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# A bidentate borane as colorimetric fluoride ion sensor†

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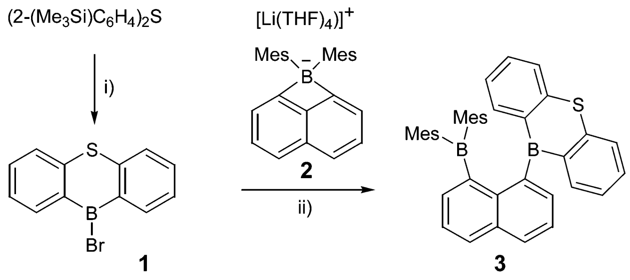
**The bright yellow bidentate diborane (3), obtained by reaction of 10-bromo-9-thia-10-boraanthracene (1) with dimesityl-1,8-naphthalenediylborate (2), serves as a colorimetric anion sensor and selectively complexes fluoride with an association constant greater than $5 \times 10^9$ M$^{-1}$ in THF.**

Anions display remarkably high solvation energy and their molecular recognition by abiotic hosts continues to be a challenge.[1] This is especially true for the small fluoride anion which enjoys a high solvation energy. Taking into account the importance of this anion in the treatment of osteoporosis[2] and in dental care,[3] a great deal of effort has been devoted to the design of selective fluoride sensors. Recently, the detection of fluoride as a by-product of sarin hydrolysis has emerged as an added impetus for the study of such receptors.[4] In addition to receptors capable of hydrogen bonding with the anionic guest,[5] Lewis acidic receptors that can covalently bind fluoride ion have also been reported.[6,7] In this domain, the study of colorimetric fluoride sensors based on boron-containing π-electron systems is especially noteworthy.[7] In such derivatives, fluoride ion complexation leads to a perturbation of the frontier orbitals thereby altering the photophysical properties of the receptor. Important advances have also been realized with bidentate Lewis acidic boranes[8,9] such as 1,8-bis(boryl)naphthalene derivatives.[10,11] These derivatives have been shown to chelate small anions including fluoride with apparently high selectivity;[10] yet their incorporation in a colorimetric sensor remains to be described. In this communication, we report our original results on the synthesis of a colorimetric fluoride sensor based on a bidentate Lewis acid.

The successful design of such a sensor necessitates the incorporation of a chromophoric boron moiety in a bidendate Lewis acid. To this end, we first prepared 10-bromo-9-thia-10-boraanthracene (**1**) by reaction of bis-(2-trimethylsilylphenyl)sulfide with boron tribromide. This compound was isolated as a yellow crystalline solid and was allowed to react with dimesityl-1,8-naphthalenediylborate (**2**)[12] to afford diborane **3** in a 68% yield (Scheme 1). This bright yellow diborane is soluble in chloroform, THF and pyridine. The $^1$H NMR spectrum of **3** confirms the attachment of the 9-thia-10-boraanthryl moiety and exhibits the expected number of resonances for an unsymmetrically substituted naphthalene derivative. In addition, the spectrum indicates the existence of a rigid structure since four aryl protons and six distinct methyl groups are observed for the mesityl substituents. The $^{11}$B NMR spectrum of **3** shows two resonances at 56 and 74 ppm confirming the presence of two different boron centres. The structure of **3** was computationally optimized using DFT methods (B3LYP, 6-31+G* for the boron and sulfur centres, 6-31G for all other atoms).†‡ The optimized geometry is close to that observed for other diboranes bearing a dimesitylboryl group.[12] Most importantly, examination of the DFT orbitals reveals that the boron $p_z$ orbitals contribute to the LUMO and are oriented toward one another in a transannular fashion (Fig. 1) as observed for 1,8-bis(diphenylboryl)naphthalene.[11] Also, the UV-Vis spectrum of this derivative features a broad band centered at 363 nm, $\varepsilon$ = 17400 mol$^{-1}$ cm$^{-1}$. As indicated by a time-dependent DFT calculations, electronic excitations from the HOMO, HOMO-1 and HOMO-2 to the LUMO are the major contributors to this broad band. Hence, any events leading to the disruption of the LUMO should greatly affect the absorption spectrum of compound **3**.

In the presence of $[Me_3SiF_2]^-[S(NMe_2)_3]^+$ in THF, compound **3** readily reacts with fluoride anions. This reaction is accompanied by a rapid loss of the yellow colour (*vide infra*) and affords the anionic chelate complex $[\mathbf{3}\cdot\mu_2\text{-F}]^-$ which has been fully characterized. Its NMR spectra differ from those of **3** but are still characteristic of an unsymmetrically substituted naphthalene species. Both boron resonance are shifted to high field and appear at 12.3 ppm and 17.1 ppm confirming coordination of the fluoride anion. The $^{19}$F NMR resonance of the bridging fluoride appears at −188 ppm which is comparable to the chemical shift observed in other fluoride bridged species.[9] As confirmed by single crystal X-ray analysis,†‡ the fluorine atom is bound to both boron centres *via* B–F bonds of comparable lengths (F–B(1) 1.633(5) Å, F–B(2) 1.585(5) Å) (Fig. 2). Owing to the bridging location of the fluoride anion, these bonds are slightly longer than terminal B–F bonds observed in other borate anions (1.47 Å).[7c] The sum of the coordination angles ($\Sigma_{(C\text{–}B1\text{–}C)}$ = 347.8°, $\Sigma_{(C\text{–}B1\text{–}C)}$ = 341.2°) indicates that both boron centres are substantially pyramidalized.

Fluoride complexation leads to population of the LUMO of **3** and is logically accompanied by an instantaneous loss of the yellow colour. Remarkably, no changes in the colour of the solution or in



**Scheme 1** Synthesis of **3**. i) BBr$_3$, Et$_2$O, 25 °C; ii) Et$_2$O, 25 °C.

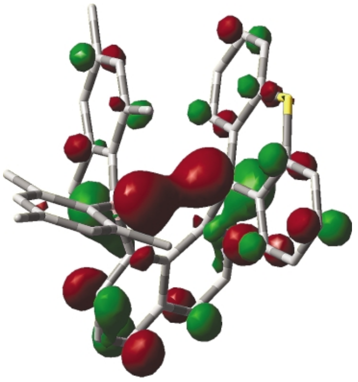


**Fig. 1** DFT orbital picture of **3** showing the LUMO (surface isovalue = 0.04). H-atoms omitted for clarity.

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† Electronic supplementary information (ESI) available: electronic supplementary information (ESI) available: synthetic and analytical results, including elemental analysis, for **1** and **3** and $[\mathbf{3}\cdot\mu_2\text{-F}]^-[S(NMe_2)_3]^+$. DFT calculation details for **3**. See http://www.rsc.org/suppdata/cc/b4/b403596h/

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the NMR of diborane **3** are observed in the presence of chloride, bromide and iodide anions indicating that fluoride anion complexation is infinitely selective. As previously proposed, the size of the binding pocket provided by this bidentate borane can be held responsible for this phenomenon.[10] Incremental addition of fluoride anions to a solution of **3** leads to a steady and linear decrease of the absorbance at 363 nm which reaches the baseline after a total addition of exactly one equivalent (Fig. 3). Further addition of fluoride anions does not lead to additional perturbation of the spectrum. These observations reflect the formation of a 1 : 1 complex whose stability constant exceeds the range measurable by direct titration. In order to evaluate the stability constant of this complex in THF, a titration experiment in the presence of a competing fluoride acceptor was designed. Since triarylboranes have been shown to complex fluoride anions,[7] trimesitylborane ($Mes_3B$) was chosen as a competing fluoride acceptor. As determined by a UV-Vis titration experiment, $Mes_3B$ complexes fluoride anions with a binding constant of $3.3(0.4) \times 10^5$ $M^{-1}$ which falls within the range established for other monofunctional borane receptors.[7] Remarkably, addition of fluoride anion to a solution containing **3** and over twelve equivalents of $Mes_3B$ resulted in the essentially quantitative formation of [**3**·$\mu_2$-F]$^-$ therefore indicating that **3** possesses a fluoride binding constant of at least $5 \times 10^9$ $M^{-1}$. Moreover, addition of water does not lead to decomplexation of the fluoride anion as typically observed for fluoride adducts of monofunctional boranes.[7c] This difference substantiates the chelating ability of **3** which leads to the formation of a thermodynamically more stable fluoride complex. Finally, we note [**3**·$\mu_2$-F]$^-$ can be converted back into **3** *via* treatment with $B(C_6F_5)_3$.

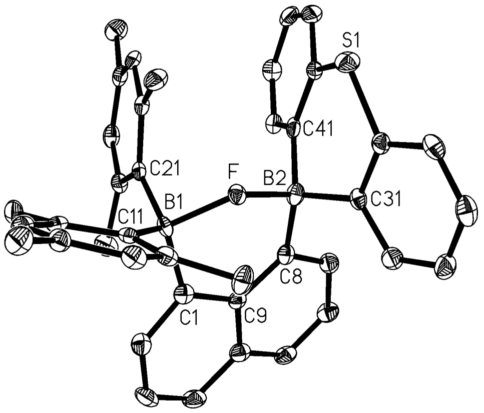

**Fig. 2** Structure of the borate anion in [**3**·$\mu_2$-F]$^-$ (50% ellipsoid). H atoms omitted for clarity. Selected bond lengths [Å] and angles [°] F–B(2) 1.585(5) F–B(1) 1.633(5), B(1)–C(1) 1.607(6), B(1)–C(11) 1.626(6), B(1)–C(21) 1.641(6), B(2)–C(8) 1.604(6), B(2)–C(41) 1.609(6), B(2)–C(31) 1.621(6), B(2)–F–B(1) 126.0(3), C(1)–B(1)–C(11) 112.8(3), C(1)–B(1)–C(21) 116.5(3), C(11)–B(1)–C(21) 118.5(3), C(8)–B(2)–C(41) 115.8(3), C(8)–B(2)–C(31) 114.0(3), C(41)–B(2)–C(31) 111.4(3).

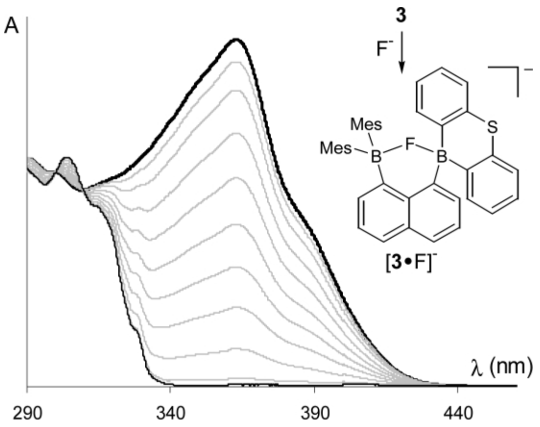

**Fig. 3** Spectral change accompanying the formation of [**3**·$\mu_2$-F]$^-$ upon addition of $n$Bu$_4$NF to a THF solution of **3** ($5.5 \times 10^{-5}$ M).

In conclusion, we report the synthesis of a colorimetric fluoride sensor whose molecular recognition unit is a bidentate Lewis acidic borane. The charge neutrality of this sensor as well as the short space available between the boron centres makes this sensor highly selective for fluoride. Finally, by virtue of its bidentate nature, the fluoride association is remarkably high and by far exceeds that measured for monofunctional borane receptors.

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‡ CCDC 233190. See http://www.rsc.org/suppdata/cc/b4/b403596h/ for crystallographic data in .cif or other electronic format.

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