

Review

A modular approach to organic, coordination complex and polymer based podand hosts for anions

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Abstract

A range of novel host molecules with various degrees of preorganisation for the supramolecular complexation of anionic guest species are analysed within the context of other recent advances in the field. A modular approach to the design of cationic podands incorporating both organic and coordination compound cores is discussed. Special attention is given to ‘pinwheel’ hosts with functionalities including pyridyl, bipyridyl, aminopyridyl and ureas. The electrochemical and photochemical anion sensing by these functionalised podands is also reviewed. Much larger and more pre-organised calixarene units with consequent alteration of complexation properties, as well as the extension of this work to polystyrene-based and coordination polymer systems and metallogels are also covered.

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1. Introduction

Anion binding continues to attract growing interest among supramolecular chemists [1–10]. There is a very considerable range of possible applications of synthetically created receptors with affinities and selectivities that rival biological anion receptors [11] particularly in a sensing context [12] either using colorimetric methods or in systems with appended redox-active or fluorescent groups [13–25]. Attachment of anion binding

groups to nanoparticles also offers a novel alternative sensing paradigm [26]. In addition, there is considerable current interest in anion transport, particularly chloride because of its biological relevance [27,28].

Anion binding hosts may be broadly classed as either cationic or neutral. In general, positively charged hosts offer scope for obtaining the largest binding constants. However, due to the non-directional and non-selective nature of electrostatic interactions, cationic hosts [29,30] are generally modulated by adding hydrogen bonding moieties. Charged hosts must also have an associated counter-anion, just as the target guest must have a counter-cation, therefore a competition situation is created which must be engineered to lie in favour of the host–guest

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complex. Neutral hosts [31,32] rely solely upon the correct orientation of hydrogen bonding or Lewis acid groups to bind guests, therefore if the fit is not exact the binding can be weak and similarly suffer from potential interference from the counter-cation which is necessarily bound along with the anion.

The hydrogen bond is arguably the most important non-covalent interaction in the design of supramolecular systems, because of its strength and high degree of directionality [33,34]. There are a number of naturally occurring building blocks that are rich source of hydrogen bonding donors and acceptors, for example amino acids and nucleobases, and many have been incorporated into the design of anion binding hosts [35,36]. Particularly effective donors are those in which the acidity of the donor hydrogen atom is amplified by the presence of adjacent electron withdrawing groups. This effect occurs naturally in guanidine systems, ureas and amides. Hydrogen bond acidity may also be enhanced by remote substitution of electron withdrawing groups [8,37]. Irrespective of whether the host species is neutral or positively charged there remains a dependence upon dipole-based interactions to select and retain the guest species. Well positioned directional interactions are essential for selectivity in such systems. Although not as strong as coordination interactions, a cumulative effect may be obtained leading to comparable binding strengths to those achieved by cation receptors in many instances.

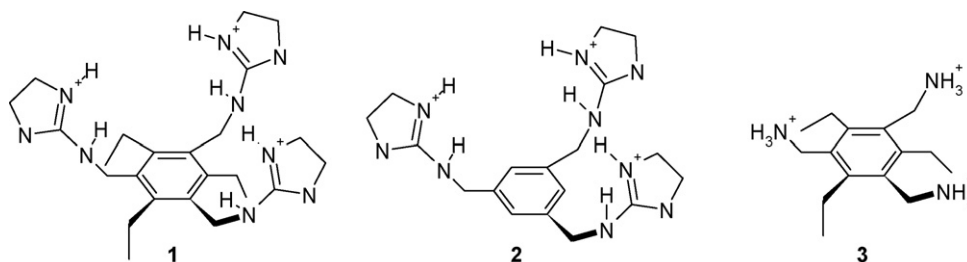
Anion binding hosts may also be divided on the basis of their flexibility or degree of preorganisation. If the host does not undergo a significant conformational change upon guest binding it is said to be pre-organised [38]. Host preorganisation is a key concept because it represents a major contribution to the overall free energy of guest complexation. During the binding process the host undergoes conformational readjustment in order

The vast majority of both macrocyclic and podand anion receptors are organic compounds. Work by Beer and co-workers has resulted in a parallel body of receptors based on ferrocene, cobalticinium, dithiocarbamate, metalloporphyrin and tris(bipyridyl)ruthenium and rhenium derived coordination compounds [13,44–54] all of which incorporate substitutionally inert metal centres. In the mid 1990's we reported a range of calixarene and CTV-derived organometallic bowl shaped receptors [22,23,55–60]. More recently, parallel work by Loeb and Gale and by ourselves among others has seen the introduction of more labile coordination complex anion hosts. Such systems have the potential advantage of self-assembling under anion templated conditions and can prove to be highly synthetically efficient [25,45,61–70].

In this review we focus on our work on a modular approach to anion binding hosts that illustrates *inter alia* the frequent supramolecular structural and binding homology between the organic and coordination complex systems. In particular this structural understanding allows facile tuning of inter-anion selectivity through judicious choice of each module of the host structure. Our results are placed into context against selected examples of other relevant work in the field.

2. Pinwheel hosts

A very elegant design introducing an array of guanidinium group functionalities situated around an aryl core was reported by Anslyn and co-workers in 1997 [15] producing a cavity that is functionalised with three hydrogen bond donor moieties in order to bind tricarboxylate anions such as citrate. The host–guest interaction is enhanced by positive charge on the guanidinium side arm.



to arrange its binding sites in the fashion most complementary to the guest and at the same time minimising unfavourable interactions between one binding site and another on the host. Rigidly pre-organised hosts such as anion binding cryptands [39] may quite often have high complexation activation energy and tend to exhibit slower guest binding kinetics. In contrast, conformationally mobile hosts are able to adjust rapidly to changing conditions and both complexation and decomplexation are usually rapid. Although generally having less intrinsic affinity for their guest than conformationally rigid molecules, flexible hosts are potentially more useful receptors in sensing applications because of their fast response times, reversible binding and the possibility of detecting binding by means of the altered conformation [13,14,20,40–43].

Preorganisation is achieved by incorporating these recognition groups into a trisubstituted 1,3,5-triethylbenzene core, generating a cone shape cavity [15]. The introduction of steric bulk around the benzene-derived core predisposes the compound to adopt the preferred conformation by 3.5 kcal mol⁻¹ in similar systems [71]. The concept has also been used in cation-binding hosts [10,72–74]. Compound **1** binds citrate with an association constant of $7 \times 10^3 \text{ M}^{-1}$ in aqueous solution. This value is much higher than for control compounds, either without the ethyl substituents (**2**) to test the advantage of preorganisation, or functionalised with ammonium groups (**3**) to emphasize the significance of the multi-point hydrogen bonding of the guanidinium groups with the carboxylate units. However, in the presence of buffer the binding affinity of **1** for citrate drops by nearly two orders in magnitude. Anslyn has used this pinwheel

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