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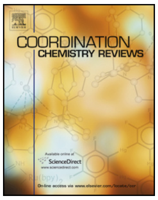

Review

Interlocked host molecules for anion recognition and sensing

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ABSTRACT

This review describes the concept and exploitation of a strategic anion templation methodology in the construction of a range of interlocked host molecular frameworks designed to recognize anionic guest species in competitive aqueous media. Rotaxane and catenane receptors that contain unique anion binding cavity domains are demonstrated to exhibit high levels of anion selectivity in aqueous media. The incorporation of redox-active ferrocene and photo-active transition metal bipyridyl and naphthalene groups into interlocked host structures enables such materials to selectively sense anions by electrochemical and optical means. Importantly, halogen bonding interlocked host systems are shown to display enhanced anion recognition properties when compared with hydrogen bonding analogues. The assembly of interlocked architectures capable of displaying anion induced molecular motion, and of increased complexity, such as [3]rotaxanes and a handcuff catenane serves to further illustrate the scope and versatility of this anion templation approach.

1. Introduction

Inspired by the fundamental roles negatively charged species play in a range of chemical, biological, medical and environmental processes [1–11], the field of anion supramolecular chemistry has expanded enormously during the past few decades. Although many acyclic and macrocyclic two-dimensional receptors have shown success in the binding and sensing of anions, it can be argued that the challenge of recognizing anions selectively in protic solvents necessitates the construction of more elaborate three-dimensional receptors where the binding site is in a protected buried pocket, which enables the total encapsulation of the anionic guest species. Taking this into account we surmised that the construction of such sophisticated target receptors would require unprecedented innovative anion templation synthetic methodologies. Various serendipitous discoveries of where anions have been shown to control the assembly of polymetallic cluster and cage complexes abound in the literature [12–18], however, the strategic use of anions as potential templating reagents for the designed assembly of molecular architectures remains largely underdeveloped [19–30]. In spite of the huge interest being currently shown in the construction of mechanically bonded molecules for nanotechnological applications as molecular switches and machines [31–35], the potential of their unique topological cavities in host-guest chemistry has been in the main neglected [36]. This is especially the case for the recognition of anions.

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This review will describe the development of a general anion templation strategy which has been successfully exploited for the synthesis of a variety of rotaxane and catenane molecular host systems whose three-dimensional interlocked binding domain cavities exhibit high degrees of anion selectivity in competitive aqueous solvent mixtures.

Furthermore, the incorporation of redox- and photo-active groups into these interlocked frameworks has enabled anion sensors to be fabricated.

2. Principle of strategic interweaving anion templation and pseudorotaxane formation

Since their initial proposition, interpenetrated and interlocked molecular architectures have provided a significant challenge to the synthetic chemist. The unique topological features of mechanically interlocked molecules has opened up a new field in supramolecular chemistry stimulated by their exciting potential nanotechnological applications in molecular machines, switches, sensors, and even computers. Since the initial statistical approaches, a range of cationic and neutral template methods have enabled a large catalogue of mechanically bonded systems to be constructed. However, the use of anion templates to construct interlocked molecules is relatively underdeveloped, which has been attributed to the problems encountered in the binding of anions: namely, their small charge/radius ratio compared to cations, pH dependence, high solvation energies, weak coordination preferences (e.g. lack of any ligand field effects) and range of geometries.

Influenced by Sauvage's metal-directed synthesis of a pseudotetrahedral copper(I) bis-1,10-phenol-phenanthroline complex **1** as a precursor to interlocked catenane structures (Fig. 1 left) [37–40], we set ourselves the challenge to investigate whether anions may be exploited in an analogous templating fashion (Fig. 1 right). More specifically, the role of the anionic template is to simultaneously coordinate two components in an orthogonal fashion.

Crabtree and co-workers had shown that simple isophthalamide derivatives **2** (Fig. 2) are receptors for anions in polar organic solvents [41]. In particular they bind halide anions through highly favourable amide–anion hydrogen bonding interactions exclusively in a 1:1 stoichiometry [42], which is clearly unsuitable for the formation of the desired orthogonal template assembled stoichiometry of 2 receptors to 1 anion. We overcame this problem by the utilisation of a mono-cationic pyridinium receptor **3** containing a bis-amide cleft anion recognition site as one of the ligands [43].

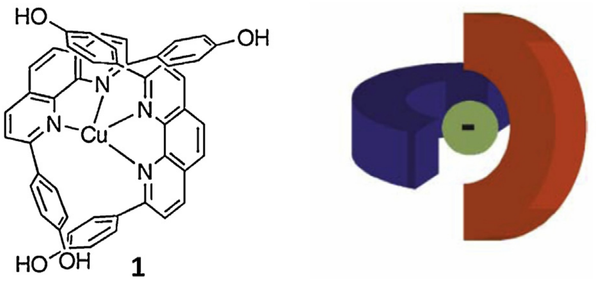
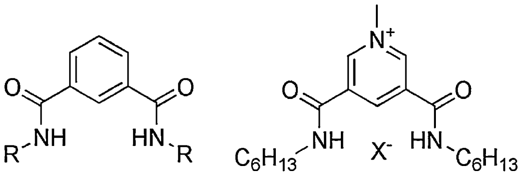


Fig. 1. (left) Sauvage [2]catenane **1**. (right) Cartoon of two ligands arranged orthogonally about a spherical anion [37].



2a R = Ph
2b R = C_6H_{13}

3a X = Cl^-
3b X = Br^-
3c X = $PF6^-$

Fig. 2. Structures of **2** and **3** [42,43].

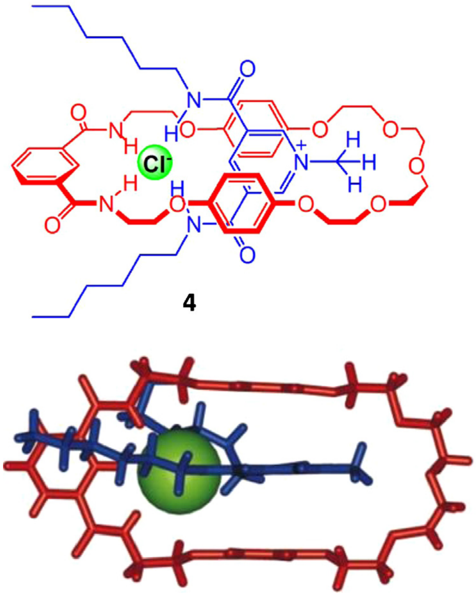


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Fig. 3. (Top) Chloride templated orthogonally interweaving pseudorotaxane **4** formation. (Bottom) X-ray structure of the pseudorotaxane **4** [44].

In polar organic solvents, a positively charged 3,5-bis-amide substituted pyridinium receptor binds a chloride anion strongly via electrostatics and hydrogen bonding to form a tight ion-pair. Due to the coordinatively unsaturated nature of the halide anion, the pyridinium chloride ion pair can orthogonally associate with a neutral isophthalamide motif via hydrogen bonding [44]. The integration of the isophthalamide motif into a cyclic structure design that contained hydroquinol diether groups to facilitate secondary aromatic donor–acceptor interactions and a polyether linkage for hydrogen bonding interactions with the pyridinium N-methyl group, led to the first chloride anion templated [2]pseudorotaxane assembly **4** in d_6-acetone solution (Fig. 3) [44]. Importantly, no evidence of interpenetrative assembly was noted with the corresponding pyridinium hexafluorophosphate salt which highlights the critical, primary role the chloride anion template is playing in the [2]pseudorotaxane formation process. The versatility of this anion templation interpenetrative assembly methodology was further illustrated with a series of pyridinium nicotinamide, imidazolium, 2-bromoimidazolium, benzimidazolium, triazolium and guanidinium chloride salt threading components all forming [2]pseudorotaxanes with the isophthalamide macrocycle [22,138].

We also demonstrated using the sulphate anion as a templating reagent, the first example of anion templated pseudorotaxane formation between a neutral indolocarbazole thread and an isophthalamide macrocycle **5** (Fig. 4) [45].

Recently Sessler and co-workers [46] have described the formation of pseudorotaxanes between the tetracationic imidazolium macrocycle ($\mathbf{6}^{4+}$ $4PF_6^-$) and bis-carboxylate guests (Fig. 5) where the assembly process was shown to be responsive to pH.

2.1. Anion templated synthetic strategies for the construction of rotaxanes and their anion binding properties

Having demonstrated the feasibility of using anions to direct the assembly pseudorotaxanes, this anion templation methodology