Electronic Supplementary Information

Adjustable Chiral Self-sorting and Self-discriminating Behaviour between Diamond-like Tröger's Base-linked Cryptands

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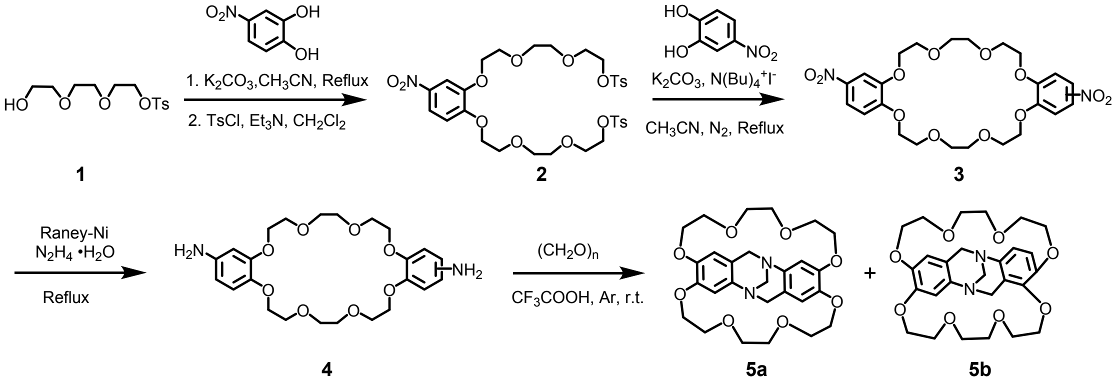
1. General information

All reactions were performed in air atmosphere unless otherwise stated. All reagents and solvents, unless otherwise indicated, were obtained from commercial sources. Melting points (M.p.) were determined using a Focus X-4 apparatus (made in China) and were not corrected. All yields were given as isolated yields. NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer with internal standard tetramethylsilane (TMS) and solvent signals as internal references at 298 K. High-resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on an Agilent 6540Q-TOF LCMS equipped with an electrospray ionization (ESI) probe operating in positive-ion mode with direct infusion.

2. Synthetic procedures and characterization data

Compound **1** were synthesized according to the previously reported methods. (Scheme S1).[S1]



Scheme S1 Synthesis of cryptand **5a** and **5b**.

Synthesis of Compound **2** and characterization data

The mixture of 4-nitrobenzene-1,2-diol (0.620 g, 4.00 mmol) and potassium carbonate (1.49 g, 10.8mmol) in dry CH_3CN (60.0 mL) was stirred at 50 °C for 2 hours, then compound **1** (2.68 g, 8.80 mmol) was added slowly, the mixture was heated under reflux for 24h. After cooling to room temperature, The resulting product was used for next step without purification. which was dissolved in dried CH_2Cl_2 (60.0 mL) and TsCl (1.91 g, 10.0 mmol) and Et_3N (1.01 g, 10.0 mmol) were added. The reaction mixture was stirred at room temperature for 10h, The precipitate was filtered off and extracted by CH_2Cl_2. After being washed with saturated sodium chloride solution and dried by anhydrous sodium sulfate, the product was purified by column chromatography on silica gel (eluent: 1/3, *v/v*, ethyl acetate: petroleum ether) to give **2** as an oil liquid (2.11 g, 73%). ^1H NMR (400 MHz, DMSO-d_6) $\delta = 7.90$-7.87 (m, 1H), 7.78-7.76 (m, 5H), 7.46 (d, $J = 8.0$ Hz, 4H), 7.19 (d, $J = 8.8$ Hz, 4H), 4.24-4.19 (m, 4H), 4.10-4.08 (m, 4H), 3.75-3.72 (m, 4H), 3.58-3.52 (m, 8H), 3.48-3.45 (m, 4H), 2.40 (s, 6H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): 154.6, 148.3, 145.4, 141.1, 132.8, 130.6, 128.1, 118.3, 112.7, 108.6, 70.4-68.4 ppm(***C***H_2). HRMS (ESI-TOF) *m/z*: calcd. for $[C_{32}H_{41}NO_{14}S_2 + Na]^+$ 750.1861; found: 750.1859.

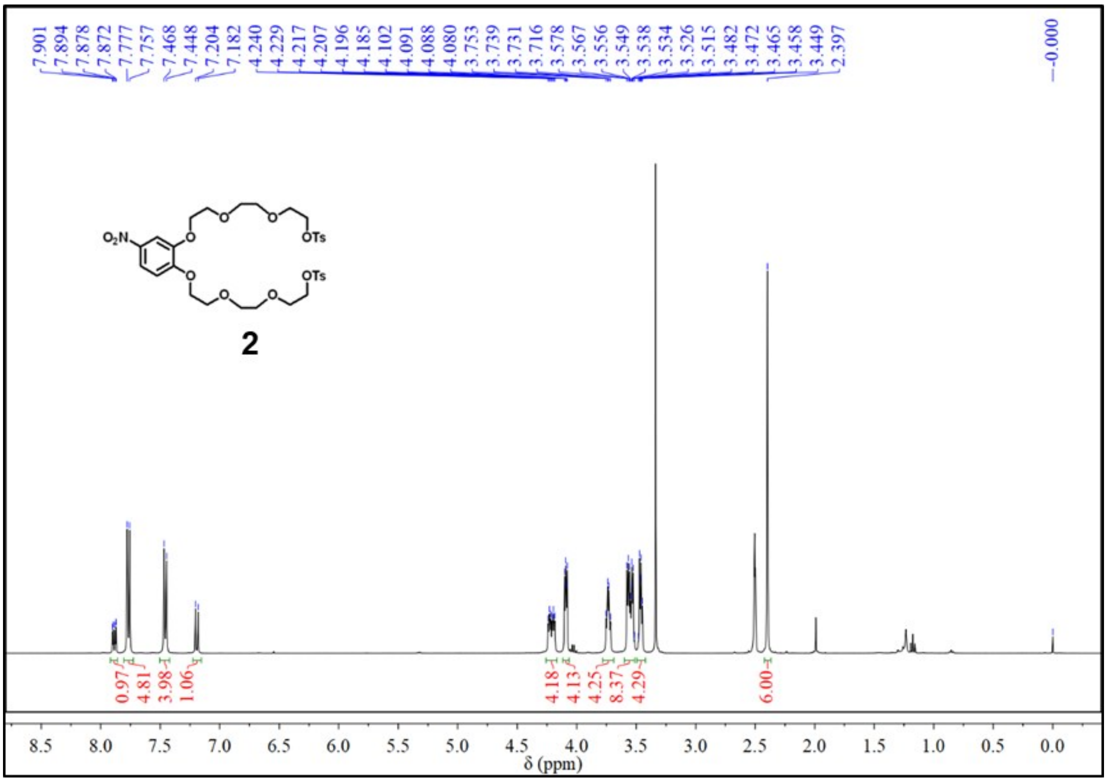


Fig. S1 ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298 K) of compound **2**.

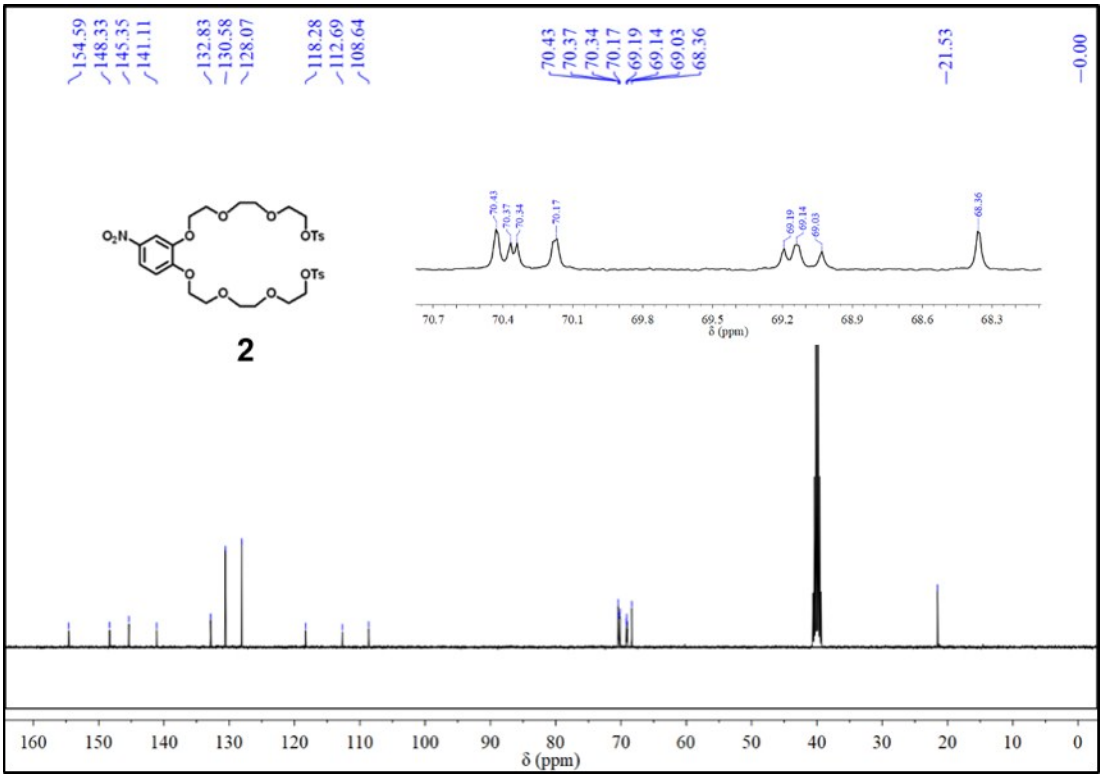


Fig. S2 ^{13}C NMR spectrum (100 MHz, DMSO-d_6, 298 K) of compound **2**.

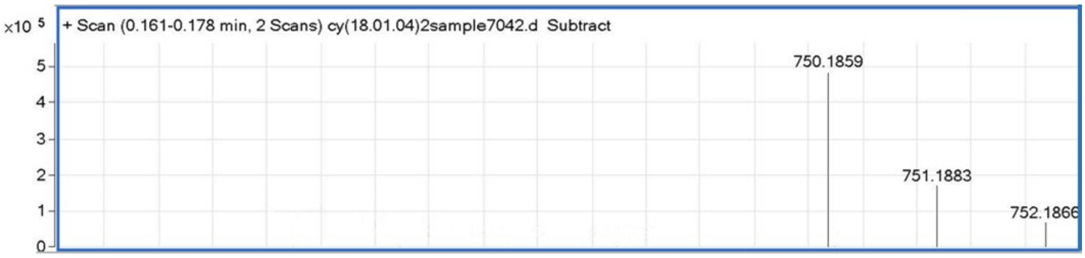


Fig. S3 High Resolution ESI-MS of compound **2** with the parent ion [M + Na]$^+$ at 750.1859, corresponding to $C_{32}H_{41}NO_{14}S_2$ with the calculated *m/z* = 750.1861.

Synthesis of compound **3** and characterization data

A single-necked flask equipped with a magnetic stirrer was charged with compound **2** (1.09 g, 1.50 mmol)**,** potassium carbonate (1.04 g, 7.50 mmol) and Tetrabutylammonium iodide (4.00 mg, 0.010 mmol) in dry CH_3CN (100 mL) under nitrogen, then 4-nitrobenzene-1,2-diol (0.230 g, 1.50 mmol) was added slowly by using a syringe, and the solution was refluxed for 48h. After cooling to room temperature, the product was first filtrated and the filtrate was evaporated under high vacuum, and extracted with CH_2Cl_2. The organic phase was washed with saturated sodium chloride solution and dried with anhydrous sodium sulfate and concentrated. The product was purified by column chromatography on silica gel (eluent: 1/50, *v/v*, methanol : dichloromethane gradually changing to 1/25) to give **3** as yellow solid (0.460 g, 57%). M.p. (153-154 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89-7.86 (m, 2H), 7.72-7.71 (m, 2H), 6.86 (d, *J* = 8.8 Hz 2H), 4.24-4.22 (m, 8H), 3.97-3.95 (m, 8H), 3.85-3.84 (m, 8H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 153.2, 147.3, 140.5, 117.0, 110.2, 107.2, 70.6-68.5 ppm(***C***H$_2$). HRMS (ESI-TOF) *m/z*: calcd. for [$C_{24}H_{30}N_2O_{12}$ + Na]$^+$ 561.1691; found: 561.1698.

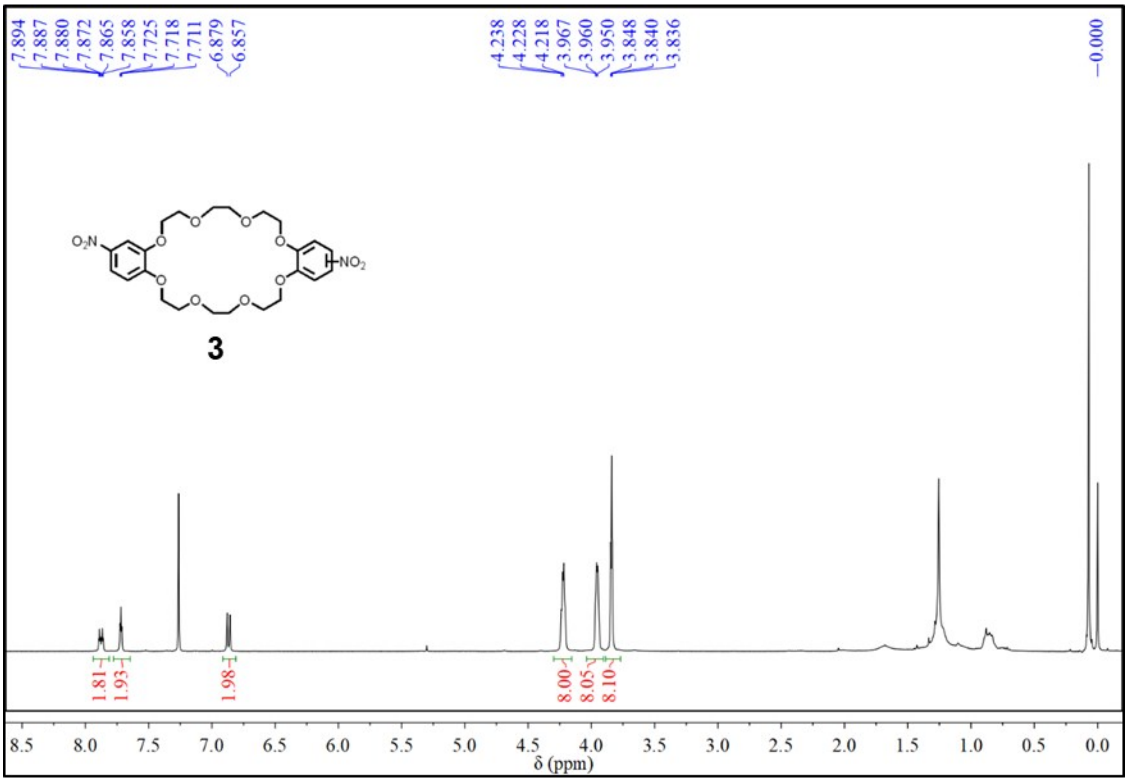


Fig. S4 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **3**.

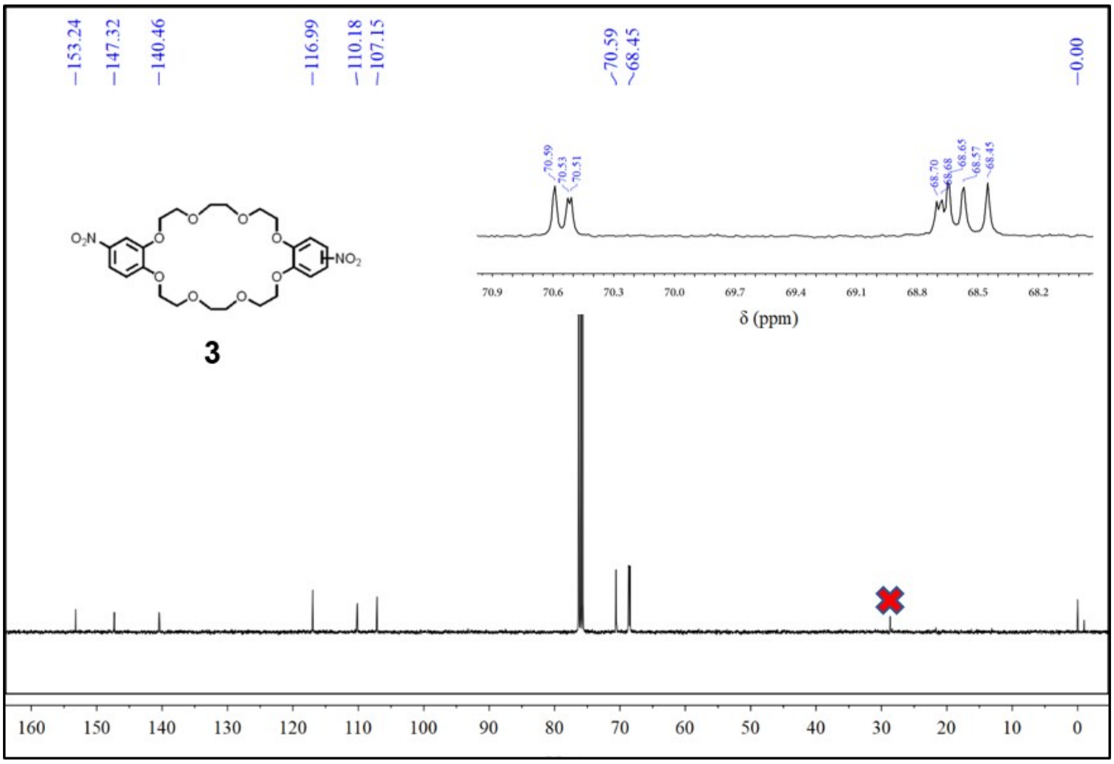


Fig. S5 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of compound **3**.

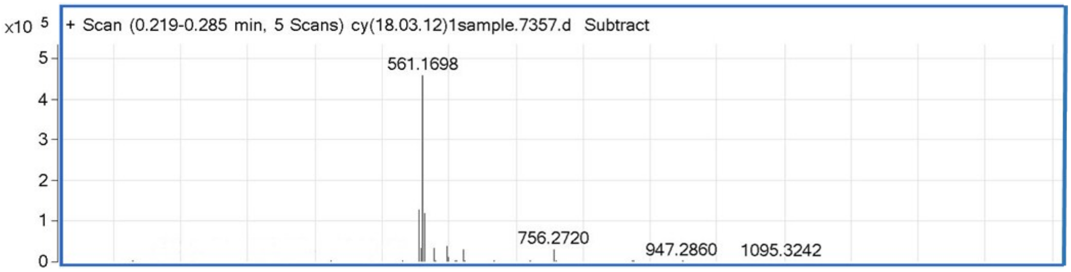


Fig. S6 High Resolution ESI-MS of compound **3** with the parent ion $[M + Na]^+$ at 561.1698, corresponding to $C_{24}H_{30}N_2O_{12}$ with the calculated *m/z* = 561.1691.

Synthesis of compound **4** and characterization data

A single-necked flask equipped with a magnetic stirrer was charged with compound **3** (0.810 g, 1.50 mmol), 10% Raney-Ni (2.00 mL, Ni > 90%, 50.0 μm) and $N_2H_4 \cdot H_2O$ (10.0 mL) were added in MeOH (100 mL). The reaction mixtures were stirred and heated under reflux for 5 h under an N_2 atmosphere. The hot reaction solution was filtered immediately in order to avoid early crystallization of the product, and after cooling the filtrate solution, the white solid was obtained, which was washed with cold EtOH (3 × 10.0 mL) further to give compound **4** as white solid (0.590 g, 82%).

M.p. (135-136 °C) ^{1}H NMR (400 MHz, DMSO-d_6) $\delta = 6.64$ (d, $J = 8.4$ Hz, 2H), 6.23 (d, $J = 2.4$ Hz, 2H), 6.06-6.03 (m, 2H), 4.69 (s, 4H), 3.98-3.89 (m, 8H), 3.74-3.62 (m, 16H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): 150.4, 144.7, 139.8, 118.3, 106.3, 101.9, 70.8-68.7 ppm (***C***H_2). HRMS (ESI-TOF) *m/z*: calcd. for $[C_{24}H_{34}N_2O_8 + Na]^+$ 501.2207; found: 501.2212.

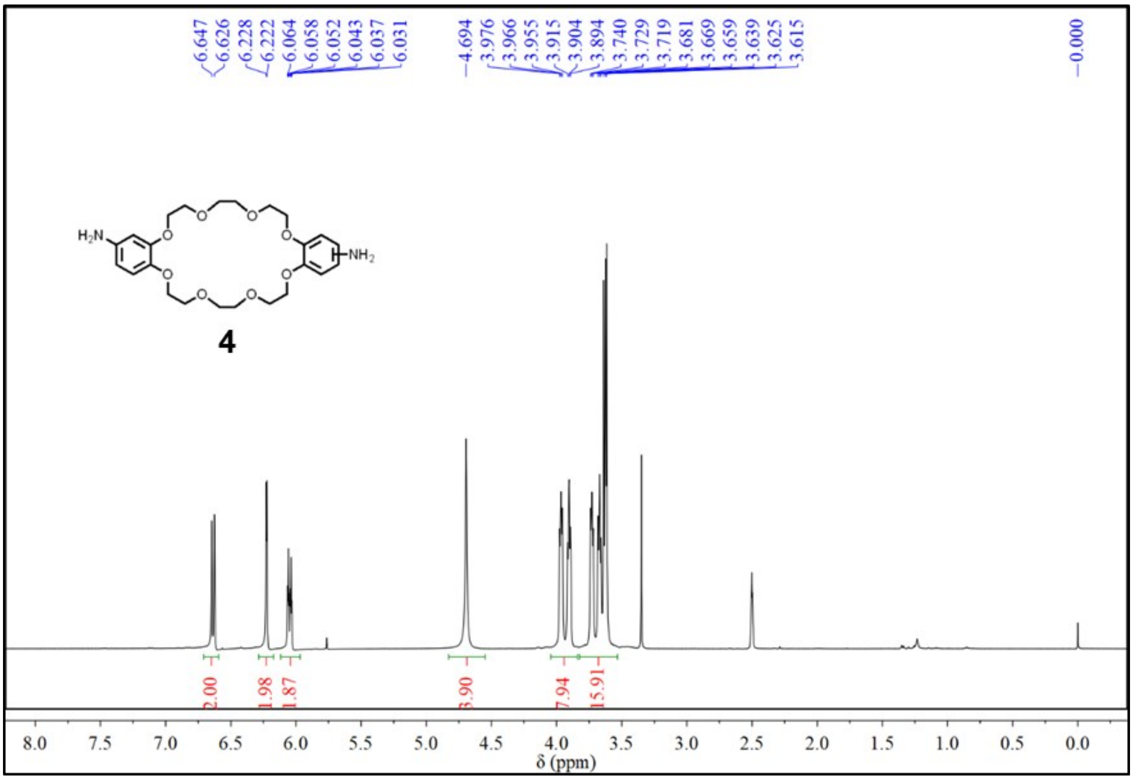


Fig. S7 ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298 K) of compound **4**.

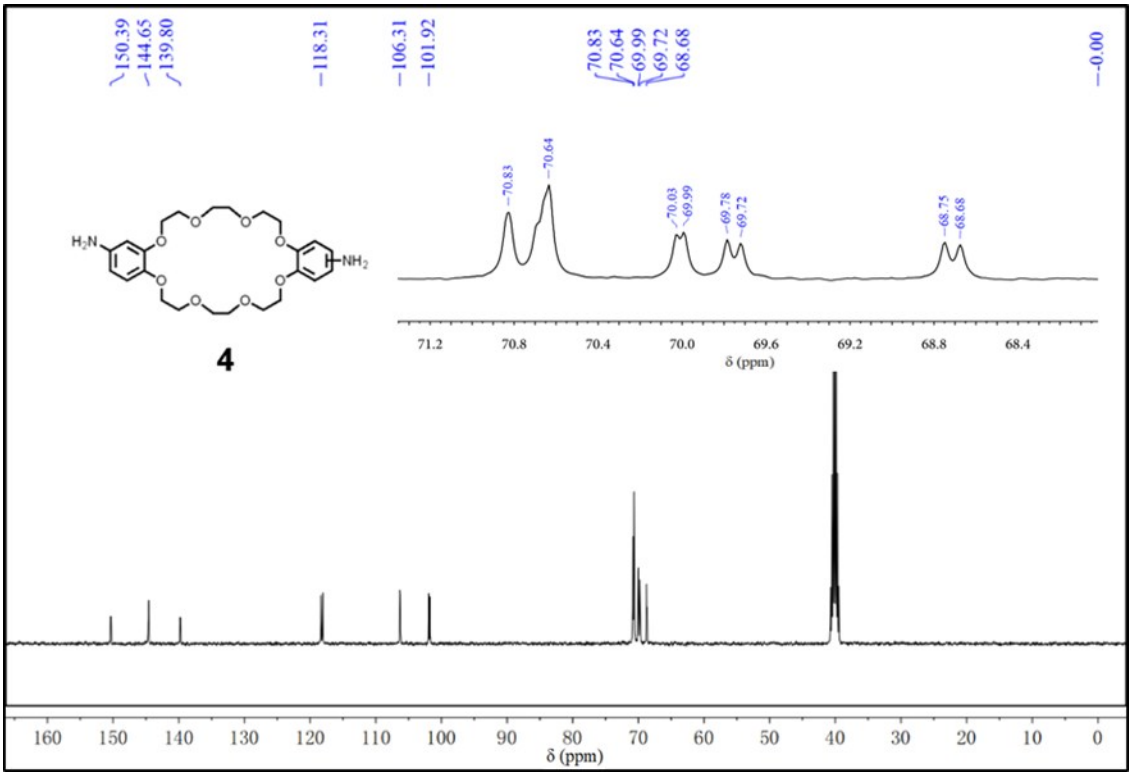


Fig. S8 ^{13}C NMR spectrum (100 MHz, DMSO-d_6, 298 K) of compound **4**.

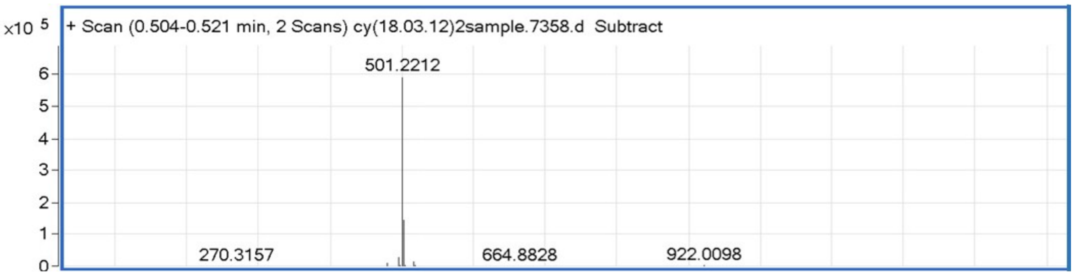


Fig. S9 High Resolution ESI-MS of compound **4** with the parent ion $[M + Na]^+$ at 501.2212, corresponding to $C_{24}H_{34}N_2O_8$ with the calculated *m/z* = 501.2207.

Synthesis of cryptand **5a** and **5b** and characterization data

A single-necked flask equipped with a magnetic stirrer was charged with compound **4** (0.720 g, 1.50 mmol) and triformaldehyde (0.410 g, 4.50 mmol) under nitrogen at 0 ˚C, trifluoroacetic acid (500 ml) was slowly added by syringe at 0 ˚C, and then the mixture was stirred at room temperature for 48 hours. Then the reaction was quenched by addition of water (200 mL) after neutralization with aq. NH_3 to pH = 6.5, the mixture was extracted by CH_2Cl_2 (3 × 100 mL), and the organic phase was dried with anhydrous Na_2SO_4. After filtration and rotary evaporation, the product was purified by column chromatography on silica gel (eluent: 1/50, *v/v*, methanol : dichloromethane gradually changing to 1/25) to give **5a** as white solid (0.220 g, 28%) and **5b** as brown solid (0.210 g, 27%).

Compound 5a: M.p. (177-178 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.79 (s, 2H), 6.69 (s, 2H), 4.56-4.42 (m, 8H), 4.2-4.00 (m, 6H), 3.86-3.77 (m, 4H), 3.72-3.66 (m, 2H), 3.48-3.43 (m, 2H), 3.24-3.12 (m, 4H), 3.0-2.88 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 147.7, 145.2, 140.1, 119.9, 114.4, 111.2, 73.3, 72.5, 70.6, 68.9, 68.1, 67.1, 60.5 ppm. HRMS (ESI-TOF) *m/z*: calcd. for $[C_{27}H_{34}N_2O_8 + Na]^+$ 537.2207; found: 514.2218.

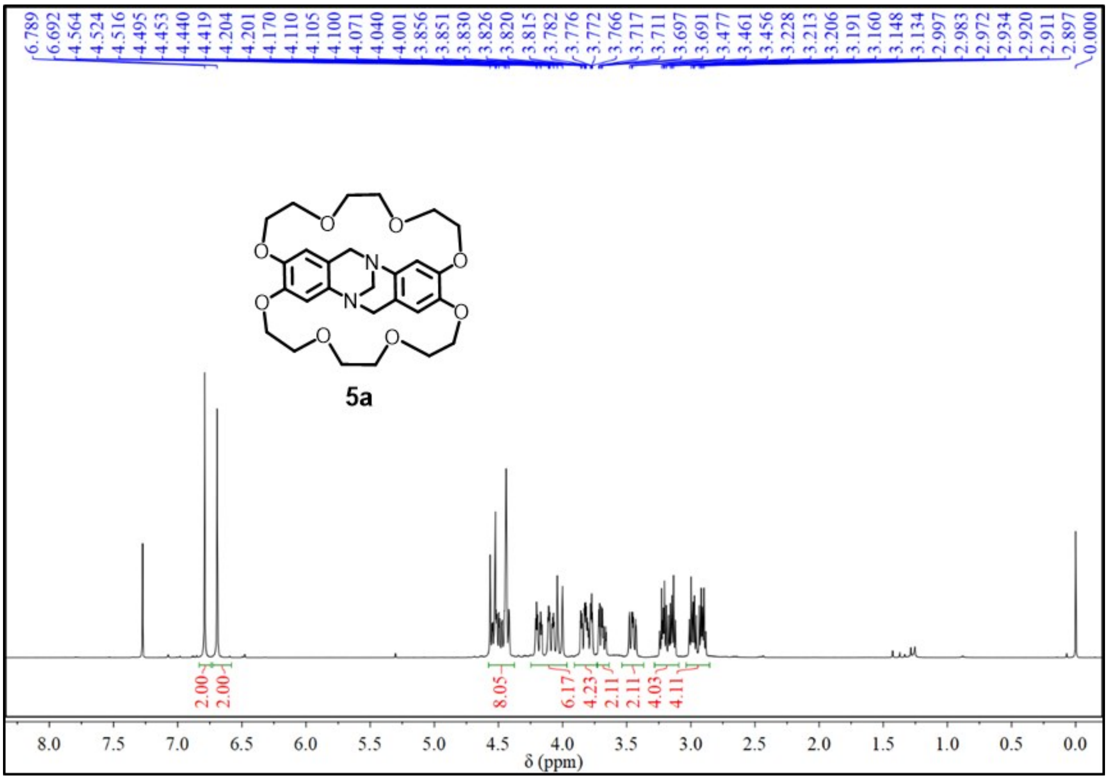


Fig. S10 ^{1}H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of compound **5a**.

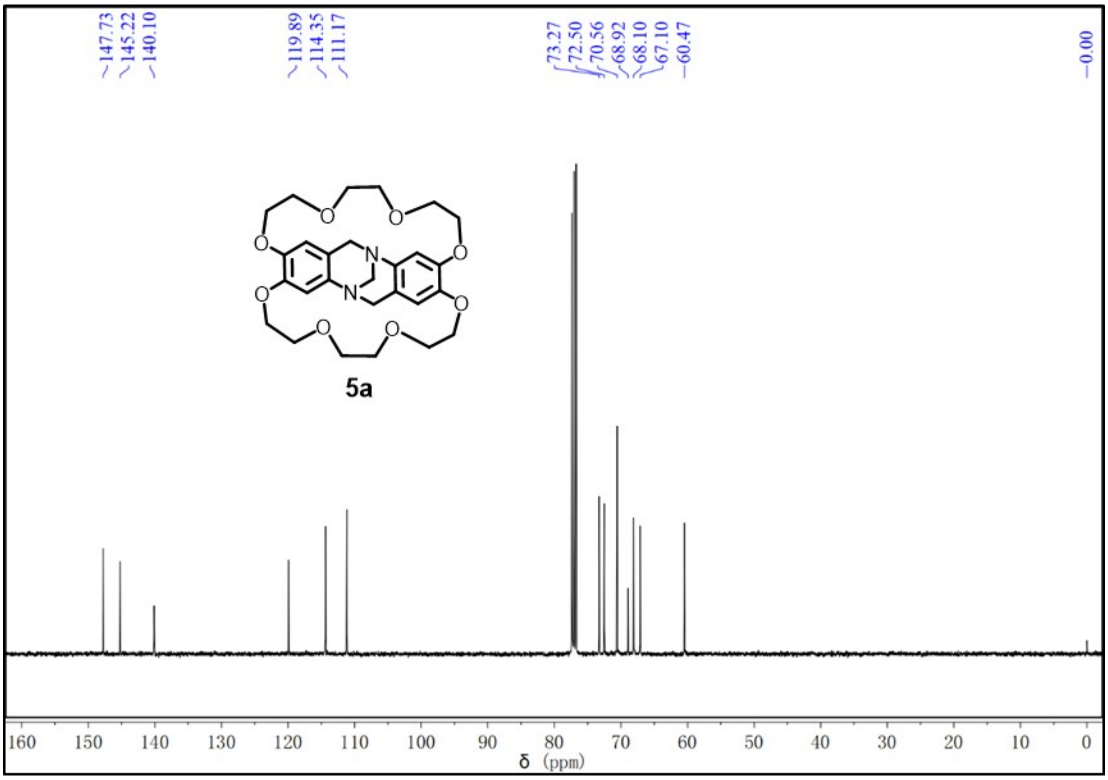


Fig. S11 ^{13}C NMR spectrum (100 MHz, CDCl$_3$, 298 K) of compound **5a**.

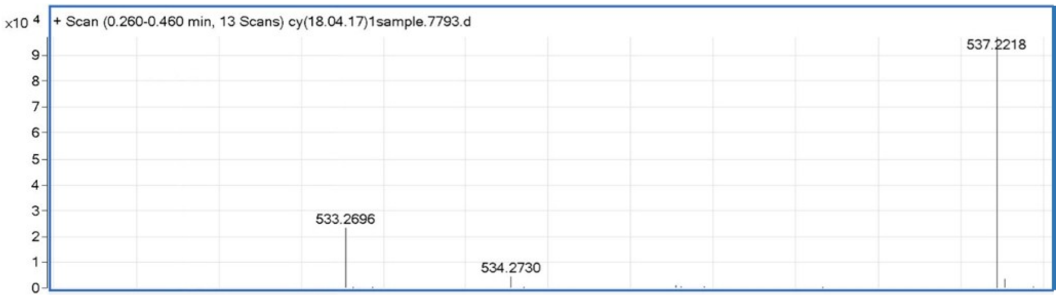


Fig. S12 High Resolution ESI-MS of compound **5a** with the parent ion $[M + Na]^+$ at 537.2218, corresponding to $C_{27}H_{34}N_2O_8$ with the calculated *m/z* = 537.2207.

Compound 5b: M.p. (133-134 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.05 (s, 1H), 6.86 (d, J = 8.8 H$_Z$ 1H), 6.76 (d, J = 8.8 H$_Z$ 1H), 6.47 (s, 1H), 4.67-4.63 (m, 1H), 4.54-4.23 (m, 9H), 4.13-4.06 (m, 2H), 3.92-3.54 (m, 13H), 3.44-3.39 (m, 1H), 3.03-2.97 (m, 1H), 2.87-2.82 (m, 1H), 2.69-2.63 (m, 1H), 2.48-2.42 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 150.1, 146.8, 145.5, 143.4, 142.5, 141.4, 122.3, 119.4, 118.7, 118.3, 116.0, 110.2, 72.3, 71.8, 71.3, 70.8, 70.3, 70.1, 69.9, 69.4, 69.0, 67.9, 67.8, 67.1, 60.3, 55.9 ppm. HRMS (ESI-TOF) *m/z*: calcd. for $[C_{27}H_{34}N_2O_8 + Na]^+$ 537.2207; found: 537.2213.

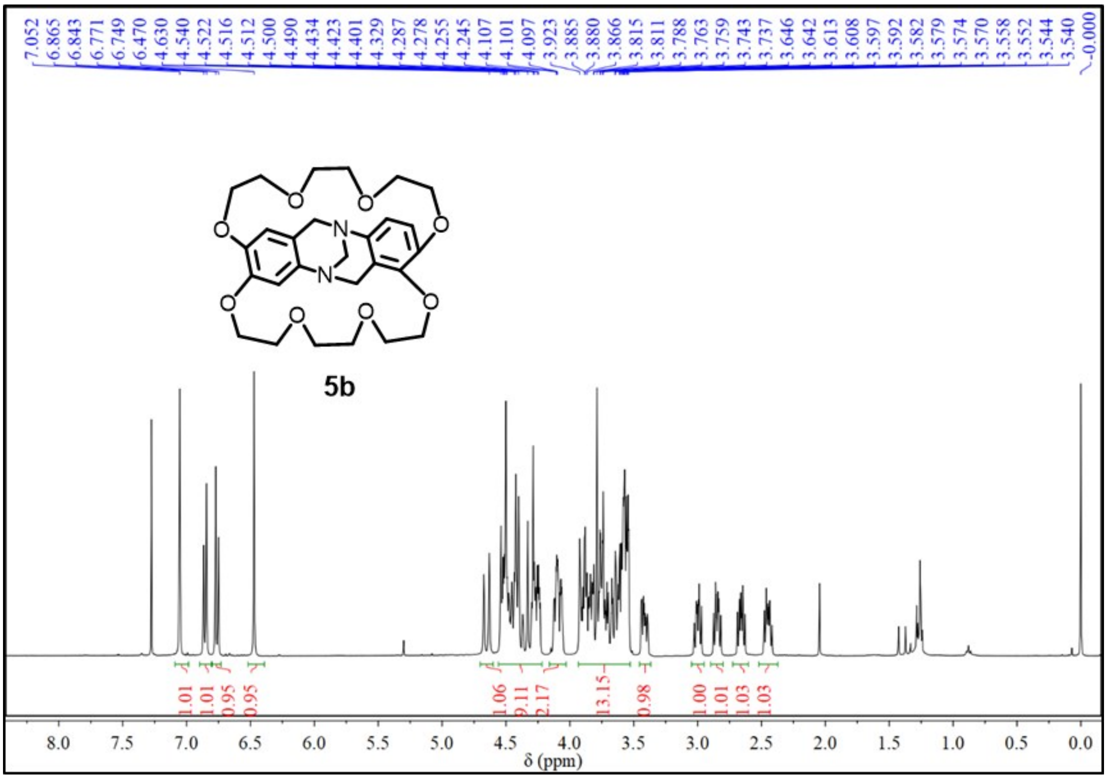


Fig. S13 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **5b**.

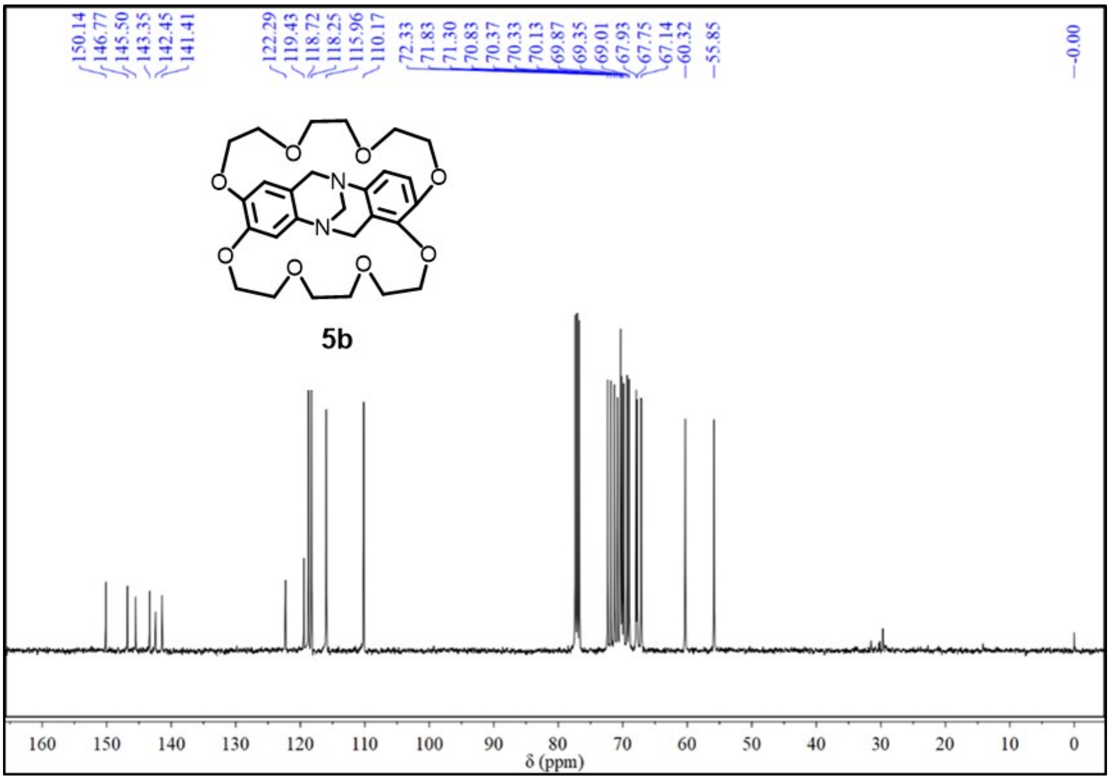


Fig. S14 ^{13}C NMR spectrum (100 MHz, CDCl$_3$, 298 K) of compound **5b**.

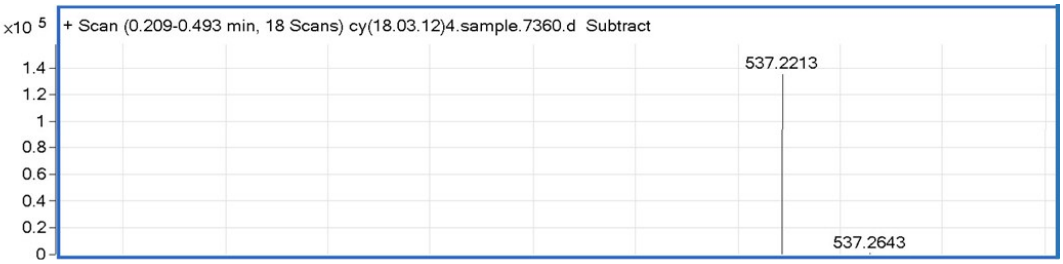
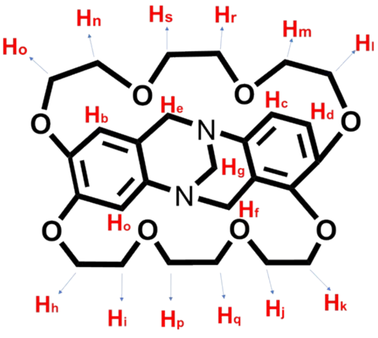
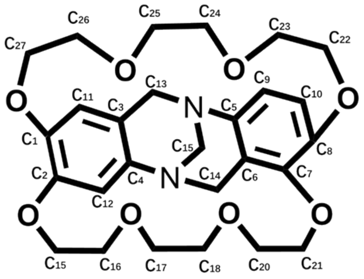
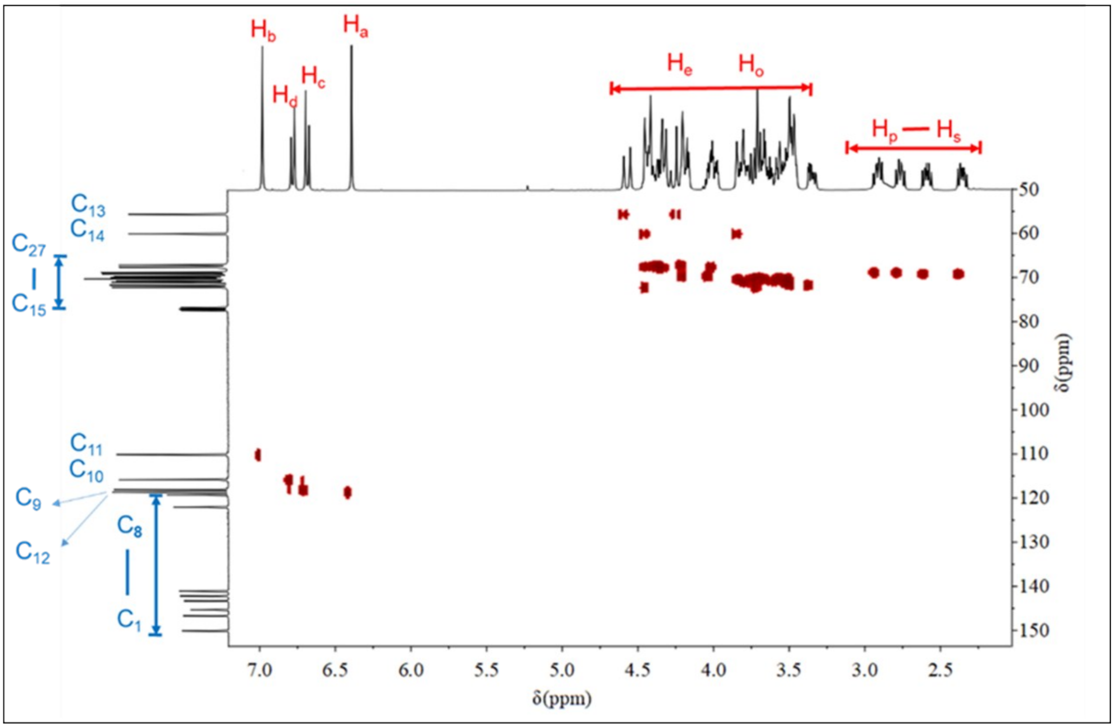


Fig. S15 High Resolution ESI-MS of compound **5b,** with the parent ion [M + H]$^+$ at 537.2213, corresponding to $C_{27}H_{34}N_2O_8$ with the calculated *m/z* = 537.2207.







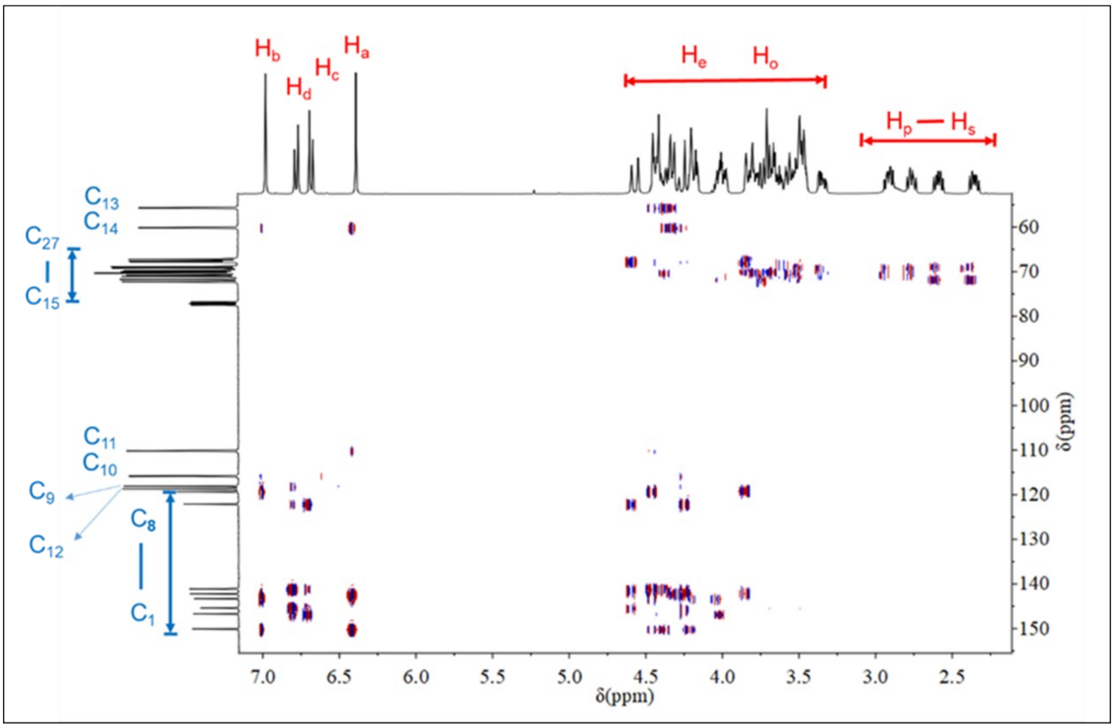


Fig. S16 ^{1}H-^{13}C HSQC (top) and ^{1}H-^{13}C HMBC (bottom) NMR spectrum (100 MHz, CDCl$_3$, 298 K) of **5b**.

3. X-ray Crystallography Experimental, Data and Analysis

The crystal structures were determined by single-crystal X-ray analyses. Data collections were performed using a Bruker Apex Smart CCD diffractometer with Mo-Kα radiation with an *φ–ω* mode (λ = 0.71073 Å). The structures were solved with direct methods using the SHELXTL program [S2] and refined anisotropically with SHELXTL using full-matrix least-squares procedures. Crystallographic data and structural refinements parameters for all these crystals are given in Table S1 – S2.

Single crystals of **5a** were obtained as color less plates by slow evaporation of isopropyl ether into a dichloromethane solution of the **5a** at 25 ˚C

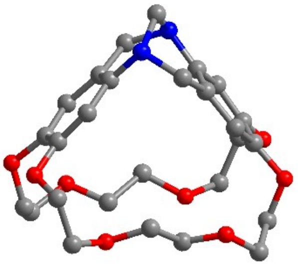


Fig. S17 View of cryptand **5a**.

Table S1 Crystal data and structure refinement for cryptand **5a**

CCDC number	1888549	
Identification code	**5a**	
Empirical formula	$C_{27} H_{34} N_2 O_8$	
Formula weight	514.56	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$C222_1$	
Unit cell dimensions	a = 33.681(11) Å	α= 90°.
	b = 13.162(5) Å	β= 90°.
	c = 11.381(4) Å	γ = 90°.
Volume	5045(3) Å^3	
Z	4	

Density (calculated)	0.677 Mg/m^3
Absorption coefficient	0.050 mm^{-1}
F(000)	1096
Crystal size	0.260 × 0.230 × 0.220 mm^3
Theta range for data collection	2.160 to 25.010°.
Index ranges	-40<=h<=39, -15<=k<=11, -13<=l<=11
Reflections collected	11724
Independent reflections	4417 [R(int) = 0.1355]
Completeness to theta = 25.010°	99.7%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4417 / 0 / 169
Goodness-of-fit on F^2	1.193
Final R indices [I>2sigma(I)]	R1 = 0.0887, wR2 = 0.1997
R indices (all data)	R1 = 0.1239, wR2 = 0.2163
Absolute structure parameter	3(3)
Extinction coefficient	n/a
Largest diff. peak and hole	0.285 and -0.262 e.$Å^{-3}$

Single crystals of **5a-CF_3COOH** were obtained as color less plates, 2.0 equiv. trifluoroacetic acid (TFA) was added into the solution to protonate **5a**. And then, by slow diffusion of isopropyl ether into a dichloromethane solution of the protonated **5a**.

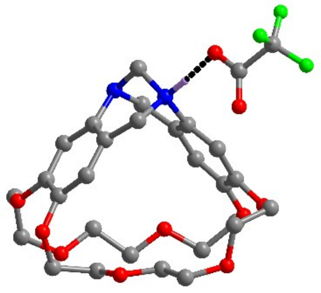


Fig. S18 View of **5a-CF_3COOH**.

Table S2 Crystal data and structure refinement for **5a-CF_3COOH**

CCDC number	1889896

Identification code	**5a-CF_3COOH**	
Empirical formula	$C_{29} H_{35} F_3 N_2 O_{10}$	
Formula weight	628.59	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.8086(12) Å	α= 87.221(4)°.
	b = 11.8096(16) Å	β= 88.432(3)°.
	c = 15.178(2) Å	γ = 88.271(4)°.
Volume	1575.8(4) $Å^3$	
Z	2	
Density (calculated)	1.325 Mg/m^3	
Absorption coefficient	0.111 mm^{-1}	
F(000)	660	
Crystal size	0.190 × 0.170 × 0.160 mm^3	
Theta range for data collection	2.137 to 25.009°.	
Index ranges	-10<=h<=10, -10<=k<=14, -17<=l<=18	
Reflections collected	10541	
Independent reflections	5498 [R(int) = 0.0494]	
Completeness to theta = 25.009°	98.8%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5498 / 36 / 425	
Goodness-of-fit on F^2	0.985	
Final R indices [I>2sigma(I)]	R1 = 0.0590, wR2 = 0.1335	
R indices (all data)	R1 = 0.1163, wR2 = 0.1593	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.297 and -0.244 e.$Å^{-3}$	

4. References

S1. C. Li, W. Huang, L. Zhou, P. Huang, Y. Pang, X. Zhu and D. Yan, *Polym. Chem.*, 2015, **6**, 6498-6508.

S2. G. M. Sheldrick, *Acta Crystallogr.*, *Sect. C: Struct. Chem.*, 2015, **71**, 3-8.