

Supporting Information

A novel fluorogenic hybrid material for selective sensing of thiophenols †

Wenwen Zhao,^a Weimin Liu,^a Jiechao Ge,^a Jiasheng Wu,^a Wenjun Zhang,^{*b} Xiangmin Meng^a and Pengfei Wang^{*a}

Contents

1. Synthesis routes of Material **I**.
2. Synthesis routes of compound **2** and **3**.
3. **Figure S1** Time resolved fluorescence measurements of Material **III** towards p-toluenethiol.
4. **Figure S2** TGA calculations.
5. **Table S1** Surface areas, pore volumes, and pore diameters of the Materials **II** and **III**.
6. **Figure S3** Calculation the Detection Limit of Material **III** towards p-toluenethiol.
7. **Figure S4** ESI-MS and ¹H NMR Spectrum Analysis.

1. Synthesis of Material I.

A typical method was used to synthesize Material I according to the procedure described previously. Cetyltrimethylammonium bromide (CTAB) (0.1 g) was dissolved in the deionized water (48 g), to which NaOH (0.7 mL, 2M) was added with vigorous stirring at room temperature. Then the temperature of the solution was raised to 80 °C and kept for 0.5 h. To the clear solution, tetraethyloxysilane (TEOS) (0.6 g) was added quickly. A white precipitate was observed after 2 min and the mixture was continuously stirred for additional 2 h. After the mixture cooling down to the room temperature, the white solid products were isolated by filtration, washed thoroughly with water, and dried under vacuum for 4 h at 40 °C. The surfactant was removed by acid/solvent extraction, using a solution of methanol (15 mL) containing aqueous HCl (0.15 mL, 37.5%). The mixture was stirred at room temperature for 24 h, then filtered, washed with methanol several times and dried under vacuum.

2. Synthesis of 2 and 3.

Under nitrogen atmosphere, a solution of relevant thiols (4.6 mmol, 1.1 mL of 3-mercaptopropyltrimethoxysilane for **2** and 0.35 mL of $\text{CH}_3(\text{CH}_2)_2\text{SH}$ for **3**) in dry CH_2Cl_2 (15 mL) was added dropwise at room temperature for 40 min into a solution of compound **1** (3.84 mmol, 900 mg) dissolved in dry CH_2Cl_2 (20 mL). After the addition, the mixture was stirred at room temperature for another 3 h. The reaction solution was treated with the same process as compound **1** to produce the crude yellow oil product. Finally, the crude product was further purified by column chromatography on silica gel (pure dichloromethane for **2** and petroleum: dichloromethane = 70:50 for **3**) to give **2** (300 mg, 22%) or **3** (200 mg, 26.2%) as yellowish liquid.

2-((3-triethoxysilyl)propyl)disulfanyl)benzenamine (2): ^1H NMR (CDCl_3 , 400 MHz, δ): $\delta=7.47(\text{dd}, 1\text{H}, J=7.5\text{ Hz}, J=1.4\text{ Hz}, \text{Ar H}), 7.14(\text{td}, 1\text{H}, J=7.9\text{ Hz}, J=1.4\text{ Hz}, \text{Ar H}), 6.73(\text{dd}, 1\text{H}, J=8.0\text{ Hz}, J=1.0\text{ Hz}, \text{Ar H}), 6.67(\text{td}, 1\text{H}, J=7.5\text{ Hz}, J=1.0\text{ Hz}, \text{Ar H}), 4.29(\text{br}, 2\text{H}, \text{NH}_2), 3.80(\text{q}, 6\text{H}, J=7.0\text{ Hz}, 3\text{OCH}_2\text{CH}_3), 2.75(\text{t}, 2\text{H}, J=7.1\text{ Hz}, \text{SCH}_2), 1.84(\text{m}, 2\text{H}, \text{SCH}_2\text{CH}_2), 1.22(\text{t}, 9\text{H}, J=7.0\text{ Hz}, 3\text{OCH}_2\text{CH}_3), 0.72(\text{t}, 2\text{H}, J=6.0\text{ Hz}, \text{SiCH}_2)$. ^{13}C NMR (CDCl_3 , 100 MHz, δ): $\delta=147.9, 135.5, 131.0, 119.3, 118.6, 115.8, 58.5, 41.2, 22.4, 18.4, 9.7$. HRMS (EI, m/z): $[\text{M}^+]$, calcd for $\text{C}_{15}\text{H}_{27}\text{NO}_3\text{SiS}_2$, 361.1202, found, 361.1207.

2-(propyl)disulfanyl)benzenamine (3): ^1H NMR (CDCl_3 , 400 MHz, δ): $\delta=7.42(\text{dd}, 1\text{H}, J=7.6\text{ Hz}, J=1.4\text{ Hz}, \text{Ar H}), 7.16(\text{m}, 1\text{H}, J=8\text{ Hz}, J=1.4\text{ Hz}, \text{Ar-H}), 6.75(\text{dd}, 1\text{H}, J=8\text{ Hz}, J=1.0\text{ Hz}, \text{Ar-H}), 6.68(\text{m}, 1\text{H}, J=7.6\text{ Hz}, J=1.0\text{ Hz}, \text{Ar-H}), 3.83(\text{br}, 2\text{H}, \text{NH}_2), 2.72(\text{t}, 1\text{H}, J=7.0\text{ Hz}, \text{SCH}_2), 1.73(\text{m}, 2\text{H}, \text{SCH}_2\text{CH}_2), 0.96(\text{t}, 3\text{H}, J=7.0\text{ Hz}, \text{CH}_3)$. ^{13}C NMR (CDCl_3 , 100 MHz, δ): $\delta=147.7, 135.4, 131.1, 119.4, 118.7, 116, 40.4, 22.1, 13.2$. HRMS (EI, m/z): $[\text{M}^+]$, calcd for $\text{C}_9\text{H}_{13}\text{NS}_2$, 199.0489, found, 199.0491.

3. Time resolved fluorescence measurements.

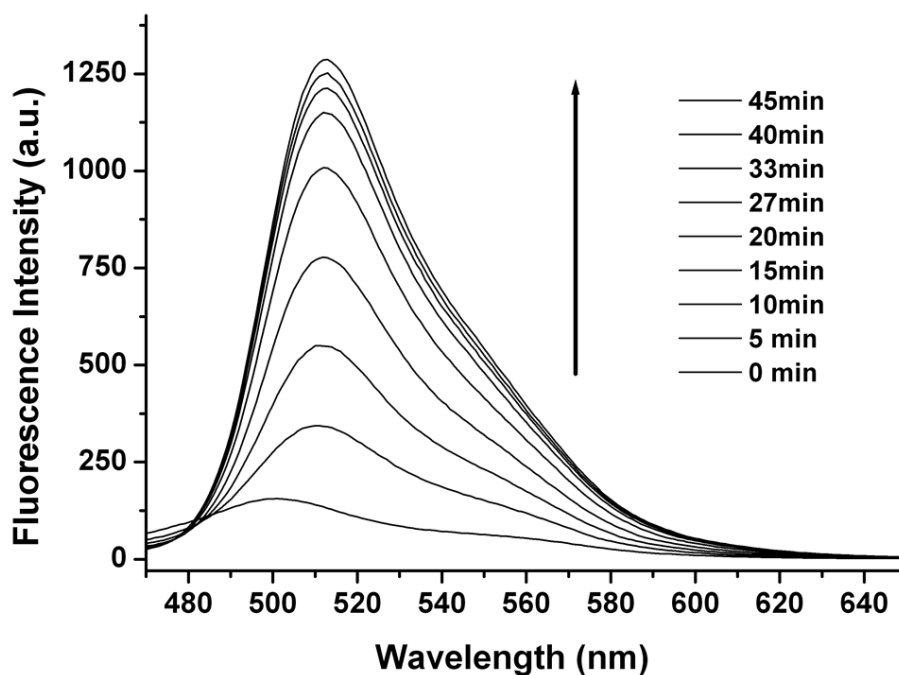


Figure S1. Reaction–time profile of Material **III** (100 ppm) sensing of *p*-toluenethiol. Material **III** was studied in a citric acid (0.1 M)-phosphate (0.2 M) buffer solution (pH 3, ethanol/water = 1/4, v/v) at room temperature upon addition of 170 μ M *p*-toluenethiol. The reaction solution was sampled for fluorescence measurement after the specified time period.

4. TGA calculations.^{S1}

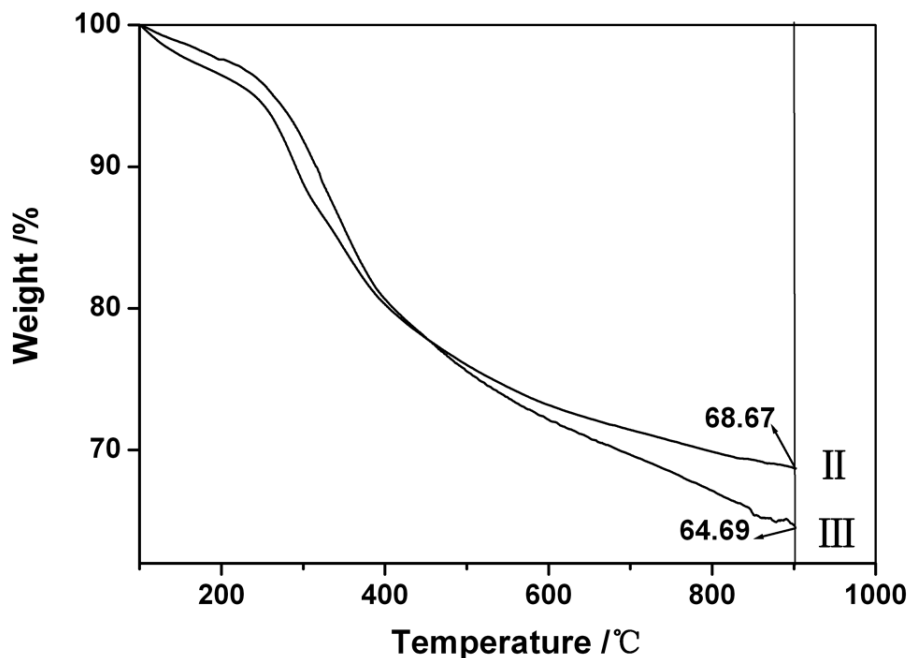


Figure S2. TGA plot of Materials **II** and **III**

In contrast to Materials **II** and **III**, the mass loss of 3.98% is attributed to the loss of the coumarin-residues during the heating process, which shows that 1 g of Material **III** contains 39.8mg of coumarin-residues.

$$\frac{0.0398g}{228g/mol} = 1.746 \times 10^{-4} mol = 0.1746 mmol$$

39.8 mg corresponds to 0.1746 mmol coumarin-residues residues per g Material **III**.

This value is divided by 0.9602 (100%-3.98%) to give the amount of coumarin-residues bound to 1g of Material **II**.

$$\frac{0.1746mmol}{0.9602} = 0.1814 mmol$$

It means that 0.1814 mmol of coumarin-residues has bound to 1g Material **II**.

5. Table S1. Surface areas, pore volumes, and pore diameters of the Materials II and III.

Sample Name	Surface Area (m ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)	Pore Diameter (nm)
Material II	621.0	0.92	2.21
Material III	270.3	0.65	1.93

6. Calculation the Detection Limit for Material III.

The detection limit was determined from the fluorescence titration data based on a reported method.^{S2} According to the result of titrating experiment, the fluorescence intensity data at 512 nm were normalized between the minimum intensity and the maximum intensity. A linear regression curve was then fitted to these normalized fluorescence intensity data, and the point at which this line crossed the ordinate axis was considered as the detection limit 7.4×10^{-6} M.

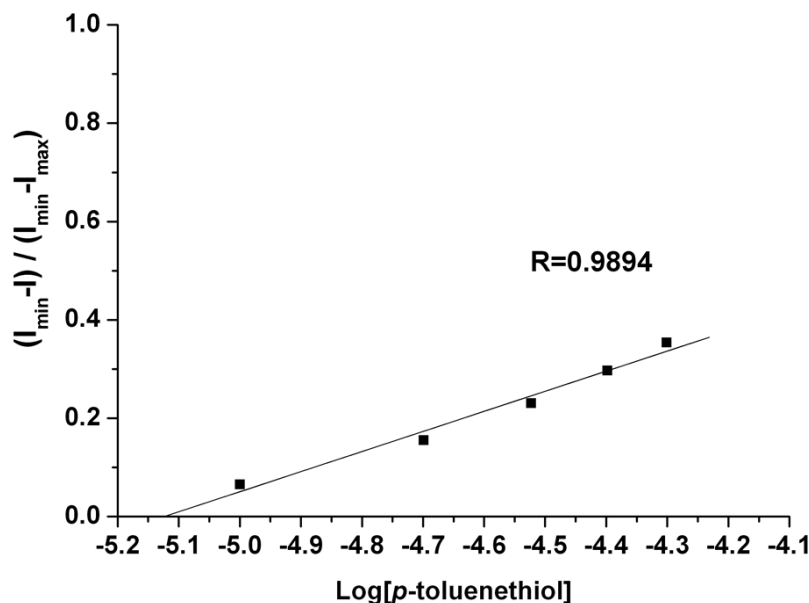


Figure S3. Normalized fluorescence intensity of Material III versus the added concentration of *p*-toluenethiol.

7. ESI-MS and ^1H NMR Spectrum Analysis.

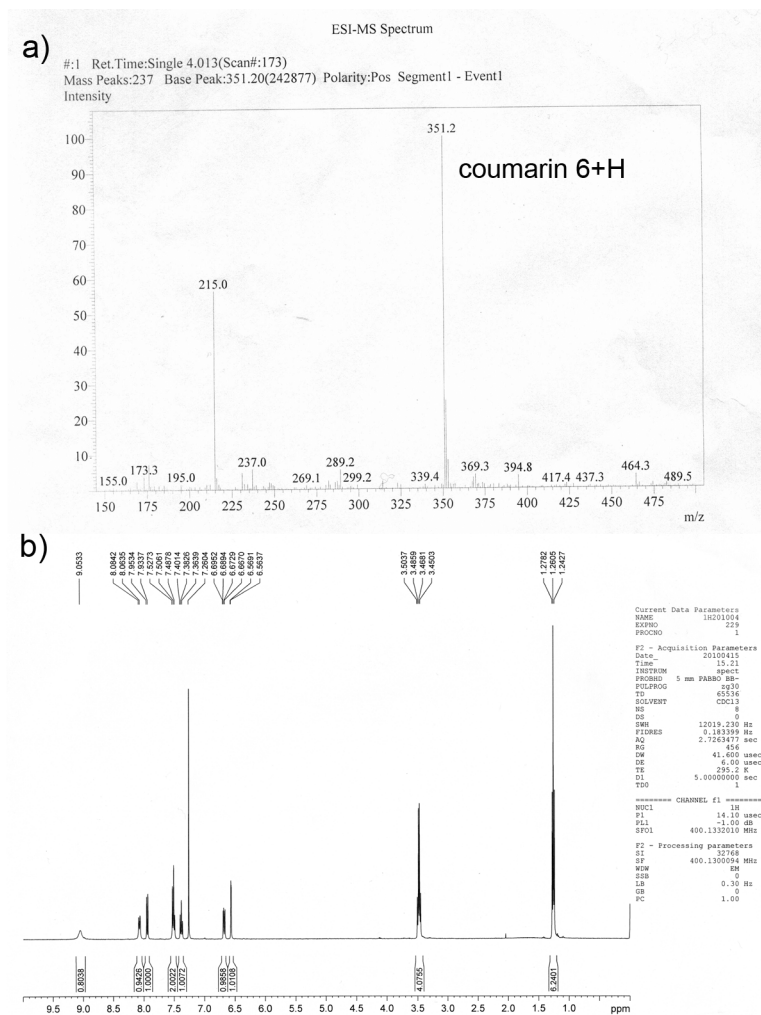


Figure S4. a) ESI-MS spectrum of the solution of Material **III** after the addition of excess *p*-toluenethiol. b) ^1H NMR spectrum of the isolated reaction product of Material **III** + *p*-toluenethiol.

8. References.

- S1 (a) A. Schlossbauer, D. Schaffert, J. Kecht, E. Wagner, T. Bein, *J. Am. Chem. Soc.*, 2008, **130**, 12558 (b) Z. Jin, X. B. Zhang, D. X. Xie, Y. J. Gong, J. Zhang, X. Chen, G. L. Shen, R. Q. Yu, *Anal. Chem.*, 2010, **82**, 6343.
- S2 (a) W. Y. Lin, L. Yuan, Z. M. Cao, Y. M. Feng, L. L. Long, *Chem. Eur. J.*, 2009, **15**, 5096. (b) A. Caballero, R. Martinez, V. Lloveras, I. Ratera, J. Vidal-Gancedo, K. Wurst, A. Tarraga, P. Molina, J. Veciana, *J. Am. Chem. Soc.*, 2005, **127**, 15666.