Supporting information for Cu(II)-directed synthesis of neutral heteroditopic [2]rotaxane ion-pair host systems incorporating hydrogen and halogen bonding anion binding cavities

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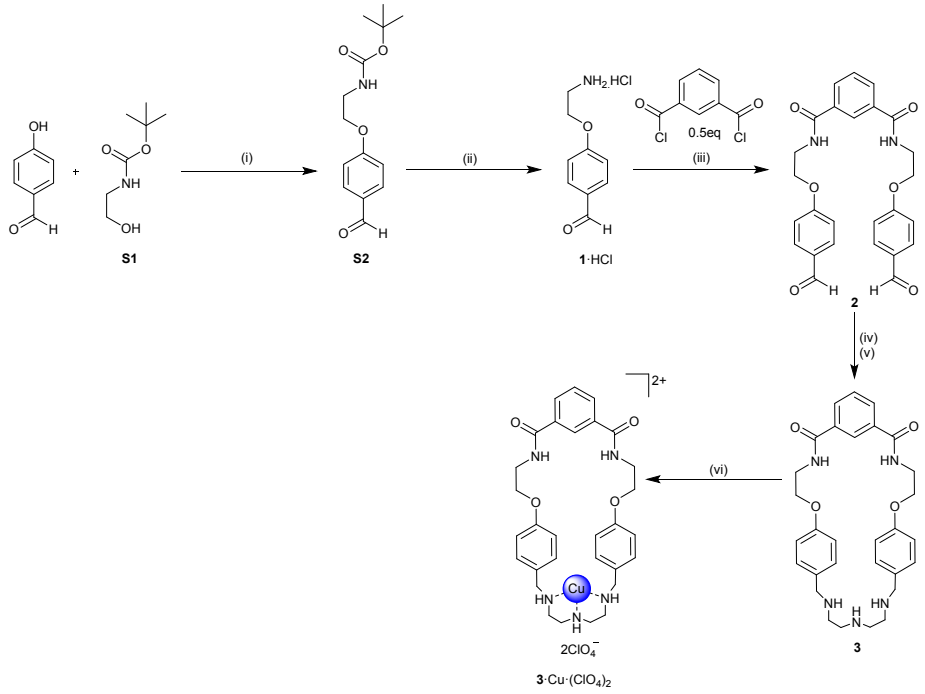
Contents

S1. Synthetic procedures and characterisation data

All solvents and reagents were purchased from commercial suppliers and used as received unless otherwise stated. Dry solvents were obtained by purging with N_2 and then passing through an MBraun MPSP-800 column. H_2O was de-ionised and micro filtered using a Milli-Q ® Millipore machine. Et_3N was distilled and stored over KOH. TBA salts were stored in a vacuum desiccator containing P_2O_5 prior to use. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury-VX 300, a Varian Unity Plus 500 or a Bruker AVD500 at 298 K. Chemical shifts are quoted in parts per million relative to the residual solvent peak. Mass spectra were obtained using a Micromass LCT (ESMS) instrument or a MALDI Micro MX instrument. Electronic absorption spectra were recorded on a PG instruments T60U spectrometer. Compounds **S1**,[1] **S2**,[2] **S3**,[3] **S4**,[4] **S6**,[5,6] **7**,[7] **10**[8] and **13**[9] were synthesised by slight adaptation of previously reported procedures.

Synthesis of tris-amine/isophthalamide-functionalised heteroditopic macrocycle 3



Scheme S1. Synthesis of the tris-amine/isophthalamide-functionalised heteroditopic macrocycle **3.** *Reagents and conditions*: (i) diethyl azodicarboxylate, PPh_3, THF, 0 °C to r.t., 12 hours, 69%; (ii) $HCl_{(g)}$, Et_2O, r.t., 16 hours, 75%; (iii) 4-dimethylaminopyridine, Et_3N, CH_2Cl_2 r.t., 48 h, 44%; (ii) diethylenetriamine, CH_2Cl_2, MeOH, r.t., overnight; (iv) $NaBH_4$, CH_2Cl_2, MeOH, r.t., 6 h, 70%; (v) $Cu(ClO_4)_2{\cdot}6H_2O$, CH_2Cl_2, MeOH, r.t, 16 h, 98%.

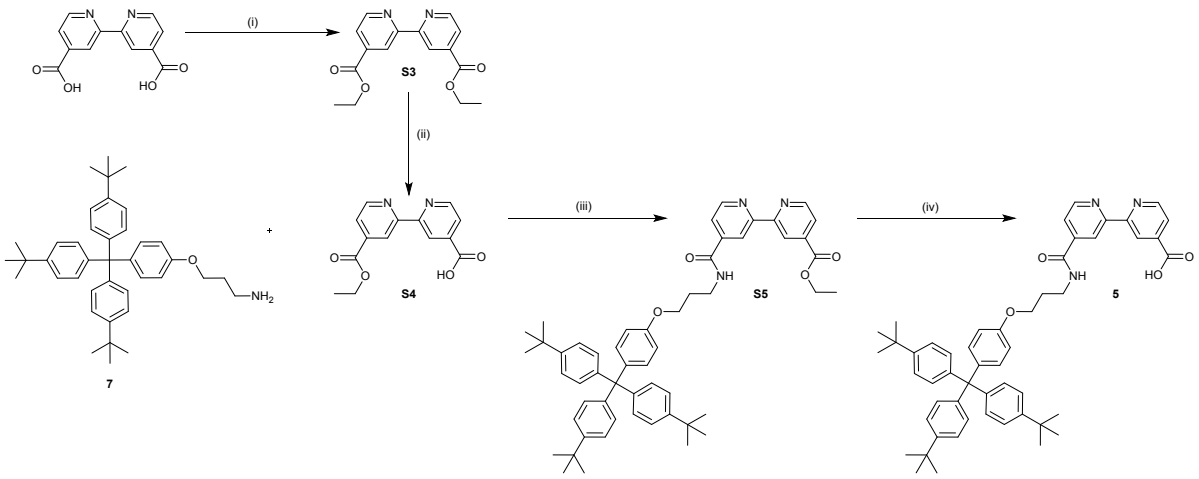
Compound 1·HCl. Compound **S2**[2] (1.00 g, 3.77 mmol) was dissolved in dry Et_2O (50 mL) and a saturated solution of $HCl_{(g)}$ in dry Et_2O (50 mL) was added. The solution was stirred at room temperature for 2 hours, during which time a precipitate began to form. Additional $HCl_{(g)}$ (generated by dropwise addition of conc. H_2SO_4 onto NaCl) was bubbled through the solution for 2 hours. The reaction mixture was then allowed to stir at room temperature for a further 12 hours, at which point TLC analysis indicated complete consumption of the starting material. The precipitate was collected by suction filtration, washed with Et_2O (4 × 15 mL) and dried under vacuum to deliver the product as an off-white solid (0.57 g, 75%). δ_H(400 MHz; DMSO-d_6) 3.21–3.25 (2 H, m, CH_2), 4.32 (2 H, t, ^3J = 5.1 Hz, CH_2), 7.17 (2 H, d, ^3J = 8.7 Hz, Ar*H*), 7.90 (2 H, d, ^3J = 8.7 Hz, Ar*H*), 8.4 (3 H, br s, NH_3^+), 9.89 (1 H, s, C*H*O); δ_C(75.5 MHz; DMSO-d_6) 38.1, 64.7, 115.1, 130.1, 131.9, 162.7, 191.5; ESMS *m/z* 166.08 9 [M – Cl]$^+$).

Compound 2. Compound 1·HCl (1.36 g, 6.72 mmol) was suspended in dry CH_2Cl_2 (75 mL). The suspension was cooled to 0 °C in an ice bath. DMAP (0.041 g, 0.336 mmol) and isophthaloyl dichloride (0.682 g, 3.36 mmol) were added. Et_3N (4 mL) was added dropwise via syringe over approximately 1 minute. After addition was complete the ice bath was removed and the reaction mixture was allowed to stir at room temperature for 48 hours, before being washed with 1 M $HCl_{(aq)}$ (2 x 50 mL), sat. $NaHCO_{3(aq)}$ (2 x 50 mL) and brine (50 mL), dried over $MgSO_4$ and concentrated on a rotary evaporator. Purification of the residue by column chromatography (2–5% MeOH in CH_2Cl_2) afforded the product as a white solid (0.683 g, 44%). δ_H(400 MHz; $CDCl_3$) 3.88–3.92 (4 H, m, CH_2), 4.23 (4 H, t, ^3J = 5.1 Hz, CH_2), 6.91 (2 H, t, ^3J = 5.6 Hz, amide-N*H*), 6.99 (4 H, d, ^3J = 8.7 Hz, Ar*H*)**, 7.50 (1 H, t, ^3J = 7.7 Hz, isophthalamide-Ar*H*), 7.80 (4 H, d, ^3J = 8.7 Hz,**

Ar*H*), 7.94 (2 H, dd, ^3J = 7.7 Hz, ^4J = 1.7 Hz, isophthalamide-Ar*H*), 8.25 (1 H, t, ^4J = 1.7 Hz, isophthalamide-Ar*H*), 9.86 (2 H, s, C*H*O); δ_C(75.5 MHz; $CDCl_3$) 39.0, 66.5, 114.3, 125.2, 128.6, 129.5, 129.8, 131.6, 134.0, 163.0, 166.4, 190.4; ESMS *m/z*: 461.2 ([M + H]$^+$), 483.1 ([M + Na]$^+$); HRMS (ES): *m/z* 483.1513.([M + Na]$^+$. $C_{26}H_{24}N_2O_6Na$ requires 483.1527).

Macrocycle 3. Diethylene triamine (0.112 g, 0.117 mL, 1.09 mmol) was added to a solution of the bis-aldehyde **2** (0.500 g, 1.09 mmol) in CH_2Cl_2 (110 mL) and MeOH (110 mL). The solution was stirred at room temperature under N_2 overnight. $NaBH_4$ (0.082 g, 2.17 mmol) was added and the reaction mixture was stirred at room temperature under N_2 for a further 6 hours. The solvent was removed on a rotary evaporator. The residue was partitioned between CH_2Cl_2:MeOH 95:5 (50 mL) and brine (30 mL). The layers were separated and the organic layer was washed with brine (30 mL), dried over $MgSO_4$ and concentrated on a rotary evaporator to give a white solid, which was purified by column chromatography on SiO_2, eluting with CH_2Cl_2:MeOH:35% NH_3(aq) 90:9:1 graded to 85:13.5:1.5). The pure fractions were combined and concentrated on a rotary evaporator, then re-dissolved in CH_2Cl_2 (70 mL). This solution was washed with H_2O (2 x 35 mL), dried over $MgSO_4$ and concentrated on a rotary evaporator. The residue was dried under high vacuum to yield the product as a white solid (0.402 g, 70%). δ_H(400 MHz; $CDCl_3$) 2.72 (8 H, apparent s, C*H*$_2$), 3.70 (4 H, s, C*H*$_2$), 3.86–3.90 (4 H, m, C*H*$_2$), 4.13 (4 H, t, ^3J = 4.8 Hz), 6.76 (2 H, t, ^3J = 5.4 Hz, amide-N*H*), 6.82 (4 H, d, ^3J = 8.6 Hz, Ar*H*), 7.20 (4 H, d, ^3J = 8.6 Hz, Ar*H*), 7.53 (1 H, t, ^3J = 7.7 Hz, isophthalamide-Ar*H*), 7.99 (1 H, t, ^4J = 1.6 Hz, isophthalamide-Ar*H*), 8.03 (2 H, dd, ^3J = 7.7 Hz, ^4J = 1.6 Hz, isophthalamide-Ar*H*); δ_C(75.5 MHz; $CDCl_3$) 39.6, 48.0, 48.6, 53.2, 66.4, 114.4, 116.9, 125.0, 129.0, 130.1, 130.7, 134.3, 158.4, 168.0; ESMS *m/z*: 532.3 ([M + H]$^+$), 554.3 ([M + Na]$^+$); HRMS (ES) *m/z* 532.2902 ([M + H]$^+$. $C_{30}H_{38}N_5O_4$ requires 532.2918).

Macrocycle 3·Cu(ClO$_4$)$_2$. The metal-free macrocycle **3** (0.15 g, 0.28 mmol) was dissolved in CH_2Cl_2 (10 mL) and MeOH (2 mL). A solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.11 g, 0.30 mmol) in MeOH (8 mL) was added. The solution was stirred at room temperature under N_2 overnight. The solvent was removed on a rotary evaporator and the residual solid was recrystallised from MeOH to afford the product as a blue solid (0.223 g, 98%). *m/z* (ES) 639.24 ([M – 2ClO_4 + HCO_2]$^-$; UV/vis (DMSO): λ_{max} (ε) = 634 nm (114 M^{-1} cm^{-1}).



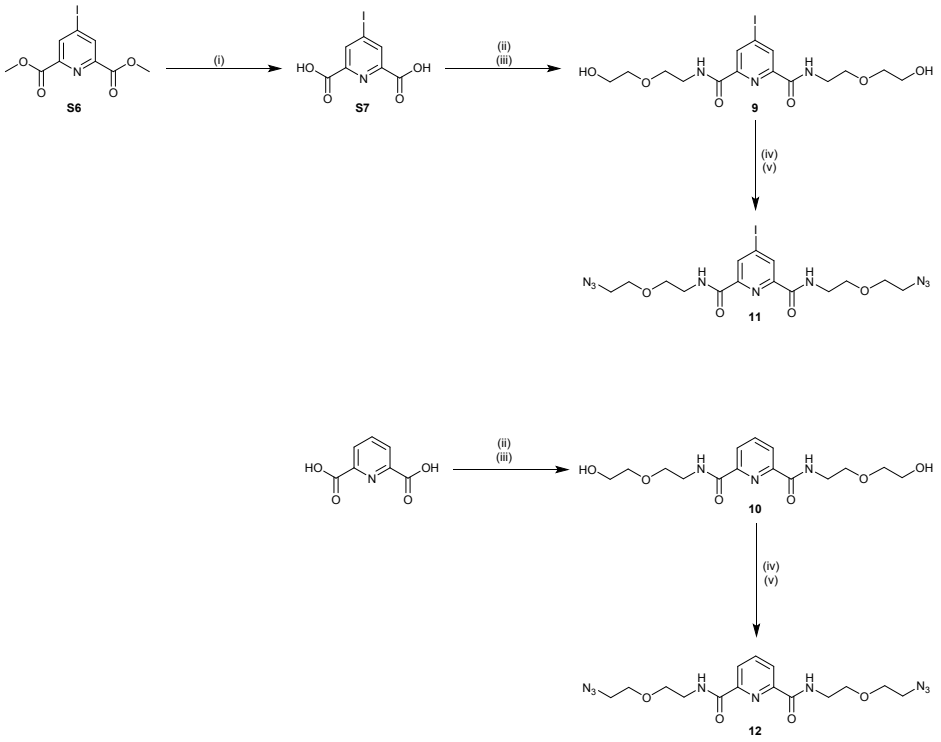
Scheme S2. Synthesis of the mono-stoppered acid-functionliased 2,2-bipyridyl axle precursor **5**. *Reagents and conditions*: (i) $SOCl_2$, EtOH, reflux, 16 h, 85%; (ii) KOH, CH_2Cl_2, EtOH, 0 °C to r.t. 24 h, 59%; (iii) EDC·HCl, DMAP, CH_2Cl_2, r.t., 72 h, 60%; (iv) KOH, CH_2Cl_2, MeOH, r.t., 48 h, 84%.

Compound S5. Compound **S4**[4] (0.25 g, 0.92 mmol) was suspended in dry CH_2Cl_2 (50 mL). 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (0.22 g, 0.92 mmol), 4-dimethylaminopyridine (0.028 g, 0.23 mmol) and compound **7**[7] (0.52 g, 0.92 mmol) were added. The mixture was stirred vigorously under an atmosphere of N_2 for 72 hours. After removal of the solvent was removed on a rotary evaporator the residue was purified by column chromatography (EtOAc:hexane 7:3) to give the product as a white solid (0.45 g, 60%). δ_H(400 MHz; $CDCl_3$) 1.31 (27 H, s, C(C*H*$_3$)$_3$), 1.45 (3 H, t, ^3J = 7.2 Hz, CH_2CH_3), 2.13–2.19 (2 H, m, C*H*$_2$), 3.74–3.78 (2 H, m, C*H*$_2$), 4.18 (2 H, t, ^3J = 5.4 Hz, C*H*$_2$), 4.46 (2 H, quartet, ^3J = 7.2 Hz, C*H*$_2$CH$_3$), 6.91 (2 H, d, ^3J = 8.9 Hz, stopper-Ar*H*), 7.09 (6 H, d, ^3J = 8.6 Hz, stopper-Ar*H*), 7.12 (2 H, d, ^3J = 8.9 Hz, stopper-Ar*H*), 7.25 (6 H, d, ^3J = 8.6 Hz, stopper-Ar*H*), 7.82 (1 H, dd, ^3J = 5.1 Hz, ^4J = 1.6 Hz, bipy-Ar*H*), 7.84 (1 H, dd, ^3J = 4.9 Hz, ^4J = 1.6 Hz, bipy-Ar*H*), 8.60 (1 H, d, ^3J = 5.1 Hz, bipy-Ar*H*), 8.74 (1 H, d, ^4J = 1.6 Hz, bipy-Ar*H*), 8.85 (1 H, d, ^3J = 4.9 Hz, bipy-Ar*H*), 8.97 (1 H, d, ^4J = 1.6 Hz, bipy-Ar*H*); δ_C(101 MHz; $CDCl_3$) 14.2, 28.6, 31.4, 34.2, 39.0, 61.8, 63.0, 67.2, 112.9, 117.3, 120.4, 122.1, 123.2, 124.0, 130.7, 132.3, 138.9, 140.2, 142.7, 144.0, 148.3, 149.8, 150.2, 156.1, 156.2, 156.3, 165.0, 165.1; ESMS *m/z*: 816.54 ([M + H]$^+$); HRMS (ES) *m/z*: 838.4550 ([M + Na]$^+$. $C_{54}H_{61}N_3NaO_4$ requires 838.4554).

Compound 5. Compound **S5** (0.42 g, 0.51 mmol) was dissolved in CH_2Cl_2 (22.5mL) and MeOH (22.5 mL). A solution of KOH (0.072 g) in H_2O (1.5 mL) was added. The reaction mixture was stirred at room temperature under N_2 for 48 hours. The organic solvents were removed on a rotary evaporator and the remaining aqueous suspension was diluted with H_2O (25 mL). 10% citric $acid_{(aq)}$ was added slowly until the pH reached 5. The precipitate was collected by filtration, washed with H_2O (5 x 15 mL) and dried under high vacuum to afford the product as a white solid (0.34 g, 84%). δ_H(400 MHz; DMSO-d_6) 1.25 (27 H, s, C(CH_3)$_3$), 1.97–2.04 (2 H, m, CH_2), 3.45–3.49 (2 H, m, CH_2), 4.02 (2 H, t, ^3J = 5.9 Hz, CH_2), 6.86 (2 H, d, ^3J = 8.9 Hz, stopper-Ar*H*), 7.02 (2 H, d, ^3J = 8.9 Hz, stopper-Ar*H*), 7.06 (6 H, d, ^3J = 8.7 Hz, stopper-Ar*H*), 7.29 (6 H, d, ^3J = 8.7 Hz, stopper-Ar*H*), 7.85 (1 H, dd, ^3J = 5.0 Hz, ^4J = 1.6 Hz, bipy-Ar*H*), 7.89 (1 H, dd, ^3J = 4.9 Hz, ^4J = 1.6 Hz, bipy-Ar*H*), 8.79 (1 H, d, ^4J = 1.6 Hz, bipy-Ar*H*), 8.84–8.87 (3 H, m, bipy-ArH), 9.02 (1 H, t, ^3J = 5.6 Hz, amide-N*H*), 13.86 (1 H, br s, CO_2H); δ_C(75.5 MHz; DMSO-d_6) 28.7, 31.1, 34.1, 36.6, 62.6, 65.1, 113.4, 118.0, 120.1, 121.6, 123.6, 124.4, 130.0, 131.4, 138.9, 142.8, 144.0, 147,7, 149.6, 150.0, 155.2, 155.9, 156.3, 164.8, 166.3; ESMS *m/z* 788.53; HRMS (ES) *m/z* 786.4262 ([M + H]$^+$. $C_{52}H_{58}N_3O_4$ requires 788.4422).

[2]Rotaxane 8. Compound **5** (0.070g, 0.089 mmol) was suspended in dry CH_2Cl_2 (15 mL). *N*-hydroxysuccinimide (0.011 g, 0.098 mmol), and *N*,*N*'-dicyclohexylcarbodiimide (0.022 g, 0.107 mmol) were added and the mixture was stirred under N_2 for 18 hours. The solution was filtered to remove insoluble dicyclohexylurea and the filtrate concentrated on a rotary evaporator. The residue was re-dissolved in dry CH_2Cl_2 (2 mL). This solution was added to a solution of **3**·$Cu(ClO_4)_2$ in dry CH_3CN (10 mL). After brief stirring a solution of the stopper amine **7**[7] (0.050 g, 0.089 mmol) in dry CH_2Cl_2 (18 mL) was added. Et_3N (1 drop) was added and the solution was stirred at room temperature under a N_2 atmosphere for 72 hours. The solvent was removed on a rotary evaporator and the residue re-dissolved in CH_2Cl_2 (20 mL). This solution was washed with EDTA/$NH_4OH_{(aq)}$ (2 x 15 mL) followed by H_2O (20 mL), dried over $MgSO_4$ and concentrated on a rotary evaporator. The residue was purified by preparative thin layer chromatography (SiO_2; CH_2Cl_2:MeOH:NH_4OH 93:6.3:0.7) to afford the pure product as a white solid (0.039 g, 24%). δ_H(400 MHz; $CDCl_3$:CD_3OD 1:1) 1.26 (54 H, s, C(CH_3)$_3$, 1.96–2.03 (4 H, m, axle-CH_2), 2.72–2.75 (4 H, m, macrocycle-CH_2), 2.83–2.86 (4 H, m, macrocycle-CH_2), 3.43 (4 H, s, macrocycle-CH_2), 3.45 (4 H, t, ^3J = 6.2 Hz, axle-CH_2), 3.61 (4 H, t, ^3J = 4.8 Hz, macrocycle-CH_2), 3.73 ((4 H, t, ^3J = 4.8 Hz, macrocycle-CH_2), 3.94 (4 H, t, ^3J = 5.9 Hz, axle-CH_2), 6.16 (4 H, d, ^3J = 8.6 Hz, macrocycle-Ar*H*), 6.66 (4 H, d, ^3J = 8.6 Hz, macrocycle-Ar*H*), 6.73 (4 H, d, ^3J = 8.9 Hz, axle-stopper-Ar*H*), 7.03–7.07 (14 H, m, axle-stopper-Ar*H*), 7.19 (12 H, d, ^3J = 8.7 Hz, axle-stopper-Ar*H*), 7.48 (1 H, t, ^3J = 7.9 Hz, macrocycle-isophthalamide-Ar*H*), 7.52 (2 H, dd, ^3J = 5.2 Hz, ^4J = 1.6 Hz, axle-bipy-Ar*H*), 8.00 (2 H, dd, ^3J = 7.9 Hz, ^4J = 1.7 Hz, macrocycle-isophthalamide-CH_2), 8.24 (2 H, t, ^4J = 1.6 Hz, axle-bipy-Ar*H*), 8.49 (2 H, d, ^3J = 5.2 Hz, axle-bipy-Ar*H*), 8.67 (1 H, t, ^4J = 1.7 Hz, macrocycle-isophthalamide-Ar*H*); δ_C(126 MHz; $CDCl_3$) 29.1, 29.4, 31.1, 31.7, 34.0, 37.9, 39.6, 49.2, 53.6, 62.8, 65.7, 112.6, 113.5, 118.3, 121.4, 123.8, 124.7, 128.7, 130.4, 131.1, 132.1, 134.0, 141.6, 143.8, 148.1, 149.4, 155.2, 156.1, 165.2, 167.1; ESMS *m/z* 932.12 ([M + 2H]$^+$, 1864.27 ([M + H]$^+$; HRMS (ES) *m/z* 1863.1149 ([M + H]$^+$. $C_{122}H_{144}N_9O_8$ requires 1163.1162).

[2]Rotaxane 8·$Zn(ClO_4)_2$**.** Compound **8**·(0.015 g, 0.0080 mmol) was dissolved in CH_2Cl_2 (3 mL) and a solution of $Zn(ClO_4)_2$·$6H_2O$ (0.015 g, 0.040 mmol) in MeOH (3 mL) was added. The solution was stirred at room temperature under N_2 for 60 minutes and the solvent was removed on a rotary evaporator. The residue was taken up in CH_2Cl_2 (3 mL) and the resulting suspension was filtered through a small plug of Celite to remove excess $Zn(ClO_4)_2$. The filtrate was concentrated on a rotary evaporator and the reside recrystallized (CH_2Cl_2/MeOH) to afford the product as a white solid (0.014 g, 82%). δ_H(500 MHz; $CDCl_3$:CD_3OD 1:1) 1.23 (27 H, s, C(CH_3)$_3$), 1.24 (27 H, s, C(CH_3)$_3$), 1.92 (2 H, t, ^3J = 6.1 Hz, axle-CH_2), 2.09 (2 H, t, ^3J = 6.1 Hz, axle-CH_2), 2.89–2.92 (2 H, m, macrocycle-CH_2), 3.07–3.10 (2 H, m, macrocycle-CH_2), 3.31–3.35 (4 H, m (partially obscured by CD_2HOD signal), 2 axle-CH_2 + 2 macrocycle-CH_2), 3.42–3.54 (6 H, m, macrocycle-CH_2), 3.60–3.71 (m, 8 H, 2 axle-CH_2 + 6 macrocycle-CH_2), 3.75–3.79 (2 H, m, macrocycle-CH_2), 3.87 (2 H, t, ^3J = 5.6 Hz, axle-CH_2), 4.01 (2 H, t, ^3J = 5.6 Hz, axle-CH_2), 5.91 (4 H, d, ^3J = 8.2 Hz, macrocycle ArH), 6.19 (4 H, d, ^3J = 8.2 Hz, macrocycle Ar*H*), 6.69 (2 H, d, ^3J = 8.9 Hz, axle-stopper-Ar*H*), 6.73 (2 H, d, ^3J = 8.9 Hz, axle-stopper-Ar*H*), 7.01–7.04 (12 H, m, axle-stopper-Ar*H*), 7.06–7.09 (4 H, m, axle-stopper-Ar*H*), 7.14–7.17 (12 H, m, axle-stopper-Ar*H*), 7.48 (1 H, t, ^3J = 7.9 Hz, macrocycle-isophthalamide-Ar*H*), 7.91 (1 H, d, ^3J = 5.3 Hz, bipy-Ar*H*), 8.03 (2 H, d, ^3J = 7.9 Hz, macrocycle-isophthalamide-Ar*H*), 8.07 (1 H, s, bipy-Ar*H*), 8.23 (1 H, d, ^3J = 5.0 Hz, bipy-Ar*H*), 8.46 (1 H, s, bipy-Ar*H*), 8.79 (1 H, s, macrocycle-isophthalamide-Ar*H*), 8.84 (1 H, d, ^3J = 5.3 Hz, bipy-Ar*H*), 9.09 (1 H, d, ^3J = 5.0 Hz, bipy-Ar*H*), δ_C(125 MHz; $CDCl_3$:CD_3OD 1:1) 29.3, 29.5, 30.4, 31.8 (x 2), 34.9, 38.8, 41.3, 47.0, 53.8, 63.8, 66.2, 66.3, 66.9, 113.7 (x 2), 114.7, 122.2, 122.4, 124.3, 124.8 (x 2), 125.1,, 127.1, 127.7, 129.8, 131.3, 131.4 (x 2), 132.0, 133.0 (x 2), 134.8, 140.7, 140.8, 145.0, 145.3, 147.1, 148.7, 149.0, 149.1, 150.6, 151.1, 157.3, 157.4, 158.8, 164.8, 165.5, 169.5; ESMS *m/z* 932.65 ([M – Zn – 2ClO_4 + 2H]$^{2+}$), 1864.31 ([M – Zn – 2ClO_4 + H]$^+$); MALDI-TOF MS *m/z* 1927.19 ([M – 2ClO_4 – H]$^+$), 2028.05 ([M – ClO_4]$^+$).



Scheme S3. Synthesis of 2,6-pyridyl-bis-amide-based bis-axide terminated threading ligands **11** and **12**. *Reagents and conditions:* (i) NaOH, MeOH, H_2O, r.t., 2.5 h, 32%; (ii) oxalyl dichloride, DMF, CH_2Cl_2, r.t., 20 h; (iii) 2-(2-aminoethoxy)ethan-1-ol. Et_3N, CH_2Cl_2, 0 °C to r.t., 5 h, 67% (compound **9**) or 18 h, 70% (compound **10**); (iv) methanesulfonyl chloride, Et_3N, CH_2Cl_2, 0 °C to r.t. 2 h (for substrate **9**) or 18 h (for substrate **10**) (v) NaN_3. DMF, 50 °C, 6 h, 63% (compound **11**) or 48 h, 62% (compound **12**).

Compound S7. The bis-ester **S6,**[5,6] (0.90 g, 2.80 mmol) was dissolved in MeOH (75 mL) with the aid of gentle heating. After cooling to room temperature a solution of NaOH (0.247 g, 6.17 mmol) in H_2O (75 mL) was added. The solution as stirred at room temperature under N_2 for 2.5 hours. The MeOH was removed on a rotary evaporator and 10% citric $acid_{(aq)}$ (10 mL) was added to the remaining aqueous solution, which caused the immediate formation of a white precipitate. The precipitate was collected by filtration, washed thoroughly with H_2O (8 x 20 mL) and dried under high vacuum to give the product as a white solid (0.264 g, 32%). δ_H(500 MHz; DMSO-d_6) 8.47 (2 H, s, py-Ar*H*); EIMS *m/z*: 292.9178 (M^+. $C_7H_4INO_4$ requires 292.9185). This characterisation agrees with that previously reported in the literature.[10,11]

Compound 9. Compound **S7** (0.85 g, 2.90 mmol) was suspended in dry CH_2Cl_2 (65 mL). Oxalyl dichloride (01.29 g, 0.86 mL, 10.2 mmol) and de-gassed DMF (1 drop) were added. The mixture was stirred at room temperature under N_2 for 20 hours, by which time it had formed a homogenous solution. The solvent was removed on a rotary evaporator and the residue was dried under high vacuum for 2 hours before being re-dissolved in dry CH_2Cl_2 (15 mL). This solution was added dropwise at 0 °C to a solution of 2-(2-aminoethoxy)ethan-1-ol (4.57 g, 4.37 mL, 43.5 mmol) and Et_3N (0.59 g, 0.81 mL, 5.80 mmol) in dry CH_2Cl_2 (50 mL) over a period of approximately one minute. After addition was complete the reaction mixture was stirred at 0 °C under N_2 for 10 minutes and then allowed warm to room temperature and stirred a further 5 hours. The solution was washed with H_2O (50 mL) and brine (50 mL), dried over $MgSO_4$ and concentrated on a rotary evaporator to give the crude product as a colourless oil. This was purified by column chromatography (CH_2Cl_2:MeOH 95:5, then EtOAc) to afford the product as a colourless oil, which solidified to a white solid on standing (0.91 g, 67%). δ_H(500 MHz; $CDCl_3$) 3.27 (2 H, s, O*H*), 3.65–3.66 (4 H, m, CH_2), 3.70–3.72 (8 H, m, CH_2), 3.81–3.82 (4 H, m, CH_2), 8.69–8.71 (4 H, m, 2 py-Ar*H* + 2 amide-N*H*); δ_C(101 MHz; $CDCl_3$) 39.1, 61.3, 69.5, 71.8, 107.8, 133.8, 148.6, 162.2; ESMS m/z 490.1 ($[M + Na]^+$). HRMS (ES) *m/z* 466.04472 ($[M – H]^-$. $C_{15}H_{21}IN_3O_6$ requires 466.04805).

Compound 11. Compound **9** (0.90 g, 1.93 mmol) was dissolved in dry CH_2Cl_2 (50 mL). Et_3N (2.5 mL) was added. The solution was cooled to 0 °C. Methanesulfonyl chloride (0.77 g, 0.52 mL, 6.74 mmol) was added dropwise. The reaction mixture was stirred at 0 °C under N_2 for 20 minutes and then allowed to warm to room temperature and stirred for a further 100 minutes, before being washed with sat. $NaHCO_{3(aq)}$ (30 mL) and brine (30 mL), dried over $MgSO_4$ and concentrated on a rotary evaporator to give the bis-mesylate intermediate as a viscous orange oil. This was dried under high vacuum and then re-dissolved in dry, de-gassed DMF (25 mL). NaN_3 (0.26 g, 4.04 mmol) was added and solution was heated at 50 °C under N_2 for 6 hours, then cooled to room temperature, diluted with H_2O (100 mL) and extracted with Et_2O (8 x 45 mL). The combined Et_2O extracts were washed with brine (150 mL), dried over $MgSO_4$ and concentrated on a rotary evaporator. Purification of the residue by column

chromatography (EtOAc) afforded the product as a colourless oil (0.63 g, 63%). δ_H(400 MHz; $CDCl_3$) 3.37 (4 H, t, ^3J = 4.6 Hz, CH_2), 3.67–3.72 (12 H, m, CH_2), 8.08 (2 H, br s, amide-N*H*), 8.72 (2 H, s, py-Ar*H*); δ_C(101 MHz; $CDCl_3$) 39.5, 50.5, 69.8, 70.2, 108.1, 134.3, 148.9, 162.5; ESMS *m/z* 540.1 ([M + Na]$^+$). HRMS (ES) *m/z* 518.07541. ([M + H]$^+$. $C_{15}H_{21}IN_9O_4$ requires 518.07667).

Compound 12. Compound **10**[8] (2.40 g, 7.03 mmol) was dissolved in dry CH_2Cl_2 (100 mL) and Et_3N (5 mL) was added. The solution was cooled to 0 °C and methanesulfonyl chloride (2.82 g, 1.90 mL, 24.6 mmol) was added dropwise. The reaction mixture was then stirred at 0 °C under N_2 for 10 minutes and then allowed to warm to room temperature and stirred for a further 18 hours, before being washed with sat. $NaHCO_{3(aq)}$ (50 mL) and brine (50 mL), dried over $MgSO_4$ and concentrated on a rotary evaporator. The residual pale yellow oil was dried thoroughly under high vacuum to remove traces of CH_2Cl_2 and then re-dissolved in dry, de-gassed DMF (40 mL). NaN_3 (0.96 g, 14.8 mmol) was added and the solution was heated to 50 °C under N_2 for 48 hours. After cooling to room temperature sat. $NaCl_{(aq)}$ (150 mL) was added and the solution was extracted with Et_2O (8 x 100 mL). The combined Et_2O extracts were dried over $MgSO_4$ and concentrated on a rotary evaporator and the residue was purified by column chromatography (CH_2Cl_2:MeOH 98:2) to give the product as a colourless oil (1.71 g, 62%). δ_H(400 MHz; $CDCl_3$) 3.41 (4 H, br t, CH_2), 3.71–3.74 (12 H, m, CH_2), 8.03 (1 H, t, ^3J = 7.7 Hz, py-Ar*H*), 8.15 (2 H, br s. amide-N*H*), 8.37 (2 H, d, ^3J = 7.7 Hz, py-Ar*H*); δ_C(101 MHz; $CDCl_3$) 39.3, 50.4, 69.9, 70.0, 124.9, 138.7, 148.7, 163.7; ESMS *m/z*: 392.2 ([M + H]$^+$), 414.2 ([M + Na]$^+$); HRMS (ES) *m/z*: 414.1627 ([M + Na]$^+$. $C_{15}H_{21}N_9NaO_4$ requires 414.1614).

General procedure for the synthesis of [2]Rotaxanes 14 and 15. The bis-azide thread **11** or **12** (0.060 mmol) was dissolved in dry CH_2Cl_2 (15 mL) and a solution of **3**·$Cu(ClO_4)_2$ (0.048 g, 0.060 mmol) in dry CH_3CN (7.5 mL) was added. After purging with N_2 for 5 minutes, tris[(1-benzyltriazolylmethyl)amine (0.0072 g, 0.0135 mmol), $Cu(CH_3CN)_4PF_6$ (0.0067 g, 0.018 mmol) and the alkyne stopper **13**[12] (0.072 g, 0.13 mmol) were added and the solution was again purged with N_2 for 5 minutes. DiPEA (0.016 g, 0.021 mL, 0.12 mmol) was added and the solution was stirred at room temperature under N_2 for 48 hours. The solvent was removed on a rotary evaporator and the residue re-dissolved in CH_2Cl_2 (25 mL) and this solution was washed with an EDTA/$NH_4OH_{(aq)}$ solution (2 x 15 mL) followed by H_2O (2 x 15 mL), dried over $MgSO_4$ and concentrated on a rotary evaporator. Purification of the residue by preparative thin layer chromatography (CH_2Cl_2:MeOH:sat $NH_{3(aq)}$ 92.5:6.75:0.75) afforded the [2]rotaxane product as a white solid.

[2]Rotaxane 14. (0.035 g, 27%). δ_H(400 MHz; $CDCl_3$:CD_3OD 1:1) 1.28 (54 H, s, C(CH_3)$_3$), 2.53–2.69 (8 H, m, macrocycle-CH_2), 3.36–3.38 (8 H, br m, CH_2), 3.53–3.55 (8 H, br m, CH_2), 3.66 (4 H, t, ^3J = 4.8 Hz, macrocycle-CH_2), 3.83 (4 H, t, ^3J = 4.8 Hz, macrocycle-CH_2), 4.17–4.20 (4 H, m, CH_2), 4.75 (4 H, s, axle-CH_2), 6.41 (4 H, d, ^3J = 8.7 Hz, macrocycle-Ar*H*), 6.67 (4 H, t, ^3J = 9.1 Hz, axle-stopper-Ar*H*), 6.89 (4 H, d, ^3J = 8.7 Hz, macrocycle-Ar*H*), 7.04–7.07 (16 H, m, axle-stopper-Ar*H*), 7.20 (12 H, d, ^3J = 8.6 Hz, axle-stopper-Ar*H*), 7.38 (1 H, t, ^3J = 7.8 Hz, macrocycle-isophthalamide-Ar*H*), 7.57 (2 H, s, axle-triazole-C*H*), 7.91 (2 H, dd, ^3J = 7.8 Hz, ^4J = 1.7 Hz, macrocycle-isophthalamide-Ar*H*), 8.26 (1 H, t, ^4J = 1.7 Hz, macrocycle-isophthalamide-Ar*H*), 8.54 (2 H, s, axle-py-Ar*H*); δ_C(126 MHz; $CDCl_3$:CD_3OD 1:1) 31.8, 34.9, 39.8, 40.6, 50.7, 53.6, 61.8, 63.8, 66.7, 69.3, 69.9, 113.9, 114.8, 124.8, 125.2, 129.7, 130.3, 131.4, 131.5, 131.6, 133.0, 134.7, 134.8, 135.0, 141.2, 144.2, 144.9, 149.1, 149.6, 156.7, 158.3, 164.1, 168.9; ESMS *m/z*: 1067.56 ([M + 2H]$^{2+}$), 2134.15 ([M + H]$^+$.); HRMS (ES) *m/z*: 2134.07970 ([M + H]$^+$. $C_{125}H_{150}IN1_4O_{10}$ requires 2134.06986).

[2]Rotaxane 15. (0.027 g, 22%) δ_H(400 MHz; $CDCl_3$:CD_3OD 1:1) 1.27 (54 H, s, C(CH_3)$_3$), 2.66–2.69 (4 H, macrocycle-CH_2), 2.73–2.75 (4 H, macrocycle-CH_2), 3.40 (8 H, apparent br s, CH_2), 3.54–3.57 (8 H, m, CH_2), 3.67 (4 H, t, ^3J = 4.7 Hz, CH_2), 3.86 (4 H, t, ^3J = 4.9 Hz), 4.21 (4 H, t, ^3J = 4.9 Hz), 4.74 (4 H, s, axle-CH_2), 6.43 (4 H, d, ^3J = 8.6 Hz, macrocycle-Ar*H*), 6.67 (4 H, d, ^3J = 9.1 Hz, axle-stopper-Ar*H*), 6.89 (4 H, d, ^3J = 8.6 Hz, macrocycle-Ar*H*), 7.06–7.08 (16 H, m, axle-stopper-Ar*H*), 7.21 (12 H, d, ^3J = 8.6 Hz, axle-stopper-Ar*H*), 7.38 (1 H, t, ^3J = 7.8 Hz, macrocycle-isophthalamide-Ar*H*), 7.65 (2 H, s, axle-triazole-Ar*H*), 7.79 (1 H, t, ^3J = 7.8 Hz, axle-py-Ar*H*), 7.92 (2 H, dd, ^3J = 7.8 Hz, ^4J = 1.7 Hz, macrocycle-isophthalamide-Ar*H*), 8.14 (2 H, d, ^3J = 7.8 Hz, axle-py-Ar*H*), 8.33 (1 H, t, ^4J = 1.7 Hz, macrocycle-isophthalamide-Ar*H*); δ_C(126 MHz; $CDCl_3$:CD_3OD 1:1) 31.8, 34.9, 39.7, 40.6, 48.2, 50.7, 53.5, 61.7, 62.0, 63.9, 66.7, 69.3, 69.9, 113.9, 114.8, 124.8, 125.3, 125.5, 126.3, 128.7, 129.7, 130.5, 131.4, 131.5, 133.0, 135.0, 139.9, 141.2, 144.2, 144.9, 149.1, 149.4, 156.7, 158.5, 165.4, 168.8; ESMS *m/z* 2008.26 ([M + H]$^+$, 1004.62 ([M + 2H]$^{2+}$; HRMS (ES) *m/z* 1005.09216 ([M + 2H]$^{2+}$. $C_{125}H_{152}O_{10}N_{14}$ requires 1005.09192).

[2]Rotaxane 14. **$Zn(ClO_4)_2$**. The metal-free rotaxane **14** (0.030 g, 0.014 mmol) was dissolved in CH_2Cl_2 (4 mL) and a solution of $Zn(ClO_4)_2$·$6H_2O$ (0.026 g, 0.070 mmol) in MeOH (2 mL) was added. The solution was stirred at room temperature under N_2 for 60 minutes and then concentrated on a rotary evaporator. The residue was taken up in CH_2Cl_2 (5 mL) and the resulting suspension was filtered through a plug of cotton wool to remove excess $Zn(ClO_4)_2$. The filtrate was diluted with CH_2Cl_2 (10 mL), washed with H_2O (3 x 10 mL) and concentrated on a rotary evaporator. Recrystallisation of the residual solid (CH_2Cl_2/MeOH) provided the zinc-complexed [2]rotaxane product as a white solid (0.029 g, 86%). δ_H(400 MHz; $CDCl_3$:CD_3OD 1:1) 1.26 (54 H, s, C(CH_3)$_3$), 2.64–2.69 (2 H, m, CH_2), 2.91–2.96 (2 H, m, CH_2), 3.05 (2 H, d, ^2J = 12.4 Hz, macrocycle-CH_2), 3.21 (2 H, d, ^2J = 12.4 Hz, macrocycle-CH_2), 3.63–3.72 (6 H, m, CH_2), 3.75–3.77 (2 H, m, CH_2), 3.82–3.84 (6 H, m, CH_2), 3.90–3.94 (2 H, m, CH_2), 4.00 (2 H, t, ^3J = 4.9 Hz, axle-CH_2), 4.05 (2 H, t, ^3J = 4.9 Hz, axle-CH_2), 4.10–4.16 (4 H, m, CH_2), 5.00 (2 H, s, axle-CH_2), 5.04 (2 H, s, axle-CH_2), 6.34 (4 H, d, ^3J = 8.4 Hz, macrocycle–Ar*H*), 6.40 (4 H, d, ^3J = 8.4 Hz, macrocycle–Ar*H*), 6.73 (2 H, d, ^3J = 9.0 Hz, axle-stopper-Ar*H*), 6.76 (2 H, d, ^3J = 9.0 Hz, axle-stopper-Ar*H*), 7.02–7.07 (16 H, m, axle-stopper-Ar*H*), 7.19 (12 H, ^3J = 7.9 Hz, axle-stopper-Ar*H*), 7.52 (1 H, t, ^3J = 7.9 Hz, macrocycle-isophthalamide-Ar*H*), 7.96 (1 H, s, axle-triazole-Ar*H*), 7.99 (1 H, s, axle-triazole-Ar*H*), 8.03 (2 H, dd,

^3J = 7.9 Hz, ^4J = 1.8 Hz, macrocycle-isophthalamide-Ar*H*), 8.04 (1 H, s, axle-py-Ar*H*), 8.44 (1 H, t, ^4J = 1.8 Hz, macrocycle-isophthalamide-Ar*H*), 8.51 (1 H, s, axle-py-Ar*H*); δ_H(126 MHz; $CDCl_3$:CD_3OD 1:1) 31.8, 34.9, 40.3, 41.9, 42.3, 47.7, 50.3, 50.9, 51.2, 54.3, 62.1, 62.2, 63.8, 66.9, 68.9, 69.5, 69.8, 113.9, 114.9, 124.8, 125.1, 125.2, 126.5, 128.3, 129.0, 130.0, 131.4, 131.8, 133.0 (x 2), 135.1, 135.5, 141.1, 141.2, 142.8, 143.2, 144.9 (x 2), 149.1 (x 2), 156.9 (x 2), 158.5, 162.4, 163.6, 168.8; ESMS *m/z* 2135 ([M – Zn −2ClO_4 + H]$^+$), 1099.61 ([M − 2ClO_4]$^{2+}$), 1068.15 ([M – Zn −2ClO_4 + 2H]$^{2+}$); MALDI-TOF MS *m/z* 2197.76 ([M – 2ClO_4 – H]$^+$.

[2]Rotaxane 15·Zn(ClO$_4$)$_2$. The metal-free rotaxane **15** (0.015 g, 7.5 μmol) was dissolved in CH_2Cl_2 (3 mL) and a solution of $Zn(ClO_4)_2{\cdot}6H_2O$ (0.014 g, 37.3 μmol) in MeOH (1 mL) was added. The reaction mixture was stirred at room temperature under N_2 for 60 minutes before being concentrated on a rotary evaporator. The residual solid was partitioned between CH_2Cl_2 (5 mL) and H_2O (5 mL) in a separatory funnel. The layers were separated and the oranic layer was washed with H_2O (2 x 5 mL), dried over MgSO4 and concentrated on a rotary evaporator to afford the product as a white solid (0.011 g, 65%). δ_H(400 MHz; $CDCl_3$:CD_3OD 1:1) 1.26 (54 H, s, C(C*H*$_3$)$_3$), 2.68–2.74 (2 H, m, C*H*$_2$), 2.91–2.96 (2 H, m, C*H*$_2$), 3.20–3.26 (4 H, m, C*H*$_2$), 3.54–3.69 (6 H, m, C*H*$_2$), 3.79–3.84 (12 H, m, C*H*$_2$), 3.96–4.04 (10 H, m, C*H*$_2$), 5.04 (2 H, s, axle-C*H*$_2$), 5.05 (2 H, s, axle-C*H*$_2$), 6.19 (4 H, d, ^3J = 8.4 Hz, macrocycle-isophthalamide-Ar*H*), 6.43 (4 H, d, ^3J = 8.4 Hz, macrocycle-isophthalamide-Ar*H*), 6.76–6.79 (4 H, m, axle-stopper-Ar*H*), 7.02–7.07 (16 H, m, axle-stopper-Ar*H*), 7.19–7.20 (12 H, m, axle-stopper-Ar*H*), ESMS *m/z* 2009.37 ([M – Zn −2ClO_4 + H]$^+$), 1036.13 ([M – 2ClO_4]$^{2+}$), 1004.66 ([M – Zn – 2ClO_4 + 2H]$^{2+}$; MALDI-TOF MS *m/z* 2071.12 ([M – 2ClO_4 – H]$^+$).

S2. ^{1}H NMR spectra of new compounds

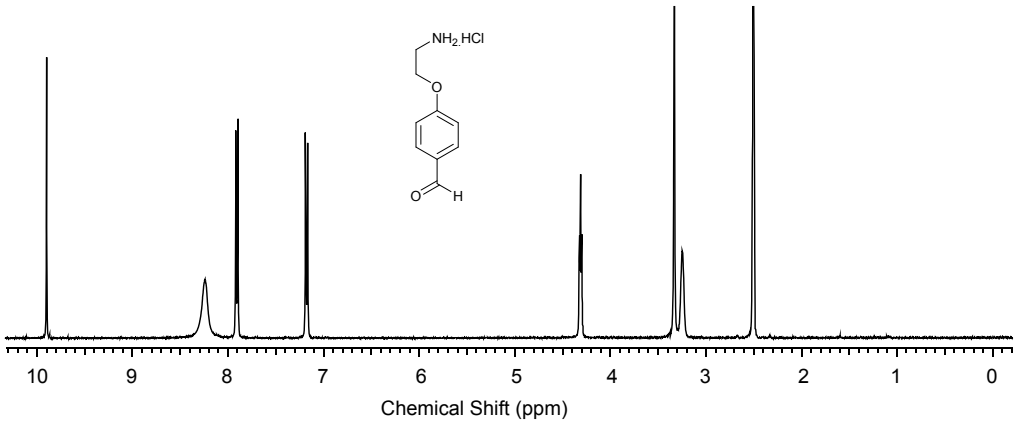


Figure S1. ^{1}H NMR spectrum of compound **1**·HCl (DMSO, 400 MHz, 298 K)

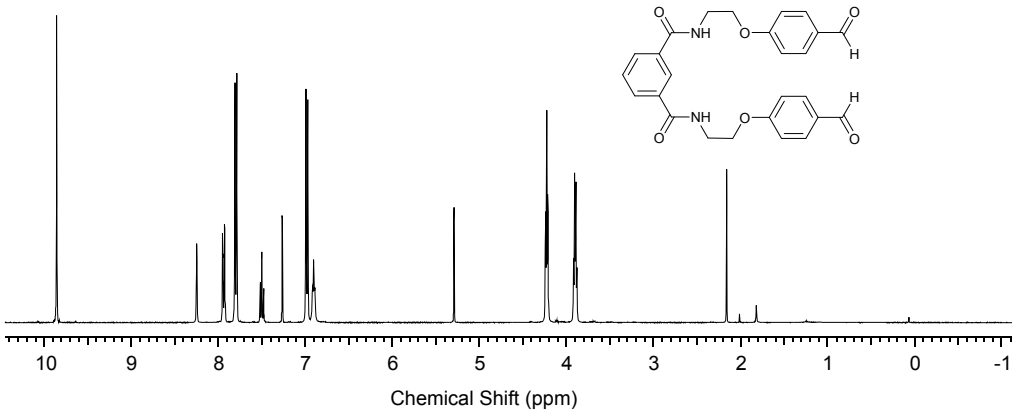


Figure S2. ^{1}H NMR spectrum of compound **2** ($CDCl_3$, 400 MHz, 298 K)

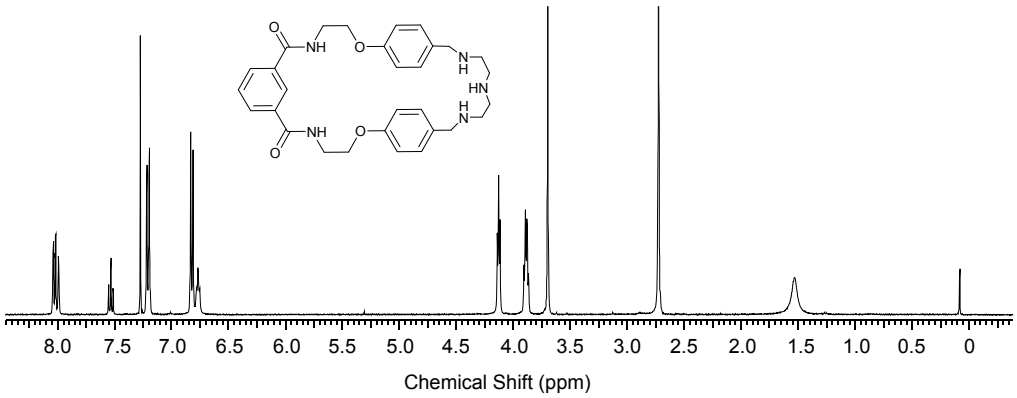


Figure S3. ^{1}H NMR spectrum of compound **3** ($CDCl_3$, 400 MHz, 298 K)

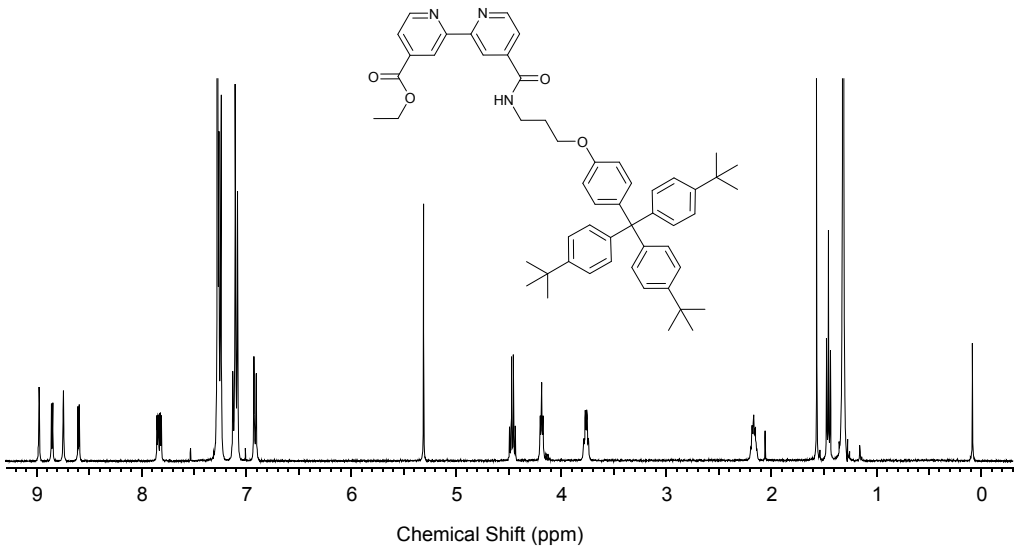


Figure S4. ^{1}H NMR spectrum of compound **S5** ($CDCl_3$, 400 MHz, 298 K)

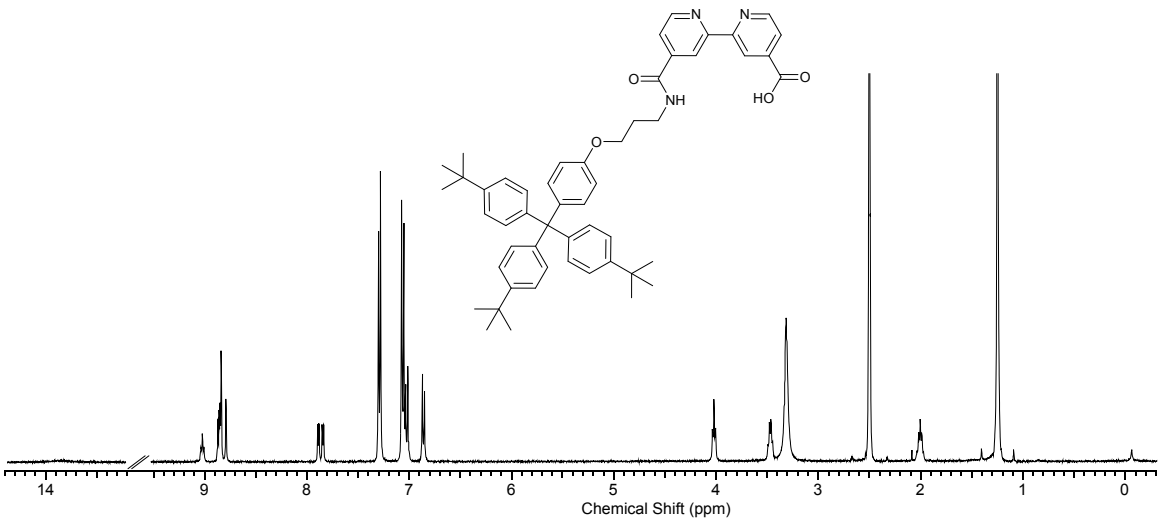


Figure S5. ^{1}H NMR spectrum of compound **5** (DMSO-d_6, 400 MHz, 298 K)

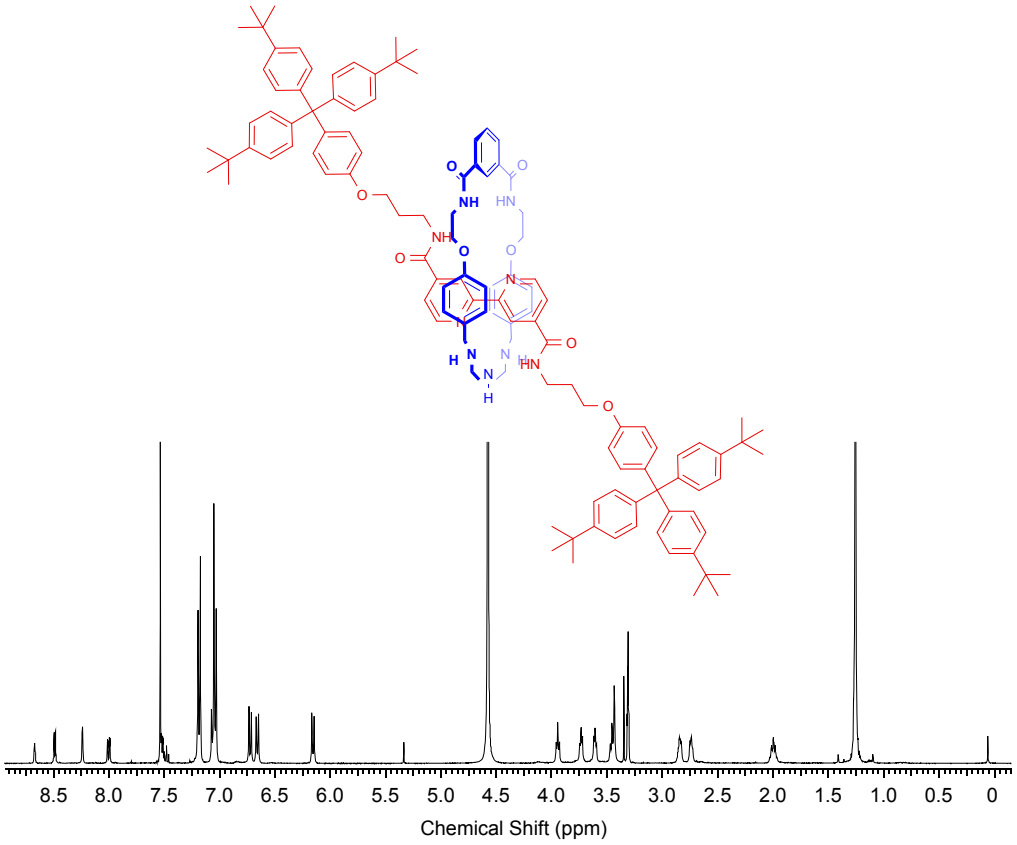


Figure S6. ^{1}H NMR spectrum of compound **8** ($CDCl_3$:CD_3OD 1:1, 400 MHz, 298 K)

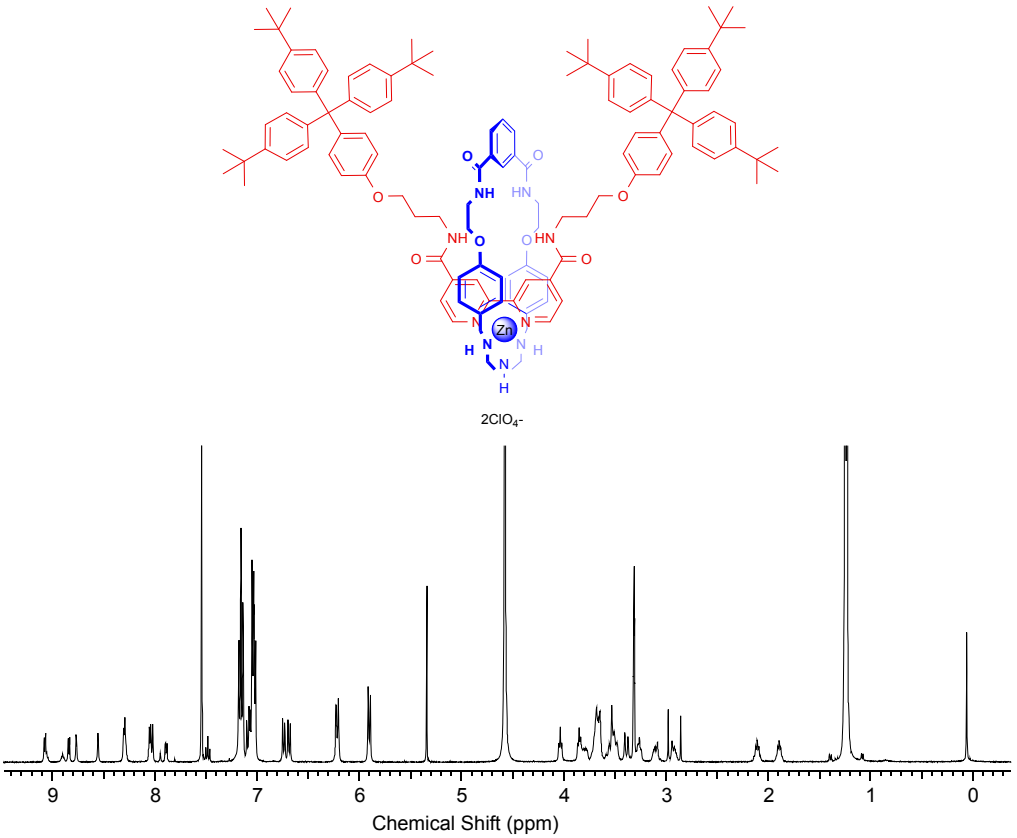


Figure S7. ^{1}H NMR spectrum of compound **8**·$Zn(ClO_4)_2$ ($CDCl_3$:CD_3OD 1:1, 400 MHz, 298 K)

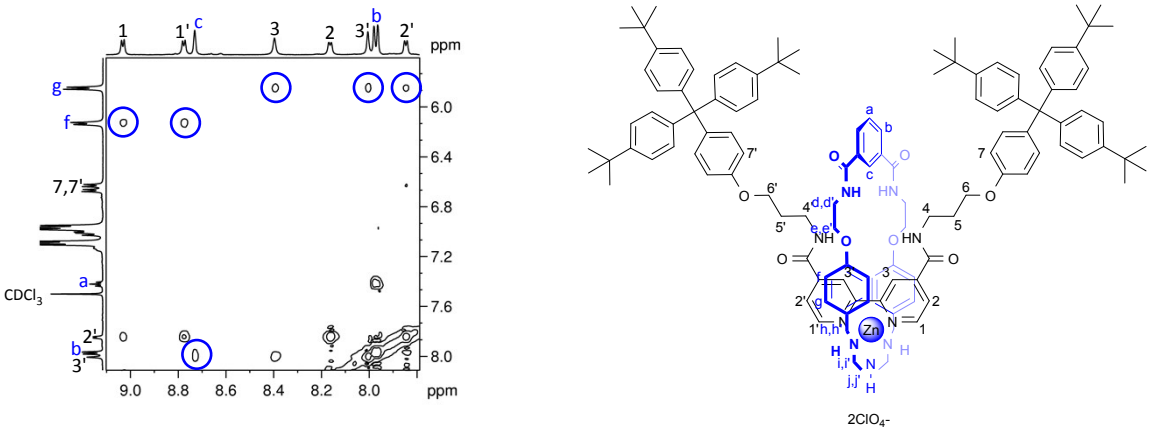


Figure S8. Section of the ^{1}H-^{1}H ROESY NMR spectrum of the [2]rotaxane **8**·Zn(ClO$_4$)$_2$ in CDCl$_3$:CD$_3$OD 1:1 at 298 K. ROE interactions between the macrocycle and axle components of the rotaxane are highlighted with blue circles.

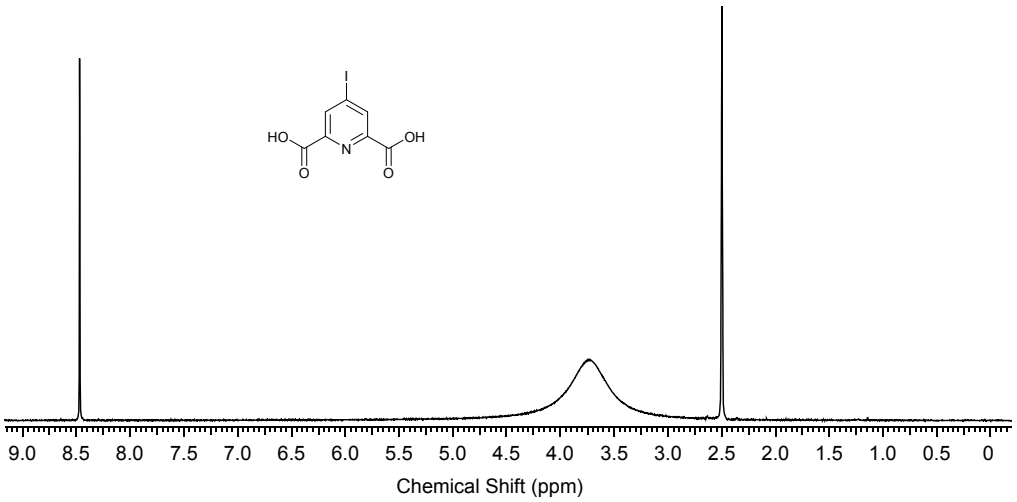


Figure S9. ^{1}H NMR spectrum of compound **S7**·(ClO$_4$)$_2$ (DMSO-d$_6$, 500 MHz, 298 K)

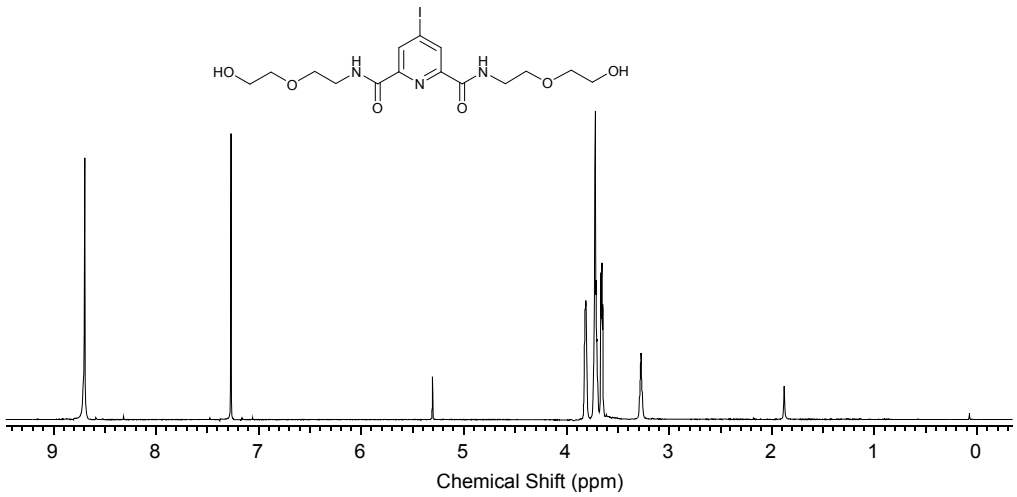


Figure S10. ^{1}H NMR spectrum of compound **9** (CDCl$_3$, 400 MHz, 298 K)

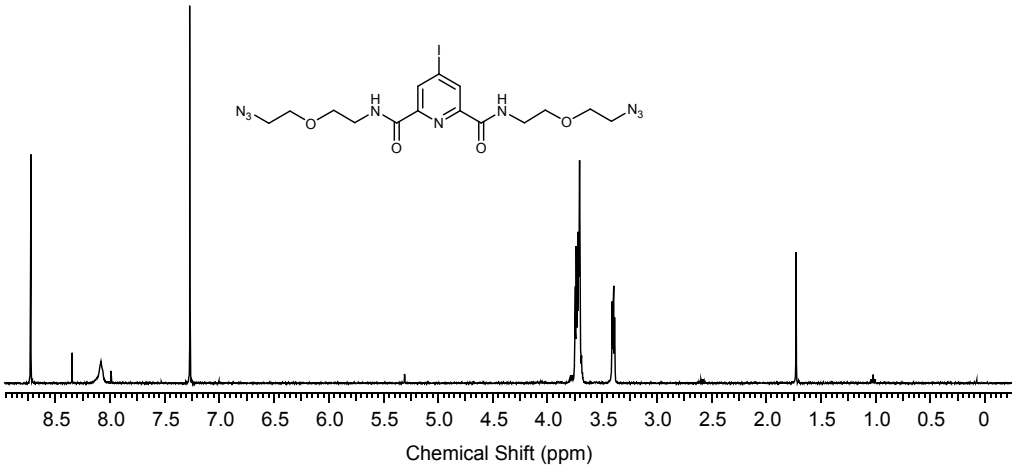


Figure S11. ^{1}H NMR spectrum of compound **11** ($CDCl_3$, 400 MHz, 298 K)

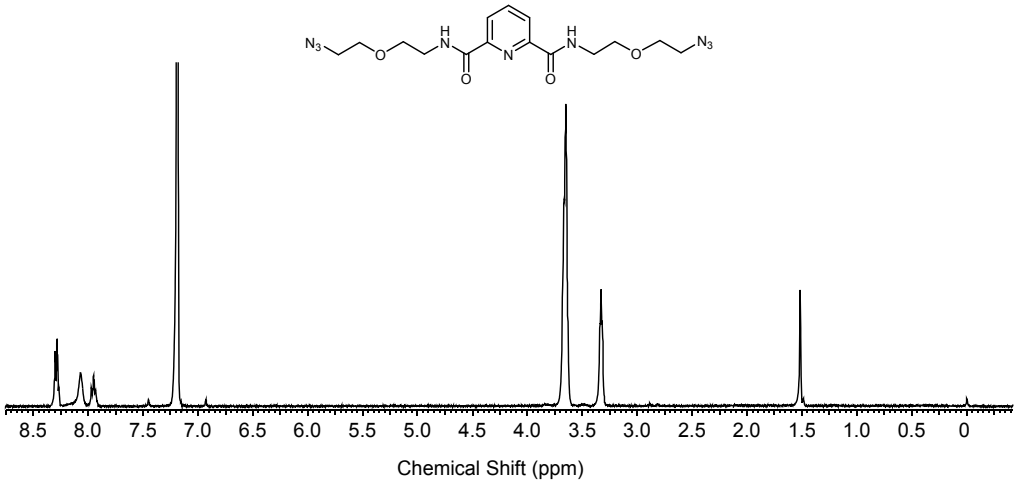


Figure S12. ^{1}H NMR spectrum of compound **12** ($CDCl_3$, 400 MHz, 298 K)

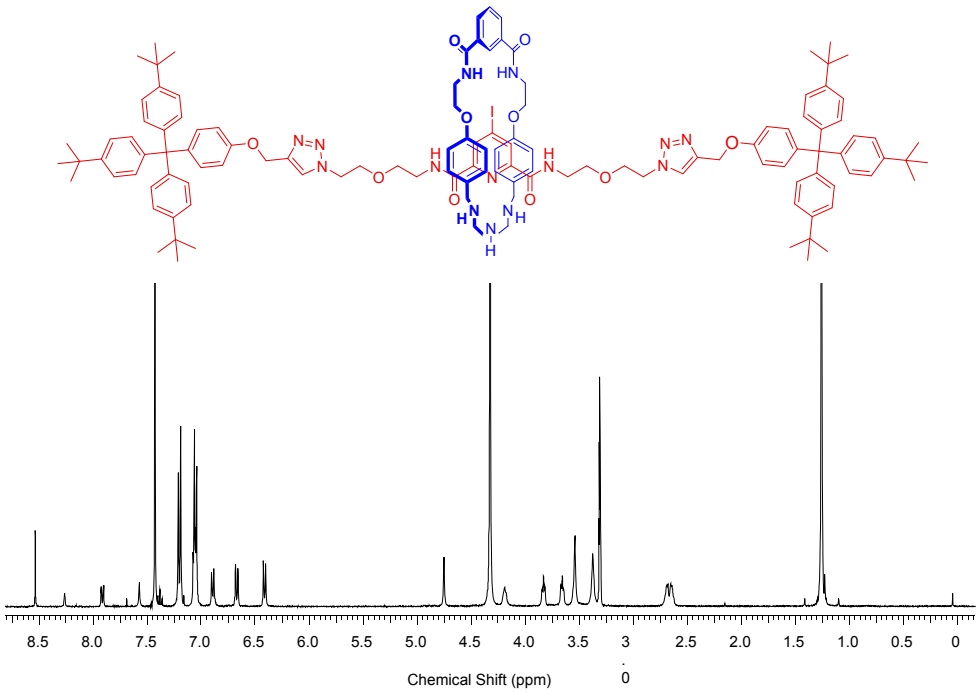


Figure S13. ^{1}H NMR spectrum of compound **14** ($CDCl_3$:CD_3OD 1:1, 400 MHz, 298 K)

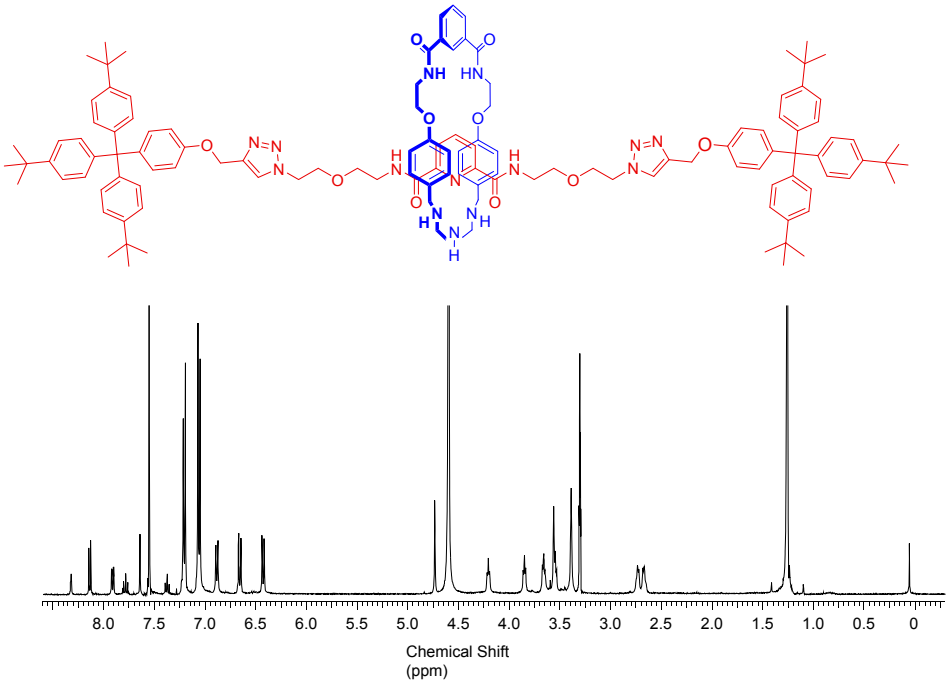


Figure S14. ^{1}H NMR spectrum of compound **15** ($CDCl_3$:CD_3OD 1:1, 400 MHz, 298 K)

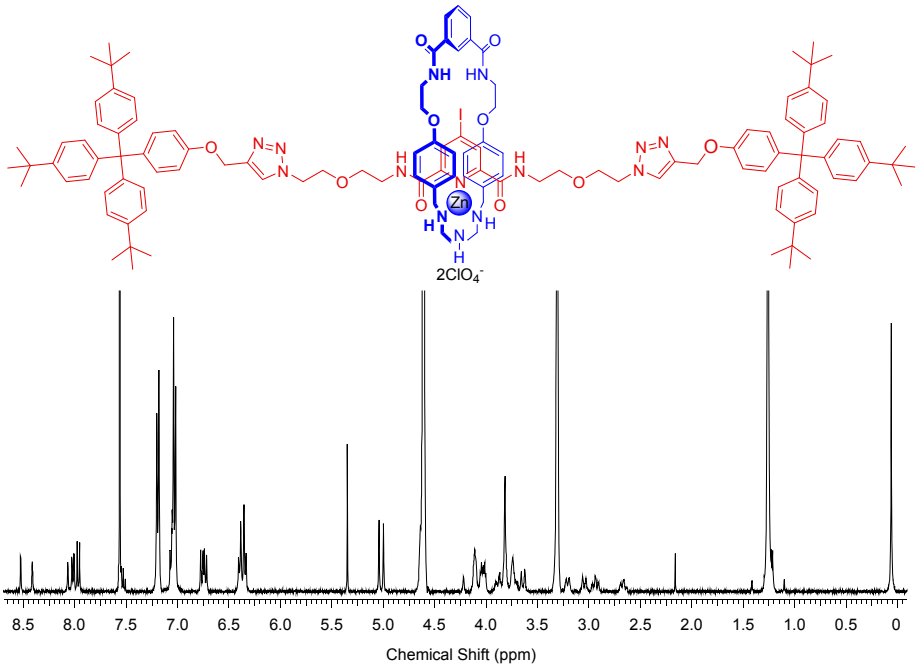


Figure S15. ^{1}H NMR spectrum of compound **14**·$Zn(ClO_4)_2$ ($CDCl_3$:CD_3OD 1:1, 400 MHz, 298 K)

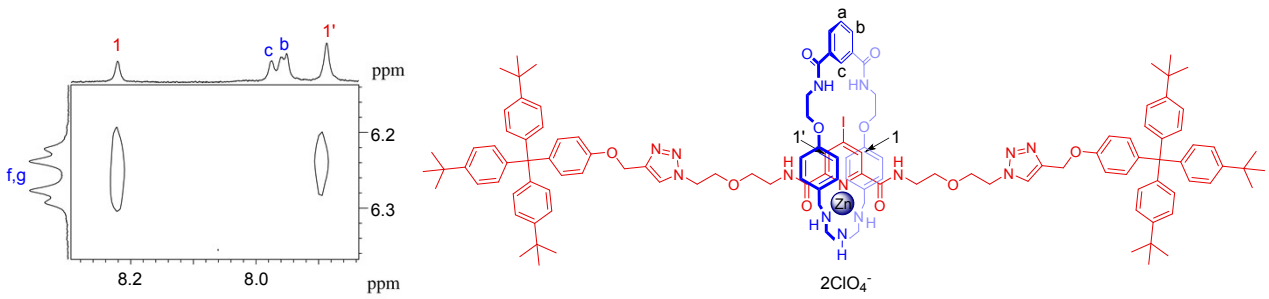


Figure S16. Section of the ^{1}H-^{1}H ROESY NMR spectrum of the [2]rotaxane **14**·Zn(ClO$_4$)$_2$ in CDCl$_3$:CD$_3$OD 1:1 at 298 K, showing through space ROE interactions between the macrocycle aromatic protons f and g and and axle iodopyridyl protons 1 and 1'.

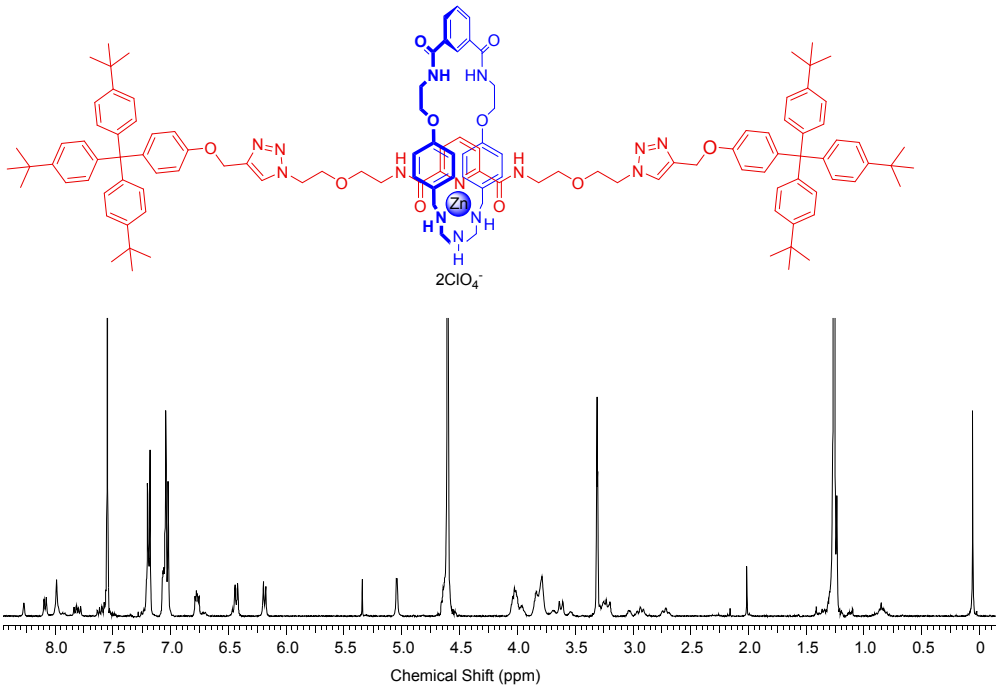


Figure S17. ^{1}H NMR spectrum of compound **15**·Zn(ClO$_4$)$_2$ (CDCl$_3$:CD$_3$OD 1:1, 400 MHz, 298 K)

S3. UV-Visible pseudorotaxane assembly titration experiments

UV-visible titration experiments were conducted using a PG instruments T60U spectrometer. During each titration experiment, aliquots of a solution of the threading ligand were repeatedly added to a 3 mM solution of the Cu(II)-complexed macrocycle **3**·Cu(ClO$_4$)$_2$ in a cuvette. After each addition, the sample was mixed thoroughly and the spectrum was recorded. The concentration of the host compound was kept constant throughout each experiment.

The stability constant for the **3**·4·Cu(ClO$_4$)$_2$ assembly was obtained by analysis of the resulting titration data using the SPECFIT[13] computer program. The parameters were refined by global analysis using singular value decomposition and non-linear modelling by the Levenberg-Marquardt method. The parameters were varied until the values for the stability constants converged. Comparison of the theoretical binding isotherms, calculated concentration profiles and the predicted spectrum of the pseudorotaxane complex with the experimental data confirmed that the model used was correct.

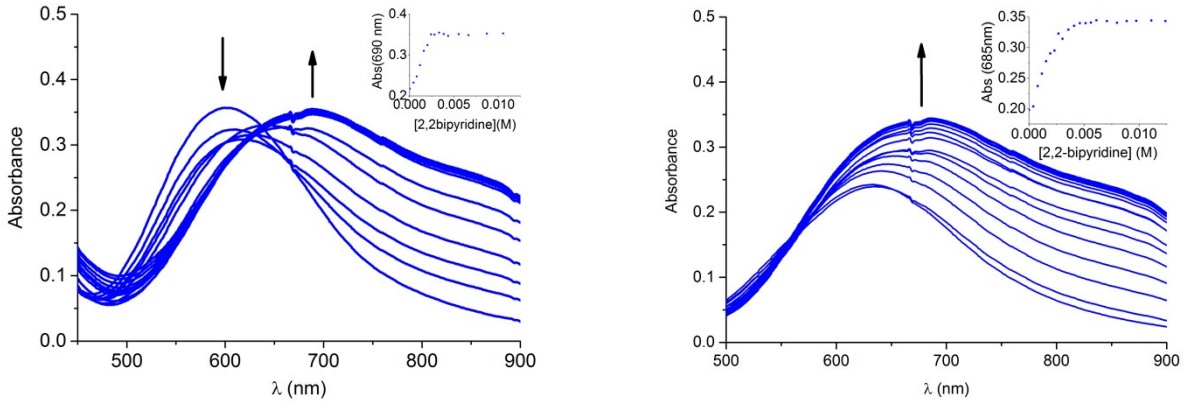


Figure S18. Left: changes in the visible absorption spectra of a 3 mM solution of macrocycle **3**·$Cu(ClO_4)_2$ in CH_3CN on addition of an increasing concentration of 2,2-bipyridine. Inset: change in absorbance at 690 nm as a function of [2,2-bipyridine]. Right: changes in the visible absorption spectra of a 3 mM solution of macrocycle **3**·$Cu(ClO_4)_2$ in DMSO on addition of an increasing concentration of 2,2-bipyridine. Inset: change in absorbance at 685 nm as a function of [2,2-bipyridine].

S4. ^{1}H NMR titration experiments

All ^{1}H NMR titration experiments were conducted on a Bruker Avance III 500 MHz NMR spectrometer, at 298K. Initial sample volumes were 600 µl. The starting concentration of the host was 1.5 mM. All anions were added as their TBA salts. The concentrations of the TBAX solutions were 45 mM. 17 aliquots of the TBAX solutions were added until a total of 10 equivalents of the anion had been added. Spectra were recorded after each addition, and the sample shaken thoroughly before measurement.

Stability constants were obtained by analysis of the titration data using the WinEQNMR2[14] computer program. Estimates for the binding constant, the limiting chemical shifts and the complex stoichiometry were also added to the input file. The various parameters were refined by non-linear least-squares analysis to achieve the best fit between observed and calculated chemical shifts. Comparison of the calculated binding isotherm with that obtained experimentally, along with careful inspection of the residuals distribution and estimated errors, helped to verify that the model used was appropriate.

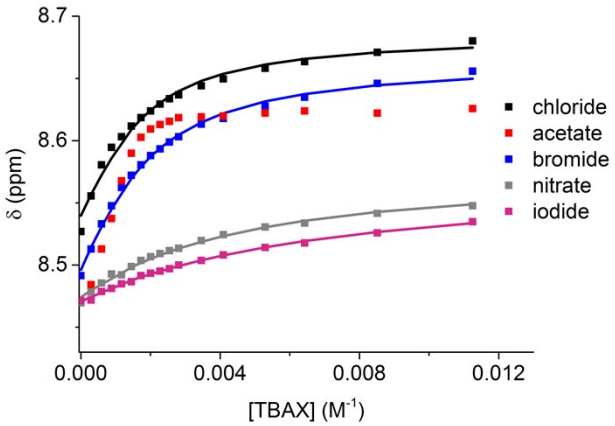


Figure S19. Changes in the chemical shift of the internal macrocycle proton c upon addition of halide, acetate and nitrate anions as their TBA salts to a 1.5 mM solution of the [2]rotaxane **8**·$Zn(ClO_4)_2$ in $CDCl_3$:CD_3OD 1:1 at 298 K. Square points represent experimental data; continuous lines represent calculated binding isotherms for the association constant values shown in Table 1 of the main article.

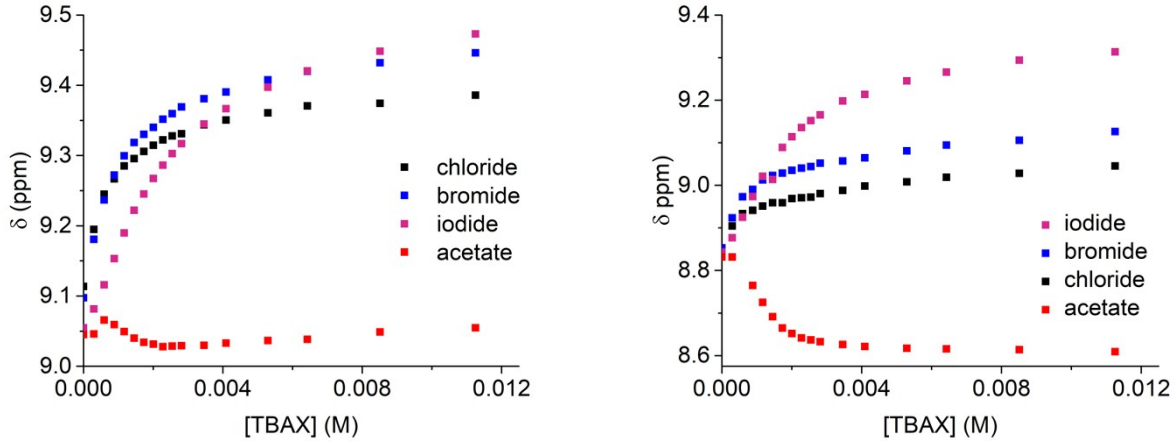


Figure S20. Changes in the chemical shift of the bipyridine aromatic protons 1 (left) and 1′ (right) upon addition of halide and acetate anions as their TBA salts to a 1.5 mM solution of the [2]rotaxane **8**·$Zn(ClO_4)_2$ in $CDCl_3$:CD_3OD 1:1 at 298 K.

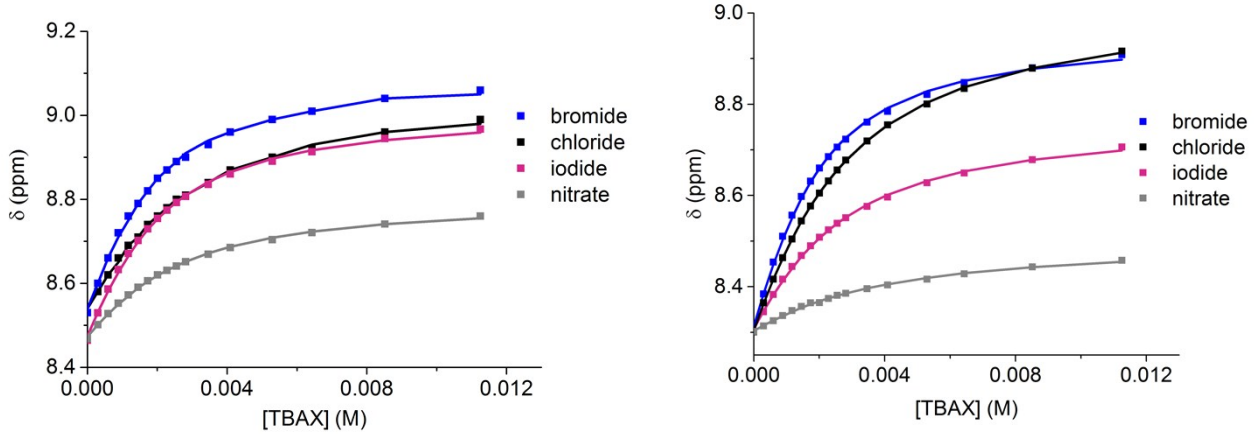


Figure S21. Changes in the chemical shift of the internal macrocycle proton c upon addition of halide and nitrate anions as their TBA salts to a 1.5 mM solution of the [2]rotaxane **14**·$Zn(ClO_4)_2$ (left) and to the [2]rotaxane **15**·$Zn(ClO_4)_2$(right) in $CDCl_3$:CD_3OD:CD_3OD 45:45:10 at 298 K. Square points represent experimental data; continuous lines represent calculated binding isotherms for the association constant values shown in Table 1 of the main article.

S5. Single crystal X-Ray diffraction experiments

Single crystals of the macrocycle **3**·$Cu(ClO_4)_2$ suitable for X-ray structural determination were grown by vapour diffusion of di-isopropyl ether into a solution of the macrocycle in CH_3CN. Single crystals of the pseudorotaxane assemblies **3**·2,2-bipyridine·$Cu(ClO_4)_2$, **3**·**4**·$Cu(ClO_4)_2$ and **3**·**9**·$Cu(ClO_4)_2$ were grown by either vapour or layered diffuson of di-siopropyl ether into a mixed solution containing the macrocycle **3**·$Cu(ClO_4)_2$ and an excess of the threading ligand 2,2-bipyridine, **4** or **9** in CH_3CN.

Diffraction data for the pseudorotaxane assembly **3**·2,2-bipyridine·$Cu(ClO_4)_2$ were collected at 150(2) K using graphite monochromated Mo Kα radiation (λ = 0.7107 Å) on a Nonius Kappa CCD diffractometer. Unit cell parameter determination and refinement and raw frame data integration were carried out using the DENZO-SMN package.[15] Diffraction data for compounds **3**·$Cu(ClO_4)_2$ and the pseudorotaxane assemblies **3**·**4**·$Cu(ClO_4)_2$ and **3**·**9**·$Cu(ClO_4)_2$ and were collected at 100(2) K using silicon double crystal monochromated synchrotron radiation (λ = 0.6889 Å) at Diamond Light Source, beamline I19,[16] using a custom-built Rigaku diffractometer.[17] Unit cell parameter determination and refinement and raw frame data integration were carried out using the CrysAlisPro[18] package.

The structures were solved by charge-flipping methods using SUPERFLIP[19] and refined by full matrix least squares on F^2 using the CRYSTALS[20] suite. All non-hydrogen atoms were refined with anisotropic displacement parameters. Where appropriate,

disordered regions were modelled over two sites using refined partial occupancies, geometric restraints were applied to ensure a physically reasonable model, and thermal and vibrational restraints were applied to maintain sensible ADPs. In addition, for the **3**·2,2-bipyridine·$Cu(ClO_4)_2$ and **3**·**4**·$Cu(ClO_4)_2$ structures the difference maps indicated the presence of some diffuse electron density, presumed to originate from diffuse disordered solvent molecules, which could not be sensibly modelled. This was included in the refinement by treating the discrete Fourier transform of the void region as contributions to the calculated structure factors with PLATON/SQUEEZE[21] (342 Å^3 containing 28 electrons and 524 Å^3 containing 128 electrons for the **3**·2,2-bipyridine·$Cu(ClO_4)_2$ and **3**·**4**·$Cu(ClO_4)_2$ structures respectively). Hydrogen atoms were generally visible in the difference map but were initially positioned geometrically and refined with restraints on bond lengths and angles, after which their positions were used as the basis for a riding model.[22] Since the hydrogen atoms on the partially occupied water molecule in the **3**·**4**·$Cu(ClO_4)_2$ structure were not clearly visible in the difference maps and it was not possible to sensibly refine their positions these hydrogen atoms were inserted at idealised hydrogen bonding positions with O—H distances of 0.9 Å and constrained to ride on the attached oxygen atom.

Crystallographic data (including structure factors) have been deposited with the Cambridge Crystallographic Data Centre (CCDC 1560763–1560766). Full data and refinement details are provided as supporting information in cif format, and selected data are also summarised in Table S1 below.

Table S1. Selected X-ray crystallographic data

Compound	**3**·$Cu(ClO_4)_2$	**3**·2,2-bipyridine·$Cu(ClO_4)_2$[a]	**3**·**4**·$Cu(ClO_4)_2$ [a]	**3**·**9**·$Cu(ClO_4)_2$
CCDC number	1560763	1560764	1560765	1560766
Formula	$C_{30}H_{37}CuN_5O_4\cdot 2Cu(ClO_4)\cdot 3.19(C_2H_3N)$	$2(C_{40}H_{45}CuN_7O_4)\cdot 4(ClO_4)\cdot 3(C_2H_3N)$	$C_{39}H_{45}CuN_6O_8I\cdot 2(ClO_4)\cdot 0.45(H_2O)$	$C_{45}H_{59}CuIN_8O_{10}\cdot 2(ClO_4)$
Formula weight	924.86	2023.73	1123.33	1261.36
a (Å)	9.0433(1)	14.4868(1)	11.1228(2)	11.8265(3)
b (Å)	23.7126(4)	16.0097(2)	13.2793(2)	12.4818(3)
c (Å)	39.6408(5)	21.0577(2)	33.7959(6)	19.5954(5)
α (°)	90	89.3102(5)	90	72.764(2)
β (°)	90	89.6569(5)	98.2505(15)	89.197(2)
γ (°)	90	83.8028(5)	90	69.746(2)
Unit cell volume (Å^3)	8500.6(2)	4854.94(8)	4940.09(15)	2560.57(12)
Crystal system	Orthorhombic	Triclinic	Monoclinic	Triclinic
Space group	*Pbca*	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
Z	8	2	4	2
Temperature (K)	100	150	100	100
Radiation type	Synchrotron	Mo $K\alpha$	Synchrotron	Synchrotron
λ (Å)	0.6889	0.7107	0.6889	0.6889
No. of measured, independent and observed [$I > 2.0\sigma(I)$] reflections	104310, 8969, 6419	197575, 22025, 11584	59945, 9986, 6311	36137, 11094, 8502
R_{int}	0.091	0.078	0.077	0.047
R_1 [$F^2>2\sigma(F^2)$]	0.087	0.070	0.055	0.042
$wR_2(F^2)$ (all data)	0.245	0.190	0.129	0.108
S	1.00	0.95	0.98	0.95

[a]PLATON-SQUEEZE[21] used.

Table S2. X—Cu bond lengths and X—Cu—X bond angles (X = N or O) from the X-ray crystal structures of the complexes **3**·$Cu(ClO_4)_2$, **3**·2,2-bipyridine·$Cu(ClO_4)_2$, **3** ·**4**·$Cu(ClO_4)_2$ and **3**·**9**·$Cu(ClO_4)_2$. Atom labels are shown in Figures 2, 4 and 5 of the main article.

3·$Cu(ClO_4)_2$ CCDC number 1560763		**3**·2,2-bipyridine·$Cu(ClO_4)_2$ CCDC number 1560764		**3**·**4**·$Cu(ClO_4)_2$ CCDC number 1560765		**3**·**9**·$Cu(ClO_4)_2$ CCDC number 1560766	
Bond lengths (Å)							
N20—Cu40	2.086(4)	N20—Cu52	2.071(4)	N20—Cu55	2.090(5)	N20—Cu65	2.075(2)
N23—Cu40	1.994(4)	N23—Cu52	2.019(4)	N23—Cu55	1.909(17)	N23—Cu55	1.997(3)
N26—Cu40	2.071(3)	N26—Cu52	2.198(4)	N26—Cu55	2.005(11)	N26—Cu55	2.081(3)
N41—Cu40	2.009(4)	N40—Cu52	2.003(5)	N40—Cu55	2.030(5)	N40—Cu65	2.052(3)
N44—Cu40	2.190(5)	N51—Cu52	2.078(4)	N123—Cu55	2.060(15)	O48—Cu55	2.363(2)
O48—Cu40	2.829(4)	N120—Cu152	2.110(5)	N126—Cu55	2.117(11)	O57—Cu55	2.244(2)
		N123—Cu152	2.035(5)	O48—Cu55	2.370(5)		
		N126—Cu152	2.112(5)	O52—Cu55	2.406(55)		
		N140—Cu152	2.002(4)				
		N151—Cu152	2.074(5)				
Bond angles (°)							
N20—Cu40—N23	83.49(13)	N20—Cu52—N23	84.01(17)	N20—Cu55—N23	81.30(20)	N20—Cu65—N23	84.28(11)
N20—Cu40—N26	162.47(14)	N20—Cu52—N26	118.67(16)	N20—Cu55—N26	163.00(40)	N20—Cu65—N26	160.11(11)
N20—Cu40—N41	94.30(15)	N20—Cu52—N40	94.75(17)	N20—Cu55—N40	94.93(17)	N20—Cu65—N40	97.34(10)
N20—Cu40—N44	96.01(18)	N20—Cu52—N51	136.78(16)	N20—Cu55—N123	85.30(30)	N23—Cu65—N26	83.23(11)
N23—Cu40—N26	83.19(12)	N23—Cu52—N26	84.22(17)	N20—Cu55—N126	164.10(30)	N23—Cu65—N40	169.66(11)
N23—Cu40—N41	164.62(16)	N23—Cu52—N40	177.75(17)	N23—Cu55—N26	86.00(30)	N26—Cu65—N40	97.73(10)
N23—Cu40—N44	98.17(15)	N23—Cu52—N51	99.69(18)	N23—Cu55—N40	170.40(40)	N20—Cu65—O48	86.25(9)
N26—Cu40—N41	95.52(14)	N26—Cu52—N40	98.03(17)	N26—Cu55—N40	99.30(30)	N20—Cu65—O57	96.20(9)
N26—Cu40—N44	97.11(16)	N26—Cu52—N51	104.53(16)	N40—Cu55—N123	163.70(30)	N23—Cu65—O48	116.67(10)
N41—Cu40—N44	97.20(17)	N40—Cu52—N51	79.90(20)	N40—Cu55—N126	95.00(20)	N23—Cu65—O57	93.68(10)
N20—Cu40—O48	79.93(15)	N120—Cu152—N123	86.60(20)	N123—Cu55—N126	81.80(30)	N26—Cu65—O48	85.61(9)
N23—Cu40—O48	85.79(14)	N120—Cu152—N126	127.00(18)	N20—Cu55—O48	87.86(19)	N26—Cu65—O57	99.99(10)
N26—Cu40—O48	87.77(12)	N120—Cu152—N140	95.82(18)	N20—Cu55—O52	97.96(18)	N40—Cu65—O48	73.66(8)
N41—Cu40—O48	78.84(16)	N120—Cu152—N151	115.24(17)	N23—Cu55—O48	95.90(40)	N40—Cu65—O57	76.01(9)
N44—Cu40—O48	174.02(15)	N123—Cu152—N126	82.90(20)	N23—Cu55—O52	115.10(40)	O48—Cu65—O57	149.63(8)
		N123—Cu152—N140	175.20(20)	N26—Cu55—O48	104.70(50)		
		N123—Cu152—N151	102.10(30)	N26—Cu55—O52	77.30(40)		
		N126—Cu152—N140	92.35(17)	N26—Cu55—O48	104.70(50)		
		N126—Cu152—N151	117.77(17)	N26—Cu55—O52	77.30(40)		
		N140—Cu152—N151	80.61(17)	N123—Cu55—O48	88.60(20)		
				N123—Cu55—O52	122.10(30)		
				N126—Cu55—O48	82.70(40)		
				N126—Cu55—O52	96.70(30)		
				O48—Cu55—O52	149.02(14)		

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