Supporting Information

Understanding coordination equilibria in solution and gel-phase [2]rotaxanes

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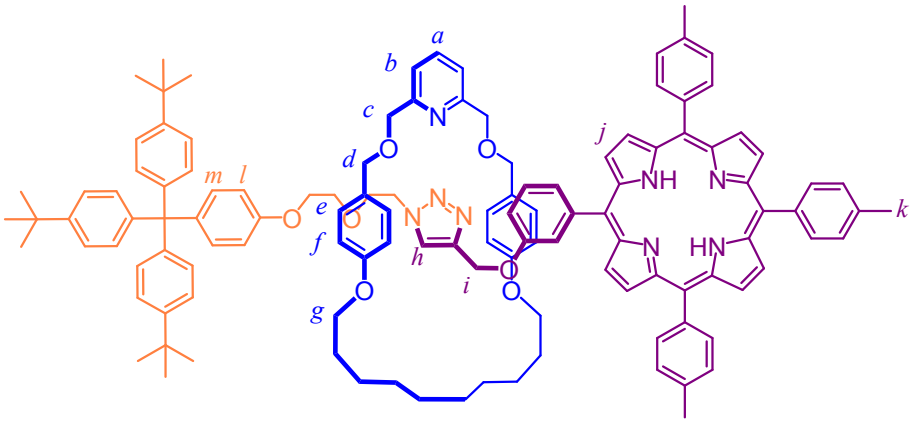
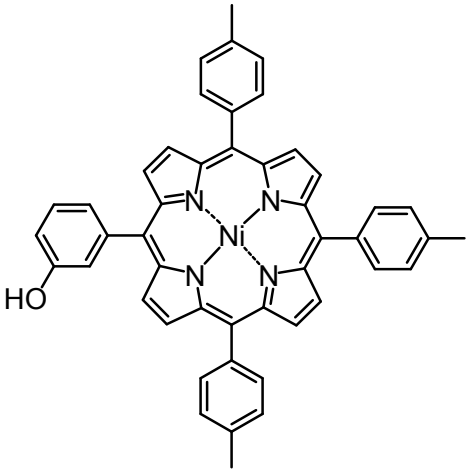
1. Experimental Procedures

Synthesis of the free base porphyrin rotaxane 6-H_2



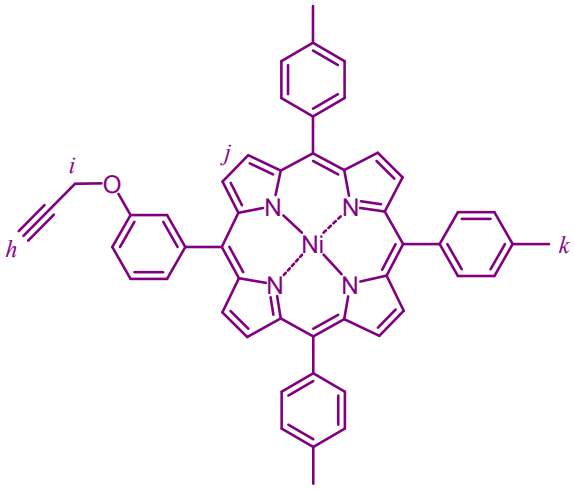
Porphyrin rotaxane **6-Zn** (10 mg, 10 µmol) was dissolved in dichloromethane (5 mL) and washed with 2M hydrochloric acid (3 x 10 mL), water (1 x 15 mL), 2M sodium bicarbonate$_{(aq)}$ (1 x 10 mL) and brine (1 x 20 mL). The organic layer was then dried over sodium sulphate and the solvent was removed in vacuo to give the free-base rotaxane **6-H_2** as a deep purple solid (9.8 mg, 99%). m/z (HR ESI-MS) $[M+H]^+$ 1817.9960 $C_{122}H_{128}N_8O_7$ (calc. 1817.9979); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.88 (d, 8H, J=3.4 Hz, H_j), 8.13 (d, 6H, J=7.8 Hz, Ar-H), 7.84 (d, 1H, J=7.4 Hz, Ar-H), 7.77 (s, 1H, Ar-H), 7.63 (t, 1H, J=7.9 Hz, Ar-H), 7.58 (d, 6H, J=7.8 Hz, Ar-H), 7.51 (s, 1H, H_h), 7.33 (m, 2H, H_a, Ar-H), 7.24 (d, 6H, J=8.4 Hz, Ar-H), 7.11 (m, 8H, H_b, Ar-H), 7.02 (d, 2H, J=9.0 Hz, H_l), 6.99 (d, 4H, J=8.3 Hz, H_e), 6.57 (d, 4H, J=8.3 Hz, H_f), 6.52 (d, 2H, J=9.0 Hz, H_m), 5.10 (s, 2H, H_i), 4.43 (s, 4H, H_d), 4.26 (s, 4H, H_c), 3.93 (t, 2H, J=5.4 Hz, OCH_2), 3.78 (t, 4H, J=6.5 Hz, H_g), 3.58 (t, 2H, J=4.3 Hz, OCH_2), 3.20 (m, 4H, OCH_2), 2.73 (s, 9H, H_k), 1.36 (m, 4H, alkyl-H), 1.30 (s, 27H, t-butyl), 1.23-1.15 (m, 12H, alkyl-H), -2.76 (s, 2H, NH). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.8, 158.7, 157.5, 156.9, 156.3, 148.3, 144.2, 143.5, 143.2, 139.6, 139.3, 139.3, 137.3, 136.9, 134.5, 132.1, 130.7, 130.1, 129.9, 129.6, 129.1, 127.9, 127.4, 127.4, 124.3, 124.1, 121.5, 120.3, 120.2, 119.9, 119.4, 114.6, 114.6, 114.5, 114.4, 114.3, 113.9, 113.0, 77.2, 72.4, 71.4, 71.3, 69.1, 68.8, 68.1, 67.5, 67.1, 66.5, 63.0, 61.9, 49.5, 34.3, 31.4, 29.7, 29.6, 28.6, 25.6, 21.5.

Synthesis of Nickel Hydroxy Porphyrin S1



5-[*m*-Hydroxyphenyl]10,15,20-*tris*-[*p*-tolyl] porphyrin (100mg, 0.15 mmol) was dissolved in DMF (5 mL). To this reaction mixture was added nickel acetate hydrate (112 mg, 0.4 mmol) and the reaction was then refluxed overnight. The solvent was reduced *in vacuo* and the crude material was redissolved in DCM (30 mL). The organic solution was then washed with water (3 x 50 mL) and brine (50 mL) and then dried over anhydrous sodium sulphate. The solvent was removed *in vacuo* to give the pure product as a deep reddish purple solid (108 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.78 (d, 8H, J=4.0 Hz), 7.91 (d, 6H, J=6.0 Hz), 7.62 (d, 1H, J=7.7 Hz), 7.53 (m, 8H, J=8.0 Hz), 7.20 (d, 1H, J=8.4 Hz), 2.74 (s, 9H).

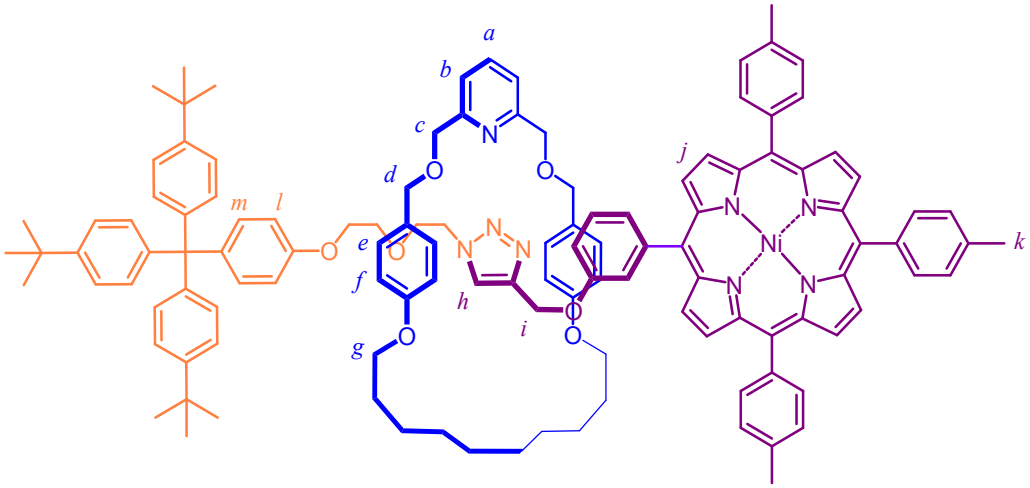
Synthesis of Nickel Alkyne Porphyrin 1-Ni



Hydroxy nickel porphyrin **S1** (108 mg, 0.15 mmol) was dissolved in dry degassed DMF (12 mL). To this, propargyl bromide (80% in toluene solution; 0.05 mL, 0.525 mmol), and

anhydrous cesium carbonate (200 mg, 0.61 mmol) were added and the reaction was then stirred at 90°C under argon for 24 hours. Upon cooling the reaction mixture was diluted with dichloromethane (100 mL) and washed with water (3 x 200 mL) and brine (200 mL). The organic layer was dried over anhydrous sodium sulphate and reduced *in vacuo* to give the crude product which was then purified by flash column chromatography (eluent CH_2Cl_2) to give the nickel alkyne porphyrin blocker **1-Ni** as a deep purple-red solid (91 mg, 85%). m/z (LR ESI-MS) $[M+H]^+$ 766.42 $C_{50}H_{36}N_4ONi$ (calc. 767.23); ^1H NMR (400 MHz, $CDCl_3$) δ: 8.79 (m, 8H, H_j), 7.91 (d, 6H, J=7.3 Hz, Ar-H), 7.69 (s, 1H, Ar-H), 7.66 (d, 1H, J=7.4 Hz, Ar-H) 7.60 (t, 1H, J=7.7 Hz, Ar-H), 7.50 (d, 6H, J=7.3 Hz, Ar-H), 7.35 (d, 1H, J=8.0 Hz, Ar-H), 4.85 (d, 2H, J=2.3 Hz, H_i), 2.66 (s, 9H, H_k), 2.58 (t, 1H, J=2.3 Hz, H_h).

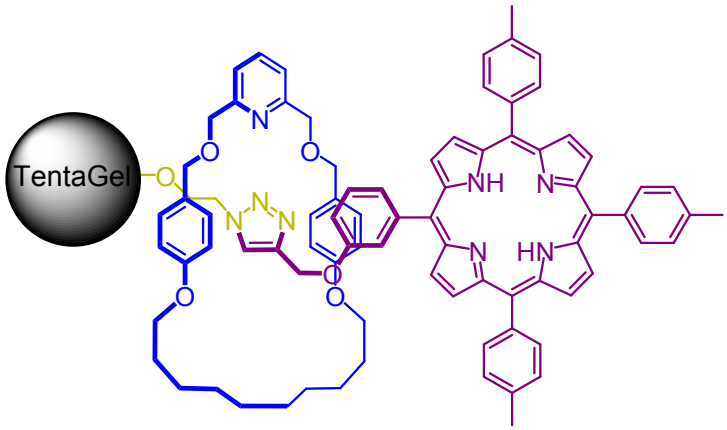
Synthesis of Porphyrin Rotaxane 6-Ni



Pyridine macrocycle **3** (100 mg, 0.20 mmol) and tetrakis(acetonitrile)copper(I) hexafluorophosphate (8 mg, 0.020 mmol) were dissolved in dry degassed dichloromethane (10 mL) and stirred for 15 minutes under argon. To this, alkyne porphyrin **1-Ni** (15 mg, 0.020 mmol) and azide blocker **5** (12 mg, 0.020 mmol) were added and the reaction was stirred at room temperature under argon for 3 days. 17% ammonia sat. $EDTA_{(aq)}$ (10 mL) was added and the reaction was vigorously stirred for 1 hour. The mixture was then diluted with dichloromethane (15 mL) and washed with 17% ammonia sat. $EDTA_{(aq)}$ (3 x 20 mL), water (2 x 25mL) and brine (1 x 20 mL). The organic layer was dried over sodium sulphate and reduced *in vacuo* to give the crude product which was subsequently purified by flash column chromatography (gradient eluent CH_2Cl_2 to 7:3 CH_2Cl_2:EtOAc) to give the pure product **6-Ni**

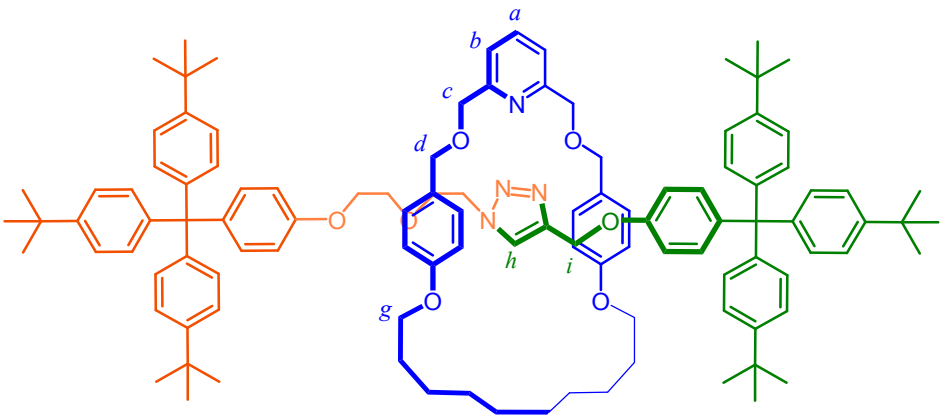
as a deep purple solid (29 mg, 78%). m/z (HR ESI-MS) $[M+H]^+$ 1873.9159 $C_{122}H_{126}N_8O_7Ni$ (calc. 1873.9176); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.77 (d, 8H, J=3.4 Hz, H_j), 7.91 (d, 6H, J=7.9 Hz, Ar-H), 7.65 (d, 1H, J=7.6 Hz, Ar-H), 7.52 (m, 9H, Ar-H), 7.47 (s, 1H, H_h), 7.34 (t, 1H, J=7.8 Hz, H_a), 7.23 (d, 2H, J=8.6 Hz, Ar-H), 7.11 (d, 2H, J=7.8 Hz, H_b), 7.10 (d, 6H, J=8.6 Hz, Ar-H), 7.01 (d, 2H, J=8.8 Hz, H_l), 6.96 (d, 4H, J=8.7 Hz, H_e), 6.55 (d, 4H, J=8.7 Hz, H_f), 6.52 (d, 2H, J=8.8 Hz, H_m), 5.03 (s, 2H, H_i), 4.45 (d, 2H, 11.9 Hz, H_d), 4.40 (d, 2H, 11.9 Hz, $H_{d'}$), 4.23 (s, 4H, H_c), 3.90 (t, 2H, J=5.5 Hz, OCH_2), 3.76 (t, 4H, J=5.7 Hz, H_g), 3.58 (t, 2H, J=4.9 Hz, OCH_2), 3.19 (m, 4H, OCH_2), 2.66 (s, 9H, H_k), 1.60 (p, 4H, J=5.7 Hz, alkyl-H), 1.28 (s, 27H, t-butyl), 1.21-1.06 (m, 12H, alkyl-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.7, 157.5, 157.0, 156.3, 148.3, 148.2, 144.2, 144.1, 142.8, 142.8, 142.8, 142.5, 142.3, 139.7, 138.0, 138.0, 137.4, 136.9, 133.7, 132.2, 132.1, 132.1, 131.8, 131.0, 130.7, 130.6, 129.9, 129.1, 127.7, 127.6, 124.1, 123.9, 120.5, 119.9, 119.1, 119.0, 118.4, 114.3, 113.0, 112.7, 77.3, 77.2, 72.4, 71.3, 69.1, 67.1, 66.6, 63.1, 49.5, 34.3, 31.5, 31.4, 29.6, 28.6, 25.6, 21.5.

Synthesis of the free base porphyrin rotaxane functionalised Beads 4-H_2



Porphyrin rotaxane functionalised polystyrene beads **4-Zn** (10 mg) were transferred to a fritted funnel and then washed thrice with the following series of solvents: water (2 x 5 mL), 20% hydrochloric acid in EtOH (2 x 5 mL) and then water (2 x 5 mL), 2M sodium bicarbonate solution (2 x 5 mL) and finally with water (5 mL) and acetone (5 mL). The beads are then dried in air to give deep purple rotaxane functionalised beads **4-H_2** (10 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.86 (8H, H_j), 8.04 (6H, Ar-H), 7.74 (3H, Ar-H), 7.48 (7H, Ar-H), 7.20 (4H, H_e), 6.75 (4H, H_f), 5.34 (4H, OCH_2), 5.15 (4H, OCH_2), 4.44 (4H, OCH_2), 4.25 (4H, OCH_2), 3.83 (4H, OCH_2), 2.64 (9H, H_k), 1.34-1.28 (12H, alkyl-H), -2.75 (2H, NH).

Synthesis of generic rotaxane S2



Pyridine macrocycle **3** (100 mg, 0.20 mmol) and tetrakis(acetonitrile)copper(I) hexafluorophosphate (8 mg, 0.020 mmol) were dissolved in dry degassed dichloromethane (10 mL) and stirred for 15 minutes under argon. To this, generic alkyne blocker **9** (12.0 mg, 0.020 mmol) and azide blocker **5** (12.2 mg, 0.020 mmol) were added and the reaction was stirred at room temperature under argon for 3 days. 17% ammonia sat. $EDTA_{(aq)}$ (10 mL) was added and the reaction was vigorously stirred for 1 hour. The mixture was then diluted with dichloromethane (15 mL) and washed with 17% ammonia sat. $EDTA_{(aq)}$ (2 x 20 mL), water (2 x 25 mL) and brine (1 x 20 mL). The organics were dried over sodium sulphate and reduced in vacuo to give the crude product which was subsequently purified by flash column chromatography (gradient eluent CH_2Cl_2 to EtOAc) to give the rotaxane **S1** as an amorphous white solid (3 mg, 9 %). m/z (HR ESI-MS) $[M+H]^+$ 1650.0488 $C_{112}H_{137}N_4O_7$ (calc. 1650.0482, Δ(ppm): 0.37); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 (t, 1H, J=6.8 Hz, H_a), 7.45 (s, 1H, H_h), 7.25 (m, 14H, Ar-H), 7.11 (m, 12H, Ar-H), 7.02 (m, 8H, Ar-H), 6.71 (d, 2H, J=6.9 Hz, Ar-H), 6.57 (m, 6H, Ar-H), 4.88 (s, 2H, H_i), 4.49 (s, 4H, H_d), 4.31 (s, 4H, H_c), 3.91 (s, 2H, OCH_2), 3.80 (t, 4H, J=6.2 Hz, H_g), 3.63 (s, 2H, OCH_2), 3.25 (s, 2H, OCH_2), 3.21 (s, 2H, OCH_2), 1.66 (quin, 4H, J=6.2 Hz, alkyl-H), 1.32 (s, 54H, t-butyl), 1.28-1.20 (m, 12H, alkyl-H).

2. Supplementary Schemes and Figures

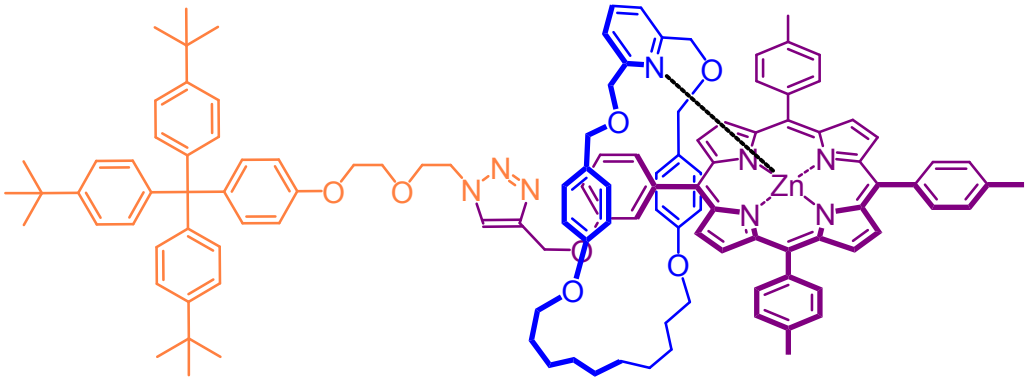
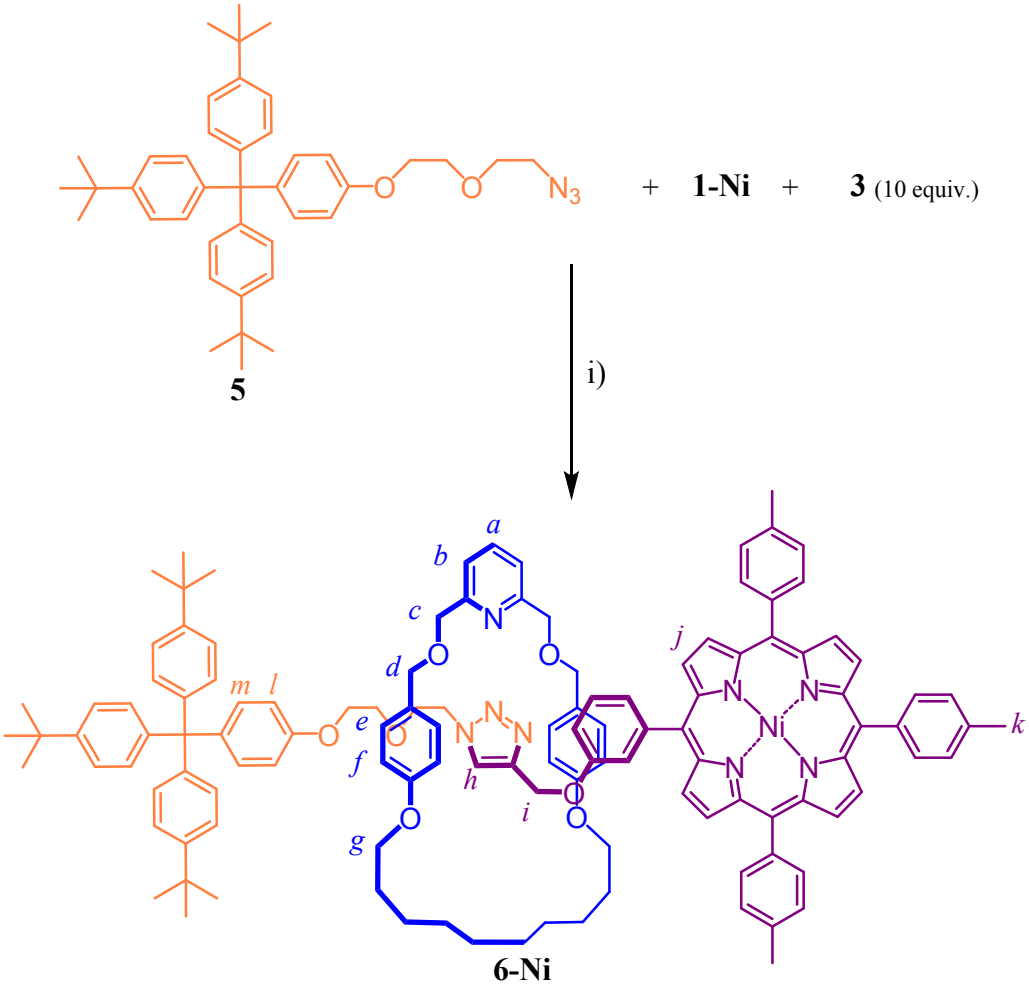


Figure S1: Proposed conformation of [2]rotaxane **6-Zn**.



Scheme S1: Synthesis of nickel [2]rotaxane **6-Ni** using nickel alkyne porphyrin **1-Ni**. Reagents and Conditions: *i*) $[Cu(MeCN)_4].PF_6$ (10 equiv), CH_2Cl_2, RT, 72 hours.

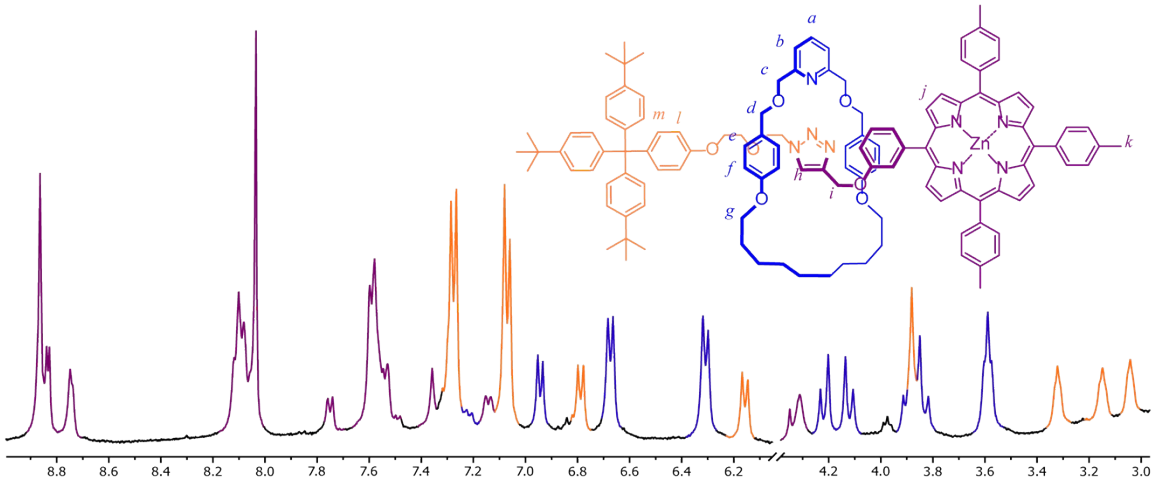


Figure S2: ^{1}H NMR (400 MHz, $(CD_3)_2CO$, 298K) spectrum of **6-Zn**.

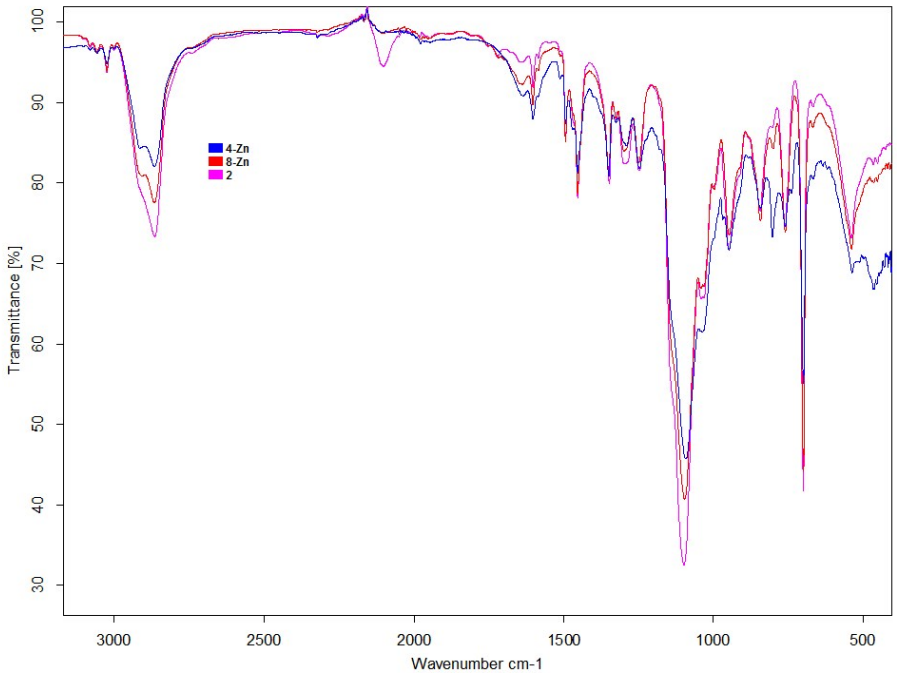


Figure S3: FT-IR spectrum of azide beads **2** (pink), rotaxane beads **4-Zn** (blue) and porphyrin thread beads **8-Zn** (red).

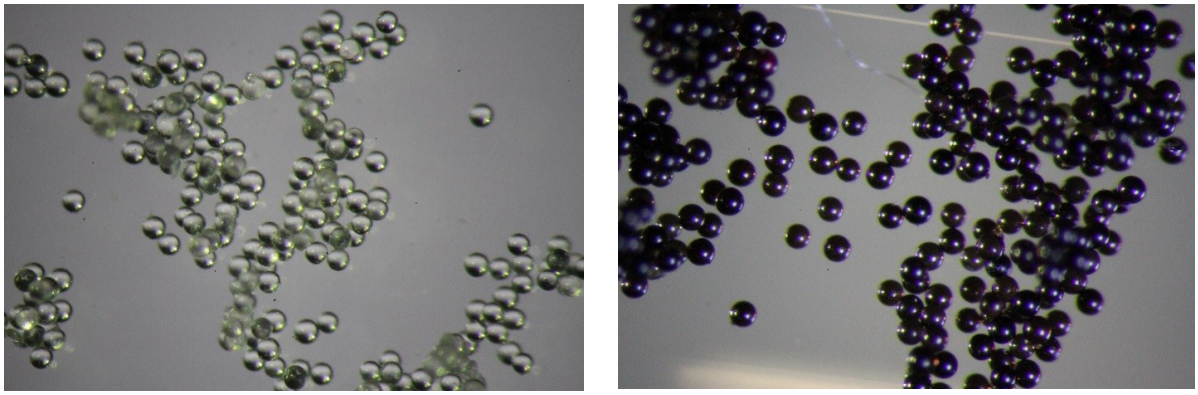


Figure S4: Optical microscope images (5x magnification) of azide beads **2** (left) and [2]rotaxane beads **4-Zn** (right).

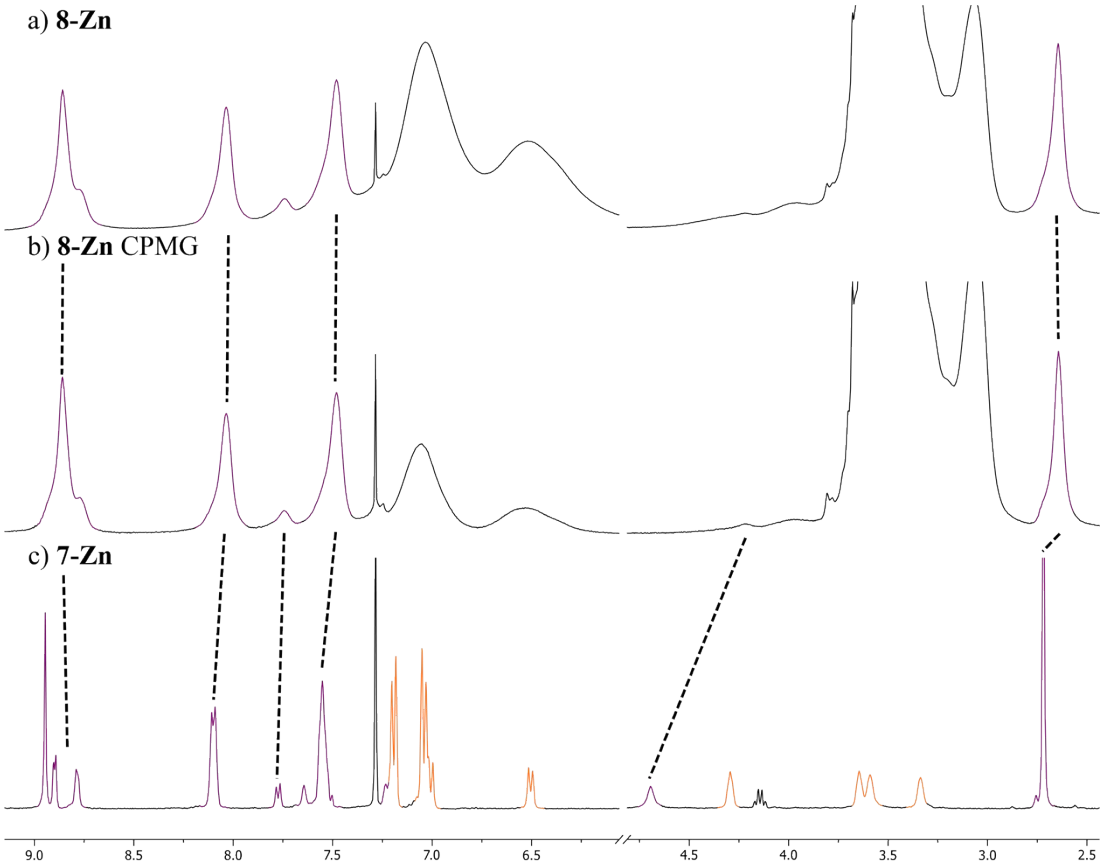


Figure S5: Stack plot showing the ^{1}H NMR (400 MHz, $CDCl_3$, 298K) spectra of porphyrin thread **7-Zn** (bottom), Porphyrin Beads **8-Zn** HR MAS CPMG pulse sequence 64 loops (middle), and Porphyrin Beads **8-Zn** HR MAS (top).

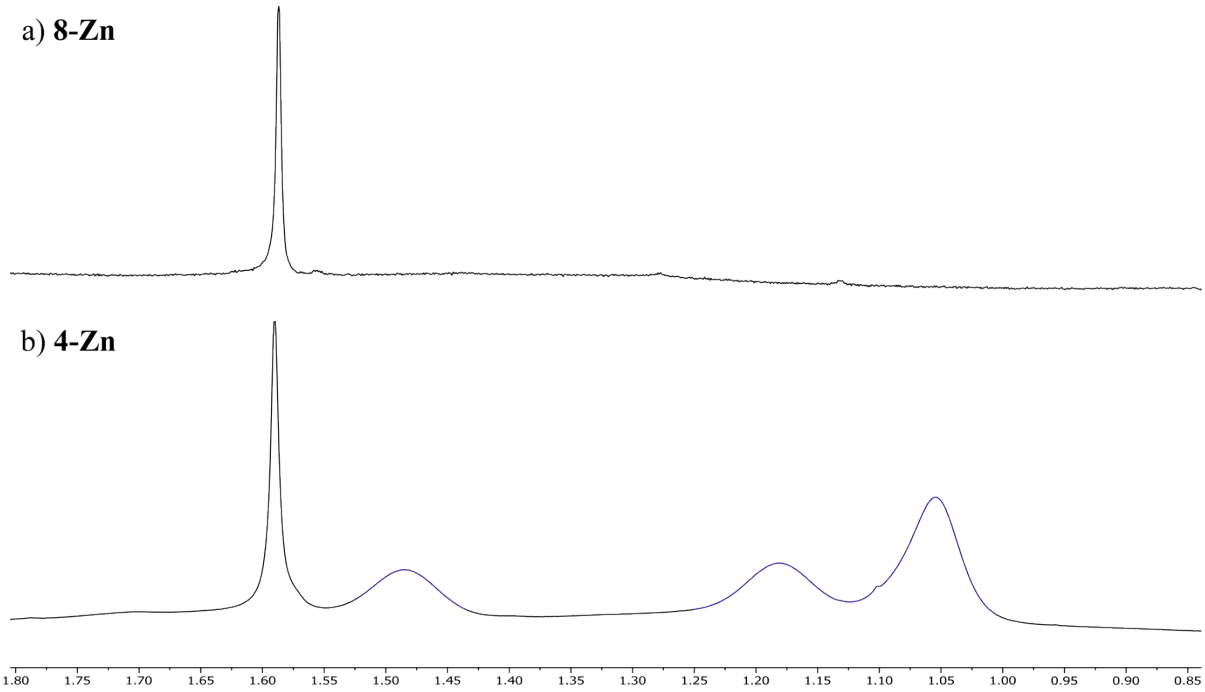
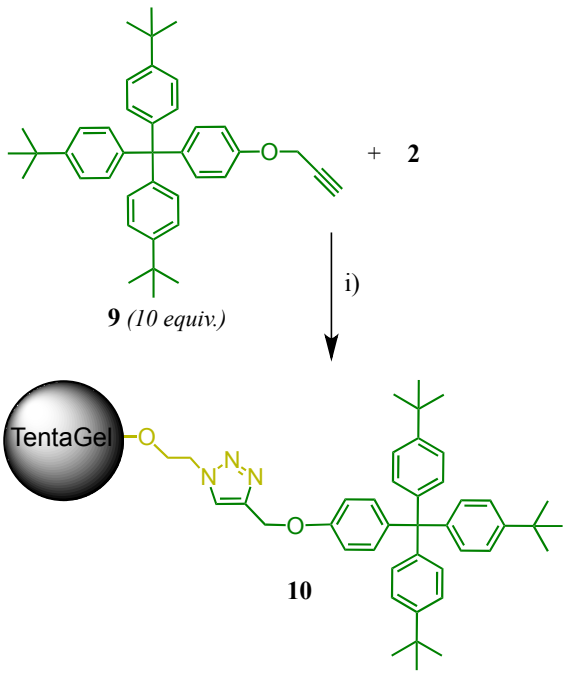
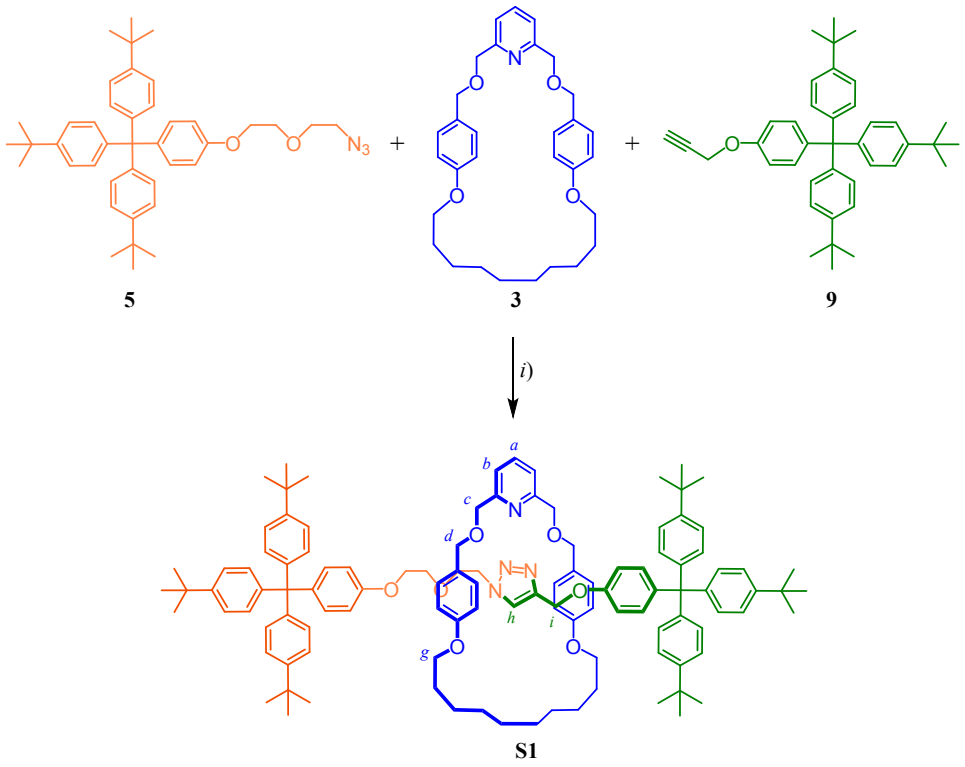


Figure S6: Stack plot of ^{1}H NMR (400 MHz, $CDCl_3$, 298K) spectra showing decyl chain proton area used for integration of a) porphyrin beads **8-Zn** and b) rotaxane beads **4-Zn**.



Scheme S2: Reagents and Conditions: *i*) $[Cu(MeCN)_4].PF_6$ (10 equiv), 2,6-lutidine (100 equiv), CH_2Cl_2, RT, 7 days.



Scheme S3: Reagents and Conditions: *i*) $[Cu(MeCN)_4].PF_6$ (1 equiv), CH_2Cl_2, RT, 72 hrs.

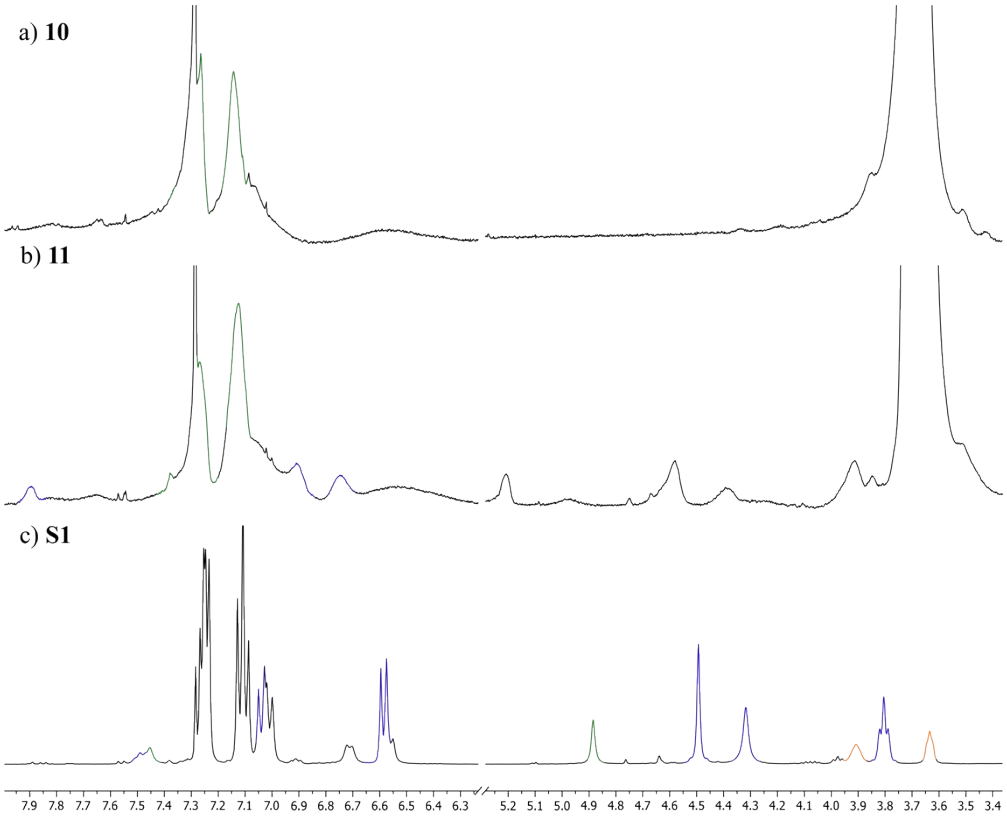


Figure S7: Stack plot showing the ^1H NMR (400 MHz, $CDCl_3$, 298K) of a) Blocker Beads **10** HR MAS CPMG 16 loops, b) [2]Rotaxane Beads **11** HR MAS CPMG 16 loops and c) [2]Rotaxane **S1** (bottom)

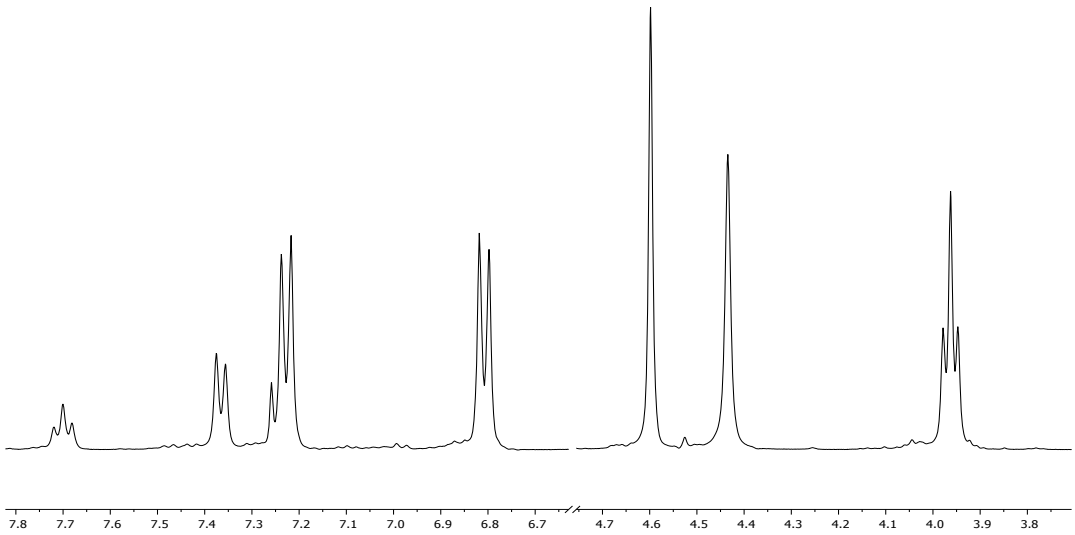


Figure S8: ^{1}H NMR (400 MHz, $CDCl_3$, 298k) of macrocycle **3** after being treated with 2M HCl.

3. Titration Data and Equilibrium Expressions used in Effective Molarity Calculations.

Titration with pyridine

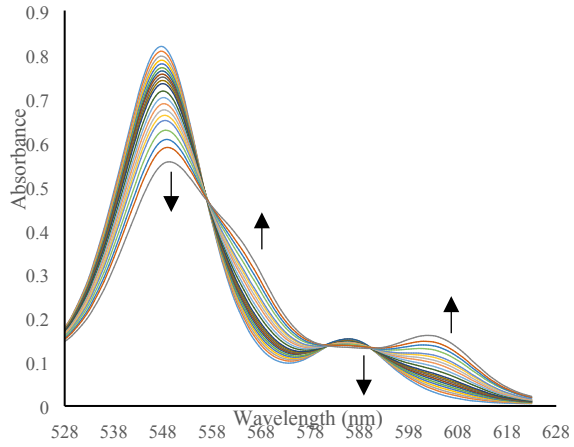
UV-visible titrations to determine binding constants were performed in 2.5 mL $CHCl_3$ (cuvette volume) at an approximate host concentration of $3x10^{-5}$ M. Fresh $CHCl_3$ for titrations was percolated through a column of basic alumina before use. Ten 4µL additions, six 10µL additions, three 20µL additions and one 40 µL addition of an approximately 0.004 M pyridine solution were made and the UV-Visible absorption spectrum was measured after each addition. This covers a range approximately up to 10 equivalency of pyridine ligand to host. The data was then fitted to a 1:1 binding model using the ReactLab Equilibria software Version 1.1, fitting all the data in range between 528-623 nm.

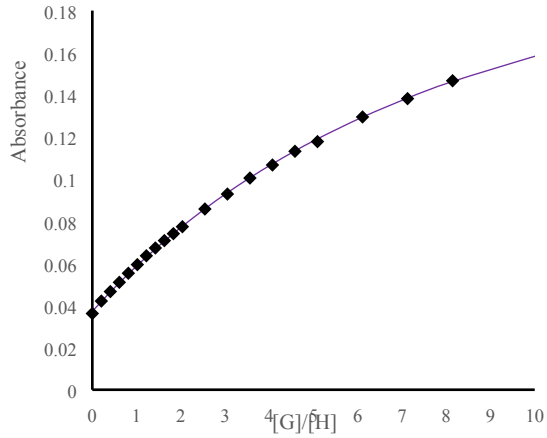
Titration with macrocycle **3**

UV-visible titrations to determine binding constants were performed in 2.5 mL $CHCl_3$ (cuvette volume) at an approximate host concentration of $1.8x10^{-5}$ M. Fresh $CHCl_3$ for titrations was percolated through a column of basic alumina before use. Ten 8µL additions, six 20µL additions, three 40µL additions and one 80 µL addition of an approximately 0.2 M pyridine solution were made and the UV-Visible absorption spectrum was measured after each addition.

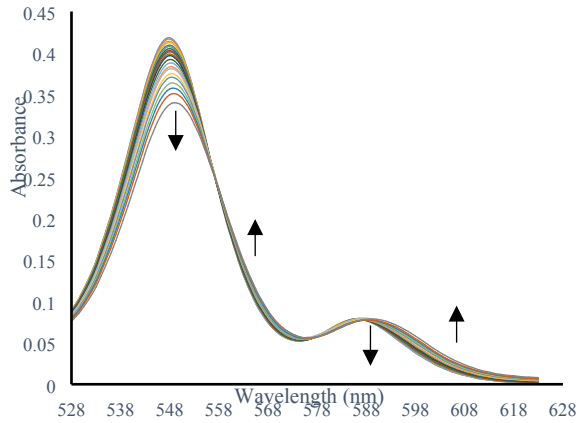
This covers a range approximately up to 2000 equivalency of macrocycle ligand to host. The data was then fitted to a 1:1 binding model using the ReactLab Equilibria software, fitting all the data in range between 528-623 nm.

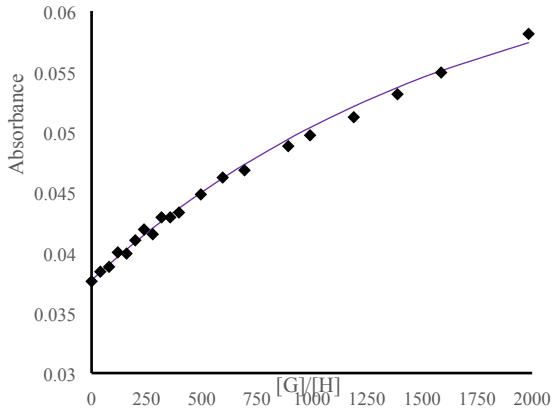
Example Titration Data



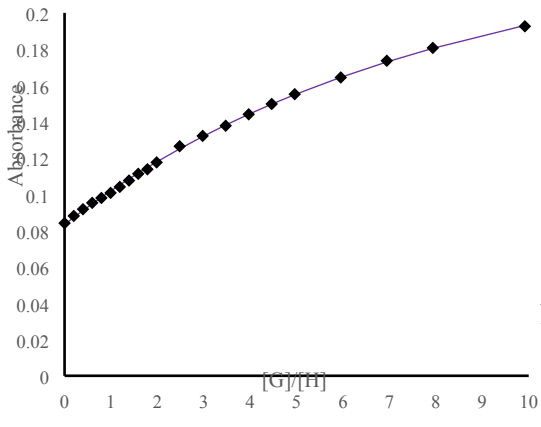


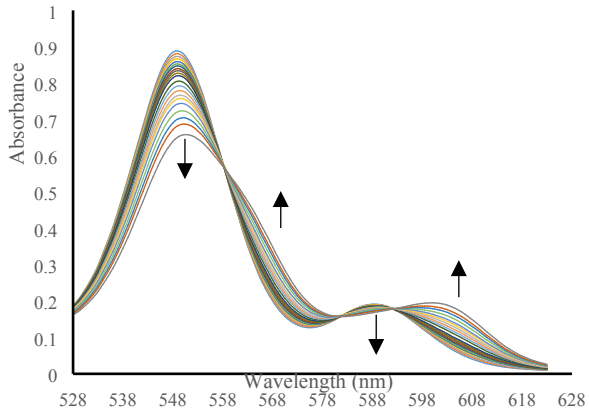
Titration data of pyridine to **7-Zn** (left **Figure S9**: whole spectrum, right **Figure S10**: 602 nm against software fit).





Titration data of **3** to **7-Zn** (left **Figure S11**: whole spectrum, right **Figure S12**: 598 nm against software fit).





Titration data of pyridine to **6-Zn** (left **Figure S13**: whole spectrum, right **Figure S14**: 602 nm against software fit).

Determination of Equation 2.

K_{intra} is the equilibrium constant between the self-included (macrocycle bound) form of the rotaxane **6-Zn$_{sic}$**, and the not included (macrocycle free) form of the rotaxane **6-Zn$_{ni}$** given by eq. 3.

$$K_{intra} = \frac{[6Zn_{sic}]}{[6Zn_{ni}]} \quad \ldots..(3)$$

The titration of pyridine to **6-Zn** gives the equilibrium constant K_1 which is expressed in eq. 4.

$$K_1 = \frac{[6Zn - L]}{[6Zn][L]} \quad \ldots(4)$$

Where [L] is the concentration of pyridine ligand, [**6Zn**-L] is the concentration of **6-Zn** that is bound to pyridine and [**6Zn**] is the total concentration of rotaxane (eq 5).

$$[6Zn] = [6Zn_{sic}] + [6Zn_{ni}] \quad \ldots(5)$$

The titration of pyridine to **7-Zn** gives the equilibrium constant K_2 which is expressed in eq. 6. In this case we approximate that **7-Zn** behaves as a host for pyridine in the same manner that pure **6-Zn$_{ni}$** would.

$$K_2 = \frac{[7Zn - L]}{[7Zn][L]} \cong \frac{[6Zn - L]}{[6Zn_{ni}][L]} \quad \ldots(6)$$

Equation 4 can be rearranged to eq. 2 by substitution of eq. 5 into eq. 4:

$$K_1 = \frac{[6Zn - L]}{[6Zn][L]}$$

Substitution of eq. 5

$$K_1 = \frac{[6Zn - L]}{[L]([6Zn_{sic}] + [6Zn_{ni}])}$$

Substitution of rearranged eq. 6

$$K_1 = \frac{K_2[6Zn_{ni}]}{[6Zn_{sic}] + [6Zn_{ni}]}$$

$$K_1 = \frac{K_2}{[6Zn_{ni}]^{-1}([6Zn_{sic}] + [6Zn_{ni}])}$$

Substitution of eq 3.

$$K_1 = \frac{K_2}{K_{intra} + 1}$$

$$\frac{1}{K_1} = \frac{K_{intra} + 1}{K_2}$$

$$\frac{K_2}{K_1} - 1 = K_{intra}$$

Determining the proportion of self-included complex.

The value of K_{intra} obtained from eq. 2 be used to determine the proportion of **6-Zn$_{sic}$** to **6-Zn$_{ni}$** by solving the simple simultaneous equation problem between eq. 3 and eq. 5:

$$K_{intra} = \frac{[6Zn_{sic}]}{[6Zn_{ni}]}$$

$$K_{intra}[6Zn_{ni}] = [6Zn_{sic}]$$

Substitution into eq. 5:

$$[6Zn] = K_{intra}[6Zn_{ni}] + [6Zn_{ni}]$$

$$[6Zn] = [6Zn_{ni}](K_{intra} + 1)$$

$$[6Zn_{ni}] = \frac{[6Zn]}{K_{intra} + 1}$$

Any arbitrary value of [**6Zn**] can be chosen to calculate [$\mathbf{6Zn_{ni}}$] and then eq. 5 is used to calculate [$\mathbf{6Zn_{sic}}$], here a value of 1 is chosen for [**6Zn**] to make the calculation of percentage values simple.

$$[6Zn_{ni}] = \frac{[6Zn]}{K_{intra} + 1} = \frac{1}{1.51} = 0.66$$

$$[6Zn_{sic}] = [6Zn] - [6Zn_{ni}] = 1 - 0.66 = 0.34$$

4. Resin Loading Methodologies

UV Loading Methodology

Two experiments were setup reacting azide functionlised beads **2** with one equivalent of porphyrin alkyne **1-Zn** relative to the bead loading. In one experiment 2,6-lutidine was used as the base resulting in the functionalisation of the resin with the porphyrin dumbbell **8-Zn**. Whereas is the second experiment, the macrocycle **3** was used to allow the formation of rotaxane **4-Zn** on the bead (see Table S1).

	N_3 Beads **2** (mg)	Cu (I)* (mg)	**1-Zn** (mg)	Pyridine Derivative
Exp.1	10, 4.25 µmol	3.5, 8.5 µmol	3.25, 4.25	2,6-Lutidine (42.5 µmol)

			µmol	
Exp. 2	10, 4.25 µmol	3.5, 8.5 µmol	3.25, 4.25 µmol	Macrocycle **3** (42.5 µmol)

Table S1: Conditions for UV loading study experiments, S: CH_2Cl_2 (3 mL). *Due to the stoichiometric nature of the reaction to form **4-Zn**, compared to the catalytic nature of the reaction to form **8-Zn**, a slight excess of copper(I) salt is used to better mimic the expected loadings of **4-Zn** in the 10 equivalent reaction.

After 7 days the solvent was reduced in vacuo and the residue was redissolved in 3 mL of CH_2Cl_2. 80 µL aliquots were taken and diluted to 3 mL with CH_2Cl_2 and the UV-Visible absorbance of the Q-band at 550 nm was measured (Figure S9). The reduction in absorbance was then used to calculate the bead loading (Table S1).

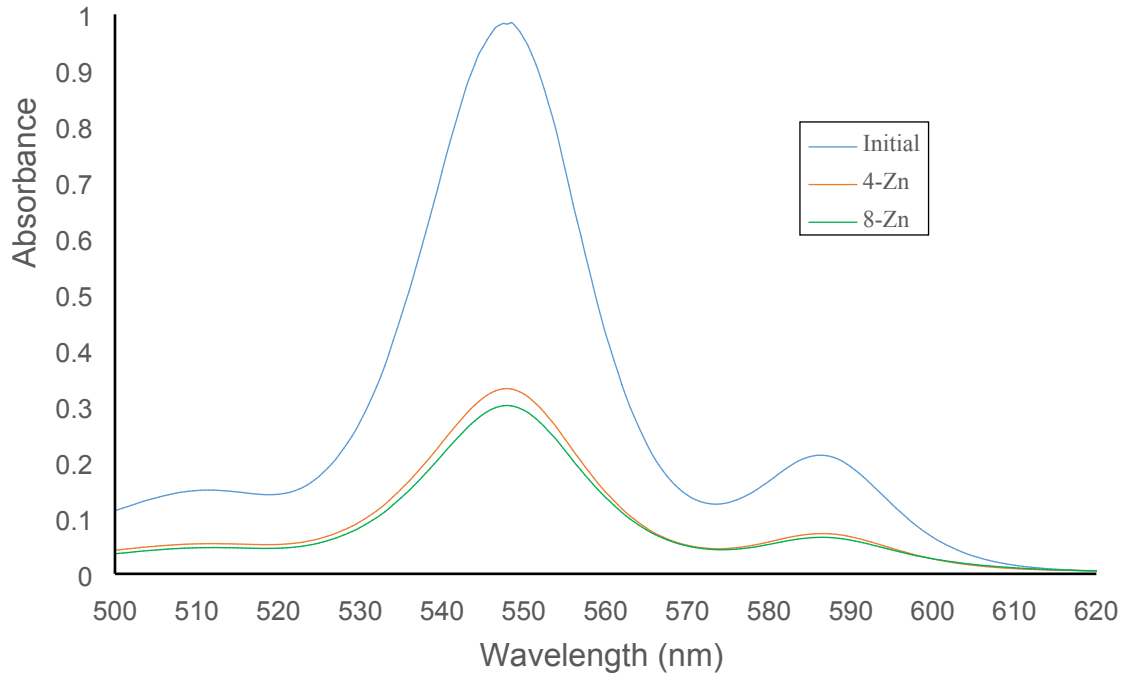


Figure S15: Change in absorbance observed during reaction of **1-Zn** with azide beads **2** in the presence of lutidine (green) **and** macrocycle **3** (red).

LA ICP-MS Methodology

LA ICP-MS was recorded with an Agilent 8800 Triple Quad ICP-MS in conjunction with an ESI *f(x)* 193 Laser Ablation tool under a helium atmosphere. The laser was operating at 7 Hz with a beam intensity of 60 J/cm^2 and a 15 second warmup time. Samples were mounted on

sticky tape and further suspended in an epoxy resin. After curing the sticky tape was removed and the surface polished. Individual beads were selected and the top layer (150 μM spot diameter) was ablated using a 10 second laser exposure. They were then further ablated using a 45 second laser exposure over a central 50 μM spot diameter and this data was used for analysis and the zinc to carbon ratio was examined. The zinc to carbon ratio can be converted to a zinc value (wt%) with knowledge of the carbon content from elemental analysis.

For a given bead loading (***L*** (mol/g)) there is an expected zinc content (***Z*** (wt%)) given by eq. 7.

$$Z = \frac{M_{Zn}L}{M_{rotax}L + 1} \quad \ldots(7)$$

Where M_{Zn} is the molar mass of zinc and M_{rotax} is the molar mass of the total attached molecules in the reaction, macrocycle **3** and porphyrin **1-Zn** ($M_{\mathbf{3}}$+$M_{\mathbf{1\text{-}Zn}}$). Eq. 7 for *Z* as a function of *L* can be rearranged to an expression for *L* as a function of *Z* and this can be easily used to compute the loading from the zinc content:

$$L = \frac{Z}{M_{Zn} - M_{rotax}Z}$$

5. ^{1}H and ^{13}C NMR of Select Molecules.

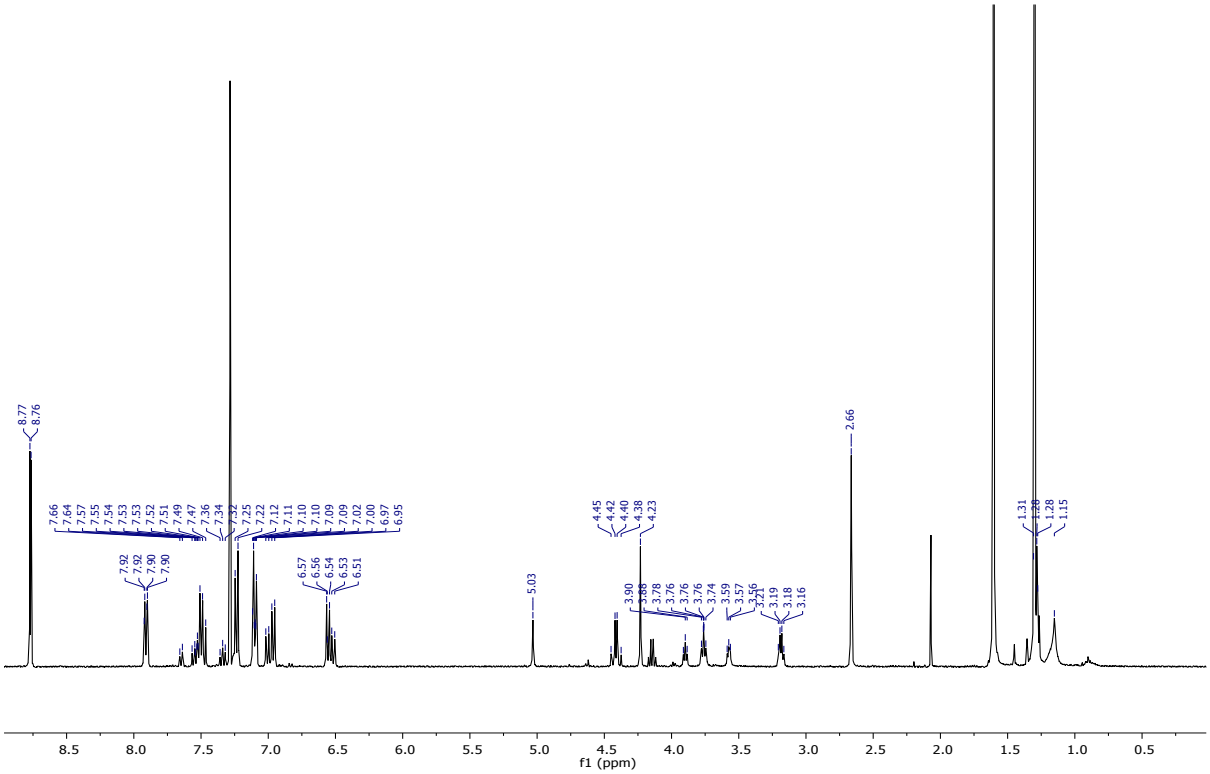


Figure S16: ^{1}H NMR (400 MHz, $CDCl_3$) of nickel [2]rotaxane **4-Ni**.

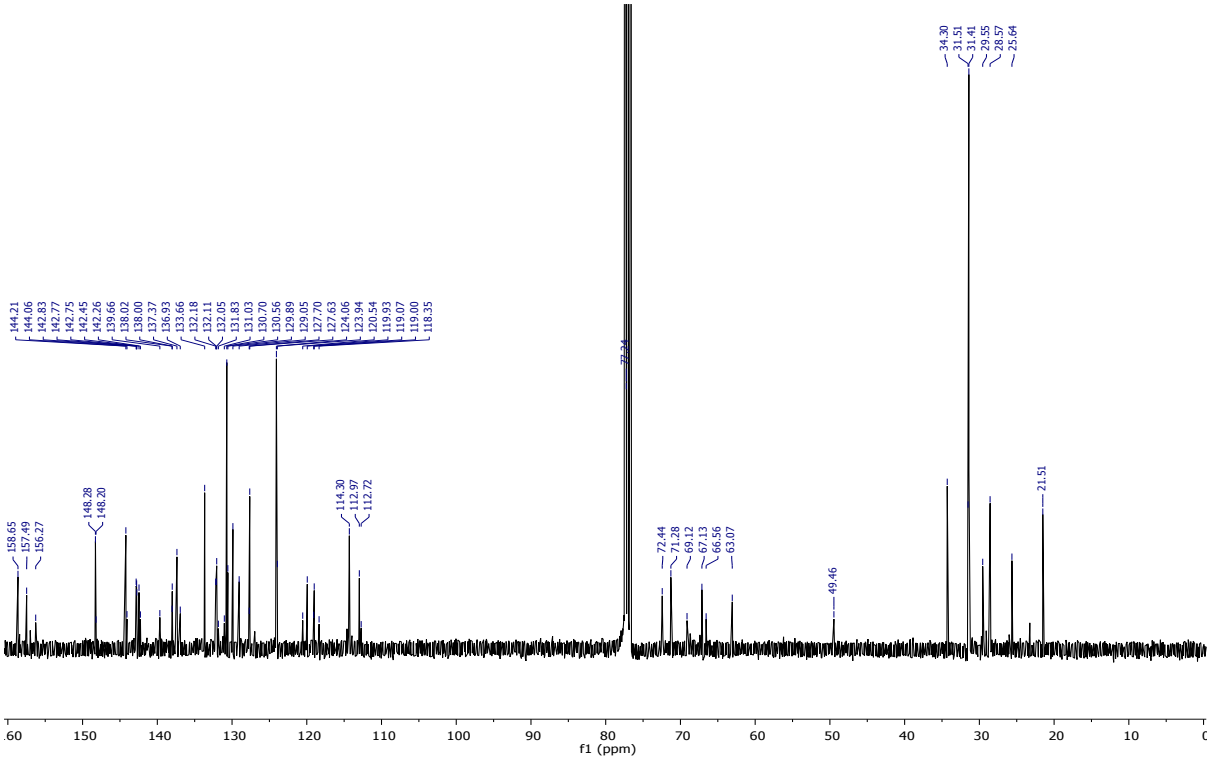


Figure S17: ^{13}C NMR (100 MHz, $CDCl_3$) of nickel [2]rotaxane **4-Ni**.

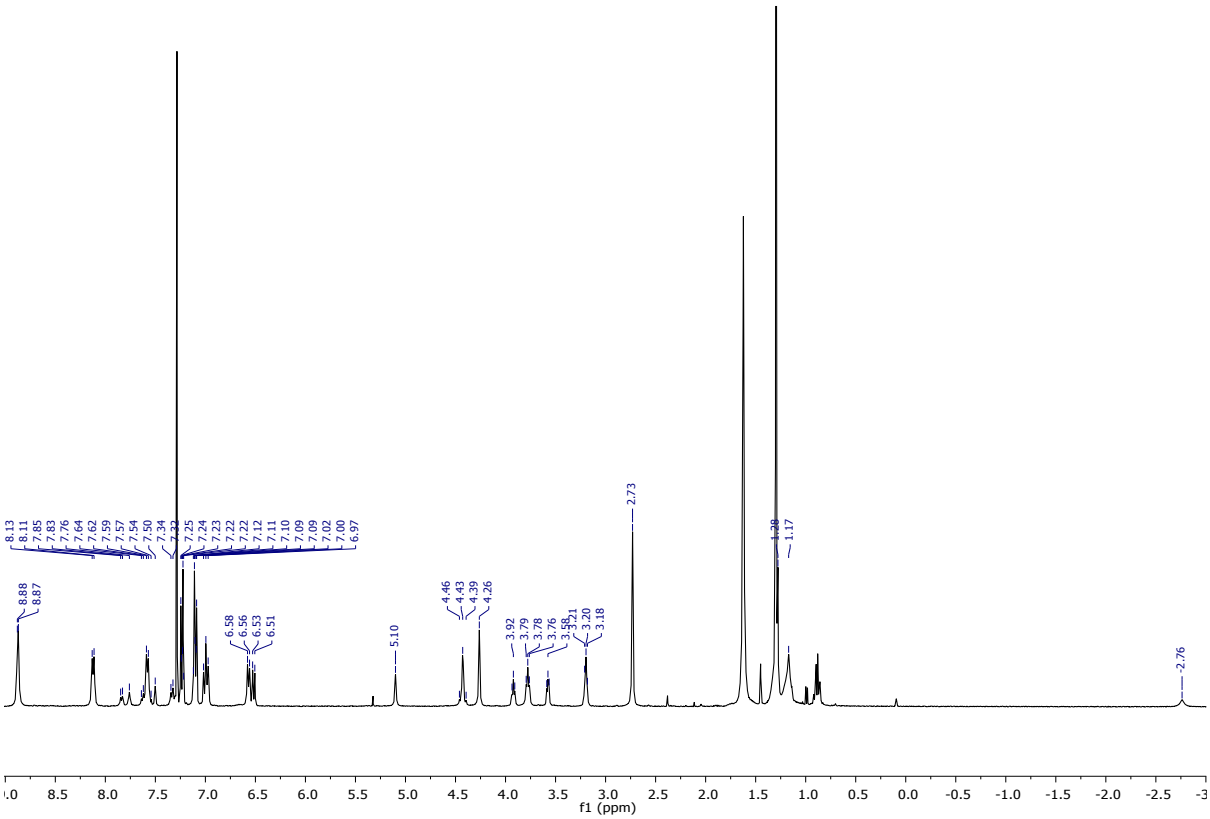


Figure S18: ^{1}H NMR (400 MHz, $CDCl_3$) of free-base [2]rotaxane **4-H_2**.

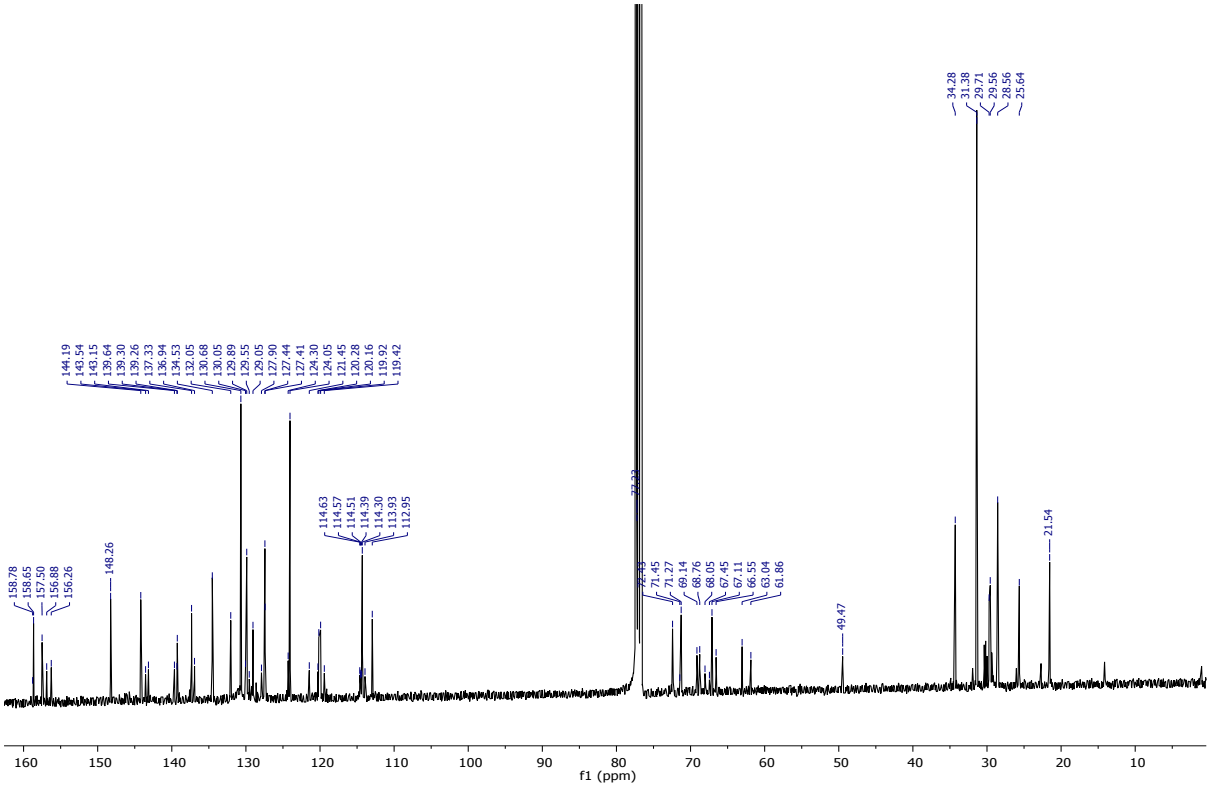


Figure S19: ^{13}C NMR (100 MHz, $CDCl_3$) of free-base [2]rotaxane **4-H$_2$**.

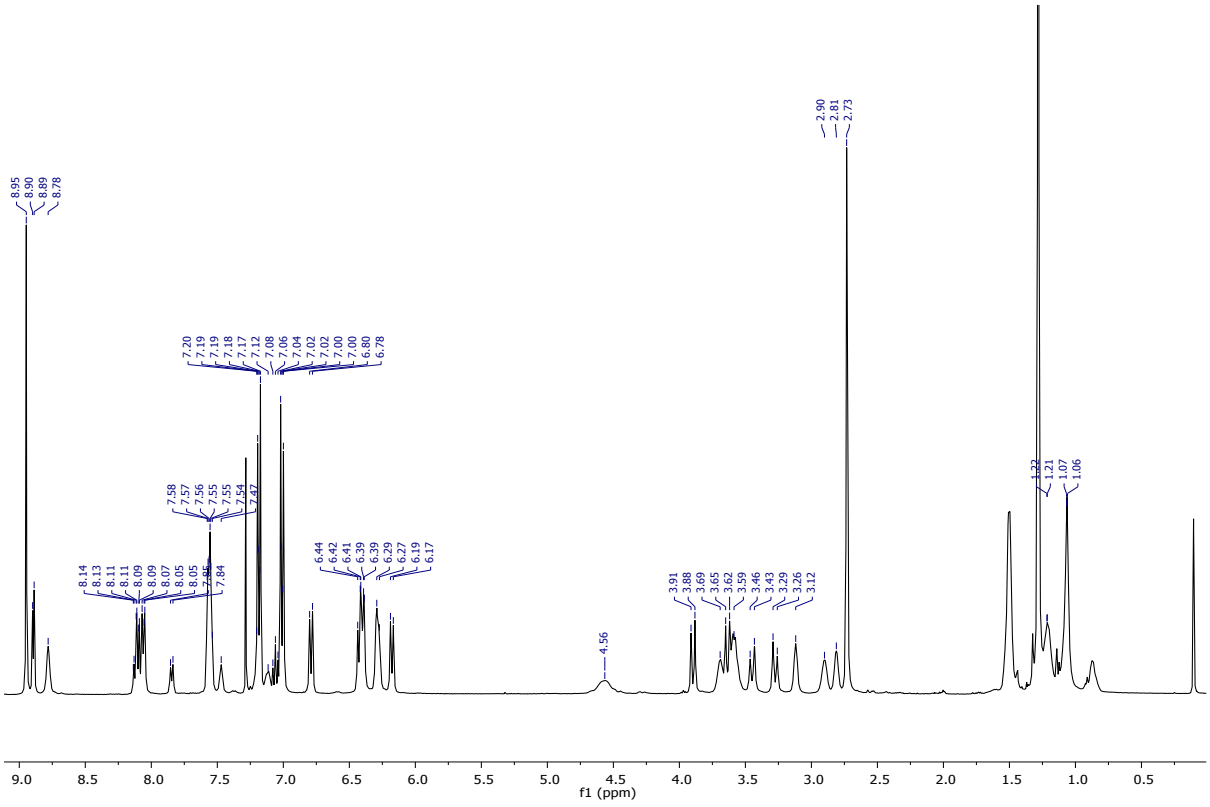


Figure S20: ^{1}H NMR (400 MHz, $CDCl_3$) of zinc [2]rotaxane **4-Zn**.

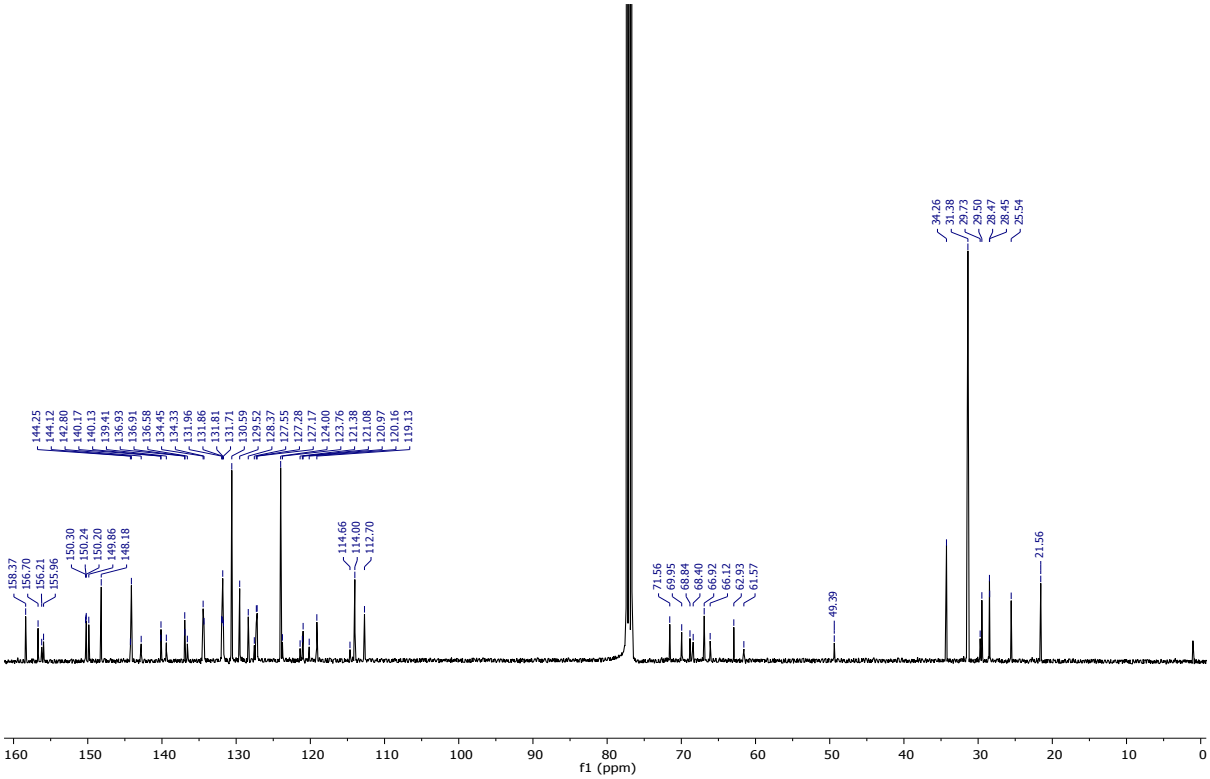


Figure S21: ^{13}C NMR (100 MHz, $CDCl_3$) of zinc [2]rotaxane **4-Zn**.

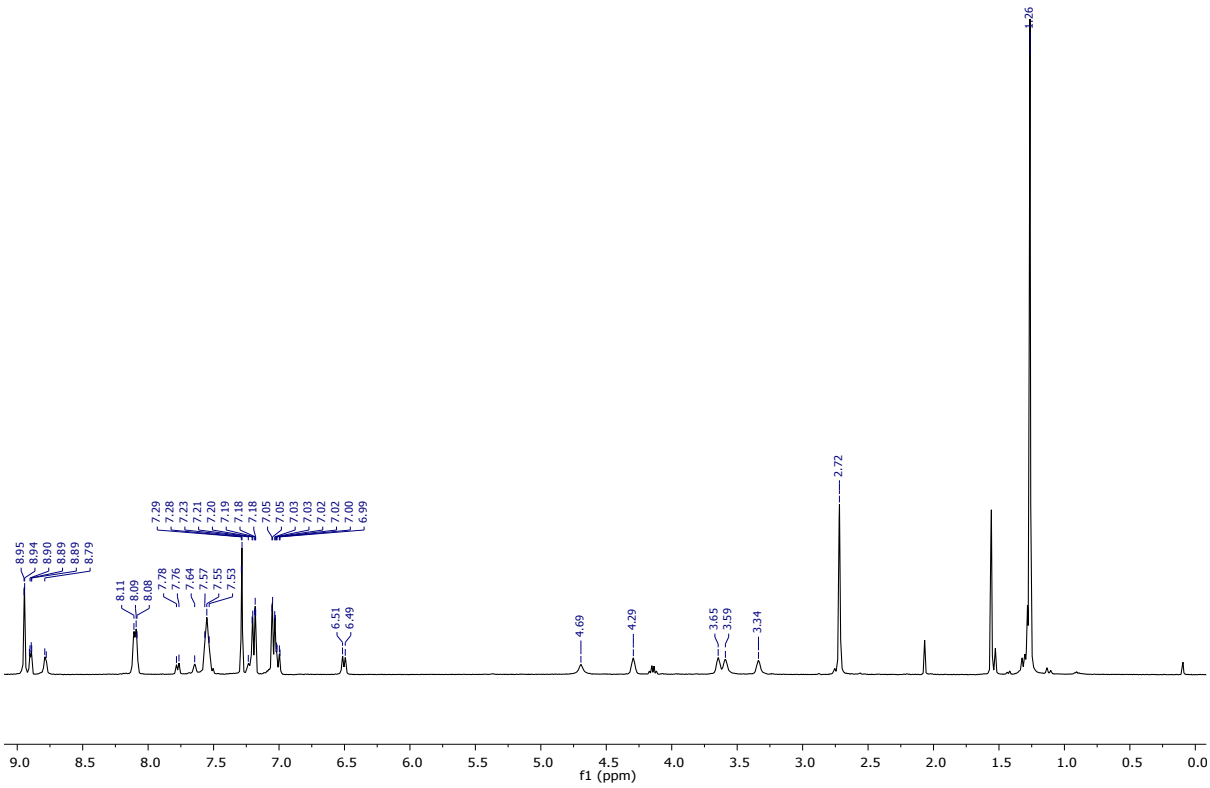


Figure S22: ^{1}H NMR (400 MHz, $CDCl_3$) of free thread **7-Zn**.

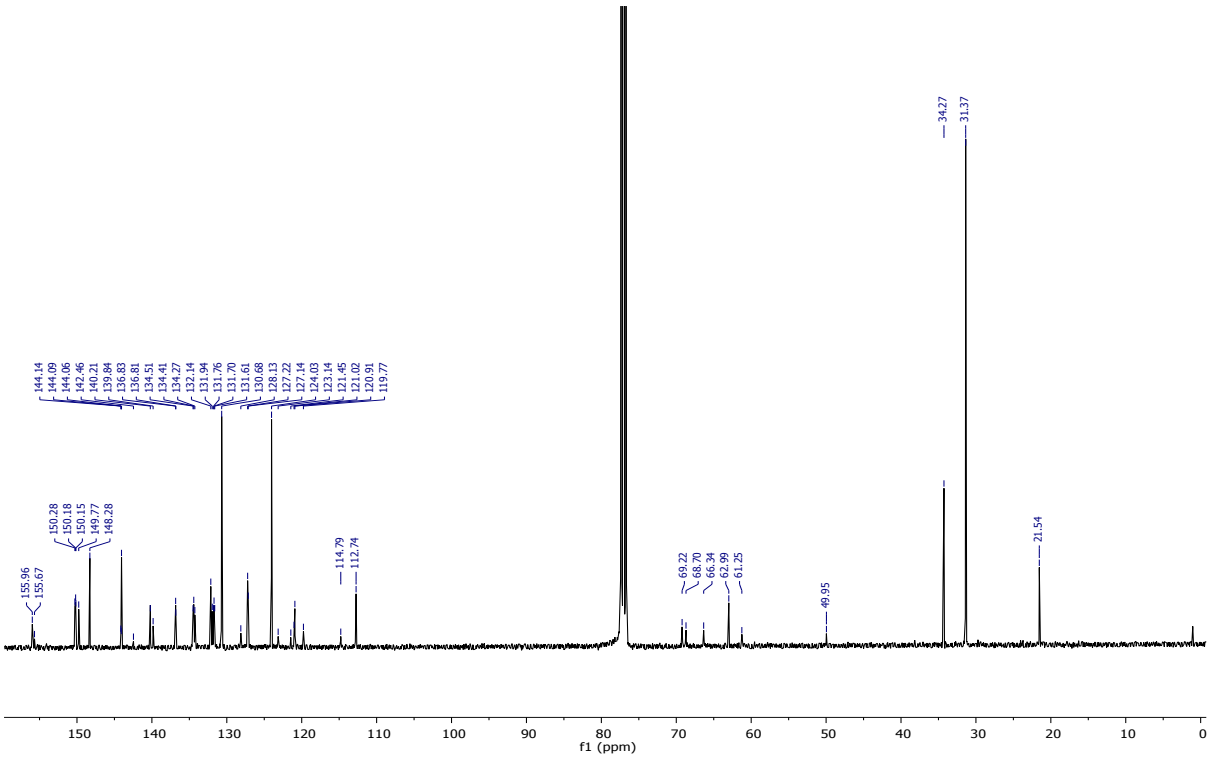


Figure S23: ^{13}C NMR (100 MHz, $CDCl_3$) of free thread **7-Zn**.

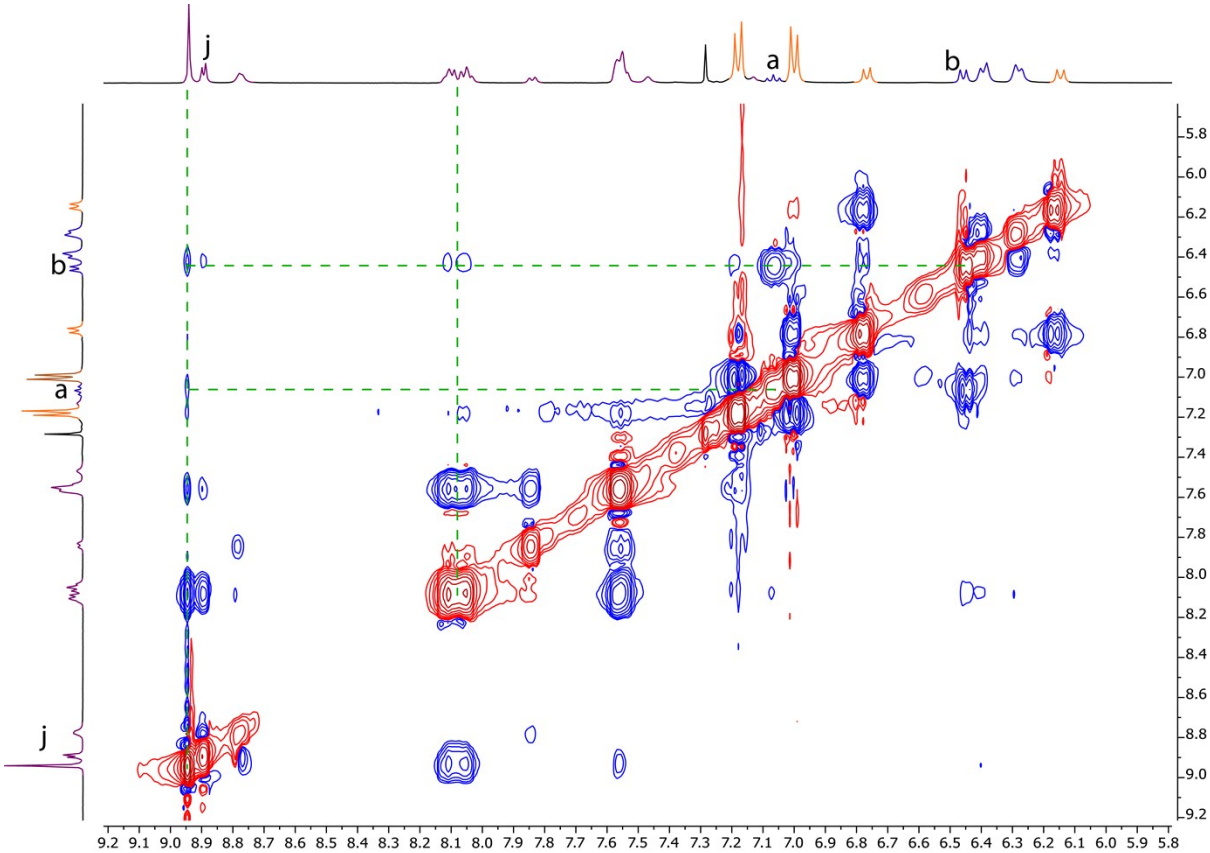


Figure S24: Partial ROESY spectrum (400 MHz, $CDCl_3$) of **6-Zn** showing NOE signals between pyridyl proton *b* to the porphyrin pyrrole *j* and meso-tolyl hydrogens as well as an NOE signal between pyridyl proton *a* and the porphyrin pyrrole hydrogens.