Anion templated assembly of mechanically interlocked structures

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This tutorial review describes the evolution of the field of chemical templation, in particular, emphasising the impact its application has made to the synthesis of mechanically interlocked structures. Recent advances in the use of negatively charged template species for the synthesis of interlocked structures are detailed, with the main focus of this review describing the development of a general anion templation strategy that combines anion recognition with ion-pairing. The versatility of this methodology is demonstrated by the chloride anion templated synthesis of a series of interpenetrated pseudorotaxane, rotaxane and catenane structures. Upon template removal, the mechanically interlocked rotaxanes and catenanes are shown to bind anions within their topologically unique anion binding clefts by virtue of electrostatic and hydrogen bonding interactions, exhibiting a strong selectivity for the chloride halide anion template. The incorporation of the photo-active rhenium(I) bipyridyl signalling group into the rotaxane structural framework highlights the potential of these interlocked systems in future chemical sensor design.

1. Introduction

We are all familiar with everyday examples of templates as models for making a variety of diverse objects. Indeed, the Oxford English Dictionary definition of a template is ''a shaped piece of rigid material used as a pattern for processes such as cutting out, shaping, or drilling''. The concept of templation is equally applicable to the molecular scale and the formative example of the concept came from Busch's metal ion templated macrocycle syntheses during the 1960's. In recent years, the increasingly detailed study of biological systems has provided the inspiration for the synthesis of a huge variety of

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Paul Beer was born in Totnes, Devon, and gained a first class honours degree in chemistry from King's College, London, in 1979. He remained there to receive a PhD (1979–1982) in the area of organophosphorus chemistry, under the supervision of Dr C. Dennis Hall. A Royal Society European postdoctoral fellowship (1982–1983) enabled him to conduct research in supramolecular chemistry with Professor Jean-Marie Lehn at the Université Louis Pasteur, Strasbourg, France. After a demonstratorship at the University of Exeter (1983–1984) he took up a New Blood Lectureship at the University of Birmingham in 1984. In 1990 he moved to the Inorganic Chemistry Laboratory, University of Oxford, where he is also a tutorial fellow at Wadham College. He became a Professor of Chemistry in 1998. He was awarded the Royal Society of Chemistry Meldola Medal in 1987, the UNESCO Javed Husain prize in 1993, the Royal Society of Chemistry Corday-Morgan Medal in 1994 and the Royal Society of Chemistry Tilden Lectureship and Medal in 2004. Professor Beer is author of over 280 research papers including a book, co-authored with previous graduates of his research group, Dr Philip Gale and Dr David Smith. His research interests cover many areas of coordination and supramolecular chemistry, including the construction of novel redox- and photo-active macrocyclic ligand systems designed to selectively bind and sense target cationic and anionic guest species of biological and environmental importance, ion-pair recognition, anion templation of interlocked molecular structures and transition metal directed assembly of polymetallic nanosized molecular host systems, catenanes, macrocycles and cryptands.

templated molecular architectures. By the simple manipulation of intermolecular forces, molecular topologies that would be impossible to form *via* traditional synthetic routes have been prepared using ionic and molecular templates of different shapes, sizes and charges.

The advent of supramolecular chemistry, dating from the pioneering work of Pedersen,[1] Cram[2] and Lehn[3a,b] in the late 1960's and 1970's has led to the increasing level of research into the non-covalent interactions that stabilise host : guest systems. A host or receptor is the supramolecular analogue of a ligand in classical coordination chemistry with the species it binds to being defined as the guest or substrate. The existence of hosts capable of binding cationic guests was highlighted by Pedersen's discovery of the ability of crown ethers to solubilise Group I metal salts.[1] In recent years, an increasing amount of research interest has been focused on the synthesis of receptors able to recognise anionic guests in solution due to the realisation of the ubiquitous importance of anions in many biological, chemical and environmental processes.[4]

The progressive understanding of, and subsequent ability to control, the intermolecular forces between host and guest has enabled the design of increasingly elaborate templated molecular architectures. Surprisingly, despite the widespread application of cations and neutral molecular species as templates, the analogous use of anions remains under exploited. Many of the reported illustrations of anion templation are a result of serendipity and proof of the templating role of the anion often relies solely on X-ray determined solid state structural evidence.[5]

The extensive use of molecular templation has enabled the construction of, amongst other assemblies, mechanically interlocked structures. These assemblies are of great interest due to their potential to act as sophisticated molecular switches, sensors and machines. This article will focus primarily on the synthesis of two families of mechanically interlocked structures, namely [*n*]-catenanes (from the latin *catena*; chain) and the closely related [*n*]-rotaxanes (from the latin *rota*; wheel and *axis*; axle), both of which consist of molecular components that are locked together without a direct covalent bond, but are joined by a so called mechanical bond and cannot be separated without breaking a covalent bond. Members of the [*n*]-catenane family consist of interlocking macrocycles whilst [*n*]-rotaxanes all feature a macrocyclic component around a stoppered axle or thread (Fig. 1). In each case, [*n*] denotes the total number of components in the interlocked system. In the course of this discussion another related structure, the [*n*]-pseudorotaxane, will often be mentioned as a key intermediate to interlocked structure formation. It is important to note however, that the formation of a [*n*]-pseudorotaxane is a reversible process and as such, the components are not mechanically interlocked.

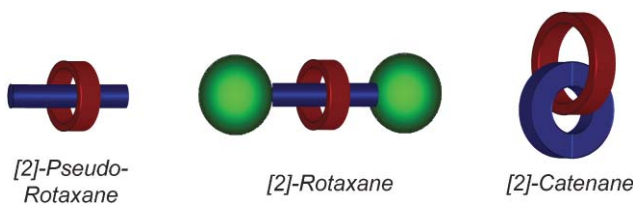


Fig. 1 Cartoon representation of a [2]-pseudorotaxane, a [2]-rotaxane and a [2]-catenane.

In the course of this review the historical origins of templation will be examined with particular emphasis focussing on the synthesis of mechanically interlocked structures. We will also highlight the progress recently made towards the strategic design and synthesis of anion templated mechanically interlocked architectures.

2. Chemical templates

By Busch's definition, '*a chemical template organises an assembly of atoms with respect to one or more geometric loci in order to achieve a particular linking of atoms*'.[6a] A template, as distinct from a reagent, must interact non-covalently with the reactive components but must not alter the intrinsic chemistry of the system.

Metal cations were initially used almost exclusively for templation studies because of their well known stereochemical preferences and ability to form labile coordinate bonds with a large number of organic ligands. These properties allow the relative geometric alignment of reagents to be controlled simply by changing the nature of the metal cation template.

The intermolecular interactions that can be utilised between the template and reagents present are generally much weaker than covalent bonds; however, these interactions are not limited to coordinate bonds. In many of the examples covered in this review, electrostatic (ion–ion or ion–dipole) and hydrogen bonded interactions between template and reagent are used to facilitate the synthesis of many fascinating architectures. Importantly, the comparatively weak nature of the interactions between the template and reagent offers the important advantage that the template can be easily removed from the final assembly. It is noteworthy however, that one or more of the reagents in an assembly process can act as the template for the reaction. In these cases, the template is not always removed from the final assembly and we shall discover examples of this type of templation in Section 3.

The ever expanding number of reported examples of templation has led to the convenient classification of templates by Sanders *et al.* according to the geometric role of the template (Fig. 2).[7] For the purposes of this review the interweaving template will be mainly considered as a necessary prelude to interlocked structure formation. Cyclisation templates will also be encountered in order to demonstrate the basic principles of template strategies, whilst linear templates, including DNA and RNA in biological self-replicating systems, are beyond the scope of this review.

During the early investigations into molecular templation it was quickly ascertained that a template can act on a system in two apparent ways, that is, it is said to act as either a thermodynamic, or as a kinetic template. The thermodynamic template effect arises when the addition of a template to an equilibrium mixture of products leads to a shifting of the equilibrium in favour of one or more products due to energetically favourable host : guest interactions. This principal is demonstrated by considering the case shown in Fig. 3a in which the nickel(II) cation favours the formation of the Schiff base ligand *via* complexation.[6b]

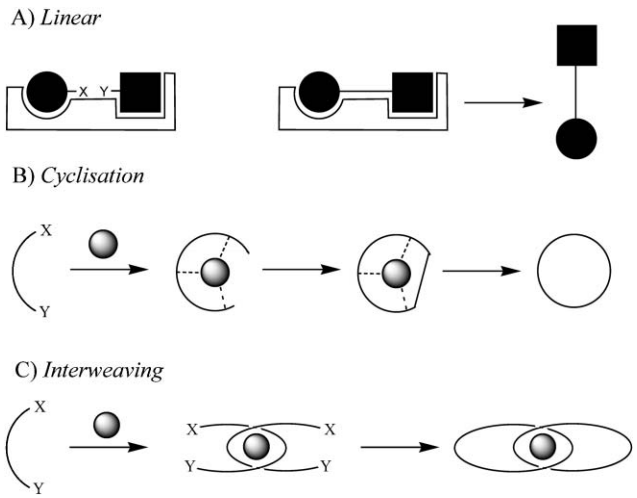


Fig. 2 Sanders' template classification.

The kinetic template effect also arises from the preferential binding of the template to one or more of the components in a mixture. This effect is illustrated by the potassium ion which acts as a cyclisation template in the synthesis of 18-crown-6 (Fig. 3b).[8] The acyclic polyether chain encircles the potassium ion due to electrostatic ion-dipole interactions, thereby causing a geometric alignment of the nucleophilic alkoxide and tosylate reactive groups to favour the macrocycle formation pathway.

It should be noted however, that the full mechanisms of many reported examples of templation have not been rigorously investigated. Indeed, Anderson concludes that the energetic classification of the observed template effect depends primarily on whether the reaction is performed under kinetic or thermodynamic control.[6]

Whilst the use of molecular templation has dramatically increased the efficiency of the synthesis of many acyclic and macrocyclic structures, molecular templation strategies have revolutionised the possibilities for the design and synthesis of mechanically interlocked structures and the evolution of the field will be described in the following section.

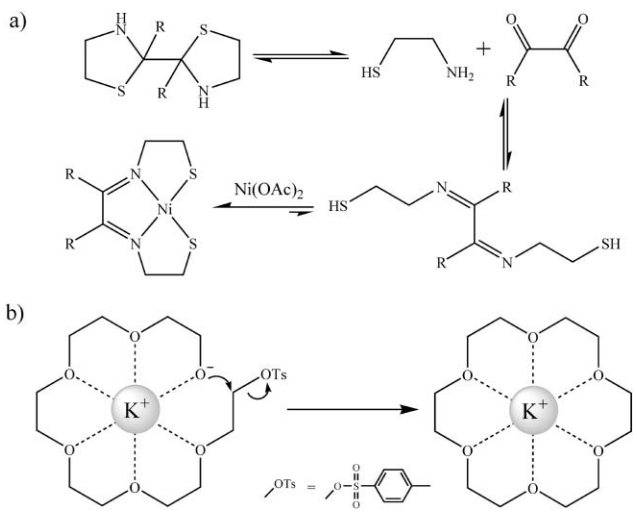


Fig. 3 (a) thermodynamic template effect (b) kinetic template effect.

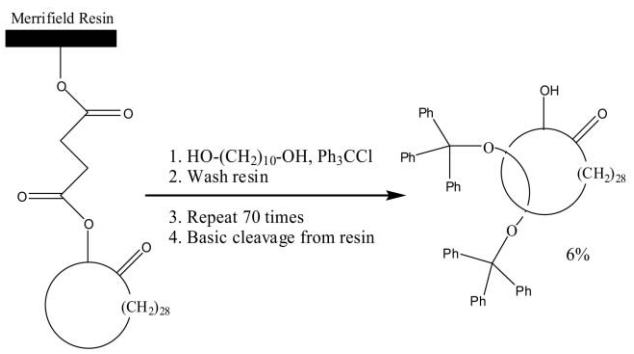
3. Mechanically interlocked structures

Isomerism is a familiar theme in chemistry and the occurrence of geometrical and spatial isomerism has long been known. The mechanical interlocking of two molecules results in a structure that is identical in terms of atoms and bonds to the non-interlocked system, however, the structures are clearly not identical. Such systems cannot be described in terms of geometric or spatial isomerism and are classed as topological isomers of the corresponding non-interlocked system.

Although the synthesis of a chain linked or catenane molecule was first proposed nearly a century ago, the synthesis of interlocked molecules is now more than just abstract scientific curiosity. The discovery of topological isomers of DNA, including catenanes, and their role in the DNA replication process, has provided a clear illustration of the importance of mechanically interlocked structures in nature.[9]

Before the application of molecular templation, the synthesis of interlocked structures was accomplished using a statistical threading approach. Wasserman demonstrated that the statistical probability of threading a linear molecule through the annulus of a macrocycle to form an interpenetrated [2]-pseudorotaxane, was approximately 0.01%. Despite this, the first successful catenane synthesis was reported by Wasserman in 1960 but the reaction yield was so small that the catenane could not be isolated.[10] Ingeniously, Harrison and Harrison reported the first example of rotaxane synthesis *via* a statistical threading approach.[11] The problem of the low yielding synthesis was partially overcome by affixing the macrocyclic component to a solid support and repeating the threading and capping process 70 times, leading to the isolation of the [2]-rotaxane, after removal from the resin, in 6% yield (Scheme 1).

Although the statistical threading approach was subsequently improved, it was not until the early 1980's that Sauvage demonstrated the seminal cation templated synthesis of a [2]-catenane.[12] The application of templation strategies enabled chemists for the first time to contemplate the efficient synthesis of rotaxanes and catenanes. Two parallel strategies were found by Sauvage to give rise to the catenane, in each case the interweaving Cu(I) template (Fig. 2c) imposes a tetrahedral stereochemical preference on the datively coordinated phenanthroline ligands. Concomitant macrocyclisation of the phenanthroline ligands with polyether chains produced the catenane in 27% yield (Fig. 4A) whilst an improved yield of



Scheme 1 Harrison and Harrison's statistical rotaxane synthesis

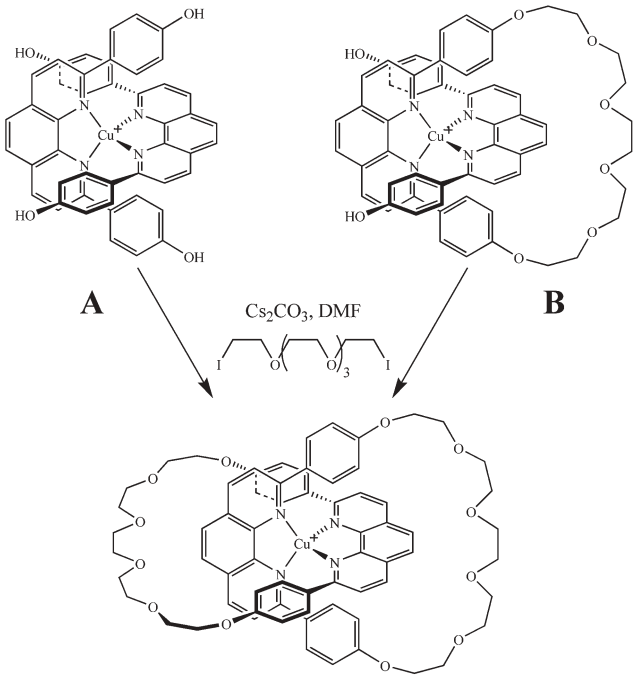


Fig. 4 Sauvage's Cu(I) templated [2]-catenane.

42% was achieved by ring closure of a pseudorotaxane intermediate (Fig. 4B). It is noteworthy that the cationic template does not influence the locking of the individual macrocycles and this must be carried out under high dilution conditions to avoid polymerisation. The Cu(I) template can be removed from this interlocked structure to generate the [2]-catenane by addition of a competing ligand such as cyanide.

The stereochemical preferences of transition metal cations make them ideally suited as interweaving templates. This concept has been extended to utilise transition metals that enforce square planar or octahedral geometries in order to construct a number of impressive architectures,[13] most notably Stoddart's Borromean ring system which harnesses the zinc(II) cation's preference for an five coordinate geometry (Fig. 5).[14a]

Similarly, the directional nature of the hydrogen bond also allows control of the geometric alignment of reagents. Hunter demonstrated the possibility for hydrogen bonded templation with his serendipitous synthesis of a [2]-catenane in 1992 (Scheme 2).[15] Stimulated by this discovery, Vogtle and co-workers have rigorously investigated the mechanism of interlocked structure formation with similar amide hydrogen bond templated systems in chlorobenzene.[16a,b,c] It has been demonstrated that the key intermediate in the reaction occurs after the formation of a single macrocyclic component from the reaction of one equivalent of the di-amine and di-acid chloride. After this stage, a further equivalent of the di-acid chloride is shown to be capable of interweaving through the macrocyclic cavity, by virtue of intermolecular hydrogen bonds between the carbonyl groups and amides, to give an orthogonal interpenetrated complex. A further amine condensation reaction results in the observed mechanically interlocked product.

Cyclodextrins (rigid conical molecules formed by the macrocyclic linkage of six (alpha), seven (beta) or eight (gamma) D-glucose units) are well known to form inclusion complexes in aqueous solution with a multitude of organic guests due to the solvatophobic interactions between them.[17]

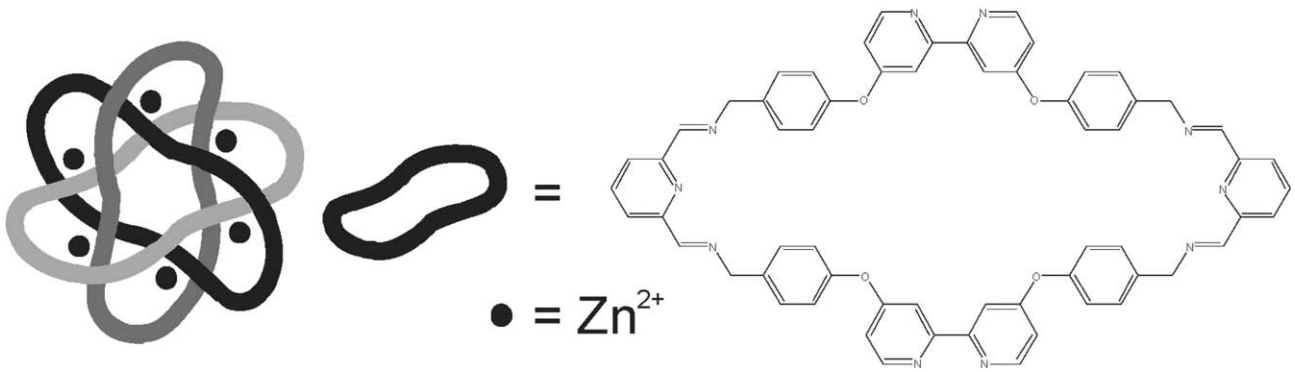
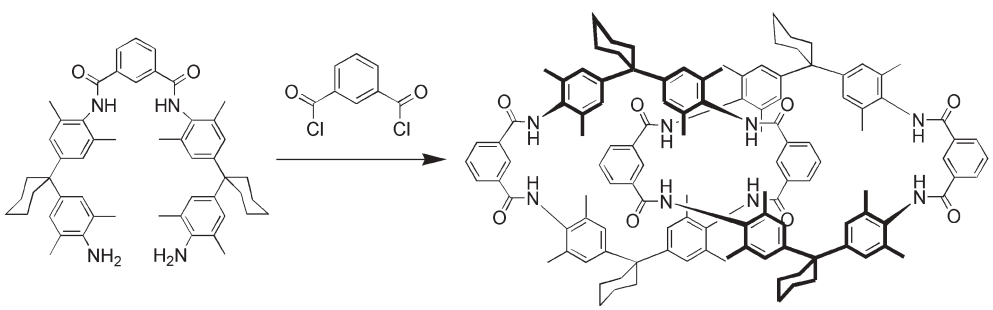


Fig. 5 Stoddart's Borromean ring.



Scheme 2 Hunter's amide hydrogen bond templated [2]-catenane.

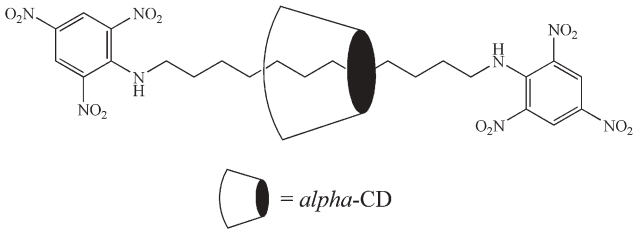


Fig. 6 Harada's hydrophobic templated α-cyclodextrin [2]-rotaxane.

The hydrophobic binding cavity of cyclodextrin has been shown to be a highly effective template for the synthesis of a number of rotaxanes.[18] The first covalent [2]-rotaxane featuring a cyclodextrin group was reported by Harada in 1997.[19] A [2]-pseudorotaxane intermediate was generated by the threading of 1,6-diaminohexane through the hydrophobic binding cavity of α-cyclodextrin in water, and subsequent capping reactions with sodium 2,4,6-trinitrobenzenesulfonate generated the [2]-rotaxane in 42% yield (Fig. 6).

The exploitation of π–π stacking charge transfer interactions as templates for interlocked structure formation has been pioneered by Stoddart *et al.*, utilising the strong interactions between electron rich π systems, for example the hydroquinone moiety, with electron deficient aromatic systems, such as paraquat, in relatively polar solvents including acetonitrile.[14b] As shown in Fig. 7a, a [2]-pseudorotaxane assembles in solution as a result of these aromatic charge transfer interactions and, following a simple capping reaction with bulky silyl stoppers, the resultant [2]-rotaxane was isolated.[14c] Continuing investigations into this methodology have yielded many multi-component catenanes and rotaxanes, for example the so called olympiadane [5]-catenane (Fig. 7b).[14d]

It is noteworthy that in both the amide hydrogen bonded and π–π stacking templated systems there is no discrete template that can be removed from the system. In such cases Busch suggests that '*the anchor (template) is best regarded as the cumulative forces that bind the two systems, and that it (the template) may be regarded as located at the point in space between those systems*'.[6a]

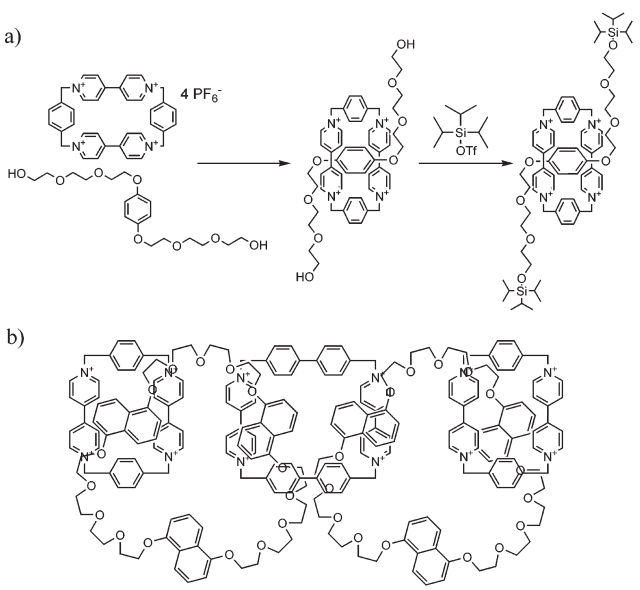


Fig. 7 Stoddart's π stacking templated (a) [2]-rotaxane (b) olympiadane [5]-catenane

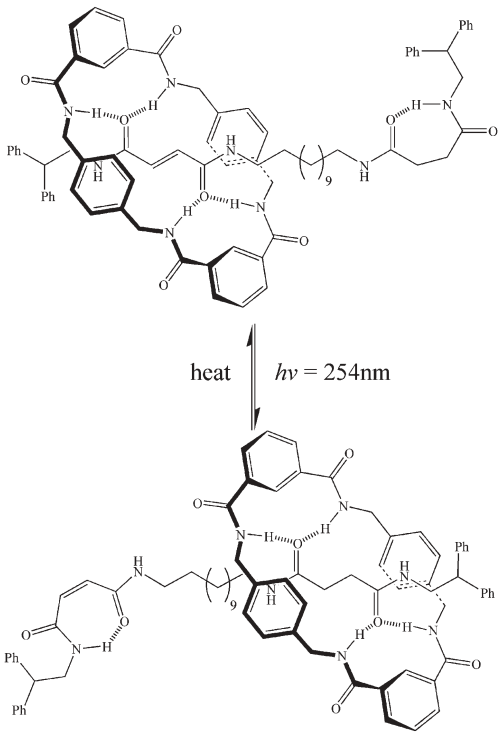


Fig. 8 Leigh's photoinduced molecular shuttle.

The elegant rotaxane and catenane paradigms described in this section have provided the inspiration for the synthesis of some of the first molecular machines. Control of the rotational or translational motion of one of the components in an interlocked molecule, using an external physical stimulus, generates a simple molecular machine. Dave Leigh and co-workers have utilised the aforementioned amide hydrogen bond templation[20a] to produce a photoswitchable 'molecular shuttle' based on a [2]-rotaxane (Fig. 8).[20b]

At room temperature in non-competitive solvents, the macrocycle shows greater than 95% positional variance in favour of the *trans* fumaramide group of the threading component, which is geometrically unable to form stabilising hydrogen bonds to itself. Photoisomerisation of the fumaramide group from the *trans* to *cis* isomer results in translational motion of the macrocycle from the fumaramide to the succinamide hydrogen bonding site, or 'station', approximately 1.5 nm along the axle. This molecular motion results from the stronger intramolecular hydrogen bonded self-association of the *cis* fumaramide group than the more flexible succinamide group, ensuring that, after isomerisation, the greatest hydrogen bonded stability for the [2]-rotaxane is achieved with the macrocycle located at the succinamide station position.

Anion templation

We have seen that the use of cations and neutral molecules as templates for the synthesis of interlocked molecules is a well

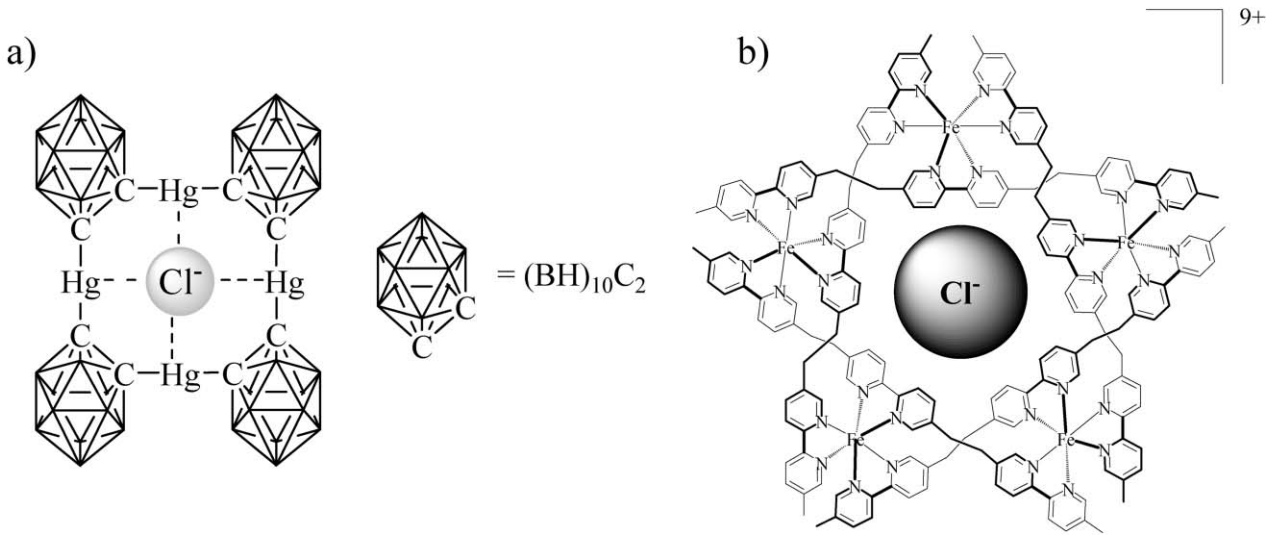


Fig. 9 (a) Hawthorne's chloride templated [12]mercuracarborand (b)Lehn's chloride templated circular double helicate.

established field. As was explained earlier, the use of anions as templates for the assembly of molecular architectures is far less common. This maybe attributed to the intrinsic properties of anions such as their diffuse nature, pH sensitivity and their relatively high energies of solvation.[5]

Groundbreaking work in the field of anion templation was performed by Hawthorne and co-workers with the chloride anion templated synthesis of the macrocyclic tetranuclear [12]mercuracarborand-4 from the direct reaction of 1,2-dilithiocarborane and $HgCl_2$ (Fig. 9a).[21] Structural analysis of the macrocycle revealed the central cavity to be very similar to the size of the chloride anion and although an analogous complex is produced using the larger iodide anion, the template is found to bind partially outside the macrocyclic cavity due to its larger size. The importance of the geometry of the anion template is revealed by the analogous reaction using $Hg(OAc)_2$ where only acyclic products are isolated.

Lehn *et al.* have provided one of the most striking examples of anion templation with the serendipitous discovery of a chloride templated circular double helicate (Fig. 9b).[3c] Reaction of a linear tris-bipyridine ligand with an equimolar amount of $FeCl_2$ results in the pentametallic complex as the thermodynamic product. Similar to the example provided by Hawthorne, the central cavity of the double helicate is complementary to the size of the chloride anion. It is noteworthy that the chloride template cannot be removed from the final structure and if an alternative iron salt, such as $Fe(BF_4)_2$, is used a hexametallic assembly is observed instead, pointing to the pivotal templating role of the halide anion.

The assembly of metal cage complexes around halide templates is demonstrated by the spontaneous assembly of a hexametallic nickel amidinothiourea cage around a templating chloride anion (Fig. 10a).[22] Single crystal X-ray structural analysis confirms the existence of eight NH–Cl hydrogen bonds which are thought to mediate the assembly.

The strategic use of halide anions as cyclisation templates (Fig. 2b) is illustrated by Alcade *et al.* in the synthesis of bis-imidazolium cyclophanes (Fig. 10b).[23] An increase in reaction rate and yield in the presence of either chloride or bromide anions is attributed to anion recognition by the imidazolium motif which results from a combination of electrostatic and hydrogen bonded interactions with the anion.

These examples serve to illustrate the potential untapped wealth of the field of anion templation. In this section we have highlighted examples of the anion templated assembly of helicates, cages and macrocycles and yet the use of anionic templates in the construction of interpenetrated and mechanically interlocked systems remains underexploited.

The possibilities for negatively charged template species in this field were highlighted by the crucial organisational role of the octahedral hexafluorophosphate anion in Stoddart's templated assembly of [5]- and [6]-pseudorotaxanes from dibenzylammonium threads and polyether macrocycles (Fig. 11a).[14e] Indeed, the first interlocked molecule synthesis based on anion recognition between the components was reported by Vogtle *et al.*[16d,e,f] An asymmetrically substituted, sterically bulky phenoxide anion is strongly bound within a

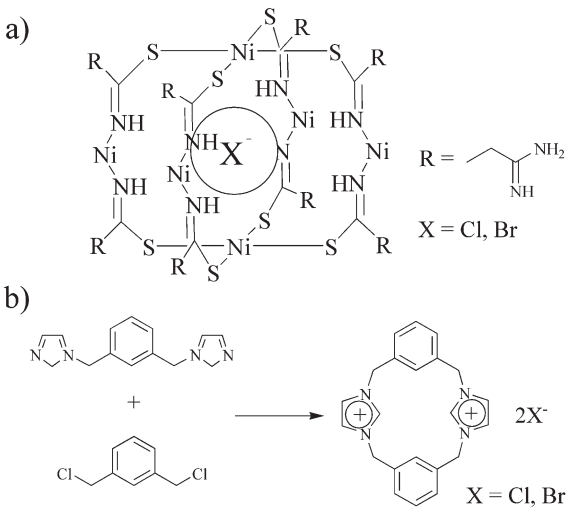


Fig. 10 (a) Schematic representation of an anion templated metallic cage (b) Anion templated imidazolium cyclophane.

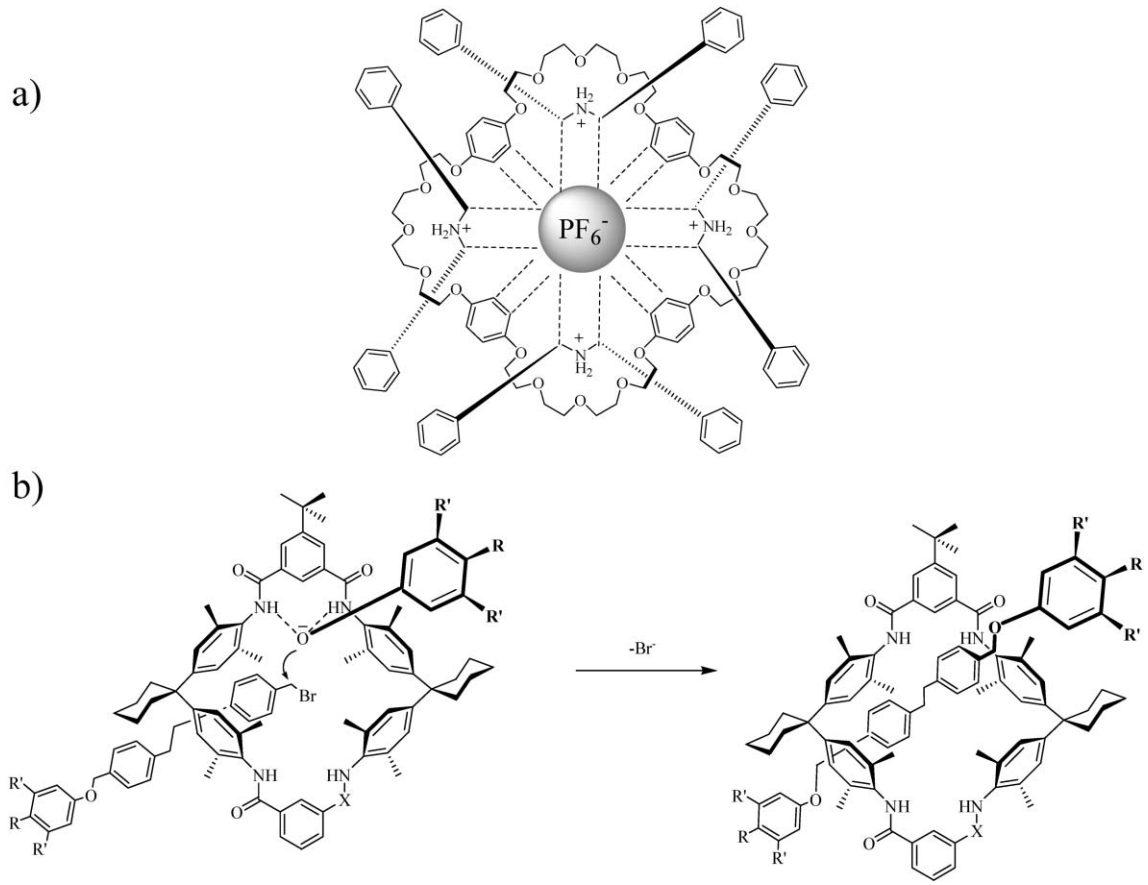


Fig. 11 (a) Stoddart's hexafluorophosphate assisted assembly of a [5]-pseudorotaxane (b) Vogtle's [2]-rotaxane, synthesised by a 'phenoxide trapping' mechanism.

tetralactam macrocycle *via* hydrogen bonded interactions with the amide functionalities and reaction with a suitably aligned electrophile affords the [2]-rotaxane formation in high yield (Fig. 11b). Smith and co-workers have further exploited this methodology in the preparation of [2]-rotaxanes containing an ion-pair receptor and more recently in the synthesis of rotaxinated squarine dyes.[24]

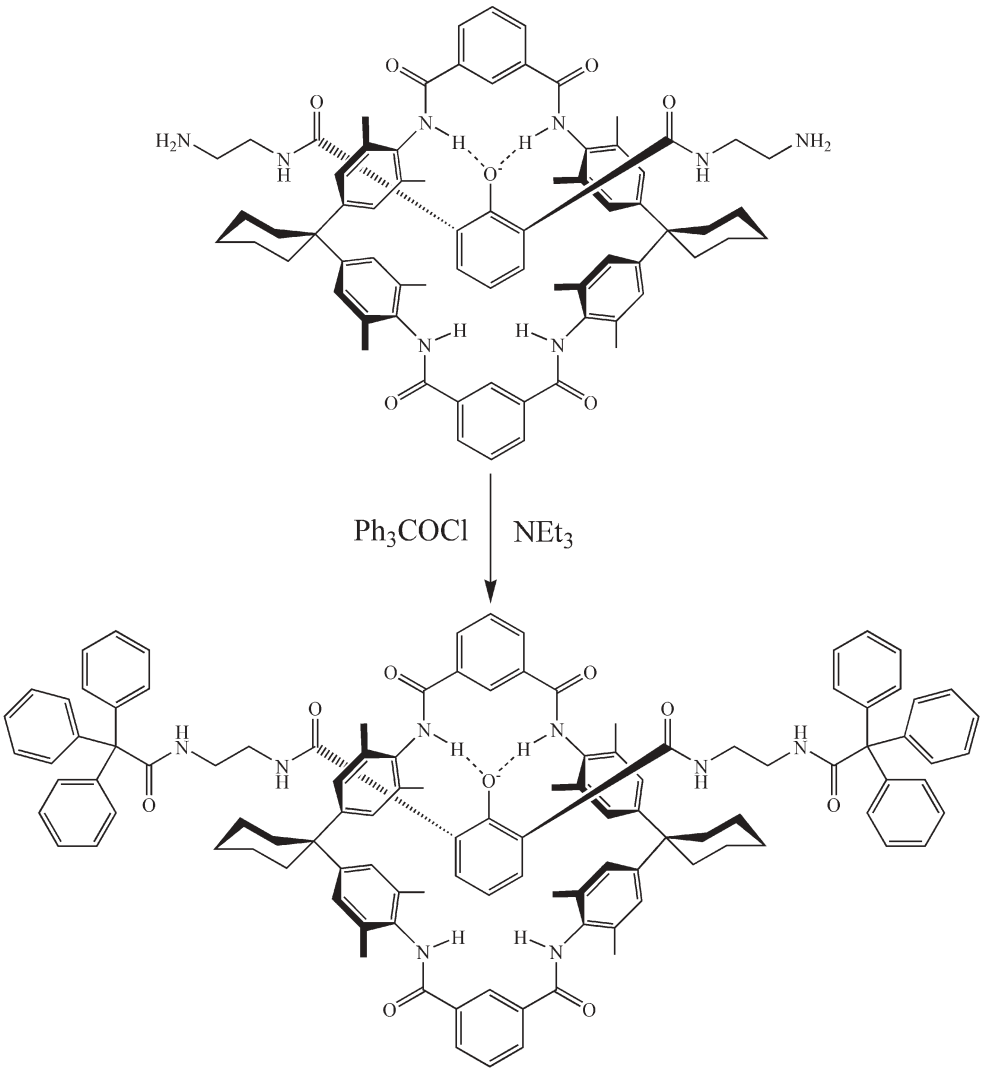
Further investigation of this template motif by Schalley has revealed that recognition of the highly reactive phenoxide anion by the macrocycle inhibits the nucleophilic reactivity of the phenoxide anion, even with highly reactive electrophiles such as methyl iodide.[25a] As an alternative strategy, terminal amine functionalities were appended to the phenoxide anion and, following anion recognition by the macrocycle to form a [2]-pseudorotaxane, amine condensation reactions with sterically bulky acid chloride frameworks generated the [2]-rotaxane (Scheme 3).[25b]

Recently within the Beer group,[26] a novel anion templation strategy for the construction of mechanically interlocked molecules has been developed. These interlocked structures are designed with a view to their use as hosts for anionic guests in which, after template removal, a unique, topologically constrained, anion binding cavity is created as a consequence of the templated synthesis. It is hoped that the high degree of preorganisation in the receptors' interlocked cleft will lead to strong association with anions of similar size and geometry to the template, thus creating a highly selective anion host system.

Anion templated mechanically interlocked structures

Taking inspiration from Sauvage's use of copper(I) metal ions as interweaving templates, we have sought to determine whether anions, in particular halides, could coordinate two simple organic ligands in an orthogonal arrangement, utilising a combination of electrostatic and hydrogen bonded interactions between the two components (Fig. 12a).

Crabtree has demonstrated that simple acyclic isophthalamide derivatives can form 1 : 1 complexes with a range of anions in non-competitive solvents *via* the formation of favourable amide-anion hydrogen bonds.[27] Although such systems were inappropriate for our requirements, namely that two organic ligands assemble around one anion, this problem was overcome by the inclusion of a positive charge into one of the components. The resulting pyridinium cation **1**·PF_6 was shown to form a strong ion-pair ($K_a > 10^5$) with chloride in acetone-d_6 solution as a consequence of strong hydrogen bonding and electrostatic interactions. This tight ion-pair leaves the chloride anion with an unsaturated coordination sphere and a vacant meridian orthogonal to the pyridinium cation. A second hydrogen bond donor **2** has been shown to saturate the coordination sphere of the chloride anion of the



Scheme 3 Schalley's phenoxide templated [2]-rotaxane.

ion-pair **1**·Cl to afford the desired orthogonal assembly with a 1 : 1 stability constant of 100 M^{-1} in acetone-d_6 (Fig. 12b). Importantly, the hexafluorophosphate salt of the pyridinium cation **1**·PF_6 fails to mediate the association of the organic ligands, thus revealing the templating role of the halide anion.

[2]-Pseudorotaxane assembly

This promising preliminary result of using the chloride anion as a potential interweaving template encouraged investigation into the development of a general anion templation strategy to

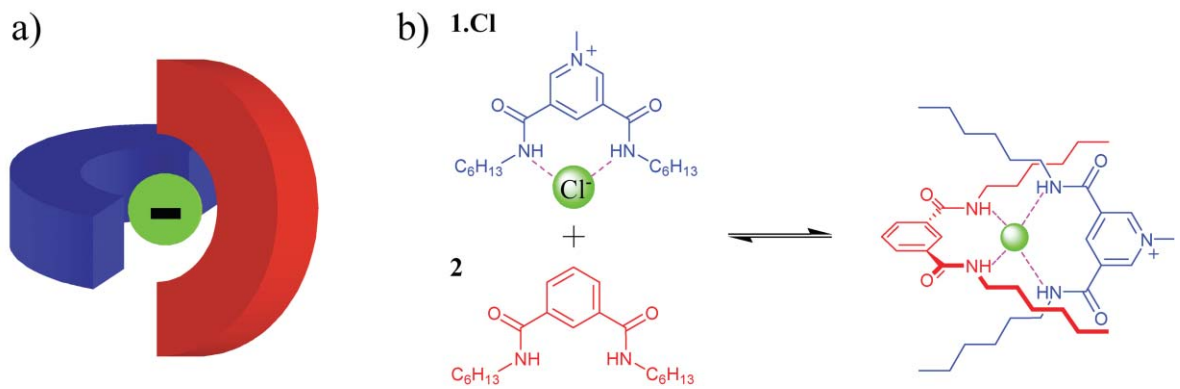


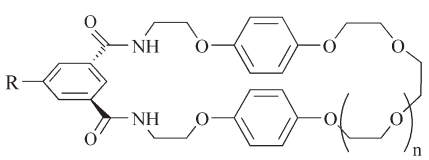
Fig. 12 (a) Cartoon representation of an interweaving template (b) Strong ion-pairing in **1**·Cl allows orthogonal coordination of a neutral isophthalamide hydrogen bond donor **2**.

promote the assembly of a range of [2]-pseudorotaxanes.[26a,b] In non-competitive solvent media the chloride anion has been shown to form a strong ion-pair with amide functionalised pyridinium cations. The coordinative unsaturation of the halide anion has allowed the formation of an orthogonal complex upon binding with an isophthalamide hydrogen bond donor. If this anion recognition site was incorporated within a macrocyclic cavity, [2]-pseudorotaxane assembly would be expected resulting from the mutual association of the macrocycle and pyridinium thread with the anion.

New macrocycles **3–6** were designed to incorporate an isophthalamide anion binding cleft within a macrocyclic cavity so as to saturate the halide anion's coordination sphere of a pyridinium ion-pair. In addition, the integration of hydroquinone groups and polyether linkages into the macrocycle structural framework was expected to aid interpenetration of the positively charged pyridinium thread by providing additional π–π stacking and hydrogen bonded stabilising interactions with the thread (Fig. 13). As expected, the high binding affinity of these macrocycles for chloride in acetone-d_6 was shown to increase relative to **2** due to the macrocyclic effect.

Addition of the halide salts of pyridinium cation $\mathbf{1}^+$ to isophthalamide macrocycles **3–6** was monitored by ^{1}H NMR spectroscopic titration in acetone-d_6. In each case, addition of the ion-pair resulted in significant downfield shifts of the macrocycle's amide protons, with concomitant upfield shifts of the hydroquinone protons of the macrocycle (Fig. 14). Pseudorotaxane assembly was inferred from these upfield shifts, presumed to be caused by the π–π stacking interactions between the electron rich hydroquinone groups and the positively charged, interpenetrated pyridinium thread. The magnitudes of the stoichiometric 1 : 1 association constant values for the macrocycle : ion-pair pseudorotaxane assembly formation were found to decrease in the order of $Cl^- > Br^- > I^-$ and furthermore, the inclusion complex was not observed upon addition of $\mathbf{1}\cdot PF_6$. This observed stability trend in pseudorotaxane assembly arises from a combination of a complementary size match between the macrocyclic binding cleft and the halide template and from the greater hydrogen bond acceptor ability of chloride with respect to the larger more diffuse anions.

Further evidence of pseudorotaxane formation was obtained from single crystal X-ray structural analysis. In the solid state, the amide hydrogen bond donors are shown to form an approximately tetrahedral coordination sphere around the spherical halide anion, resulting in an orthogonal arrangement of the organic components. Short distances are observed between the aromatic groups, indicative of charge transfer interactions between the electron deficient pyridinium thread



3 n = 1, R = ^{t}Bu
4 n = 2, R = ^{t}Bu
5 n = 3, R = ^{t}Bu
6 n = 2, R = H

Fig. 13 Isophthalamide macrocycles **3**, **4** and **5** and their association constant for the addition of TBACl in acetone-d_6.

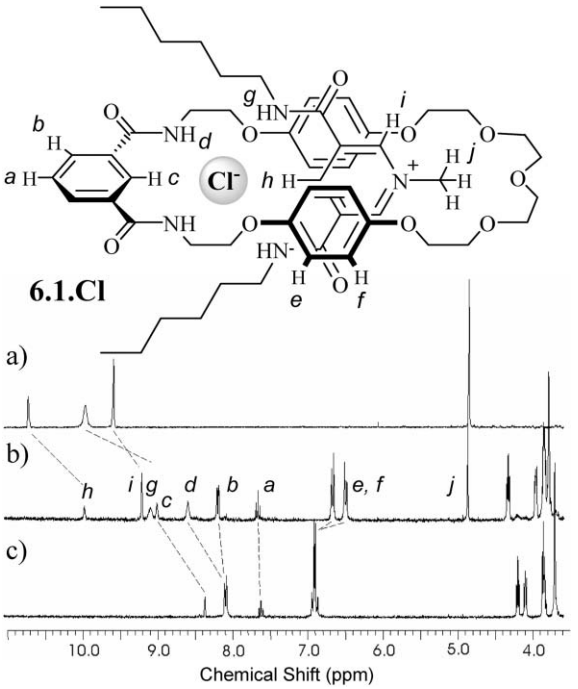


Fig. 14 Proton NMR spectrum of thread **1**·Cl(a) macrocycle **6** (c) and a 1 : 1 mixture of **6**·**1**·Cl (b) in acetone-d_6.

and the electron rich hydroquinone π system. Secondary hydrogen bonding interactions are also observed between the protons of the pyridinium thread's methyl group and the polyether linkages of the macrocycle (Fig. 15).

The versatility of this pseudorotaxane anion templation methodology was further illustrated with the assembly of a series of pseudorotaxane structures where macrocyclic recognition of an anion of an ion-pair results in the formation of an interpenetrated structure (Fig. 16). As in the previous example, the macrocyclic component featured the isophthalamide anion recognition motif whilst the thread contained a coordinatively unsaturated halide anion strongly bound to an appropriately designed cationic organic framework.

The range of pseudorotaxanes accessible *via* this templation strategy was demonstrated using a series of cationic thread

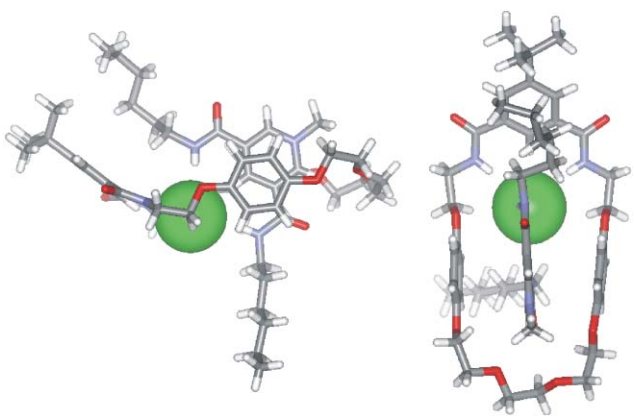


Fig. 15 Solid state structure of the anion templated [2]-pseudorotaxane assembly promoted by the anion recognition between macrocycle **3** and ion-pair **1**·Cl.

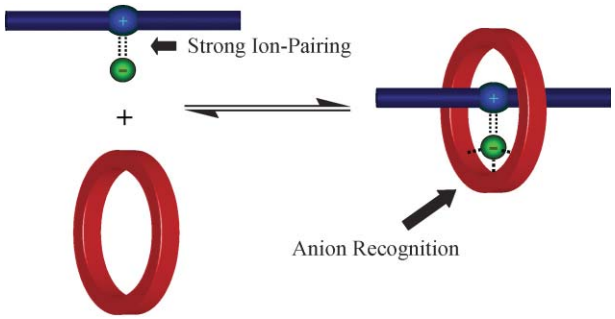


Fig. 16 Cartoon representation of anion templated [2]-pseudorotaxane assembly.

components including pyridinium nicotinamide (thread **7** shown in Fig. 17) as well as imidazolium, benzimidazolium and guanidinium functionalities. For each new system, the stability of the interpenetrated assembly was found to be critically dependent on the nature of the halide template with evidence for [2]-pseudorotaxane formation obtained from ^{1}H NMR and 2D NOESY NMR spectroscopic experiments, as well as from solid state X-ray structural analysis.[26b]

Alternative macrocycles containing a halide binding cleft were also shown to afford [2]-pseudorotaxane assemblies using this anion templation methodology.[26c] Macrocycle **8**, appended with the photo-active rhenium(I) bipyridyl reporter group, was shown by ^{1}H NMR spectroscopy and solid state X-ray crystallography to form interpenetrated species with the halide salts of pyridinium and pyridinium nicotinamide chloride ion-pair salts (Fig. 18). Addition of **1**·Cl to the macrocycle was found to result in an increase in intensity of the rhenium(I) ^{3}MLCT emissive response, presumably due to the increasing rigidity of the complex decreasing the probability of non-radiative decay.[28]

Anion templated assembly of rotaxanes

Having demonstrated the anion templated assembly of a variety of pseudorotaxanes, attention now focused on whether this methodology could be exploited in the synthesis of mechanically interlocked molecules. The synthesis of [2]-rotaxanes has been commonly achieved by slippage and stoppering strategies however, after careful consideration, a clipping reaction using Grubbs' metathesis catalyst was used to effect rotaxane formation (Fig. 19).

An acyclic isophthalamide binding cleft was functionalised with hydroquinone and polyether functionalities, and additionally with two terminal allyl groups, producing the macrocyclic precursor **9**. Two sterically bulky aromatic stopper groups, too large to fit through the macrocycle annulus, were appended to the pyridinium di-amide moiety to form the cationic stoppered axle **10**·Cl. Addition of the macrocycle precursor **9** and ion-pair **10**·Cl resulted in an orthogonal complex assembly and subsequent ring closing metathesis reaction using Grubbs' catalyst between the allyl groups in dichloromethane yielded the [2]-rotaxane **11**·Cl in 47% yield (Scheme 4).[26d] It is noteworthy that no interlocked products were obtained from the reaction of the corresponding bromide, iodide or hexafluorophosphate salts of the pyridinium thread **10**$^+$, unambiguously demonstrating the pivotal templating role of the chloride anion.

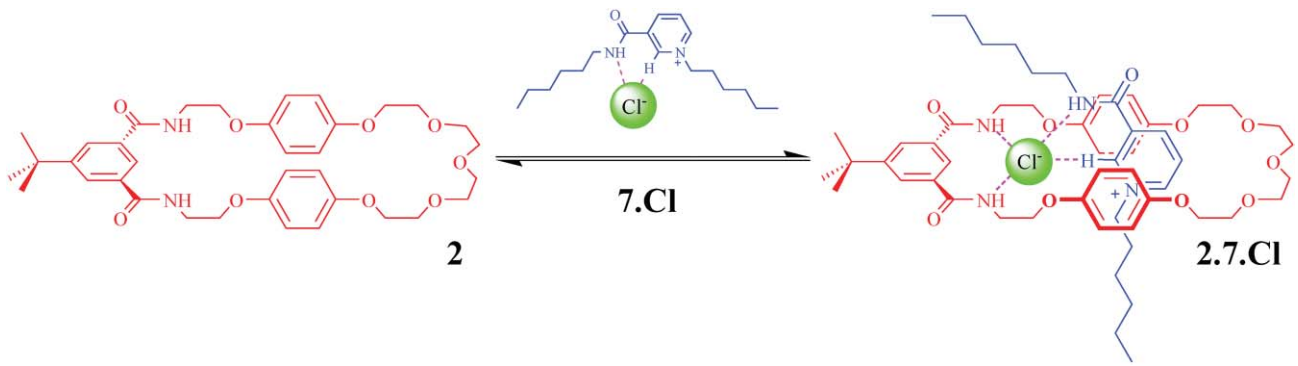


Fig. 17 Anion templated [2]-pseudorotaxane formed between macrocycle **2** and nicotinamide ion-pair **7**·Cl in acetone-d_6.

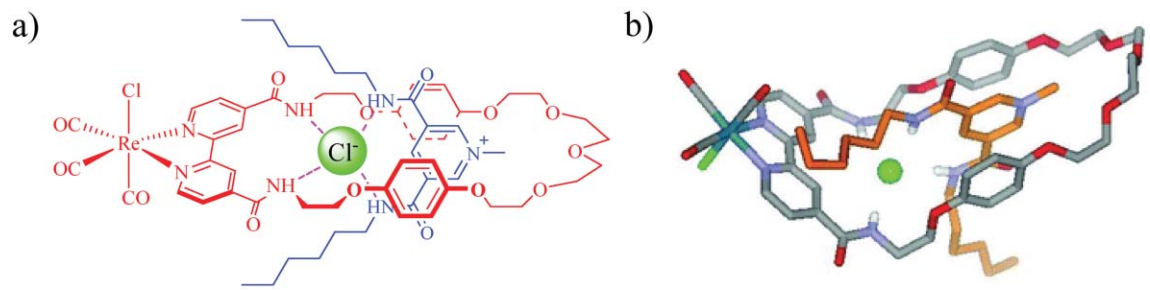


Fig. 18 (a) Chloride anion templated [2]-pseudorotaxane formed between luminescent macrocycle **8** and pyridinium thread **1**·Cl in acetone-d_6 (b) Solid state structure of [2]-pseudorotaxane **8**·**1**·Cl (hydrogen atoms omitted for clarity).

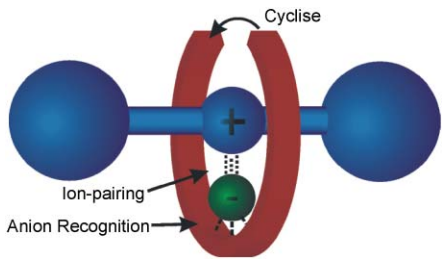
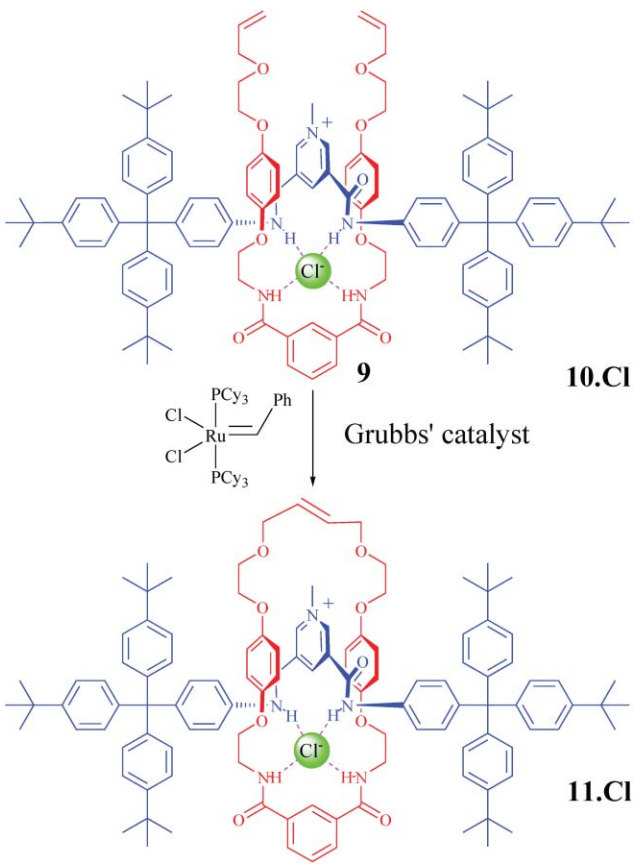


Fig. 19 Clipping methodology for the anion templated synthesis of a [2]-rotaxane.

^{1}H NMR spectroscopic experiments and single crystal X-ray structural analysis of **11**·Cl revealed multiple hydrogen bonded interactions between the [2]-rotaxane and chloride anion within the rotaxane's unique binding cavity. As was observed in the [2]-pseudorotaxanes, significant π–π stacking and hydrogen bonding interactions were found between the organic components.

Anion exchange of the chloride template for the non coordinating hexafluorophosphate anion was achieved by the addition of $AgPF_6$, leaving an anion binding cavity in the [2]-rotaxane with four amide hydrogen bond donor groups pointing inward to the receptors' cleft. ^{1}H NMR spectroscopic titrations revealed that halide anion recognition occurs within



Scheme 4 Ring closing metathesis of the interweaving complex formed between **9** and stoppered thread **10**·Cl leads to the [2]-rotaxane **11**·Cl in CH_2Cl_2.

this interlocked binding pocket and upon anion addition significant downfield shifts were observed for each of the amide protons, indicating hydrogen bond formation. Analysis of the titration data revealed that [2]-rotaxane **11**·PF_6 binds anions with a remarkable reversal of selectivity to the pyridinium thread **10**·PF_6 in $CDCl_3$:MeOD (1 : 1), which is highly selective for acetate, with a notable preference for chloride (K = 1130 M^{-1}) over dihydrogenphosphate (K = 300 M^{-1}) and acetate (K_{11} = 100 M^{-1}, K_{12} = 40 M^{-1}). Whilst it is presumed that **10**·PF_6 binds anions in preference according to their increasing oxo-basicity, rotaxane **11**·PF_6 is shown to bind chloride selectively due to the high degree of complementarity between the binding pocket and anion. The complexation of larger, non-complementary anions, results in the unfavourable distortion of the binding cavity and the full complement of hydrogen bonds are not accessible to the incoming anion, thus reducing complex stability.

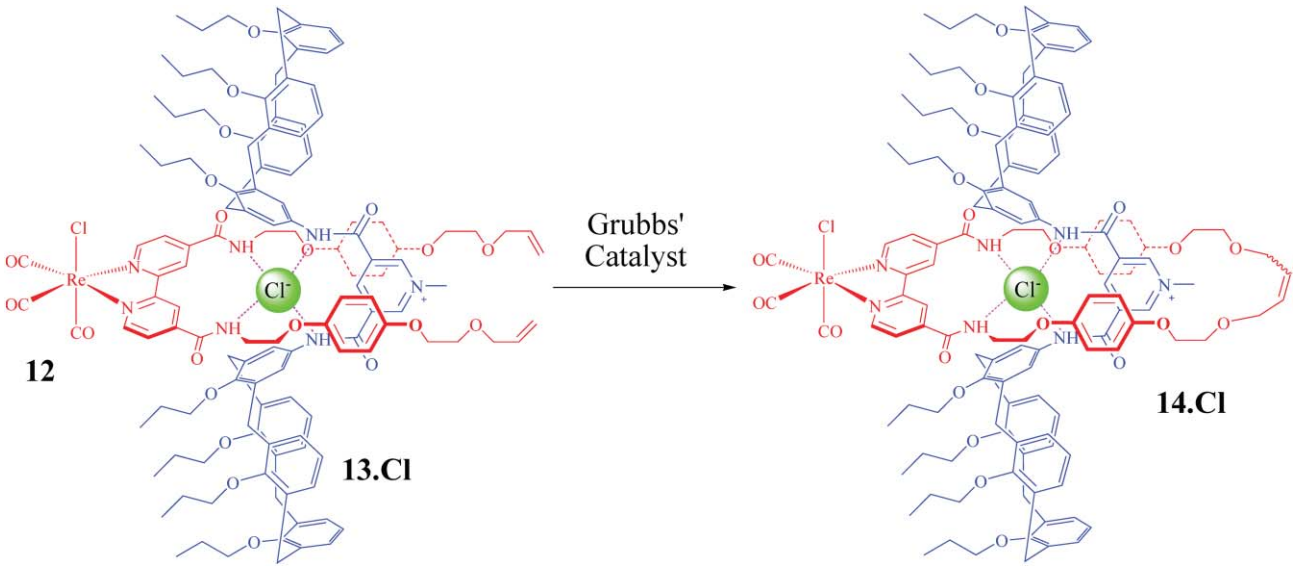
Satisfyingly, these results justify the use of anion templation to create receptors containing unique, highly preorganised, anion binding cavities. In the pursuit of mechanically interlocked anion sensors, the success of the assembly of a photo-active [2]-pseudorotaxane (Fig. 16a) inspired the application of an analogous anion templated clipping synthetic strategy to produce a luminescent [2]-rotaxane. As such, the bis-vinyl appended rhenium(I) bipyridyl derivative **12** was synthesised and, due to the large size of the bipyridyl anion binding cleft, larger calix[4]arene stoppering groups were required to prevent the pyridinium axle **13**·Cl from simply passing through the macrocyclic cavity. A mixture of **12** and **13**·Cl followed by a metathesis reaction with Grubbs' catalyst in dichloromethane led to isolation of the luminescent [2]-rotaxane **14**·Cl in 21% yield (Scheme 5).[26e]

Following replacement of the chloride template with the non-coordinating hexafluorophosphate anion, ^{1}H NMR spectroscopic experiments of [2]-rotaxane **14**·PF_6 with TBACl in acetone-d_6 confirmed that chloride anion recognition occurs *via* the formation of hydrogen bonds with each of the amide donors.

Pleasingly, the [2]-rotaxane was able to function as a luminescent anion sensor *via* notable enhancements in the rhenium(I) ^{3}MLCT emissive response. Interestingly, 1 : 1 anion association constants obtained by luminescence spectroscopy in acetone, revealed **14**·PF_6 to exhibit hydrogen sulfate selectivity over a variety of other anionic guests such as chloride and nitrate. It is noteworthy that this result contrasts sharply with the chloride selectivity of rotaxane **11**·PF_6, and is thought to result from the larger rotaxane binding cavity of $\mathbf{14}^+$ which results in a complementary topology for the tetrahedral hydrogensulfate anion.

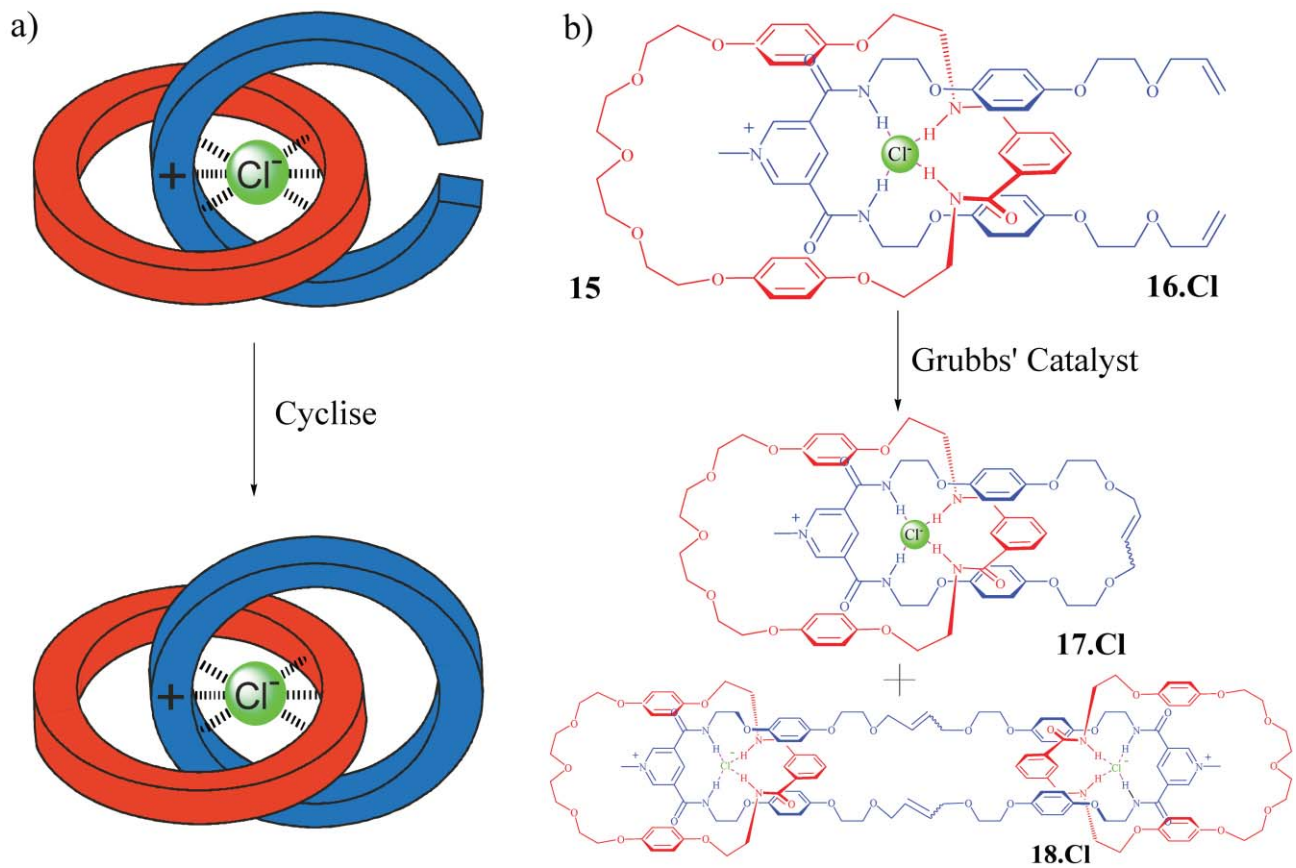
Anion templated assembly of catenanes

In a major development of this methodology, the first example of the use of anion templation to synthesise catenanes was demonstrated. The strategy employed for preparing a [2]-catenane is shown in Scheme 6a where a chloride anion, as part of a tight ion-pair, promotes the formation of a [2]-pseudorotaxane and a subsequent clipping reaction affords the [2]-catenane.[26e]



Scheme 5 Clipping mechanism for the synthesis of luminescent [2]-rotaxane **14**·Cl in CH_2Cl_2 from the chloride anion templated interweaving complex between **12** and **13**·Cl.

A dichloromethane solution of isophthalamide macrocycle **15** and the allyl functionalised pyridinium chloride component **16**·Cl was treated with Grubbs' catalyst to afford the [2]-catenane **17**·Cl in 45% yield (Scheme 6b). Unexpectedly, the reaction also yielded the corresponding [3]-catenane **18**·Cl as a side product in 5% yield. The analogous reaction using a bromide template afforded the [2]-catenane in a much reduced yield of 6% and no mechanically interlocked products were observed using iodide or hexafluorophosphate anions as templates. As was demonstrated in [2]-rotaxane synthesis,



Scheme 6 (a) Clipping methodology for [2]-catenane formation (b) Synthesis of [2]-catenane **17**·Cl and the [3]-catenane **18**·Cl in CH_2Cl_2 from the chloride anion templated interpenetrated complex formed between macrocycle **15** and pyridinium thread **16**·Cl.

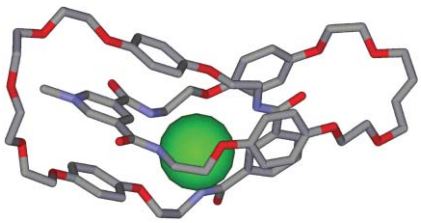


Fig. 20 X-Ray crystal structure of [2]-catenane **17**·Cl (hydrogen atoms omitted for clarity).

the formation of the interlocked product depends critically on the size and shape of the anionic template.

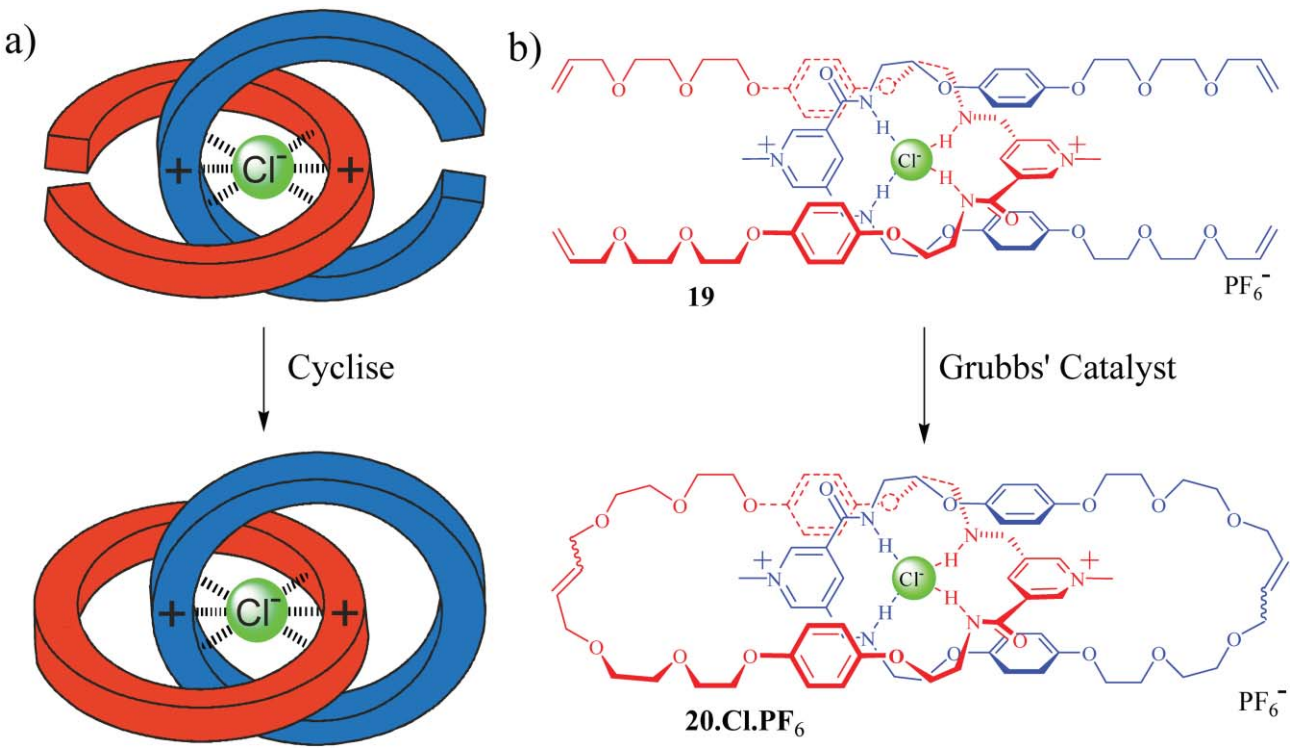
The single crystal X-ray structure of **17**·Cl confirms the orthogonal interlocked arrangement of the two macrocycles, with the chloride anion shown to bind within the topologically unique amide binding cavity (Fig. 20).

As with the [2]-rotaxane structures, following chloride anion exchange using $AgPF_6$, the anion binding properties of [2]-catenane **17**·PF_6, and its acyclic pyridinium precursor **16**·PF_6 were assessed by ^{1}H NMR spectroscopic titrations in acetone-d_{10} solutions. The acyclic pyridinium ligand, **16**·PF_6 was found to exhibit a strong affinity for dihydrogen phosphate and acetate with the calculated 1 : 2 stoichiometric stability constants of K_{11} = 1360 M^{-1}, K_{12} = 370 M^{-1} and K_{11} = 1500 M^{-1}, K_{12} = 340 M^{-1} respectively, where as only weak binding of K = 230 M^{-1} was calculated for the chloride anion. In contrast, catenane **17**·PF_6 was found to reverse this selectivity trend and bind chloride (K = 730 M^{-1}) more strongly than acetate (K = 230 M^{-1}).

The changes in binding selectivity between the acyclic pyridinium ligand **16**·PF_6 and catenane **17**·PF_6 is a result of the creation of a unique, topologically constrained, binding pocket formed by the amide clefts of the two macrocyclic components. This pocket is shown to be complementary in size to the templating chloride anion used to assemble the structure. As was explained in the case of the [2]-rotaxanes, larger anions such as acetate must bind externally to this cavity which may lead to an unfavourable conformational change upon the interlocked structure.

As was noted in Section 3, Sauvage has elegantly used copper(I) cations as interweaving templates for the synthesis of [2]-catenanes using two simultaneous macrocyclic ring closures (Fig. 4). Emulating this catenane synthetic strategy using anions was the next defining challenge. Indeed, a significant advance has very recently been made with the assembly of two acyclic cationic pyridinium components around a single chloride anion template (Scheme 7a). In this experiment, a new pyridinium derivative **19**$^+$, featuring an extended polyether linkage was synthesised. Addition of TBACl to **19.PF$_6$** in $CDCl_3$ led to the observation by ^{1}H NMR spectroscopy of the co-existence of 1 : 1 and 1 : 2 host : guest binding modes, indicating the presence of an interweaving assembled species. Further evidence of the orthogonal assembly was provided by the upfield shifts of the hydroquinone protons, due to the familiar effect of favourable π–π stacking interactions.

Mixing an equimolar solution of **19**·Cl and **19**·PF_6 in dichloromethane, followed by double ring cyclisation using Grubbs' catalyst afforded the di-cationic [2]-catenane **19** in the exceptionally high yield of 78% (Scheme 7b). In contrast to the



Scheme 7 (a) Simultaneous clipping methodology for [2]-catenane formation (b) Synthesis of [2]-catenane **20**·Cl·PF_6 in CH_2Cl_2 from the anion templated interweaving complex formed between **19**·PF_6 and **19**·Cl.

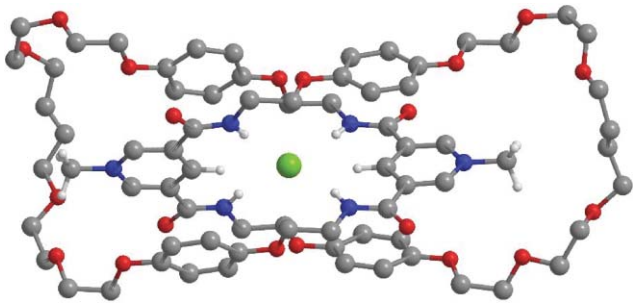


Fig. 21 Solid state structures of [2]-catenane **20**·Cl·PF_6 (hydrogen atoms and hexafluorophosphate anion omitted for clarity).

example shown in Scheme 6, an interlocked product was also obtained by cyclising **19**·PF_6 without a halide template in 16% yield.[26g] This result demonstrates the importance of the secondary π–π stacking and hydrogen bonding interactions in this case, and the reduced yield confirms the templating role of the anion.

Single crystal X-ray structural analysis of **20**·Cl·PF_6 once again highlights the crucial nature of the chloride template which is found to lie in a distorted octahedral binding cavity formed between the amide and *para*-pyridinium protons (Fig. 21).

Anion exchange with $AgPF_6$ gave **20**·$2PF_6$ and the anion binding properties of the catenane were investigated by ^{1}H NMR spectroscopic titration in $CDCl_3$: acetone-d_6 (1 : 1). Analysis of the titration data obtained upon the addition of chloride, bromide and acetate produced association constants with a major 1 : 1 host : guest binding stoichiometry and a minor 1 : 2 binding component. The association constants reveal a remarkable selectivity for chloride (K_{11} = 9240 M^{-1}, K_{12} = 160 M^{-1}) over bromide (K_{11} = 790 M^{-1}, K_{12} = 40 M^{-1}) and acetate (K_{11} = 420 M^{-1}, K_{12} = 40 M^{-1}). In the case of larger anions, significant shifts in the *ortho*-pyridinium protons were also observed indicating anion binding is taking place outside the interlocked cavity.

Conclusions and future prospects

In the course of this review we have charted the evolution of the field of ionic and molecular templation and in particular, the revolution its application has produced in the synthesis of mechanically interlocked structures.

The focus of this article has been the rational development of a general anion templation strategy that combines halide anion recognition and ion-pairing for the purposes of interpenetrated assembly and interlocked structure synthesis. This methodology is demonstrated by the halide anion templated assembly of a series of pseudorotaxanes containing various pyridinium, nicotinamide, imidazolium and guanidinium cationic threading components together with a range of isophthalamide macrocycles. In each case, interpenetrated assembly is found to be critically dependent upon the nature of the anion template. The general applicability of this methodology to interlocked structure synthesis is demonstrated by the synthesis of a number of rotaxanes and catenanes whose formation is determined by the nature of the templating anion.

After template removal, the [2]-rotaxanes and [2]-catenanes are found to bind anions within their preorganised, topologically unique binding pockets by a combination of electrostatic and hydrogen bonding interactions. These interlocked structures are found to be highly selective for chloride, the templating anion. Incorporation of the photo-active rhenium(I) bipyridyl reporter group into the rotaxane structural framework using chloride anion templation has been shown to produce a luminescent anion sensor, selective for the hydrogensulfate anion in acetone solution.

These results demonstrate the potential of this strategic anion templation methodology, both in the synthesis of previously inaccessible molecular architectures and more importantly in future chemical sensor design and fabrication.

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