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Notes

Fluorescence Chemosensor for Fluoride Anion with Coumarin Bipyridine Derivative

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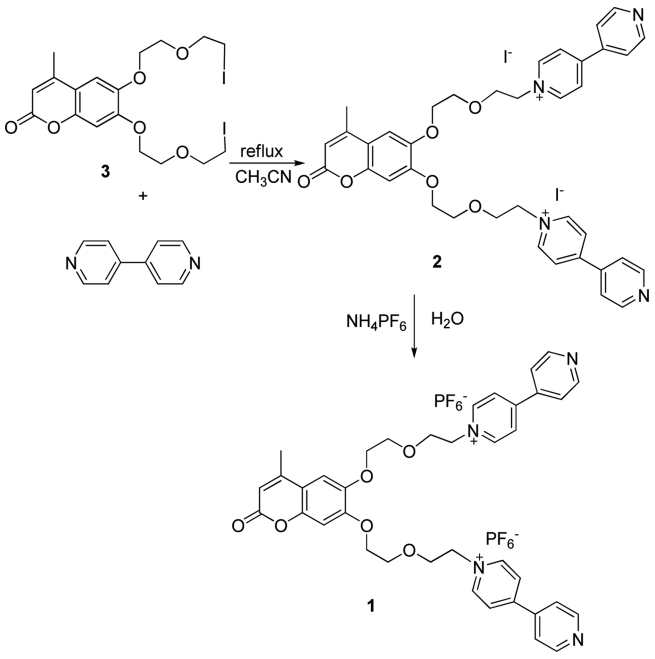
On account of the important roles of anion in biological, clinical, environmental, catalysis, and chemical processes, the selective and efficient recognition of anion is an area of growing interest in supramolecular chemistry.[1,2] In particular, the studies of chemosensors toward fluoride anion are quite intriguing because of its beneficial effects in human physiology.[3,4] Also, fluoride is of interest due to its established role in dental care and osteoporosis. However, an excess of fluoride ion can lead to fluorosis. Therefore, developments of reliable sensors for fluoride ion are needed for environment and human health care. Among anion receptors, colorimetric and fluorescent chemosensors are important because they provide high sensitivity and convenience for monitoring the anion recognition. [5-7]

Coumarin is a fragrant compound in the benzopyrone chemical class, found in many plants. Although coumarin itself has no anticoagulant properties, it is transformed into the natural anticoagulant dicoumarol by a number of species of fungi. Coumarin is also used as a gain medium in some dye lasers,[8-10] and as a sensitizer in older photovoltaic technologies.[11] Recently, a chromogenic and fluorogenic fluoride chemosensor made of coumarin derivative has been reported. [12-15] In most fluorescent sensors involves photophysical changes such as photoinduced electron transfer (PET), photoinduced charge transfer (PCT), metal-to-ligand charge transfer (MLCT) for fluorescent chemosensors.[16-18] Here, we report a novel coumarine chemosensor **1** with a specific optical response to fluoride ion.

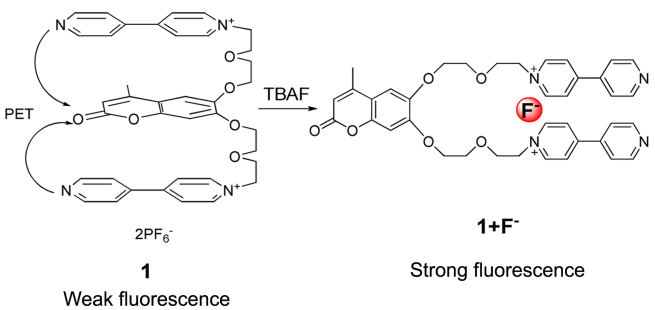
In pursuit of a selective fluoride chemosensor, a coumarine derivative **1** was synthesized, and its anion binding properties were investigated by ^{1}H NMR and fluorescence titration analysis. Coumarin derivative **1** was prepared by treating **3** with bipyridine in high yield. Finally, the iodide ions of **2** were replaced with PF_6^- by a simple reaction with $NaPF_6$ as shown in Scheme 1.

Results and Discussion

The ^{1}H NMR spectrum of **1** showed a singlet at δ 2.10 ppm for the methyl protons, a mixture of multiplets at δ 3.93 to δ 4.74 ppm for the methylene protons, three singlets at 5.99, 6.62 and 6.73 for coumarine protons and two doublets and a multiplet at 7.58, 8.13 and 8.76 for dipyridine protons. To investigate the anion binding properties, a series of anions such as tetrabutylammonium (TBA) fluoride, chloride, bromide, iodide, acetate, hydrogen sulfate, and dihydrogen phosphate were studied using fluorescence titration with chemosensor **1** in CH_3CN. In the absence of anions, coumarine bipyridine derivative **1** exhibits nearly no fluorescence



Scheme 1. Synthetic Route to Ligand **1**.



Scheme 2. The proposed interaction mode of **1** and the fluoride ion.

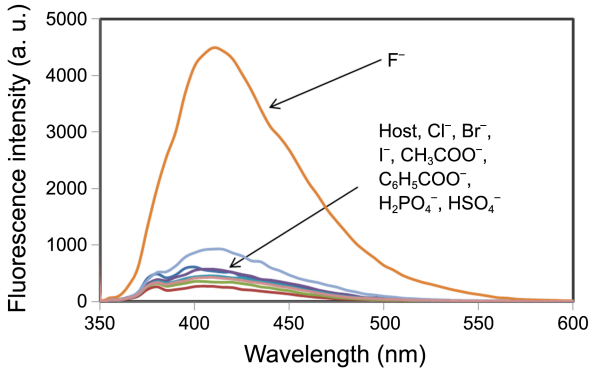


Figure 1. Emission spectra of **1** (10 μM) upon addition of tetrabutylammonium anions (100 eq.) in CH_3CN. (The excitation wavelength is 360 nm).

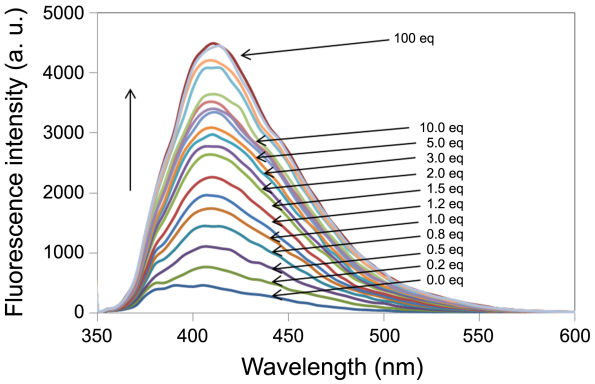


Figure 2. Emission spectra of **1** (10 μM) upon the addition of F^- from 0 eq to 100 eq. in CH_3CN. (The excitation wavelength is 360 nm).

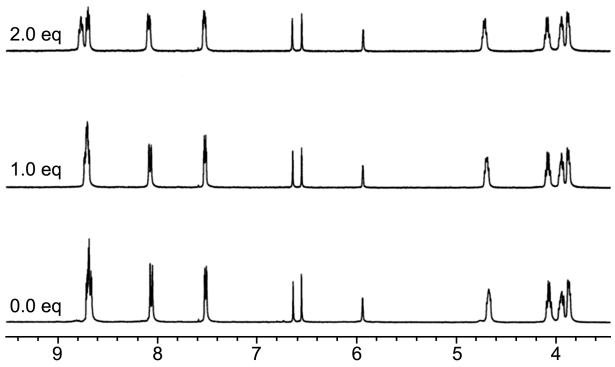


Figure 3. The partial ^1H NMR spectra of compound **1** with fluoride ions in CH_3CN.

in acetonitrile solution. Only in the presence of fluoride ion, a "turn-on" fluorescence was observed a strong fluorescence at 415 nm presumably from the interaction of bipyridine and fluoride ion. From the titration experiment as shown in Figure 2, the association constant (K_a) of **1** with F^- was calculated to be $4.0 \times 10^4\ M^{-1}$.[19]

Fluorescence emission suggests that the PET (photoinduced electron transfer) between nonbonding electron of nitrogen and coumarine unit was changed to the π-π interaction between bipyridine and coumarine that was induced by the interaction of bipyridine and fluoride ion as shown in Scheme 2.

Ligand **1** do not have acidic protons such as amide and urea groups which was the most frequent cases for fluoride receptor. Figure 3 shows the partial ^1H NMR spectra of **1** in the presence of fluoride ions. When fluoride ions were added, only a multiplet at 8.76 ppm was moved to downfield and became to two triplets, indicating that fluoride ions interacted with bipyridine protons near to cation charge.

In conclusion, a new chemosensor with coumarine derivative of bipyridine is synthesized. In the free ligand, coumarine derivative has nearly no fluorescence in acetonitrile solution. However, in the presence of fluoride ion, a "turn-on" fluorescence was observed. This phenomenon suggest that the PET (photoinduced electron transfer) between anion electron and coumarine unit was changed the π-π interaction between bipyridine and pyrene that was modified structure by deprotonation

Experimental

Synthesis of 2. To a solution of 1.0 g (017 mmol) of 6,7-bis(2-(2-iodoethoxy)ethoxy)-4-methyl-2*H*-chromen-2-one **3** in 40 mL of CH_3CN, 4,4'-bipyridine (0.80 g, 0.51 mmol) was added and refluxed for 24 h under the nitrogen atmosphere. After cooling the reaction mixture, the solid was collected to give 0.92 g (60%) of **2**. ^1H NMR (DMSO) δ 9.08, 8.72, 8.43, 7.79 (d, 16H, pyridil-H), 6.73, 6.67 (s, 2H, Ar-H), 5.99 (s, 1H, allylic-H), 4.84, 4.08, 4.00, 3.85 (t, 16H, OCH_2CH_2O), 2.20 (s, 3H, $-CH_3$).

Synthesis of 1. After dissolving 0.92 g (1.02 mmol) **2** in hot water (20 mL), ammonium hexafluorophosphate(V) (0.67 g, 4.08 mmol) was added. The solid was collected after cooling and washed with water several times and dried to give a white solid (0.91 g, 95%). ^1H NMR (CD_3CN) δ 8.76, 8.13, 7.58 (d, 16H, pyridil-H), 6.73, 6.62 (s, 2H, Ar-H), 5.99 (s, 1H, allylic-H), 4.74, 4.14, 4.02, 3.93 (t, 16H, OCH_2CH_2O), 2.10 (s, 3H, $-CH_3$); ^{13}C NMR (DMSO) δ 160.00 (-COO-), 152.79, 121.36 (allylic), 150.73, 148.24, 145.58 (Ar), 100.48, 69.36, 68.65 ($-OCH_2CH_2O-$), 68.39 ($-NCH_2CH_2-$), 18.15 (CH_3).

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