Anion Selective Colorimetric Chemosensor with Nitronaphthalene Urea Derivative

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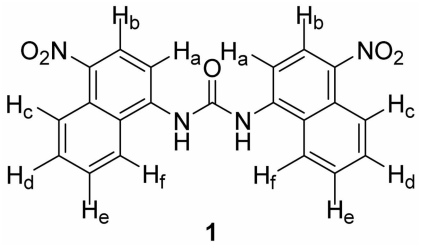
Anions play an important role in a wide range of chemical and biological processes, and considerable attention has been focused on the design of host molecules that can recognize and sense anion species selectively through the naked eye, electrochemical, and optical responses.[1,2] Color changes, as signaling an event detected by naked eye, are widely used owing to the inexpensive equipment required or no equipment at all. Those chemosensors are constructed according to the receptor-chromophore binomial, which involves the binding a specific anion substrate with receptor sites and a chromophore responsible for translating the receptor-anion association into an optical signal.[3-7]

Among the important anions, fluoride is of particular interest owing to its established role in preventing dental caries[8] and acetate for the biological importance. Even though some receptor compounds for fluoride have reported,[9-11] there is a paucity of reports on a selective naked eye chemosensor for those anions.[12,13] Most of those chemosensors have been constructed based on nitrophenyl group as a signal unit.[14] In pursuit of naked-eye fluoride ion chemosensors a new nitronaphthalene urea derivative **1** was synthesized and its anion binding properties were investigated by UV-vis spectroscopy, ^{1}H NMR and color changes. Ligand **1** showed a significant bathochromic shifts in the presence of fluoride, indicating that it could be utilized as a naked eye chemosensor owing to the noticeable color change in the presence of fluoride ion.



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Results and Discussion

Ligand **1** was synthesized from the reaction of 4-nitro-1-aminonaphthalene with the corresponding isocyanate which was prepared by the reaction of 4-nitro-1-aminonaphthalene with triphosgene in 72% yield. The ^{1}H NMR spectrum of ligand **1** showed one characteristic singlet at δ 10.01 for two N-H protons and two multiplets at δ 7.83-7.93 and δ 8.37-8.64 ppm for twelve aromatic protons.

The UV-vis experiments were carried out in a DMSO solution. A receptor solution (3×10^{-5} M) was treated with the representative anions such as tetrabutylammonium (TBA) fluoride, chloride, bromide, acetate and benzoate. When compound **1** forms a complex with F^-, the absorption peak at 401 nm disappears and a new peak appears at 535 nm with a red-shifted by a $\Delta\lambda_{max}$ of 134 nm. When acetate and benzoate form a complex with ligand **1**, the absorption peak at 401 nm disappears and a new peak appears at 521 nm with a red-shifted by a $\Delta\lambda_{max}$ of 120 nm. However, a bathochromic shift of other ions such as chloride and bromide was also observed with a small change as shown in Figure 1.

A color change could be observed easily by mixing the ligand and anion as shown in Figure 2. A receptor solution was simply treated with various anions such as F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, HSO_4^-, CH_3COO^- and $C_6H_5COO^-$. Noticeable color changes were observed when ligand **1** was treated with the anions. In particular, it was remarkable that a pale yellow ligand solution became red when fluoride ions were added to compound **1** in DMSO, but no color changes were observed when the other anions such as chloride, bromide and hydrogen sulfate were added. A similar red color was observed when acetate and benzoate were added into the ligand solution.

To look into the nature of a new peak in the presence of fluoride, NMR titration was carried out. The ^{1}H NMR spectrum of **1** shows dramatic changes in the presence of F^-. When F^- is added, a amide N-H at signal disappear rapidly,

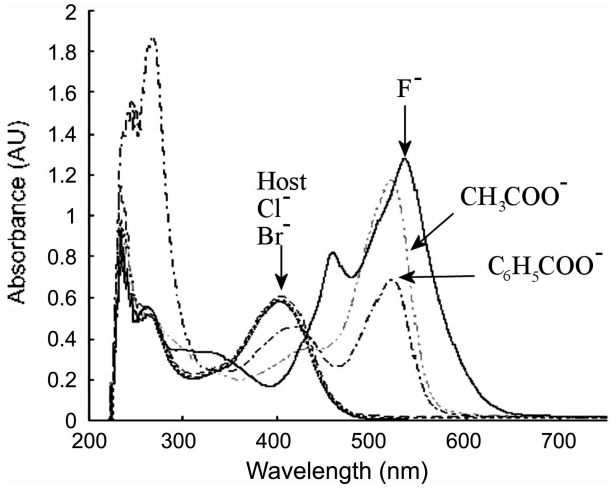


Figure 1. Absorption spectra of compound **1** (3×10^{-5} M) upon addition of tetrabutylammonium chloride, bromide, acetate, benzoate and fluoride (3×10^{-3} M) in DMSO.

Figure 2. Color changes of ligand **1** (3×10^{-5} M) in DMSO with the addition of tetrabutylammonium anions (3×10^{-3} M). From left, Free receptor, Fluoride, Chloride, Bromide, Acetate, and Benzoate.

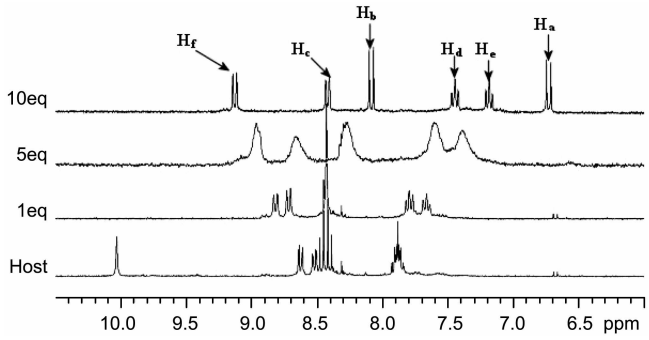
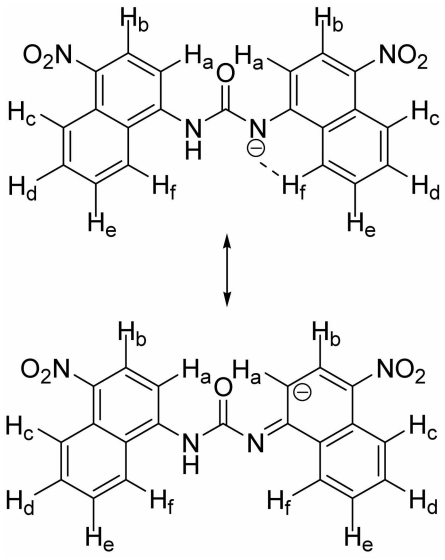


Figure 3. A partial ^{1}H NMR spectra of ligand **1** in the presence of fluoride ions in DMSO-d_6. Numbers on left indicate the equivalents of fluoride ions added.

and aromatic protons signals shift downfield or upfield. The correlation spectrum of 2D COSY indicates that H_a is correlated with H_b, while H_c and H_f with H_d and H_e. H_a protons at *ortho* of urea group show a significant up-filed shift ($\Delta\delta = -1.80$) upon addition of F^-.

H_b proton signal shows a slight up-field shift ($\Delta\delta = -0.30$), and also moderate up-field shifts are observed from H_d and H_e proton signals ($\Delta\delta = -0.80$ and -0.60, respectively). On the other hand, a considerable down-field shift of H_f signal



was observed ($\Delta\delta = +0.60$) as shown in Figure 3. A significant up-field shift of H_a and H_c protons could be the results of the enhanced resonance of naphthalene from the anionic character of urea nitrogen. A considerable down-field shift of H_f signal ($\Delta\delta = +0.60$) could suggest that nitrogen anion formed a cyclic H-bond directly with H_f proton.

Summary

A new nitronaphthalene urea derivative **1** was synthesized by the simple reaction of 1-naphthylamine and its corresponding isocyanate. A distinct color change was observed when ligand **1** was treated with fluoride ions by extending the conjugated system of the ligand anion which is formed only when complexed with a fluoride ion.

Experimental

1,3-*Bis*(4-nitronaphthalen-1-yl)urea (1). To a solution of 1-amino-4-nitronaphthalene (0.188 g, 1.0 mmol) in 30 mL of dry 1,4-dioxane, 0.894 g (3.0 mmol) of triphosgene was added and the reaction mixture was refluxed for 20 hours under the nitrogen atmosphere. Solvent was removed completely under the vacuum condition. The residue was treated with 1-amino-4-nitronaphthalene (0.188 g, 1.0 mmol) in 20 mL of dry 1,4-dioxane. The reaction mixture was refluxed for 24 hours under the nitrogen atmosphere. The precipitate was collected to give 0.292 g (72%) of 1,3-*bis*(4-nitronaphthalen-1-yl)urea; ^{1}H NMR (DMSO-d_6) δ 10.01 (s, 2H, NH), 7.83-7.93 (m, 4H, ArH), 8.37-8.64 (m, 8H, ArH).

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