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Review

Anion coordination and anion-templated assembly: Highlights from 2002 to 2004

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Contents

Abstract

This review article highlights advances made in abiotic anion coordination chemistry from 2002 to 2004. The structure of this review is that similar to the previous reviews in this series that covered 1997–2001 [P.A. Gale, Coord. Chem. Rev. 199 (2000) 181; P.A. Gale, Coord. Chem. Rev. 213 (2001) 79; P.A. Gale, Coord. Chem. Rev. 240 (2003) 191]. The first section examines anion receptors that do not contain metal ions. This is followed by a review of metal containing anion receptors and finally the role of anions in directing the self-assembly of complex molecular architectures are presented in the final section.
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Keywords: Anion complexation; Hydrogen bonds; Crystallography

1. Introduction

Molecular receptors designed to bind anionic guests or ion-pairs have attracted much interest recently [1–5]. Anions are ubiquitous throughout biological systems playing many essential roles [6–9]. On the other hand, anions can have deleterious effects on the environment. For example, anionic pollutants, such as phosphate and nitrate from the overuse of agricultural fertilisers are the cause of eutrophication of lakes and inland waterways [10]. Other anions, such as pertechnetate are generated from the re-processing of nuclear fuel and their release to the environment strictly controlled or prohibited. There is therefore a demand for the production of selective anion receptor and sensor species that can allow in the field detection of particular species. The aim of this review is to highlight advances made in the area of anion receptor chemistry in the years 2002–2004.

This overview of progress is split into three sections covering anion receptors that operate *via* hydrogen-bonding interactions, metal-containing anion receptors and finally the use of anions to template assemblies.

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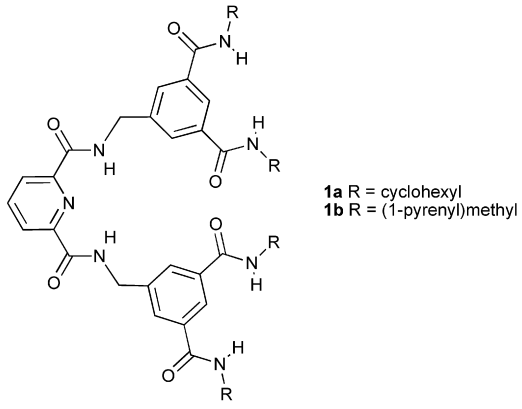
2. Metal-free anion receptors

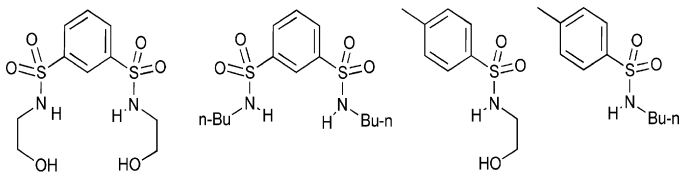
2.1. Amide-based receptors

Amide NH groups have been employed to produce a wide range of receptors capable of coordinating anions. General reviews covering anion receptors containing amide groups have been recently published [11]. Fang and co-workers have designed a neutral receptor **1** containing six amide groups in a 'pseudotetrahedral' cleft arrangement, which displays a high selectivity for phosphates [12]. This compound was also functionalized with pyrene groups so introducing a fluorescent probe into the receptor. The binding constants for $H_2PO_4^-$ were calculated by ^{1}H NMR titration experiments in DMSO-d_6 and found to be 1374 and 549 M^{-1} for **1a** and **1b**, respectively.



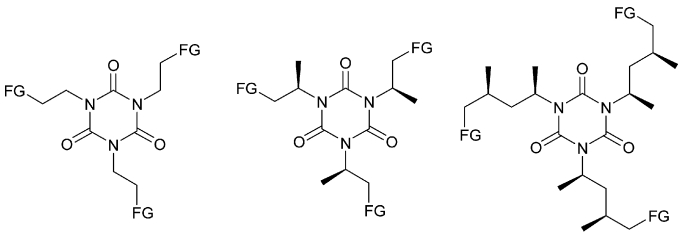
1a R = cyclohexyl
1b R = (1-pyrenyl)methyl

Sulfonamides have also been incorporated into a number of hosts [1–3]. Kondo et al. have investigated the role of hydroxyl group in sulfonamide cleft receptors **2** and **4** and compared their behaviour with the non-hydroxyl containing control compounds **3** and **5** [13]. Association constants were calculated by ^{1}H NMR titration experiments in deuterated acetonitrile and the results demonstrated the involvement of the –OH group in anion complexation as evidenced by the higher affinity of the hydroxyl functionalized compounds for anionic guests. For example, acetate and dihydrogenphosphate association constants rose from approximately 585 and 209 M^{-1}, respectively, in receptor **3** to 23,800 and 1890 M^{-1} for receptor **2**.



2 **3** **4** **5**

Hoffmann has employed a triazine-trione scaffold bearing three *p*-nitrophenylsulfonamide groups to assess the effect of preorganization on binding properties [14]. The conformationally preorganized receptor **7** binds chloride more strongly than the more flexible system **6** and significantly the selectivity is greatly improved. Further preorganization of the side arms in compound **8** showed no positive effect on the binding properties of this compound. Binding constants for chloride, added as the tetrabutylammonium salt in $CDCl_3$/DMSO 95:5, were found at 4870 ± 170, $12{,}630 \pm 1100$ and 4170 ± 130 M^{-1} for **6**, **7** and **8**.



6 **7** **8**

FG = NH-SO_2-(*p*)C_6H_4-NO_2

Isophthalamides and their analogues have received a great deal of attention due to their high affinity for anions, and a variety of cyclic and acyclic receptors have been reported [15]. Yamamoto and co-workers have published the synthesis and binding properties of the macrocyclic polythiolactam **9a** [16], which showed a higher anion affinity than the previously reported tetralactam **9b** [17]. The association constants were calculated by ^{1}H NMR titration experiments in deuterated dimethylsulfoxide and found to be 1.4×10^4 M^{-1} (AcO^-), 3.9×10^3 M^{-1} ($H_2PO_4^-$), 1.1×10^3 M^{-1} (Cl^-), 1.5×10^2 M^{-1} (Br^-) and 9.6×10^3 M^{-1} (F^-, slow exchange was observed at room temperature). The structure of the complex [PPh_4][**9a**·Cl] was determined by X-ray crystallography and revealed the chloride interacting with the four N–H groups lying above the plane of the macrocycle (Fig. 1).

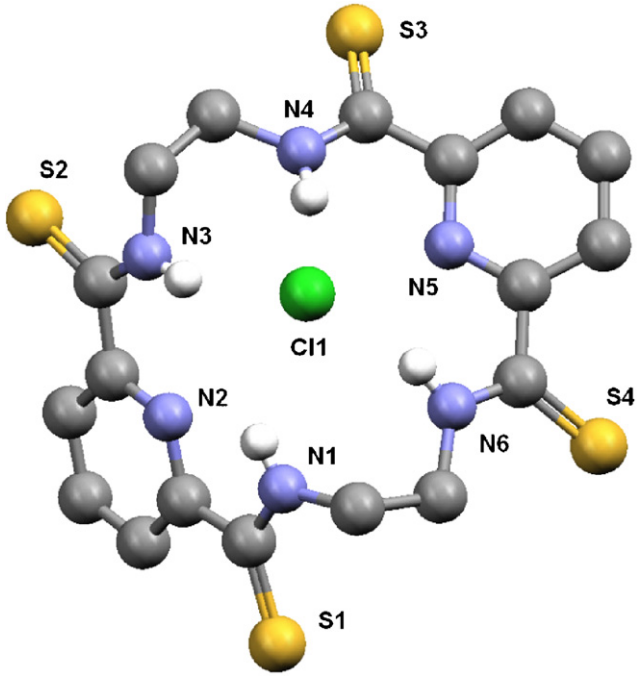
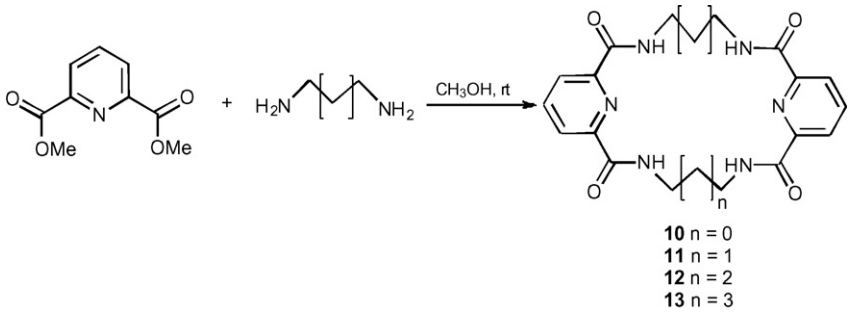
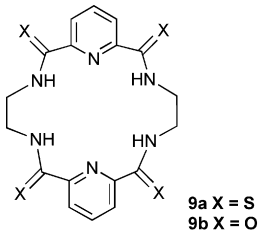


Fig. 1. X-ray crystal structure of the chloride complex of receptor **9a**.



Scheme 1.



Chmielewski and Jurczak have reported a series of neutral macrocyclic tetraamides **10–13** containing two 2,6-diamidopyridine groups linked *via* short aliphatic chains (Scheme 1) [18]. These receptors contain well-defined and relatively rigid cavities, with all the amide hydrogen atoms directed inwards by intramolecular hydrogen bonding to the lone pairs of the pyridine nitrogen atoms. The stability constants of receptors **10**, **11** and **13** with various anions were determined by ^{1}H NMR titrations in DMSO-d_6 solution (Table 1). Enlargement of the size of the macrocyclic ring from 18 (**10**) to 20 (**11**) atoms resulted in a 30-fold increase in the respective binding constant for chloride, whereas further enlargement by four methylene units causes reduction of affinity towards Cl^- by two orders of magnitude (Table 1). This suggests a very good size complementarity between chloride and 20-membered macrocycle **11**. The 24-membered macrocycle **13** is large enough to accommodate two of the oxygen atoms of phosphate, sulfate or carboxylate anions therefore, strong interactions between the receptor and these anions were expected. However, the binding constants of receptor **13** with carboxylate, phosphate and sulfate anions are relatively small. This suggests that in all these cases, only one oxygen atom of the anion is involved in binding with the receptor. The hypothesis of monodentate binding mode of oxoanions with tetraamides **10–13** also explains why the effect of ring size on binding constant trend with chloride is qualitatively the same as the binding constants with acetate, phosphate and sulfate.

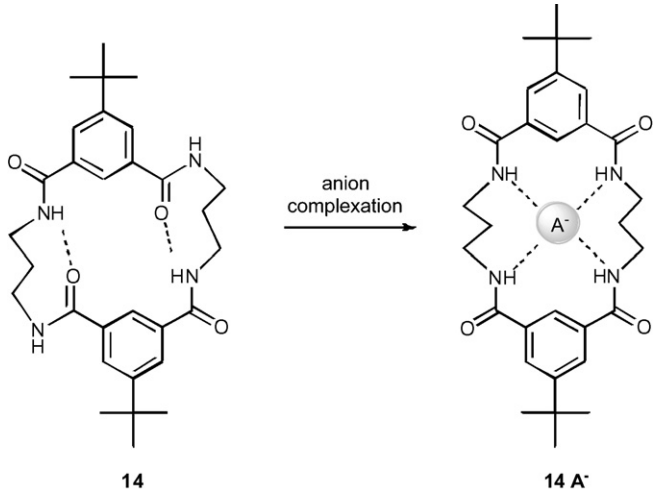
Table 1
Association constants[a] K_a (M^{-1}) for the formation of 1:1 complexes of receptors **10**, **11** and **13** with various anions in DMSO-d_6 at 298 K

Anion	10	11	13
Cl^-	65[b]	1930	18
$PhCOO^-$	202	2283	301
AcO^-	2640[b]	3240	310
$H_2PO_4^-$	1680[b]	7410	450
HSO_4^-	<5	75	<5

[a] Errors are estimated to be <10%. Tetrabutylammonium salts used as anion sources.
[b] Values from ref. [17].

The same authors also examined whether isophthalamide analogues of these systems would function as more efficient anion receptors [19]. The stability constants of receptor **14** with various putative anionic guests were determined under analogous conditions to that employed for receptor **10** with the results revealing that the isophthalamide-based receptor **14** has a lower anion affinity than the pyridine containing receptor **10**. This result could be explained in terms of competition between anion complexation and intramolecular hydrogen bonding, arising from the preferred *syn-anti* conformation existing in the free macrocyclic amide. These studies demonstrated that anion complexation is able to switch both isophthalamide groups into a *syn–syn* conformation, breaking two intramolecular hydrogen bonds (Scheme 2).

Crystal structures of the tren-based polyamide cryptand **15** with HCl and fluoride were reported by Bowman-James and co-workers revealing that the anions are encapsulated inside the receptor cavity (Fig. 2) [20]. This compound showed high affinity and selectivity for fluoride, with the anion symmetrically bonded to the six N–H groups. Association constants (log K) for this receptor and different anions, added as tetra-



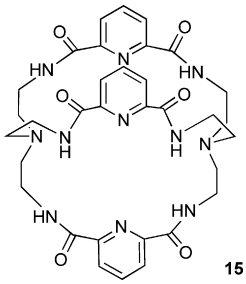
Scheme 2.

Table 2
Association constants[a] K_a (M^{-1}) and binding free energies (kcal mol^{-1}) for the formation of 1:1 complexes of receptor **17a** with halide anions in $CDCl_3$ at 298 K

	F^-	Cl^-	Br^-	I^-
K_a	4.44×10^2	9.91×10^2	1.91×10^2	80
ΔG°_{298}	−3.59	−4.07	−3.09	−2.58

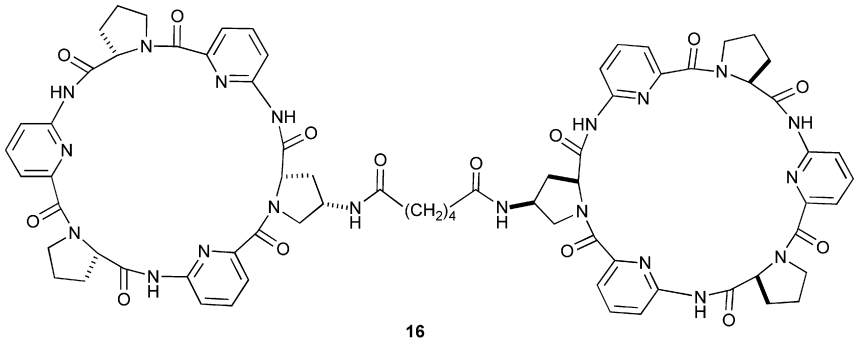
[a] Errors are estimated to be <10%. Tetrabutylammonium salts used as anion source.

butylammonium salts, were calculated by ^1H NMR titration experiments in DMSO-d_6 at >5 (F^-, slow exchange), 3.47 (Cl^-), 3.38 (AcO^-), 3.3 ($H_2PO_4^-$), 1.93 (NO_3^-), 1.83 (HSO_4^-) and 1.60 (Br^-).



15

Kubik et al. prepared a receptor **16** containing two linked hexapeptide units [21]. This receptor binds anions in 1:1 methanol/water mixtures efficiently, with high affinity and selectivity for sulfate. Stability constant for compound **16** for sulfate (added as Na_2 SO_4) was calculated at $3.5 \times 10^5\ M^{-1}$ by ^1H NMR titration experiments in 1:1 D_2O/CD_3OD mixtures versus $710\ M^{-1}$ for chloride (added as NaCl). The same authors reported a combinatorial optimization of the linker in this system [22].



16

Cheng and co-workers have synthesized two cystine–glycine-based cyclopeptides containing alkyl bridges (Fig. 3) [23]. Binding studies with halide ions showed that macrocycle **17a** possessed good affinities for F^-, Cl^- and Br^- and a low affinity with I^- (Table 2), whereas macrocycle **17b** failed to bind any of the halide ions and no changes were observed in the proton NMR spectrum of this receptor upon addition of the anions. Two-dimensional NMR studies suggest that all the amide NH groups are oriented into the interior of the ring in the case of **17a**, while receptor **18b** presents an unfavourable conformation

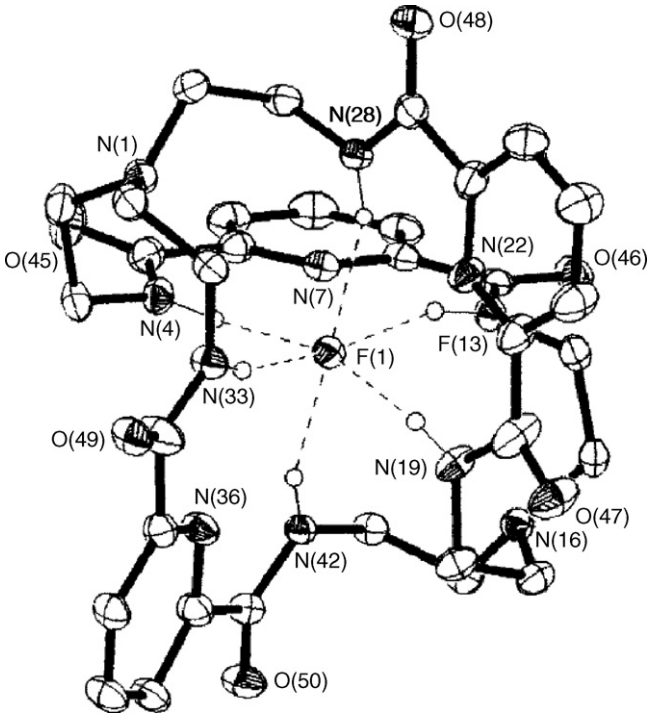
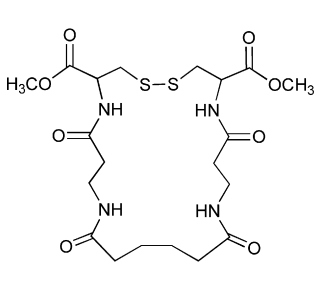
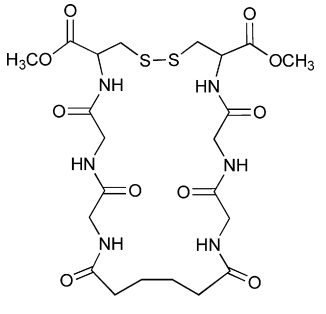


Fig. 2. X-ray crystal structure of the fluoride complex of cryptand **15**. Reproduced with permission from J. Am. Chem. Soc. 125 (2003) 10152. Copyright American Chemical Society 2004.

for anion recognition, with two carbonyl groups oriented into the cavity.



17a



17b

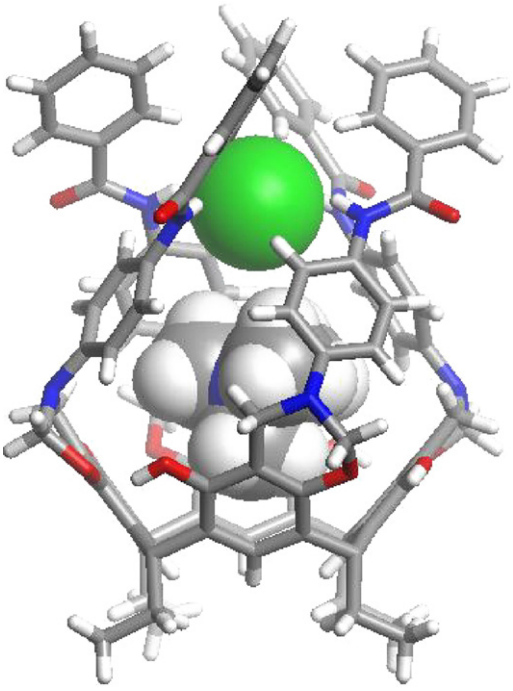
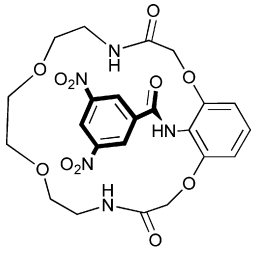


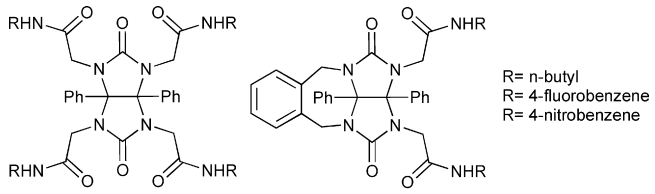
Fig. 3. X-ray crystal structure of **21**·TMACl.

Piatek and Jurczak reported the macrocyclic compound **18** bearing a 3,5-dinitrophenyl group that is able to act as colorimetric anion sensor [24]. Solutions of this receptor in both DMSO and acetonitrile showed dramatic changes of colour upon addition of fluoride, acetate and dihydrogenphosphate added as tetrabutylammonium salts, from colourless to blue, yellow and purple, respectively. ^{1}H NMR titration experiments in DMSO-d_6 allowed the calculation of association constants for compound **18** and F^- ($7.8 \times 10^6\,M^{-1}$), AcO^- ($337\,M^{-1}$), $H_2PO_4^-$ ($142\,M^{-1}$), HSO_4^- ($32\,M^{-1}$) and Cl^- ($5\,M^{-1}$). When these experiments were repeated in deuterated acetonitrile, roughly similar values are obtained in the case of fluoride and acetate. However, the value obtained for dihydrogen phosphate is enhanced to $4271\,M^{-1}$, which is attributed to additional interactions of the –OH groups of the anion and the ethereal oxygen atoms of the receptor in this solvent.



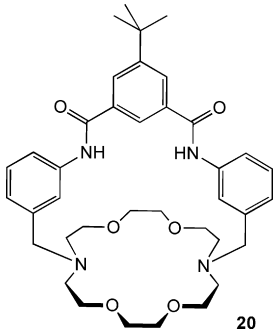
18

Kang et al. have reported the synthesis of several anion receptors based on a glycoluril molecular scaffold containing either two (**19a**) or four (**19b**) amide groups (Fig. 2) [25]. Receptor **19a** is selective for fluoride and acetate ions, forming 1:1 complexes in which all four amide groups are involved. The binding constant for **19a** when R = *n*-butyl in CD_3CN was found to be $1.8 \times 10^5\,M^{-1}$ with acetate and $2263\,M^{-1}$ with fluoride. Bigger or less basic anions are bound only weakly. Receptor **19b**, containing two amide hydrogen bonds in a tweezer-type arrangement shows selectivity for Y shaped carboxylate anions.



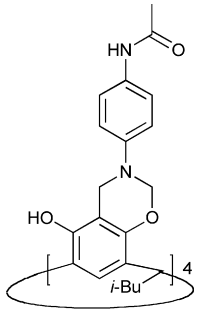
19a **19b**

Smith and co-workers have continued their studies on macrobicyclic ion-pair receptors containing adjacent anion and cation binding sites [26,27], and demonstrated the steric selectivity of the macrobicyclic compound **20** toward different alkylammonium cations, enhanced by the simultaneous binding of the anion [28]. The association constants towards different alkyl ammonium chloride salts were calculated in $CDCl_3$/DMSO-d_6 85:15 at $50\,M^{-1}$ for Bu_4N·Cl, $2.0 \times 10^4\,M^{-1}$ for *n*-$PrNH_3$·Cl, $2.0 \times 10^2\,M^{-1}$ for *i*-$PrNH_3$·Cl and $10\,M^{-1}$ for Et_2NH_2·Cl. The binding selectivity is attributed to the deep penetration of the ammonium cation into the receptor cavity.



20

Atwood and Szumna have reported an ion-pair receptor based on a calixarene type molecular capsule **21** that forms complexes with tetramethylammonium halide salts [29]. The cation is deeply included into the capsule whereas the anion is bound through the sum of electrostatic attraction and the interaction with four amide N–H groups. The X-ray structure of this receptor binding TMACl is shown in Fig. 3.



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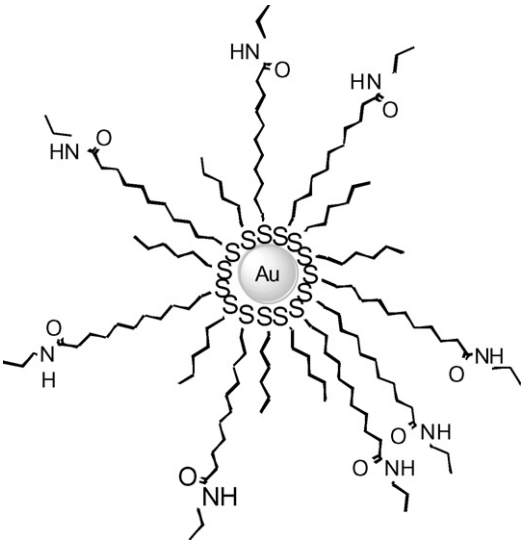


Fig. 4. An amide functionalized gold nanoparticle.

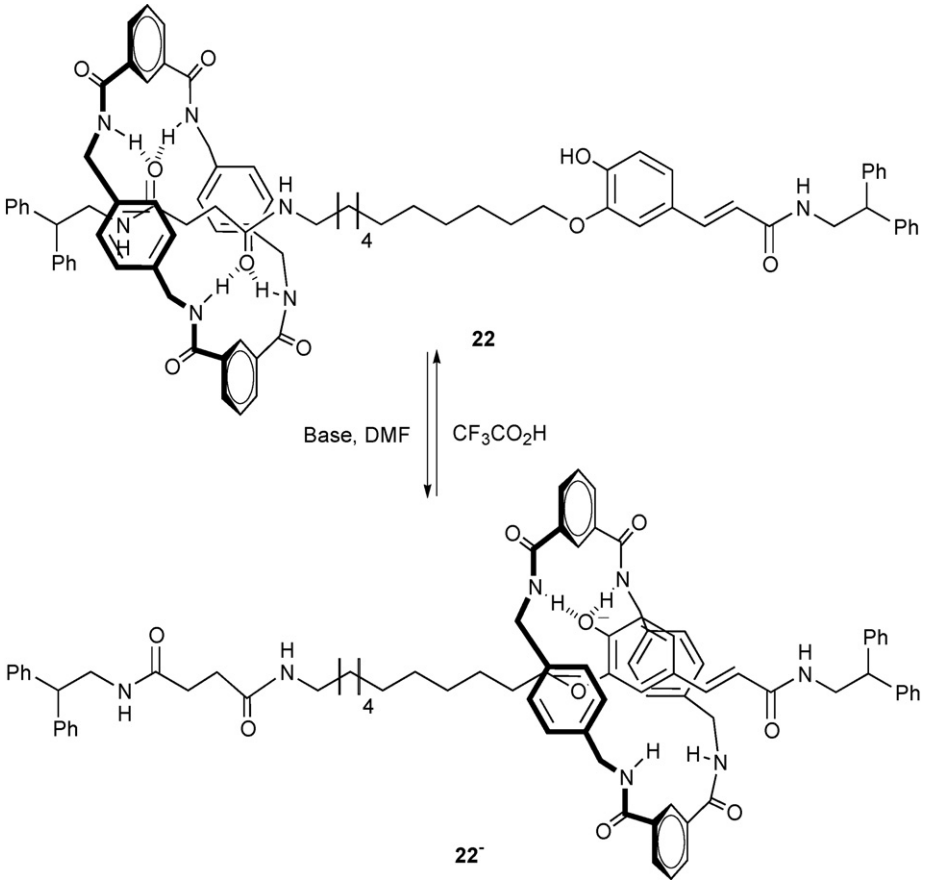
Watanabe et al. investigated the use of gold nanoparticles, functionalized with amide groups, as anion sensors [30] (Fig. 4). The binding properties of the nanoparticles were evaluated through UV titrations experiments and revealed that they are capable of optically sensing changes in the anion concentration at 10^{-6} M level, improving by three orders of magnitude the detection limit of simple neutral amide ligands.

Keaveney and Leigh have reported the use of hydrogen bonding to an anion to switch the position of a macrocycle in a bistable molecular shuttle [31]. Rotaxane **22** was synthesized from a thread equipped with two (succinamide and cinnamate) potential hydrogen-bonding stations. The succinamide group displays favourable hydrogen-bonding interactions with benzylic amide macrocycles, whereas the cinnamate group is a powerful hydrogen-bond acceptor in its deprotonated form. Protonation–deprotonation processes on the thread induced translation of the macrocycle between the hydrogen-bond acceptor stations (Scheme 3). The shuttle has several remarkable features, including that translocation of the macrocycle only occurs in solvent systems where the designed hydrogen-bonding interactions are relatively weak (and competing hydrogen-bonding interactions weaker still), and that under these conditions shuttling is unaffected by the nature of the counter-cation or the presence of alternative anionic hydrogen-bond acceptors.

2.2. Urea-based receptors

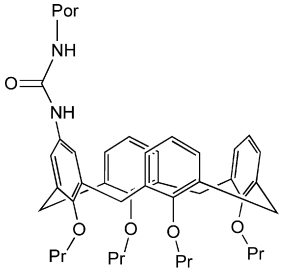
Urea and thiourea binding groups have been widely used as anion receptor moieties as they are excellent hydrogen-bond donors, forming particularly strong complexes with carboxylates [32–34].

Equipping calixarene scaffolds with anion binding units, and particularly urea groups, has been widely used to pro-



Scheme 3. Reversible acid–base induced displacement of the macrocycle along the thread in rotaxane **22**.

duce anion receptors [35]. Lhòtak and co-workers have reported calix[4]arene-porphyrin conjugates **23–26** that are connected *via* urea groups and studied their binding properties by UV–vis titration experiments in dichloromethane. They found that the binding constants of chloride and bromide halides are very similar for **24**, **25** and **26**, indicating that the urea spacers are flexible enough to accommodate these anions regardless of their mutual position. Larger anions like iodide or nitrate showed significant differences in their association constants owing to steric hindrance in the binding site [36].



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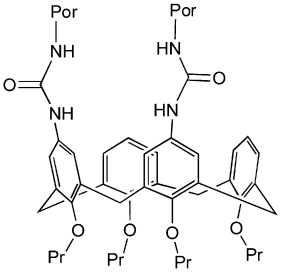

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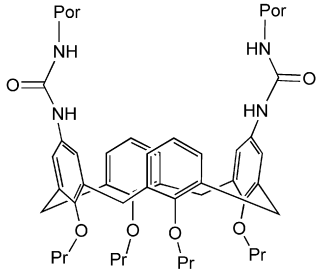

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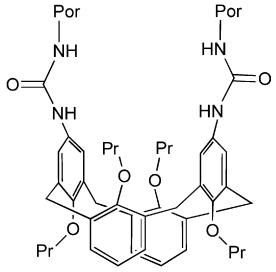
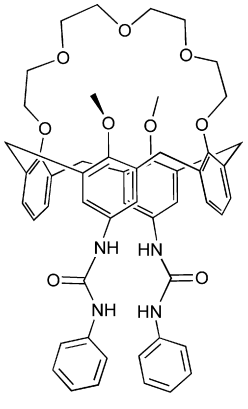


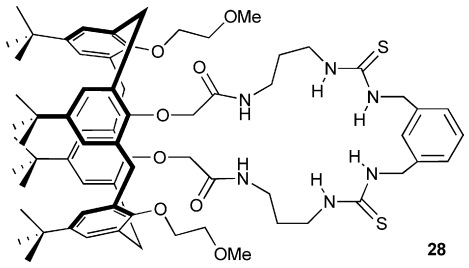
26

Tuntulani and co-workers have synthesized a crown ether strapped calix[4]arene containing two urea groups (**27**) and demonstrated that in the presence of Na^+ ions the affinity of the receptor for dihydrogen phosphate anions increases notably. Association constants calculated by ^1H NMR titration experiments in DMSO-d_6 were 200 and 1028 M^{-1} in the absence/presence of 1.2 equivalents of $NaPF_6$ [37].



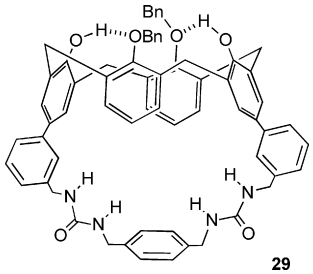
27

Kilburn and co-workers have described the synthesis of the ditopic receptor **28**, which contains an amide/ether functionality and a bisthiourea moiety for cation and anion binding, respectively [38]. This compound binds effectively acetate and phenyl phosphinate whereas diphenyl phosphonate is bound less strongly. The receptor also binds group 1 metal cations, and in the presence of Na^+, the binding affinity for acetate is quenched, as addition of the anion leads to the sequestration of the cation from the receptor [39]. On the other hand, diphenyl phosphonate binding is favoured by the presence of the cation (K_a 1800 and 2200 M^{-1} for **28** and **28**·Na^+, respectively).



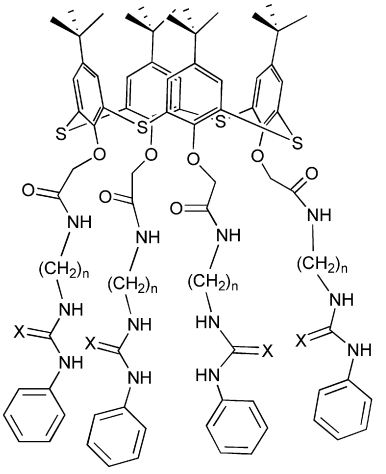
28

Fukazawa and co-workers have synthesized an upper rim bridged calix[4]arene-based receptor **29** containing two urea groups and evaluated its anion binding ability by ^1H NMR titration experiments in DMSO-d_6 [40]. This molecule is capable of selectively binding dicarboxylates over monocarboxylates. For example, the stability constant for the benzoate complex was found to be $43 \pm 2\ M^{-1}$ meanwhile isophthalate was bound with a stability constant of $490 \pm 30\ M^{-1}$. The authors compared the observed behaviour with a previously reported bisureidocalix[4]arene [41] and *N*,*N*′′-(*p*-xylylene)bis(*N*′-benzylurea) [42], concluding that it is the combination of the *p*-xylylenebisurea and the calix[4]arene (which presumably pre-organizes the binding site for dicarboxylate recognition) that is responsible for the selectivity.



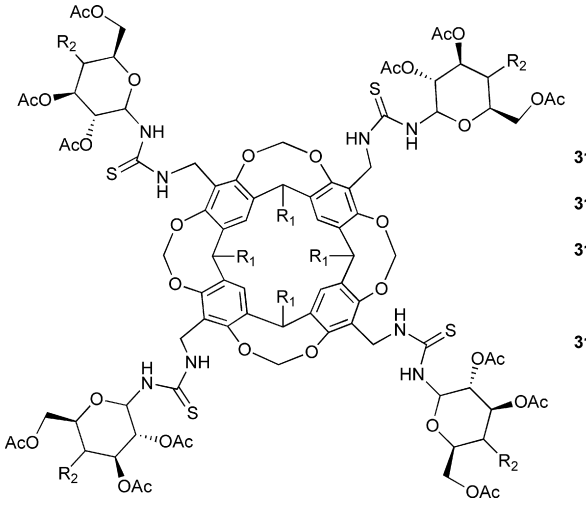
29

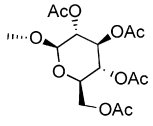
Lhoták and co-workers have reported the first example of anion recognition by a thiacalixarene [43]. This group synthesized several thiacalix[4]arene derivatives **30a–d** bearing ureido or thioureido functions on the lower rim, and studied the complexation abilities of these receptors towards chloride and other anions by ^1H NMR titrations in $CDCl_3$–CD_3CN 4:1 (v/v) solvent mixtures. They found these derivatives to be more effective chloride receptors than analogous receptors based on regular calix[4]arenes (3480 M^{-1} for compound **30a** against 2670 M^{-1} for the parent calix[4]arene).



30a X= S, n= 2
30b X= S, n= 3
30c X= S, n= 6
30d X= O, n= 2

Resorcinarene-based cavitands have also been used as molecular scaffolds to prepare anion receptors [44,45]. Verboom and Reinhoudt have constructed a series of saccharide-thiourea functionalized cavitands **31**. Saccharide functionalization improved the solubility of these derivatives. Association constants with different anions were calculated by using ESI-MS based methods. The receptor showed the higher affinities for chloride with values up to $1.5 \times 10^4\ M^{-1}$ in acetonitrile, more than 20 times higher than the corresponding values for bromide.



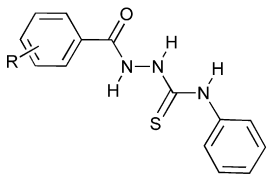
31a R_1= Me, R_2= ····OAc
31b R_1= Me, R_2= —OAc
31c R_1= C_5H_{11}, R_2= ····OAc
31d R_1= Me, R_2= 

Jiang and co-workers have reported a series of neutral *N*-(substituted-benzamido)-*N*′-phenylthioureas **32a–h** [46] that show large red shifts in their absorption spectra upon anion binding and substantially enhanced anion affinities (13–590 times) compared with their *N*′-phenylthiourea counterparts. The binding constants towards different anions were determined measuring the absorption spectra of the receptor in acetonitrile (Table 3). Interestingly, the authors found that *N*-(*p*-ethoxybenzamido)-*N*′-(*p*-nitrophenyl) thiourea showed sensitive and selective binding to AcO^- in acetonitrile containing 10% water by volume with a binding constant of $1.74 \times 10^5\ M^{-1}$ (that is higher than that of *N*-phenyl-*N*′-(*p*-nitrophenyl)-thiourea for binding AcO^- in pure acetonitrile).

Table 3
Binding constants[a] K_a (M^{-1}) of receptor **32** with different anions in acetonitrile

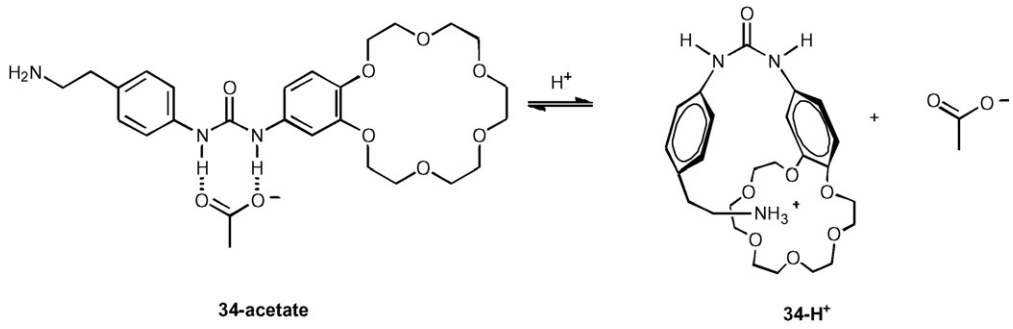
Compound	F^-	AcO^-	$H_2PO_4^-$
32a R = *p*-OC_2H_5	0.188×10^6	1.71×10^6	0.0123×10^6
32b R = *p*-CH_3	0.157×10^6	1.84×10^6	0.0169×10^6
32c R = *m*-CH_3	11.5×10^6	12.1×10^6	32.4×10^6
32d R = H	0.0694×10^6	0.297×10^6	0.0053×10^6
32e R = *p*-Cl	0.510×10^6	5.58×10^6	0.0399×10^6
32f R = *p*-Br	0.158×10^6	1.47×10^6	0.509×10^6
32g R = *m*-Cl	0.0562×10^6	4.05×10^6	0.090×10^6
32h R = *p*-NO_2	0.685×10^6	2.48×10^6	0.138×10^6

[a] Anions added as their tetrabutylammonium salts.

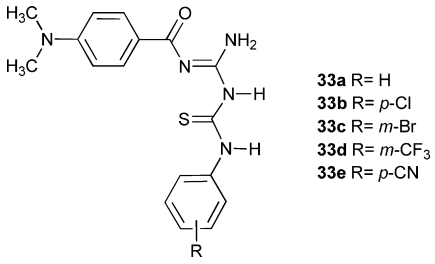


32a R= *p*-OC_2H_5
32b R= *p*-CH_3
32c R= *m*-CH_3
32d R= H
32e R= *p*-Cl
32f R= *p*-Br
32g R= *m*-Cl
32h R= *p*-NO_2

The same authors have developed a series of intramolecular charge transfer (ICT) dual fluorescent anion receptors **33** in which a phenylthiourea anion-binding site is linked to a charge transfer (CT) fluorophore, *p*-dimethylaminobenzamide, through an iminoyl linker [47]. The binding constants of the receptor with different anions were calculated employing both the ICT dual fluorescence intensity ratio and absorption titrations, and found to range from 10^4 to $10^6\ M^{-1}$ and vary in general in the order of $F^- > OAc^- > H_2PO_4^- \gg HSO_4^-, Br^-, Cl^-$, in agreement with that observed with other neutral thiourea-based receptors. The anion sensing was signaled by a blue shift in the CT emission and by a decrease in the CT to locally excited state (LE) intensity ratio.

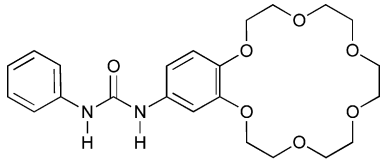


Scheme 4. Proton switchable anion binding by receptor **34**.



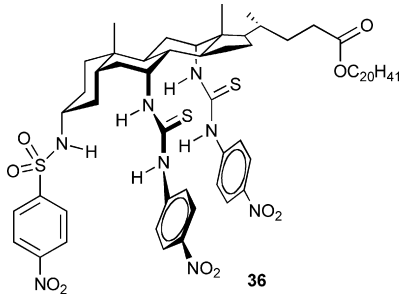
Al-Sayah and Branda reported a *N*,*N*′-diphenylurea receptor **34** equipped with 18-crown-6-ether and primary amine groups in the aromatic rings [48]. This compound represents an example of a proton switchable system. While this receptor is able to coordinate anions, such as acetate, protonation of the amine groups produces a conformational change on the receptor because of the complexation of the ammonium group by the crown ether, quenching the anion receptor ability of the this compound, which is only reactivated in the presence of a large excess of the anion (Scheme 4).

Barboiu et al. have synthesized a similar ion-pair receptor based, consisting in a 4-phenyl urea-benzo-15-crown-5 receptor **35**, and demonstrated its ability to transport NaX salts through liquid chloroform membranes, favoured by the cooperativity between the anion and cation binding [49].



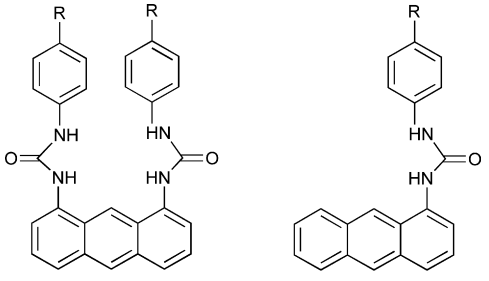
35

Davis and co-workers have continued their work on cholapods, receptors derived from cholic acid [50–52]. They demonstrated the ability of urea-substituted cholapods to transport chloride and promote phospholipid translocation in vesicle and cell membranes. They equipped this molecular scaffold with two thiourea and a sulfonamide groups as anion binding units, and calculated the association constants of this receptor **36** towards different anions, employing voltammetry at the interface between two immiscible electrolyte solutions (ITIES) [53]. The values obtained for the association of fluoride, chloride and bromide, respectively, with **36** in dichloroethane were found to be 1×10^{12} ($\pm 0.5 \times 10^{12}$), 5×10^{12} ($\pm 2 \times 10^{12}$) and 2×10^{11} ($\pm 0.5 \times 10^{11}$) M^{-1}, respectively, values which are amongst the highest yet reported to an electroneutral receptor.

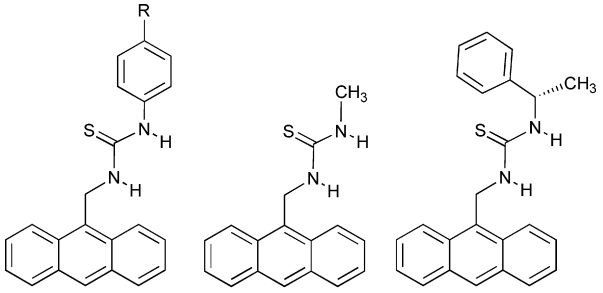


36

Several reports have appeared discussing anion receptors containing urea and thiourea derivatives attached to anthracene groups employed as fluorescent probes. Yoon and co-workers reported a series of new colorimetric and fluorescent sensors for fluoride and pyrophosphate ions in which two *p*-nitrophenylurea groups or two phenylurea groups are attached to the first- and eight-positions of anthracene **37**, **38** [54]. The stability constants for receptor **38** were calculated from fluorescent titration experiments in DMSO, and were found to be 108,000, 9700 and 6000 M^{-1} for fluoride, bromide and pyrophosphate, respectively. Receptor **38** showed a higher affinity for anions (approximately 250 times) than receptor **40** owing to the cooperative effect of the two thiourea groups. Anion complexation was enhanced by the formation of a hydrogen bond from the 9-H of anthracene (between the two urea groups) to both fluoride or pyrophosphate ions.



Gunnlaugsson et al. have studied several receptors **41–44** that contain a thiourea group linked to an anthracene fluorophore *via* a methylene spacer [55]. These receptors behave as ideal photoinduced electron transfer (PET) chemosensors with the fluorescence emission quenched upon anion recognition and no other spectral changes being observed. The anion recognition occurred through 1:1 hydrogen-bonding complexes between the thiourea NH groups and the anion, with a higher degree of fluorescence quenching by fluoride followed by acetate and dihydrogenphosphate, while chloride and bromide do not induce any changes on the fluorescence spectra (all experiments carried out in DMSO).



41 R= H
42 R= CF_3

43

44

The mode of interaction of certain basic anions with neutral hydrogen-bond donor anion receptors is currently being re-examined by a number of research groups. In 2002, Gale and co-workers reported that fluoride, rather than binding to 2,5-diamidopyrrole based anion receptors containing electron-withdrawing substituents, would deprotonate the receptor leading to the formation of an anionic pyrrole species as confirmed by X-ray crystallography [56,57]. If the receptor was appropriately functionalized, this deprotonation process could result in a colour change with the receptor functioning as a colorimetric fluoride sensor [58]. Contemporaneously with these latter findings, Gunnlaugsson et al. discovered that an anion receptor containing a secondary amine and a urea group could be deprotonated (at the amine group) upon addition of fluoride leading to a colour change [59]. Fabbrizzi and co-workers have reported a detailed study of the interaction of anions with a simple urea (1,2-bis(4-nitrophenyl)urea) **45** [60]. They found that the association constants of several oxoanions depends on the partial negative charge located on each oxygen atom of the anion, so K_a values increase with the basicity of the anion following the natural order ($NO_3^- < HSO_4^- < NO_2^- < H_2PO_4^- < C_6H_5COO^- < CH_3COO^-$). Chloride interacts with both NH protons of the urea subunit, leading to a binding behavior similar to that found for oxoanions. On the other hand, fluoride behaves peculiarly because its small size and high basicity. It establishes a strong hydrogen-bond interaction with the urea protons, and in the presence of a second fluoride ion, proton transfer occurs with formation of the stable complex HF_2^- and deprotonation of the urea subunit. This process is signalled by the presence of a charge transfer complex absorption band in the visible region, leading to a change of colour in the receptor. A view of the X-ray structure of the complex **45**-benzoate is shown in Fig. 5.

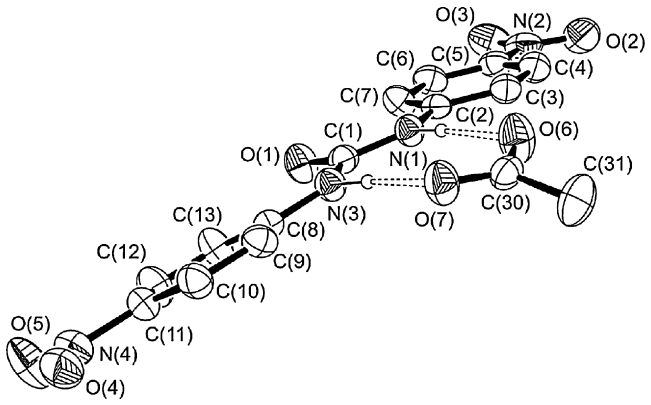
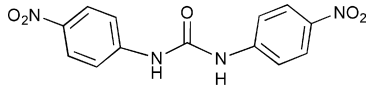
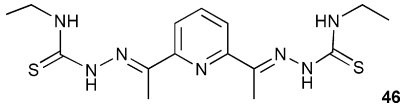


Fig. 5. The X-ray crystal structure of the benzoate complex of **45**. Reproduced with permission from J. Am. Chem. Soc. 125 (2004) 16507. Copyright American Chemical Society 2004.



45

In a related work, Fabbrizzi and co-workers have reported a chromogenic sensor for fluoride ions **46**, which possesses two thiourea-containing unsaturated arms appended to a pyridine ring (Fig. 13) [61]. In the presence of fluoride, the interaction with the thiourea hydrogen atoms enhances π delocalization and shifts the π–π^* transition from the UV to the visible region resulting in the generation of a yellow colour, even in the absence of a defined chromophore. Spectrophotometric titrations in MeCN indicated the 1:1 stoichiometry of the adduct and with an association constant $\log K_{ass} = 4.14 \pm 0.02$. This receptor appears to be a specific sensor for the fluoride ion and the spectrophotometric response of **46** to the fluoride concentration does not suffer interference from any other anionic analyte even when present at millimolar concentrations.



46

2.3. Pyrrole-based receptors

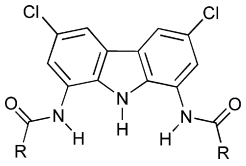
Pyrrole-based receptors have continued to attract a great deal of interest in the last few years, and several groups have reported anion-binding receptors containing this group. Jurczak and co-workers have reported a new family of receptors containing a carbazole group functionalized with two amide groups in the first- and eight-positions **47a–b** [62]. The rigidity of these systems and enhanced acidic character of the pyrrole ring resulting from the conjugation with the two benzene rings provide an interesting and versatile building block for the construction of anion receptors. The stability constants of receptors **47a** and **b** with various anions, added as tetrabutylammonium salts, were determined by ^{1}H NMR titration experiments in DMSO-d_6/0.5% H_2O solution and found to be 13 M^{-1} (**47a**-chloride), 115 M^{-1} (**47b**-chloride), 1230 M^{-1} (**47a**-benzoate), 8340 M^{-1}

Table 4
Binding constants[a] K_a (M^{-1}) of receptor **48** with different carboxylates in water (10% DMSO)

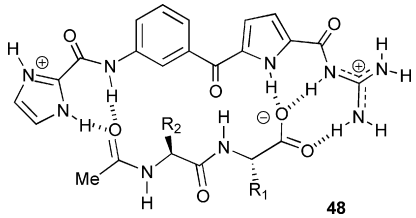
	Carboxylate					
	Gly–Gly	Ala–Ala	Val–Ala	Val–Val	Ala	Gly
K_a	15900	30600	43800	54300	7400	5200

[a] Errors are estimated to be <±25%.

(**47b**-benzoate), 1910 M^{-1} (**47a**-dihydrogenphosphate) and 19,800 M^{-1} (**47b**-dihydrogenphosphate).



Schmuck and Geiger have reported a cationic receptor containing a guanidiniocarbonylpyrrole unit **48**, designed based on theoretical calculations, to bind dipeptides containing free carboxylate groups [63]. The guanidiniocarbonylpyrrole moiety binds the carboxylate whereas the rest of the receptor is expected to stabilize the complex by additional hydrogen bonds with the dipeptide backbone (Fig. 15). The complexation properties of **48** were studied by UV titration in water/10% DMSO and the association constants of the receptor with various peptides and dipeptides calculated (Table 4). Dipeptides were bound with $K_{ass} > 10^{-4}\ M^{-1}$ (up to 10 times more efficiently than simple amino acids), making this receptor one of the most effective known so far for dipeptides in water. Interestingly, the same authors reported the dimerization of this receptor in the presence of chloride [64].



Gale has reported a variety of anion receptors based on the 2,5-diamidopyrrole skeleton [65]. As previously mentioned, this group has shown that deprotonation of diamidopyrroles containing electron-withdrawing groups in the three- and four-positions leads to the formation of orthogonally arranged hydrogen-bonded dimers (Fig. 6), a promising building block for the synthesis of interlocked materials [66,67].

Gale, Brooker and co-workers have produced a series of diamidopyrrole anion receptors **49–52** derived from pyrrole-2,5-diacetic acid [68]. The stability constants with a variety of anionic guests were studied by ^{1}H NMR titration techniques in acetonitrile-d_3 and were found to be moderately higher to those previously reported for 2,5-diamidopyrroles. As these compounds contain a more flexible hydrogen-bonding array compared with the simple 2,5-diamidopyrroles, this fact suggests that the expanded hydrogen-bonding site is closer to being optimal for these anions despite their increased flexibility.

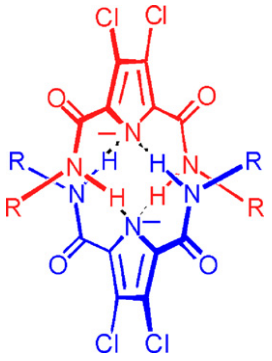
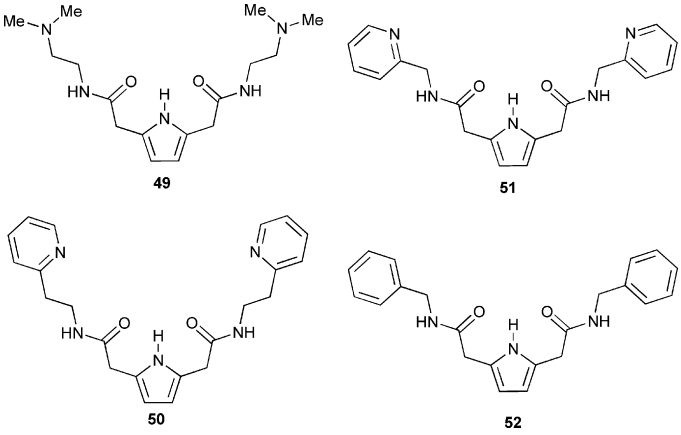
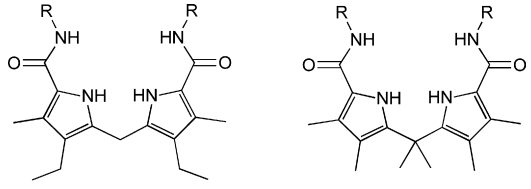


Fig. 6. Hydrogen-bonding array between 2,5-diamidopyrrole anions.



Gale and co-workers have also explore the binding properties of the 5,5′-dicarboxamido-dipyrrolylmethanes [69,70]. These systems displayed a remarkable affinity and selectivity for dihydrogenphosphate in competitive solvent media. Association constants for compound **53a**,**b** required a highly competitive solvent mixture (DMSO-d_6/25% water) to make possible it calculation through ^{1}H NMR titration experiments (234 and 20 M^{-1}, respectively). The limited stability of these derivatives in solution prompted this group to synthesize similar compounds with methyl groups attached to the *meso*-carbon **54a**,**b** in order to prevent oxidation of the receptor to the corresponding dipyrromethene.

The resulting receptors showed a lower affinities for anions than the first systems produced, however, compound **54a** showed good selectivity for dihydrogenphosphate (1092 M^{-1} for dihydrogenphosphate against 124 M^{-1} for fluoride or 41 M^{-1} for benzoate) in DMSO-d_6/5% water solution.

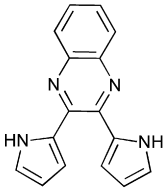


Causey and Allen have reported the anion binding properties of a series of biimidazole diamides **55** [71]. The fluorescence of the biimidazole unit avoids the need to functionalize the receptor with other fluorophore or chromophore groups in order to signal the binding event. The association constants of these receptors towards dihydrogenphosphate and chloride were calculated at 6.8×10^4 to 2×10^4 for $H_2PO_4^-$ and 1.4×10^5 to 4×10^3 for Cl^- by fluorescence spectroscopy in dichloromethane.

Table 5
Binding constants[a] K_a (M^{-1}) of receptors **56–62** with different anions in dichloromethane

Anion	56	57	58	62
F^-	18200	32000	>1000000	
Cl^-	50	550	5800	48000
$H_2PO_4^-$	60	4300	300000	30000
Acetate			46000	175000
Oxalate			30000	24000

[a] Anions added as their tetrabutylammonium salts.



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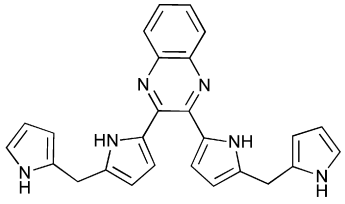

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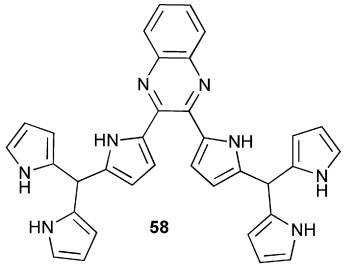

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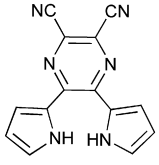

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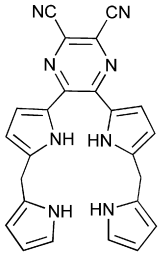

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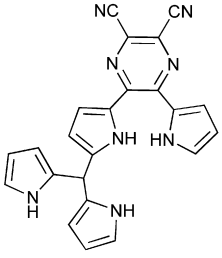

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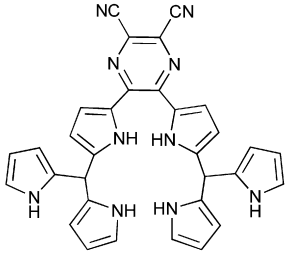

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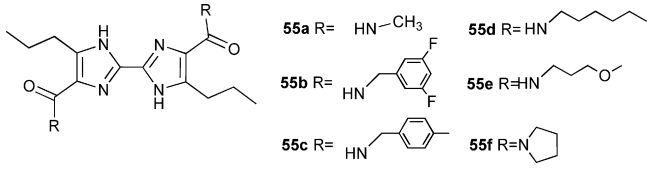
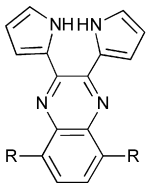


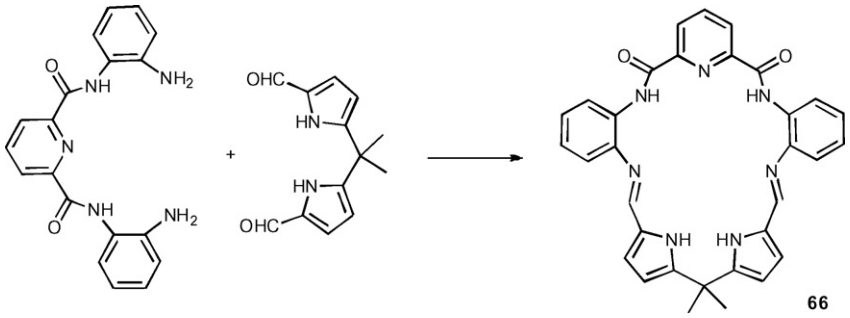
The dipyrrolylquinoxaline (DPQ) group, which was first used as an anion receptor by Sessler and co-workers [72], has been employed in a variety of fluorometric and colorimetric sensors for anions by a number of groups. Sessler has recently prepared a series of oligopyrrolylquinoxalines **56–58** and pyrazine analogues **59–62**. The association constants of these compounds towards different anions were calculated by UV–vis spectroscopy titration experiments in dichloromethane and appear in Table 5 [73,74]. The increasing number of pyrrole groups in **56–58** is reflected in an increase of the association constants values, especially in the case of dihydrogenphosphate, in which case a chelating binding mode is favoured. Changes in the structure of the receptor were shown to result in major changes in anion affinities. For example, compound **62** binds chloride more strongly, while the affinity for dihydrogenphosphate is greatly reduced relative to compound **58**.

Aldakov and Anzenbacher have synthesized a series of DPQs containing different aromatic substituents in the five- and eight-positions, obtaining an improvement of the sensor performance by enhancement of emissivity [75]. These compounds **63a–d** showed a strong selectivity for pyrophosphate over phosphate anion in dichloromethane solutions. Fluorescence quenching experiments gave binding constant between 93,700 and 39,000 M^{-1} for pyrophosphate under these conditions against less than 200 M^{-1} for phosphate.



63a R = Ph
63b R = Ph-OMe
63c R = 3,4 ethylenedioxythiophene (EDOT)
63d R = Ph-N(Me)$_2$

The same group has designed a polythiophene conductive polymer with integrated quinoxaline moieties modified with two pyrrole groups **64** [76,77]. This polymer combines a DPQ group, which is capable of binding anions via hydrogen-bonding, with potential coulombic interactions derived from p-doping the



Scheme 5. Synthesis of macrocycle **66**. *Reagents and conditions*: MeOH, 2.5 equiv. TFA, 15 min, followed by Et_3N.

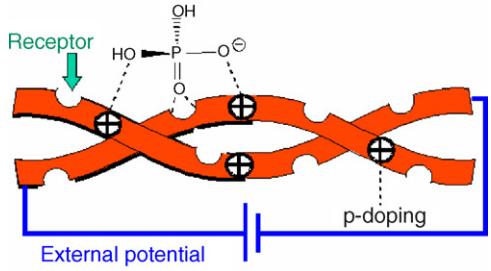
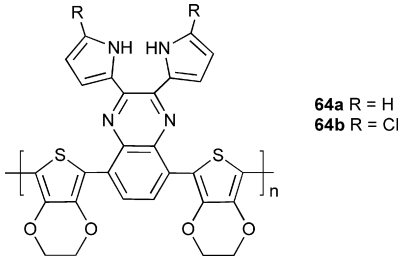
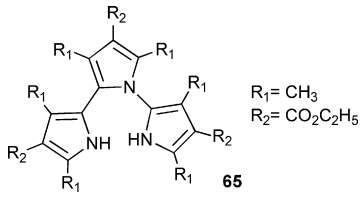


Fig. 7. A schematic drawing of synergy in a p-doped conductive polymer with integrated hydrogen-bonding receptors. Reproduced with permission from J. Am. Chem. Soc. 126 (2004) 4752. Copyright American Chemical Society 2004.

polymer, achieved by using an external voltage, which results in a dramatic increase in the anion-sensor affinity (Fig. 7). An electrochemical quartz crystal microbalance was used to weigh the polymers, which were deposited on a probe before and after exposure to aqueous solutions of anions. Pyrophosphate, dihydrogen phosphate and fluoride (but not chloride) caused a significant increase in the mass of the polymer, suggesting complexation of these species by the polymer. This sensor shows reversible anion-specific changes both in colour and in conductivity upon increasing concentration of anions, thus providing two independent modes of signal transduction and has been employed to sense aqueous phosphate-related anions.

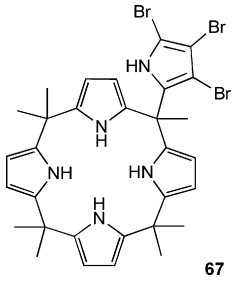


A terpyrrolic analogue of DPQ, that contains two pyrrole anion recognition groups bridged by a central 1,2-linked pyrrole, **65** was described by Sessler and co-workers [78]. This receptor undergoes a visible change of colour when treated with the tetrabutylammonium salts of fluoride, chloride and dihydrogen phosphate. The anion binding constants in dichloromethane were calculated by fluorescence titration experiments and found to be 182,000 M^{-1} for fluoride, 160 M^{-1} for chloride, 60 M^{-1} for bromide and 17,500 M^{-1} for dihydrogen phosphate. These represent an order of magnitude higher than those displayed for the dipyrrolylquinoxaline derivative under identical conditions.



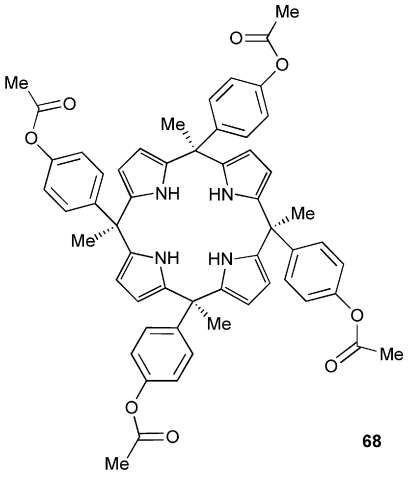
Moving onto macrocyclic systems, Sessler et al. have reported a 2,6-diamidopyridinedipyrromethane **66** derived from the condensation reaction of bis(2-aminophenyl)pyridine-2,6-dicarboxamide and diformyldimethyldipyrrolylmethane (Scheme 5) [79]. This receptor has a large cavity that favours the formation of well-oriented, directional NH-anion hydrogen bonds, allowing it to bind hydrogen sulfate in a strong, 1:1 fashion in acetonitrile ($K_a = 64{,}000 \pm 2600\ M^{-1}$ from UV–vis spectroscopic titrations). Only weak binding interactions were seen in the case of cyanide, chloride and bromide and no detectable affinity for nitrate anion. This feature makes it an attractive candidate for nuclear waste remediation applications, removing sulfate from nitrate-rich low-activity nuclear wastes.

Gale and co-workers have reported synthesis of the pentapyrrrolic calix[4]pyrrole **67**, and compared the anion binding affinity with the parent calix[4]pyrrole using ^1H NMR titration experiments in dicholoromethane-d_2 [80]. The presence of an extra pyrrole unit increased the anion stability constants, specially in the case of carboxylate anions, which are calculated to be higher than $10^4\ M^{-1}$ compared to the 196 and 668 M^{-1} for acetate and benzoate reported in the case of regular calix[4]-pyrrole under these experimental conditions. Modelling studies led to the suggestion that the ability of the macrocycle to interact with both oxygen atoms of the carboxylate anion simultaneously might be the cause of the enhanced carboxylate binding.



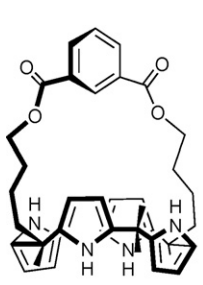
67

Gale and co-workers have reported a deep cavity calix[4]pyrrole **68** which was found to bind fluoride very selectively in DMSO solutions (in fact no binding with other anions was observed) [81]. Theoretical calculations using adaptive umbrella WHAM calculations revealed that this selectivity may be caused by the presence of a small electrostatic positive pocket into which the small fluoride ion can fit. The crystal structure of the fluoride complex was also elucidated (Fig. 8).



68

Calix[4]pyrroles **69**, **70**, **71** and **72** were prepared by the Lee and Sessler groups bearing ether or ester straps of different lengths on one side of the tetrapyrrolic core [82,83]. The authors demonstrated an increase in affinity towards chloride and bromide in DMSO and acetonitrile displayed by these systems compared to simple calix[4]pyrrole derivatives by iso-thermal calorimetry (ITC) experiments.



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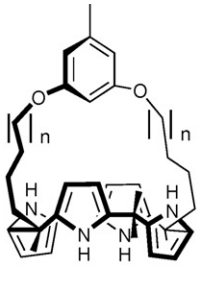


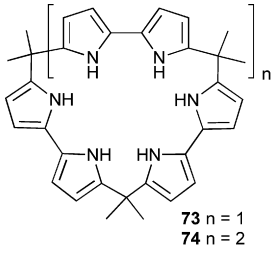
70 n=1
71 n=2
72 n=3

Sessler et al. have also synthesized other bipyrrole-based macrocycles, such as calix[3]bipyrrole **73**, calix[4]bipyrrole **74**, calix[2]bipyrrole[2]furan **75** and calix[2]bipyrrole[2]thiophene **76** [84,85]. The binding constants of these compounds were calculated in acetonitrile-d_3 using ^{1}H NMR titration experiments (Table 6), revealing that calix[3]bipyrrole **73** shows improved affinity for bromide than the parent calix[4]pyrrole, and that calix[2]bipyrrole[2]furan **75** and calix[2]bipyrrole[2]thiophene **76** derivatives display selectivity for carboxylate anions against chloride.

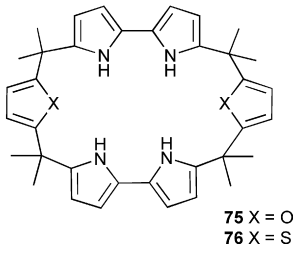
Table 6
Binding constants[a] K_a (M^{-1}) of receptors **73–75** with different anions in acetonitrile

Anion	**73**	**75**	**76**
Cl^-	110000	960	1540
Br^-	100000	37	103
HSO_4^-		125	28
Benzoate	937000	63000	99600
Acetate		78000	139000

[a] Anions added as their tetrabutylammonium salts.

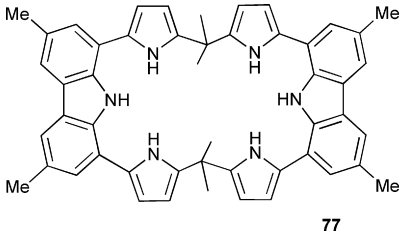


73 n = 1
74 n = 2



75 X = O
76 X = S

Sessler and co-workers have also reported the synthesis of an expanded calixpyrrole-type macrocycle incorporating two carbazole subunits **77** [86]. The anion binding properties of this macrocycle were studied using standard fluorescence titration methods, and revealed that **77** displayed a preference for acetate ($K_a = 229{,}000\ M^{-1}$) relative to larger carboxylate-type anions (benzoate, succinate and oxalate). It also showed good affinity for dihydrogenphosphate ($K_a = 72{,}000\ M^{-1}$) and chloride ($K_a = 35{,}000\ M^{-1}$) anions but no evidence of binding was seen in the case of bromide, nitrate and hydrogen sulfate. Solid state structure of the 1:1 complex formed between receptor **77** and tetrabutylammonium benzoate were obtained by X-ray diffraction analysis (Fig. 9).



77

2.4. Metal-free charged receptors

Anion sensing *via* the use of an indicator displacement strategy was pioneered by Anslyn and co-workers [87–89]. Recently,

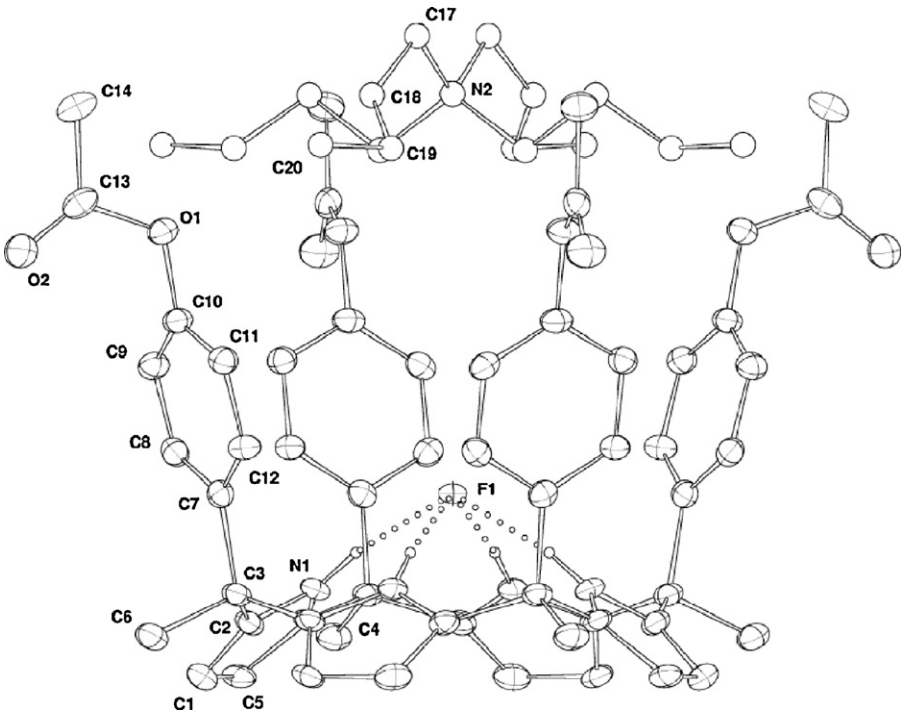


Fig. 8. Crystal structure of the tetrabutylammonium fluoride complex of calix[4]pyrrole **68**. Reproduced with permission from J. Am. Chem. Soc. 124 (2002) 8644. Copyright American Chemical Society 2002.

Zhong and Anslyn have prepared receptor **78**, based on a 1,3,5-trisubstituted-2,4,6-triethylbenzene scaffold [90]. This receptor contains aminoacid-boronic acid side chains and was designed to interact with heparin, a negatively charged oligosaccharide, achieving good affinity and selectivity for this substrate over other similar polysaccharides in HEPES buffer solution at pH 7.4. In order to detect this substrate, the indicator displacement strategy was employed, using pyrocathecol violet as indicator. Heparin is able to displace the indicator from the receptor cavity, producing a change of colour from purple to yellow.

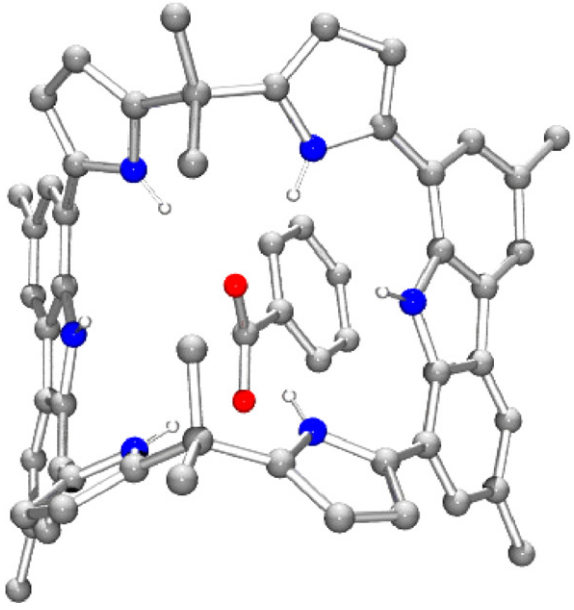
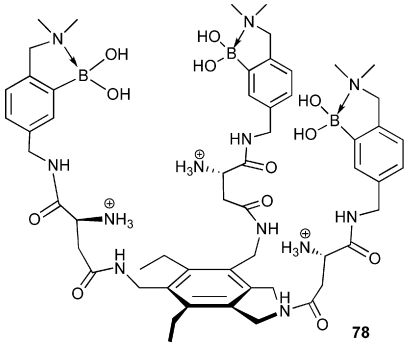
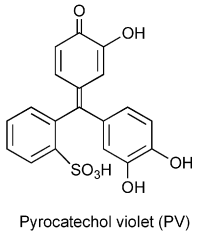
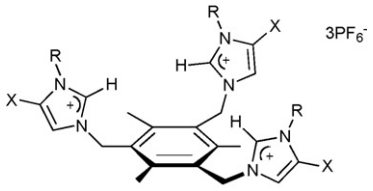


Fig. 9. Crystal structure of the benzoate complex of macrocycle **77**. Reproduced with permission from J. Am. Chem. Soc. 126 (2004) 16073. Copyright American Chemical Society 2004.



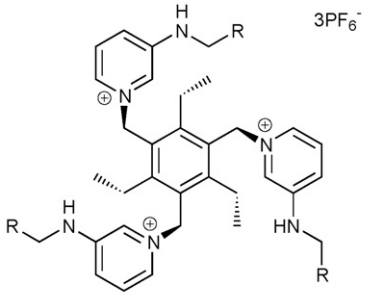


Kim and co-workers reported benzene-based tripodal imidazolium systems **79–81** and studied their binding properties using ^{1}H NMR titration experiments in DMSO-d_6, MeCN-d_3 and mixtures of these solvents [91]. The nitroimidazolium-substituted compound **79** recognizes chloride anions in a 9:1 DMSO-d_6/MeCN-d_3 mixture, with an association constant of 1.1×10^6 M^{-1}. Addition of fluoride causes a nucleophilic attack on the receptor, so derivatives **80** and **81** where used in the studies with this anion, and both showed a high affinity in acetonitrile. The presence of a butyl substituent in **81** reduces the polarity of the microenvironment around the binding site, resulting in an enhanced selectivity for fluoride in more polar solvents compared to the methyl substituted **80**, with association constants in DMSO-d_6 of 1.3×10^3 M^{-1} (**80**) and 2.4×10^3 M^{-1} (**81**).



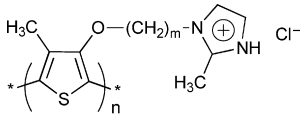
79 R = Me, X = NO_2
80 R = Me, X = H
81 R = *n*-Bu, X = H

Steed and co-workers synthesized a series of tripodal tricationic hosts **82–87** based on a hexasubstituted benzene core with alternating 3-aminopyridinium and alkyl arms to introduce a degree of preorganization in the host [92,93]. This moiety is easily functionalized with redox active (ferrocene) or fluorescent (anthracene) probes. A cone geometry is destabilized by steric interactions in the case of **85–87**, and conformational switch from an alternate 2-up 1-down situation to a cone situation can be monitored by ^{1}H NMR spectroscopy upon anion binding. ^{1}H NMR titration experiments in MeCN-d_3 were used to determine the association constants towards different anions, added as tetrabutylammonium salts. Compound **85** showed very good selectivity for chloride, with $K_a > 10^6\ M^{-1}$ more than 25 times the affinity for other anions, whereas compound **87** is selective for acetate over spherical anions, with K_a values of 49,000 M^{-1} for acetate and 5270 M^{-1} for chloride.

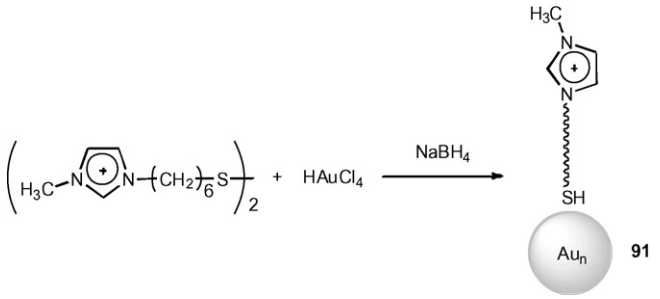


82 R = H
83 R = Fe
84 R = CH_3
85 R = C_6H_5
86 R = $C_6H_4CH_2CH_2CH_2CH_2CH_3$
87 R = 9-anthracenyl

Ho and Leclerc have prepared water-soluble cationic polythiophenes **88** which undergo a change of colour in the presence of iodide [94]. This response is selective over a wide range of anions (F^-, Cl^-, Br^-, CO_3^{2-}, $H_2PO_4^-$, HPO_4^{2-}, CH_3COO^-, $EDTA^{4-}$, SO_4^{2-}) and is based on conformational modifications of the conjugated backbone of the cationic polythiophene upon iodide binding. Fluorimetric detection is also possible since the fluorescence is also selectively quenched by this anion.

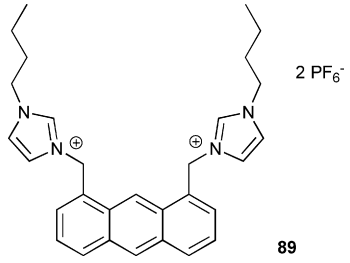


88a m = 2
88b m = 3



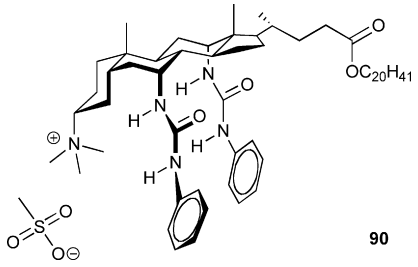
Scheme 6. Synthesis of functionalized gold nanoparticles with methylimidazolium ionic liquids **91**.

Kim et al. have studied the anion binding properties of the imidazolium functionalized anthracene compound **89** [95]. This receptor forms strong (C–H)$^+\cdots$X hydrogen bonds with anions, and, as theoretical calculations predict, selectively recognizes HPO_4^{2-} over other halides in acetonitrile. Binding can be monitored through ^{1}H NMR titration experiments and also *via* fluorescence quenching of the anthracene moiety. Using this method, association constants were found to be ~1,300,000, 7900, 4500 and 600 M^{-1} for $H_2PO_4^-$, Cl^-, Br^- and I^-, respectively, in acetonitrile.



89

Davis and co-workers prepared a "cholapod" derivative **90** equipped with two urea and one quaternary ammonium group, designed to bind spherical anions through N–H and C–H$\cdots$anion interactions [96]. The authors demonstrated its ability to extract anions from aqueous solutions into chloroform solutions and transport anions through non-polar barriers, employing a U-tube apparatus and two aqueous phases separated by a chloroform solution, favouring halides over oxoanions of comparable lipophilicity.



90

Naka and co-workers have synthesized a series of gold nanoparticles functionalized with imidazolium groups **91** (Scheme 6) [97]. Anion exchange on the methyl imidazolium moieties induced changes in the aggregation of the nanoparticles, which led to changes in the solubility of the sample and

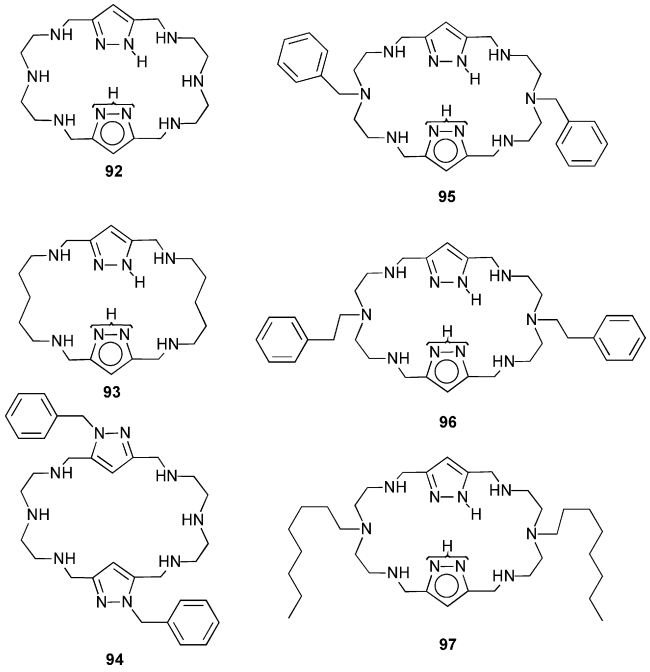
Table 7
First association constants[a] $\log K_a$ observed for macrobicycle **98** at different states of protonation using potentiometry

Species	F^-	Cl^-
98·H_6X	9.54(12)	4.19(13)
98·H_5X	7.84(8)	3.88(9)
98·H_4X	5.65(12)	2.06(26)
98·H_3X	4.86(9)	–

[a] Potentiometric titrations of an approximately 10^{-3} M ligand solution containing an excess of TsOH in the presence of 0.01 M of the corresponding NaX salt and TsONa (0.1 M) to maintain the ionic strength.

colour of the solution, demonstrating that this system may have application as an optical sensor for anions.

Garcia-España and co-workers have reported a detailed study of a series of hexaaza 2 + 2 dipodal macrocycles **92–97** containing 1*H*-pyrazole rings as spacers, as receptors for L-glutamic acid in water [98]. The effect of several structural modifications is reported. The stability of the macrocycle-glutamic acid adduct was found to be higher for receptors bearing a benzyl group on the central nitrogen atoms due to π-cation interactions. Substitution of these central nitrogen atoms with carbon atoms lead to a decrease of the stability constants and the receptors with secondary nitrogens in the middle of the side chains show a reverse dependence of the stability constants with pH.



Steed and co-workers have reported a macrobicyclic azaphane **98** displaying high affinities for fluoride and chloride in its protonated forms (Table 7) [99]. The receptor is selective for fluoride in solution while no binding is observed for either bromide or nitrate. The authors reported X-ray crystal structures of hydrogen halide salts of **98**, showing formation of 1:1 complexes with halide located inside of the cavity of the macrobycicle. Fluoride and chloride anions are held into the azaphane cryptand *via* three N–H and three C–H hydrogen bonds (Fig. 10). Formation

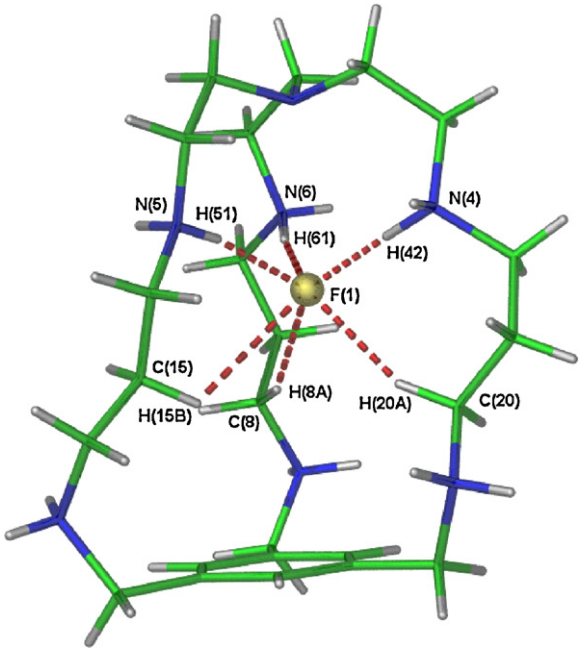
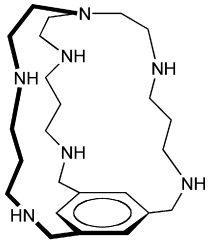
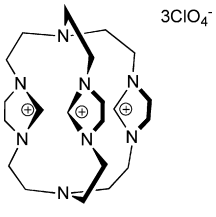


Fig. 10. The X-ray crystal structure of the fluoride complex of compound **98**. Reproduced with permission from J. Am. Chem. Soc. 126 (2004) 12395. Copyright American Chemical Society 2004.

of the bromide and iodide complexes was achieved by the use of highly acidic crystallization conditions, unsuitable for solution studies.



Duan and co-workers reported an imidazolinium based cryptand **99** displaying very high affinity and selectivity for fluoride [100]. The steric requirements of the host prevent anions larger than the fluoride entering the cavity. The stability constant of **99** with fluoride was determined using a competition ^{1}H NMR titration experiments and found to be $\log K_a \sim 12.5$.



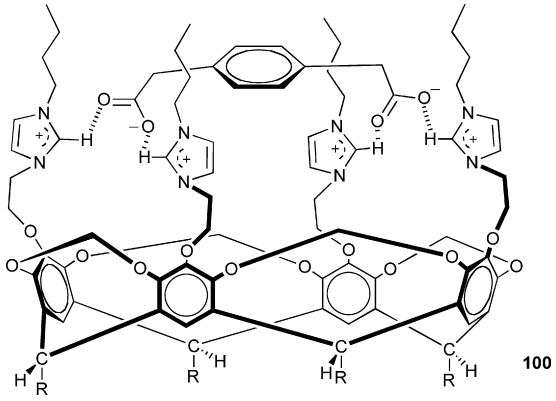
Lee and co-workers have reported the synthesis of a cavitand **100** containing four appended imidazolium groups designed for the recognition of dicarboxylates [101]. The binding properties of this receptor were examined by ^{1}H NMR titration experiments in either DMSO-d_6 or CD_3CN (Table 8). The host is able

Table 8
Association constants of cavitand **100** with different anions

Anion	K_a (M^{-1})[a]	K_a (M^{-1})[b]
1,3-Adamantanedicarboxylate	2100	
Adipate	8100	
Terephthalate	7300	
1,4-Phenylenediacetate	16200	96200
Succinate	200[c]	
Acetate	400[c]	2100[c]
Chloride	210[c]	840[c]
Bromide	100[c]	

[a] In DMSO-d_6.
[b] In CD_3CN.
[c] K_{11}.

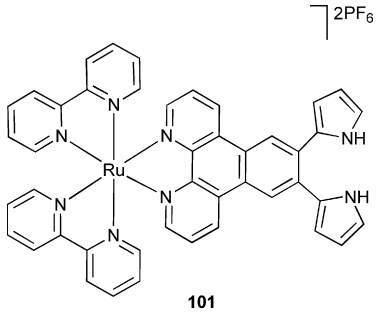
to bind certain dicarboxylates with 1:1 stoichiometry. The highest stability constant was found for 1,4-diphenylenediacetate (K_a = 16,200 M^{-1}), whereas succinate, acetate, chloride and bromide form weaker 1:2 host to guest complexes.



100

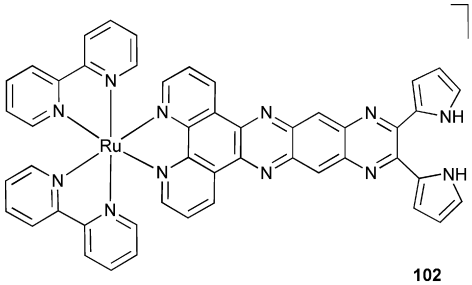
3. Metal and Lewis acid containing anion receptors

A number of research groups have succeeded in synthesizing transition metal complexes containing phenanthroline ligands connected to dipyrrolylquinoxaline units which function as anion receptors. For example, Anzenbacher et al. have prepared the Ru(II) complex **101**, and examined its affinity towards different anions in 2% acetonitrile-dichloromethane solution using UV–vis titration experiments [102]. Complexation of the ligand enhances its anion binding properties by orders of magnitude and the anion-induced changes in the luminescence lifetime allow their use in anion sensing. Association constants were found at 640,000, 428,000, 1700 and 14,000 M^{-1} for F^-, CN^-, Cl^- and $H_2PO_4^-$, respectively.

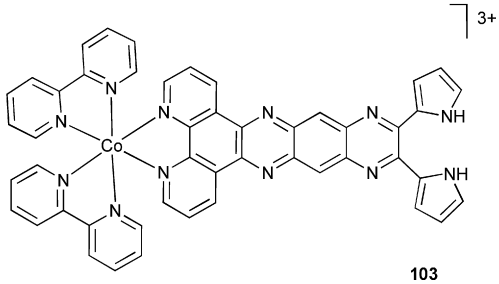


101

Sessler and co-workers have reported similar Ru(II) **102** and Co(III) **103** complexes as perchlorate salts, and studied their anion binding properties by UV–vis spectroscopy in DMSO [103]. Both complexes have strong selectivity for fluoride with association constants of 12,000 (**102**) and 54,000 M^{-1} (**103**) against 10–50 M^{-1} of both complexes with chloride and dihydrogenphosphate. Moreover, addition of tetrabutylammonium fluoride to a red-pink solution of **103** in DMSO causes a change of colour to pale purple.

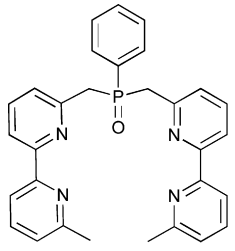


102



103

Luminescent lanthanide complexes have demonstrated their use as anion sensors. Ziessel and co-workers prepared Eu^{3+} and Tb^{3+} complexes equipped with the bis-bipyridine-phenylphosphine oxide ligand **104** as triflate salts [104]. Addition of the tetrabutylammonium salts of different anions (NO_3^-, Cl^-, F^-, CH_3COO^-) to acetonitrile solutions of the complexes result in the displacement of solvent molecules from the coordination of the metal cation, and in the case of nitrate in a dramatic increase in luminescence intensity.



104

Loeb and co-workers have continued their studies of anion receptors based on square planar platinum complexes [105,106], and have reported a platinum(II) complex **105**, containing four urea functionalized *iso*quinoline ligands [107]. The stability constants of the complex towards different anions were calculated by ^1H NMR titrations in DMSO-d_6 (Table 9). The results suggest that, in solution, the receptor adopts a 1,2- or 1,3-alternate conformation in the presence of halides so form-

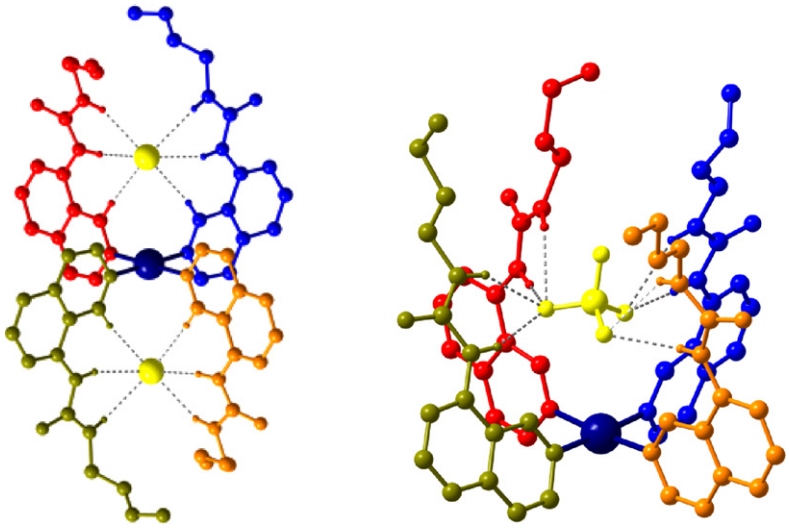


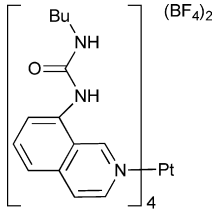
Fig. 11. Ball and stick representations of the chloride and sulfate complexes of **105**. Reproduced with permission from J. Am. Chem. Soc. 126 (2004) 5030. Copyright American Chemical Society 2004.

Table 9
Association constants K_a (M^{-1}) for the formation of complex **105** with various anions[a] in DMSO-d_6 at 298 K

Anion	K_1	K_2
Cl^-	11693	2223
Br^-	1364	450
I^-	1431	52
$H_2PO_4^-$	>10[5b]	
SO_4^{2-}	>10[5b]	

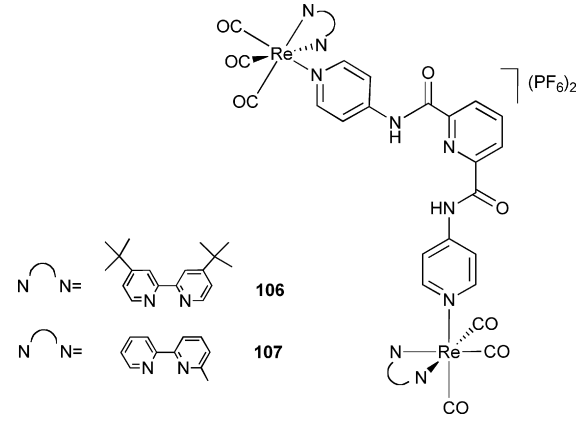
[a] Anions added as $[nBu_4N]^+$ salts except SO_4^{2-} which was added as K_2SO_4.
[b] Estimated value—saturation is seen on addition of one equivalent of the anion.

ing two binding sites for the anions. However, in the presence of dihydrogenphosphate and sulfate, the receptor may adopt a cone conformation, forming a single binding pocket containing eight NH hydrogen-bond donor groups. This was confirmed in the solid state with the crystal structures of the chloride and sulfate salts showing 1,2-alternate and cone conformations, respectively (Fig. 11).



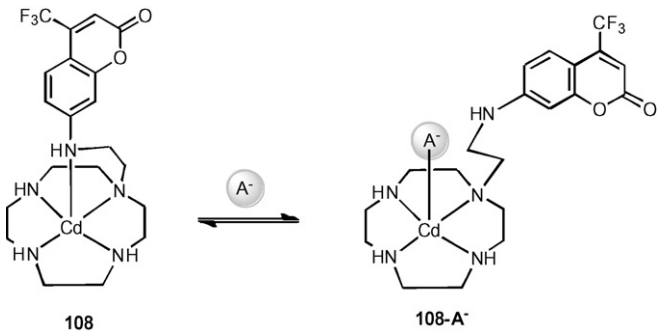
105

Lees and co-workers reported binuclear rhenium(I) complexes bridged by a pyridine ligand bearing an amide-type binding site **106** and **107** [108]. The luminescence of the rhenium(I) tricarbonyl pyridine units allows the sensing of different anions. Luminescence titration experiments in dichloromethane showed a binding affinity trend $CN^- > F^- > I^- > Cl^- \sim Br^- \sim OAc^- \gg H_2PO_4^- > NO_3^- > ClO_4^-$. The higher binding affinity found for I^- than for Cl^- and Br^- is explained in terms of the involvement of an excited state in the quenching process.



Kikuchi and co-workers developed a fluorescent sensor for anions which works in neutral aqueous solutions, based in a Cd(II)-cyclen complex equipped with a fluorescent aromatic amine **108** [109]. Anions are able to displace this weakly coordinated amine producing a shift of the λ_{max} in the excitation spectra. This sensing mechanism is reversible (Scheme 7).

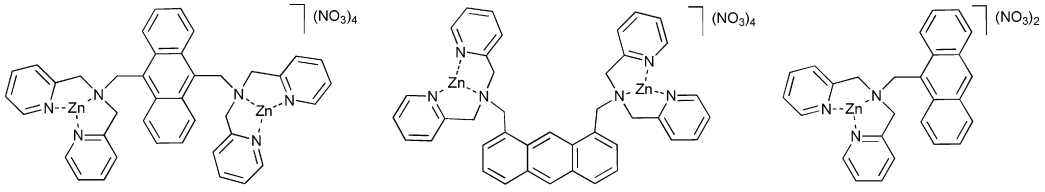
Hamachi and co-workers have prepared fluorescent chemosensors **109**, **110** and **111** based on anthracene deriva-



108 **108-A⁻**

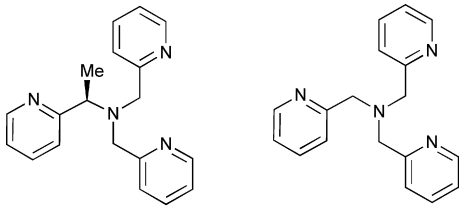
Scheme 7. The signalling mechanism in fluorescent sensor **108**.

tives equipped with Zn(II) dipicolylamine complexes [110]. These complexes bind phosphorylated peptides in aqueous solution, resulting in an increase of the fluorescence emission of the anthracene moiety, whereas non-phosphorylated peptides do not produce any response at all.



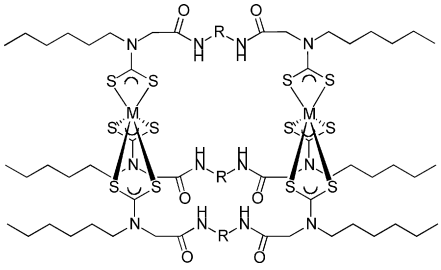
109 110 111

Tsukube and co-workers have prepared other Eu^{3+} and Tb^{3+} triflate salts bearing tris(2-pyridylmethyl)amine ligands **112** and **113** [111]. The authors determined the anion selectivity showed by the complexes adding tetrabutylammonium salts in acetonitrile to solutions of the hosts and observing the luminescence spectral changes. [Eu-**112**][CF_3SO_3]$_3$ responded selectively to NO_3^- whereas in the case of [Tb-**112**][CF_3SO_3]$_3$ the biggest increase of the luminescence intensity was observed for chloride. When complexes bearing the achiral ligand **113** were evaluated, the same selectivity was observed, but the sensitivity was much lower.



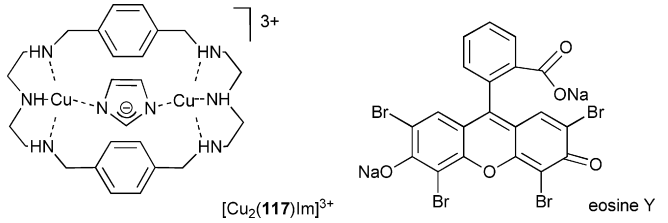
112 113

Beer et al. have prepared a series of bimetallic cryptands, **114a**,**b–116a**,**b**, by self-assembly of redox-active metals with dithiocarbamate ligands [112]. These species are able to sense different anions by following the perturbations of the metal redox couple. Addition of tetrabutylammonium dihydrogenphosphate in dichloromethane produced the biggest cathodic shift of the redox couple Co(III)/Co(IV) in compounds **115a** and **116a**: 125 and 90 mV, respectively.



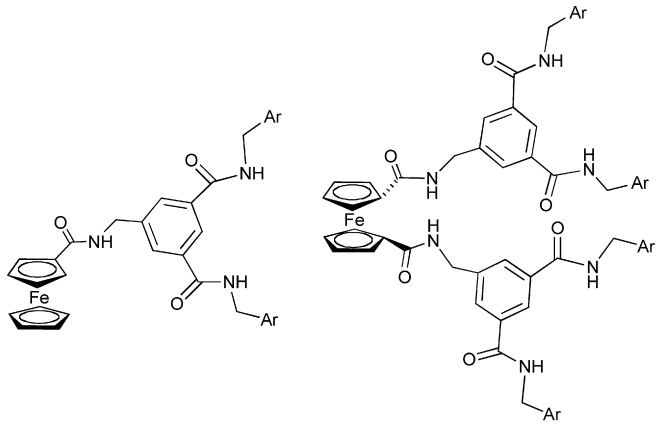
a M = Co(III), **b** M = Fe(III)
114 R = ethyl
115 R = *o*-phenyl
116 R = *m*-phenyl

Fabbrizzi and co-workers have used an indicator displacement strategy to produce a fluorescent sensor for histidine [113]. Macrocyclic ligand **117** can coordinate two copper(II) metal ions in an appropriate fashion to bind an additional carboxylate group binding both metals in a cascade complex arrangement. When [Cu_2(**117**)]$^{4+}$ is treated with fluorescent indicators containing a carboxylate group, the fluorescence is quenched by coordination of the latter to the metal complex. Addition of an amino acid produced a competitive displacement of the fluorescent indicator restoring the fluorescence emission. This process is most efficiently performed by the imidazole group, so favouring histidine. The authors demonstrate the selective sensing of this amino acid at pH 7 using eosine Y as fluorescent indicator.



[Cu_2(**117**)Im]$^{3+}$ eosine Y

Ferrocene units have been attached to a variety of anion receptors to produce electrochemically active sensors [114]. Chen and co-workers reported the ferrocene compounds **118–123** bearing multiple amide groups, which bind selectively dihydrogenphosphate over other anions [115]. Two arm ferrocene hosts **121–123** form complexes with a 1:2 stoichiometry, whereas the one arm compounds **118–120** forms 1:1 complexes.

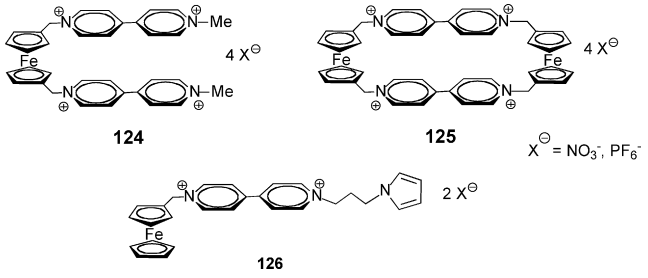


118 Ar = Ph
119 Ar = 4-nitrophenyl
120 Ar = 1-pyrenyl

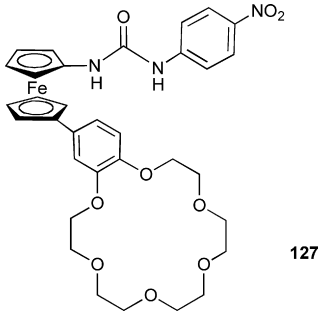
121 Ar = Ph
122 Ar = 4-nitrophenyl
123 Ar = 1-pyrenyl

Moutet and co-workers have reported a series of ferrocene containing 4,4′-bipyridinium receptors **124–126** [116]. These systems provide strong electrostatic interactions with anionic guests in addition to possible charge transfer complexes with the electron acceptor bipyridinium groups. The anion recognition abilities of these compounds were measured through the shifts in the ferrocene oxidation waves. Sensing of ATP^{2-} in water

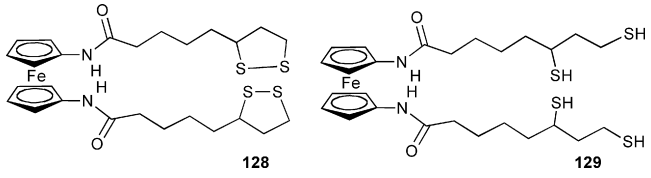
was achieved. The anion recognition properties of **124** and **125** are amplified by using *poly*-**126** films deposited onto electrode surfaces by oxidative electropolymerization.



Tucker and co-workers reported compound **127**, a ferrocene unit bearing a 4-nitrophenyl urea group as anion binding unit and a crown ether moiety as cation binding motif [117]. Addition of TBAF to an acetonitrile solution of this compound produced a change of the colour to yellow, which is reverted by addition of K^+ resulting in an optical output in the presence/absence of a combination of anion and cation.



Beer et al. have reported the synthesis of 1,1-diamidoferrocene systems **128** and **129**, designed to form monolayers on the surface of gold electrodes [118]. Formation of the monolayers produces a sensing amplification effect, and redox responses to addition of anions show an enhanced cathodic shift. Competition experiments reveal that monolayers of **128** and **129** selectively sense dihydrogenphosphate over other anions in organic media (CH_3CN:$CHCl_3$), meanwhile perrhenate detection is favoured in water.



Astruc and co-workers reported related amidoferrocenyl alkanethiol derivatives **130**, **131** and prepared gold colloids with these ligands adsorbed in different proportions and with different chain lengths of the alkanethiol moiety [119]. The authors studied the electrochemical recognition of anions by these systems, finding that permethylation of the Cp ring produced a weakening of the recognition properties, which are enhanced by the acetylation, highlighting the importance of the amidoferrocenium form

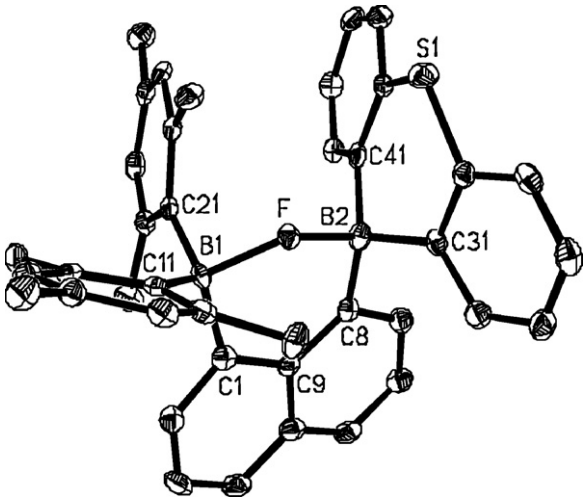
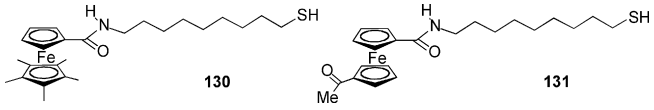
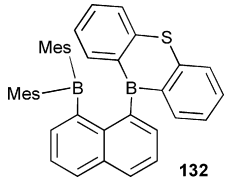


Fig. 12. Crystal structure of the fluoride complex of diborane **132**. Reproduced with permission from Chem. Commun. (2004) 1284 (Fig. 2). Copyright Royal Society of Chemistry 2004.

in the recognition process. Dihydrogenphosphate and hydrogensulfate can be sensed using these particles, whereas chloride, bromide and nitrate did not produce any potential shifts.



Solé and Gabbaï have reported a bidentate diborane derivative **132** capable of acting as a colorimetric sensor for fluoride [120]. This receptor displays a rigid structure providing a binding pocket with an optimum size to bind fluoride (Fig. 12), larger halides are not accommodated into this site and no interaction is observed in the case of chloride, bromide or iodide. Coordination of fluoride leads to population of the LUMO of the molecule and loss of the yellow colour. This complex is very stable and competitive titration experiments indicate that the binding constant for fluoride is at least $5 \times 10^9\ M^{-1}$ in tetrahydrofuran.



In the past few years, a number of theoretical studies highlighted the existence of anion–π interactions, involving typically electron deficient systems, such as perfluoroaromatic compounds and electron-poor heteroaromatic derivatives [121–123]. There are a number of metal complexes structures reported displaying short contacts between anions and π-electron clouds, mainly involving coordination compounds, but it is only very recently that these interactions have been classed as 'anion–π interactions'. Gamez and co-workers have reported a supramolecular copper complex of a dendritic octadentate ligand *N*,*N*′,*N*″,*N*‴-tetrakis{2,4-bis(di-2-pyridylamino)-1,3,5-

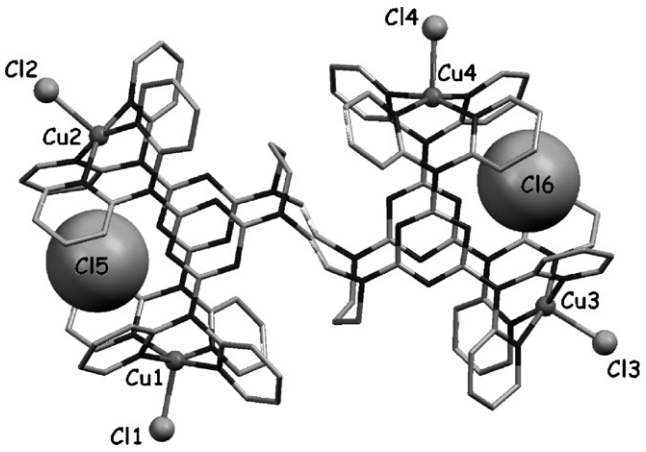
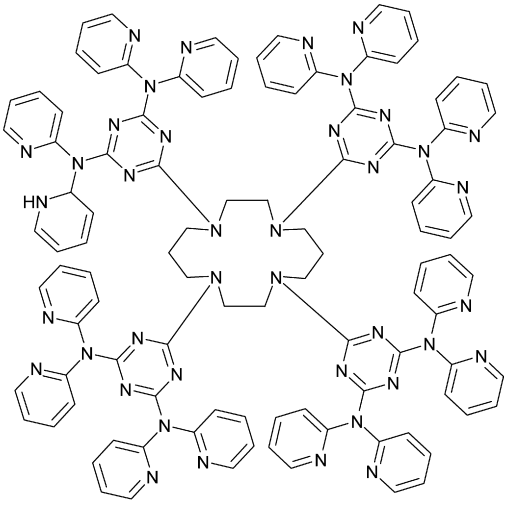


Fig. 13. Representation of the encapsulated chloride anions in the tetracopper complex of ligand **133**. Reproduced with permission from Angew. Chem. Int. Ed. 43 (2004) 5815. Copyright 2004, Wiley-VCH.

triazinyl}-1,4,8,11-tetraazacyclotetradecane (azadendtriz) **133** [124]. This supramolecular entity is capable of encapsulating two chloride anions in a cavity formed by four pyridine rings (Fig. 13). The anion–π interactions are favoured by the enhanced electron-poor character of the pyridine rings by coordination to the copper(II) ions.



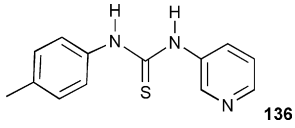
133

Meyer and co-workers have observed chloride-triazine interactions in a copper(II) chloride complex containing the hexakis(pyridin-2-yl)-[1,3,5]-triazine-2,4,6-triamine ligand **134** [125]. The chloride anion is situated about 3.17 Å above the ring matching the C_3 axis of the triazine moiety (Fig. 14), which is perfectly correlated with the theoretical predictions for this system. This interaction appears to persist in solution and in the gas phase and can be detected in the ESI mass spectrum.

4. Anion directed assembly

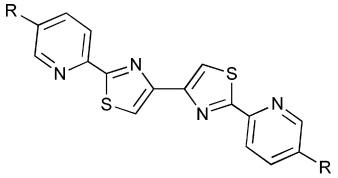
Anion directed assembly is an emerging area of supramolecular chemistry and has been recently reviewed [126,127]. A number of reports concerning the synthesis of various metal complexes involving anion templation have appeared. Champness and co-workers have reported a hexanuclear cage complexes $[M_6L_6X](X)_5$ [M = Cu(I), Ag(I); L = 6,6′-bis(4-ethynylpyridine)2,2′-bipyridine; X = BF_4^-, SbF_6^-] **135**, which encapsulate one BF_4^- or SbF_6^- anion inside their cavity (Fig. 15) [128]. When a significantly larger anion, such as $[Co(C_2H_{11}B_9)_2]^-$, is used no hexanuclear but binuclear complexes are obtained. Similarly, when a hexanuclear cage complex with X = BF_4^-, SbF_6^- is treated with solutions of $Na[Co(C_2H_{11}B_9)_2]$, only substitution of the non-encapsulated anions is achieved.

Steed and co-workers have reported a study regarding the templation role of nitrate in the assembly of a silver(I) complex containing a pyridyl ligand **136** bearing an urea group in the three position [129]. Reaction of the free ligand with different silver salts yield complexes of 1:2 stoichiometry $[Ag(\mathbf{136})_2]^+$. Non-complementary anions, such as $CF_3SO_3^-$ and SO_4^{2-} form infinite hydrogen-bonded assemblies in the solid state, whereas the nitrate complex displays a discrete 1:1 assembly as a result of the chelation of the anion by two ligands attached to the same metal centre (Fig. 16). NMR titration experiments proved difficult due precipitation of complexes, but binding constants for $[Ag(\mathbf{136})_2]^+$ towards nitrate where calculated at 17,000 M^{-1} (K_{11}) and 1660 M^{-1} (K_{12}) in the presence of triflate.



136

Rice and co-workers have studied the ligand–ligand self-recognition processes within complexes of the type $[Co_2(L)_3]^{4+}$ in which L is a tetradentate N-donor ligand [130]. When L contains an amide group, e.g. **137**, an anion receptor cavity is formed upon metal complexation, and as X-ray crystallography confirmed the cavity is suitable for nitrate complexation (Fig. 17). A statistical sample of homo- and heteroleptic complexes is formed upon mixing the metal and a mixture of ligands **137** and **138** (the latter species does not contain any hydrogen-bond donor groups). However, upon addition of nitrate, the mixture is resolved and only the homoleptic species are observed. On the other hand, presence of the perchlorate anion, which does not interact with the amide groups, makes no significant difference to the statistical mixture.



137 R=(*S*)-CONHCH(CH(CH$_3$)$_2$)CO$_2$Me
138 R=H

Vilar et al. continued their studies on metallacages [131,132] and reported the templating role of chloride and bromide in the synthesis of hexanickel and nickel–palladium clusters $[M_2Ni_4(atu)_8X][X]_3$ (atu = deprotonated form of amidinothiourea; M = Ni, X = Cl, **138**; Br, **139**; M = Pd, X = Cl, **140**; Br, **141**), forming an octahedral cage around the encapsulated halide

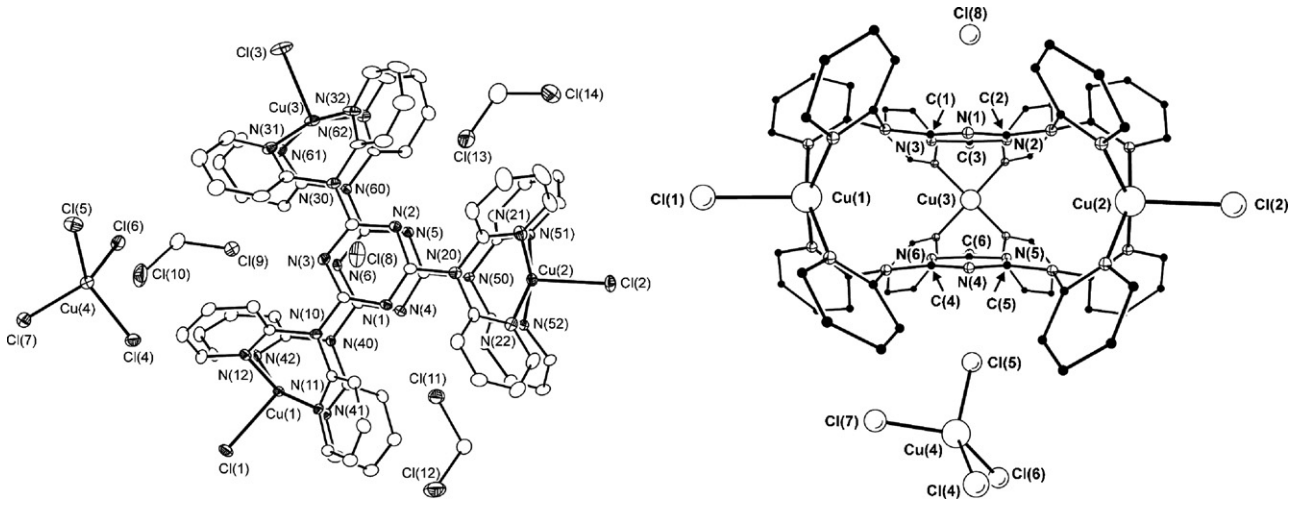


Fig. 14. Two different views of the crystal structure of complex **134** showing the chloride-triazine interaction. Reproduced with permission from J. Am. Chem. Soc. 126 (2004) 4508. Copyright American Chemical Society 2004.

(Scheme 8) [133]. Synthesis of these species is dependent of the presence of these halides and the presence of other anions, such as I^-, $NO_3{}^-$, OAc^- and $ClO_4{}^-$ does not lead to the formation of the cages but rather mononuclear complexes. Assembly of the chloride cage **138** in methanol is accompanied by a dramatic change of colour from orange to green, an effect that has been successfully employed for the colorimetric detection of micromolar amounts of chloride.

Beer and co-workers have reported the synthesis of a family of luminescent pseudorotaxanes synthesized by halide anion directed assembly [134]. When a rhenium(I) complex **142**, bearing a bipyridyl macrocycle ligand containing two amide groups capable of binding anions, is titrated in acetone solution with

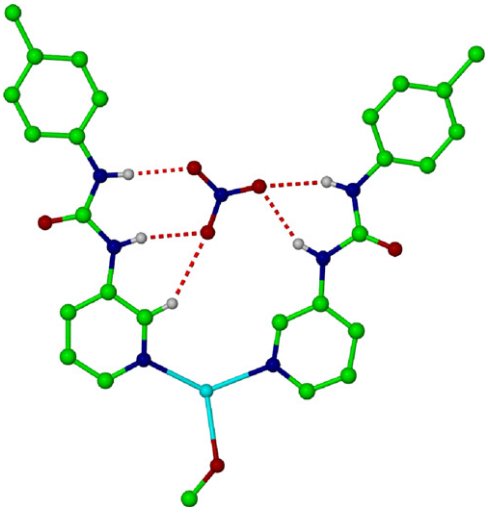


Fig. 16. X-ray structure of complex $[Ag(\mathbf{136})_2](NO_3)\cdot MeOH$ Reproduced with permission from Chem. Commun. (2004) 1352. Copyright Royal Society of Chemistry 2004.

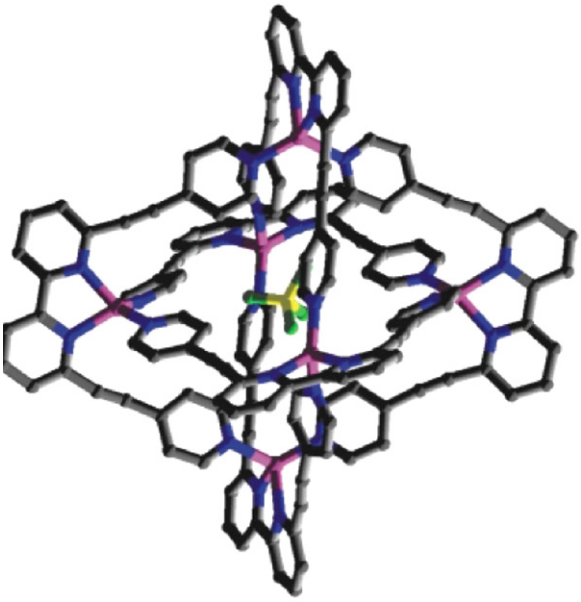


Fig. 15. Crystal structure of the hexanuclear cage complex $[Cu_6L_6BF_4](BF_4)_5$ showing the encapsulation of the tetrafluoroborate anion in the solid state. Reproduced with permission from Chem. Commun. (2003) 682. Copyright Royal Society of Chemistry 2003.

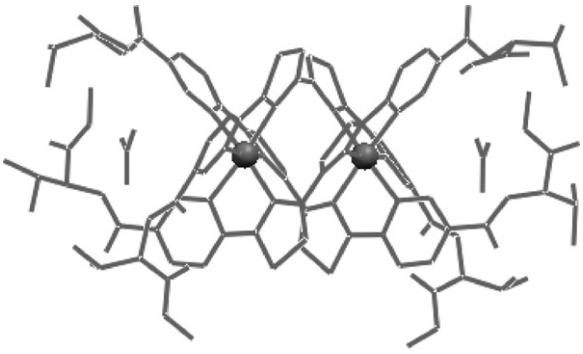
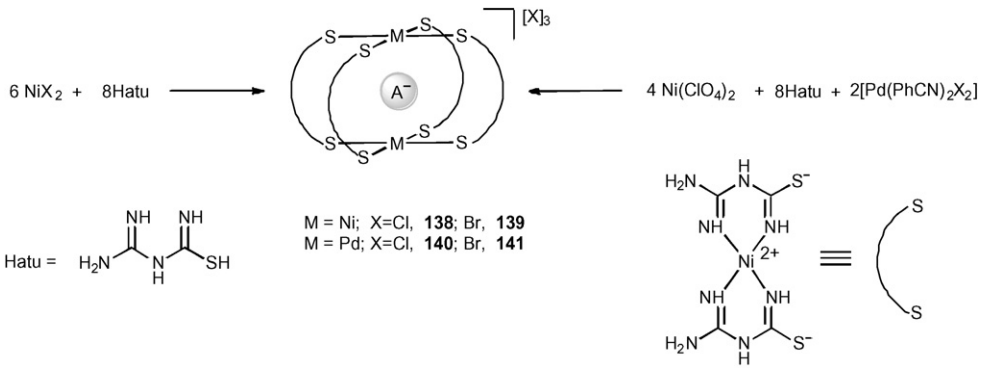


Fig. 17. Crystal structure of the complex cation $[Co_2(\mathbf{137})_3](NO_3)_2{}^{2+}$ showing the amide-nitrate interactions. Reproduced with permission from *Chem. Commun.*, 2004, 654. Copyright Royal Society of Chemistry 2004.



Scheme 8. Schematic representation of the synthesis of metallacages **138–141**.

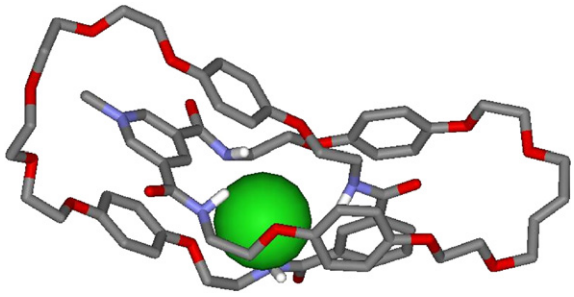
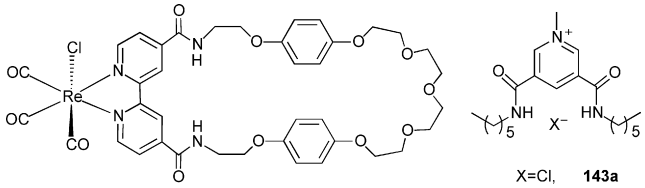
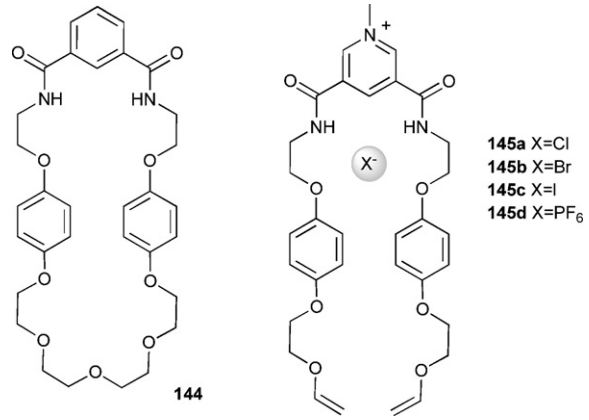


Fig. 18. Crystal structure of the [2]catenane **146** binding the chloride anion.

pyridinium bisamide halide salts **143a–c**, pseudorotaxane formation takes place. In this solvent medium, ion-pairing between the pyridinium cation and halide anion is very strong, and consequently halide complexation at the rhenium(I) bipyridyl amide recognition site of **142** results in the cationic pyridinium moiety forming an interlocked assembly with the macrocycle. Halide anion templation is demonstrated as no evidence of interpenetration was seen when a hexafluorophosphate pyridinium salt was employed.



Analogous strategies can be used in the synthesis of interlocked molecules [135] and were used by the same authors to produce the first examples of [2]- and [3]catenane structures synthesized by anion templation [136]. The strategy used was to mix a macrocyclic receptor **144**, containing an amide cleft for anion recognition, with a pyridinium chloride thread **145a**, designed to complement the binding sites of this molecule, allowing rotaxane formation. As the thread is equipped with terminal allyl groups, subsequent ring-closing metathesis (RCM) affords the catenane structure **146** (Fig. 18). The crucial template role of the chloride ion is demonstrated by the dramatic decrease in the yield achieved by using a pyridinium bromide **145b**, and the fact that no catenanes are isolated from reaction with iodide or hexafluorophosphate salts **145c** and **145d**.



5. Conclusions

The examples cited in this review give a broad overview of advances in anion receptor chemistry and anion-templated assembly over a 3-year period. This review and the other reviews in this issue of coordination chemistry reviews illustrate the tremendous effort that is still being applied to the production of anion receptor systems. The challenge now is to apply these systems to real-world problems. Progress in this area is being made with new generations of compounds being used for transport of anions in separation processes. Additionally, anion transport across biological membranes in order to treat diseases, such as cystic fibrosis and cancer is attracting increasing attention and this area is likely to see rapid growth in the coming years.

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