

## Supporting Information

### **Novel fluorescent probes for fluoride anion based on Hydroxy-substituted perylene tetra-(alkoxycarbonyl) derivatives**

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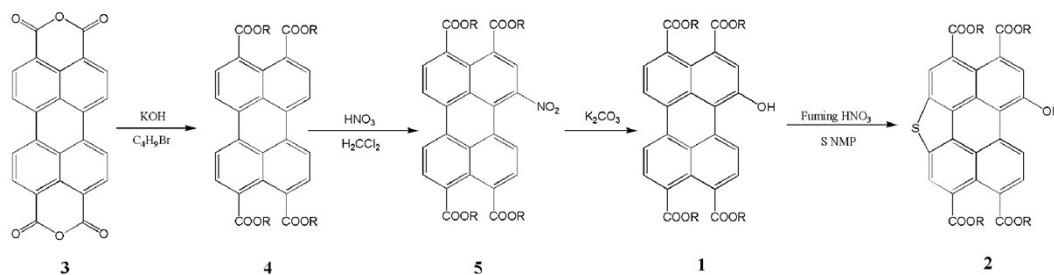
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## Experimental section



Scheme s-1. The synthesis route of probes **1** and **2**.

### General procedure for the synthesis of **4**

Compound **3** (4.0 g, 10.2 mmol) was dissolved in 200 mL KOH (0.1 mol/L) solution and heated under reflux for 6 hours. After being cooled to room temperature, the reaction mixture was added dropwise into acetone: isopropanol (1:1, v/v, 400.0 mL). The resulting precipitate was filtered and washed three times with 15 mL of acetone and isopropanol, respectively. After drying, the solid was dissolved in a flask (250 mL) with 100 mL of water, then butyl bromide (10.88 g, 80 mmol) was added into the solution after tetrabutylammonium bromide (3.0 g, 9.4 mmol), anhydrous potassium carbonate (6.0 g, 43.4 g) and KI (0.125 g, 1 mmol) were charged into the solution and stirred vigorously for 15 min. The mixture was refluxed for 24 h. Subsequently, the reaction mixture was cooled to room temperature and poured into 100 mL of methylene chloride, and the methylene chloride phase layer was washed thrice with 30 mL of aqueous solution. A yellow solid was obtained by adding methanol into the concentrated chloroform solution and dried under vacuum condition at 70°C. Yield: 4.58 g (70%). Yellow solid.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.08 (d,  $J=7.9\text{ Hz}$ , 4H), 7.93 (d,  $J=7.9\text{ Hz}$ , 4H), 4.39 (d, 8H), 1.87 (m, 8H), 1.59 (m, 8H), 1.02 (m, 12H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 168.51, 132.78, 130.35, 130.26, 128.81, 126.62, 121.26, 65.29, 53.39, 30.68, 19.28, 13.78. FT-IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  = 2952, 2868, 2109, 1893, 1714, 1584, 1511, 1469, 1405, 1266, 1164, 1128, 1097, 1032, 939, 890, 841, 803, 743, 588, 507, 436. MALDI-TOF MS: calcd 652.3; found, 652.3046 ( $\text{M} + \text{Na}^+$ ).

Elemental analysis: Calculated for  $C_{40}H_{44}O_8$  C 73.60, H 6.79, O 19.61%; found C 73.48, H 6.43, O 19.82%.

#### **General procedure for the synthesis of 5.**

Compound **4** (1.0g, 1.5 mmol) was dissolved in 150mL of dichloromethane at room temperature. Fuming nitric acid (1.5mL) was then added dropwise into the solution and the reaction mixture was kept stirring for 2h at room temperature. The resulting mixture was diluted with 50 mL of sodium bicarbonate (20%) solution. The organic phase was separated, washed with water three times (50 ml $\times$ 3), dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The crude product was purified by gel column chromatography using dichloromethane/petroleum ether (2:1, v/v) as the eluent to afford target product. Yield: 0.9g (86%). Red solid.  $^1H$ -NMR(300 MHz,  $CDCl_3$ , ppm):  $\delta$ =8.40 (s, 1H), 8.37 (m, 2H), 8.26 (d, 1H), 8.14 (d, 1H,  $J$ =6 Hz), 7.97 (d, 1H,  $J$ =6 Hz), 7.93 (d, 1H,  $J$ =9 Hz), 4.37 (m, 8H), 1.82 (m, 8H), 1.55 (m, 8H), 1.03 (m, 12H).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ , ppm)  $\delta$ : 168.06, 167.86, 167.79, 166.60, 146.32, 133.91, 132.53, 131.96, 131.61, 130.83, 130.51, 130.38, 130.00, 129.15, 128.73, 128.48, 127.92, 127.40, 126.63, 125.62, 123.13, 122.61, 66.02, 65.64, 65.58, 30.60, 19.23, 13.74. FT-IR (KBr,  $cm^{-1}$ ):  $\nu$  = 2959, 2871, 1711, 1589, 1529, 1460, 1394, 1353, 1274, 1249, 1163, 1108, 1062, 1021, 959, 899, 846, 801, 736, 702, 604, 506, 434. MALDI-TOF MS: calcd 697.29; found, 697.2913 ( $M + Na^+$ ). Elemental analysis: Calculated for  $C_{40}H_{43}NO_{10}$  C 68.85, H 6.21, N 2.01, O 22.93%; found C 68.75, H 6.33, O 2.04, O 22.87%.

#### **General procedure for the synthesis of 1.**

Compound **5** (70mg, 0.1mmol), potassium carbonate (69 mg, 0.50 mmol) were dissolved in N-methylpyrrolidone (NMP, 10ml). The resulting solution was heated to 60°C with vigorous stirring for 12h, then cooled and poured into 100ml of 2 M HCl. The precipitate was collected by vacuum filtration, washed with water and dried under vacuum condition. The residue was purified by column chromatography on silica gel with dichloromethane /ethyl acetate (20/1) as eluent and a carmine solid of was obtained. Yield: 52 mg (79%). Red solid.  $^1H$ -NMR ( $CHCl_3$ , TMS, ppm):  $\delta$  =

10.67 (s, 1H), 9.34 (d, 1H), 8.25 (d, 1H), 7.99-7.95 (m, 3H), 7.84 (d, 1H), 7.82 (s, 1H), 4.23-4.17(m, 8H), 2.62-2.39(m, 8H), 1.71-1.64(m, 8H), 1.44-1.34(m, 12H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 168.78, 167.80, 167.71, 157.31, 144.10, 133.47, 132.33, 131.95, 131.82, 129.85, 129.30, 128.61, 127.65, 127.40, 126.34, 125.87, 125.64, 122.24, 120.78, 113.56, 80.00, 65.35, 65.27, 65.21, 30.66, 30.58, 19.25, 13.77. FT-IR (KBr, cm<sup>-1</sup>):  $\nu$  = 2957, 2928, 2870, 1708, 1588, 1514, 1460, 1406, 1344, 1271, 1196, 1160, 1063, 1024, 961, 939, 896, 837, 801, 750, 707, 580, 507, 438. MALDI-TOF MS: calcd 667.3; found, 667.29 (M + Na<sup>+</sup>). Elemental analysis: Calculated for C<sub>40</sub>H<sub>44</sub>O<sub>9</sub> C 71.84, H 6.63, O 21.53%; found C 71.76, H 6.25, O 21.61%.

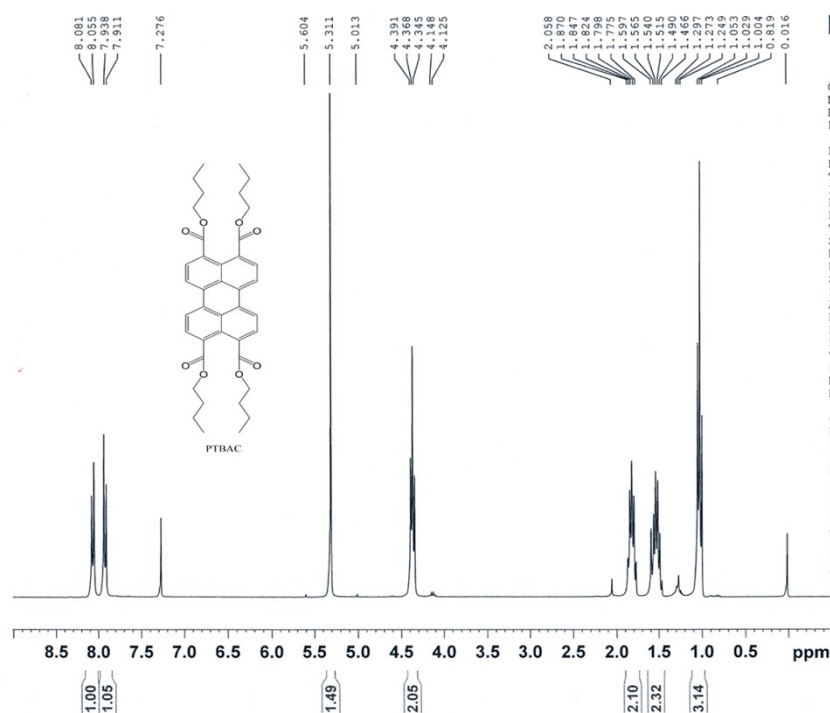
#### **General procedure for the synthesis of 2.**

Compound **1** (335 mg, 0.5 mmol) was dissolved in 50mL of dichloromethane at room temperature. Fuming nitric acid (2.5 mL) was then added dropwise into the solution and the reaction mixture was kept stirring for 1h at room temperature. The resulting mixture was diluted with 100 mL of sodium bicarbonate (20%) solution. The organic phase was separated, washed with water three times (50 ml×3), dried over anhydrous MgSO<sub>4</sub> and concentrated under reduced pressure. Then a mixture of the crude product (250mg, 0.4mmol) and sulfur powder (160mg 5.0mmol) was dissolved in 150mL anhydrous N-methylpyrrolidine. The resulting solution was heated to 110°C with vigorous stirring for 5h, then cooled and poured into 200ml of 2 M HCl. The precipitate was collected by vacuum filtration, washed with water three times (50 ml×3), and dried under vacuum condition. The residue was purified by gel column chromatography with dichloromethane /ethyl acetate (20/1) as eluent to afford target product **2** (196mg, 82%). Characterization data: <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz, ppm):  $\delta$  = 11.09 (s, 1H), 9.73 (d, J = 9.0 Hz, 1H), 8.71 (s, 1H), 8.55 (s, 1H), 8.33 (s, 1H), 8.11 (d, 1H), 4.34-4.43 (m, 8), 1.74 (m, 8H), 1.48 (m, 8H), 0.88-0.99 (m, 12H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 169.59, 169.20, 168.81, 153.19, 129.87, 129.08, 128.16, 127.77, 126.94, 126.77, 125.43, 124.15, 123.01, 122.27, 119.10, 116.71, 65.71, 65.61, 65.42, 30.81, 29.67, 19.34, 13.84. FT-IR (KBr, cm<sup>-1</sup>):  $\nu$  = 3365 (s, O-H stretching),

3189 (s, aliphatic C-H), 2922 (vs, aliphatic C-H), 2854 (vs, aliphatic C-H), 1651 (s, C=O), 1462 (s, aromatic C=C), 1410 (s, C-O), 1067 (s, C-C), 873 (s, C-S), 732, 661, 586, 528, 486, 437. HRMS:  $C_{40}H_{42}SO_9$  ( $M^+ - H$ ), calcd, 697.2352, found 697.2469.

# Spectra of NMR, FTIR and MALDI-TOF-MS

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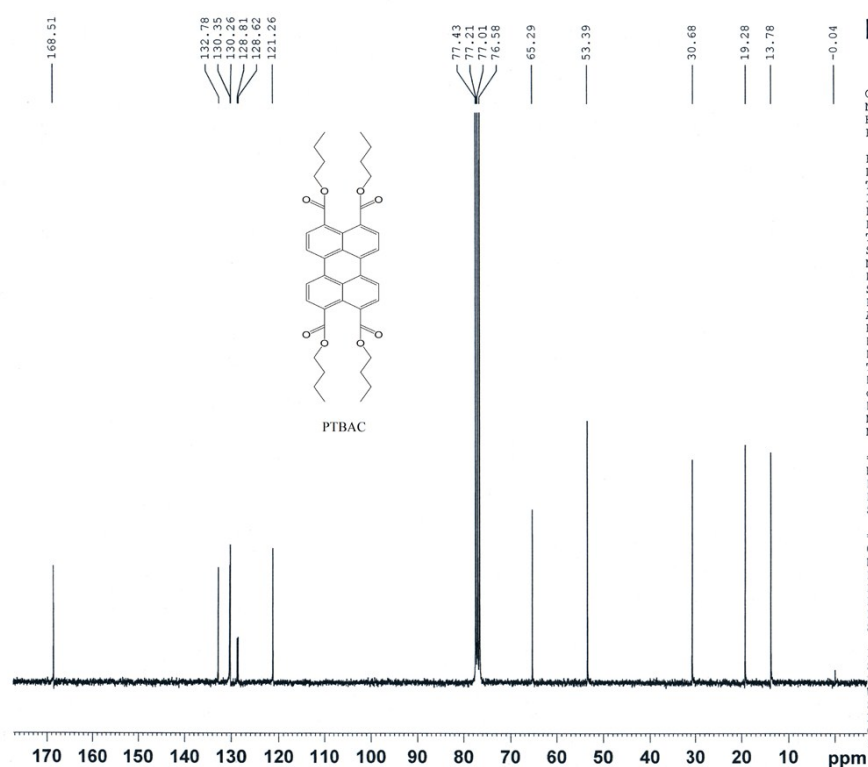
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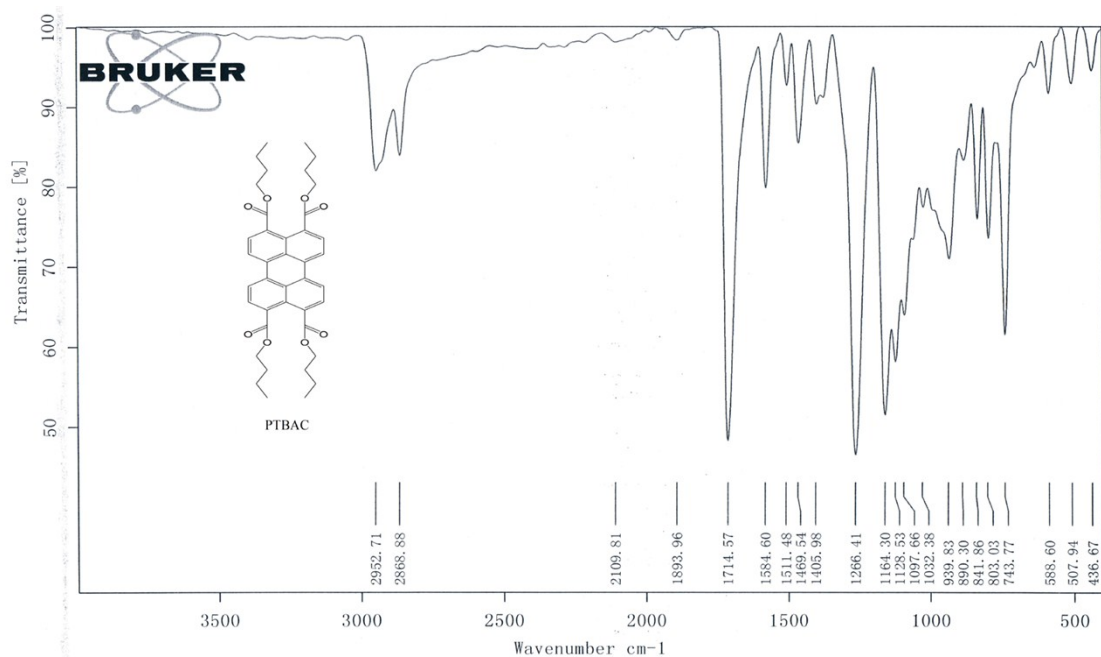
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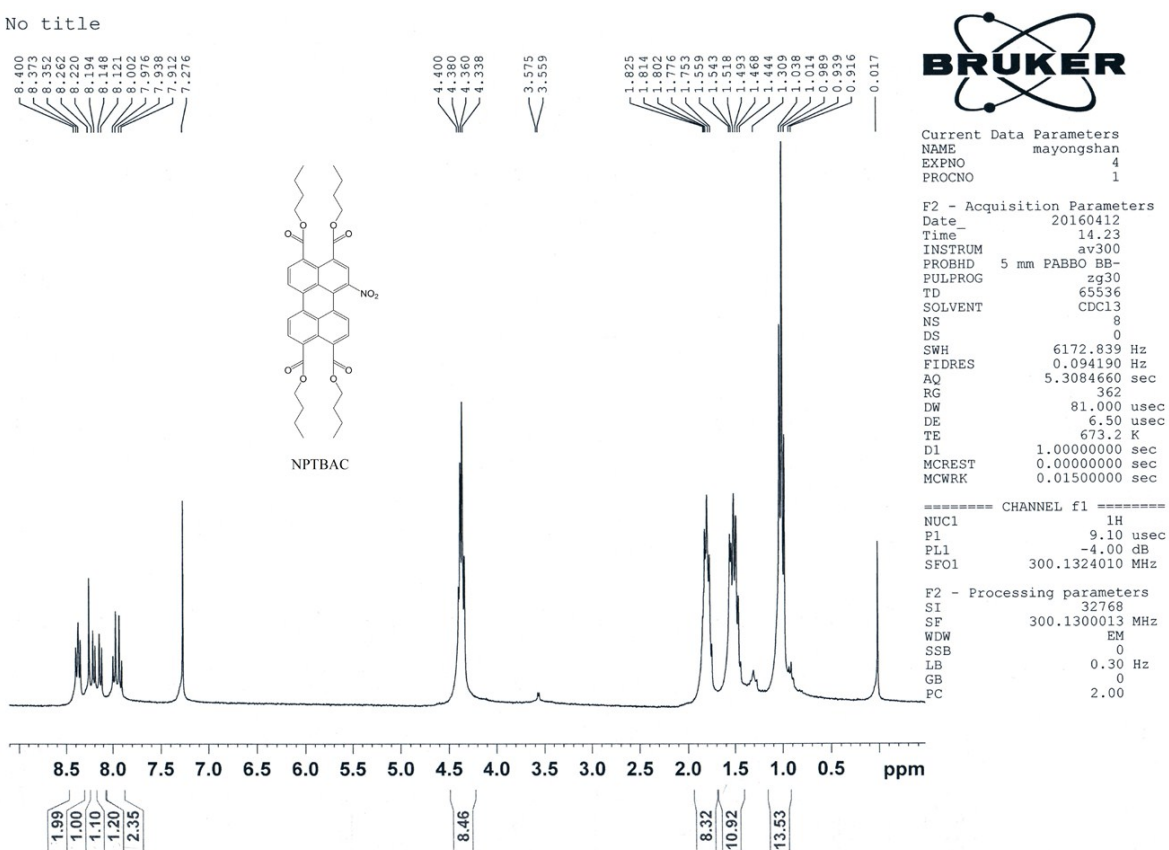
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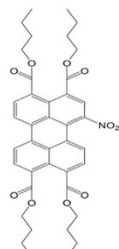
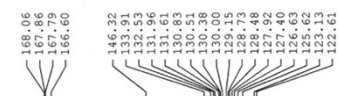
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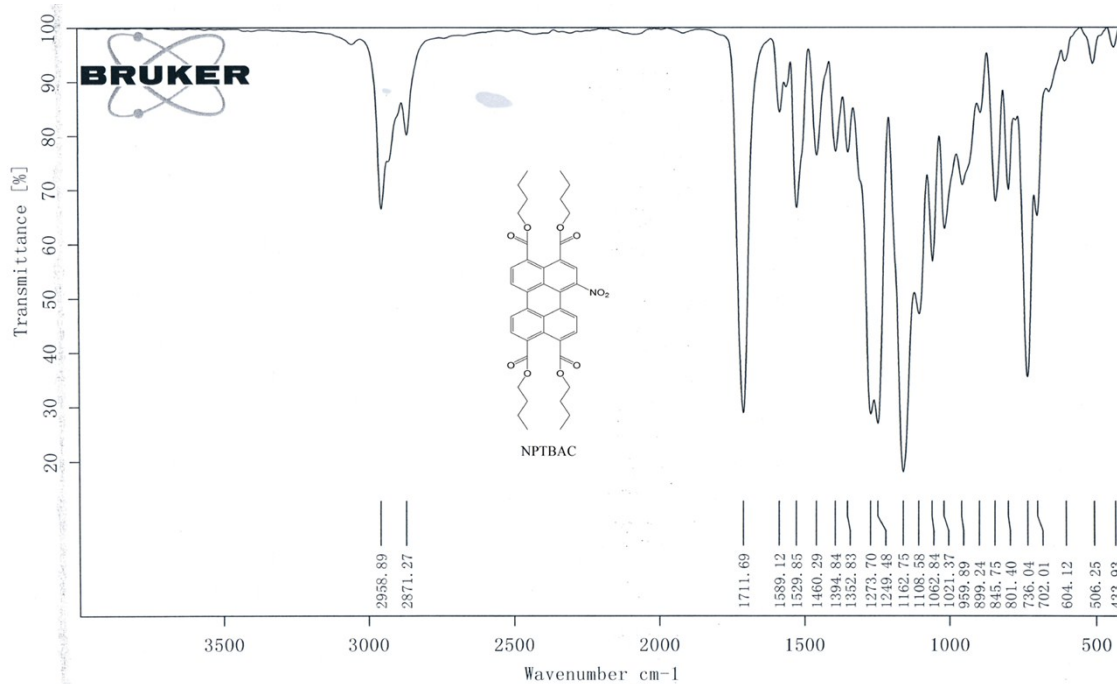
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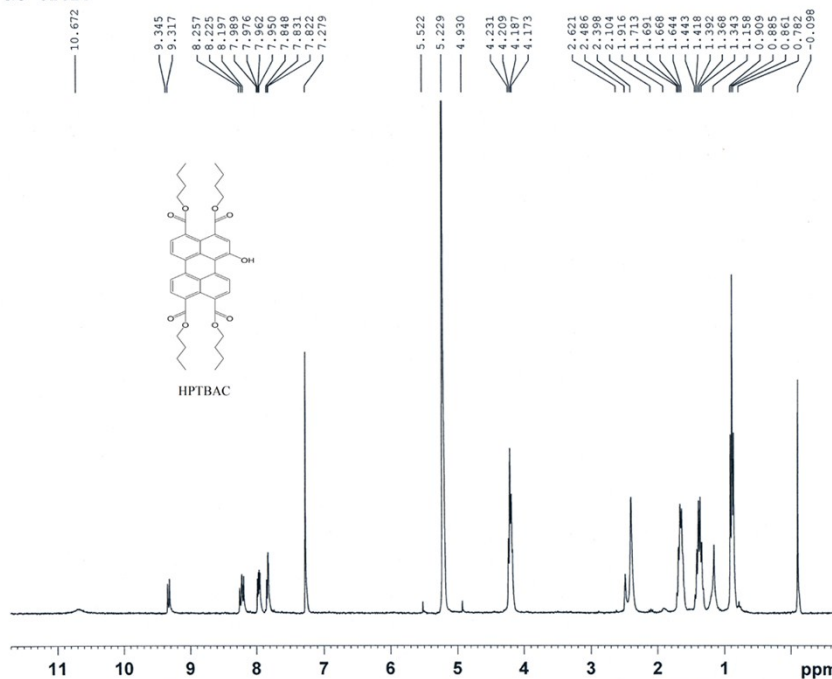
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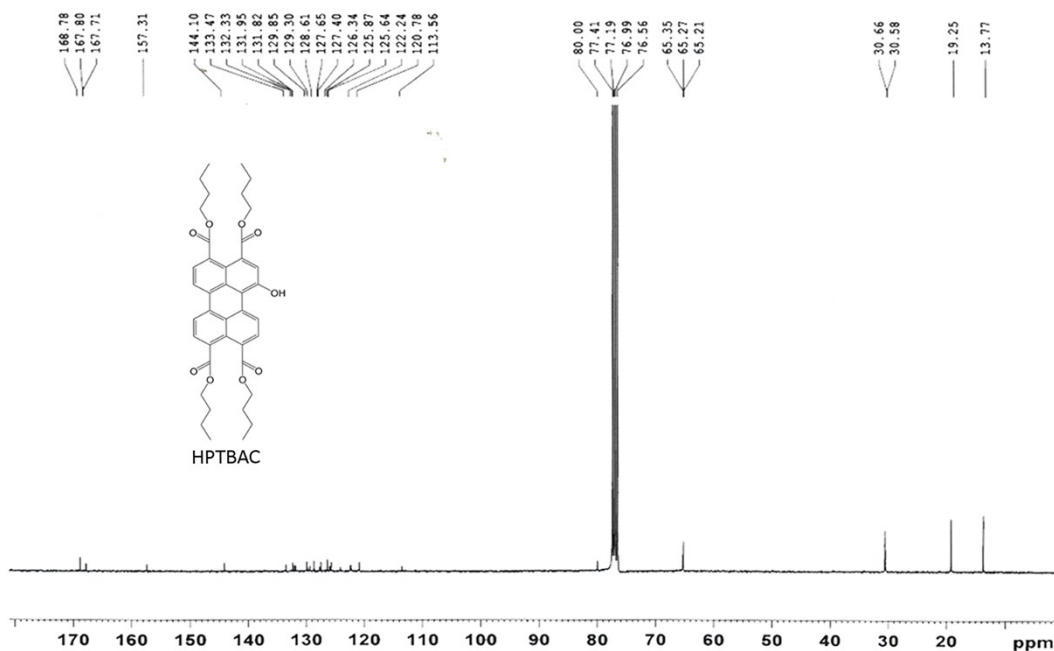


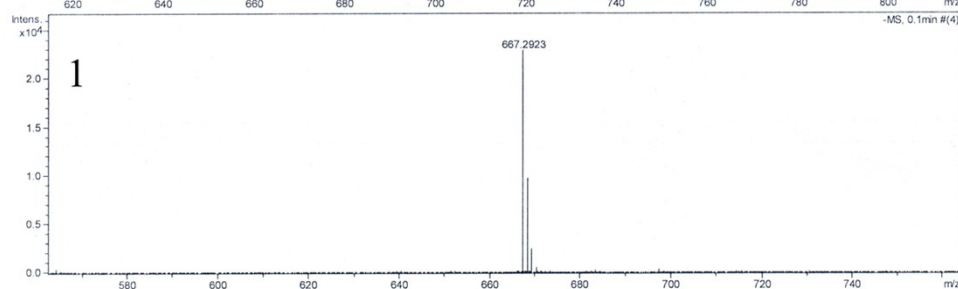
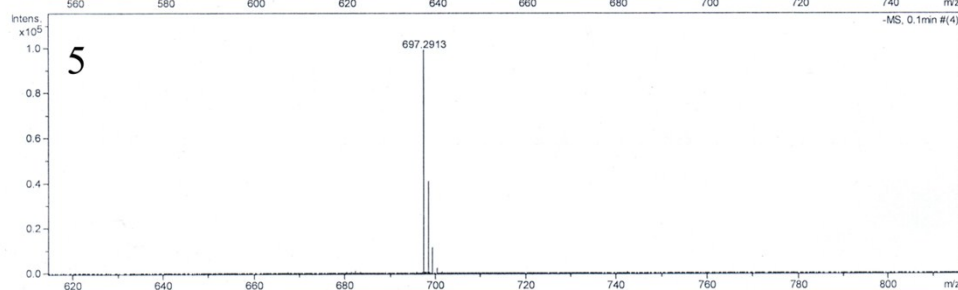
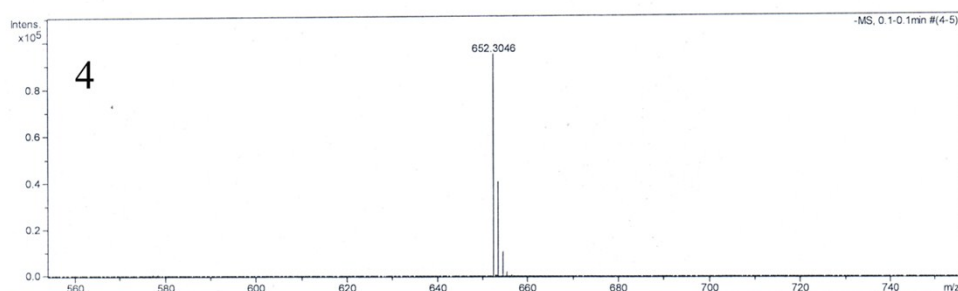
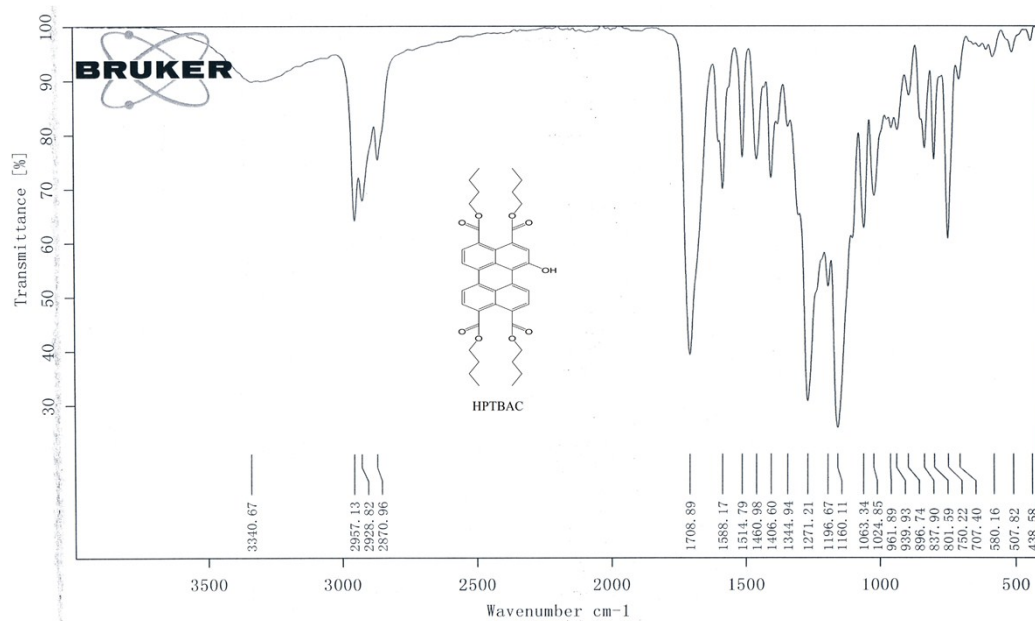
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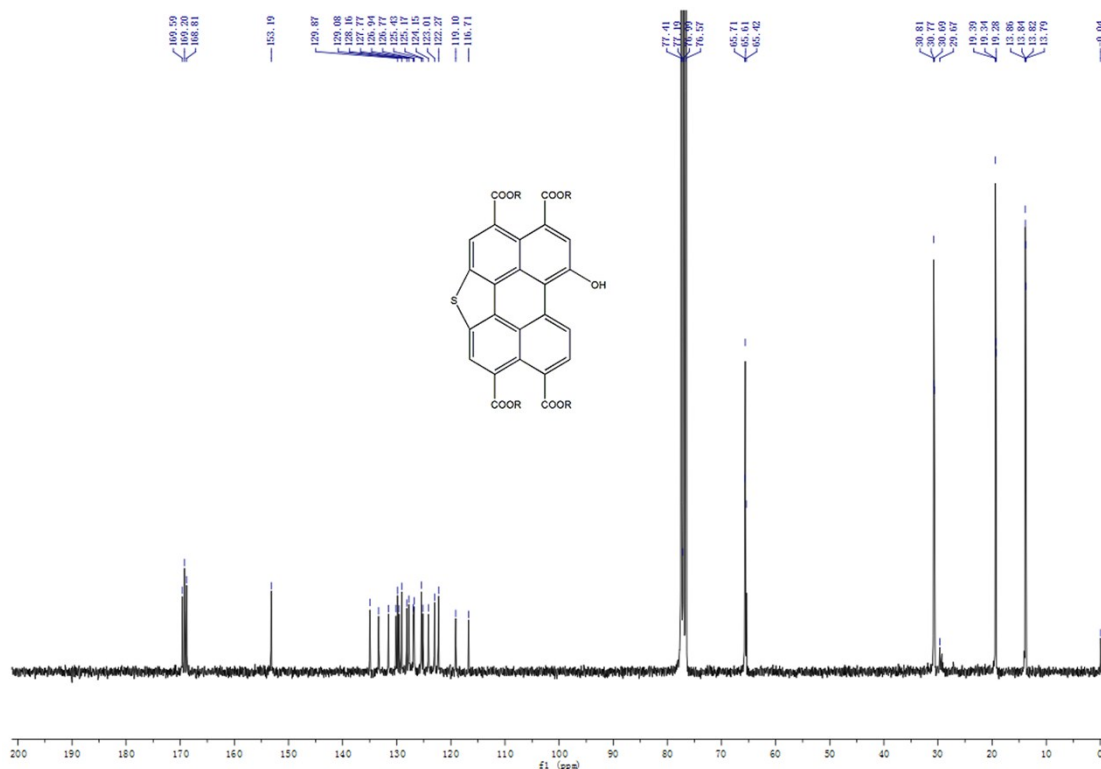
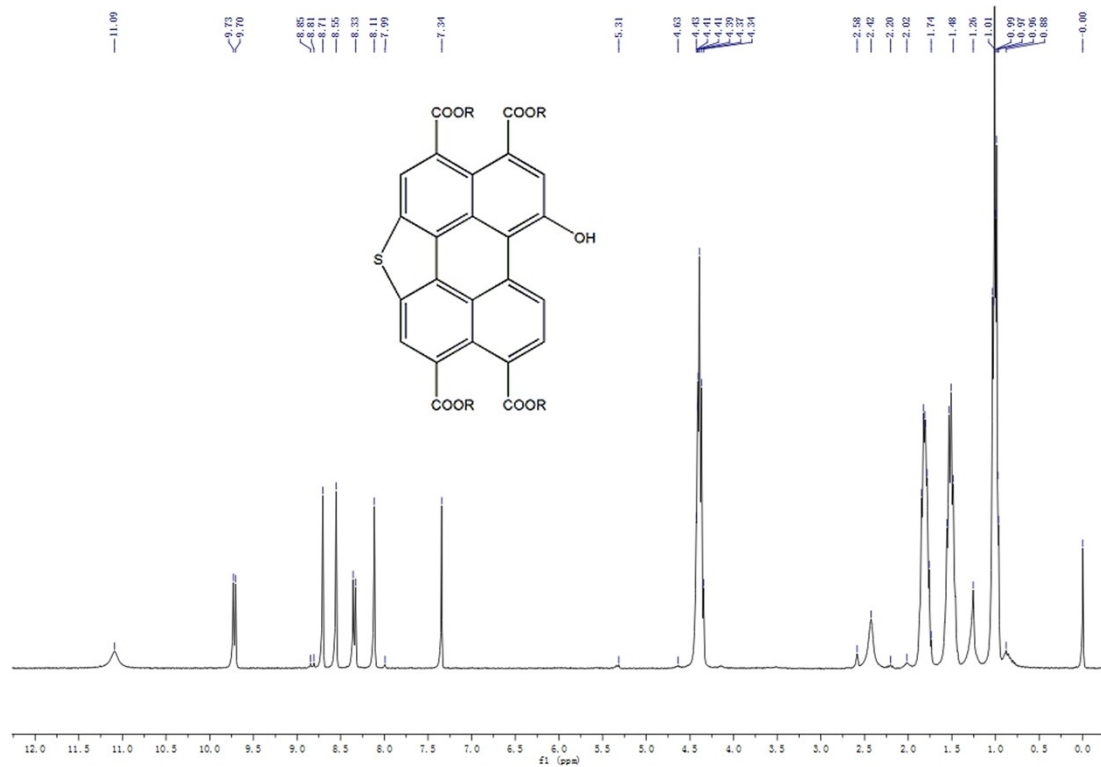
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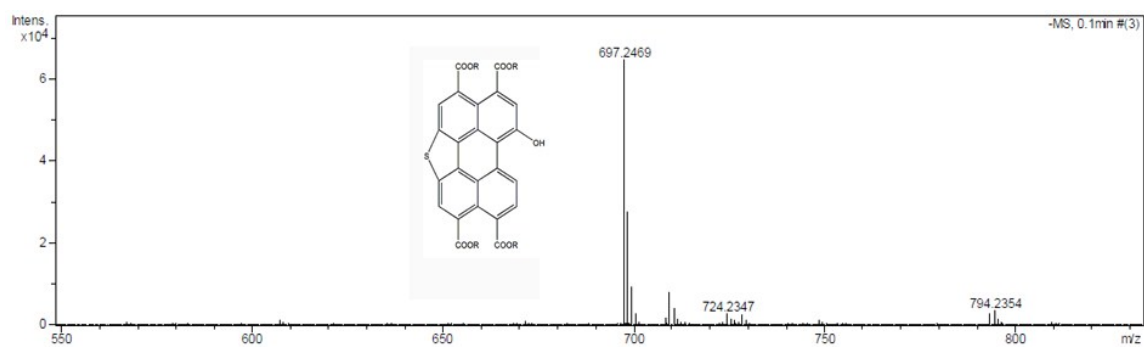
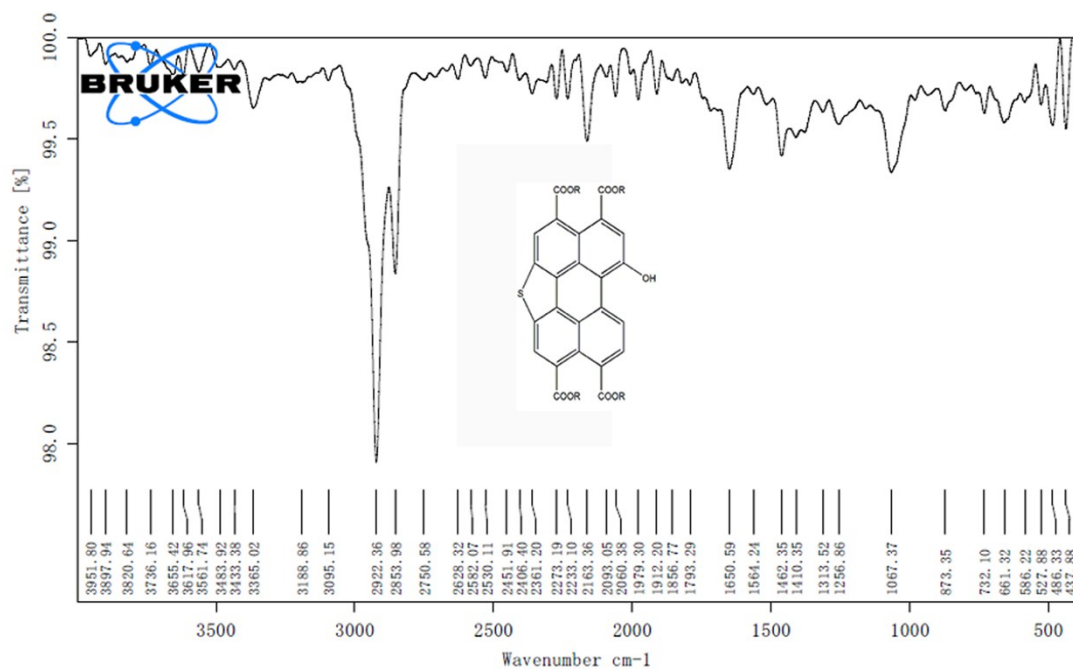


Fig. S-1 Job's plot for probes **1** and **2** with  $F^-$  ions.

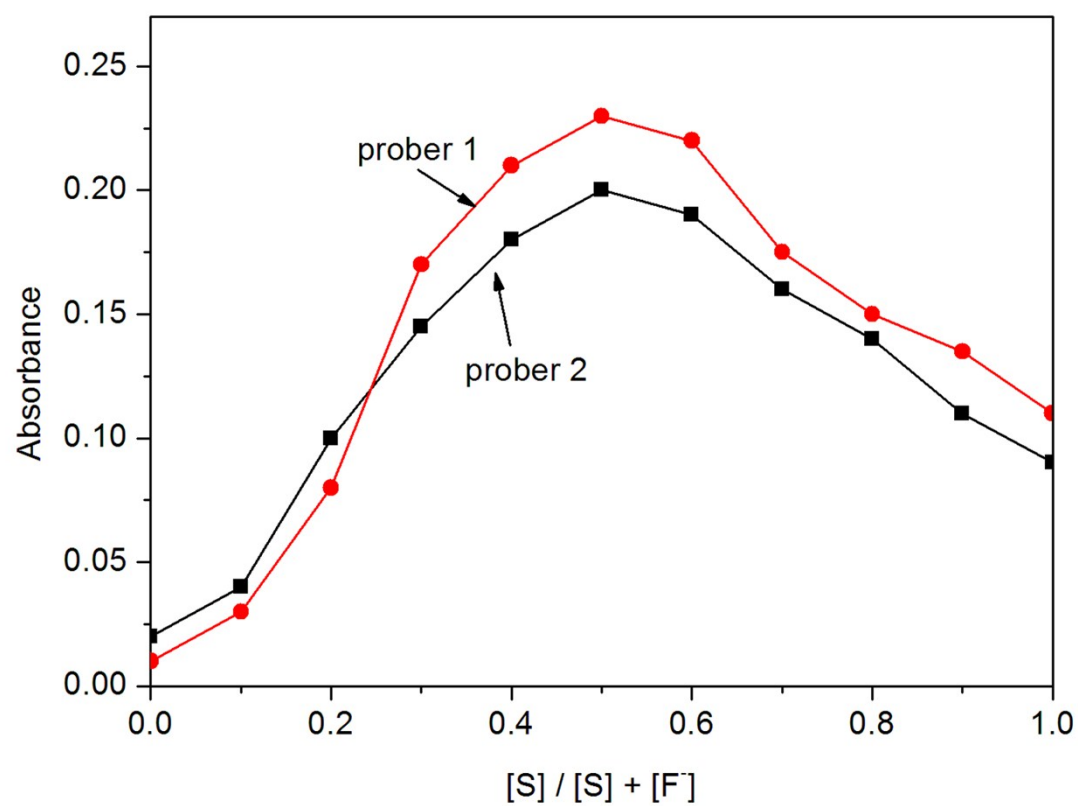


Fig. S-2 Plot of (a) the emission intensity of sensor **1** at 517 nm, (b) the emission intensity of sensor **2** at 475 nm vs concentration of F<sup>-</sup> in DCM.

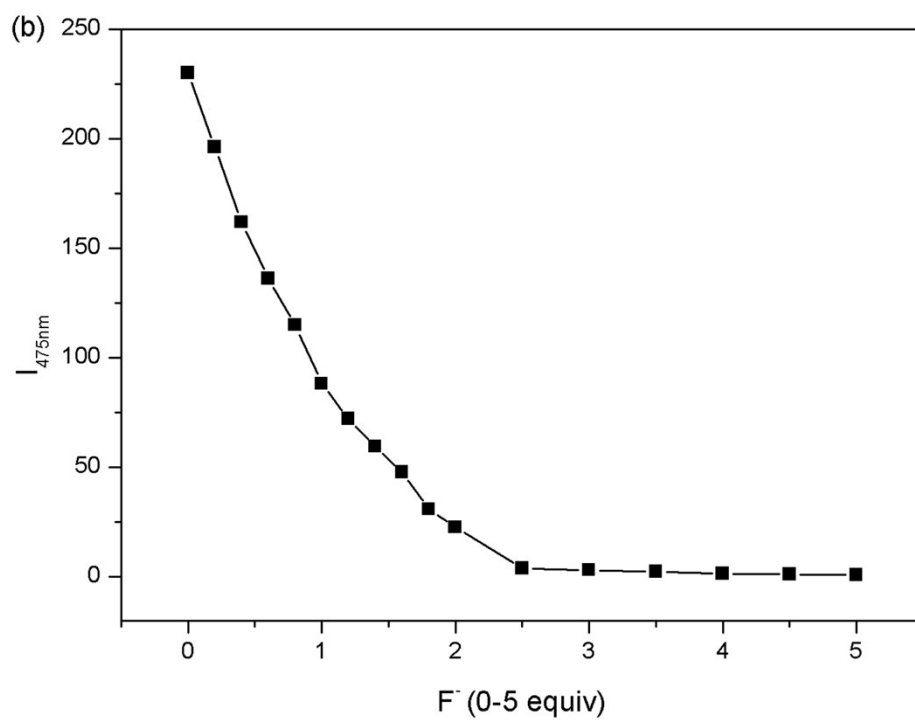
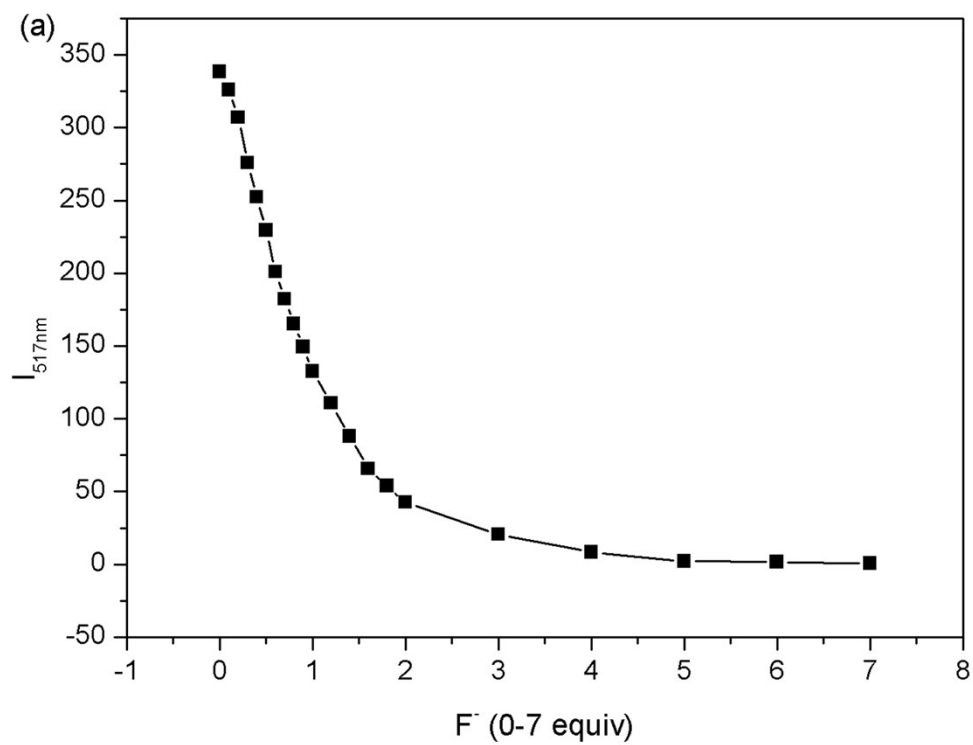


Fig. S-3 Cell cytotoxic effect of (a) probes **1** and (b) **2** on Human Lung Cancer A549 Cells. (1, control; 2, 0.01  $\mu$ M; 3, 0.1 $\mu$ M; 4, 1  $\mu$ M; 5, 10  $\mu$ M; 6, 50  $\mu$ M. Data are expressed as mean values standard error of the mean of five independent experiments).

