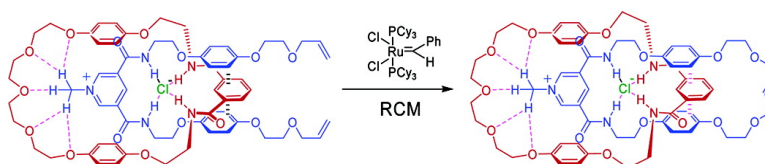


Anion-Templated Assembly of a [2]Catenane

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Anion-Templated Assembly of a [2]Catenane

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The assembly of mechanically bonded molecules such as rotaxanes and catenanes is of great interest to the supramolecular chemist,¹ not only for the challenge of their synthesis but also for the potential uses these systems may have such as molecular switches, sensors, and machines.² Access to the assembly of these interpenetrated structures has been dominated by templated strategies using π - π donor-acceptor interactions,³ hydrogen bonding,⁴ metal-ligand coordination,⁵ and hydrophobic effects⁶ between two or more species that are neutral or cationic in nature. The challenge of using anions to direct the assembly of interlocked supramolecular architectures remains underexploited,⁷ which may be attributed to their diffuse nature, pH dependence, and relative high solvation energy as compared to cations.⁸ We have recently reported a general method of using anions to template the formation of a wide range of [2]pseudorotaxanes.⁹ The assembly process is based on coupling anion recognition with ion-pairing where in noncompetitive solvent media a coordinatively unsaturated chloride anion of a tight ion-pair threading component facilitates the interpenetration of a pyridinium, imidazolium, or guanidinium thread through the annulus of an isophthalamide macrocycle. In a major development of this anion templation methodology, herein, we describe the first example of using anion templation to synthesize [2]-¹⁰ and [3]catenanes and demonstrate after template removal that the [2]catenane exhibits chloride anion-selective binding behavior. The anion templation strategy employed for preparing a [2]catenane is shown in Figure 1 where a chloride anion templates the initial formation of a pseudorotaxane assembly and a subsequent clipping reaction using ring-closing metathesis (RCM) affords the catenane structure.¹¹

Compound **1** (Figure 2) provides one macrocyclic unit of the target catenane, incorporating an amide cleft for anion recognition. The pyridinium chloride thread component, **2a**, has been designed to complement the binding sites of the macrocycle: a pyridinium chloride tight ion-pair where the chloride anion's coordination sphere can be satisfied by the macrocycle's amide cleft, the presence of an electron-deficient aromatic ring capable of favorable second-sphere π - π stacking to the hydroquinone moieties of the macrocycle and a methyl group suitable for hydrogen bonding to the macrocyclic polyether chain. In addition, functionalization of the thread with terminal allyl groups enables a RCM reaction to be carried out.

Mixing components **1** and **2a** in dichloromethane followed by addition of 10 wt % Grubbs' catalyst and stirring overnight allows the metathesis reaction to proceed. Separation of the reaction mixture on preparative TLC using dichloromethane-methanol (94:6) afforded the isolation of the [2]catenane, **3a**, in 45% yield in addition to a small amount (<5%) of the [3]catenane, **4** (Scheme 1). Both catenane systems were characterized by electrospray mass spectrometry, elemental analysis, and ¹H NMR. It is noteworthy that analogous RCM reactions of **1** with **2b** gave the bromide [2]catenane **5** in only 6% yield and no catenanes were isolated from RCM reactions of **1** with **2c** or **2d**. This highlights the crucial role

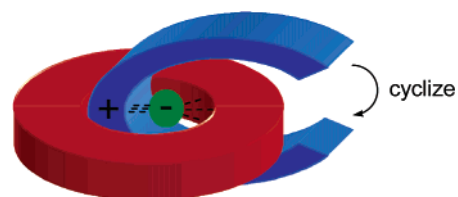


Figure 1. Strategy for assembly of [2]-catenanes via anion templation.

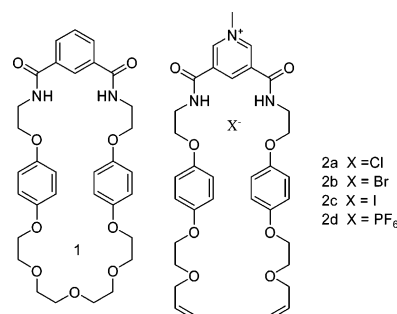
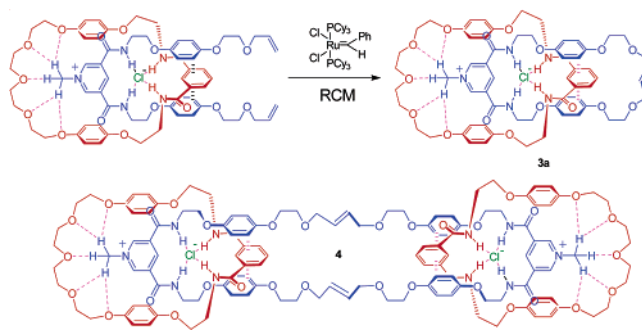


Figure 2. Anion-binding macrocycle, **1**, and catenane precursor, **2**.

Scheme 1. Catenane Synthesis



the chloride ion template plays where threading of the pyridinium cation **2**⁺ is driven by recognition of the halide anion by the macrocycle.

Pale yellow crystals were grown by slow diffusion of diisopropyl ether into a chloroform solution of the [2]catenane and analyzed by single-crystal X-ray diffraction. The crystal structure is shown in Figure 3 and confirms the interlocked nature of the two macrocyclic rings and the location of the chloride anion within the amide cavity. Aromatic stacking and pyridinium-N⁺-CH₃...polyether hydrogen bonds are also observed.

Chloride anion template removal was achieved by addition of AgPF₆ to produce the [2]catenane PF₆⁻ salt, **3b**. Interestingly, only small changes in the ¹H NMR spectrum are observed upon chloride removal, indicating that the catenane, **3b**, retains a nearly identical molecular structure. To determine the effect that catenane formation has upon anion recognition, both the pyridinium allyl component, **2d**, and [2]catenane, **3b**, were titrated with three different anions

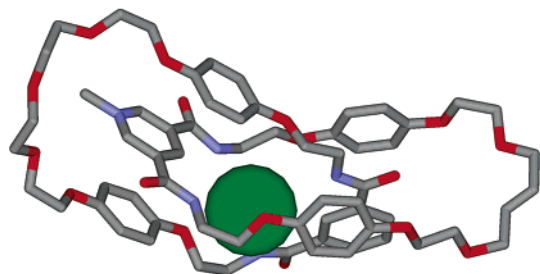


Figure 3. Crystal structure of the [2]-catenane. The polyether chain has been modeled as disordered over two positions, but one of these has been omitted for clarity. Chloride is represented as a green CPK sphere.

Table 1. Association Constants, M^{-1} , for Various Anions with **2d** and **3b** at 298 K in 1:1 CD_3OD-CD_3Cl ^a

host molecule	Cl^-	$H_2PO_4^-$	^-OAc
2d	$K_{11} = 230$	$K_{11} = 1360$ $K_{12} = 370$	$K_{11} = 1500$ $K_{12} = 345$
3b	$K_{11} = 730$	$K_{11} = 480$ $K_{12} = 520$	$K_{11} = 230$

^a Errors less than 10%.

in a 1:1 CD_3OD-CD_3Cl solvent mixture, monitoring the aromatic protons by 1H NMR. WinEQNMR¹² analysis of the respective titration curves gave association constant values shown in Table 1. The pyridinium allyl component, **2d**, displays a strong affinity for acetate and dihydrogen phosphate, with only weak chloride binding being observed. It would appear from these results that the basicity of the oxoanions is the dominant factor in dictating the strength of anion association with **2d**.

By contrast, titrations with the [2]catenane, **3b**, give a reverse binding trend: $Cl^- > H_2PO_4^- > ^-OAc$. The binding of chloride is enhanced significantly, whereas the binding of the oxoanions is much weaker. These dramatic changes in anion selectivity are postulated to be the result of the creation of a unique, topologically constrained catenane binding pocket formed by the two amide clefts of **3b**. Large anions such as dihydrogen phosphate and acetate must either bind outside of the cavity or force a large, and unfavorable, conformational change upon the catenane. In both cases, it is unlikely that a full complement of hydrogen bond donors will be available to complex the oxo anionic guest. Association stoichiometries also appear to be affected, with only a 1:1 binding ratio observed for acetate as opposed to a mixed 1:1 and 1:2 with the pyridinium allyl precursor, **2d**. The reason for the cooperative binding of a second $H_2PO_4^-$ guest species by the catenane is still undetermined.

In conclusion, we have described the first [2]- and [3]catenane structures to be synthesized using anion templation. The choice of anion has been demonstrated to be crucial to the assembly process, with only chloride producing the [2]catenane in acceptable yield. Anion binding by the pyridinium component is greatly influenced by catenation, leading to dramatic changes in anion selectivity trends. The use of rotaxane and catenane cavities as binding domains remains underexploited,¹³ and we are currently pursuing a greater range of mechanically interlocked species with desirable anion binding properties in our laboratories.

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Supporting Information Available: Full experimental details and tables giving the crystal data and structure refinement information, bond lengths and angles, atomic and hydrogen coordinates, and isotropic and anisotropic displacement coordinates for **3a** (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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