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Calix[4]arene-Based Rotaxane Host Systems for Anion Recognition

Anna J. McConnell,[a] Christopher J. Serpell,[a] Amber L. Thompson,[a] David R. Allan,[b] and Paul D. Beer*[a]

Abstract: The synthesis, structure and anion binding properties of the first calix[4]arene-based [2]rotaxane anion host systems are described. Rotaxanes **9**·Cl and **12**·Cl, consisting of a calix[4]arene functionalised macrocycle wheel and different pyridinium axle components, are prepared via adaption of an anion templated synthetic strategy to investigate the effect of preorganisation of the interlocked host's binding cavity on anion binding. Rotaxane **12**·Cl contains a conformationally flexible pyridinium axle, whereas rotaxane **9**·Cl incorporates a more preorganised pyridinium axle component. The X-ray crystal structure of **9**·Cl and solution phase ^{1}H NMR spectroscopy demonstrate the successful interlocking of the calix[4]arene macrocycle and pyridinium axle components in the rotaxane structures. Following removal of the chloride anion template, anion binding studies on the resulting rotaxanes **9**·PF_6 and **12**·PF_6 reveal the importance of preorganisation of the host binding cavity on anion binding. The more preorganised rotaxane **9**·PF_6 is the superior anion host system. The interlocked host cavity is selective for chloride in 1:1 $CDCl_3/CD_3OD$ and remains selective for chloride and bromide in 10% aqueous media over the more basic oxoanions. Rotaxane **12**·PF_6 with a relatively conformationally flexible binding cavity is a less effective and discriminating anion host system although the rotaxane still binds halide anions in preference to oxoanions.

Keywords: anions · calixarenes · rotaxanes · supramolecular chemistry · templation

Introduction

The imaginative design and construction of rotaxane and catenane interlocked molecules of increasing complexity and functionality is an area of intense current interest.[1] This has been stimulated by their promising applications as components of molecular machines and switches in which external stimuli can control the mechanical-bond dynamics.[2] Despite this, the potential of these molecules to function as selective-host systems in molecular recognition applications has been largely overlooked, which is somewhat surprising given their unique three-dimensional topological binding cavities.[3]

Calixarenes are attractive molecular structural frameworks renowned for their versatility and ease of functionalisation at both the narrow lower, and wide upper rim.[4,5] As a result a multitude of calixarene derivatives have been utilised as cation,[6] anion[4,7] and ion-pair receptors.[8] They have also recently begun to be incorporated into interlocked structures including rotaxanes[9,10] and catenanes.[11–13]

We have undertaken a research programme with the objective of exploiting the unique topological cavities of rotaxanes and catenanes in anion host-guest chemistry.[10–12,14–16] We have previously reported the synthesis of heteroditopic calix[4]arene receptors which exhibit unprecedented cooperative and ion-pair binding behaviour.[17,18] Through suitable modification of this heteroditopic receptor design, together with exploitation of a strategic anion templation methodology, calix[4]arene functionalised [2]catenane anion receptors were assembled.[11,12] Herein we describe the preparation of the first calix[4]arene-based [2]rotaxane anion host systems, which consist of a calix[4]arene functionalised macrocycle wheel and pyridinium axle components, through adaptation of a new synthetic pathway that involves anion templation in combination with favourable π–π stacking interactions.[15] Anion binding investigations reveal the more preorganised rotaxane exhibits an impressive high affinity for chloride

[a] A. J. McConnell, C. J. Serpell, Dr. A. L. Thompson, Prof. P. D. Beer
Inorganic Chemistry Laboratory, Department of Chemistry
University of Oxford, South Parks Road, Oxford, OX1 3QR (UK)
Fax: (+44) 1865-272-690
E-mail: paul.beer@chem.ox.ac.uk

[b] Dr. D. R. Allan
Diamond Light Source, Harwell Science and Innovation Campus
Didcot, OX11 0QX (UK)

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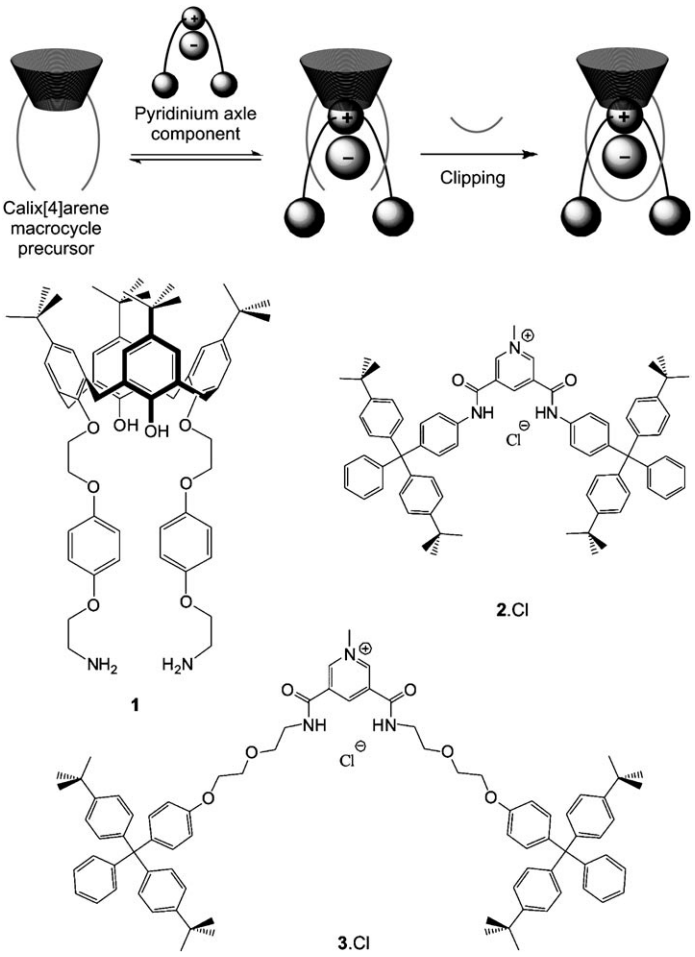
and bromide in aqueous solvent media in preference to basic oxoanions.

Results and Discussion

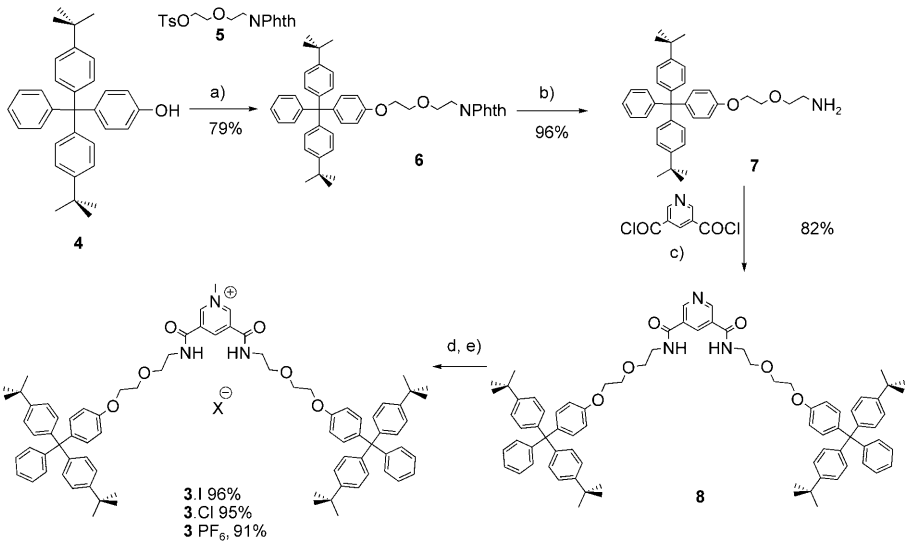
Synthetic strategy: The strategy for the synthesis of the target calixarene-based [2]rotaxanes is depicted in Scheme 1. Anion templation and favourable π–π stacking interactions between the calix[4]arene-based macrocycle precursor and stoppered pyridinium axle component are exploited prior to reaction with a clipping component to form the [2]rotaxane. The calix[4]arene macrocycle precursor **1** incorporates electron rich hydroquinone groups to facilitate π–π stacking interactions with the electron deficient pyridinium axle component. In addition, it is functionalised with terminal amine groups for the clipping condensation reaction with an appropriate bis-acid chloride derivative. Calix[4]arene-based rotaxanes containing the two pyridinium axle components, **2**·Cl and **3**·Cl, are synthesised to investigate the effect of preorganisation of the axle component on the anion binding properties of the resulting rotaxane host systems.

Macrocycle precursor **1**[12] and axle component **2**·Cl[16] were prepared according to literature procedures. The synthesis of the new axle component **3**·Cl is outlined in Scheme 2. Compound **6** was synthesised in 79% yield by heating a suspension of compounds **4**[19] and **5**[17] and K_2CO_3 in acetonitrile in a microwave at 160°C for four hours. The phthalimide protecting groups were removed in 96% yield using hydrazine monohydrate. The resulting amine **7** was reacted with 3,5-*bis*(chlorocarbonyl) pyridine in CH_2Cl_2 to give **8** in 82% yield. Methylation of **8** with methyl iodide afforded **3**·I in 96% yield. The iodide anion was exchanged for chloride by repeated aqueous washings with ammonium chloride to give **3**·Cl in 95% yield. In addition the non-coordinating hexafluorophosphate salt **3**·PF_6 was prepared for anion binding studies by repeated washing of a solution of **3**·Cl in $CHCl_3$ with aqueous NH_4PF_6.

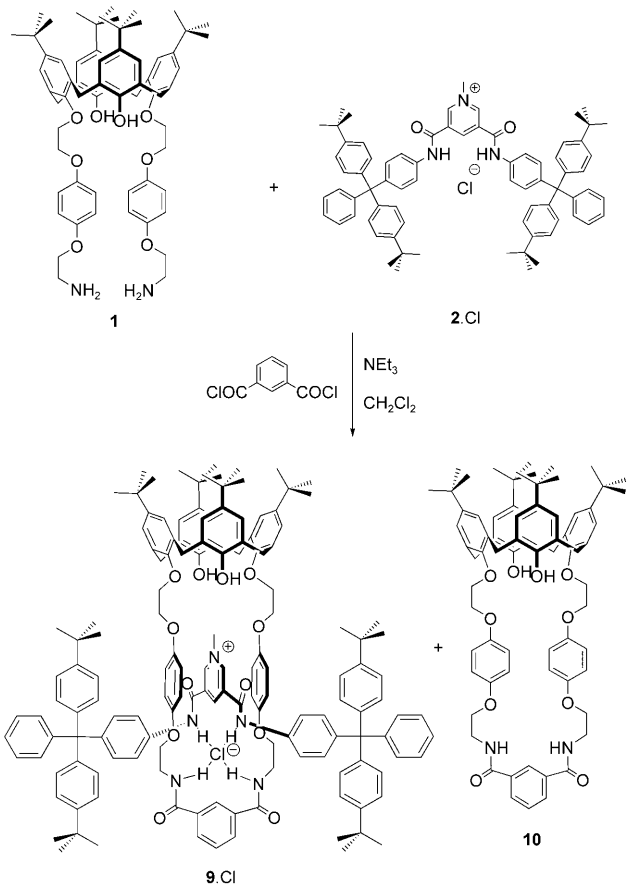


Scheme 1. A diagram of the ion-pair templation strategy for the synthesis of calix[4]arene-based rotaxanes.

Synthesis of rotaxanes: The [2]rotaxane **9**·Cl was prepared by adding isophthaloyl dichloride to a 1:1 mixture of compounds **1** and **2**·Cl in dry CH_2Cl_2 in the presence of triethylamine (Scheme 3). Rotaxane **9**·Cl was isolated in 11% yield following purification by preparative thin-layer chromatography and recrystallisation from $CHCl_3$/MeOH. In addition the macrocycle by-product **10** was isolated in 30% yield. The



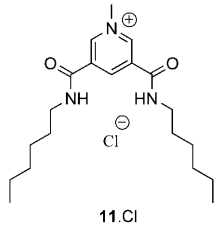
Scheme 2. Synthesis of axle component **3**·Cl. a) K_2CO_3, CH_3CN, μW, 160°C, 4 hr; b) $N_2H_4.H_2O$, EtOH, reflux, 16 hr; c) NEt_3, CH_2Cl_2, RT, 19 hr; d) MeI, acetone, reflux, 3 days; e) Anion exchange.



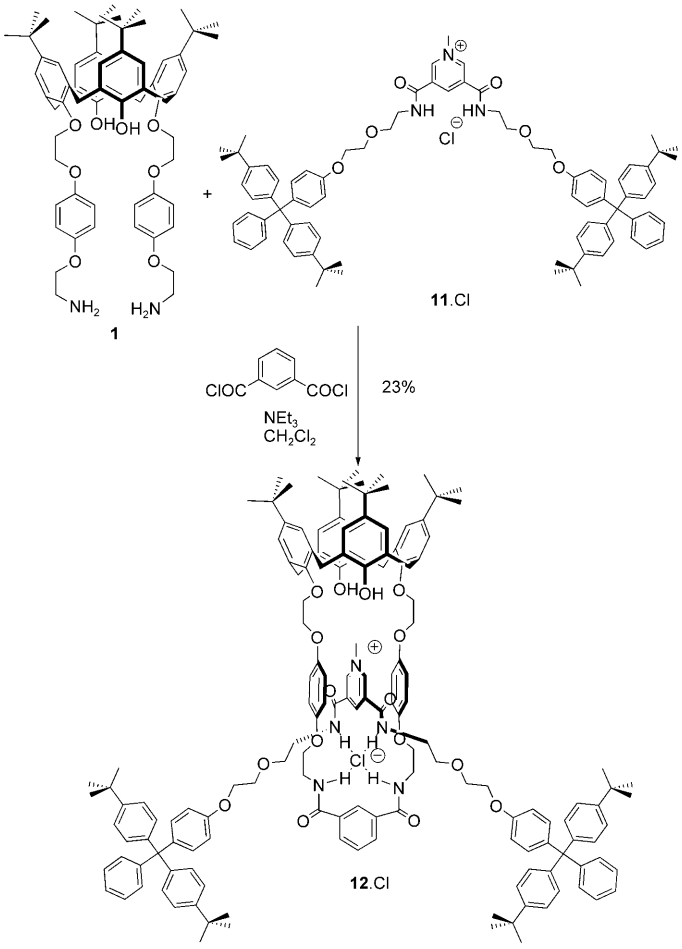
Scheme 3. Synthesis of rotaxane **9**·Cl and macrocycle by-product **10**.

formation of the macrocycle by-product accounts for the lower yield of rotaxane as compared with our previously reported rotaxane system where a flexible polyether hydroquinone bis-amine is used as the macrocycle precursor component instead of the relatively more preorganised calix[4]arene bis-amine synthon.[15]

Interestingly, whereas the macrocyclisation of bis-amine **1** and isophthaloyl dichloride in the absence of the axle component gave macrocycle **10** in 25% yield, the analogous condensation reaction in the presence of the unstoppered 3,5-bis-amide pyridinium chloride axle component **11**·Cl afforded the macrocycle in an improved yield of 38%. This suggests chloride anion templation in combination with favourable π–π donor-acceptor interactions contribute to the efficacy of macrocycle formation, and in rotaxane formation using the stoppered axle. In an effort to improve the yield of the rotaxane, a number of the reaction conditions were varied. Compound **2**·Cl has limited solubility in CH_2Cl_2 and therefore the chloride anion was exchanged to hexafluorophosphate using $AgPF_6$[16] to improve the organic solvent solubility. The hexafluorophosphate anion was not expected to interfere with any anion templation effects due to the large excess of chloride anions produced in the condensation reaction as a consequence of amide formation. Although the solubility of the axle component was improved upon anion exchange, the yield of the rotaxane did not significantly increase. Despite the solubility problems with **2**·Cl, the rotaxane synthesis was repeated in the presence of 1.5 equivalents of **2**·Cl and the rotaxane was isolated in an improved yield of 17%. The macrocycle by-product **10** was also isolated in 23% yield.



Rotaxane **12**·Cl was synthesised using an analogous synthetic procedure and owing to the improved solubility of **3**·Cl compared to **2**·Cl, it was possible to carry out the reaction at a higher concentration (Scheme 4). The rotaxane was isolated in 23% yield following purification by preparative thin layer chromatography and recrystallisation from $CHCl_3$/diisopropyl ether (iPr_2O). The macrocycle by-product **10** was also formed, but owing to its impure nature it was not possible to obtain an accurate yield.



Scheme 4. Synthesis of rotaxane **12**·Cl.

Rotaxanes **9**·Cl and **12**·Cl were characterised by ^{1}H and ^{13}C NMR spectroscopy, high-resolution electrospray mass spectrometry and melting point analysis.[20] A comparison of the ^{1}H NMR spectra of the macrocycle **10**, axle **2**·Cl and rotaxane **9**·Cl in $CDCl_3$ are shown in Figure 1. The downfield shifts of the isophthalamide protons a and b are indicative of halide anion complexation in the rotaxane's interlocked host binding cavity. In addition the upfield shifts of the axle proton e can be attributed to the competitive binding of chloride in the rotaxane compared with the ion-paired free axle. The upfield shifts and splitting of the hydroquinone protons c and d result from π–π stacking interactions between the electron deficient pyridinium unit of the axle and electron rich hydroquinone rings of the macrocycle. The ROESY spectra of **9**·Cl and **12**·Cl (Figure S10) reveal a number of through space correlations between the respective macrocycle and axle components, as illustrated in Figure 2.

X-ray crystal structure of rotaxane 9·Cl: Single crystals of rotaxane **9**·Cl were obtained by slow evaporation of a solution of the rotaxane in 45:45:10 $CDCl_3/CD_3OD/D_2O$. Although of a good size, the crystals were found to diffract poorly under standard MoKα radiation. Despite these difficulties, it was possible to collect a useable dataset and the X-ray crystal structure unambiguously confirmed the connectivity and interlocked nature of the structure (Figure S12).

However, a higher quality dataset was obtained from another crystal from the same sample, analysed using synchrotron radiation on beamline I19 at Diamond Light Source (Figure 3). Interestingly, structural differences were observed as established by examination of the conformation of

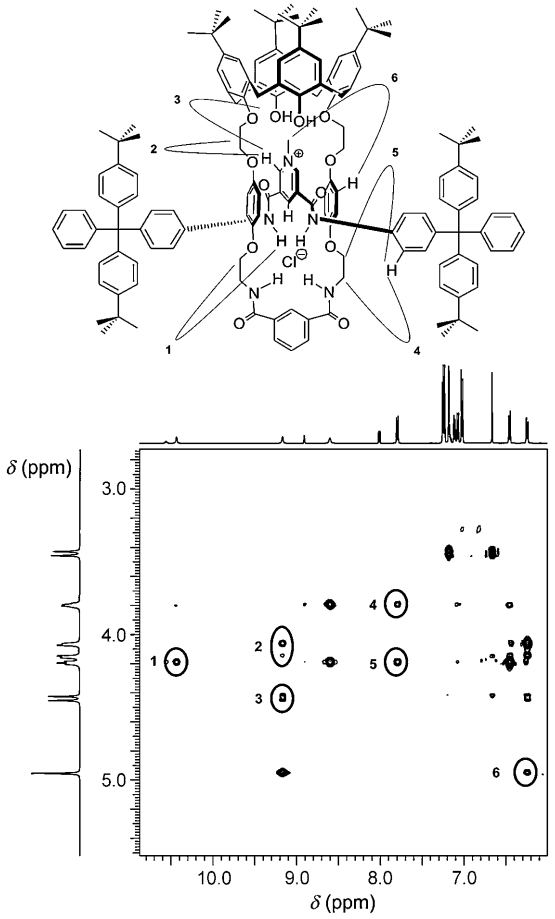


Figure 2. Portion of the ROESY spectrum of rotaxane **9**·Cl in $CDCl_3$ at 298 K illustrating the through space correlations between the calixarene macrocycle and ion-pair thread components.

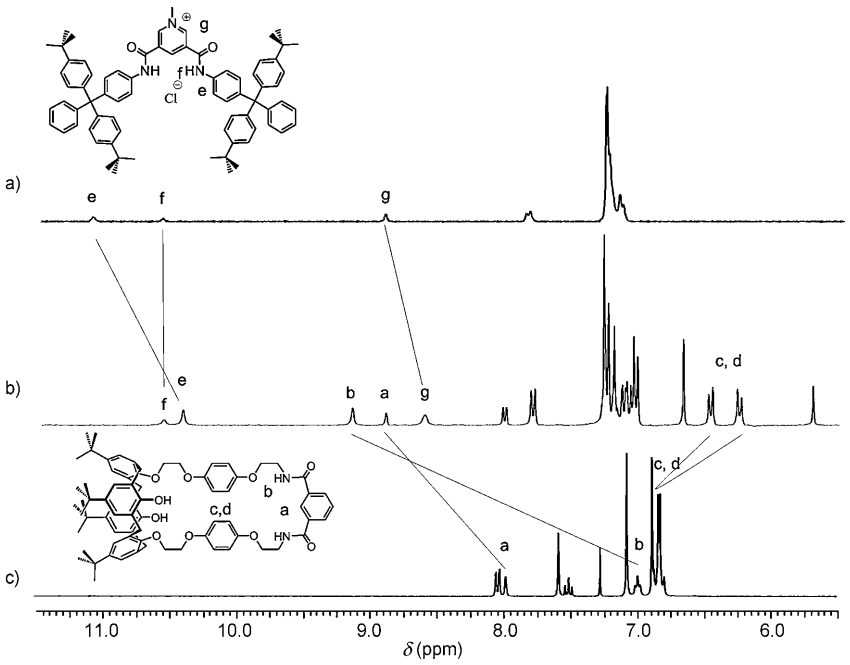


Figure 1. ^{1}H NMR spectra of a) axle **2**·Cl, b) rotaxane **9**·Cl and c) macrocycle **10** in $CDCl_3$ at 298 K.

the stopper groups (Figure S12). Contraction of one of the cell axes indicates that this results from solvent loss (Table S1). However, with respect to the supramolecular forces involved, there is little difference between the two samples. A top-down view makes it clear that slippage of the stoppers is impossible. The intermolecular forces used to template the rotaxane in solution are still present in the solid state: hydrogen bonds from both components to the chloride anion; π–π stacking between the electron poor pyridinium unit and the electron rich hydroquinone groups (though with a high degree of offset); and secondary hydrogen bonding of the pyridinium methyl group to calixarene oxy-

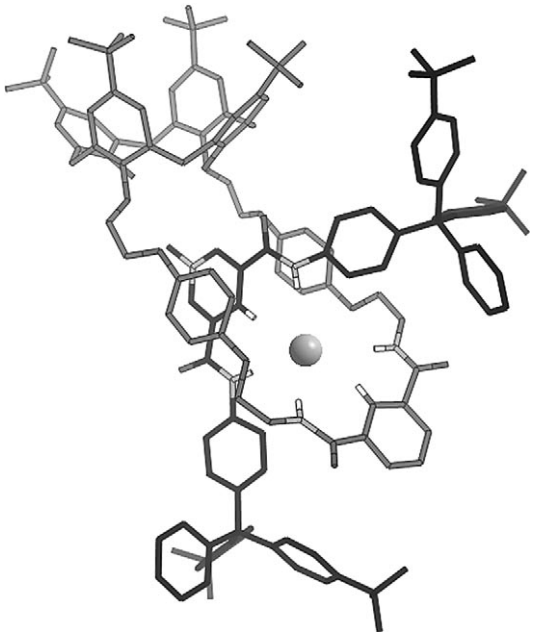


Figure 3. X-ray crystal structure of **9**·Cl obtained by synchrotron radiation displaying anion coordination. Disorder and non-coordinating hydrogen atoms are omitted for clarity.

gens (Table 1). The chloride anion is tetrahedrally coordinated with respect to the amide protons (a mean N(H)···Cl distance of 3.36 Å), but central aryl protons also form close contacts with a mean C(H)···Cl distance of 3.32 Å.

Table 1. Selected crystallographic data for rotaxane **9**·Cl. Distances are given for atoms labelled in numerical order.

N(H)···Cl distances [Å][a]	3.222(11), 3.544(37)
	3.340(9),[c] 3.246(9)[c]
	3.511(12),[c] 3.273(40)[c]
C(H)···Cl distances [Å][a]	3.366(14), 3.276(12)
π–π centroid–centroid distances [Å][b]	4.015(8), 3.749(8)
π–π stacking angle[b] [°]	17.2(7), 8.7(6)
Pyr^+-C(H_3)-O distances [Å][a]	3.734(16), 3.428(16)
	3.113(13), 3.559(14)

[a] Calculated within CRYSTALS[21] by using the full variance-covariance matrix. [b] Calculated by using PLATON[22] without inclusion of the covariance. [c] Multiplicity of value occurs owing to disorder.

Anion binding studies: To study the anion binding properties of the rotaxanes, the chloride anion template was removed from the respective interlocked host cavity by washing a $CHCl_3$ solution of the rotaxanes with aqueous NH_4PF_6. The resulting rotaxanes **9**·PF_6 and **12**·PF_6 and axle **3**·PF_6 were characterised by ^1H, ^{19}F, ^{31}P, ^{13}C NMR spectroscopy, electrospray mass spectrometry and melting point analysis. The ROESY NMR spectra of **9**·PF_6 (Figure 4) and **12**·PF_6 (Figure S11) both demonstrate through space correlations between the macrocycle and axle components indicating that anion exchange has preserved the interlocked structure.

^1H NMR titration experiments in 1:1 $CDCl_3/CD_3OD$ were undertaken to study the anion binding properties of the rotaxanes and axle. Chemical shift changes were monitored upon addition of a variety of anions, added as their tetrabutylammonium (TBA) salts. In the presence of anions such as chloride and bromide, downfield shifts of the cavity protons a, f and g were observed for both rotaxanes **9**·PF_6 and **12**·PF_6 (Figure 5). However, the addition of acetate and dihydrogen phosphate induced an upfield shift of proton f and downfield shifts of protons a and g. This is suggestive of a different binding mode for these anions, most likely outside the interlocked cavity due to their large size. In contrast, downfield shifts of protons a, f and g were observed upon addition of all anions to the axle **3**·PF_6. WinEQNMR2[23] analysis of the titration data gave association constant values for the 1:1 rotaxane/anion stoichiometric complexes shown in Table 2.

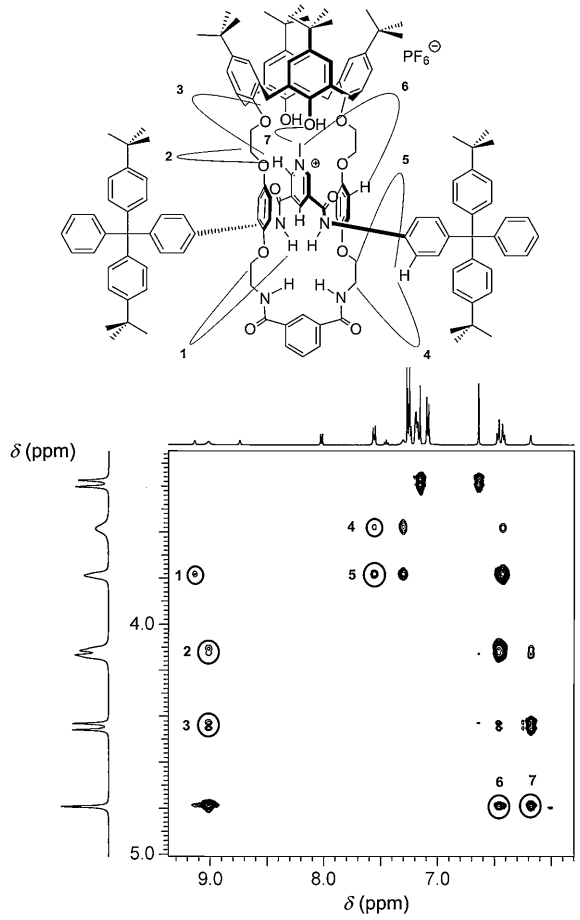


Figure 4. Portion of the ROESY spectrum of rotaxane **9**·PF_6 in $CDCl_3$ at 298 K illustrating the through space correlations between the calixarene macrocycle and ion-pair thread components.

The association constant values reveal the more preorganised rotaxane **9**·PF_6 is the superior anion discriminating and complexing host system. Rotaxane **9**·PF_6 is selective for chloride over bromide and the more oxobasic anions acetate and dihydrogen phosphate. This selectivity is due to a complementary size match between the preorganised interlocked binding cavity and the chloride anion, as evidenced in the solid state structure of **9**·Cl (Figure 3). Owing to the

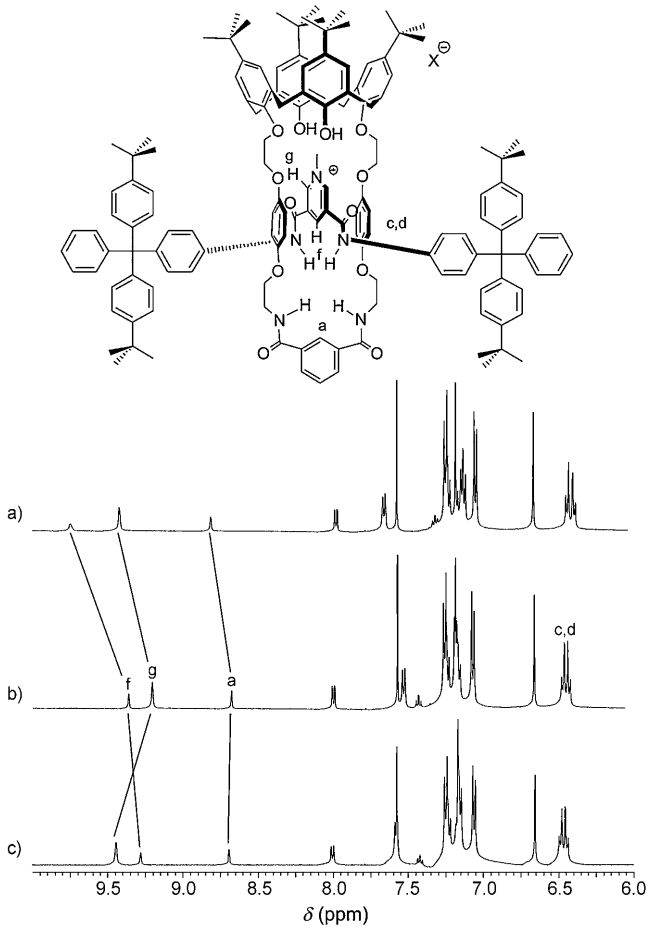


Figure 5. ^{1}H NMR spectra of a) **9**·Cl, b) **9**·PF_6 and c) **9**.H_2PO_4 in 1:1 $CDCl_3/CD_3OD$ at 298 K.

Table 2. Anion binding properties of rotaxanes **9**·PF_6, **12**·PF_6 and axle **3**·PF_6.[a]

X^-	**9**·PF_6[b]	**9**·PF_6[c]	**3**·PF_6[b]	**12**·PF_6[b]
Cl^-	3820	620	300	650
Br^-	1560	630	440	630
$H_2PO_4^-$	1140	70[d]	710	420
OAc^-	530	80	160	140[d]

[a] Association constants derived from winEQNMR2[23] analysis of the ortho pyridinium proton g data from ^{1}H NMR titration experiments in [b] 1:1 $CDCl_3/CD_3OD$ and [c] 45:45:10 $CDCl_3/CD_3OD/D_2O$ at 298 K. Errors $<10\%$. [d] Errors $<20\%$.

lack of conformational flexibility of the binding cavity, the larger anions bromide, acetate and dihydrogen phosphate cannot be completely encapsulated within the rotaxane cavity. As a result, the magnitude of the association constants for these anions is significantly lower than for chloride. In addition, the large oxoanions most likely associate on the periphery of the cavity in a different binding mode to chloride as evidenced by the upfield shift of proton f in Figure 5.

As the rotaxane displays strong binding of chloride in 1:1 $CDCl_3/CD_3OD$, its anion binding properties in aqueous media were also investigated (Table 2). In a 45:45:10 $CDCl_3/CD_3OD/D_2O$ solvent mixture the rotaxane binds the halide anions in preference to the oxoanions and as expected the association constant values are lower in this more competitive aqueous mixture. It is noteworthy the rotaxane is no longer selective for chloride over bromide with both anions exhibiting similar binding affinities in the aqueous mixture. This loss of chloride anion selectivity is presumably a consequence of the smaller halide anion's larger hydration energy which effectively competes with the overall anion recognition process.[24]

The axle **3**·PF_6 and rotaxane **12**·PF_6 exhibit significantly weaker anion binding compared with rotaxane **9**·PF_6 in 1:1 $CDCl_3/CD_3OD$ solutions. Rotaxane **12**·PF_6 has a similar shaped binding cavity to rotaxane **9**·PF_6 and as a result, still binds the halides in preference to the larger oxoanions. However, it cannot discriminate chloride from bromide since the binding cavity is more conformationally flexible and can accommodate the larger bromide in the cavity with a similar affinity to chloride. The axle **3**·PF_6 also cannot significantly discriminate between the halides and as commonly observed for acyclic receptor systems, it binds the basic dihydrogen phosphate more strongly.

Conclusion

The first calix[4]arene-based [2]rotaxane anion host systems have been prepared via adaption of a recently discovered anion templated synthetic methodology. Two rotaxanes, **9**·Cl and **12**·Cl, incorporating different axle components were synthesised to investigate the effect of preorganisation of the interlocked host's binding cavity on anion binding. Rotaxane **12**·Cl contains a conformationally flexible axle whereas rotaxane **9**·Cl incorporates a more preorganised axle component. Solution phase ^{1}H NMR spectroscopy experiments provided evidence for the successful interlocking of the calix[4]arene macrocycle and pyridinium axle components in the rotaxane structures. Additionally the first X-ray crystal structure of a calix[4]arene-based rotaxane anion host system reveals the axle is threaded through the calix[4]arene macrocycle with a chloride anion complexed within the rotaxane host cavity. Following removal of the chloride anion template, the anion binding properties of the resulting rotaxanes **9**·PF_6 and **12**·PF_6 were studied by ^{1}H NMR titration experiments. These reveal that the degree of preorganisation of the host cavity governs the strength and selectivity of anion binding. The more preorganised rotaxane **9**·PF_6 is the superior anion host system exhibiting selectivity for chloride in 1:1 $CDCl_3/CD_3OD$ and selectivity for the halide anions in 45:45:10 $CDCl_3/CD_3OD/D_2O$ over the more basic oxoanions. Rotaxane **12**·PF_6 having a relatively conformationally flexible binding cavity, however is a less effective and discriminating anion host system. The rotaxane still binds halide anions in preference to the oxoanions, unlike the axle **3**·PF_6.

Experimental Section

All commercial-grade chemicals and solvents were used without further purification unless otherwise stated. Where dry solvents were used, they were degassed with nitrogen, dried by passing through an MBraun MPSP-800 column and then used immediately. Triethylamine was distilled over and stored over potassium hydroxide. Thionyl chloride was distilled over triphenyl phosphite. TBA salts were stored prior to use under vacuum in a desiccator containing phosphorus pentoxide and self-indicating silica gel. Deionised water was used in all cases.

^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded by using a Varian Mercury 300, a Varian Unity Plus 500 or a Bruker AVII500 with cryoprobe spectrometer. Mass spectra were obtained by using a Bruker micrOTOF or a MALDI Micro MX spectrometer. Melting points were recorded by using a Gallenkamp capillary melting point apparatus and are uncorrected. Elemental analysis was carried out by the service at London Metropolitan University. Microwave reactions were carried out by using a Biotage Initiator 2.0 microwave.

Compounds **1**,[12] **2**,[16] **4**,[19] **5**[17] and **11**·Cl[25] were prepared according to literature procedures. The synthesis and characterisation of macrocycle **10** has been described elsewhere.[12] The characterisation of macrocycle **10** was consistent with the literature data.

Synthesis of 3·I: A solution of **8** (0.27 g, 0.23 mmol) and methyl iodide (0.5 mL, excess) in acetone (15 mL) was heated under reflux under a N_2 atmosphere for three days. The solvent was removed to give **3·I** as an orange solid in 96% yield (0.30 g, 0.22 mmol). M.p. 158–160 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 9.87$ (s, 1H; py H^4), 9.22 (s, 2H; py H^2 and H^6), 8.79 (br. s., 2H; NH), 7.19 (m, 18H; ArH), 7.08 (m, 12H; ArH), 6.73 (d, $^{3}J = 8.8$ Hz, 4H; ArH), 4.21 (s, 3H; N^+CH_3), 4.10 (m, 4H; CH_2), 3.85 (m, 8H; CH_2), 3.71 (m, 4H; CH_2), 1.29 ppm (s, 36H; *t*Bu); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 160.63$, 156.34, 148.35, 147.33, 146.26, 143.89, 141.57, 139.79, 134.42, 132.16, 131.03, 130.58, 127.26, 125.66, 124.18, 113.20, 69.40, 68.89, 67.41, 63.41, 49.36, 40.19, 34.27, 31.35 ppm; ESMS: *m*/*z*: 1216.7144 $[M-I]^+$.

Synthesis of 3·Cl: A biphasic mixture of **3·I** (0.26 g, 0.20 mmol) in $CHCl_3$ (100 mL) and 1 M $NH_4Cl_{(aq)}$ (100 mL) was stirred vigorously for 30 mins. The aqueous layer was decanted and the procedure was repeated a further four times. The organic layer was dried over $MgSO_4$, filtered and the solvent was removed. Compound **3·Cl** was obtained as a yellow solid in 95% yield (0.23 g, 0.19 mmol). M.p. 186–188 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 10.53$ (s, 1H; py H^4), 9.47 (t, $^{3}J = 4.7$ Hz, 2H; NH), 9.26 (s, 2H; py H^2 and H^6), 7.20 (m, 18H; ArH), 7.07 (m, 12H; ArH), 6.72 (d, $^{3}J = 8.8$ Hz, 4H; ArH), 4.30 (s, 3H; N^+CH_3), 4.11 (m, 4H; CH_2), 3.86 (m, 8H; CH_2), 3.71 (t, $^{3}J = 5.0$ Hz, 4H; CH_2), 1.29 ppm (s, 36H; *t*Bu); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 160.39$, 156.34, 148.31, 147.30, 146.65, 143.85, 141.37, 139.72, 133.96, 132.16, 131.03, 130.58, 127.22, 125.64, 124.13, 113.09, 69.41, 69.01, 67.30, 63.39, 49.28, 40.38, 34.25, 31.33 ppm; ESMS: *m*/*z*: 1216.7087 $[M-Cl]^+$.

Synthesis of 3·PF$_6$: **3·**Cl (0.066 g, 0.053 mmol) was dissolved in $CHCl_3$ (10 mL) and washed with 0.2 M $NH_4PF_{6(aq)}$ (5×10 mL). The organic layer was separated, dried over $MgSO_4$, filtered and the solvent was removed to give **3·**PF_6 as a white solid in 91% yield (0.066 g, 0.049 mmol). M.p. 142–144 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.14 (s, 1H; py H^4), 8.94 (s, 2H; py H^2 and H^6), 7.59 (t, $^{3}J = 4.4$ Hz, 2H; NH), 7.21 (m, 18H; ArH), 7.08 (m, 12H; ArH), 6.70 (d, $^{3}J = 8.8$ Hz, 4H; ArH), 4.17 (s, 3H; N^+CH_3), 4.03 (m, 4H; CH_2), 3.78 (m, 4H; CH_2), 3.68 (m, 8H; CH_2), 1.29 ppm (s, 36H; *t*Bu); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 160.56$, 156.17, 148.37, 147.33, 145.78, 143.88, 141.21, 139.95, 135.10, 132.18, 131.02, 130.57, 127.27, 125.68, 124.19, 113.19, 69.42, 68.97, 67.29, 63.43, 49.17, 40.41, 34.27, 31.35 ppm; ^{19}F NMR (282.5 MHz, $CDCl_3$): $\delta = -72.01$ ppm (d, $^{1}J = 713$ Hz, PF_6^-); ^{31}P NMR (121.6 MHz, $CDCl_3$): $\delta = -144.63$ ppm (septet, $^{1}J = 713$ Hz, PF_6^-); ESMS: *m*/*z*: 1216.7160 $[M-PF_6]^+$.

Synthesis of 6: A suspension of compounds **4** (1.27 g, 2.8 mmol), **5** (1.33 g, 3.4 mmol) and K_2CO_3 (0.79 g, 5.7 mmol) in CD_3CN (15 mL) was heated in a microwave for 4 hr at 160 °C. The reaction mixture was cooled to room temperature and the solvent was removed. The crude material was redissolved in $CHCl_3$ (50 mL), washed with 1 M $HCl_{(aq)}$ (30 mL) and H_2O (2×30 mL). The organic layer was dried over $MgSO_4$, filtered and the solvent was removed. Following purification by silica gel chromatography (99:1 $CHCl_3$/MeOH), the product **6** was obtained as a white solid in 79% yield (1.43 g, 2.2 mmol). M.p. 82–84 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.81$ (dd, $^{3}J = 5.4$, $^{4}J = 3.1$ Hz, 2H; PhthH), 7.66 (dd, $^{3}J = 5.4$, $^{4}J = 3.1$ Hz, 2H; PhthH), 7.21 (m, 9H; ArH), 7.06 (m, 6H; ArH), 6.68 (d, $^{3}J = 8.8$ Hz, 2H; ArH), 4.04 (t, $^{3}J = 4.8$ Hz, 2H; CH_2), 3.93 (m, 2H; CH_2), 3.83 (m, 4H; CH_2), 1.31 ppm (s, 18H; *t*Bu); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 168.26$, 156.43, 148.30, 147.35, 143.92, 139.45, 133.85, 132.07, 132.04, 131.10, 130.64, 127.17, 125.62, 124.09, 123.21, 113.06, 69.06, 67.99, 67.18, 63.40, 37.20, 34.26, 31.34 ppm; ESMS: *m*/*z* calcd for $C_{45}H_{47}NO_4Na$: 688.3397; found: 688.3398 $[M+Na]^+$.

Synthesis of 7: Compound **6** (0.32 g, 0.48 mmol) was suspended in ethanol (20 mL), hydrazine monohydrate (0.7 mL, excess) was added and the resulting mixture was heated under reflux for 16 hr. The resulting white suspension was cooled to room temperature, poured in water (50 mL) and then extracted using CH_2Cl_2 (3×50 mL). The combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed to give **7** as an off-white solid in 96% yield (0.26 g, 0.48 mmol). M.p. 68–70 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.24$ (m, 9H; ArH), 7.10 (m, 6H; ArH), 6.79 (d, $^{3}J = 9.1$ Hz, 2H; ArH), 4.11 (t, $^{3}J = 4.8$ Hz, 2H; CH_2), 3.82 (t, $^{3}J = 4.8$ Hz, 2H; CH_2), 3.59 (t, $^{3}J = 5.1$ Hz, 2H; CH_2), 2.91 (br. s., 2H; CH_2N), 1.83 (br. s., 2H; NH_2), 1.31 ppm (s, 18H; *t*Bu); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 156.50$, 148.33, 147.34, 143.92, 139.63, 132.19, 131.11, 130.65, 127.20, 125.65, 124.11, 113.13, 73.11, 69.50, 67.15, 63.43, 41.62, 34.28, 31.35 ppm; ESMS: *m*/*z* calcd for $C_{37}H_{46}NO_2$: 536.3523; found: 536.3539 $[M+H]^+$.

Synthesis of 8: A suspension of 3,5-pyridinedicarboxylic acid (0.05 g, 0.30 mmol) in $SOCl_2$ with a drop of DMF was heated under reflux under a N_2 atmosphere for 17 hr. The excess $SOCl_2$ was removed by distillation in vacuo and the resulting solid was redissolved in dry CH_2Cl_2 (15 mL). This was added dropwise over 1 hr to a solution of compound **7** (0.32 g, 0.60 mmol) and NEt_3 (0.15 mL, 1.1 mmol) in dry CH_2Cl_2 (20 mL) under a N_2 atmosphere. The reaction mixture was left to stir for 19 hr, then washed with 1 M $HCl_{(aq)}$ (2×30 mL) and brine (30 mL). The organic layer was dried over $MgSO_4$, filtered and the solvent was removed to give **8** as a white solid in 82% yield (0.30 g, 0.25 mmol). M.p. 130–132 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.12 (s, 2H; py H^2 and H^6), 8.53 (t, $^{4}J = 2.1$ Hz, 1H; py H^4), 7.20 (m, 18H; ArH), 7.09 (m, 12H; ArH), 6.86 (br. s., 2H; NH), 6.74 (d, $^{3}J = 9.1$ Hz, 4H; ArH), 4.06 (m, 4H; CH_2), 3.81 (m, 4H; CH_2), 3.70 (m, 8H; CH_2), 1.30 ppm (s, 36H; *t*Bu); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 164.73$, 156.16, 150.75, 148.36, 147.30, 143.87, 139.90, 133.31, 132.21, 131.06, 130.61, 129.56, 127.23, 125.67, 124.15, 113.10, 69.76, 69.57, 67.07, 63.43, 39.89, 34.27, 31.35 ppm; ESMS: *m*/*z*: 1224.6626 $[M+Na]^+$.

Synthesis of 9·Cl: A solution of isophthaloyl dichloride (0.015 g, 0.072 mmol) in dry CH_2Cl_2 (20 mL) was added to a solution of bis-amine **1** (0.070 g, 0.069 mmol), axle **2·**Cl (0.11 g, 0.10 mmol) and NEt_3 (0.02 mL, 0.14 mmol) in dry CH_2Cl_2 (15 mL). The reaction mixture was stirred at room temperature under a N_2 atmosphere for 1 hr and then washed with 1 M $HCl_{(aq)}$ (2×10 mL) and brine (10 mL). The organic layer was dried over $MgSO_4$, filtered and the solvent was removed. Following purification by preparative thin-layer chromatography (4:1 EtOAc/$CHCl_3$) and recrystallisation from $CHCl_3$/MeOH, the rotaxane **9·**Cl was isolated as a yellow solid in 17% yield (0.021 g, 0.0097 mmol). M.p. 250 °C (dec.); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 10.59$ (s, 1H; py H^4), 10.44 (br. s., 2H; NH), 9.16 (s, 2H; py H^2 and H^6), 8.92 (s, 1H; isoH), 8.62 (br. s., 2H; NH), 8.02 (d, $^{3}J = 7.9$ Hz, 2H; isoH), 7.81 (d, $^{3}J = 8.8$ Hz, 4H; ArH), 7.13 (m, 35H; ArH, calix ArH, isoH), 6.67 (s, 4H; calix ArH), 6.47 (d, $^{3}J = 9.0$ Hz, 4H; hydroqH), 6.25 (d, $^{3}J = 9.0$ Hz, 4H; hydroqH), 5.69 (s, 2H; OH), 4.97 (s, 3H; N^+CH_3), 4.45 (d, $^{2}J = 13.6$ Hz, 4H; $ArCH_{in}H_{out}Ar$), 4.19 (m, 8H; CH_2), 4.09 (m, 4H; CH_2), 3.82 (m, 4H; CH_2), 3.46 (d, $^{2}J = 13.6$ Hz, 4H; $ArCH_{in}H_{out}Ar$), 1.39 (s, 18H, *t*Bu), 1.33 (s, 36H, *t*Bu), 0.87 ppm (s, 18H; *t*Bu); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 167.11$, 158.10, 154.01, 151.70, 150.58, 149.97, 148.32, 147.54, 146.97, 144.99, 144.67, 143.52, 142.78, 134.62, 134.06, 133.21, 131.75, 131.58, 131.09, 130.64, 128.46, 127.33, 125.93, 125.69, 125.52, 125.11, 124.26, 120.85, 114.86, 114.35, 75.19, 67.68, 65.88, 63.77, 50.81, 41.24, 34.30, 34.02, 33.85, 31.75, 31.39, 31.16, 30.90 ppm; ESMS: *m*/*z*: 2177.0742 $[M-Cl]^+$; elemental anal-

ysis calcd (%) for $C_{146}H_{162}N_5O_{12}Cl$: C 79.19, H 7.37, N 3.16; found C 79.04, H 7.25, N 3.23.

Synthesis of 9·PF_6: A solution of **9**·Cl (0.048 g, 0.021 mmol) in $CHCl_3$ (10 mL) was washed with 0.2 M $NH_4PF_{6(aq)}$ (5×10 mL) and water (10 mL). The combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed to give **9**·PF_6 as a yellow solid in 100% yield (0.049 g, 0.021 mmol). M.p. 240 °C (dec.); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.40 (br. s., 2H; NH), 9.12 (s, 1H; py H^4), 9.00 (br. s., 2H; py H^2 and H^6), 8.73 (s, 1H; isoH), 8.02 (dd, ^3J = 7.9, ^4J = 1.5 Hz, 2H; isoH), 7.56 (d, ^3J = 8.5 Hz, 4H; ArH), 7.45 (t, ^3J = 7.5 Hz, 2H; NH), 7.15 (m, 35H; calix ArH, ArH), 6.64 (s, 4H; calix ArH), 6.44 (m, 8H; hydroqH), 6.18 (s, 2H; OH), 4.77 (s, 3H; N^+CH_3), 4.44 (d, ^2J = 13.8 Hz, 4H; $ArCH_{in}H_{out}Ar$), 4.12 (m, 8H; CH_2), 3.79 (m, 4H; CH_2), 3.58 (m, 4H; CH_2N), 3.38 (d, ^2J = 13.8 Hz, 4H; $ArCH_{in}H_{out}Ar$), 1.36 (s, 18H; *t*Bu), 1.32 (s, 36H; *t*Bu), 0.85 ppm (s, 18H; *t*Bu); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.05, 158.08, 152.92, 152.12, 150.10, 149.91, 148.54, 147.25, 146.82, 145.27, 144.19, 143.40, 142.52, 141.61, 134.12, 133.93, 133.72, 131.86, 131.64, 131.02, 130.85, 130.59, 128.86, 128.33, 127.39, 125.98, 125.84, 125.74, 125.53, 124.32, 120.37, 115.69, 114.65, 75.11, 67.34, 67.16, 63.82, 50.35, 39.86, 34.31, 33.94, 33.82, 31.74, 31.49, 31.38, 30.91 ppm; ^{19}F NMR (282.5 MHz, $CDCl_3$): δ = −70.10 ppm (d, ^1J = 715 Hz, PF_6^-); ^{31}P NMR (202.4 MHz, $CDCl_3$): δ = −142.71 ppm (septet, ^1J = 715 Hz, PF_6^-); ESMS: *m*/*z*: 2177.1363 $[M-PF_6]^+$.

Synthesis of 12·Cl: A solution of isophthaloyl dichloride (0.014 g, 0.071 mmol) in dry CH_2Cl_2 (2 mL) was added to a solution of bis-amine **1** (0.070 g, 0.069 mmol), axle **2**·Cl (0.13 g, 0.11 mmol) and NEt_3 (0.02 mL, 0.14 mmol) in dry CH_2Cl_2 (5 mL). The reaction mixture was stirred at room temperature under a N_2 atmosphere for 1 hr and then washed with 1 M $HCl_{(aq)}$ (2×5 mL) and brine (5 mL). The organic layer was dried over $MgSO_4$, filtered and the solvent was removed. Following purification by preparative thin-layer chromatography (4:1 EtOAc/$CHCl_3$) and recrystallisation by vapour diffusion of iPr_2O into a $CHCl_3$ solution of the rotaxane, the rotaxane **12**·Cl was isolated as a yellow solid in 24% yield (0.039 g, 0.016 mmol). M.p. 200 °C (dec.); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.82 (br. s., 1H; py H^4), 9.28 (br. s., 1H; isoH), 9.03 (br. s., 2H; py H^2 and H^6), 8.76 (br. s., 2H; NH), 8.68 (br. s., 2H; NH), 8.27 (d, ^3J = 7.9 Hz, 2H; isoH), 7.53 (t, ^3J = 7.9 Hz, 1H; isoH), 7.18 (m, 22H; ArH), 7.04 (m, 12H; ArH), 6.71 (d, ^3J = 8.8 Hz, 4H; ArH), 6.65 (s, 4H; calix ArH), 6.47 (d, ^3J = 8.8 Hz, 4H; hydroqH), 6.19 (d, ^3J = 8.8 Hz, 4H; hydroqH), 5.71 (br. s., 2H; OH), 4.89 (s, 3H; N^+CH_3), 4.40 (d, ^2J = 13.6 Hz, 4H; $ArCH_{in}H_{out}Ar$), 4.24 (m, 4H; CH_2), 4.10 (m, 4H; CH_2), 4.03 (m, 8H; CH_2), 3.87 (m, 4H; CH_2), 3.76 (t, ^3J = 4.4 Hz, 4H; CH_2), 3.67 (t, ^3J = 4.8 Hz, 4H; CH_2), 3.57 (m, 4H; CH_2), 3.43 (d, ^2J = 13.6 Hz, 4H; $ArCH_{in}H_{out}Ar$), 1.39 (s, 18H; *t*Bu), 1.28 (s, 36H; *t*Bu), 0.86 ppm (s, 18H; *t*Bu); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.83, 159.83, 156.55, 153.78, 151.54, 150.51, 149.97, 148.29, 147.49, 147.36, 144.34, 143.91, 142.75, 139.42, 133.62, 133.53, 132.09, 131.88, 131.51, 131.10, 130.85, 130.63, 128.99, 128.41, 127.17, 125.89, 125.60, 125.51, 124.26, 124.08, 114.74, 114.07, 113.09, 75.21, 69.13, 67.49, 67.16, 65.25, 63.39, 50.61, 41.23, 39.78, 34.25, 34.01, 33.83, 31.74, 31.66, 31.34, 31.08, 30.89 ppm; ESMS: *m*/*z*: 2353.0742 $[M-Cl]^+$.

Synthesis of 12·PF_6: A solution of **12**·Cl (0.057 g, 0.024 mmol) in $CHCl_3$ (20 mL) was washed with 0.2 M $NH_4PF_{6(aq)}$ (5×10 mL) and water (10 mL). The combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed to give **12**·PF_6 as a yellow solid in 100% yield (0.061 g, 0.024 mmol). M.p. 210 °C (dec.); ^{1}H NMR (500 MHz, 1:1 $CDCl_3$/CD_3OD): δ = 8.95 (s, 2H; py H^2 and H^6), 8.88 (s, 1H; py H^4), 8.64 (s, 1H; isoH), 8.09 (d, ^3J = 7.8 Hz, 2H; isoH), 7.60 (t, ^3J = 7.8 Hz, 1H; isoH), 7.07 (m, 34H; calix ArH, ArH), 6.72 (d, ^3J = 8.8 Hz, 4H; ArH), 6.64 (s, 4H; calix ArH), 6.38 (m, 8H; hydroqH), 4.69 (s, 3H; N^+CH_3), 4.37 (d, ^2J = 13.7 Hz, 4H; $ArCH_{in}H_{out}Ar$), 4.10 (m, 4H; CH_2), 4.01 (m, 8H; CH_2), 3.86 (t, ^3J = 4.6 Hz, 4H; CH_2), 3.80 (m, 4H; CH_2), 3.70 (m, 4H; CH_2), 3.60 (t, ^3J = 4.9 Hz, 4H; CH_2), 3.48 (m, 4H; CH_2), 3.35 (d, ^2J = 13.7 Hz, 4H; $ArCH_{in}H_{out}Ar$), 1.33 (s, 18H; *t*Bu), 1.20 (s, 36H; *t*Bu), 0.81 ppm (s, 18H; *t*Bu); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.00, 160.34, 156.43, 152.85, 151.53, 149.85, 149.62, 148.35, 147.53, 147.28, 143.84, 143.38, 143.07, 142.21, 139.66, 134.00, 133.08, 132.17, 131.65, 131.43, 131.04, 130.59, 129.20, 128.39, 127.20, 125.82, 125.69, 125.65, 124.11, 115.64, 115.53, 114.49, 112.99, 75.28, 69.39, 68.35, 67.30, 67.15, 66.77, 63.39, 49.95, 40.90, 39.80, 34.26, 34.03, 33.85, 31.75, 31.35, 30.91 ppm; ^{19}F NMR (282.5 MHz, $CDCl_3$): δ = −70.70 ppm (d, ^1J = 713 Hz, PF_6^-); ^{31}P NMR (121.6 MHz, $CDCl_3$): δ = −143.76 ppm (septet, ^1J = 714 Hz, PF_6^-); ESMS: *m*/*z*: 2353.1877 $[M-PF_6]^+$.

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