ORGANIC
LETTERS

2008
Vol. 10, No. 14
2931−2934

A Novel Fluoride Ion Colorimetric Chemosensor

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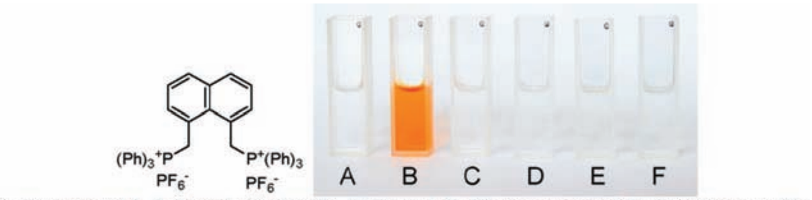
Received April 11, 2008

ABSTRACT



A=Free receptor **5**, B=Fluoride, C=Chloride, D=Bromide, E=Dihydrogen phosphate, F=Hydrogen sulfate

A novel phosphonium derivative of naphthalene was synthesized by the reaction of 1,8-dibromomethylnaphthalene with triphenylphosphine, which only showed a distinct color change when treated with fluoride ions.

Anion recognition is an area of growing interest in supramolecular chemistry due to its important role in a wide range of environmental, clinical, chemical, and biological applications, and considerable attention has been focused on the design of host molecules that are able to selectively recognize and sense anion species.[1,2] 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.[3–5]

Among the biologically important anions, fluoride is of particular interest due to its established role in dental care[6] and osteoporosis.[7]

Even though some receptor compounds for fluoride ions have been reported,[8] there is a paucity of reports on selective naked eye chemosensors for fluoride.[9,10] Nitrophenyl and nitronaphthalene urea, as a signal unit for fluoride, have been reported as chromogenic chemosensors,[11–13] but a naphthalene triphenylphosphonium ligand for the anion remains to be developed.

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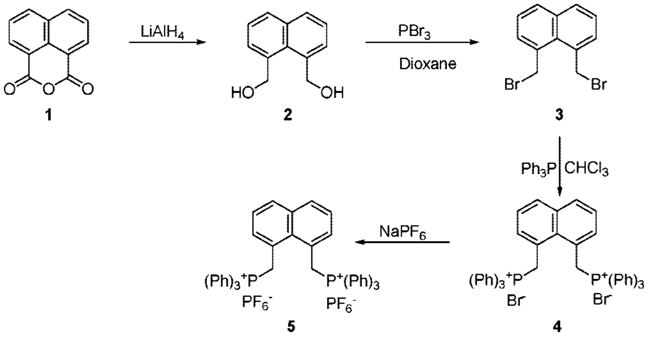
In pursuit of a selective fluoride ion chemosensor, a naphthalene phosphonium derivative **5** was synthesized, and its anion binding properties were investigated by ^{1}H NMR, UV−vis spectroscopy, color changes, and X-ray structural analysis. To our knowledge, it is the first report of a colorimetric chemosensor based on phosphonium ions.[14]

Using a previously reported method, 1,8-naphthalene bicarboxylic dianhydride **1** was reduced to the corresponding alcohol **2**[15] and following bromination with PBr_3 produced **3**[16] in high yield. Treatment with triphenylphosphine yielded **4**,[17] and the bromide ions were replaced with PF_6^- by a simple reaction with $NaPF_6$ (Scheme 1).

Scheme 1. ynthesis of 1,8-Bis(triphenylphosphoniomethyl)naphthalene Dihexafluorophosphate **5**



The ^{1}H NMR spectrum of **5** showed a doublet at δ 5.65 ppm (J = 16.2 Hz) for the methylene protons due to the coupling of the phosphorus atom and a mixture of multiplets at δ 7.01 to δ 7.69 ppm for the phenyl and naphthalene aromatic protons. To investigate the selectivity, a series of anions such as tetrabutylammonium (TBA) fluoride, chloride, bromide, iodide, perchlorate, hydrogen sulfate, and dihydrogen phosphate were treated with ligand **5** in DMSO-d_6, as shown in Figure S1. The most obvious spectral changes were observed when fluoride ions were treated. A methylene peak at δ 5.65 ppm, as a doublet, disappeared, and several aromatic peaks at δ 7−8 ppm were moved to multiplets at δ 7.6 ppm; however, no noticeable changes were observed with bromide, iodide, hydrogen sulfate, and perchlorate. However, similar changes were observed when **5** was treated with dihydrogen phosphate ions: the aromatic signals became broad, and the doublets at δ 5.65 ppm disappeared.

The binding properties of **5** toward anions were also investigated using ^{31}P NMR spectroscopy. The ^{31}P NMR spectrum of ligand **5** showed an interesting feature (Figure 1). In the presence of fluoride ions, the phosphorus signal shifts from δ 24.238 to δ 26.776 ppm, 2.538 ppm downfield, but in the presence of chloride ions, only a 0.385 ppm upfield shift was observed (Figure S3).

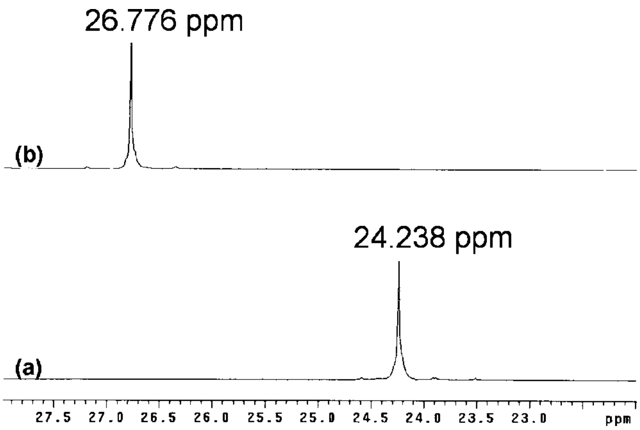


Figure 1. S^{31}P NMR spectra of ligand **5** (a) and on the addition of F^- (b).

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, hydrogen sulfate, and dihydrogen phosphate. When compound **5** forms a complex with F^-, a new peak appears at 447 nm. However, a bathochromic shift of other ions was observed with a small change as shown in Figure 2. Figure S22 explains the absorption titration data for **5** with F^-. From the absorption titration, the association constant of complex **5** with F^- was observed to be 1.38×10^4 M^{-1}.

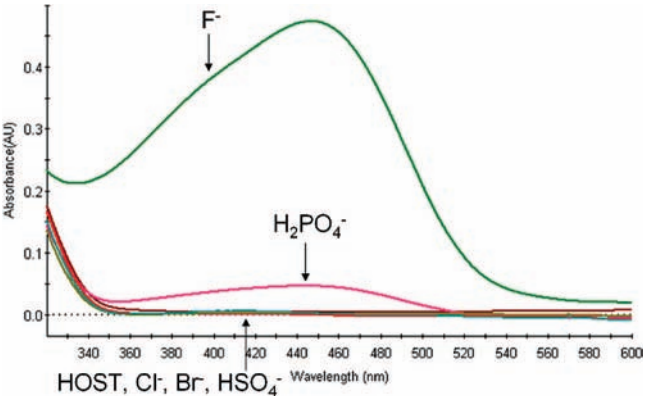


Figure 2. SAbsorption spectra of compound **5** (3.0×10^{-5} M) on the additions of tetrabutylammonium fluoride, chloride, bromide, hydrogen sulfate, and dihydrogen phosphate (3.0×10^{-4} M) in DMSO.

A color change was easily observed on mixing the ligand and anions, as shown in Figure 3. A receptor solution was simply treated with various anions such as tetrabutylammonium (TBA) fluoride, chloride, bromide, dihydrogen phosphate, and hydrogen sulfate, for which noticeable color changes were observed. In particular, the colorless ligand

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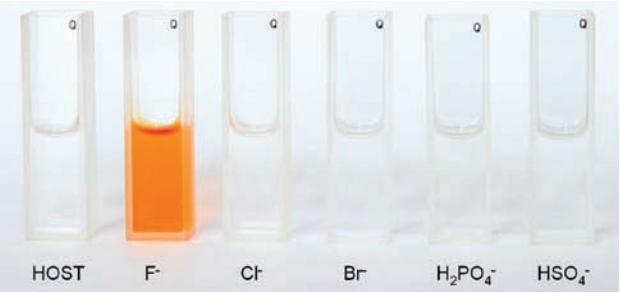

Figure 3. SColor changes of ligand **5** (3.0×10^{-4} M) on the additions of tetrabutylammonium (TBA) fluoride, chloride, bromide, dihydrogen phosphate, and hydrogen sulfate (3.0×10^{-3} M) in DMSO.

Table 1. Distance between Methylene Carbons and Anions in the Ligand[18]

the counteranion	carbon−anion	distance (Å)
PF_6^-	C11−P3	8.888
	C11−P4	15.012
	C30−P3	9.639
	C30−P4	14.973
Br^-	C11−Br1	7.966
	C11−Br2	3.669
	C30−Br1	9.505
	C30−Br2	3.623
Cl^-	C11−Cl1	7.890
	C11−Cl2	3.514
	C30−Cl1	9.404
	C30−Cl2	3.472

solution became markedly orange when fluoride ions were added to compound **5** in DMSO, but no color changes were observed on the additions of chloride, bromide, and hydrogen sulfate ions. A pale yellow color appeared on the addition of dihydrogen phosphate ions.

The crystal structure of the ligand revealed the unsymmetrical location of the two anions (Table 2). One stayed close to the middle of the two phosphorus atoms, whereas the other was positioned slightly outside of the phosphorus atoms (Figures 4, S5, and S6). Two anions may be able to hydrogen bond with the methylene protons, depending on the anion species, especially a small anion, such as the fluoride ion. The distance between the methylene carbon and the anions showed an interesting feature. Large anions such as PF_6^- were reasonably distant from the methylene carbons. Table 1 shows 8.888 and 9.639 Å between the methylene carbons and phosphorus atoms of the two PF_6^-, but 3.669 and 3.623 Å between the methylene carbons and the bromides and 3.514 and 3.472 Å between the methylene carbons and the chlorides. The X-ray structure for fluoride is not currently available, but a short distance would be expected.

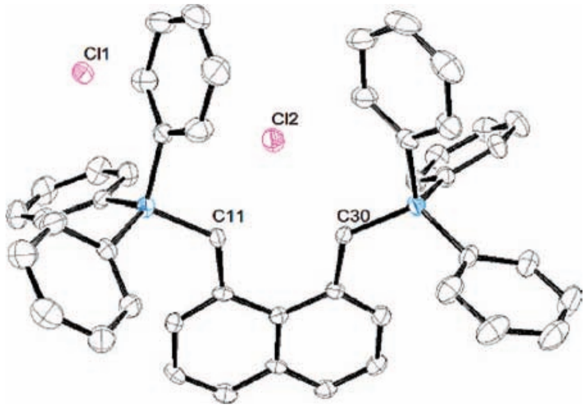

Figure 4. SCrystal structure of the ligand with two chloride ions.

Recently, colorimetric changes due to the deprotonation of NH have been utilized as sensors for F^-.[19] It is reported that F^- is sufficiently basic to deprotonate NH, which can cause usually long wavelength color change. The ^1H NMR experiments also support the deprotonation process. In our case, a new triplet, which corresponds to the formation of FHF,[20] was observed at around 16 ppm (Figure S19). From the UV−vis titration (Figures S22 and S23), the new absorption peak appeared at 447 nm on the addition of 2 equiv of fluoride, and then the absorption maxima shifted to 407 nm as further aliquots of fluoride were added. We interpreted this behavior as the fluoride binding to the receptor, and further additions of fluoride trigger deprotonation.[21] A similar spectral change was observed when treated with 100 equiv of KO^{t}Bu. But, when treated with 1 equiv of KO^{t}Bu, the intensity of the new peak was quite low and the color change was not observed, indicating the ligand **5** as an effective colorimetric chemosensor for fluoride ions (Figures S20 and S21).

In conclusion, a new phosphonium derivative of naphthalene was synthesized by the reaction of 1,8-dibromometh-

Table 2. Crystal Data and Structure Refinement for the Ligand with Two Chloride Ions

empirical formula	C50 H43 Cl2 N P2
formula weight	790.69
crystal system	triclinic
space group	$P\bar{1}$
unit cell dimensions	a = 11.2692(11) Å, α = 108.221(2)°
	b = 13.1613(13) Å, β = 98.803(3)°
	c = 14.7442(14) Å, γ = 93.853(2)°
goodness-of-fit on F^2	0.944
final R indices [$I > 2\sigma(I)$]	R1 = 0.0720, wR2 = 0.1157
R indices (all data)	R1 = 0.1662, wR2 = 0.1556
largest diff. peak and hole	0.581 and −0.365 e.Å^{-3}

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(18) Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC NO 676782 for chloride, 676783 for bromide, and 676784 for PF_6^-.

ylnaphthalene with triphenylphosphine, which only showed a distinct color change when treated with fluoride ions. The high selectivity for fluoride can be attributed to the acidity of the methylene protons and the small size of fluoride ions.

Acknowledgment. The NMR spectra were obtained at the Korea Basic Science Institute, Kwangju, Korea. This work was supported by the Korea Science and Engineering Foundation (KOSEF) grant funded by the Korea government (MOST) (No. R01-2007-000-20245-0).

Supporting Information Available: Spectroscopic data for ligand **5**, ^{1}H NMR titration spectra, and X-ray structure for Cl^-, Br^-, PF_6^-, and their data. This material is available free of charge via the Internet at http://pubs.acs.org.

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