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PERSPECTIVE

Anion capture and sensing with cationic boranes: on the synergy of Coulombic effects and onium ion-centred Lewis acidity

Haiyan Zhao, Lauren A. Leamer and François P. Gabbaï*

Stimulated by the growing importance and recognized toxicity of anions such as fluoride, cyanide and azides, we have, in the past few years, developed a family of Lewis acidic triarylboranes that can be used for the complexation of these anions in organic and protic solvents, including water. A central aspect of our approach lies in the decoration of the boranes with peripheral ammonium, phosphonium, sulfonium stibonium or telluronium groups. The presence of these cationic groups provides a Coulombic drive for the capture of the anion, leading to boranes that can be used in aqueous solutions where anion hydration and/or protonation are usually competitive. The anion affinity of these boranes can be markedly enhanced by narrowing the separation between the anion binding site (*i.e.* the boron atom) and the onium ion. In such systems, the latent Lewis acidity of the onium ion also plays a role as manifested by the formation of B–X→E (E = P, S, Sb, or Te; X = F, CN or N_3) chelate motifs that provide additional stability to the resulting complexes. These effects, which are maximum in stibonium and telluronium boranes, show that the Lewis acidity of heavy onium ions can be exploited for anion coordination and capture. The significance of these advances is illustrated by the development of applications in anion sensing, fluorination chemistry and ^{18}F radiolabeling for positron emission tomography.

Introduction and background

The field of anion recognition has become a very active research area fuelled by the role that these species play in biological systems and in the environment.[1] In turn, molecular receptors that can selectively bind specific anions, especially in protic media, have become increasingly coveted synthetic

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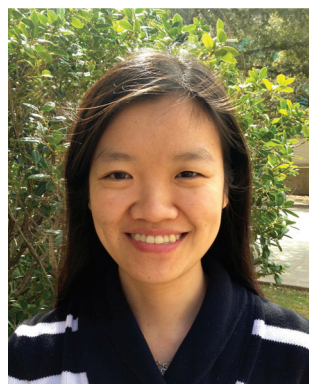
Haiyan Zhao

Haiyan Zhao was born in 1984 in Hebei, China. She earned a B.S. degree from Nankai University, in 2007. The same year, she joined the group of François Gabbaï in department of chemistry at Texas A&M University to obtain her PhD in 2012. During her PhD, she studied the chemistry of cationic boranes and authored several papers included in this article. She is currently enrolled as a graduate student in the Department of Petroleum Engineering at Texas A&M University and is involved in a project dealing with the oilfield applications of polymers and fibers.

Lauren A. Leamer

Lauren Leamer was born in 1988 in Dallas, Texas. She earned a B.S. degree from The University of Texas at Tyler in 2010. She joined the graduate program at Texas A&M in the fall of the same year. For the last two and half years, she has been working in the Gabbaï group on the synthesis and anion affinity of cationic boranes and stiboranes. She successfully defended her MS and will graduate in May 2013.

targets. The approach chosen in the design of such receptors depends largely on the nature of the anionic analyte. While organic receptors with hydrogen-bond donor groups as recognition sites are well suited for large anions,[1,2] Lewis acidic receptors based on main group elements have proven especially well-adapted to the recognition of small nucleophilic anions.[3–9] One of these anions is the cyanide anion. It is highly toxic because of its ability to inhibit cell respiration by deactivating the cytochrome-*c* oxidase enzyme.[10] Unfortunately, cyanide is widely available in both research and industrial settings such that its unintentional release or its use for harmful purposes have occurred in the recent past.[11] Another important nucleophilic anion is the fluoride anion. This anion is often added to drinking water and toothpaste because of its beneficial effects in dental health. It is also administered in the treatment of osteoporosis.[12] However, high doses of this anion are dangerous and can lead to dental or skeletal fluorosis.[13] Thus, as for cyanide, the development of methods that can sense this anion in water has become a topical objective. Ideally, such methods should be sufficiently sensitive to allow for the detection of these anions near or below their drinking water maximum contaminant level set at 4 ppm (210 μmol) for fluoride and 0.2 ppm (7.7 μmol) for cyanide by the Environmental Protection Agency.[14] Designing water compatible receptors that are competent in these concentration ranges is complicated by the high hydration enthalpy of the fluoride ion ($\Delta H^{\circ} = -504$ KJ mol^{-1}). An added challenge exists for the cyanide ion whose competitive protonation (pK_a(HCN) = 9.3) complicates its capture in neutral water. As documented by

extensive available studies, triarylboranes appear well suited for the complexation of these anions.[4–7,9,15] However, to be useful in water, their Lewis acidity should be sufficiently elevated to overcome the hydration enthalpy and/or competitive protonation of these anions.

The introduction of electron-withdrawing substituents in triarylboranes constitutes a well-established method for enhancing their Lewis acidity.[16–18] Noteworthy applications for these fluorinated boranes include the activation of transition metal and main group species *via* anionic ligand abstraction.[17,19] These fluorinated boranes have also been combined with bulky Lewis bases to generate frustrated Lewis pairs that promote the heterolytic cleavage of H_2[16,20] or add to unsaturated compounds such as CO_2, N_2O, alkenes, and alkynes to name a few.[16,19,21] While additional exciting applications may be discovered for the use of these boranes in organic media, their electron-deficiency, as well as the exposed nature of the boron centre, may preclude applications that require the use of water.

An approach that may be better suited to applications in water was pioneered two decades ago by Shinkai who showed that oxidation of Fc–B(OH)$_2$ (Fc = ferrocenyl) into the ferrocenium derivative [Fc–B(OH)$_2$]$^+$ leads to a significant increase of the Lewis acidity and fluoride ion affinity of the boron centre.[22] As stated by Shinkai, his pioneering studies showed that the oxidized species of ferroceneboronic acid has a stronger interaction with fluoride ions compared to the neutral boronic acid. Inspired by this work, we decided in 2005 to determine whether this strategy could be implemented with triarylboranes. In this concept article, we will review some of the results that we have obtained in pursuit of this idea. While the content of this Perspective article largely concentrates on the results obtained by our group, an effort is made to also include related results that have appeared in the recent literature. Finally, the reader is encouraged to consult a few other related reviews that offer a different angle and often partial view into the chemistry of cationic boranes.[1,6,7,23]

Systems with remote and/or charge-delocalized cationic groups

Since the Coulombic attraction between two oppositely charged species is inversely proportional to the distance separating the species involved, it can be predicted that a cationic borane with cationic functionality adjacent to the boron atom will display the highest anion affinity. While this reasoning is certainly verified by some of the results that we will present later in this review, we have observed that the presence of a somewhat distant and diffuse cationic group in organoboranes can have a marked effect on the anion affinity of the boron centre. This phenomenon is appropriately illustrated by the behavior of the four cationic boranes [**1**]$^{+,24}$ [**2**]$^{+,24}$ [**3**]$^{+25}$ and [**4**]$^{+26}$ which have been synthesized by a simple electrophilic methylation procedure using MeOTf in the case of [**1**]$^+$ or [**2**]$^+$, by reaction of the pyridyl precursor with (bpy)$_2$RuCl$_2$ and

François P. Gabbaï

François Gabbaï was born in 1968 in Montpellier. After a Maîtrise in Bordeaux, he joined the group of A. H. Cowley at the University of Texas at Austin (UT). For part of his graduate studies, he collaborated with the group of Guy Bertrand then in Toulouse. After obtaining his PhD from UT in 1994, he joined the group of Hubert Schmidbaur at the Technische Universität München where he was successively awarded an Alexander von Humboldt Fellowship and a Marie Curie Fellowship. In 1998, he completed his Habilitation work and moved to Texas A&M where he now holds a Davidson Professorship in Science. His research focuses on the chemistry of p-block and late transition metal elements with applications in the domain of molecular recognition, nuclear imaging and energy research. He is a fellow of the American Chemical Society and serves as an associate Editor for Organometallics. In 2009 he was recognized as the North American Dalton Lecturer in Inorganic Chemistry; he has also just been admitted as Fellow of the Royal Society of Chemistry.
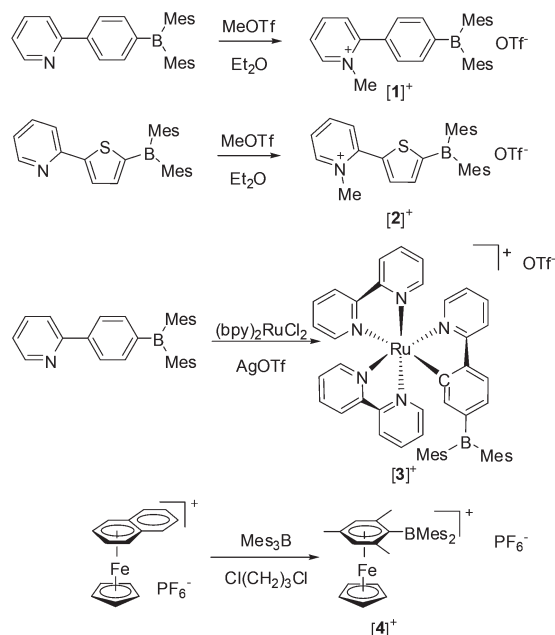
Scheme 1 Synthesis of the cationic boranes [1]⁺, [2]⁺, [3]⁺ and [4]⁺.

AgOTf in the case of [3]⁺ or by attachment of CpFe⁺ group in the case of [4]⁺ (Scheme 1). A feature common to these three species is the distance and relative diffuseness of the cationic functionality. In the case of [1]⁺ and [2]⁺, the positive charge is delocalized over the entire pyridinium ring, a factor that may further contribute to a lessening of Coulombic effects.

A similar argument could be advanced in the case of [3]⁺ and [4]⁺ where the charge is delocalized over the entire metal complex. Despite the diffuseness of these cationic groups, these compounds feature a distinctly higher fluoride and cyanide affinity than neutral boranes with similar steric encumbrances around the boron atom (Fig. 1). This has been verified by anion binding studies monitored by following the quenching of the absorbance of the boron-centred chromophore in the 330–340 nm range. These experiments show that unlike neutral boranes of comparable bulk, these three cationic derivatives react quantitatively with fluoride and cyanide in organic solvents but show no activity for other anions such as Cl⁻, Br⁻, and I⁻. Another distinguishing quality of such compounds pertains to their ability to capture fluoride ions under biphasic conditions as verified for [1]⁺, [2]⁺ and [3]⁺. These observations show that the presence of a distant cationic
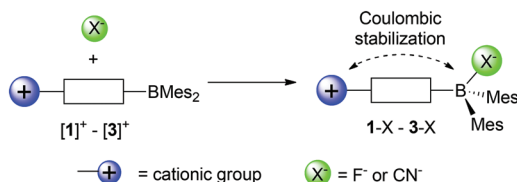

**Fig. 1** Schematic representation of the anion complexation by boranes [1]⁺, [2]⁺ and [3]⁺.

group can still favorably impact the Lewis acidic properties. For complexes such as [3]⁺ and [4]⁺, we note that the cationic groups are large coordination or organometallic complexes which efficiently delocalize the positive charge. Drawing a parallel with the properties of weakly coordinating anions,[27] we propose that the charge delocalization occurring in such systems negatively impacts the anion affinity of the boron centres.

The unique anion binding properties of these compounds are supported by a series of results obtained by other researchers who have described compounds such as [5]⁺ and [6]⁺ as water compatible sensors for fluoride anions,[28] with structures and properties that are reminiscent of those displayed by [1]⁺ and [2]⁺.
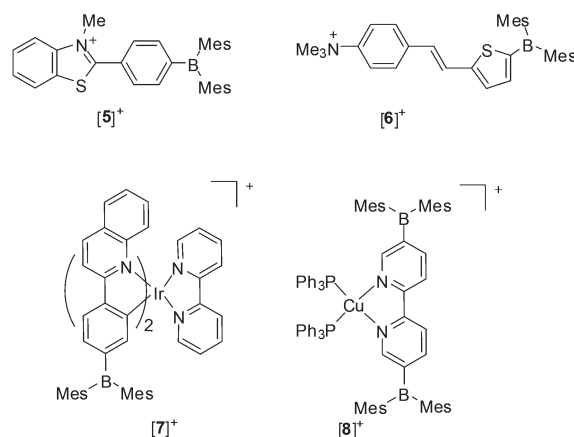

Other examples include the Ir(III) derivative [7]⁺, isolated as PF₆⁻ salt, which captures two equivalents of fluoride ions in acetonitrile (CH₃CN).[29] The first binding constant K_1 of [7]⁺ significantly exceeds that of the free ligand 2-(4-dimesitylboryl-phenyl)quinoline. Similarly, the Cu(I) derivative [8]⁺, shows a fluoride affinity that exceeds that of the corresponding free ligand, namely 5,5′-bis(dimesitylboryl)-2,2′-bipyridine.[30] Reference should also be made to additional examples of cationic coordination complexes with peripheral triarylborane moieties.[6,31] Like [7]⁺ and [8]⁺, these cationic derivatives show a high affinity for nucleophilic anions such as fluoride and cyanide.

Another compound that we have investigated is the cationic borane [10]⁺, which could be obtained by reaction of the tetra-kis(THF)lithium salt of dimesityl-1,8-naphthalenediylborate with [Me₂NCH₂]I and subsequent methylation of the resulting borane **9** with MeOTf (Scheme 2).[32] This cationic borane [10]⁺, containing a remote but localized cationic functionality, shows a much higher affinity towards fluoride and cyanide than the neutral borane **9** in organic solvents. More interestingly, [10]⁺ could capture fluoride and cyanide ions under biphasic conditions (H₂O/CHCl₃). These results confirm that the introduction of the ammonium group can efficiently enhance the Lewis acidity of the triarylboranes. The fluoride binding constant ($K > 10^8$ M⁻¹) of [10]⁺ exceeds the cyanide binding constant (8.0 (±0.5) $\times 10^5$ M⁻¹) in THF.[33] This selectivity can be
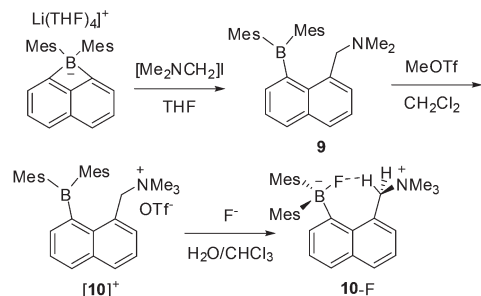
Scheme 2 Synthesis of the cationic borane [10]$^+$ and its reaction with fluoride under biphasic conditions to form **10**-F.

Scheme 3 Behavior of *para*-phenylene ammonium and phosphonium boranes toward fluoride in aqueous solution. The inset on the right hand side shows the fluorescence turn-off response induced by fluoride anion binding to [13]$^+$.

attributed to the higher basicity reported for fluoride in organic solvents (pK_a = 15 for HF and 12.9 for HCN in DMSO).[34] The steric crowding of the boron centre in [10]$^+$ and the larger size of the cyanide ion may be another important contributing factor. The stability of **10**-F also benefits from a BF–HC hydrogen bond, the presence of which has been confirmed by NMR spectroscopy, X-ray diffraction (Fig. 2), and computational analysis. Analogous electrostatic and hydrogen bonding effects have been used to explain the elevated fluoride affinity of [11]$^+$.[35]
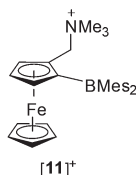
The results discussed in this section indicate that the incorporation of a distant cationic moiety leads to a notable increase of the anion affinity *via* Coulombic effects. These effects are, however, limited, as none of these compounds show an affinity for any anions including fluoride and cyanide in aqueous solutions.
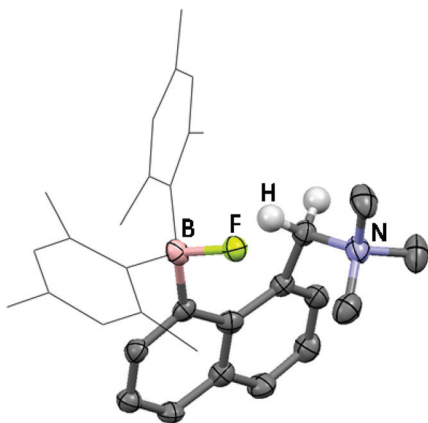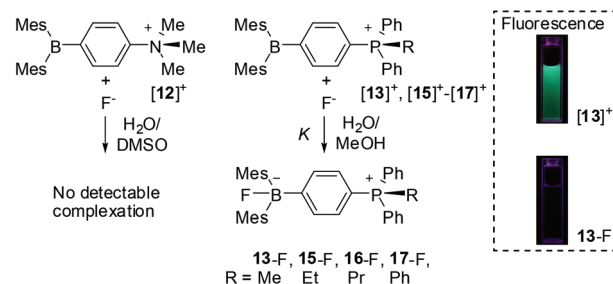

Fig. 2 Crystal structure of **10**-F. Thermal ellipsoids are drawn at the 50% probability level.

para-Phenylene ammonium and phosphonium boranes

Fluoride anion complexation

Based on the results summarized in the above section, we logically aimed to study cationic boranes that feature a shorter separation between the anion binding site and the cationic group. With this in mind, we synthesized the ammonium borane [12]$^+$ by methylation of the known aminoborane precursor.[36] This new derivative readily interacts with fluoride anions in organic solvents such as CHCl$_3$ to afford the resulting zwitterionic adduct. By contrast, no fluoride anion complexation is observed in aqueous solutions consisting of H$_2$O–DMSO (6 : 4, vol., HEPES 6 mM, pH 7). Interestingly, we noted that variation in the nature of the onium group has a profound impact on the anion affinity of these complexes. Such differences are illustrated by the ability of the phosphonium borane [13]$^+$ to complex fluoride anions in water,[37,38] thus outperforming its ammonium analog [12]$^+$. A fluoride titration carried out with [13]$^+$ in H$_2$O–MeOH (9 : 1, vol.) at pH 7 afforded a binding constant in the order of 10^3 M^{-1}.[37,38] Fluoride binding to this compound leads to a quenching of the absorbance of the boron-centred chromophore at 330 nm leading to a turn-off response as described above for [1]$^+$, [2]$^+$ and [3]$^+$. A similar turn-off response is observed in the fluorescence spectrum (λ_{max} = 495 nm) of this compound.[37] In terms of selectivity, these compounds show no measurable affinity for anions such as Cl$^-$, Br$^-$, NO$_3^-$ and I$^-$. The observation that fluoride anions could bind to [13]$^+$ in water was certainly an important benchmark in our efforts to design useful sensors, but the fluoride binding constant of this cationic borane remained too low for fluoride sensing applications in the ppm range.
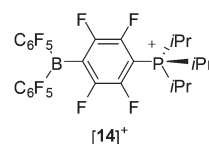
As demonstrated by Stephan,[39] the Lewis acidity and hence the anion affinity of such phosphonium boranes can be drastically enhanced by fluorination of the backbone as in [14]$^+$. However, such boranes are too acidic for applications in water.

For this reason, we decided to determine whether other more subtle variations in the structure and composition of these phosphonium boranes would afford derivatives competent for fluoride binding in water. The contrasting behavior of $[12]^+$ and $[13]^+$ toward fluoride suggested that the nature of the onium group and possibly its hydrophilic character may be responsible for the noted differences in the fluoride anion affinities of these two compounds. To investigate this hypothesis further, we prepared additional examples of phosphonium boranes of general formula $[p\text{-}Mes_2B\text{–}C_6H_4\text{–}PPh_2R]^+$ with R = Et ($[15]^+$), Pr ($[16]^+$), and Ph ($[17]^+$) (Scheme 3).[38] The Lewis acidity and fluoride affinity of these new compounds were studied in H_2O–MeOH (9 : 1, vol.) and compared to those of $[13]^+$. The phosphonium boranes are water-stable under acidic conditions but a conversion into the corresponding zwitterionic hydroxide adducts is observed as the pH approaches neutrality.[38] This process can be quantified by measuring the absorbance of the boron-centred chromophore at 330–340 nm as a function of pH (Fig. 3). The resulting spectrophotometric titration data can be treated using eqn (1), affording pK_{R+} values as a measure of the Lewis acidity of each phosphonium borane. As shown in Table 1, the most hydrophobic boranes are the most Lewis acidic.

$$[R_3B]^+ + 2H_2O \underset{}{\overset{K_{R+}}{\rightleftharpoons}} R_3B-OH + H_3O^+ \tag{1}$$

The fluoride binding constant of these compounds has also been measured by UV-vis titration experiments (Fig. 4).[38] These titrations indicate that a similar trend is reflected in the fluoride affinity of this series of cationic boranes with the fluoride binding constant of $[17]^+$ exceeding that of $[13]^+$ by more than one order of magnitude. We rationalize this increase by
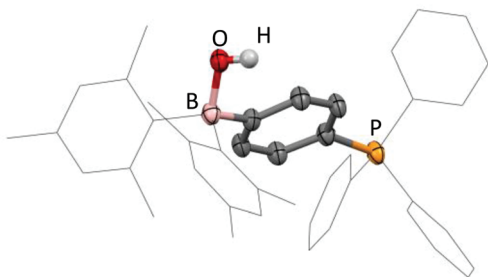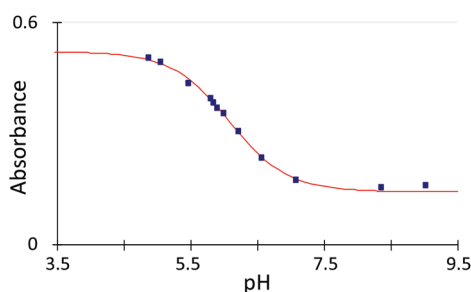

Fig. 3 Spectrophotometric acid–base titration for $[17]^+$ (top) and the crystal structure of **17**-OH (bottom, thermal ellipsoids are drawn at the 50% probability level). The titration was carried out in H_2O–MeOH (9 : 1 vol.) and the data was fitted to eqn (1) affording pK_{R+} = 6.08($\pm$0.09).

Table 1 The Lewis acidity and fluoride affinity of the phosphonium boranes $[13]^+$, $[15]^+$, $[16]^+$ and $[17]^+$ [a]

R	Cpd	pK_{R+}	K (M^{-1})
Me	$[13]^+$	7.3	840
Et	$[15]^+$	6.9	2500
Pr	$[16]^+$	6.6	4000
Ph	$[17]^+$	6.1	10 500

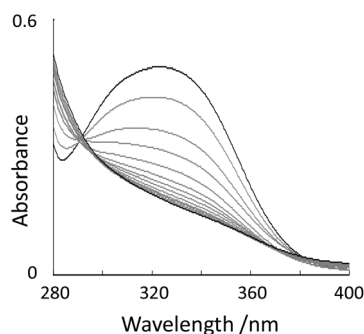[a] Cpd = compound, pK_{R+} = $-\log(K_{R+})$ (eqn (1)), K = fluoride binding constant.

Fig. 4 UV-vis titration data showing the absorbance change of a solution of $[17]^+$ after successive additions of fluoride anions in H_2O–MeOH (9 : 1 vol.; 9 mM pyridine buffer, pH 4.6).

invoking the lesser solvation of the most hydrophobic derivative $[17]^+$. This decreased solvation will magnify Coulombic effects thus promoting the pairing of the fluoride anion with the cationic borane. A similar effect is invoked for the complexation of hydroxide ions. Like $[13]^+$, none of these phosphonium boranes interact with other commonly encountered anions, such as Cl^-, Br^-, I^-, OAc^-, NO_3^-, $H_2PO_4^-$, and HSO_4^-. These effects are significant because $[17]^+$ captures fluoride at ppm concentrations in water. It can therefore be used to tackle fluoride anion concentrations around or below the EPA maximum contaminant level of 4 ppm. This gratifying result comes with the caveat that ppm fluoride anion sensing with $[17]^+$ can only be carried out at pH's that are at least 1 unit lower than the pK_{R+} of the phosphonium borane. Above this value, hydroxide binding becomes competitive and interferes with fluoride anion binding to the boron centre.

Cyanide anion complexation and sensing

Fluorescence turn-on sensors for cyanide anions. *para*-Phenylene ammonium and phosphonium boranes display an even higher affinity for cyanide than fluoride ions. Indeed, while $[12]^+$ does not show any affinity for fluoride anions in H_2O–DMSO (6 : 4, vol., HEPES 6 mM, pH 7), cyanide binding is highly favoured as indicated by the cyanide binding constant of $(K(CN^-))$ of 3.9($\pm$0.1) × 10^8 M^{-1} measured under the same conditions.[36] This dichotomy is rationalized by the notably higher basicity of cyanide (pK_a (HCN) = 9.3) *versus* fluoride (pK_a(HF) = 3.18) in water. A similar selectivity for cyanide is displayed by several other cationic boranes including $[3]^+$ and
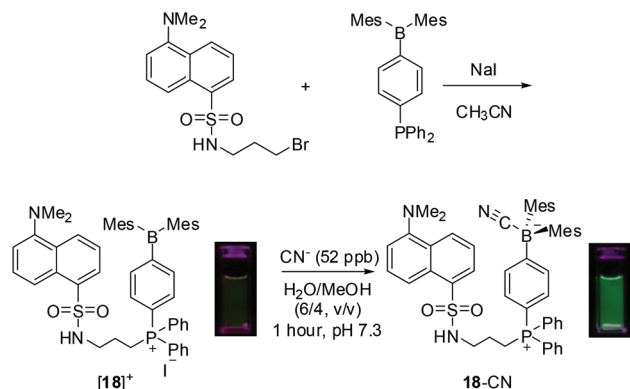
Scheme 4 Synthesis of [18]+ and visible fluorescence turn-on response observed with this cationic borane (4.02 μM) in the presence of 52 ppb of CN− at pH 7.3 under UV lamp (right).

para-phenylene phosphonium boranes which also form very stable complexes with cyanide anions.[25,40] With the view to capitalize on these elevated binding constants, the design of fluorescent cyanide sensors was investigated. As explained above, anion binding to cationic boranes such as [12]+ and [13]+ results in a fluorescence turn-off response which is not ideal from an analytical point of view. To overcome this limitation, we synthesized cationic boranes such as [18]+ which feature a pendant chromophore (Scheme 4).[40] In this compound, the fluorescence of the pendant dansyl chromophore is efficiently quenched by photoinduced electron transfer from the dansyl chromophore to the electron deficient cationic borane. Cyanide binding to the boron atom leads to the formation of 18-CN (Fig. 5) and, in the process, also neutralizes the electron accepting properties of the cationic borane, leading to a revival, or turn-on, of the fluorescence of the dansyl chromophore. Moreover, this derivative displays a very high affinity for cyanide and can be used to detect concentrations as low as 52 ppb (∼2 μM) with the naked eye in aqueous solutions (Scheme 4). These cationic boranes are also very selective and do not show measurable interactions with Cl−, Br−, I−, NO₃⁻, H₂PO₄⁻, SO₄²⁻, and CH₃CO₂⁻.
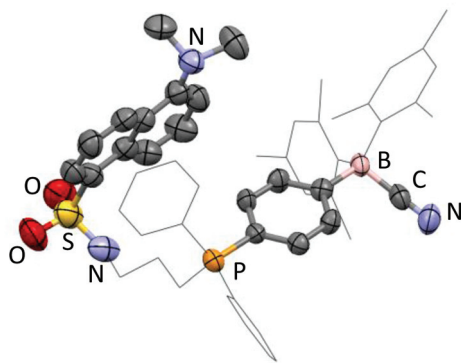

Fig. 5 Crystal structure of 18-CN. Thermal ellipsoids are drawn at the 50% probability level.
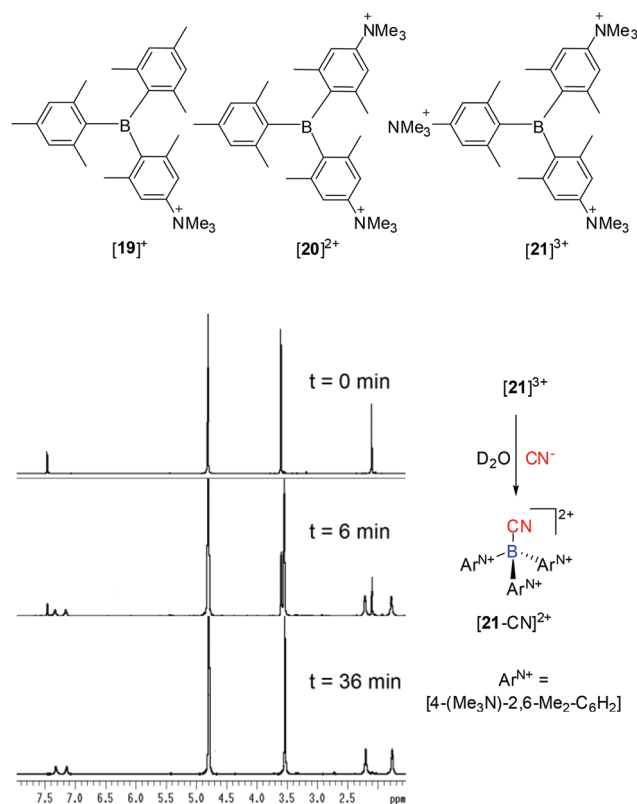

Fig. 6 Top: the structures of [19]+, [20]²⁺ and [21]³⁺ (triflate anion was omitted). Bottom: cyanide binding by [21]³⁺ in water monitored by ¹H NMR spectroscopy. Ar^{N+} = [4-(Me₃N)-2,6-Me₂-C₆H₂]⁺.

Effects imparted by the presence of multiple cationic groups. In another part of our efforts, we questioned whether the introduction of multiple remote cationic groups would have additive effects on the electron deficiency and Lewis acidity of the boron centre. In order to answer this question, we synthesized [19]+, [20]²⁺ and [21]³⁺ as their triflate salts (Fig. 6).[41] The reduction potential of Mes₃B, [19]+, [20]²⁺ and [21]³⁺ have been measured by cyclic voltammetry in CH₃CN. A comparison of the reduction peak potentials of these four boranes (−2.63 V, −2.41 V, −2.16 V and −1.86 V for Mes₃B, [19]+, [20]²⁺ and [21]³⁺, respectively) shows that substitution of a Mes group by a [4-(Me₃N)–2,6-Me₂–C₆H₂]⁺ (Ar^{N+}) group leads to a linear increase of the reduction potential, indicating that [21]³⁺ is the most electron-deficient compound in the series. Following these results, the use of these boranes for the complexation of the small anions in water has been investigated. Among the three cationic boranes, only [21]³⁺ could capture cyanide in pure water, in accordance with its highest reduction potential. This cyanide recognition has been confirmed by multinuclear NMR spectroscopy and UV-vis spectroscopy (Fig. 6). In addition, [21]³⁺ shows a high selectivity for cyanide since there is negligible change of the absorbance of the boron-centred chromophore in the presence of F⁻, Cl⁻, Br⁻, I⁻, OAc⁻, NO₃⁻, H₂PO₄⁻, and HSO₄⁻. The absence of affinity for fluoride is noteworthy. Since monocations such the

phosphonium boranes $[17]^+$ capture fluoride in water, we believe that the absence of fluoride binding by $[21]^{3+}$ originates from the steric encumbrance provided by six *ortho* methyl groups. Related results have been obtained by the groups of Kawashima[42] and Lee[43] who independently described the synthesis and anion binding affinity of derivatives such as $[22]^{2+}$, $[23]^{2+}$ and $[24]^{3+}$.[43]

[22]²⁺ (RₙE = Me₃N)
[23]²⁺ (RₙE = MePh₂P)

[24]³⁺
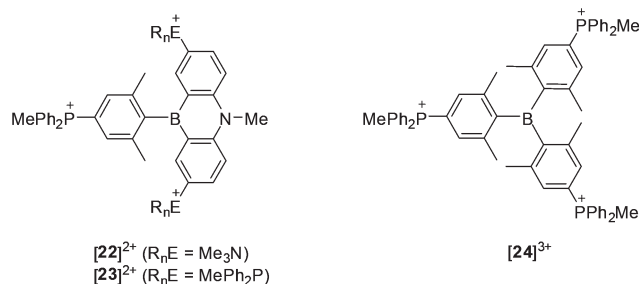
Steric undressing of the boron atom. A common feature uniting most of the cationic boranes discussed thus far in this review concerns the use of sterically encumbered dimesitylboryl moieties which are inert to most nucleophiles except fluoride and cyanide. To increase the reactivity of the boron centre, we have also studied cationic boranes that feature a more sterically accessible boron atom. Toward this end, we synthesized a cationic borane ($[25]^+$) featuring a 9-thia-10-boraanthracene moiety substituted at boron by the cationic anilinium group $[4-(Me_3N)-2,6-Me_2-C_6H_2]^+$ (Scheme 5).[44] This cationic borane has been fully characterized. Its UV-vis spectrum features a low-energy band at $\lambda_{max} = 392$ nm which, as confirmed by computational studies, arises from a π–π^* transition of the 9-thia-10-boraanthracene chromophore. As a result of the low steric bulk present around the boron centre and the inductive effects imparted by the anilinium group, $[25]^+$ possesses unusual Lewis acidic properties and reacts with
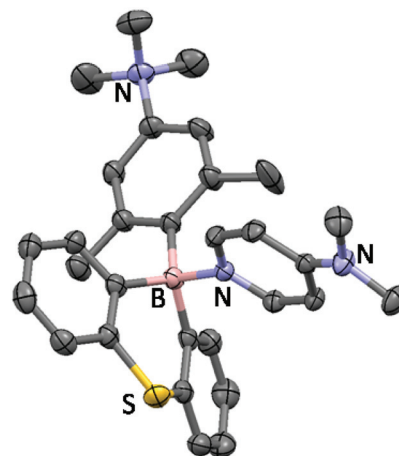

Fig. 7 ORTEP drawings of $[25\text{-DMAP}]^+$. Thermal ellipsoids are drawn at the 50% probability level.

DMAP to form the corresponding adduct (Scheme 5, Fig. 7). Formation of DMAP adducts with cationic boranes containing dimesitylboryl functionalities has not been observed. Hence, formation of $[25\text{-DMAP}]^+$ may be assigned to the low steric protection of the boron centre in $[25]^+$.

This derivative also binds both fluoride and cyanide anions in THF to afford 25-F and 25-CN (Scheme 5). Titration experiments indicate that the stability constants of these zwitterions exceed 10^7 M^{-1} thus reflecting the accessibility of the boron atom as well as the favourable inductive and Coulombic effects imparted by the anilinium substituent. Although $[25]^+$ is unstable in pure water, it can be used to selectively extract cyanide under biphasic conditions in nitromethane/water.

ortho-Phenylene ammonium and phosphonium boranes

From anion complexation to anion chelation

Because Coulombic effects should increase as the distance between the anion binding site and the onium group decreases (Fig. 8), we synthesized the *ortho*-ammonium borane $[26]^+$ by simple methylation of the aminoborane precursor.[36] By contrast with the *para*-isomer $[12]^+$, we observed that $[26]^+$ complexes fluoride in H$_2$O–DMSO (6 : 4, vol.) with a fluoride
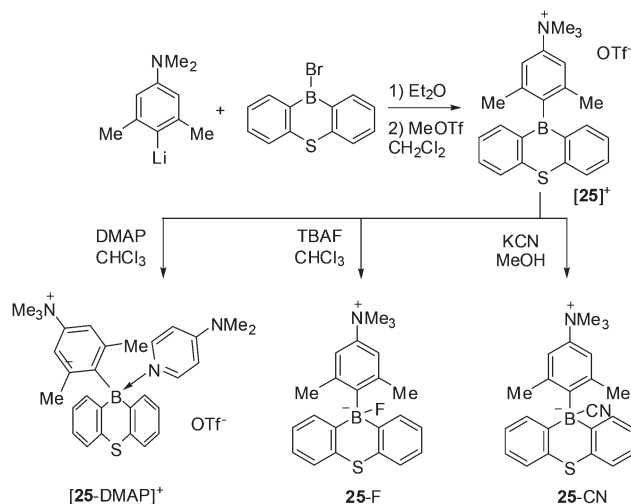
Scheme 5 Top: synthesis of $[25]^+$ and reaction with DMAP in CHCl$_3$ to form $[25\text{-DMAP}]^+$. Bottom: Reaction of $[25]^+$ with TBAF in CHCl$_3$ to form 25-F and with KCN in MeOH to form 25-CN.
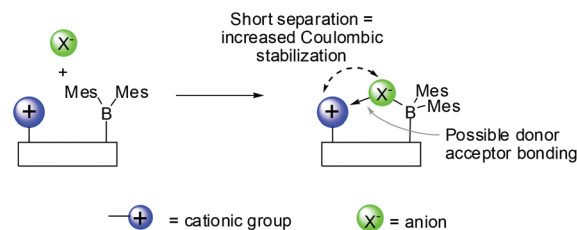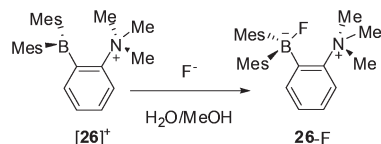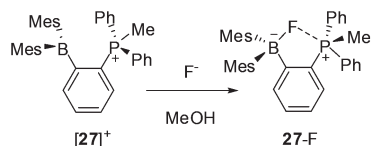

Fig. 8 Scheme showing the increased Coulombic stabilization expected in cationic boranes with a narrow separation between the boron atom and the onium group.

Scheme 6 Reaction of [**26**]$^+$ with fluoride under biphasic conditions to form **26**-F.


Scheme 7 Reaction of [**27**]$^+$ with fluoride in MeOH to form **27**-F.

Scheme 8 Formation of **27**-N$_3$.

binding constant of 910 ($\pm$50) M^{-1} thus supporting the notion that the anion affinity of such complexes can be enhanced by the closer positioning of the onium group. The *ortho* positioning of the onium group with respect to the boron atom in **26**-F may facilitate the formation of stabilizing CH–FB hydrogen bonds involving the nitrogen-bound methyl groups; it also leads to an increase of the steric congestion around the boron atom. This increase in steric congestion is held responsible for the fact that [**26**]$^+$ does not interact with the larger cyanide anion under the same conditions as those used for fluoride complexation (Scheme 6).

We have also synthesized and evaluated the phosphonium borane [**27**]$^+$ (Scheme 7).[45,46] Although [**27**]$^+$ cannot be evaluated in water, we have studied its fluoride affinity in organic solvents.[45] In MeOH, the fluoride binding constant of [**27**]$^+$ ($K > 10^6$ M^{-1}) exceeds the measurable range and is at least four orders of magnitude higher than that measured for the *para*-isomer [**13**]$^+$ ($K = 400$ ($\pm$50) M^{-1}). Clues to the higher fluoride affinity of [**27**]$^+$ were derived from a structural and Natural Bond Orbital (NBO) analysis of **27**-F, which pointed to the presence of a bonding B–F$\rightarrow$P donor–acceptor interaction of 2.66 Å involving a fluorine lone-pair and the σ^* orbital of a P–C bond. Energetically, this interaction contributes 5.0 kcal mol^{-1} to the stability of the complex. Thus, [**27**]$^+$ can be regarded as a cationic bidentate Lewis acid, whose high fluoride affinity arises from both anion chelation and Coulombic attractions. These results are significant because they show that the latent Lewis acidity of phosphonium ions can be exploited for anion sensing applications. However, unlike the para isomer [**13**]$^+$, [**27**]$^+$ is not stable in neutral water. It can be observed by UV-vis spectroscopy at pH 2.3 in water, but the absorption band associated with the cationic borane quickly disappears above pH 3.5, indicating its high Lewis acidity.

We have also found that [**27**]$^+$ can be used for the complexation of the toxic N$_3^-$ anion (Scheme 8).[46] This complexation, which is selective in biphasic organic solvent–water mixtures, originates from favourable Coulombic effects which stabilize the B–N$_3$ linkage against dissociation as well as the ability of the azide anion to interact with both the boron and phosphorus
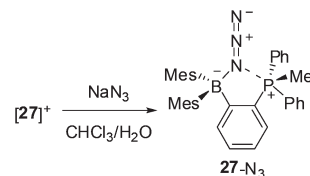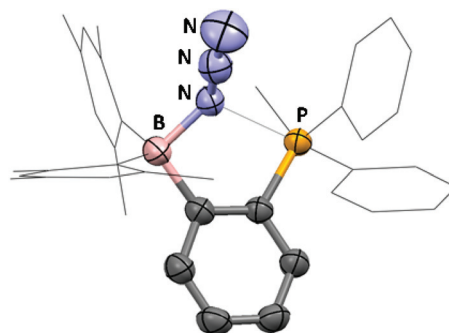

Fig. 9 Crystal structure of **27**-N$_3$. Thermal ellipsoids are drawn at the 50% probability level.

Lewis acidic sites of the receptor. This view is confirmed by a crystal structure of **27**-N$_3$ (Fig. 9) as well as Natural Bond Orbital (NBO) calculations which indicate the presence of a bonding B–N$\rightarrow$P donor–acceptor interaction involving a nitrogen sp^2 lone-pair and the σ^* orbital of a P–C bond. Energetically, this interaction contributes 5.8 kcal mol^{-1} to the stability of the complex.

Phosphonioborins [**28**]$^+$ and [**29**]$^+$ constitute another class of *ortho*-phenylene phosphonium boranes.[37,47] In this case, the boron and phosphonium units are confined to a doubly benzannulated six-membered ring. As in the case of the cationic thiaborin [**25**]$^+$, the boron atom is sterically exposed and thus readily accessible to nucleophilic anions. The mesityl derivative [**29**]$^+$, which possesses the less sterically demanding boron substituent, is expectedly the most reactive. It undergoes rapid conversion into the corresponding fluoroborate phosphonium zwitterion when dissolved in CHCl$_3$ and layered with an aqueous KF solution. It also scavenges fluoride anions from pure water as a solid (Scheme 9).[47]
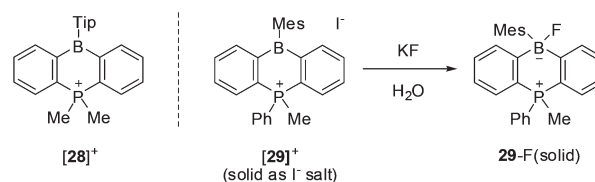
Scheme 9 Structure of [**28**]$^+$ and fluoride scavenging reaction observed when solid [**29**]I is exposed to an aqueous KF solution (Tip = 1,3,5-tri-(iso-propyl)-benzene).
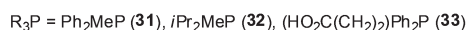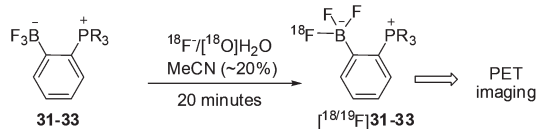
Applications in radiofluorination chemistry

Novel strategies for the capture of fluoride are attracting an increasing interest because of their relevance to the preparation of ^{18}F-labeled radiotracers for Positron Emission Tomography (PET).[48] Inspired by the demonstrated stability of *ortho*-phosphonium trifluoroborates such as **30**,[49] as well as by the contribution of Perrin who showed that electron deficient aryltrifluoroborates can serve as water resistant captors for ^{18}F fluoride anions,[50] we have decided to determine if some of the scaffolds investigated in our group could be applied to the design of boron-based fluoride captors. With this in mind, we synthesized the phosphonium trifluoroborate zwitterions **31**, **32** and **33** (Scheme 10) and studied their hydrolytic conversion into the corresponding boronic acids. Kinetic measurements carried out with **31**, **32** and **33** in D_2O–CD_3CN (8 : 2 vol.) at pH 7.5 afforded a hydrolysis reaction half-life of 12 days for **32** and 32 days for **33**, thus pointing to a marked dependency on the nature of the phosphorus substituents.[51,52] The most hydrolytically resistant derivative is **31**. It displays a hydrolysis reaction half-life of 142 days, a value that far exceeds that measured for $[PhBF_3]^-$ (29 min).[51] Moreover, we found that **31**, **32** and **33** can be radiofluorinated by [18]F–[19]F isotopic exchange at acidic pH through simple mixing with a $[^{18}F]$-fluoride/$[^{18}O]$-water solution produced in the cyclotron (Scheme 10). The best results have been obtained with $[^{18}F]$**31** which could be obtained with specific activities as high as 0.5 Ci μmol^{-1}.[52] Moreover, PET studies carried out in mice have shown that fluoride dissociation does not occur on the time scale of the imaging experiment.
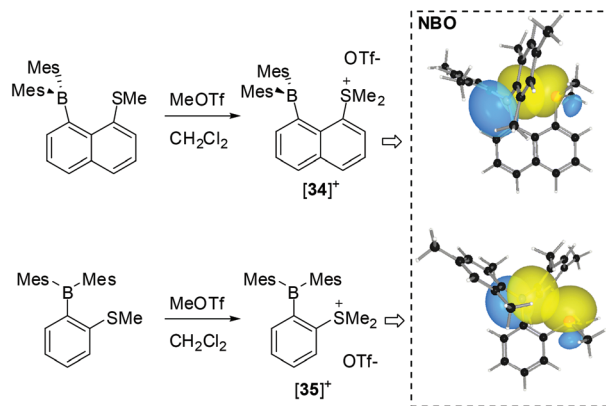

30
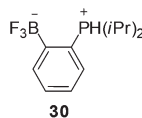
ortho-Phenylene and peri-substituted naphthalenediyl sulfonium boranes

Influence of the backbone on the anion affinity

Anticipating that similar synergistic effects may also be observed in sulfonium boranes, we synthesized $[34]^+$ and $[35]^+$ by simple methylation of the corresponding thioethers (Scheme 11).[53] Spectrophotometric titrations carried out in H_2O–MeOH (95 : 5, vol.) indicated that $[34]^+$ is stable up to pH 9.5 while $[35]^+$ already begins to bind hydroxide at pH ≥ 7. These observations also led to the conclusion that $[35]^+$ is


Scheme 11 Synthesis of $[34]^+$ and $[35]^+$ as triflate salts.

more acidic than $[34]^+$ by at least two orders of magnitude. This *a priori* surprising difference could be rationalized by a combination of structural and computational results. The crystal structures of the two boranes show similar boron–sulfur separation (3.07 Å for $[34]^+$ and 3.12 Å for $[35]^+$) that are within the sum of the van der Waals radii of the two elements. This relatively short separation is consistent with the presence of a lp(S)→p(B) donor–acceptor interaction which, in effect, partially quenches the Lewis acidity of the boron atom. Because of the more convergent orientation of the sulfonium and boryl units, this donor–acceptor interaction is expected to be more intense in $[34]^+$, leading to a lower Lewis acidity. This argument is supported by NBO analyses which confirm the presence of a lp(S)→p(B) donor–acceptor interaction which contributes 6.8 kcal mol^{-1} to the stability of $[34]^+$ and only 2.3 kcal mol^{-1} to the stability of $[35]^+$.

In accordance with the above, $[34]^+$ shows negligible affinity for common anions, such as F^-, CN^-, Cl^-, Br^-, I^-, NO_3^-, HSO_4^-, $H_2PO_4^-$, and $CH_3CO_2^-$ in H_2O–MeOH (95 : 5, vol.).[53] However, under the same conditions, $[35]^+$ behaves as a selective cyanide sensor (Scheme 12). Cyanide complexation can be conveniently followed by monitoring the green fluorescence of $[35]^+$ (λ_{max} = 460 nm) which is efficiently quenched upon cyanide coordination to the boron centre. Using this monitoring method, $[35]^+$ can be used for the fluorescence detection of cyanide at the EU maximum allowable concentration of

Scheme 10 Aqueous radiofluorination reaction of **31**, **32** and **33**.
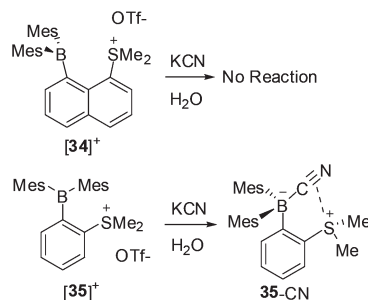
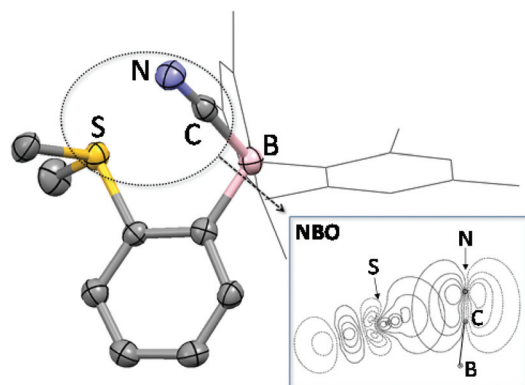**Scheme 12** Cyanide binding of $[34]^+$ and $[35]^+$ in water.

Fig. 10 Crystal structure and NBO contour plots for **35**-CN (right). Thermal ellipsoids are drawn at the 50% probability level.

50 ppb. The fluorescence quenching phenomenon can be observed with the naked eye under a hand-held UV lamp. Like for the phosphonium borane $[27]^+$, both Coulombic and chelate effects contribute to the high cyanide affinity of $[35]^+$. Indeed, a structural and NBO analysis of **35**-CN shows that the sulfonium moiety interacts with the cyanide guest *via* both a bonding $\pi(C\equiv N)\rightarrow\sigma^*(S-C)$ and back-bonding $lp(S)\rightarrow\pi^*(C\equiv N)$ interaction (Fig. 10). Collectively, these secondary interactions increase the stability of the complex by 4.1 kcal mol^{-1}. Supporting results have also been obtained in the chemistry of a *ortho*-phenylene sulfonium fluorosilane which complexes fluoride to afford a Si–F→S chelate complex.[54]

Sulfonium boranes for the capture and release of fluoride ions

Because of applications in the biomedical and materials areas, the fluorination of organic compounds is experiencing a surge of interest. While electrophilic fluorination strategies remain preponderant, there is a growing need for the development of nucleophilic pathways. Unfortunately, the fluoride ion has a high hydration energy making most of its salts hygroscopic, difficult to dry, and thus, poorly suited for nucleophilic fluorination reactions. For these reasons, we have become interested in strategies that would allow for: (i) the capture of fluoride under wet conditions; (ii) the release and transfer of fluoride to organic substrates in dry organic solutions. While we observed that $[34]^+$ does not bind fluoride anions in H$_2$O–MeOH (95 : 5, vol.) under dilute conditions, we found that the zwitterionic fluoroborate **34**-F precipitates when $[34]^+$ is mixed with fluoride anions in wet methanol. Precipitation also occurs in MeOH–H$_2$O mixtures containing up to ~40% of water.[55] The zwitterionic fluoroborate **34**-F can be recovered by simple filtration as a non-hygroscopic solid. In dry acetonitrile, **34**-F reacts with PhS$^-$ yielding the anionic fluoroborate **36**-F$^-$. The latter is very labile and acts as a nucleophilic fluorination reagent toward a variety of substrates, including 1-bromooctane which could be converted into 1-fluorooctane in 45% yield (70 °C, 1 hour) or 1-chloro-2-cyano-3-nitrobenzene which could be converted into 1-chloro-2-fluoro-3-nitrobenzene in >95% (25 °C, 2 hours) (Scheme 13). These results suggest that
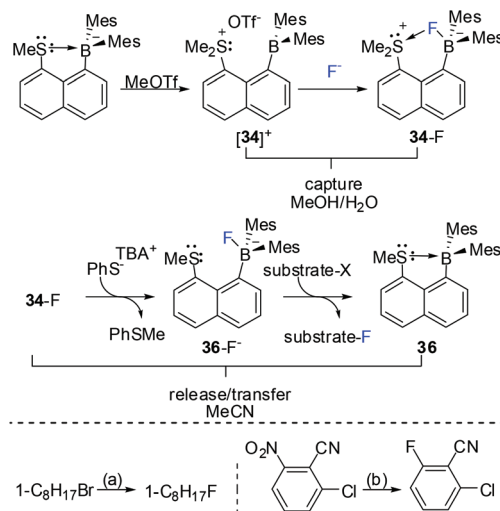

Scheme 13 Top: Fluoride capture and release protocol using $[34]^+$. Bottom: Examples of fluorination reactions.

the tetrabutylammonium salt of **36**-F$^-$ dissociates upon elevation of the temperature to produce **36** and anhydrous TBAF. While previously reported preparations of anhydrous TBAF necessitate the use of dry conditions,[56] our approach can be implemented in two simple steps starting from aqueous fluoride solutions.

Sulfonium diboranes

Inspired by Katz's seminal contribution on the anion affinity of 1,8-dimethylborylnaphthalene,[57] we have investigated the synthesis of numerous naphthalene-based diboranes as anion sensors.[9,58–61] In this context, we have shown that the reaction of 1,8-dilithionaphthalene with Mes$_2$BF leads to the formation of the Li(THF)$_4$ salt of dimesityl-1,8-naphthalenediylborate (**37**) (Scheme 14).[58] This borate can be converted into diboranes such as **38** by reaction with boron halide reagents (Scheme 14).[59,61] An investigation of the anion binding properties of **38** show that this diborane chelates fluoride in THF with a binding constant in excess of 10^9 M^{-1}.[59] To further enhance the anion affinity of such diboranes, we have more
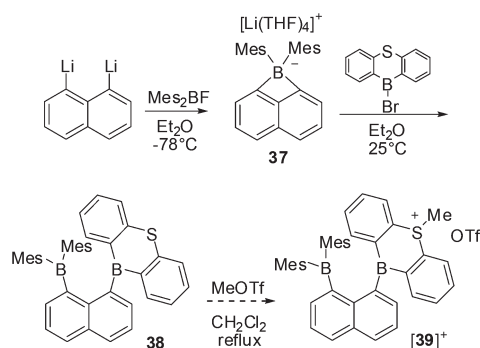
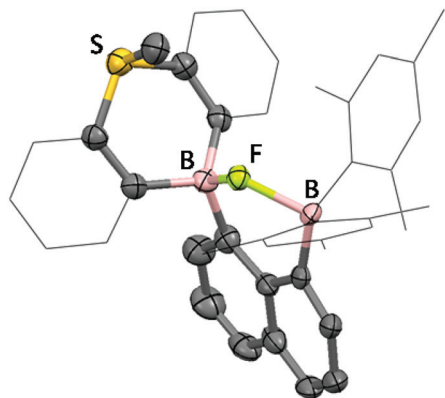**Scheme 14** Synthesis of **37**, **38**, and $[39]^+$.

Fig. 11 Crystal structure of **39**-F. Thermal ellipsoids are drawn at the 50% probability level.

recently described the sulfonium derivative [**39**]$^+$, obtained by alkylation of the sulfur atom of **38** with MeOTf.[62] This new diborane, which has been isolated as the triflate salt, reacts with azide to form the corresponding chelate complex **39**-N$_3$. It also reacts with fluoride anions to form **39**-F. The structure of this fluoride complex shows formation of an asymmetrical B–F–B bridge with the fluoride atom forming a shorter B–F bond (1.540(5) Å vs. 1.882(4) Å) with the boron atom of the thiaborinium unit (Fig. 11). DFT calculations suggest that fluoride binding first involves an exo-coordination to the boron of the thiaborinium unit followed by rotation of the resulting fluoroborate sulfonium unit about the B–C$_{napthalenediyl}$ bond. In support of this scenario, a change in the orientation of the sulphur-bound methyl group from exo to endo is observed upon conversion of [**39**]$^+$ into **39**-F. The most significant aspect of these results pertains to the greater thermodynamic stability of **39**-F vs. [**38**-F]$^-$ which demonstrates that chelate and Coulombic effects are additive and can be combined to boost the anion affinity of bidentate Lewis acids. A similar anion affinity enhancement has been observed upon decoration of a heteronuclear B/Hg bidentate Lewis acid with a peripheral ammonium moiety as in [**40**]$^+$.[63]

[**40**]$^+$
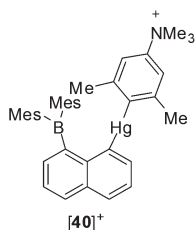
Cationic boranes featuring heavy onium ions

Stibonium boranes

The anion affinity of compounds such as [**27**]$^+$ and [**35**]$^+$ show that the latent Lewis acidity of third row onium ions can be exploited to induce anion chelation.[45,53] This fact is well
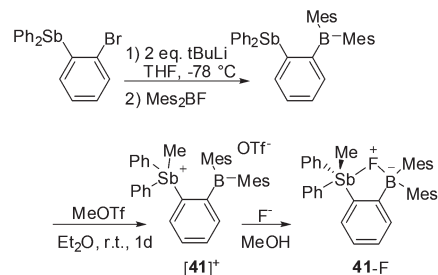
Scheme 15 Synthesis of [**41**]$^+$ and reaction with fluoride in MeOH to form **41**-F.

illustrated by the behavior of the phosphonium derivative [**27**]$^+$ which forms a fluoride complex stabilized by a relatively weak F→P$^+$ donor–acceptor interaction.[45] In principle, such a F→onium donor–acceptor interaction could be strengthened by increasing the anion affinity of the onium ion. A survey of the literature shows that stibonium ions tend to form covalent species with small anions.[64,65] This is, for example, the case of Ph$_4$SbF which is a trigonal bipyramidal molecule,[66] while [Ph$_4$Sb][ClO$_4$] is ionic.[65] In fact, the tetraphenylstibonium cation has been used for the extraction of fluoride ions from water into CCl$_4$.[67] Encouraged by these precedents, we have synthesized the stibonium derivative [**41**]$^+$ by the sequence of steps presented in Scheme 15.[68] Competition experiments carried out with [o-(Ph$_2$MeP)(Mes$_2$FB)C$_6$H$_4$] (**27**-F) confirm that [**41**]$^+$ exhibits a much higher fluoride affinity than its lighter phosphorus congener. The resulting B–F–Sb chelate complex **41**-F features a Sb–F separation of 2.450(2) Å which is close to that measured for the Sb–F–Sb bridges of polymeric Me$_4$SbF (2.369(14) and 2.382(12) Å). The strength of the Sb–F bond is also supported by the relatively long B–F (1.53 Å) bond which exceeds the value of 1.48 Å typically observed for aryldimesitylfluoroborate species. According to Natural Bond Orbital (NBO) calculations, the B–F–Sb chelate motif present in **41**-F can be described as a B–F→Sb donor–acceptor interaction involving a fluorine lone-pair and the σ* orbital of a Sb–C bond (Fig. 12). This interaction, which contributes at

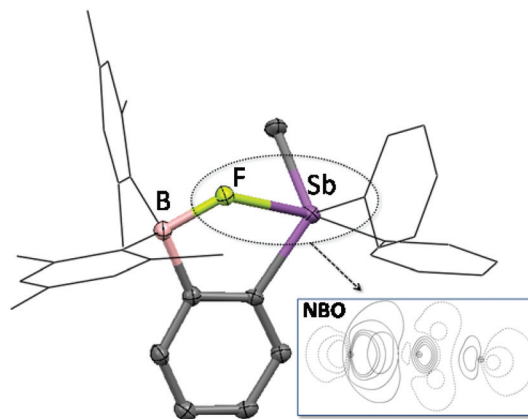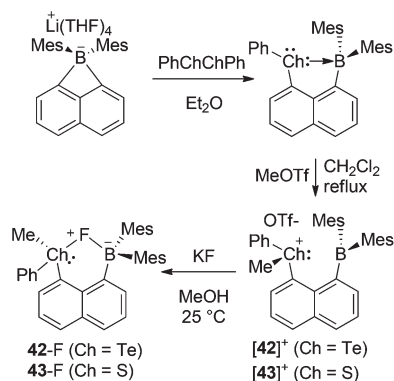**Fig. 12** Crystal structure and NBO contour plot showing the lp(F)→σ*(Sb–C) interaction in **41**-F. Thermal ellipsoids are drawn at the 50% probability level.

least 15 kcal mol⁻¹ to the stability of the complex, illustrates the enhanced Lewis acidic properties of the stibonium ion. This enhancement can be assigned to the greater energetic and spatial accessibility of the accepting σ^* orbital in the heavy pnictogenium ion. The F→Sb interaction observed in **41**-F is reminiscent of donor–acceptor interactions found in halogen-bonded complexes. Thus, as for halogen bonded complexes which become more stable as the halogen group is descended, the larger size, polarizability and electropositivity of antimony *vs.* phosphorus are also important factors that contribute to the strength of the F→Sb interaction.

Telluronium boranes

We have also questioned whether a similar anion affinity increase would be observed in chalcogenium boranes as the group is descended. To this end, we synthesized the telluronium and sulfonium cation [**42**]⁺ and [**43**]⁺ and compared their properties (Scheme 16). The UV-vis spectra of both [**42**]⁺ and [**43**]⁺ in MeOH bear two distinct low-energy bands in the 280–390 nm range, for which the LUMO and LUMO + 1 are the main accepting orbitals.[69] The LUMO and LUMO + 1 carry an important contribution from the boron *p*- and the Ch–C σ^*-orbital, respectively, as illustrated for [**42**]⁺ in Fig. 13. The localization of the LUMO and LUMO + 1 orbitals on these two atoms underscores their predisposition for anion chelation. It also suggests that anion coordination to these two atoms will lead to noticeable photophysical changes.

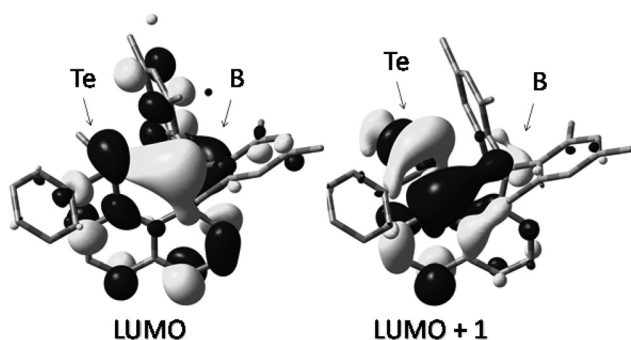**Scheme 16** Synthesis of [**42**]⁺ and [**43**]⁺ and their reaction with KF in MeOH.

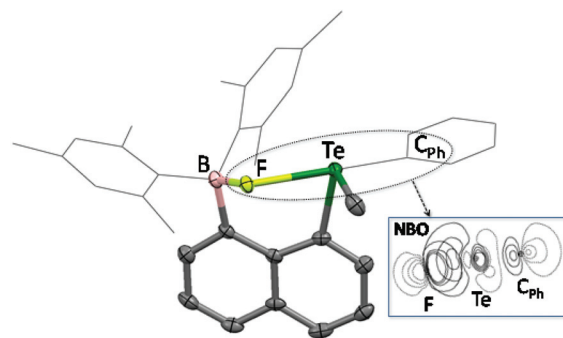**Fig. 13** LUMO and LUMO + 1 of [**43**]⁺.

Fig. 14 Crystal structure and NBO contour plots for **42**-F. The mesityl groups are represented by thin lines. Thermal ellipsoids are drawn at the 50% probability level.

Indeed, upon addition of fluoride ions to a 0.0673 mM solution of [**42**]⁺, these low energy bands undergo progressive quenching indicating formation of **42**-F.[69] Fitting of the resulting data to a one to one isotherm affords a binding constant of 750 (±100) M⁻¹. By contrast, [**43**]⁺ shows negligible fluoride affinity under these dilute conditions. Compound **43**-F can, however, be isolated by mixing [**43**]OTf with a saturated KF solution in MeOH. While the ¹⁹F NMR signal of **43**-F (−150.7 ppm) appears in the expected range for a typical triarylfluoroborate anion, that of **42**-F at −130.4 ppm is significantly shifted downfield. Moreover, **42**-F displays as $^1J_{\text{Te-F}}$ of 940 Hz, a value comparable to that observed in *o*-(C₆H₄–CH₂NMe₂)₂TeF₂. These spectroscopic features suggest that the boron bound fluorine atom in **42**-F also forms a strong bond with the tellurium atom. The crystal structure of **42**-F shows that the Te–F distance (2.506(2) Å) is shorter than the S–F distance (2.548(1) Å) in **43**-F, despite the larger size of the tellurium atom. Another conspicuous feature is the close linearity of the F–Te–C_ph angle (174.0(1)°). An NBO analysis confirms a much stronger lp(F)→σ^*(Ch–C) interaction for **42**-F (E_{del} = 22.8 kcal mol⁻¹) than that for **43**-F (E_{del} = 9.2 kcal mol⁻¹) (Fig. 14). These results further illustrate the larger onium-centred Lewis acidity observed for fifth period elements.

Conclusions and outlook

In the past several years, our group has investigated the chemistry of organoboranes whose ligands are decorated by cationic groups. In addition to improving the water solubility of the boranes, the presence of the cationic groups increases the anion affinity of the borane *via* favorable Coulombic effects. As a result, some of the cationic boranes described here can be used to sense fluoride or cyanide in aqueous environments or in pure water. Another important outcome of this body of work is the finding that cationic boranes with a narrow separation between the anion binding site (*i.e.* the boron atom) and the onium ion display a markedly enhanced Lewis acidity, a phenomenon that is logically assigned to Coulombic effects and their reversed dependency on the distance separating the boron-bound anion from the onium ion. These forces can be

complemented by the formation of B–X→E (E = P, S, Sb, or Te; X = F, CN or N_3) chelate motifs in which the central atom of the onium groups acts as a Lewis acid *via* a low lying σ* orbital. Because the energy of this orbital will decrease as the size of the element increases, Lewis acidity is maximum with the 5th period elements Sb and Te. As a result, the stibonium and telluronium boranes described in this article are some of the most potent anion binders studied in our group. In fact, we have recently found that simple tetraarylstibonium ions can be used for the complexation of fluoride ions in water.[70]

As this field continues to develop, increasing the selectivity of these sensors for the target anionic guest over hydroxide should become the primary objective. This is especially true for fluoride sensing which currently necessitates the use of slightly acidic pH's in order to avoid competing hydroxide binding. The discovery of Lewis acidic fluoride sensors that are compatible with neutral pH's should open the door to a number of exciting sensing applications in biological systems. As a prelude to these opportunities, we have shown that some of the new anion-binding paradigms emerging from our fundamental studies can be applied to the design of new ^{18}F positron emission tomography imaging agents.

Acknowledgements

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