Supporting Information for

A structural study of triazole and amide containing anion templated pseudorotaxanes

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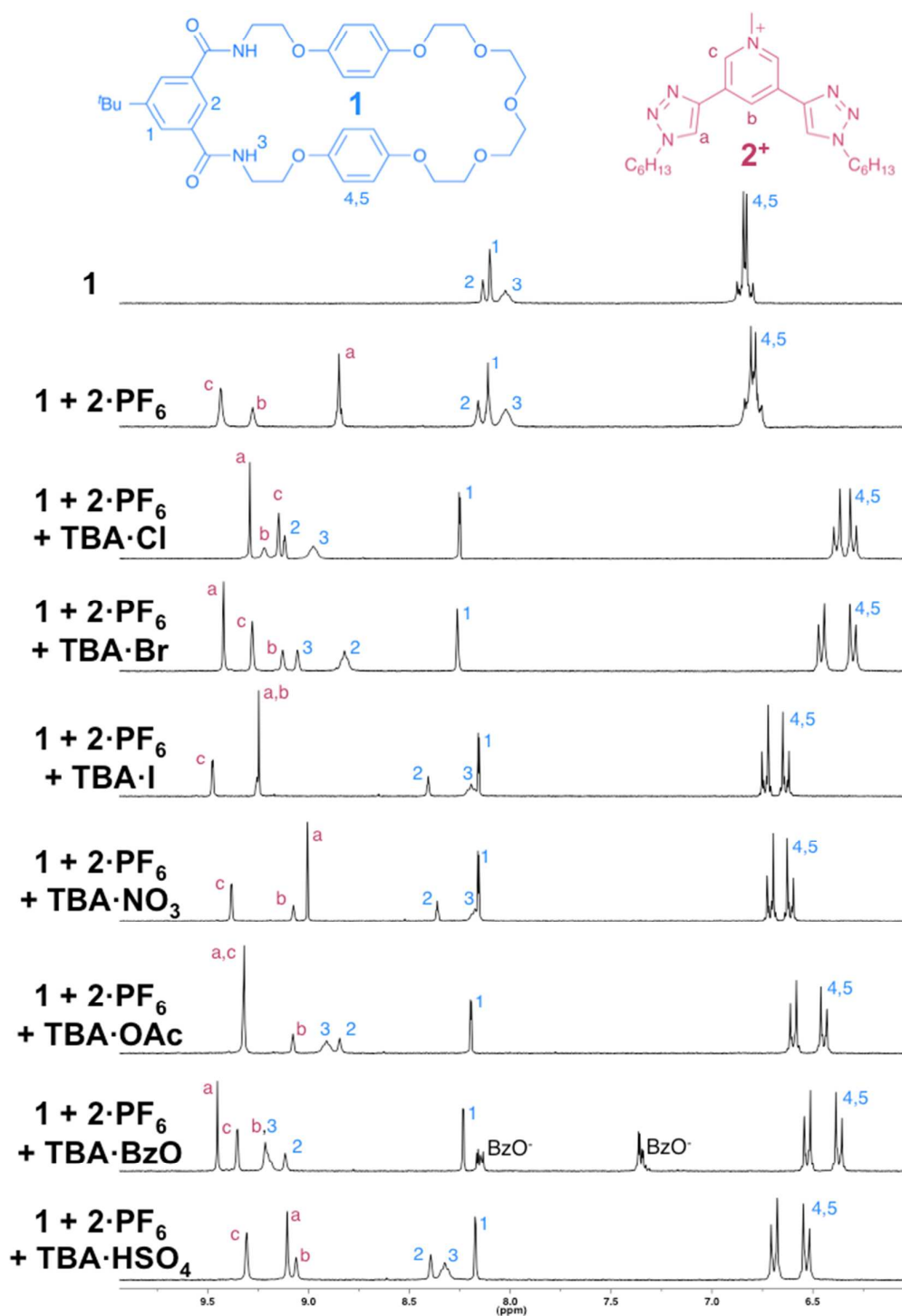
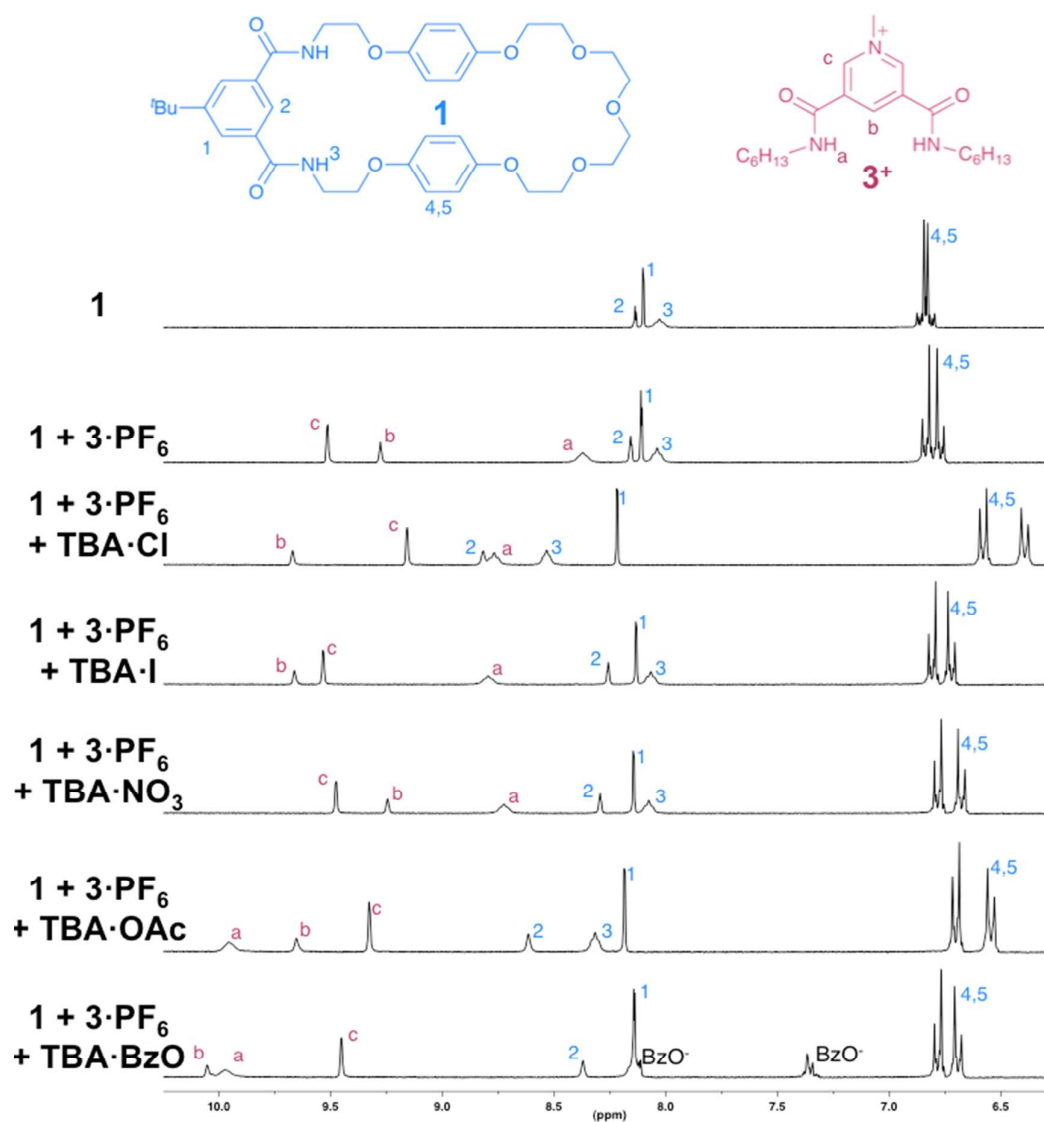**Solution pseudorotaxane formation**

Figure S1. Truncated ^{1}H NMR spectra of **1**, **2·PF$_6$** and TBA·X (d$_6$-acetone, 293 K, 300 MHz).

Figure S2. Truncated ^{1}H NMR spectra of **1**, **3·PF$_6$** and TBA·X (d$_6$-acetone, 293 K, 300 MHz).
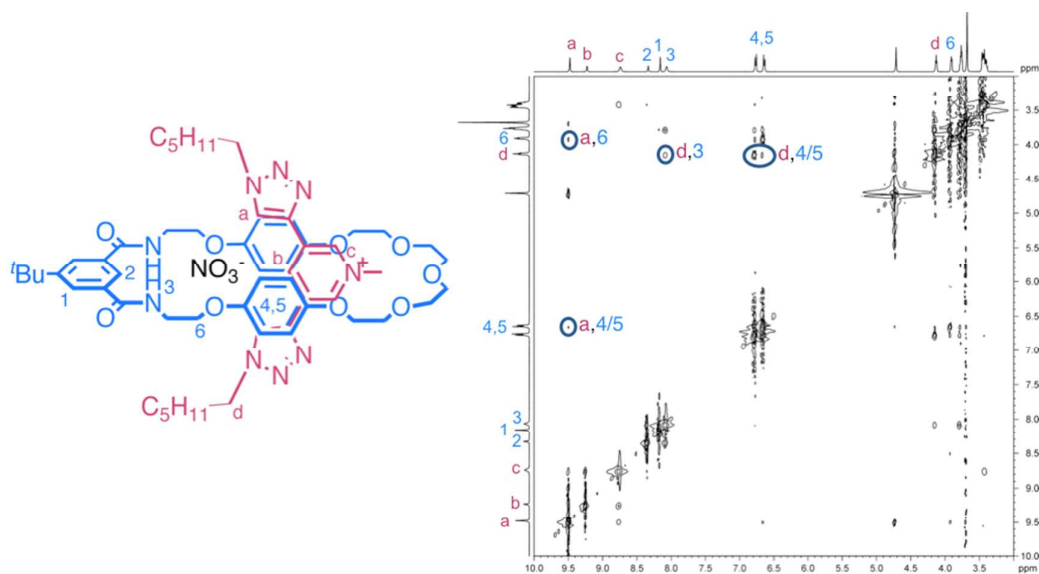
Figure S3. Truncated 2D ROESY NMR spectra of **1·NO₃·3** showing selected inter-component couplings; couplings involving macrocycle CH₂ protons other than 6 are not highlighted due to the overlap of these resonances in the 1D spectrum (293 K, 500 MHz, d₆-acetone).
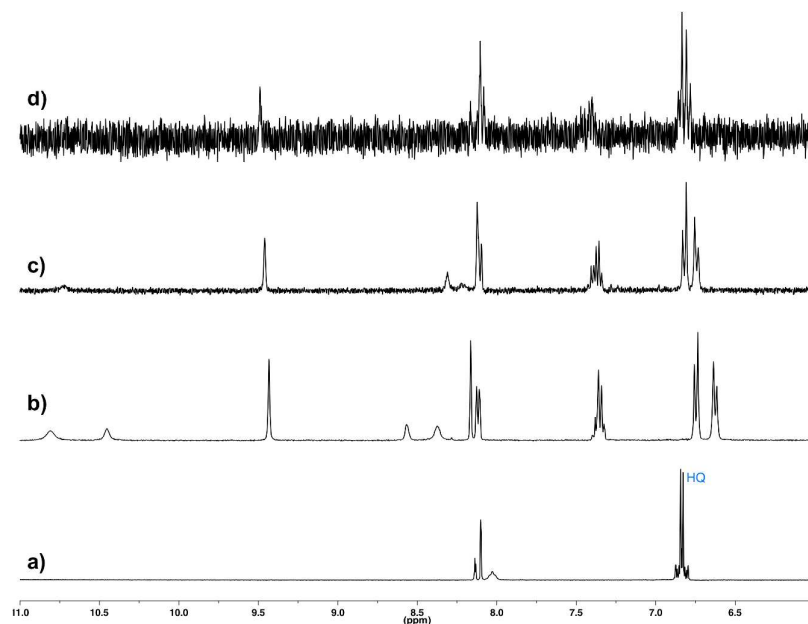
Figure S4. Truncated ¹H NMR spectra of a) macrocycle **1**; b) 1:1:1 mixture of **1**, **3·PF₆** and TBA·BzO at 10 mM; c) 1:1:1 mixture of **1**, **3·PF₆** and TBA·BzO at 1.0 mM; d) 1:1:1 mixture of **1**, **3·PF₆** and TBA·BzO at 0.10 mM (293 K, 500 MHz, d₆-acetone). The hydroquinone resonances of **1** are labelled HQ.

At 0.10 mM (which equals 0.033 mg of **1**, 0.025 mg of **3·PF₆** and 0.018 mg of TBA·BzO in 0.50 mL d₆-acetone), the macrocycle's hydroquinone resonances are shifted noticeably upfield relative to the free macrocycle, suggesting significant pseudorotaxane formation, even at this very low concentration.

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Table S1. Upfield chemical shift (ppm) of centre of hydroquinone resonances of **1** upon addition of threading component and TBA·X.[a]

Anion, X	Threading component 2^+	Threading component 3^+
none[b]	0.04	0.03
Cl^{-}	0.50	0.35
Br^{-}	0.46	–[c]
I[-]	0.15	0.07
NO$_3$[-]	0.17	0.11
OAc[-]	0.31	0.21
BzO[-]	0.39	0.10
HSO$_4$[-]	0.22	–[c]

[a]d_6-acetone, 293 K. [b]These small shifts occur due to addition of threading component as the hexafluorophosphate salt with no added anion. [c]Experiment not carried out due to a lack of material.

Full details of non-covalent interactions in pseudorotaxanes

Table S2. Non-covalent interactions in solid structures of **1·X·2**.[a]

X	Cl^{-}	Br^{-}	I[- b]	NO$_3^{- c}$
Receptor⋯anion hydrogen bonding				
*Macrocycle **1***				
N–H⋯X[-]	3.300(4)	3.596(4)	3.803(2)	3.121(2)
%vdW$_{N,X}$	95	102	103	99
∠N–H⋯X[-]	159	164	161	169
H⋯X[-]	2.43	2.75	2.97	2.27
%vdW$_{H,X}$	80	90	92	84
N–H⋯X[-]	3.348(4)	3.639(4)	3.846(2)	3.161(2)
%vdW$_{N,X}$	96	103	103	100
∠N–H⋯X[-]	152	159	147	170
H⋯X[-]	2.51	2.82	3.09	2.28
%vdW$_{H,X}$	83	92	95	84
C$_{phenylene}$–H⋯X[-]	3.445(4)	3.801(5)	4.036(2)	3.114(2)
%vdW$_{C,X}$	96	105	106	95
∠C$_{phenylene}$–H⋯X[-]	142	175	173	177
H⋯X[-]	2.66	2.87	3.09	2.15
%vdW$_{H,X}$	88	94	95	80
Receptor⋯anion hydrogen bonding				
*Threading component **2**$^+$*				
C$_{triazole}$–H⋯X[-]	3.431(4)	3.694(5)	3.885(3)	3.189(5), 3.210(4)
%vdW$_{C,X}$	96	102	102	98, 98
∠C$_{triazole}$–H⋯X[-]	166	168	166	140, 168
H⋯X[-]	2.54	2.77	2.98	2.43, 2.30
%vdW$_{H,X}$	84	91	92	90, 85
C$_{triazole}$–H⋯X[-]	3.679(5)	3.882(5)	3.985(3)	3.597(5), 3.655(4)
%vdW$_{C,X}$	102	107	105	110, 112
∠C$_{triazole}$–H⋯X[-]	163	160	156	157, 144
H⋯X[-]	2.78	2.99	3.11	2.76, 2.89
%vdW$_{H,X}$	92	98	96	102, 107
C$_{pyridinium}$–H⋯X[-]	3.641(5)	4.013(5)	4.187(3)	3.268(3), 3.431(4)
%vdW$_{C,X}$	101	111	110	100, 105
∠C$_{pyridinium}$–H⋯X[-]	178	169	167	150, 175
H⋯X[-]	2.69	3.08	3.25	2.39, 2.46
%vdW$_{H,X}$	89	101	100	89, 91
Pyridinium⋯hydroquinone donor–acceptor interactions				
centroid⋯centroid	3.499(2)	3.546(3)	3.6123(14)	3.5863(11)
mean plane angle	7.1(2)	9.5(2)	11.25(12)	9.60(9)
centroid⋯centroid	3.623(3)	3.889(3)	–	–
mean plane angle	5.64(19)	10.4(2)	–	–
Pyridinium–methyl⋯polyether hydrogen bonding				
C$_{methyl}$–H⋯O	3.379(5)	3.395(7)	3.369(3)	3.354(3)
%vdW$_{C,O}$	103	104	103	103
∠C$_{methyl}$–H⋯O	172	164	158	143
H⋯O	2.41	2.47	2.47	2.54
%vdW$_{H,O}$	89	91	91	94
C$_{methyl}$–H⋯O	3.288(5)	3.391(7)	3.413(3)	3.606(2)
%vdW$_{C,O}$	101	104	104	110
∠C$_{methyl}$–H⋯O	119	148	147	143
H⋯O	2.69	2.55	2.57	2.61
%vdW$_{H,O}$	100	94	95	97

[a]Distances in Angstroms, angles in degrees. Estimated errors in parentheses. No errors are given for distances/angles/%vdW values involving hydrogen atom positions, for the reasons outlined on p. 12. [b]The minor component of the disordered iodide anion is excluded from this analysis. [c]Values are given for both half-occupancy positions of the nitrate anion. The data for the lower-numbered position of the anion are given first (*i.e.* before the comma) in each case.

Table S3. Non-covalent interactions in solid structures of **1·X·3**.[a]

X	Cl⁻	I⁻ [a]	NO₃⁻ [b]	OAc⁻ [b]	BzO⁻
Receptor···anion hydrogen bonding					
Macrocycle 1					
N–H···X⁻	3.426(2)	3.780(3)	3.140(11), 3.026(10)	3.002(18), 3.025(18)	2.942(5)
%vdW$_{N,X}$	98	102	99, 96	95, 96	93
∠N–H···X⁻	167	160	166, 166	169, 173	173
H···X⁻	2.56	2.97	2.26, 2.15	2.10, 2.13	2.08
%vdW$_{H,X}$	85	92	84, 80	78, 79	77
N–H···X⁻	3.515(2)	3.902(3)	3.301(15), 2.987(11)	3.365(18), 3.231(18)	3.187(5)
%vdW$_{N,X}$	101	105	104, 96	106, 102	101
∠N–H···X⁻	169	158	169, 153	151, 150	164
H···X⁻	2.67	3.11	2.41, 2.16	2.53, 2.42	2.34
%vdW$_{H,X}$	88	96	89, 80	94, 90	87
C$_{phenylene}$–H···X⁻	3.604(2)	4.039(3)	3.295(12), 3.441(11)	3.215(13), 3.153(14)	3.101(3)
%vdW$_{C,X}$	100	106	101, 105	98, 96	95
∠C$_{phenylene}$–H···X⁻	165	175	132, 152	152, 154	133
H···X⁻	2.70	3.10	2.60, 2.55	2.31, 2.26	2.39
%vdW$_{H,X}$	89	96	96, 94	86, 84	89
Receptor···anion hydrogen bonding					
Threading component 3⁺					
N–H···X⁻	3.337(2)	3.621(3)	3.000(15), 2.813(10)	3.066(18), 3.035(18)	3.059(5)
%vdW$_{N,X}$	96	98	95, 89	98, 96	97
∠N–H···X⁻	163	158	159, 139	173, 161	171
H···X⁻	2.44	2.81	2.14, 2.07	2.14, 2.16	2.16
%vdW$_{H,X}$	81	87	79, 77	79, 80	80
N–H···X⁻	3.323(2)	3.735(3)	3.349(16), 2.848(12)	3.207(18), 3.059(18)	3.087(5)
%vdW$_{N,X}$	95	101	106, 89	102, 97	98
∠N–H···X⁻	163	158	172, 147	147, 168	162
H···X⁻	2.52	2.90	2.46, 2.06	2.39, 2.13	2.23
%vdW$_{H,X}$	83	90	91, 76	89, 80	83
C$_{pyridinium}$–H···X⁻	3.477(2)	3.912(3)	3.102(17), 3.365(16)	3.054(15), 3.041(16)	2.978(3)
%vdW$_{C,X}$	97	103	95, 103	93, 93	91
∠C$_{pyridinium}$–H···X⁻	163	161	176, 163	169, 166	166
H···X⁻	2.57	3.04	2.18, 2.66	2.11, 2.07	2.00
%vdW$_{H,X}$	85	94	81, 99	78, 77	74
Pyridinium···hydroquinone donor–acceptor interactions					
centroid···centroid	3.6072(11)	3.701(6)	3.881(5), –	–, –	–
mean plane angle	11.00(9)	13.41(14)	8.6(4), –	–, –	–
centroid···centroid	3.6282(11)	3.915(6)	–, –	–, –	–
mean plane angle	8.81(9)	12.40(14)	–, –	–, –	–
Pyridinium–methyl···polyether hydrogen bonding					
C$_{methyl}$–H···O	3.491(3)	3.467(4)	3.367(10), 3.290(9)	3.516(14), 3.548(14)	3.409(3)
%vdW$_{C,O}$	107	106	103, 101	107, 109	104
∠C$_{methyl}$–H···O	168	150	169, 163	156, 157	157
H···O	2.54	2.56	2.42, 2.36	2.62, 2.66	2.49
%vdW$_{H,O}$	94	95	90, 87	97, 98	92
C$_{methyl}$–H···O	3.535(3)	3.414(4)	–, –	–, –	–
%vdW$_{C,O}$	108	104	–, –	–, –	–
∠C$_{methyl}$–H···O	153	155	–, –	–, –	–
H···O	2.63	2.58	–, –	–, –	–
%vdW$_{H,O}$	97	96	–, –	–, –	–

[a]Distances in Angstroms, angles in degrees. Estimated errors in parentheses No errors are given for distances/angles/%vdW values involving hydrogen atom positions, for the reasons outlined on p. 12. [b]These structures have Z′ = 2, the data from the lower-numbered complex are given first (*i.e.* before the comma) in each case.

Table S4. Comparison of average hydrogen bond strength and anion basicity.

Anion (X⁻)	pK_a of HX in H_2O^a	Mean %vdW$_{H,X}$ in 1·X·2	Mean %vdW$_{H,X}$ in 1·X·3
BzO⁻	4.204 [S1]	83	82
OAc⁻	4.756 [S1]	–	83
NO$_3$⁻	–1.6 [S2]	88	86
Cl⁻	~ –7 [S2]	86	85
Br⁻	~ –9 [S2]	94	–
I⁻	~ –11 [S2]	95	93

[a]While these pK_a values were determined in water, and so are clearly not directly relevant to our studies which were conducted in d$_6$-acetone, they are provided to give an approximation of anion basicity.

Anion recognition properties of 2·PF$_6$ and 3·PF$_6$

An initial ^{1}H NMR titration experiment revealed that association of chloride anion with **2·PF$_6$** in d$_6$-acetone was too strong for WINEQNMR2[S3] to quantify ($K_a > 10^4$ M^{-1}), so titration experiments were conducted in more competitive CD$_3$CN.

Table S5. Association constants, K_a (M^{-1}) of threading components **2·PF$_6$** and **3·PF$_6$** and various anions.[a]

Anion	2·PF$_6$	3·PF$_6$
Cl$^-$	206(11)	> 10^4
Br$^-$	106(3)	3342(143)
I$^-$	59(2)	664(52)
BzO$^-$	402(12)	> 10^4

[a]Anions added as TBA salts, estimated standard errors are given in parentheses. Association constants calculated using WINEQNMR2[S3] (293 K, CD$_3$CN).
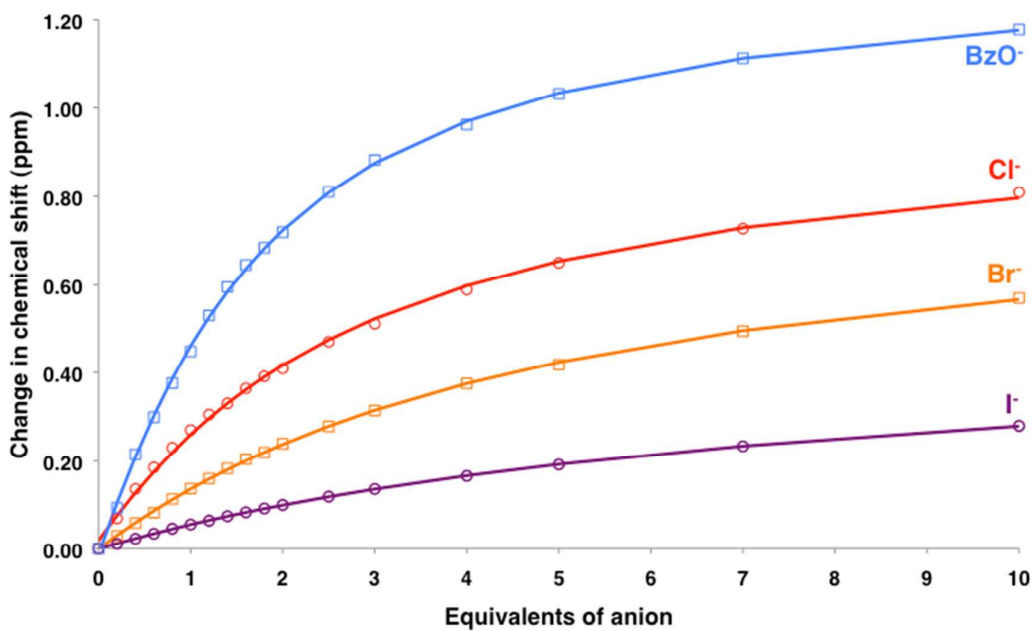
Figure S4. Experimental titration data (points) and fitted binding isotherms (lines) for addition of anions to **2·PF$_6$** (CD$_3$CN, 293 K, 500 MHz).
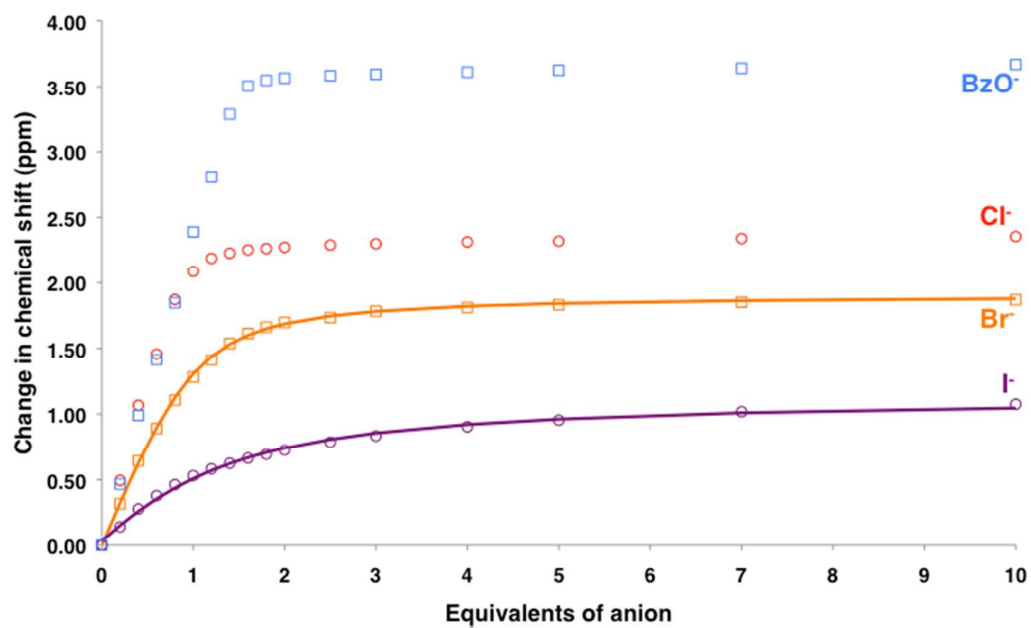
Figure S5. Experimental titration data (points) and fitted binding isotherms (lines) for addition of anions to **3·PF$_6$**; association of **3·PF$_6$** with chloride and benzoate was too strong for WINEQNMR2[S3] to quantify (CD$_3$CN, 293 K, 500 MHz).

Further crystallographic details

Generally, pseudorotaxane crystals were reasonably weakly diffracting, so for all-but-one dataset (**1·Cl·3**), it was necessary to use either copper or synchrotron radiation. In most structures, the thermal ellipsoids of the threading components' hexyl chains are much larger than the better-defined central part of the pseudorotaxane (as would be expected), leading to B and C level CIFcheck alerts.

Several structures contain positional disorder, typically involving solvent molecules and/or the threading component's hexyl chains; this was modelled by having multiple positions for the affected atoms. The occupancy of each position was refined and then fixed. In some cases, areas of diffuse electron density (believed to arise from disordered solvent molecules) were present, which could not be sensibly modelled. In these cases, the SQUEEZE[S4,S5] program within the PLATON suite[S5] was used to include this electron density in the refinement.
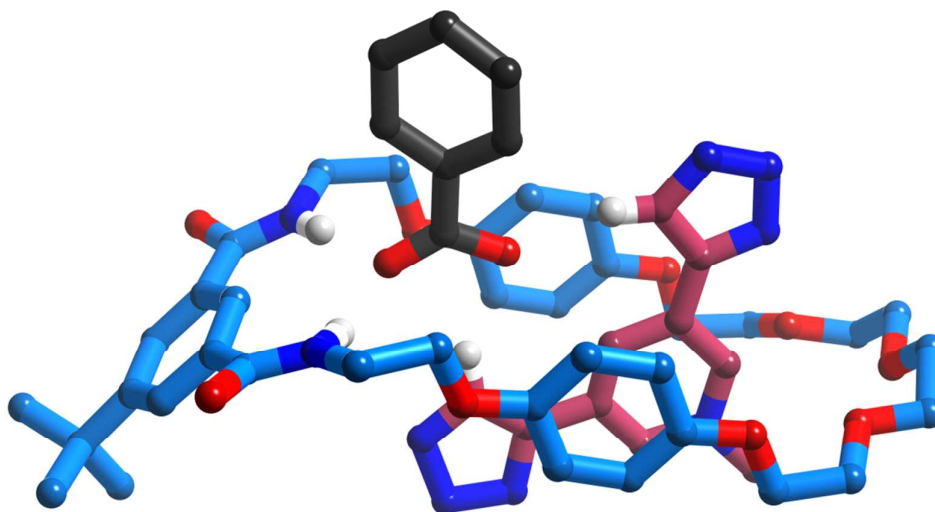
The structures of **1·NO$_3$·3** and **1·OAc·3** crystallize in the non-centrosymmetric space groups P2$_1$, and both have a Z' of 2. No further symmetry could be found, either by visual inspection of atomic coordinates of "pairs" of atoms in the two structures, or using PLATON ADDSYM.[S5] In both cases, the hydrogen bonding with the anion and the arrangements of the hexyl chains differ significantly between the two different pseudorotaxane complexes in the asymmetric unit cell. Both of these structures are also twinned, appropriate twin laws were determined using the ROTAX package[S6] within the CRYSTALS suite;[S7] the relative twin fraction of each twin component was refined.

Crystals of **1·BzO·2** were very small and very weakly-diffracting. Despite the use of Cu $K\alpha$ radiation and long collection times (3 days to collect a quarter-sphere of data), it was only possible to collect data to a resolution of 1.0 Å, and numerous reflections could not be distinguished from the background. The threading component's hexyl chains were severely disordered, and a region of diffuse electron density was also present (presumably arising from disordered solvent molecules). These could not be sensibly modelled, despite the use of extensive restraints on bond distances, bond angles and thermal ellipsoids parameters, therefore PLATON-SQUEEZE was used to include the electron density in the refinement.

Errors associated with hydrogen bonding distances and angles

Errors can be obtained for distances and angles involving hydrogen atoms using standard crystallography programs. Even for a poor quality dataset, these estimated errors are small (typically around 0.01 Å for H···X distances, 0.2˚ for D–H···X angles, 0.4% for $\%vdW_{H,X}$ values), while for high quality datasets they are considerably smaller (typically around 0.002 Å for H···X distances, 0.05˚ for D–H···X angles, 0.15% for $\%vdW_{H,X}$ values). Due to the weak scattering of X-rays by hydrogen atoms, these values have little or no chemical significance, therefore errors are not reported for these values. Instead, values are given to a small number of significant figures, and the error is expected to be significantly less than the range the value reflects.

Structure of 1·BzO·2

Figure S6. Solid state structure of 1·**BzO**·2. Most hydrogen atoms omitted for clarity.

Table S6. Non-covalent interactions in solid structures of **1·X·2.**[a]

Receptor···anion hydrogen bonding (%vdW$_{H,X}$)	
Macrocycle 1	
N–H···X$^-$	77
N–H···X$^-$	82
C$_{phenylene}$–H···X$^-$	86
Threading component 2$^+$	
C$_{triazole}$–H···X$^-$	82
C$_{triazole}$–H···X$^-$	90
C$_{pyridinium}$–H···X$^-$	83
Pyridinium···hydroquinone donor–acceptor interactions (Å)	
centroid···centroid	–
centroid···centroid	–
Pyridinium–methyl···polyether hydrogen bonding (%vdW$_{H,O}$)	
C$_{methyl}$–H···O	97
C$_{methyl}$–H···O	–
Distance between central cavity carbon atoms of macrocycle and threading component (Å)	
C$_{phenylene}$···C$_{pyridinium}$	7.60

Structure of 1·BzO·2

Figure S6. Solid state structure of 1·**BzO**·2. Most hydrogen atoms omitted for clarity.

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Receptor···anion hydrogen bonding (%vdW$_{H,X}$)	
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Threading component 2$^+$	
C$_{triazole}$–H···X$^-$	82
C$_{triazole}$–H···X$^-$	90
C$_{pyridinium}$–H···X$^-$	83
Pyridinium···hydroquinone donor–acceptor interactions (Å)	
centroid···centroid	–
centroid···centroid	–
Pyridinium–methyl···polyether hydrogen bonding (%vdW$_{H,O}$)	
C$_{methyl}$–H···O	97
C$_{methyl}$–H···O	–
Distance between central cavity carbon atoms of macrocycle and threading component (Å)	
C$_{phenylene}$···C$_{pyridinium}$	7.60

References

[S1] CRC Handbook of Chemistry and Physics (92nd Ed.), **2011-2012**, Editor-in-Chief: W.M. Haynes.

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