Supporting information for Active metal template synthesis of a neutral indolocarbazole-containing [2]rotaxane host system for selective oxoanion recognition

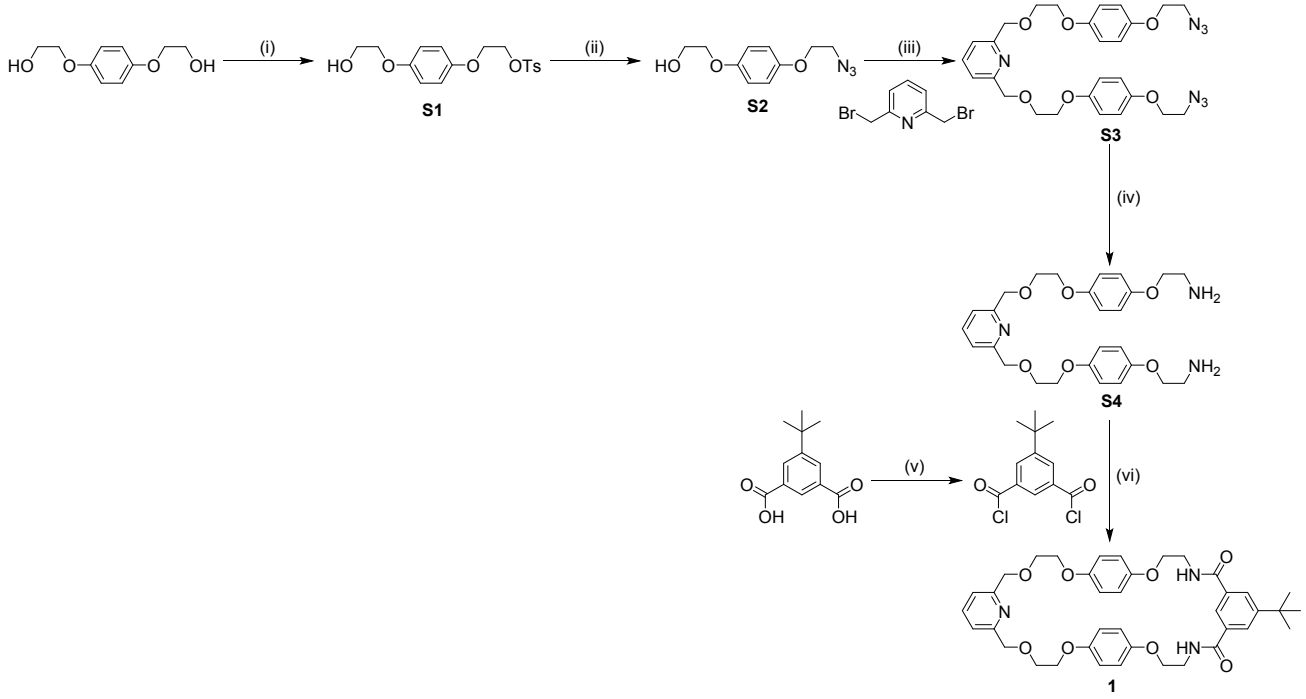
Asha Brown,[a] Thomas Lang,[a] Kathleen M. Mullen[a] and Paul. D. Beer[a*]

[a]Department of chemistry, University of Oxford, Mansfield Road, Oxford OX1 3TA. E-mail: paul.beer@chem.ox.ac.uk

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. $(TBA)_2SO_4$ was purchased as a 50%$_{wt}$ solution in water. Solid $(TBA)_2SO_4$ was obtained by removal of the water by rotary evaporation, followed by thorough drying of the residue over P_2O_5 in a vacuum desiccator. All 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 Bruker Avance III HD nanobay NMR spectrometer equipped with a 9.4T magnet or a Bruker Avance III NMR spectrometer equipped with a 11.75T magnet 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. Compounds **S1**,[1] **S5**,[2] **S6**,[2] **S7**[3] and **3**[4] were synthesised by slight adaptation of previously reported procedures.



Scheme S1. Synthesis of the pyridyl and isopthalamide-functionalised macrocycle **1**. *Reagents and conditions*: (i) *p*-toluenesulfonyl chloride, 4-(dimethylamino)pyridine, Et_3N. THF r.t., 20 h, 43%; (ii) NaN_3, DMF, r.t., 48 h, 98%; (iii) NaH (60% dispersion in mineral oil), r.t., 1 h, 50 °C, 48 h, 78%; (iv) Hydrazine monohydrate, 10% Pd/C, MeOH, reflux, 18 h, 95%; (v) oxalyl dichloride, DMF (cat.), CH_2Cl_2, r.t., 18 h, quantitative yield; (vi) Et_3N, CH_2Cl_2, 18 h, 36%.

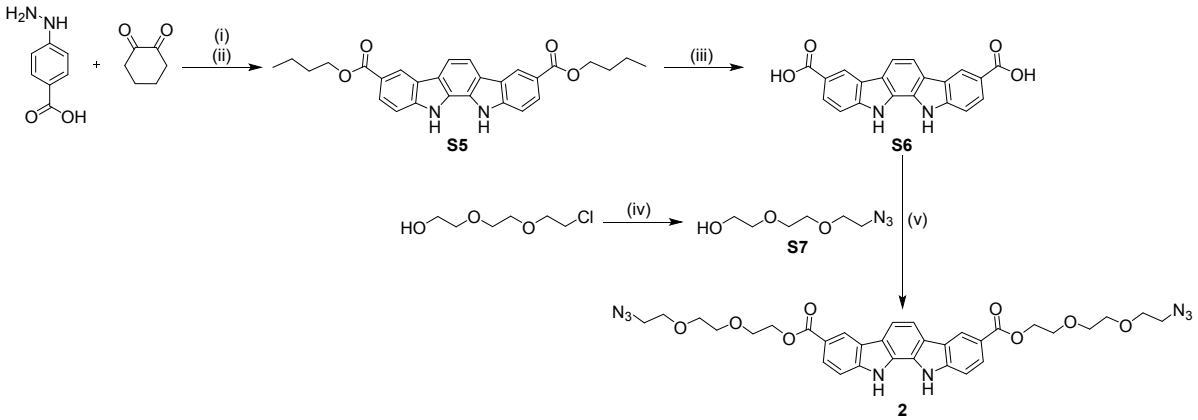
Compound S2. 2-(4-(2-Hydroxyethoxy)phenoxy)ethyl 4-methylbenzenesulfonate **S1** (5.00 g, 14.2 mmol) was dissolved in dry, de-gassed DMF (20 mL) and NaN_3 (0.922 g, 14.2 mmol) was added. The mixture was stirred at room temperature under N_2 for 48 hours, before removal of the solvent on a rotary evaporator. The residue was partitioned between EtOAc (50 mL) and H_2O (50 mL). The layers were separated and the aqueous layer was extracted with EtOAc (2 x 50 mL). The combined EtOAc solutions were washed with H_2O (2 x 100 mL) and brine (150 mL), dried over $MgSO_4$ and concentrated on a rotary evaporator to give a colourless oil, which solidified on standing. After drying under high vacuum, the product was obtained as a white solid (3.12 g, 98%). δH(400 MHz, $CDCl_3$) 2.11 (1 H, br s, OH), 3.58 (2 H, t, ^3J = 5.0 Hz, CH_2), 3.95 (2 H, br s, CH_2), 4.05 (2 H, t, ^{3}J = 4.5 Hz, CH_2), 4.12 (2 H, t, ^3J = 5.0 Hz, CH_2), 6.87 (4 H, app s, ArH); ESMS *m/z* 246.1 ([M + Na]$^+$).

Compound S3. 2-(4-(2-Azidoethoxy)phenoxy)ethan-1-ol **S2** (1.20 g, 5.38 mmol) was dissolved in dry THF (50 mL). NaH (0.236 g of a 60% dispersion in mineral oil, 5.91 mmol) was added and the mixture was stirred at room temperature under N_2 for 20 minutes before addition of 2,6-bis(bromomethyl)pyridine (0.712 g, 2.69 mmol). The reaction mixture was stirred at room temperature under N_2 for 60 minutes and then heated at 50 °C for 48 hours. After cooling to room temperature the solvent was removed on a rotary evaporator and the residue partitioned between CH_2Cl_2 (50 mL) and brine (50 mL). The layers were separated and the organic layer was washed with brine (50 mL) dried over $MgSO_4$ and concentrated on a rotary evaporator. The residue was purified by column chromatography (1–2% MeOH in CH_2Cl_2) to give the product as a waxy white solid (1.15 g, 78%). δH(400 MHz; $CDCl_3$) 3.58(4 H, t, ^3J = 5.0 Hz, CH_2), 3.92 (4 H, t, ^3J = 4.8 Hz, CH_2), 4.11 (4 H, t, ^3J = 5.0 Hz, CH_2), 4.16 (4 H, t, ^3J = 4.8 Hz, CH_2), 4.74 (4 H, s,

CH_2), 6.85–6.90 (8 H, m, Ar*H*), 7.40 (2 H, d, ^3J = 7.7 Hz, py-Ar*H*), 7.72 (1 H, t, ^3J = 7.7 Hz, py-Ar*H*); δC (126 MHz, $CDCl_3$ 50.1, 67.5, 67.9, 69.9, 74.0, 115.5, 115.5, 119.9, 137.2, 152.4, 153.3, 157.7; ESMS *m/z* 550.16 ([M + H]$^+$); 572.21 ([M + Na]$^+$); HRMS (ES) *m/z* 550.2403 ([M + H]$^+$. $C_{27}H_{32}N_7O_6$ requires 550.2409).

Compound S4. 2,6-Bis((2-(4-(2-Azidoethoxy)phenoxy)ethoxy)methyl)pyridine **S3** (2.5 g, 4.55 mmol) was dissolved in MeOH (250 mL). 10% Pd/C (0.25 g) and hydrazine monohydrate (2.21 mL, 2.28 g, 45.5 mmol) were added and the mixture was heated at reflux under N_2 for 18 hours. After cooling to room temperature the mixture was filtered through a plug of Celite® and the filtrate was concentrated on a rotary evaporator to give a white solid which was dried under high vacuum and then used in the next step without further purification (2.14 g, 95%). δH(400 MHz; $CDCl_3$) 3.03–3.07(4 H, m, CH_2), 3.90–3.96(8 H, m, CH_2), 4.15(4 H, t, ^3J = 4.8 Hz, CH_2), 4.74 (4 H, s, CH_2), 6.83–6.89 (8 H, m, Ar*H*), 7.40 (2 H, d, ^3J = 7.7 Hz, py-Ar*H*), 7.71 (1 H, t, ^3J = 7.7 Hz, py-Ar*H*); δC (126 MHz, $CDCl_3$:CD_3OD 1:1) 41.3, 68.8, 69.8, 70.3, 74.2, 116.2, 116.4, 121.4, 138.7, 153.8, 153.9, 158.3; ESMS *m/z* 249.63 ([M + 2H]$^{2+}$); 498.26 ([M + H]$^+$; 520.24 ([M + Na]$^+$); HRMS (ES) *m/z* 498.2582 ([M + H]$^+$. $C_{27}H_{36}N_3O_6$ requires 498.2599).

Compound 1. 5-(Tert-butyl)isophthalic acid (0.45 g, 2.01 mmol) was suspended in dry CH_2Cl_2 (30 mL). Oxalyl chloride (0.68 mL, 1.02 g, 8.04 mmol) and DMF (2 drops) were added and the mixture was stirred at room temperature under N_2 for 18 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, before being re-dissolved in dry CH_2Cl_2 (30 mL). This solution was added dropwise over 2 minutes to a solution of the bis-amine **S4** (1.00 g, 2.01 mmol) and Et_3N (1.40 mL, 1.02 g, 10.0 mmol) in dry CH_2Cl_2 (370 mL). After stirring at room temperature under N_2 for 18 hours the reaction mixture was washed sequentially with 10% citric $acid_{(aq)}$ (2 x 75 mL), sat. $NaHCO_{3(aq)}$ (2 x 75 mL) and brine (75 mL), dried over $MgSO_4$ and concentrated on a rotary evaporator to give a white solid. After purification by column chromatography (2% MeOH in CH_2Cl_2) the product was obtained as a white solid (0.50 g, 36%). δH (400 MHz; $CDCl_3$) 1.33 (9 H, s, C(CH_3)$_3$), 3.82–3.86 (4 H, m, CH_2), 3.89 (4 H, t, ^3J = 4.6 Hz, CH_2), 4.07–4.11 (8 H, m, CH_2), 4.70 (4 H, s, CH_2), 6.77 (8 H, app s, Ar*H*), 6.79 (2 H, t, ^3J = 5.6 Hz, N*H*), 7..29 (2 H, d, ^3J = 7.7 Hz, py-Ar*H*), 7.62 (1 H, t, ^3J = 7.7 Hz, py-Ar*H*), 7.85 (1 H, s, Ar*H*), 8.01 (2 H, s, Ar*H*); δC (101 MHz, $CDCl_3$:CD_3OD 1:1) 31.5, 35.7, 40.6, 67.8, 68.9, 70.2, 74.2, 116.2, 116.5, 121.9, 123.2, 128.6, 134.9, 138.6, 153.2, 153.9, 158.2, 169.3; ESMS *m/z* 684.26 ([M + H]$^+$); 706.28 ([M + Na]$^+$); HRMS (ES) *m/z*: 684.3304 ([M + H]$^+$. $C_{39}H_{46}N_3O_8$ requires 684.3285).



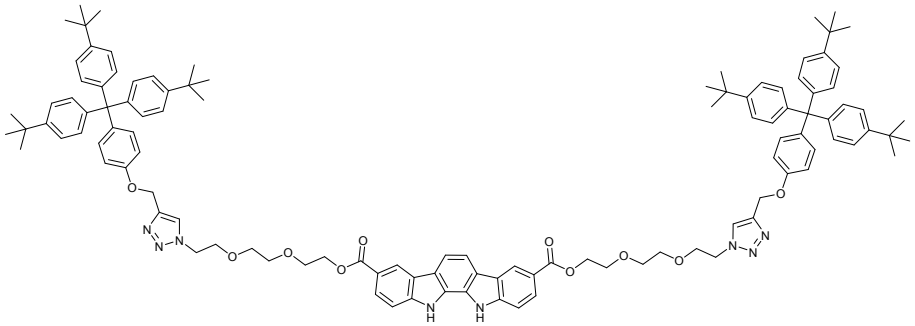
Scheme S2. Synthesis of the indolocarbazole bis-azide threading compound **2**. *Reagents and conditions*: (i) conc. H_2SO_4, n-BuOH, reflux, 60 h; (ii) 10% Pd/C, DMF, reflux, 24 h, 68%; (iii) KOH, 2-propanol, H_2O, reflux, 48 h, 91%; (iv) NaN_3, DMF,9 °C, 18 h, 84%, (v) EDC·HCl, 4-dimethylaminopyridine, DMF, r.t., 70 h, 17.5%.

Compound 2. A solution of 11,12-dihydroindolo[2,3-a]carbazole-3,8-dicarboxylic acid **S6** (0.200 g, 0.581 mmol), 2-(2-(2-azidoethoxy)ethoxy)ethan-1-ol (0.407 g, 2.32 mmol), N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC·HCl) (0.225 g, 1.17 mmol) and 4-(dimethylamino)pyridine (0.035 g, 0.286 mmol) in dry, de-gassed DMF (15 mL) was stirred at room temperature under N_2 for 70 hours. The mixture was filtered to remove an insoluble precipitate. After concentration of the filtrate on a rotary evaporator the residue was purified by column chromatography (CH_2Cl_2:EtOAc 7:3). The product was obtained as a waxy white solid (0.067 g, 17.5%). δH(400 MHz; DMSO-d_6) 3.37(4 H, t, ^3J = 5.0 Hz, CH_2), 3.61–3.64 (8 H, m, CH_2), 3.66–3.69 (4 H, m, CH_2), 3.83 (4 H, t, ^3J = 4.7 Hz, CH_2), 4.46 (4 H, t, ^3J = 4.7 Hz, CH_2), 7.81 (2 H, d, ^3J = 8.7 Hz, Ar*H*), 8.05 (2 H, dd, ^3J = 8.7 Hz, ^4J = 1.5 Hz, ArH), 8.11 (2 H, s, Ar*H*), 8.85 (2 H, d, ^4J = 1.5 Hz, Ar*H*), 11.61 (2 H, br s, N*H*); δC (126 MHz; DMSO-d_6) 50.0, 63.7, 68.6, 69.4, 69.8, 70.0, 111.6, 112,7, 120.3, 120.8, 122.1, 123.4, 125.9, 126.5, 142.1, 166.6; ESMS *m/z* 659.26 ([M + H]$^+$); HRMS (ES) *m/z* 659.25717 ([M + H]$^+$. $C_{32}H_{35}O_8N_8$ requires 659.25724).

[2]Rotaxane 4. The macrocycle **1** (0.010 g, 0.015 mmol) and Cu(CH_3CN)4PF_6 (0.0055 g, 0.015 mmol) were dissolved in dry, de-gassed CH_2Cl_2 (2 mL). A solution of the bis-azide **2** (0.029 g, 0.44 mmol) and stopper alkyne **3** (0048 g, 0.88 mmol) in dry CH_2Cl_2 (1 mL) was added. The reaction mixture was purged with N_2 and then stirred at room temperature under a N_2 atmosphere for

48 hours, before being diluted with CH_2Cl_2 (10 mL).The solution was washed with EDTA/$NH_4OH_{(aq)}$ (2 x 10 mL) followed by brine (10 mL), dried over $MgSO_4$ and concentrated on a rotary evaporator to give the crude product as an-off-white solid. This mixture was separated by preparative thin layer chromatography (CH_2Cl_2:MeOH 97:3, then CH_2Cl_2:EtOAc:MeOH 49:49:2, then CH_2Cl_2:MeOH, 97:3) to afford the product as a white solid (0.0185 g, 52%). δH (500 MHz; $CDCl_3$) 1.30 (54 H, s, axle C(CH_3)$_3$), 1.43 (9 H, s, macrocycle C(CH_3)$_3$), 3.03 (4 H, t, ^3J = 4.3 Hz, macrocycle-OCH_2CH$_2$O), 3.53 (4 H, t, ^3J = 4.3 Hz, macrocycle-OCH$_2$CH_2O), 3.61–3.66 (8 H, m, axle-OCH_2CH_2O), 3.77–3.81 (8 H, m, 4 axle-OCH_2CH$_2$N + 4 macrocycle-OCH$_2$CH_2N), 3.87 (4 H, t, ^3J = 5.03 Hz, axle-OCH_2CH$_2$O), 3.91 (4 H, ^3J = 5.3 Hz, macrocycle-OCH_2CH$_2$N), 4.43 (4 H, t, ^3J = 4.6 Hz, axle-OCH$_2$CH_2N), 4.49 (4 H, t, ^3J = 5.03 Hz, axle-OCH$_2$CH_2O), 4.77 (4 H, s, macrocycle-py-CH_2-O), 5.18 (4 H, s, axle-O-CH_2-triazole), 5.63 (4 H, d, ^3J = 8.9 Hz, macrocycle-hydroquinone-Ar*H*), 6.12 (4 H, d, ^3J = 8.9 Hz, macrocycle-hydroquinone-Ar*H*), 6.85 (4 H, d, ^3J = 8.9 Hz, axle-stopper-Ar*H*), 7.08 (12 H, d, ^3J = 8.5 Hz, axle-stopper-Ar*H*), 7.10 (4 H, d, ^3J = 8.9 Hz, axle-stopper-Ar*H*), 7.20 –7.24 (14 H, m, 12 axle-stopper-ArH + 2 axle indolocarbazole-Ar*H*), 7.47 (2 H, d, ^3J = 7.6 Hz, macrocycle-py-Ar*H*), 7.51 (2 H, t, ^3J = 5.0 Hz, macrocycle-amide-N*H*), 7.77 (2 H, s, axle-triazole-C*H*), 7.88 (2 H, s, axle-indolocarbazole-Ar*H*), 7.88–7.92 (3 H, m, 2 axle-indoloccarbazole-ArH + 1 macrocycle-py-Ar*H*), 8.32 (2 H, d, ^4J = 1.2 Hz, macrocycle-isophthalamide-Ar*H*), 8.51 (1 H, t, ^4J = 1.2 Hz, macrocycle-isophthalamide-Ar*H*), 8.57 (2 H, s, axle-indolocarbazole-Ar*H*), 10.91 (2 H, s, axle-indolocarbazole-N*H*); δC (126 MHz; $CDCl_3$) 31.3, 31.4, 34.3, 35.2, 40.1, 50.3, 61.9, 63.0, 63.9, 66.7 (x 2), 69.3, 69.5, 69.8, 70.5, 70.6, 74.0, 110.3, 112.8, 113.2, 114.0, 114.4, 120.0, 121.2, 121.5, 122.7, 123.1, 123.9, 124.0, 126.1, 126.6, 129.0, 130.7, 132.3, 133.9, 138.8, 140.1, 142.4, 144.1 (x 2), 148.3, 151.6, 152.0, 152.8, 156.2, 157.5, 167.6, 168.4; ESMS *m/z* 1214.62 ([M + 2H]$^{2+}$); 2429.28 ([M + H]$^+$); HRMS (ES) *m/z* 1214.1482 ([M + 2H]$^{2+}$). $C_{151}H_{173}N_{11}O_{18}$ requires 1214.1479).

Compound S8. Isolated as a white solid in variable yields, as a side-product of the synthesis of [2]rotaxane **4**. δH (500 MHz; $CDCl_3$) 1.29 (54 H, s, C(CH_3)$_3$), 3.72–3.75 (8 H, m, CH_2), 3.90 (4 H, br t, ^3J = 4.4 Hz, CH_2), 3.96 (4 H, t, ^3J = 4.8 Hz, CH_2), 4.51 (4 H, t, ^3J = 4.8 Hz, CH_2), 4.55 (4 H, br t, ^3J = 4.4 Hz, CH_2), 5.05 (4 H, s, CH_2), 6.83 (4 H, d, ^3J = 9.2 Hz, stopper-Ar*H*), 7.07 (12 H, d, ^3J = 8.5 Hz, stopper-Ar*H*), 7.10 (4 H, d, ^3J = 9.2 Hz, stopper-Ar*H*), 7.19–7.23 (14 H, m, 12-stopper Ar*H* + 2 indolocarbazole-Ar*H*), 7.63 (2 H, s, triazole-C*H*), 7.85 (2 H, s, indolocarbazole-Ar*H*), 7.98 (2 H, d, ^3J = 8.5 Hz, indolocarbazole-Ar*H*), 8.41 (2 H, s, indolocarbazole-Ar*H*), 10.3 (2 H, br s, indolocarbazole-N*H*); δC (126 MHz; $CDCl_3$) 31.4, 34.3, 50.5, 61.5, 63.1, 63.4, 69.3, 69.4, 70.6, 100.0, 110.3, 112.1, 113.3, 120.3, 121.0, 122.1, 123.5, 124.1, 124.2, 125.9, 130.7, 132.3, 140.3, 141.8, 143.8, 144.1, 148.3, 156.1, 167.3; ESMS *m/z* 1744.97 ([M + H]$^+$). HRMS (ES) *m/z* 1743.9675 ([M + H]$^+$. $C_{112}H_{127}N_8O_{10}$ requires 1743.9675).



S8

Figure S1. Chemical structure of the axle compound **S8**, isolated as a side-product of the synthesis of the [2]rotaxane **4**.

S2. NMR spectra of new compounds

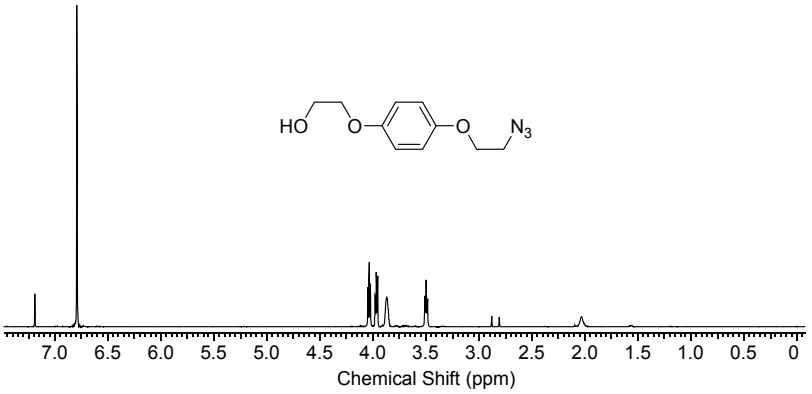


Figure S2. ^{1}H NMR spectrum of compound **S2** ($CDCl_3$, 400 MHz, 298 K)

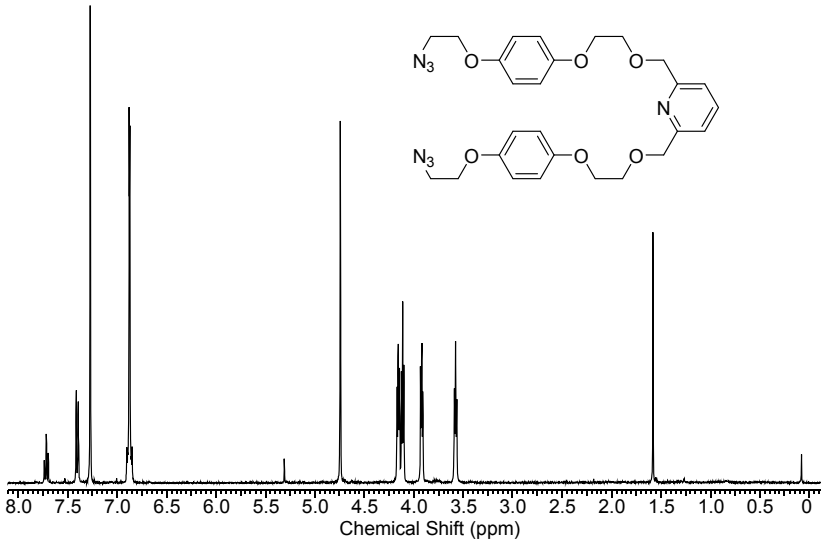


Figure S3. ^{1}H NMR spectrum of compound **S3** ($CDCl_3$, 400 MHz, 298 K)

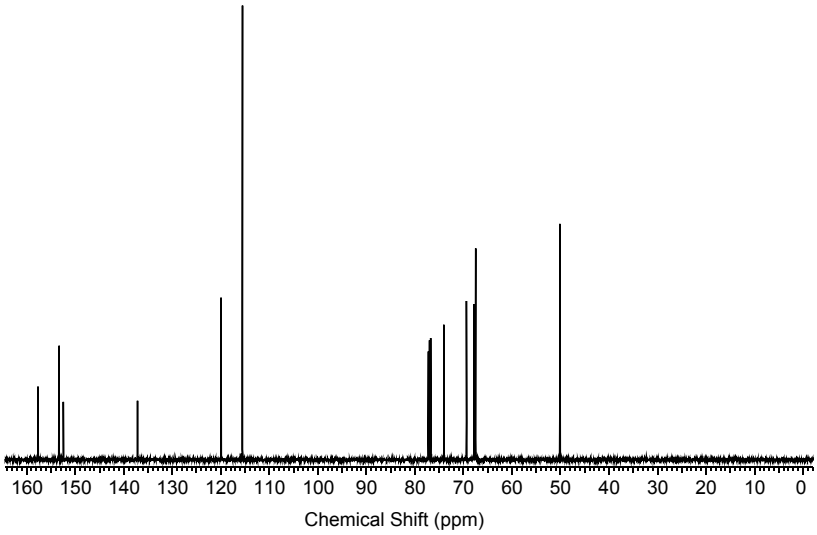


Figure S4. ^{13}C NMR spectrum of compound **S3** ($CDCl_3$, 126 MHz, 298 K)

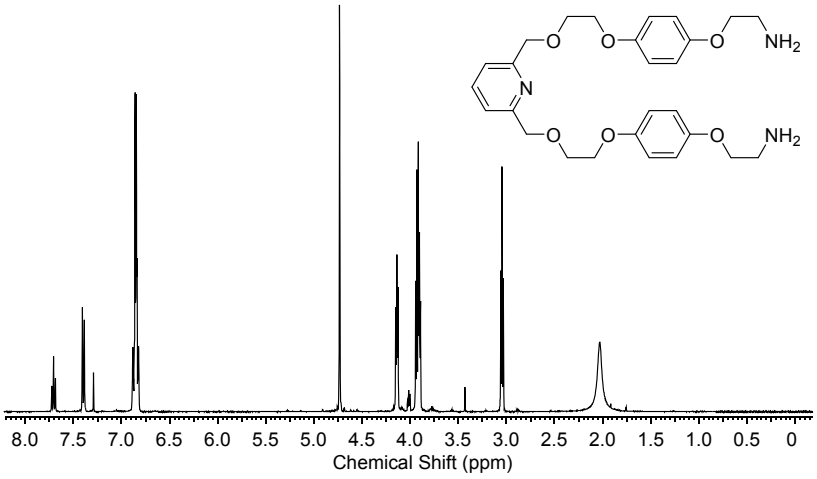


Figure S5. ^{1}H NMR spectrum of compound **S4** ($CDCl_3$, 400 MHz, 298 K)

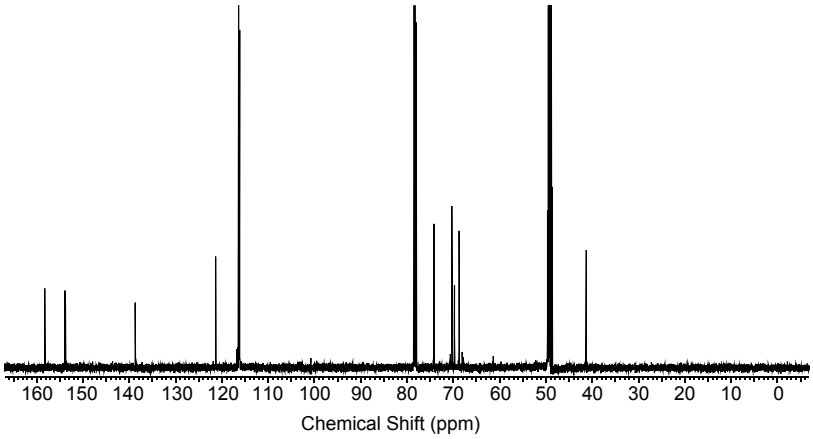


Figure S6. ^{13}C NMR spectrum of compound **S4** ($CDCl_3$:CD_3OD 1:1, 126 MHz, 298 K)

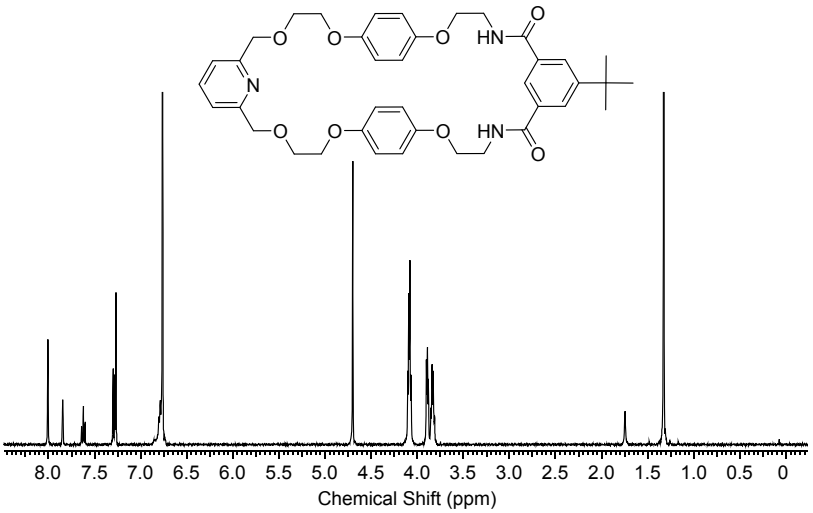


Figure S7. ^{1}H NMR spectrum of macrocycle **1** ($CDCl_3$, 400 MHz, 298 K)

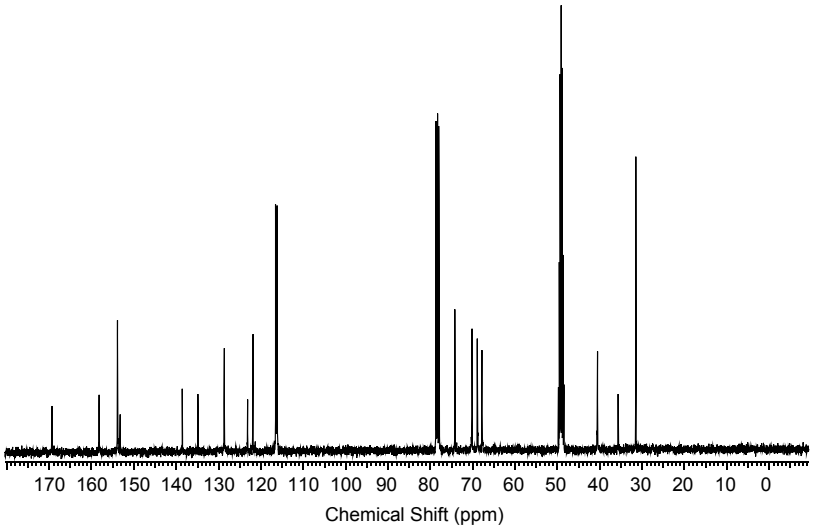


Figure S8. ^{13}C NMR spectrum of macrocycle **1** ($CDCl_3$:CD_3OD 1:1 101 MHz, 298 K)

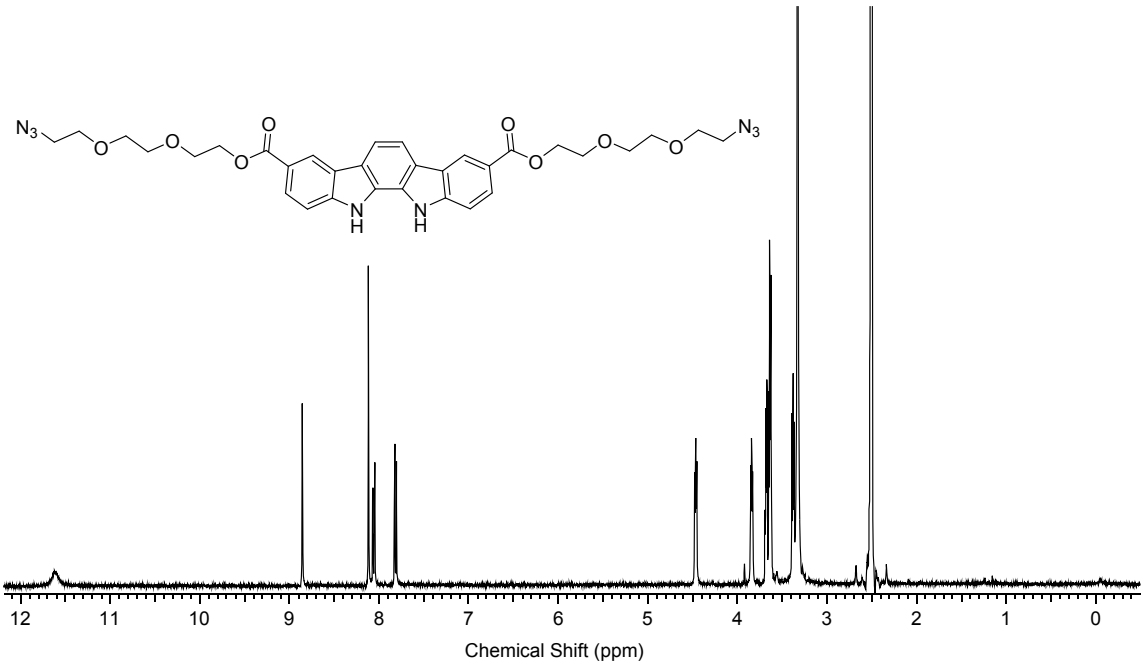


Figure S9. ^{1}H NMR spectrum of compound **2** (DMSO-d_6, 400 MHz, 298 K)

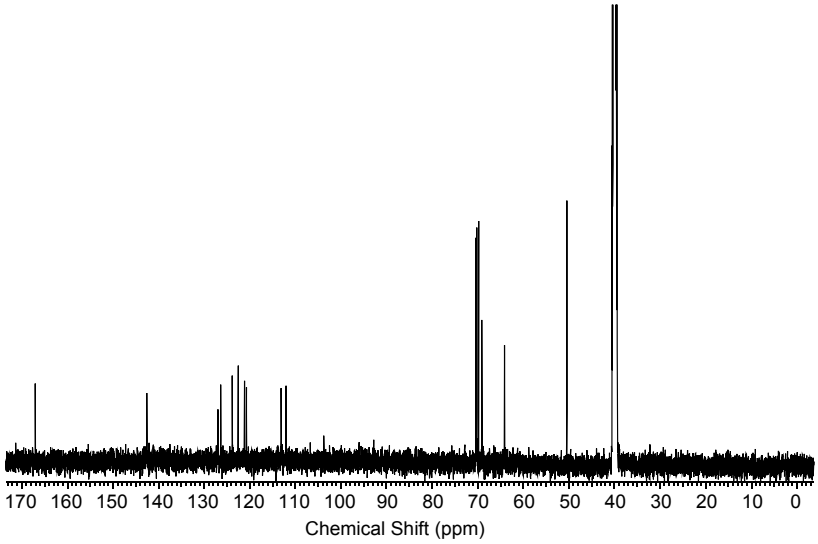


Figure S10. ^{13}C NMR spectrum of compound **2** (DMSO-d_6, 126 MHz, 298 K)

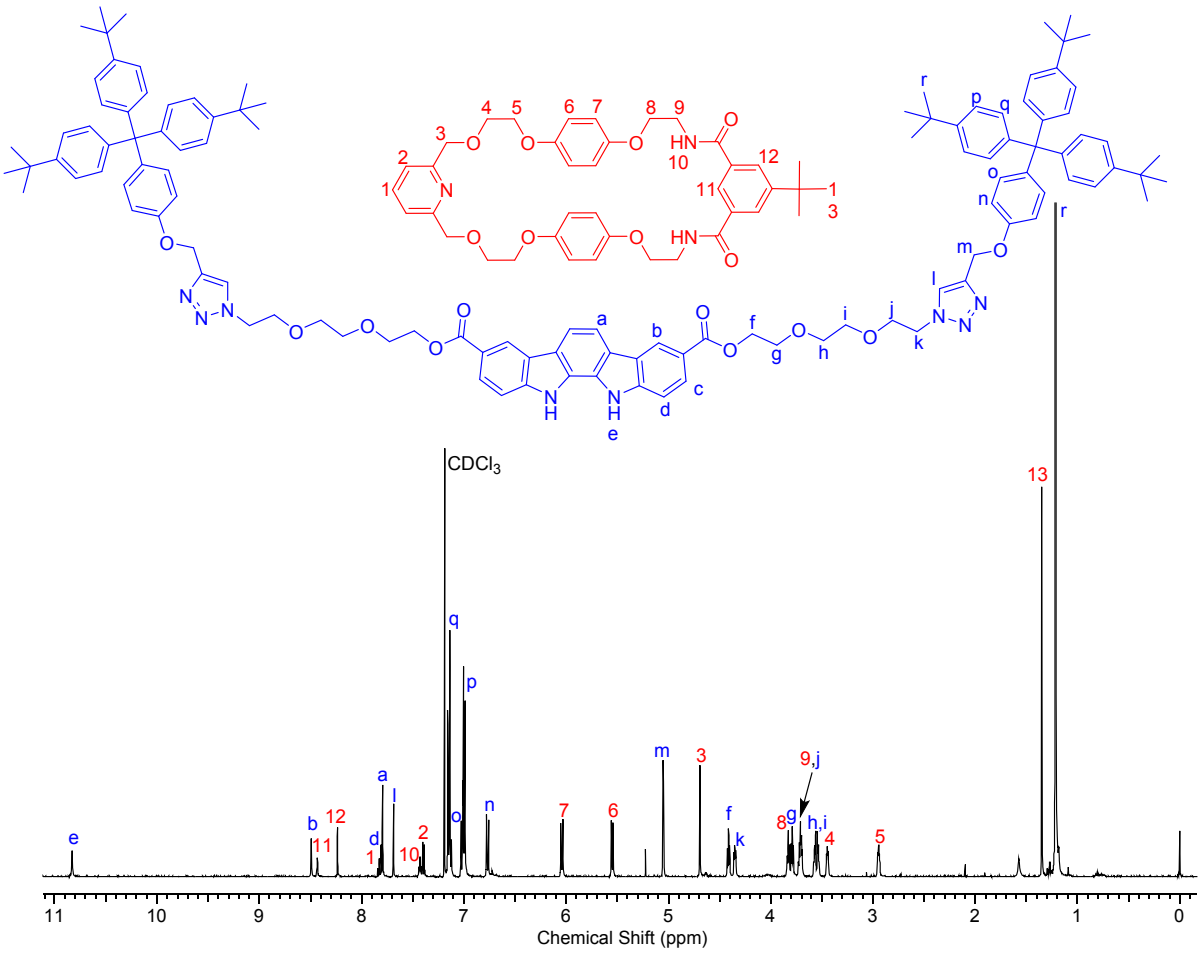


Figure S11. ^{1}H NMR spectrum of the [2]rotaxane **4** ($CDCl_3$, 500 MHz, 298 K)

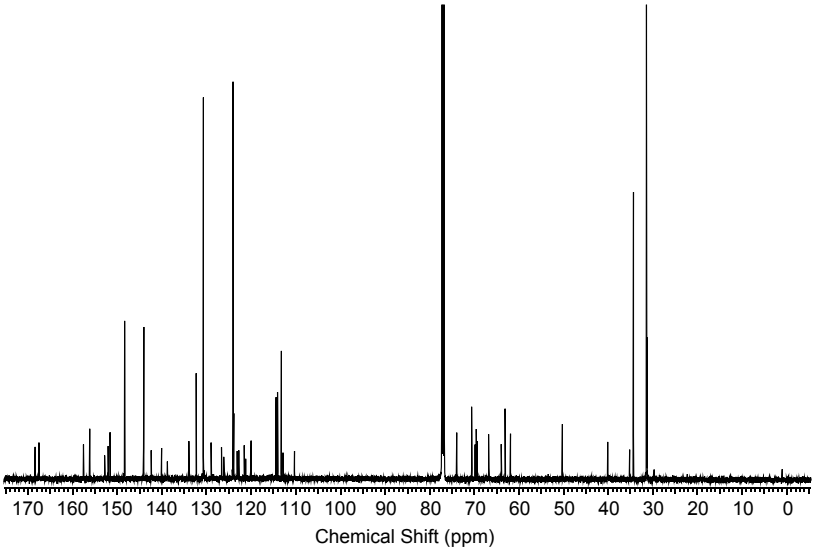


Figure S12. ^{13}C NMR spectrum of the [2]rotaxane **4** ($CDCl_3$, 126 MHz, 298 K)

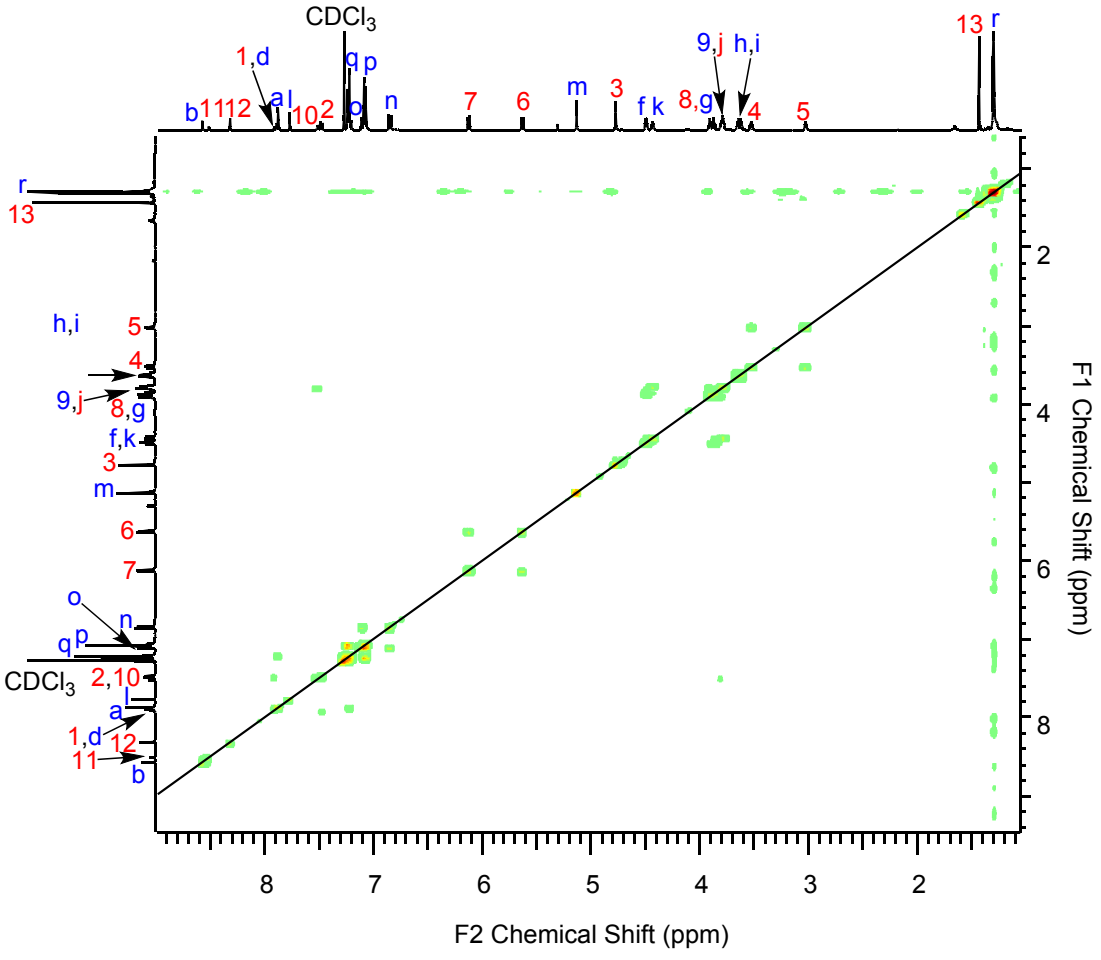


Figure S13. ^{1}H NMR COSY spectrum of the [2]rotaxane **4** ($CDCl_3$, 500 MHz, 298 K)

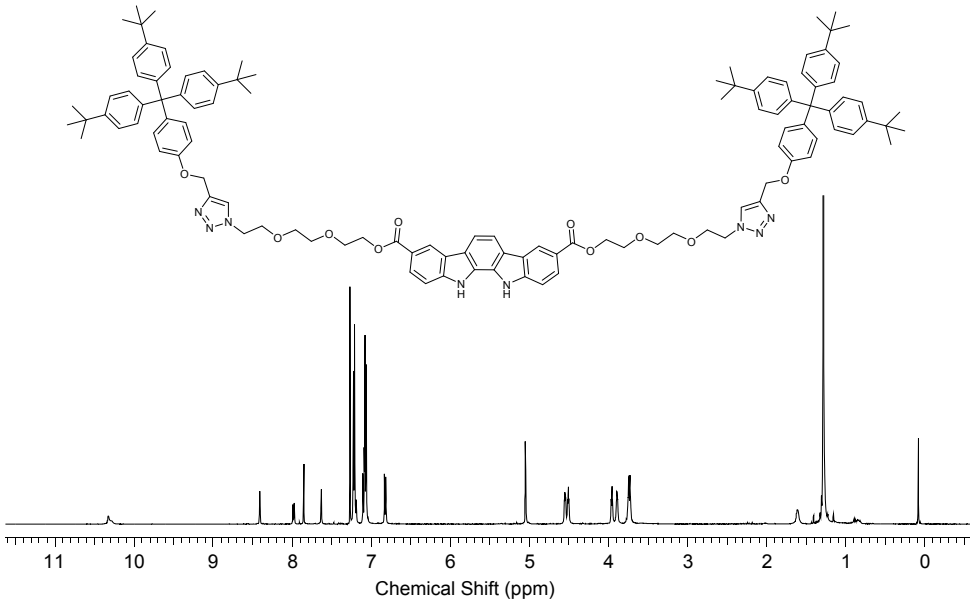


Figure S14. ^{1}H NMR spectrum of the axle compound **S8**, isolated as a side-product of the synthesis of the [2]rotaxane **4** ($CDCl_3$, 500 MHz, 298 K).

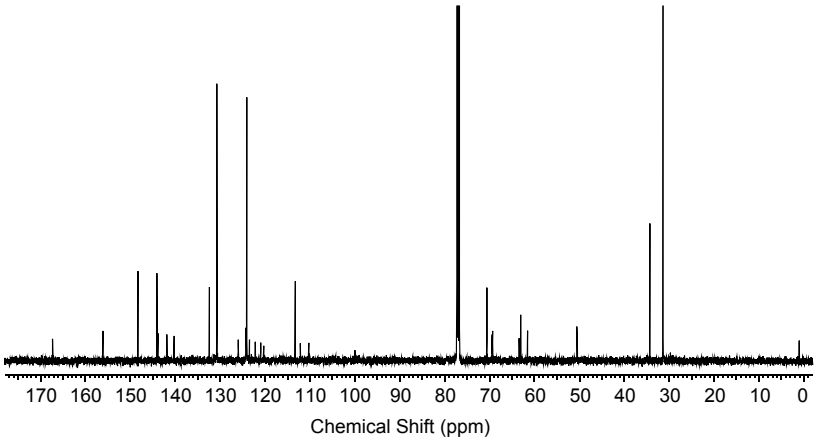


Figure S15. ^{1}H NMR spectrum of the axle compound **S8**, isolated as a side-product of the synthesis of the [2]rotaxane **4** ($CDCl_3$, 126 MHz, 298 K).

S3. ^{1}H NMR titration experiments

All ^{1}H NMR titration experiments were conducted on a Bruker Avance III 500 MHz NMR spectrometer, at 298 K. Initial sample volumes were 600 µl. The starting concentration of the host was 1.5 mM. All anions were added as their TBA salts. Seventeen aliquots of a 45 mM solution of the TBAX guest 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[5] 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.

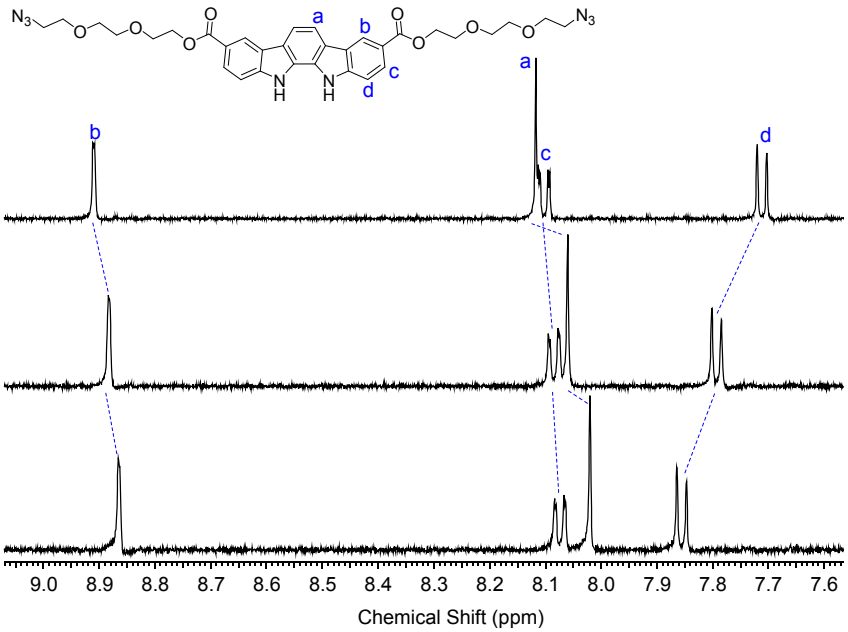


Figure S16. Aromatic regions of the ^{1}H NMR spectra of a 1.5 mM solution of the compound **2** in acetone-d_6:D_2O 95:5 (500 MHz; 298 K) in the presence of (i) 0, (ii) 1 and (iii) 5 equivalents of TBA·AcO.

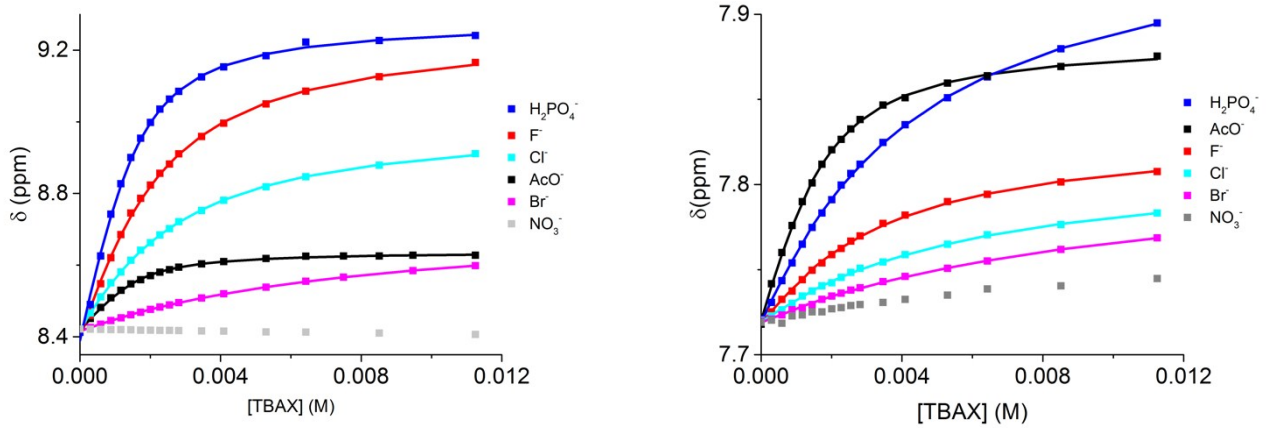


Figure S17. Changes in the chemical shift of the internal macrocycle proton 11 upon addition of monoanions as their TBA salts to a 1.5 mM solution of the [2]rotaxane **4** in acetone-d_6:D_2O 95:5 (left) and changes in the chemical shift of the indolocarbazole aromatic proton e on addition of monoanions as their TBA salts to a 1.5 mM solution of the indolocarbazole bis-azide **2** in acetone-d_6:D_2O 95:5. Square points represent experimental data; continuous lines represent theoretical binding curves for the calculated association constants shown in Table 1.

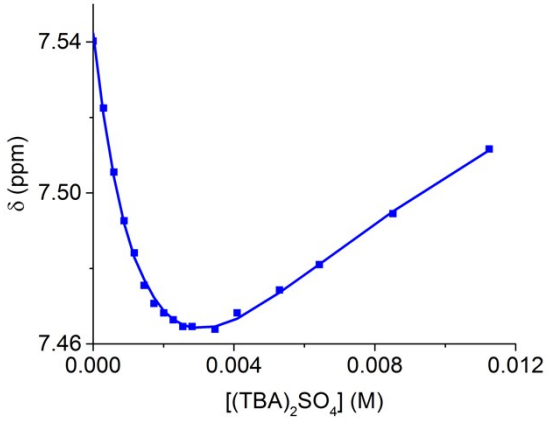


Figure S18. Changes in the chemical shift of the indolocarbazole proton c upon addition of $(TBA)_2SO_4$ to a 1.5 mM solution of the [2]rotaxane **4** in acetone-d_6:D_2O 90:10 at 298 K. Square points represent experimental data; continuous line represents theoretical binding curve for the calculated association constants shown in Table 2.

Table S1. Comparison of association constants for 2:1 and 1:1 complexes of the [2]rotaxane **4** with SO_4^{2-} anions in acetone-d_6:D_2O 95:5 at 298 K calculated by monitoring the chemical shift changes in the signals for protons 11, c and d using WineQNMR software. SO_4^{2-} added as a TBA salt.

	proton 11	proton d	proton c
$K_{11} = \beta_1$ (M^{-1})	4518 (872)	4707 (284)	4412 (955)
K_{21} (M^{-1})	48 (12)	57 (5)	57 (15)
$K_{11} \cdot K_{21} = \beta_2$ (M^{-2})	216315 (33950)	270141(16760)	250212 (36480)

S4. Fluorescence titration experiments

Fluorescence titration experiments were conducted using a Horiba Jobin Yvon FluoroLog3. During each titration experiment aliquots of a TBAX guest solution were repeatedly added to a solution of the [2]rotaxane host compound **4** 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.

Stability constants were determined by analysis of the resulting titration data using the SPECFIT[6] 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 rotaxane·anion complexes with the experimental data confirmed that the model used was correct.

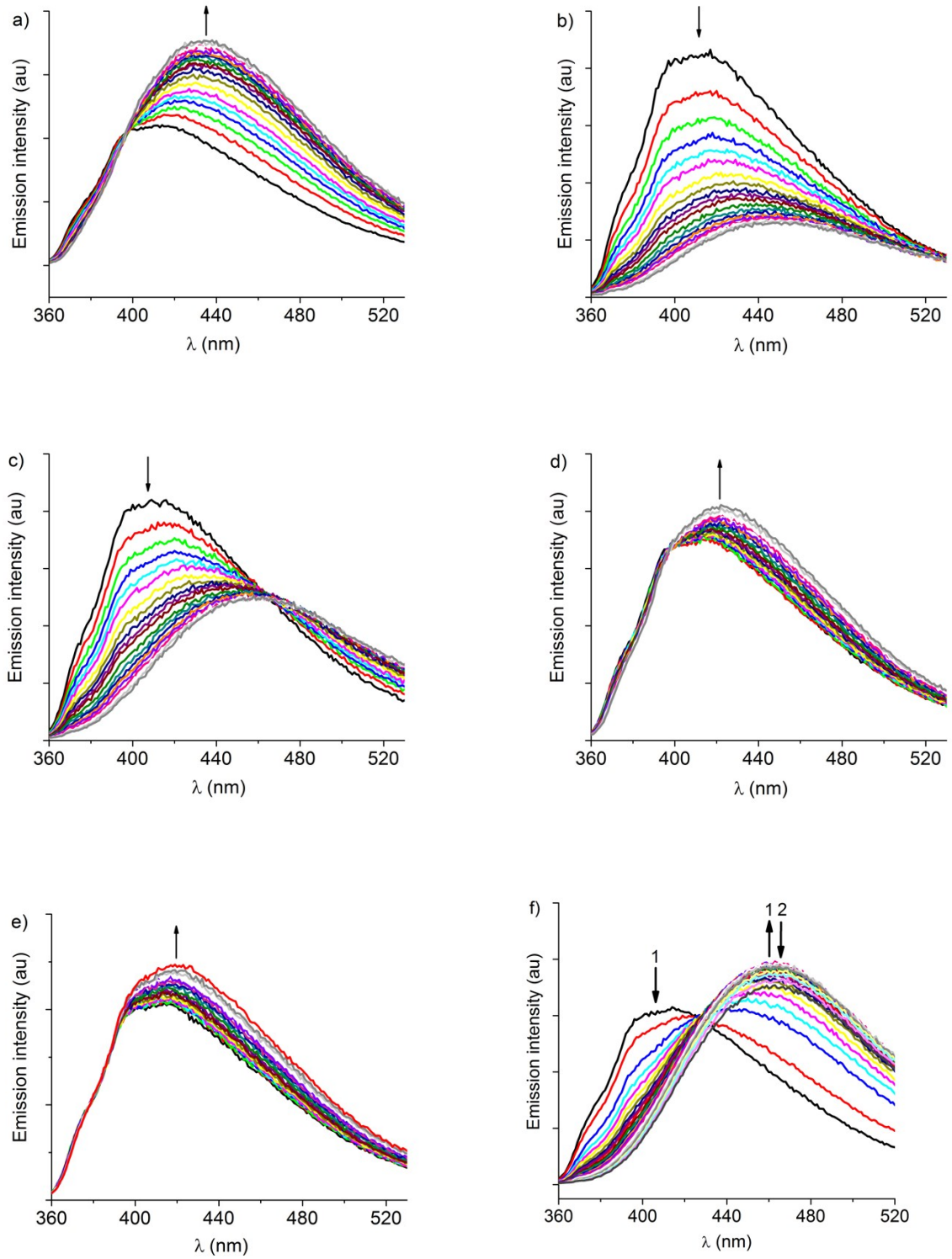


Figure S19. Fluorescence emission spectra of 15 µM solutions of compound 4 in acetone:H_2O 95:5 recorded after progressive addition of increasing concentrations of a) TBACl, b) TBAAcO, c) TBAF, d) TBABr, e) $TBANO_3$ and f) $(TBA)_2SO_4$. Final TBAX concentrations: 9.6–10.0 mM for X = Cl^-, AcO^-, F^-, Br^- and NO_3^-; 3.8 mM for X = SO_4^{2-}.

S5. References

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