PAPER

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Ammonium halide selective ion pair recognition and extraction with a chalcogen bonding heteroditopic receptor†

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The first example of a heteroditopic receptor capable of cooperative recognition and extraction of ammonium salt (NH_4X) ion-pairs is described. Consisting of a bidentate 3,5-bis-tellurotriazole chalcogen bond donor binding cleft, the appendage of benzo-15-crown-5 (B15C5) substituents to the tellurium centres facilitates binding of the ammonium cation *via* a co-facial bis-B15C5 sandwich complex, which serves to switch on chalcogen bonding-mediated anion binding potency. Extensive quantitative ion-pair recognition ^{1}H NMR titration studies in $CD_3CN/CDCl_3$ (1 : 1, v/v) solvent media reveal impressive ion-pair binding affinities towards a variety of ammonium halide, nitrate and thiocyanate salts, with the heteroditopic receptor displaying notable ammonium halide salt selectivity. The prodigious solution phase NH_4X recognition also translates to efficient solid–liquid and liquid–liquid extraction capabilities.

Introduction

The ammonium cation (NH_4^+) is implicated in pivotal roles across various domains from biological metabolism[1–4] to environmental monitoring,[5–9] and industrial processes.[10] Indeed, in biotic systems NH_4^+ is a crucial intermediate in nitrogen metabolism, amino acid synthesis and pH regulation,[11] whilst, from an anthropogenic perspective NH_4^+ constitutes a key component in agricultural fertiliser, and a crucial reagent in chemical manufacturing.[12] Considering the importance of ammonium, it is surprising that more effort has not been directed towards designing receptors capable of its molecular recognition,[13] wherein the majority of reports to date primarily rely on tripodal pyrazolyl- or cryptand-based host systems.[14–21] The development of heteroditopic receptors for ion pair recognition *via* the simultaneous binding of a cation and an anion has proven a powerful strategy in augmenting ion affinity and selectivity profiles of supramolecular host systems.[22–24] Typically such ditopic hosts target alkali metal salts, employing a crown ether motif for metal cation binding covalently linked to hydrogen bond donors for recognition of the counter-anion guest species.

In recent decades the supramolecular toolbox for anion recognition has been expanded to include sigma (σ)-hole type interactions,[25,26] with halogen bonding (XB)[27–30] and chalcogen bonding (ChB)[31–34] monotopic host systems commonly exhibiting remarkable anion binding affinity enhancements and unique selectivity behaviours relative to more traditionally employed hydrogen bonding based receptors.[35–41] Despite this, the integration of sigma (σ)-hole interactions into heteroditopic host structural design remains rare.[42–44] In light of these advantages and paucity of receptors targeting ammonium ion-pairs,[45] we sought to apply our recent report of a ChB heteroditopic ion-pair receptor,[46] **1·ChB^PFP**, consisting of a 3,5-bis-tellurotriazole nitro-benzene central scaffold functionalised with electron-deficient perfluorophenyl substituents and benzo-15-crown-5 appended telluro-triazoles (Fig. 1), for the purpose of ammonium ion-pair (NH_4X) recognition. Herein, we report to the best of our knowledge the first example of a heteroditopic receptor capable of cooperative solution phase recognition of NH_4X ion-pairs, where extensive quantitative ion-pair affinity measurements demonstrate considerable selectivity towards ammonium halides. Crucially, the anion affinity of the receptor relies on NH_4^+ complexation *via* an intramolecular co-facial sandwich complex by the B15C5 units which not only conformationally preorganises the tellur-otriazole ChB donors, but also switches on Te σ-hole Lewis acidity for anion recognition. This prodigious cooperative ion-pair recognition behaviour of **1·ChB^PFP** is further exploited for successful ammonium salt solid–liquid and liquid–liquid extraction purposes.

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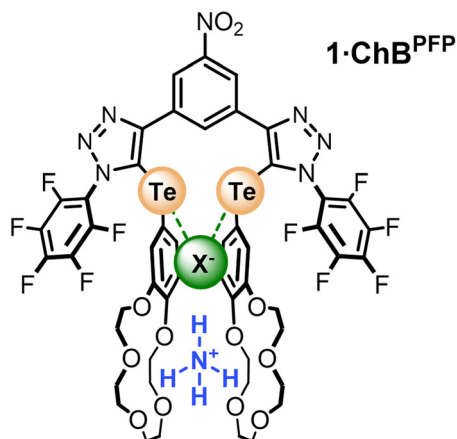
Fig. 1 Ammonium salt (NH₄X) binding chalcogen bonding heteroditopic receptor **1·ChB**^{PFP}.

Results and discussion

Anion and ion-pair recognition studies

It is well known that B15C5 is capable of forming 2 : 1 host–guest stoichiometric complexes with alkali metal cations K$^+$,

Rb$^+$, Cs$^+$,[47–49] and similar sandwich complex formation has also been reported with NH₄$^+$.[50] Motivated by this, we sought to determine whether **1·ChB**^{PFP} could bind an ammonium cation in an analogous intramolecular manner between the two pendant B15C5 units and thereby potentially function as a receptor for NH₄X ion-pairs (Fig. 2a). To this end, a qualitative ^{1}H NMR titration experiment was initially conducted, wherein to a CD₃CN/CDCl₃ (1 : 1, v/v) solution of **1·ChB**^{PFP} was added an equimolar amount of solid NH₄PF₆. Upon comparison of the ^{1}H NMR spectra of pre- and post-ammonium salt addition, dramatic perturbations and broadening of the resonances associated with the crown ether aromatic and methylene regions, namely signals c, d, e, f and h respectively were observed relative to the free receptor (Fig. 2b). Specifically, the dramatic *ca.* 1 and 0.5 ppm upfield shifts of CH₂ signals f and h of the polyether chain, evidence a strong shielding effect from a proximal aromatic ring current, supporting the formation of a cofacial NH₄$^+$ bis-B15C5 sandwich complex and is wholly consistent with previously reported diagnostic chemical shift changes associated with this type of complex.[47–49] The sequential addition of further equivalents of NH₄PF₆ elicited no further changes in the ^{1}H NMR spectrum, indicative of 1 : 1 NH₄$^+$: **1·ChB**^{PFP} complex stoichiometry and the association of ammonium cation to the B15C5 units is of considerable

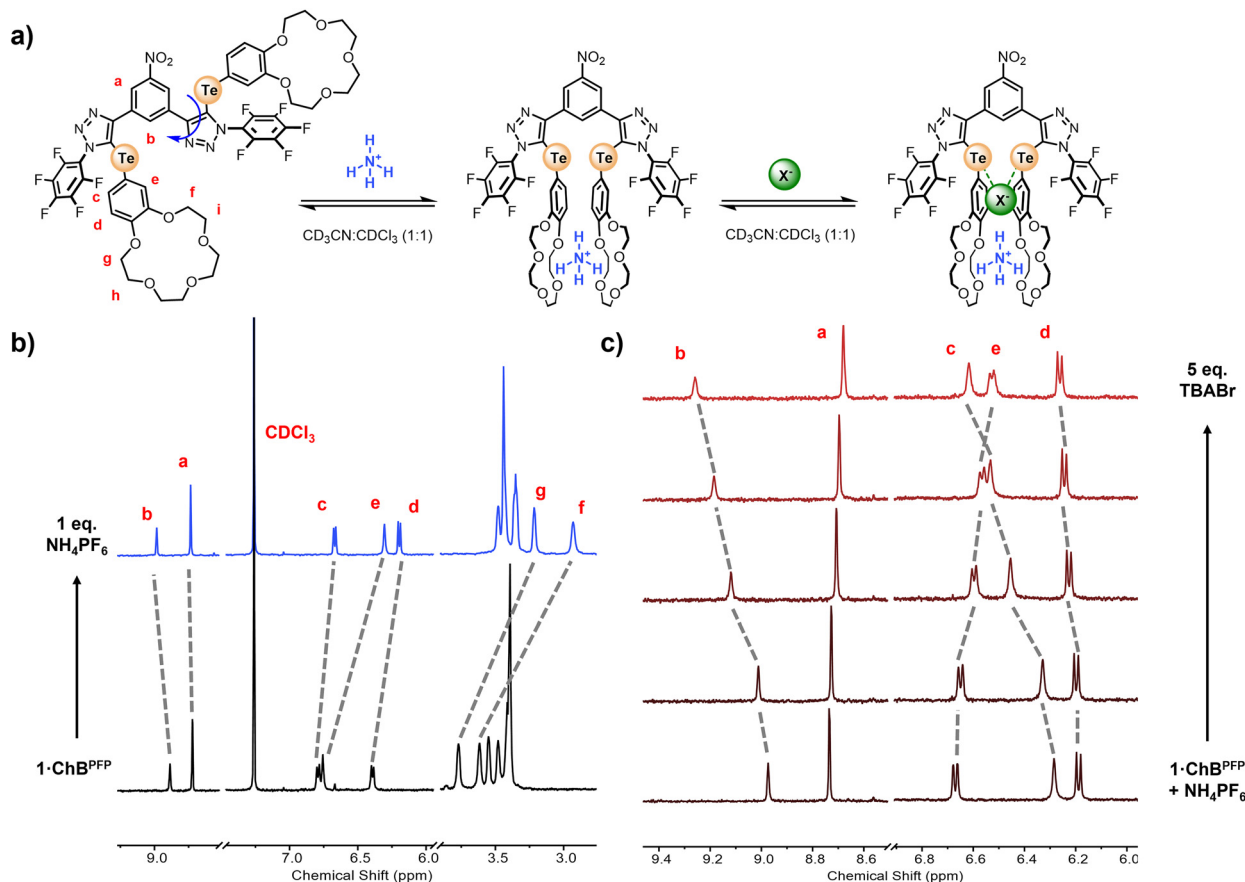**Fig. 2** (a) NH₄X **1·ChB**^{PFP} binding equilibria. ^{1}H NMR titration experiments of (b) NH₄PF₆ and **1·ChB**^{PFP} (c) TBABr and **1·ChB**^{PFP} in the presence of 1 equivalent of NH₄PF₆ (CD₃CN/CDCl₃ 1 : 1 (v/v), 500 MHz, 298 K).

strength ($K_a > 10^4$ M^{-1}). Furthermore, the relatively minor perturbations observed in the nitro phenyl signals a and b suggest minimal perturbation of the ChB binding cleft, as anticipated from the non-coordinating nature of the hexafluorophosphate counter-anion.

Encouraged by this strong evidence for NH_4^+ sandwich complexation, we investigated the ammonium salt ion-pair recognition properties of **1·ChB^{PFP}**. To this end, a series of ^{1}H NMR anion titration experiments were conducted on a CD$_3$CN/CDCl$_3$ (1 : 1, v/v) solution of **1·ChB^{PFP}** in the presence of equimolar NH$_4$PF$_6$. The addition of increasing equivalents of tetrabutylammonium halide, nitrate and thiocyanate salts all induced progressive downfield shifts of the heteroditopic receptor's internal aromatic proton signal b, providing strong evidence for the participation of the tellurotriazole ChB donors mediating the anion recognition process (a representative example for bromide is shown in Fig. 2c). During the course of anion addition, it was noted that characteristic features of the NH_4^+ bis-B15C5 sandwich complex in the ^{1}H NMR spectrum persisted, indicating that the anion binding and cation binding events occur concomitantly *i.e.* genuine ion-pair binding. Monitoring proton b, Bindfit[51] analysis of the resulting anion-induced chemical shift perturbation isotherm titration data (Fig. 3) determined 1 : 1 stoichiometric host/guest apparent association constants (K_a)[52] for a range of halides and polyatomic anions. Table 1 shows the co-bound ammonium complex receptor (**1·ChB^{PFP}·NH$_4^+$**) displays strong halide affinities, with a particularly impressive affinity for chloride with K_a(Cl$^-$) = 2530 M^{-1}, notably greater than both K_a(Br$^-$) and K_a(I$^-$) by at least a factor of two. Interestingly, relative to the halides the affinities for nitrate and thiocyanate are considerably diminished (K_a(NO$_3^-$) = 357 M^{-1} and K_a(SCN$^-$) = 294 M^{-1}). It is also noteworthy that whilst anion affinity trends in simple acyclic HB based receptors are typically governed by the anion's inherent basicity, usually correlated with pK_a values, this is not observed for **1·ChB^{PFP}**, and empirically appears to be a consistent feature of sigma-hole based anion receptors.[53]
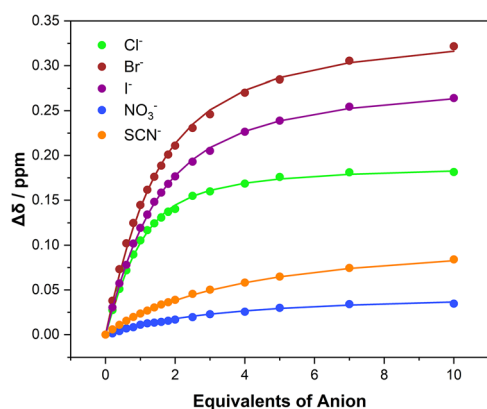
Table 1 Anion association constants for **1·ChB^{PFP}** from ^{1}H NMR titration experiments (1 : 1 CD$_3$CN/CDCl$_3$ (v/v), 500 MHz, 298 K)

Anion association constant (K_a, M^{-1}) of **1·ChB^{PFP}** in the presence of equimolar NH$_4$PF$_6$ ^{a,b}		Anion pK_a
Cl$^-$	2530	−8.0
Br$^-$	1140	−9.0
I$^-$	1130	−10
NO$_3^-$	357	−1.3
SCN$^-$	294	4.0

^{a} Determined from Bindfit analysis, monitoring signal b, error <5%.
^{b} Anions added as their tetrabutylammonium salts.

Interestingly, the co-bound ammonium complex receptor **1·ChB^{PFP}·NH$_4^+$** halide association constant values are of significantly larger magnitude than those determined with the potassium complex **1·ChB^{PFP}·K$^+$** [46] with a particularly notable 2-fold enhancement in chloride affinity. Whilst the exact origin of this enhancement is not definitively known, it is postulated the N–H···O hydrogen bonding interactions formed between NH_4^+ and the crown ether oxygens more effectively electronically polarise the Te ChB donor centres than a potassium cation thereby raising anion binding potency. Importantly, in the absence of NH$_4$PF$_6$, **1·ChB^{PFP}** exhibited no measurable anion binding affinity, thereby confirming the crucial role of bis-B15C5 sandwich bound NH_4^+ in switching on ChB mediated anion recognition *via* favourable proximal electrostatic interactions and preorganised through bond polarisation of the Te sigma-hole donors.

Solid state single-crystal X-ray diffraction study of NH$_4$Br ion-pair complex

Further insight into the ammonium halide salt ion-pair recognition mode of **1·ChB^{PFP}** in the solid state was provided by single crystal diffraction X-ray analysis of **1·ChB^{PFP}** complexed with NH$_4$Br (Fig. 4). Consistent with the ^{1}H NMR solution phase evidence, the ammonium cation is complexed *via* a cofa-

Fig. 3 Anion-binding isotherms for **1·ChB^{PFP}** in the presence of 1 equivalent of NH$_4$PF$_6$ (CD$_3$CN/CDCl$_3$ 1 : 1 (v/v), 500 MHz, 298 K).
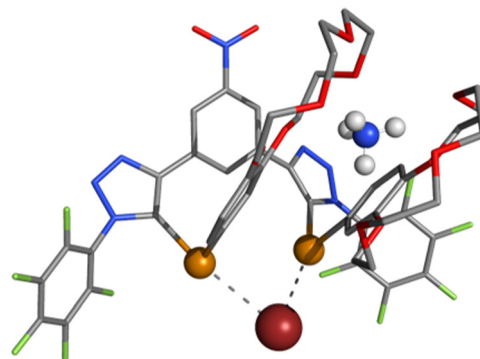

Fig. 4 Solid-state structure of **1·ChB^{PFP}** complexed with NH$_4$Br (solvent molecules and hydrogen atoms, except those of NH$_4^+$, are omitted for clarity). Grey = carbon, blue = nitrogen, red = oxygen, light green = fluorine, orange = tellurium and dark red = bromine.

cial B15C5 sandwich complex. However, in contrast to the structure of alkali metal cation (M$^+$) complexes previously obtained for **1·ChB^{PFP}**,[46] there are notable differences. Specifically, in the M$^+$ crystal structures the orientation of the crown ether rings appear relatively symmetric, typically allowing all five oxygen atoms of each B15C5 unit to coordinate the cation. In contrast, the somewhat skewed conformations of the B15C5 units observed in the ammonium bromide complex of **1·ChB^{PFP}** seem to suggest a less symmetric NH$_4^+$ complexation mode.[46] This is presumably due to the formation of directional hydrogen bonds between the ammonium and crown ether oxygens; N–H···O. The Br$^-$ counteranion is shown to be chelated, moderately asymmetrically, by bifurcated chalcogen bond formation, exhibiting short Te···Br contacts of 3.241 Å and 3.583 Å, corresponding to contractions in their van der Waal radii of 83% and 92% respectively. Determination of the C–Te···Br angles; 174° and 167° reveals a commonly observed preference for ChB interactions in which the preferential bonding geometry approaches linearity.

Ammonium salt solid–liquid and liquid–liquid ion-pair extraction studies

Motivated by the impressive ion-pair affinity of **1·ChB^{PFP}** for ammonium salts, as evidenced by quantitative solution phase ^{1}H NMR binding studies, attention was directed toward investigating the heteroditopic receptor's potential as an extraction agent for NH$_4$X salts under solid–liquid (SLE) and liquid–liquid extraction (LLE) conditions. In a typical SLE experiment, a CDCl$_3$ solution of **1·ChB^{PFP}** was exposed to a 5-fold molar excess microcrystalline solid sample of NH$_4$X (X = Cl$^-$, Br$^-$, I$^-$, NO$_3^-$, SCN$^-$) and stirred for 10 minutes (Fig. 5a). With the

exception of NH$_4$Cl, the ^{1}H NMR spectrum of the resultant post-extraction solution in general revealed dramatic changes relative to the pre-extraction spectrum and closely resembled spectroscopic features observed during the solution phase ion-pair titration experiments with NH$_4$PF$_6$ and TBAX (Fig. 5b). Specifically, in the case of NH$_4$Br, NH$_4$I, NH$_4$NO$_3$ and NH$_4$SCN, dramatic broadening of the methylene and aromatic signals of B15C5 units, indicative of the NH$_4^+$ sandwich complexation binding mode and downfield perturbations of the internal aromatic signal b, consistent with ChB mediated anion binding, were observed. It was also noted a new signal appeared presenting as a triplet consistent with the heteronuclear spin–spin coupling between ^{1}H and ^{14}N of NH$_4^+$, further confirming successful extraction of these NH$_4$X salts into CDCl$_3$. The extraction efficiency for each NH$_4$X salt was estimated by integration of the N–H signals of NH$_4^+$ relative to signal a of **1·ChB^{PFP}**, thereby determining the ratio of NH$_4$X extracted by **1·ChB^{PFP}**, the results of which are summarised in Table 2, together with graphical presentation shown in Fig. 6. The efficiency of a host to perform SLE is a subtle balance

Table 2 Solid–liquid extraction efficiencies of **1·ChB^{PFP}**

Ammonium salt	NH$_4$Cl	NH$_4$Br	NH$_4$I	NH$_4$NO$_3$	NH$_4$SCN
Extraction^a	0%	85%	>95%	~5%^{b}	>95%
ΔH_L/kJ mol^{-1}	705	647	608	646	597

^{a} Determined from relative integration of proton signals a of **1·ChB^{PFP}** and of NH$_4^+$, error estimated at ±5%. ^{b} Despite evident extraction of NH$_4$NO$_3$ from the post SLE ^{1}H NMR spectrum the very low signal intensity of the co-extracted NH$_4^+$ precluded precise extraction percentage determination.
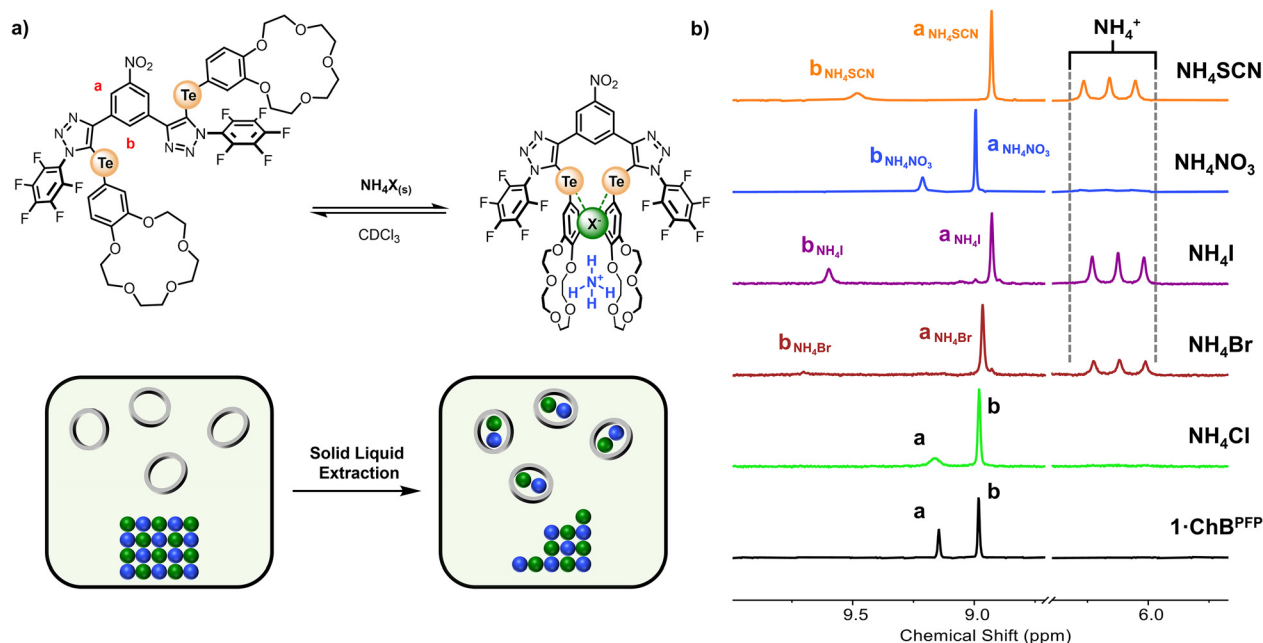

Fig. 5 (a) Representative SLE equilibrium of ammonium salt (NH$_4$X) by **1·ChB^{PFP}** and cartoon representation of the SLE process (b) Pre and post-SLE ^{1}H NMR spectra (CDCl$_3$, 500 MHz, 298 K), with various ammonium salts.
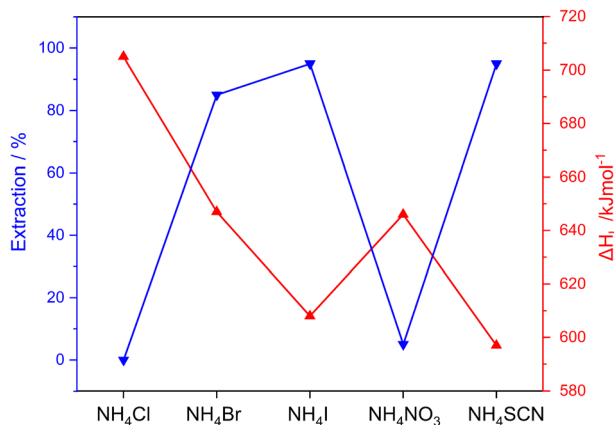
Fig. 6 Plot showing extraction efficiency (blue) and lattice energy ΔH_L (red) versus NH$_4$X (X = Cl, Br, I, NO$_3$).

between two competing factors: the affinity of the host for the ion-pair and the lattice enthalpy (ΔH_L) of the salt to be extracted. In the former, a higher ion-pair binding affinity usually translates to improved SLE (or LLE) extraction performance, whilst in the latter a larger ΔH_L is energetically unfavourable to extraction performance. Inspection of Table 2 reveals that whilst NH$_4$I and NH$_4$SCN are extracted with the highest efficiencies >95%, as expected on the basis of their low ΔH_L values, interestingly, in stark contrast, the extraction efficiencies observed for NH$_4$Br and NH$_4$NO$_3$, are 85% and ~5% respectively. Considering their near identical lattice enthalpies; ΔH_L(NH$_4$Br) = 647 kJ mol^{-1} and ΔH_L(NH$_4$NO$_3$) = 646 kJ mol^{-1}, it is apparent the 3-fold enhancement in solution phase ion-pair affinity for K_a(Br$^-$) relative to K_a(NO$_3^-$) notably translates to an improved extraction capability providing strong evidence for **1·ChB^{PFP}** functioning as a genuine ion-pair receptor. However, despite **1·ChB^{PFP}** exhibiting the largest NH$_4$Cl ion-pair affinity from solution phase experiments (Table 2), no evidence of SLE was noted, suggesting the appreciable magnitude of ΔH_L(NH$_4$Cl) dominates in this case.

Liquid–liquid extraction (LLE) experiments were undertaken for ammonium chloride, bromide and iodide. In a typical LLE experiment a CDCl$_3$ solution of **1·ChB^{PFP}** (2 mM) was exposed to an ammonium halide D$_2$O solution (4 M), stirred vigorously for 30 minutes and ^{1}H NMR spectrum of the post-extraction CDCl$_3$ organic phase recorded. As for the SLE experiment, while for NH$_4$Cl no receptor proton perturbations were observed, in the case of NH$_4$Br and NH$_4$I a comparison of the pre- and post-extraction spectra revealed successful extraction of the ammonium halides as evidenced by similar proton perturbations to those observed in the SLE experiments (Fig. S7†). However, unlike in the SLE experiment, the signal corresponding to the co-extracted NH$_4^+$ was significantly broadened or not observable, presumably due to deuterium-proton isotope exchange from the deuterated aqueous source phase, which prevented quantitative determination of LLE efficiencies.

Conclusions

In summary, the unprecedented cooperative ion-pair recognition of ammonium salt ion-pair species (NH$_4$X) is achieved by a heteroditopic receptor **1·ChB^{PFP}**. Exploiting the bis-tellurotriazole ChB donor framework, wherein the Te-centres are directly appended with B15C5 units, co-facial intramolecular bis-B15C5 NH$_4^+$ sandwich complex formation not only preorganises the receptor's ChB donor groups, but also effectively serves to enhance and switch on the Lewis acidity of the Te-centres for anion recognition. Quantitative ^{1}H NMR binding studies demonstrate prodigious NH$_4$X ion-pair binding properties, highlighting a significant selectivity preference for ammonium halide salts over NH$_4$NO$_3$ and NH$_4$SCN. Solid state X-ray structural analysis of the **1·ChB^{PFP}**·NH$_4$Br ion-pair complex supports the postulated bis-crown ether NH$_4^+$ sandwich binding mode, concomitant with strong ChB···Br– interactions driving anion coordination. The notable solution phase NH$_4$X ion-pair binding properties of **1·ChB^{PFP}** are also reflected in the heteroditopic receptor's efficient solid–liquid and liquid–liquid extraction NH$_4$Br and NH$_4$I salt capabilities. Importantly, these results highlight the exciting potential of sigma (σ)-hole based heteroditopic host structural design for the future development of ammonium salt selective ion-pair recognition applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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