

Selective Recognition of Fluoride by using a Benzobisimidazolium Derivative through Aggregation-Induced Fluorescence

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A new benzobisimidazolium derivative (**1**) bearing four naphthalene moieties was synthesized and demonstrated as an F⁻ ion-selective fluorescent chemosensor. The fluorescence of **1** in acetonitrile (CH₃CN) is significantly stronger with F⁻ and acetate (CH₃CO₂⁻), but not with other anions (Cl⁻, Br⁻, I⁻, HSO₄⁻, and H₂PO₄⁻). The fluorescence of **1** is enhanced selectively with F⁻ in the presence of a small amount of water. Our DFT calculations indicate that the electrostatic interactions between the positively charged benzobisimidazolium moieties and F⁻ play an important role in the formation of stable aggregates. The formation of stable aggregates of **1** with F⁻ in CH₃CN is a key step for the selective sensing of F⁻, and the fluorescence of the aggregates is further enhanced in a mixture of 95% CH₃CN and 5% water, which can be attributed to the aggregation-induced emission.

Anion recognition, especially fluoride (F⁻) anion recognition, has been actively investigated for the last few decades.^[1] Hydrogen bonding interactions, anion- π interactions, boronic acid/boron interactions, and so forth, are known to play a key role for F⁻ recognition or sensing.^[1] Even though the recognition of F⁻ in aqueous solution has been successfully demonstrated through irreversible silyl deprotection, through some boronic-acid-based receptors, as well as a few others, there are only a few papers in which F⁻ can be recognized by hydrogen bonding interactions in the presence of water.

Among the various types of anion-selective probes,^[2] imidazolium-based sensors have been extensively investigated in recent years.^[3] Imidazolium salts can be formed from protonation or substitution at the nitrogen atom of imidazole, where the positive charge is delocalized in the imidazole ring. In imi-

dazolium-based anion receptors, the charge-charge electrostatic interaction dominates. This novel type of charged hydrogen bonding is very different and intriguing in comparison with many other conventional hydrogen bonds. Imidazolium derivatives as well as benzobisimidazolium derivatives (Figure 1) have been extensively utilized as anion-selective receptors.^[3] In contrast, naphthoimidazolium derivatives (Figure 1) have been reported as anion-selective fluorescent chemosensors relatively recently.^[4] Naphthoimidazolium groups can recognize anions through ionic hydrogen bonding, and thus in addition serve as fluorescent sensors.

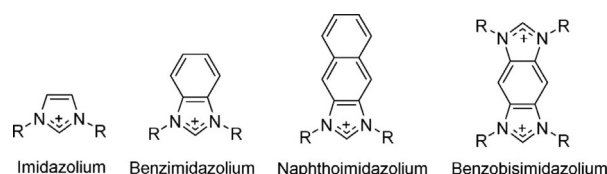


Figure 1. Structures of the imidazolium derivatives.

Benzobisimidazolium derivatives bearing two imidazolium moieties (Figure 1) are also fluorescent. Recently, benzobisimidazolium derivatives have been actively studied as biscarbene ligands for metal ions by Bielawski and co-workers^[5] and Hahn et al.^[6] In recent years, benzobisimidazoliums have actively been used as a class of fluorescent materials^[7] and anion-selective fluorescent probes.^[8]

An aggregation-induced emission (AIE)-based fluorophores are induced to emit strong emission when they undergo spatially restricted aggregation.^[9] As a result, fluorescent probes based on the AIE mechanism have several advantages, such as higher sensitivity and selectivity. Even though tetraphenylethene derivatives have been extensively used for AIE-based fluorescent probes, other fluorophores, especially benzobisimidazoliums, have not been actively investigated as aggregation-based fluorescent probes.

In this study, we prepared a new benzobisimidazolium derivative (**1**), bearing four naphthalene moieties as an anion-selective fluorescent chemosensor. Compound **1** displayed a large fluorescent enhancement with F⁻ and acetate (CH₃CO₂⁻) in acetonitrile (CH₃CN). On the other hand, Cl⁻, Br⁻, I⁻, HSO₄⁻, and H₂PO₄⁻ did not show any significant change in the fluorescence intensity. A clear red-shifted peak was observed in the UV/Vis absorption spectra of **1** when F⁻ and CH₃CO₂⁻ ions were added. Interestingly, the fluorescence of **1** with F⁻ was amplified in the presence of a small amount of deionized water (DW) (5 or 10%) and was also confirmed by using time-

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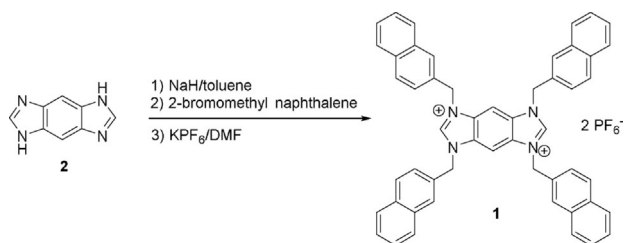
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resolved fluorescence (TRF) experiments. More interestingly, this amplification was selective only for F^- , and not for $CH_3CO_2^-$. Accordingly, compound **1** could selectively recognize F^- among the various anions in the presence of water. The optimized structure of aggregates of **1** with F^- was successfully obtained by using quantum chemical calculations, providing an important clue to understanding the selective sensing of F^- by compound **1** at the molecular level.

For the synthesis of **1**, benzo-bis(imidazole) (**2**) was first synthesized from 1,2,4,5-benzenetetraamine tetrachloride by following the reported procedure.^[10] Briefly, the treatment of **2** with NaH followed by the addition of 2-(bromomethyl)-naphthalene and counter-ion exchange using KPF_6 afforded **1** in 24% yield (Scheme 1).

Figure 2 shows the UV/Vis absorption spectra and fluorescence spectra of **1** (10 μM) in CH_3CN upon the addition of $H_2PO_4^-$, HSO_4^- , $CH_3CO_2^-$, I^- , Br^- , Cl^- , and F^- (10 equiv, as tetrabutylammonium salts). With F^- and $CH_3CO_2^-$ added, the peaks at 340 nm appeared in UV/Vis absorption spectra and a large fluorescence enhancement at $\lambda_{max}=430$ nm was observed. As shown below, the peaks at 340 nm resulted from the aggregates of **1** with anions and were responsible for the emission of fluorescence in the solutions. From the fluorescence titrations, the association constants of **1** for F^- and $CH_3CO_2^-$ were calculated as 1.15×10^4 and $8.45 \times 10^3 M^{-1}$, respectively (Figures S4 and S5), and the detection limits for F^- and $CH_3CO_2^-$ were determined to be 2.02×10^{-7} and $3.27 \times 10^{-7} M$, respectively (Figure S6).

More interestingly, when 5% DW was added to these solutions, the fluorescence intensity of **1** with F^- was further enhanced in the mixture of 95% CH_3CN + 5% DW, as shown in Figure 3a; however, the fluorescence intensity of **1** with $CH_3CO_2^-$ in the mixed solution was dramatically suppressed. In



Scheme 1. Synthesis of benzobisimidazolium derivatives **1**.

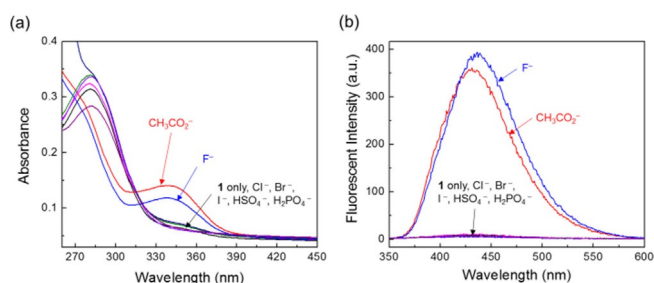


Figure 2. a) UV/Vis absorption spectra of **1** (10 μM) upon addition of various anions (10 equiv) in CH_3CN . The peaks at 340 nm result from the aggregates of **1** with anions. b) Fluorescence spectra of **1** (10 μM) upon addition of various anions (10 equiv) in CH_3CN (excitation at 340 nm).

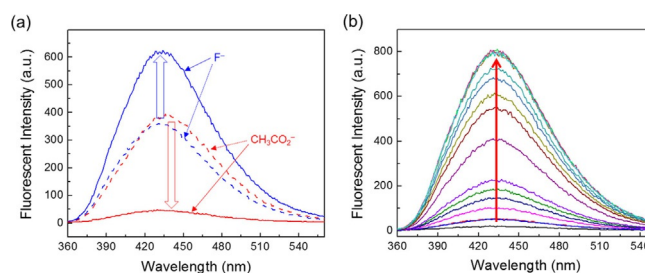


Figure 3. a) Fluorescence intensity changes of **1** (10 μM) with F^- and $CH_3CO_2^-$ (10 equiv) in CH_3CN (excitation at 340 nm) followed by the addition of 5% DW. Dashed lines are fluorescence spectra of **1** with F^- (blue) and $CH_3CO_2^-$ (red) in CH_3CN . With DW added, the fluorescence intensity of **1** with F^- (blue) is further significantly increased, but the fluorescence intensity of **1** with $CH_3CO_2^-$ (red) is substantially suppressed. b) Fluorescent titrations of **1** (10 μM) with various amounts of F^- in CH_3CN (excitation at 340 nm) followed by the addition of 5% DW.

addition, the UV/Vis absorption spectra show that the intensity of the peak at 340 nm is substantially decreased in the case of **1** with $CH_3CO_2^-$ in the mixed solution, as shown in Figure S7, resulting from the disruption of aggregates of **1** with $CH_3CO_2^-$. The association constant of **1** for F^- in the presence of water was determined to be $7.73 \times 10^3 M^{-1}$ from the fluorescent titrations, as shown in Figures 3b and S8.

The fluorescence lifetimes were measured by TRF experiments. Figure 4 displays the TRF signals of **1** with F^- or $CH_3CO_2^-$ in CH_3CN and in the mixed solution (95% CH_3CN + 5% DW). The TRF signals were fitted well by a bi-exponential function, and the average fluorescence lifetimes were used here for comparison. When compared to the TRF signal with **1** only ($T_{avg}=3.0$ ns), the TRF signal of **1** with F^- ($T_{avg}=3.6$ ns) or **1** with $CH_3CO_2^-$ ($T_{avg}=5.1$ ns) in CH_3CN decays more slowly. With the addition of DW, the average fluorescence lifetime of **1** with F^- in the mixed solution is increased by a factor of approximately 2 ($T_{avg}=7.1$ ns), but that of **1** with $CH_3CO_2^-$ is decreased by a factor of around 2 ($T_{avg}=2.7$ ns). These results are well correlated with the fluorescence intensity measurements of **1** with F^- or $CH_3CO_2^-$ in CH_3CN and in the mixed solution. As shown below, the fluorescence is emitted from the aggregates of **1** with anions. The aggregates of **1** with F^- are stably formed and they become more stable when DW is added. The prolonged fluorescence lifetime of aggregates of **1** with F^- in the mixed solution can be explained by the AIE, as shown below. In contrast, the aggregates of **1** with $CH_3CO_2^-$ are

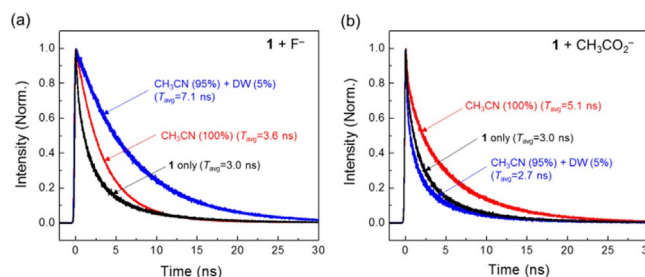


Figure 4. TRF signals of **1** with a) F^- and b) $CH_3CO_2^-$ in CH_3CN and in the mixed solution (95% CH_3CN + 5% DW). The TRF signals were measured at 430 nm. The average fluorescence lifetimes (T_{avg}) are given.

found to be stably formed, but are disrupted when DW is added.

To understand the formation of aggregates of **1** with F^- in CH_3CN and in the mixed solution, quantum chemical calculations were carried out with the DFT method (B3LYP) with a 6–31 g basis set implemented in the Gaussian 09 package.^[11] First, the optimized structure of **1** was obtained, and its electronic transitions were calculated by using time-dependent DFT (TD-DFT). Second, we optimized a dimer of **1**, but found that the dimer was not stably produced because of the repulsive interactions between the positively charged benzobisimidazolium moieties in the dimeric configuration. However, the aggregate of **1** with two F^- ions was stably optimized. It turns out that F^- ions are placed in between the two benzobisimidazolium moieties, and the electrostatic interactions between the positive and negative charges allow the formation of stable aggregates, as shown in Figure 5. The calculated spectra of **1** and its aggregate, resulting from the major electronic transitions with relatively large oscillator strengths, are shown in Figure 5. The calculated electronic transition spectrum of the aggregate is red-shifted when compared to **1**, which agrees well with our experimentally measured UV/Vis absorption spectrum. Therefore, aggregates of **1** with F^- might be stably formed in CH_3CN . These types of aggregates of **1** with anions seem to be associated with the peaks at 340 nm in the UV/Vis absorption spectra in Figure 2a and are responsible for the fluorescence emission at 430 nm.

In our experiments, F^- is a small anion with a relatively large charge density, thus favorably allowing the formation of aggregates of **1** in CH_3CN . In the presence of DW, the peak at 340 nm gets narrower with a slight increase in its amplitude, indicating that the inhomogeneity of the aggregates is reduced. The naphthalene moieties of aggregates in CH_3CN interact favorably with CH_3CN molecules with a wide spatial distribution. Upon the addition of DW, they are exposed to relatively hydrophilic environments because of the nearby water molecules. Under such conditions, the naphthalene moieties

become spatially more restricted within the aggregates, forming less flexible configurations. Such a spatial restriction of naphthalene moieties within the aggregates can significantly enhance the fluorescence intensity, which is usually explained by the AIE.^[9] On the other hand, the aggregates of **1** with $CH_3CO_2^-$ are structurally less stable in CH_3CN , because the methyl group of $CH_3CO_2^-$ is bulky and is unfavorably placed in between the neighboring naphthalene moieties in the aggregates. Therefore, the aggregates of **1** with $CH_3CO_2^-$ in CH_3CN are not as stable as those of **1** with F^- . It is likely that the aggregates of **1** with $CH_3CO_2^-$ are readily disrupted by water molecules and they dissociate into **1**. In addition, the aggregates of **1** with other anions (Cl^- , Br^- , I^- , HSO_4^- , and $H_2PO_4^-$, in our current experiments) do not seem to be favorably formed in CH_3CN . These anions might be relatively bulky and their electrostatic interactions with two positively charged benzobisimidazolium moieties might not be strong enough for the formation of stable aggregates in CH_3CN .

In this study, we have demonstrated that the addition of a small amount of water selectively enhances the fluorescence emission of F^- through a combination of unique electrostatic interactions between F^- and the imidazolium moiety and selective aggregation in the presence of water and F^- .

In summary, a new benzobisimidazolium derivative (**1**) as an F^- -selective fluorescent chemosensor has been synthesized. Compound **1** exhibits a strong fluorescence at 430 nm in the presence of F^- and $CH_3CO_2^-$ in CH_3CN , but not with Cl^- , Br^- , I^- , HSO_4^- , or $H_2PO_4^-$, thereby showing anion selectivity. Upon the addition of a small amount of water, fluorescence amplification was only observed with F^- . Accordingly, our benzobisimidazolium derivative (**1**) was effectively used as a F^- -selective fluorescent chemosensor. The fluorescence resulted from the aggregates of **1** with F^- or $CH_3CO_2^-$. TRF experiments were used to directly measure the fluorescence lifetimes of aggregates of **1** with F^- or $CH_3CO_2^-$. Quantum chemical calculations were successfully used to obtain the optimized structure and electronic transitions of **1** and aggregates of **1** with F^- . Our experimental and computational results indicate that F^- plays an important role in the formation of stable aggregates, which is a key mechanistic factor for F^- -selective fluorescent chemosensors. A selective amplification of the fluorescence of aggregates of **1** with F^- in CH_3CN upon the addition of water is attributed to the combination of unique electrostatic interactions between F^- and the imidazolium moiety, as well as the formation of spatially restricted aggregates through unfavorable interactions of the naphthalene moieties in **1** with nearby water molecules, often described by the AIE. These results indicate that **1** has the potential to serve as a F^- sensor in practical applications.

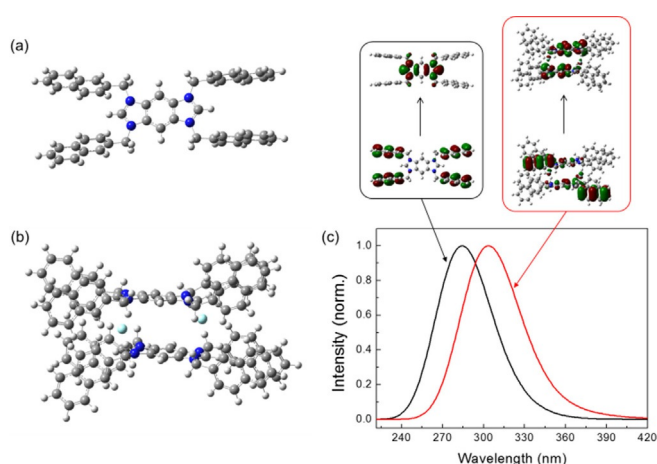


Figure 5. Optimized structures of a) **1** and b) its aggregate with two F^- ions. To form an aggregate, two F^- ions are placed in between two units of **1** in (b). c) Calculated electronic absorption spectra of **1** and its aggregate. The electronic absorption of the aggregate is red-shifted. The molecular orbitals associated with the dominant transitions are shown as well.

Experimental Section

General Methods

Unless otherwise noted, materials were purchased from commercial suppliers and were used without further purification. Thin layer chromatography (TLC) was carried out by using Merck 60 F_{254}

plates with a thickness of 0.25 mm. Preparative TLC was performed by using Merck 60 F₂₅₄ plates with the thickness of 1 mm.

Melting points were measured by using Büchi 530 melting point apparatus. ¹H NMR and ¹³C NMR spectra were recorded by using a Bruker 250 MHz. Chemical shifts were given in ppm and coupling constants (*J*) in Hz. Mass spectra were obtained by using a JMS-HX 110A/110A Tandem Mass Spectrometer (JEOL). UV absorption spectra were obtained with UVIKON 933 Double Beam UV/VIS Spectrometer. Fluorescence spectra were obtained by using an RF-5301/PC spectrofluorometer (Shimadzu).

Time-Resolved Fluorescence Spectroscopy

Time-resolved fluorescence (TRF) experiments were carried out by using a time-correlated single-photon counting (TCSPC) method (PicoHarp 300, picoquant). The sample solutions were excited with a 375 nm pulse (LDH-P-C-375, Picoquant) and the TRF signals from the sample solutions were collected at 430 nm. The instrumental response function (IRF) of our TCSPC setup was about 0.23 ns in FWHM. TRF signals, *P*(*t*), measured in our experiments were well fit by a bi-exponential function, that is, $P(t) = A_1 \exp(-t/T_1) + A_2 \exp(-t/T_2)$ with $A_1 + A_2 = 1$ (see the Supporting Information). The average fluorescence lifetime, $T_{\text{avg}} = T_1 * A_1 / (A_1 + A_2) + T_2 * A_2 / (A_1 + A_2)$, was calculated and used for comparison.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: aggregation-induced emission • chemosensors • fluorescent probes • fluoride • imidazolium

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