Synthetic indole, carbazole, biindole and indolocarbazole-based receptors: applications in anion complexation and sensing

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Indole, biindole, carbazole and indolocarbazole-based receptors are rapidly emerging as an important new class of anion-binding agents. This Feature Article provides a comprehensive overview of the molecular recognition and structural chemistry of these neutral, yet highly effective, anion receptors and sensors.

Introduction

Neutral anion receptors containing hydrogen bond donor groups, such as amides, ureas and pyrroles, have attracted much attention recently, with many systems being synthesised that include these groups in both macrocyclic and acyclic frameworks.[1] Whilst secondary amides and ureas contain both hydrogen bond donor and acceptor groups (making internal competition for hydrogen bond donors an important factor to consider when designing systems containing these groups), pyrrole contains only a single NH hydrogen bond donor. Sessler and co-workers have pioneered the use of pyrrole in anion complexation, with many highly selective receptor systems being reported over the last two decades.[2] It is perhaps surprising then that indole, and groups such as carbazole, biindole and indolocarbazole, have been neglected as potential components of hydrogen bond donor-based anion receptors. Indole and carbazole, like pyrrole, each contain a single NH hydrogen bond donor and are more acidic (pK_a in DMSO: pyrrole 23.0, indole 21.0 and carbazole 19.9)[3] so whilst indole and carbazole are better hydrogen bond donors than pyrrole, they are also more prone to deprotonation,[4] which may not be desirable when trying to complex with anionic guests.[5]

Indoles have previously found applications unrelated to anion complexation in the arena of supramolecular chemistry. In pioneering work, Black and co-workers synthesised macrocyclic calixindoles, consisting of indole rings linked *via* the 2- and 7-positions by methylene groups.[6] This group have also employed indoles in Schiff base-containing receptors for transition metals.[7]

Compounds containing indole have biological activity. For example, bisindolylmaleimides and indolocarbazoles function as potent protein kinase C inhibitors.[8] Nature employs

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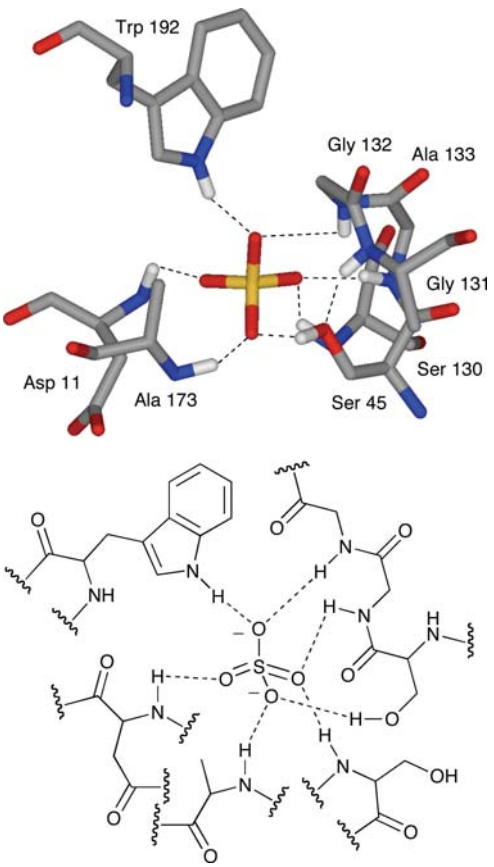


Fig. 1 The X-ray crystal structure and schematic of the sulfate-binding site in the sulfate-binding protein. The anion is bound by seven hydrogen bonds from neutral hydrogen bond donor groups, including Trp 192. Figure reproduced from J. L. Sessler, P. A. Gale and W.-S. Cho, Anion Receptor Chemistry, 2006. Reproduced by permission of The Royal Society of Chemistry (RSC).

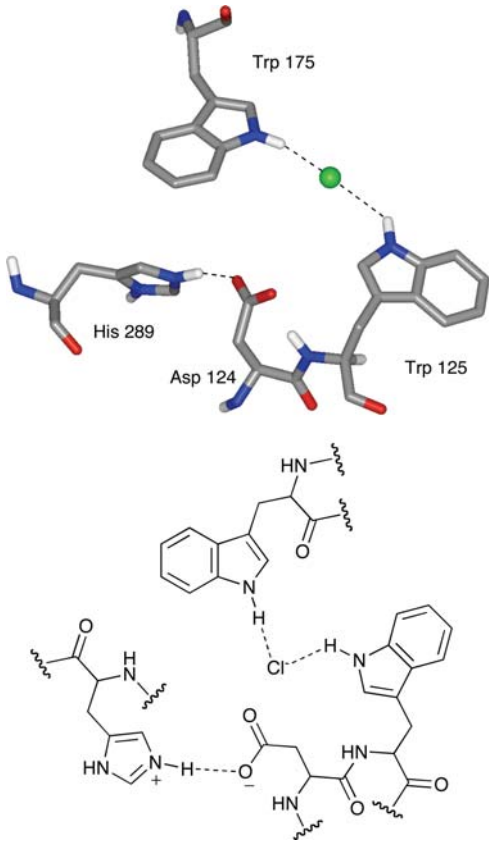


Fig. 2 The X-ray crystal structure and schematic of the enzymatic active site of haloalkane dehalogenase, revealing the presence of a chloride anion bound by Trp 125 and Trp 175. Figure reproduced from J. L. Sessler, P. A. Gale and W.-S. Cho, Anion Receptor Chemistry, 2006. Reproduced by permission of The Royal Society of Chemistry (RSC).

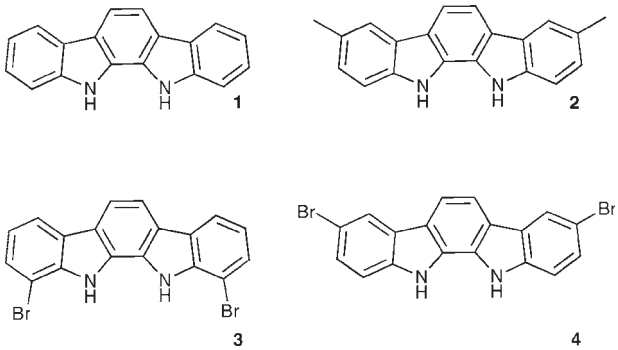
tryptophan (Trp) as a hydrogen bond donor in the anion-binding site of the sulfate-binding protein[9] (Fig. 1), and it has been shown by X-ray crystallography to complex with chloride in haloalkane dehalogenase (Fig. 2).[10]

Very recently, the first examples of synthetic indole-based anion receptors have been reported. This Feature Article will focus on the rapid progress made in the development of these systems from 2004 to date. We will start by looking at systems based on biindole and indolocarbazole, both of which contain two NH groups.

Indolocarbazoles and biindoles

In 2005, Beer and co-workers at the University of Oxford reported the first anion complexation studies with indolocarbazole.[11] Compounds **1–4** were synthesised *via* a modification of the Fischer indolisation reaction, using an appropriate aryl functionalised hydrazine and 1,2-cyclohexanedione. Binding studies conducted by UV-vis titrations in acetone showed that under these conditions, the compounds were very effective benzoate receptors, with all four indolocarbazoles forming the strongest complex with this anion (Table 1). Fluorescence spectroscopy was used to assess whether compounds **1** and **2** could be used as fluorimetric sensors for anions. Significant

Table 1 Stability constants (log K_a)[a] in acetone solution



	1	2	3	4
F^-	4.7	4.7	3.6	5.0
Cl^-	4.5	4.1	4.0	4.9
$PhCO_2^-$	5.3	5.4	4.4	5.9
$H_2PO_4^-$	4.9	5.2	4.1	5.3
HSO_4^-	—[b]	—[b]	—[b]	—[b]

[a] Determined by UV-vis spectroscopy; T = 25 °C; [host] = 3×10^{-5} M^{-1}. [b] Very weak complexation. Stability constant could not be determined; error <10%.

fluorescence enhancement was observed with fluoride, chloride and dihydrogen phosphate, whilst the addition of benzoate quenched the fluorescence and hydrogen sulfate had little effect (Fig. 3). Receptor **2** was crystallised in the presence of two equivalents of tetrabutylammonium fluoride by the slow diffusion of diisopropyl ether into a solution of the receptor

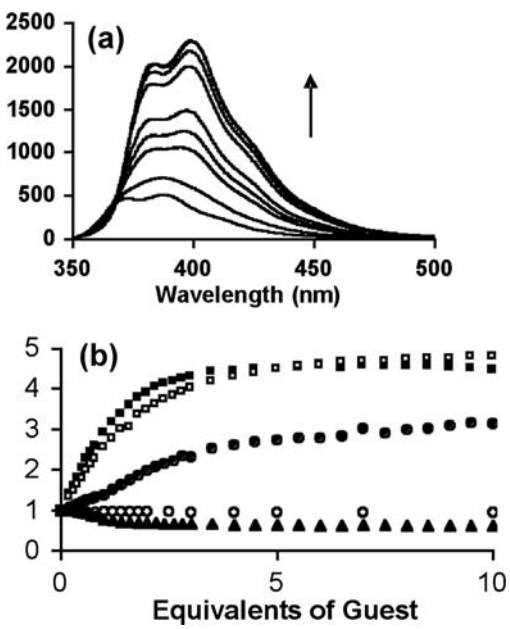


Fig. 3 (a) Fluorescence enhancement upon titration of receptor **2** (3×10^{-5} M in acetone) with TBAF (λ_{exc} = 320 nm): 0, 0.2, 0.5, 0.7, 1, 2, 3, 5 and 10 equivalents of TBAF. (b) Titration curves: ■ TBAF, □ TBACl, ● $TBAH_2PO_4$, ▲ TBA benzoate and ○ TBA HSO_4. Figure reproduced with from D. Curiel, A. Cowley and P. D. Beer, *Chem. Commun*., 2005, 236–238. Reproduced by permission of The Royal Society of Chemistry (RSC).

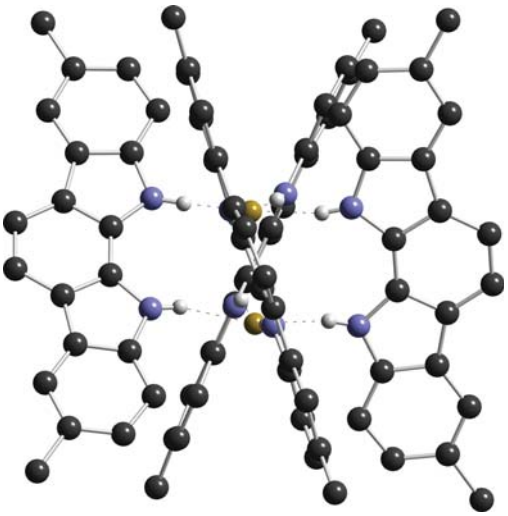


Fig. 4 The crystal structure of the fluoride complex of receptor **2**.

and a tetrabutylammonium salt. X-Ray crystallographic elucidation of the structure revealed that four indolocarbazoles surround two fluoride anions in a helical arrangement (Fig. 4).

Very recently, Davis, Beer and co-workers have revisited indolocarbazole, with a study of the sulfate anion templation of these compounds.[12] In their Communication, the Oxford group showed that two indolocarbazoles assemble around the sulfate (added as tetrabutylammonium sulfate) in CD_3CN solution in a 2 : 1 receptor : anion stoichiometry by ^1H NMR. The structure of the crystals grown by the slow diffusion of pentane or ether into a 2 : 1 receptor : anion solution in dichloromethane was elucidated and confirmed this stoichiometry in the solid state (Fig. 5). This assembly process around sulfate allowed pseudo-rotaxane formation (**5**, Fig. 6) when a hybrid crown ether-isophthalamide macrocycle was combined with a 1 : 1 mixture of sulfate and compound **1**. This work demonstrates that indolocarbazoles may have important roles to play in anion-templated assembly processes in the future.

Jeong and co-workers at Yonsei University in Seoul, Korea have emerged as one of the leading groups in the area of indole-based anion receptors.[13] In 2005, this group reported the synthesis and anion-binding properties of alkyne-linked biindole- and indolocarbazole-containing macrocycles **6** and **7**.[14]

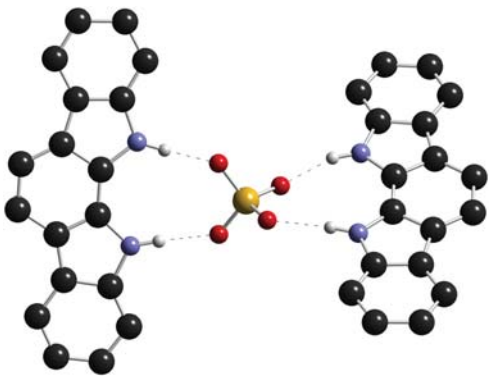


Fig. 5 The X-ray structure of the sulfate complex of indolocarbazole **1**. Only one of the two crystallographically-independent complexes is shown.

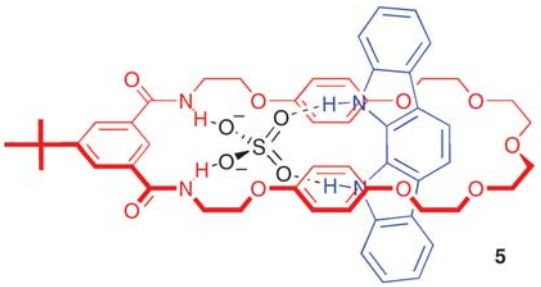
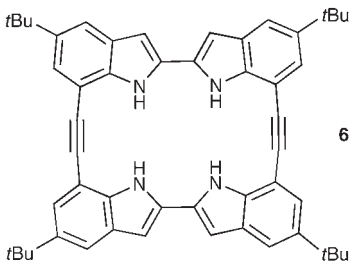


Fig. 6 The structure of sulfate-templated pseudo-rotaxane **5**.

Compound **6** was synthesised from 7,7′-diiodo-2,2′-biindole, which was converted into a diethynyl derivative and then coupled with the original diiodo compound using the copper-free conditions described by Soheili *et al.*[15] A similar procedure was used to synthesise macrocycle **7** from an analogous diiodoindolocarbazole. These compounds proved to have very high affinities for fluoride, binding this anion selectively with stability constants of 2.0×10^8 and 5.6×10^8 M^{-1}, respectively, in CH_3CN. These values were determined by a UV-vis competition experiment at 295 ± 1 K with the chloride complex of each receptor. Chloride was found to bind to compounds **6** and **7**, with stability constants of 1.5×10^6 and 2.1×10^6 M^{-1}, respectively. The crystal structure of the chloride complex of receptor **7** was elucidated, showing the anion perching on one face of the macrocycle (Fig. 7). Hydrogen bonding distances and angles between the indole nitrogen atoms and chloride ion were 3.13–3.15 Å and 149–153°, respectively. Interestingly, upon addition of sub-stoichiometric quantities of anions to NMR solutions of the receptors in CD_3CN, slow exchange was observed on the NMR timescale, and resonances corresponding to the free receptor and complex could both be observed. The addition of each anion caused a unique chemical shift of the NH group in the complex, allowing the macrocycles to function as chemosensors. The anions studied were found to bind with a 1 : 1 stoichiometry, except for bromide and iodide, which bound with a 2 : 1 receptor : anion stoichiometry in solution, presumably forming sandwich-type complexes.



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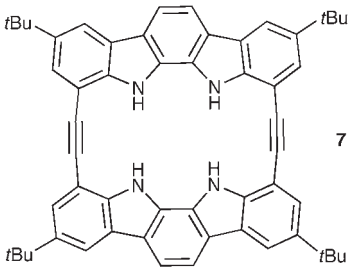

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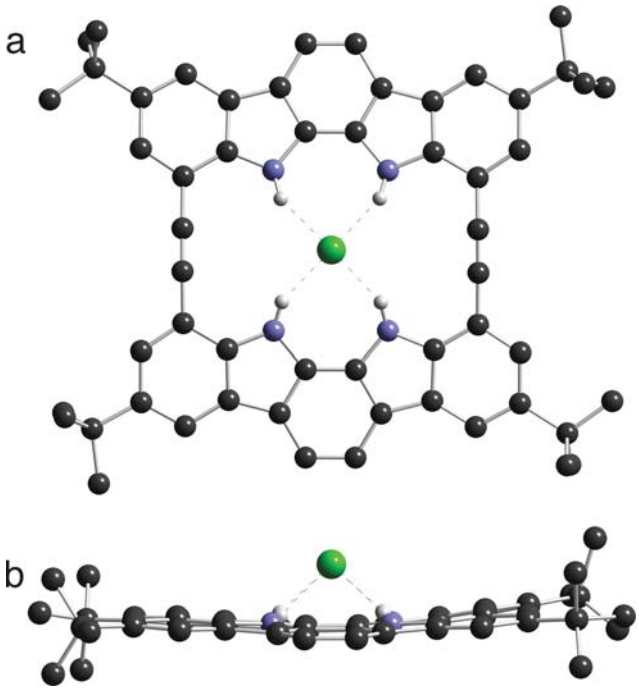
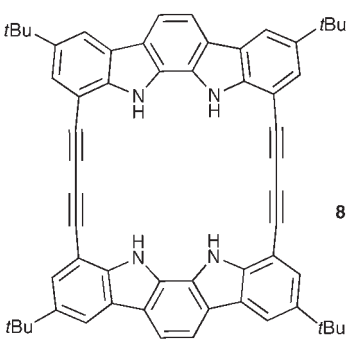


Fig. 7 (a) Top and (b) side views of the chloride complex of compound **7**.

The same group have also reported the synthesis of expanded macrocycle **8**.[16] The anion complexation properties of the smaller macrocycle, **7**, and expanded system, **8**, were compared in 10% (v/v) methanol/acetone at 23 ± 1 °C by UV-vis titration techniques, adding the anions as their tetrabutylammonium salts. Under these conditions, macrocycle **7** had a higher affinity for chloride than the larger system (1800 *vs.* 430 M^{-1}), but all of the other (larger) anions studied bound more strongly to the larger receptor. The greatest enhancement in binding on going from compound **7** to **8** was observed with iodide, which bound to compound **7** with a stability constant of less than 10 *vs.* 2400 M^{-1} for complexation to the larger receptor **8**. Interestingly, X-ray crystallography revealed that azide binds to the two macrocycles *via* different coordination modes. Compound **7** forms four hydrogen bonds to a single terminal nitrogen atom of the azide anion. However, larger macrocycle **8** encapsulates azide and forms two hydrogen bonds to each of the terminal nitrogen atoms (Fig. 8). Stability constant determinations with azide showed weaker binding with smaller macrocycle **7** K_a = 2300 *vs.* 81 000 M^{-1} with compound **8**.



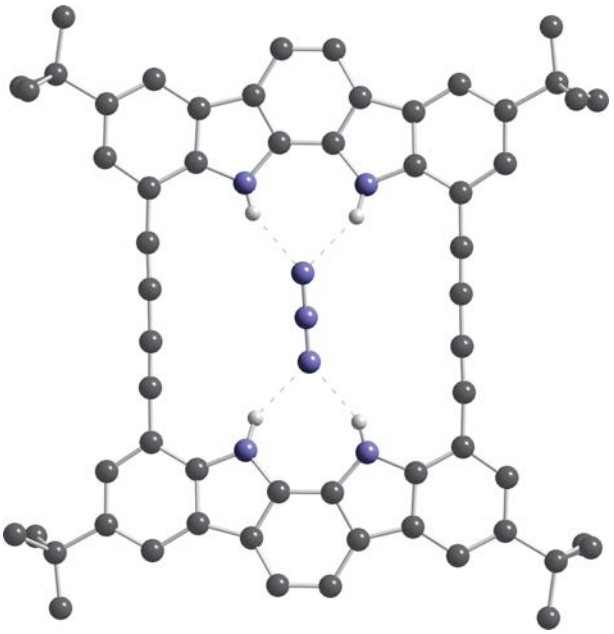
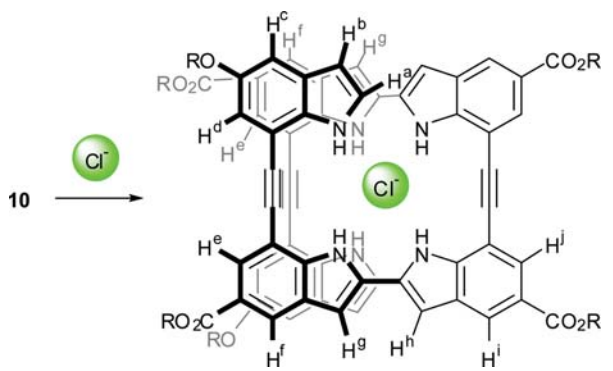
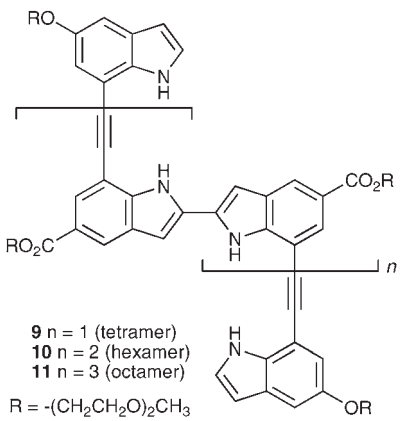


Fig. 8 The X-ray crystal structure of the azide complex of compound **8**.

In very elegant work, Jeong and co-workers have employed alkynyl-linked biindole oligomers as anion-templated foldamers.[17] A series of compounds, **9–11**, were synthesised, containing four, six and eight indole groups, respectively. ^{1}H NMR studies with these three compounds in CD_3CN in the absence and presence of one equivalent of chloride showed significant upfield shifts of the aromatic protons in compounds **10** and **11** upon addition of the anion, but much less significant shifts in the case of compound **9**. The authors attributed these shifts to the compounds folding-up around the chloride template, with compounds **10** and **11** making one-and-a-half (Scheme 1) and two turns, respectively, resulting in stacking of the indole rings and consequent deshielding, which is not possible in the shorter tetramer. The helical conformation was confirmed by ^{1}H ROESY NMR studies, which showed NOE cross-peaks (and hence through-space coupling) between H^b and H^g, H^c and H^f, and H^d and H^e in compound **10** in the presence of chloride (Scheme 1). In the absence of chloride, these couplings were not present.

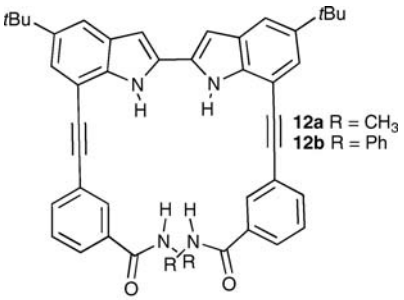


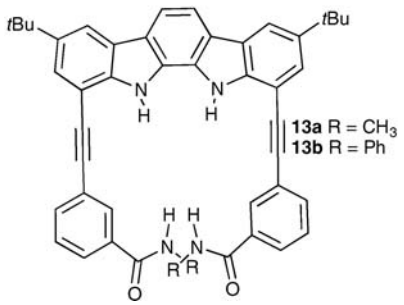
Scheme 1 Chloride-induced helix formation by hexamer **10**.



The same group has synthesised a series of cleft molecules based on biindole and indolocarbazole. For example, amide groups have been appended to the biindolyl and carbazole scaffolds to afford a series of receptors, **12–13**.[18] Stability constant determinations showed that carbazole derivative **13a** had a significantly higher affinity for anions than biindole derivative **12a** in CH_3CN (Table 2). The authors attributed the higher affinity to the greater degree of preorganisation present in the carbazole derivative when compared with the biindole derivative, which can rotate about the indole–indole bond. A pyridine-functionalised carbazole has also been synthesised,[19] with NMR studies in CD_3CN leading the authors to suggest that receptor **14** adopts different conformations when binding to dihydrogen phosphate (pyridine nitrogens accepting hydrogen bonds from the anion) and chloride (pyridine nitrogens orientated out of the cavity, allowing $CH\cdots Cl^-$ interactions (Fig. 9)).

Table 2 Stability constants ($K_a/M^{-1} \pm 20\%$) of clefts **12a** and **13a**, and anions in CH_3CN at 22 ± 1 °C[a]





Anion	**12a**	**13a**	K_a(**13a**)/K_a(**12a**)
Cl^-	5×10^3	1.1×10^5	22
Br^-	2.1×10^2	8.7×10^3	41
I^-	6[b]	1.8×10^2	30
HSO_4^-	77	2.1×10^3	27
$CH_3CO_2^-$[c]	1.4×10^5	$>2 \times 10^6$	—

[a] Titration experiments were all duplicated by UV-vis spectroscopy, in which the concentration of **12a** (or **13a**) remained constant (2.0×10^{-5} M) throughout each titration and the anions were used as their tetrabutylammonium salts. [b] The stability constant between **12a** and I^- was evaluated by ^1H NMR spectroscopy. [c] The stability constants of **12a** and **13a** with acetate were determined in 10% (v/v) DMSO/CH_3CN.

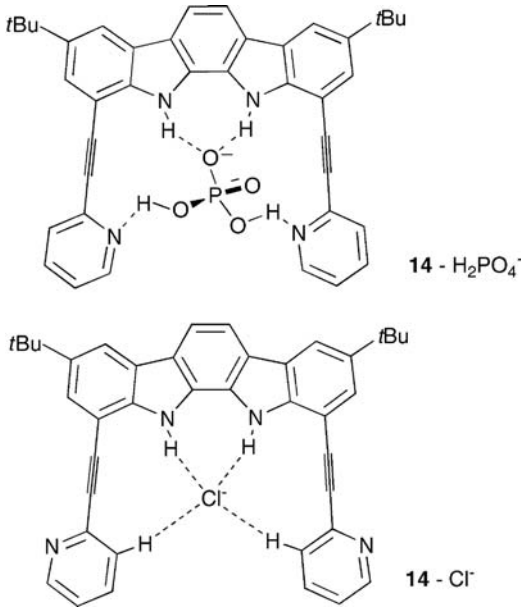
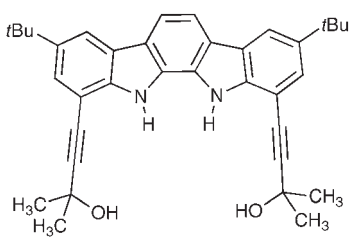


Fig. 9 Receptor **14** adopts different conformations when binding to dihydrogen phosphate and chloride.

Very recently, the synthesis and anion-binding properties of compound **15**, which contains two carbazole NH groups and two hydroxy groups, was reported.[20] Proton NMR and UV-vis titrations in 1% H_2O/CD_3CN demonstrated that the compound forms stable complexes with oxo-anions (AcO^- $K_a = 1\,100\,000\ M^{-1}$; $H_2PO_4^-$ $K_a = 29\,000\ M^{-1}$) and chloride ($K_a = 56\,000\ M^{-1}$). Job plot analysis showed 1 : 1 complex stoichiometry in all cases. Interestingly, in the solid state, compound **15** forms a 2 : 2 complex with dihydrogen phosphate, with each receptor binding one anion *via* two $NH\cdots O$ hydrogen bonds and one $OH\cdots O$ interaction. The other OH group forms a hydrogen bond with the other receptor in the 2 : 2 complex. The dihydrogen phosphate anions form a hydrogen-bonded dimer *via* $OH\cdots O$ interactions (Fig. 10).



Jeong and co-workers have also synthesised bis-amido and bis-urea biindole derivatives **16** and **17**.[21] These compounds proved to have a high affinity for dihydrogen phosphate and

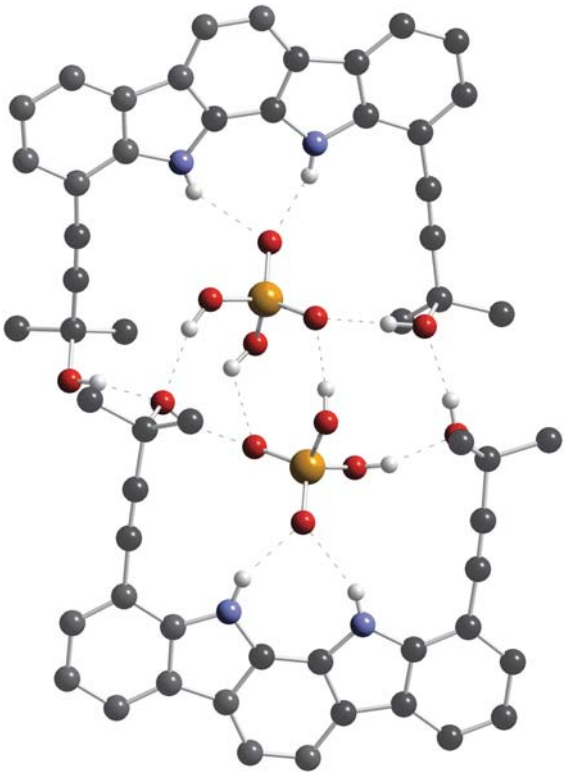
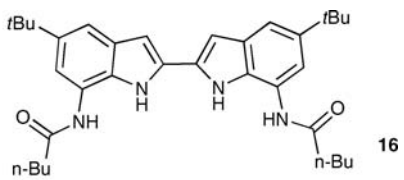


Fig. 10 The X-ray crystal structure of $(\mathbf{15}\cdot H_2PO_4)_2^{2-}$. The non-acidic hydrogen atoms and counter-cations are omitted for clarity.

pyrophosphate in DMSO (Table 3). Additional studies with dicarboxylates and compound **17** in 10% (v/v) MeOH/DMSO (stability constants in DMSO alone were too high to measure) showed uniformly high affinities for malonate, succinate, glutarate and adipate, with stability constants in the order of 10^5 M^{-1}.

Table 3 Stability constants (K_a/M^{-1}) for receptors **16** and **17** with anions (tetrabutylammonium salts) in DMSO (containing 0.1–0.2% water) at 22 ± 1 °C



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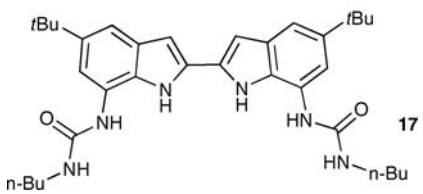
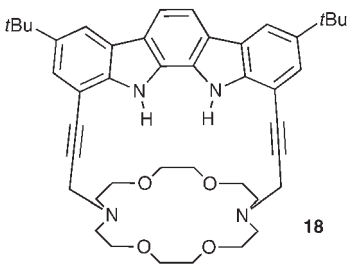


17

Anion	**16**	**17**
AcO^-	$(4.3 \pm 0.3) \times 10^4$	$(7.5 \pm 0.4) \times 10^4$
$H_2PO_4^-$	$(1.4 \pm 0.1) \times 10^5$	$(3.9 \pm 0.1) \times 10^5$
$HP_2O_7^{3-}$	$(5.2 \pm 0.3) \times 10^5$	$> 5 \times 10^6$

Strapping an anion receptor across a diaza-crown ether to create a receptor for a contact ion-pair has previously been a successful strategy for producing new systems that show high cooperativity between cation and anion binding processes.[22] The Seoul group have followed a similar strategy and employed carbazole in ion-pair receptor **18**.[23] In 10% (v/v) DMSO-d_6/CD_3CN, the receptor showed a very low affinity for halide anions. However, in the presence of one equivalent of an alkali metal salt, significant enhancement of the halide affinity was observed, with the highest halide affinities being measured in the presence of one equivalent of sodium perchlorate (Table 4).

Table 4 Stability constants (K_a/M^{-1}) between ion-pair receptor **18** and halides in the presence of alkali metal salts (1 equiv.) in 10% (v/v) DMSO-d_6/CD_3CN at 24 ± 1 °C[a]



18

Halide[b]	Cation additive	Stability constant
Cl^-	None	7
	$LiClO_4$	120
	$NaClO_4$	14 000
	KPF_6	6200
Br^-	None	[c]
	$LiClO_4$	24
	$NaClO_4$	600
	KPF_6	200
I^-	None	[c]
	$LiClO_4$	9
	$NaClO_4$	61
	KPF_6	45

[a] ^1H NMR titration experiments were duplicated and stability constants determined from the downfield shifts of the indole NH proton resonances. Errors in the stability constants are less than 15%, except those of $K_a < 10$ M^{-1}, in which cases errors are up to 30%. [b] Halides were used as their tetrabutylammonium salts. [c] The chemical shift changes during the titration were too small to determine the stability constant.

The interactions of indole and biindole analogues **19** and **20** (pyreno[2,1-*b*]pyrrole and bis(pyreno[2,1-*b*]pyrrole) with anions have been studied by Fang, Chou and co-workers using UV-vis, fluorescence and NMR techniques.[24] They found that compound **19** bound to fluoride in CH_3CN in the ground state, but fluorescence studies led the authors to suggest that proton transfer occurred in the excited state, causing a bathochromic shift in fluorescence emission upon addition of this basic anion. In contradistinction to these results, compound **20** was deprotonated by fluoride in the ground state in acetonitrile, and both compounds were deprotonated in DMSO

solution. DMSO solutions of compound **20** are a distinct greenish-yellow colour, but upon addition of excess tetrabutylammonium fluoride, a colour change to bright red was observed, whilst other anions did not cause a change in colour (Fig. 11). The authors rationalise the fact that compound **19** is not deprotonated by fluoride in acetonitrile, but that compound **20** is, as on deprotonation of **20**, the resultant anion, $[\mathbf{20} - H^+]^-$, can be stabilised by accepting a hydrogen bond from the adjacent NH group present in the system (resulting in a conformational change from the *anti*- to the *syn*-conformation) (Fig. 12), which, of course, is not present in compound **19**. This work further demonstrates that anion-induced deprotonation can give rise to significant colour changes in neutral hydrogen bond donor-based anion receptors.[5]

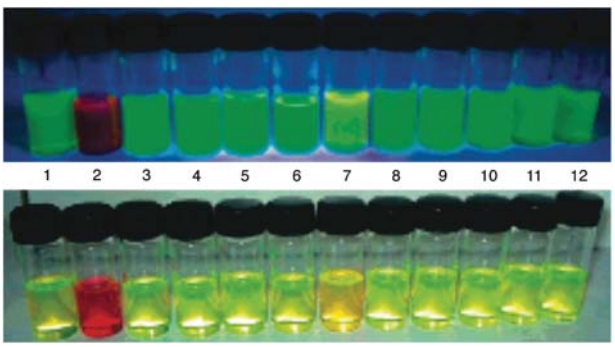
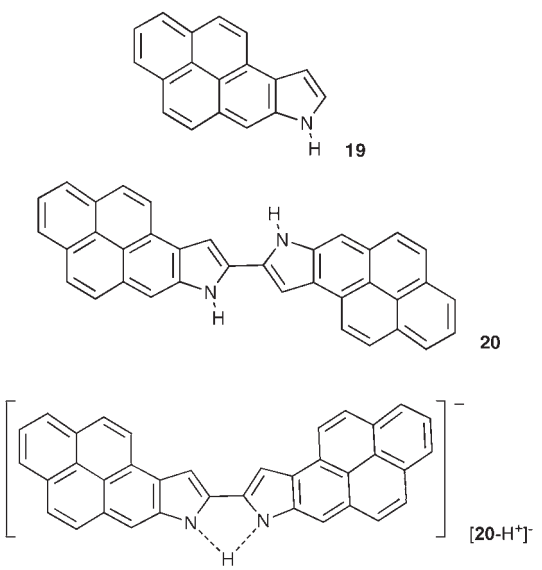


Fig. 11 The colour change induced upon addition of anions (100 equivalents as their tetrabutylammonium salts) to receptor **20** (1×10^{-4} M in DMSO): (top series) under irradiation with 364 nm light and (bottom series) under daylight. From left to right: (1) no anion, (2) F^-, (3) Cl^-, (4) Br^-, (5) I^-, (6) AcO^-, (7) $H_2PO_4^-$, (8) HSO_4^-, (9) ClO_4^-, (10) NO_3^-, (11) SCN^- and (12) benzoate ion. Reproduced with permission from *J. Org. Chem.*, 2007, **72**, 3537–3542. Copyright 2007 American Chemical Society.



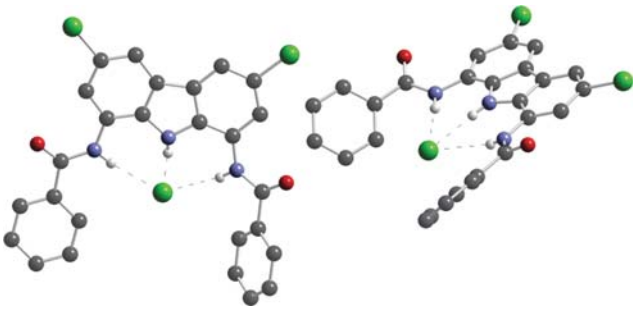
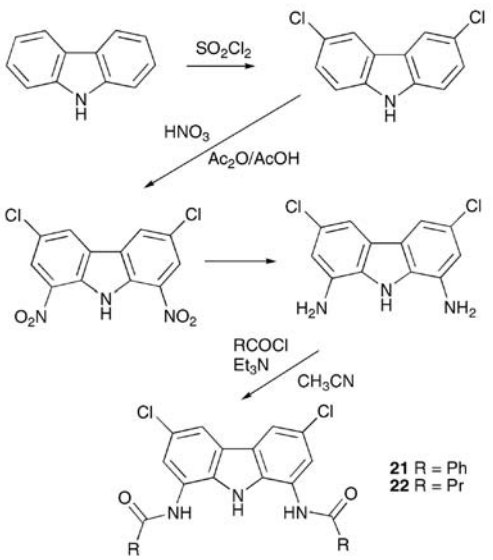


Fig. 12 Two crystallographically-independent chloride complexes of receptor **21**. Non-acidic hydrogen atoms and counter-cations have been omitted for clarity.

Indole and carbazole

In the second section of this Feature Article, we move on from biindole and indolocarbazoles and look at receptors consisting either of functionalised indoles, containing pendant indole groups, or carbazoles. Each one of these moieties can donate a single NH hydrogen bond.

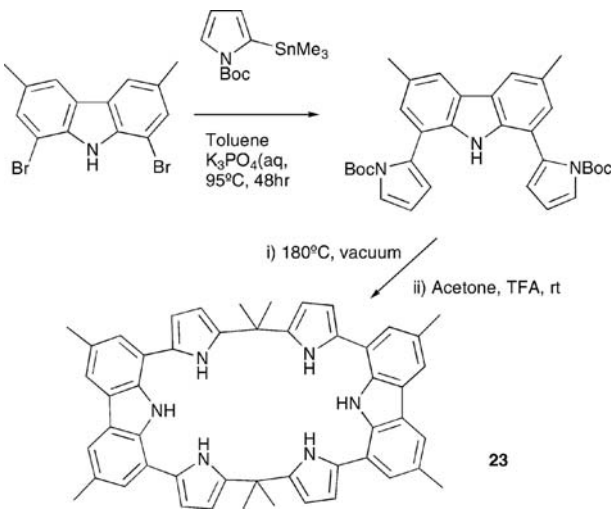
In 2004, Jurczak and co-workers reported the synthesis of receptors based on carbazole functionalised with two amide groups (Scheme 2).[25] The anion-binding properties of compounds **21** and **22** were studied in DMSO-d_6/0.5% water. It was found that compound **21** bound to chloride with a stability constant of 13 M^{-1}, benzoate 1230 M^{-1} and dihydrogen phosphate 1910 M^{-1}. Compound **22** bound to these anions with stability constants of 115, 834 and 19 800 M^{-1}, respectively. In all cases, significant downfield shifts of the amide and carbazole NH protons were observed, indicating that all three NH groups are involved in anion complexation in solution. Single crystals of the chloride complex of receptor **21** were obtained and the structure elucidated (Fig. 12). Two crystallographically-independent chloride complexes were observed in the asymmetric unit and in both cases, the chloride anions were bound by the amide and carbazole NH groups. In one of the complexes, the amide N···Cl distances



Scheme 2 The synthesis of carbazole-based bis-amide receptors **21** and **22**.

are 3.603 and 3.376 Å, whilst the carbazole N···Cl distance is 3.043 Å. In the other complex, the amide N···Cl distances are 3.579 and 3.572 Å, and the carbazole N···Cl distance is 3.065 Å. The authors also attribute aromatic CH···Cl interactions as contributors to the stability of the complex.

Contemporaneously with Jurczak *et al*., Sessler and co-workers at the University of Texas at Austin reported the synthesis of calix[4]pyrrole[2]carbazole (**23**) in 2004 (Scheme 3).[26] This compound was found to adopt a folded 'wing-like' conformation in the solid state. The crystal structure of the tetrabutylammonium benzoate complex of **23** was elucidated and revealed that the anion is bound by the four pyrrole NH groups and potentially interacts with the carbazole NH moieties (although these NH groups are not oriented directly at the oxygen atoms), with the anion sitting in the cleft formed by the folded macrocycle (Fig. 13). Stability constants were obtained from static fluorescence quenching experiments in dichloromethane or dry acetonitrile (illustrating the potential of carbazole as a reporter group), revealing a selectivity for acetate over larger carboxylates.



Scheme 3 The synthesis of calix[4]pyrrole[2]carbazole (**23**).

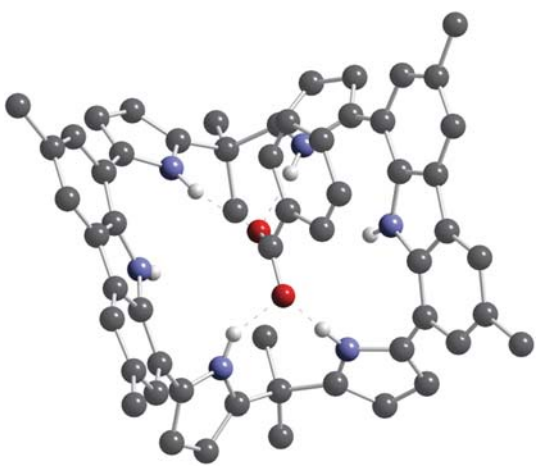
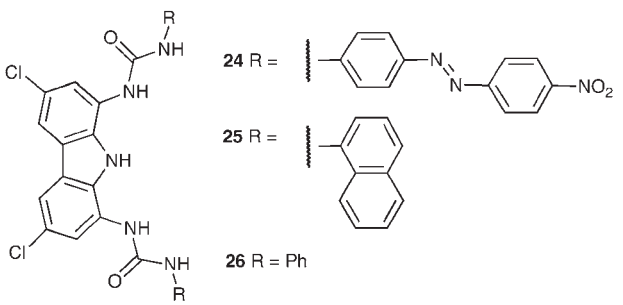


Fig. 13 A view of the X-ray crystal structure of the benzoate complex of receptor **23**. Disorder, non-acidic hydrogen atoms and counter-cations have been omitted for clarity.

Kim and co-workers have synthesised a series of compounds, **24–26**, which can function as dual channel sensors, having both a colourimetric and a fluorescent response to anionic guests.[27] By plotting fluorescence relative intensity *vs*. absorption shift of the UV-vis spectrum in the presence of a variety of anions, the authors could identify diverse sets of anions. The structure of the acetate complex of compound **25** was elucidated (Fig. 14), showing the receptor binding the anion *via* four urea NH···O interactions and one bifurcated hydrogen bond from the carbazole.



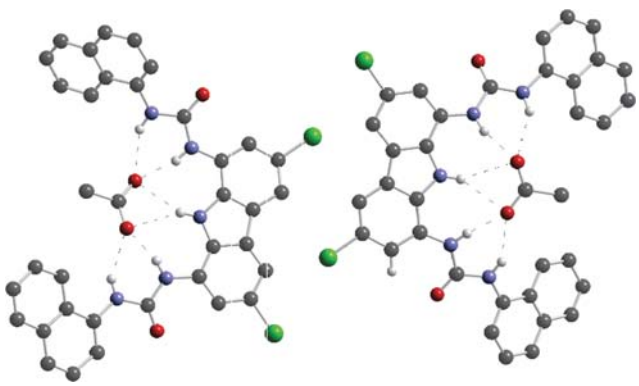
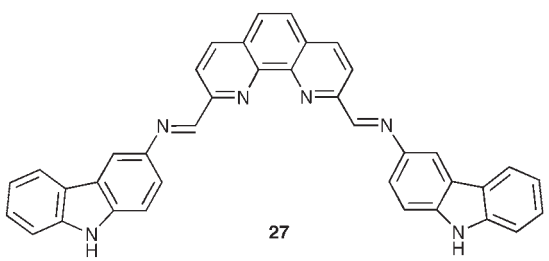


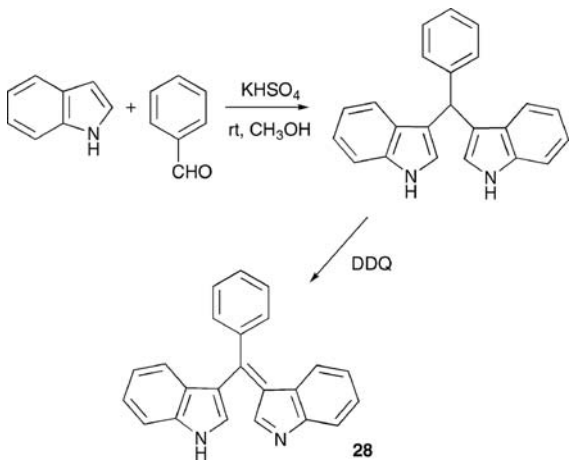
Fig. 14 The X-ray crystal structure of the acetate complex of receptor **25**, showing two crystallographically-independent complexes. Non-acidic hydrogen atoms and counter-cations have been omitted for clarity.

Lin and co-workers have reported the synthesis of compound **27**, which contains two pendant carbazole groups linked to a central phenanthroline *via* Schiff base linkages.[28] The compound was shown by UV-vis titration experiments in DMF to bind to iodide with a stability constant of 5×10^4 M^{-1}, while not interacting with other halides under these conditions.



Carbazoles have been employed in included systems designed to sense iodide *via* fluorescence and colour changes.[29]

Indoles have also been employed as pendant groups in anion receptor systems. Shao and co-workers have described the synthesis of a bis(indolyl)methene receptor by the condensation of indole with benzaldehyde in methanol, followed by treatment of the precursor bis(indolyl)methane in acetonitrile with DDQ to afford compound **28** (Scheme 4).[30] In an acetonitrile solution, the receptor is deprotonated by fluoride, giving rise to a yellow-to-red colour change. However, under different conditions (namely acetonitrile : water 4 : 1 (v/v) mixtures), the receptor can accept a proton from HSO_4^-, giving a selective yellow-to-pink colour change. Colour changes have also been observed by Lin and co-workers in phenylhydrazone-functionalised indoles upon addition of anions.[31]

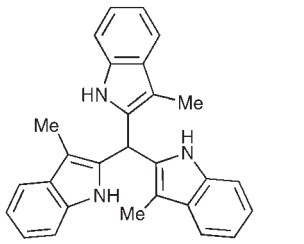


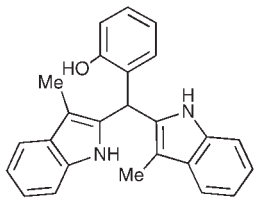
Scheme 4 The synthesis of compound **28**.

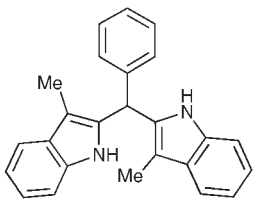
A series of indolylmethanes, **29–33**, containing 2- or 3-linked indole groups have been synthesised by Ito and co-workers and their anion complexation properties studied by ^{1}H NMR titration techniques in $CDCl_3$.[32] All of the compounds were shown to form 1 : 1 complexes with the anions studied (by Job plot analysis), except for compound **32**, which was found to have more a complex stoichiometry. Stability constants for the anion complexes of compounds **29**, **30**, **31** and **33** are shown in Table 5. The compounds showed selectivity for chloride, but it should be noted that more basic anions, such as acetate, benzoate or dihydrogen phosphate, were not studied.

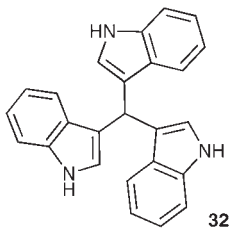
The synthesis and anion binding properties of tris-2-(3-methylindolyl)phosphine (**34**) has been reported by Browning and co-workers.[33] This compound was synthesised by the lithiation of 1-[*N*,*N*-dimethylamino)methyl]-3-methylindole, followed by the addition of trichlorophosphine and subsequent reaction with $NaBH_4$. The compound proved to be air stable. ^{1}H NMR titrations were used to elucidate the stability constants of receptor **34** with anions (added as their tetrabutylammonium salts) in CD_2Cl_2 solution at 298 K. The compound was found to bind chloride, acetate and bromide in a 1 : 1 stoichiometry, with stability constants of 3920, 2730 and 320 M^{-1}, respectively, under these conditions. Fluoride caused the largest downfield shift of the NH proton resonances of the anions studied, but the titration profile could not be fitted to a 1 : 1 binding model. Crystals of the tetraethylammonium

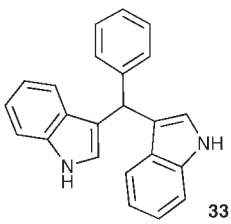
Table 5 Stability constants (K_a/M^{-1} in $CDCl_3$ at 297 K) for 1 : 1 complexes of indolylmethanes **29–31**, and **33** and tetrabutylammonium anion salts[a]







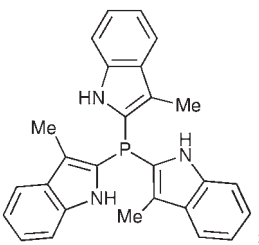




	Host			
Anion	**29**	**30**	**31**	**33**
Cl^-	1200	150	75	26
Br^-	105	55	25	16
I^-	27	16	22	7
HSO_4^-	34	27	12	13
NO_3^-	36	125	31	23

[a] Errors were estimated to be 10%.

fluoride complex of **34** showed 1 : 1 binding in the solid state *via* three NH···F^- hydrogen bonds in the range 2.632(3) to 2.790(2) Å (Fig. 15). Interestingly, BF_4^- was found to bind to the receptor with a stability constant of 150 M^{-1}. The copper phenanthroline complex of **34** was prepared by reacting compound **34** with 1,10-phenanthroline (phen) and $[Cu(MeCN)_4]BF_4$ in CH_2Cl_2. Crystals of this material were grown by vapour diffusion of diethyl ether into a dichloromethane solution of the receptor, revealing the BF_4^- anion hydrogen-bonded to the indole NH groups, with three single hydrogen bonds to three different fluorine atoms in the anion (Fig. 16).



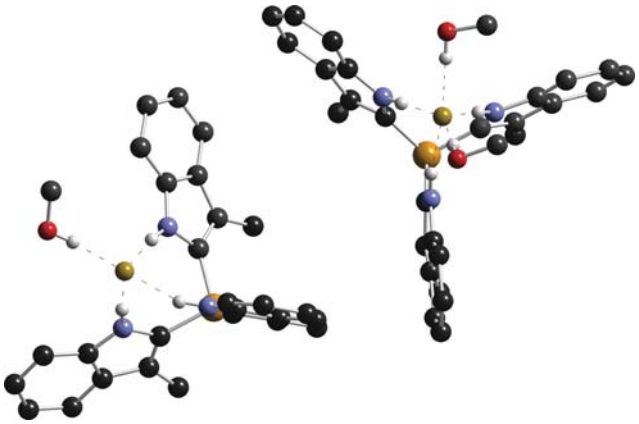


Fig. 15 The X-ray crystal structure of the two crystallographically-independent fluoride complexes of receptor **34** in the asymmetric unit. The fluorides are solvated with methanol. Non-acidic hydrogen atoms and tetraethylammonium counter-cations are omitted for clarity.

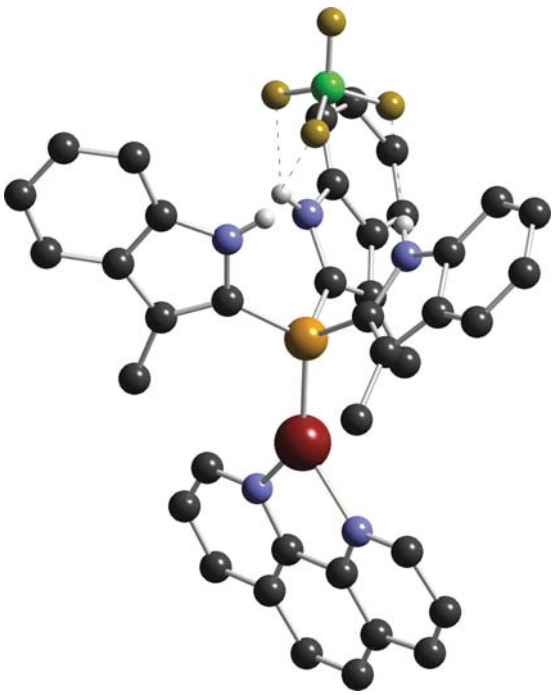
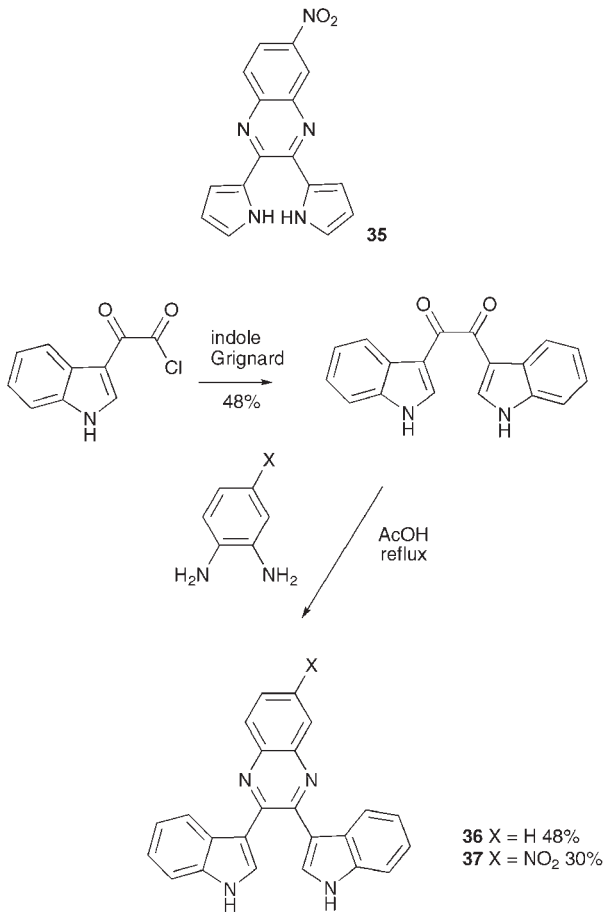


Fig. 16 The X-ray crystal structure of the [Cu(**34**)phen]BF_4 complex. The Cu(I) coordinates to the phosphorus donor of receptor **34**, while the BF_4^- anion hydrogen-bonds to the indole NH groups. Non-acidic hydrogen atoms are omitted for clarity.

Over the last decade, Sessler and co-workers have reported a number of studies on the synthesis and anion binding properties of 2,3-dipyrrolyl-2′-yl quinoxalines (DPQs), such as compound **35**.[34] Recently, the Austin group have extended this chemistry and have synthesised diindolylquinoxalines **36** and **37** (Scheme 5).[35] These compounds have a slightly different topology to the DPQs, as the indole groups in **36** and **37** are linked through the 3-position whilst the pyrrole groups in **28** are linked through the 2-position. The DIQ receptors proved to be selective for dihydrogen phosphate anions (Table 6); the findings are in marked contrast to DPQ **35**, which was selective for fluoride under these conditions. Single crystal X-ray diffraction was used to elucidate the structure of the $H_2PO_4^-$ complex of receptor **37**. The structure (shown in Fig. 17) shows that the receptors complex to a continuous chain of $H_2PO_4^-$ anions in the solid state, with two crystallographically-distinct receptors: one complexing to adjacent $H_2PO_4^-$ anions and the other forming hydrogen bonds to one dihydrogen phosphate and its next but one neighbour.



Scheme 5 The synthesis of diindolylquinoxalines **36** and **37**.

Yan and co-workers have taken Sessler's DIQ chemistry a step further by oxidising compounds **36** and **37** with DDQ,

Table 6 The stability constants (K_a/M^{-1}) of **35**, **36** and **37** with anions in dichloromethane at 22 °C[a]

	Host		
Anion	**35**	**36**	**37**[c]
F^-	118 000	2100	[b]
Cl^-	65	170	470
HSO_4^-	n.d.	80	250
Benzoate	n.d.	600	2700
$H_2PO_4^-$	80	6800	20 000

[a] Values were determined by UV-vis spectroscopic titrations; errors are $< \pm 10\%$. All anions were used in the form of their respective tetrabutylammonium salts. n.d. = not determined. [b] A reliable stability constant could not be determined due to the observation of biphasic behaviour. [c] The stability constant for the interaction of receptor **37** with $H_2PO_4^-$ was also examined in acetone, acetonitrile and DMSO; the K_a values were 5600, 2400 and 300 M^{-1}, respectively.

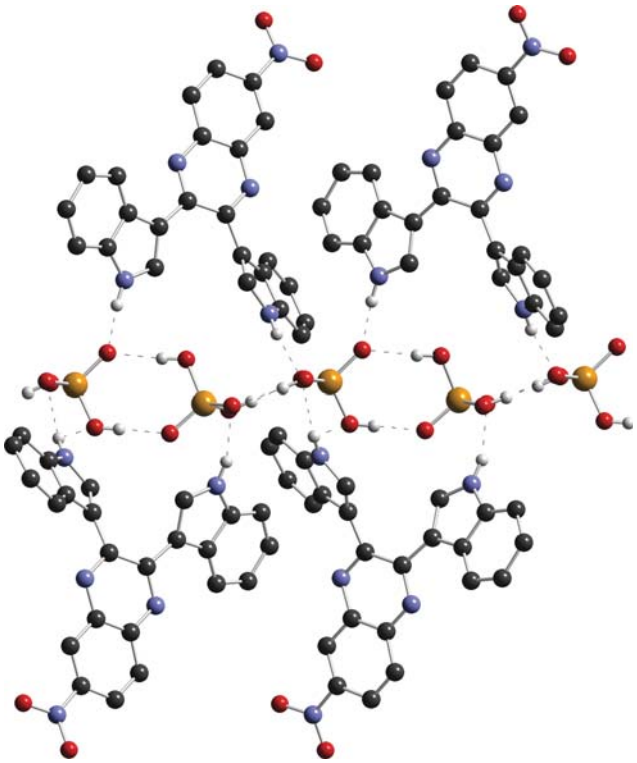
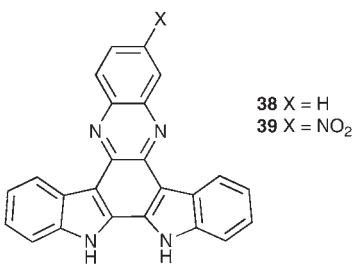


Fig. 17 The X-ray crystal structure of the tetrabutylammonium dihydrogen phosphate complex of receptor **37**. Non-acidic hydrogen atoms and counter-cations have been omitted for clarity.

refluxing them in TFA to afford the corresponding indolocarbazole-quinoxalines **38** and **39**.[36] These species showed a high affinity for basic anions, such as fluoride, acetate and dihydrogen phosphate, in DMSO solution. The X-ray crystal structure of the acetate complex of compound **39** was determined, showing the anion accepting two hydrogen bonds from the carbazole unit (Fig. 18).



38 X = H
39 X = NO_2

Gale and co-workers at the University of Southampton have synthesised pyridine-2,6-dicarboxamide and isophthalamide[37] cleft molecules, containing pendant 2,3-dimethylindole groups linked *via*- the 7-position.[38] Compounds **40** and **41** showed a high selectivity for fluoride in DMSO/water mixtures (Table 7), which the authors attributed to the receptor adopting a 'twisted' conformation when binding to fluoride, which more completely encapsulated this smaller anion (the X-ray crystal structure of the fluoride complex of compound **41** is shown in Fig. 19) than the perching binding mode observed for chloride (see Fig. 20), resulting in stronger complexation under these polar solvent conditions.

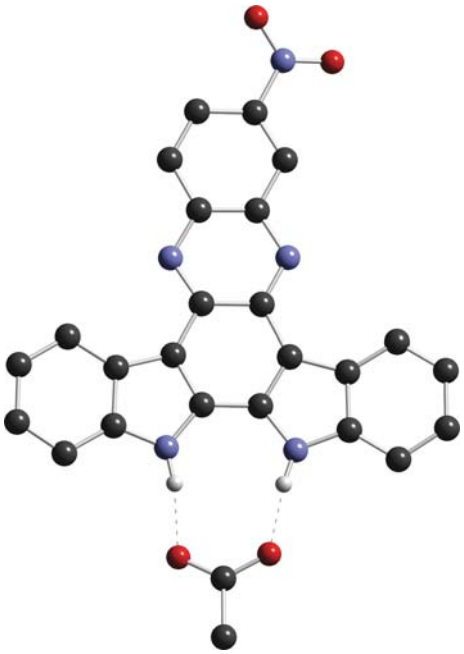
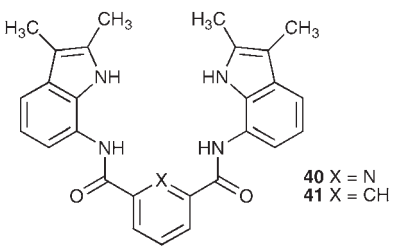


Fig. 18 The crystal structure of the acetate complex of receptor **39**. Tetrabutylammonium counter-cations, non-acidic hydrogen atoms and solvent molecules have been removed for clarity.

Subsequently, Jurczak and co-workers published the synthesis and anion-binding properties of cleft-type receptors **42–44**, containing pendant indole groups linked *via* the

Table 7 The stability constants (K_a/M^{-1}) of compounds **40** and **41** with a variety of putative anionic guests, added as their tetrabutylammonium salts at 298 K, in DMSO-d_6/0.5% water or DMSO-d_6/5% water solution. A 1 : 1 receptor : anion stoichiometry was observed except where noted.



40 X = N
41 X = CH

Anion	**40**	**41**
Fluoride[a]	$>10^4$	[c]
Chloride[a]	<10	17
Bromide[a]	No interaction	No interaction
Acetate[a]	250	880
Dihydrogen phosphate[a]	70	1140
Benzoate[a]	17	120
Fluoride[b]	1360	K_1 = 940 K_2 = 21
Chloride[b]	<10	15
Acetate[b]	14	110
Dihydrogen phosphate[b]	26	260
Benzoate[b]	<10	35

[a] DMSO-d_6/0.5% water solution. [b] DMSO-d_6/5% water solution. [c] The NMR titration data was consistent with strong binding, but could not be successfully fitted to either 1 : 1 or 1 : 2 receptor : anion binding models.

Fig. 19 A space-filling view of the crystal structure of the fluoride complex of receptor **41**. Reproduced from G. W. Bates, P. A. Gale and M. E. Light, *Chem. Commun.*, 2007, 2121. Reproduced by permission of The Royal Society of Chemistry (RSC).

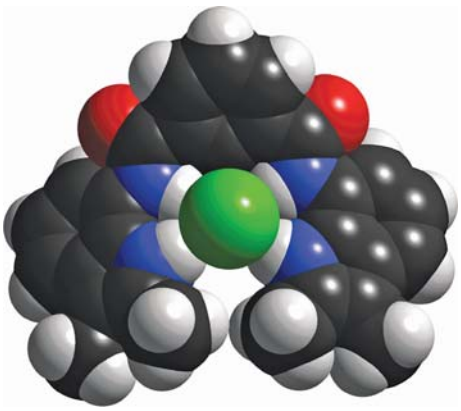
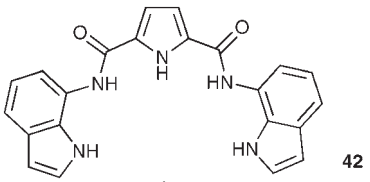


Fig. 20 A space-filling view of the crystal structure of the chloride complex of receptor **41**. Reproduced from G. W. Bates, P. A. Gale and M. E. Light, *Chem. Commun.*, 2007, 2121. Reproduced by permission of The Royal Society of Chemistry (RSC).

7-position.[39] Compound **43** had the highest affinity for anions of the three compounds reported, binding to dihydrogen phosphate selectively (over chloride or benzoate) with a stability constant of approximately 2400 M^{-1} in DMSO-d_6/0.5% water. Molecular modelling studies were used to determine the conformational preferences of these compounds, findings that were successfully correlated to the affinity of these species for anionic guests.

Pfeffer and co-workers from Deakin University have reported the synthesis and anion-binding properties of the series of compounds, **45–47**, that contain a 2-carboxamidoindole linked *via* an alkyl chain to a urea or thiourea group.[40] Upon addition of fluoride to compound **45**, significant broadening of the NH resonances was observed, and after the addition of 1.2 equivalents of fluoride, one of the urea resonances and the indole NH signal completely disappeared. When >2 equivalents of fluoride had been added, resonances corresponding to bifluoride $[FHF]^-$ were visible at *ca.* 16 ppm, indicative of deprotonation of the host by fluoride. Similar behaviour was observed with compounds **46** and **47**, and notably in the case of compound **47**, the addition of fluoride was accompanied by a colour change from colourless to yellow-orange. Other anions were bound by the receptors, with NMR titration curves illustrating which NH groups were predominantly involved in binding in each case. The determined stability constants are summarised in Table 8.



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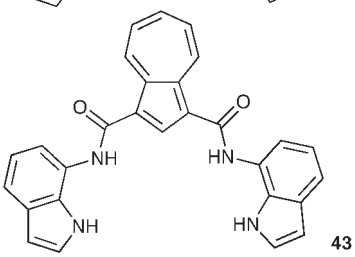

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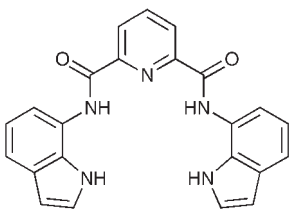
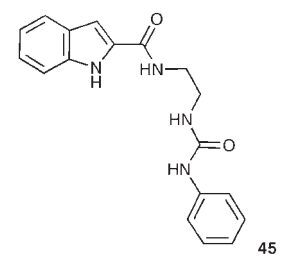


44

Gale and co-workers have also studied the anion-binding properties of 2-amidoindoles and have reported the anion complexation properties of compounds **48–51**, which each

Table 8 The stability constants (log β) for compounds **45**, **46** and **47** against a selection of anionic guests in DMSO solution



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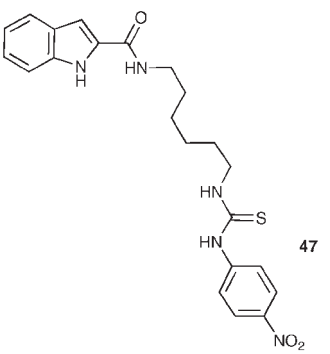
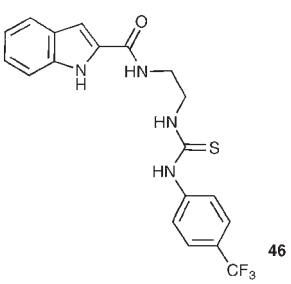


47



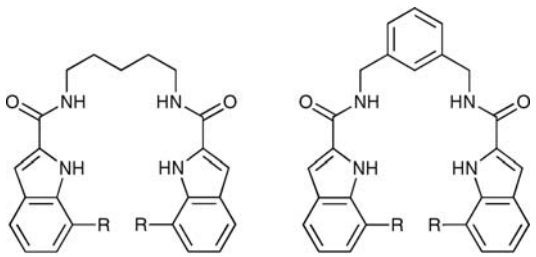
46

	Anion		
Receptor	Cl^-	AcO^-	$H_2PO_4^-$
45	2.1[a]	3.1 ± 0.2	3.5 ± 0.3
46	2.2[a]	2.8 ± 0.4	3.5[a]
47	—	3.9 ± 0.7	3.4 ± 0.2

[a] Estimation only due to error > 20%.

consist of either two 2-carboxyamidoindoles or two 7-nitro-2-carboxamidoindoles, linked *via* either a pentyl or 1,3-phenylenediamine linker.[41] The compounds showed moderate affinities for anions in DMSO-d_6/0.5% water with, in most cases, a slight selectivity for dihydrogen phosphate (Table 9). The complexes formed were found to adopt a 1 : 1 stoichiometry in all cases, except for compound **51** and dihydrogen phosphate, which was shown by Job plot analysis to bind in a 1 : 2 receptor : anion stoichiometry. Crystals of the dihydrogen phosphate complex of receptor **48** were grown by slow evaporation of an acetonitrile solution of the receptor and tetrabutylammonium dihydrogen phosphate. As was seen with Sessler's diindolylquinoxaline (**37**) dihydrogen phosphate complex, compound **48** forms hydrogen bonds to a dihydrogen phosphate ion-pair, which is part of a continuous chain of $H_2PO_4^-$ anions in the solid state (Fig. 21 and Fig. 22).

Table 9 The stability constants (K_a/M^{-1}) for compounds **48–51** with anionic guests, added as their tetrabutylammonium salts, in DMSO-d_6/0.5% water solution at 298 K. 1 : 1 stoichiometries were observed except where noted. Errors in fitting estimated <15% except for chloride



Anion	**48**	**49**	**50**	**51**
F^-	82.5	[a]	<10	[a]
CH_3COO^-	46	149	38	97
$PhCOO^-$	25	24	18	11
$H_2PO_4^-$	260	99	176	K_1 = 108 K_2 = 216
Cl^-	<10	<10	<10	<10

[a] The NH proton resonance disappeared during the titration.

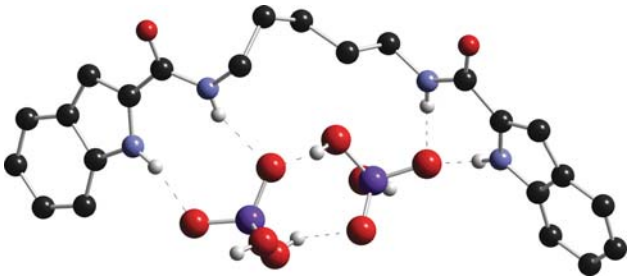


Fig. 22 A closer view showing receptor **48** binding a dihydrogen phosphate dimer in the solid state. Note the two different binding modes of the carboxamidoindole groups. Counter-cations and non-acidic hydrogen atoms have been omitted for clarity.

The Southampton group, in collaboration with Albrecht and Triyanti from the University of Aachen, have reported the synthesis of a series of 2,7-disubstituted indoles with pendant amide and urea groups.[42] This work arose as a collaboration employing design principles from Gale's work on amidopyrroles[43] and Albrecht's work on functionalised quinolines as anion receptors.[44] A series of six compounds were synthesised, of which bis-amide **52** and mono-amide-mono-urea **53** are exemplars. By following the chemical shifts of each NH group during the titration in DMSO-d_6/0.5% water at 298 K, it was demonstrated that while compound **52** employed all three NH groups when binding oxo-anions, such as acetate (with downfield shifts >1 ppm for all three groups—Fig. 23), compound **53** bound carboxylates predominantly *via* the urea/thiourea NH groups and the indole NH (Fig. 24). This is indicated by the greater shifts of the urea and indole NH groups, and their titration profiles reaching a plateau compared to the amide NH group resonance, which shifted downfield by a significantly smaller degree and did not reach a plateau. Presumably, the amide can orient out of the binding site and is able to interact weakly with further additions of anions. These findings were supported by crystallographic studies on the chloride complex of compound **53**, which shows the receptor hydrogen-bonded to two chlorides—one *via* the indole and urea NH groups, and the other *via* a single hydrogen bond from the amide (Fig. 25).

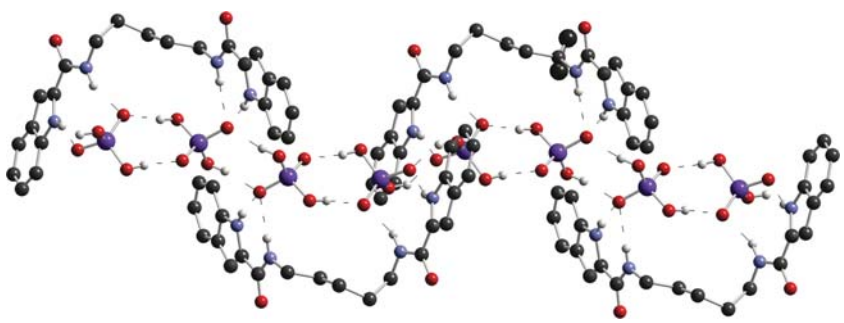
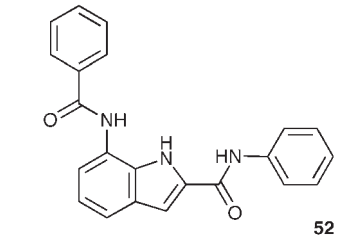


Fig. 21 The X-ray crystal structure of the tetrabutylammonium dihydrogen phosphate complex of receptor **48**, showing the receptors complexing with dihydrogen phosphate anion pairs, which form part of a continuous chain. Counter-cations and non-acidic hydrogen atoms have been omitted for clarity.



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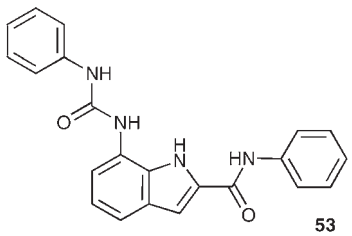

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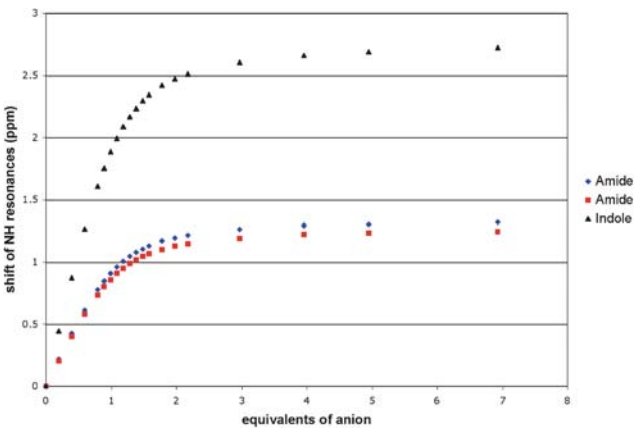


Fig. 23 Proton NMR titration curves for the NH protons in compound **52** upon addition of acetate in DMSO-d_6/0.5% water. Reproduced with permission from *J. Org. Chem.*, 2007, **72**, 8921–8927. Copyright 2007 American Chemical Society.

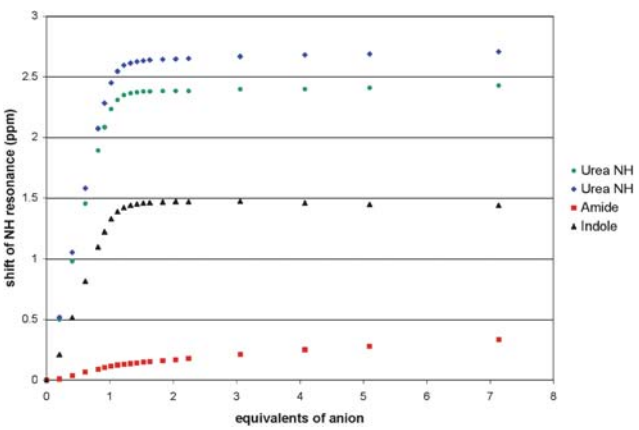


Fig. 24 Proton NMR titration curves for the NH protons in compound **53** upon addition of acetate in DMSO-d_6/0.5% water. Reproduced with permission from *J. Org. Chem.*, 2007, **72**, 8921–8927. Copyright 2007 American Chemical Society.

Building on this design, Gale and co-workers synthesised 1,3-diindolylureas **54** and **55**, which consist of a central urea group linked to two indoles *via* the 7-position.[45] These

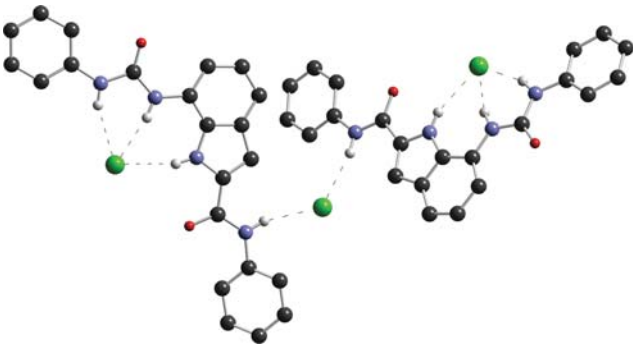


Fig. 25 The X-ray crystal structure of the chloride complex of receptor **53**. Non-acidic hydrogen atoms and tetrabutylammonium counter-cations have been omitted for clarity.

compounds proved to have a high affinity for oxo-anions, with compound **54** binding to dihydrogen phosphate, acetate and benzoate with stability constants $>10^4$ M^{-1} in DMSO-d_6/0.5% water, and 4790, 567 and 736 M^{-1}, respectively, in DMSO-d_6/10% water. Similar results were obtained with compound **55**. However, this latter compound proved to be more soluble than compound **54**, allowing stability constants to be measured in DMSO-d_6/25% water. It was found that under these very competitive conditions, compound **55** bound to $H_2PO_4^-$ with an apparent stability constant of 160 *vs.* 20 M^{-1} for acetate. Single crystals of the tetrabutylammonium benzoate complex of receptor **54** were grown by the slow evaporation of a DMSO solution of the complex. The structure revealed that the anion was bound by the four hydrogen bond donors in the receptor, with N···O interactions in the range 2.846–2.907 Å (Fig. 26).

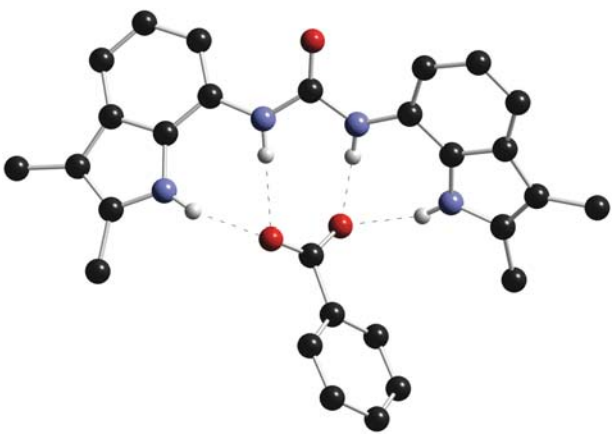
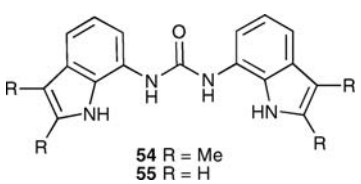
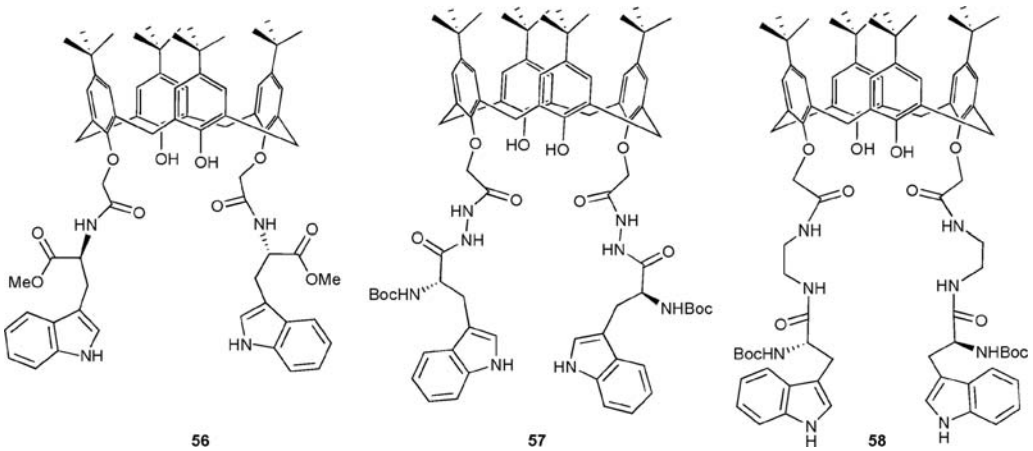


Fig. 26 The X-ray crystal structure of the benzoate complex of compound **54**. Non-acidic hydrogen atoms and counter-cations have been omitted for clarity.



54 R = Me
55 R = H



He and co-workers have synthesised three chiral fluorescent receptors, **56**, **57** and **58**, based on *para-tert*-butylcalix[4]arene functionalised at the lower rim with L-Trp units.[46] The selectivities towards different chiral carboxylates have been studied by fluorescence titration methods. Fig. 27 shows the fluorescence emission spectra of a mixture of receptor **56** and different concentrations of L-Ala or D-Ala in DMSO. The dramatically different fluorescent response and quenching efficiency (10% for L-Ala and 48% for D-Ala) observed for the two enantiomers indicate that compound **56** has good enantioselective fluorescence recognition properties towards the Ala anion. Similarly, the fluorescence emission of receptor **57** was selectively quenched (quenching efficiency 88%) upon addition of excess D-mandelate, while the quenching was negligible (11%) when the L-enantiomer was added (Fig. 27). In the case of receptor **58**, the peak emission was at 445 nm, whereas the maximum fluorescence emission of **56** and **57** was at 345 nm. This is due to the longer linkers in this system, allowing an intramolecular interaction between the two indole groups, causing the formation of an excimer. This is not possible in receptors **56** and **57**, which have more rigid amide and hydrazine linkers, respectively. Upon addition of anions, an anion-induced fluorescence enhancement was observed, and in particular, receptor **58** showed a good enantioselective recognition ability towards D-phenylananinol. The same group have also synthesised cleft-like receptors carrying similar Trp groups and studied the fluorescence of these species in the presence of chiral carboxylates.[47]

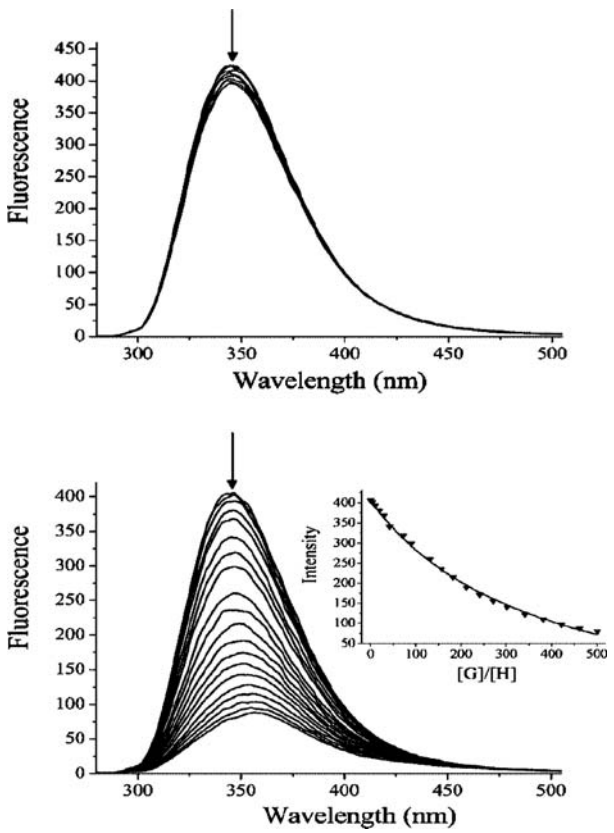


Fig. 27 The fluorescence spectra of receptor **56** with L-Ala anion (top) and D-Ala anion (bottom) in DMSO. Inset: changes in the fluorescence intensity of **56** at 346 nm upon addition of D-Ala anion. Reproduced with permission from *Eur. J. Org. Chem.*, 2007, 1768–1778. Copyright 2007 Wiley-VCH.

Conclusions

In the last four and a half years, indoles have been incorporated into a variety of anion receptor and sensor frameworks as either functionalised indoles, carbazoles, biindoles or indolocarbazoles. The pace of development has been fast, and many of the compounds developed have high affinities and selectivities for specific anionic guests. We can look forward to further exciting developments in indole, carbazole, biindole and indolocarbazole-based anion receptor chemistry in the coming years.

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