

Fluorescent Selective Chemosensor for Fluoride Ion with Pyrene Based on Triphenylphosphine

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Received November 1, 2013, Accepted November 14, 2013

Key Words : Fluoride, Triphenylphosphine, Chemosensor, Fluorescent

Design and development of artificial molecular systems for sensing anions in biologically relevant conditions is a challenging task in supramolecular chemistry.¹ In particular, sensing fluoride anion has attracted increasing interest in the molecular recognition community because of its pivotal importance in many areas of biological and chemical sciences.² Also, fluoride is interest due to its established role in dental care and osteoporosis. 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.^{3,4} Most of the fluorescent chemosensors for anions are composed of an anion recognition unit together with a fluorogenic unit and are called fluoroionophores.⁵ An effective fluorescence chemosensor must convert the event of anion recognition by the ionophore into an easily monitored and highly sensitive light signal from the fluorophore. Fluorescent moieties available to the scientist are typically aromatics such as substituted benzenes, anthracenes, naphthalenes, and pyrenes. Pyrenes are a particularly elegant basis for ratiometric based optical sensors, where the ratio of two emission wavelengths comprised the analytical signal. To date the pyrene excimer/monomer system has been exploited mainly for cation sensing and increasingly for anion sensing.⁷⁻²⁰ We developed herein a simple and highly selective indicator system. It can detect fluoride anion in organic media by utilizing chromogenic and fluorogenic “turn-on” signals. In pursuit of a selective fluoride chemosensor, a pyrene triphenylphosphine derivative **1** was synthesized and characterized with X-ray crystal structure analysis. Anion binding properties were investigated by ¹H NMR, UV-vis spectroscopy, color changes, and fluorescence titration analysis. Pyrene triphenylphosphine derivative **1** was prepared by treating **2** with triphenylphosphine in high yield. The bromide ion was replaced with PF₆⁻ by a simple reaction with NaPF₆ as shown in Scheme 1.

Results and Discussion

The ¹H NMR spectrum of **1** showed a doublet at δ 5.34 ppm (*J* = 14.4 Hz) for the methylene protons due to the coupling of the phosphorus atom and a mixture of multiplets at δ 7.40 to δ 8.31 ppm for the phenyl and pyrene aromatic protons. To investigate the anion binding properties, a series of anions such as tetrabutylammonium (TBA) fluoride, chloride, bromide, iodide, acetate, benzoate, hydrogen sulfate, and dihydrogen phosphate were studied using fluorescence titration with chemosensor **1** in CH₃CN. In the absence of anions, pyrene triphenylphosphine derivative **1** exhibits nearly weak fluorescence in acetonitrile solution.

Upon addition of fluoride ion, the fluorescence intensity emission of the dosimeter at 375 and 395 nm was increased 5-fold. Only in the presence of fluoride ion, a strong fluorescence was observed at 375 and 395nm. However, other anions such as chloride, bromide, iodide, acetate, benzoate, hydrogen sulfate, and dihydrogen phosphate did not cause any significant changes in the fluorescence emission inten-

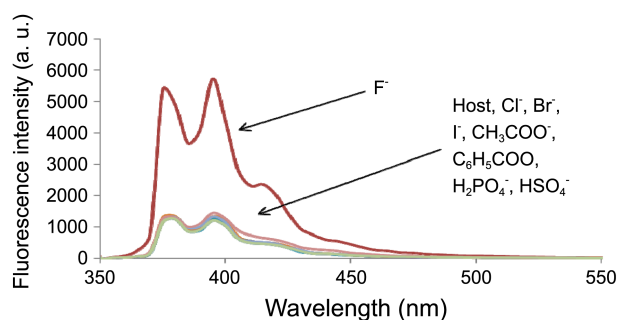
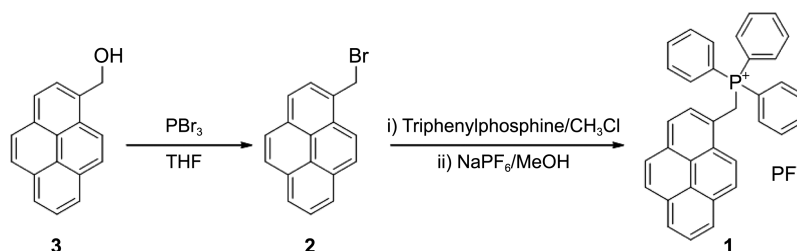


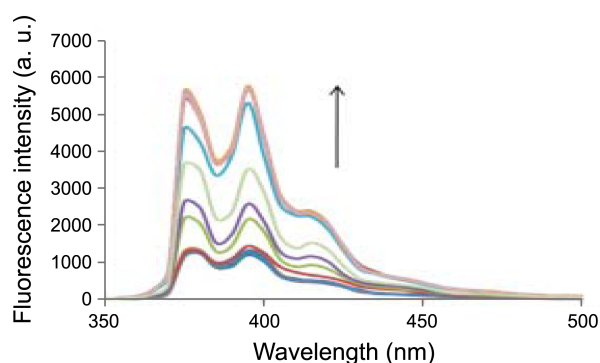
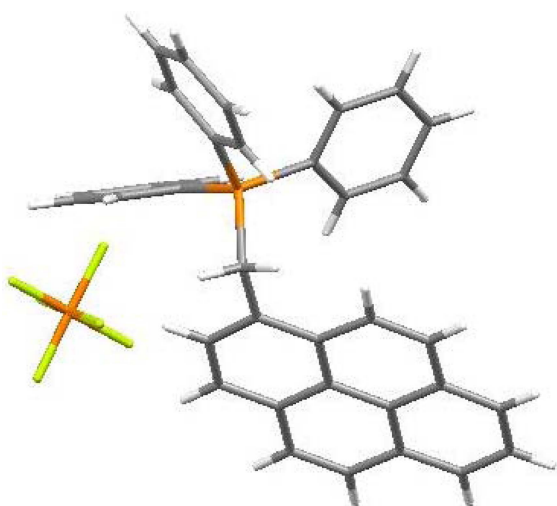
Figure 1. Emission spectra of **1** (2 μM) upon the addition of anions to 5 equivalents in CH₃CN. (The excitation wavelength is 340 nm).



Scheme 1. Synthetic Route to Chemosensor **1**.

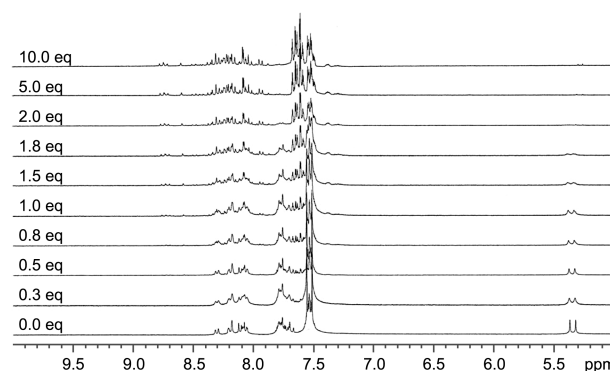
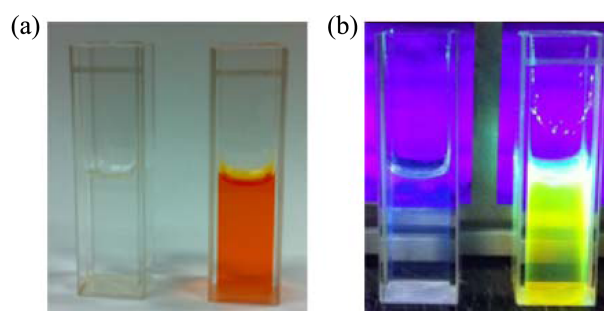
Table 1. Crystal data and structure refinement for **1**

Empirical formula	C ₃₅ H ₂₆ F ₆ P ₂
Formula weight	622.50
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	a = 8.8364(13) Å b = 15.950(2) Å c = 20.304(3) Å
Goodness-of-fit on F ²	0.876
Final R indices [I > 2σ(I)]	R1 = 0.0608, wR2 = 0.1148
R indices (all data)	R1 = 0.1260, wR2 = 0.1475
Largest diff. peak and hole	0.315 and −0.368 e.Å ^{−3}

**Figure 2.** Emission spectra of **1** (2 μM) upon the addition of F[−] to 5 equivalents in CH₃CN. (The excitation wavelength is 340 nm).**Figure 3.** Crystal structure of the chemosensor **1**.

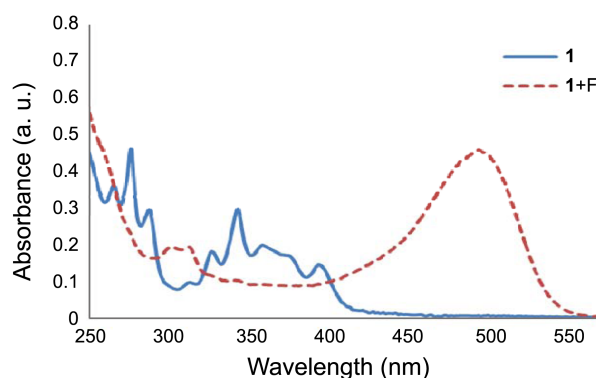
sity, even at excesses guest ions as shown in Figure 1.

The crystal structure of chemosensor **1** for X-ray analysis was grown by slow evaporation of acetonitrile solution. Figure 3 showed X-ray structure of chemosensor **1**. Table 1 showed the detail data for X-ray structure of chemosensor **1**. The crystal system is triclinic and P2(1)2(1)2(1) space group. Unit cell dimension are a = 8.8364(13) Å, b = 15.950(2) Å and c = 20.304(3) Å. The final R indices are R1 = 0.0608 wR2 = 0.1148.

**Figure 4.** The partial ¹H NMR spectra of compound **1** with fluoride ions.**Figure 5.** (a) Color change of **1** on the addition of fluoride in CH₃CN. (b) fluorescence change of **1** on the addition of fluoride in CH₃CN.

A quite drastic ¹H NMR spectral change was observed when treating with fluoride ions as showed in Figure 4. A methylene doublet at δ 5.34 was disappeared and several aromatic peaks at δ 8.31–7.40 ppm were moved slightly downfield at δ 8.78–7.40 ppm upon addition of fluoride ions. The stability constant could not be determined due to the completely disappearance of observing peaks at δ 5.34 with even small addition of anions. But, a new triplet at 16.1 ppm was appeared over 1 equivalents of fluoride addition. It is the typical characteristics of hydrogen fluoride ion (F–H–F).

Color and fluorescence change were easily observed on mixing the compound **1** and anions, as shown in Figure 5. A receptor solution was simply treated with various anions such as tetrabutylammonium (TBA) fluoride, chloride, bro-

**Figure 6.** UV-visible spectra of **1** and **1**+F[−] in CH₃CN.

mide, 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 were observed on the additions of chloride, bromide, and hydrogen sulfate ions. Figure 6 showed the UV-visible spectra of **1**. In the presence of fluoride ions a new peak at around 500 nm appeared as color indicated in Figure 5.

Conclusion

In conclusion, pyrene triphenylphosphine derivative **1** was synthesized successfully by the reaction of triphenylphosphine with **2**, which only showed a dramatic color and fluorescence change when treated with fluoride ions. The high selectivity for fluoride can be attributed to deprotonation of the methylene protons.

Experimental

Compound (1). To a solution 0.295 g (1.0 mmol) of 1-bromomethyl pyrene **2** in 30 mL of CH₃CN was added 0.524 g (0.5 mmol) of triphenylphosphine and the reaction mixture was refluxed for 1 days under the nitrogen atmosphere. After cooling down to room temperature, the pale yellow solid was obtained by filtration. The filtered solid was added in 20 mL MeOH with NaPF₆. The yellow solid was obtained by filtration to yield 0.5 g (95%) of **1**. ¹H NMR (CD₃CN, 300 MHz) δ 8.31–7.48 (m, 24H, aromatic). 8.27 (d, 2H, Ar-CH₂, *J* = 14.4 Hz), ¹³C NMR (CD₃CN, 300 MHz) δ 136.36, 136.32, 135.42, 135.29, 132.84, 132.80, 132.25, 132.23, 131.62, 131.54, 131.24, 131.23, 131.20, 131.03, 130.26, 130.20, 129.84, 129.45, 129.42, 128.88, 128.86, 128.33, 128.30, 127.78, 127.07, 127.06, 126.72, 126.71, 125.96, 125.91, 125.67, 124.92, 123.22, 121.39, 121.27, 118.87, 117.73, 29.01, 28.36.

Acknowledgments. This work was supported by Ministry of Education of Korea (BK21 project). NMR spectra were taken at the Korea Basic Science Institute, Kwangju, Korea. “This research was supported by Basic Science Research

Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (No. 2012R1A1A4A01011316)”.

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