

## A Versatile Colorimetric Chemosensor for Anion Detection with Phosphonium Derivative<sup>†</sup>

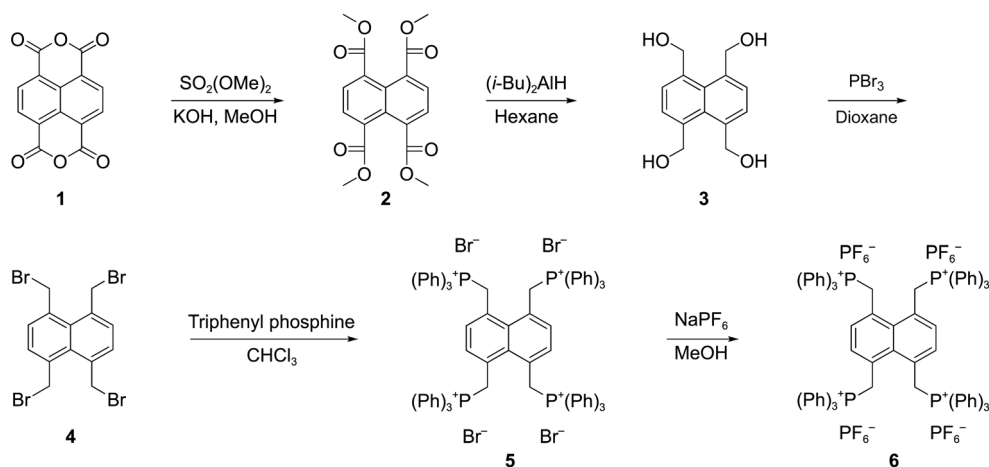
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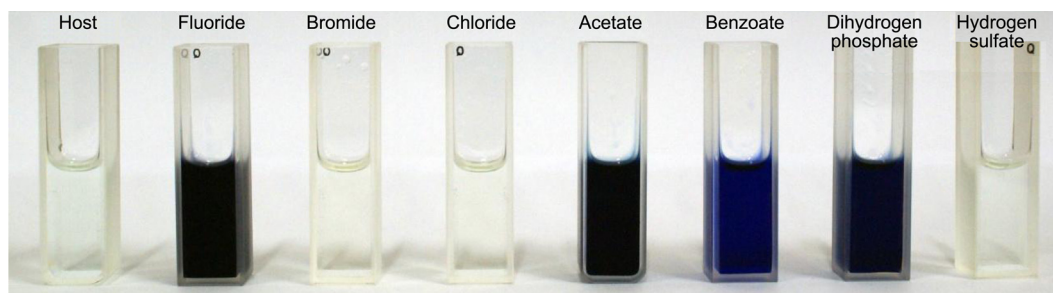
**Key Words :** Anion detection, Chemosensor, Color change, Phosphonium ion, Naphthalene

In a wide range of environmental, clinical, chemical, and biological applications, anion recognition in supramolecular chemistry is important role.<sup>1</sup> The design of host molecules that are able to selectively recognize and sense anion species has to do considerable attention. Color changes can be detected by the naked eye. So it is widely used as signals for events owing to the inexpensive equipment required or no equipment at all.<sup>2-4</sup> In viewing of biological importance, excessive fluoride anion may cause hair loss, skin inflammation, osteoporosis<sup>5</sup> and mutation of especially children's teeth enamel<sup>6</sup>. Even though some receptor compounds for fluoride ions have been reported,<sup>7</sup> there is a paucity of

reports on selective naked eye chemosensors for fluoride.<sup>8,9</sup> Nitrophenyl and nitronaphthalene urea, as a signal unit for fluoride, have been reported as chromogenic chemosensors,<sup>10-12</sup> As we mentioned previous papers<sup>13</sup>, only few phosphonium salt receptor was developed although importance of anion receptor. We reported here a further developed novel phosphonium derivative of naphthalene for anion sensors. In pursuit to develop a sensitive and versatile anion chemosensor, a naphthalene *tetrakis* phosphonium derivative **6** was synthesized, and its anion binding properties were investigated by <sup>1</sup>H NMR, UV-vis spectroscopy, color changes and X-ray structural analysis.



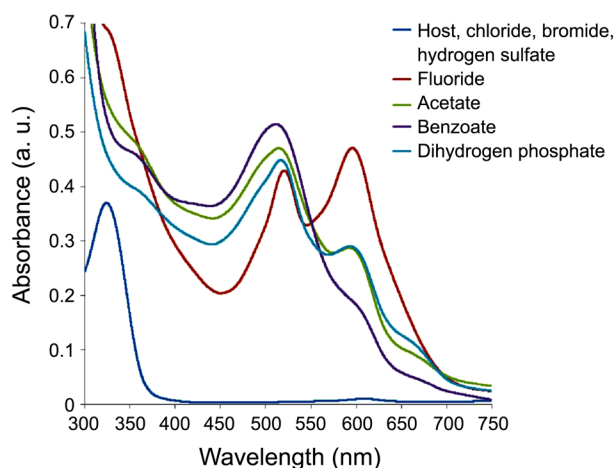
**Scheme 1.** Synthesis of 1,4,5,8-*tetrakis*(triphenylphosphoniomethyl)naphthalene tetrahexafluorophosphate **6**.



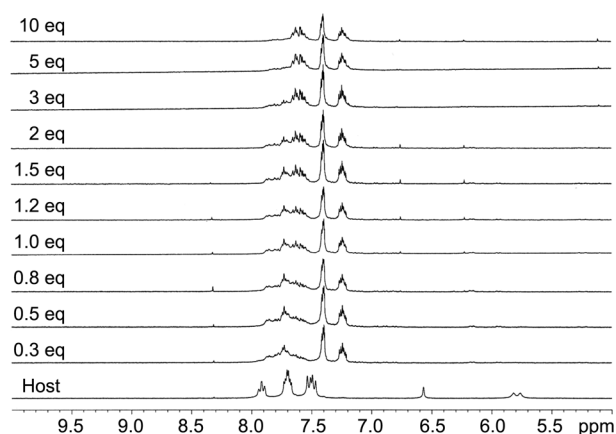
**Figure 1.** Color changes of ligand **6** ( $3.0 \times 10^{-4}$  M) upon addition of tetrabutylammonium fluoride, chloride, bromide, acetate, benzoate, dihydrogen phosphate and hydrogen sulfate (10 equiv.) in DMSO.

<sup>†</sup>This paper is dedicated to Professor Eun Lee on the occasion of his honourable retirement.

1,4,5,8-Tetrakisbromomethyl naphthalene **4** was easily obtained from the bromination of alcohol **3** with  $\text{PBr}_3$ , followed by reduction of **2** which was obtained from the hydrolysis of **1** with methylation. Treatment with triphenyl-



**Figure 2.** Absorption spectra of ligand **6** ( $3 \times 10^{-5}$  M) upon the additions of tetrabutylammonium anions to 100 equiv. in DMSO.



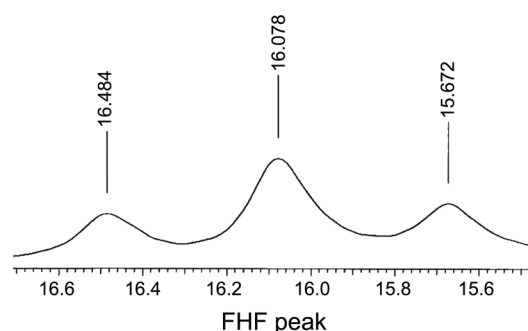
**Figure 3.**  $^1\text{H}$  NMR spectra of ligand **6** upon addition of fluoride anion.

phosphine yielded **5**, and the bromide ions were replaced with  $\text{PF}_6^-$  by a simple reaction with  $\text{NaPF}_6$  (Scheme 1).

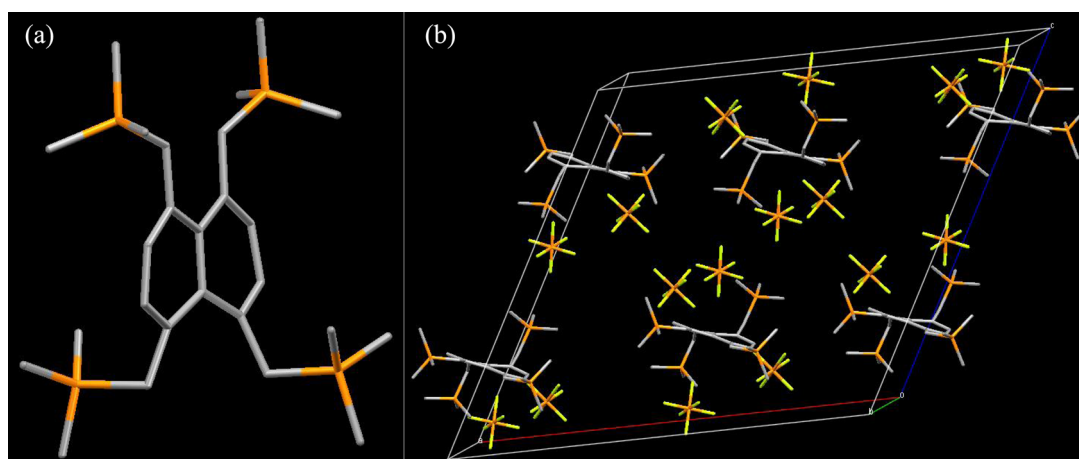
$^1\text{H}$  NMR spectrum of ligand **6** showed a doublet at  $\delta$  5.79 ppm for the methylene protons between triphenylphosphine and naphthalene due to the coupling of phosphorous atom. Naphthalene protons appeared singlet at  $\delta$  6.57. Aromatic protons appeared a mixture of multiplets at  $\delta$  7.47 to  $\delta$  7.95.

A color change was observed easily by mixing the ligand and anion. A receptor solution was simply treated with various anions such as tetrabutylammonium (TBA) fluoride, chloride, bromide, hydrogen sulfate, and dihydrogen phosphate. Impressive color changes were observed when **6** was treated with the anions. In particular, it was remarkable that a colorless ligand solution became almost black when fluoride ions were added to compound **6** in DMSO as shown in Fig. 2. In case of acetate and dihydrogen phosphate anions, a dark blue color was appeared and a light blue was appeared for benzoate. But color change was not observed when chloride, bromide and hydrogen sulfate anions were added.

The UV-vis experiments were carried out in a DMSO solution. A receptor solution ( $3 \times 10^{-5}$  M) was treated with the representative anions such as tetrabutylammonium (TBA) fluoride, chloride, bromide, hydrogen sulfate, and dihydrogen phosphate. When ligand **6** was treated with 100 equivalents of dihydrogen phosphate, acetate, benzoate, and



**Figure 4.** Partial  $^1\text{H}$  NMR spectra (300 MHz) of **6** (4 mM) with  $\text{F}^-$  in  $\text{DMSO}-d_6$ .



**Figure 5.** (a) Crystal structure (b) Packing diagram of ligand **6**. (Solvent molecules, hexafluorophosphate and hydrogen atoms have been omitted for clarity. Triphenylphosphine group was modified trimethylphosphine for clarity).

**Table 1.** Crystal data and structure refinement for ligand **6**

Empirical formula	C <sub>88</sub> H <sub>74</sub> Cl <sub>6</sub> F <sub>24</sub> P <sub>8</sub>	
Formula weight	2047.93	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	$a = 25.461(3) \text{ \AA}$ $b = 16.6709(19) \text{ \AA}$ $c = 23.893(3) \text{ \AA}$	$\alpha = 90^\circ$ . $\beta = 118.666(2)^\circ$ . $\gamma = 90^\circ$ .
Goodness-of-fit on F <sup>2</sup>	1.051	
Final R indices [I > 2σ(I)]	$R_1 = 0.0582$ , $wR_2 = 0.1568$	
R indices (all data)	$R_1 = 0.0789$ , $wR_2 = 0.1795$	
Largest diff. peak and hole	1.184 and -0.903 e.Å <sup>-3</sup>	

In summary, we have developed a novel anion receptor **6**, by combine naphthalene and positive charged triphenylphosphonium which showed fluoride selective. The crystal showed the direction of the triphenylphosphinio methyl group toward anion.

fluoride, a new peak appear at 510 nm and a second peak at 596 nm was appeared for fluoride shown in Fig. 3.

A quite drastic <sup>1</sup>H NMR spectral change was observed when treating with fluoride ions as showed in Fig. 4. A methylene doublets at δ 5.79 and naphthalene singlet at δ 6.57 were disappeared and a several aromatic peaks at δ 7.47-7.95 ppm were moved to a multiplets at δ 7.18-7.65 ppm upon addition of fluoride ions. The stability constant could not be determined due to the completely disappearance of observing peaks at δ 5.79 and δ 6.57 with even small addition of anions. But, a new triplet at 16.1 ( $J = 122$  Hz) was appeared over 1 equivalents of fluoride addition. It is to the typical characteristics of hydrogen fluoride ion (F-H-F). The <sup>1</sup>H NMR experiments also support the deprotonation process on aliphatic protons.

The crystals of ligand **6** suitable for the X-ray analysis were grown by slow evaporation of a chloroform solution. Fig. 5 showed a X-ray structure of ligand **6**. Two triphenylphosphonium units stayed right and left side of naphthalene, and two others units stayed up and down side of naphthalene. Table 1 showed the detail data for X-ray structure of ligand **6**. The Crystal system is Monoclinic and C2/c space group. Unit cell dimension are  $a = 25.461(3) \text{ \AA}$ ,  $b = 16.6709(19) \text{ \AA}$ ,  $c = 23.893(3) \text{ \AA}$  and  $\alpha = 90^\circ$ ,  $\beta = 118.666(2)^\circ$ ,  $\gamma = 90^\circ$ .

### Experiment Section

**Tetramethyl-1,4,5,8-naphthalenetetracarboxylate 2.** To a solution of 10 g (37.3 mmol) of 1,4,5,8-naphthalic anhydride **1** in 35 mL of MeOH was added 29.3 g (233 mmol) of dimethyl sulfate under nitrogen atmosphere. The reaction mixture was stirred and added 14.5 g (259 mmol) of KOH in 120 ml of MeOH carefully. The reaction mixture was stirred for 1 hour and than cool down room temperature. Cool, The precipitated white solide **2** (10.3 g, 77%) was filtered and dried. mp 200-203 °C; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 8.10 (s, 4H, Ar), 3.85 (s, 12H, OCH<sub>3</sub>)

**1,4,5,8-Tetrakis(hydroxymethyl)naphthalene 3.** To a solution of 9.0 g (25.0 mmol) of Tetramethyl-1,4,5,8-Naphthalenetetracarboxylate **2** in 365 mL (365 mmol) diisobutylaluminum hydride (1.0M solution in hexane) was

stirred for 30 hours under nitrogen atmosphere at room temperature. The reaction mixture was poured to 120 mL of MeOH and 275 mL of 6M HCl and filtrated. After recrystallization from hexane and chloroform, the white solid **3** (5.84 g, 94%) was obtained. mp 231-233 °C; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 5.05 (d, 8H,  $J = 5.5$  Hz, ArCH<sub>2</sub>), 5.22 (t, 4H,  $J = 5.5$  Hz, OH), 7.56 (s, 4H, Ar).

**1,4,5,8-Tetrakis(bromomethyl)naphthalene 4.** To a solution of 1.7 g (6.84 mmol) of 1,4,5,8-tetrakis (hydroxymethyl) naphthalene **3** in 60 mL of anhydrous dioxane was added 7.2 mL (76 mmol) of PBr<sub>3</sub> under nitrogen atmosphere. After 1 hour, additional 7.2 mL of PBr<sub>3</sub> was added, and stirred for 20 hours at room temperature. To 12 mL of H<sub>2</sub>O, the reaction mixture was added. The white solid (2.7 g, 93%) was obtained. mp 248-250 °C; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 7.84 (s, 4H, Ar), 5.39 (s, 8H, CH<sub>2</sub>Br).

**1,4,5,8-Tetrakis(triphenylphosphoniomethyl)-naphthalene tetrabromide 5.** To a solution of 0.2 g (0.40 mmol) of 1,4,5,8-tetrakis(bromomethyl)naphthalene **4** in 10 mL of CHCl<sub>3</sub> was added 0.2 g (0.78 mmol) of triphenylphosphin under nitrogen atmosphere. The reaction mixture was refluxed for 10 days. After cooling down to room temperature, the white solid was obtained by filtration to yield 0.54 g (88%) of **5**. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 5.18 (d, 8H,  $J = 16.2$  Hz, ArCH<sub>2</sub>), 6.15 (s, 4H, Ar), 7.56-7.89 (60H, P-Ar)

**1,4,5,8-Tetrakis(triphenylphosphoniomethyl)-naphthalene tetrahexafluorophosphate 6.** To a solution of 0.5 g (0.32 mmol) of 1,4,5,8-tetrakis-(triphenylphosphoniomethyl)-naphthalene tetrabromide **5** in 20 mL of MeOH was added a solution of 0.5 g (3.0 mmol) of NaPF<sub>6</sub>. The reaction mixture was stirred for 30 min. The white solid was obtained by filtration to yield 0.53 g (92%) of **6**. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 5.79 (d, 8H,  $J = 16.2$  Hz, ArCH<sub>2</sub>), 6.57(s, 4H, Ar), 7.46-7.94 (60H, P-Ar); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>): δ 30.38 (d, ArCH<sub>2</sub>P-), δ 115.81 to 135.30 (Ar- and P-Ar).

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