# A Naked-eyes Chemosensor for Fluoride Ion: a Selective Easy-to-prepare Test Paper

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#### **Experiments Section**

## **General Information**

Unless otherwise stated, all the chemicals used in this study were purchased from Aldrich or Tokyo Kasei Kogyo Co., Ltd. (TCI, Tokyo, Japan).

<sup>1</sup>H (400 MHz) and <sup>13</sup>C (100 MHz) NMR spectra were recorded on a Bruker Avance/DMX 400-MHz NMR spectrometer with CH<sub>3</sub>CN-*d*<sub>3</sub> or THF-*d*<sub>8</sub> as solvents and tetramethylsilane as an internal reference. IR spectra were measured using a Shimadzu FTIR-8100 spectrophotometer. Melting points (mp) was measured on a Yanaco micro-melting point apparatus. Mass spectra (MS) were carried out on a GCT Premier CAB 048 mass spectrometer operating in a chemical ionization mode (CI). Elemental analysis was performed on an Eager 300 elemental microanalyzer. UV–vis spectra was recorded in a quartz cell (thickness: 1 cm) at room temperature using a JASCO J-820 spectropolarimeter.

### Typical Experimental Procedure for UV-vis Absorption Measurements.

All UV-vis absorption measurements were performed in dry solvent. The concentration of probe 1, was 100  $\mu$ M for all the measurements.

A typical experimental procedure is described as follows: Stock solutions of probe **1** (26.4 mg/10mL) and *tetra*-n-butylammonium fluoride (TBAF) (1.0 mM) in CH<sub>3</sub>CN were prepared in flasks equipped with stopcocks, respectively. The probe **1** solution (0.1 mL) and the TBAF solution (0.1 mL) were transferred to a vial, and then the resulting mixture was diluted to 10 mL with dry CH<sub>3</sub>CN to give the sample solution, of which [**1**] and [TBAF]/[**1**] were adjusted to be 100  $\mu$ M and 10, respectively. The

UV-vis absorption spectrum of the resulting sample solution was measured in a quartz cell with a 10 mm path length at 25  $^{\circ}$ C.

#### Synethsis of probe 1



Into a 100 mL flask was added (4.34 g, 20 mmol) of 2-amino-2-(4-hydroxyphenyl) acetic acid methyl ester hydrochloride in 30 mL of THF and 10 mL Et<sub>3</sub>N. (2.30 g, 20 mmol) of butyl isothiocyanate was then added into the flask. The reaction mixture was stirred at room temperature overnight. The filtrate was concentrated by a rotary evaporator and the residue was extracted with 200 mL of  $CH_2Cl_2$ . The organic phase was with 1 M HCl, statured aq. NaHCO<sub>3</sub> and brine. The organic layer was dried over anhydrous MgSO<sub>4</sub> and evaporated to dryness. After filtration and solvent evaporation, the crude product was purified by a silica gel column using hexane/ethyl acetate mixture (1:1 by volume) as eluent. White solid was obtained in 84% yield (4.44 g).

**Mp** 291.5~292.5 °C.

<sup>1</sup>H NMR (400 MHz, THF-*d*<sub>8</sub>):δ 10.09(s, 1H), 8.59(s, 1H), 7.54(d, *J* = 8.8 Hz, 2H),
6.71 (d, *J* = 8.8 Hz, 2H), 5.28(s, 1H), 3.48 ~3.35 (m, 2H), 1.14 (dd, *J* = 34.2, 27.4 Hz,
4H), 0.85 (t, *J* = 7.2 HZ, 3H).

<sup>13</sup>C NMR (100 MHz, THF-*d*<sub>8</sub>): δ182.36, 171.76□, 158.54, 128.46, 121.75, 114.66,
61.44, 40.38, 29.24, 19.69, 13.08.

**IR** (cm<sup>-1</sup>, KBr): 3330, 2962, 2878, 1898, 1719, 1617, 1589, 1517, 1481, 1351, 1191,

1144,930, 817, 744, 631.

## Elemental analysis: Anal. Calcd for C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>S: C, 59.07; H, 6.10; N, 10.60; O,

12.11; S, 12.13. Found: C, 59.11; H, 6.08; N, 10.77.

**MS**(ESI): calcd. 264.0932 found ES+, *m/z*: = 263.1 [M+H]<sup>+</sup>.



Fig S1 <sup>1</sup>H NMR spectrum of probe **1** in THF- $d_8$ . The solvent and water peaks are marked with asterisks.



Fig S2  $^{13}$ C NMR spectrum of probe 1 in THF- $d_8$ . The solvent peaks are marked with asterisks.



Fig S3 ESI-MS spectrum of probe 1



Fig S4 IR spectrum of probe 1



Fig S5 UV-vis spectrum of probe 1 in  $CH_3CN$  after the addition of TBA salts of a series of anions ([1] = 1.0 mM, [anion]/[1] =10).