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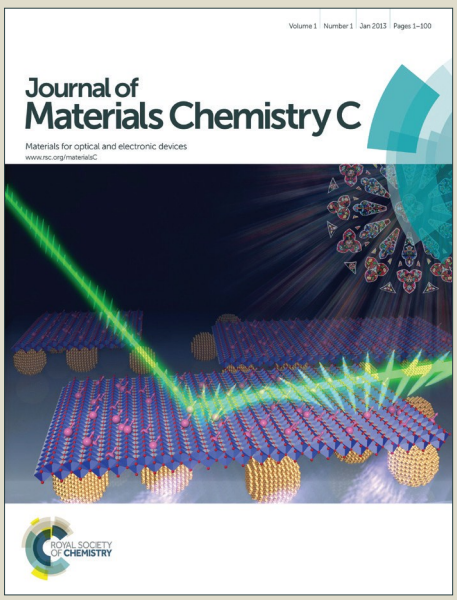





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ARTICLE

# A fluorescent probe for benzenethiols and its application on test paper, in water samples and living cells

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It is significant to develop probes for rapid, selective, and sensitive detection of the highly toxic benzenethiols in both environmental and biological science. In this work, based on the selective cleavage reaction by benzenethiols under mild condition, a novel naphthalimide-based fluorescent probe was designed and synthesized for rapid recognition of benzenethiol with excellent selectivity and anti-interference over other various species including some nucleophilic species, aliphatic thiols, anions and metal ions. The limit of quantification (LOQ) value was 0–4.0 $\mu$M and the detection limit could be as low as 10.3 nM. The fluorescence enhancement of this probe upon addition of benzenethiol on test paper and the application of the probe for selective detection in water samples and living cells have been successfully demonstrated.

## Introduction

Benzenethiols, also named as thiophenols, as a kind of very useful organic compounds, play a vital role in organic synthesis and are widely used in preparing pharmaceuticals, agrochemicals, and various industrial products.[1,2] However, benzenethiols are a class of highly toxic and pollutant compounds and their toxicity is even more serious than that of aliphatic thiols. As reported, the median lethal dose ($LC_{50}$) values for fish are in a low range of 0.01−0.4 *m*M.[3,4] In addition, prolonged exposure to benzenethiols can cause a series of serious health problems such as increased respiration, central nervous system damage, muscle weakness, hind limb paralysis, coma, and even death.[5] Considering their high toxicity and the continuing environmental concerns, an efficient and simple method for determining benzenethiol level is therefore urgently needed in both environmental and biological science.

In recent years, the development of small molecular fluorescent probes toward metal ions, anions and biomolecules has attracted great attention due to their simplicity, high sensitivity, and instantaneous response.[6,7] Significant effort has been paid to the development of fluorescent probes toward thiols to achieve high sensitivity, low cost, and ease of detection, and as a result, many fluorescent probes toward thiols have been developed in the past few decades.[8–11] However, the goal of such work is to discriminate aliphatic thiols such as cysteine and homocysteine from other amino acids,[12–20] and in general, they cannot clearly discriminate benzenethiols over aliphatic thiols. In fact, Wang et al. reported the first fluorescent probe capable of selective detection of benzenethiols over aliphatic thiols in 2007.[21] In his work, a reaction-based fluorescent probe for selective detection of benzenethiols was innovatively developed with good water solubility and selectivity, in spite of the drawbacks of this probe such as relatively weak fluorescence intensity and low sensitivity. Since then, several fluorescent probes have been developed for benzenethiols.[22–33] However, available fluorescent probes for benzenethiols are still very limited and it is still significant to design and synthesize novel fluorescent probes for benzenethiols.

As widely used fluorophores, 1,8-naphthalimide-based derivatives posses many favorable optical properties such as excellent photostability, high fluorescence quantum yields and large Stokes' shift. Moreover, their photophysical properties can be easily tuned through judicious structural modifications.[34–43] In fact, based on 1,8-naphthalimide, one benzenethiol-fluorescent probe has been reported.[26] However, the reported naphthalimide-based fluorescent probes for benzenethiol are very limited and it is necessary to design and synthesize novel naphthalimide derivatives for sensing benzenethiol.

In this paper, we synthesized a highly sensitive and stable fluorescent dye compound **1**, which can quantitatively detect benzenethiol with dramatically enhanced fluorescence within 3 minutes. The detection limit on fluorescence response of the probe can be as low as 10.3 nM. The fluorescence enhancement of this probe upon addition of benzenethiol on test paper and the application of the probe for selective detection in water samples and living cells have been successfully demonstrated.

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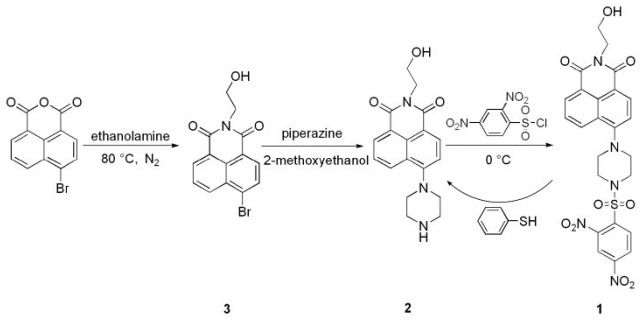
## Experimental section

### Methods and materials

All commercial grade chemicals and solvents were purchased and were used without further purification. Compound **1** was synthesized according to **Scheme 1** and following the recently reported method.[44,45]




**Scheme 1** Synthetic route to probe **1**.

Mass spectra were obtained on high resolution mass spectrometer (IonSpec4.7 Tesla FTMS-MALDI/DHB). $^{1}$H and $^{13}$C NMR spectra were recorded on a Bruker 400 NMR spectrometer. Chemical shifts are reported in parts per million using tetramethylsilane (TMS) as the internal standard.

### Spectral characterizations

All spectral characterizations were carried out in HPLC-grade solvents at 20 °C within a 10 mm quartz cell. Fluorescence spectroscopy was determined on a Hitachi F-4500 spectrometer. HPLC was determined on a LC-16 (Liquid Chromatography-16) chromatographic instrument.

### Fluorescence imaging experiments in Living A549 cells

A549 were gifted from the center of cells, Peking Union Medical College and were grown in RPM1640, McCoy's 5A or DMEM respectively, supplemented with10% fetal bovine serum and 1% penicillin/streptomycin, incubated under 5% $CO_2$ at 37℃. Cells were seeded on confocal dish for imaging 12-24 h prior to conduction of experiment. Images were acquired with a Nikon C1si laser scanning confocal microscopy with 60 × oil objective. The probe was excited by a sapphire solid laser at 405 nm with 61.1% intensity ratio and M pin hole and the emission fluorescence was recorded by the 515/15 nm detecting channel.

The cells were firstly incubated with thiophenol (100 $\mu$M) for 30 min at 37 °C and then incubated with Probe **1** (10 $\mu$M) for another 5 min, 15 min and 30 min, respectively. After washing with PBS buffer, cell images were obtained. For a control experiment, A549 cells were only incubated with probe **1** (10 $\mu$M) for 5 min, 15 min and 30 min at 37 °C, respectively and then cell images were performed.

### DFT calculations

DFT calculations using the Becke three-parameter exchange/Lee–Yang–Parr correlation hybrid functional (B3LYP) with 6-31G(d,p) basis sets as implemented in the Gaussian 09 suite of programs were carried out for the energies of **1** and the fluorophore (compound **2** also the product from the reaction of **1** with benzenethiol, Scheme 1) were obtained using time-dependent DFT (TD-DFT) with the same basis sets.

### Synthesis of compound 1

10 mL dichloromethane solution of 2,4-dinitrobenzenesulfonyl chloride (163.8 mg, 0.62 mmol) was slowly added to the 35 mL dichloromethane solution of compound **2** (200 mg, 0.62 mmol) and the mixture was reacted for 1 h at 0 °C. The final product **1** (0.1886 g, 54.8 %) was obtained by column chromatography over silica gel column using dichloromethane/ethanol (100:1) as eluent. Characterization of **1**: HRMS (EI) m/z: calcd for $C_{20}H_{18}N_2O_4$ $[M + Na]^+$, 578.0958; found, 578.0955. $^{1}$H NMR (400 MHz, DMSO-$d_6$, TMS): $\delta_H$ 9.06 (s, 1H), 8.65 (d, 1H), 8.39 (m, 4H), 7.76 (m, 1H), 7.34 (d, 1H), 4.80 (s, 1H), 4.10 (t, 2H), 3.60 (t, 6H), 3.35 (t, 2H), and 3.30 (t, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta_C$ 164.02, 163.51, 155.00, 150.73, 148.38, 134.58, 132.86, 132.32, 131.07, 130.63, 129.41, 127.49, 126.73, 125.85, 123.12, 120.57, 117.05, 116.26, 58.28, 52.54, 46.36, and 42.11.

### Synthesis of the product from the reaction of 1 with benzenethiol

45 mg (0.081 mmol) probe **1** was dissolved in 10 mL ethanol and 83 $\mu$L (0.081 mmol) benzenethiol was dissolved in the above mixture. The mixture was stirred for 2 h at 20 °C and the final product (compound **2**, 17 mg, 65.4 %) was obtained by column chromatography over silica gel column using dichloromethane/ethanol (1:1) as eluent. Characterization of the product from the reaction of **1** with benzenethiol (**2**): HRMS (EI) m/z: calcd for $C_{18}H_{20}N_3O_3$ [M+H], 326.1505; found, 326.1506. $^{1}$H NMR (400 MHz, DMSO-$d_6$, TMS): $\delta_H$ 8.41(t, 2H), 8.35 (d, 1H), 7.76 (t, 1H), 7.27 (d, 1H), 4.12 (t, 2H), 3.60 (t, 2H), 3.23 (s, 1H), 3.14 (t, 4H), 3.01 (t, 4H).

## Results and discussion

### Fluorescence studies of probe 1 towards benzenethiol

To investigate the changes in fluorescence emission spectrum of **1** upon exposure to benzenethiol, fluorescence titrations were conducted with ethanol solution of benzenethiol in aqueous solution of **1** ($5.0 \times 10^{-6}$ M, water/ethanol = 7:3, v/v) (**Fig. 1**). Upon excitation at 380 nm, the fluorescence emission intensity of **1** gradually increased (≈32-fold, excited at 380 nm) as the concentration of benzenethiol increased within 3 min. **Fig. S1** indicates the relationship between the fluorescence peak intensity at 517 nm and the concentration of benzenethiol. A good linear relationship between the fluorescence peak at 517 nm and the concentration of benzenethiol was obtained in concentration range of 0 and $4.0 \times 10^{-6}$ M (inset of **Fig. 1**), implying that benzenethiol can be quantitatively detected in a wider concentration range. From this linear calibration graph, the detection limit of probe **1** for benzenethiol is found to be about 10.3 nM based on signal-to-noise ratio (S/N) = 3.[33,46] This result proved that probe **1** shows high sensitivity to benzenethiol.

Time-dependent fluorescence experiments on probe **1** toward benzenethiolbenzenethiol is completely accomplished

within 10 min and benzenethiol can be detected within 3 min when the concentration of benzenethiol is higher or equal to 2.5× $10^{-6}$ M. such result further proved the fast response and high sensitivity of **1** for detection of benzenethiol.

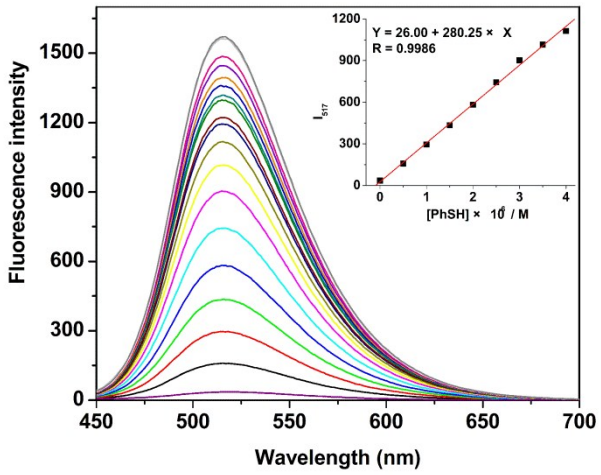



**Fig. 1** Emission spectra of **1** (5.0 × $10^{-6}$ M, $V_{water}$:$V_{ethanol}$ = 7:3) upon titration of benzenethiol ethanol solution (0–10 equiv to **1**) with excitation at 380 nm. The linearity of peak intensity with respect to benzenethiol concentrations (inset).

**The sensing mechanism of probe 1 toward benzenethiol**

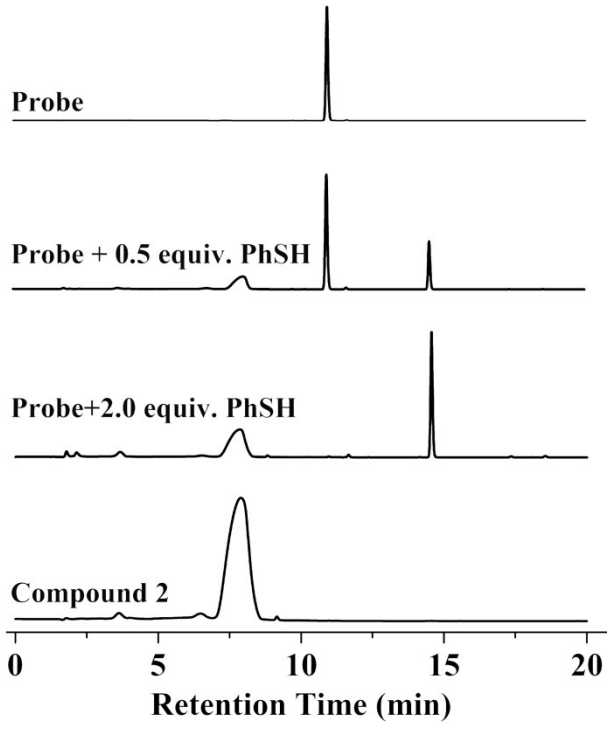



**Fig. 2** The HPLC chromatograms: (a) Probe **1** (100.0 μM); (b) Probe **1** (100.0 μM) with 0.5 equiv. benzenethiol; (c) 2.0 equiv. benzenethiol respectively incubated for 30 min in HEPES buffer (10.0 mM, pH = 7.4) containing 30% EtOH; Compound **2** (100.0 μM). Condition: eluent, $CH_3CN/H_2O$; gradient, 40–90% $CH_3CN$ (0–10 min), 90% $CH_3CN$ (10–20 min), flow rate, 1.0 mL/min; temperature, 25°C; detection wavelength, 390 nm; injection volume, 20.0 μL.

The sensing mechanism was studied by $^1$H NMR and Mass spectra. The reaction product was isolated by column chromatography to confirm that compound **2** was formed through the reaction of benzenethiol with probe **1** (**Scheme 1**). $^1$H NMR spectra of the isolated product, the probe **1** itself and the reference compound **2** are shown in **Fig. S3**. Upon reaction of benzenethiol, three protons of probe **1** corresponding to the protons of 2,4-dintrobenzenesulfonyl group around 9.06, 8.65 and 8.39 ppm dramatically disappeared. For pure probe **1**, a characteristic peak at m/z = 578.0958 was obtained which corresponds to the species [1 + Na]$^+$, whilst on reaction of benzenethiol, the peak at 578.0958 disappeared and one new peak appeared at m/z = 326.1506 corresponding to the species [2+H] (Figures **S4**, **S5** and **S6** in the Supporting Information). HPLC is an effective method widely used for the seperation and analysis of mixtures of organic compounds. Thus, we conducted HPLC analysis on compound **2**, probe **1** and the reaction product of probe **1** with benzenethiol (shown in **Fig. 2**). Probe **1** displayed a single peak with a retention time at 10.978 min while compound **2** produced a single peak with a retention time at 7.855 min. Upon the addition of benzenethiol to the solution of probe **1**, the peak at 10.386 min disappeared with the appearance of a new peak at 7.896 min, which is almost the same as that of compound **2**. Such results indicated that the sensing mechanism of probe **1** toward benzenethiol is most likely the cleavage of the sulfonamide process mediated by benzenethiol as shown in **Fig. 3**.

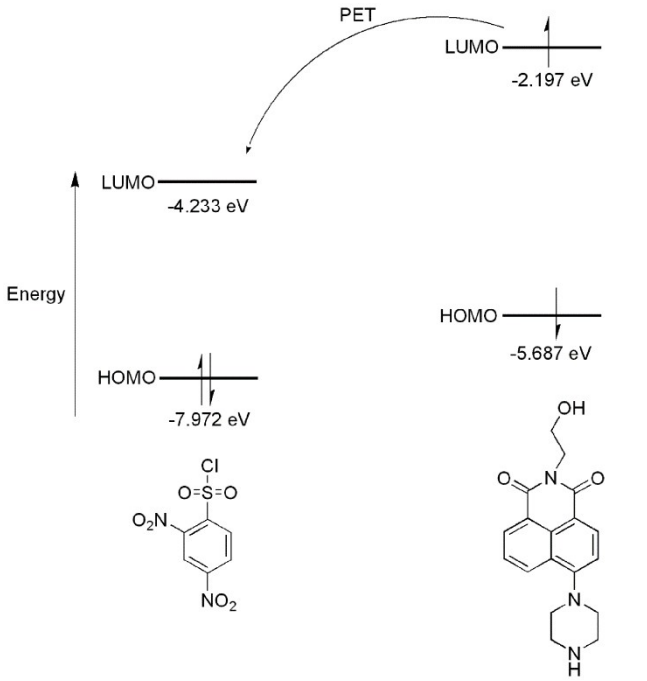



**Fig. 3** Frontier molecular orbital energies of **1** in different conditions, which are relevant to PET process.

To interpret further the sensing mechanism of **1** toward benzenethiol, DFT calculations were carried out on the energies of probe **1,** and the product from the reaction of **1** with benzenethiol (**Fig. 3**). Frontier orbital diagram indicates

that the LUMO energy of the fluorophore (the product from the reaction of **1** with benzenethiol) (-2.197 eV) was higher than the LUMO energy of the electron withdrawing group 2,4-dinitrobenzenesulfonyl chloride (-4.232 eV) before the reaction of **1** with benzenethiol, which implied that PET process can happen from the fluorophore moiety to the 2,4-dintrobenzenesulfonyl group. However, after reaction of probe **1** with benzenethiol, because of the disappearance of the electron withdrawing group 2,4-dintrobenzenesulfonyl group, PET process became less feasible.

**pH range in application of probe 1 toward benzenethiol**

The pH value of solution was found to be essential to the cleavage reaction. To investigate the pH effect, the fluorescence intensities of 5.0 $\mu$M probe **1** at 517 nm in the absence and presence of 10 $\mu$M benzenethiol were examined at pH range from 0 to 14.0. As shown in **Fig. S7** in Supporting Information, the probe **1** itself does not show fluorescence emission in a wide pH range from 0.0 to 14.0. However, upon addition of benzenethiol, there was a significant fluorescence increase in pH range of 5.0–11.0. Notably, the fluorescence changes of probe **1** to benzenethiol reached a maximum at about 7.0 and became almost constant in the pH range of 8.0–10.0, which is consistent with the $pK_a$ value of benzenethiol ($pK_a \approx 6.5$). Such result implies that probe **1** is able to detect benzenethiol in a relatively wide pH range.

**The selectivity study of probe 1 for benzenethiol**

To evaluate the selectivity of probe **1** for benzenethiol, various species including some nucleophilic species (KI, $NaN_3$, NaSH, PhOH, $PhNH_2$, Gly, Ala), aliphatic thiols (Cys, Hcy, GSH), various anions and metal ions ($CaCl_2$, $CoCl_2$, $CrCl_3$, $HgCl_2$, KCl, $MgCl_2$, $MnCl_2$, NaCl, $NiCl_2$, $PbCl_2$, $ZnSO_4$, $CdCl_2$, $Al(NO_3)_3$, NaBr, $K_2Cr_2O_7$, NaCl, $NaClO_3$, $NaClO_4$, NaF, $NaH_2PO_4$, $NaHSO_3$, $NaNO_2$, $NaNO_3$, $Na_2S_2O_3$, NaSCN, $NaSO_4$) were tested. As shown in **Fig. 4**, only the introduction of benzenethiol to the probe **1** solution induced a significant enhancement in the fluorescent intensity at 517 nm. In the same condition, other tested species mentioned above including aliphatic thiols, metal ions and shared anions did not induce any obvious fluorescence enhancement to the probe **1** solution (left part of **Fig. 4**, red bars of Figures **4** and **S8** in Supporting Information). Considering that GSH is the most abundant intracellular nonprotein biothiol, fluorescence titration experiment was also done to check the influence of GSH on the detection of benzenethiol. As shown in **Fig. S9**, when the concentration of GSH is lower or equal to 7 mM, the fluorescence intensity increased about 6 times, which is so small compared with that upon addition of $1.0 \times 10^{-5}$ M benzenethiol (about 32 times). Such result indicates that probe **1** has very high selectivity toward benzenethiol against other species. As is well known, the dinitrobenzene sulfonamide moiety is usually used as a detecting group for thiols such as GSH, Cys and Hcy.[47–49] However, probe **1** can detect benzenethiol against GSH, Cys and Hcy, which may be ascribed to the lower pKa of benzenethiol (6.5) than that of GSH, Cys and Hcy (8.5).[22]

**The anti-disturbance effect study of 1 for benzenethiol detection**

To further assess its utility as a benzenethiol-selective fluorescent probe, its fluorescence spectrum response to benzenethiol in the presence of other species mentioned above (green bars of Figures **4** and **S8** in Supporting Information) was also tested. The results demonstrated that all of the selected species have no interference in the detection of benzenethiol. This result strongly indicates that compound **1** could be an excellent fluorescent probe towards benzenethiol with strong anti- interference ability.

**The Application on Test Paper, in Water Samples and Living cells**

Considering the toxicity of benzenethiols and their potential as pollutants, probe **1** was employed to determine benzenethiol concentrations in water samples to validate its practical utility in environmental science. The water samples were collected from Eyebrow Lake, tap water, and a pond in Zhengzhou University. These water samples were directly analyzed first and then spiked with benzenethiol at different levels (0, 1, 1.5, 2, 2.5, 3, 3.5 and 4 $\mu$M), and the fluorescence responses of probe **1** at 517 nm toward all these samples were examined, respectively. The results are shown in **Fig. 5**, and they are compared with those determined in distilled water. It can be seen that they have a good consistency between each other (**Fig. 5**). For each real water sample, a linear relationship between the responses of the fluorescent intensity at 517 nm to the spiked benzenethiol concentrations from 0 to 4 $\mu$M was observed (Figures **5b**–**d**), which is in good agreement with the result obtained in distilled water (inset of **Fig. S1**, The LOQ value was 0–4.0 $\mu$M). In addition, the recoveries of benzenethiol ranged from 90% to 106% (**Table S1** in Supporting Information), which indicates that benzenethiol in the water samples could be accurately measured with good recovery when probe **1** was applied as the probe. Such result suggested that probe **1** has potential application for quantitative detection of benzenethiol in water samples.

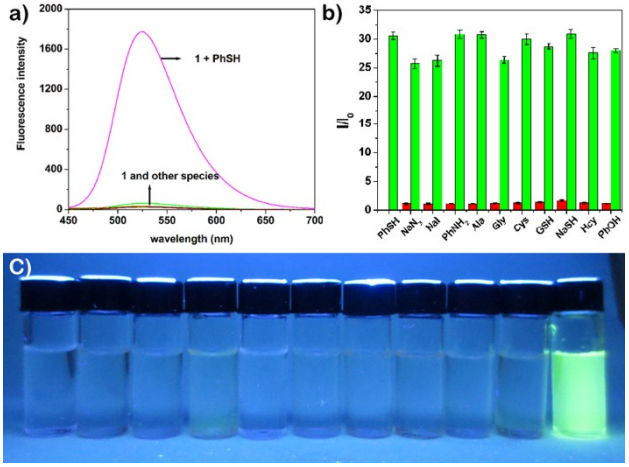



**Fig. 4** Fluorescence spectra ($5.0 \times 10^{-6}$ M, $V_{water}$:$V_{ethanol}$ = 7:3) (a) and photographs (c) of **1** ($5.0 \times 10^{-5}$ M, $V_{water}$:$V_{ethanol}$ = 7:3) upon addition of 2 equiv. of various species (KI, $NaN_3$, PhOH, $PhNH_2$, Gly, Ala, Cys, Hcy, GSH, and PhSH) with excitation at

380 nm and under a 365 nm UV lamp (c). The reaction time was 3 min. Fluorescence responses (b) of **1** ($5.0 \times 10^{-6}$ M, $V_{water}$:$V_{ethanol}$ = 7:3) upon addition of different species (10 equiv of species relative to **1**) (red bars of b) and fluorescence changes of the mixture of **1** and benzenethiol after addition of an excess of the indicated species (10 equiv relative to **1**) (green bars of b). The excitation wavelength was 380 nm. $I_0$ represents the emission intensity at 517 nm in the fluorescence spectroscopy of compound **1**. I represents the emission intensity at 517 nm in the fluorescence spectroscopy of compound **1** after addition of the species to the solution of **1** (red bars of b) and of the mixture of **1** and benzenethiol after addition of an excess of the species (green bars). The species used were PhSH, $NaN_3$, NaI, $PhNH_2$, Ala, Gly, Cys, GSH, NaSH, Hcy and PhOH.

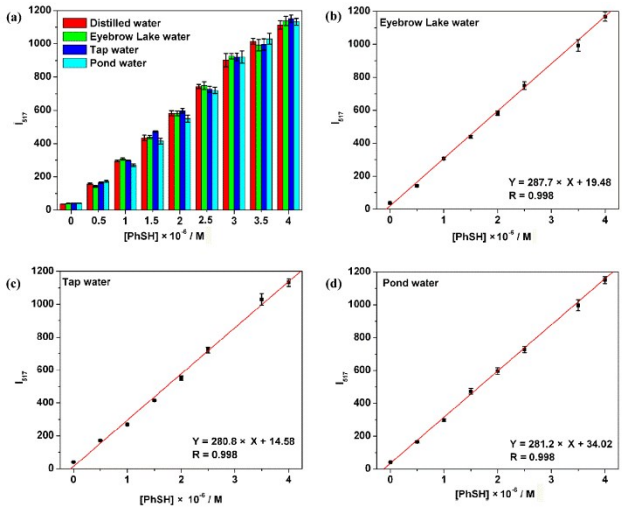



**Fig. 5** (a) Fluorescent detection of different concentrations of benzenethiol in "Eyebrow Lake water", "tap water", and "pond water" by probe **1** ($5.0 \times 10^{-6}$ M) in water solution with 30% ethanol at 20 °C. The reaction is monitored at 517 nm with excitation at 380 nm. Each condition was measured three times, and the average values are shown. Benzenethiol is spiked in 0, 1, 1.5, 2, 2.5, 3, 3.5, and 4 $\mu$M, respectively. (b–d) linear plot of fluorescence intensity changes of probe **1** at 517 nm against the spiked concentrations of benzenethiol from 0 to 4 $\mu$M for each real water samples.

As shown in the above, probe **1** can detect benzenethiol in aqueous solution, it inspired us to further investigate the possibility of detection as solid materials for point-of-care detection application. Test paper was selected and the fluorescence detection properties were studied by a UV lamp with photography as well as solid fluorescence spectroscope. In the detection process, the probe spots were prepared by dropping 5 $\mu$L 50 $\mu$Msolutions of **1** benzenethiolbenzenethiolportable ultraviolet lamp. As shown in **Fig. 6**, the probe spots emitted bright blue-green fluorescence upon the addition of benzenethiol under UV illumination, while an enhancement of the fluorescence intensity at 493 nm could be recorded. Additionally, the probe spots emitted fluorescence only upon the addition of benzenethiol (**Fig. S9** in Supporting Information), demonstrating the high selectivity of probe **1** as solid materials toward benzenethiol.

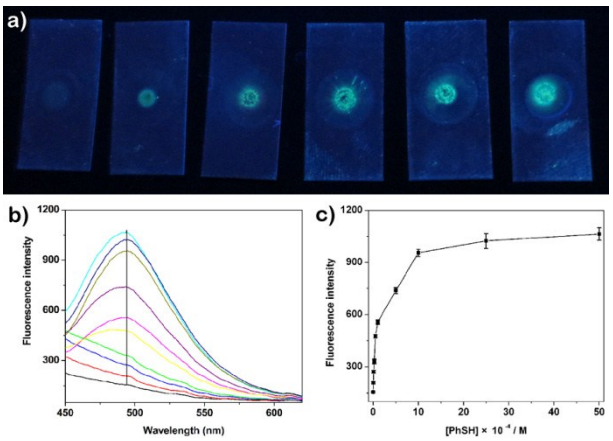



**Fig. 6** (a) Images of test papers for the detection of benzenethiol at various concentrations (0, $1.0 \times 10^{-5}$ M, $5.0 \times 10^{-5}$ M, $1.0 \times 10^{-4}$ M, $5.0 \times 10^{-4}$ M, $1.0 \times 10^{-3}$ M, $5.0 \times 10^{-3}$ M, from left to right) in aqueous solutions under a UV lamp (365 nm). (b) Fluorescence spectra and (c) fluorescence intensity at 493 nm of the probe spots of **1** on test papers upon addition of various concentrations of benzenethiol (0–5.0 mM). Other conditions are the same as in Figure S1.

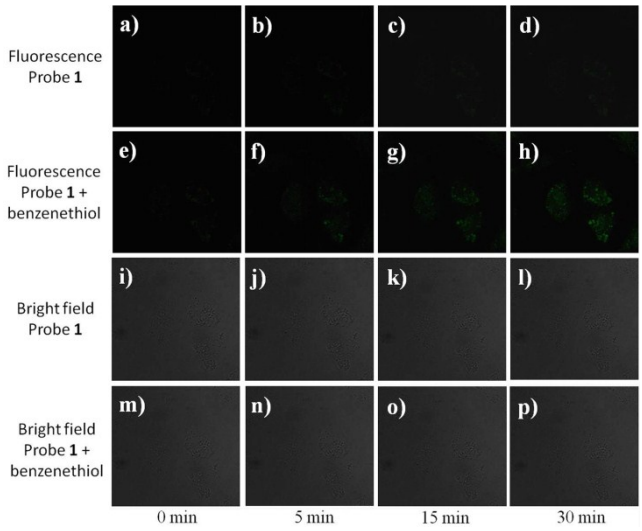



**Fig. 7** Confocal fluorescence contrast images of living A549 incubated with 10 $\mu$M probe **1** for 0, 5, 15 and 30 min at 37 °C (a, b, c and d respectively) and pretreated with 100 $\mu$M benzenethiol, followed by incubation with probe **1** for 0, 5, 15 and 30 min at 37°C (e, f, g and h respectively); Bright field images of living A549 cells incubated with 10 $\mu$M probe **1** only for 0 min (i), 5 min (j), 15 min (k), and 30 min (l) at 37 °C; Bright field images of living A549 cells incubated with 10 $\mu$M probe **1** and 100 $\mu$M benzenethiol for 0 min (m), 5 min (n), 15 min (o), and 30 min (p) at 37 °C.

The practical utility of using probe **1** to detect thiols in an imagewise manner within living A549 cells was explored (**Fig. 7**). When A549 cells were incubated with 10 $\mu$M probe **1** only for equal or less than 30 min at 37 °C, no obvious fluorescence was observed (a, b, c, and d of **Fig. 7**), indicating that the reaction of probe **1** and intracellular biothiol cannot result in green emission within 30 min. However, when A549 cells were preincubated with benzenethiol (100 $\mu$M) and then incubated with probe **1** (10 $\mu$M) for equal or more than 15 min, a

significant green fluorescence inside the cells was observed with the aid of an inverted fluorescence microscope (e, f, g and h of **Fig.7**), implying that the stimulation of benzenethiol toward probe **1** only for 15 min can give green emission. Thus, probe **1** is capable of permeating into cells and distinguishing benzenethiol from biothiol in living cells.

## Conclusions

Based on 1,8-naphthalimide and selective cleavage of 2,4-dinitro-benzenesulfonamide by benzenethiols under mild condition, a novel off-on fluorescent probe was designed and synthesized for highly sensitive and excellent selective recognition of benzenethiol. Probe **1** exhibited an ultra sensitivity (the LOD could be as low as 10.3 nM), a good linear relationship between benzenethiol concentration and the fluorescence enhancement in concentration range of 0–4.0 $\mu$M, and excellent selectivity and anti-interference over other various species including many nucleophilic species, aliphatic thiols, anions and metal ions. The fluorescence enhancement of this probe upon addition of benzenethiol on test paper and the application of the probe for selective detection in water samples and living cells have been successfully demonstrated.

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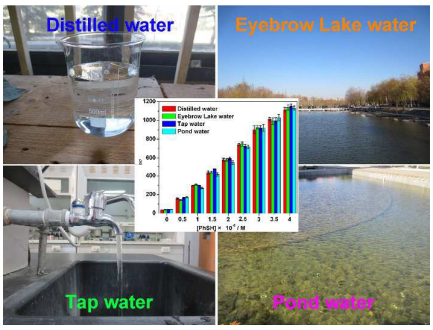
## Notes and references

1 J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo and G. M. Whitesides, *Chem. Rev.*, 2005, **105**, 1103.
2 K. M. Ro, In Ullmann's Encyclopedia of Industrial Chemistry, 7th ed.; Wiley: New York, 2007.
3 T. P. Heil and R. C. Lindsay, *J. Environ. Sci. Health B*, 1989, **24**, 349.
4 R. Munday, *Free Radical Biol.*, 1989, **7**, 659.
5 P. Amrolia, S. G. Sullivan, A. Stern and R. Munday, *J. Appl. Toxicol.: JAT*, 1989, **9**, 113.
6 X. Chen, T. Pradhan, F. Wang, J. S. Kim and J. Yoon, *Chem. Rev.*, 2012, **112**, 1910.
7 X. Li, X. Gao, W. Shi and H. Ma, *Chem. Rev.*, 2014, **114**, 590.
8 Y. Zhou and J. Yoon, *Chem. Soc. Rev.*, 2012, **41**, 52.
9 H. S. Jung, X. Chen, J. S. Kim, J. Yoon, *Chem. Soc. Rev.*, 2013, **42**, 6019.
10 C. Yin, F. Huo, J. Zhang, R. Martinez-Manez, Y. Yang, H. Lv and S. Li, *Chem. Soc. Rev.*, 2013, **42**, 6032.
11 J. Yin, Y. Kwon, D. Kim, D. Lee, G. Kim, Y. Hu, J.-H. Ryu and J. Yoon, *J. Am. Chem. Soc.*, 2014, **136**, 5351.
12 X. Dai, T. Zhang, Y. Li, T. Yan, P.-C. Wang, J.-Y. Miao and B.-X. Zhao, *RSC Adv.*, 2014, **4**, 54650.
13 M. Li, X. Wu, Y. Wang, Y. Li, W. Zhu and T. D. James, *Chem. Commun.*, 2014, **50**, 1751.
14 C. S. Lim, G. Masanta, H. J. Kim, J. H. Han, H. M. Kim and B. R. Cho, *J. Am. Chem. Soc.*, 2011, **133**, 11132.
15 S. Y. Lim, K. H. Hong, D. I. Kim, H. Kwon and H. J. Kim, *J. Am. Chem. Soc.*, 2014, **136**, 7018.
16 J. Liu, Y. Q. Sun, Y. Huo, H. Zhang, L. Wang, P. Zhang, D. Song, Y. Shi and W. Guo, *J. Am. Chem. Soc.*, 2014, **136**, 574.
17 X. F. Yang, Y. X. Guo and R. M. Strongin, *Angew. Chem. Int. Ed.*, 2011, **50**, 10690.
18 X. F. Yang, Q. Huang, Y. Zhong, Z. Li, H. Li, M. Lowry, J. O. Escobedo and R. M. Strongin, *Chem. Sci.*, 2014, **5**, 2177.
19 F. Wang, Z. Guo, X. Li, X. Li and C. Zhao, *Chem. -Eur. J.*, 2014, **20**, 11471.
20 X. Wang, J. Lv, X. Yao, Y. Li, F. Huang, M. Li, J. Yang, X. Ruan and B. Tang, *Chem. Commun.*, 2014, **50**, 15439.
21 W. Jiang, Q. Fu, H. Fan, J. Ho and W. Wang, *Angew. Chem. Int. Ed.*, 2007, **46**, 8445.
22 W. Jiang, Y. Cao, Y. Liu and W. Wang, *Chem. Commun.*, 2010, **46**, 1944.
23 W. Lin, L. Long and W. Tan, *Chem. Commun.*, 2010, **46**, 1503.
24 W. Zhao, W. Liu, J. Ge, J. Wu, W. Zhang, X. Meng and P. Wang, *J. Mater. Chem.*, 2011, **21**, 13561.
25 C. Zhao, Y. Zhou, Q. Lin, L. Zhu, P. Feng, Y. Zhang and J. Cao, *J. Phys. Chem. B*, 2011, **115**, 642.
26 Z. Wang, D.-M. Han, W.-P. Jia, Q.-Z. Zhou and W.-P. Deng, *Anal. Chem.*, 2012, **84**, 4915.
27 D. Kand, P. K. Mishra, T. Saha, M. Lahiri and P. Talukdar, *Analyst*, 2012, **137**, 3921.
28 X.-L. Liu, X.-Y. Duan, X.-J. Du and Q.-H. Song, *Chem.-Asian J.*, 2012, **7**, 2696.
29 Y. Shiraishi, K. Yamamoto, S. Sumiya and T. Hirai, *Chem. Commun.*, 2013, **49**, 11680.
30 C. Zhao, X. Wang, J. Cao, P. Peng, J. Zhang, Y. Zhang, Y. Yang and Z. Yang, *Dyes Pigm.*, 2013, **96**, 328.
31 D. Kand, P. S. Mandal, A. Datar and P. Talukdar, *Dyes Pigm.*, 2014, **106**, 25.
32 J. Li, C.-F. Zhang, S.-H. Yang, W.-C. Yang and G.-F. Yang, *Anal. Chem.*, 2014, **86**, 3037.
33 D. Yu, F. Huang, S. Ding and G. Feng, *Anal. Chem.*, 2014, **86**, 8835.
34 D. Kand, P. S. Mandal, T. Saha and P. Talukdar, *RSC Adv.*, 2014, **4**, 59579.
35 X. Shao, R. Kang, Y. Zhang, Z. Huang, F. Peng, J. Zhang, Y. Wang, F. Pan, W. Zhang and W. Zhao, *Anal. Chem.*, 2015, **87**, 399.
36 Z. Wang, D. M. Han, W. P. Jia, Q. Z. Zhou and W. P. Deng, *Anal. Chem.*, 2012, **84**, 4915.
37 M. H. Lee, B. Yoon, J. S. Kim and J. L. Sessler, *Chem. Sci.*, 2013, **4**, 4121.
38 J. Du, M. Hu, J. Fan and X. Peng, *Chem. Soc. Rev.*, 2012, **41**, 4511.
39 C. Huang, T. Jia, M. Tang, Q. Yin, W. Zhu, C. Zhang, Y. Yang, N. Jia, Y. Xu and X. Qian, *J. Am. Chem. Soc.*, 2014, **136**, 14237.
40 M. H. Lee, N. Park, C. Yi, J. H. Han, J. H. Hong, K. P. Kim, D. H. Kang, J. L. Sessler, C. Kang and J. S. Kim, *J. Am. Chem. Soc.*, 2014, **136**, 14136.
41 M. H. Lee, H. M. Jeon, J. H. Han, N. Park, C. Kang, J. L. Sesser and J. S. Kim, *J. Am. Chem. Soc.*, 2014, **136**, 8430.
42 M. H. Lee, J. H. Han, P.-S. Kwon, S. Bhuniya, J. Y. Kim, J. L. Sessler, C. Kang and J. S. Kim, *J. Am. Chem. Soc.*, 2012, **134**, 1316.
43 M. H. Lee, J. H. Han, J.-H. Lee, H. G. Choi, C. Kang and J. S. Kim, *J. Am. Chem. Soc.*, 2012, **134**, 17314.
44 H. Tian, J. Gan, K. C. Chen, J. He, Q. L. Song and X. Y. Hou, *J. Mater. Chem.*, 2002, **12**, 1262.
45 J. Zhou, H. Liu, B. Jin, X. Liu, H. Fu and D. Shangguan, *J. Mater. Chem. C*, 2013, **1**, 4427.
46 Y. Liu, H. Li, M. Pei, G. Zhang, L. Hu and J. Han, *Talanta*, 2013, **115**, 190.
47 M. Wei, P. Yin, Y. Shen, L. Zhang, J. Deng, S. Xue, H. Li, B. Guo, Y. Zhang and S. Yao, *Chem. Commun.*, 2013, **49**, 4640.
48 S. Chen, P. Hou, B. Zhou, X. Song, J. Wu, H. Zhang and J. W. Foley, *RSC Adv.*, 2013, **3**, 11543.

49 L. Peng, Z. Zhou, R. Wei, K. Li, P. Song and A. Tong, *Dyes Pigm.*, 2014, **108**, 24.




**Graphical Abstract**

Using the selective cleavage of 2,4-dinitro-benzenesulfonamide by benzenethiols, a 1,8-naphthalimide-based OFF-ON fluorescent probe was synthesized and the application was demonstrated.