

## Supporting information

### Design of a ratiometric fluorescent probe for benzenethiols based on thiol-sulfoxide reaction

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### Table of contents

General Methods and Instruments.....	S2
Experimental Section.....	S3-S4
Figure S1. Absorption and emission of <b>BSFO</b> and <b>BSFI</b> in buffer solution.....	S5
Figure S2. HRMS spectrum of <b>BSFO</b> + benzenethiols.....	S6
Figure S3. Comparison <sup>1</sup> H NMR spectra.....	S7
Figure S4. Visible color and fluorescence color changes.....	S8
Figure S5. Plot of the emission response to benzenethiols.....	S9
Figure S6. Time course kinetic measurement.....	S10
Figure S7-8. HPLC analysis of <b>BSFO</b> and <b>BSFI</b> .....	S11-12
Table S1. Measurement of benzenethiol concentrations in Huangpu River....	S13
<sup>1</sup> H NMR and <sup>13</sup> C NMR spectra of <b>BSFO</b> and <b>BSFI</b> .....	S14-15

## General Methods and Instruments

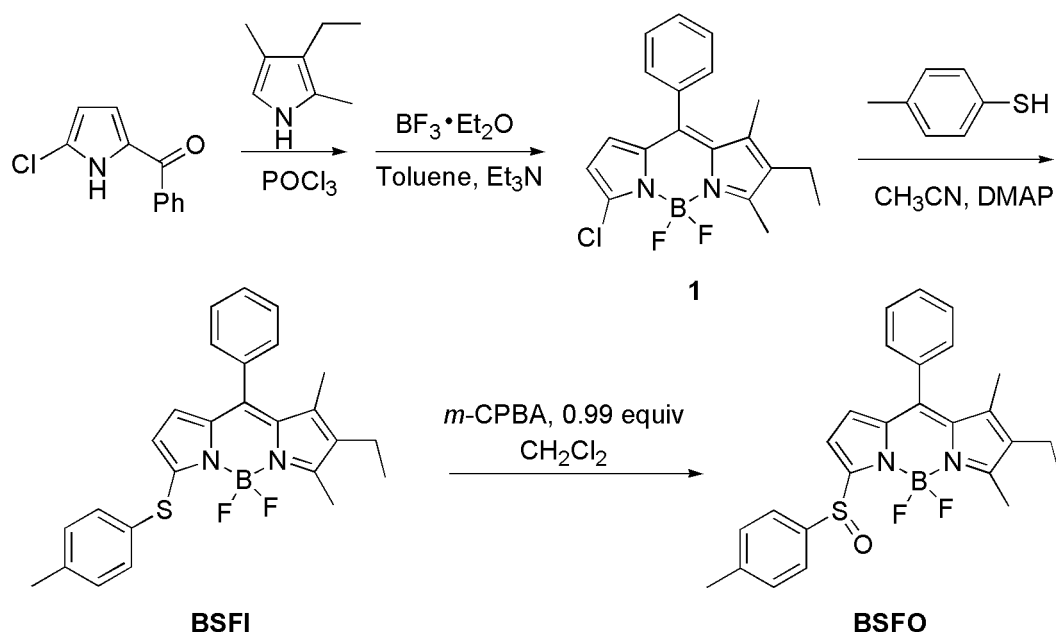
All chemicals were purchased from commercial suppliers and used without further purification unless otherwise specified. 2-Chloro-5-benzoyl-pyrrole<sup>1</sup>, 2,4-dimethyl-3-ethylpyrrole<sup>2</sup>, 3-chloro-5,7-dimethyl-6-ethyl-8-phenyl-BODIPY<sup>3</sup> were prepared according to literature procedures.

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on spectrometer operating at 400 MHz and 100 MHz, respectively. Deuterated chloroform was used as the solvent, TMS as internal standard. Mass spectra were measured on a HP 1100 LC-MS spectrometer. UV-vis spectra were measured using a Shimadzu UV-2550 spectrophotometer. Fluorescence spectroscopic measurements were conducted on a Varian Cary Eclipse fluorescence spectrophotometer. TLC analysis was performed on silica gel plates and column chromatography was conducted over silica gel (mesh 200–300), both of which were obtained from the Qingdao Ocean Chemicals.

For absorption or fluorescence measurements, compounds were dissolved in EtOH to obtain stock solutions (2-5 mM). These stock solutions were diluted with aqueous solutions to the desired concentration.

1. Petruso, S.; Caronna, S. *J. Hetero. Chem.* **1992**, *29*, 355-357.
2. Mula, S.; Ray, A. K.; Banerjee, M.; Chaudhuri, T.; Dasgupta, K.; Chattopadhyay, S. *J. Org. Chem.* **2008**, *73*, 2146-2154.
3. Zhao, C.; Zhang, Y.; Feng, P.; Cao, J. *Dalton Trans.* **2012**, *41*, 831-838.

## Experiential Section



Scheme S1. Synthesis of **BSFO** and **BSFI**.

**Synthesis of 3-(4-methylphenyl)sulfenyl-5,7-dimethyl-6-ethyl-8-phenyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BSFI).** A reaction mixture of **1** (0.358 g, 1 mmol), *p*-thiocresol (0.149 g, 1.2 mmol) and Et<sub>3</sub>N (3 mL) in 20 mL CH<sub>3</sub>CN was stirred for 24h at room temperature. Excess CH<sub>3</sub>CN was removed under vacuum, and the residue was dissolved in ethyl acetate, washed H<sub>2</sub>O, dried over Na<sub>2</sub>SO<sub>4</sub>. The crude product was purified by flash chromatography (silica gel) to afford **BSFI** (0.289 g, 65%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 7.51 (d, 2H), 7.46-7.43 (m, 3H), 7.32-7.27 (m, 2H), 7.20 (d, 2H), 6.21 (d, *J* = 4 Hz, 1H), 5.77 (d, *J* = 4 Hz, 1H), 2.62 (s, 3H), 2.38-2.32 (m, 5H), 1.41 (s, 3H), 1.02 (t, *J* = 8 Hz, 3H); <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 158.8, 152.2, 139.9, 139.3, 139.0, 134.3, 130.2, 129.0, 128.3, 127.7, 127.0, 116.9, 21.3, 17.1, 14.4, 13.0, 12.1; HRMS (ESI) calcd for C<sub>26</sub>H<sub>24</sub>N<sub>2</sub>BF<sub>2</sub>S [M - H]<sup>-</sup>: 445.1721. Found: 445.1760.

**Synthesis of 3-(4-methylphenyl)lsulfinyl-5,7-dimethyl-6-ethyl-8-phenyl-4,4-difluoro-4-bora- 3a,4a-diaza-s-indacene (BSFO).** TO a solution of **BSFI** (0.223 g, 0.5 mmol) in 20 mL dichloromethane was added 0.99 equivalents of *m*-CPBA (0.085 g, 0.49 mmol) at 0 °C. The reaction was then stirred for 30 minutes. Excess potassium carbonate was added to neutralize any acids, and washed with water. The organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and evaporated in vacuo. The crude product was further purified by flash chromatography (silica gel) to afford **BSFO** (0.169 g, 73%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ.7.79 (d, 2H), 7.52-7.47 (m, 4H), 7.35-7.28 (m, 3H), 6.73 (d, *J* = 4 Hz, 1H), 6.26 (d, *J* = 4 Hz, 1H), 2.69 (s, 3H), 2.38 (m, 5H), 1.47 (s, 3H), 1.04 (t, *J* = 7.6 Hz, 3H); <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 166.6, 152.0, 143.5, 141.9, 141.6, 141.3, 137.8, 137.8, 135.9, 134.88, 133.5, 129.8, 129.6, 128.8, 128.6, 128.6, 128.5, 125.2, 124.4, 114.2, 21.4, 17.1, 14.0, 13.7, 12.4; HRMS (ESI) calcd for C<sub>26</sub>H<sub>24</sub>N<sub>2</sub>BF<sub>2</sub>SO [M - H]<sup>-</sup>: 461.1670. Found: 461.1445.

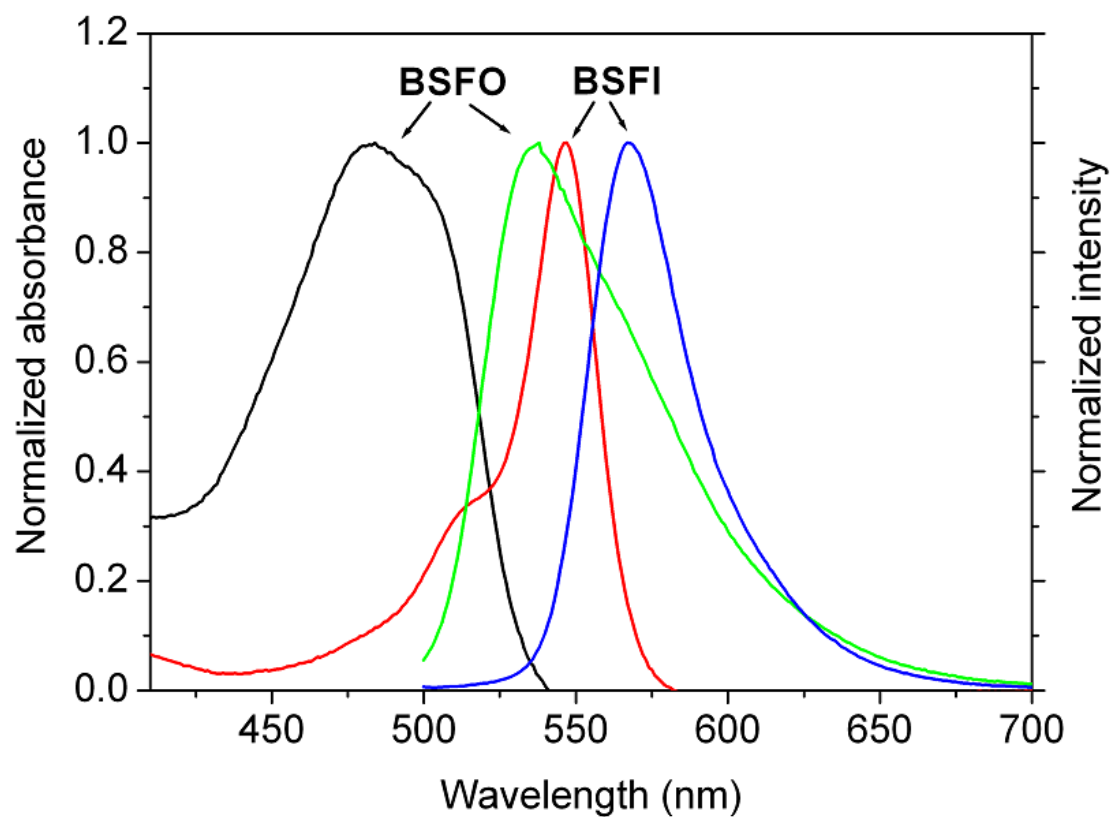


Figure S1. (a) Normalized absorption spectra and (b) Normalized fluorescent emission spectra of **BSFO** and **BSFI** in a phosphate buffer (pH 6.1, 25 mM sodium phosphate buffer, 50% EtOH as co-solvent) at room temperature.

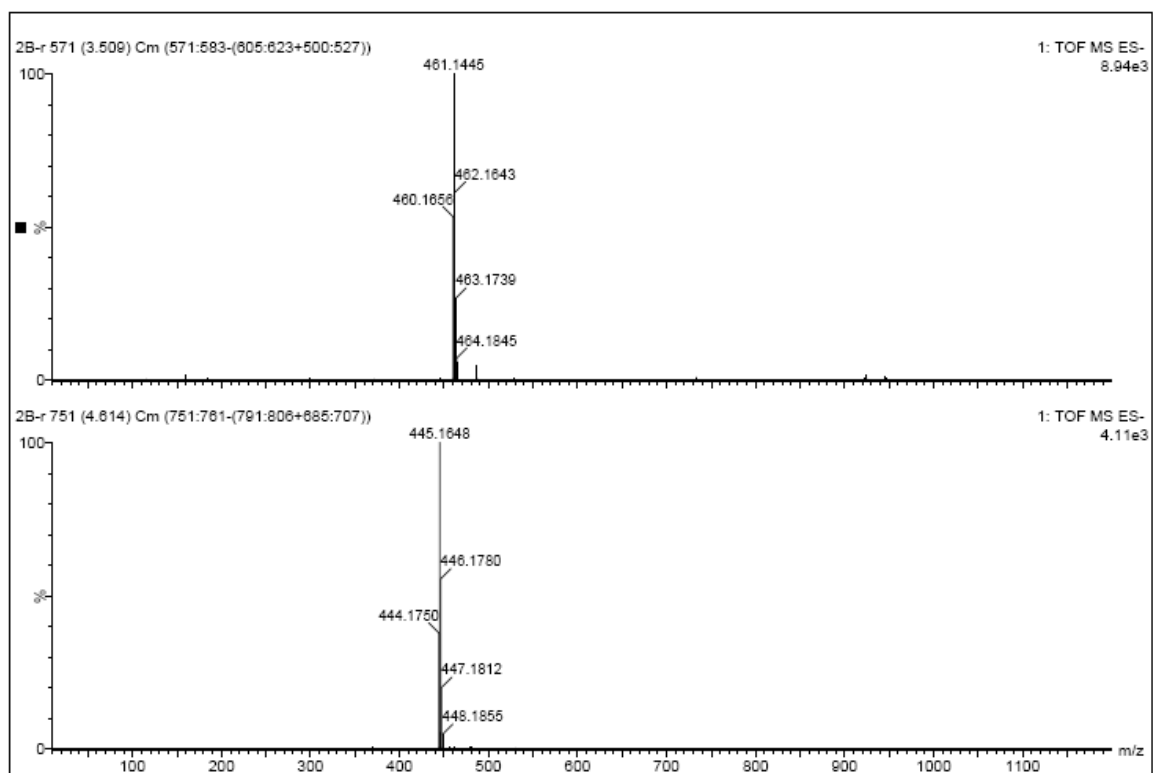


Figure S2. HRMS spectrum of **BSFO** + benzenethiols.

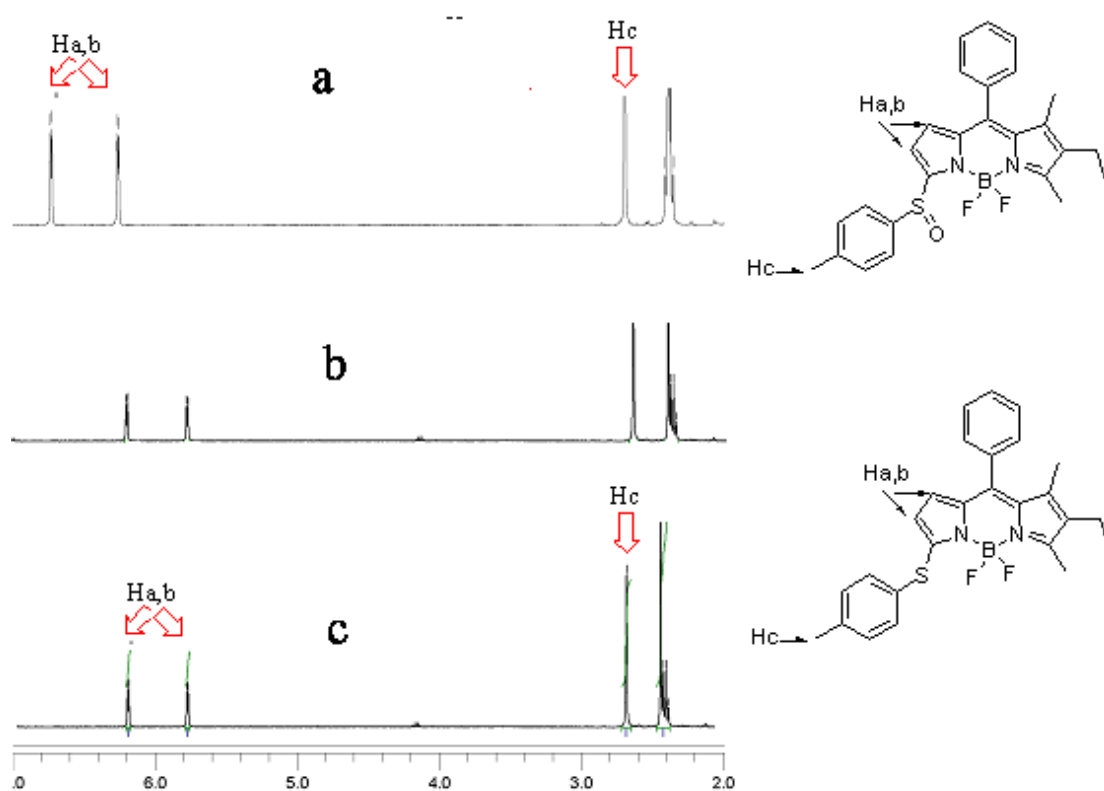


Figure S3. Partial  $^1\text{H}$  NMR spectra of (a) **BSFO**, (b) the isolated product of **BSFO** + benzenethiols, (c) **BSFI**.

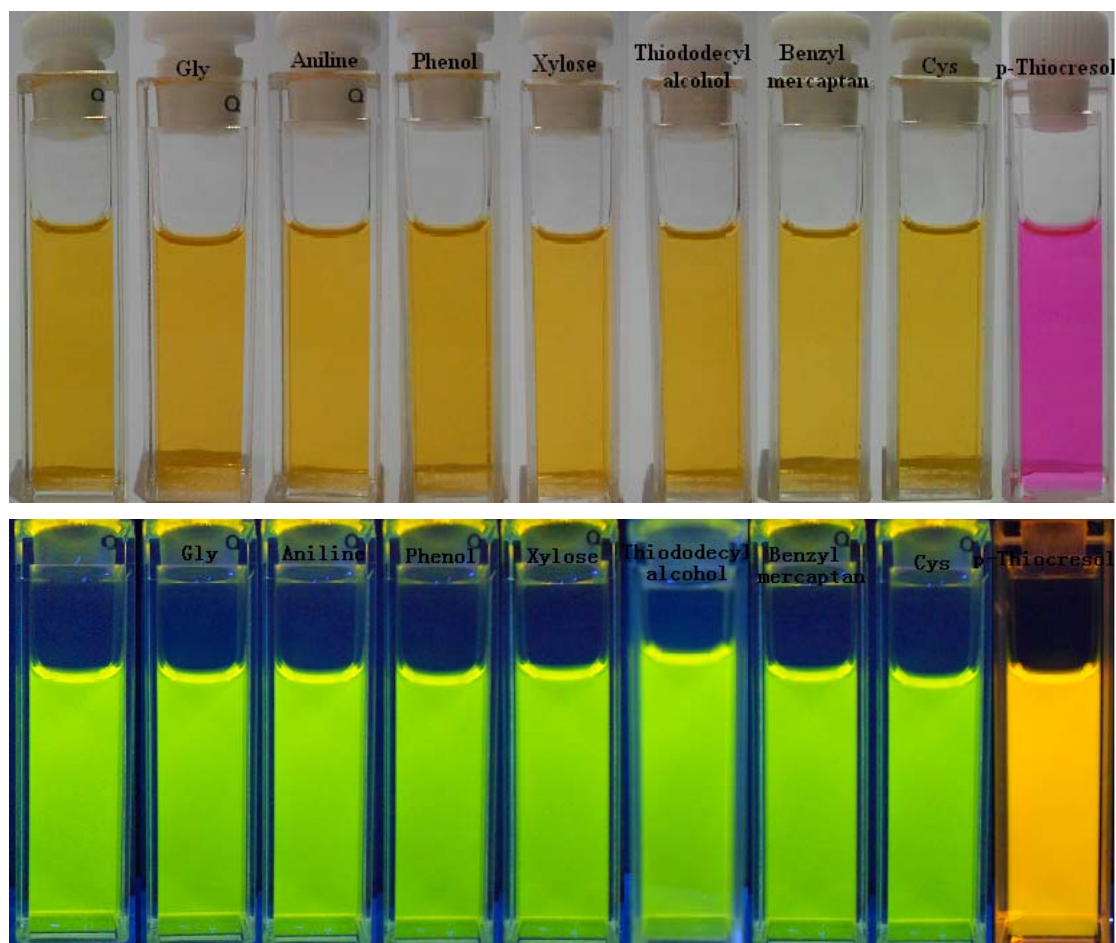


Figure S4. Visible color changes (up) and fluorescence color changes (bottom) of **BSFO** after the addition of 100 equiv of various related species (from left to right represents **BSFO** only, glycine,  $\text{PhNH}_2$ ,  $\text{PhOH}$ , D-xylose,  $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$ ,  $\text{PhCH}_2\text{SH}$ , cysteine, and p-thiocresol respectively).



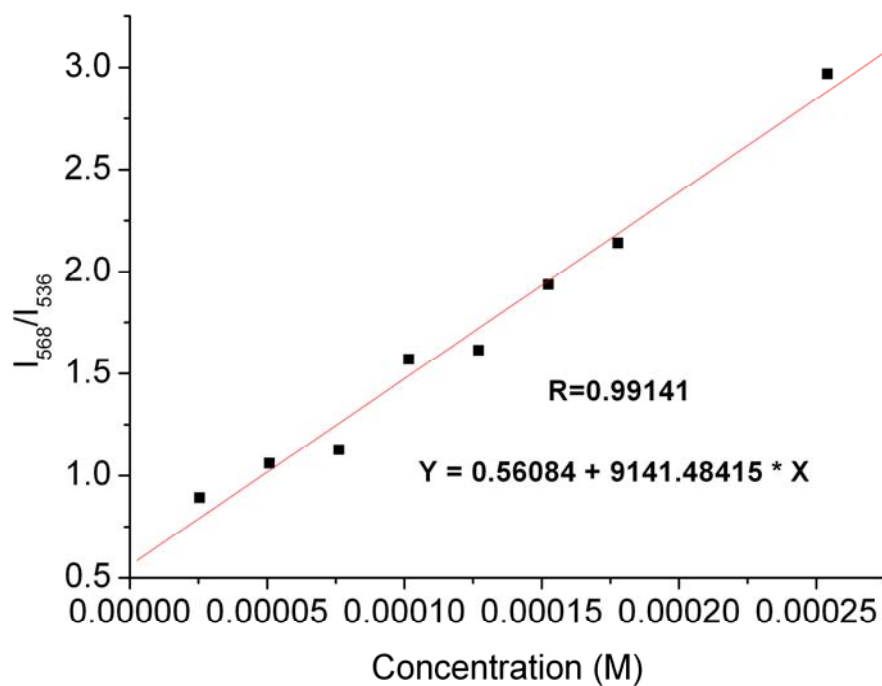


Figure S5. Calibration plot of the emission response to benzenethiols concentrations. The Standard Deviation was obtained by fluorescence responses to be  $\sigma = 2.26 \times 10^{-3}$ , therefore, the detection limit was calculated by the formula  $(3\sigma/k)$  and gave a result as  $7.41 \times 10^{-7}$  M.

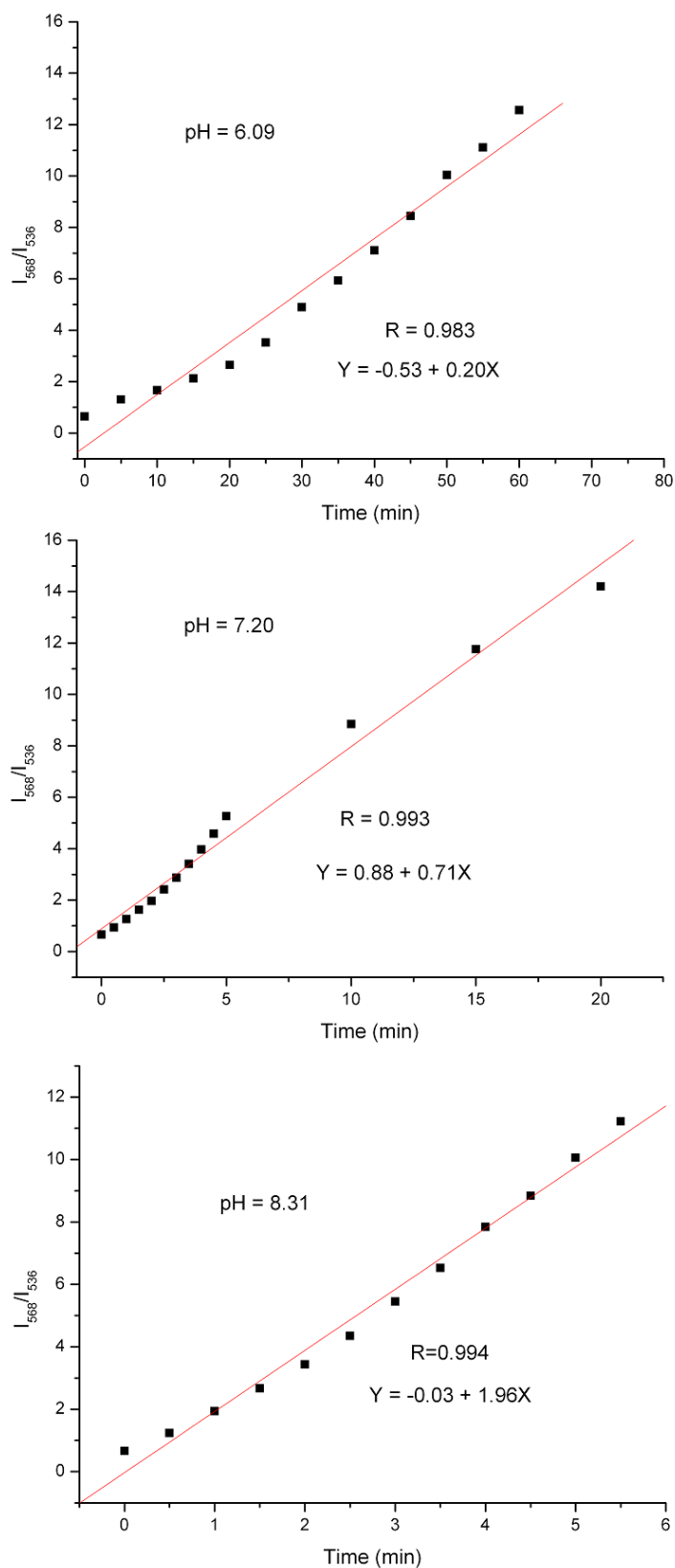


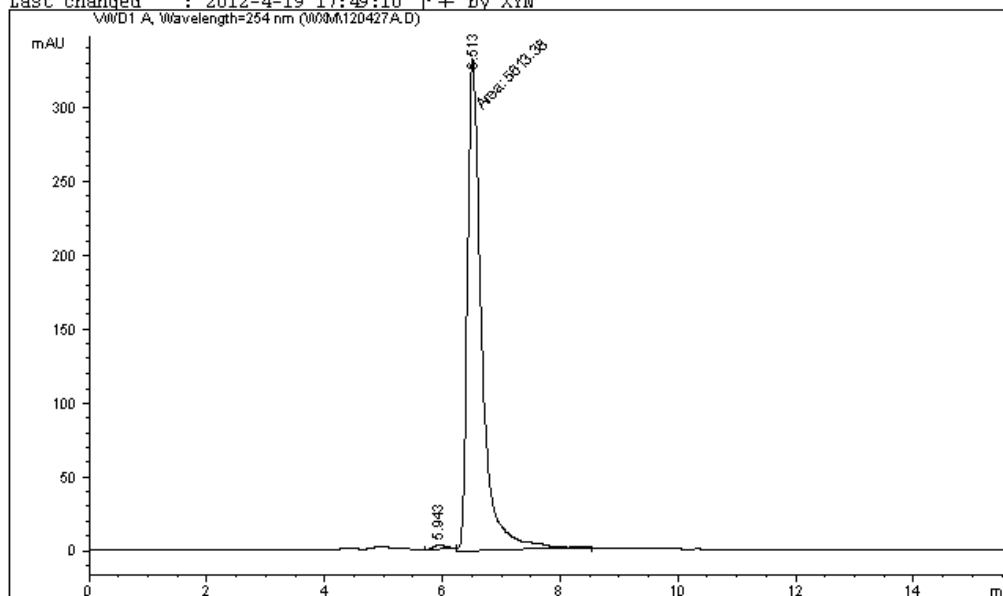
Figure S6. Time course kinetic measurement of the emission response of **BSFO** to benzenethiols. Data ( $I_{568}/I_{536}$ ) were collected under pseudo-first-order conditions (10  $\mu\text{M}$  **BSFO**, 1 mM thiophenol) with excitation at  $\lambda_{\text{ex}} = 484$  nm.

Data File C:\HPCHEM\1\DATA\WXM\120427A.D

Sample Name: a

254nm 0.6ml/min CH3OH

=====  
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Sample Name : a Location : Vial 1  
Acq. Operator : wxm  
Acq. Instrument : Instrument 1  
Method : C:\CW.M  
Last changed : 2012-4-19 17:49:10 下午 by XYN



=====  
Area Percent Report  
=====  
Sorted By : Signal  
Multiplier : 2.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs  
  
Signal 1: WVD1 A, Wavelength=254 nm  

Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	5.943	PV	0.2257	42.34183	2.89913	1.4973
2	6.513	MM	0.2816	5613.38232	332.20569	198.5027

  
Totals : 5655.72415 335.10482  
  
Results obtained with enhanced integrator!  
=====  
\*\*\* End of Report \*\*\*

Instrument 1 2012-4-27 16:16:01 下午 wxm

Page 1 of 1

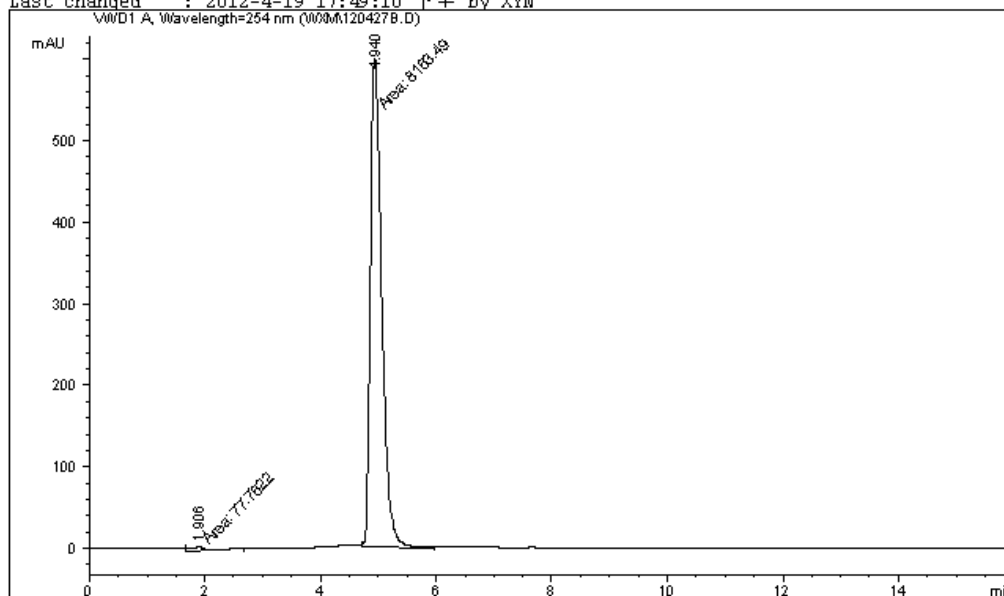
Figure S7. HPLC analysis of **BSFL**.

Data File C:\HPCHEM\1\DATA\WXM\120427B.D

Sample Name: b

254nm 0.6ml/min CH3OH

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Acq. Operator : wxm  
Acq. Instrument : Instrument 1  
Method : C:\CW.M  
Last changed : 2012-4-19 17:49:10 下午 by XYN



=====  
Area Percent Report  
=====  
Sorted By : Signal  
Multiplier : 2.0000  
Dilution : 1.0000  
Use Multiplier & Dilution Factor with ISTDs  
  
Signal 1: WVD1 A, Wavelength=254 nm  

Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	1.906	MM	0.2742	77.76221	4.72676	1.8871
2	4.940	MM	0.2273	8163.48633	598.68280	198.1129

  
Totals : 8241.24854 603.40956  
  
Results obtained with enhanced integrator!  
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\*\*\* End of Report \*\*\*

Instrument 1 2012-4-27 15:43:06 下午 wxm

Page 1 of 1

Figure S8. HPLC analysis of **BSFO**.

Table S1. Measurement of benzenethiol concentrations in water samples from Huangpu River.

The amount of benzenethiols in the Huangpu river sample was estimated by using the internal standard method with standard benzenethiols solution (5 mM stock) in ethanol.

The crude water samples from Huangpu River were adjusted to pH 6.1 phosphate buffer, and different concentrations of benzenethiol (0.3, 1, 5, 10, 30, 100  $\mu\text{M}$ ) were obtained by diluting the stock solution into a solvent mixture of ethanol and PB buffer (3 mL, V/V = 1:1, pH 6.1). The resulting samples were further treated with probe **BSFO** (10  $\mu\text{M}$ ). The resulting solution was shaken well. After 30 min, the emission was recorded. The ratiometric emission response ( $I_{568}/I_{520}$ ) of **BSFO** was plotted against different concentrations of benzenethiols, a calibration curve revealing a good linear relationship was obtained, with R-value = 0.99. Then the unknown concentration of benzenethiols in the Huangpu river sample was determined by the calibration curve.

sample	Concentration of benzenethiols (mol/L)	Concentration of benzenethiols determined by <b>BSFO</b> (mol/L)
1	$2.40 \times 10^{-4}$	$2.82 \times 10^{-4}$
2	$6.84 \times 10^{-5}$	$6.51 \times 10^{-5}$
3	$3.42 \times 10^{-6}$	$3.10 \times 10^{-6}$
4	0	No detection

