Anion-templated assembly of interpenetrated and interlocked structures

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Received (in Cambridge, UK) 18th November 2005, Accepted 19th January 2006
First published as an Advance Article on the web 8th March 2006
DOI: 10.1039/b516435b

The rational development of a general anion templation strategy for the construction of a variety of interpenetrated and interlocked molecular structures based upon the coupling of anion recognition with ion-pairing is described. The success of this anion templation methodology is demonstrated with the halide anion directed assembly of a series of novel [2]pseudorotaxanes containing pyridinium, pyridinium nicotinamide, imidazolium, benzimidazolium and guanidinium threading components and anion binding macrocyclic ligands. Interlocked [2]rotaxane and [2]catenane molecular structures are also synthesised using this anion templation protocol. These interlocked structures feature unique topologically defined hydrogen bond donating binding domains that exhibit a high degree of selectivity for chloride, the templating anion. A series of rhenium(I) bipyridyl containing [2]pseudorotaxane assemblies and a [2]rotaxane further highlight the potential this strategic anion templation approach has in future chemical sensor design and fabrication.

Introduction

Inspired by the ubiquitous roles negatively charged species play in a range of chemical, biological and environmental processes, interest in the recognition of anions has grown over the past few decades to the extent that the field is now an established and important area of supramolecular chemistry.[1]

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A variety of inorganic and organic based receptors have been designed which utilise favourable electrostatic, hydrogen bonding and Lewis acidic interactions to selectively bind and, in more recent years, sense target anionic guest species.[2] By incorporating redox- and/or photo-active transition metal signalling probes into various acyclic, macrocyclic and calixarene ligand frameworks we, and others, have produced a series of selective optical and electrochemical responsive reagents for anions.[3] With the ultimate objective of constructing novel anion receptor systems with increasingly superior

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binding behaviour we have recently undertaken the challenge of exploiting anions to template the formation of mechanically interlocked supramolecular assemblies such as rotaxanes and catenanes.[4] Access to these interlocked structures has been dominated by assembling strategies that utilise π–π donor–acceptor interactions,[5] hydrogen bonding,[6] metal–ligand coordination[7] and solvophobic effects[8] between two or more species that are neutral or cationic in nature. In contrast, manipulating anions to direct supramolecular assembly remains largely under-developed, which may be attributed to their diffuse nature (small charge to radius ratio), pH dependence and relatively high solvation energies as compared to cations. Although various serendipitous discoveries of cases where anions have templated the formation of, in particular, inorganic-based polymetallic cage complexes and circular double helicates[9] have now appeared, strategic anion-templated syntheses and assemblies remain rare.[10] This is strikingly the case when employing anions in the construction of interpenetrated compounds.

Stoddart *et al.* reported the organisational role the octahedral geometry of the hexafluorophosphate anion can play in the anion-assisted self-assembly of large [5]- and [6]-pseudorotaxanes from dibenzylammonium threads and polyether macrocycles (Fig. 1a).[11] Vögtle *et al.* introduced an approach to rotaxane synthesis in which anion recognition of a phenolic nucleophile by a tetralactam wheel is used to assemble a complex termed a 'wheeled nucleophile'. This complex, or 'semi-rotaxane', is shielded on one side by a bulky stopper group but still retains sufficient nucleophilicity to react with a sterically demanding electrophile (*e.g.* bulky acyl chlorides or alkyl bromides) to form a [2]rotaxane. In these systems the anion template used to assemble the intermediate template is effectively used up in the formation of the rotaxane product and consequently the properties of the anion do not 'live-on' in the final structure (Fig. 1b).

This elegant anion trapping methodology has been exploited by Smith and co-workers in the preparation of [2]rotaxanes in which the cyclic component is an ion-pair receptor and recently in the synthesis of rotaxinated squarine dyes.[12] Schalley reported a related approach for [2]rotaxane preparation in which a phenolic nucleophile is complexed by a tetralactam wheel to form a [2]pseudorotaxane which can be

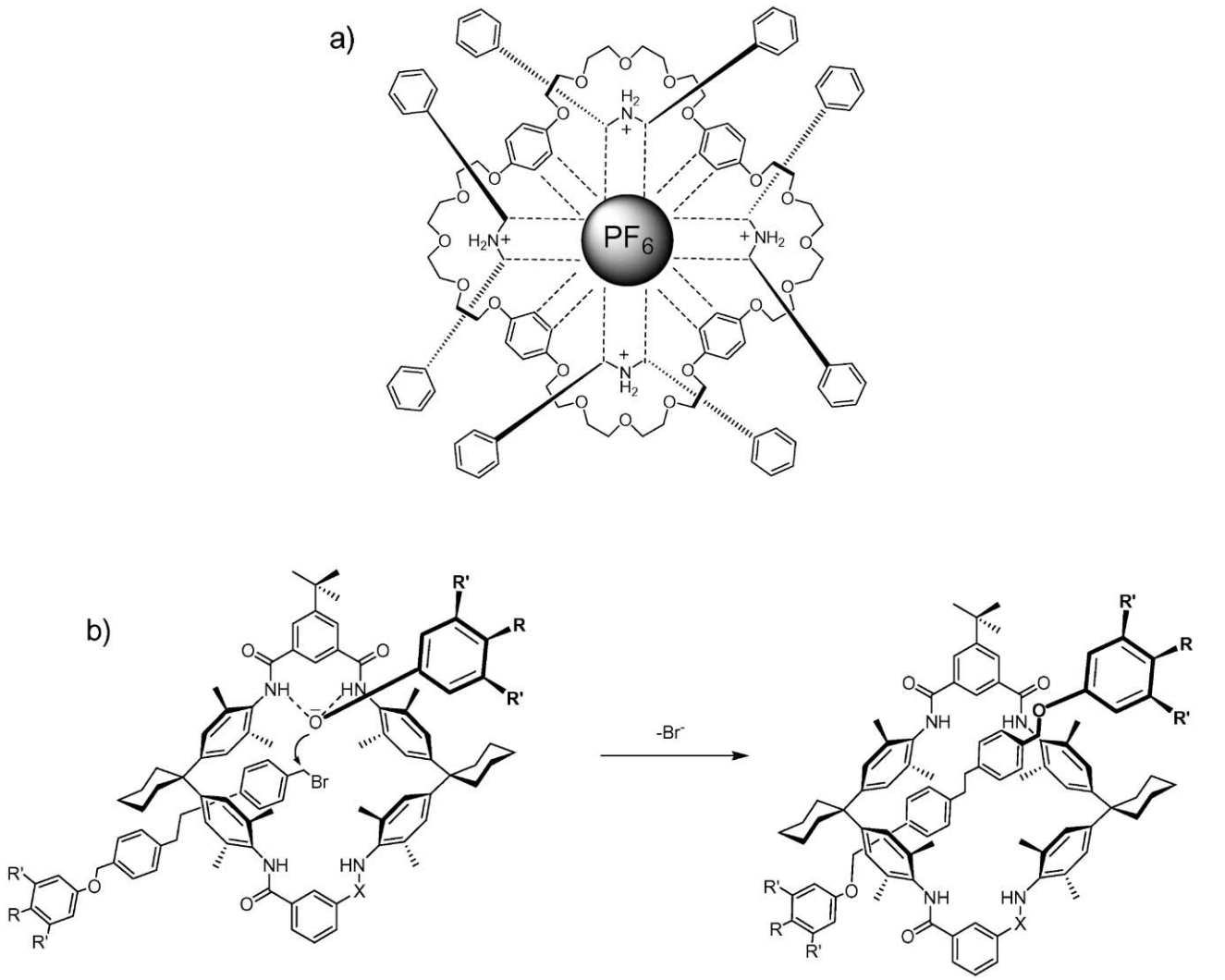
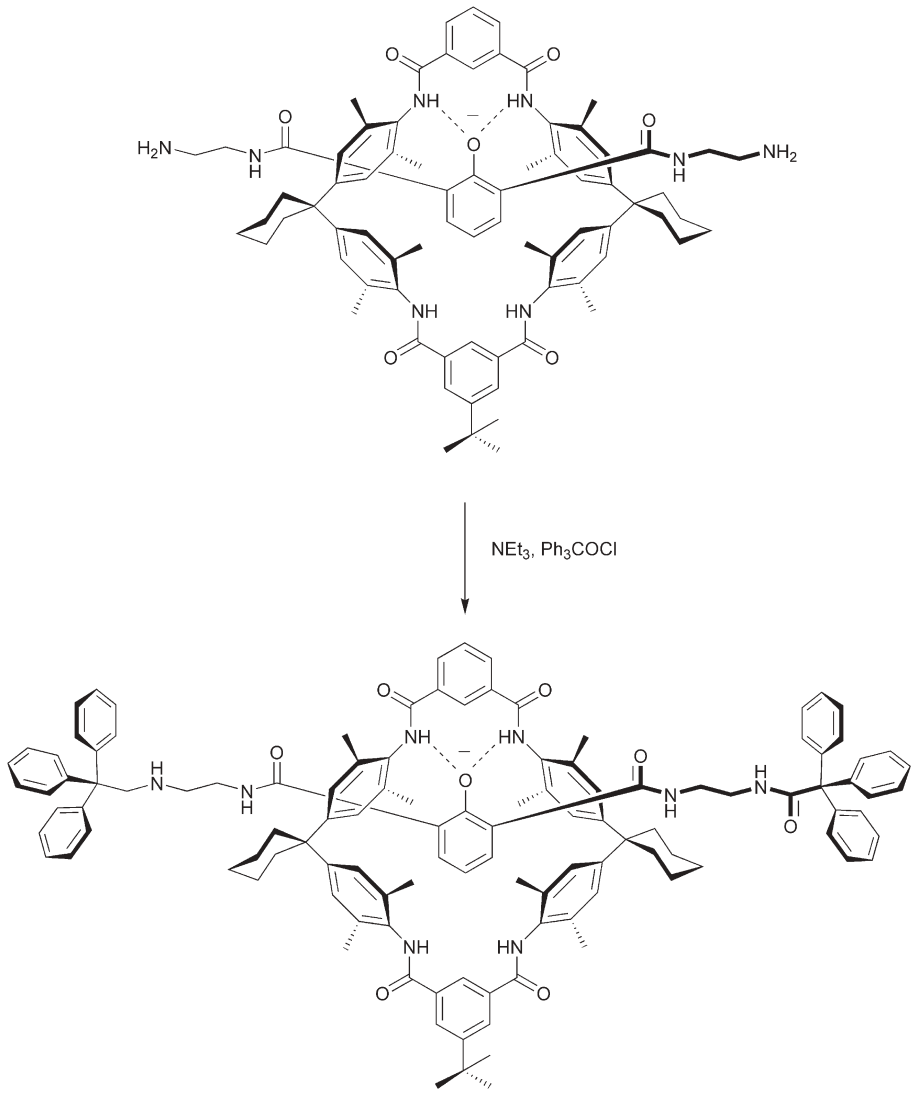


Fig. 1 (a) Stoddart's anion-assisted assembly of a [5]pseudorotaxane. (b) Reaction of a 'wheeled nucleophile' with a sterically hindered alkyl bromide furnishes a [2]rotaxane in Vögtle's 'trapping' strategy.



Scheme 1

subsequently stoppered to form the interlocked structure.[13] Interestingly, the encirclement of the, usually, highly reactive phenoxide anion was found to provide significant protection towards substitution with powerful alkylating agents such as methyl iodide (Scheme 1). Leigh and co-workers have also exploited the phenoxide anion binding properties of hydrogen bond donating amide clefts to enable molecular motion in a bistable [2]rotaxane molecular shuttle.[14]

In this Feature Article we describe the recent development of a novel anion templation strategy for the construction of a variety of interpenetrated and interlocked supramolecular and molecular assemblies designed to display unique properties with regards to anion recognition and sensing.

Anion templation design strategy for [2]pseudorotaxane assembly

Influenced by Sauvage's metal-directed synthesis of a pseudo-tetrahedral copper(I) bis-1,10-phenol-phenanthroline complex as a precursor to interlocked catenane structures (Fig. 2a),[15] we set ourselves the challenge to investigate whether anions may be exploited in an analogous templating fashion (Fig. 2b). More specifically, the role of the anionic template is to simultaneously coordinate two components in an orthogonal fashion.

Crabtree and co-workers have shown that simple isophthalamide derivatives such as **1a** (Fig. 3) are receptors for anions in polar organic solvents.[16] In particular they bind halide anions

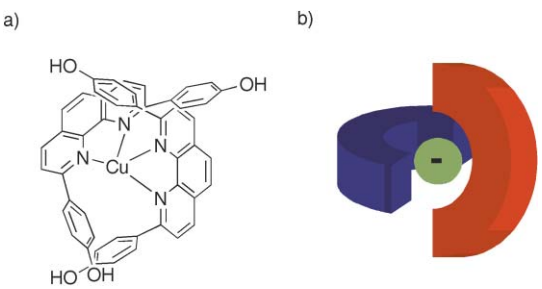


Fig. 2 (a) $[Cu(phen)_2]^+$ as exploited by Sauvage in metal-templated [2]catenane synthesis. (b) Cartoon of two ligands arranged orthogonally about a spherical anion.

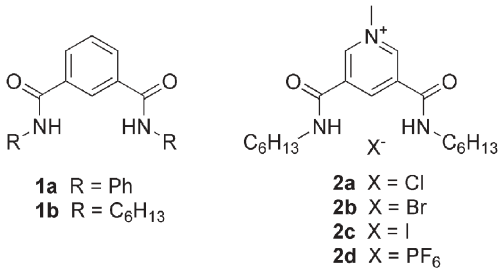


Fig. 3 Structures of **1a**, **1b** and **2a–d**

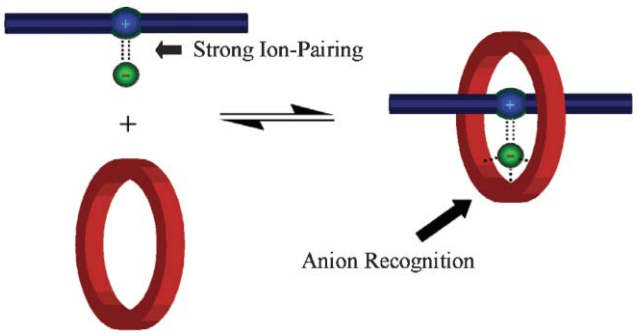
through highly favourable amide–anion hydrogen bonding interactions exclusively in a 1 : 1 stoichiometry,[17] which is clearly unsuitable for the formation of the desired template stoichiometry of 2 receptors to 1 anion. This problem was overcome by the utilisation of a mono-cationic receptor containing an amide cleft anion recognition site as one of the ligands.[18]

Acyclic anion receptors

As a consequence of favourable electrostatics and increased amide and aryl proton acidity, the new 3,5-bis amide substituted pyridinium receptor $\mathbf{2}^+$ is designed to bind anions strongly in non-competitive solvent media. Indeed, in acetone solution, ion-pairing between the pyridinium cation and the chloride counter-anion in **2a** is very strong as confirmed by ^{1}H NMR titration experiments with tetrabutylammonium (TBA) chloride, where an association constant of $>10^5$ M^{-1} was obtained for the equilibrium:

$$\mathbf{2d} + TBA^+Cl^- \rightleftharpoons \mathbf{2a} + TBA^+PF_6^-$$

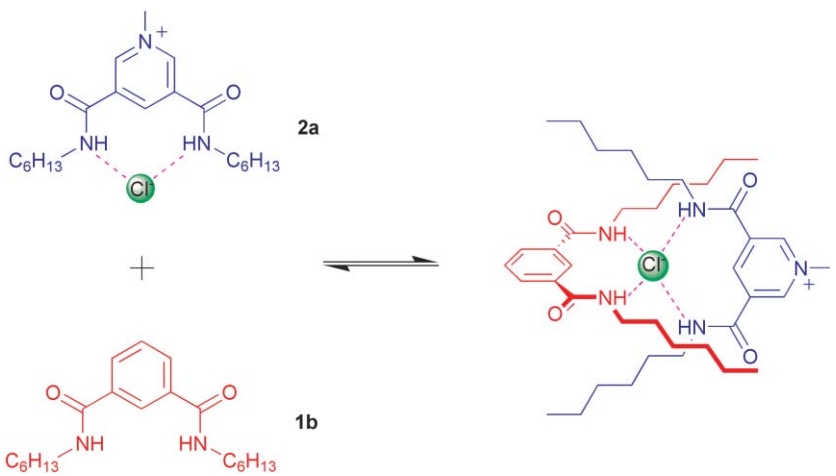
Complexation of the chloride anion occurs in the hydrogen bond donor cleft formed by the amide groups and their mutually *ortho*-aryl proton. The resulting tight ion-pair, **2a**, crucially leaves the chloride anion with an unsaturated coordination sphere and presents an empty meridian orthogonal to the pyridinium cation which is available for further



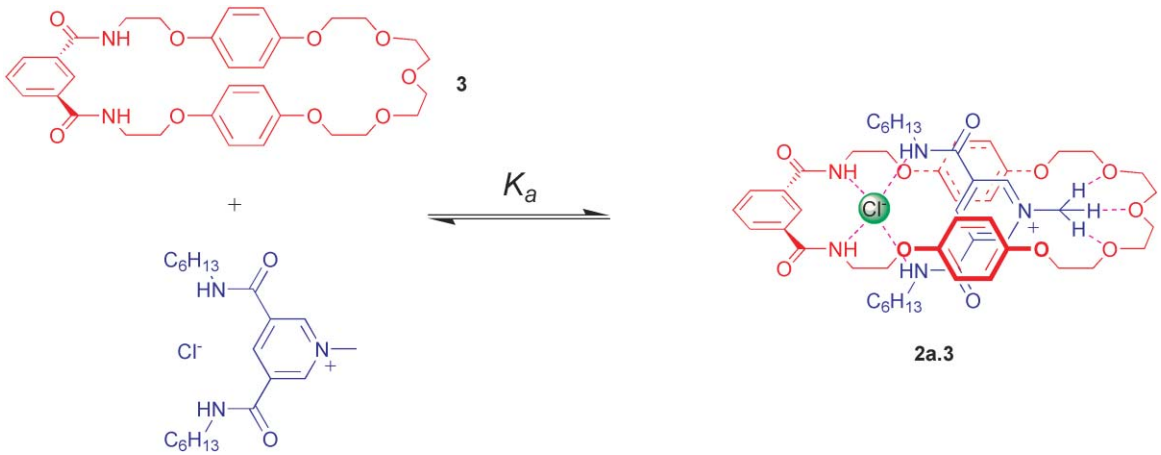
Scheme 3 Anion-templated assembly of [2]pseudorotaxanes. Recognition of the anion by the macrocycle results in the formation of an interpenetrated structure.

complexation to a second hydrogen bond donor ligand in the absence of a competitive solvent. As a preliminary test of this hypothesis, quantitative ^{1}H NMR titration experiments with isophthalamide compound **1b** and pyridinium chloride ligand **2a** produced a 1 : 1 association constant of 100 M^{-1} in acetone-d_6 (Scheme 2), while an analogous titration experiment of pyridinium hexafluorophosphate derivative **2b** gave no evidence of association. This is highly indicative that the chloride anion is of paramount importance in simultaneously coordinating the two ligand systems.

We were now in a position to exploit the use of this anion templation strategy in order to develop a general method of using anions to template the formation of a wide range of [2]pseudorotaxanes based on the coupling of anion recognition with ion-pairing. Operating in non-competitive solvent media in which the anion of the ion-pair is strongly associated with the potential cationic threading component and remains coordinatively unsaturated, anion recognition by a suitably designed macrocyclic ligand results in [2]pseudorotaxane formation as the cationic thread strongly associates with the complexed anion within the macrocyclic cavity (Scheme 3). Considering the macrocycle ligand design it was anticipated that an isophthalamide anion recognition binding site incorporated within the macrocyclic cavity would satisfy the



Scheme 2 Strong ion-pairing in a pyridinium chloride salt allows, in non-competitive solvents, coordination of a second, neutral ligand orthogonally to the first.



Scheme 4 In non-competitive solvent media, recognition of an ion-paired chloride anion by a macrocyclic receptor leads to [2]pseudorotaxane assembly.

coordinatively unsaturated chloride anion of a pyridinium ion-pair **2a**. In addition, the integration of hydroquinone groups and polyether functionalities into the cyclic framework would further stabilise the cationic pyridinium component of the ion-pair in the interpenetrated structure.

The first success using this general anion template procedure was illustrated by the halide anion directed assembly of pyridinium [2]pseudorotaxanes with macrocycle **3** (Scheme 4).[17]

Quantitative ^{1}H NMR titration experiments carried out in acetone-d_6 revealed the efficacy of [2]pseudorotaxane formation was dependent on the nature of the halide anion, with association constants (Table 1) illustrating a halide anion template order $Cl^- > Br^- > I^-$. Crucially, no evidence of [2]pseudorotaxane assembly was noted with the pyridinium hexafluorophosphate salt **2d**. This trend arises from a combination of a complementary size match between the macrocycle's amide cleft and the size and geometry of the guest anion, and from the greater hydrogen bond acceptor ability of chloride with respect to the larger, more diffuse halide counter-anions. Whilst anion-templation is the predominant driving force in the assembly of the [2]pseudorotaxane, ^{1}H NMR titration data also revealed the presence of secondary stabilising interactions, specifically π–π stacking between the positively charged pyridinium and the electron rich hydroquinone aromatic rings and hydrogen bonding between the pyridinium *N*-methyl group and the macrocyclic polyether chain.

Single crystal X-ray diffraction reveals the interpenetrated nature of the [2]pseudorotaxane **2a.3** in the solid state, highlighting the key templating role of the chloride anion in coordinating *via* hydrogen bonding and electrostatic interactions to both the cationic pyridinium thread and the neutral macrocycle's amide cleft (Fig. 4).

Interestingly, variation in the size of the macrocyclic polyether chain significantly affects the stability of the [2]pseudorotaxane assemblies, with the smallest macrocycle **4** binding the pyridinium chloride thread **2a** with much greater affinity than macrocycles **3**, **5** and **6** (Fig. 5).[19]

Proton NMR titration data suggests near identical π–π stacking interactions in all three chloride templated

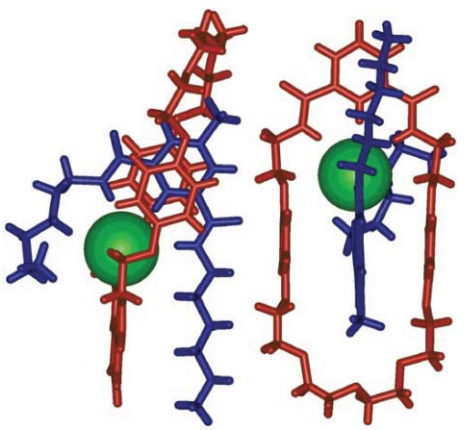


Fig. 4 Solid-state molecular structure chloride templated [2]pseudorotaxane **2a.3** shown from two different perspectives, confirming the interpenetrated nature of the assembly.

Table 1 Association constants and free energy of association for components **2a, 2b and 2c** with anion binding macrocycle **3** as determined by quantitative ^{1}H NMR titrations in acetone-d_6 at 293 K and 2.5×10^{-3} M

Thread	Association constant K_a/M^{-1}	ΔG/kJ mol^{-1}
2a	2400	19.3
2b	700	16.2
2c	65	10.3

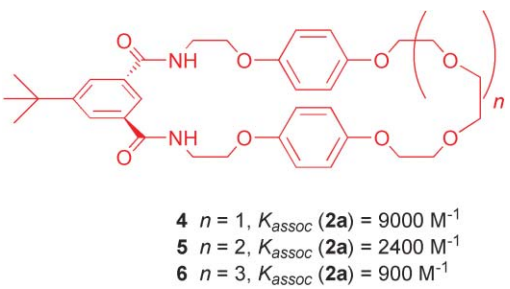


Fig. 5 Macrocycles **4–6** and association constants for [2]pseudorotaxane formation with pyridinium chloride thread **2a**.

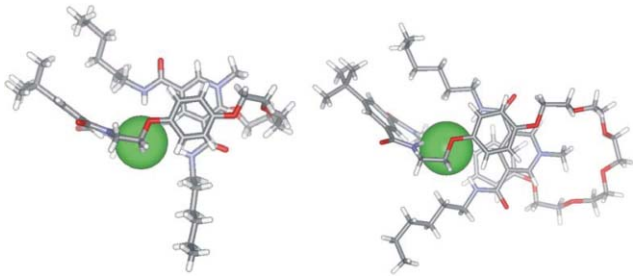


Fig. 6 Left: solid-state molecular structure of chloride templated [2]pseudorotaxane **2a.4**. Right: solid-state molecular structure of chloride templated [2]pseudorotaxane **2a.6**. (Chloride anion represented as CPK sphere for clarity).

[2]pseudorotaxane complexes (**4.2a, 5.2a** and **6.2a**) and single crystal X-ray structure determinations indicate more effective $N^+CH_3\cdots O$ hydrogen bonding in the most weakly associated [2]pseudorotaxane **6.2a** (Fig. 6). These findings indicate an unfavourable entropic contribution determines the observed binding affinities. Isothermal calorimetry (ITC) was utilised to confirm that macrocycle **4** accrues the smallest entropic deficit upon binding ion-pair threads and that this gives rise to the significant differences observed in [2]pseudorotaxane stability with changing macrocycle ring size, *i.e.* macrocycle **4** is the most preorganised macrocycle and thus maximises enthalpic gain whilst minimising entropic loss.

Single crystal X-ray diffraction structure determination of the bromide templated [2]pseudorotaxane **2b.4** (Fig. 7) also reveals the interpenetrated nature of the final complex.

The versatility of this [2]pseudorotaxane anion-templation methodology was further illustrated with the assembly of a series of [2]pseudorotaxanes containing pyridinium nicotinamide, imidazolium, benzimidazolium and guanidinium threading components (Fig. 8).[20]

Extensive ^{1}H NMR titration investigations revealed the thermodynamic stability of the pyridinium nicotinamide–macrocycle [2]pseudorotaxane assembly, as with the 3,5-bis-amide pyridinium system, depended critically on the nature of the halide anion template, with chloride proving to be the optimum template anion as a result of comparatively greater hydrogen bond acceptor ability and size match with the macrocycle's isophthalamide cleft (Table 2).

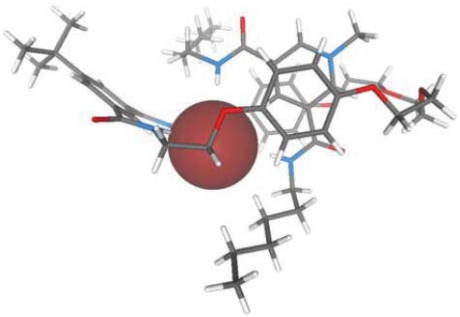


Fig. 7 Solid-state molecular structure of the bromide templated [2]pseudorotaxane **2b.4** as determined by single crystal X-ray diffraction. The templating bromide anion is represented as a red CPK sphere for clarity.

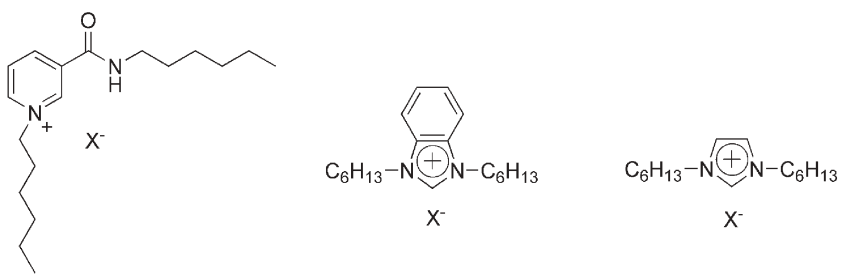
Table 2 Association constants for threads **7a–c** with macrocycles **4–6** as determined by ^{1}H NMR titrations in acetone-d_6 at 293 K (errors less than 10%)

	Association constants K_{assoc}/M^{-1}		
Thread	**4**	**5**	**6**
7a	1900	950	318
7b	200	240	180
7c	65	<50	50

[a] Accurate fitting of titration data could not be achieved due to very weak binding.

In comparison with the 3,5-bis-amide pyridinium threads, however, the pyridinium nicotinamide threads were observed to form relatively weaker associations with all three macrocycles. A possible reason for this is the loss of stability provided by second-sphere $N^+CH_3\cdots O$ hydrogen bonds. This is demonstrated in the X-ray crystal structure determination of a pyridinium nicotinamide chloride–macrocyle, **7a.5**, [2]pseudorotaxane assembly, shown in Fig. 9.

As with the pyridinium systems Table 2 shows that the most strongly associated [2]pseudorotaxanes are found with the chloride imidazolium and benzimidazolium salts, which mirrors the macrocycle's preference for this halide guest. Large perturbations of the imidazolium methine proton are observed upon titration, indicating that the orientation of the imidazolium threads within the macrocycle are as shown in Fig. 10. It is noteworthy that whereas ion-pairing is extremely



7a X = Cl
7b X = Br
7c X = I
7d X = PF_6

8a X = Cl
8b X = Br
8c X = I
8d X = PF_6

9a X = Cl
9b X = Br
9c X = I
9d X = PF_6

Fig. 8 Potential pyridinium nicotinamide, benzimidazolium and imidazolium ion-pair threading components.

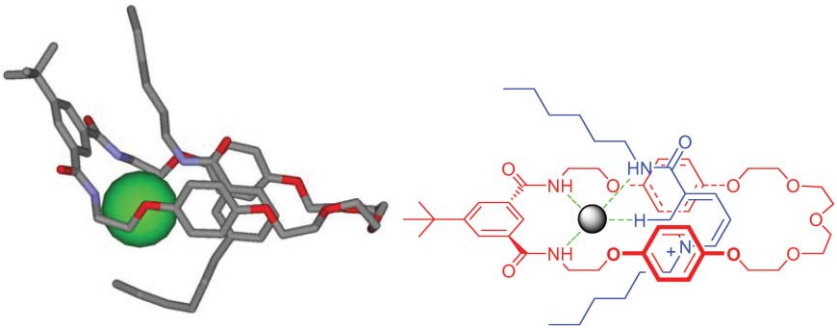


Fig. 9 Left: solid-state molecular structure of the chloride templated nicotinamide pyridinium pseudorotaxane **7a.5** (hydrogens omitted and chloride shown as CPK sphere for clarity). Right: a schematic of the interpenetrated structure (chloride shown as grey sphere).

strong for the pyridinium based systems ($>10^4$ M^{-1}), for the imidazolium threads relatively weaker ion-pair association (2000 M^{-1}) results in free anion–macrocycle complexation competing with [2]pseudorotaxane formation. The additional ion-pair dissociation and macrocycle-anion complex equilibria, together with weaker second-sphere π–π stacking interactions and the absence of stabilising hydrogen bonding interactions to the macrocycle polyether chain, lead to a decrease in the imidazolium–macrocycle pseudorotaxane association constant values when compared to the pyridinium chloride threading components.

Anion-templated assembly of [2]rotaxanes

Having demonstrated successfully the anion templated assembly of a variety of [2]pseudorotaxanes, our attention turned to the question of whether this anion templation approach could be applied to the more challenging task of constructing interlocked molecules. Commonly used synthetic strategies for the preparation of interlocked molecules include slippage[21] and stoppering,[22] however, we selected a clipping methodology[23] to effect rotaxane formation (Fig. 11).

A pyridinium chloride thread, **11a**, stoppered with tetraphenyl groups was prepared, designed to act as the axle of the target rotaxane. The second component synthesised was a neutral acyclic molecule incorporating an isophthalamide anion binding cleft functionalised with two hydroquinone containing side chains terminating with allyl groups, **10**, capable of undergoing a ring-closing metathesis (RCM) reaction. By virtue of the chloride anion template the two components associate strongly in non-competitive solvents and RCM reaction with Grubbs' catalyst in dichloromethane facilitated [2]rotaxane formation in yields of up to 47% (Scheme 5).[24] No rotaxane formation was detected with analogous bromide, iodide and hexafluorophosphate pyridinium salts, indicating the critical templating role of the chloride anion.

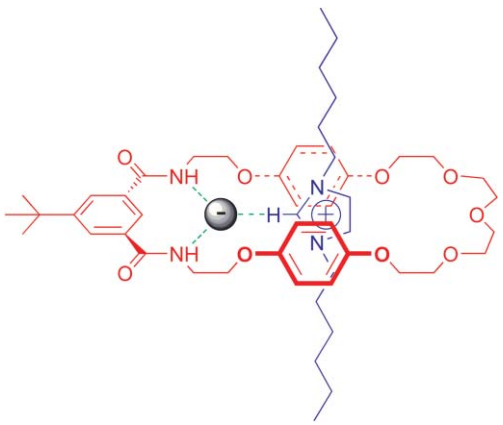


Fig. 10 Proposed orientation of the imidazolium chloride threading component **9a** within the anion templated [2]pseudorotaxane assembly **9a.5** (chloride anion represented by grey sphere).

Solution ^{1}H NMR and a single crystal X-ray structure determination of the [2]rotaxane **12a** confirm the presence of four NH···Cl^- hydrogen bonds and secondary stabilising π–π stacking interactions and N^+CH_3···O hydrogen bonding (Fig. 12).

An impressive feature of this method of rotaxane assembly is that the resultant product retains a degree of functionality based on the anion template itself. Anion exchange of the templating chloride anion for the non-competitive hexafluorophosphate anion using $AgPF_6$, leaves a highly selective anion binding site within the rotaxane. Proton NMR anion titration studies revealed that although the pyridinium PF_6^- thread **11b** alone binds anions with a selectivity trend $AcO^- >> H_2PO_4^- > Cl^-$, indicating that oxobasicity is the dominant factor in selectivity, the rotaxane PF_6^- receptor (**12b**) exhibits a selectivity trend reversal with a high selectivity for chloride (Table 3). This is postulated to be the result of a unique hydrogen bond donating pocket, formed by the diamide clefts of the thread and macrocycle, that lies within the superstructure of the [2]rotaxane and is of complementary topology to the guest chloride anion. The binding of larger, non-complementary anions would require either peripheral binding

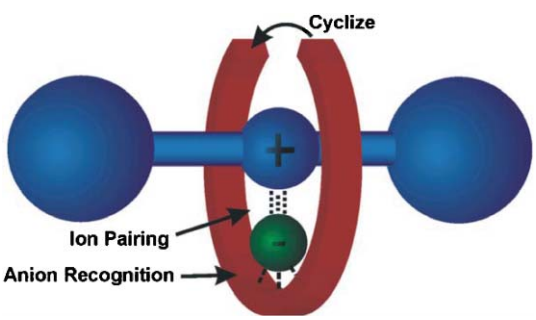
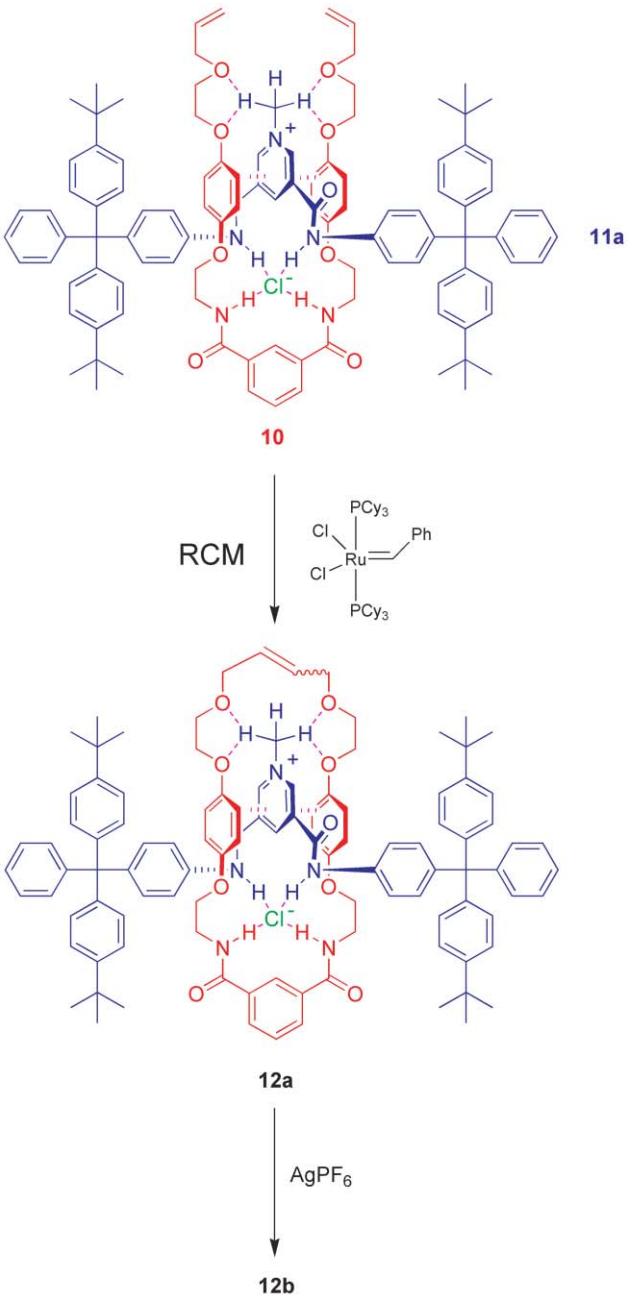


Fig. 11 The 'clipping' method for rotaxane formation based on an anion template.



Scheme 5 In dichloromethane components **10** and **11a** associate strongly and subsequent RCM leads to [2]rotaxane **12a**.

or a significant distortion of the [2]rotaxane structure, neither of which would present the full complement of hydrogen bond donors available to the chloride anion.

Anion-templated assembly of a [2]catenane

In a major development of this methodology, the first example of using anion templation to synthesise catenanes was demonstrated.[25] The strategy employed for preparing a [2]catenane is shown in Scheme 6 where a chloride anion templates the initial formation of a [2]pseudorotaxane assembly and a subsequent clipping reaction affords the [2]catanene structure.

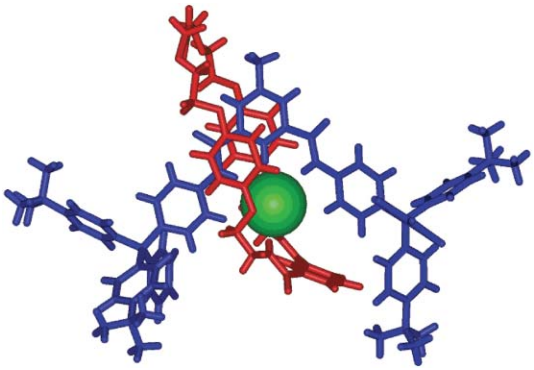
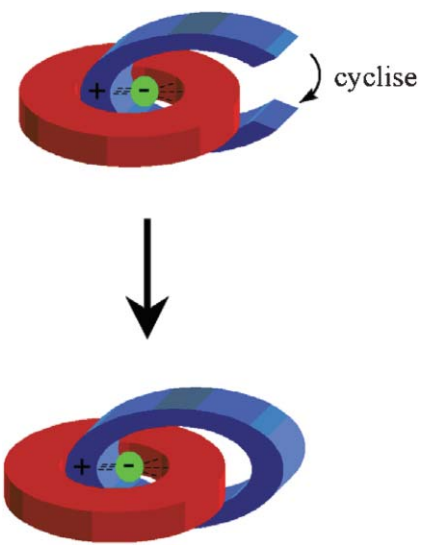


Fig. 12 Solid-state molecular structure of [2]rotaxane **12a** as determined by single crystal X-ray diffraction. Pyridinium chloride thread shown in blue, neutral isophthalamide-based macrocycle shown in red and chloride as green CPK sphere for clarity.

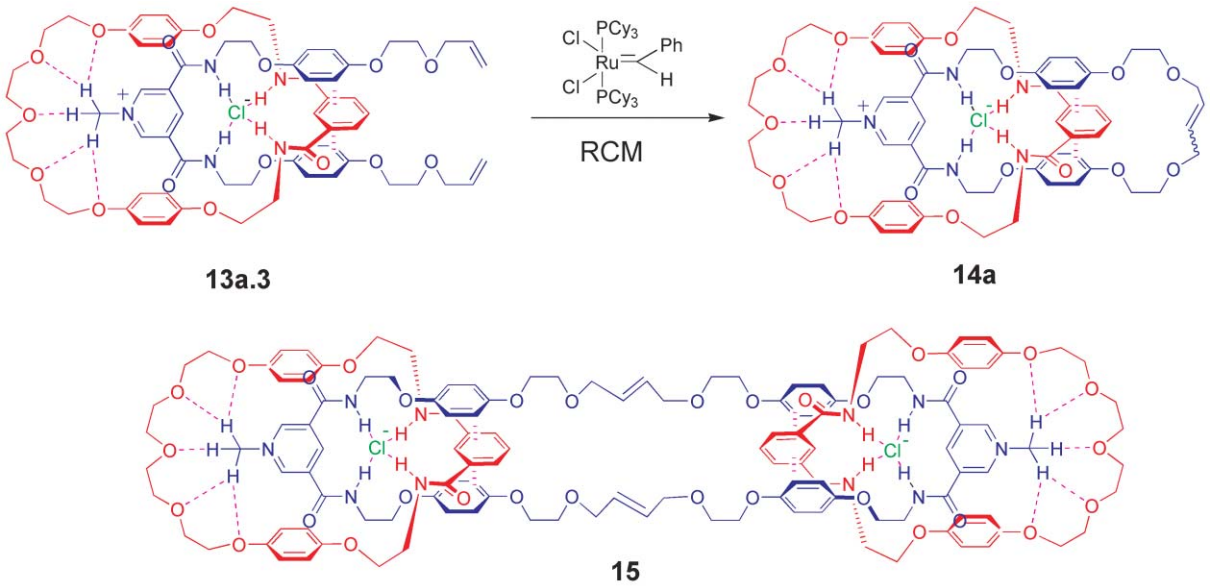
Table 3 Anion association constants for the pyridinium hexafluorophosphate thread, **11b**, and the hexafluorophosphate [2]rotaxane, **12b**, as determined by ^{1}H NMR titration in $CDCl_3$: CD_3OD 1 : 1 at 293 K (errors less than 10%)

	Association constants K_{assoc}/M^{-1}	
Anion	Pyridinium PF_6 Thread **11b**	[2]Rotaxane PF_6 **12b**
Cl^-		
K_{11}	125	1130
$H_2PO_4^-$		
K_{11}	260	300
AcO^-		
K_{11}	2200	100
K_{12}	140	40



Scheme 6 Proposed strategy for the anion-templated synthesis of a [2]catenane.

Mixing macrocycle **3** and pyridinium chloride allyl functionalised derivative **13a** in dichloromethane followed by addition of Grubbs' catalyst afforded the [2]catanene **14a** in 45% yield and a [3]catenane, **15**, in 5% yield (Scheme 7). It is noteworthy that analogous RCM reactions of macrocycle **13** with the



Scheme 7 [2]Catenane, **14a**, formation proceeds *via* RCM of an anion-templated [2]pseudorotaxane, **13a.3**.

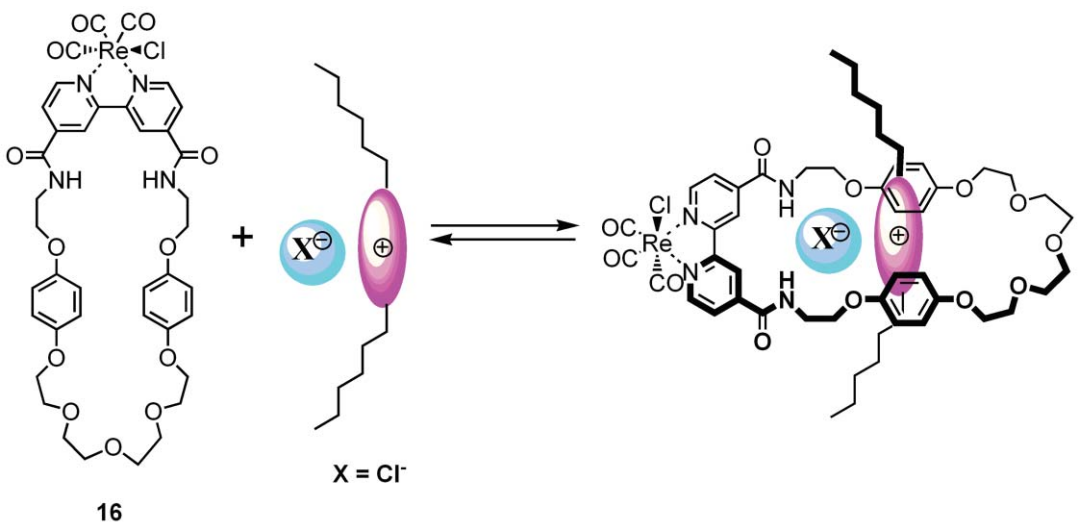
corresponding bromide pyridinium component gave the bromide [2]catenane in only 6% yield and no catenanes were isolated from RCM reactions of the macrocycle with iodide or hexafluorophosphate pyridinium derivatives. As with the [2]rotaxane synthesis discussed previously, this again highlights the crucial role the chloride ion template plays whereby threading of the pyridinium cation $\mathbf{13}^+$ is driven by recognition of the halide anion by the macrocycle.

The single crystal X-ray determined molecular structure of [2]catenane **14a** shown in Fig. 13 confirms the interlocked nature of the two macrocyclic rings and the location of the chloride anion within the diamide catenane cavity.

Chloride anion template removal was achieved by addition of silver hexafluorophosphate to produce the [2]catenane$^+$ PF_6^- salt. Quantitative ^{1}H NMR binding studies revealed that the hexafluorophosphate pyridinium allyl component **13b** displays a strong affinity for acetate and dihydrogen phosphate and only binds chloride weakly, whereas the catenane **14b** exhibits a reverse binding trend: $Cl^- > H_2PO_4^- > {}^-OAc$. Table 4 shows that chloride anion binding is significantly enhanced upon catenane formation, whereas the binding of the oxoanions is much weaker. In a similar fashion to the [2]rotaxane binding studies discussed previously, the removal of the templating anion creates a unique topologically defined hydrogen bond donating pocket which is highly selective for chloride anions.

Halide anion directed assembly of luminescent pseudorotaxanes

As mentioned in the Introduction section there is currently intense interest being shown in the preparation of receptors



Scheme 8 Anion-templated assembly of luminescent [2]pseudorotaxanes based upon the rhenium(I)bipyridyl containing macrocycle **16** and cationic threading components $\mathbf{2}^+$, $\mathbf{7}^+$ and $\mathbf{8}^+$.

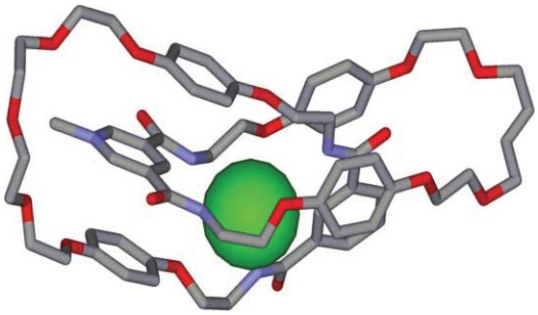


Fig. 13 Solid-state molecular structure of [2]catenane **14a** as determined by single crystal X-ray diffraction. Hydrogens omitted and chloride represented as green CPK sphere for clarity.

Table 4 Anion binding constants for the pyridinium hexafluorophosphate ligand, **13b**, and the hexafluorophosphate [2]catenane, **14b**, as determined by ^{1}H NMR titration in $CDCl_3$: CD_3OD 1 : 1 at 293 K (errors less than 10%)

	Association constants K_{assoc}/M^{-1}	
Anion	Pyridinium PF_6 **13b**	[2]Catenane PF_6 **14b**
Cl^-		
K_{11}	230	730
$H_2PO_4^-$		
K_{11}	1360	480
K_{12}	370	520
AcO^-		
K_{11}	1496	230
K_{12}	343	—

that are highly proficient at sensing anions in solution *via* optical or electrochemical signalling methodologies. The use of rotaxane and catenane cavities as potential binding domains for the recognition and in particular, sensing, of guest species remains underdeveloped, which is surprising given the unique three dimensional cavities formed in the centre of these interlocked structures. In a first step towards the fabrication of novel luminescent interlocked receptor systems we recently adapted our anion templation protocol to the halide anion templated assembly of a range of new photo-active rhenium(I)bipyridyl-based [2]pseudorotaxanes.[26]

Initial ^{1}H NMR titration experiments of the new rhenium(I) bipyridyl macrocycle **16** with pyridinium, pyridinium nicotinamide, benzimidazolium and guanidinium halide salts indicated interpenetration, and hence pseudorotaxane assembly, was occurring. Stability constant determinations (Table 5) show that the stability of the pseudorotaxane complex mirror the strength of halide binding by the receptor where pyridinium chloride and bromide salts form the strongest [2]pseudorotaxane complexes.

The single crystal X-ray structure determination of the macrocycle-pyridinium chloride complex **2a.16** shows the expected interpenetrated nature of the assembly (Fig. 14).

As was hoped, the addition of the various ion-pair chloride threading components was signalled through a significant enhancement in the rhenium–bipyridine ^{3}MLCT luminescent emission centred at 640 nm; increased macrocycle rigidity upon ion-pair binding leads to a disfavouring of non-radiative decay pathways (Fig. 15).

Table 5 Association constants for macrocycle **16** with pseudorotaxane threads **2a–c** and **7a** as determined by quantitative ^{1}H NMR titration experiments in acetone-d_6 at 293 K

Thread	Association constants K_{assoc}/M^{-1}
2a	1500
2b	1200
2c	140
7a	6100

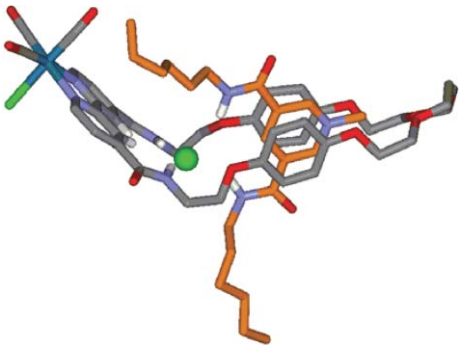


Fig. 14 Solid-state molecular structure of the luminescent [2]pseudorotaxane **2a.16** as determined by single-crystal X-ray diffraction.

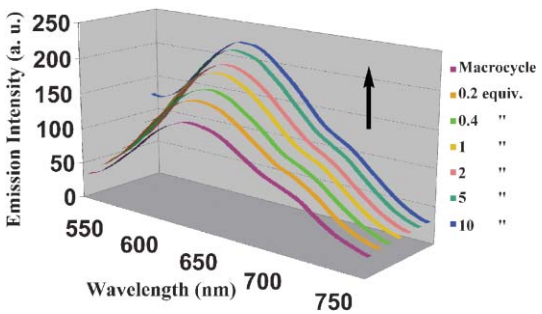
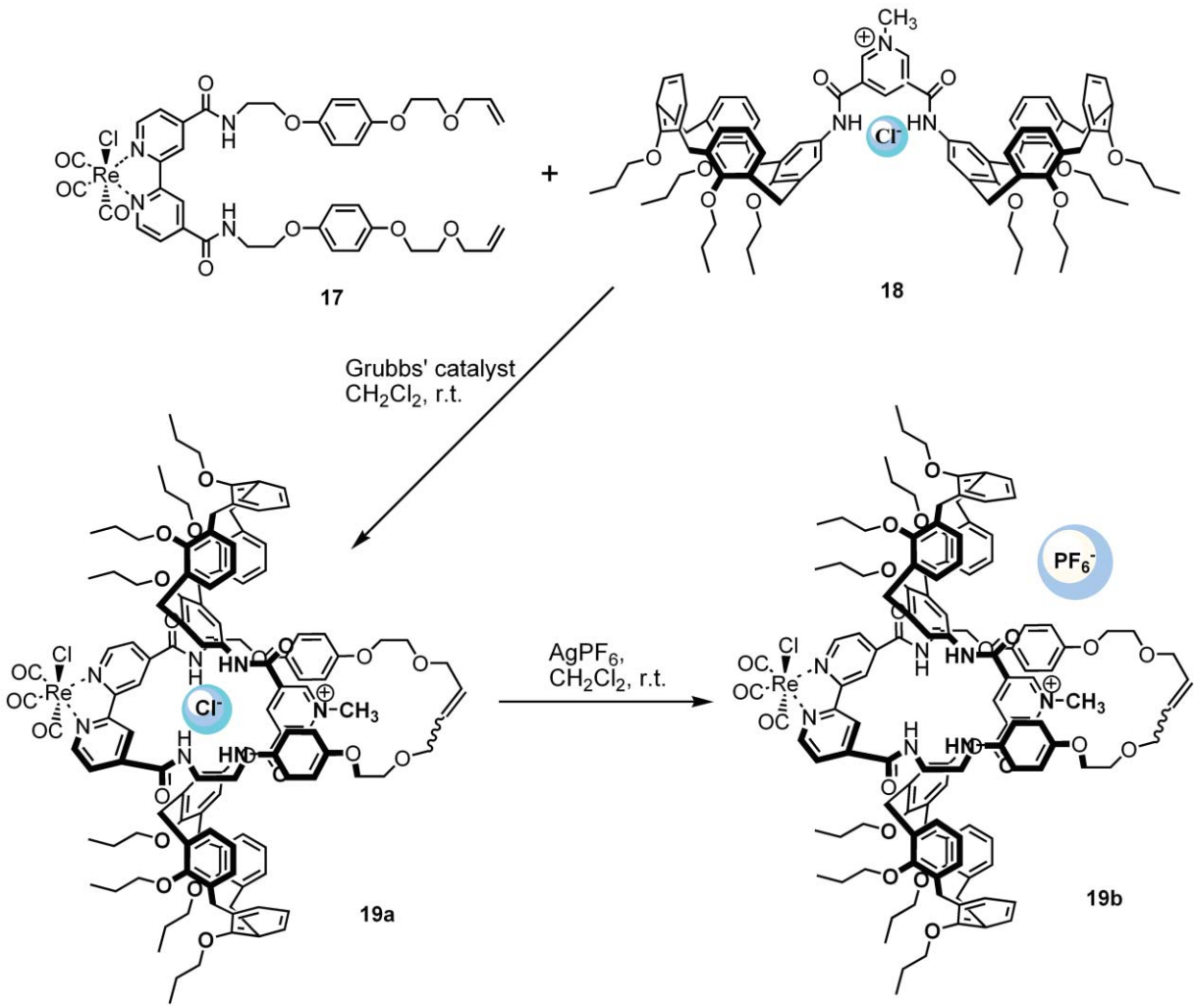


Fig. 15 Enhancement in the rhenium–bipyridine ^{3}MLCT luminescent emission intensity of macrocycle **16** upon titration of pyridinium chloride thread **2a** in dichloromethane at 293 K.

Anion directed synthesis of a hydrogensulfate selective luminescent rotaxane

Building on the luminescent pseudorotaxane results led to the anion directed synthesis of a novel photo-active rhenium(I)-bipyridyl based [2]rotaxane (Scheme 9).[27] Mixing a bis-vinyl appended rhenium(I)bipyridyl derivative, **17**, with a calix[4]-arene stoppered pyridinium chloride axle component, **18**, in dichloromethane followed by RCM reaction with Grubbs' catalyst produced the [2]rotaxane **19a** in 21% yield. Exchange of the chloride template for the non-coordinating hexafluorophosphate anion to afford [2]rotaxane **19b** was achieved using silver hexafluorophosphate.

Proton NMR titrations of [2]rotaxane **19b** with TBA chloride in acetone-d_6 confirmed that anion recognition takes place in the rotaxane binding pocket where, in particular, significant downfield shifts of the respective amide protons were observed. Luminescence spectroscopy binding studies with chloride, nitrate and hydrogen sulfate in acetone solution



Scheme 9 Novel luminescent [2]rotaxanes **19a** and **19b** incorporating rhenium(I)bipyridyl functionality and utilising calix[4]arenas as stoppers.

demonstrated the ability of [2]rotaxane **19b** to operate as an anion sensor *via* significant enhancements in the rhenium–bipyridine ^{3}MLCT emission intensity (Fig. 16).

It is noteworthy that anion stability constant determinations for the 1 : 1 stoichiometric complexes (Table 6) reveal the rotaxane exhibits selectivity for hydrogen sulfate anions in preference to both chloride and nitrate. This contrasts with the preferential chloride binding of acyclic and macrocyclic receptors and suggests that rotaxane **19b** possesses a binding domain of complementary topology for the tetrahedral

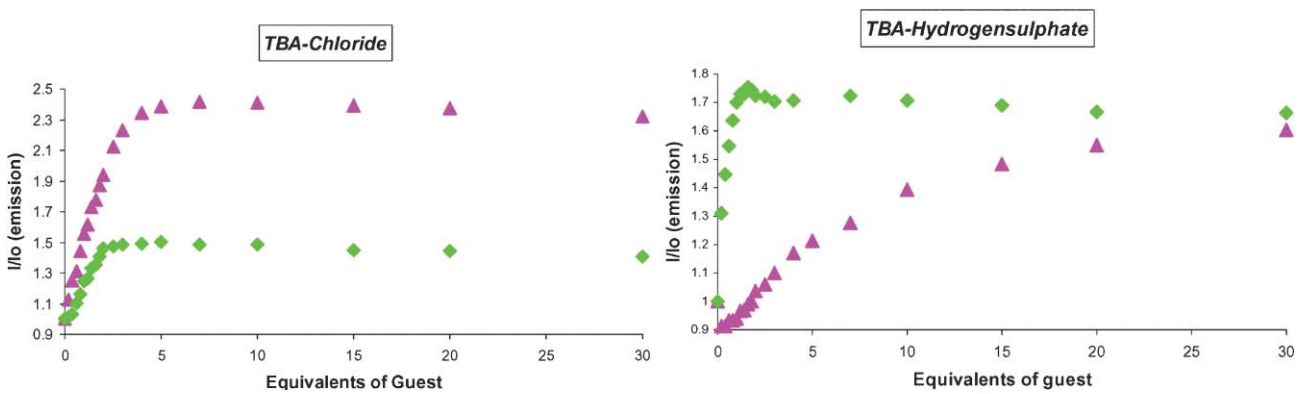


Fig. 16 Titration curves for the binding of chloride (TBA Cl) and hydrogen sulfate (TBA HSO_4) for the free macrocycle (▲) and for the rotaxane PF_6 compound **19b** (◆) as determined by luminescent titrations (λ_{ex} = 400 nm, λ_{em} = 640 nm) in acetone at 293 K.

Table 6 Association constants for the binding of chloride, hydrogen sulfate and nitrate anions by ligand **17** and macrocycle **19b** as determined by quantitative luminescence titrations in acetone at 293 K

	Association constant K_{assoc}/M^{-1}	
Anion	**17**	**19b**
Cl^-	3.10×10^5	1.81×10^5
HSO_4^-	3.52×10^3	$>10^6$
NO_3^-	1.82×10^3	5.13×10^4

hydrogen sulfate anion. This rotaxane receptor system serves to illustrate the real potential that such interlocked systems have in future chemical sensor design and fabrication.

Conclusions and future prospects

This Feature Article has discussed the rational, design-oriented development of a general anion templation methodology for the fabrication of interpenetrated and interlocked structures based upon the coupling of anion recognition with ion-pairing. This templation strategy operates in non-competitive solvent media in which the anion of an ion-pair is strongly associated with a potential cationic threading component and, importantly, remains coordinatively unsaturated. The subsequent anion recognition step by a suitably designed macrocyclic ligand leads to an orthogonal arrangement of both ligands about the spherical anion and results in the assembly of an interpenetrated structure. The success of this anion templation strategy has been illustrated with the halide anion directed assembly of a series of novel [2]pseudorotaxanes containing pyridinium, pyridinium nicotinamide, imidazolium, benzimidazolium and guanidinium threading components and neutral macrocyclic ligands. The efficacy of [2]pseudorotaxane assembly was found to depend critically on three key factors: (i) the nature of the halide anion template, (ii) the anion recognition ability of the macrocyclic ligand and, (iii), the strength of the ion-pair association. Applying this anion templation approach to the construction of interlocked molecular structures led to the chloride anion templated assembly of a [2]rotaxane and the first example of anion templated catenanes. After template removal the [2]rotaxane and [2]catenane, by virtue of the mechanically bonded assemblies' unique interlocked topologically confined binding site, both exhibit a high degree of selectivity for chloride, the templating anion.

The photoactive rhenium(I) bipyridyl functionality has been successfully incorporated into pseudorotaxane assemblies and a rotaxane structural framework *via* halide templation where the latter interlocked receptor system selectively senses hydrogen sulfate *via* luminescence spectroscopy. These preliminary results highlight the real potential this anion templation approach has in producing novel interlocked receptor systems for selective anion recognition and sensing purposes.

Acknowledgements

We thank the EPSRC for postdoctoral fellowships (James A. Wisner, Fridrich Szemes, David Curiel) and a studentship (Mark R. Sambrook). Financial support for Dr Wisner from the Natural Sciences and Engineering Research Council of Canada and a Marie Curie Postdoctoral Fellowship of the European Union for Dr Curiel is also gratefully acknowledged. We also thank Professor Mike Drew (University of Reading), Dr Andrew Cowley (University of Oxford) and Dr Rowena Paul (University of Oxford) for their invaluable crystallographic X-ray structural determinations.

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