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Ultrasensitive dicyanoisophorone-based near-infrared fluorescent probe for rapid and specific detection of thiophenols in river water

Shunzhou Chang[1] · Kaiqiang Xiang[2] · Wei Ming[2] · Xiaojun Cheng[2] · Changdong Han[2] · Zhizhong Zhang[1] · Baozhu Tian[2] · Jinlong Zhang[2]

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Abstract Thiophenols are a class of highly toxic pollutant compounds, which can cause severe damage to the central nervous system and other nervous systems after long-term exposure. Therefore, it is of significance to develop an effective method to detect trace thiophenols in the environment. Herein, we synthesized a dicyanoisophorone-based near-infrared fluorescent probe (probe **1**) with large stokes shift ($\lambda_{em} - \lambda_{abs}$ = 203 nm) for the selective detection of thiophenols. Probe **1** exhibited very high response speed (less than 200 S), sensitivity, and selectivity towards thiophenols, regardless of the presence of aliphatic thiols and other analytes. The detection limit was as low as 3.4 nM and the signal-to-background ratio of fluorescence intensity reached 30. Moreover, probe **1** displayed ultrasensitivity and high reliability in the quantitative detection of trace thiophenol in three river water samples.

Keywords Fluorescence probe · Thiophenols · Ultrasensitive · Near-infrared (NIR)

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✉ Baozhu Tian
baozhutian@ecust.edu.cn

Zhizhong Zhang
Zhangzhizhong333@sina.com

Jinlong Zhang
jlzhang@ecust.edu.cn

[1] Research Institute of Physical and Chemical Engineering of Nuclear Industry, 168 JinTang Road, Tianjin 300180, People's Republic of China

[2] Key Lab for Advanced Materials and Institute of Fine Chemicals, School of Chemistry and Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, People's Republic of China

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Introduction

Thiols (including aliphaticthiols and thiophenols) are widely used in the fields of chemical, biological, and environmental sciences [1, 2]. Thereinto, aliphaticthiols (including cysteine, homocysteine, and glutathione) have aroused tremendous interest due to their essential roles in many physiological processes of living organisms [3–8]. On the contrary, thiophenols are also considered to be a class of highly toxic compounds to organisms, in spite of their wide applications in raw materials and intermediates. In this regard, the median lethal concentration (LC_{50}) of thiophenols for fish is 0.01 − 0.4 mM [9, 10]. Long-term intake of superfluous thiophenols can lead to severe damage to the central nervous system, shortness of breath, muscular weakness, and even death [9, 11]. Consequently, it is very necessary to exploit a highly sensitive and selective detection technique to identify toxic thiophenols and aliphaticthiols [12, 13]. In recent years, fluorescent detection has attracted much attention owing to its simple operation, high sensitivity, and real-time imaging [14, 15]. However, most fluorescent probes are unable to distinguish aliphatic thiols and thiophenols, due to their low selectivity to the two types of thiols [16–18]. In 2007, Wang et al. first reported a new fluorescent probe for recognizing thiophenols over aliphatic thiols through S_NAr process [1]. Therein, 4-chloro-7-nitro-2,1,3-benzoxadiazole was used as the fluorophore and 2,4-dinitrobenzenesulfonyl (DNBS) as the response unit. This probe showed high selectivity for the detection of thiophenols in spite of the drawbacks of low sensitivity. Subsequently, Lin et al. explored a 3-benzothiazole coumarin-based fluorescent probe for the detection of thiolphenols via the thiolysis of a dinitrophenyl ether [19]. This probe shows excellent selectivity and the detection limit reaches as low as 1.8 nM. In 2014, Yang et al. reported a new type of fluorescent probe for the detection of thiophenols via an intramolecular charge transfer mechanism, which exhibited high selectivity and sensitivity in the quantitative determination of thiophenols in biological systems [20]. However, all three examples suffered from short emission wavelength, which limited its real application.

So far, the thiolphenol probes based on S_NAr mechanism have been studied for 10 years [21–30], but most of these probes still suffer from the following two main shortages: one is the low sensitivity, which limits their applications in low concentration of thiophenols; the other is that these probes mostly emit in the UV to green light region, which always leads to the interference between excitation light and emission light. Herein, it is of considerable importance to develop the highly sensitive fluorescence probes for recognizing thiophenols that emit in NIR light region, because the NIR fluorescence detection has unique advantages such as deep tissue penetration, light scattering decrease, autofluorescence reduction, and optical transparency increase [31–36].

Dicyanoisophorone-based fluorescent dyes are well recognized as an excellent fluorophore in the field of functional fluorescent materials due to their excellent spectroscopic characteristics, such as internal charge transfer (ICT), emission at NIR region, and large Stokes shift [37–42]. In the previous work, we have made some exploration in the synthesis and application of this type of fluorescence

materials [37, 43]. Herein, we designed a novel NIR fluorescence probe (probe **1**) for recognition of thiophenols (Scheme 1). As expected, probe **1** exhibited a turn-on response around 658 nm, high sensitivity and selectivity, and large stokes shift (203 nm). Moreover, probe **1** was also successfully applied in the quantitative detection of low concentration of thiophenols in the three river water samples.

Experimental

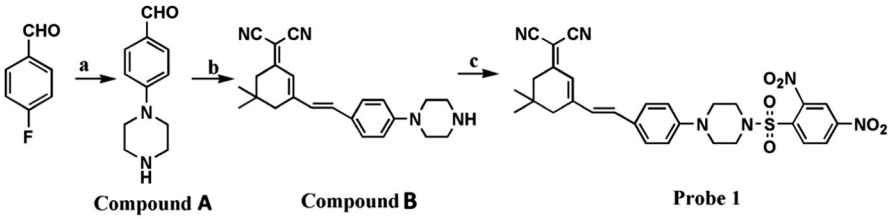
Synthesis

*Synthesis of compound **A***

4-Fluorobenzaldehyde (2.0 mL, 18.6 mmol) and piperazine (6.0 g, 69.6 mmol) were dissolved in 2-methoxyethanol (25 mL). The mixture solution was refluxed for 3 h and poured into 200 mL of water to obtain a yellow precipitate. After filtration, the yellow solid was further purified by silica column chromatography using dichloromethane/methanol (50/1, v/v) as the eluent to give a light yellow solid (Compound **A**, 2.3 g, 65%). ^{1}H-NMR (400 MHz, $CDCl_3$): 9.78 (s, 1H), 7.76 (d, J = 8 Hz, 2 H), 6.92 (d, J = 8 Hz, 2 H), 3.36 (t, J = 4 Hz, 4 H), 3.02 (t, J = 4 Hz, 4 H) (Fig. S1). ^{13}C-NMR (100 MHz, $CDCl_3$): 190.48, 155.41, 131.86, 127.05, 113.48, 48.19, 45.81 (Fig. S2).

*Synthesis of compound **B***

Under a nitrogen atmosphere, compound **A** (380 mg, 2.0 mmol) and dicyanoisophorone (372 mg, 2 mmol) were dissolved in toluene (20 mL), followed by addition of piperidine (0.5 mL) and acetic acid (0.5 mL). The mixture was refluxed for 8 h and then concentrated under vacuum. Finally, the residue was purified by silica gel column chromatography with dichloromethane/methanol as the eluent (20/1, v/v) to give a red solid (Compound **B**, 316 mg, 42%) ^{1}H-NMR (400 MHz, $CDCl_3$): 7.56 (d, J = 8 Hz, 2 H), 7.20 (d, J = 8 Hz, 2 H), 6.94 (d, J = 8 Hz, 2 H), 6.78 (s, 1H), 3.21 (t, J = 4 Hz, 4 H), 2.83 (t, J = 4 Hz, 4 H), 2.58 (s, 2H), 2.51 (s, 2H), 1.01 (s, 6H)



Reagent and conditions: (a) piperazine, 2-methoxyethanol, 3 h, 60%; (b) dicyanoisophorone, piperidine, AcOH, ethylbenzene, 10 h, 45%; (c) 2,4-Dinitrobenzenesulfonyl chloride, Et_3N, CH_2Cl_2, 12 h, 32%.

Scheme 1 Synthetic route of probe **1**

(Fig. S3). ^{13}C-NMR (100 MHz, $CDCl_3$): 169.32, 154.63, 151.76, 137.10, 129.13, 127.11, 126.31, 122.39, 115.60, 113.91, 113.14, 47.46, 44.22, 43.00, 39.21, 32.03, 28.06, 22.59 (Fig. S4).

*Synthesis of probe **1***

Compound **B** (107 mg, 0.3 mmol) and triethylamine (0.5 mL) was dissolved in 15 mL of CH_2Cl_2 at 0 °C. Then, a mixture solution of 2,4-dinitrobenzenesulfonyl chloride (80 mg, 0.3 mmol) and CH_2Cl_2 (5 mL) was added dropwise to the solution and stirred for 30 min. The mixture was warmed to room temperature for another 10 h, followed by removal under vacuum and purification by silica column chromatography (probe **1**, dichloromethane/methanol = 30/1, v/v) to obtained a red solid. (68 mg, yield: 11%). ^{1}H-NMR (400 MHz, $CDCl_3$): 9.01 (d, J = 8 Hz, 1 H), 8.58 (d, J = 8 Hz, 1 H), 8.31 (d, J = 8 Hz, 1 H), 7.57 (d, J = 8 Hz, 2 H), 7.21 (s, 2 H), 6.96 (d, J = 12 Hz, 2 H), 6.79 (s, 1H), 3.41 (t, J = 4 Hz, 4 H), 3.36 (t, J = 4 Hz, 4 H), 2.58 (s, 2H), 2.51 (s, 2H), 1.00 (s, 6H) (Fig. S5). ^{13}C-NMR (100 MHz, $CDCl_3$): 172.28, 170.04, 156.99, 152.07, 138.59, 129.51, 125.40, 120.85, 114.32, 113.49, 73.83, 47.46, 44.86, 42.27, 38.15, 31.62, 27.42, 21.35 (Fig. S6). HRMS (ESI): calcd. For $[C_{29}H_{28}N_6O_6S–H]^-$ 587.1713; found 587.1710 (Fig. S7).

Characterization

^{1}H NMR and ^{13}C NMR spectra were performed on a Bruker AM400 NMR spectrometer with TMS as the internal standard. High resolution mass spectrum (HRMS) was recorded on a Waters LCT Premier XE spectrometer. Absorption spectra and fluorescence spectra were recorded on a SHIMADZU UV-2450 spectrophotometer and SHIMADZU RF-5301PC fluorescence spectrophotometer at room temperature, respectively.

Measurements of HS^- in water samples

We collected three various water samples from Qingchun River, Huangpu River, and Changjiang River. The water samples were filtered first, then the pH was modulated in terms of PBS buffer solution (20 mM, pH 7.4). Finally, each water sample (3 mL, containing 5 μM probe **1**) was spiked with different concentrations (0, 0.1, 0.4, 0.7, 1 μM) of thiophenol solutions.

Results and discussion

Synthesis route

The synthetic routes of probe **1** and its intermediates compound **A** and compound **B** are illustrated in Scheme 1. The key intermediate dicyanoisophorone was synthesized according to our established procedures [35, 43]. The detailed synthetic procedures for compound **A**, compound **B** and probe **1** are described as follows.

Absorption and fluorescence properties

We firstly examined the absorption and emission spectra of probe **1** (5 μM) in the absence and presence of thiophenol in PBS buffer. As shown in Fig. 1a, b, the free probe **1** (5 μM) displayed an absorption band at 450 nm and a relatively weak emission peak at 596 nm. Upon addition of four equivalents of thiophenol, a new absorption band at 455 nm appeared. Although the absorption spectra between probe **1** and compound 2 only had a slight difference, their fluorescence spectra exhibited a significant difference. As showed in Fig. 1b, a strong emission enhancement at 658 nm appeared, which is ascribed to the cleavage of 2,4-dinitrobenzenesulfonyl (DNBS). Moreover, a remarkable large stokes shift of 203 nm (λ_{abs} = 455 nm, λ_{em} = 658 nm) was observed. The large stokes shift is

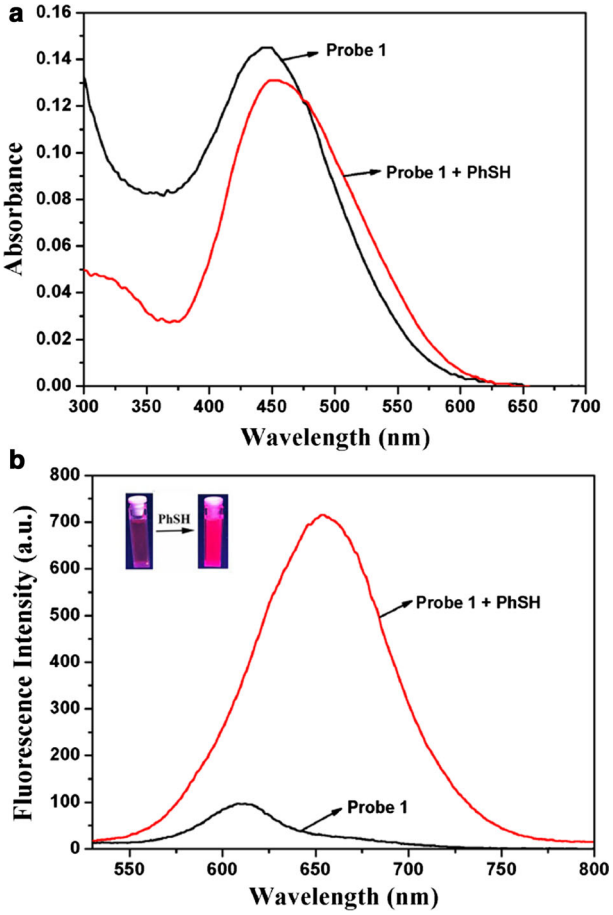


Fig. 1 UV–vis absorption (**a**) and fluorescence spectra (**b**) of probe **1** (5 μM) upon addition of thiophenol (20 μM). All spectra were recorded in DMSO/PBS buffer solution (20/80, v/v, pH = 7.4, 20 mM). λ_{ex} = 455 nm; slit width = 5/5 nm. The inset of Fig. 1b is the color change of probe **1** in DMSO/PBS buffer solution after addition of thiophenol (20 μM) under UV (365 nm) light irradiation

generally desired in fluorescence microscopy studies, because the large gap between the excitation wavelength and the emission wavelength can effectively diminish the measurement error caused by the excitation light and scattered light [32]. Additionally, the signal-to-background ratio can be achieved 30.4 (t = 0, Fluorescence Intensity = 22.4; t = 180 s, Fluorescence Intensity = 681.2), implying that probe **1** is quiet sensitive for thiophenol detection.

Response kinetics

The reaction kinetics of probe **1** in presence of thiophenol was investigated and is displayed in Fig. 2. In absence of thiophenol, almost no fluorescence can be detected throughout the detection process. Under different concentrations of thiophenol (0–20 μM), the fluorescence emission response speed was extremely fast (less than 160 s), which is allowed for real time detection. To verify whether our probe can work at low level of organic solvent, the influences of different ratios of DMSO (1, 5, 10, 20, 30, 40%) on the fluorescence response of probe **1** toward thiolphenol were also investigated. As shown in Fig. S8, probe **1** was effective at low level (1%) of organic solvent, indicating that probe **1** can be potentially used in water-rich detection system.

Effect of pH

As shown in Fig. 3, the emission band of probe **1** at 658 nm showed almost no change in the pH range from 2 to 12 in the absence of thiophenol, indicating that probe **1** is quiet stable. The emission band at 658 nm showed a remarkable increase in the pH range from 2 to 6 with thiophenol, which can be attributed to protonation of amino group [34] (Scheme 2). Then the fluorescence intensity had almost no

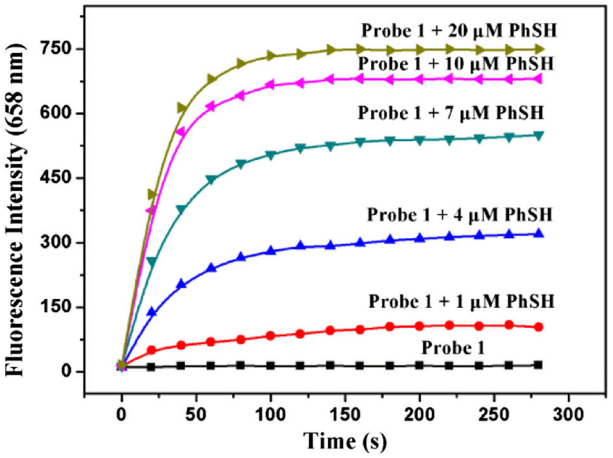


Fig. 2 Change of fluorescence intensities of probe **1** (5 μM) at 658 nm as a function of reaction time under different thiophenol concentrations (0, 1, 4, 7, 10, 20 μM) in DMSO/PBS buffer solution (20/80, v/v, pH = 7.4, 20 mM). λ_{ex} = 455 nm; slit width = 5/5 nm

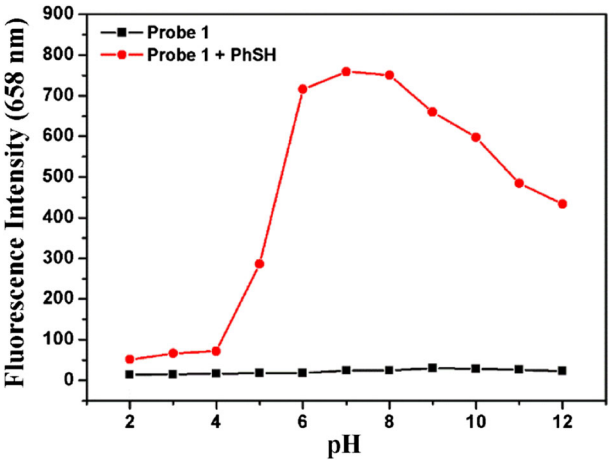
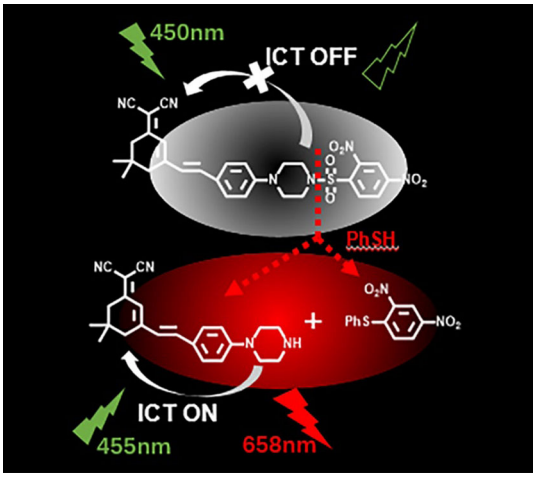


Fig. 3 Effect of pH on the fluorescence intensity of probe **1**(5 μM) at 658 nm in DMSO/PBS buffer solution (20/80, v/v, pH = 7.4, 20 mM) with (filled circle) and without (filled square) thiophenol (20 μM). λ_{ex} = 455 nm; slit width = 5/5 nm

Scheme 2 Proposed reaction mechanism of detecting thiophenol



change in the pH range from 6 to 8. These results suggested that probe **1** is suitable for detection of thiophenols in both environmental and biological systems.

Sensitivity

The fluorescence titration experiments was investigated in PBS buffer solution (containing 20% DMSO, pH = 7.4, 20 mM). As shown in Fig. 4, probe **1** exhibited a weak fluorescence band at 596 nm without thiophenol. The intensity of emission band at 658 nm was strong enhanced upon addition of thiophenol from 0 to 30 μM. Figure 4b shows the plot of emission band at 658 nm versus thiophenol

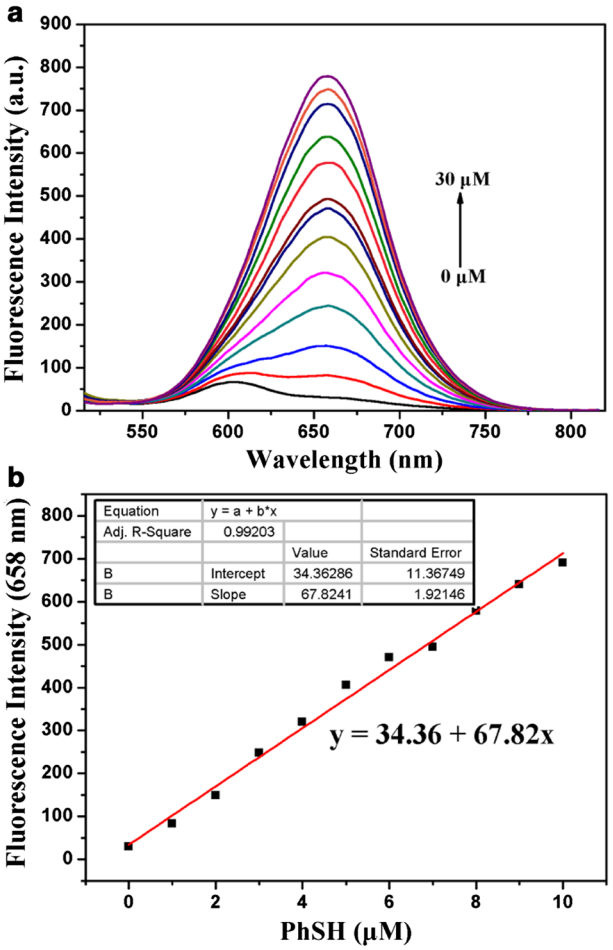


Fig. 4 Fluorescence spectra (**a**) of probe **1** (5 μM) in the presence of different concentrations of thiophenol (0–30 μM) in DMSO/PBS buffer solution (20/80, v/v, pH = 7.4, 20 mM). **b** Fluorescence intensity at 658 nm as a function of thiophenol concentration (0–10 μM). λ_{ex} = 455 nm; slit width = 5/5 nm

concentration. Notably, a good correlation coefficient of 0.992 was obtained when the thiophenol concentration was in the range of 0–10 μM, suggesting that probe **1** could be used for the quantitative detection of thiophenol. The detection limit of probe **1** for thiophenol was determined to be 3.4 nM ($3\sigma/\kappa$). Moreover, a considerable fluorescence enhancement was also observed upon addition of thiophenol from 0 to 1 μM (Fig. S9). All these results indicated that probe **1** is ultrasensitive and quite suitable to detect low concentrations of thiophenol quantitatively compared to previously reported thiophenol probes (Table S1).

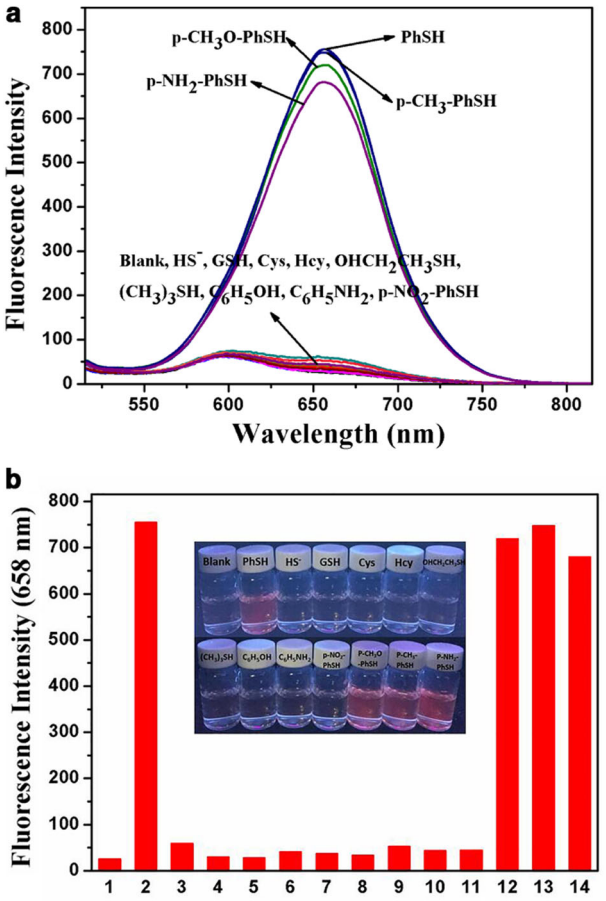


Fig. 5 **a** Fluorescence spectra of probe **1** toward various species: (1) Blank, (2) C_6H_5SH (20 μM); (3) HS^- (100 μM); (4) GSH (100 μM); (5) Cys (100 μM); (6) Hcy (100 μM); (7) $OHCH_2CH_2SH$ (100 μM); (8) $(CH_3)_3CSH$ (100 μM); (9) C_6H_5OH (100 μM); (10) $C_6H_5NH_2$ (100 μM); (11) *p*–NO_2–C_6H_4SH (20 μM); (12) *p*–CH_3O–C_6H_4SH (20 μM); (13) *p*–CH_3–C_6H_4SH (20 μM); (14) *p*–NH_2–C_6H_4SH (20 μM). **b** Corresponding fluorescence intensity at 658 nm in the presence of different species. Inset B: Color change of probe **1** in DMSO/PBS buffer solution (20/80, v/v, pH = 7.4, 20 mM) after addition of various species. λ_{ex} = 455 nm; slit width = 5/5 nm

Response mechanism

According to previous reported literatures, the fluorescence enhancement of probe **1** in the presence of thiophenol implies the formation of compound **2**. To verify the proposed reaction mechanism, mass spectra were measured to confirm reaction product of probe **1** and thiophenol. As shown in Fig. S10, the reaction product of probe **1**–thiophenol is confirmed by HRMS, in which the dominant peaks at *m*/*z* = 359.2242 (calcd. 359.2236) and 291.0434 (calcd. 291.0440) correspond to [probe **1**–thiophenol + H]$^+$ and [DNS–thiophenol + H]$^+$, respectively. Additionally, both absorbance and fluorescence spectra of probe **1**–thiophenol adduct were

Table 1 Determination of thiophenol concentrations in water samples

Sample	Concentration of spiked thiophenol (μM)	Concentration of recovered thiophenol (μM)	Recovery (%)
Changjiang river water	0	Not detected	–
	0.1	0.09 ± 0.12	90
	0.4	0.46 ± 0.04	115
	0.7	0.71 ± 0.21	101
	1	0.97 ± 0.06	97
Huangpu river water	0	Not detected	–
	0.1	0.89 ± 0.15	89
	0.4	0.43 ± 0.06	107
	0.7	0.74 ± 0.16	106
	1	1.04 ± 0.32	104
Qingchun river water	0	Not detected	–
	0.1	0.11 ± 0.13	110
	0.4	0.42 ± 0.11	105
	0.7	0.72 ± 0.09	103
	1	0.98 ± 0.18	98

consistent with compound **2** (Fig. S11). All these results suggested that the reaction process of probe **1** toward thiophenol follows the sulfonamide cleavage mechanism mediated by thiophenol (Scheme 2).

Selectivity

To evaluate the selectivity of probe **1** toward thiophenol, we examined the fluorescence spectra of probe **1** toward various species including thiophenol derivatives (C_6H_5SH, *p*–CH_3–C_6H_4SH, *p*–NH_2–C_6H_4SH, *p*–NO_2–C_6H_4SH, *p*–CH_3O–C_6H_4SH), aliphatic thiols (Cys, Hcy, GSH, $(CH_3)_3CSH$, and $OHCH_2CH_2SH$), and various interfering substances such as nucleophilic species (HS^-, C_6H_5OH, $C_6H_5NH_2$), various anions and metal ions (NaF, NaCl, NaBr, NaI, NaOAc, Na_2SO_3, Na_2HSO_3, Na_2S, KCl, $ZnCl_2$, $FeCl_3$, $AlCl_3$, $CuCl_2$, $Co(NO_3)_3$, $HgCl_2$), and some oxygen species (H_2O_2, ClO^-, ClO_4^-). As shown in Fig. 5, the fluorescence intensity of probe **1** exhibited a significant enhancement upon addition of thiophenols including C_6H_5SH, *p*–CH_3–C_6H_5SH, *p*–NH_2–C_6H_5SH, and *p*–CH_3O–C_6H_5SH. Exceptionally, probe **1** cannot respond to *p*–NO_2–C_6H_4SH, which is due to the existence of strong a electron-withdrawing NO_2 group [12, 25, 29]. *p*–NO_2–$C_6H_4S^-$ showed very low activity in the S_NAr reaction toward sulfonamide because of its relatively large local softness (S^-_{sulfur}) value [44]. As shown in Fig. 5 and Fig. S12, probe **1** displayed slight response to other species except for thiophenols, indicating that probe **1** has a very high selectivity to thiophenols. From the insets of Fig. 5 and Fig. S11, it can be seen that probe **1** exhibits a significant fluorescence enhancement in the presence of thiophenols (except for *p*–NO_2–C_6H_4SH). To investigate the influence of coexisting species to probe **1**, the

fluorescence spectra of probe **1** in the presence of both thiophenols (20 μM) and other species (100 μM) were examined. As shown in Fig. S13 and Fig. S14, probe **1** displayed excellent selectivity to thiophenols and anti-interference ability in the co-existence of various species. As for the selectivity of probe **1** toward thiophenols over aliphatic thiols, it is relative to the weak nucleophilicity of probe **1**. Since the pK_a value of aliphatic thiols is about 8.5, whereas that of thiophenols is around 6.5 [45] the probe **1** preferentially reacts with thiophenols rather than aliphatic thiols.

Determination of the thiophenols in water samples

Considering the toxicity of thiophenols as environmental pollutants, we investigated the feasibility of probe **1** for analysing the thiophenols in environmental water samples. Three water samples were obtained from Changjiang River, Huang-Pu River of Shanghai, and Qing-Chun River of East China University of Science and Technology. These water samples were filtered before analysis, then spiked with different concentrations of thiophenols (0, 0.1, 0.4, 0.7, 1 μM). Then, the fluorescence intensities for different samples at 658 nm were collected. As displayed in Table 1 and Fig. 6, for all of the three river water samples, the

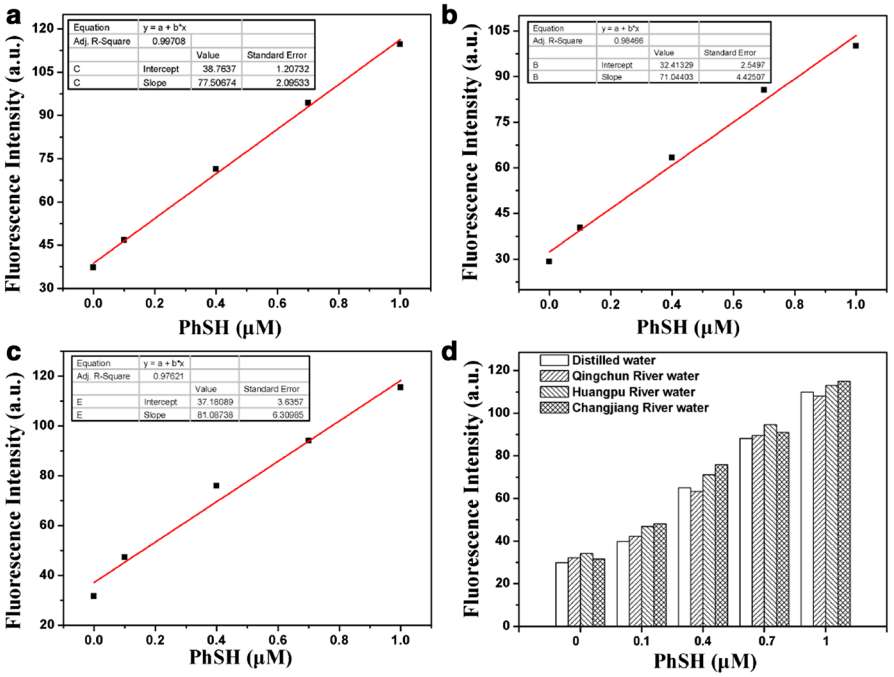


Fig. 6 **a–c** Linear plots of fluorescence intensity changes of probe **1** at 658 nm against the spiked concentrations of PhSH from 0 to 10 μM for "Changjiang River water" (**a**), "Huang-Pu River water" (**b**) and "Qing-Chun River water" (**c**). **d** Fluorescent intensities of probe **1** (5 μM) toward different concentrations of thiophenol in "Qing-Chun River water", "Huang-Pu River water" and "Changjiang River water". All results were conducted in DMSO/PBS buffer solution (20/80, v/v, pH = 7.4, 20 mM). λ_{ex} = 455 nm; slit width = 5/5 nm

fluorescent intensities at 658 nm showed good linear relationships to the spiked thiophenol concentrations (0–1 μM). These results demonstrated that probe **1** is ultrasensitive and has a potential application in quantitative detection of extremely small amount (10^{-7}) of thiophenol in real water samples.

Conclusion

In summary, we have synthesized a new near-infrared (NIR) fluorescent probe (probe **1**) for the highly selective detection of thiophenols. On the basis of the highly efficient cleavage reaction mediated by thiophenols, probe **1** showed high response speed, sensitivity, and selectivity toward thiophenols (except for *p*–NO_2-C_6H_4SH) under room temperature. Probe **1** shows a large stokes shift (203 nm) and significantly enhanced fluorescence intensity which can be easily distinguished by naked eyes. The detection limit was as low as 3.4 nM and the corresponding signal-to-background ratio reached 30.4. Additionally, probe **1** showed good anti-interference ability in the co-existence of the environmental and biologic species. Moreover, probe **1** was ultrasensitive and successfully used in the quantitative detection of thiophenol in three river water samples.

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References

1. W. Jiang, Q.Q. Fu, H.Y. Fan, J. Ho, W. Wang, Angew. Chem. **119**, 8597 (2007)
2. H.W. Liu, X.B. Zhang, J. Zhang, Q.Q. Wang, X.X. Hu, P. Wang, W. Tan, Anal. Chem. **87**, 8896 (2015)
3. S. Shahrokhian, Anal. Chem. **735**, 972 (2001)
4. I. Rahman, W. MacNee, Free Radic. Biol. Med. **28**, 1405 (2000)
5. J. Yin, Y. Kwon, D. Kim, D. Lee, G. Kim, Y. Hu, J.H. Ryu, J. Yoon, J. Am. Chem. Soc. **136**, 5351 (2014)
6. H.S. Jung, X. Chen, J.S. Kim, J. Yoon, Chem. Soc. Rev. **42**, 6019 (2013)
7. O. Nygard, J.E. Nordrehaug, H. Refsum, P.M. Ueland, M. Farstad, S.E.N. Vollset, Eng. J. Med. **337**, 230 (1997)
8. M.T. Heafield, S. Fearn, G.B. Steventon, R.H. Waring, A.C. Williams, S.G. Sturman, Neurosci. Lett. **110**, 216 (1990)
9. P. Amrolia, S.G. Sullivan, A. Stern, R. Munday, J. Appl. Toxicol. **9**, 113 (1989)
10. T.P. Heil, R.C. Lindsay, J. Environ. Sci. Health, Part B **24**, 349 (1989)
11. T.R. Juneja, R.L. Gupta, S. Samanta, Toxicol. Lett. **21**, 185 (1984)
12. X.M. Shao, R.X. Kang, Y.L. Zhang, Z.T. Huang, F.F. Peng, J. Zhang, Y. Wang, F.C. Pan, W.J. Zhang, W.L. Zhao, Anal. Chem. **87**, 399 (2015)
13. L.Y. Niu, Y.Z. Chen, H.R. Zheng, L.Z. Wu, C. Tung, Q.Z. Yang, Chem. Soc. Rev. **44**, 6143 (2015)
14. J. Chan, S. Dodani, C.J. Chang, Nat. Chem. **4**, 973 (2012)
15. C.R. Liu, W. Chen, S. Wen, B. Peng, Y. Zhao, H.M. Ma, M. Xian, J. Am. Chem. Soc. **136**, 7257 (2014)
16. Y. Tang, H.R. Yang, H.B. Sun, S.J. Liu, J.X. Wang, Q. Zhao, X.M. Liu, W.J. Xu, S.B. Li, W. Huang, Chem. Eur. J. **19**, 1311 (2013)
17. X. Li, S.J. Qian, Q.J. He, B. Yang, J. Li, Y.Z. Hu, Org. Biomol. Chem. **8**, 3627 (2010)
18. W. Sun, W.H. Li, J. Li, J. Zhang, L.P. Du, M.Y. Li, Tetrahedron **68**, 5363 (2012)

19. W.Y. Lin, L.L. Long, W. Tan, Chem. Commun. **46**, 1503 (2010)
20. J. Li, C.F. Zhang, S.H. Yang, W.C. Yang, G.F. Yang, Anal. Chem. **86**, 3037 (2014)
21. X.Q. Chen, Y. Zhou, X.J. Peng, J. Yoon, Chem. Soc. Rev. **39**, 2120 (2010)
22. L. Peng, Z.J. Zhou, R.R. Wei, K. Li, P.S. Song, A.J. Tong, Dyes Pigments **108**, 24 (2014)
23. L. Lin, X.Q. Zeng, Y.N. Shen, H.L. Zhu, Y. Qian, Talanta **165**, 321 (2017)
24. Q.J. Ma, J.H. Xu, X.B. Zhang, L.Y. Zhou, H.W. Liu, J. Zhang, Sens. Actuators, B **229**, 434 (2016)
25. W. Jiang, Y.T. Cao, Y. Liu, W. Wang, Chem. Commun. **46**, 1944 (2010)
26. D.H. Yu, F.H. Huang, S.S. Ding, G.Q. Feng, Anal. Chem. **86**, 8835 (2014)
27. C.C. Zhao, Y. Zhou, Q.N. Lin, L.Y. Zhu, P. Feng, Y.L. Zhang, J.A. Cao, J. Phys. Chem. B **115**, 642 (2011)
28. W.W. Zhao, W.M. Liu, J.C. Ge, J.S. Wu, W.J. Zhang, X.M. Meng, P.F. Wang, J. Mater. Chem. **21**, 13561 (2011)
29. D. Kand, P.K. Mishra, T. Saha, M. Lahiri, P. Talukdar, Analyst **137**, 3921 (2012)
30. R. Zhang, Z.Q. Ye, Y.J. Yin, G.L. Wang, D.Y. Jin, J.L. Yuan, J.A. Piper, Bioconjugate Chem. **23**, 725 (2012)
31. Y. Ji, L.J. Xia, L.C. Chen, X.F. Guo, H. Wang, H.J. Zhang, Talanta **181**, 104 (2018)
32. P. Hou, S. Chen, H.B. Wang, J.X. Wang, K. Voitchovsky, X.Z. Song, Chem. Commun. **50**, 320 (2014)
33. X.M. Wu, X.R. Sun, Z.Q. Guo, J.B. Tang, Y.Q. Shen, T.D. James, H. Tian, J. Am. Chem. Soc. **136**, 3579 (2014)
34. Q.S. Lin, Y.L. Huang, X.X. Fan, X.L. Zheng, X.L. Chen, X.Q. Zhan, H. Zheng, Talanta **170**, 496 (2017)
35. K.Q. Xiang, Y.C. Liu, C.J. Li, B.Z. Tian, J.L. Zhang, RSC Adv. **5**, 52516 (2015)
36. L.H. Li, W. Shi, X.F. Wu, Q.Y. Gong, X.H. Li, H.M. Ma, Biosens. Bioelectron. **81**, 395 (2016)
37. K.Q. Xiang, S.Z. Chang, J.J. Feng, C.J. Li, W. Ming, Z.Y. Liu, Y.C. Liu, B.Z. Tian, J.L. Zhang, Dyes Pigment **134**, 190 (2016)
38. Z.Q. Guo, W.H. Zhu, H. Tian, Chem. Commun. **48**, 6073 (2012)
39. B. Liu, W.H. Zhu, Q. Zhang, W.J. Wu, M. Xu, Z.J. Ning, Y.S. Xie, H. Tian, Chem. Commun. **13**, 1766 (2009)
40. Z.J. Ning, Q. Zhang, W.J. Wu, H.C. Pei, B. Liu, H. Tian, J. Org. Chem. **73**, 3791 (2008)
41. O.P. Kwon, S.J. Kwon, M. Jazbinsek, F. Brunner, J. Seo, C. Hunziker, A. Schneider, H. Yun, Y.S. Lee, P. Günter, Adv. Funct. Mater. **18**, 3242 (2008)
42. O.P. Kwon, B. Ruiz, A. Choubey, L. Mutter, A. Schneider, M. Jazbinsek, V. Gramlich, P. Günter, Chem. Mater. **18**, 4049 (2006)
43. K.Q. Xiang, Y.C. Liu, C.J. Li, B.Z. Tian, T.Z. Tong, J.L. Zhang, Dyes Pigments **123**, 78 (2015)
44. Y. Shiraishi, K. Yamamoto, S. Sumiya, T. Hirai, Chem. Commun. **49**, 11680 (2013)
45. X.L. Liu, X.Y. Duan, X.J. Du, Q.H. Song, Chem. Asian J. **7**, 2696 (2012)