Communication

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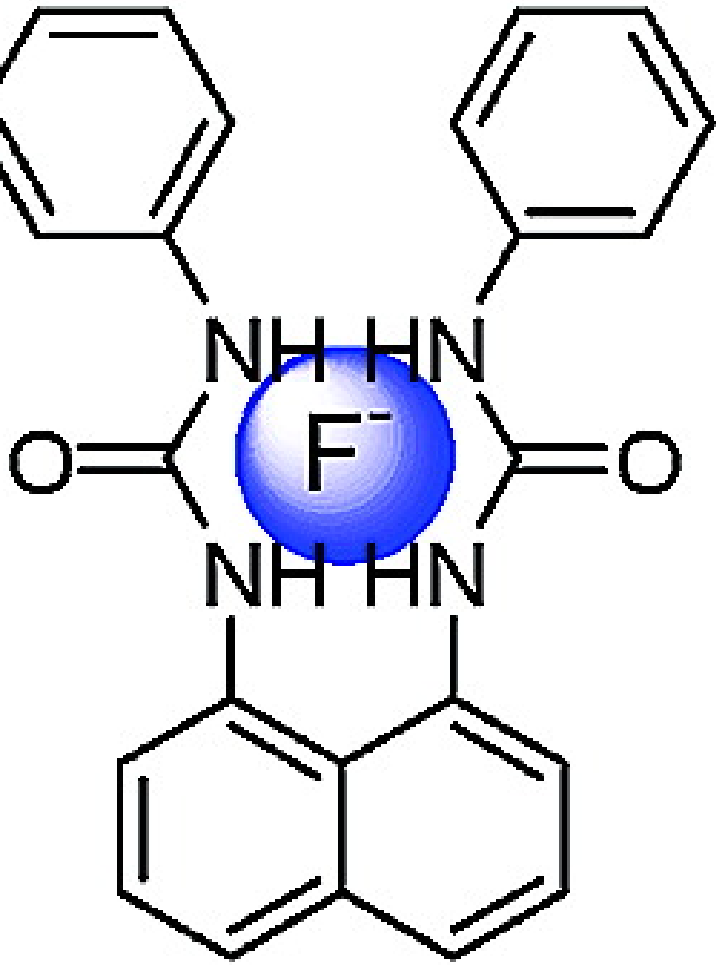

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A New Fluoride Selective Fluorescent as Well as Chromogenic Chemosensor Containing a Naphthalene Urea Derivative

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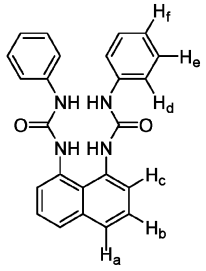
Considerable attention has been focused upon the design of supramolecules which have the ability to selectively recognize and sense anionic analytes through the naked eye, electrochemical, and optical responses.[1] On account of its simplicity and high sensitivity, fluorescence is becoming of increasing importance for chemical trace detection. The linkage of cation crown ethers with fluorescent dyes[2] provides a novel method for monitoring low concentrations of alkali and alkaline earth metals, and, in this connection, considerable effort has been devoted to developing fluorescent chemosensors for cations and neutral guests.[3] However, it has been only a few years since fluorescent chemosensors for anions have been extensively investigated.[4,5] Fluoride ions are biologically important anions because of their important role in dental care[6] and the treatment of osteoporosis,[7] etc. Even though some receptor compounds for fluoride ions have been reported,[8] there is a paucity of reports regarding a selective fluorescent sensor for fluoride ions.[5] We synthesized a fluoride selective fluorescent as well as chromogenic chemosensor **1**, based on a naphthalene urea derivative, which shows a unique fluorescent and absorption peak in the presence of fluoride ions.



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The synthesis of **1** was carried out by refluxing the solution of 1,8-diaminonaphthalene with phenylisocyanate in THF/DMF (2:1 ratio) for 5 h (80% yield). ^{1}H, ^{13}C NMR, elemental analysis, and mass spectra are consistent with the proposed structure of **1**.[9] Our host **1** displays a unique new peak (λ_{max} = 445 nm) upon the addition of fluoride ion in its fluorescence study as shown in Figure 1; on the other hand, only changes at 379 nm were observed when chloride, bromide, or iodide ions were added. All of the fluorescence experiments were done in an acetonitrile−DMSO mixture (9:1, v/v). From the fluorescence titration experiments, the association constants for F^- and Cl^- were calculated as 14 200 and 380 M^{-1} (errors < 10%), respectively.[10] The selectivity for F^- is almost 40-fold as compared to that of Cl^-. Even though the selectivity for F^- over Cl^- is not that high, the appearance of a new peak in the presence of F^- could provide a great advantage for detecting fluoride ions. Similar behavior was observed in the absorption spectra.

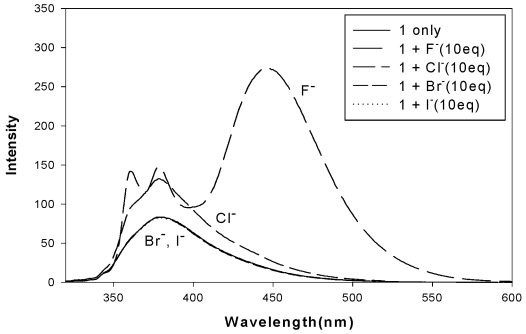

Figure 1. Fluorescent emission changes of **1** (6 μM) upon the addition of tetrabutylammonium fluoride, bromide, chloride, and iodide (60 μM) in acetonitrile−DMSO (9:1, v/v) (excitation wavelength = 310 nm).

To look into the nature of a new peak in the presence of fluoride, NMR and ab initio calculations were carried out. The ^{1}H NMR spectrum of **1** shows dramatic changes in the presence of F^-. When F^- is added, two amide N−H signals disappear rapidly, and aromatic proton signals shift downfield or upfield. The correlation spectrum of 2D COSY (Figure 2) indicates that H_a and H_c are correlated with H_b, and H_d and H_f are correlated with H_e. H_c and H_d protons at the ortho position of the urea group show a moderate downfield shift ($\Delta\delta$ = +0.35 and +0.44, respectively) upon addition of F^-. On the other hand, the H_a proton signal shows a significant upfield shift ($\Delta\delta$ = −0.88), and also slight upfield shifts are observed from H_b, H_e, and H_f proton signals ($\Delta\delta$ = −0.45, −0.14, and −0.28, respectively). Obviously, fluoride ions bind with four urea N−H protons, which could cause the H_c and H_d protons to be downfield shifted by the hydrogen bond of urea oxygen. A significant upfield shift of H_a and H_f protons could be the result of the enhanced resonance of naphthalene as well as phenyl electrons from the anionic character of urea nitrogen.

The structures of **1** and **1**F^- were optimized by AM1 using Gaussian 98.[11] There are four acidic protons in molecule **1**, two at nitrogen atoms attached to naphthalene (we name these as lower protons) and two at those to benzene (we name these as upper protons). We compared the acidity of those protons from the energies of anions with a lower proton detached (**1**$^-$) and an upper proton detached (**1**$^{-\prime}$). The energy of **1**$^-$ is lower than that of **1**$^{-\prime}$ by 5.37 kcal/mol; hence, the lower proton is more acidic. As a result, F^- interacts with lower protons more favorably than upper protons, as is evident from the fact that the energy of **1**F^- is lower than that of **1**$F^{-\prime}$ by 4.78 kcal/mol. When the fluoride anion forms a complex with **1**, it attacks more acidic lower protons of **1** and breaks the N−H bond to make the F−H bond. The binding energy

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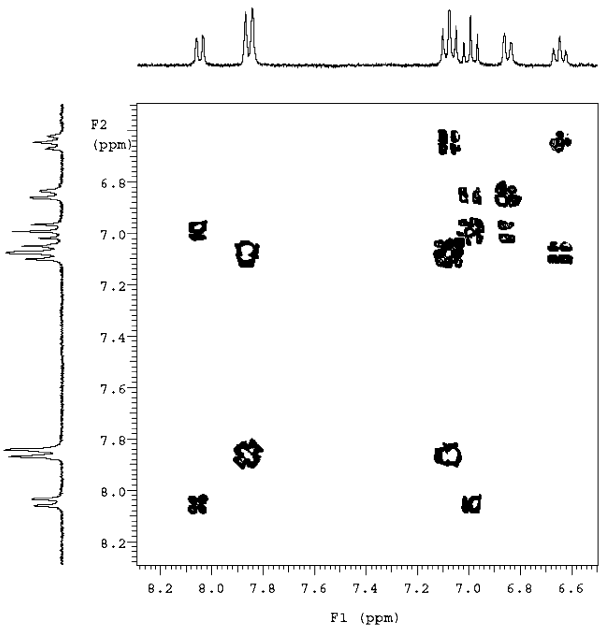

Figure 2. 2D COSY of **1** in the presence of 100 equiv of fluoride ions in DMSO-d_6.

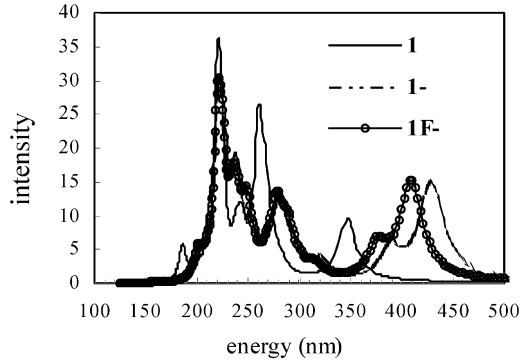

Figure 3. Absorption spectra of **1**, $\mathbf{1}^-$, and ($\mathbf{1}F^-$) calculated by CEO.[12]

is very large ($\Delta E = -126.43$ kcal/mol), mainly because of the charged hydrogen bonding between F−H and the anionic character of N. The interatomic distances between oxygen and the ortho protons in **1** are 2.2076 and 2.5669 Å, while those in $\mathbf{1}F^-$ are 2.1581, 2.1649, 2.1145, and 2.1116 Å. Thus, the hydrogen bonds between oxygen atoms and protons at the ortho positions of phenyl and naphthalenyl are stronger in $\mathbf{1}F^-$ than in **1**. The absorption peak appears at about 350 nm for **1** (Figure 3). When **1** forms a complex with F^-, the absorption peak at 345 nm disappears and appears at about 408 nm, red-shifted by 63 nm, which is in good agreement with the experimental absorption change of 53 nm. The F^- interaction with **1** results in large anionic character of **1** as rationalized from the similarity of absorption spectra of $\mathbf{1}^-$ and $\mathbf{1}F^-$.

In conclusion, two phenylurea groups were introduced at the 1,8-position of naphthalene in our system. The naphthalene moiety acts not only as a fluorescent source but also as a template for introducing the binding selectivity. Naphthalene urea derivative **1** displays selective fluorescent effects with fluoride ions. The binding selectivity of **1** for fluoride ions is 40 times as high as that for chloride ions. Furthermore, **1** displays a unique new peak at 445 nm in the presence of fluoride ion. The NMR and ab initio calculations are in good agreement with fluorescence changes. Host **1** interacts with the fluoride anion by strong charged hydrogen bonding. This compound has a potential for practical application, which is currently being investigated.

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Supporting Information Available: UV−vis spectra, binding energies, and optimized structures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Selected data for **1**:**1**, mp 190−192 °C, decomp.; ^{1}H NMR (DMSO-d_6) δ 9.01 (s, 2H, NH), δ 8.85 (s, 2H, NH), δ 7.70 (two d, 4H, J = 7.5 Hz, ArH), δ 7.46 (t, 2H, J = 7.5 Hz, ArH), δ 7.41 (d, 4H, J = 7.5 Hz, ArH), δ 7.22 (t, 4H, J = 7.5 Hz, ArH), δ 6.92 (t, 2H, J = 7.5 Hz, ArH). ^{13}C NMR (DMSO-d_6) δ 153.5, 140.1, 135.8, 134.1, 128.8, 125.6, 125.2, 122.5, 121.8, 118.5, 114.0 (−CO− and Ar). FAB MS *m*/*z* 397 (M + 1, Calcd 397). Anal. Calcd for $C_{24}H_{20}N_4O_2$: C, 72.73; H, 5.05; N, 14.14. Found: C, 72.68; H, 5.10; N, 14.10.

(10) Association constants were obtained using the computer program ENZFITTER, available from Elsevier-BIOSOFT, 68 Hills Road, Cambridge CB2 1LA, United Kingdom.

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