A modular approach to anion binding podands: adaptability in design and synthesis leads to adaptability in properties

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Progress in the development of a modular approach towards flexible anion-binding and sensing systems is reviewed within the context of related developments in conformationally flexible anion- and salt-binding hosts. The transferability of concepts and structural features across chemically distinct systems is emphasised along with the use of modular components in polymer and gel-phase systems.

Introduction

In a feature article written a decade ago[1] I said that the field of anion binding had been slow to develop compared to the field of cation binding. It is fair to say that since that time anion binding chemistry has undergone a veritable explosion[2–11] and it would not be unfair to describe it as a vibrant and highly active area of endeavour. The difficulties and challenges inherent in anion binding, and its potential rewards have been extensively discussed.[12,13] The "problem of selective anion binding" and, perhaps more pertinently, the problem of discrimination[14,15] between different anions has been at least partially solved by the development of a vast array of artificial receptors coupling information gleaned from solid state[12,16] and computational studies.[17,18] Correlation of optimal anion binding groups and their preorganisation with solution data on affinity and conformational flexibility is of particular importance. In effect there exists a virtual database in the literature of designs that allow a fair assessment of structure activity relationships for both binding and application, *e.g.* in sensing.[19] As particular anion binding systems become more optimised, increasing refinement has led to truly impressive affinities and selectivities even in competitive media. For example the combination of rigid preorganisation and optimised hydrogen bond acidity engineered into the cholapods.[20] While not all anion binding systems are sharply peak-selective, it is clear that with sufficient synthetic ingenuity and labour, such optimisation is possible in the majority of cases. We may thus truly talk of design rather than serendipity in this field, while at the same time recognising and looking forward to plenty of surprises!

In the design and synthesis of anion binding (including ion-pair binding[21–25]) host compounds, as in many aspects of discrete host–guest chemistry, there are a number of approaches that must be tensioned against one another according to objective and available resources. Some of these considerations are as follows.

Preorganisation

Is a rigidly preorganised host that may well display sharp peak selectivity, perhaps at the cost of some synthetic effort (*e.g.* macrocyclisation) required? Or, is it more appropriate to look to the induced fit paradigm and prepare a flexible molecule that will adapt to fit the guest species? Such conformational change or other adaptability may have use in amplification and signal transduction types of application.[26–28]

Charge

Cationic hosts are an obvious choice for binding anions but suffer from competition from associated counter anions.

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Jonathan W. Steed was born in Wimbledon, UK in 1969. He obtained his BSc and PhD degrees at University College London, working with Derek Tocher on coordination and organometallic chemistry directed towards inorganic drugs and new metal-mediated synthesis methodologies. He graduated in 1993 winning the Ramsay Medal for his PhD work. Between 1993 and 1995 he was a NATO postdoctoral fellow at the University of Alabama and University of Missouri, working with Jerry Atwood, where he developed a new class of supramolecular hosts for anions, an area of chemistry which is still part of his current research work. In 1995 he was appointed as a Lecturer at Kings College London where he built up a reputation for supramolecular chemistry including anion binding and sensing, and crystal engineering studies using strong and weak hydrogen bonds. In 1998 he was awarded the Royal Society of Chemistry Meldola Medal and he was promoted to Reader in 1999. In 2004 he was appointed as Reader in Inorganic Chemistry at the University of Durham and was elected FRSC in 2005. Dr Steed is the author of the textbook Supramolecular Chemistry (2000) and more than 190 research papers. He has published a large number of reviews, book chapters and popular articles as well as a major edited work, the Encyclopaedia of Supramolecular Chemistry (2004). He has been an Associate Editor of New Journal of Chemistry since 2001.

Neutral anion hosts, on the other hand, may bind more weakly in absolute terms (albeit not necessarily less selectively) and must deal with the associated counter cation. They are in effect ion pair binding hosts.

Lability

The traditional concept of the equilibrium-controlled binding of a guest by an inert host makes for relatively straightforward binding stoichiometry and hence affinity analysis but possibly at the expense of the preparation of an elaborate and 'specialist' host. A recently discussed alternative consists of the anion templated,[29] equilibrium self-assembly of a number of components into a host-like assembly.[22,30]

This article will discuss our own progress in developing an overarching approach to adaptive anion binding systems that can be applied, with minimal synthetic effort, to a wide variety of anion binding applications and the study of anion-related phenomena. A key feature is the transferrability of design and concept across chemically unrelated boundaries.

Preorganisation

Classic examples of preorganised, peak-selective receptors are Lehn's Cryptands.[31] Anion-binding azamacrobicycles such as octaazacryptand (**1**) and bis(tren) (**2**) based on protonated secondary amine binding groups also exist, with **1** in particular exhibiting very high affinity for fluoride in water, log K_{assoc} = 11.2.[32] We have prepared more rigid analogues **3** and **4** based on a trisubstituted aromatic ring.[33,34] The tiny cryptand **3** is a strong organic base, binding H^+ *via* $NH^+\cdots\pi$ interactions (Fig. 1(a)), while the larger **4**, like **1**, is highly peak-selective for fluoride (log K_{assoc} = 9.5, Fig. 1(b)) despite binding *via* three $NH\cdots F^-$ and three $CH\cdots F^-$ interactions, as opposed to six $NH\cdots F^-$ hydrogen bonds in the F^- complex with **1**. These two tripodal cryptands highlight the efficacy of weak interactions ($NH\cdots\pi$ and $CH\cdots$anion) when butressed by rigid preorganisation. Moreover host rigidity can result in fascinating encapsulation effects as in the recent report of a hexametallic anion-binding cryptophane.[35] The corollary is that rigid, macrocyclic hosts are sometimes not very versatile and bind few anions, *i.e.* they are very highly selective for their target guests (host **4** binds Cl^- more then 200 000 times less effectively that F^-). They are also difficult to make.[36] Compound **4** is prepared in nine steps and requires an awkward detosylation procedure.[34]

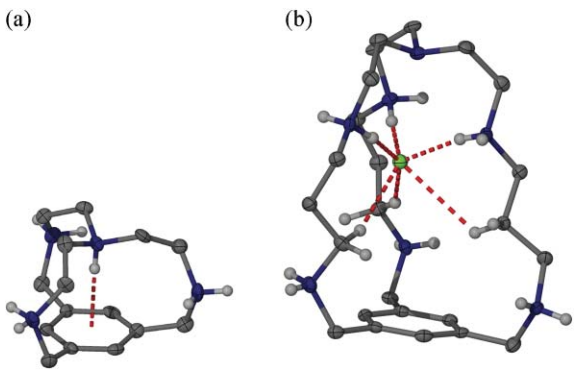
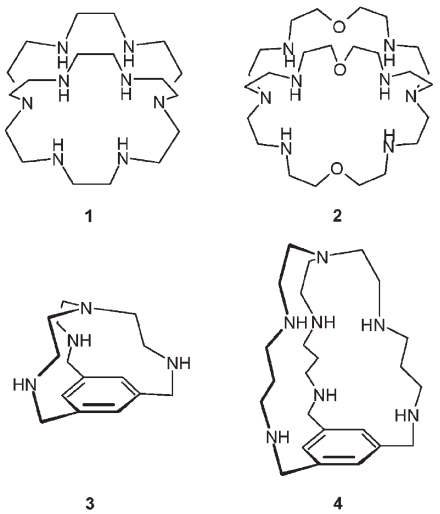
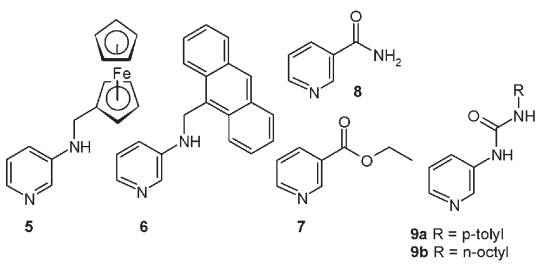


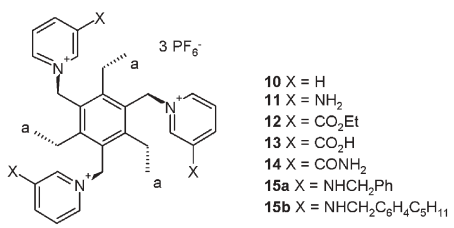
Fig. 1 (a) X-Ray crystal structure of **3**-$4H^+$ showing $NH\cdots\pi$ interactions. (b) X-Ray crystal structure of **4**-$6H^+$ with encapsulated fluoride.



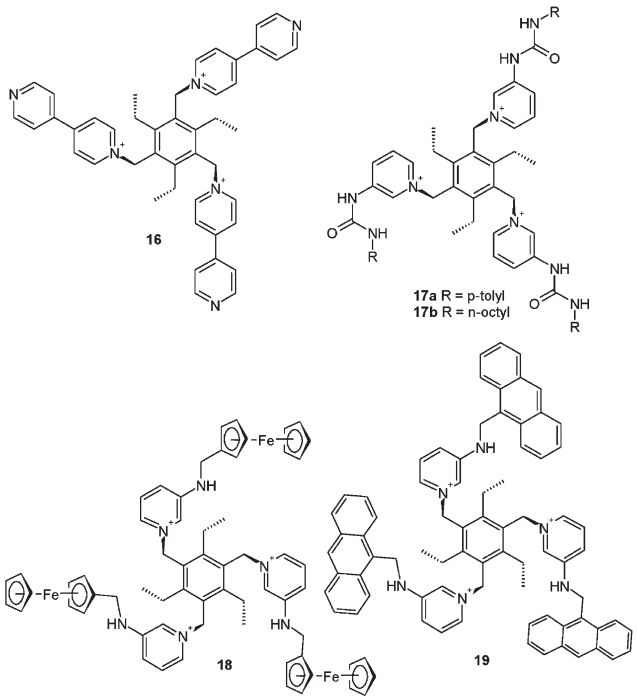
Flexible tripodal receptors

In contrast to compounds such as **4**, much more flexible tripodal receptors **10–19** may be prepared in between one and three steps,[26,37,38]





generally in overall yields in excess of 80% simply by reaction of substituted pyridines such as **5–9** with tri(bromomethyl)-triethylbenzene, followed by counter anion metathesis to PF_6^-.[39] Tripodal receptors for both anions and for cations based on hexasubstituted arene rings have been popularised, respectively, by Anslyn[40,41] and by Kim[42,43] with elegant related systems reported by Fabbrizzi,[44] Garratt,[45–48] Sun,[49] Schmuck,[27] Suzuki[50] and Duan.[28,51] In 1997 Anslyn and co-workers reported a selective receptor for citrate. The binding affinity is 6900 M^{-1} in D_2O, enhanced by the tendency towards alternation around the aryl core. This steric effect preorganises the receptor into a 'three-arms up' binding conformation and was shown to provide a stabilisation of



*ca.*15 kJ mol^{-1} in this system.[40] Hexasubstitution of an aryl ring represents one of a number of strategies for preorganising tripodal hosts.[52–55] This core moiety has since been used in a variety of novel sensing ensembles, some including metals,[41] able to discriminate between different carboxylate anions typically found in beverages, for example. This type of receptor, immobilised onto polymeric beads as part of an indicator displacement system, forms the basis for an electronic tongue sensor array capable of distinguishing between complex mixtures by principal component analysis of the multi-receptor response.[14,15,19,41,56–60]

We have taken the view that a useful moiety such as the triethyl benzene core could form part of a library of components that might be linked *via* simple, high-yielding reactions to generate a readily varied array of podand hosts for anions with their flexibility, and the nature and disposition of their binding and (if desired) sensor reporter groups, controlled by the choice of components. Thus the hosts' affinity and selectivity should be a function of the intrinsic affinity of the binding sites and their spatial organisation. While podand hosts are not expected to display the very high affinities offered by preorganised macrocycles (with some very preorganised exceptions[6,20]), their flexibility offers the interesting possibility of anion-dependent conformational behaviour. Thus a single receptor with a number of degrees of conformational freedom may be regarded as a small virtual library of equilibrating conformers. Particular anions may select and stabilise those conformers that most closely resemble the bound complex, in a version of the induced fit paradigm. Thus the shift in conformation (or distribution of conformations) induced by anion binding may be in principle used to bring widely separated signalling groups into close proximity, for example. The mutual interaction of such moieties may result in effective signal generation.

Anion binding podands

Our initial work resulted in the synthesis of the tripods **10–17** showing that this 'modular' approach is applicable to a variety of potentially anion-binding functional groups. Only the carboxylic acid **13** cannot be prepared by direct reaction of the substituted pyridine with tri(bromomethyl)triethylbenzene and is instead formed by hydrolysis of the ester **12**. The design of **10–17** includes cationic pyridinium groups. While neutral systems are increasingly popular (and successful) in the literature[61–63] they necessarily bind ion pairs rather than representing essentially a metathesis reaction. Cationic hosts also potentially offer scope for high affinity based on electrostatic charge.

Steric crowding and the mutual proximity of the pyridinium positive charges destabilise the 'three-up' conformation and comparison of Br^- binding by **10** and its non-ethylated analogue suggest that the tripodal (or cone) conformation with all the pyridinium groups on the same face of the core is stabilised by only *ca.* 10 kJ mol^{-1} in these systems.[37] Consistent with this conformational preference the bromide salt of the unfunctionalised trispyridinium host **10** exists as two pseudopolymorphs in the solid state, one with a 'three-up' conformation and one with a 'two-up, one-down' or partial cone conformation.[26] The non-convergent partial cone conformation is also observed in the X-ray crystal structures of the PF_6^- salt of the aminopyridinium host **11** (Fig. 2(a)) and the bromide salt of its 4-aminopyridinium isomer.

These conformers contrast to the extensive work of Anslyn on neutral analogues in which the three-up conformer is invariably observed.[41] While the bromide salt of the non-converging 4-amino isomer of **11** is partial cone, the analogous 3-isomer adopts a 'three-up' conformation (Fig. 2(b)). The central bromide anion is held in place by a sixfold array of two NH$\cdots$Br$^-$ and four CH$\cdots$Br$^-$ interactions. Inspection suggests that the cavity is slightly too large for Br^- and this factor may

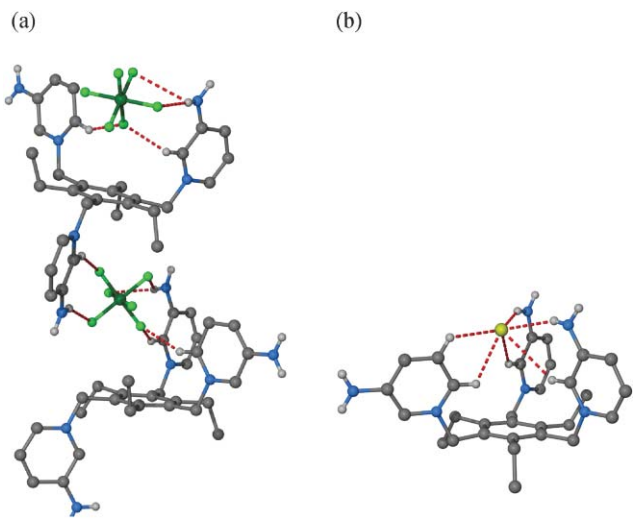


Fig. 2 (a) X-Ray crystal structure of the PF_6^-complex of **11** (two repeat units) showing the partial cone conformation. (b) X-Ray structure of the bromide salt of **11** in the 'three-up' conformation with one NH_2 group rotated outwards.

be responsible for the outward orientation of one of the NH_2 groups.

While solid-state data gives a good indication of possible conformers, it is of crucial importance to establish the solution anion affinity and conformational behaviour of the systems. We have found that a combination of variable temperature and titration experiments using ^{1}H NMR spectroscopy is extremely effective in this regard. ^{1}H NMR titration shows that receptor **11** is selective for Cl^- with K_{assoc} in MeCN in excess of 10^4 M^{-1}. Other halides are bound to a lesser extent. The intrinsic basicity of acetate also results in strong binding, while other anions are less strongly bound. On cooling in acetone-d_6 to 193 K the ^{1}H NMR spectrum of the PF_6^- salt of **11** undergoes significant splitting (Fig. 3(a)) that can readily be rationalised by a freezing of the cone–partial cone interconversion process, Scheme 1(a). The partial cone conformer (observed crystallographically for this salt) exhibits a high field resonance at 0.55 ppm assigned to the CH_3 group (labelled 'a') of an ethyl substituent that enters the shielding region of one of the pyridinium rings. Upon addition of *ca.* one equivalent of Cl^- (as the NBu_4^+ salt) this interconversion process is turned off and the spectrum is indicative of C_3 molecular symmetry throughout the accessible temperature range. However, if a sub-stoichiometric amount (0.4 equivalents) of Cl^- is added the spectrum becomes highly complex. The amount 0.4 equivalents was chosen in order to distinguish between resonances for 'complex' and 'free' host (*i.e.* Cl^- binding and unchanged PF_6^- binding host) on the basis of spectral integration. The result is a spectrum that is broad even at room temperature and resolves into two sets of C_3 symmetric host resonances at 243 K in the ratio 2:3 assigned to **11**·Cl^- and **11**·PF_6^-, respectively (Fig. 3(b)). Further cooling to 203 K results in the further splitting of the latter set of resonances according to the conformational inversion process shown in Scheme 1(a). In contrast, the minor set of resonances sharpen on further decreasing the temperature, indicating that Cl^- stabilises the C_3 symmetric cone conformation.

Addition of substituents to the amine group in **11** to give compounds **15**, **18** and **19** potentially results in unfavourable steric interactions in the C_3 cone conformation as the substituents are all drawn together when the molecule envelops guests such as chloride. This 'clenching' is suggested by

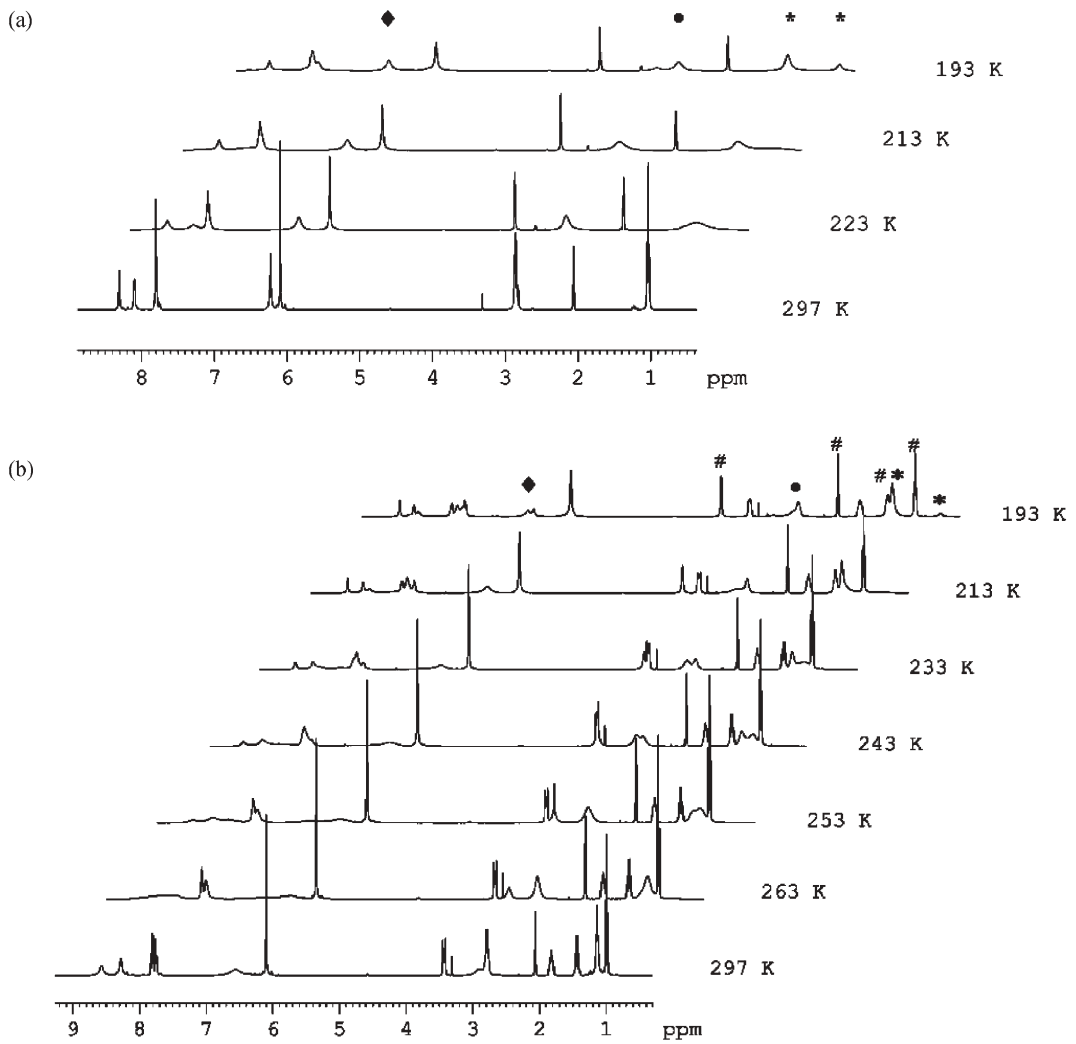
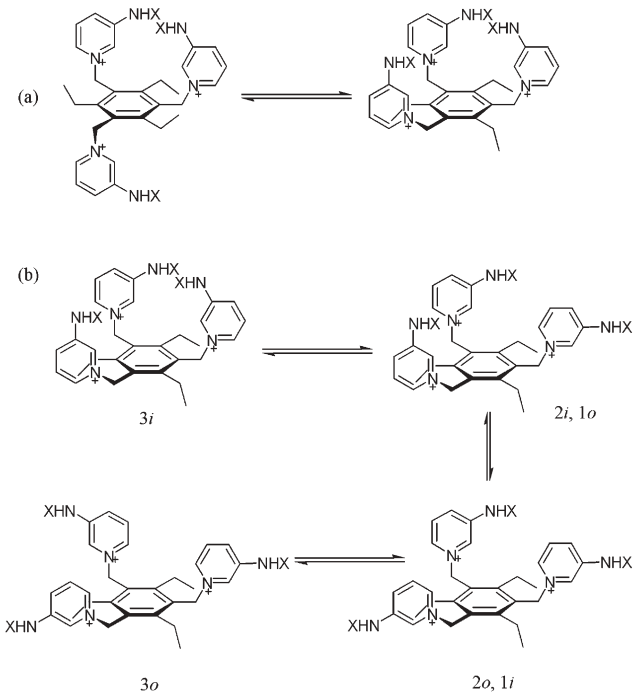


Fig. 3 Variable-temperature ^{1}H NMR spectra of tris(3-aminopyridinium) host **11** in acetone-d_6 (a) as the hexafluorophosphate salt, (b) after addition of 0.4 equivalents of NBu_4Cl. # NBu_4Cl, * ethyl CH_3, ● ethyl CH_2 and ◆ NH.



Scheme 1 Conformational change in hosts of type **11** and analogues (a) up–down and (b) in–out exchange.

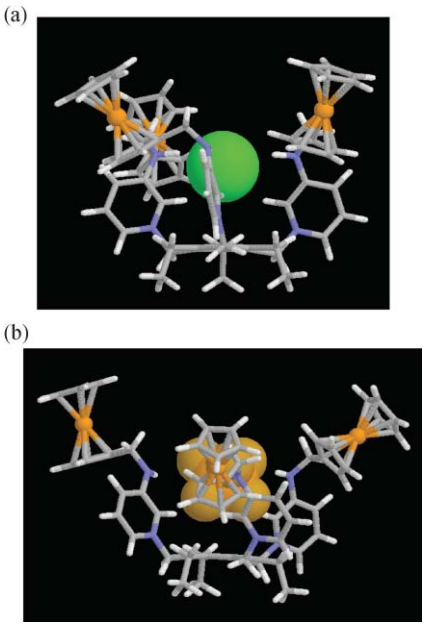


Fig. 4 Semiempirical models of (a) **18**·Cl^- and (b) **18**·PF_6^- showing the closer mutual proximity of the ferrocenyl substituents in the chloride complex.

semiempirical modelling of the Cl^- and PF_6^- salts of the ferrocene derivative **18**. The gas phase calculations indicate that, while the chloride complex is significantly more stable than the hexafluorophosphate, the three ferrocenyl groups in **18**·Cl^- are some 3 Å closer to one another than in **18**·PF_6^-, Fig. 4.

This increased steric hinderance also has an effect on the solution phase binding. Compounds **11** and **15a** bind Cl^- too strongly to measure by ^{1}H NMR methods. Compound **11** also has a high affinity for Br^-, K_{assoc} = 13 800 M^{-1} in acetonitrile-d_3. However as steric bulk increases with compounds **15a**, **18**, **15b** and the anthracenyl derivative **19**, the affinity for Br^- decreases to 3953, 2950, 2330 and 486 M^{-1} in the same solvent, respectively. Thus the very bulky anthracenyl compound is in fact a poorer host for Br^- in acetonitrile-d_3 than the unsubstituted tris(pyridinium) compound **10** (K_{assoc} = 850 M^{-1}). This lack of affinity is ascribed to a lack of convergence in **19** and is exemplified by the X-ray crystal structure of the PF_6^- salt of the host (Fig. 5(a)). While there is an alternating 'three-up, three-down' arrangement of substituents about the aryl core, the conformation is described as 'three-up, three-out' because the secondary amine hydrogen bonding groups are all pointed outwards away from the centre of the molecule and thus the anthracenyl substituents are spaced far apart. As might be expected this steric effect diminishes affinity for not only Br^- but for halides in general with Cl^- being bound with K_{assoc} = 5270 M^{-1} compared to values of over 100 000 M^{-1} for **11** and **15a** which have essentially the same binding sites. Indeed steric effects are so severe that the selectivity of the receptor is entirely changed and the compound becomes acetate selective; K_{assoc} for acetate is 49 000 M^{-1} for the bulky **19**, 3680 M^{-1} for the tris(ferrocenyl) compound **18** and only 2511 M^{-1} for the less bulky benzyl derivative **15a** (all in acetonitrile-d_3). Differential changes in the chemical shift of individual resonances in the ^{1}H NMR titration experiments indicate that acetate binding is occurring, initially *via* two NH groups followed by NH and CH interactions to a second anion possibly in a 'two-up, one-down' conformation, Fig. 5(b). At low temperature a small manifold of unsymmetrical conformations can be identified with four resonances assigned to bound acetate CH_3 protons in the region

In general, combined X-ray crystallographic, ^{1}H NMR titration and VT NMR experiements for hosts **10**, **11** and **15–19** showed that both 'up–down' (Scheme 1(a)) and 'in–out' conformational exchange (Scheme 1(b)) along with in–out exchange for the 'two-up, one-down' isomer are occurring with the proportion of various conformers influenced by the identity and geometry of the bound anion and the steric bulk of the amine substituents. The C_3 symmetric three-up, three-in isomer predominates when steric bulk is low in the presence of small spherical anions, particularly Cl^-. The activation barrier to Cl^- exchange is significant in this system and becomes even more significant in the ferrocenyl compound **18** implying a significant stability to a Cl^- binding arrangement comprising a trigonal prism of three NH···Cl^- and three CH···Cl^- hydrogen bonds, Fig. 4(a).

In addition to the secondary amine derivatives, our simple, modular approach allows the incorporation of other functional groups as in **12–14**, **16** and **17**. As with **10**, X-ray crystal structures of the ester **12** and bipyridinium derivative **16** suggest that CH···anion hydrogen bonding interactions are of considerable importance in these systems. The structure of the bromide salt of **16** is remarkable in that it gives a snapshot *in the same crystal* of the desolvation process that occurs upon anion binding with some hosts binding in a second sphere fashion to solvated Br^- and others binding directly to the Br^- anion by CH···Br^- hydrogen bonds. In acetonitrile solution,

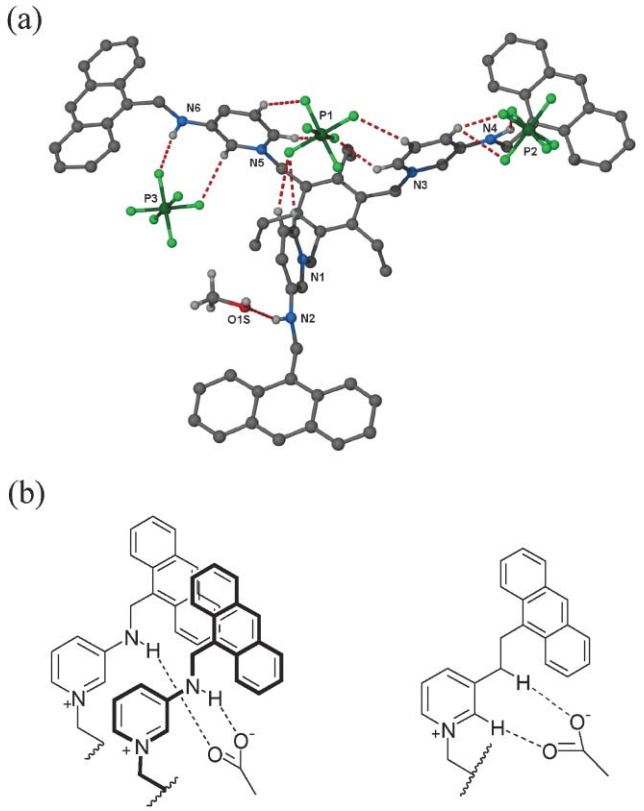
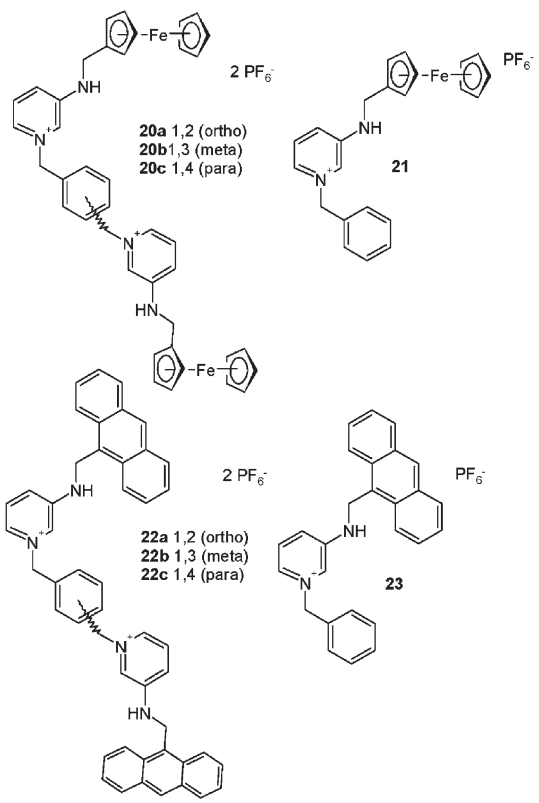


Fig. 5 (a) X-Ray crystal structure of **19** showing binding of PF_6^- anions *via* a CH···anion interactions in the centre and NH···anion interaction at the periphery. The remaining NH group interacts with solvent methanol. The molecule adopts a splayed, 'three-out' conformation to avoid steric interactions between the anthracenyl groups. (b) Binding of two equivalents of acetate by the bulky tris(anthracenyl) host **19**.

the binding constant of **12** for bromide (used as a baseline anion) is similar to that of **10** suggesting that binding is *via* the same mode in each, as in the X-ray structures. In a more polar medium (acetonitrile–water 50:50) compound **16** as the PF_6^- does not interact appreciably with common inorganic anions, but does form a weak complex with ATP^{2-}, K_{assoc} 71 M^{-1}.[64]

Studies on amide **14** have been limited by solubility constraints, while the carboxylic acid **13** (produced by hydrolysis of ester **12**) exhibits complicated deprotonation behaviour. The urea derivatives **17** proved to be highly effective hosts, however, binding in a very surprising fashion.[38] The soluble *n*-octyl derivative **17b** was shown by VT and ^1H NMR titration to bind Cl^- *via* only two of the three urea groups, K_{assoc} = 7080 M^{-1} in acetonitrile-d_3. The compound proved selective for acetate among halides and common oxoanions with K_{assoc} = 40 740 M^{-1}. Given the increased hydrogen bond donor strength of the urea groups compared to the secondary amines these values, comparable to those observed for **11** and its derivatives, are surprisingly low. Unlike the secondary amines, however, complexes **17** are also effective hosts in DMSO-d_6, a much more competitive medium. In this solvent binding measurements are also possible on the *p*-tolyl derivative **17a**. The compound binds Cl^- with K_{assoc} = 437 M^{-1} but proved selective for Br^-, K_{assoc} = 2880 M^{-1} and $H_2PO_4^-$ K_{assoc} = 5010 M^{-1} among the common anions studied. Acetate was also bound effectively. The affinity for the basic, H-bond acceptors acetate and dihydrogen phosphate in a dipolar aprotic solvent are understandable. The selectivity for Br^- over Cl^- is more surprising and was rationalised by binding occurring further up the cone-shaped cavity in a cone conformation, or between urea pairs in a partial cone as indicated for **17b** in acetonitrile. The partial cone binding mode indicated in solution for **17b** was probed computationally using DFT calculations. From a number of starting geometries (Fig. 6(a)) the calculations also suggest that the partial cone conformer with Cl^- interactions to just two urea groups is the most stable, Fig. 6(b). In contrast, the calculations suggest that π–π interactions stabilise the three-up conformer for **17a**, Fig. 6(c). The calculations also indicate binding to one NH and one CH group rather than the two NH units. This model is supported by the magnitude of chemical shift changes in the NMR titration experiments.

In addition to tripodal compounds we have also prepared a range of closely related molecular 'clips' of type **20** and **22** and, as controls, their singly-arm model analogues **21** and **23**.



The clips are much more flexible than the sterically pre-organised tripodal hosts and exhibit lower binding constants (K_{assoc} for Cl^- is 1340 for **20b** compared to 17 380 M^{-1} in acetonitrile-d_3 for the tripodal analogue **18**). The increased flexibility imparts an enhanced selectivity for oxoanions, however, with binding of acetate by **20b** being more effective than the tripod **18** (K_{assoc} = 4515 M^{-1} *vs.* 3680 M^{-1} in acetonitrile-d_3). Within the series **20a–20c** there is an interesting structural trend in NO_3^- binding in acetonitrile with the meta derivative **20b** being more effective than ortho (**20a**) and

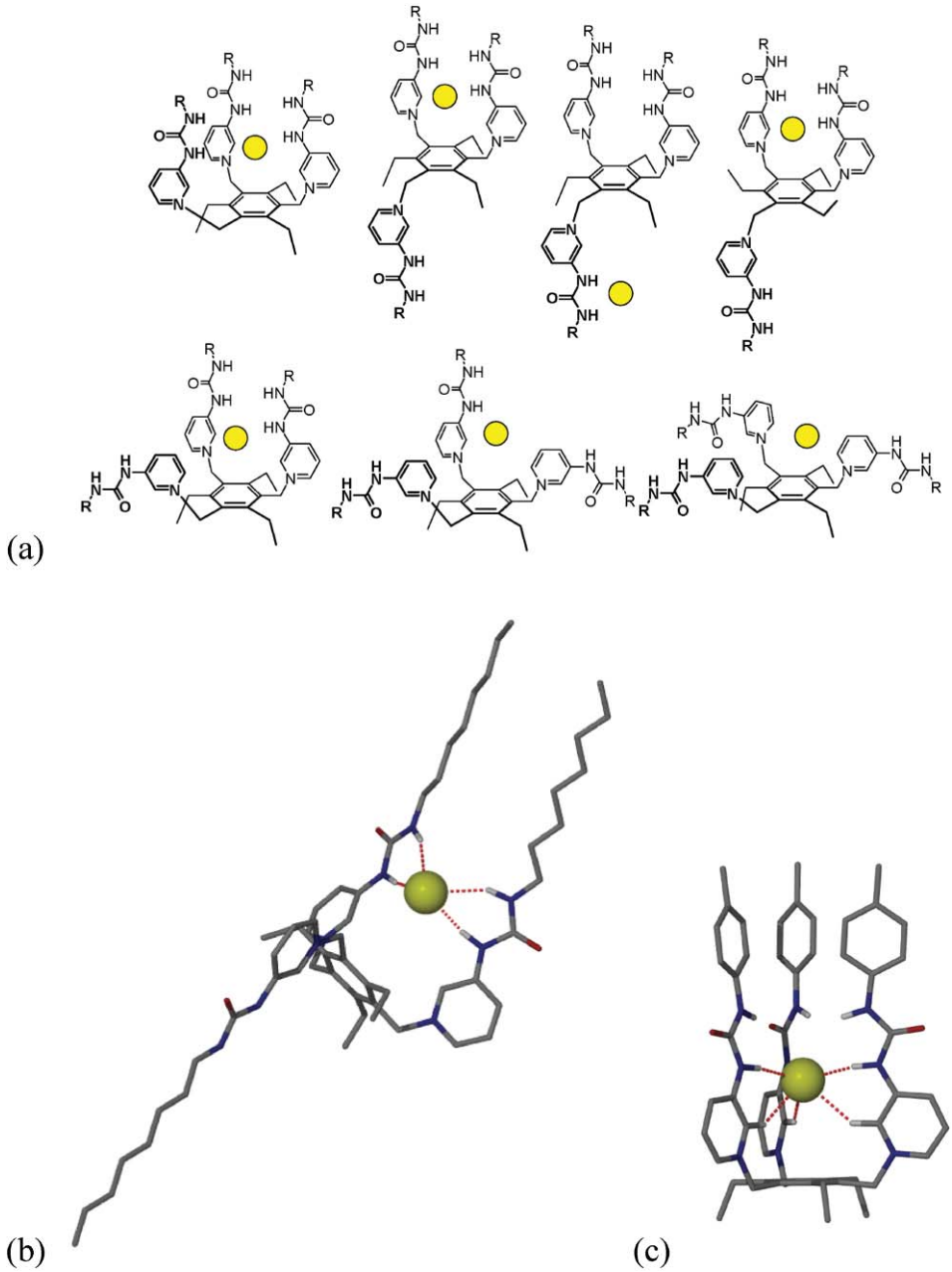
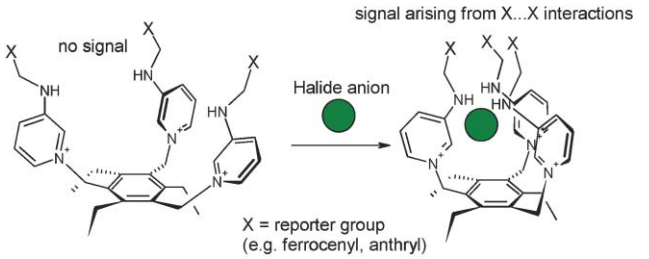


Fig. 6 (a) Starting geometries used in DFT optimisations for chloride complexes of **17**, (b) most stable optimised geometries for octyl derivative **17b**·Cl^- and (c) tolyl derivative **17a**·Cl^-

para (**20c**), K_{assoc} values 1233, 462 and 263 M^{-1}, respectively. Binding by the model compounds **21** and **23** proved extremely weak in all cases implying the importance of a significant anion chelate effect.[26,65]

Anion sensing

Compounds **18–20** and **22** follow the receptor–spacer–signalling unit design popularised for PET sensors for cations.[66–68] In general, binding at the receptor is transmitted through the spacer to give a change in fluorescent properties or, in the case of redox active moieties, a change in redox potential. This kind of redox sensing has been utilized extremely successfully by Hall[69–71] and by Beer.[9,10,72,73] In our case, in addition to engendering changes in the redox potential of the ferrocenyl units in **18** and **20** we were interested in the effect the conformational mobility of the podands would have on their electrochemistry. For example, it is likely that in cases where the ferrocenyl units are well separated as in Fig. 4(b) then oxidation of all three Fe(II) centres will occur at the same potential. On the other hand, binding of a smaller anion as in Fig. 4(a) might bring them sufficiently close to one another in order to bring about resolved, sequential oxidations, Scheme 2. We have observed such sequential reduction in the case of (arene)ruthenium(II) derivatives of cyclotriveratrylene (CTV) in which the mono-, di- and trinuclear complexes



Scheme 2 Proposed conformational sensing mechanism.

$[(p\text{-cymene})Ru(CTV)]^{2+}$, $[\{(p\text{-cymene})Ru\}_2(CTV)]^{4+}$ and $[\{(p\text{-cymene})Ru\}_3(CTV)]^{6+}$ exhibit one, two and three reduction waves respectively that are well-separated in the latter two cases.[74,75]

In fact, in solution, the tripodal host **18** exhibits three very closely spaced (unresolved) one-electron oxidation waves, both as the PF_6^- salt and in the presence of a variety of anions. Similarly the molecular clips **20a–c** exhibit unresolved two-electron waves. The magnitudes of the complexation-induced shifts are solvent dependent with the maximum values observed in less polar solvents such as CH_2Cl_2. Overall relatively modest shifts of up to 80 mV are observed with the anion response broadly in line with the binding behaviour. Surprisingly, however, it is the dipodal receptor **20b** rather than the tripod **18** that exhibits the largest change in redox potential upon anion (Cl^-), Fig. 7(a). This was rationalised on the basis of the increased flexibility and hence complexation-induced conformational change in this host, affecting its redox potential.

In contrast to solution and ionic liquid media, the solid-state electrochemistry of **18** (adsorbed onto carbon) does exhibit more than one oxidation wave in the presence of KPF_6, Fig. 7(b). The oxidation peak currents proved to be dependent on both scan number and salt concentration suggesting some dissolution, however, more than one oxidation wave arising from inter-ferrocene communication cannot be ruled out.

The anthracene-derived host **19** and its single-arm model **23** were examined as fluorescent sensors for anions. The absorption spectrum of **19** suggests a conformational change upon acetate binding consistent with an increased mutual proximity of the anthracenyl units. However, the fluorescence spectrum recorded on a fresh sample is relatively insensitive to added anions. On exposure to UV radiation, or more slowly, upon standing in solution in daylight, the compound undergoes a 2 + 2 photocycloaddition reaction well known for anthracene derivatives.[76,77] A similar reaction is observed for **23** suggesting an intermolecular reaction. Oddly, the cycloaddition product is a relatively effective fluorescent sensor, with chloride and particularly iodide causing considerable quenching. Because of the ill-defined nature of the system, however, work is proceeding with more photostable pyrene derivatives.

Calixarenes as cores

A key feature of the 'modular approach' is the ability to exchange all of the components of the anion host including the core scaffold. The triethylbenzene-derived core is most suited

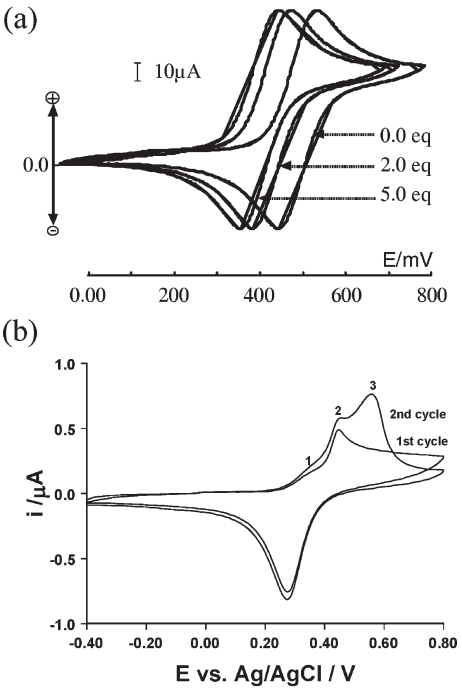


Fig. 7 (a) Cyclic voltammogram of dipodal host **20b** in titration with Cl^- in CH_2Cl_2. (b) Solid-state cyclic voltammogram of **18** in the presence of 0.1 M KPF_6.

to host species binding relatively small anions. In order to expand the range of anions bound larger hosts are required. Garratt and co-workers, have isolated a tetramethylnaphthalene-derived host with diazabicyclooctane (DABCO) 'arms' that we have crystallographically characterised. The structure reveals that the four DABCO groups are arranged in two pairs facing in opposite directions, Fig. 8.[46]

While naphthalene is somewhat larger than benzene-derivatives the geometry of the host does not provide much

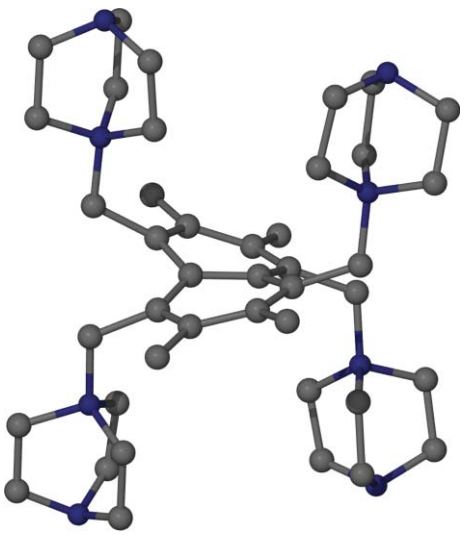
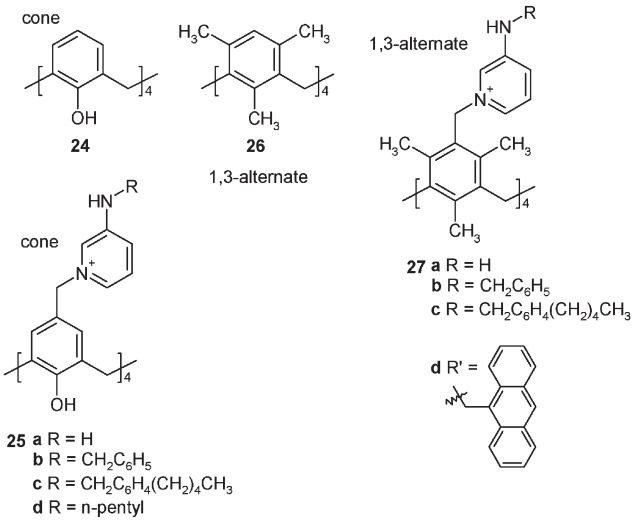


Fig. 8 X-Ray crystal structure of a naphthalene-core host based on DABCO arms.[46]

of a binding cavity. In contrast, work by Beer and Reinhoudt among others has resulted in an impressive range of anion binding hosts of varying dimensions based on calixarene cores.[78–82] The synthetic versatility of calixarenes lends them readily to our modular approach and hence we have developed two types of calixarene tetrapod with different degrees of preorganisation. The conventional tetraol calix[4]arene **24** may be readily bromomethylated and functionalised with amino-pyridine derivatives to give the cone conformers **25**. The slightly more unusual mesitylene-derived calixarene **26** also readily bromomethylates and may be derivatised to give the locked 1,3-alternate ditopic receptors **27**.[83]



The large size of the receptors and their different conformational preferences has a significant effect on their binding behaviour. The ditopic 1,3-alternate hosts are selective for dicarboxylate anions (Fig. 9) and bind in a 2:1 guest:host ratio, established by Job plot analysis. For example **27c** binds malonate with K_{assoc} = 58 800 M^{-1} in MeCN/DMSO 60:40. Binding of halides and nitrate is relatively weak. In contrast, the cone compounds bind strongly to Br^- and NO_3^- and less well to Cl^-. Their affinity for carboxylates is difficult to determine because the presence of the pyridinium group makes the hydroxy calixarenes relatively acidic (pK_a(1) = 4.4(5) in 90% DMSO–water) and hence they are deprotonated by carboxylates.

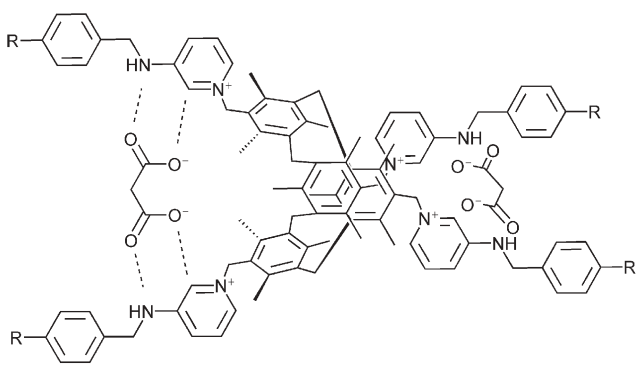
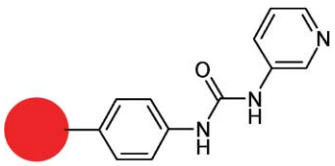


Fig. 9 ditopic binding of malonate by the 1,3-alternate calixarene **27**

Polymers as cores

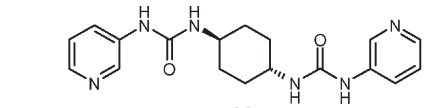
Moving to ever larger core moieties, we have prepared polystyrene-bound pyridyl urea derivatives related to compounds of type **9**. The materials are readily produced from reaction of polymer-bound isocyanate with 3-aminopyridine. The resulting polymer (**28**) has approximately a 1:4 ratio of urea:phenyl groups and differs from the pyridinium compounds such as **11**, **18**, **25** and **27** in that the pyridine group is not bound and remains available to act as a Lewis base. As a result the polymer binds both anions and cations, for example $Cu(NO_3)_2$. The nature of the bound species may be understood from model compounds and our work on such coordination compounds as hosts is described in the next section. Work on polymer, dendrimer and nanoparticle core hosts is ongoing.



28

Coordination compounds as cores

In addition to their reactivity with bromomethyl arenes, pyridyl derivatives **5–9** can act as ligands for a variety of metal centres while retaining their hydrogen bond donor ability and hence their ability to interact directionally with anions. There has been a significant amount of elegant recent work concerning hydrogen bonding ligands which may be regarded effectively as salt-binding receptors. Smith and co-workers have produced macrobicyclic ion pair receptors in which anion and cation are bond as a contact ion pair.[24,25] Work by Barboiu has resulted in urea-containing crown ethers capable of binding alkali metals and hydrogen bonding to anions.[84] Transition-metal based anion receptors have become increasingly topical in recent years and were reviewed by Beer in 2003 and 2005, who has made major contributions in the area.[72,85] Recently emphasis has shifted from metals as reporter groups as in metallocene and metal tris(bipyridyl) type complexes to metals as core structural elements. Work by Rice has resulted in the preparation of anion binding and anion templated helicates. Work by Halcrow and co-workers and by Pérez and co-workers has resulted in the preparation of halide receptors based on Zn(II) and Re(I) pyrazole derivatives.[86–88] Work by Gale, Bondy and Loeb has resulted in complexes with unidentate ligands related to **9** that form elegant anion binding coordination complexes, particularly using relatively inert Pt(II) derivatives.[21,89,90] Arene ruthenium(II) complexes are also relatively inert and have recently been used by Pérez in conjunction with biimidazoles and the non-coordinating $B(C_6H_3(CF_3)_2)_4^-$ anion.[91] In 2001 we began a programme looking at Pd(II), Pt(II) and Ru(II) derivatives of ferrocenyl and anthracenyl ligands **5** and **6**, resulting in the preparation of compounds such as **29** and **30**.[92]



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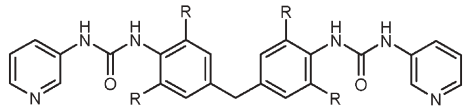


34 R = H, Et

The less highly charged Ru(II) derivative **29** proved to be far more effective than **30**, which may adopt an unfavourable conformation because of steric interactions with the phenyl groups of the diphosphine. As with the related organic core compounds, compound **29** undergoes anion-dependent conformational exchange between *syn* and *anti* forms, although both isomers can bind anions such as NO_3^- and HSO_4^-. The complexes formed were predominantly 1:1 however the evidence suggests the surprising formation of 2:1 host:guest complexes in which the anion is presumably enveloped by a pair of the singly charged hosts. Such behaviour was not observed in the dicationic organic analogues such as compounds **20**. Compound **29** also binds Cl^- with approximately the same affinity as the organic analogue **20b** but over a period of hours the nucleophilic Cl^- displaces one of the pyridyl ligands and binds directly to the metal centre.

We then turned our attention to the ureidopyridine ligand **9a** and its *para* analogue. Solid-state hydrogen bonded polymers were observed with a wide variety of metals with some degree of predictability in the urea···anion interactions observed. The R_2^1 (6) motif (in graph set nomenclature[93]) is common for halide binding, including interactions to metal-coordinated halide, while oxyanions generally exhibit either combinations of R_2^1 (6) and R_2^2 (8) motifs, or a double R_2^2 (8) geometry.[94] Reaction of **9a** with $AgNO_3$ gives the remarkable, discrete complex $[Ag(\mathbf{9a})_2(S)]NO_3$ (**31**, S = MeOH, NO_2Me) in which a nitrate anion is sandwiched between a pair of ureidopyridyl ligands both coordinated to the same metal centre, Fig. 10). ^{1}H NMR measurements indicated that the discrete entity is retained in solution, binding NO_3^- with K_1 = 30 200 M^{-1} in acetonitrile-d_3. Upon addition of excess nitrate a second anion is bound, K_2 = 2900 M^{-1} and there is evidence for further coordination of nitrate to the metal centre in larger excess. In the case of acetate this sequence is reversed with the first equivalent of acetate binding to Ag(I) before any chemical shift changes in the urea NH proton resonances that can be ascribed to anion binding.[22,30]

With divalent transition metal nitrates ligand **9a** gives a series of 1:4 complexes of formula $[M(\mathbf{9a})_4(H_2O)_2](NO_3)_2 \cdot n$MeOH (**32a** M = Co, n = 2; **32b** M = Ni, n = 2; **32c** M = Cu, n = 0). Complexes **32a** and **32b** are isostructural and show nitrate interaction with a single urea group on each complex along with interactions to methanol and water. The Cu(II) complex **32c** is remarkable, however, in forming pairwise interactions of urea groups bound to the same metal interaction with nitrate anions in a double R_2^2 (8) motif. The Jahn–Teller distortion of the Cu(II) results in the coordinated

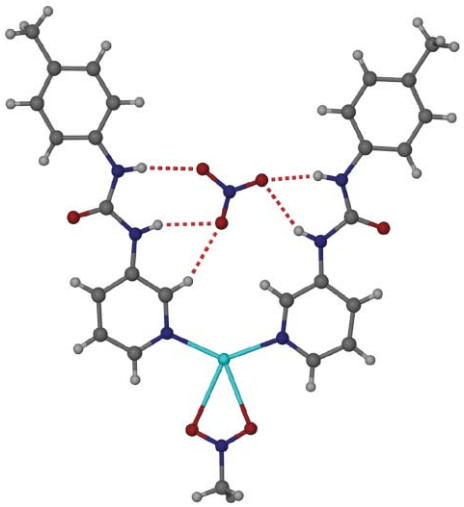
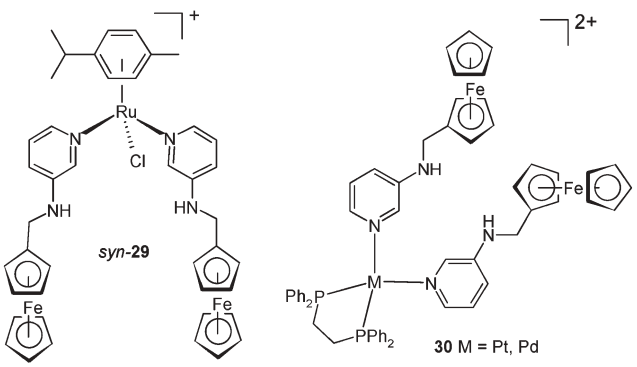


Fig. 10 X-Ray crystal structure of the discrete $AgNO_3$ complex (**31**) of ureidopyridyl ligand **9a** as the nitromethane complex.

water being too far from the nitrate to interfere with the chelating, pairwise urea hydrogen bonding, Fig. 11.[95] The complex is a possible model for the interaction of $Cu(NO_3)_2$ to the polymer bound ureidopyridyl ligand **28**. Interestingly, reaction with M(II) sulfates completely changes the behaviour of the system, which then acts as a solid-state host for a water square, characterised by neutron diffraction.[96]

Anion-dependent coordination polymers and gels

With a view to making metallamacrocyclic analogues of **31** and **32c**, we have recently extended the chemistry of **9a** to form bis(ureidopyridine) analogues such as **33** and **34**, with **34** being almost a dimer of **9a** with the CH_3 group being replaced by a methylene linker to the second half of the molecule.



syn-**29**

30 M = Pt, Pd

Ligand **33** forms coordination polymers with Ag(I) salts with the polymer conformation being highly solvent dependent.[97] Ligand **34** however, does form a metallomacrocycle with $AgNO_3$, Fig. 12. However, the interior of the macrocycle is occupied by two molecules of silver-coordinated acetonitrile solvent instead of the anions, which instead, bridge between macrocycles in a double R_2^2 (8) motif as observed for **32c**.[98] During the course of crystallisation experiments we serendipitously discovered that metal complexes of both **33** and **34** form metallogels[99,100] in some organic solvents and in thf–water,

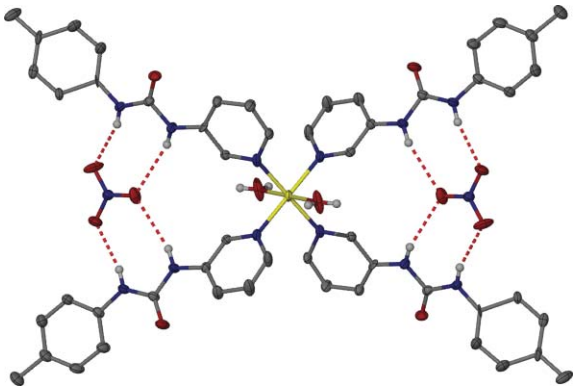


Fig. 11 Copper(II) nitrate complex **32c** showing the double interaction to nitrate.

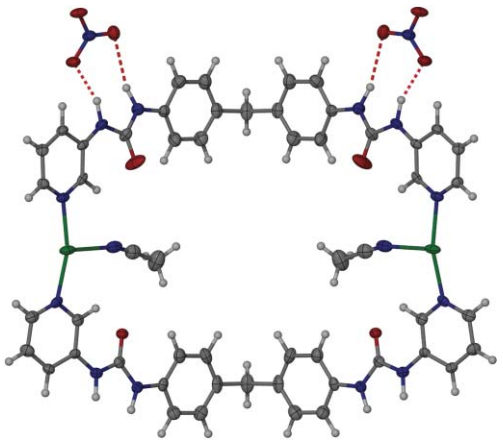


Fig. 12 Metallomacrocycle $[\{Ag(\mathbf{34})(MeCN)\}_2](NO_3)_2$.

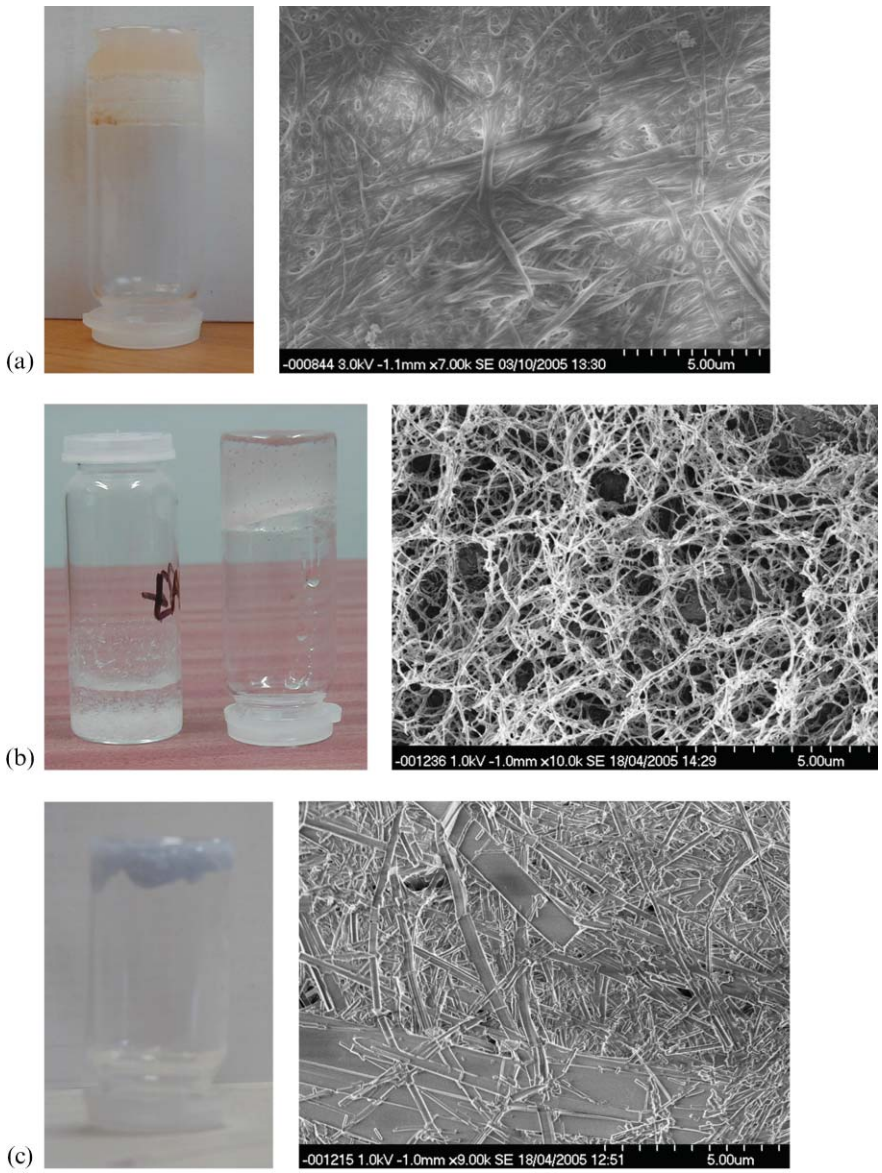


Fig. 13 Gel photographs and SEM images of the corresponding xerogels. (a) Organogel of **34** (R = Et) from chloroform–methanol. (b) Comparison of solutions of free ligand **34** (R = H) (left) and with $AgBF_4$ in thf–water (right) and xerogel image of **34** (R = Et) with $AgBF_4$. (c) Metallogel comprising **33**/$Cu(NO_3)_2$ from aqueous methanol.

Fig. 13. When R = Et ligand **34** also forms an organogel in the absence of metal salts. SEM images of the dried xerogels indicate that the gels are composed of bundles of fibres of *ca.* 50 nm diameter. The precise structure of the fibres is currently unknown and may be based on the conventional urea tape motif.[101] However, crystallographic investigations on ureidopyridines suggest that $NH\cdots N_{pyridyl}$ interactions dominate[102] and urea tape formation does not explain the significant effect metal salts have on the fibre morphology and the fact that no gels are observed for **34** (R = H) in the absence of metal salts. It is even possible that stacks of the metallomacrocycle shown in Fig. 12 could represent a model for the gel-forming unit. Work is ongoing.

Conclusion

In this Feature article we have shown that relatively straightforward synthetic chemistry may be used to generate a large library of anion and salt-binding materials that have tunable affinities, sensing ability and materials properties. These properties depend on structural, conformational and preorganisation preferences that are readily determined by a complementary variety of experimental techniques and may be incorporated into the design of further systems. In general, in the field, anion binding affinities and selectivity remain low, however. Future challenges lie in the improvement of binding constants and thermodynamic selectivity, particularly in competitive media such as water. Parallel work in inter-anion discrimination using anion-binding arrays is beginning to give excellent results. Other ways of identifying and discriminating between anions or other guest species by virtue of their induced-fit effect on a receptor system rather than simply on the basis of binding constant represents and exciting way forward.

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