat.*, 2008, **350**, 1984-1990.
S8. M. Hutin, C. A. Schalley, G. Bernardinelli and J. R. Nitschke, *Chem.-Eur. J.*, 2006, **12**, 4069-4079.
S9. COLLECT, Nonius BV, 1998
S10. Z. Otwinowski and W. Minor, *Methods in Enzymology*, 1997, **276**, 307-326.
S11. L. Farrugia, *J. Appl. Cryst.*, 1999, **32**, 837-838.
S12. A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giocavazzo, A. Gaugliardi, G. C. Moliterni, G. Polidori and S. Spagna, *J. Appl. Cryst.*, 1999, **32**, 115-119.
S13. R. H. Blessing, *Acta Cryst.*, 1995, **A51**, 33-38.
S14. G. M. Sheldrick, *SHELXL-97: Programs for Crystal Structure Analysis, University of Göttingen, Germany*, 1997.
S15. A. L. Spek, *Acta Cryst.*, 1990, **A46**, C34.