

Ratiometric Fluorescence Sensing of Fluoride Ions by an Asymmetric Bidentate Receptor Containing a Boronic Acid and Imidazolium Group

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The synthesis of the first examples of anion receptors that utilize boron–fluoride interactions and (C–H)⁺...F[−]-type ionic hydrogen-bond interactions in the binding of F[−] ions is reported herein. *o*-, *m*-, and *p*-Phenylboronic acids were linked to naphthoimidazolium through a methylene group. On the basis of fluorescence and ¹⁹F NMR studies, we have confirmed that the addition of fluoride to a boron center occurs prior to the formation of (C–H)⁺...F[−]-type ionic hydrogen bond with the imidazolium moiety. More importantly, these investigations have demonstrated that only the receptor bearing the *ortho*-directed boron and imidazolium exhibits

enhanced fluoride binding. The increased binding ability of the asymmetric bidentate receptor of *ortho*-boronic acid and imidazolium towards F[−] enables it to sense fluoride ions in a 95:5 CH₃CN/HEPES aqueous solution. The fluorescence responses to different anions were also explored; the *ortho*-boron-imidazolium receptor displayed ratiometric fluorescence changes and a high selectivity towards fluoride ions over other anions (Cl[−], Br[−], CH₃CO₂[−], HSO₄[−], and H₂PO₄[−]).

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Introduction

Anions play a fundamental role in a wide range of chemical and biological processes, and considerable effort has been devoted to the development of abiotic receptors for anionic species.^[1] Among them, fluoride is the smallest anion with a high charge density and a hard Lewis basic nature, which results in unusual chemical properties. Fluoride ions are biologically important anions because of their role in, for example, dental care^[2] and the treatment of osteoporosis.^[3] In this regard, the sensing of fluoride ions has attracted growing attention.^[1,4–6]

In a number of cases, hydrogen-bonding between the N–H of urea, pyrrole, or a naphthalimide group and the fluoride ion is the mechanism of recognition.^[4] Electron-deficient Lewis acid coordination by orbital overlap has also received considerable attention and receptors containing

boron, silicon, tin, and mercury have all emerged.^[7] The fluorescence sensing of fluoride ions using boronic acid was reported in 1998.^[5] Since this first report several other fluorescent systems utilizing the boron–fluoride interaction have been reported.^[6] We developed system **A**, shown in Scheme 1, in which the binding of fluoride ions by boronic acid induced a selective fluorescence enhancement.^[6e] More recently, stable triarylborons with high Lewis acidity were used as fluoride probes in aqueous or alcohol solvents to overcome the competitive binding of aqueous protons with fluoride ions.^[8] In particular, diborane receptors have received considerable attention because they accept fluoride more efficiently than monoborane receptors.^[9] To increase the ability of borane-based receptors to capture fluoride ions from water, Gabbai et al. developed a series of borane-containing asymmetric bidentate receptors,^[10] for example, borane with ammonium^[11] and borane with phosphonium.^[12] The ammonium site not only increases the binding ability with fluoride, but also increases the water-solubility.^[11] Kawachi et al. reported a B/Si bidentate receptor for fluoride ions.^[13] These asymmetric bidentate receptors could lead to a new design and synthesis of receptors for fluoride ions that can enhance the binding ability of fluoride ions in aqueous solutions.

The imidazolium group has also been actively studied for the recognition of anions.^[14] The imidazolium group can interact strongly with anions through a (C–H)⁺...X[−]-type ionic hydrogen bond, as shown in system **B** (Scheme 1).

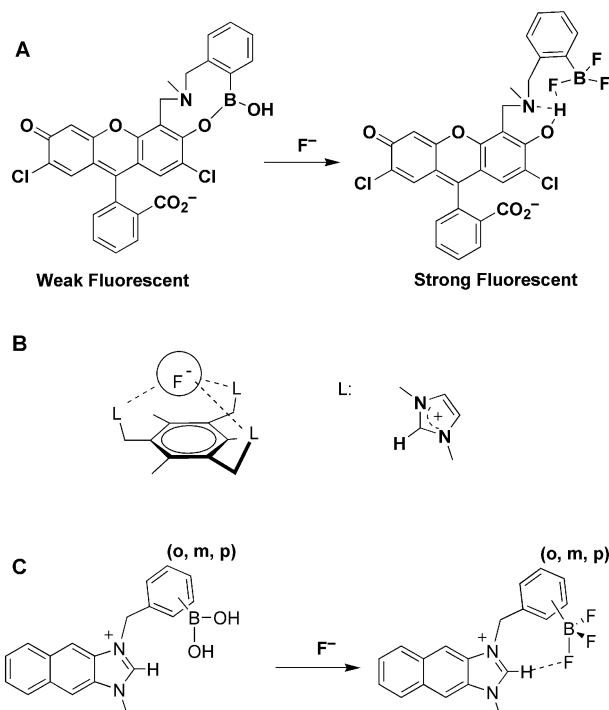
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Scheme 1. Sensing systems A, B, and C.

More attractively, the imidazolium group has also shown the ability to sense anions in aqueous solution.^[15] Encouraged by the idea of asymmetric bidentate receptors, we have synthesized the first receptors bearing boronic acid and an imidazolium group as fluorescent receptors for the fluoride ion. In our new system **C**, the naphthoimidazolium group was utilized for anion-binding and also as a fluorescent reporter. To test the potential of the borane-imidazolium system to bind fluoride ions, *o*-, *m*-, and *p*-phenylboronic acids were selected instead of triarylboron and linked to the naphthoimidazolium through a methylene group for an easy synthesis. The results are presented herein.

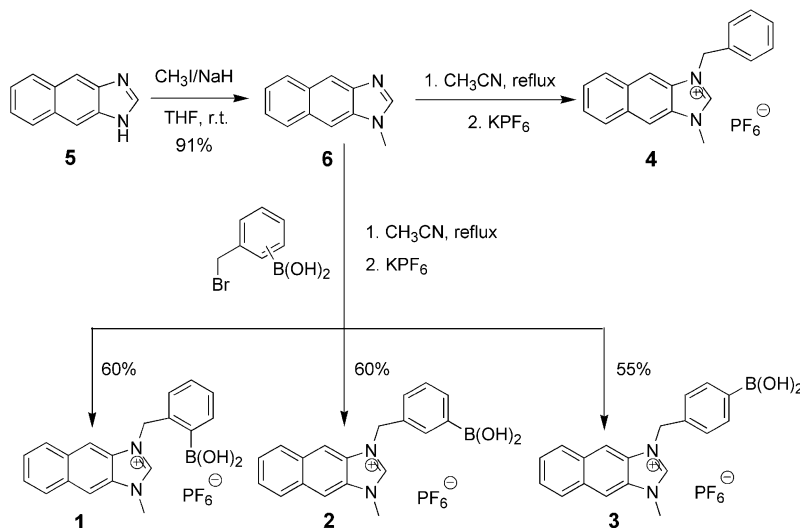
Results and Discussion

Synthesis and Characterization

Compounds **1**, **2**, and **3** were synthesized as the *ortho*, *meta*, and *para* derivatives, respectively. Compound **4** was prepared as a reference compound. The synthetic method for the preparation of compounds **1–4** is summarized in Scheme 2. 1*H*-Naphtho[2,3-*d*]imidazole (**5**) was synthesized by following a published procedure.^[16] 2,3-Diaminonaphthalene was heated at reflux in formic acid for 4.5 h. The solution was evaporated to dryness and the residue was dissolved in boiling water, treated with charcoal, and filtered. The hot filtrate was treated with conc. ammonia and on cooling the precipitate was collected. 1-Methyl-1*H*-naphtho[2,3-*d*]imidazole (**6**) was synthesized in 91% yield by the reaction of 1*H*-naphtho[2,3-*d*]imidazole (**5**) with iodomethane in THF at 0 °C followed by stirring for 1 h at room temperature. This intermediate was then treated with *o*-, *m*-, or *p*-(bromomethyl)phenylboronic acid and 1-(bromomethyl)benzene in acetonitrile at reflux for 24 h. The reaction mixtures were subsequently treated with a saturated aqueous KPF₆ solution to give the compounds **1–4** in 55–60% yields. All these compounds were fully identified by ¹H and ¹³C NMR spectroscopy and HRMS.

Fluoride Recognition Studies in Acetonitrile

Of the probes illustrated in Scheme 2, compound **1** is expected to show the strongest binding with F[−] due to the proximity of the boronic acid and imidazolium, increasing the likelihood that the boronic acid and imidazolium can bind the same fluoride ion. Compounds **2** and **3** are anticipated, in comparison with **1**, to provide a favorable geometry of the boronic acid and imidazolium to bind F[−] ions. The control compound **4** can clearly be used to test the

Scheme 2. Synthesis of compounds **1–4**.

rationality of our design, that is, that a bidentate receptor of boronic acid and imidazolium improves the binding ability towards F^- compared with a single binding site.

The emission spectroscopy and fluorescence titration experiments with F^- were performed in acetonitrile solution (Figure 1). The emission spectrum of free **1** displays a broad band with a maximum at 440 nm. When F^- was added progressively to a solution of **1**, a significant decrease in the 440 nm emission was observed with the appearance of a blue-shifted emission band centered at 372 nm, which was attributed to the formation of a **1**- F^- complex and increased in intensity, and a clear isoemission point at 406 nm. Thus, **1** is a ratiometric fluorescent probe for F^- , which means that changes in the ratio of the intensities of the emission at two wavelengths are observed. Ratiometric fluorescent probes permit signal-ratiometric and thus they increase the dynamic range and provide built-in correction for monitoring environmental effects.^[17] Figure 2a shows the dependence of the ratio of the emission intensities at 372 and 440 nm (I_{372}/I_{440}) on the concentration of F^- , which correlates directly with the amount of F^- . The addition of F^- to a solution of **1** causes a blue-shift of the emission from 440 to 372 nm, which leads to a significant color change. This color change allows **1**- F^- to be readily distinguished by the naked eye (Figure 2b), and probe **1** thus combines the sensitivity of fluorescence with the convenience and aesthetic appeal of a colorimetric assay.^[17a]

With the addition of F^- , compounds **2** and **3** showed only slight changes in emission even with more than 130 equiv. of F^- . Compound **4** displayed a similar fluorescent response, but needs larger amounts of F^- than **1**. As shown in Figure 2 (a), for compound **1**, the addition of 7 equiv. of F^- saturates the fluorescent changes. On the other hand, a larger amount of F^- (>11 equiv.) is needed in the case of **4** for saturation, notably with a weaker blue-shifted fluorescence intensity. Because the communicating source of the fluorescence is the naphthoimidazolium group, the blue-shifted emission should result from the interaction between naphthoimidazolium and the fluoride ion. Naphthoimidazolium is a donor-acceptor system and undergoes internal charge transfer (ICT) from naphthalene to imidazolium upon excitation by light, with imidazolium playing the role of acceptor.^[18] When F^- interacts with imidazolium, the electron-withdrawing ability of imidazolium would be reduced and an anion-induced blue-shift in emission would be expected. Thus, we can conclude that **1** displays a stronger $(C-H)^+ \cdots F^-$ -type ionic hydrogen bond than the other three compounds **2–4**.

Two questions arise regarding these systems. First, between the boron-fluoride interaction and the $(C-H)^+ \cdots F^-$ -type ionic hydrogen bond, which interaction occurs first? Secondly, does the *ortho* derivative **1** display enhanced binding with the fluoride ion compared with compounds **2** and **3**?

To answer these questions, a study by ^{19}F NMR spectroscopy in CD_3CN was performed at $-10^\circ C$. Figure 3 shows the ^{19}F NMR spectra of phenylboronic acid, **4**, and **1** upon the addition of F^- . James and co-workers have pre-

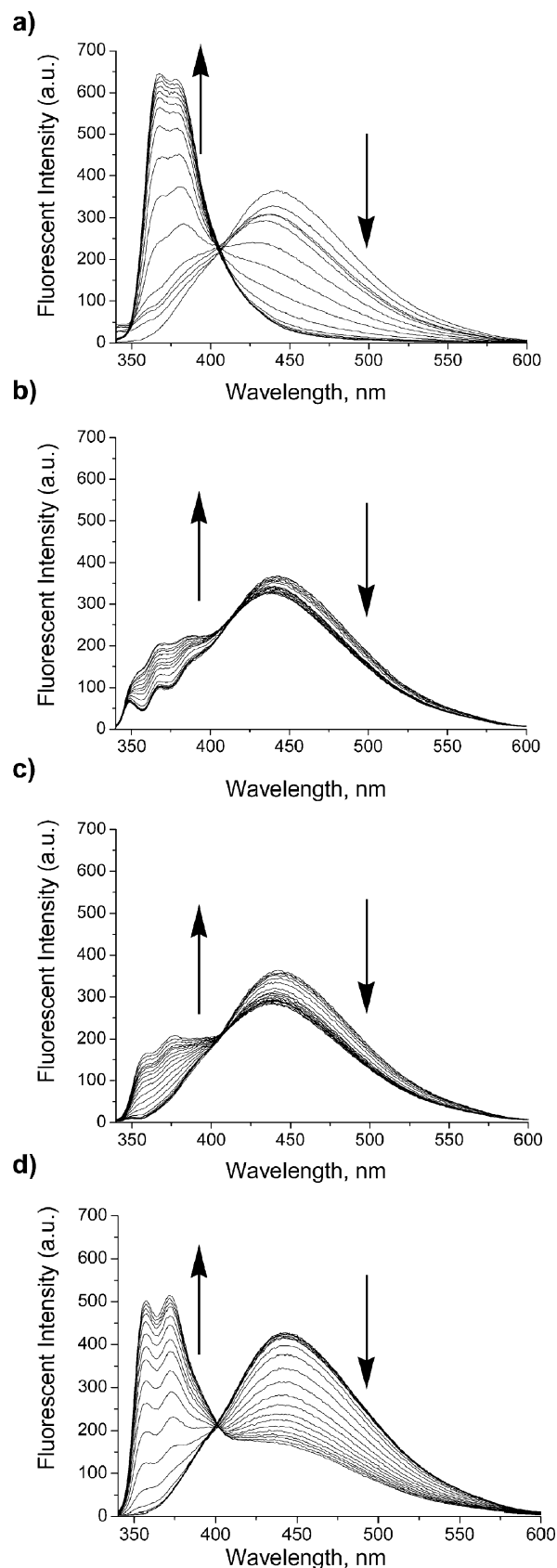


Figure 1. Fluorescent emission spectra for compounds **1–4** in the presence of different concentrations of F^- (0–130 equiv.; at intervals of 0.5 equiv.) in CH_3CN . a) **1**; b) **2**; c) **3**; d) **4**. The excitation wavelength was 323 nm. The concentrations of **1–4** were all 10 μM .

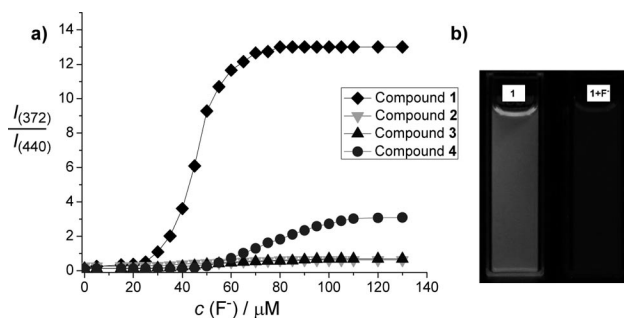


Figure 2. a) Ratiometric calibration curve for I_{372}/I_{440} as a function of F^- concentration. $[1] = [2] = [3] = [4] = 10 \mu M$. b) Emission observed from a solution of **1** and **1**- F^- .

viously reported the ^{19}F NMR spectroscopic data of phenylboronic acid in 33% methanol/ D_2O (v/v) at $0^\circ C$ upon the addition of fluoride ions.^[5] The experimental curves in Figure 2 (a) and the NMR spectroscopic data in Figure 3 (c) assume the formation of the trifluoroborate of **1** with fluoride (Scheme 3). As shown in Figure 3 (a), the peaks at -138.5 and -115.9 ppm, appeared upon the addition of F^- and correspond to $-B(OH)F_2^-$ and free F^- , which was confirmed by James and co-workers. It is notable that, even with excess fluoride ions, $-B(OH)F_2^-$ is the most stable species of phenylboronic acid in CH_3CN upon the addition of fluoride ions. In Figure 3 (b), the peaks for $(C-H)^+ \cdots F^-$ (or F_2H) and free F^- can be observed at -150.9 and -115.4 ppm, respectively. With these references, it is easy to explain the ^{19}F NMR spectra of **1** shown in Figure 3 (c). The peak at -134.5 ppm was observed first with 1 equiv. of F^- , corresponding to $-B(OH)F_2^-$. Very importantly, upon the addition of ≥ 2 equiv. of F^- , a peak at -144.4 ppm, which corresponds to $-BF_3^-$, began to appear at the expense of the $-B(OH)F_2^-$ peak, which disappeared after adding 3 equiv. of F^- . The peak at -118.1 ppm corresponds to the free fluoride peak. As shown in Figure 2 (a), the addition of ≥ 2 equiv. of F^- induced the blue-shifted fluorescence of **1**. This means that there is a $(C-H)^+ \cdots F^-$ -type ionic hydrogen-bond interaction between imidazolium and $-BF_3^-$. This suggests that the boron binds to F^- first, and then the binding is strengthened with the cooperation of naphthoimidazolium. We may ascribe the nonexistence of the $(C-H)^+ \cdots F^-$ interaction between imidazolium and $-B(OH)F_2^-$ to hydrogen-bonding between imidazolium and B-OH, which may prevent B-F from accessing the imidazolium.

To gain further proof for the above conclusion, the ^{19}F NMR spectra of **2** and **3** were also recorded upon the addition of F^- . Unfortunately, the solutions of **2**- PF_6 and **3**- PF_6 emulsified upon addition of F^- . Therefore, we studied **2**-Br and **3**-Br by ^{19}F NMR spectroscopy. Figure 4 shows the ^{19}F NMR spectra of **3** upon the addition of F^- . The *meta* adduct **2**-Br displayed similar ^{19}F NMR spectra to those of the *para* adduct **3**-Br. The peak at -133.9 ppm was observed first with 2 equiv. of F^- , which corresponds to $-B(OH)F_2^-$, as confirmed by analogy with the spectra of

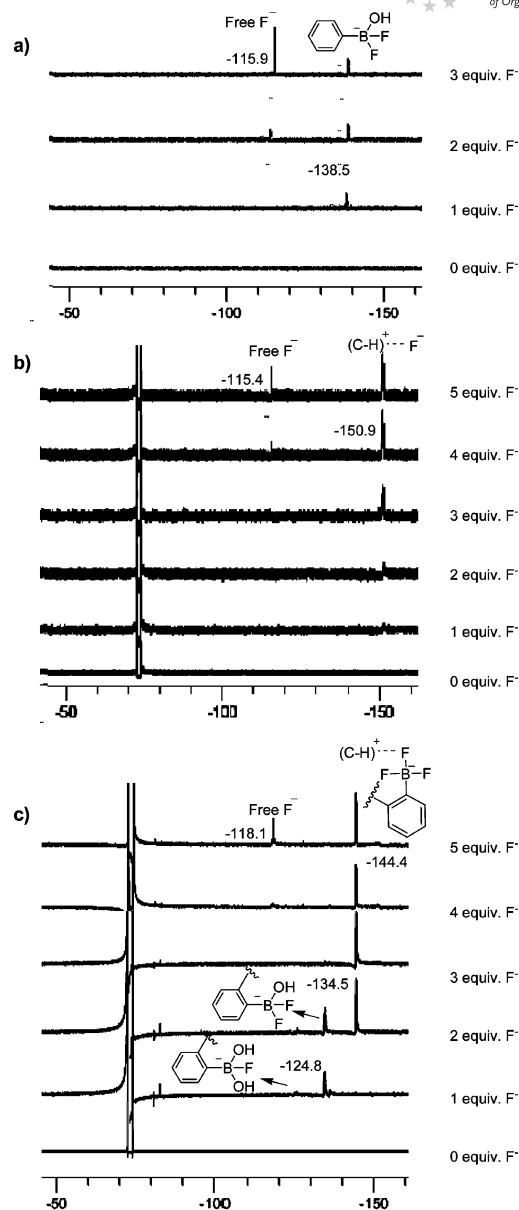
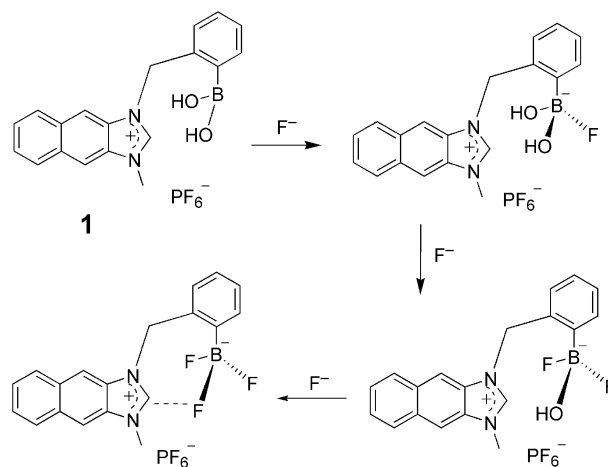


Figure 3. ^{19}F NMR spectra of solutions of fluoride ion in CD_3CN with a) phenylboronic acid, b) compound **4**, and c) compound **1**.



Scheme 3. The binding of **1** to fluoride ions.

phenylboronic acid (Figure 3, a). Upon the addition of ≥ 3 equiv. of F^- , peaks at -143.9 and -144.1 ppm began to appear, which correspond to $-BF_3^-$. The peak at -106.5 ppm corresponds to the free fluoride ion. Notably, with this amount of F^- , the peak arising from $-B(OH)F_2^-$ still exists alongside the peaks of $-BF_3^-$, which are quite weak. That means compound **3** has a much weaker ability to bind three fluoride ions than compound **1**. Thus, we can be clear why the addition of the fluoride ions does not cause a blue-shift of the fluorescence of **2** and **3**. These results also suggest that F^- adds to the boron prior to the formation of the hydrogen bond with the imidazolium moiety, and more importantly the presence of boronic acid at the *meta* or *para* position does not increase the strength of F^- -binding. Based on the variation of the fluorescence, the binding constants K_3 for **1–3** and K for **4** with F^- were estimated to be $5.1 (\pm 0.2) \times 10^5$, $6.7 (\pm 0.2) \times 10^3$, $5.7 (\pm 0.2) \times 10^3$, and $1.1 (\pm 0.2) \times 10^4 M^{-1}$, respectively.^[19] Based on Figures 1, 3, and the binding constants, we can say that the adjacent boronic acid (*ortho*) facilitates the interaction of the fluoride ion with imidazolium, whereas the more distant boronic acids (*meta* and *para*) inhibit the F^- -binding process with imidazolium. This is reasonable because boronic acid and naphthoimidazolium are competitors for binding F^- . They bind F^- cooperatively under favorable circumstances, but also they can be mutually exclusive of F^- -binding under unfavorable situations.

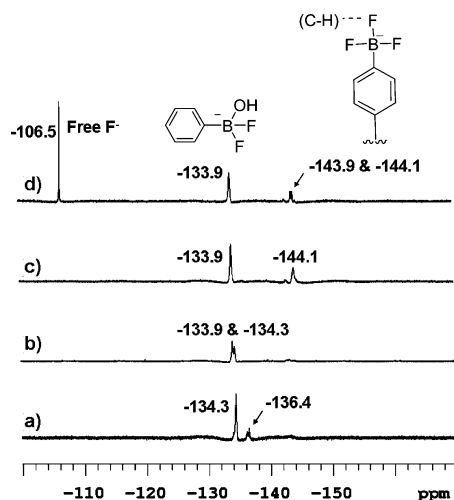


Figure 4. ^{19}F NMR spectra of **3-Br** with fluoride ion in CD_3CN . a) 1 equiv. of F^- ; b) 2 equiv. of F^- ; c) 3 equiv. of F^- ; d) 5 equiv. of F^- .

Cyclic voltammetry (CV) experiments were also performed (Table 1 and Figure 1 of the Supporting Information). The cathodic peak current (i_{pc}) for the *ortho* adduct **1** decreased to less than half (-1.63 V vs. SCE) upon addition of 2 equiv. of F^- , which can be attributed to the interaction of the fluoride ion with the imidazolium group. With 3 equiv. of F^- , **1** did not show any significant reduction current. On the other hand, such a virtual disap-

pearance of i_{pc} was not observed with the *para* adduct **3** upon addition of 3 equiv. of F^- and 17% of the reduction current still remained even upon the addition of 5 equiv. of F^- . These results also support unequivocally the proposal that fluoride-binding can be enhanced with the *ortho*-directed boron.

Table 1. Relative change of cathodic peak current (i_{pc}) at -1.6 V vs. SCE for **1** and **3** upon the addition of F^- .^[a]

F^- [equiv.]	1	3
0	1.00	1.00
1	0.94	1.00
2	0.41	0.94
3	0.00	0.78
5	0.00	0.17

[a] Cathodic peak potential (E_{pc}) was -1.63 and -1.50 V vs. S.C.E. for **1** and **3**, respectively.

Two crystal structures related to **3-Br** were obtained, as shown in Figure 5; the OH groups were replaced with OCH_3 as the crystals were grown in methanol. Figure 5 (a) represents a compound (**3-OMe**) in which one of the OH groups has been replaced with OCH_3 and the other forms

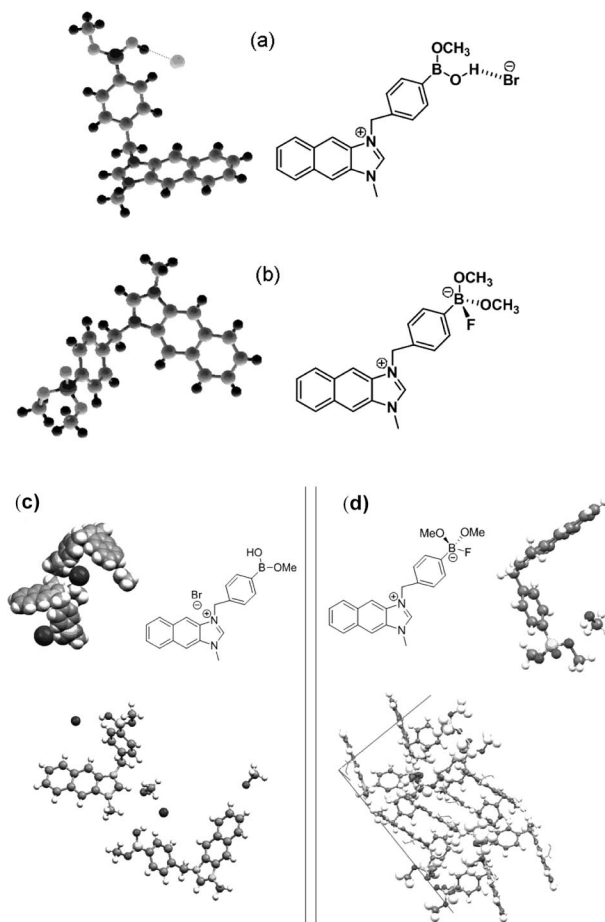


Figure 5. X-ray crystal structures of a) **3-OMe** and b) **3-2OMe- F^-** and unit cells of c) **3-OMe** and d) **3-2OMe- F^-** .

a hydrogen bond with Br^- . In the unit cell, imidazolium ($\text{C}-\text{H}$)⁺ forms a hydrogen bond with methanol, methanol then interacts with Br^- , and Br^- interacts with $-\text{B}(\text{OH})$ (Figure 5, c). On the other hand, Figure 5 (b) represents a structure (**3-2OMe-F**) in which the boron bears two OCH_3 groups and a fluoride. The unit cell displays π -stacking between the naphthoimidazolium moieties (Figure 5, d).

The fluorescence titration of **1** against various anions was conducted to examine its selectivity. The addition of Cl^- , Br^- , CH_3CO_2^- , HSO_4^- , and H_2PO_4^- produced only a nominal change in the fluorescence spectra of **1** due to their low affinity with probe **1**. Figure 6 shows the dependence of the intensity ratios (I_{372}/I_{440}) on the anions. The results show that probe **1** has a high selectivity for F^- .

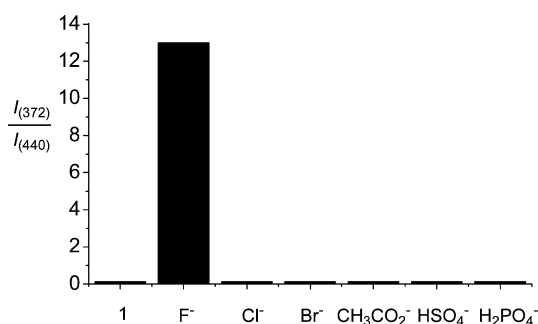


Figure 6. The responses of **1** to various anions in fluorescence titration.

Studies of Fluoride Recognition in Aqueous Solution

Probe **1** is a bidentate receptor containing a boronic acid and naphthoimidazolium that exhibits enhanced fluoride-binding. The increased ability of the boronic-based receptor to bind F^- may enable **1** to capture fluoride ions from aqueous solution.

To explore the F^- -binding ability of **1** in aqueous solution, the fluorescence responses of **1** in the presence of F^- were examined in different ratios of acetonitrile/water. In 1–5% water, **1** exhibits a blue-shifted emission centered at 372 nm due to binding with F^- . Figure 7 displays the fluorescence responses of **1–4** to F^- in $\text{CH}_3\text{CN}/\text{HEPES}$ (95:5) solution. With the addition of F^- , the emission of **1** at 440 nm first increases and then displays the same response as that in 100% acetonitrile. The other three compounds showed only slight fluorescence changes on addition of F^- because of their weak ability to bind F^- in aqueous solution. As the percentage of water increased (>5%), **1** can no longer capture fluoride ions and nominal changes in the fluorescence were observed. In aqueous solution, it may be difficult for the methylene-bridged imidazolium and boronic acid to bind the same fluoride ion, because of the flexibility of **1**. A rigid geometry of boron and the adjacent imidazolium can be expected to bind the same fluoride ion in aqueous solution. Related studies are in progress.

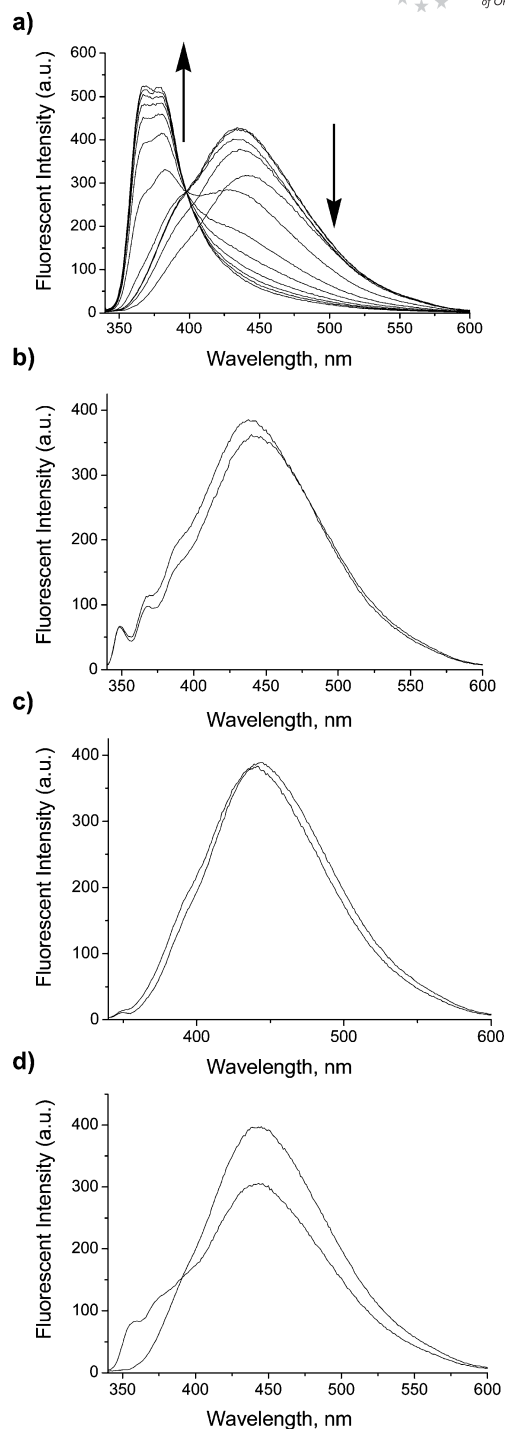


Figure 7. Fluorescent emission spectra of compounds **1–4** in the presence of different concentrations of F^- (0–100 equiv., rising in steps of 10 equiv.) in $\text{CH}_3\text{CN}/\text{HEPES}$ (95:5, 0.5 M, pH 7.4). a) **1**; b) **2**; c) **3**; d) **4**. The excitation wavelength was 323 nm. The concentrations of **1–4** were all 10 μM .

Conclusions

We have reported the synthesis of novel fluoride receptors bearing two distinct recognizing groups, boronic acid and an imidazolium moiety. The *ortho* compound **1** displayed a selective and ratiometric fluorescence change on

addition of fluoride ions. Based on the fluorescence and ^{19}F NMR studies, we confirmed that the addition of fluoride to the boron center occurs prior to the formation of the $(\text{C}-\text{H})^+\cdots\text{F}^-$ -type ionic hydrogen bond with the imidazolium moiety. More importantly, these investigations have demonstrated that only the receptor bearing the *ortho*-directed boron and imidazolium exhibits enhanced fluoride binding. This increased ability of the boronic-based receptor to bind F^- allows **1** to be used as a fluoride ion sensor in aqueous solution.

Experimental Section

General Procedures and Materials: Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Flash chromatography was carried out on silica gel 60 (230–400 mesh ASTM; Merck). Thin-layer chromatography (TLC) was carried out by using Merck 60 F₂₅₄ plates with a thickness of 0.25 mm. Preparative TLC was performed by using Merck 60 F₂₅₄ plates with a thickness of 1 mm. Melting points were measured by using a Büchi 530 melting point apparatus. ^1H and ^{13}C NMR spectra were recorded by using Bruker 250 MHz or Varian 500 MHz spectrometers. Chemical shifts are given in ppm and coupling constants (J) in Hz. UV absorption spectra were obtained with a UVIKON 933 Double Beam UV/Vis spectrometer. Fluorescence emission spectra were obtained with a RF-5301/PC spectrofluorophotometer (Shimadzu). Phenylboronic acid was purchased from Aldrich.

Synthesis of 6: NaH (330 mg, 8.3 mmol, 60% in mineral oil) was added to a mixture of **5**^[16] (690 mg, 4.1 mmol) in THF (20 mL) at 0 °C. After the reaction mixture had been stirred for 20 min at 0 °C, iodomethane (960 mg, 6.3 mmol) was added. After additional stirring for 1 h at room temperature, water (50 mL) was added to the reaction mixture and the mixture extracted with CHCl_3 . The organic layer was then separated, dried with anhydrous magnesium sulfate, and concentrated under reduced pressure. Purification by flash chromatography on silica gel ($\text{CH}_2\text{Cl}_2/\text{MeOH} = 100:1$) afforded **6** (680 mg, 91%) as a pale-yellow solid; m.p. 152–154 °C. ^1H NMR (CDCl_3 , 250 MHz): $\delta = 3.52$ (s, 3 H), 7.28 (m, 2 H), 7.47 (s, 1 H), 7.76 (m, 2 H), 7.86 (m, 1 H), 8.15 (s, 1 H) ppm. ^{13}C NMR (CDCl_3 , 62.5 MHz): $\delta = 30.92$, 105.13, 117.09, 123.49, 124.43, 127.48, 128.52, 129.97, 130.44, 135.07, 143.78, 147.51 ppm. HRMS (FAB): calcd. for $\text{C}_{12}\text{H}_{11}\text{N}_2$ [MH]⁺ 183.0922; found 183.0925.

Synthesis of 1: A mixture of **6** (100 mg, 0.55 mmol) and 2-(bromomethyl)phenylboronic acid (180 mg, 0.81 mmol) in acetonitrile (10 mL) was heated at reflux for 24 h under N_2 . After cooling to room temperature, the precipitate was filtered and washed with cold CH_2Cl_2 to give **1** as a bromide salt. The bromide salt was dissolved in methanol (10 mL). During the dropwise addition of aqueous saturated KFP₆ solution, a precipitate was formed. After washing the precipitate with water several times, the desired product was obtained as a white solid (152 mg, 60%). ^1H NMR (DMSO, 250 MHz): $\delta = 4.21$ (s, 3 H), 6.02 (s, 2 H), 7.35 (m, 1 H), 7.43 (m, $J = 2.4$ Hz, 2 H), 7.69 (m, $J = 1.4$ Hz, 2 H), 7.82 (d, $J = 4.0$ Hz, 1 H), 8.19 (m, 1 H), 8.23 (m, 1 H), 8.49 (s, 2 H, B-OH), 8.52 (s, 1 H), 8.68 (s, 1 H), 9.82 (s, 1 H) ppm. ^{13}C -NMR (DMSO, 62.5 MHz): $\delta = 33.86$, 50.78, 111.49, 127.08, 128.21, 128.71, 128.75, 130.51, 130.75, 131.33, 131.64, 135.50, 137.92, 147.48 ppm. HRMS (FAB): calcd. for $\text{C}_{19}\text{H}_{18}\text{BN}_2\text{O}_2$ [$\text{M} - \text{PF}_6$]⁺ 317.1461; found 317.1466.

Synthesis of 2: By following the same procedure as that used for **1**, combining **6** (100 mg, 0.55 mmol) and 3-(bromomethyl)phenylboronic acid (180 mg, 0.81 mmol) produced **2** (152 mg, 60% yield) as a white solid. ^1H NMR (DMSO, 250 MHz): $\delta = 4.23$ (s, 3 H), 5.88 (s, 2 H), 7.45 (m, 1 H), 7.70 (m, 3 H), 7.83 (d, $J = 7.4$ Hz, 1 H), 7.96 (s, 1 H), 8.20 (m, 4 H), 8.60 (s, 1 H), 8.69 (s, 1 H), 10.09 (s, 1 H) ppm. ^{13}C NMR (DMSO, 62.5 MHz): $\delta = 33.46$, 50.0, 110.94, 111.09, 126.63, 128.01, 128.20, 129.93, 130.82, 131.15, 132.85, 133.78, 134.30, 146.90 ppm. HRMS (FAB): calcd. for $\text{C}_{19}\text{H}_{18}\text{BN}_2\text{O}_2$ [$\text{M} - \text{PF}_6$]⁺ 317.1461; found 317.1462.

Synthesis of 3: By following the same procedure as that used for **1**, combining **6** (100 mg, 0.55 mmol) and 4-(bromomethyl)phenylboronic acid (180 mg, 0.81 mmol) produced **3** (140 mg, 55% yield) as a white solid. ^1H NMR (DMSO, 250 MHz): $\delta = 4.20$ (s, 3 H), 5.87 (s, 2 H), 7.54 (d, $J = 8.0$ Hz, 2 H), 7.68 (t, $J = 4.2$ Hz, 2 H), 7.84 (d, $J = 8.0$ Hz, 2 H), 8.17 (s, 2 H), 8.23 (m, 2 H, B-OH), 8.54 (s, 1 H), 8.66 (s, 1 H), 10.06 (s, 1 H) ppm. ^{13}C NMR (DMSO, 62.5 MHz): $\delta = 33.95$, 50.29, 111.38, 111.60, 127.14, 127.62, 128.70, 130.33, 131.30, 131.65, 135.09, 136.07, 147.48 ppm. HRMS (FAB): calcd. for $\text{C}_{19}\text{H}_{18}\text{BN}_2\text{O}_2$ [$\text{M} - \text{PF}_6$]⁺ 317.1461; found 317.1466.

Synthesis of 4: By following the same procedure as that used for **1**, combining **6** (100 mg, 0.55 mmol) and benzyl bromide (130 mg, 0.76 mmol) produced **4** (147 mg, 64% yield) as a white solid. ^1H NMR (DMSO, 250 MHz): $\delta = 4.22$ (s, 3 H), 5.90 (s, 2 H), 7.47 (m, 3 H), 7.68 (m, 4 H), 8.21 (m, 2 H), 8.61 (s, 1 H), 8.68 (s, 1 H), 10.18 (s, 1 H) ppm. ^{13}C NMR (DMSO, 62.5 MHz): $\delta = 32.34$, 48.58, 109.76, 109.95, 116.95, 125.44, 127.03, 127.12, 127.49, 127.76, 128.65, 129.63, 129.96, 132.82, 145.79 ppm. HRMS (FAB): calcd. for $\text{C}_{19}\text{H}_{17}\text{N}_2$ [$\text{M} - \text{PF}_6$]⁺ 273.1392; found 273.1388.

Supporting Information (see also the footnote on the first page of this article): ^1H and ^{13}C NMR, and CV data.

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