Electronic Supplementary Material (ESI) for ChemComm.

Imidazolium-based catenane host for bromide recognition in aqueous media

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Supplementary Information

Contents

Materials, instrumentation, and general considerations

All solvents and starting materials were purchased from Fisher Scientific, Sigma-Aldrich, Arcos Organics and Alfa Aesar. These materials were used as received from the supplier without any further purification methods carried out unless otherwise stated.

Dry solvents were obtained by purging with nitrogen and then passing through a MBraun MPSP-800 column. Water was de-ionised and microfiltered using a Milli-Q® Millipore machine. All tetrabutylammonium (TBA) salts and Grubbs' II catalyst were stored in a vacuum desiccator over phosphorus pentoxide prior to use. Et_3N was distilled over and stored over potassium hydroxide.

Microwave reactions were carried out using a Biotage Initiator 2.0 microwave.

Routine ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury VX300 spectrometer. All ^{13}C spectra were proton decoupled.

^{1}H NMR titrations were performed using the Varian Unity Plus 500 spectrometer. A solution of the intended guest species (10^{-5} mol in 0.10 mL solvent) was added in a stepwise fashion to a solution of host (10^{-6} mol in 0.50 mL solvent) at 293 K. Spectra were measured and chemical shifts recorded at 22 titration points (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, 3.0, 4.0, 5.0, 7.0 and 10 equivalents of guest to host). Due to the overwhelming dominance of the water resonance, phasing of the spectrum of interest was challenging at times, as can be seen in the titration spectra; nonetheless, it was quite possible to follow the progression of the relevant peaks throughout the titrations. The resulting titration data, along with the binding stoichiometry and estimates of binding constants and final chemical shifts, were entered into the WinEQNMR2 programme[1] to obtain stability constants. In the fast exchange regime (applicable here), the chemical shift of a proton on one of the species involved an equilibrium process occurs at the weighted average (determined by the equilibrium constant) of the same proton in fully complexed and de-complexed species. Both the equilibrium constant and the chemical shift of the fully complexed species are unknown, but are extracted from titration data[2] by WinEQNMR2 via a non-linear least squares fitting routine. Iterations were then performed to provide the most accurate result.

Routine mass spectrometry was performed on a Bruker microTOF (ESI).

Synthesis and Characterisation

2-(Allyloxy)ethyl tosylate (1).[3]

2-Allyloxyethanol (2.55 g, 25.0 mmol), and tosyl chloride (4.76 g, 25.0 mmol) were dissolved in dry CH_2Cl_2 (100 ml). Dry Et_3N (5.00 ml, 37.5 mmol) and DMAP (catalytic) were added and the solution was stirred overnight under a nitrogen atmosphere. Water (50 ml) was added to quench the reaction, and the organic layer was washed with a further 2 x 50 ml water, followed by brine (50 ml). The aqueous layers were combined and re-extracted with CH_2Cl_2 (2 x 50 ml). The organic fractions were then dried over $MgSO_4$, filtered, and the solvent removed *in vacuo*, giving **1** as a pure yellow oil (5.95 g, 93 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.82 (2H, d, ^{3}J = 8.5 Hz, Ar*H*), 7.35 (2H, d, ^{3}J = 8.5 Hz, Ar*H*), 5.82 (1H, m, C*H*=CH_2), 5.20 (2H, m, CH=CH_2), 4.18 (2H, t, ^{3}J = 4.8 Hz, CH_2), 3.95 (2H, m, CH_2CH=CH_2), 3.64 (2H, t, ^{3}J = 4.8 Hz, CH_2), 2.45 (3H, s, CH_3); ESMS: *m/z* calc. for $[M + Na]^+$ 279.07, found 279.07.

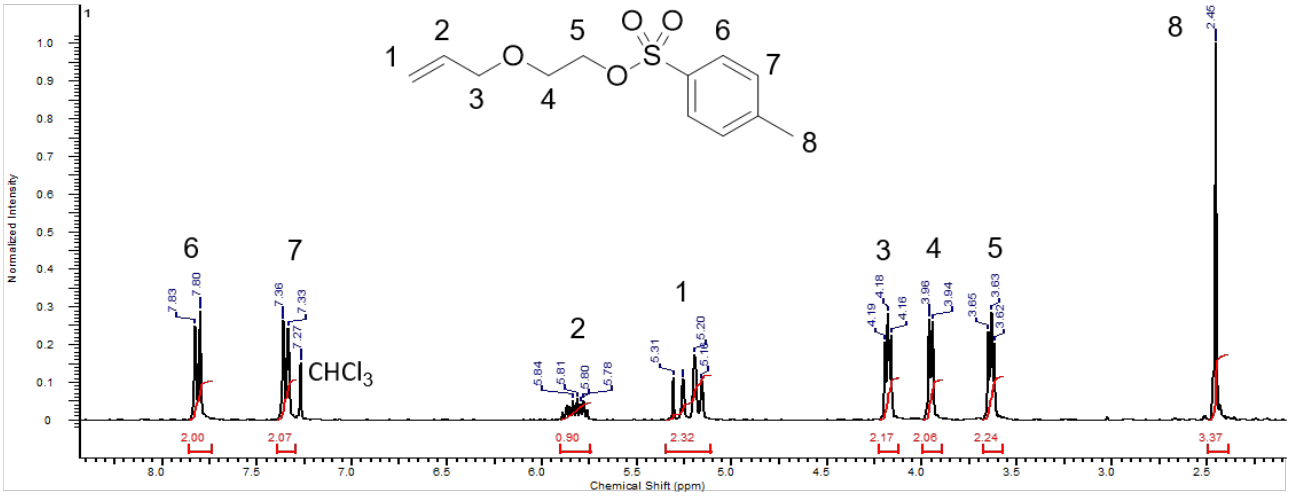


Figure S1. ^{1}H NMR spectrum of **1** in $CDCl_3$.

1-(2-(Allyloxy)ethoxy)-3-iodobenzene (2).

3-Iodophenol (2.50 g, 11.4 mmol), **1** (3.62 g, 13.6 mmol), K_2CO_3 (3.14 g, 22.7 mmol), and KI (0.38 g, 2.27 mmol) were heated in DMF (500 ml) at 150 °C for three hours under a nitrogen atmosphere. The mixture was filtered and solids washed with acetone (50 ml). The solvent was removed *in vacuo*, and 1M HCl (aq) (100 ml) was added to the residue, which was then extracted twice with CH_2Cl_2 (100 ml). The combined organic layers were then washed with 1M NaOH (aq) (2 x 100 ml) and brine (1 x 100 ml). The CH_2Cl_2 layer was separated and dried over $MgSO_4$, after which it was filtered and the solvent removed, giving **2** as a brown oil (3.39 g, 98 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.99 (1H, br, Ar*H*), 7.26 (1H, m, Ar*H*), 6.97 (1H, t, ^{3}J = 8.2 Hz, Ar*H*), 6.87 (1H, m, Ar*H*), 5.87 (1H, m, CH_2CH=CH_2), 5.26 (2H, m, CH_2CH_2=CH_2), 4.07 (4H, m, CH_2), 3.77 (2H, t, ^{3}J = 4.7 Hz, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 159.2, 134.3, 130.6, 129.9, 123.7, 117.3, 114.2, 94.2, 72.2, 68.2, 67.5; ESMS: *m/z* calc. for $[M + Na]^+$ 326.99, found 326.81.

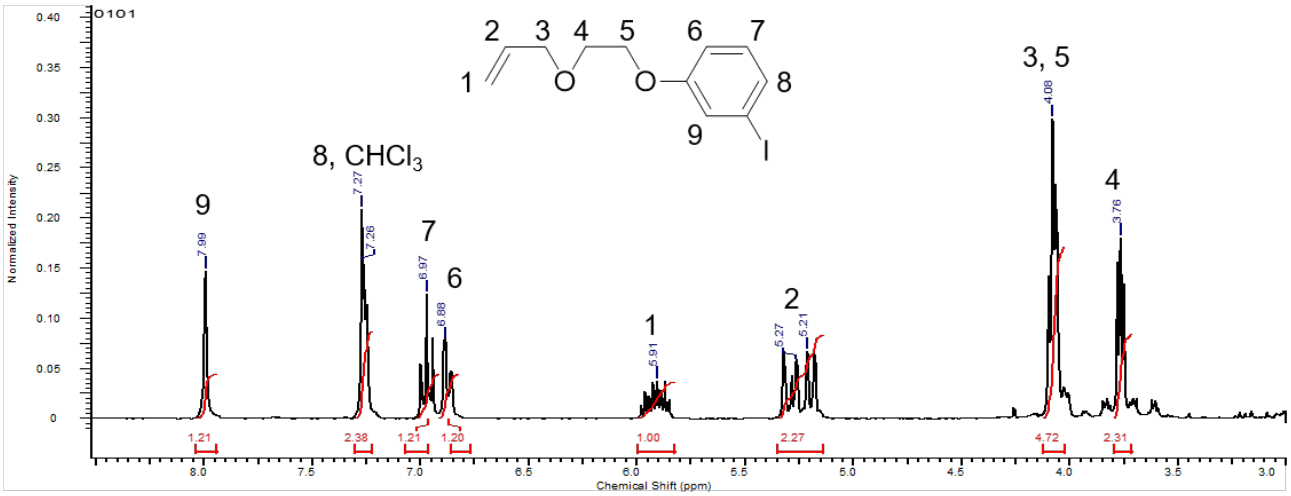


Figure S2. ^{1}H NMR spectrum of 2 in $CDCl_3$.

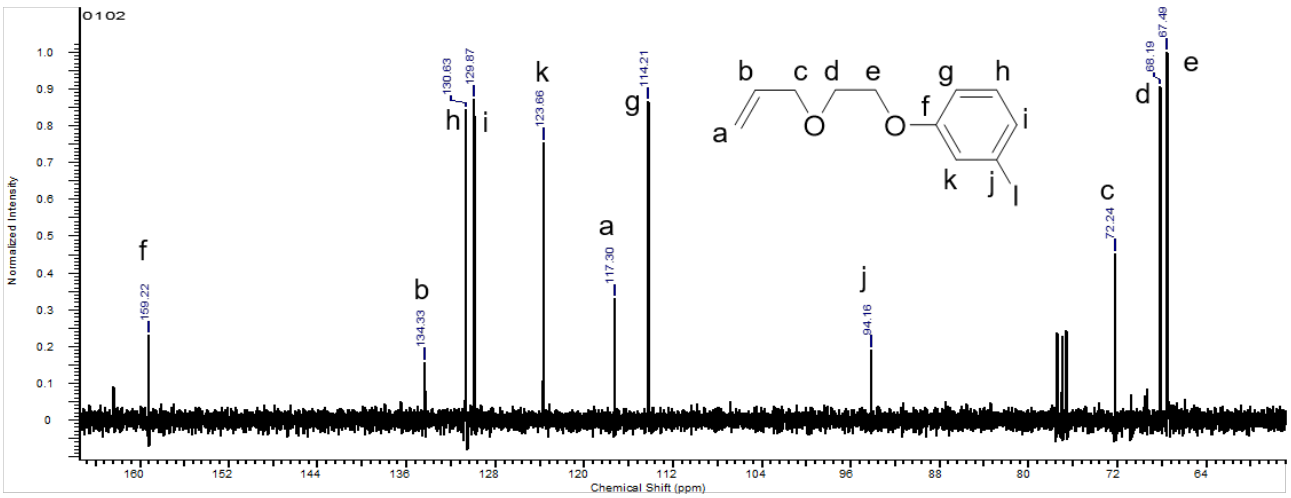


Figure S3. ^{13}C NMR spectrum of **2** in $CDCl_3$.

1-(3-(2-(Allyloxy)ethoxy)phenyl)-1*H*-imidazole (3).

Imidazole (1.68 g, 24.7 mmol), **2** (3.00 g, 9.86 mmol), Cs_2CO_3 (9.64 g, 29.6 mmol), Cu_2O (0.28 g, 1.97 mmol), salicylaldoxime (0.54 g, 3.94 mmol), and ascorbic acid (0.52 g, 2.96 mmol) were added to degassed dry acetonitrile (250 ml) under nitrogen, and refluxed for two nights. After cooling, the solvent was removed *in vacuo*, and CH_2Cl_2 was added (100 ml). The mixture was then filtered through Celite, and after solvent removal subjected to silica gel column chromatography eluted first with 1:1 ethyl acetate/hexane and then ethyl acetate, to give the product **3** as an white solid powder (1.70 g, 71 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.86 (1H, br, Im*H*), 7.37 (1H, t, ^{3}J = 8.4 Hz, Ar*H*), 7.28 (1H, br, Im*H*), 7.21 (1H, br, Im*H*), 6.96 (2H, m, Ar*H*), 5.95 (1H, ddt, ^{3}J = 17.3, 10.4, 5.7 Hz, CH_2CH=CH_2), 5.27 (2H, m, CH_2CH_2=CH_2), 4.19 (2H, t, ^{3}J = 4.7, CH_2), 4.11 (2H, d, ^{3}J = 5.7 Hz, CH_2), 3.83 (2H, t, ^{3}J = 4.7 Hz, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 159.8, 138.3, 135.5, 134.3, 130.6, 130.2, 118.1, 117.4, 113.6, 113.0, 108.3, 72.3, 68.2, 67.7; ESMS: *m/z* calc. for $[M + H]^+$ 245.1, found 245.1

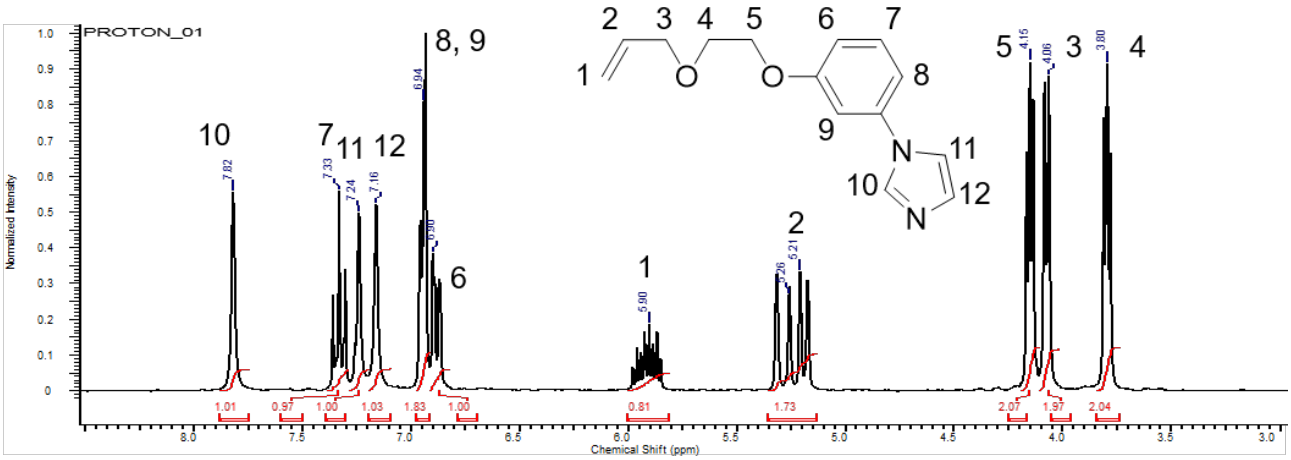


Figure S4. ^{1}H NMR spectrum of **3** in $CDCl_3$.

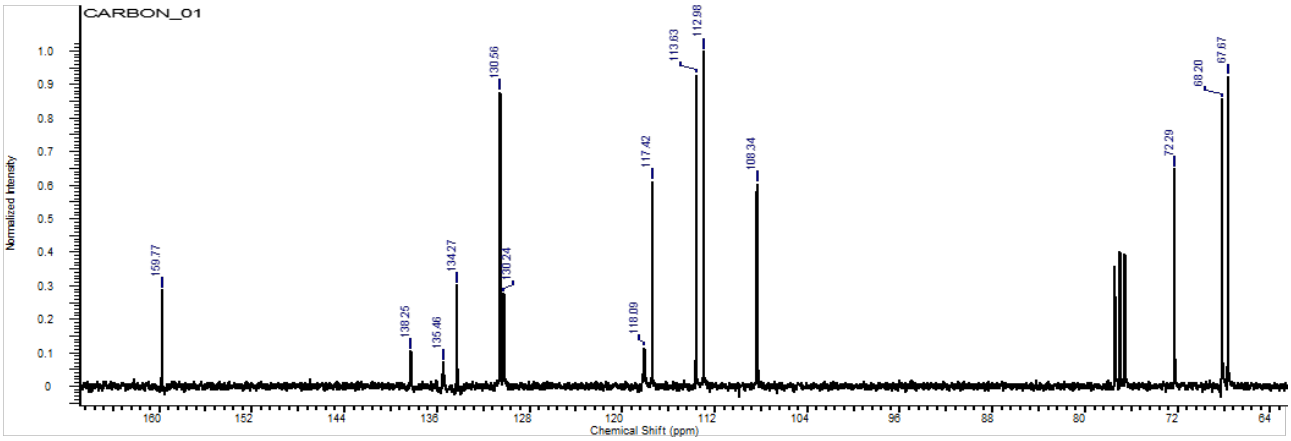
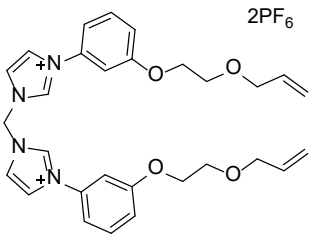


Figure S5. ^{13}C NMR spectrum of **3** in $CDCl_3$.

Allyl-appended methylene-bis-imidazolium pre-macrocycle 4.



Diiodomethane (0.50 g, 1.86 mmol) and **3** (1.00 g, 4.09 mmol) were dissolved in acetonitrile (5 ml) and heated under microwave irradiation for three hours at 130 °C. A white precipitate was obtained upon de-capping and cooling of the microwave vial, which was collected by filtration and redissolved in hot water (20 ml). Addition of NH_4PF_6 (aq, sat.) caused a thick white precipitate to form, which was collected, washed with water (20 ml), and dried under high vacuum conditions, giving pure **4**. A second crop was obtained by removing the solvent from the remaining reaction mixture and adding ethyl acetate to the residue, giving a white precipitate. The same anion exchange procedure was performed on this, resulting in a combined yield of 0.63 g (19 %). ^{1}H NMR (300 MHz, CD_3CN) δ (ppm) 9.99 (2H, br, Im*H*), 8.30 (4H, m, Im*H*), 7.50 (2H, t, ^3J = 8.4 Hz, Ar*H*), 7.29 (4H, m, Ar*H*), 7.15 (6H, m, Ar*H* + Im_2CH_2), 5.80 (2H, m, CH_2CH=CH_2), 5.10 (4H, m, CH_2CH_2=CH_2), 4.16 (4H, t, ^3J = 4.6, CH_2), 3.96 (4H, d, ^3J = 5.3 Hz, CH_2), 3.70 (4H, t, ^3J = 4.6 Hz, CH_2); ^{13}C NMR (75 MHz, 10:1 $CDCl_3$/CD_3OD) δ (ppm) 159.8, 146.8, 134.9, 133.9, 130.9, 122.7, 117.8, 117.2, 114.2, 107.8, 71.9, 67.9, 67.6; HR-ESMS: *m/z* calc. for $[M - 2PF_6]^{2+}$ 251.1285, found 251.1279; mp 129 °C.

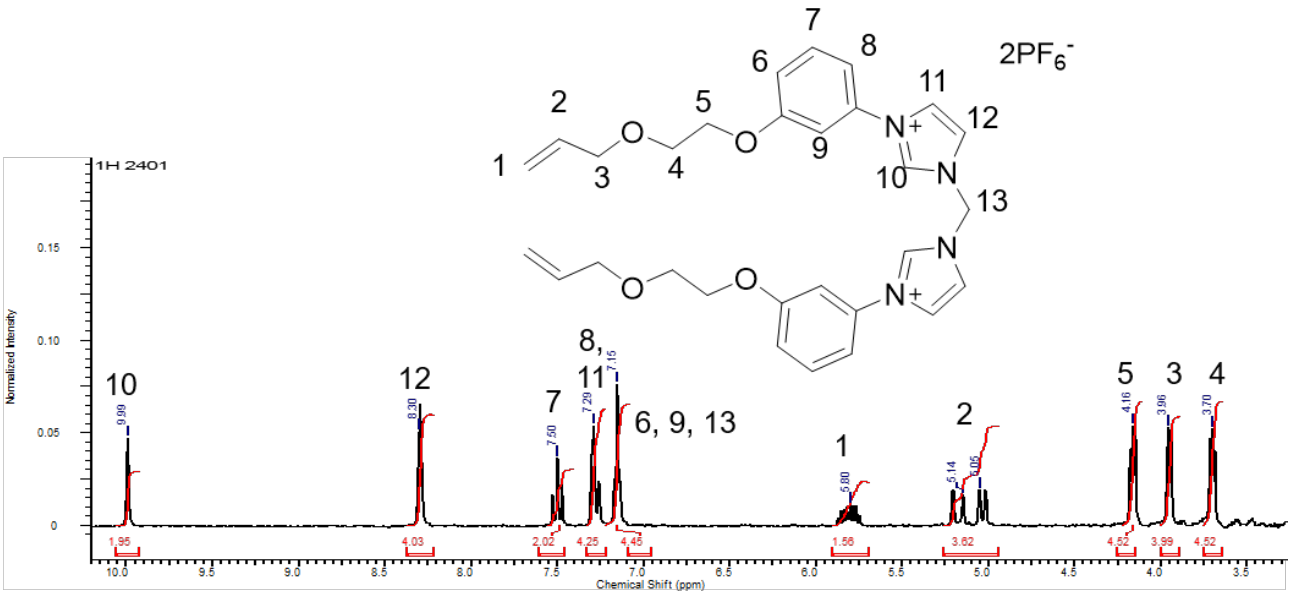


Figure S6. ^{1}H NMR spectrum of **4** in CD_3CN.

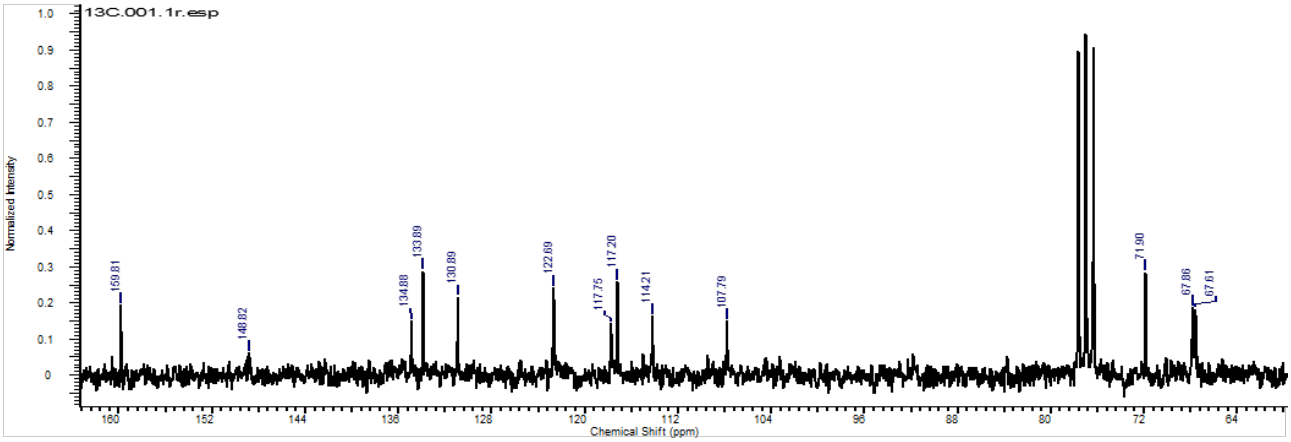


Figure S7. ^{13}C NMR spectrum of **4** in 10:1 $CDCl_3/CD_3OD$.

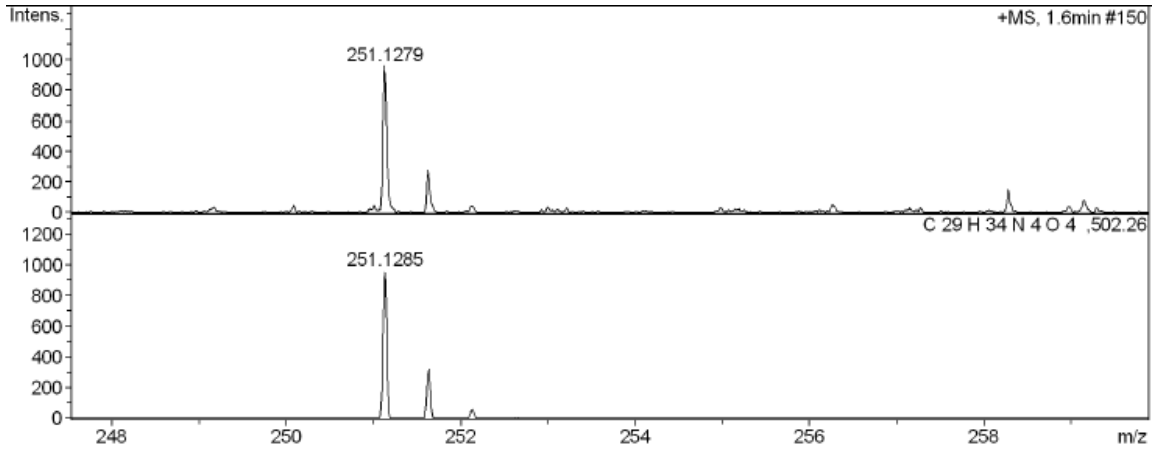
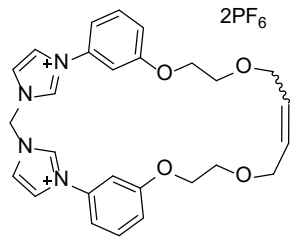


Figure S8. HR-ESI MS of **4** showing experimental (top) and calculated (bottom) spectra.

Methylene-bis-imidazolium-methylene macrocycle 5.



Bis-imidazolium compound **4** (30 mg, 3.92 x 10^{-5} mol) was stirred with TBA Cl (11 mg, 3.92 x 10^{-5} mol) in dry CH_2Cl_2 (20 ml) under a nitrogen atmosphere. Grubbs II catalyst (1.5 mg, 5 wt%) was added and the solution was stirred overnight. After TLC eluted with 17:2:1 acetonitrile/water/KNO_3 (aq, sat.) confirmed that the macrocycle precursor had been consumed, the solvent was removed *in vacuo*, and the residue loaded onto a preperative TLC plate using acetone. The plate was eluted with the same KNO_3 solvent system, giving one major band which corresponded to the macrocycle. This was isolated and the silica was extracted using 97:2:1 acetone/water/NH_4PF_6 (aq, sat.). Removal of the organic solvent gave a white precipitate consisting of **5**, which was collected by filtration, washed with water, and dried under high vacuum, giving the product (6.0 mg, 20 %). ^{1}H NMR (300 MHz, CD_3CN) δ (ppm) 9.44 (2H, br, Im*H*), 7.91 (2H, br, Im*H*), 7.88 (2H, br, Im*H*), 7.61 (2H, t, ^{3}J = 8.1 Hz, Ar*H*), 7.28 (6H, m, Ar*H*), 6.66 (2H, s, Im_2CH_2), 5.82 (2H, m, C*H*=C*H*), 4.24 (4H, t, ^{3}J = 4.1 Hz, CH_2), 4.03 (4H, m, CH_2), 3.79 (4H, t, ^{3}J = 4.1 Hz, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 161.2, 136.7, 133.1, 132.9, 130.4, 124.7, 124.2, 116.5, 115.8, 112.2, 72.9, 71.9, 71.7, 69.3; HR-ESMS: *m/z* calc. for $[M - PF_6]^+$ 619.1903, found 619.1898 (singly charged); mp 189 °C (decomp.).

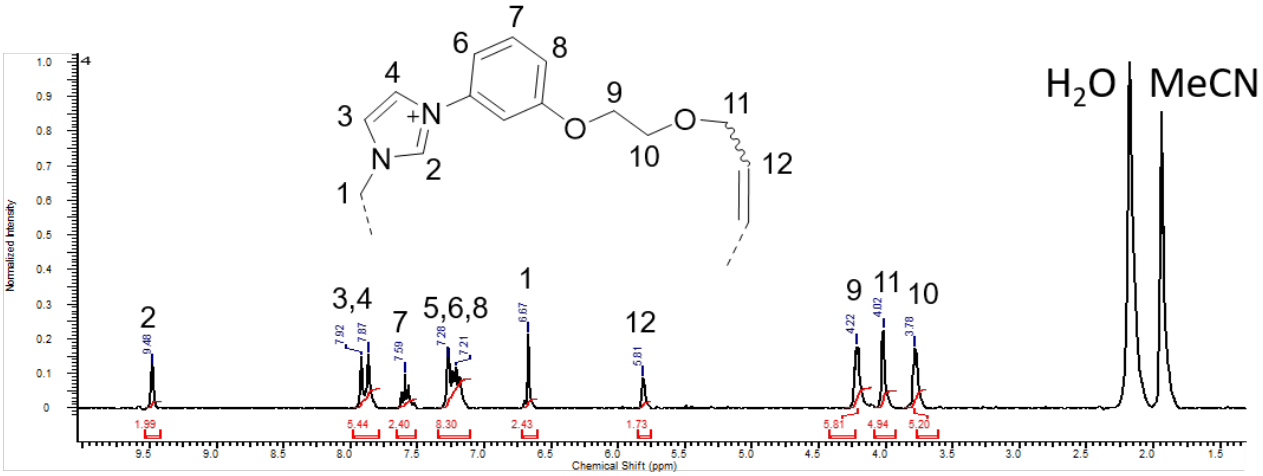


Figure S9. ^{1}H NMR spectrum of **5** in CD_3CN

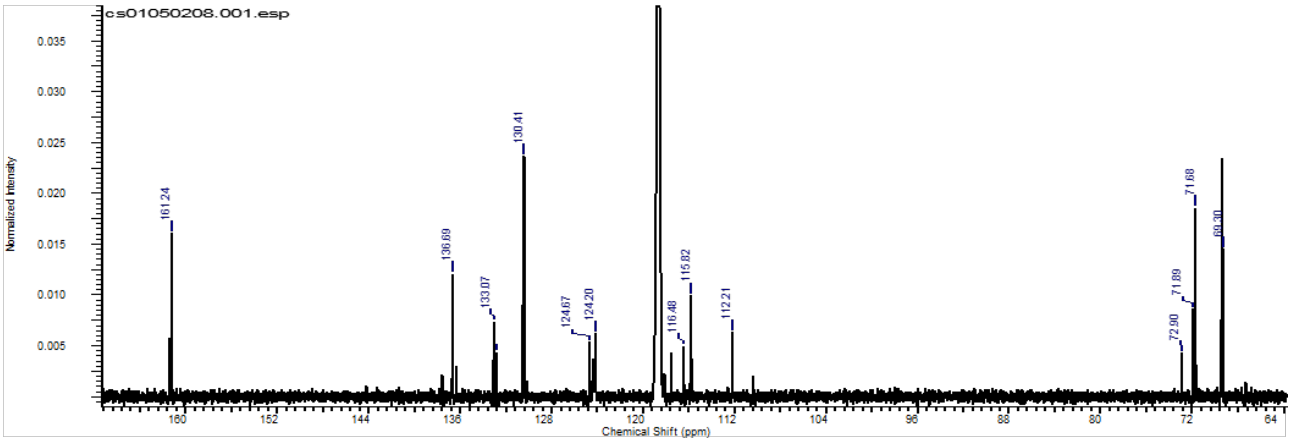


Figure S10. ^{13}C NMR spectrum of **5** in CD_3CN

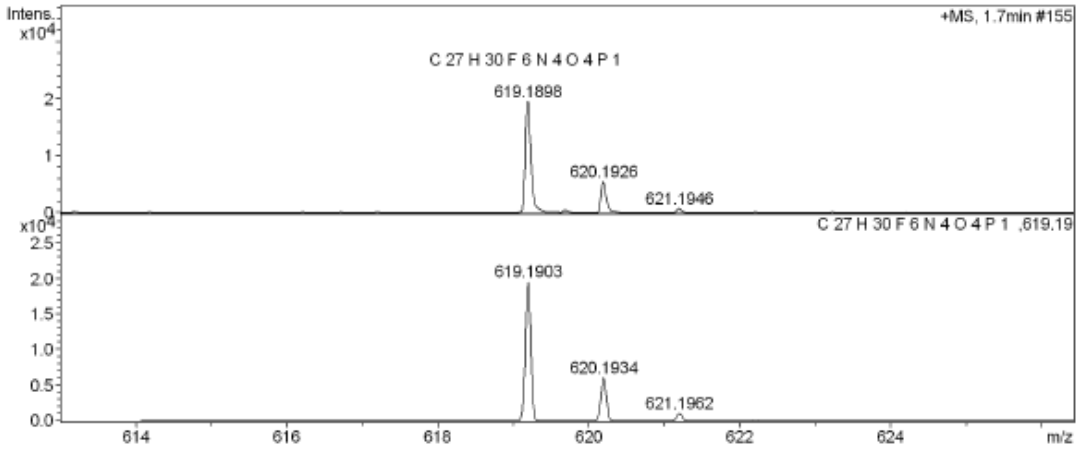
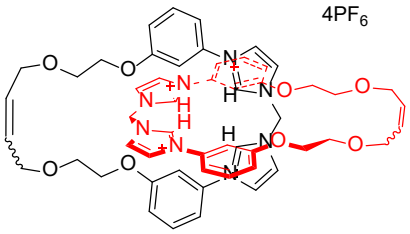


Figure S11. HR-ESI MS of **5** showing experimental (top) and calculated (bottom) spectra.

Methylene-bis-imidazolium catenane 6.



Bis-imidazolium compound **4** (100 mg, 7.84 x 10^{-5} mol) was stirred with TBA Cl (18.3 mg, 3.92 x 10^{-5} mol) in dry CH_2Cl_2 (20 ml) under a nitrogen atmosphere. Grubbs II catalyst (5.0 mg, 5 wt%) was added and the solution was stirred overnight. After TLC eluted with 17:2:1 acetonitrile/water/KNO_3 (aq, sat.) confirmed that the macrocycle precursor had been consumed, the solvent was removed *in vacuo*, and the residue loaded onto a preperative TLC plate using acetone. The plate was eluted with the same KNO_3 solvent system, giving two major bands which corresponded to the macrocycle **5** and the catenane **6**. These were isolated and the silica was extracted separately using 97:2:1 acetone/water/NH_4PF_6 (aq, sat.). Removal of the organic solvent gave a white precipitate which was collected by filtration, washed with water, and dried under high vacuum, giving **6** (9.9 mg, 16.5 %) and **5** (5.1 mg, 8.5 %). ^{1}H NMR (300 MHz, CD_3CN) δ (ppm) 10.20 (2H, br, Im*H*), 8.28 (2H, br, Im*H*), 8.21 (2H, br, Im*H*), 7.86 (2H, s, Ar*H*), 7.44 (2H, t, ^{3}J = 8.2 Hz, Ar*H*), 7.28 (2H, m, Ar*H*), 7.10 (4H, m, Ar*H*, Im2CH_2), 5.70 (2H, m, C*H*=C*H*), 4.15 (4H, t, ^{3}J = 4.2 Hz, CH_2), 3.94 (4H, m, CH_2), 3.67 (4H, t, ^{3}J = 4.2 Hz, CH_2); ^{13}C NMR (125 MHz, CD_3CN) δ (ppm) 161.4, 136.7, 132.8, 130.5, 130.4, 124.4, 124.2, 117.5, 115.8, 110.5, 72.9, 71.9, 71.8, 69.4; HR-ESMS: *m/z* calc. for $[M - PF_6]^+$ 1383.3465, found 1383.3466 (singly charged); mp 110 °C.

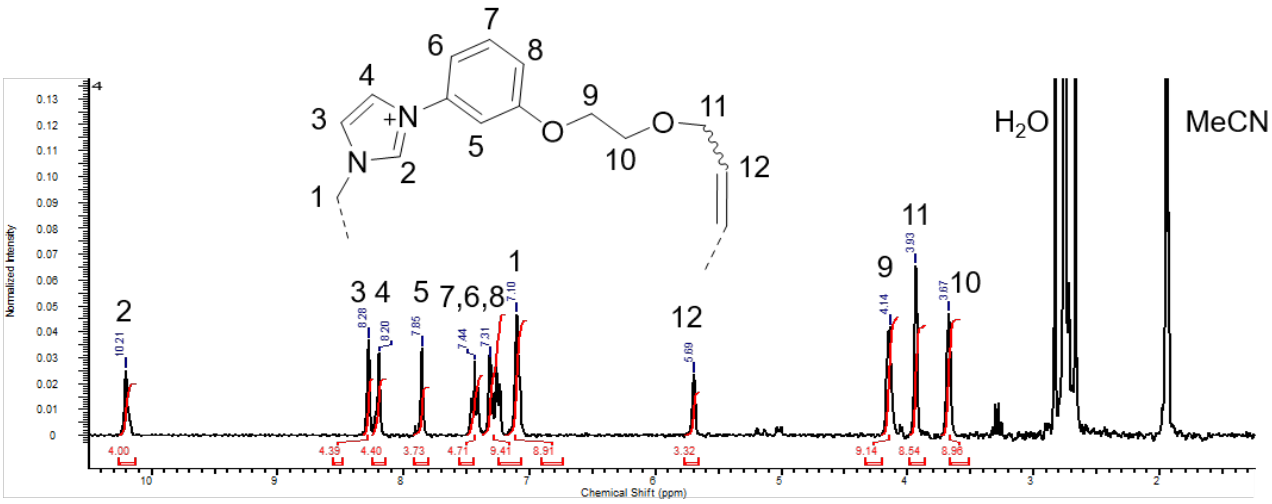


Figure S12. ^{1}H NMR spectrum of **6** in CD_3CN

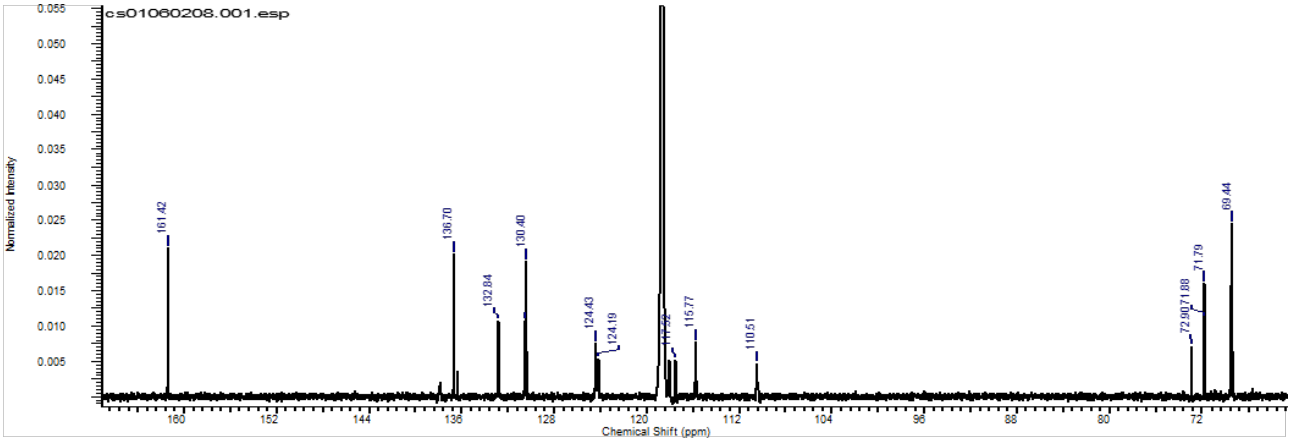


Figure S13. ^{13}C NMR spectrum of **6** in CD_3CN

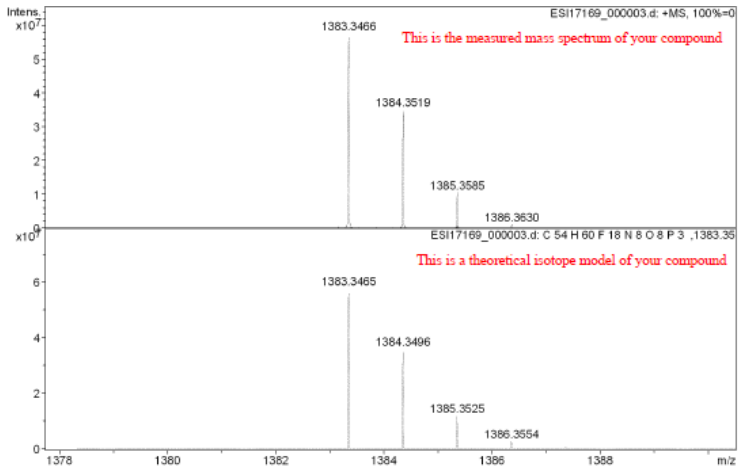


Figure S14. HR-ESI MS of **6** showing experimental (top) and calculated (bottom) spectra.

Crystallography

Single crystal X-ray diffraction data were collected using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) on a Nonius KappaCCD diffractometer equipped with a Cryostream N_2 open-flow cooling device,[4] and the data were collected at 150(2) K.

Series of ω-scans were performed in such a way as to collect every independent reflection to a maximum resolution of 0.77 Å, aiming for 99.5 % completeness. Cell parameters and intensity data (including inter-frame scaling) were processed using the DENZO-SMN package.[5]

The structures were solved by direct methods using the SIR92[6] software or by charge flipping using Superflip.[7] The structures were refined using full-matrix least-squares on F^2 or F within the CRYSTALS suite.[8] All non-hydrogen atoms were refined with anisotropic displacement parameters, unless specified otherwise. Disordered portions were modelled using refined partial occupancies. Geometric and vibrational restraints were applied where appropriate to ensure physically reasonable models. The H atoms were usually located in the difference map, but those attached to carbon atoms were repositioned geometrically. Protic H atoms which could not be located in the difference map were positioned to satisfy hydrogen bonding requirements. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularise their geometry (C-H in the range 0.93-0.98 Å, N-H in the range 0.86-0.89 Å, and O-H = 0.82 Å and isotropic displacement factors in the range 1.2-1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.

After the construction of a stable, physically reasonable, and complete model, the weights were optimised,[9,10] anomalous reflections were omitted, and absent high-angle data (in the case of poorly diffracting samples) was pruned using the Wilson plot. This generally led to convergence of the refinement, giving the final structure.

Notes and parameters for each structure are given below.

Bis-imidazolium Macrocycle Precursor 4 – Hexafluorophosphate salt

Crystals were grown by gaseous diffusion of diisopropyl ether into an acetone solution of **4**. The $2PF_6^-$ salt crystallised with Z' = 2, with slightly different conformations being adopted by the two cationic species. Although the anions are included in close proximity to the imidazolium units, satisfying electrostatic requirements, there are no strong hydrogen bonds formed, which is not unexpected given the diffuse charge of the PF_6^- anion.

The sample was found to diffract very weakly, which was ascribed to the lack of rigidity in the pendant arms of the molecule. For this reason, many of the weak reflections were measurements of noise rather than data. Examination of the Wilson plot after full construction and refinement of the model led to omission all reflections with $\sin^2(\theta/\lambda) > 0.2384$. Upon filtering the reflections in this way the R-factor dropped significantly, and convergence was observed. However, it did reduce the ratio of reflections to parameters to 6.69. Since the weak reflections could not be measured, this was regarded as discarding only spurious data and was therefore justified in this case.

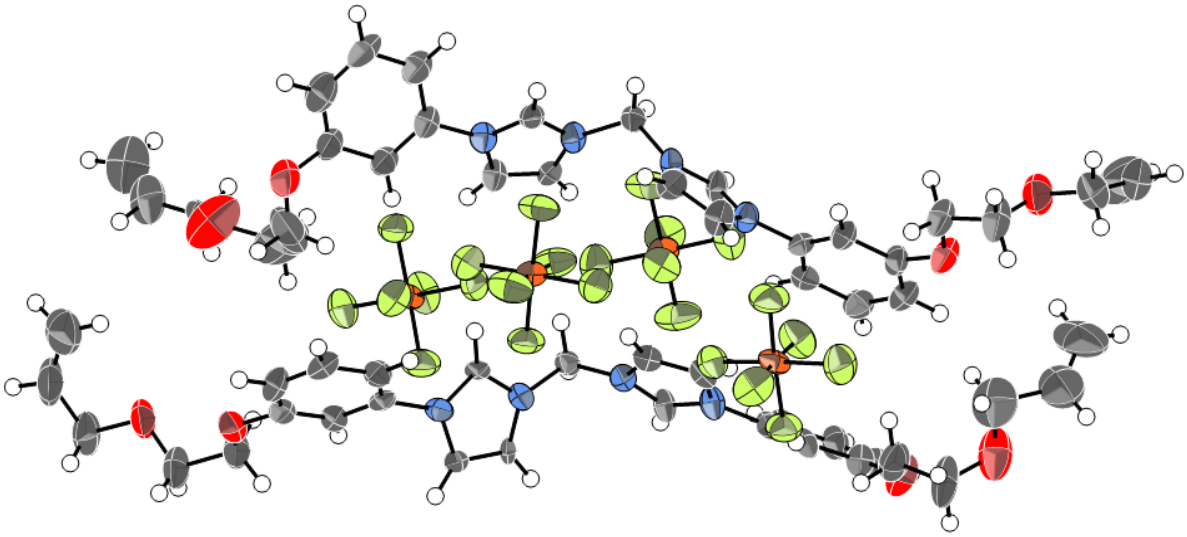
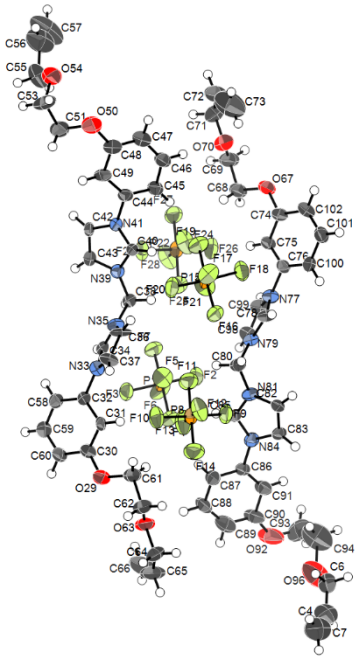


Figure S15. X-ray crystal structure of **4**. Anisotropic displacement parameters shown at 50 % probability.

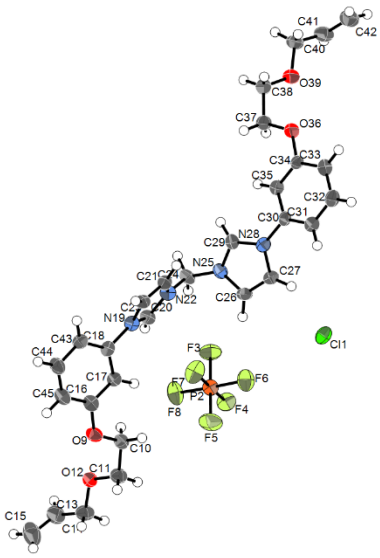


Chemical formula moiety	$C_{29}H_{34}N_4O_4$, $2(F_6P)$	
Empirical formula	$C_{29}H_{34}F_{12}N_4O_4P_2$	
Mr = 792.54	Orthorhombic (*P*na2$_1$)	
a = 19.7417 (4) Å	b = 8.2997 (2) Å	c = 41.8665 (10) Å
α = 90º	β = 90º	γ = 90º
V = 6859.8 (3) Å^3	Z = 8	
μ = 0.233 mm^{-1}	D_{calc} = 1.535 mg/m^3	
T = 150 (2) K		

43464 reflns collected, 12189 independent [R(int) = 0.173]
R1 = 0.0739, wR2 = 0.1673 [I>2 σ (I)].

Bis-imidazolium Macrocycle Precursor 4 – Mixed Chloride Salt

Crystals were grown by gaseous diffusion of diethyl ether into an acetonitrile solution of 2:1 **44**/TBA Cl.



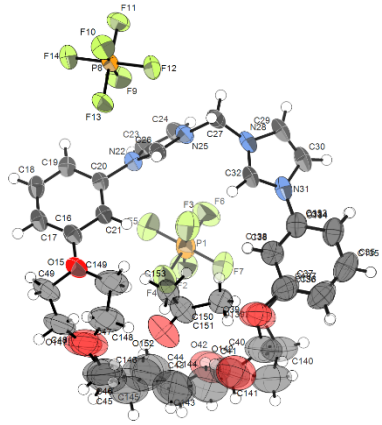
Chemical formula moiety	$C_{29}H_{34}N_4O_4$, Cl, F_6P	
Empirical formula	$C_{29}H_{34}Cl_1F_6N_4O_4P_1$	
Mr = 683.02	Monoclinic ($P2_1/c$)	
a = 22.115 (2) Å	b = 8.2941 (8) Å	c = 17.1145 (10) Å
α = 90º	β = 93.599 (5)º	γ = 90º
V = 31333.1 (5) Å^3	Z = 4	
μ = 0.250 mm^{-1}	D_{calc} = 1.448 mg/m^3	
T = 150 (2) K		

17197 reflns collected, 5220 independent [R(int) = 0.071]
R1 = 0.0747, wR2 = 0.1368 [I>2σ(I)].

Bis-imidazolium Macrocycle 5

Crystals were grown by gaseous diffusion of diisopropyl ether into an acetone solution of **5**.

The crystal diffracted very weakly, especially at high angle. Additionally, the disorder in the aliphatic portion of the molecule made it difficult to locate all the atoms, and numerous Fourier cycles were required. Eventually a bipartite model for the disorder was constructed, permitting anisotropic refinement using partial occupancies. Restraints were required both for geometric the thermal parameters, indicating that there is a very large degree of freedom within this volume. A partially occupied acetone was also located in the vicinity.



Chemical formula moiety	$C_{27}H_{30}N_4O_4$, 0.24(C_3H_6O), 2(F_6P)	
Empirical formula	$C_{27.72}H_{31.44}F_{12}N_4O_{4.24}P_2$	
Mr = 778.44	Monoclinic ($P2_1/c$)	
a = 24.6850 (4) Å	b = 6.87090 (10) Å	c = 19.9436 (3) Å
α = 90º	β = 97.1114 (6)º	γ = 90º
V = 3356.58 (9) Å^3	Z = 4	
μ = 0.237 mm^{-1}	D_{calc} = 1.540 mg/m^3	
T = 150 (2) K		

43900 reflns collected, 7619 independent [R(int) = 0.035]
R1 = 0.0866, wR2 = 0.2459 [I>2σ(I)].

Mass Spectrometry

IM-MS measurements were carried out on a modified Synapt HDMS system (Waters Corp., UK).[11] Specifically, ion mobility cell is replaced by a RF drift tube so a drift time of an ion can be measured directly. Instrument parameters were typically: capillary voltage, 1.0 kV; cone voltage, 100 V; trap collision energy, 20 V; bias, 20V; source temperature, 20 °C; backing pressure, 5 mBar. To optimize IM separation, measurements were recorded at 40-90V. The RF drift tube contained He_2 at a pressure of 2.5 Torr.

The collision cross section of model structures were calculated using a modified version of the MOBCAL program[12] and the projection approximation (PA) method was employed for the CCS calculation.

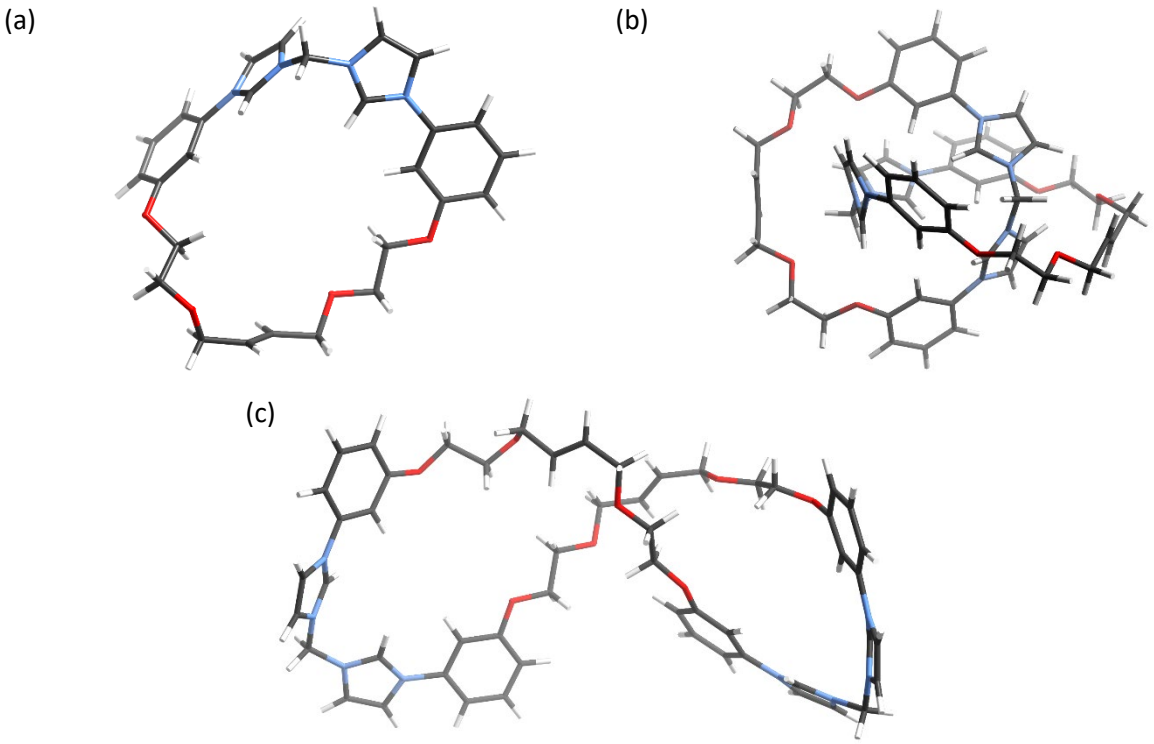


Figure S16. MMFF94 minimised models used for IM-MS analysis (calculated collision cross sections given in brackets): a) macrocycle **5** (147.08 Å^2); b) catenane **6** (204.93 Å^2); c) macrocyclic topological isomer of **6** (248.26 Å^2).

Anion Binding Titration Data

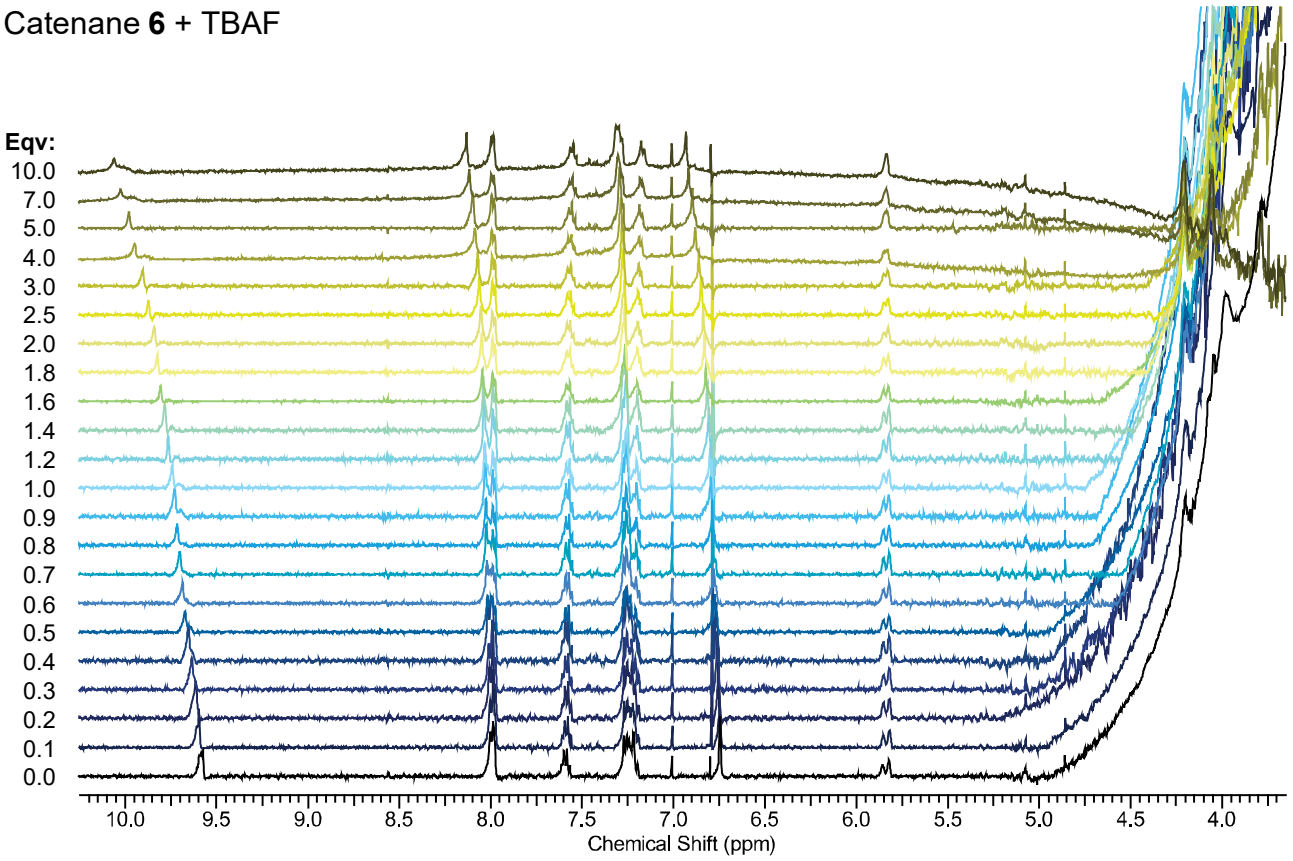


Figure S17. ^{1}H NMR spectra for catenane **6** titrated with TBAF in 9:1 MeCN:H_2O.

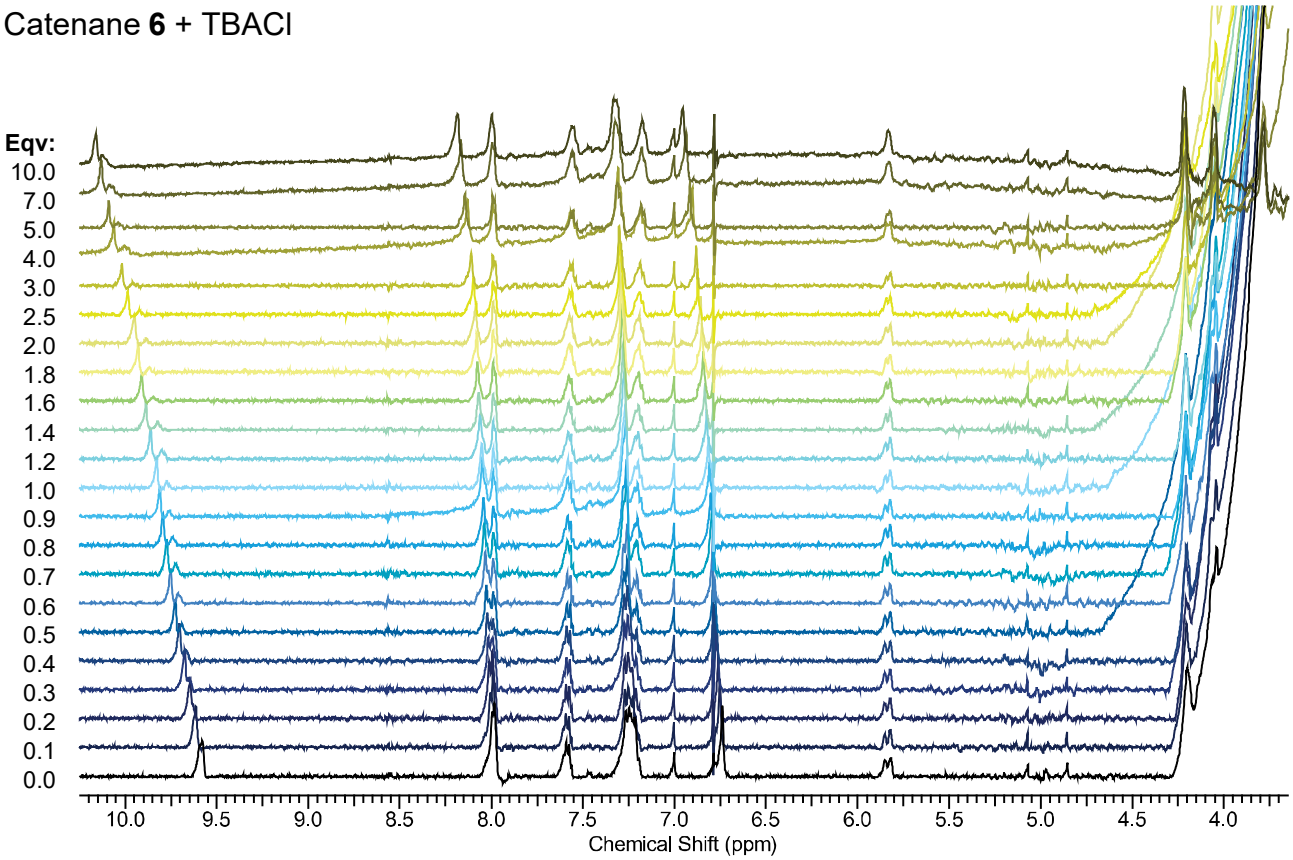


Figure S18. ^{1}H NMR spectra for catenane **6** titrated with TBACl in 9:1 MeCN:H_2O.

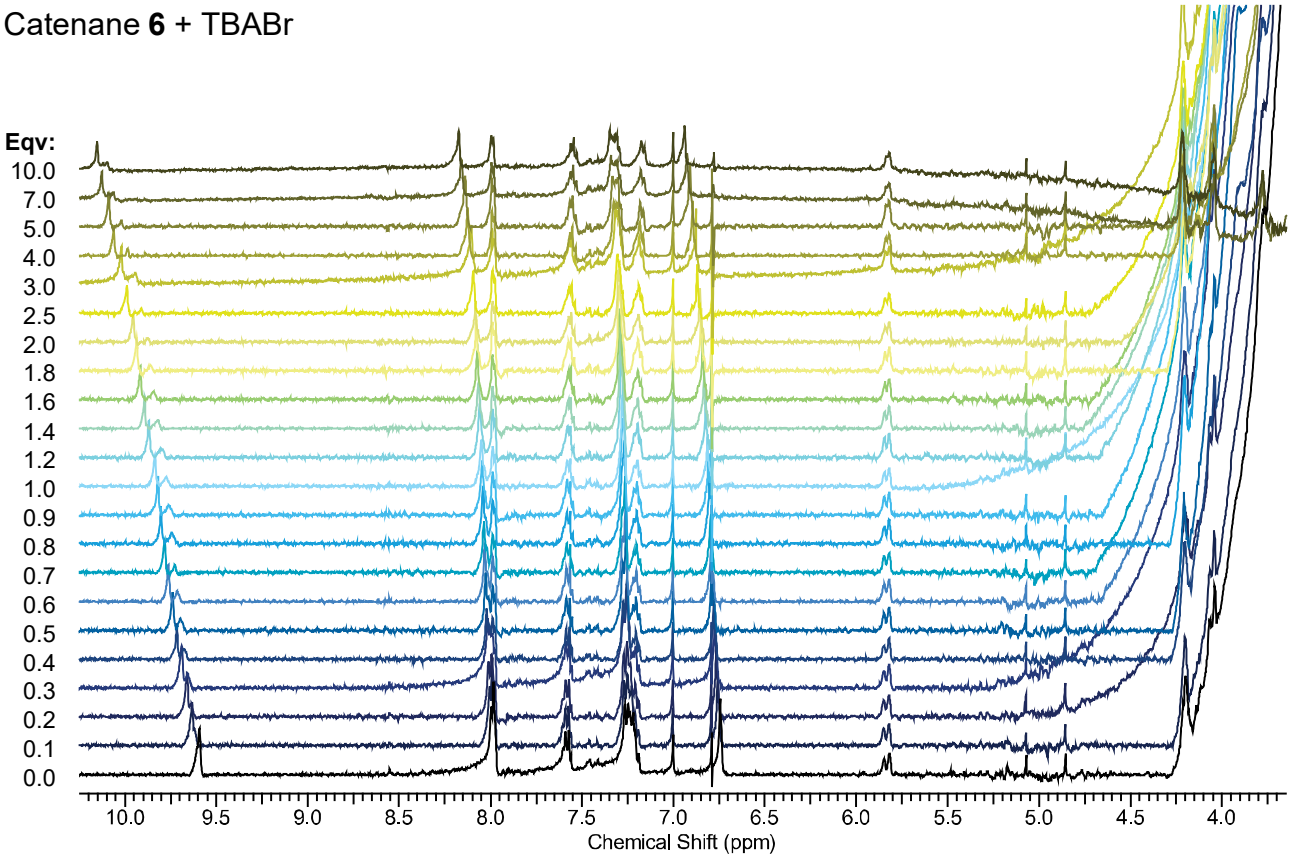


Figure S18. ^{1}H NMR spectra for catenane **6** titrated with TBABr in 9:1 MeCN:H_2O.

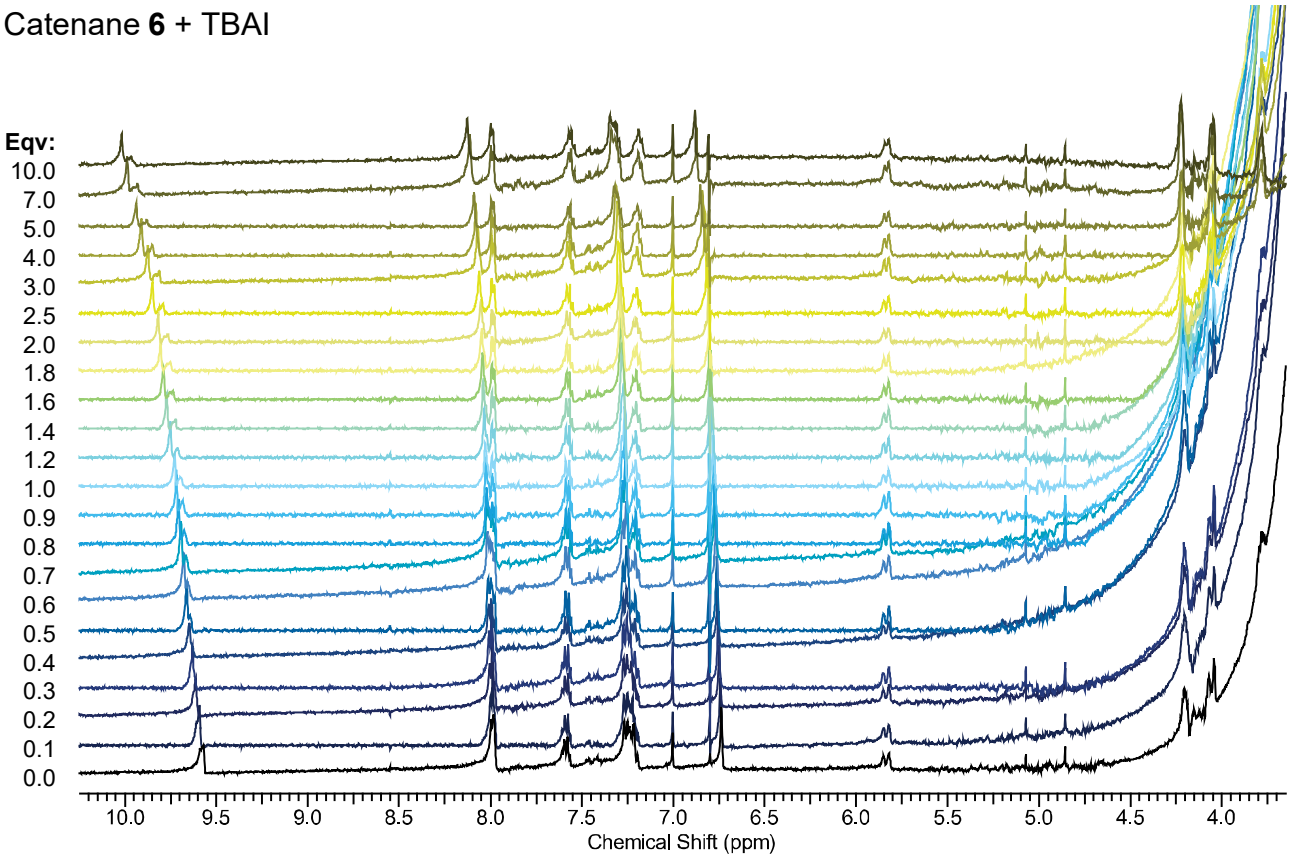


Figure S20. ^{1}H NMR spectra for catenane **6** titrated with TBAI in 9:1 MeCN:H_2O.

Catenane **6** + TBAOAc

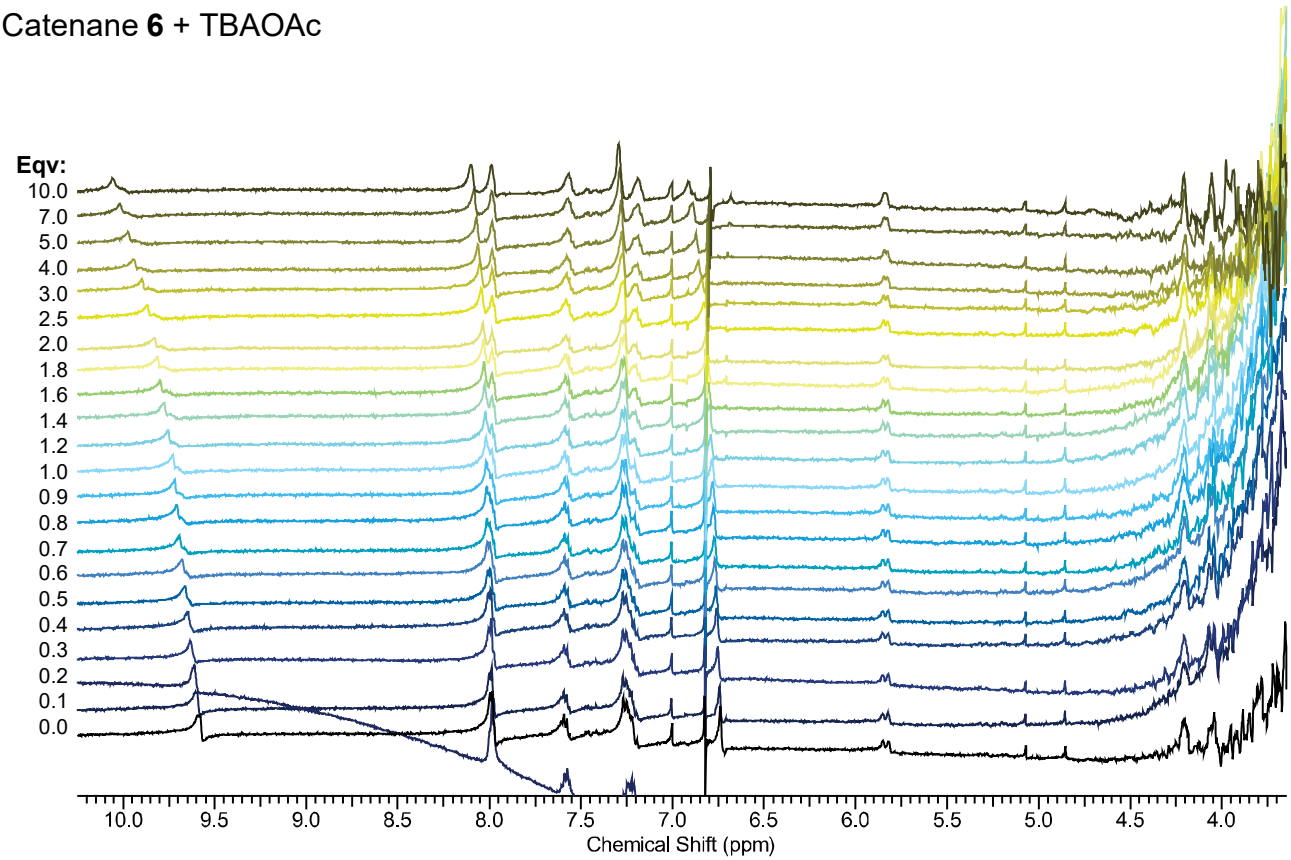


Figure S21. ^{1}H NMR spectra for catenane **6** titrated with TBAOAc in 9:1 MeCN:H_2O.

Macrocycle **5** + TBAF

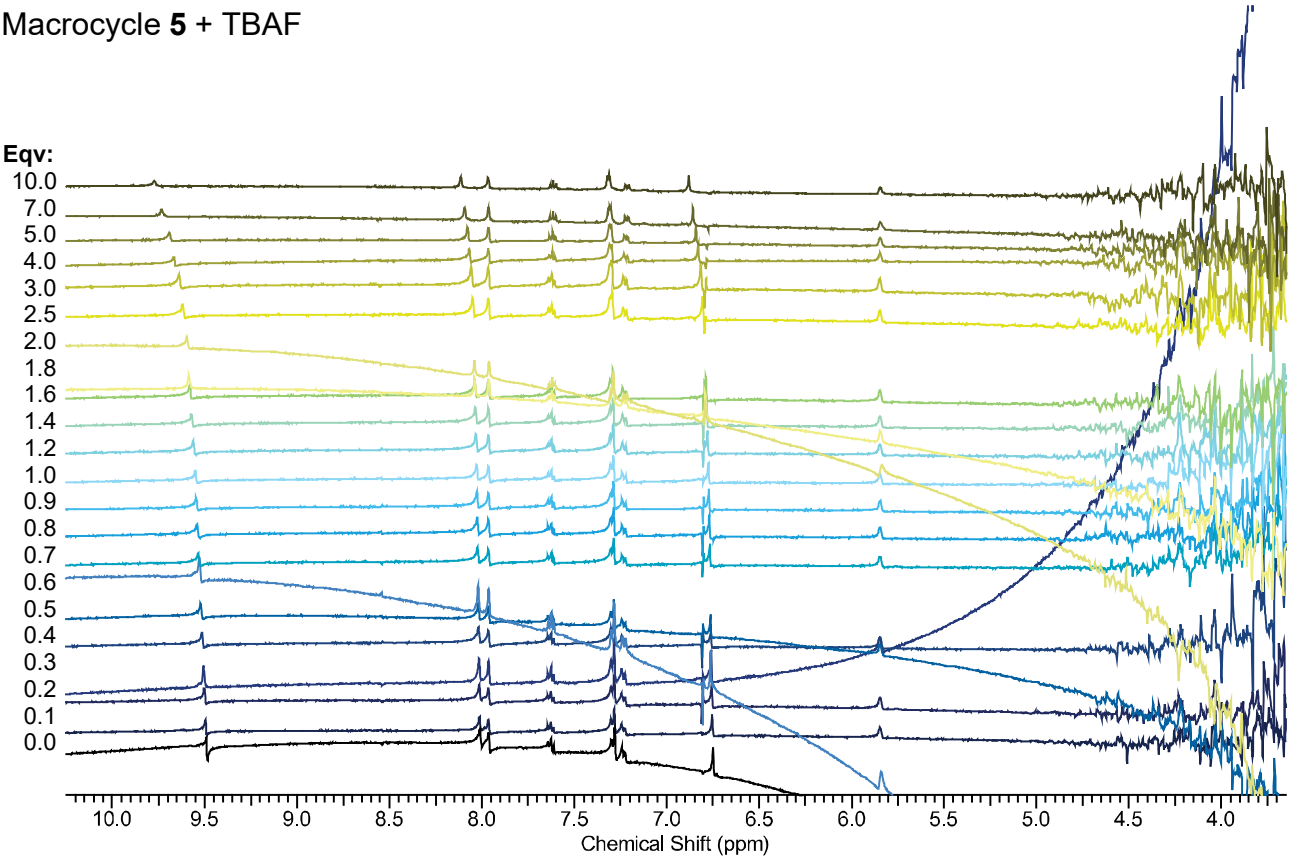


Figure S22. ^{1}H NMR spectra for macrocycle **5** titrated with TBAF in 9:1 MeCN:H_2O.

Macrocycle **5** + TBACl

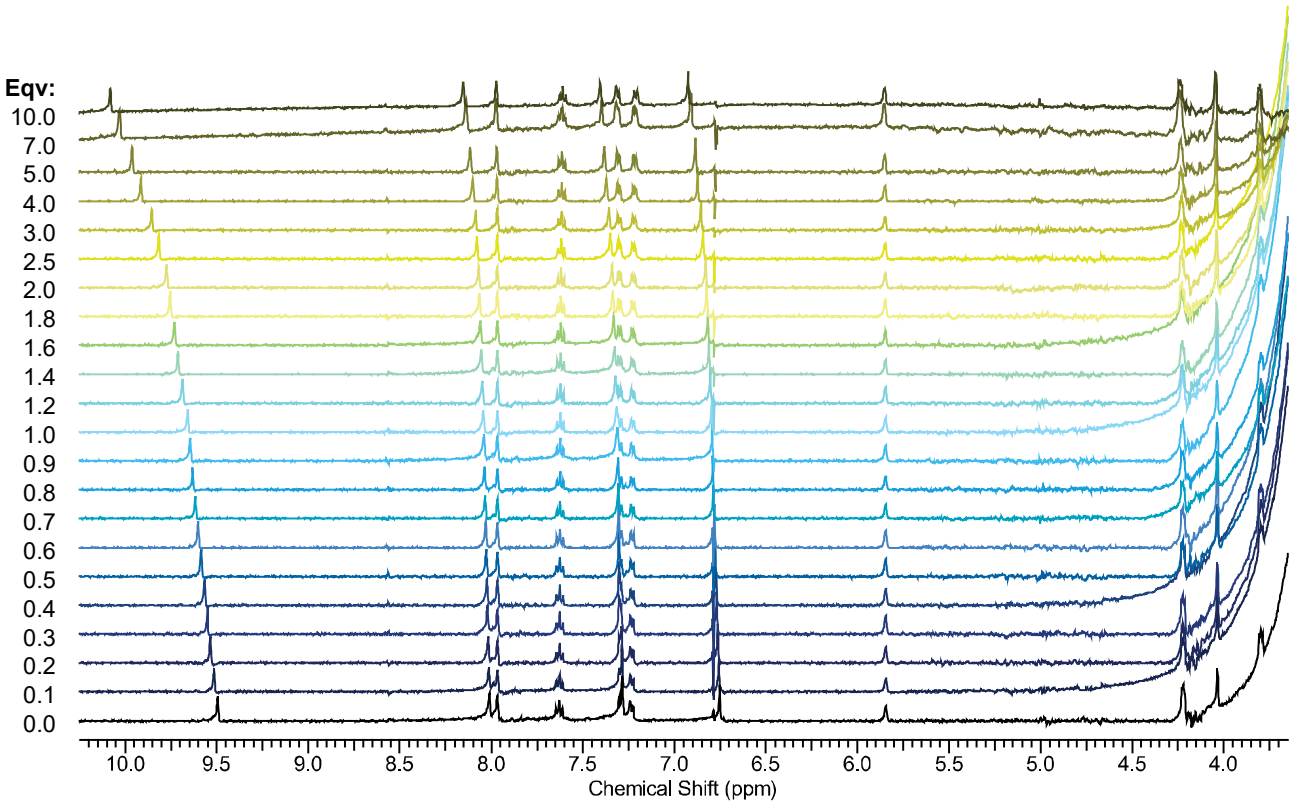


Figure S23. ^{1}H NMR spectra for macrocycle **5** titrated with TBACl in 9:1 MeCN:H_2O.

Macrocycle **5** + TBABr

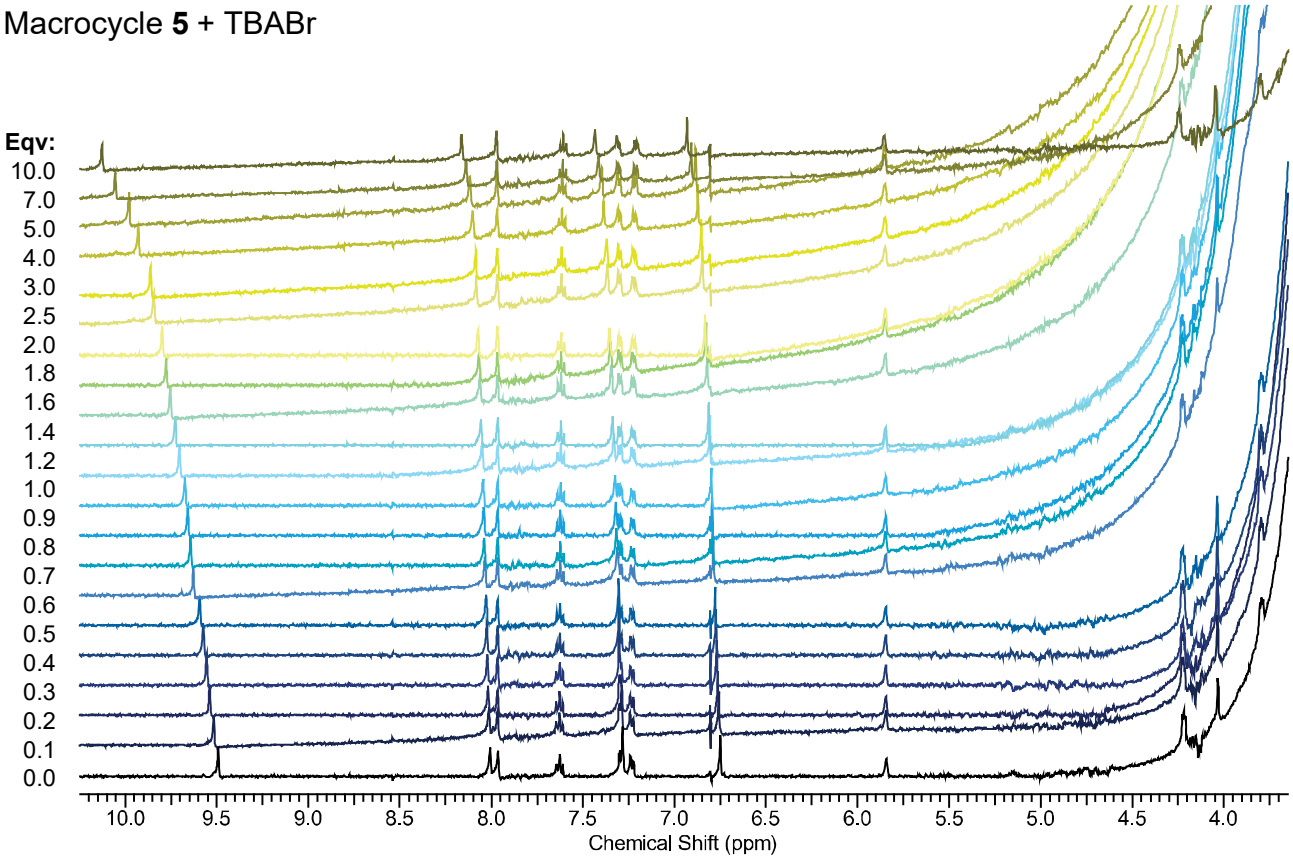


Figure S24. ^{1}H NMR spectra for macrocycle **5** titrated with TBABr in 9:1 MeCN:H_2O.

Macrocycle **5** + TBAI

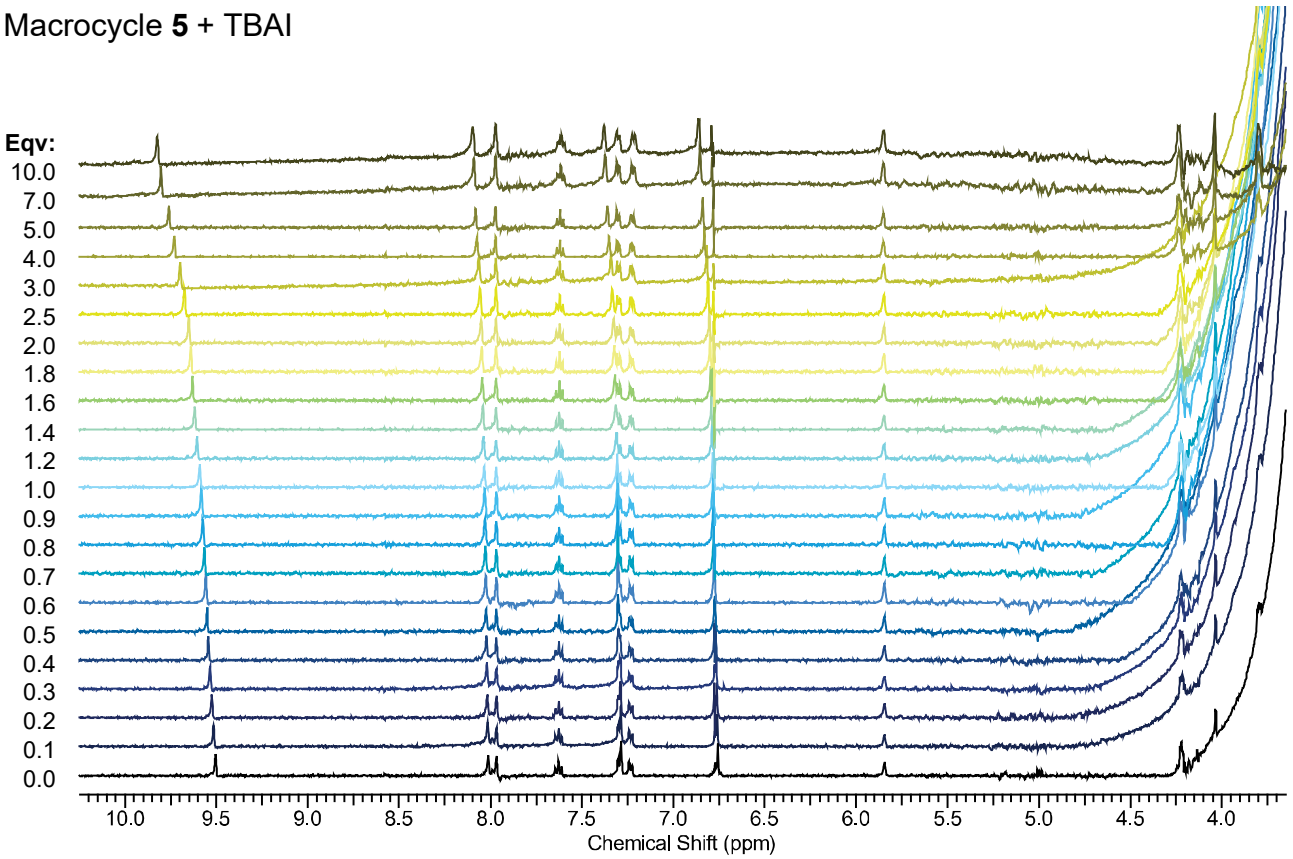


Figure S25. ^{1}H NMR spectra for macrocycle **5** titrated with TBAI in 9:1 MeCN:H_2O.

Macrocycle **5** + TBAOAc

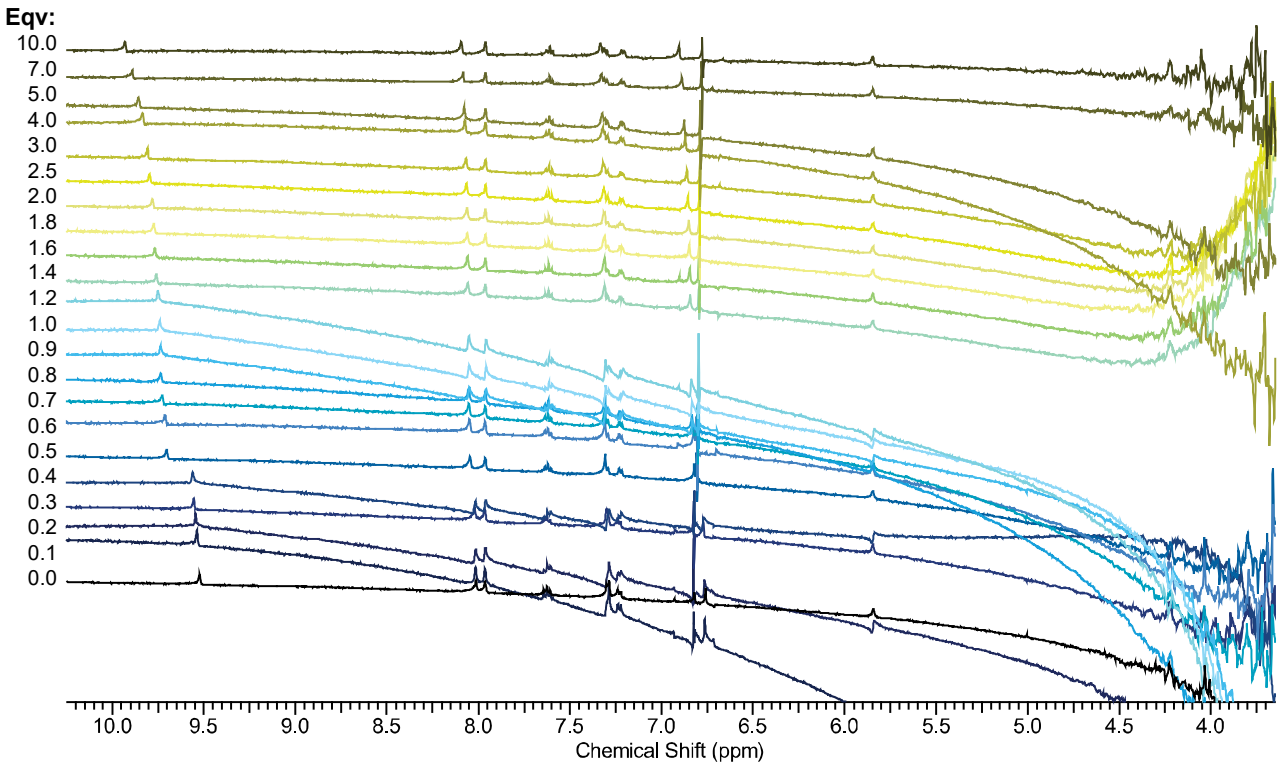


Figure S26. ^{1}H NMR spectra for macrocycle **5** titrated with TBAOAc in 9:1 MeCN:H_2O.

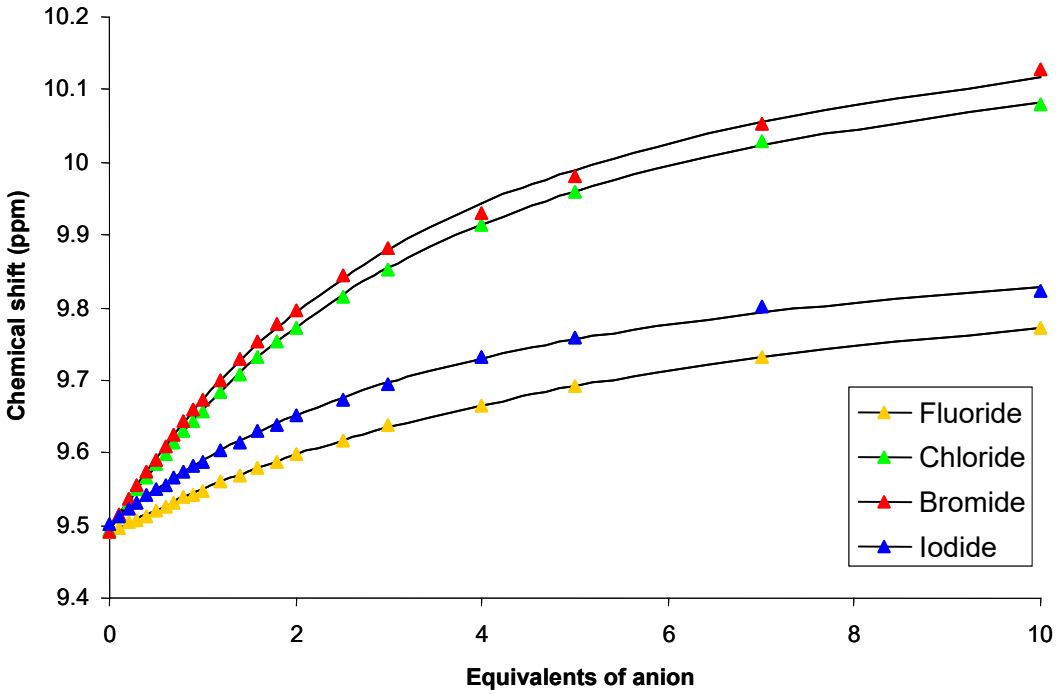


Figure S27. ^{1}H NMR titration binding curve for halide binding derived from the imidazolium C2 proton peak for macrocycle **5** (5:1 MeCN-d_3/H_2O, 293 K). Black lines represent the calculated fit (1:1 host:guest model).

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