



## A ratiometric fluorescent probe for fluoride ions with a tridentate receptor of boronic acid and imidazolium

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### ABSTRACT

A new ratiometric fluorescent probe for fluoride ions was developed which complexed fluoride by a tridentate receptor of boronic acid and imidazolium. In the current study, a tridentate receptor **1** with one ortho boronic acid and two imidazolium groups was designed. The boron center can co-operate with imidazolium to bind F<sup>-</sup>. The formation of B–F complex stabilizes the interaction between fluoride and imidazolium which induces a ratiometric fluorescence response. With the addition of F<sup>-</sup>, a strongly increased fluorescent emission centered at 370 nm appears at the expense of the fluorescent emission centered at 445 nm.

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The development of abiotic receptors for anionic species is currently of great interest because of their fundamental roles in a wide range of chemical and biological processes.<sup>1</sup> Among them, fluoride is the smallest anion, with a high charge density and a hard Lewis basic nature that result in unusual chemical properties. Fluoride ions are biologically important anions because of their important role in dental care<sup>2</sup> and the treatment of osteoporosis,<sup>3</sup> etc. In this regard, the sensing of a fluoride ion has attracted growing attention.<sup>4</sup>

In a number of cases, hydrogen bonding between the N–H of urea,<sup>5</sup> indole,<sup>6</sup> imidazole,<sup>7</sup> amide,<sup>8</sup> pyrrole<sup>9</sup> or O–H of phenol<sup>10</sup> and fluoride is the mechanism of recognition. Electron-deficient Lewis acid co-ordination via orbital overlap has also received a lot of attention and receptors containing boron,<sup>1a,4b,11</sup> silicon,<sup>12</sup> tin,<sup>13</sup> aluminium<sup>14</sup> and antimony<sup>15</sup> have all emerged. In recent years, receptors using anion– $\pi$  interactions<sup>16</sup> and specific reactions<sup>17,18</sup> have been developed to sense fluoride ions. Among these type receptors, boron–base complex is the most attractive one. The fluorescence sensing of fluoride using boronic acid was first reported by Tony Jams in 1998.<sup>19</sup> Since then a lot of fluorescent systems utilizing boron–fluoride interaction have been reported.<sup>1h,4b,11</sup> Recently, stable triarylborons with a high Lewis acidity were used as fluoride probes in aqueous or alcohol solvents to overcome the competing binding of aqueous protons for fluoride ions.<sup>20</sup> Particularly, diborane receptors have received much atten-

tion because they can efficiently accept fluoride compared to monoborane receptors.<sup>21</sup> In order to increase the ability of borane-based receptors to capture fluoride ions from water, Gabbai and co-workers developed a series of borane-containing bidentate receptors, such as borane with ammonium,<sup>22</sup> borane with phosphonium,<sup>23</sup> borane with antimony<sup>24</sup>, and borane with tellurium.<sup>25</sup> Kawachi et al. reported B/Si bidentate receptor for fluoride ions.<sup>26</sup> These combined or hybrid receptors would illumine a new route to devise receptors for fluoride ions which can enhance the binding ability of fluoride ions.

In this Letter, we reported a new combined receptor of boronic acid and imidazolium to construct a ratiometric fluorescent probe **1** (Fig. 1). The imidazolium group can interact strongly with anions through a (C–H)<sup>+</sup>...X<sup>-</sup> type ionic hydrogen bond.<sup>27</sup> In our system,

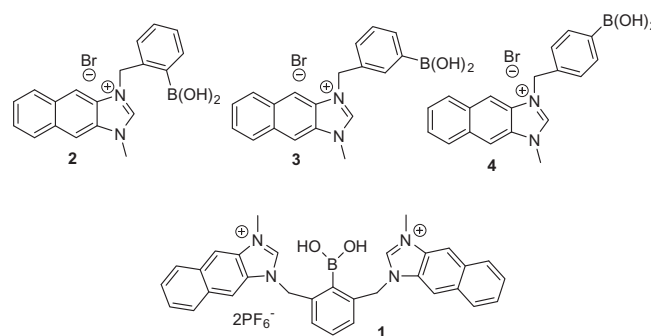
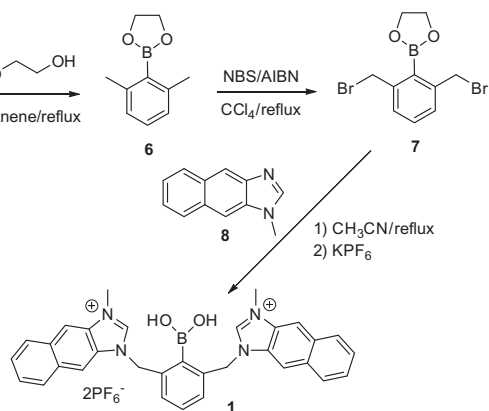


Figure 1. Structures of naphthoimidazolium–boronic acid derivatives **1–4**.

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Scheme 1. Synthesis of compound **1**.

the naphthoimidazolium group was utilized for anion binding and also as a fluorescent reporter. In our previous study, we have proved that only the *ortho* phenylboronic acid **2** other than *meta*, and *para* ones (**3** and **4**) can co-operate with imidazolium as a hybrid receptor for fluoride (Fig. 1).<sup>28</sup> In order to increase the affinity with fluoride, a reasonable way is to introduce more binding sites to the receptor. In the current study, a tridentate receptor **1** with one *ortho* boronic acid and two imidazolium groups was designed.

2-(2,6-Dimethylphenyl)-1,3,2-dioxaborolane **6** and bis(bromomethyl) adduct **7** were synthesized by modifying the reported procedures from 2,6-dimethylphenylboronic acid **5** (Scheme 1).<sup>29</sup> Then, treatment of the bis(bromomethyl) adduct **7** with 1-methyl-naphthoimidazole **8**<sup>30</sup> in acetonitrile followed by the anion exchange with KPF<sub>6</sub> gave the desired product **1** in 47% yield. The detailed synthetic procedure as well as the characterization data including <sup>1</sup>H NMR, <sup>13</sup>C NMR, and ESI mass spectra are reported in the Supplementary data.

The emission spectra and fluorescence titration experiments with F<sup>-</sup> were first recorded in acetonitrile solution (Fig. 2). The emission spectrum of free **1** displays a broad band with a maximum at 445 nm. When F<sup>-</sup> was added progressively to the solution of **1**, a significant decrease of the 445 nm emission and a blue-shifted emission band centered at 370 nm were seen, which were attributed to the formation of **1**/F<sup>-</sup> complex and increase in intensity. The (C–H)<sup>+</sup>...F<sup>-</sup> interaction blue-shifts the fluorescence emission. We have found the electrostatic interaction between the imidazolium cation and F<sup>-</sup> can only quench the fluorescence without a shift in emission. The emission shift is due to the hydrogen bonding between imidazolium C<sub>2</sub>–H and F<sup>-</sup>.<sup>30</sup> This indicates the key role of the C<sub>2</sub>–H in the interaction with fluoride. Therefore, the  $\delta$  of C<sub>2</sub>–H and the blue-shift in the fluorescence emission can be used to probe the hydrogen bond between C<sub>2</sub>–H and F<sup>-</sup>. Then **1** is a ratiometric fluorescent probe for F<sup>-</sup> which involves the observation of changes in the ratio of the intensities of the emission at two wavelengths. Ratiometric fluorescent probes have the important feature in that they permit signal rationing and thus increase the dynamic range and provide built-in correction for environmental effects. Based on the variation of the fluorescence, the binding constant of F<sup>-</sup> with imidazolium moiety is  $2.3(\pm 0.2) \times 10^6 \text{ M}^{-1}$ , which is much larger than the one of bidentate receptors.<sup>28</sup> Addition of F<sup>-</sup> to the solution of **1** sufficiently blue shifts the emission from 445 to 370 nm that makes a significant color change. This color change allows **1**/F<sup>-</sup> to be readily distinguished by the naked eye (Fig. 2, inset), and probe **1** thus combines the sensitivity of fluorescence with the convenience and esthetic appeal of a colorimetric assay.

The fluorescence titration of **1** with various anions was conducted to examine the selectivity. As shown in Figure 3, the addi-

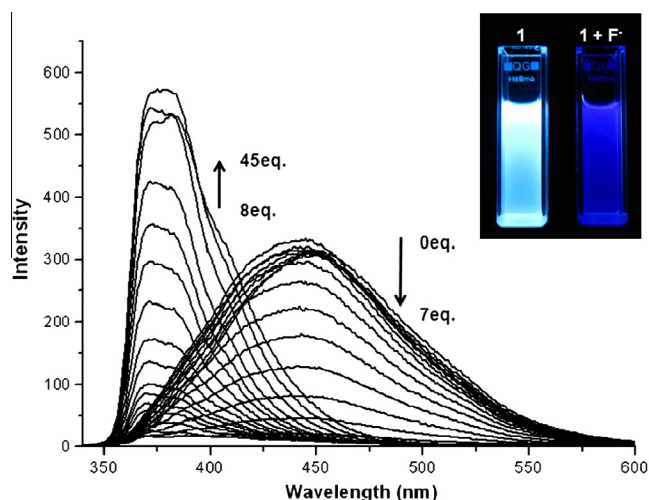


Figure 2. Fluorescent emission spectra of compound **1** (10  $\mu\text{M}$ ) in the presence of different concentrations of F<sup>-</sup>. Inset: emission observed from solution of **1** and **1**/F<sup>-</sup>. Excitation at 325 nm.

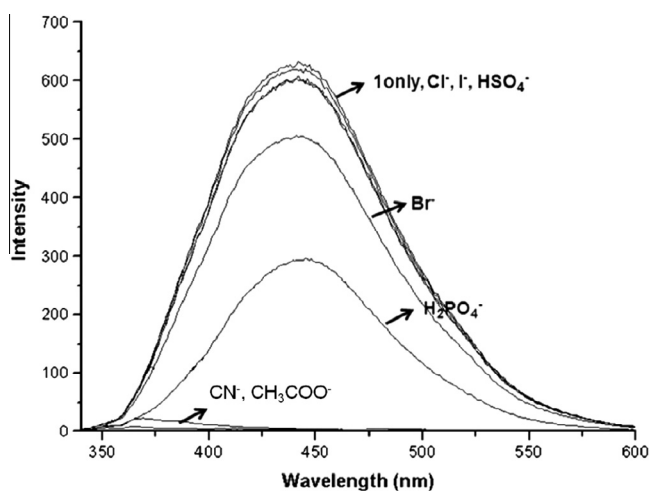


Figure 3. Fluorescence responses of **1** (10  $\mu\text{M}$ ) to various anions (45 equiv). Excitation at 325 nm.

tion of Cl<sup>-</sup>, I<sup>-</sup> and HSO<sub>4</sub><sup>-</sup> produced a nominal change in the fluorescence spectra of **1** due to their low affinity with probe **1**. Other tested anions including Br<sup>-</sup>, CN<sup>-</sup>, CH<sub>3</sub>CO<sub>2</sub><sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> quench the fluorescence without a shift in emission, while the extent of quenching depends on the nature of the anion. These results indicate these anions except F<sup>-</sup> interact with the imidazolium part of **1** only by electrostatic attraction. Then probe **1** has a very high selectivity for F<sup>-</sup>. The fluorescence titrations with other anions and fluorescence changes of F<sup>-</sup> in the presence of other anions are explained in the Supplementary data.

In our previous work,<sup>28</sup> based on fluorescence and NMR studies, we confirmed that the addition of fluoride to boron center can occur prior to the (C–H)<sup>+</sup>...F<sup>-</sup> type ionic hydrogen bond from the imidazolium moiety. Only after binding 2 equiv F<sup>-</sup> by the boron center, the imidazolium part can interact with the third fluoride ion.<sup>28</sup> In this Letter, <sup>1</sup>H NMR and <sup>19</sup>F NMR of **1** with F<sup>-</sup> were also investigated to clarify the binding process. Tetrabutylammonium fluoride hydrate is used as the fluoride source. As shown in Figure 4, with the addition of first equivalent fluoride, the peak of C<sub>2</sub>–H in **1** shifted downfield slightly from 9.11 to 9.29 ppm. This means, unlike our previous bidentate B/imidazolium receptor,<sup>28</sup> the tridentate one has a better architecture, that is the boron center can

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