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# Turn-On Fluorescent Chemosensor for Fluoride Based on Pyreneamide Derivative

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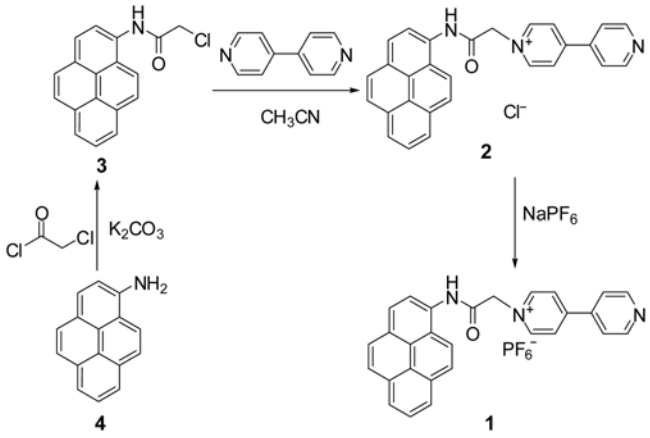
On account of the important roles of anion in biological, clinical, environmental, catalysis, and chemical processes, the selective and efficient recognition of anion is an area of growing interest in supramolecular chemistry.[1,2] In particular, the studies of chemosensors toward $F^-$ anion are quite intriguing because of its beneficial effects in human physiology.[3,4] Also, fluoride is interest due to its established role in dental care and osteoporosis. However, an excess of fluoride ion can lead to fluorosis. Therefore, the development of reliable sensors for $F^-$ is needed for environment and human health care. Color changes that can be detected by the naked eye are widely used as signals for events owing to the inexpensive equipment required or no equipment at all.[5-7]

Among anion receptors, colorimetric and fluorescent chemosensors are important because they provide high sensitivity and convenience for monitoring the anion recognition.[8-10] Especially, pyrenes are a particularly elegant basis for ratiometric based optical sensors, where the ratio of two emission wavelengths comprise the analytical signal. To date the pyrene excimer/monomer system has been exploited mainly for cation sensing and increasingly for anion sensing.[11-13] 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.[14-17] Here, we report a novel pyreneamide chemosensor **1** with a specific optical response to $F^-$.

In pursuit of a selective fluoride chemosensor, a pyreneamide derivative **1** was synthesized, and its anion binding properties were investigated by $^1$H NMR, UV-vis spectroscopy, color changes, and fluorescence titration analysis. Pyreneamide derivative **1** was prepared by treating **3** with bipyridine in high yield. Finally, the chloride ion of **2** was replaced with $PF_6^-$ by a simple reaction with $NaPF_6$ as shown in Scheme 1.



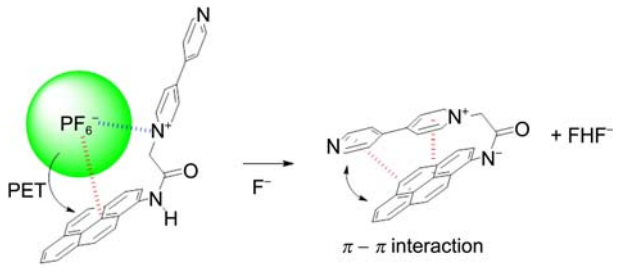

**Scheme 1.** Synthetic Routes to Fluorescent Chemosensor **1**.

## Results and Discussion

The $^1$H NMR spectrum of **1** showed a singlet at $\delta$ 5.95 ppm for the methylene protons, a mixture of multiplets at $\delta$ 8.07 to $\delta$ 9.32 ppm for the bipyridine and pyrene aromatic protons and a singlet at $\delta$ 11.06 ppm for the amide proton. 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, pyreneamide derivative **1** exhibits nearly no fluorescence in acetonitrile solution. Only in the presence of fluoride ion, a "turn-on" fluorescence was observed with a weak fluorescence at 385 nm and a strong fluorescence at 420 nm presumably from the interaction of bipyridine and pyrene. Form the titration experiment as shown in Figure 2, the association constant ($K_a$) of **1** with $F^-$ was calculated to be $2.0 \times 10^4\ M^{-1}$.[18]

This fluorescence emission suggests that the PET (photoinduced electron transfer) between anion electron and pyrene unit was changed to the π-π interaction between bipyridine and pyrene that was induced by the deprotonation as shown in Scheme 2. It is reported[19] that $F^-$ is sufficiently basic to deprotonate NH. The deprotonation was supported from the $^1$H NMR experiment. A new triplet at around 16 ppm, which corresponds to the formation of $FHF^-$, was observed.

The UV-vis experiments were carried out in an acetonitrile solution. A receptor solution 10 μM was treated with the




**Scheme 2.** Proton transfer between **1** and the fluoride ion.

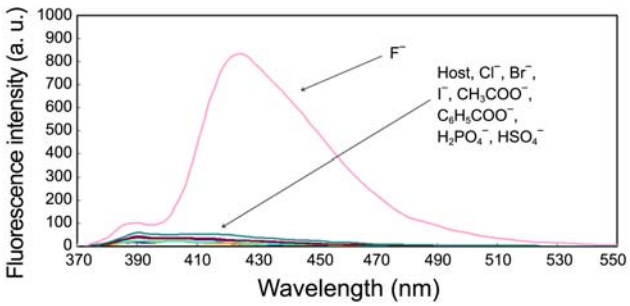



**Figure 1.** Emission spectra of **1** (10 μM) upon addition of tetrabutylammonium anions (100 eq.) in $CH_3CN$ (The excitation wavelength is 360 nm).

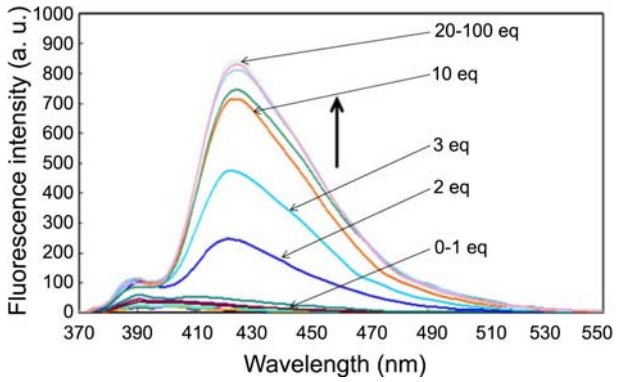



**Figure 2.** Emission spectra of **1** (10 μM) upon the addition of $F^-$ from 0 eq to 100 eq. in $CH_3CN$ (The excitation wavelength is 360 nm).

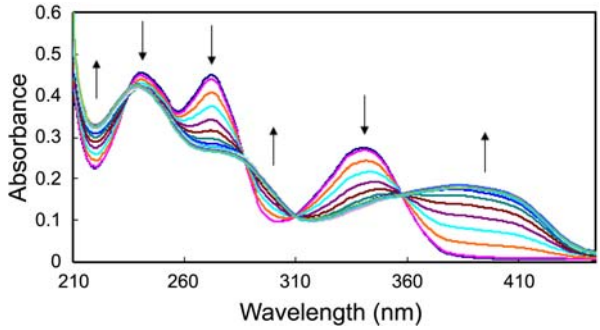



**Figure 3.** Absorbance spectra of **1** (10 μM) upon the addition of $F^-$ in $CH_3CN$ (From 0 to 10 eq.).

representative anions such as tetrabutylammonium (TBA) fluoride, chloride, bromide, iodide, acetate, hydrogen sulfate, and dihydrogen phosphate. Free ligand **1** displays a strong absorbance band centered at 340 nm. When compound **1** forms a complex with $F^-$, a new peak appears at 390 nm. However, a slight red shift was observed for the other anions.

A color change was easily observed on mixing the ligand and anions, as shown in Figure 4. A receptor solution was simply treated with various anions such as tetrabutylammonium (TBA) fluoride, chloride, bromide, iodide, acetate, dihydrogen phosphate, and hydrogen sulfate. The colorless solution became orange when fluoride ion was added to compound **1** in acetonitrile, but no color changes

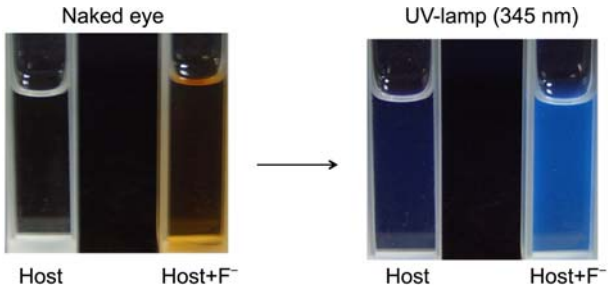



**Figure 4.** Photograph of the enhanced emission of **1** in $CH_3CN$.

were observed on the additions of chloride, bromide, and hydrogen sulfate ions.

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

## Experimental

**1-(2-Oxo-2(pyren-1-ylamino)ethyl)-4-(pyridin-4-yl)pyridinium chloride (2).** To a solution of 0.35 g (1.2 mmol) of 2-chloro-*N*-(pyren-1-yl)acetatamide (**3**) in 20 mL of MeCN, 0.3 g (1.9 mmol) of 4,4-dipyridyl was added and the reaction mixture was refluxed for 12 hours under the nitrogen atmosphere. The precipitate was occured in reaction mixture. The reaction mixture was cooled and filtered to give 0.5 g (94%) of (**2**). mp 258.7-259.1 °C.; $^1$H NMR (DMSO-$d_6$): 11.62 (s, 1H, ArNH-), 8.02 to 9.41 (13H, Ar-, N-Ar), 6.13 (s, 2H, -$CH_2$N-). $^{13}$C NMR (DMSO-$d_6$): 164.53 (-CO), 121.93 to 152.80 (Ar-). 61.90 (Ar$CH_2$N-). ESI-Mass: *m/z*: 414.1605.

**1-(2-Oxo-2(pyren-1-ylamino)ethyl)-4-(pyridin-4-yl)pyridinium hexafluorophosphate (1).** To a solution of 0.5 g (1.1 mmol) of 1-(2-oxo-2(pyren-1-ylamino)ethyl)-4-(pyridin-4-yl)pyridinium chloride (**2**) in 20 mL of MeOH, $NaPF_6$ (0.5 g, 3.0 mmol) was added. The reaction mixture was stirred for 30 min. The deep yellow solid was collected by filtration to yield 0.5 g (90%) of (**1**). mp 258.7-259.1 °C.; $^1$H NMR (DMSO-$d_6$): 11.08 (s, 1H, ArNH-), 8.07 to 9.32 (13H, Ar-, N-Ar), 5.95 (s, 2H, -$CH_2$N-). $^{13}$C NMR (DMSO-$d_6$): 164.47 (-CO), 122.00 to 153.03 (Ar-). 61.85 (Ar$CH_2$N-). ESI-Mass: *m/z*: 414.1605.

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