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# Anion-Templated Calix[4]arene-Based Pseudorotaxanes and Catenanes

**Michael D. Lankshear, Nicholas H. Evans, Simon R. Bayly, and Paul D. Beer*[a]**

**Abstract:** We present the rational design and anion-binding properties of the first anion-templated pseudorotaxanes and catenanes in which the "wheel" component is provided by a calix[4]arene macrobicyclic unit. The designs and syntheses of two new calix[4]arene macrobicycles, **2** and **3**, are presented, and the abilities of these new species both to bind anions and to undergo anion-dependent pseudorotaxane formation are demonstrated. Furthermore, it is shown that performing ring-closing metathesis reactions on some of these pseudorotaxane assemblies gives novel catenane species **14** and **15**, in which the yield of interlocked molecule obtained is critically dependent on the presence of a suitable anion template, namely, chloride. Exchange of the chloride anion in catenane **14a** for hexafluorophosphate gives catenane **14d**, which contains a unique anion-binding domain defined by the permanently interlocked hydrogen-bond-donating calix[4]arene macrobicycle and pyridinium macrocycle fragments. The anion-binding properties of this domain are presented, and shown to differ from non-interlocked components.

**Keywords:** anions · calixarenes · catenanes · self-assembly · supramolecular chemistry

## Introduction

The generation of novel, topologically complex, interpenetrated architectures remains a formidable task for the synthetic chemist.[1] The recent emergence of general templation methodologies based on cationic[2] and neutral[3] motifs has allowed access to a multitude of highly sophisticated structures, which in addition to their natural aesthetic appeal have also begun to be exploited for their potential molecular-machine-like behaviours.[4] To date, the similar development and exploitation of strategic anion templation approaches to these species is markedly less well explored, probably owing to the inherent challenges associated with the coordination of anions.[5] Recently, however, approaches that involve anion-templation methods for the generation of a range of interpenetrated and interlocked structures have been elucidated.[6] In particular, our group has shown that the orthogonal arrangement of two components around a central halide anion can give rise to pseudorotaxane, rotaxane and catenane formations.[7]

[a] M. D. Lankshear, N. H. Evans, Dr. S. R. Bayly, 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

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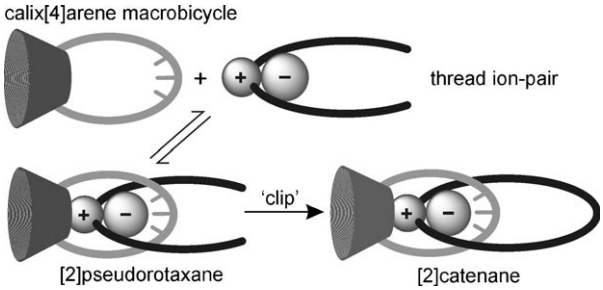
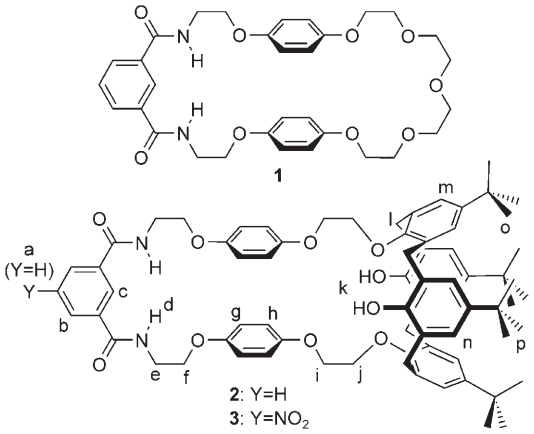
The calix[4]arene motif has received considerable attention as a scaffold for the design of numerous receptor systems, owing to its highly preorganised and readily functionalised nature.[8] Although examples are much rarer, it has also been exploited in the formation of interpenetrated and interlocked species in which the association of the components is mediated by hydrogen bonding or cationic templation effects,[9] whereas the steric bulk of calix[4]arene also renders it to be used as a stopper in the formation of rotaxanes.[10] However, as yet, no examples of anion-templated systems in which the calix[4]arene unit forms part of the "wheel" component of the interpenetrated species have been reported. In an effort to address this absence, we detail herein the first such calix[4]arene-based anion-templated assemblies.

The design of these new systems exploits the established methodology for the anion-mediated assembly of two components. This method involves the association of a charged pyridinium chloride ion pair and neutral isophthalamide components in a pseudotetrahedral fashion to yield pseudorotaxane species, which may further be clipped to form catenane derivatives (Scheme 1).[7h,11] The association is aided by employing secondary forces, namely, π-stacking interactions and hydrogen bonding. The replacement of the crown ether portion of previously reported isophthalamide macrocycle **1** with a calix[4]arene moiety yields system **2**, which is equally capable of undergoing anion-mediated threading, but with greatly increased complexity.




Scheme 1. General schematic representation for the formation of anion-templated calix[4]arene pseudorotaxanes and catenanes.

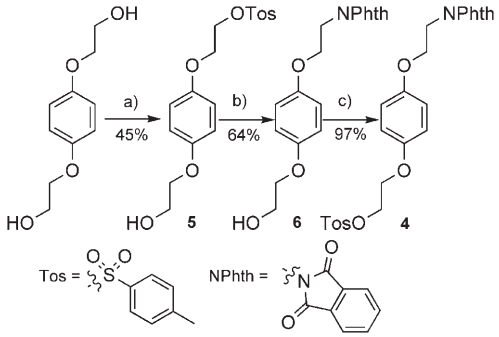



This article provides a description of the syntheses of macrocycle **2** and related macrocycle **3**, their anion-binding properties and their propensities to form anion-templated pseudorotaxanes. We also show that such macrocycles may provide the basis for catenane formation, in which the yield of the catenane product is dependent on the nature of the anion template. Furthermore, the anion-binding properties of one of the resulting catenanes depends on the formation of a hydrogen-bond-donating pocket by interlocking the two components.

## Results and Discussion

**Syntheses of calix[4]arene macrobicycles 2 and 3**: To prepare these new macrobicycles, it was first necessary to prepare "arm" precursor **4** (Scheme 2). Commercially available hydroquinone bis(2-hydroxyethyl)ether was statistically monotosylated by treating it with a stoichiometric quantity of tosyl chloride (TosCl) in THF to give **5** in 45% yield. Compound **5** was treated with potassium phthalimide (KNPhth) in dry DMF at 100°C to give **6** in 64% yield, which was subsequently tosylated under standard conditions (catalytic DMAP, tosyl chloride and triethylamine) to give **4** in 97% yield.

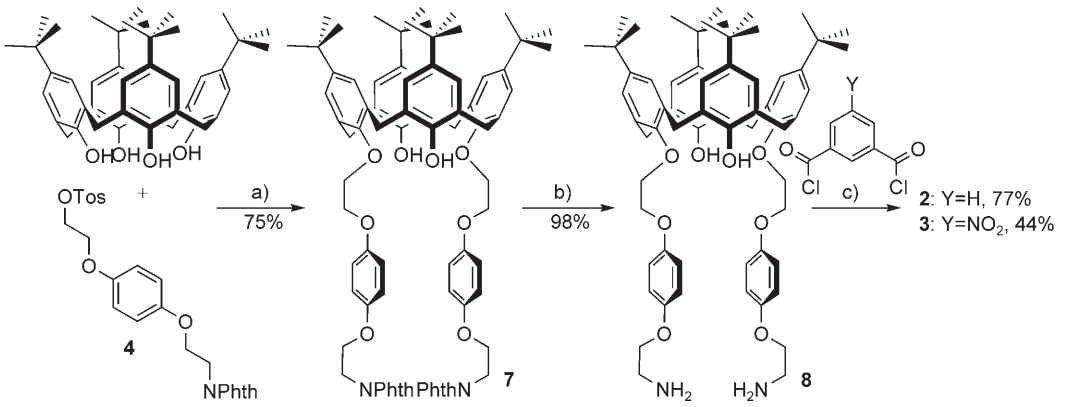
The syntheses of macrobicycles **2** and **3** were then accomplished by employing the three-step procedure illustrated in Scheme 3. *p-tert*-Butyl calix[4]arene was heated at reflux with precursor **4** and potassium carbonate in dry acetonitrile for four days to give compound **7** in 75% yield after an aqueous workup was performed. The phthalimide units of **7** were then cleaved to give amine **8** in 98% yield by heating the reaction mixture at reflux with hydrazine in ethanol for 16 h. Amine **8** was treated under high dilution conditions with an appropriate bis(acid chloride) and triethylamine in dry dichloromethane to give target compounds **2** and **3** in 77 and 44% yields, respectively. Only the [1+1] condensation products were obtained, which were verified by mass spectrometric analyses of the reaction mixtures. These processes represent remarkably facile syntheses of such highly functional macrobicycle derivatives.




Scheme 2. Preparation of "arm" precursor **4**. a) TosCl, $NEt_3$, DMAP (cat.), THF, 16 h; b) KNPhth, DMF, 100°C, 16 h; c) TosCl, $NEt_3$, DMAP (cat.), $CH_2Cl_2$, 16 h.

**Anion-binding properties of calix[4]arene macrobicycles 2 and 3**: To demonstrate the efficacy of chloride as a template for the formation of interpenetrated assemblies, the anion-binding properties of **2** and **3** were investigated by $^1$H NMR spectroscopy of solutions in [$D_6$]acetone at 298 K. Unsurprisingly, the isophthalamide clefts of these macrobicycles strongly bind halides in 1:1 stoichiometry, which can be seen by large downfield shifts in the $^1$H NMR spectrum for the isophthalamide (c, d) and hydroquinone (g) protons on addition of TBA salts (Figure 1a), as expected from the numerous literature studies into this motif.[12] Notably, the signal that corresponds to hydroxyl proton k is not affected by the addition of TBA salts. Association constants were derived by using the WinEQNMR program[13] (Table 1) from results obtained by monitoring the change in chemical shift of the signal that arises from the amide protons (d) of the macrocycles, which demonstrated that the selectivity order was $Cl^- > Br^- > I^-$. Again this trend was as expected, and confirmed the use of chloride as the anion of choice in the formation of interpenetrated species. Although both macrobicycles also bound acetate strongly, this anion is less suitable for putative interpenetration because it lacks the spherical symmetry necessary to mediate the threading process. Furthermore, it is clear that **3** binds anions more strongly than **2** because the nitro group increases the acidity of the amide groups.




Scheme 3. Preparations of calix[4]arene macrocycles **2** and **3**. a) $K_2CO_3$, $CH_3CN$, Δ, 4 d; b) $N_2H_4$, EtOH, Δ, 16 h; c) $NEt_3$, $CH_2Cl_2$, 16 h.

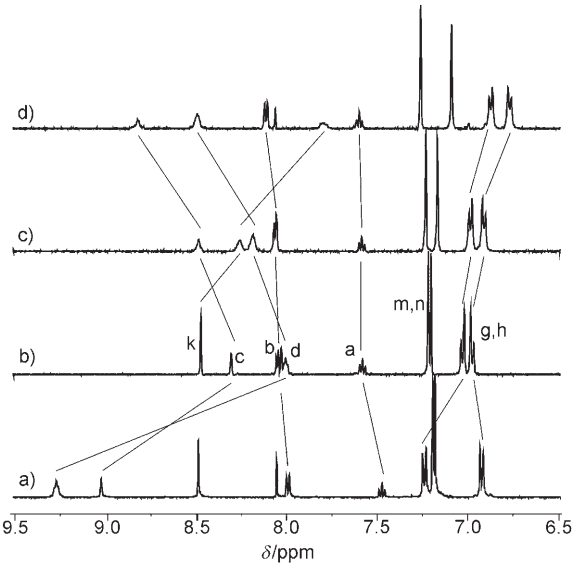


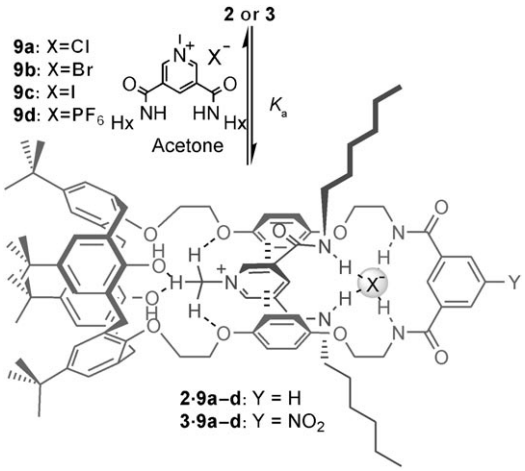

Figure 1. $^1$H NMR spectral changes observed for **2** induced on addition of TBACl or **9a**. a) **2**·TBACl, b) **2**, c) **2·9a** and d) **2**+2.5 equiv of **9a**. Solvent: [$D_6$]acetone, 298 K.

Table 1. Anion-binding properties of macrobicycles **2** and **3**.[a]

| | **2** | | **3** | |
|---|---|---|---|---|
| Anion | $\Delta\delta_{NH}$ [ppm][b] | $K_a$ [$M^{-1}$] | $\Delta\delta_{NH}$ [ppm][b] | $K_a$ [$M^{-1}$] |
| $Cl^-$ | 1.45 | 5700 | 1.84 | $>10^4$ |
| $Br^-$ | 0.69 | 930 | 1.11 | 7600 |
| $I^-$ | 0.10 | 90[c] | 0.25 | 380 |
| $AcO^-$ | 1.51 | 4000 | 2.72 | $>10^4$ |
| $HSO_4^-$ | 0.21 | 370 | 0.48 | 1700 |

[a] $K_a$ ($M^{-1}$) 1:1 binding. Solvent: [$D_6$]acetone, 298 K. Association constant errors $<10\%$. [b] Chemical shift change of the amide proton signal that occurs on addition of TBA salt (one equiv). [c] Association constant derived from monitoring isophthalamide proton c.

**Formation of anion-templated pseudorotaxanes**: The formation of pseudorotaxane derivatives based on the inclusion of the simple dihexyl pyridinium threads **9a–d** in the macrocyclic clefts of **2** and **3** (Scheme 4) was then investigated by $^1$H NMR spectroscopy of solutions in [$D_6$]acetone at




Scheme 4. Formation of anion-templated [2]pseudorotaxanes **2·9a–d** and **3·9a–d**, in [$D_6$]acetone at 298 K.

298 K.[7f] The existence of the desired interpenetrated species **2·9a** could be inferred from chemical shift data. Figure 1b and c illustrates the differences in the spectra of **2** and **2·9a**, in which a downfield shift in the amide and isophthalyl proton signals (c, d) occurs to indicate that there is primary coordination to the chloride anion. The spectra also show upfield shifts in the signals that arise from the hydroxy (k) and hydroquinone (g, h) protons, which confirms the interpenetrated nature of the products through the presence of secondary hydrogen-bonding and π-stacking interactions. Notably, this upfield shift of the hydroquinone protons is in sharp contrast to the downfield shift that is observed when TBA chloride is added to receptor **2**, as is the upfield shift in the hydroxyl proton signal. Similar changes were observed in the $^1$H NMR spectrum of **3** upon the addition of thread species **9a–d**. The stoichiometries of these interactions were 1:1 and association constants for the assembly process could be inferred by monitoring the dependence of the pertinent proton chemical shifts of the macrocycles on the concentration of **9a–d** added (Table 2).[13] No discernible evidence for the formation of **2·9d** or **3·9d** was obtained,

Table 2. [2]Pseudorotaxane association constants for **2** and **3** with threads **9a–d**.[a]

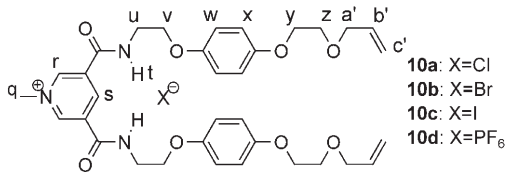
| Macrocycle | **9a** | **9b** | **9c** | **9d** |
|---|---|---|---|---|
| **2** | 170 | 30 | <5 | –[b] |
| **3** | 240 | 70 | 20 | –[b] |

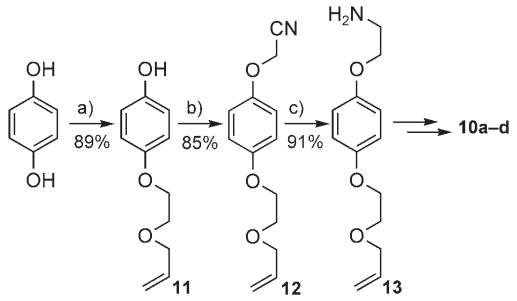
[a] $K_a(M^{-1})$. Solvent: $[D_6]$acetone, 298 K. Association constant errors <10%. Constants are derived by monitoring the chemical shift of hydroxyl proton k. [b] No interaction could be inferred.

which emphasised the importance of the templating anion in the threading process.

The importance of the anion template in mediating pseudorotaxane assembly is underscored by the magnitudes of the association constants obtained. Thus, for both **2** and **3** the association is strongest when the counterion is chloride (**9a**) and weakest for hexafluorophosphate (**9d**). The thermodynamic stabilities of the pseudorotaxane assemblies based on bromide (**9b**) and iodide (**9c**) lie intermediate between these two extremes. Thus, the strength of the interaction is dependent on the size, basicity and shape of the anionic template. Furthermore, the nature of the anion-binding cleft of the macrobicycle is important because the strength of pseudorotaxane formation is enhanced by the presence of the nitro functionality in **3** relative to **2**. As in the case of simple anion binding, this functionality increases the acidity of the amide hydrogen-bond-donating groups of the macrobicycle, and thus, enhances the association of the anion, and in this case also the thread, component.

**Formation of anion-templated catenanes**: After showing that the anion-mediated penetration of the simple dihexyl pyridinium chloride thread **9a** into the cavities of **2** and **3** occurred, we then aimed to form permanently interlocked species, namely, [2]catenanes. Therefore, it was necessary to form a reactive anion-templated pseudorotaxane complex in which the terminal functionalities of the incorporated thread could be joined together, or "clipped" by using ring-closing metathesis,[11,14] to form the [2]catenane. Catenane formation could be achieved by the assembly of pseudorotaxanes that include the known bisallyl pyridinium chloride thread **10a** within the macrobicycles **2** and **3**, followed by ring-closing metathesis to form the catenanes.[7h] The synthesis of **10a–d** reported previously is somewhat lengthy,[7i] and therefore, an alternative procedure was devised, the novel parts of which are summarised briefly in Scheme 5. *p*-Hydroquinone was mono-functionalised with a substoichiometric quantity of 2-allyloxyethanol-*p*-toluene sulfonate[15] by



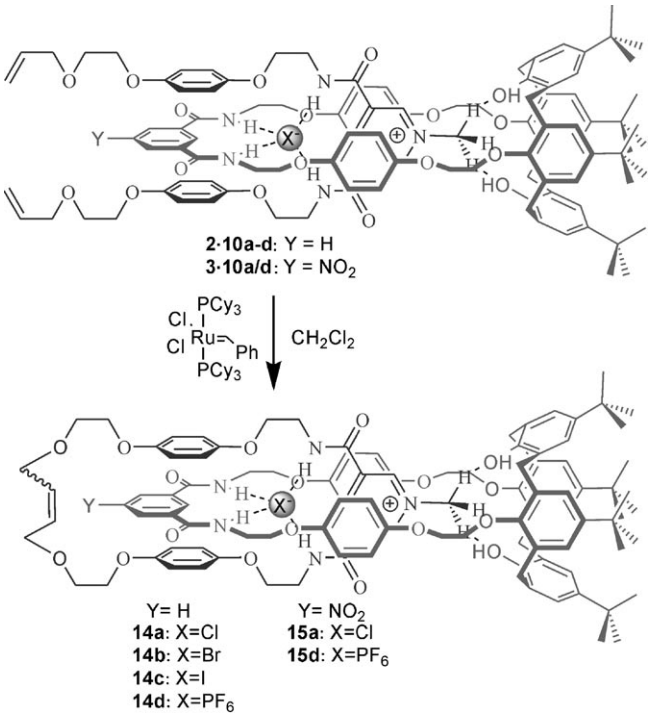

Scheme 5. Alternative route to precursors **10a–d**. a) 2-Allyloxyethanol-*p*-toluene sulfonate, $K_2CO_3$, EtOH, Δ, 16 h; b) $BrCH_2CN$, $K_2CO_3$, acetone, Δ, 16 h; c) $LiAlH_4$, $Et_2O$, Δ, 1 h.

heating the reactants at reflux in ethanol in the presence of potassium carbonate to give **11** in 89% yield. This mono-functionalised material was then treated with bromoacetonitrile and potassium carbonate in acetone and heated at reflux to give **12** in 85% yield. Amine precursor **13** could then be obtained by reducing **12** with lithium aluminium hydride in ether by heating at reflux. Precursor **13** was further modified by following known procedures[7i] to give the pyridinium salts **10a–d**. This new procedure makes the preparation of similar precursors substantially more accessible, and improves the facility of this general anion-templation strategy.

The formation of [2]pseudorotaxanes **2·10a** and **3·10a** in $CD_2Cl_2$ was shown by $^1H$ NMR spectroscopic experiments that are analogous to those used for **2·9a**. Again, there was no evidence for the formation of hexafluorophosphate-directed pseudorotaxanes **2·10d** and **3·10d** from these experiments, which indicates that an analogous anion-templation effect was operating in these systems. These pseudorotaxane precursors were shown to exist, and ring-closing metathesis reactions were carried out on a solution of **2** with thread **10a** in $CH_2Cl_2$ in the presence of Grubbs' first-generation catalyst to give [2]catenane **14a** in 29% yield (69% based on recovered starting material **2**) after purification by chromatography (Scheme 6). When **10b** was used, the yield of catenane **14b** was only 8% and no interlocked product was obtained for threads **10c** and **10d**. Pseudorotaxane complex **3·10a** was similarly treated to give **15a** in 29% yield; the stronger anion-binding properties of this receptor did not enhance the yield of catenane obtained. However, no product was detected when complex **3·10d** was treated in a similar manner. These observations serve to emphasise the critical nature of the anion template in mediating the assembly process, and the yields compare favourably to those obtained for previous systems.[7h]

Although mass spectrometric and TLC analysis of the reaction mixture revealed the presence of a new product of the requisite mass, confirmation of the interlocked nature of catenane product **14a** was obtained from one- and two-dimensional NMR experiments (Figures 2 and 3). As in the case of pseudorotaxane **2·9a**, shifts in the primary coordination spheres of the pyridinium (s, t) and isophthalamide (c,




Scheme 6. Synthesis of catenanes **14a–d** and **15a**. Yields: **14a** 29%, **14b** 8%, **14c** and **14d** 0%, **15a** 29% and **15d** 0%. Catenane **14d** was prepared in 75% yield by treatment of **14a** with $AgPF_6$.

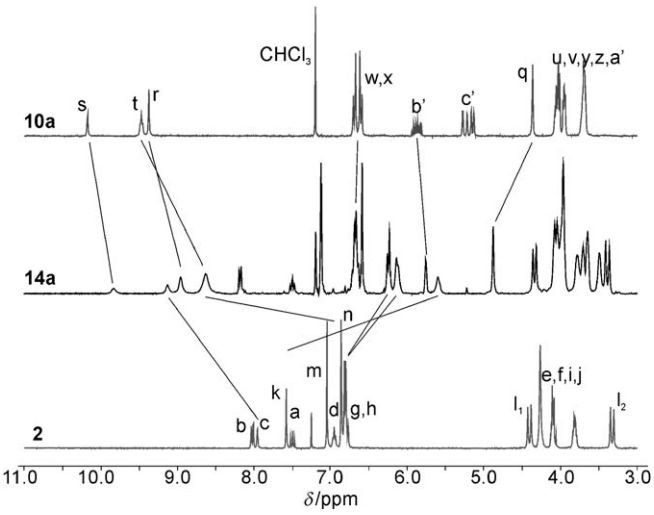



Figure 2. Differences between the $^1$H NMR spectra of **2**, **10a** and **14a**, which illustrates the interlocked nature of the catenane product. Solvent: $CDCl_3$ (298 K).

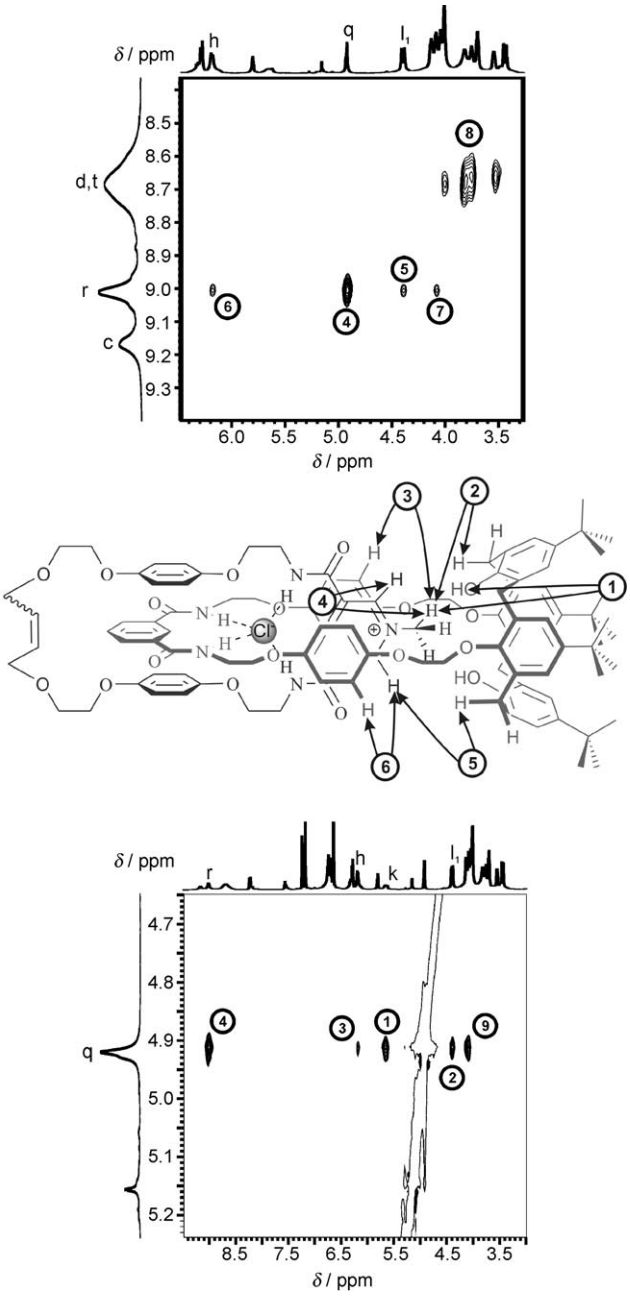



Figure 3. Portions of the ROESY spectrum of catenane **14a**. The spectra illustrate the coupling interactions between pyridinium $H^2$ proton r and the calixarene component (top) and the interactions between pyridinium *N*-methyl proton q and the calixarene component (bottom). Additional couplings (7–9) correspond to those to the $OCH_2$ protons of the molecule, which could not be assigned. Solvent: $CDCl_3$ (298 K).

d) units indicate competitive complexation of the chloride anion relative to the "free" components. A downfield shift of the pyridinium methyl proton signal (q), coupled with upfield shifts in the macrocycle hydroxyl (k) and hydroquinone (g, h) proton signals, further serves to illustrate the interpenetration of the two components. The existence of a macrocyclic thread, rather than the unclosed precursor, is indicated by the disappearance of the signal arising from proton c′, and the resolution of that arising from b′ owing to the formation of the double bond. In addition, a ROESY NMR spectrum of **14a** indicated that there were coupling interactions between a number of proximal protons, which included those illustrated in Figure 3.

**Catenane anion-binding properties**: Exchange of the residual chloride template of **14a** with the non-competitive hexa-

fluorophosphate anion by using $AgPF_6$ formed catenane derivative **14d**, which contained a topologically unique anion-binding domain that is defined by the interlocked hydrogen-bond-donating components.[7,16] Confirmation that species **14d** remains interlocked on exchange of the anion was obtained by performing an NOE experiment (Figure 4), in

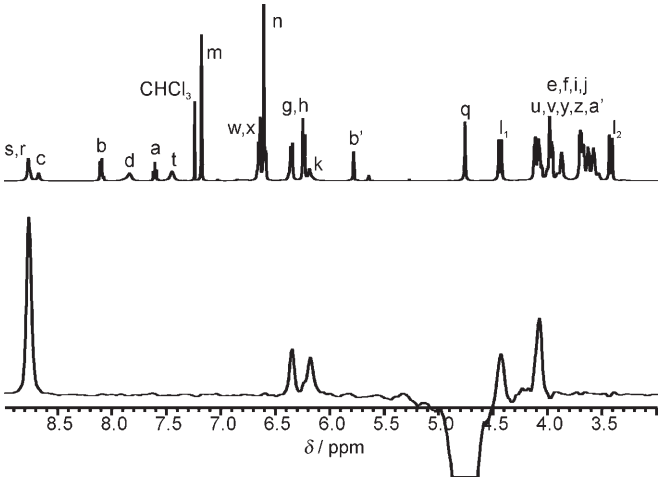



Figure 4. Results from the NOE experiment performed on *N*-methylpyridinium proton q in **14d**. Top: $^1$H NMR spectrum of **10d**. Bottom: NOE of proton q in **14d**.

which the expected coupling interaction between the pyridinium *N*-methyl and calixarene macrocycle proton signals was observed. The nature of the binding domain of **14d** was probed by $^1$H NMR spectroscopic titration experiments by using a $CDCl_3/CD_3OD$ (1:1) solvent mixture, and compared with the properties of free macrocycle **2** and thread **10d**.[13] It was found that macrocycle **2** displayed no affinity for anions in this solvent system, whereas the addition of anions to **14d** induced downfield shifts (0.3–0.5 ppm) in the pyridinium (s) and isophthalyl (c) protons. The amide protons were not observed in this solvent system owing to exchange phenomena. The interaction was 1:1 for all of the anions studied, with the exceptions of acetate and dihydrogensulfate in the presence of thread **10d**. Monitoring the dependence of chemical shift on the concentration of TBA salt added allowed association constant data to be derived (Table 3). These data reveal some interesting trends. Catenane **14d** binds halide anions strongly, with a selectivity for chloride, owing to the provision of a pseudotetrahedral binding environment by the interlocked components, which is able to satisfy the coordination sphere of spherical anions. Catenane **14d** binds the oxoanions acetate and dihydrogenphosphate more weakly than halide anions, and less strongly than **10d** binds acetate and dihydrogenphosphate, and interacts strongly with hydrogensulfate. This latter observation is not easy to explain, but is almost certainly as a result of the topologically unique binding site provided by interlocking the two components. Indeed, this selectivity for hydrogensulfate has been previously observed in rotaxane systems by luminescence spectroscopy techniques.[7e] Thread **10d** binds all of the halides with similar strengths, all of which are weaker than that of **14d**, and shows a preference for binding bromide. Otherwise, the anion association constants observed correlate well with oxoanion basicity.

Table 3. Anion-binding properties of catenane **14d**.[a]

| | $Cl^-$ | $Br^-$ | $I^-$ | $AcO^-$ | $H_2PO_4^-$ | $HSO_4^-$ |
|---|---|---|---|---|---|---|
| **10d** | 460 | 590 | 440 | 1500[c] | 1360[c] | –[b] |
| **14d** | 960 | 740 | 550 | 400 | 480 | 1000 |

[a] $K_a$ ($M^{-1}$) 1:1 binding. Solvent: $CDCl_3/CD_3OD$ 1:1, 298 K. Association constant errors $<10\%$. [b] No association could be inferred. [c] See ref. [7i]. 1:2 binding observed. $K_a(AcO^-) = 345\,M^{-1}$, $K_a(H_2PO_4^-) = 370\,M^{-1}$.

These anion-binding results clearly illustrate that the provision of a unique hydrogen-bond-donating pocket formed by interlocking the two components in catenane **14d** results in novel anion-binding behaviour. Relative to the free components, this anion-binding behaviour manifests as an enhancement in affinity for spherical anions, such as the halides, which allow size and shape complementarity for this pocket, but a reduction in affinity for the oxoanions acetate and dihydrogenphosphate. Catenane **14d** also demonstrates selectivity for hydrogensulfate, which must also arise from the provision of a topologically unique binding pocket.[17]

## Conclusion

A new class of interpenetrated and interlocked motifs that incorporate a calix[4]arene unit have been successfully assembled by means of a strategic anion-templating method. The syntheses of these systems represent a significant step forward in the preparation of anion-templated derivatives, both in terms of synthetic viability and of their ultimate application, such as in molecular sensory devices. It has also been demonstrated that exchanging the templating chloride anion of a catenane that contains a calix[4]arene for non-coordinating hexafluorophosphate yields a system that contains a unique anion-binding domain, which is defined by the interlocked nature of the catenane. This emphasises the potential use of similar species as sensory devices. The further exploitation of such interpenetrated derivatives is currently a subject of intense interest, because modification of the highly adaptable calixarene framework will lead to increasingly sophisticated derivatives, the applicability of which appears to be limited only by the imagination.

## Experimental Section

All commercial-grade chemicals were used without further purification. TBA salts, silver hexafluorophosphate and Grubbs first-generation catalyst were stored prior to use under vacuum in a desiccator that contained phosphorus pentoxide and self-indicating silica gel. Solvents were dried by being degassed with nitrogen and then dried by passing them through a column of activated alumina by using Grubbs apparatus. Elemental analyses were carried out by the service at the Inorganic Chemistry Lab-

oratory, University of Oxford. Mass spectra were obtained by using a Micromass LCT (ESMS) instrument. NMR spectra were recorded by using a Varian Mercury 300, an Oxford Instruments Venus 300 or a Varian Unity Plus 500 spectrometer, in which the solvent serves as the lock and internal reference.

**Isophthalamide calix[4]arene macrobicycle (2)**: A solution of bis(amine) **8** (1.50 g, 1.49 mmol) in dry $CH_2Cl_2$ (75 mL) and a solution of isophthaloyl dichloride (0.30 g, 1.49 mmol) in dry $CH_2Cl_2$ (75 mL) were added dropwise, simultaneously, to a stirred solution of triethylamine (0.5 mL, 3.28 mmol) in dry $CH_2Cl_2$ (1200 mL) over a period of 1 h, under an atmosphere of nitrogen. The reaction mixture was allowed to stir at room temperature for a further 16 h, before it was reduced in vacuo to approximately 100 mL, and this concentrated solution was washed consecutively with 1 M aqueous HCl solution (2×100 mL), $H_2O$ (100 mL), 1 M aqueous NaOH solution (100 mL) and brine (100 mL). The organic layer was then dried over $MgSO_4$, filtered, and the solvent was removed in vacuo. Purification was completed by silica gel chromatography (EtOAc/hexane 90:10 v/v) in which the first band that eluted was collected. The combined fractions were concentrated in vacuo to give **2** as a white solid (1.31 g, 77%). M.p. 242–244°C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=1.03 (s, 18H; C$H_3$), 1.29 (s, 18H; C$H_3$), 3.35 (d, $^2J$=12.9 Hz, 4H; ArCH$_{in}H_{out}$Ar), 3.83 (m, 4H; NC$H_2$), 4.11 (m, 4H; OC$H_2$), 4.28 (m, 8H; 2×OC$H_2$), 4.43 (d, $^2J$=12.9 Hz, 4H; ArC$H_{in}$H$_{out}$Ar), 6.83 (m, 8H; hydroq Ar$H$), 6.88 (s, 4H; calix Ar$H$), 6.99 (brs, 2H, N$H$), 7.07 (s, 4H; calix Ar$H$), 7.51 (t, $^3J$=7.6 Hz, 1H; isoph Ar$H^5$), 7.58 (s, 2H; O$H$), 7.98 (s, 1H; isoph Ar$H^2$), 8.03 ppm (d, 2H, $^3J$=7.6 Hz; isoph Ar$H^4$, Ar$H^6$); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$=31.06, 31.66, 33.80, 33.97, 39.68, 67.33, 74.07, 116.09, 115.58, 123.39, 125.11, 125.66, 127.87, 129.55, 131.15, 132.83, 134.45, 141.43, 147.04, 149.88, 150.56, 152.76, 153.23, 166.86 ppm; ESMS: $m/z$: 1159.60 [$M$+Na]$^+$; elemental analysis calcd (%) for $C_{72}H_{84}N_2O_{10}$: C 76.0, H 7.4, N 2.5; found: C 75.8, H 7.4, N 2.6.

**5-Nitroisophthalamide calix[4]arene macrobicycle (3)**: This compound was prepared in an analogous manner to macrobicycle **2** by using 5-nitroisophthaloyl dichloride (49.2 mg, 0.199 mmol), calix[4]arene amine **8** (200 mg, 0.199 mmol) and triethylamine (0.1 mL, 0.7 mmol) in dry $CH_2Cl_2$ (200 mL total volume). Purification was accomplished by preparative TLC (silica gel, $CH_2Cl_2$/MeOH 65:35 v/v) to give **3** as a bright yellow solid (104 mg, 44%). M.p. 234–236°C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=1.01 (s, 18H; C$H_3$), 1.29 (s, 18H; C$H_3$), 3.34 (d, $^2J$=12.9 Hz, 4H; ArCH$_{in}H_{out}$Ar), 3.87 (m, 4H; NC$H_2$), 4.12 (m, 4H; OC$H_2$), 4.30 (m, 8H; 2×OC$H_2$), 4.42 (d, $^2J$=12.9 Hz, 4H; ArC$H_{in}$H$_{out}$Ar), 6.75 (m, 4H; hydroq Ar$H$), 6.86 (m, 8H; calix Ar$H$, hydroq Ar$H$), 7.07 (s, 4H; calix Ar$H$), 7.15 (brs, 2H; N$H$), 7.44 (s, 2H; O$H$), 8.38 (s, 1H; isoph Ar$H^2$), 8.82 ppm (s, 2H; isoph Ar$H^4$, Ar$H^6$); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$=31.03, 31.66, 33.81, 33.94, 40.13, 67.04, 67.27, 74.22, 115.43, 115.94, 125.13, 125.50, 125.65, 127.91, 129.22, 132.65, 136.08, 141.51, 147.04, 148.69, 149.93, 150.47, 152.28, 153.16, 164.75 ppm; ESMS: $m/z$: 1204.51 [$M$+Na]$^+$; elemental analysis calcd (%) for $C_{72}H_{83}N_3O_{12}$·$^3/_4CH_2Cl_2$: C 70.1, H 6.8, N 3.4; found: C 70.2, H 6.8, N 3.5.

**(2-Tosyloxyethoxy)-4-(2-phthalimidoethoxy)benzene (4)**: Triethylamine (2 mL, 14.2 mmol) and DMAP (cat. 10 mg) were added to a solution of **6** (1.22 g, 3.73 mmol) and tosyl chloride (0.78 g, 4.10 mmol) in dry $CH_2Cl_2$ (50 mL), and the reaction mixture was then stirred under a nitrogen atmosphere for 16 h. $H_2O$ (25 mL) was added to the solution, and the vigorously stirred biphasic mixture was then carefully neutralised with 10% aqueous citric acid solution. The phases were then separated, and the organic layer was subsequently washed with $H_2O$ (2×25 mL) and brine (50 mL), before it was dried over $MgSO_4$ and filtered. Subsequent removal of the solvent in vacuo gave **4** as a white solid (1.74 g, 97%). M.p. 123–125°C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=2.44 (s, 3H; C$H_3$), 4.07 (m, 4H; 2×C$H_2$), 4.17 (m, 2H; C$H_2$), 4.32 (t, $^3J$=4.7 Hz, 2H; C$H_2$), 6.66 (d, $^3J$=9.4 Hz, 2H; Ar$H$), 6.77 (d, $^3J$=9.4 Hz, 2H; Ar$H$), 7.33 (d, $^3J$=8.0 Hz, 2H; Tos$H$), 7.73 (dd, $^3J$=5.4, $^4J$=3.1 Hz, 2H; Phth$H$), 7.80 (d, $^3J$=8.0 Hz, 2H; Tos$H$), 7.87 ppm (dd, $^3J$=5.4, $^4J$=3.1 Hz, 2H; Phth$H$); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$=21.61, 37.33, 65.27, 66.05, 68.18, 115.55, 123.29, 127.95, 129.79, 131.94, 132.77, 134.01, 144.87, 152.35, 152.89, 154.49, 168.13 ppm. ESMS: $m/z$ calcd for $C_{25}H_{23}NO_7SNa$: 504.1093; found: 504.1089 [$M$+Na]$^+$.

**Hydroquinone bis(2-hydroxylethyl)ether monotosylate (5)**: Tosyl chloride (6.06 g, 31.8 mmol) was added to a stirred solution of hydroquinone bis(2-hydroxylethyl)ether (6.00 g, 30.3 mmol), triethylamine (5.5 mL, 39.4 mmol) and DMAP (cat. 10 mg) in dry THF (150 mL), and the resulting reaction mixture was stirred under a nitrogen atmosphere for 16 h. The resulting white suspension was filtered, and the filtrate was concentrated in vacuo to give a crude yellow material that was purified by silica gel chromatography (EtOAc/hexane 50:50 v/v) and eluted as the third band. The fractions were concentrated in vacuo to give **5** as a yellow oil (4.81 g, 45%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=2.46 (s, 3H; C$H_3$), 3.95 (m, 2H; OC$H_2$), 4.03 (m, 2H; OC$H_2$), 4.10 (t, $^3J$=4.7 Hz, 2H; OC$H_2$), 4.34 (t, $^3J$=4.7 Hz, 2H; OC$H_2$), 6.73 (d, $^3J$=9.4 Hz, 2H; Ar$H$), 6.82 (d, $^3J$=9.4 Hz, 2H; Ar$H$), 7.36 (d, $^3J$=8.1 Hz, 2H; Tos$H$), 7.82 ppm (d, $^3J$=8.1 Hz, 2H; Tos$H$); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$=21.64, 61.49, 66.14, 68.21, 69.71, 115.43, 115.69, 127.98, 129.82, 132.77, 144.91, 152.39, 153.22 ppm; ESMS: $m/z$: 375.08 [$M$+Na]$^+$.

**(2-Hydroxylethoxy)-4-(2-phthalimidoethoxy)benzene (6)**: Potassium phthalimide (2.60 g, 14.1 mmol) was added to a solution of **5** (3.30 g, 9.38 mmol) in anhydrous DMF (25 mL), and the resulting suspension was heated to 100°C for 16 h, under a nitrogen atmosphere. The reaction mixture was subsequently allowed to cool to room temperature and was then poured onto $H_2O$ (100 mL). The resulting milky suspension was extracted with $CH_2Cl_2$ (3×50 mL), before the organic extracts were combined, dried over $MgSO_4$, filtered, and the filtrate concentrated in vacuo. The product was purified by silica gel chromatography (EtOAc/hexane 50:50 v/v) and eluted as the third band. The fractions were concentrated in vacuo to give **6** as a white solid (1.96 g, 64%). M.p. 114–116°C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=2.04 (t, $^3J$=6.2 Hz, 1H; O$H$), 3.93 (m, 2H; C$H_2$OH), 4.03 (m, 2H; C$H_2$CH$_2$OH), 4.09 (m, 2H; C$H_2$), 4.19 (m, 2H; C$H_2$), 6.82 (m, 4H; Ar$H$), 7.73 (dd, $^3J$=5.4, $^4J$=3.1 Hz, 2H; Phth$H$), 7.87 ppm (dd, $^3J$=5.4, $^4J$=3.1 Hz, 2H; Phth$H$); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$=37.34, 61.45, 65.29, 69.70, 115.38, 115.61, 123.28, 131.93, 133.97, 152.67, 152.98, 168.14 ppm; ESMS: $m/z$ calcd for $C_{18}H_{17}NO_5Na$: 350.1004; found: 350.1012 [$M$+Na]$^+$.

**5,11,17,23-Tetra-*tert*-butyl-25,27-di{2-[4-(2-phthalimidoethoxy)phenoxy]-ethoxy}-26,28-dihydroxycalix[4]arene (7)**: A suspension of *p*-*tert*-butylcalix[4]arene (0.4 g, 0.56 mmol) and potassium carbonate (0.06 g, 1.2 mmol) in dry $CH_3CN$ (25 mL) was stirred under a nitrogen atmosphere for 1 h. Compound **4** (0.72 g, 1.5 mmol) was then added and the reaction mixture heated at reflux under a nitrogen atmosphere for 4 d. The suspension was then allowed to cool to room temperature, and the solvent was carefully removed in vacuo. The resulting off-white residue was triturated with 1 M aqueous HCl solution (50 mL) to give an aqueous suspension that was extracted with $CH_2Cl_2$ (3×50 mL). The combined organic extracts were washed with $H_2O$ (2×50 mL), dried over $MgSO_4$ and filtered. Removal of the solvent in vacuo gave a crude material that was purified by silica gel chromatography (EtOAc/hexane 40:60 v/v) and eluted as the first (intense) band. The fractions were combining and the solvent was removed in vacuo to give **7** as a white solid (0.50 g, 75%). M.p. 194–196°C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=1.01 (s, 18H; C$H_3$), 1.28 (s, 18H; C$H_3$), 3.30 (d, $^2J$=12.9 Hz, 4H; ArCH$_{in}H_{out}$Ar), 4.09 (m, 4H; C$H_2$), 4.19 (m, 8H; 2×C$H_2$), 4.26 (m, 4H; C$H_2$), 4.40 (d, $^2J$=12.9 Hz, 4H; ArC$H_{in}$H$_{out}$Ar), 6.81 (m, 8H; hydroq Ar$H$), 6.86 (s, 4H; calix Ar$H$), 7.04 (s, 4H; calix Ar$H$), 7.59 (s, 2H; O$H$), 7.66 (dd, $^3J$=5.4, $^4J$=3.1 Hz, 2H; Phth$H$), 7.83 ppm (dd, $^3J$=5.4, $^4J$=3.1 Hz, 2H; Phth$H$); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$=31.03, 31.65, 33.77, 33.91, 37.43, 65.31, 67.16, 73.97, 115.52, 123.26, 125.57, 127.76, 131.96, 132.85, 133.97, 141.19, 146.83, 149.79, 150.61, 153.04, 168.15 ppm; ESMS: $m/z$: 1289.52 [$M$+Na]$^+$.

**5,11,17,23-Tetra-*tert*-butyl-25,27-di{2-[4-(2-aminoethoxy)phenoxy]-ethoxy}-26,28-dihydroxycalix[4]arene (8)**: Compound **7** (1.04 g, 8.20 mmol) was dissolved in ethanol (50 mL) before hydrazine monohydrate (1 mL, excess) was added, and the stirred solution was heated at reflux for 16 h. After the reaction mixture was allowed to cool to room temperature, it was added to $H_2O$ (100 mL) and then extracted by using EtOAc (4×50 mL). The combined organic layers were dried over $MgSO_4$, filtered and solvent removed in vacuo to give **8** as a white solid (0.81 g, 98%). M.p. 205–207°C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=1.03 (s, 18H; C$H_3$), 1.28 (s, 18H; C$H_3$), 3.07 (m, 4H; C$H_2$N), 3.31 (d, $^2J$=12.9 Hz, 4H; Ar-

$CH_{in}H_{out}Ar$), 3.94 (t, $^3J=5.0$ Hz, 4H; $CH_2CH_2N$), 4.28 (m, 8H; 2× $OCH_2$), 4.41 (d, $^2J=12.9$ Hz, 4H; $ArCH_{in}H_{out}Ar$), 6.83 (d, $^3J=8.8$ Hz, 4H; hydroq Ar*H*), 6.87 (s, 4H; calix Ar*H*), 6.90 (d, $^3J=8.8$ Hz, 4H; hydroq Ar*H*), 7.05 (s, 4H; calix Ar*H*), 7.56 ppm (s, 2H; O*H*); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta=31.06$, 31.66, 33.78, 33.95, 41.63, 67.22, 70.65, 73.97, 115.33, 115.96, 125.05, 125.60, 127.81, 132.86, 141.25, 146.87, 149.82, 150.59, 152.89, 153.23 ppm; ESMS: *m*/*z*: 1007.55 $[M+H]^+$.

**4-[2-(Allyloxy)ethoxy]phenol (11)**: 2-Allyloxyethanol-*p*-toluene sulfonate (13.09 g, 0.051 mol), *p*-hydroquinone (22.55 g, 0.204 mol) and potassium carbonate (7.76 g, 0.056 mol) were suspended in ethanol (350 mL) and heated at reflux for 18 h under a nitrogen atmosphere. The reaction mixture was allowed to cool to room temperature, filtered, and the solvent was removed in vacuo. The residue was then redissolved in $H_2O$ (100 mL) and acidified to pH 3 by the addition of 1 M aqueous HCl solution. The crude product was extracted with $CHCl_3$ (3×100 mL), before the combined organic extracts were dried over $MgSO_4$, filtered, and the solvent removed in vacuo. Purification of this crude product by silica gel chromatography (hexane/EtOAc 60:40 v/v) gave **11** as a brown oil (8.83 g, 89%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta=3.80$ (m, 2H, $ArOCH_2CH_2$), 4.09 (m, 4H, $OCH_2CHCH_2$, $ArOCH_2$), 5.20–5.34 (m, 2H, $OCH_2CHCH_2$), 5.69 (br s, 1H; O*H*), 5.88–6.01 (m, 1H; $OCH_2CHCH_2$), 6.75 ppm (m, 4H; hydroq Ar*H*); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta=67.96$, 68.96, 72.36, 115.72, 116.01, 117.72, 134.22, 149.82, 152.55 ppm; ESMS: *m*/*z*: 217.08 $[M+Na]^+$.

**2-{4-[2-(Allyloxy)ethoxy]phenoxy}acetonitrile (12)**: Compound **11** (2.05 g, 10.6 mmol) was dissolved in acetone (50 mL) before bromoacetonitrile (1.39 g, 11.6 mmol) and potassium carbonate (1.60 g, 11.6 mmol) were added, and the reaction mixture was heated at reflux for 16 h under a nitrogen atmosphere. The suspension was then allowed to cool to room temperature, filtered, and the filtrate was concentrated in vacuo. The resulting brown oil was dissolved in $CHCl_3$ and filtered through a plug of silica gel. Removal of solvent from the filtrate in vacuo yielded **12** as a yellow oil (2.10 g, 85%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta=3.78$ (t, $^3J=$ 4.7 Hz, 2H; $ArOCH_2CH_2$), 4.09 (m, 4H; $OCH_2CHCH_2$, $ArOCH_2$), 4.69 (s, 2H; $NCCH_2$) 5.20–5.34 (m, 2H; $OCH_2CHCH_2$), 5.88–6.01 (m, 1H; $OCH_2CHCH_2$), 6.91 ppm (m, 4H; hydroq Ar*H*); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta=54.67$, 67.83, 68.35, 72.21, 115.62, 116.44, 117.28, 134.37, 150.65, 154.63 ppm; ESMS: *m*/*z* calcd for $C_{13}H_{16}NO_3$: 234.1140; found: 234.1130 $[M+H]^+$.

**2-{4-[2-(Allyloxy)ethoxy]phenoxy}ethylamine (13)**: A solution of **12** (3.75 g, 16.0 mmol) in dry diethyl ether (50 mL) was slowly added to a suspension of $LiAlH_4$ (0.92 g, 24.1 mmol) in dry diethyl ether (250 mL), and the resulting suspension was then heated at reflux, under a nitrogen atmosphere, for 1 h. The reaction mixture was subsequently allowed to cool to room temperature, and unreacted $LiAlH_4$ was neutralised by the careful addition of 10% aqueous NaOH solution (40 mL). $H_2O$ (100 mL) was then added, and the phases separated. The diethyl ether layer was then decanted, and the remaining aqueous layer extracted by using diethyl ether (8×100 mL). The organic layers were combined, dried over $MgSO_4$, filtered and the filtrate was concentrated in vacuo to give **13** as a red-brown oil (3.47 g, 91%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta=1.50$ (br s, 2H; $NH_2$), 3.04 (t, $^3J=5.1$ Hz, 2H; $CH_2NH_2$), 3.77 (m, 2H; $OCH_2$), 3.93 (t, $^3J=5.1$ Hz, 2H; $CH_2CH_2N$), 4.08 (m, 4H; 2×$OCH_2$), 5.18–5.34 (m, 2H; $OCH_2CHCH_2$), 5.88–6.01 (m, 1H; $OCH_2CHCH_2$), 6.84 ppm (m, 4H; hydroq Ar*H*); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta=41.60$, 67.98, 68.53, 70.65, 72.29, 115.27, 115.54, 117.28, 134.50, 152.98, 153.11 ppm; ESMS: *m*/*z* calcd for $C_{13}H_{20}NO_3$: 238.1443; found: 238.1432 $[M+H]^+$.

**Isophthalamide calix[4]arene catenane chloride (14a)**: Macrobicycle **2** (100.0 mg, 0.0879 mmol) and chloride thread **10a** (86.8 mg, 0.132 mmol) were dissolved in dry $CH_2Cl_2$ (65 mL) and stirred for 20 minutes. Grubbs first-generation catalyst (17 mg, 20% by mass) was added, and the reaction mixture was stirred for 16 h under an atmosphere of nitrogen. The solvent was then removed in vacuo to give the crude material, which was purified by preparative TLC (silica gel, $CH_2Cl_2$/MeOH 96:4 v/v) to give impure catenane **14a**. Trituration of this product in diisopropyl ether gave the pure catenane as a pale yellow solid (45 mg, 29% or 69% including recovered starting material **2**). $^1$H NMR (300 MHz, $CDCl_3$): $\delta=$ 0.87 (s, 18H; $C(CH_3)_3$), 1.40 (s, 18H; $C(CH_3)_3$), 3.47 (d, $^2J=13.3$ Hz, 4H; $ArCH_{in}H_{out}Ar$), 3.57 (m, 4H; $CH_2$), 3.73 (m, 4H; $CH_2$), 3.79 (m, 4H; $CH_2$), 3.85 (m, 4H; $CH_2$), 4.08 (m, 16H; $CH_2CHCHCH_2$, 3×$CH_2$), 4.15 (m, 4H, $CH_2$), 4.42 (d, $^2J=13.3$ Hz, 4H; $ArCH_{in}H_{out}Ar$), 4.94 (s, 3H; $N^+CH_3$), 5.66 (s, 2H; O*H*), 5.84 (s, 2H; $CH_2CHCHCH_2$), 6.19 (m, 4H; calix-hydroq Ar*H*), 6.31 (m, 4H; calix-hydroq Ar*H*), 6.68 (s, 4H, calix Ar*H*), 6.76 (m, 8H; py-hydroq Ar*H*), 7.21 (s, 4H; calix Ar*H*), 7.59 (t, $^3J=7.6$ Hz, 1H; isoph $ArH^5$), 8.27 (d, $^3J=7.6$ Hz, 2H; isoph $ArH^4$, $ArH^6$), 8.71 (br s, 4H; 2×CON*H*), 8.99 (s, 2H; py$H^2$, $H^6$), 9.23 (s, 1H; isoph $ArH^2$), 9.90 ppm (s, 1H; py$H^4$); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta=$ 30.89, 31.75, 34.03, 39.92, 41.33, 50.84, 65.13, 66.36, 66.76, 67.53, 68.32, 68.67, 70.62, 71.21, 75.22, 109.97, 113.88, 114.70, 115.93, 124.09, 125.53, 125.91, 128.41, 129.00, 129.37, 131.51, 131.93, 133.50, 133.69, 142.77, 144.37, 147.51, 149.98, 150.46, 151.57, 152.63, 152.80, 153.80, 159.72, 166.80 ppm; ESMS: *m*/*z*: 1729.81 $[M-Cl]^+$; elemental analysis calcd (%) for $C_{104}H_{122}ClN_5O_{18}\cdot CH_2Cl_2$: C 68.2, H 6.8, N 3.8; found: C 68.3, H 7.0, N 3.5.

**Isophthalamide calix[4]arene catenane bromide (14b)**: This compound was prepared in an analogous method to that used for the formation of **14a** by using macrocycle **2** (100.0 mg, 0.0879 mmol), bromide thread **10b** (92.4 mg, 0.132 mmol) and Grubbs first-generation catalyst (19 mg, 20% by mass). After an identical workup to that used to prepare **14a**, product **14b** was isolated as a pale yellow solid (13 mg, 8% or 42% including recovered starting material **2**). $^1$H NMR (300 MHz, $CDCl_3$): $\delta=0.87$ (s, 18H; $C(CH_3)_3$), 1.40 (s, 18H; $C(CH_3)_3$), 3.47 (d, $^2J=13.6$ Hz, 4H; $ArCH_{in}H_{out}Ar$), 3.58 (m, 4H; $CH_2$), 3.73 (m, 4H; $CH_2$), 3.80 (m, 4H; $CH_2$), 3.86 (m, 4H; $CH_2$), 4.05–4.15 (m, 20H; $CH_2CHCHCH_2$, 4×$CH_2$), 4.42 (d, $^2J=13.6$ Hz, 4H; $ArCH_{in}H_{out}Ar$), 4.94 (s, 3H; $N^+CH_3$), 5.66 (s, 2H; O*H*), 5.84 (s, 2H; $CH_2CHCHCH_2$), 6.22 (m, 4H; calix-hydroq Ar*H*), 6.32 (m, 4H; calix-hydroq Ar*H*), 6.67 (s, 4H; calix Ar*H*), 6.74 (m, 8H; py-hydroq Ar*H*), 7.21 (s, 4H; calix Ar*H*), 7.59 (t, $^3J=7.6$ Hz, 1H; isoph $ArH^5$), 8.26 (d, $^3J=7.6$ Hz, 2H; isoph $ArH^4$, $ArH^6$), 8.69 (br s, 4H; 2×N*H*), 8.99 (s, 2H; py$H^2$, $H^6$), 9.22 (s, 1H; isoph $ArH^2$), 9.92 ppm (s, 1H; py$H^4$); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta=30.89$, 31.74, 33.84, 39.99, 66.23, 66.76, 67.52, 68.30, 68.72, 69.96, 71.18, 75.24, 109.97, 113.98, 114.74, 115.85, 116.16, 124.17, 125.53, 125.89, 128.39, 128.99, 129.31, 131.51, 131.94, 133.52, 142.75, 144.48, 147.48, 149.95, 150.42, 151.56, 152.60, 152.82, 161.91, 166.84 ppm; ESMS: *m*/*z*: 1729.85 $[M-Br]^+$; elemental analysis calcd (%) for $C_{104}H_{122}N_5O_{18}Br\cdot{}^2/_3CH_2Cl_2$: C 67.4, H 6.7, N 3.8; found: C 67.1, H 6.9, N 3.7.

**Isophthalamide calix[4]arene catenane hexafluorophosphate (14d)**: Chloride catenane **14a** (73 mg, 0.0413 mmol) was dissolved in dry $CH_2Cl_2$ (100 mL) and stirred with $AgPF_6$ (52 mg, 0.207 mmol) for 2 h under a nitrogen atmosphere in the absence of light. The suspension was then filtered, and the brown solid obtained was triturated with $CH_3CN$. This mixture was then filtered and the yellow filtrate concentrated in vacuo. The solid obtained was then redissolved in $CH_2Cl_2$ (30 mL) and vigorously stirred with $H_2O$ (30 mL) for 15 min. The organic layer was separated, dried over $MgSO_4$, filtered and the solvent removed in vacuo to give **14d** as a bright yellow solid (58 mg, 75%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta=$ 0.85 (s, 18H; $C(CH_3)_3$), 1.39 (s, 18H; $C(CH_3)_3$), 3.45 (d, $^2J=13.7$ Hz, 4H; $ArCH_{in}H_{out}Ar$), 3.61–3.73 (m, 16H; 4×$CH_2$), 3.90 (m, 4H; $CH_2$), 4.01 (m, 8H; $CH_2CHCHCH_2$, $CH_2$), 4.12 (m, 8H; 2×$CH_2$), 4.46 (d, $^2J=13.7$ Hz, 4H; $ArCH_{in}H_{out}Ar$), 4.78 (s, 3H; $N^+CH_3$), 5.82 (s, 2H; $CH_2CHCHCH_2$, cis 26%), 5.82 (s, 2H; $CH_2CHCHCH_2$, trans 74%), 6.27 (m, 6H; calix-hydroq Ar*H*, O*H*), 6.38 (m, 4H; calix-hydroq Ar*H*), 6.64 (m, 12H; calix Ar*H*, py-hydroq Ar*H*), 7.21 (s, 4H; calix Ar*H*), 7.44 (br s, 2H; CON*H*), 7.64 (t, $^3J=7.7$ Hz, 1H; isoph $ArH^5$), 7.83 (br s, 2H; CON*H*), 8.13 (d, $^3J=$ 7.6 Hz, 2H; isoph $ArH^4$, $ArH^6$), 8.70 (s, 1H; isoph $ArH^2$), 8.77 ppm (s, 3H; py*H*); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta=26.05$, 30.91, 31.73, 33.81, 33.97, 39.98, 40.70, 50.22, 65.49, 66.68, 66.95, 68.14, 69.04, 71.02, 75.10, 114.85, 114.17, 115.44, 115.74, 125.61, 125.72, 128.31, 128.97, 129.25, 131.11, 131.52, 133.52, 134.04, 142.58, 143.83, 147.22, 149.91, 150.06, 151.74, 152.43, 152.69, 152.96, 160.58, 167.08 ppm. $^{19}$F NMR (282.4 MHz, $CDCl_3$): $\delta=-70.90$ ppm (d, $^1J=715$ Hz, 6F; $PF_6^-$). $^{31}$P NMR (121.5 MHz, $CDCl_3$): $\delta=156.45$ ppm (septet, $^1J=715$ Hz, 1P; $PF_6^-$); ESMS: *m*/*z*: 1729.87 $[M-PF_6]^+$; elemental analysis calcd (%) for $C_{104}H_{122}N_5O_{18}PF_6\cdot 5H_2O$: C 63.6, H 6.8, N 3.6; found C 63.3, H 6.8, N 3.3.

**5-Nitroisophthalamide calix[4]arene catenane chloride (15a)**: This compound was prepared in an analogous method to that used to form chloride catenane **14a** by using nitro calix[4]arene macrocycle **3** (93 mg, 0.0786 mmol), chloride thread **10a** (77 mg, 0.0118 mmol) and Grubbs first-generation catalyst (17 mg, 20% by mass). The solvent system used for the preparative TLC was 95:5 v/v $CH_2Cl_2$/MeOH. The pure product was isolated as a pale yellow solid (41 mg, 29% or 61% from recovered starting material **3**). $^1$H NMR (500 MHz, $CDCl_3$): $\delta = 0.84$ (s, 18H; C-($CH_3$)$_3$), 1.39 (s, 18H; C($CH_3$)$_3$), 3.46 (d, $^2J = 13.6$ Hz, 4H; Ar-$CH_{in}H_{out}$Ar), 4.10–4.16 (br m, 32H; 8×$CH_2$), 3.76 (m, 4H; $CH_2$), 4.40 (d, $^2J = 13.6$ Hz, 4H; Ar$CH_{in}H_{out}$Ar), 4.94 (s, 3H; $N^+CH_3$), 5.62 (s, 2H; O*H*), 5.73 (s, 2H; $CH_2CHCHCH_2$ cis 13%), 5.94 (s, 2H; $CH_2CHCHCH_2$ trans 87%), 6.22 (m, 4H; calix-hydroq Ar*H*), 6.37 (m, 4H; calix-hydroq Ar*H*), 6.68 (m, 8H; calix Ar*H*, py-hydroq Ar*H*), 6.78 (m, 4H; py-hydroq Ar*H*), 7.22 (s, 4H; calix Ar*H*), 8.70 (s, 2H; isoph Ar$H^4$, Ar$H^6$), 8.75–8.95 (br s, 4H; 2×N*H*), 9.00 (s, 2H; py$H^2$, $H^6$), 9.65 (s, 1H; isoph Ar$H^2$), 9.92 (s, 1H; py$H^4$). ESMS *m*/*z*: 1774.64 $[M-Cl]^+$; elemental analysis calcd (%) for $C_{104}H_{121}N_6O_{20}\cdot{}^1/_2CH_2Cl_2$: C 66.1, H 6.5, N 4.4; found: C 66.1, H 6.6, N 4.4.

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