Colorimetric turn-on sensing of fluoride ions in $H_2O/CHCl_3$ mixtures by pyridinium boranes†

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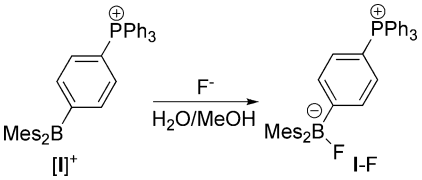
As part of our interest in chemistry of cationic boron compounds as anion receptors, we have synthesized 2-(4′-dimestylborylphenyl)-*N*-methyl-pyridinium triflate ([**3**]OTf) and 2-(5′-dimesitylborylthiophen-2′-yl)-*N*-methyl-pyridinium triflate ([**4**]OTf) by reaction of the corresponding pyridyl derivatives with MeOTf. Both [**3**]OTf and [**4**]OTf extract fluoride ions biphasically ($H_2O/CHCl_3$) to form the zwitterionic fluoroborates **3**-F and **4**-F, which have been structurally characterized. Remarkably, fluoride binding induces a red-shift of the low energy absorption band of these boranes (from 319 nm to 368 nm for **3**/**3**-F and from 355 nm to 430 nm for **4**/**4**-F) leading to the appearance of a yellow color. The origin of this turn-on colorimetric response is attributed to an intramolecular charge transfer process involving the triorganofluoroborate moiety as the donor and the pyridinium moiety as the acceptor.

Introduction

The recognition of fluoride anions is attracting a great deal of interest because of the importance of this anion in dental health and its possible toxicity when administered in high doses. Because of their inherent fluorophilicity, organoboranes have been recently used as receptors for fluoride anions.[1-9] Simple triarylboranes such as tris(9-anthryl)borane[3] or trimesitylborane[5] complex fluoride in non-polar organic solvents to form the corresponding fluoroborate anions whose stability constants range from 10^5 to 10^6 M^{-1}. In the case of cationic boranes[10,11] such as **I** (Scheme 1),[12] fluoride binding is assisted by favorable Coulombic attractions and occurs in aqueous solutions where fluoride is highly hydrated.[12-14]

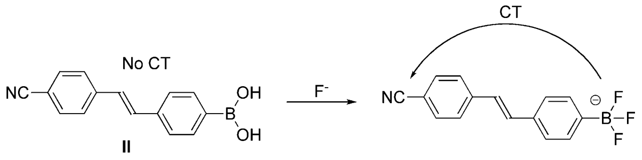


Scheme 1

In most cases, the aromatic substituents of triarylboranes are conjugated *via* the vacant boron p-orbital leading to the formation of a chromophore whose absorption and emission are red-shifted when compared to that of the individual aromatic substituents.[3] Fluoride binding leads to population of the boron p-orbital, interrupting conjugation and, as a result, providing a turn-off response both in the absorption and emission spectra of the borane. The turn-off rather than turn-on nature of the observed response inherently limits the sensitivity of triarylborane-based anion sensors.

Realizing this limitation, Wang recently reported a series of bifunctional molecules containing both a triarylborane and triarylamine moiety. In such systems, the emission of the triarylamine moiety is quenched by an intramolecular electron transfer process.[6] Because the emission of the triarylamine moiety can be revived upon addition of fluoride to the boron center, such derivatives behave as turn-on fluoride sensors.[8] These derivatives are neutral and can only be expected to be compatible with organic solvents.

Arylboronic acids such as **II**[4] have also been considered as fluoride sensors (Scheme 2). In the case of **II**, formation of the corresponding trifluoroborate species is accompanied by the appearance of an intramolecular charge transfer band involving the borate moiety as a donor and the electron deficient aryl group as the acceptor.[4] Appearance of this charge transfer band results in an intense turn-on colorimetric response. Although this strategy has proved quite general,[7,11] it has not been applied to the case of simple triorganoborane fluoride receptors. In this paper, we describe cationic boranes with electron deficient pyridinium moieties which serve for the turn-on colorimetric sensing of fluoride ions in organic solvents or under biphasic conditions in water/organic solvent mixtures.



Scheme 2

Results and discussion

The reaction of 2-(4′-lithiophenyl)pyridine and 2-(5′-lithiothiophen-2′-yl)pyridine with dimesitylboron fluoride (Mes_2BF) afforded boranes **1**[15] and **2** in moderate yields (Scheme 3). Subsequent treatment of **1** and **2** with MeOTf in Et_2O yielded the

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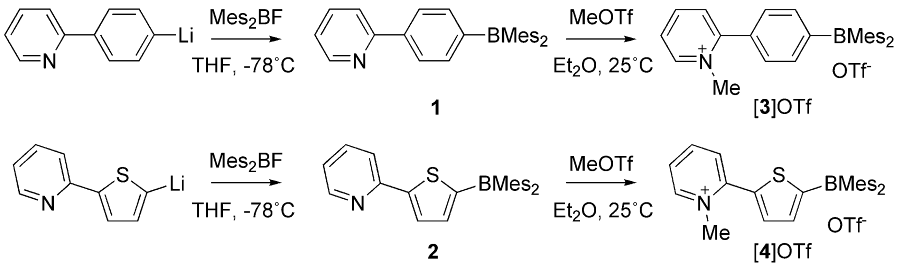
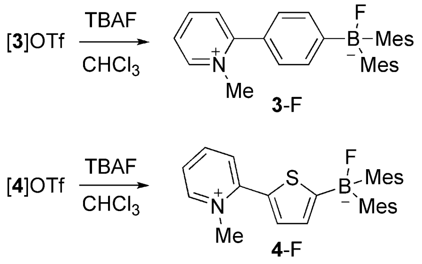


Scheme 3 Synthesis of cationic boranes [**3**]OTf and [**4**]OTf.

new cationic boranes [**3**]OTf and [**4**]OTf which have been fully characterized. These salts dissolve in polar solvents such as acetone, acetonitrile and DMSO but are insoluble in hydrocarbon solvents and diethyl ether. The ^{1}H NMR spectra of [**3**]OTf and [**4**]OTf in acetone-d_6 feature all expected resonances for the aromatic C*H* groups of the aryl, pyridinium, and mesityl groups. The proton resonance of the *N*-methyl groups in [**3**]OTf and [**4**]OTf appear at 4.43 ppm and 4.59 ppm, respectively. The broad ^{11}B NMR signals at 76 ppm for [**3**]OTf and 68 ppm for [**4**]OTf indicate that the boron atom of these derivatives adopts a trigonal planar geometry in solution. Broad UV bands are observed at 319 nm and 355 nm for [**3**]OTf and [**4**]OTf, respectively, in $CHCl_3$ solution and are assigned to the absorbance of the boron centered chromophore.

Both [**3**]OTf and [**4**]OTf are quantitatively converted into the zwitterionic fluoroborate adducts **3**-F and **4**-F upon addition of TBAF (*n*-tetrabutylammonium fluoride) in $CDCl_3$ (Scheme 4). These zwitterions have been characterized by multinuclear NMR spectroscopy and single crystal X-ray diffraction (Table 1). In both cases, the ^{11}B NMR signal is in the expected range for a four-coordinate boron center (5.6 ppm for **3**-F, 4.9 ppm for **4**-F). The ^{19}F NMR signals, which appear at −173 ppm for **3**-F and −168 ppm for **4**-F, indicate the presence of fluoroborate moieties.[2,3,5,14] The structures of **3**-F and **4**-F (Fig. 1) confirm the presence of a fluorine atom coordinated to the boron center *via* B(1)-F(1) lengths of 1.482(3) and 1.460(5) Å which are comparable to those found in triarylfluoroborate anions (1.47 Å).[3,14]



Scheme 4 Synthesis of fluoroborates **3**-F and **4**-F.

Interestingly, conversion of [**3**]OTf and [**4**]OTf into **3**-F and **4**-F is accompanied by the appearance of an intense yellow color in solution (Fig. 2). These colorimetric changes indicate that both [**3**]OTf and [**4**]OTf act as turn-on sensors for fluoride. In order to better understand the origin of this turn-on response, the UV-spectra of these compounds in $CHCl_3$ solutions were monitored upon incremental addition of TBAF (Fig. 3). In both cases, addition of fluoride results in a quenching of the borane absorption band indicating a break in conjugation due to fluoride binding to the boron center.[3,5] However, in each case, this quenching is also accompanied by the appearance of a new absorption band (at 368 nm for **3**-F and 430 nm for **4**-F) which is responsible for the observed visible color change. The shape of the fluoride binding isotherms suggests that the fluoride binding constants of these cationic boranes are above the 10^7–10^8 M^{-1} range. Addition of chloride, bromide, or iodide anions does not affect the UV-Vis spectra of the cationic boranes, indicating that these anions do not bind to the boranes. Although [**3**]OTf and [**4**]OTf are soluble and undergo no noticeable decomposition in 9:1 H_2O:MeOH solvent mixtures, addition of fluoride to these solutions does not result in the formation of the fluoroborates indicating that these cationic boranes are not sufficiently Lewis acidic to overcome the high hydration energy of the fluoride anion. Similarly, NMR measurements in the same deuterated solvent mixture show no indication of formation of the fluoroborate species.

Table 1 Crystal data, data collections, and structure refinements

Crystal data	**3**-F	**4**-F
Formula	$C_{32.24}H_{36.71}BFN_{1.76}O_{0.24}$	$C_{28}H_{31}BFNS$
Mr	482.51	443.41
Crystal size/mm	0.24 × 0.10 × 0.05	0.12 × 0.11 × 0.08
Crystal system	Monoclinic	Tetragonal
Space group	*P*2(1)/*c*	*I*4(1)/*a*
a/Å	13.924(3)	22.51(3)
b/Å	12.520(3)	22.51(3)
c/Å	15.974(4)	17.90(3)
β/°	101.333(3)	
V/Å^3	2730.4(11)	9071(22)
Z	4	16
ρ_{calc}/g cm^{-3}	1.174	1.299
μ/mm^{-1}	0.072	0.168
F(000)	1034	3776
T/K	110(2)	110(2)
Scan mode	ω	ω
hkl Range	−15 → +15	−25 → +25
	−14 → +14	−25 → +23
	−18 → +18	−20 → +20
Measd reflns	22904	22185
Unique reflns [R_{int}]	4278 [0.0831]	3557 [0.0956]
Reflns used for refinement	4278	3557
Refined parameters	351	289
GooF	1.001	1.000
$R1$,[a] $wR2$[b] (all data)	0.0986, 0.1433	0.0839, 0.1290
ρ_{fin} (max., min.)/e Å^{-3}	0.318, −0.272	0.404, −0.365

[a] $R1 = \sum \|F_o| - |F_c\| / \sum |F_o|$. [b] $wR2\ ([\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2])^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$ with $a = 0.069$ for **3**-F and 0.0415 for **4**-F and $b = 0$ for **3**-F and 21 for **4**-F.

Despite the inability of these compounds to complex fluoride directly in aqueous media, we investigated their capacity to extract

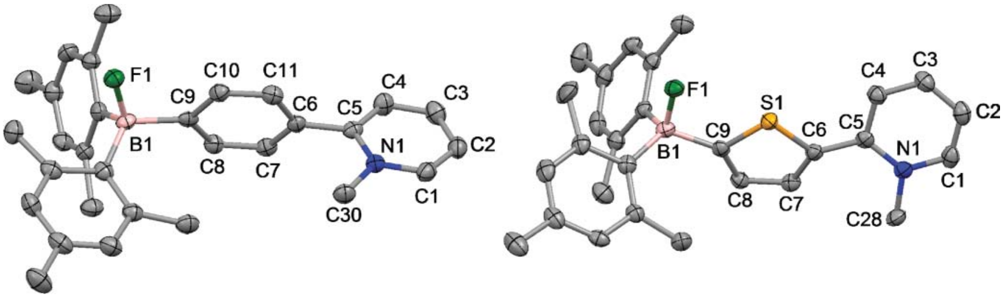


Fig. 1 Structure of fluoroborates **3**-F (left) and **4**-F (right). Displacement ellipsoids are scaled to the 50% probability level.

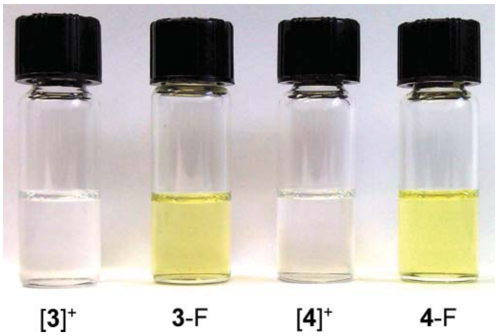


Fig. 2 Observed color change of solutions of [**3**]$^+$ and [**4**]$^+$ (0.017 M, $CHCl_3$) upon addition of TBAF.

fluoride from aqueous solutions into a less polar solvent where binding might be more favorable. When $CDCl_3$ solutions of [**3**]OTf and [**4**]OTf (0.5 mL, 0.07 M) were layered with solutions of TBAF in D_2O (0.125 mL, 0.28 M, 1 eq.), the organic layers quickly developed a yellow color indicative of the fluoroborate species. Changes in both the ^{1}H and ^{19}F NMR spectra were consistent with the formation of the corresponding zwitterionic fluoride adducts **3**-F and **4**-F. Conversion to the fluoroborate species was monitored by integration of ^{1}H NMR signals corresponding to the aromatic C*H* groups of the mesityl substituents, which undergo an upfield shift (*ca.* 0.4 ppm) upon fluoride binding. Based on integration of the ^{1}H NMR spectra, [**3**]OTf was converted to **3**-F in 50% yield while [**4**]OTf underwent full conversion to **4**-F. The greater fluoride affinity of [**4**]$^+$ when

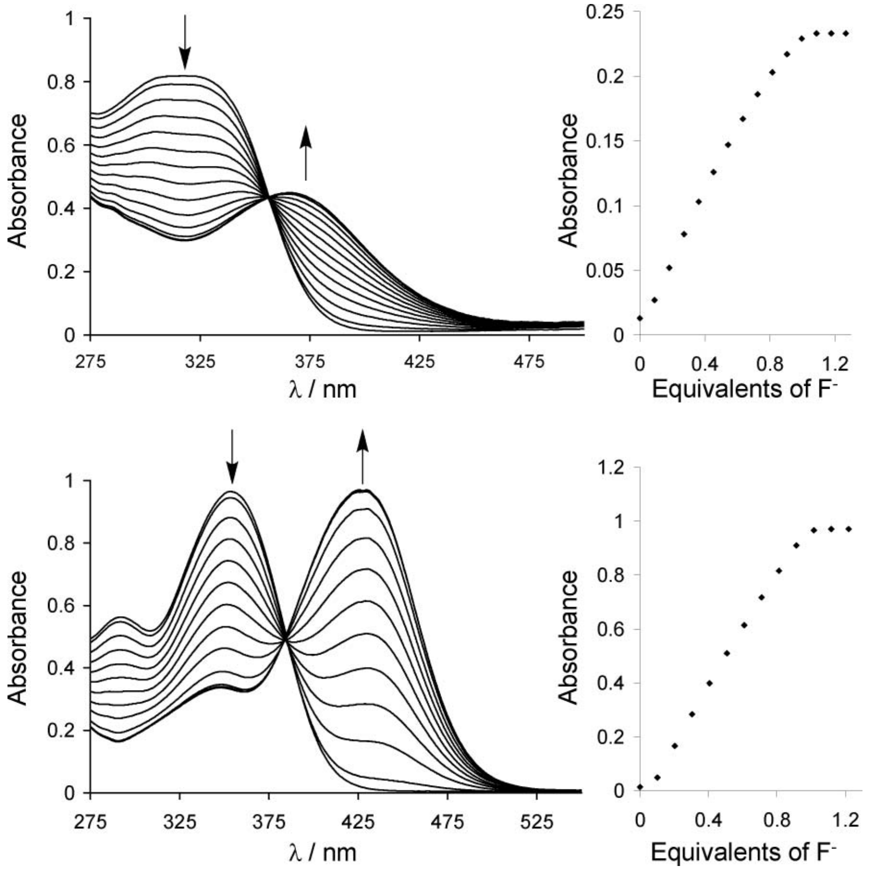


Fig. 3 Spectral changes in the UV-Vis absorption spectra of [**3**]OTf (top, 6.3×10^{-5} M) monitored at 406 nm and [**4**]OTf (bottom, 5.6×10^{-5} M) monitored at 430 nm in $CHCl_3$ upon incremental addition of a TBAF solution (3.4×10^{-3} M in $CHCl_3$).

compared to [**3**]$^+$ can be assigned to the electron withdrawing properties[9] and possibly the lower steric requirement of the five-membered thienyl group. By layering a solution of [**3**]OTf with a total of four equivalents of TBAF solution (0.500 mL) the conversion to **3**-F increased to 74%. We performed the same experiments by layering with a NaF/D$_2$O (0.125 mL, 0.28 M, 1 eq.) solution. Under these conditions only 5% conversion to **3**-F and 30% conversion to **4**-F was observed thus indicating that the *n*-tetrabutylammonium cation acts a phase transfer agent for fluoride anions. The percent conversion to **3**-F remained low when layered with a total of four equivalents of NaF/D$_2$O (0.500 mL) while **4**-F was formed in a 42% yield (Fig. 4). In the experiments performed with NaF, a slight upfield shift of the pyridinium C*H* signals is observed for the remaining [**4**]OTf. Similar changes were observed in the spectra of [**3**]OTf upon layering with NaF/D$_2$O and are attributed to the changing ionic strength of the organic layer.

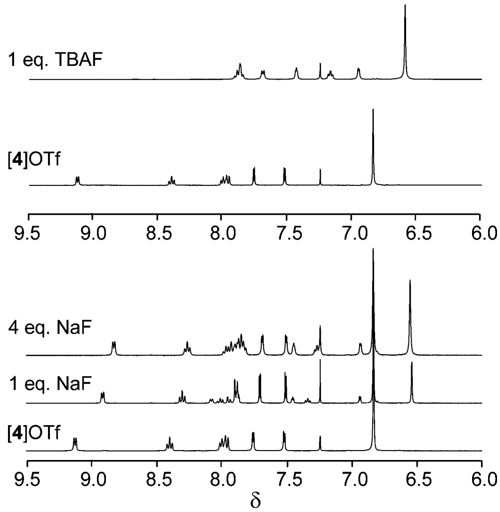


Fig. 4 ^{1}H NMR spectra of [**4**]OTf in CDCl$_3$ upon layering with a D$_2$O solution of TBAF (top) or NaF (bottom).

The structures of [**3**]$^+$, [**4**]$^+$, **3**-F and **4**-F have been optimized using DFT methods (B3LYP, 6-31+g(d′) for all atoms) and subjected to single point energy calculations using the Polarizable Continuum Model[16] (PCM) and chloroform as a solvent. Inspection of the frontier orbitals shows that the lowest unoccupied molecular orbital (LUMO) of each molecule is localized on the pyridinium portion of the molecule while the highest occupied molecular orbital (HOMO) is localized exclusively on the mesityl rings (Fig. 5). Although common TD-DFT methods cannot be used to study such chromophores,[17] it appears reasonable to assume that the lowest energy absorption band of these compounds is dominated by a HOMO-LUMO transition. Because of the localization of the frontiers orbital, these transitions can be regarded as intramolecular charge transfer transitions involving the boron moiety as the donor and the pyridinium moiety as the

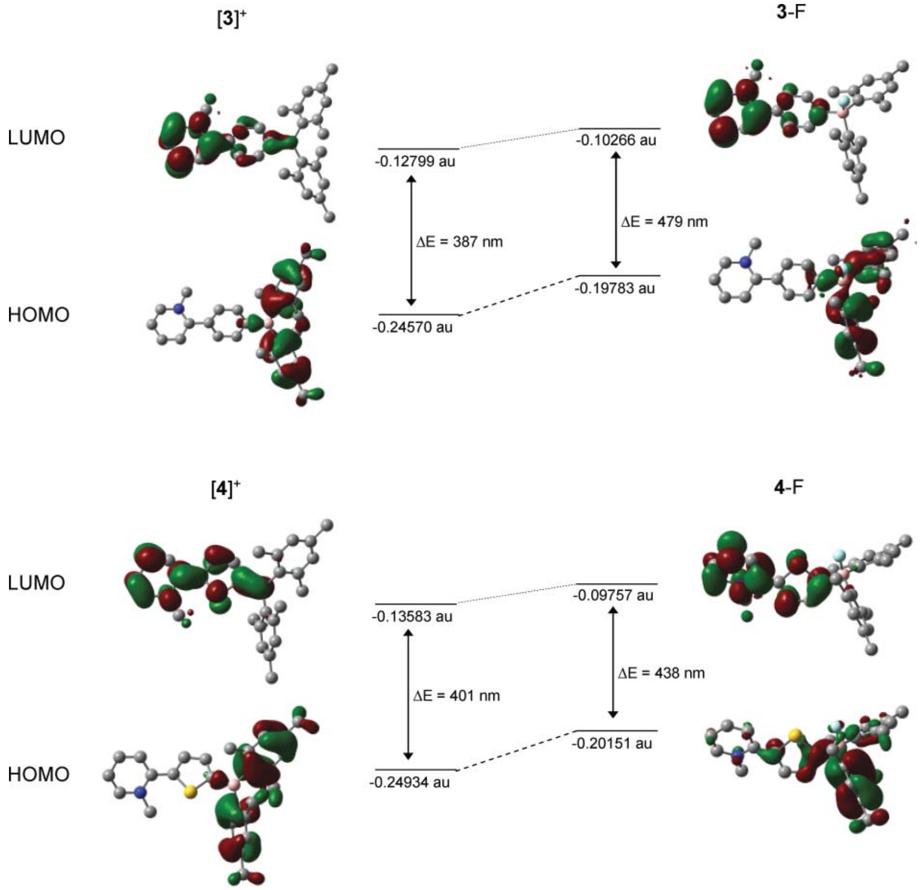


Fig. 5 Rendering of the HOMOs and LUMOs of [**3**]$^+$ and [**3**]F (top) and [**4**]$^+$ and [**4**]F (bottom) along with relative orbital and HOMO-LUMO gap energies. Isovalues are set at 0.03.

acceptor. In agreement with this assumption, we note that the HOMO-LUMO energy gap undergoes a noticeable decrease on going from the cationic borane [**3**]$^+$ and [**4**]$^+$ to the corresponding fluoroborate species **3**-F and **4**-F, respectively. Presumably, this fluoride induced decrease of the HOMO-LUMO gap of the compounds is responsible for the experimentally observed red-shift, thus allowing to rationalize the turn-on response given by [**3**]$^+$ and [**4**]$^+$ in the presence of fluoride.

Experimental

General considerations

2-(4′-Bromophenyl)pyridine was synthesized by a published procedure.[18] NaF and dimesitylboron fluoride were purchased from Aldrich. *n*-Bu4NF·3H_2O (TBAF) and 2-(2-thienyl)pyridine were purchased from Alfa Aesar and used as received. Solvents were dried by passing through an alumina column (*n*-hexane, CH_2Cl_2) or refluxing under N_2 over Na/K (Et_2O and THF). Air-sensitive compounds were handled under a N_2 atmosphere using standard Schlenk and glovebox techniques. UV-vis spectra were recorded on an Ocean Optics USB4000 spectrometer with an Ocean Optics ISS light source. Elemental analyses were performed at Atlantic Microlab (Norcross, GA). NMR spectra were recorded on Varian Unity Inova 400 FT NMR (399.59 MHz for ^{1}H, 375.99 MHz for ^{19}F, 128.19 MHz for ^{11}B, 100.45 MHz for ^{13}C) spectrometer at ambient temperature unless otherwise stated. Chemical shifts δ are given in ppm, and are referenced against external Me4Si (^{1}H, ^{13}C) and $BF_3\cdot Et_2O$ (^{11}B, ^{19}F).

Crystallography

Single crystals of **3**-F could be obtained by slow evaporation of a solution of [**3**]OTf and TBAF in CH_3CN/acetone. Single crystals of **4**-F could be obtained by cooling a concentrated acetone-d_6 solution of [**4**]OTf and TBAF. The crystallographic measurements were performed using a Bruker-AXS APEX-II CCD area detector diffractometer, with a graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). A specimen of suitable size and quality was selected and mounted onto a nylon loop. The structure was solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinement on F^2 using the allowed location of the remaining non-hydrogen atoms. The structure solution and refinement were carried out using the SHELXTL/PC package (version 6.10).[19]

Theoretical calculations

Density functional theory (DFT) calculations (full geometry optimization) were carried out with *Gaussian03* using the gradient-corrected Becke exchange functional (B3LYP) and the Lee-Yang-Parr correlation functional. A 6-31+g(d′) basis set was used for all atoms. Frequency calculations were also carried out on the optimized geometry. In the case of **4**-F, an imaginary frequency corresponding to low energy rotation of a para-methyl group of a mesityl ligand was observed and ignored.

Synthesis of 2-(4′-dimesitylborylphenyl)-*N*-methyl-pyridinium triflate ([3]OTf)

n-BuLi (0.790 mL, 2.5 M in hexanes, 1.97 mmol) was added to a THF (10 mL) solution of 2-(4′-bromophenyl)pyridine (0.440 g, 1.88 mmol) at −78 °C. The resulting reaction mixture was stirred at −78 °C for 1 h and mixed with a solution of Mes_2BF (0.529 g, 1.97 mmol) in THF (10 mL). The reaction was stirred overnight at room temperature before removing the solvent *in vacuo*. The solids were extracted with CH_2Cl_2 (20 mL) and filtered through Celite to remove LiF. The filtrate was evaporated to dryness and the residue recrystallized from Et_2O/pentane to afford 2-(4′-dimestylborylphenyl)pyridine (**1**) (0.400 g, 53% yield). ^{1}H NMR (399.9 MHz, CDCl3): δ 2.04 (s, 12H, Mes-C*H*$_3$), 2.33 (s, 6H, Mes-C*H*$_3$), 6.85 (s, 4H, Mes-C*H*), 7.25-7.28 (m, 1H, Pyr-C*H*), 7.64 (d, $^3J_{\text{H-H}}$ = 8.42 Hz, 2H, Ph-C*H*), 7.75-7.81 (m, 2H, Pyr-C*H*), 7.98 (d, $^3J_{\text{H-H}}$ = 7.98 Hz, 2H, Ph-C*H*), 8.72 (d, $^3J_{\text{H-H}}$ = 4.58 Hz, 1H, Pyr-C*H*). ^{11}B NMR (128.2 MHz, $CDCl_3$): δ 75.10. Without further purification, **1** (0.100 g, 0.248 mmol) was treated with MeOTf (0.100 mL, 0.420 mmol) in 10 mL Et_2O at room temperature. A white solid precipitated upon standing overnight. The solid was filtered, washed with Et_2O (3 × 5 mL) and pentane (3 × 5 mL), and dried under vacuum to afford [**3**]OTf (0.115 g, 82% yield). ^{1}H NMR (399.9 MHz, acetone-d_6): δ 2.03 (s, 12H, Mes-C*H*$_3$), 2.30 (s, 6H, Mes-C*H*$_3$), 4.43 (s, 3H, N-C*H*$_3$), 6.89 (s, 4H, Mes-C*H*), 7.71 (d, $^3J_{\text{H-H}}$ = 7.88 Hz, 2H, Ph-C*H*), 7.82 (d, $^3J_{\text{H-H}}$ = 7.88 Hz, 2H, Ph-C*H*), 8.25-8.27 (m, 2H, Pyr-C*H*), 8.78 (t, $^3J_{\text{H-H}}$ = 8.06 Hz, 1H, Pyr-C*H*), 9.24 (d, $^3J_{\text{H-H}}$ = 6.05 Hz, 1H, Pyr-C*H*). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 21.22 (Mes-*p*-CH_3), 23.47 (Mes-*o*-CH_3), 47.48 (pyr-CH_3), 118.92, 122.11, 127.25, 128.21, 128.43, 129.50, 133.55, 136.45, 139.50, 140.72, 141.05, 145.26, 147.63, 149.42, 155.67. ^{11}B NMR (128.2 MHz, acetone-d_6): δ 76.3. ^{19}F NMR (375.97 MHz, acetone-d_6): δ -77.8 (OTf). Anal. Calcd for $C_{31}H_{33}BNSF_3O_3$: C, 65.61; H, 5.86. Found: C, 65.71; H, 5.92.

Synthesis of 2-(5′-dimesitylboryl-thiophen-2′-yl)-*N*-methyl-pyridinium triflate ([4]OTf)

n-BuLi (1.30 mL, 2.5 M in hexanes, 3.26 mmol) was added to a THF (10 mL) solution of 2-(2-thienyl)pyridine (0.500 g, 3.1 mmol) at −78 °C. The resulting reaction mixture was stirred at −78 °C for 1 h and mixed with a solution of Mes_2BF (0.873 g, 3.26 mmol) in THF (10 mL). The reaction was stirred overnight at room temperature before removing the solvent *in vacuo*. The crude product was extracted with CH_2Cl_2 (20 mL) and filtered through Celite to remove LiF. The filtrate was evaporated to dryness and the residue was recrystallized from Et_2O/pentane to afford the crude product 2-(2-pyridyl)-5-dimesitylboryl-thiophene (0.70 g, 55% yield). ^{1}H NMR (399.9 MHz, CDCl3): δ 2.16 (s, 12H, Mes-C*H*$_3$), 2.32 (s, 6H, Mes-C*H*$_3$), 6.84 (s, 4H, Mes-C*H*), 7.16-7.21 (m, 1H, Pyr-C*H*), 7.46 (d, $^3J_{\text{H-H}}$ = 3.85 Hz, 1H, Thioph-C*H*), 7.69-7.72 (m, 2H, Pyr-C*H*), 7.74 (d, $^3J_{\text{H-H}}$ = 3.58 Hz, 1H, Thioph-C*H*), 8.58 (d, 1H, Pyr-C*H*, $^3J_{\text{H-H}}$ = 4.67 Hz). ^{11}B NMR (128.2 MHz, acetone-d_6): δ 67.35. Without further purification, **2** (0.100 g, 0.240 mmol) was treated with MeOTf (0.10 mL, 0.420 mmol) in 10 mL Et_2O at room temperature. A white solid precipitated upon standing overnight. The solid was filtered, washed with Et_2O (3 × 5 mL) and pentane (3 × 5 mL), and dried under vacuum to afford [**4**]OTf (0.125 g, 89% yield). ^{1}H NMR (399.9 MHz, acetone-d_6): δ 2.14 (s, 12H, Mes-C*H*$_3$), 2.29 (s, 6H, Mes-C*H*$_3$), 4.59 (s, 3H, N-C*H*$_3$), 6.89 (s, 4H, Mes-C*H*), 7.60 (d, $^3J_{\text{H-H}}$ = 3.85 Hz, 1H, Thiophene-C*H*), 8.00 (d, $^3J_{\text{H-H}}$ = 3.85 Hz, 1H, Thiophene-C*H*), 8.24 (t, $^3J_{\text{H-H}}$ = 6.41 Hz, 1H, Pyr-C*H*), 8.37 (d, $^3J_{\text{H-H}}$ = 8.06 Hz, 1H, Pyr-C*H*), 8.72 (t, 1H, Pyr-C*H*, $^3J_{\text{H-H}} = 7.88$ Hz), 9.24 (d, 1H, Pyr-C*H*, $^3J_{\text{H-H}} = 6.23$ Hz). ^{13}C NMR (100.5 MHz, acetone-d_6): δ 21.20 (Mes-*p*-CH_3), 23.61 (Mes-*o*-CH_3), 48.64 (pyr-CH_3), 128.08, 129.24, 131.62, 135.86, 140.31, 140.79, 141.33, 141.54, 143.02, 146.43, 148.56, 150.28, 156.43. ^{11}B NMR (128.2 MHz, acetone-d_6): δ 68.4. ^{19}F NMR (375.97 MHz, acetone-d_6): δ -77.6 (OTf). Anal. Calcd for $C_{29}H_{31}BNS_2F_3O_3$: C, 60.73; H, 5.45. Found: C, 60.89; H, 5.53.

Generation of 3-F and 4-F

3-F and **4**-F were prepared and characterized by multinuclear NMR spectroscopy *in situ* by addition of TBAF to solutions of [**3**]OTf and [**4**]OTf in acetone-d_6. Data for **3**-F: ^{1}H NMR (399.9 MHz, acetone-d_6): δ 1.94 (s, 12H, Mes-C*H₃*), 2.08 (s, 6H, Mes-C*H₃*), 4.34 (s, 3H, N-C*H₃*), 6.45 (s, 4H, Mes-C*H*), 7.10-7.30 (bm, 3H), 8.03-8.07 (m, 3H), 8.59 (t, $^3J_{\text{H-H}} = 8.06$ Hz, 1H, Pyr-C*H*), 9.00 (d, $^3J_{\text{H-H}} = 6.05$ Hz 1H, Pyr-C*H*). ^{13}C NMR (100.5 MHz, dmso-d_6): δ 20.56 (Mes-*o*-CH_3), 24.90 (Mes-*o*-CH_3), 46.96 (pyr-CH_3), 125.34, 125.99, 126.35, 128.03, 129.72, 130.60, 133.51, 140.60, 144.81, 146.30, 154.12, 157.08, 169.42. ^{11}B NMR (128.2 MHz, acetone-d_6): δ 5.64. ^{19}F NMR (375.97, MHz, acetone-d_6): δ -176.0. Data for **4**-F: ^{1}H NMR (399.9 MHz, acetone-d_6): δ 2.03 (s, 12H, Mes-C*H₃*), 2.09 (s, 6H, Mes-C*H₃*), 4.51 (s, 3H, N-C*H₃*), 6.47 (s, 4H, Mes-C*H*), 6.90 (d, $^3J_{\text{H-H}} = 3.48$ Hz, 1H, Thioph-C*H*), 7.66 (dd, $^3J_{\text{H-H}} = 3.66$ Hz, $^4J_{\text{H-F}} = 2.56$ Hz, 1H, Thioph-C*H*), 7.74 (t, $^3J_{\text{H-H}} = 6.31$ Hz, 1H, Pyr-C*H*), 8.18 (d, $^3J_{\text{H-H}} = 8.24$ Hz, 1H, Pyr-C*H*), 8.36 (t, $^3J_{\text{H-H}} = 7.78$ Hz, 1H, Pyr-C*H*,), 8.81 (d, $^3J_{\text{H-H}} = 6.23$ Hz 1H, Pyr-C*H*). ^{13}C NMR (100.5 MHz, acetone-d_6): δ 20.92 (Mes-*p*-CH_3), 24.90 (Mes-*o*-CH_3), 48.67 (pyr-CH_3), 120.68, 123.58, 123.88, 129.13, 129.39, 130.15, 131.44, 132.22, 135.62, 141.60, 144.28, 146.72, 152.38. ^{11}B NMR (128.2 MHz, acetone-d_6): δ 4.93. ^{19}F NMR (375.97, MHz, acetone-d_6): δ -167.5.

Titration of [3]OTf and [4]OTf with fluoride in $CHCl_3$

Solutions of [**3**]OTf (3.0 mL, 6.3×10^{-5} M, $CHCl_3$) and [**4**]OTf (3.0 mL, 5.6×10^{-5} M, $CHCl_3$) were titrated with incremental (5 µL) amounts of fluoride anions by addition of a 3.4×10^{-3} M solution of TBAF in $CHCl_3$.

Biphasic fluoride capture

^{1}H NMR spectra of solutions of [**3**]OTf and [**4**]OTf in $CDCl_3$ (0.500 mL, 0.07 M) were collected after layering and shaking with 0.125 mL (1 eq. F^-) and/or 0.500 mL (4 eq. F^-) of D_2O solutions containing TBAF or NaF (0.28 M). Conversion to the fluoroborate species **3**-F and **4**-F was monitored by integration, specifically the signals corresponding to the mesityl aromatic C*H* groups which are shifted significantly upfield upon fluoride binding.

Conclusion

In conclusion, we report the synthesis and structures of two new cationic boranes. These new cationic boranes selectively bind fluoride ions in organic solvents. These compounds are sufficiently fluorophilic to capture fluoride ions under biphasic conditions in $H_2O/CHCl_3$. In addition to being selective, these new boranes give a colorimetric turn-on response upon fluoride binding. This turn-on response originates from an intramolecular charge transfer band involving the fluoroborate moiety as a donor and the pyridinium ring as the acceptor.

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