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New Fluorescent Chemosensor Based on Exciplex Signaling Mechanism

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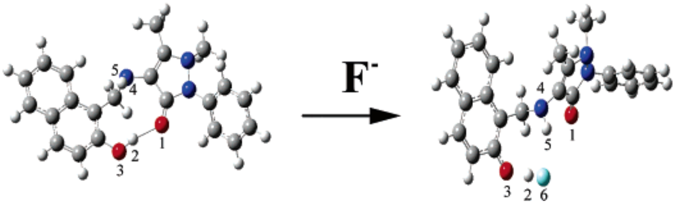
ABSTRACT



A novel fluorescent chemosensor (compound 1) containing aminonaphthol, which selectively recognizes fluoride anion with high sensitivity, was synthesized. The fluorescence of compound 1 was quenched rapidly by fluoride ion, and a new peak at a longer wavelength emerged concurrently, which constituted the signature for fluoride detection. The mechanism of exciplex formation was proposed for the interesting observation.

Fluorescent chemosensors capable of selectively recognizing anions are of current interest in supramolecular chemistry because of their high selectivity, sensitivity, and simplicity.[1,2] Among the various anionic analytes, the biologically important fluoride anion is of particular interest due to its role in dental care and treatment of osteoporosis.[3] Although many examples are available for fluoride anion testing, the simplicity and high sensitivity of the fluorescence method make it increasingly important for applications in biological, environmental, and microchemical detection.[4] When a guest species binds to a receptor, photophysical characteristics of the receptor such as fluorescence intensity, emission wavelength, and fluorescence lifetime change through various mechanisms, and such changes provide a signal indicating guest binding. Indeed, a variety of signaling mechanisms such as photoinduced electron transfer (PET),[5] metal−ligand charge transfer (MLCT),[6] excimer formation,[7] and intramolecular charge transfer (ICT)[8] have been developed so far.

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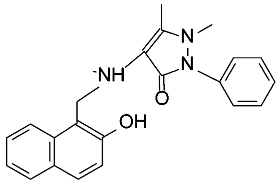

Figure 1. Molecular structure of compound **1**.

However, exciplex formation, to the best of our knowledge, is not usually used as a signaling mechanism for anion recognition, though it has been documented previously.[9]

Herein, we report a new fluorescent chemosensor consisting of aminonaphthol, which can be used for the selective detection of fluoride anion. The signal reporting of such a sensor derives from the fact that with addition of fluoride anion species, the fluorescence of compound **1** is quenched gradually and a new peak at a longer wavelength clearly appears simultaneously. The mechanism of the new peak formation in the fluorescence spectrum is also discussed.

Compound **1** was synthesized and characterized by ^{1}H NMR, MS, and elemental analysis (Supporting Information). The molecular structure was shown in Figure 1. It was designed as an efficient fluoride-selective fluorescent chemosensor on the basis of consideration that a fluoride anion can strongly interact with a hydrogen-donating group such as hydroxyl or amide through hydrogen bonding interaction to form HF. Therefore, it is necessary and important that the $-$OH or/and $-NH_2$ groups of compound **1** serve as a part of the receptor. On the other hand, to improve the sensitivity of the chemosensor with PET reporting system, it is better to have a competitive mechanism of hydrogen bonding formation introduced during the recognition process. For instance, the formation of an intramolecular hydrogen bond makes the structure of compound **1** rigid when the fluoride is absent, whereas replacement of the hydrogen bonding by the fluoride anion will change the structure of compound **1** from rigid to flexible. As a result, the presence of fluoride anion will induce an evident change in the fluorescence spectrum of compound **1**.

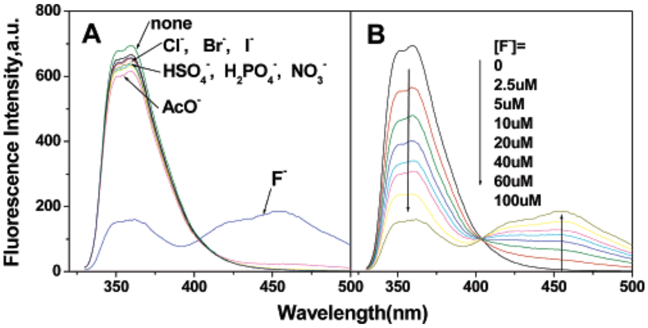

Figure 2. Fluorescence spectra of compound **1** (10 μM) in acetonitrile upon addition of (A) different anions (F^-, $H_2PO_4^-$, AcO^-, HSO_4^-, NO_3^-, Cl^-, Br^-, I^-) (100 μM) and (B) different concentrations of F^-. Excitation wavelength: 320 nm.

Figure 2A shows variations of the fluorescence spectra of compound **1** in acetonitrile in the presence of different anions such as F^-, $H_2PO_4^-$, AcO^-, HSO_4^-, NO_3^-, Cl^-, Br^-, and I^-. It is clear that compound **1** can recognize fluoride anion with excellent sensitivity and selectivity over other anions in acetonitrile. Figure 2B shows that with increasing concentration of fluoride anion, the fluorescence intensity of compound **1** at 360 nm decreases and a new broad emission band peaked at 455 nm emerges with increasing intensity. Meanwhile, a distinct isoemissive point at 405 nm is also observed. This implies that a 1:1 complex is formed and the increase of fluorescent intensity at 455 nm is closely correlated with the decrease of the intensity at 360 nm, revealing a definite relationship between peaks at 360 and 455 nm. On the basis of the spectral results and possible structural change of compound **1** upon addition of fluoride anion, the luminescence at 455 nm can be reasonably attributed to the exciplex formation by a photoinduced electron-transfer process between the naphthoxy moiety and antipyrine moiety of the molecule. As noted above, in the absence of fluoride anion, compound **1** contains an intramolecular hydrogen bonding structure and possesses a rigid structure that is difficult to fold. However, when fluoride anion is added, the original intramolecular hydrogen bonding is broken due to the stronger interaction between fluoride anion and hydroxyl group. As a result, the whole molecular structure becomes flexible, which makes it easy for the two parts of compound **1** to fold. Consequently, a photoinduced electron-transfer process may induce the interaction of the naphthoxy with the antipyrine, leading to exciplex formation, as shown in Scheme 1.

The stability constant of the complex was calculated by the linear Benesi−Hildebrand expression:[10]

$$\frac{1}{\Delta I} = \frac{1}{[\mathbf{1}]\Delta X} + \frac{1}{K_{\mathrm{ass}}[\mathbf{1}]\Delta X}\frac{1}{[\mathrm{F}]}$$

where, ΔI is the change in the fluorescence intensity at 360 nm; K_{ass} is the stability constant; ΔX is the difference of fluorescence quantum yields between the complex and compound **1**; and [**1**] and [F] are the concentrations of compound **1** and fluoride anion, respectively. On the basis

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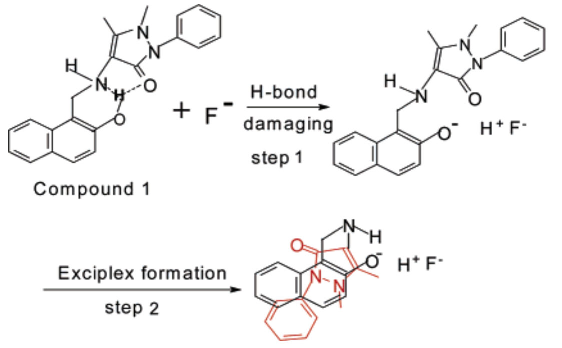
Scheme 1. Schematic Illustration of Breaking of Intramolecular Hydrogen Bonding upon Addition of Fluoride Ion: The Molecular Structure Changes from Rigid to Flexible



of the plot of $1/\Delta I$ and $1/[F]$, the stability constant was determined to be 1.8×10^5 M^{-1} with a good linear relationship ($R = 0.997$), which also indicates that the formation of the complex occurs with 1:1 stoichiometery.

To confirm the mechanism proposed above, several experiments have been carried out as follows. First, the formation and breaking of intramolecular hydrogen bonding in the molecule of compound **1** in acetonitrile are supported by ^1H NMR measurement (Figure 3). It was found that two peaks at δ 13.19 and 10.88 were present in the ^1H NMR spectrum of compound **1** in acetonitrile without fluoride anion. However, when fluoride anion was added, the distinct intensity at δ 10.88 decreased dramatically, while that at δ 13.19 almost completely disappeared. It is well recognized that the downfield chemical shifts are related to hydrogen bonding formation; therefore, the result is consistent with the breaking of hydrogen bonding when fluoride anion was added.

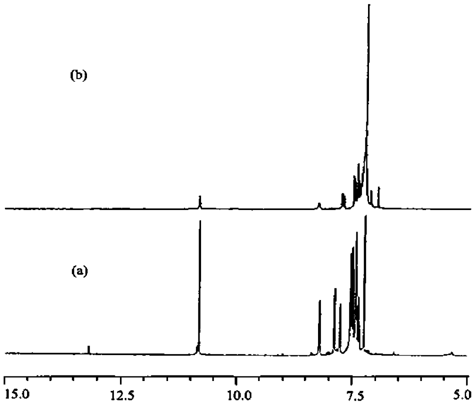


Figure 3. ^1H NMR (300 MHz) spectra of compound **1** in CD_3CN in the presence of 0 (a) and 10 equiv (b) of tetrabutylammonium fluoride.

Second, the breaking process of intramolecular hydrogen bonding was investigated by quantum chemical calculation using the Gaussian 98 program at B3LYP/6-31G* level to simulate the optimized molecular configuration of compound **1** with and without fluoride anion. The results are depicted and listed in the Abstract Graphic and Table 1, respectively. As shown in Table 1, the distance between atoms 1 and 2, which corresponds to the hydrogen bond length between the naphthol and carbonyl of antipyrine, changes to 4.590 Å in the presence of fluoride anion from its original value 1.809 Å. The distance between atoms 2 and 3, which is the bond length of hydroxyl of naphthol, is 0.988 and 1.459 Å without and with fluoride, respectively. This thus shows that introduction of fluoride anion leads to an increase in the distance between atom H and atom O. Thus, quantum chemical calculation supports the experimental observation that the intramolecular hydrogen bonding of compound **1** is broken upon fluoride addition.

Table 1. Distance of Compound **1** between Atoms with and without Fluoride Anion

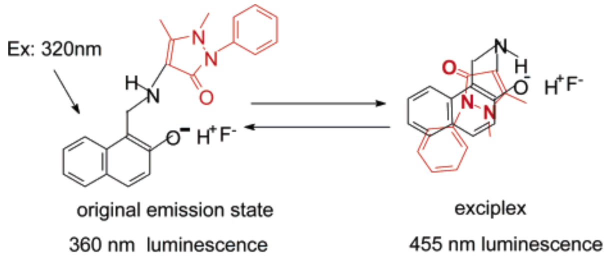
atoms	distance between atoms without F^- (Å)	distance between atoms with F^- (Å)
1–2	1.809	4.590
2–3	0.988	1.459
3–5	3.358	3.135
1–5	3.119	2.888
2–6		0.984

Third, the fluorescence decay process of compound **1** in acetonitrile was measured by a single-photon counting method, and the resulting decay curves were found to display either a good single- or double-exponential decay process with χ^2 typically below 1.2. The data are listed in Table 2. The fluorescence lifetime of compound **1** in acetonitrile without fluoride anion is 7.46 ns with a single-exponential decay process (monitored wavelength: 360 nm). Upon addition of 10 equiv of fluoride anion into the solution of compound **1**, two lifetimes (7.07 and 1.54 ns) were observed in the decay process with a double-exponential decay at the same monitored wavelength. However, when the monitored wavelength was changed to 455 nm, the lifetime with a single-exponential decay came to be 8.12 ns, which is slightly longer than that of compound **1**. This infers that a new species that appears only upon addition of fluoride anion could be assigned to the exciplex formed between the excited state of naphthoxy and the ground state of antipyrine. The decay process is shown in Scheme 2.

Table 2. Fluorescence Lifetime of Compound **1** in CH_3CN with and without F^- Anion

	lifetime (ns)		
samples	$\lambda_{em} =$ 360 nm	$\lambda_{em} =$ 450 nm	χ^2 value
compound **1**	7.46 (100%) single-exponential		0.95
compound **1** + F^- (10 equiv)	7.07 (95%) double-exponential 1.54 (5%) double-exponential		1.12
		8.12 single-exponential	1.18

Scheme 2 Fluorescence Decay Process of Compound **1** in Acetonitrile with Two Lifetimes at a Monitored Wavelength of 360 nm



Fourth, to further verify that the new species shown in Figure 2B is an exciplex formed between the naphthoxy and antipyrine, control experiments were carried out. 1-Naphthol and its sodium salt were used separately with 4-aminoantipyrine to clarify which of them participates in the formation of the exciplex. The fluorescence quenching spectra of 1-naphthol and its sodium salt due to 4-aminoantipyrine are given in Figures 4A and 4B, respectively. For the combination of 1-naphthol sodium salt and 4-aminoantipyrine, Figure 4B shows that as the naphthoxy emission at 342 nm is quenched, a new emission peak at 445 nm and a clear isoemissive point at 410 nm emerge simultaneously. In contrast, for the combination of 1-naphthol and the same quencher, Figure 4A shows no new peak at a longer wavelength, except for a gradual intensity decrease of the fluorescence peak at 342 nm (Figure 4A). These results show that naphthoxy but not 1-naphthol is involved in the exciplex formation with antipyrine after addition of fluoride anion into the solution.

Finally, when the excitation spectra of compound **1** in acetonitrile were recorded at the emission wavelengths of 360 and 455 nm, both spectra had an identical peak at 280 nm. This suggests that two fluorescence peaks observed in Figure 2B should be generated from the same source of excitation. In other words, the fluorescence peak at 455 nm can be attributed to the emission of an exciplex.

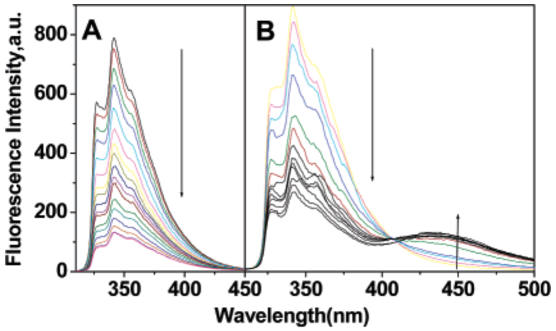


Figure 4. Fluorescence quenching of (A) 1-naphthol (10 μM) in acetonitrile upon addition of 4-aminoantipyrine (corrected concentrations: 0, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 120, 140, 160, 180, and 200 μM) and (B) 1-naphthyloxy sodium (10 μM) upon addition of different concentrations of 4-aminoantipyrine (corrected concentrations: 0, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, and 110 μM). Excitation wavelength: 300 nm.

In summary, compound **1** exhibits excellent selectivity and sensitivity for fluoride detection. Exciplex formation was responsible for the recognition process. This exciplex mechanism not only increases the sensitivity of the present sensor but also provides a new concept for development of other novel chemosensors.

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Supporting Information Available: Synthesis of compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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