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Coordination Chemistry Reviews 250 (2006) 3200–3218
COORDINATION CHEMISTRY REVIEWS
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Review

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

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Received 20 December 2005; accepted 6 June 2006
Available online 15 June 2006

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.

Keywords: Preorganisation; Supramolecular systems; Anions

Contents

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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doi:10.1016/j.ccr.2006.06.004

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.

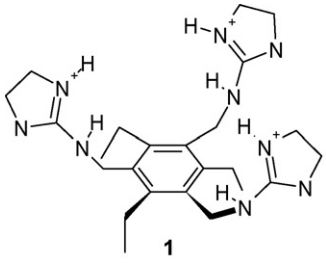
Anion binding hosts may also be divided on the basis of their flexibility or degree of preorganisation. If the host does not undergo a significant conformational change upon guest binding it is said to be pre-organised [38]. Host preorganisation is a key concept because it represents a major contribution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

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.



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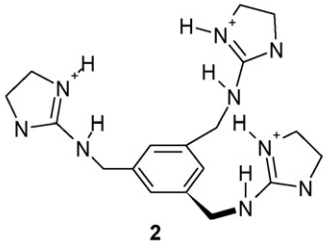

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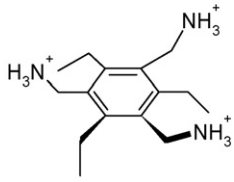

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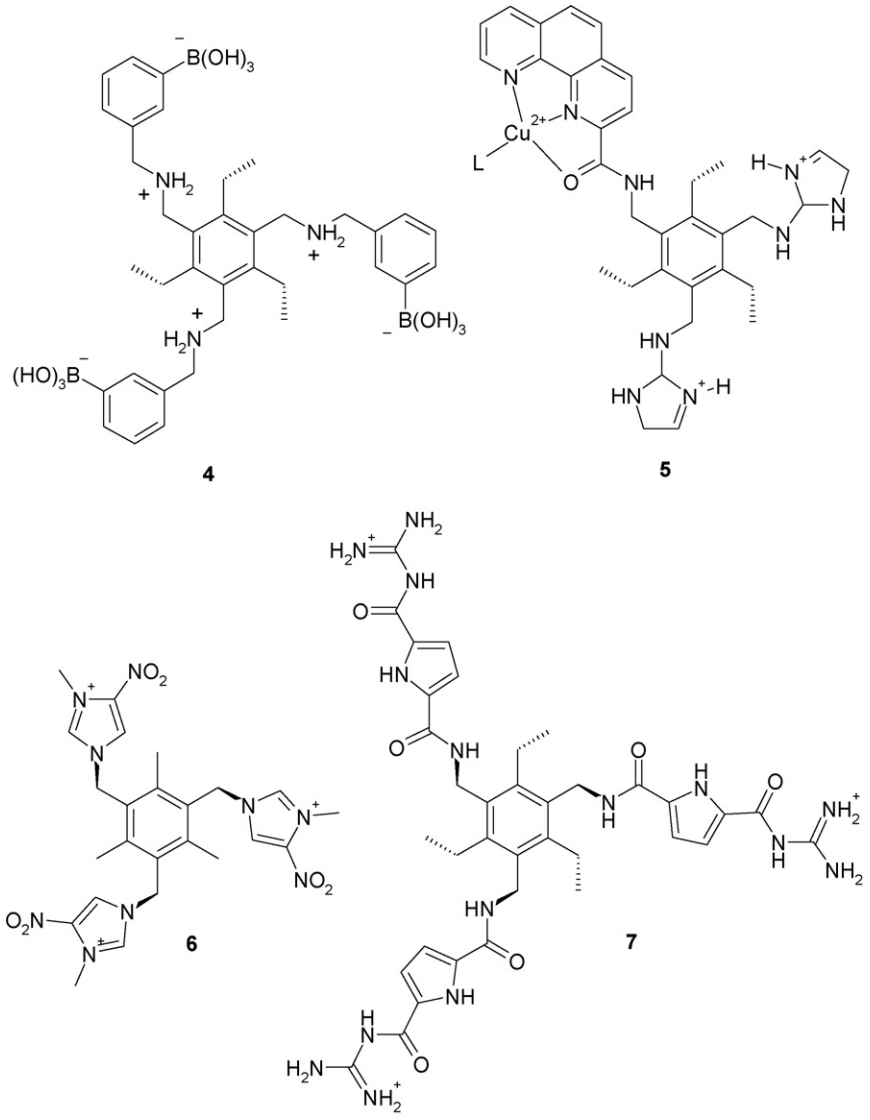
Preorganisation is achieved by incorporating these recognition groups into a trisubstituted 1,3,5-triethylbenzene core, generating a cone shape cavity [15]. The introduction of steric bulk around the benzene-derived core predisposes the compound to adopt the preferred conformation by 3.5 kcal mol^{-1} 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 $7 \times 10^3\ M^{-1}$ 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

core (for which improved syntheses are available [75,76]) as the basis for a very broad range of anion hosts such as **4** including those containing metal centres such as **5**. An array of such hosts attached to polystyrene beads form the basis for a fluorescent 'electronic tongue' able to distinguish certain beverage components or bioanalytes based on their recognition signature pattern as part of a dye displacement assay [77–79]. Parallel work by Kim and co-workers has used a similar core to produce a range of CH hydrogen bond donor systems such as **6** that also bind effectively to anions, for example $K_a = 1.1 \times 10^6$ for Cl^- binding by **6** in 9:1 MeCN:DMSO. The electron withdrawing nitro groups enhance the hydrogen bond acidity of the imidazolium CH groups [80]. This work has recently been extended by Duan and co-workers to produce functionalised derivatives useful for anion sensing applications [40]. Also, Schmuck and co-workers recently introduced guanidinio-carbonyl pyrrole binding sites with a hexasubstituted aryl core to give receptor **7** [17,43].

Host **7** contains acylated guanidinium groups which account for an increased acidity and the pyrrole amide provides an additional hydrogen bonding site. Binding between host **7** and carboxylates is much stronger as a result; association constants of $3.4 \times 10^5\ M^{-1}$ with trimesate and $1.6 \times 10^5\ M^{-1}$ with citrate were determined by UV–vis spectroscopic titrations in 10% DMSO in water. These associations were confirmed by fluorescence titration in water which provided constants of $K_a = 4.4 \times 10^5\ M^{-1}$ and $2.3 \times 10^5\ M^{-1}$, respectively. Even in excess of bis-tris buffer and chloride, the binding constant for citrate only reduced to $8.6 \times 10^4\ M^{-1}$.

Garratt and co-workers, in part in collaboration with our group, have also examined the hexasubstituted benzene core, along with a naphthalene analogue, as the basis for a series of dizazbicyclooctane (DABCO) hosts (**8**–**9**) designed to bind anions *via* electrostatic interactions [81–85]. One such tripodand (**8a**) can discriminate between the ferricyanide and ferrocyanide



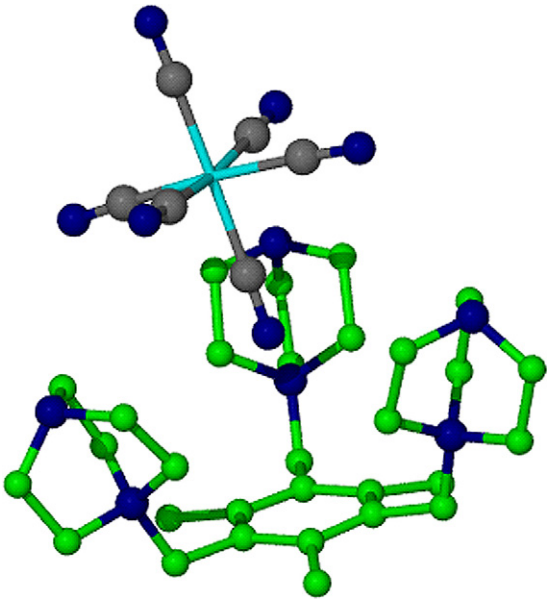
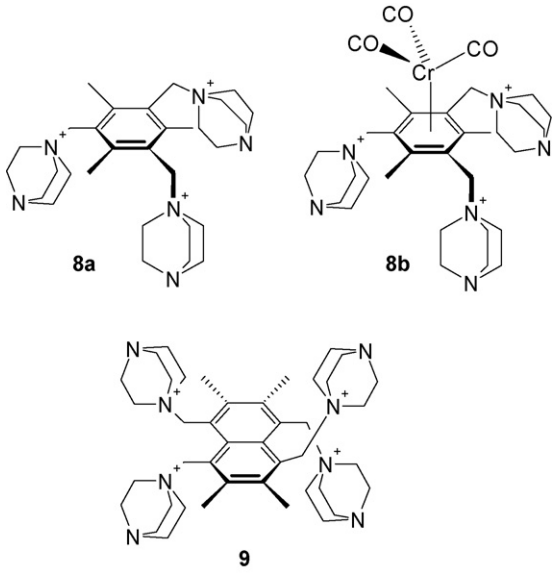


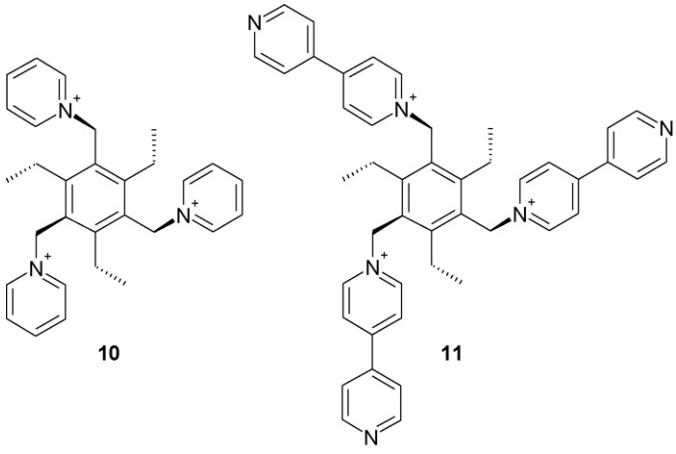
Fig. 1. X-ray crystal structure of the 1:1 ferricyanide complex of receptor **8a**.

ions. An X-ray crystallographic study of the trication host with the ferricyanide trianion shows how the tripodand co-ordinates electrostatically to the anion, Fig. 1 [84].



The presence of the $Cr(CO)_3$ group in the analogous tripodal species **8b** (and a 1,4-disubstituted analogue) as well as the three methyl substituents contributes to a marked degree of preorganisation around the core, forcing the DABCO arms to point in the same direction. ^1H NMR spectroscopic titration studies were carried out for **8a**·3Br$^-$ and **8b**·3Br$^-$ in D_2O. However, in the case of the non-complexed trication **8a** the binding constant with trimesate is considerably greater than for the complexed **8b**·3Br$^-$ ($K_a = 776\ M^{-1}$), but the data are obtained from chemical shift changes of the anion and for the host in the other which may introduce experimental error. It was suggested that the blocking of access to one face of the host outweighs the preorganisation effect of the chromium tricarbonyl unit. The $Cr(CO)_3$ group also acts as an IR reporter group in the solid-state. The carbonyl bands of the IR spectrum in KBr of various salts of **8b**, namely bromide, iodide, citrate, tetrafluoroborate, hexafluorophosphate, triflate and trifluoroacetate, were recorded. An increase in ν_{CO} from halides to trifluoroacetate indicates the diminishing effectiveness in quenching the positive charge on the trimesate anion. It was also noted that IR frequencies reflected much better binding of the anion in organic solvents as water solvation properties effectively screen the polycationic host from the electron-donating effect of the guest. It was shown that acetonitrile and acetone solvents clearly do not solvate the guest species as effectively and probably encourage tighter guest binding [82].

In our own group we began looking at organised electrostatic anion binding cations in 1999 as a follow on from our work on calixarene and cyclotriveratrylene based organometallic receptors [9,22,23,55–60,86,87]. Thus reaction of 1,3,5-tris(bromomethyl)-2,4,6-triethyl benzene [15,88] with either pyridine or 4,4′-bipyridine cleanly affords receptors **10** and **11** as the bromide salts. Such a reaction represents a simple example of a much more general modular approach in which interchangeable core, binding and signalling moieties may be simply prepared from readily available building blocks. The key objective is the tailoring of inter-anion discrimination by manipulation of the dimensions and symmetry of the host structure and binding site disposition. Our particular interests lie in conformationally flexible anion receptors that undergo a significant anion-triggered adaptation or induced-fit upon binding. Such a strategy represents a possible route to signal amplification since the conformational change and its consequences on the redox, luminescent or refractive index properties of the host material may be more readily detected than the binding itself.



The simple design of host **11** contains a pre-organised cavity of bipyridinium "arms" which are linked to a triethylbenzene core resulting in a high positive charge density within the anion binding pocket. Two different X-ray crystal structures of the bromide complex of **11** were obtained as disordered alternatives in the structure. A desolvated form in which host cation **11** acts as a first sphere ligand for bromide, interacting with the anion *via* CH···Br$^-$ hydrogen bonds, and a solvated complex in which **11**

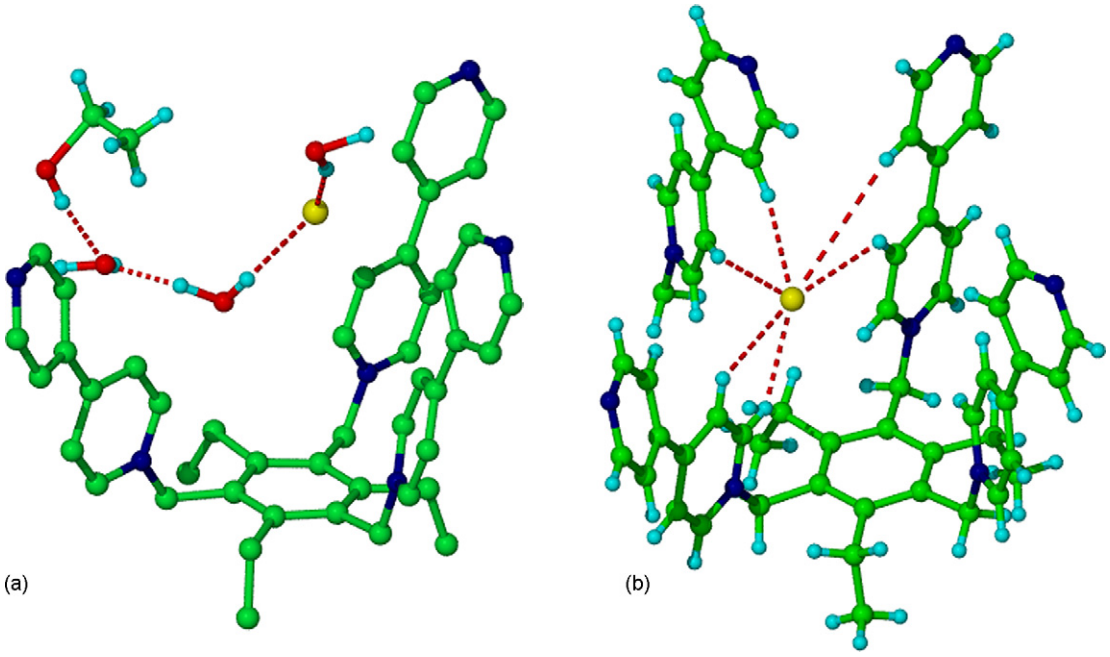


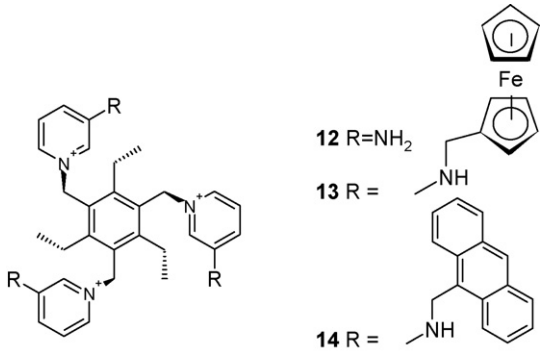
Fig. 2. (a) Structure of solvated [**11**·Br]$^{2+}$ showing positions of included water and ethanol. Selected O···Br distances: 3.222, 3.444 Å, (b) solvent free [**11**·Br]$^{2+}$ incorporating CH···Br interactions 2.660–2.977 Å.

acts as a second sphere ligand for hydrated bromide (Fig. 2). In both forms two bipyridinium arms are coplanar accounting for π-stacking interactions between pairs of cation **11** in the solid state, therefore, deviating from the ideal C_{3v} symmetry.

Conversely a PF_6^- salt crystal obtained from water/acetonitrile adopts a three-fold symmetric conformation. One PF_6^- anion is deeply included within the molecular cavity (Fig. 3).

The affinity of the PF_6^- salt of **11** for simple anions such as Cl^-, Br^-, I^-, HSO_4^-, SO_4^{2-}, $H_2PO_4^-$, $CH_3CO_2^-$ and NO_3^- in aqueous MeCN-d_3 solution was probed using ^{1}H NMR spectroscopic titrations, however, the spectra showed insignificant changes. When **11** was titrated against ATP in aqueous acetonitrile, however, it showed a moderate affinity, with $K_a = 71\ M^{-1}$ suggesting π-stacking with an aryl anion along with electrostatic forces as an important role in this interaction [89].

The behaviour of these tricationic pinwheel hosts changes dramatically when a hydrogen bonding moiety is introduced to the hexasubstitued core to give **12**. Further addition of redox-active or fluorescent signalling modules gives hosts **13** and **14** [20].



The binding constants (K_{11}) determined by ^{1}H NMR titration in MeCN-d_3 for the interaction of hosts **12**–**14** with Br^-, were 13,800, 2950 and 486 M^{-1}, respectively. Compound **12** proved a particularly effective host for chloride with binding constants too high to measure by NMR methods. Introduction of chloride to the hexafluorophosphate salt of **12** also results in remarkable changes in the dynamic behaviour of the host. Compound **12**·3PF_6 was shown by X-ray crystallography to adopt a non-C_3 symmetric geometry in which one aminopyridinium arm is on one side of the aryl core and the remaining two are on the other – a partial cone geometry, Fig. 4.

Monitoring the ^{1}H NMR spectrum of this host in acetone-d_6 revealed a slow conformational equilibrium in which the crystallographically observed partial cone conformation proved to be in equilibrium with the cone conformation in which all three arms occupy the same face of the core. The key resonances are those assigned to the CH_3 protons of the ethyl substituents (marked (*) in Fig. 5). The high field resonance is assigned to a methyl group entering the shielding region of the pyridinium units as in the crystal structure of **12**·3PF_6 show in Fig. 8. Upon addition of Cl^- this process is turned off and there is a rearrangement to the cone conformation upon chloride binding (Scheme 1). Addition of 0.4 equiv. of Cl^- also reveals a second, higher temperature equilibrium involving slow exchange of the bound chloride anion. While slow anion exchange has been observed for macrocyclic anion hosts [90] it is surprising in a tripodand and suggests a very complementary Cl^- binding array, consistent with binding by three NH and three CH donors.

Podand **12** also proved an effective host for acetate, while nitrate is bound much less strongly despite its similar geometry. The strong binding ($K_{11} = 10\,500\ M^{-1}$) is probably due to higher basicity of acetate. Titration and variable temperature

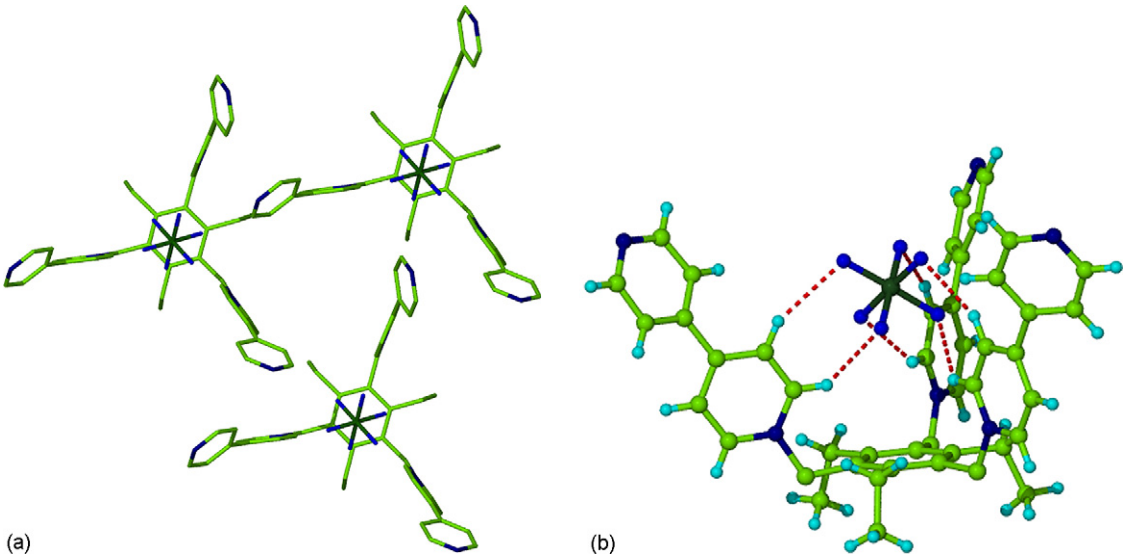


Fig. 3. (a) Encapsulation of PF_6^- by cation **11** in a three-fold symmetric conformation. (b) The achiral PF_6^- induces a rigid three-fold symmetric chiral structure on the lower pyridinium rings *via* CH· · ·F interactions (H· · ·F distances 2.39 and 2.53 Å).

NMR studies show that the bulky **13** and **14** bind non-spherical anions such as acetate in a very different manner to halides, typically in a partial cone conformation. The increasing steric bulk of the redox or luminescent substituents in hosts **13** and **14** contributes to their decreasing affinity for halides. Titration results of **13** with Cl^-, Br^- and I^- show a trend in diminishing affinity for larger anions (K_{11} = 17,380, 2950 and 1860 M^{-1}, respectively.) The electrochemistry of **13** was also explored in collaboration with Alan Bond's group. The voltammetry of **13**·3PF_6^- in MeCN solution and ionic liquids, exhibits an over-

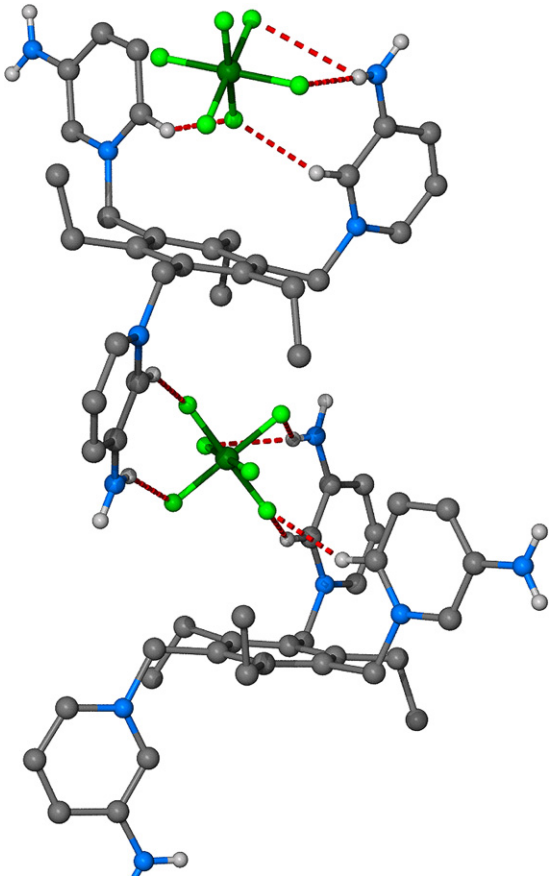
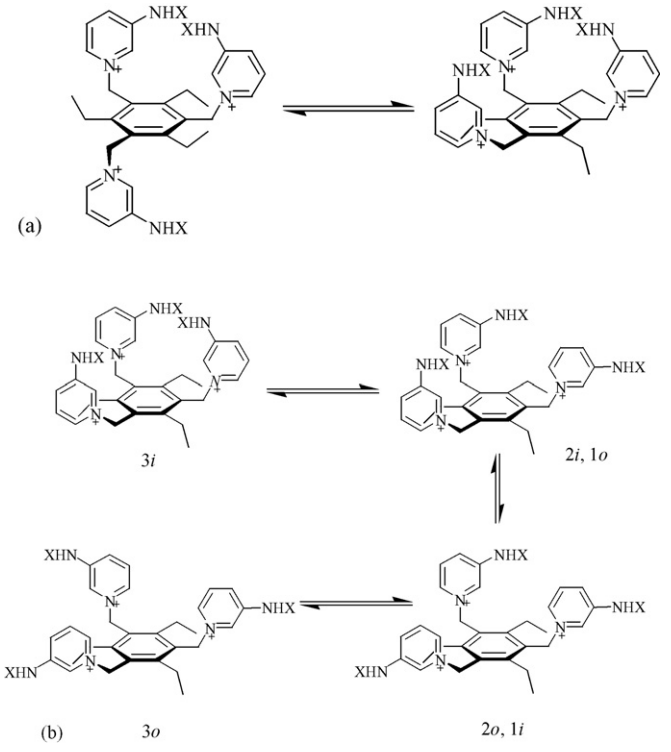


Fig. 4. Partial cone conformation of **12**·3PF_6 from X-ray crystal structure (two repeats showing PF_6^- binding in the solid).



Scheme 1. (a) conformational exchange in **12**·3PF_6. This process is 'turned off' upon addition of chloride which stabilises the cone conformation; (b) in-out conformational exchange observed in addition to the process shown in (a) over a range of different complexes in the presence of various anions.

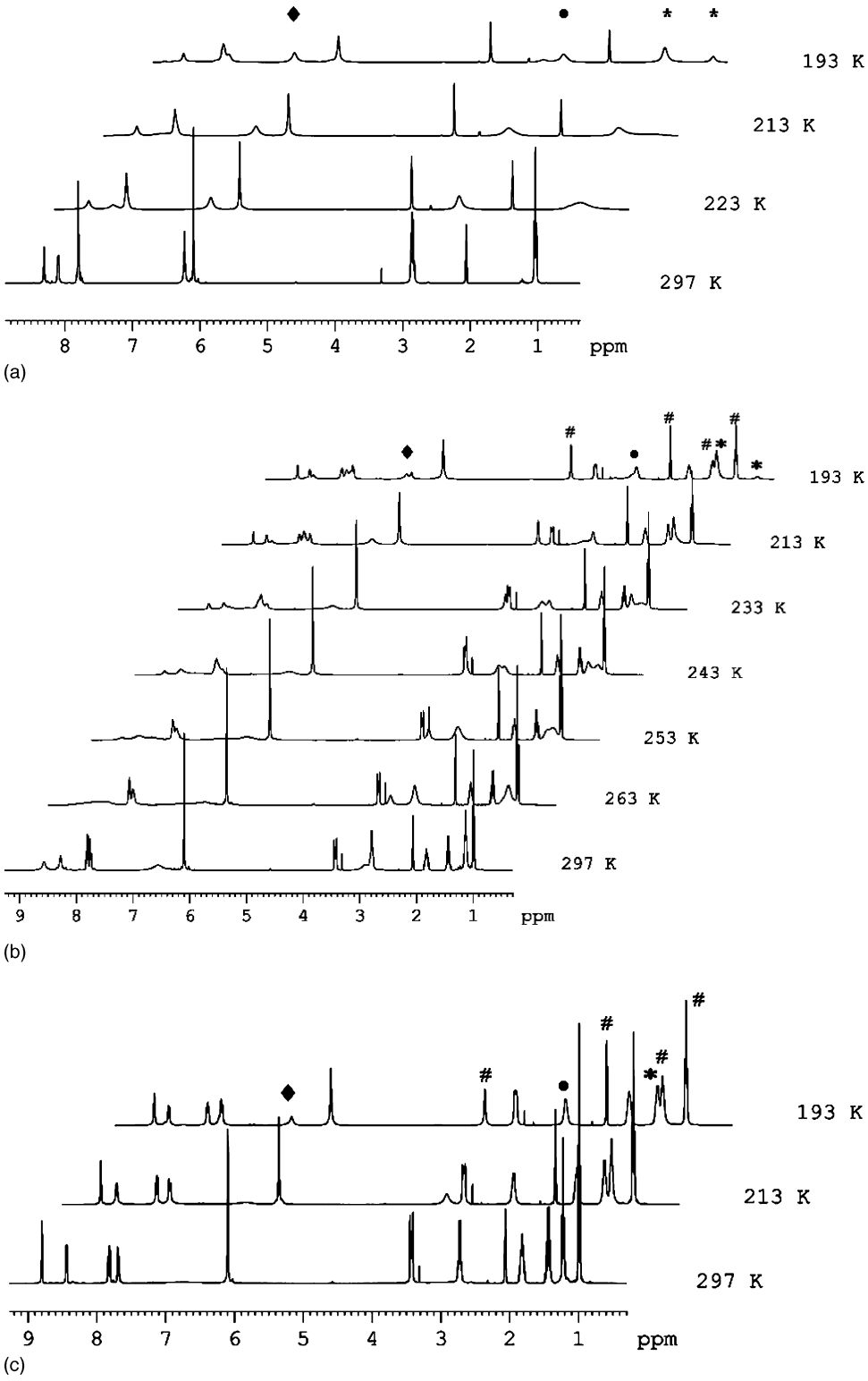


Fig. 5. Variable temperature ^{1}H NMR spectra of **12** in acetone-d_6 (a) as the hexafluorophosphate salt, (b) after addition of 0.4 equiv. of NBu_4Cl and (c) after addition of 0.8 equiv. of NBu_4Cl. (#) NBu_4Cl, (*) ethyl CH_3, (●) ethyl CH_2 and (♦) NH.

all three-electron oxidation consisting of three closely spaced one-electron-transfer steps, which implies a minimal communication between the ferrocene redox centres in the cation [19]. The solid state electrochemistry of the compound proved more complicated and highly anion-dependent. A resolved series of three oxidation waves were observed in the presence of KPF_6 with scan dependent characteristics suggesting limited solubility, Fig. 6b. However, on addition of KCl or NaCl dissolution and

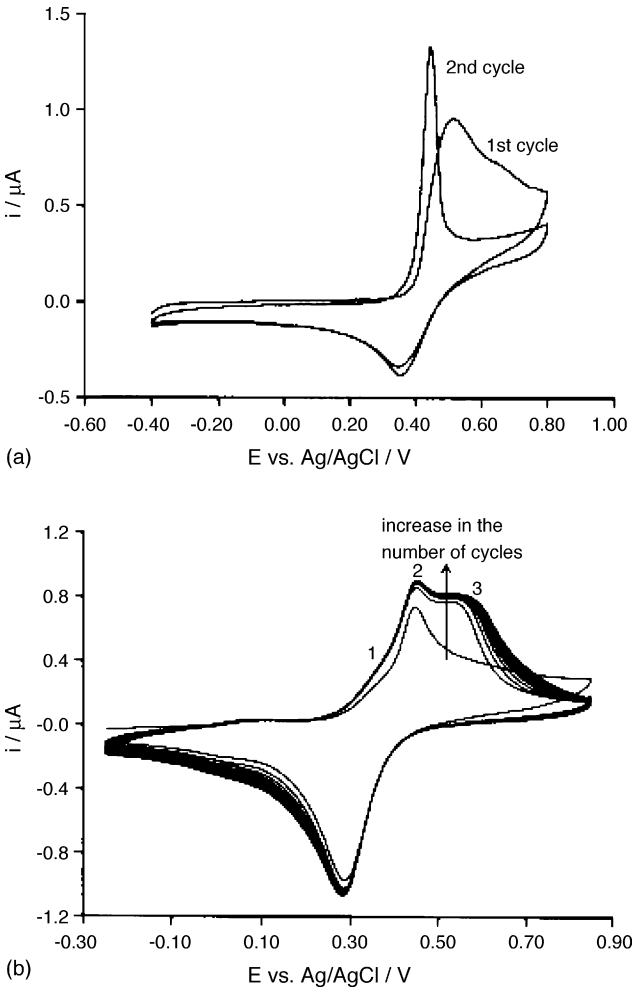


Fig. 6. (a) Cyclic voltammetry of solid **12**·3PF_6^- adhered to a 1 mm diameter GC electrode in the presence of 0.01 M NaCl. (b) Cyclic voltammetry (20 cycles) of solid **12**·3PF_6^- adhered to a 1 mm diameter GC electrode in the presence of 0.4 M aqueous KPF_6. (scan rates 0.1 V s^{-1}) (reproduced from Ref. [19]).

re-precipitation occurred to give a voltammogram with stripping characteristics, Fig. 6a.

Compound **14** falls into the category of the fluorophore-spacer-receptor model [91] where and excited anthracene unit can associate with the ground state of a second fluorophore and produce an intramolecular excimer (anthracene–anthracene). The fluorescence intensity of **14** increases when exposed to ambient light suggesting interaction of the arms with one another. Exposure of a sample **14** to a UV irradiation for 30 min resulted in an appearance of two new peaks in the ^1H NMR spectrum suggesting a $4\pi + 4\pi$ cycloaddition reaction forming cis and trans isomers of the photodimer or formation of both intra- and intermolecular addition species [92]. The fluorescence studies of this photocoupled derivative receptor, show that the intensity decreases, i.e. quenching is observed by 30% on the addition of Cl^- and 50% for I^-. This could be explained by an enhancement of electron transfer from the receptor towards the fluorophore. No significant change in fluorescence intensity occurs if anions are added to a fresh sample of receptor **14**·3PF_6^- [14]. The X-ray crystal structure of host **14**·$(PF_6)_3$·MeOH·2MeCN (Fig. 7) shows that the cationic host does adopt a cone conformation with alternation about the hexasubstituted core. The anthracenyl arms are splayed out, however, and the three NH groups do not converge. It is remarkable that the central anion is held solely by CH···F interactions and eschews the remaining secondary amine binding site.

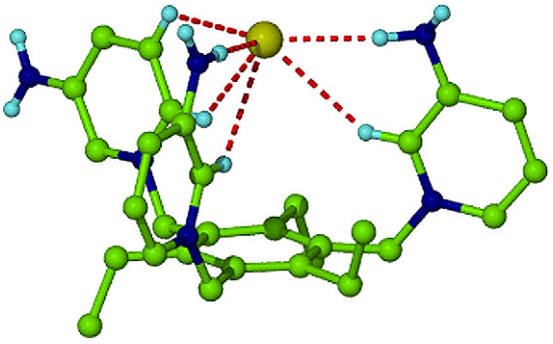


Fig. 8. X-ray crystal structure of **11**·3Br^-. Only the central Br^- anion is shown for clarity.

Conversely an X-ray crystal structure of **12**·3Br^- (Fig. 8), shows a remarkable encapsulation of an intra-cavity bro-

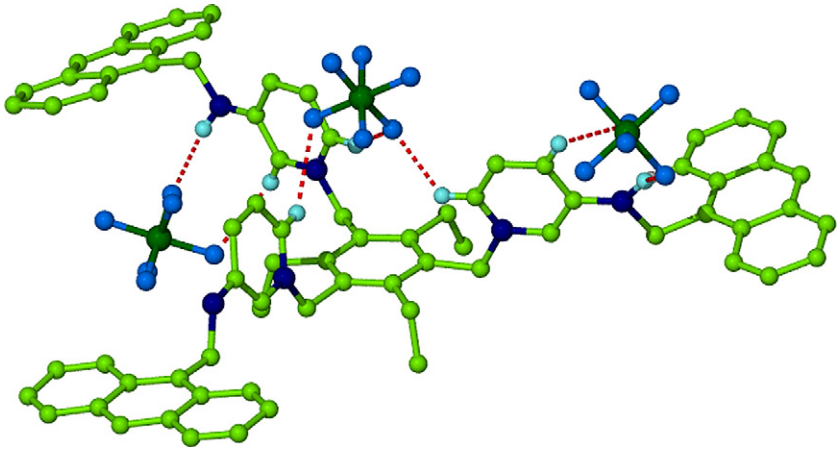
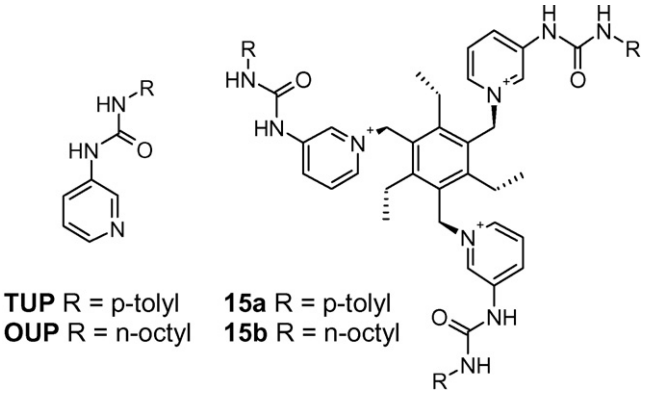


Fig. 7. X-Ray structure of receptor 14·3PF_6 showing cooperative anion binding of the central PF_6^- anion by weak hydrogen bonds.

mide anion by a six-fold array of NH···Br^- and CH···Br^- interactions. Two of the three NH groups are involved in interactions to bromide, which appears to be just slightly too large for the cavity (N···Br distances are 3.35 and 3.40 Å).

The modular strategy towards these cationic pinwheel receptors renders the synthesis of a range of compounds with different hydrogen bonding functionality readily accessible. Thus compounds with amide, ester, carboxylic acid and urea functionalities are all available. Urea compounds in particular are expected to exhibit stronger hydrogen bond donation and hence more effective anion complexation, particular in more competitive solvents (the amine receptors function well in acetonitrile but exhibit little binding in DMSO, for example). The urea moiety is known to be strong double hydrogen bond donor and, like the closely related amide group, has been utilized effectively in a number of anion binding systems [7,25,46,62,68,93–107]. In the case of urea, both donor hydrogen atoms may face towards the guest and the potential exists for the anion to be chelated to each arm in $R_1^2(6)$ motif, or R_2^2 (8) in the case of oxyanions [64]. The precursor ligands **TUP** and **OUP** are readily obtainable from the reaction of 3-aminopyridine with the appropriate isocyanates [66] and reaction with 1,3,5-tris(bromomethyl)-2,4,6-triethyl benzene [15,88] gives the tripodal receptors **15** [108].



As in previous host species **10**–**14**, counter-anion metatheses were carried out to exchange bromide for the more readily displaced hexafluorophosphate anion. These exchange reactions were carried out by stirring solutions of the bromide salts in the presence of a large excess of TBA-PF_6 (TBA = tetra-*n*-butyl ammonium). Three crystal structures of receptor **15a** were obtained, each containing different counter-anions resulting in dramatically altered geometries. The structure of **15a**·3Br^- adopts an alternating 'up-down' conformation of the substituents around the central aryl core with functionalised arms on the opposite face to the ethyl groups. The pseudo-cone geometry forms a central cavity occupied by one of the bromide anions which hydrogen bonds to only one of the urea groups. The other two bromides interact with two arms facing away from the cavity (Fig. 9).

The structure of **15a**·3PF_6^- obtained form acetone does not have a central cavity. The three functional arms are situated

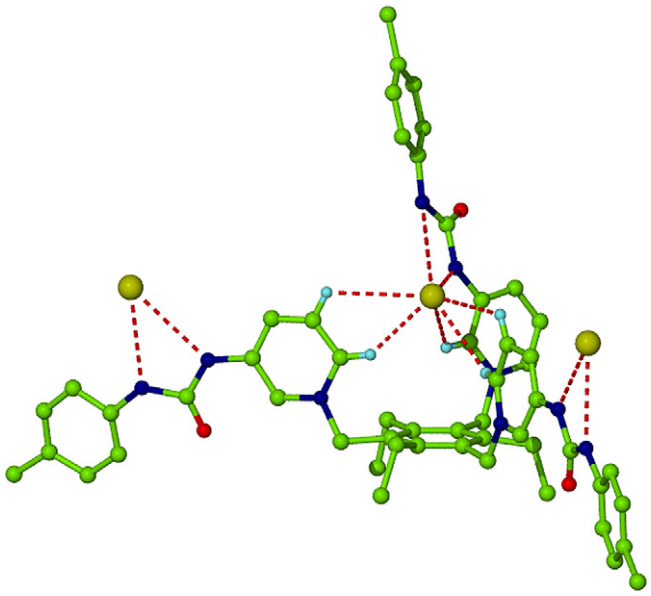


Fig. 9. One independent host–guest complex from the crystal structure of 15a·3Br^-, showing the hydrogen bonding interactions to the anions.

on one face of the central aryl core but are folded inwards over it. One of the ethyl groups is also on the same face as urea groups. Only one urea group is engaged in a hydrogen bonding to one of the PF_6^- anions. One urea proton binds the anion in a bifurcating mode, the other forms a linear NH···F interaction. The other two PF_6^- anions are incorporated in the lattice and the other two urea moieties only interact with two enclathrated acetone solvent molecules within the structure (Fig. 10a).

The third structure exhibits a mixture of nitrate and hexafluorophosphate as the counter anions in a 1:1 ratio. The structure is related to that of the PF_6^- complex but the substituents unfold somewhat in this case to accommodate the hydrogen bonding between the nitrate and the urea moiety (Fig. 10b). The solution studies of **15a** confirmed the strong bonding to bromide in particular, as seen in the crystal structure. Binding constants of **15a**·3PF_6^- with Cl^-, Br^-, I^- and NO_3^- obtained from ^{1}H NMR titrations in the very competitive solvent DMSO-d_6 were as follows $K_{11} = 437$, 2884, 41 and 347 M^{-1}. The highly basic acetate was also strongly bound, $K_{11} = 1622\ M^{-1}$ [108].

The **TUP** derivative **15a** is an effective host in DMSO but it is limited by solubility constraints. The more lipophilic analogue **15b** was developed to overcome these limitations and was studied in MeCN by both ^{1}H NMR titration and variable temperature NMR spectroscopy. These experiments revealed a very different behaviour to the amine analogues (such as **12**) with an unsymmetrical partial cone chloride binding low temperature structure. There is a considerable conformational change from this 1:1 complex upon addition of excess chloride with a series of anion binding and conformational equilibria quite different to those observed for the very similar amine analogues **12–14** (Fig. 11a). This conformer was also found to be the most stable *in silico* in the gas phase by DFT methods (Fig. 11b).

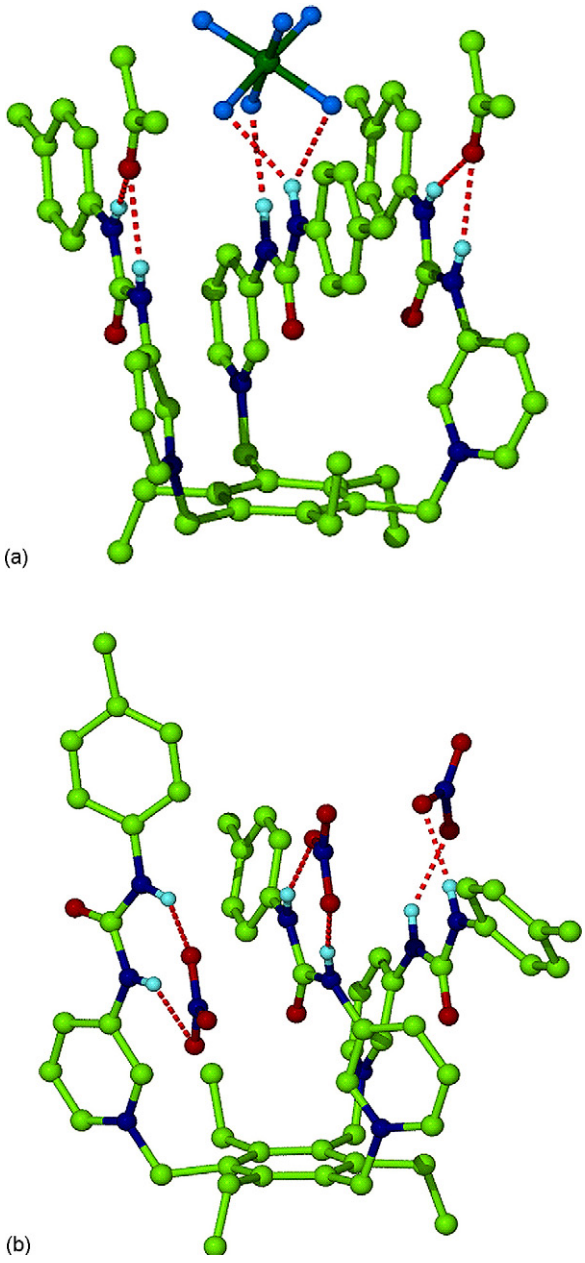


Fig. 10. (a) X-ray structure of **15a**·3PF_6^- showing the interactions between the urea protons and the PF_6^- anion; (b) X-ray structure of **15a**·1.5PF_6·1.5NO_3 showing interaction of the urea protons with two NO_3^- anions.

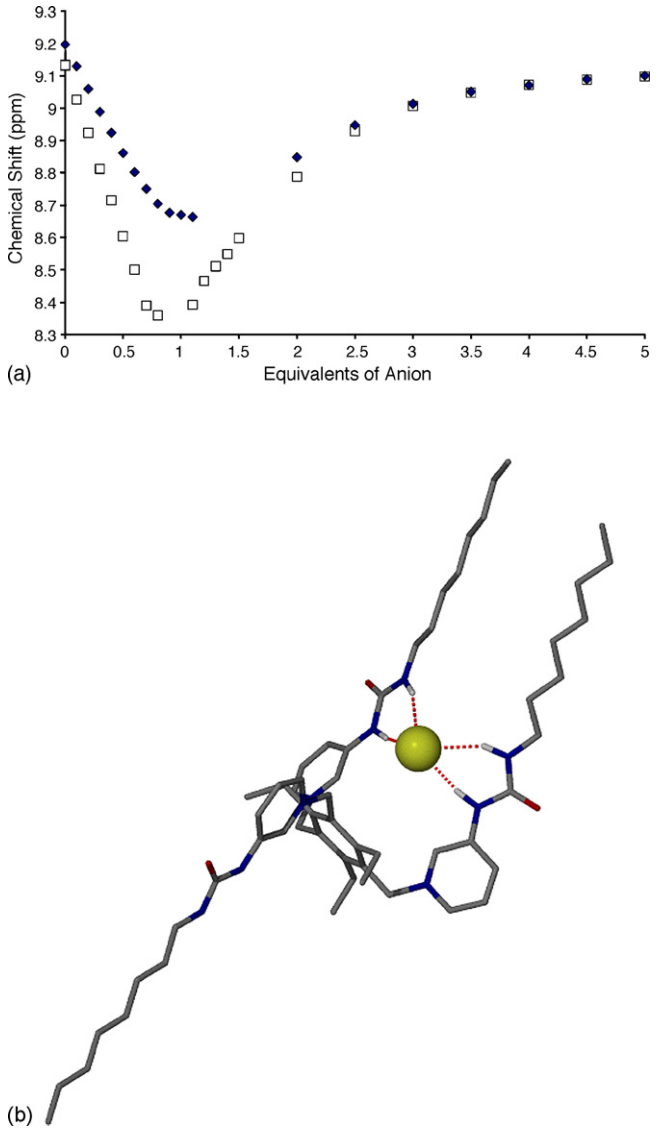
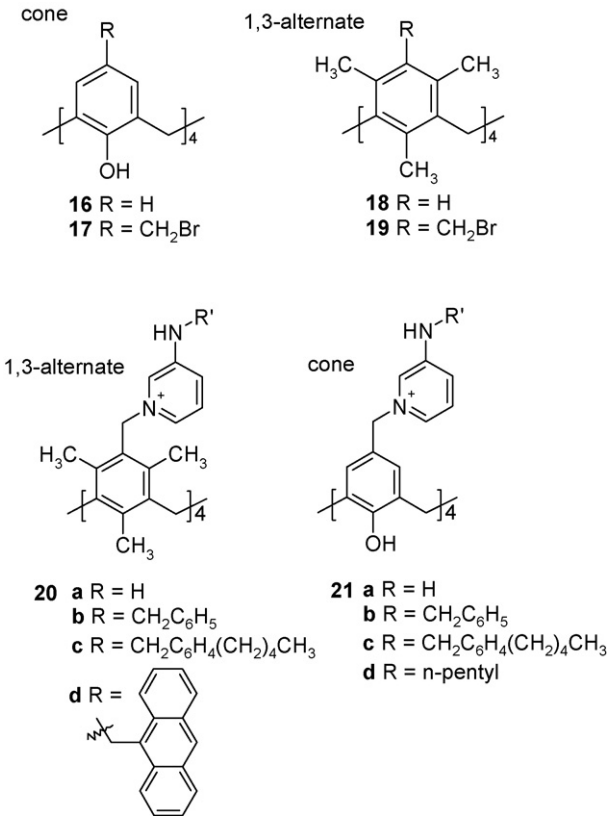


Fig. 11. (a) ^{1}H NMR titration curve for Cl^- (squares) and Br^- (diamonds) binding by 15b in MeCN-d_3; (b) lowest energy conformer of 15b·Cl^- from DFT methods.

In contrast, for the tolyl complex **15a**, calculations suggest a cone conformer [108]. While the neglect of solvation effects in these gas phase calculations renders them only loosely applicable they are highly consistent with the NMR results and provide a starting point for understanding the solution phase data.

3. Calixarene hosts

The triethylbenzene core can also be replaced by much larger units as in naphthalene derivative **9** [83]. Even larger tetrapodal hosts are available using a calix[4]arene derived core. Calixarene chemistry is well developed and the conformational properties of the calixarenes are subject to control and indeed locking by appropriate choice of functional groups [109,110]. The calixarene-derived scaffold exhibits much less flexibility despite some fluxional behaviour around the bridging methylene groups observed in hydroxyl calix[4]arene **16**, which exists predominantly in the cone conformation [111]. The mesityl hydrocarbon calix[4]arene **18** is readily prepared from α′-chloroisodurene [36,112]. It is locked into a 1,3-alternate conformation with very little flexibility. Reactions of **16** and **18** with formaldehyde in the presence of Zn-HBr results in a facile bromomethylation of the aryl rings to give **17** and **19**, respectively [113].



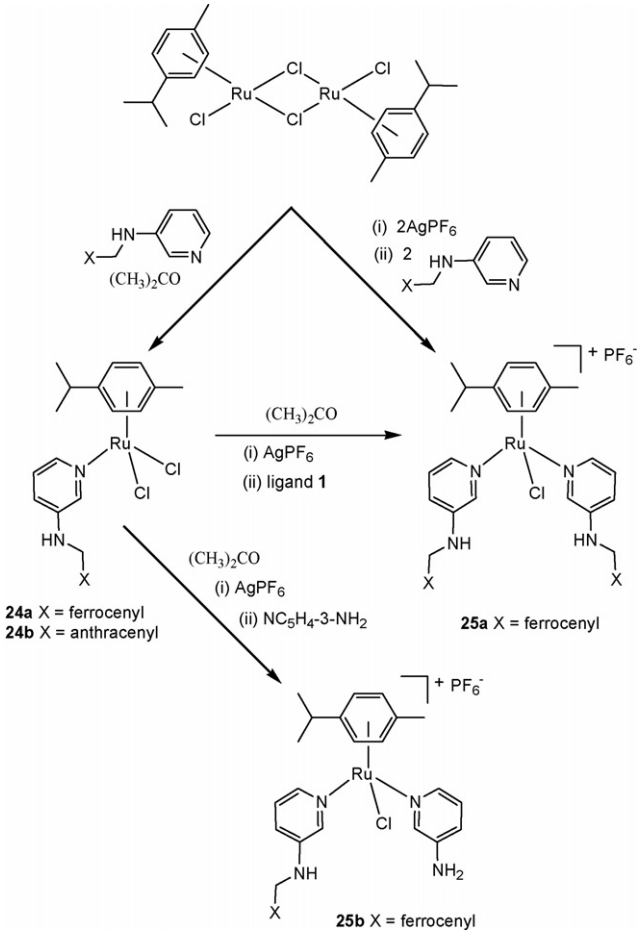
Reaction of **17** and **19** with 3-aminopyridine derived ligands results in the corresponding hosts **20**–**21**. The X-ray crystal structure of **20c**·4Br$^-$ (Fig. 12) shows that the four pyridinium arms are splayed out and bent backwards from the calixarene. Each of the arms interacts *via* a single NH unit with Br$^-$ anion *via* NH···Br$^-$ and longer CH···Br$^-$ interactions.

The ^{1}H NMR titration study of **20c**·4PF$_6^-$ in MeCN-d_3 suggests the lack of cooperativity between the arms in Br$^-$ and Cl$^-$ binding with K_{11} of only 646 and 1780 M^{-1}, respectively consistent with the crystal structure. Much stronger interactions are observed between **20c**·4PF$_6^-$ and carboxylate anions with K_{11} reaching 58,800 M^{-1} for malonate^{2-} despite more competitive solvent being used (MeCN-d_3: DMSO-d$_6$ 60:40) due to reduced solubility. The stoichiometry, determined by Job plot method, is consistent with the titration curves for malonate^{2-} as a 1:2 host:guest ratio. The postulated ditopic behaviour is depicted in Fig. 13. The malonate^{2-} anions are chelated by pairs of pyridinium arms *via* NH···O and CH···O interactions.

The cone hydroxyl calix[4]arene species **21c** and **21d** display very different behaviour with respect to halide binding. A significant affinity was observed for Br$^-$ K_{11} = 24,550 and 53,470 M^{-1}, respectively. Relatively lower affinity binding was observed for Cl$^-$ with K_{11} = 6309 and 3980 M^{-1}, respectively. This selectivity for Br$^-$ over Cl$^-$ may arise from the larger cavity of the calixarene in comparison to the tripodal species **12**–**14**. Both **21c** and **21d** become deprotonated at one OH group on addition of acetate and dicarboxylates. Little change in chemical shift of NH protons is observed during NMR titration until one equivalent of carboxylate group had been added. The enhanced acidity compared to *p-t*-butylcalix[4]arene, for example (pK_a = 4.4(5) in 90% DMSO/water) arises from the stabilisation of the phenolate anion by the pyridinium moiety.

4. Coordination complex hosts

The organic scaffold which bears hydrogen bonding ligands can be replaced by a relatively inert metal such as Pt(II) or Ru(II) forming a 'semi-labile' coordination complex. Work by Loeb and Gale has produced several urea containing Pt(II) species able to bind NO_3^-, ReO_4^- and SO_4^{2-} in a highly concerted fashion [25,61–63,114]. A neutral ion receptor must contain *a priori* binding sites for both anion and cation either as a contact or separated ion pair [16,114]. In these complexes the metal ion plays the role of both counter ion to the bound anion and core organising module. The host geometry depends on the metal ion's preferred coordination geometry. Thus, according to our modular approach the triethylbenzene module is readily exchanged for a metal ion core. Reaction of the Ru(II) species [{Ru(η^6-*p*-cymene)Cl$_2$}$_2$] with 3-aminopyridine or its ferrocenylmethylene (**22**) or anthracenylmethylene (**23**) derivatives gives both 1:1 and 2:1 complexes, **24a**, **b** and **25a**, Scheme 2. The ruthenium(II) complex **25a** proved to be an effective chloride binder exhibiting comparable affinity to the analogous dipodal benzene-derived dication **28**, however the lability of the complex is such that nucleophilic anions like Cl$^-$ displace the pyridyl ligands over a



Scheme 2. Synthesis of Ru(II) receptors.

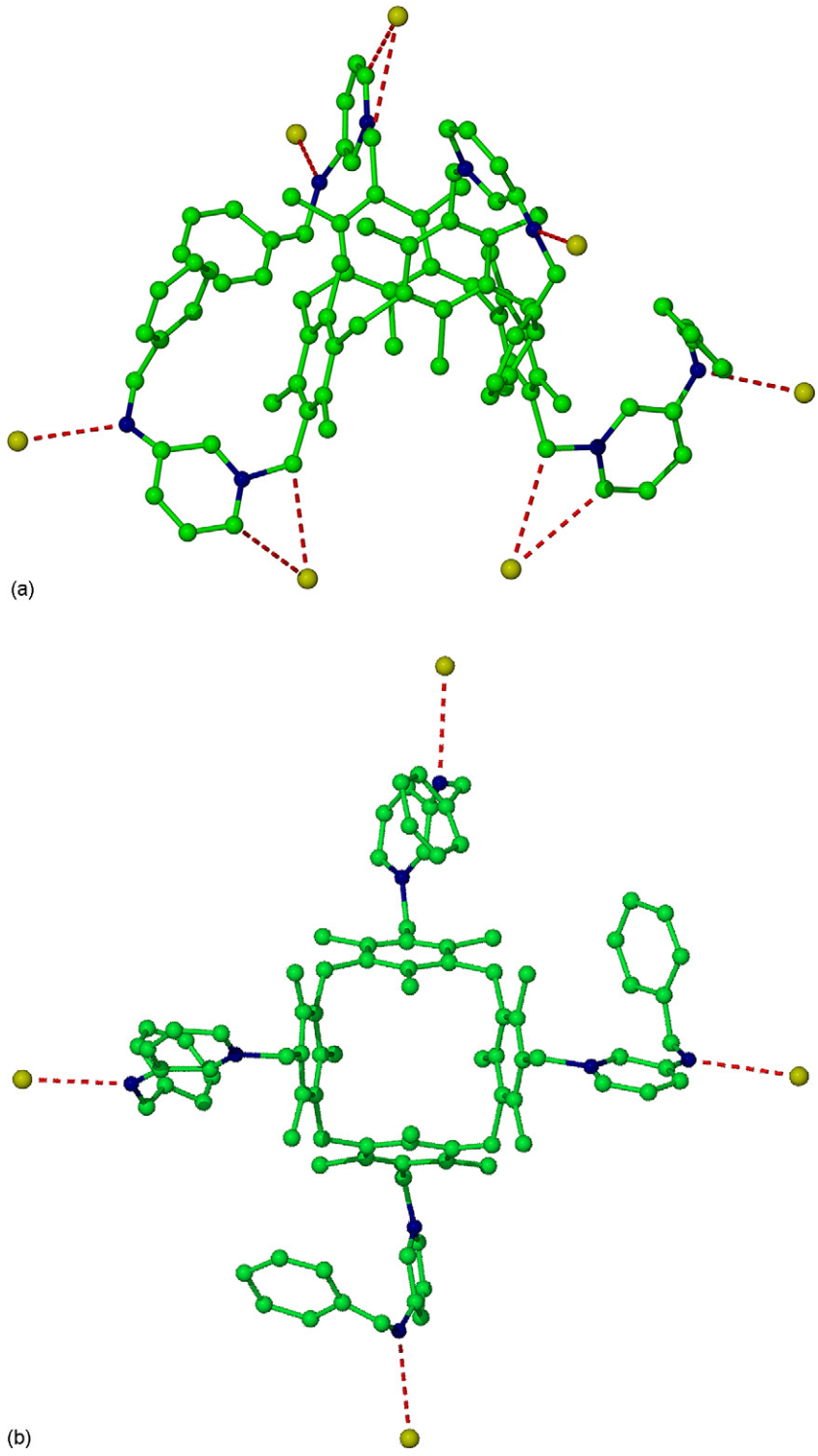


Fig. 12. X-ray crystal structure of the penylbenzyl species 20c·4Br$^-$ showing the splayed conformation of the pyridinium arms, each interacting with a single Br$^-$ anion. The *n*-pentyl chains are disordered and were not located experimentally.

period of hours, re-generating monoadduct **24a**. With less nucleophilic anions the system proved to be stable and exhibits a particularly high affinity for NO_3^-, $K_{11} = 1412$, $K_{12} = 52$. Two binding constants are observed because the lower formal positive charge on the ruthenium complex allowed the formation of a 2:1 host:guest complex as well as the target 1:1 species. This speciation was not observed for the organic analogue. The ruthenium complex also exhibited interesting dynamic NMR behaviour with two forms apparent at low temperature, Scheme 3. In CH_2Cl_2 solvent shifts in the Fc/Fc$^+$ redox couple of up to 82 mV were observed upon chloride addition. Analogous Pt(II) species $[PtCl_2(\mathbf{22})_2]$ **26a** and $[Pt(PPh_2CH_2CH_2PPh_2)(\mathbf{22})_2]^{2+}$ **27a** may also be prepared. In contrast to the success of the ruthenium species, the platinum complexes proved to be poor anion hosts.

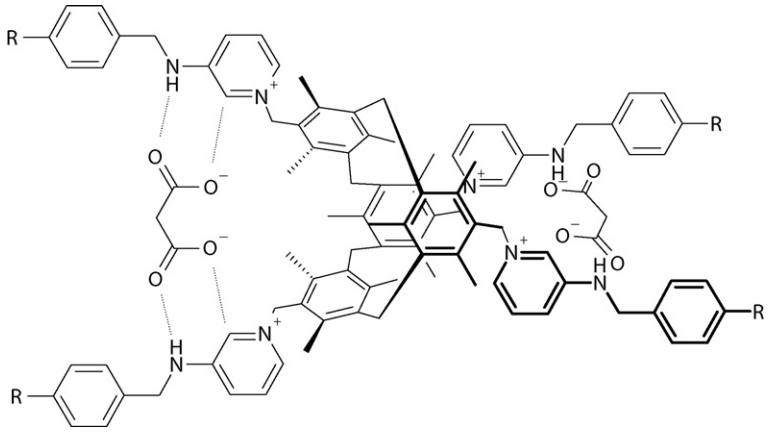
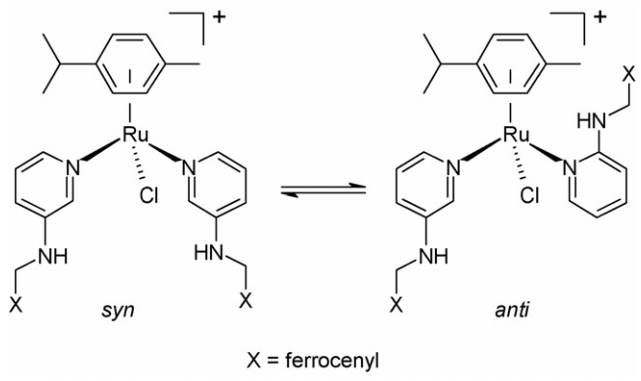


Fig. 13. Model for 1:2 ditopic anion binding by **20c**.



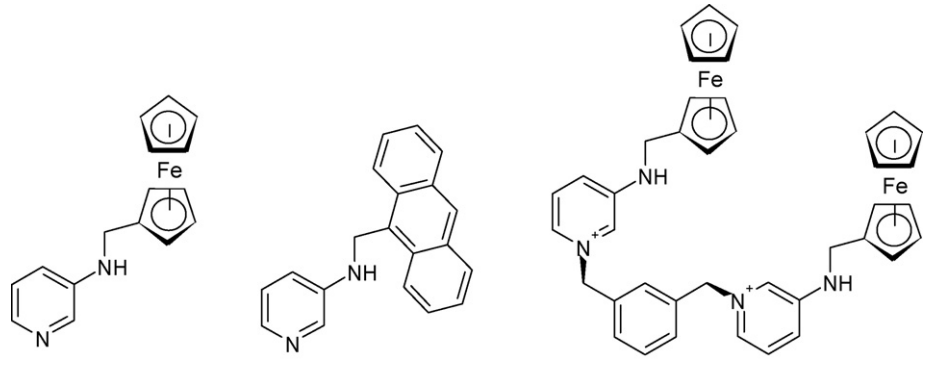
Scheme 3. Conformational exchange in **25a**.

In the case of the dichloride **26a** an X-ray crystal structure revealed a *trans* geometry, unsuitable for anion chelation while the anion binding by the dppe derivative **27a** is apparently inhibited by the bulk of the dppe spectator ligand [63].

tion chemistry is relatively unexceptional, resulting in linear 2- or 3-coordinate complexes for Ag(I) and tetrahedral or octahedral 2:1 and 4:1 complexes for transition metal ions, depending on counter-anion. The complexes prepared are summarized in Scheme 4.

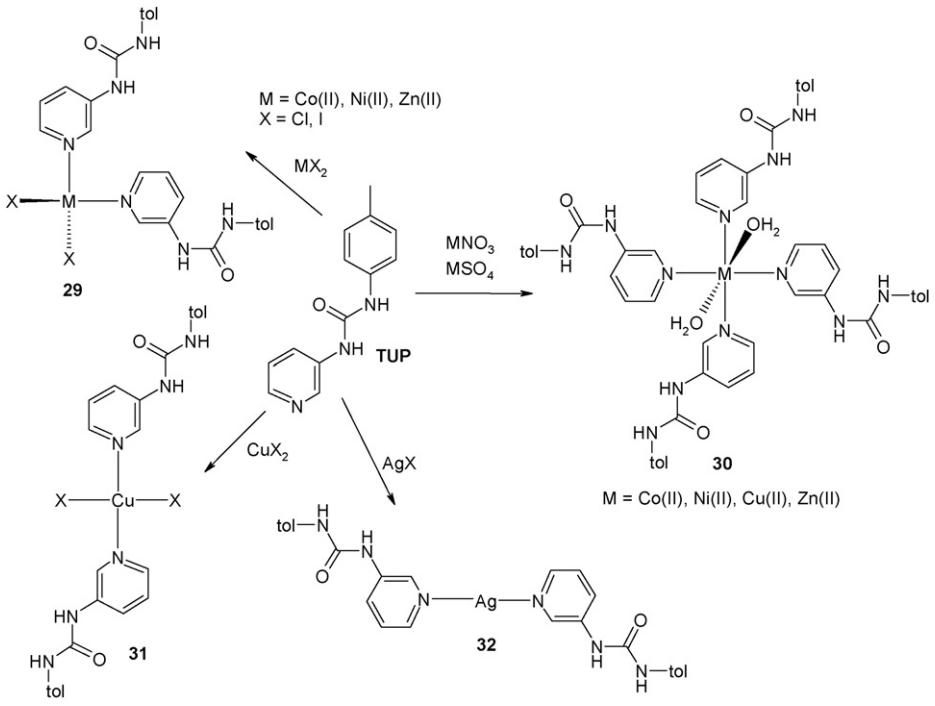
A number of tetrahedral and Jahn-Teller distorted octahedral complexes of type **29** and **31** were characterized by X-ray crystallography. The results revealed divergent hydrogen bonded polymeric systems with reproducible hydrogen bonded motifs, particularly R_1^2 (6) in graph set nomenclature [66]. The isomorphous series of sulfate salts of **30** included a very interesting water tetramer guest characterized by neutron diffraction and PACHA calculations [67].

Reaction of **TUP** with labile Ag(I) as the nitrate, triflate and sulfate salts in methanol-water (∼50:50) resulted in formation of a series of complexes of 1:2 stoichiometry, namely [Ag(**TUP**)$_2$](NO$_3$)·S (**32a**, S = MeOH or NO$_2$Me), [Ag(**TUP**)$_2$](CF$_3$SO$_3$)·0.5 H$_2$O (**32b**) and [Ag(**TUP**)$_2$](SO$_4$)



The very versatile urea ligand **TUP** used in host **15a** has also been extensively investigated within the context of coordination complex hosts. While the Ru(II) and Pt(II) complexes **25a** and **27a** are relatively kinetically inert, the chemistry of **TUP** was investigated with much more labile metal centres, particularly Ag(I) and first row transition metal dications. The coordina-

(**32c**), all of which were characterized crystallographically. Nitrate complex **32a** displays an interesting 1:1 assembly in which the nitrate anion is asymmetrically chelated by two ligands attached to the same metal centre (Fig. 14), forming a highly complementary cavity. The whole structure is almost planar and stacking effects result in either 3.5 or 2.5 crystallographicaly



Scheme 4. Metal complexes of the ligand **TUP**.

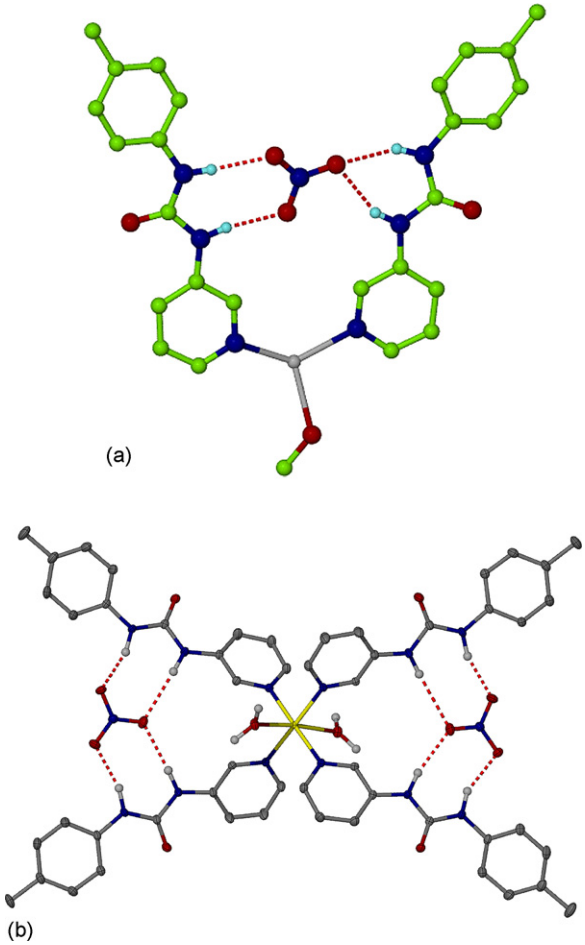


Fig. 14. (a) The discrete $[Ag(\mathbf{TUP})_2](NO_3)\cdot MeOH$ in **32a** showing the slight tilt of the nitrate anion; (b) double nitrate chelation in the Cu(II) complex **30a**.

independent molecules depending on the identity of the solvent molecule 'S' [65,115]. In the case of complexes **32b** and **32c** NH interactions with oxygen in anions result in infinite hydrogen bonded assemblies in the solid state in which each anion is surrounded by an array of two (**32b**) or four (**32c**) urea groups. The high complementarity of **32a** with nitrate is confirmed by ^{1}H NMR titrations studies in actone-d_6 which show that the complex persists in solution, $K_{11} = 30\,200\,M^{-1}$. Once again, CH···anion interactions also prove to be important. Titration of **32a** with acetate produced a notably different response to that of nitrate. There was no change in chemical shift values until after the addition of one equivalent of TBA-acetate. The addition of further aliquots of guest resulted in significant binding ($K_{11} = 4.97 \times 10^5\,M^{-1}$), Fig. 15. This process is due to the ligation of the Ag(I) centre by the first equivalent of acetate,

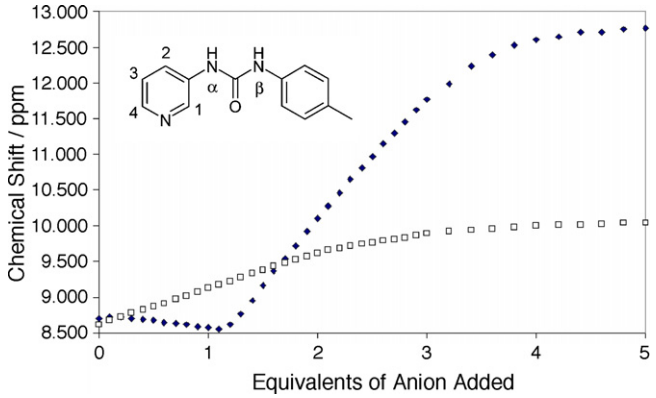


Fig. 15. ^{1}H NMR binding isotherms for the NH(α) proton of **TUP** on addition of NO_3^- (squares) and $CH_3CO_2^-$ (diamonds).

unlike nitrate, which does not ligate until an excess of nitrate is present.

A remarkable similar nitrate-binding motif is observed in the Cu(II) complex $[Cu(\mathbf{TUP})_4(H_2O)_2](NO_3)_2$ **30a**. The X-ray crystal structure shows a symmetric double chelation of the two nitrate anions between pairs of **TUP** ligands, Fig. 14b [116]. The cobalt and nickel analogues were also characterized by X-ray crystallography. They are mutually isomorphous but differ from the Cu(II) complex in that the symmetric nitrate-binding mode is disrupted. Apparently the elongation of the axial M–OH_2 binds due to the Jahn-Teller distortion in the Cu(II) complex is sufficient to favour nitrate chelation. Conversely, the coordinated water molecules are more involved in interactions to the anions in the Co(II) and Ni(II) complexes.

5. Polymer hosts

5.1. Polystyrene derivatives

The simultaneous anion and cation binding behaviour of **TUP** as exemplified by the structures shown in Fig. 14 suggested that the ligand may form the basis for a salt-selective resin. It proved easy to derivatise a commercial cross-linked polystyrene-based isocyanate resin to give a polymer-bound urea analogue, **PBU**. Analytical measurements suggested an average of one **TUP** unit every five polymer repeats. The **PBU** polymeric ligand proved readily able to take up transition metal salts, which imparted their characteristic colour to the material, although uptake proved relatively slow and required an excess of metal salt. Some very slight selectivity was noted for copper(II) nitrate over copper(II) chloride and other transition metal nitrates and it is possible that formation of polymer-bound structures analogous to the X-ray structure of the model compound shown in Fig. 14b are responsible, however, the relevance of this model to the polymer system remains to be firmly established.

5.2. Coordination polymer hosts

In addition to amorphous polymeric materials such as **PBU**, we have prepared a number of difunctional pyridyl urea ligands such as **33** and **34** in order to examine anion templated coordination polymer formation. Ligand **34** represents a 'double' analogue of **TUP** while **33** is more linear and divergent. Ligand **33** forms a 1D coordination polymer with $Ag(NO_3)$ when crystallised from DMSO solution $[Ag(\mathbf{33})(NO_3)]\cdot 2DMSO$ (**35**). The material adopts a highly pleated conformation that does include bis(urea) binding pockets, however these are occupied by DMSO solvent molecules, with the nitrate anions being

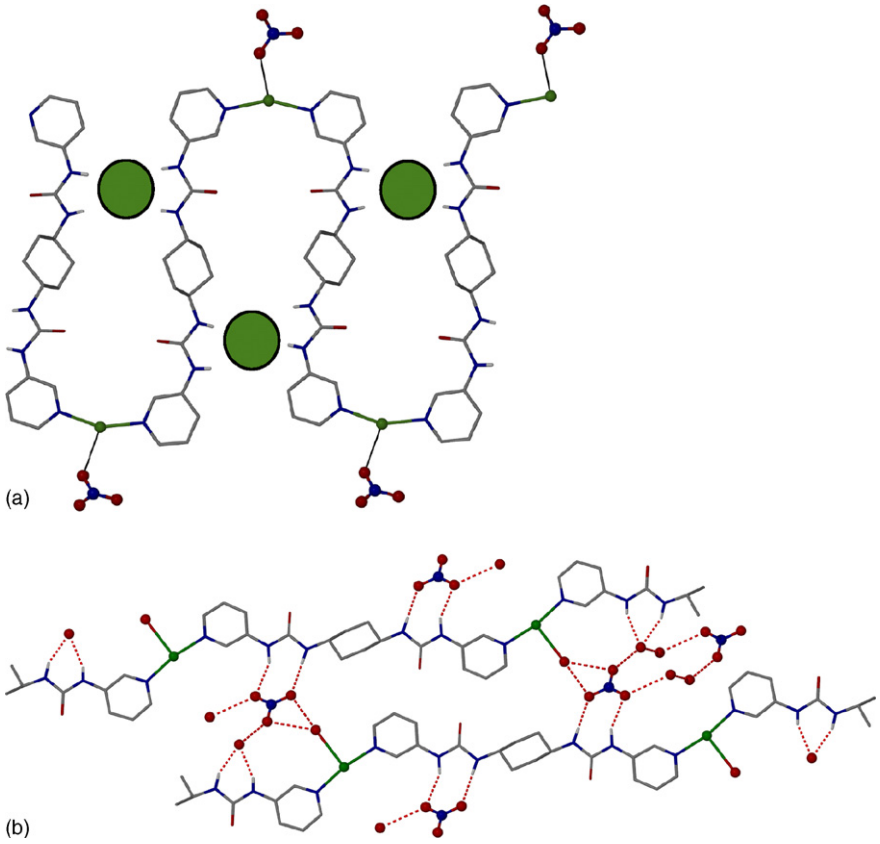
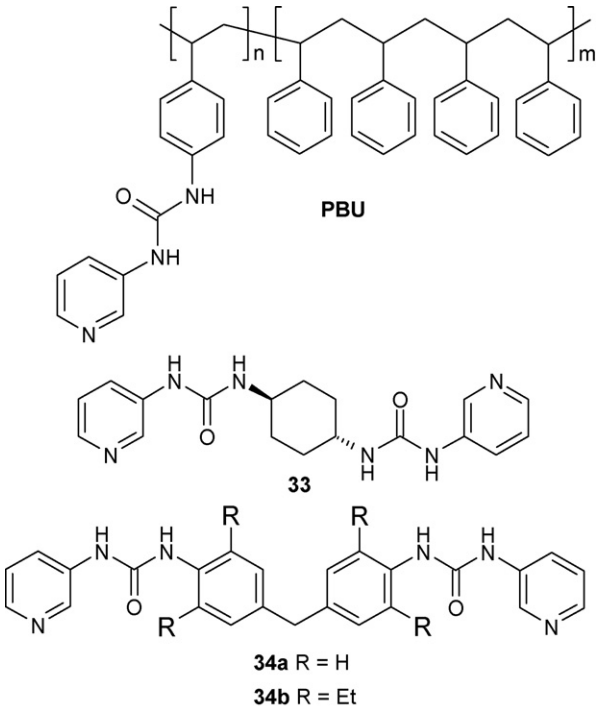


Fig. 16. (a) Convergent self-inclusion in adjacent units of $[Ag(\mathbf{33})(NO_3)]\cdot 2DMSO$ **35** mediated by DMSO molecules in the urea clefts (circles); (b) two parallel polymer chains in $[Ag(\mathbf{33})](NO_3)\cdot 3H_2O$ **36** showing the hydrogen bonding arrangement including the R_8^6 (16) unit involving two nitrate anions and four water molecules.

directly coordinated to the Ag(I) centres. Crystallisation of the same material from methanol results in a topologically similar material [Ag(**33**)]$(NO_3)\cdot 3H_2O$ (**36**) but one that exhibits a much more open conformation that does incorporate urea-nitrate interactions. Thus the coordination polymer conformation is highly dependent on the hydrogen bonding geometry adopted by the urea groups (Fig. 16).



5.3. Gel phase materials

During crystallisation experiments on **33** and **34a**,**b** a number of gel phase materials were observed. For example, a 10 mM solution of **34a** in water/thf mixture (1:2, v/v) simply results in slow crystallisation of the ligand. However, in the presence of one equivalent of $AgBF_4$ the solution gels, Fig. 17 [117]. Gellation of organic solvents by bis(ureas) is not unknown [118–123] but is usually restricted to species with long lipophilic chains. Moreover the present gels are apparently highly crystalline as exemplified by SEM images of the dried xerogels (Fig. 18), yet exhibit viscoelastic properties which, while solid-like, are characteristic of weak gels. The key to this behaviour presumably lies in the labile nature of the supramolecular interactions holding the gels together. As yet the gels' structure is a matter for speculation. Urea gels are generally taken to be based on assembly of the urea low molecular weight gelators (LMWG) by the urea tape motif, Fig. 19a. However, in the present systems this common interaction type is subject to competition with interactions with pyridyl nitrogen atoms (as exemplified in a recent study by Nangia and by our own results [124,125]) and by coordination to metal and anion, Fig. 19b–d.

Fig. 17. Comparison of solutions of free ligand **34a** (left) and **34a**/$AgBF_4$ in thf/water (right; inverted).

To date one X-ray crystal structure arising from the reaction of $Ag(NO)_3$ with **34a** provides a clue as to the type of species that might comprise the gel fibres. The product [{Ag(**34a**)(MeCN)}$_2$]$(NO_3)_2$ (**37**) comprises a discrete 2 + 2 metallomacrocycle with approximately linear coordination at the Ag(I) centres and four externally directed urea groups hydrogen bonding to NO_3^- anions. The anions bridge between adjacent macrocycles *via* unsymmetrical pairwise R_2^2 (8) hydrogen bonded rings (Fig. 20). It is possible that anion-mediated interaction between such stacks of complexes is responsible for the gels' unusual rheology. Work is in progress towards a much fuller understanding of this phenomenon.

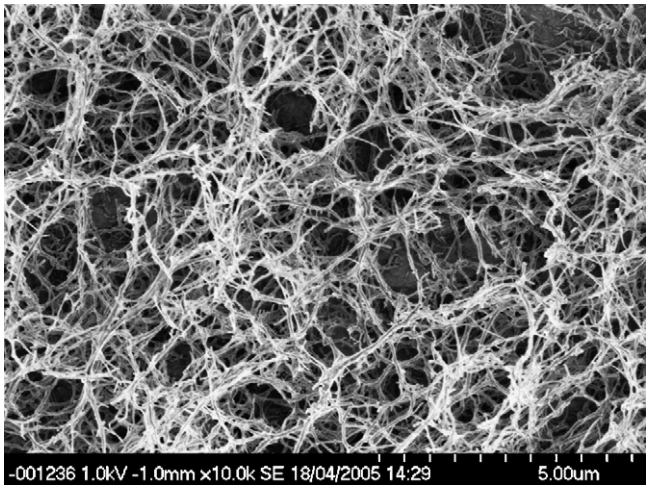


Fig. 18. SEM image of the xerogel of **33**/$AgBF_4$.

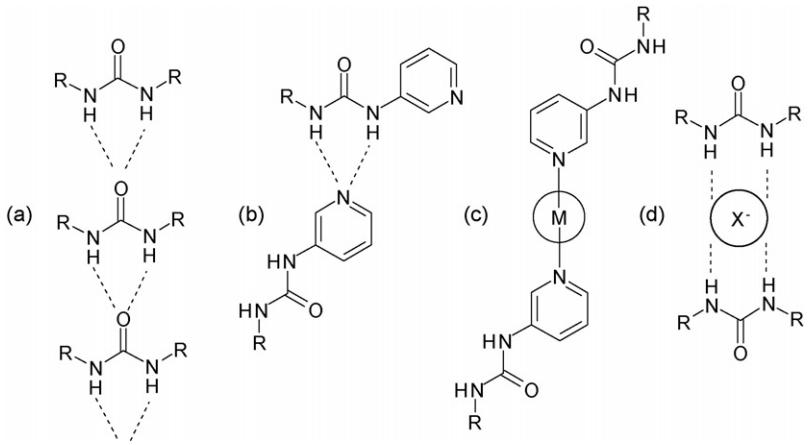


Fig. 19. Possible modes of interaction within pyridyl urea metallogels.

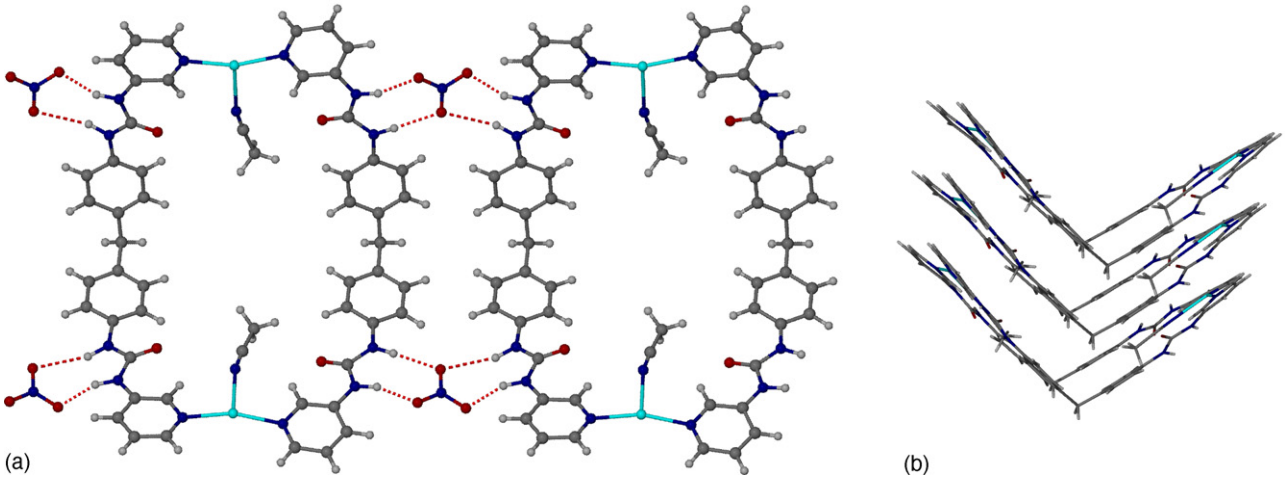


Fig. 20. (a) Molecular structure of the metallomacrocycle $[\{Ag(\mathbf{34a})(MeCN)\}_2]^{2+}$ in **37**. Each chain interacts with its neighbours *via* NH· · ·anion hydrogen bonds. (b) Polar π-stacked chains of macrocycles.

6. Conclusion

We have outlined a synthetically simple, modular approach to a versatile series of anion binding hosts. The key results are that inter-anion discrimination depends primarily on the structural characteristics of the hosts and thus a wide range of building blocks may be used in order to achieve the desired configuration. Triethylbenzene and calixarene-based compounds are highly flexible and can modulate their conformation in order to adapt to the anion guest in an induced-fit binding process. This behaviour can be well understood by a combination of VT NMR spectroscopic and NMR titration methods in conjunction with molecular modelling and X-ray crystallography. This flexibility translates into a self-assembling regime in some structurally similar metal complexes with labile metal centres in which the metal, ligands and anion all form part of a self-assembled aggregate that is structurally similar to the organic host–guest species. The versatility of this approach allows its adaptation to polymer supported materials and to the construction of guest dependent coordination polymers. Current work is directed towards the attachment of flexible anion binding moieties to metallic nanoparticles.

Acknowledgements

We thank the many outstanding collaborators and co-workers whose names appear in the references. We are also extremely grateful to the Royal Society, the EPSRC and the Leverhulme Trust for research funding.

References

[1] J.M. Llinares, D. Powell, K. Bowman-James, Coord. Chem. Rev. 240 (2003) 57.
[2] V. McKee, J. Nelson, R.M. Town, Chem. Soc. Rev. 32 (2003) 309.
[3] P.A. Gale, Coord. Chem. Rev. 240 (2003) 191.
[4] P.A. Gale, Coord. Chem. Rev. 240 (2003) 1.
[5] P.A. Gale, Coord. Chem. Rev. 199 (2000) 181.
[6] B. Dietrich, Pure & Appl., Chem. 65 (1993) 1457.
[7] C.R. Bondy, S.J. Loeb, Coord. Chem. Rev. 240 (2003) 77.
[8] A.P. Davis, J.B. Joos, Coord. Chem. Rev. 240 (2003) 143.

[9] J.L. Atwood, K.T. Holman, J.W. Steed, J. Chem. Soc. Chem. Commun. (1996) 1401.
[10] G. Hennrich, E.V. Anslyn, Chem. Eur. J. 8 (2002) 2218.
[11] Z.F. Kanyo, D.W. Christianson, J. Biol. Chem. 266 (1991) 4264.
[12] J.J. Lavigne, E.V. Anslyn, Angew Chem., Int. Ed. 40 (2001) 3118.
[13] P.D. Beer, P.A. Gale, Angew Chem., Int. Ed. 40 (2001) 487.
[14] K.J. Wallace, W.J. Belcher, D.R. Turner, K.F. Syed, J.W. Steed, J. Am. Chem. Soc. 125 (2003) 9699.
[15] A. Metzger, V.M. Lynch, E.V. Anslyn, Angew Chem., Int. Ed. Engl. 36 (1997) 862.
[16] J.L. Atwood, A. Szumna, Chem. Commun. (2003) 940.
[17] C. Schmuck, L. Geiger, J. Am. Chem. Soc. 126 (2004) 8898.
[18] P.D. Beer, J.J. Davis, D.A. Drillsma-Milgrom, F. Szemes, Chem. Commun. (2002) 1716.
[19] J. Zhang, A.M. Bond, J. Belcher, K.J. Wallace, J.W. Steed, J. Phys. Chem. B 107 (2003) 5777.
[20] L.O. Abouderbala, W.J. Belcher, M.G. Boutelle, P.J. Cragg, J.W. Steed, D.R. Turner, K.J. Wallace, Proc. Nat. Acad. Sci. U.S.A. 99 (2002) 5001.
[21] L.O. Abouderbala, W.J. Belcher, M.G. Boutelle, P.J. Cragg, M. Fabre, J. Dhaliwal, J.W. Steed, D.R. Turner, K.J. Wallace, Chem. Commun. (2002) 358.
[22] K.T. Holman, M.M. Halihan, S.S. Jurisson, J.L. Atwood, R.S. Burkhalter, A.R. Mitchell, J.W. Steed, J. Am. Chem. Soc. 118 (1996) 9567.
[23] K.T. Holman, M.M. Halihan, J.W. Steed, S.S. Jurisson, J.L. Atwood, J. Am. Chem. Soc. 117 (1995) 7848.
[24] M. Buda, A. Ion, J.-C. Moutet, E. Saint-Aman, R. Ziessel, J. Electroanal. Chem. 469 (1999) 132.
[25] C.R. Bondy, P.A. Gale, S.J. Loeb, Chem. Commun. (2001) 729.
[26] P.D. Beer, D.P. Cormode, J.J. Davis, Chem. Commun. (2004) 414.
[27] P.A. Gale, M.E. Light, B. McNally, K. Navakhun, K.E. Sliwinski, B.D. Smith, Chem. Commun. (2005) 3773.
[28] B.D. Smith, T.N. Lambert, Chem. Commun. (2003) 2261.
[29] J.W. Steed, K.J. Wallace, in: G.W. Gokel (Ed.), Advances in Supramolecular Chemistry, vol. 9, Cerberus, New York, 2003, p. 221, Chapter 5.
[30] B. Dietrich, M.W. Hosseini, J.-M. Lehn, R.B. Sessions, J. Am. Chem. Soc. 103 (1981) 1282.
[31] B.H.M. Snellink-Ruel, M.M.G. Antonisse, J.F.J. Engbersen, P. Timmerman, D.N. Reinhoudt, Eur. J. Org. Chem. (2000) 165.
[32] M.M.G. Antonisse, D.N. Reinhoudt, Chem. Commun. (1998) 443.
[33] J.J. Dannenberg, J. Mol. Struct. (2002) 219.
[34] G.A. Jeffrey, An Introduction to Hydrogen Bonding, 1st ed., OUP, Oxford, 1997.
[35] F.P. Schmidtchen, Tetrahedron Lett. 30 (1989) 4493.
[36] J. de Mendoza, A. Galán, D. Andreu, A.M. Echavarren, J. Am. Chem. Soc. 114 (1992) 1511.
[37] A.J. Ayling, M.N. Perez-Payan, A.P. Davis, J. Am. Chem. Soc. 123 (2001) 12716.
[38] J.W. Steed, J.L. Atwood, Supramolecular Chemistry, 1st ed., J. Wiley & Sons, Chichester, 2000.
[39] C.A. Ilioudis, D.A. Tocher, J.W. Steed, J. Am. Chem. Soc. 126 (2004) 12395.
[40] Y. Bai, B.G. Zhang, J. Xu, C.Y. Duan, D.B. Dang, D.J. Liu, Q.J. Meng, New. J. Chem. 29 (2005) 777.
[41] S.W. Kubik, R. Goddard, Proc. Nat. Acad. Sci. U.S.A. 99 (2002) 5127.
[42] F. Hettche, P. Reiß, R.W. Hoffmann, Chem. Eur. J. 8 (2002) 4946.
[43] C. Schmuck, M. Schwegmann, J. Am. Chem. Soc. 127 (2005) 3373.
[44] P.D. Beer, E.J. Hayes, Coord. Chem. Rev. 240 (2003) 167.
[45] M.D. Pratt, P.D. Beer, Polyhedron 22 (2003) 649.
[46] A.J. Evans, S.E. Matthews, A.R. Cowley, P.D. Beer, Dalton Trans. (2003) 4644.
[47] P.D. Beer, A.G. Cheetham, M.G.B. Drew, O.D. Fox, E.J. Hayes, T.D. Rolls, Dalton Trans. (2003) 603.
[48] L.H. Uppadine, F.R. Keene, P.D. Beer, J. Chem. Soc., Dalton Trans. (2001) 2188.
[49] N.G. Berry, M.D. Pratt, O.D. Fox, P.D. Beer, Supramol. Chem. 13 (2001) 677.
[50] P.D. Beer, N. Berry, M.G.B. Drew, O.D. Fox, M.E. Padilla-Tosta, S. Patell, Chem. Commun. (2001) 199.
[51] P.D. Beer, J. Cadman, Coord. Chem. Rev. 205 (2000) 131.
[52] P.D. Beer, D. Hesek, K.C. Nam, M.G.B. Drew, Organometallics 18 (1999) 3933.
[53] P.D. Beer, Acc. Chem. Res. 31 (1998) 71.
[54] P.D. Beer, S.W. Dent, G.S. Hobbs, T.J. Wear, Chem. Commun. (1997) 99.
[55] J.W. Steed, R.K. Juneja, J.L. Atwood, Angew Chem. Int. Ed. Engl. 33 (1994) 2456.
[56] J.W. Steed, R.K. Juneja, R.S. Burkhalter, J.L. Atwood, J. Chem. Soc. Chem. Commun. (1994) 2205.
[57] J.W. Steed, C.P. Johnson, R.K. Juneja, J.L. Atwood, R.S. Burkhalter, Supramol. Chem. 6 (1996) 235.
[58] M. Staffilani, K.S.B. Hancock, J.W. Steed, K.T. Holman, J.L. Atwood, R.K. Juneja, R.S. Burkhalter, J. Am. Chem. Soc. 119 (1997) 6324.
[59] K.T. Holman, G.W. Orr, J.W. Steed, J.L. Atwood, Chem. Commun. (1998) 2109.
[60] M. Staffilani, G. Bonvicini, J.W. Steed, K.T. Holman, J.L. Atwood, M.R.J. Elsegood, Organometallics 17 (1998) 1732.
[61] C.R. Bondy, P.A. Gale, S.J. Loeb, J. Supramol. Chem. 2 (2002) 93.
[62] C.R. Bondy, P.A. Gale, S.J. Loeb, J. Am. Chem. Soc. 126 (2004) 5030.
[63] K.J. Wallace, R. Daari, W.J. Belcher, L.O. Abouderbala, M.G. Boutelle, J.W. Steed, J. Organomet. Chem. 666 (2003) 63.
[64] D.R. Turner, B. Smith, E.C. Spencer, A.E. Goeta, I.R. Evans, D.A. Tocher, J.A.K. Howard, J.W. Steed, New J. Chem. 29 (2005) 90.
[65] D.R. Turner, E.C. Spencer, J.A.K. Howard, D.A. Tocher, J.W. Steed, Chem. Commun. (2004) 1352.
[66] D.R. Turner, B. Smith, A.E. Goeta, I.R. Evans, D.A. Tocher, J.A.K. Howard, J.W. Steed, Cryst. Eng. Comm. 6 (2004) 633.
[67] D.R. Turner, M. Henry, C. Wilkinson, G.J. McIntyre, S.A. Mason, A.E. Goeta, J.W. Steed, J. Am. Chem. Soc. 127 (2005) 11063.
[68] J.A. Tovilla, R. Vilar, A.J.P. White, Chem. Commun. (2005) 4839.
[69] L.P. Harding, J.C. Jeffery, T. Riis-Johannessen, C.R. Rice, Z.T. Zeng, Chem. Commun. (2004) 654.
[70] L.P. Harding, J.C. Jeffery, T. Riis-Johannessen, C.R. Rice, Z.T. Zeng, Dalton Trans. (2004) 2396.
[71] K.V. Kilway, J.S. Siegel, J. Am. Chem. Soc. 114 (1992) 255.
[72] J. Chin, C. Walsdorff, B. Stranix, J. Oh, H.J. Chung, S.-M. Park, K. Kim, Angew Chem., Int. Ed. 38 (1999) 2756.
[73] K.S. Oh, C.W. Lee, H.S. Choi, S.J. Lee, K.S. Kim, Org. Lett. 2 (2000) 2679.
[74] S.Y. Jon, J. Kim, M. Kim, S.H. Park, W.S. Jeon, J. Heo, K. Kim, Angew Chem., Int. Ed. 40 (2001) 2116.
[75] K.J. Wallace, R. Hanes, E. Anslyn, J. Morey, K.V. Kilway, J. Siegel, Synthesis (2005) 2080.
[76] A. Vacca, C. Nativi, M. Cacciarini, R. Pergoli, S. Roelens, J. Am. Chem. Soc. 126 (2004) 16456.
[77] Y.S. Sohn, A. Goodey, E.V. Anslyn, J.T. McDevitt, J.B. Shear, D.P. Neikirk, Biosens. & Bioelectron. 21 (2005) 303.
[78] A.T. Wright, E.V. Anslyn, Chem. Soc. Rev. 35 (2006) 14.
[79] A. Goodey, J.J. Lavigne, S.M. Savoy, M.D. Rodriguez, T. Curey, A. Tsao, G. Simmons, J. Wright, S.J. Yoo, Y. Sohn, E.V. Anslyn, J.B. Shear, D.P. Neikirk, J.T. McDevitt, J. Am. Chem. Soc. 123 (2001) 2559.
[80] H. Ihm, S. Yun, H.G. Kim, J.K. Kim, K.S. Kim, Org. Lett. 4 (2002) 2897.
[81] A.M. Christofi, P.J. Garratt, G. Hogarth, J.W. Steed, J. Chem. Soc. Dalton Trans. (2000) 2137.
[82] A.M. Christofi, P.J. Garratt, G. Hogarth, Tetrahedron 57 (2001) 751.
[83] A.M. Christofi, P.J. Garratt, G. Hogarth, A.J. Ibbett, Y.F. Ng, J.W. Steed, Tetrahedron 58 (2002) 4543.
[84] P.J. Garratt, A.J. Ibbett, J.E. Ledbury, R. O'Brien, M.B. Hursthouse, K.M.A. Malik, Tetrahedron 54 (1998) 949.
[85] P.J. Garratt, Y.F. Ng, J.W. Steed, Tetrahedron 56 (2000) 4501.
[86] J.W. Steed, P.C. Junk, J.L. Atwood, M.J. Barnes, C.L. Raston, R.S. Burkhalter, J. Am. Chem. Soc. 116 (1994) 10346.
[87] K.S.B. Hancock, J.W. Steed, Chem. Commun. (1998) 1409.
[88] C. Walsdorff, W. Saak, S. Pohl, J. Chem. Res. (S) (1996) 282.
[89] W.J. Belcher, M. Fabre, T. Farhan, J.W. Steed, Org. Biomol. Chem. 4 (2006) 781.

[90] K.H. Choi, A.D. Hamilton, Coord. Chem. Rev. 240 (2003) 101.
[91] A.P. de Silva, H.Q.N. Gunaratne, T. Gunnlaugsson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher, T.E. Rice, Chem. Rev. 97 (1997) 1515.
[92] G. McSkimming, J.H.R. Tucker, H. Bouas-Laurent, J.P. Desvergne, Angew Chem., Int. Ed. 39 (2000) 2167.
[93] M. Albrecht, J. Zauner, R. Burget, H. Röttele, R. Fröhlich, Mater. Sci. Eng. C 18 (2001) 185.
[94] P.J. Smith, M.V. Reddington, C.S. Wilcox, Tetrahedron Lett. 33 (1992) 6085.
[95] D.E. Gomez, L. Fabbrizzi, M. Licchelli, E. Monzani, Org. Biomol. Chem. 3 (2005) 1495.
[96] M. Boiocchi, L. Del Boca, D. Esteban-Gomez, L. Fabbrizzi, M. Licchelli, E. Monzani, Chem. Eur. J. 11 (2005) 3097.
[97] J.-L. Wu, Y.-B. He, Z.-Y. Zeng, L.-H. Wei, L.-Z. Meng, T.-X. Yang, Tetrahedron 60 (2004) 4309.
[98] S.-Y. Liu, Y.-B. He, J.-L. Wu, L.-H. Wei, H.-J. Qin, L.-Z. Meng, L. Hu, Org. Biomol. Chem. 2 (2004) 1582.
[99] P. Gale, in: J.W. Steed, J.L. Atwood (Eds.), Encyclopedia of Supramolecular Chemistry, vol. 1, Marcel Dekker, New York, 2004, p. 31.
[100] Y.S. Yang, S.W. Ko, I.H. Song, B.J. Ryu, K.C. Nam, Bull. Korean Chem. Soc. 24 (2003) 681.
[101] A. Fan, H.K. Hong, S. Valiyaveettil, J. Vittal, J. Supramol. Chem. 2 (2002) 247.
[102] J. Scheerder, F. Fochi, J.F.J. Engbersen, D.N. Reinhoudt, J. Org. Chem. 59 (1994) 7815.
[103] S. Nishizawa, P. Bühlmann, M. Iwao, Y. Umezawa, Tetrahedron Lett. 36 (1995) 6483.
[104] S. Nishizawa, P. Bühlmann, K.P. Xiao, Y. Umezawa, Anal. Chim. Acta 358 (1998) 35.
[105] K.H. Lee, J.-I. Hong, Tetrahedron Lett. 41 (2000) 6083.
[106] J. Budka, P. Lhotak, V. Michlova, I. Stibor, Tetrahedron Lett. 42 (2001) 1583.
[107] B.R. Linton, M.S. Goodman, E. Fan, S.A. van Arman, A.D. Hamilton, J. Org. Chem. 66 (2001) 7313.
[108] D.R. Turner, M.J. Paterson, J.W. Steed, J. Org. Chem. 71 (2006) 1598.
[109] C.D. Gutsche, Calixarenes, Royal Society of Chemistry, Cambridge, 1989.
[110] C.D. Gutsche, Calixarenes Revisited, Royal Society of Chemistry, Cambridge, 1997.
[111] C.D. Gutsche, L.J. Bauer, Tetrahedron Lett. 22 (1981) 4763.
[112] T.-T. Wu, J.R. Speas, J. Org. Chem. 52 (1987) 2330.
[113] M.H. Filby, T.D. Humphries, D.R. Turner, R. Kataky, J. Kruusma, J.W. Steed, Chem. Commun. (2006) 156.
[114] B.D. Smith, T.N. Lambert, Chem. Commun. (2003) 2261.
[115] J.W. Steed, Crystengcomm (2003) 169.
[116] J.M. Russell, A.D.M. Parker, I. Radosavljevic-Evans, J.A.K. Howard, J.W. Steed, Chem. Commun. (2006) 269.
[117] L. Applegarth, N. Clark, A.C. Richardson, A.D.M. Parker, I. Radosavljevic-Evans, A.E. Goeta, J.A.K. Howard, J.W. Steed, Chem. Commun. (2005) 5423.
[118] J. van Esch, F. Schoonbeek, M. de Loos, H. Kooijman, A.L. Spek, R.M. Kellogg, B.L. Feringa, Chem. Eur. J. 5 (1999) 937.
[119] J. Brinksma, B.L. Feringa, R.M. Kellogg, R. Vreeker, J. van Esch, Langmuir 16 (2000) 9249.
[120] F.S. Schoonbeek, J.H. van Esch, R. Hulst, R.M. Kellogg, B.L. Feringa, Chem. Eur. J. 6 (2000) 2633.
[121] Y. Jeong, K. Hanabusa, H. Masunaga, I. Akiba, K. Miyoshi, S. Sakurai, K. Sakurai, Langmuir 21 (2005) 586.
[122] K.J.C. van Bommel, C. van der Pol, I. Muizebelt, A. Friggeri, A. Heeres, A. Meetsma, B.L. Feringa, J. van Esch, Angew Chem., Int. Ed. 43 (2004) 1663.
[123] P. Terech, R.G. Weiss, Chem. Rev. 97 (1997) 3133.
[124] L.S. Reddy, S. Basavoju, V.R. Vangala, A. Nangia, Cryst. Growth. Des. 6 (2006) 161.
[125] D.R. Turner, Ph.D. thesis, King's College, London, 2004.