# **Electronic Supporting Information**

## Reaction-based fluorescent probe for selective and sensitive detection

## of thiophenols with a large stokes shift and its application in water

## samples

Mengzhao Zhang <sup>a, b</sup>, Taohua Leng <sup>b, \*</sup>, Yongjia Shen <sup>a</sup>, Chengyun Wang <sup>a, \*</sup>

a. Key Laboratory 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, P. R. China. E-mail: cywang@ecust.edu.cn.

b. Department of Chemistry, School of Chemistry and Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, P. R. China. E-mail: <u>length@sqi.org.cn</u>.

# **Table of contents**

### **Preparation of test solutions**

Table S1. Comparison of determined detection limit with those of some literatures.

Fig. S1. <sup>1</sup>H NMR spectrum of compound 2 in DMSO-d<sub>6</sub>

- Fig. S2. <sup>13</sup>C NMR spectrum of compound 2 in DMSO-d<sub>6</sub>
- Fig. S3. <sup>1</sup>H NMR spectrum of Probe 1 in DMSO-d<sub>6</sub>
- Fig. S4. <sup>13</sup>C NMR spectrum of Probe 1 in DMSO-d<sub>6</sub>
- Fig. S5. HRMS spectrum of Probe 1.
- **Fig. S6.** Time course of Probe 1 (10  $\mu$ M) upon addition of thiolphenol (20  $\mu$ M) in DMSO– HEPES (V/V = 3 : 7, 50 mM, pH 7.4) solution. Slit width: 3/5 nm.  $\lambda_{ex}$  = 454 nm.
- Fig. S7. Time dependent fluorescence spectra of Probe 1 (10  $\mu$ M) in the present of PhSH (50  $\mu$ M) in different DMSO/HEPES buffer solution (30/70, 20/80, 10/90, 5/95, pH = 7.4, 50 mM).  $\lambda_{ex} = 454$  nm.
- Fig. S8. Color changes of Probe 1 upon addition of different species under UV light (365 nm).
- Fig. S9. Fluorescence responses of Probe 1 (10  $\mu$ M) at 613 nm toward thiolphenol (20  $\mu$ M) in the presence of some competitive species (100  $\mu$ M) in DMSO–HEPES (V/V = 3 : 7, 50 mM, pH 7.4) solution.  $\lambda_{ex}$  = 454 nm.
- Fig. S10. HRMS spectrum of the reaction between Probe 1 and PhSH.
- Fig. S11. Effect of pH on the fluorescence intensity at 613 nm of Probe 1 (10  $\mu$ M) in DMSO– HEPES (V/V = 3 : 7, 50 mM, pH 7.4) solution with (•) and without (•) PhSH (20  $\mu$ M).  $\lambda_{ex}$  = 454 nm.

#### **Preparation of test solutions:**

<sup>\*</sup> Corresponding author. Tel./fax: +86-021-64252967; e-mail: cywang@ecust.edu.cn; length@sqi.org.cn.

- 1. Preparation of probe solution: The solution of Probe **1** was prepared in DMSO at 0.2 mM. The test solution of the Probe **1** (10  $\mu$ M) in 3 mL HEPES buffer (50 Mm, pH 7.4) was prepared by placing 0.15 mL stock solution of Probe **1** (10  $\mu$ M) and 0.75 mL DMSO in 2.1 mL HEPES buffer.
- Preparation of the solutions of various tested analytes: NaF, NaCl, NaBr, NaI, NaClO<sub>4</sub>, NaClO, NaHSO<sub>3</sub>, Na<sub>2</sub>SO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, KCl, ZnCl<sub>2</sub>, FeCl<sub>3</sub>, AlCl<sub>3</sub>, CuCl<sub>2</sub>, HgCl<sub>2</sub>, CoCl<sub>2</sub> were prepared at 3 mM in distilled water. PhSH, p–NH<sub>2</sub>–PhSH, p–CH<sub>3</sub>–PhSH, p–NO<sub>2</sub>–PhSH, Hcy, Cys, GSH, (CH<sub>3</sub>)<sub>3</sub>SH, HOCH<sub>2</sub>CH<sub>2</sub>SH, NaSH, Na<sub>2</sub>S, C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>OH were prepared at 3 mM in EtOH.

Probe	$\lambda_{\rm ex}/\lambda_{\rm em}$ (nm) (stokes shift)	Response speed	Detection limit	Reference	
HO COH HO COH HO COH	260/414 (154)	5 s	3.8 nM	Dyes Pigms 2015; 116: 52–57	
	465/555 (90)	20 min	2 μΜ	Chem Commun 2010; 46: 1944–1946	
Not	461/494 (33)	30 min	1.8 nM	Chem Commun 2010, 46, 1503–1505.	
$- {\underset{H^{-}}{\atop\atopH^{-}}{\underset{H^{-}}{\underset{H^{-}}{\underset{H^{-}}{\underset{H^{-}}{\atop{H^{-}}{{\atop{H^{}}}{\atop{H^{}}}{{{{\atop{H^{}}}{{{{\atop{H^{}}}{{{}{{\atop{H^{}}}{{}{{}{{\atop{H^{}$	370/515 (145)	15 min	150 nM	Anal. Chem. 2014, 86, 8835 – 8841	
→ → → → → → → → → → → → → →	484/568 (84)	30 min	0.74 μΜ	Org Biomol Chem. 2012; 10: 4689–4691.	
о,н-()-5-0-()-()-0-()-0-()-0-()-0-()-0-()-0	380/517 (137)	3 min	10 nM	J Mater Chem C 2015, 3, 8248–8254.	
	477/606 (129)	2 min	8.2 nM	J Mater Chem C 2016, 4, 4320–4326.	
NC <sub>T</sub> CN TOTAL N N O NO2 Probe 1 O C NO2	454/613 (159)	15 min	8.3 nM	This work	

Table S1. Comparison of determined detection limit with those of some literatures.



Fig. S1. <sup>1</sup>H NMR spectrum of compound 2 in DMSO-d<sub>6</sub>



Fig. S2. <sup>13</sup>C NMR spectrum of compound 2 in DMSO-d<sub>6</sub>



Fig. S3. <sup>1</sup>H NMR spectrum of Probe 1 in DMSO-d<sub>6</sub>



Fig. S4. <sup>13</sup>C NMR spectrum of Probe 1 in DMSO-d<sub>6</sub>

Multiple Mass Analysis: 2 mass(es) processed Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3



Monoisotopic Mass, Odd and Even Electron Ions 8172 formula(e) evaluated with 15 results within limits (up to 50 closest results for each mass) Elements Used: 12C: 0-50 13C: 0-1 H: 0-50 N: 4-9 O: 5-10 S: 0-1 Wc-ZWZ-EI-PHSH XEVO-G2TOF#NotSet 20170310 86 (0.870) Cm (86-(452:455+962:969))

WC-ZMZ-EI-P 20170310 86	HSH (0.870) Cm (	86-(452:455+962	:969))	0.0-10	XEVO-G2TOF#NotSet					10:14:00 16-May-2017 1: TOF MS ES+ 1.37e+004	
100	573.6757573.9370 574		74.1273	574.4501	575.0222 575.1304		575.6129		576.1335 576.4074		m/z
573.00	573.5	0 574.0	00	574.50		575.00	575.5	0	576.00	576.50	
Minimum: Maximum:	20.00 100.00		5.0	5.0	-1.5 50.0						
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula		
574.1273	100.00	574.1271 574.1277 574.1278 574.1266 574.1257	0.2 -0.4 -0.5 0.7	0.3 -0.7 -0.9 1.2 2.8	20.0 29.0 21.0 24.5 20.5	141.1 139.1 139.1 141.4 141.3	3.562 1.523 1.615 3.913 3.798	2.84 21.81 19.88 2.00 2.24	12C27 H2: 12C35 H1: 12C25 13 12C31 13 12C25 H2	2 N6 07 S 8 N4 05 C H19 N7 09 C H21 N4 05 S 0 N9 06 S	
575.1304	43.34	574.1291 575.1304 575.1302 575.1309 575.1311 575.1315 575.1291 575.1298 575.1288	-1.8 0.0 0.2 -0.5 -0.7 -1.1 1.3 1.6 -1.8	-3.1 0.0 0.3 -0.9 -1.2 -1.9 2.3 2.8 -3.1	20.5 20.0 25.0 15.5 29.0 24.5 20.5 20.5 20.0 15.0	138.2 73.4 71.9 73.6 70.9 71.6 73.9 72.3 73.0 73.9	0.669 3.436 1.889 3.568 0.902 1.652 3.952 2.272 3.026 3.901	51.23 3.22 15.12 2.82 40.57 19.17 1.92 10.31 4.85 2.02	12C27 13 12C26 13 12C28 H1 12C22 H2 12C34 13 12C30 H1 12C24 13 12C27 H2 12C27 H2 12C24 H2 12C24 H2	$ \begin{array}{cccc} {\rm H}21 & {\rm N4} & {\rm O10} \\ {\rm C} & {\rm H}22 & {\rm N6} & {\rm O7} & {\rm S} \\ {\rm 7} & {\rm N9} & {\rm O6} \\ {\rm 3} & {\rm N8} & {\rm O9} & {\rm S} \\ {\rm C} & {\rm H18} & {\rm N4} & {\rm O5} \\ {\rm 9} & {\rm N6} & {\rm O7} \\ {\rm C} & {\rm H20} & {\rm N9} & {\rm O6} & {\rm S} \\ {\rm 1} & {\rm N5} & {\rm O10} \\ {\rm 5} & {\rm N5} & {\rm O10} & {\rm S} \\ {\rm C} & {\rm H24} & {\rm N5} & {\rm O10} & {\rm S} \end{array} $	3

Fig. S5. HRMS spectrum of Probe 1.



Fig. S6. Time course of Probe 1 (10 µM) upon addition of thiolphenol (20 µM) in DMSO-HEPES (V/V = 3 : 7, 50 mM, pH 7.4) solution. Slit width: 3/5 nm.  $\lambda_{ex} = 454$  nm.



Fig. S7. Time dependent fluorescence spectra of Probe 1 (10 µM) in the present of PhSH (50  $\mu$ M) in different DMSO/HEPES buffer solution (30/70, 20/80, 10/90, 5/95, pH = 7.4, 50 mM).  $\lambda_{\rm ex} = 454$  nm.



Fig. S8. Color changes of Probe 1 upon addition of different species under UV light (365 nm).



**Fig. S9.** Fluorescence responses of Probe 1 (10  $\mu$ M) at 613 nm toward thiolphenol (20  $\mu$ M) in the presence of some competitive species (100  $\mu$ M) in DMSO–HEPES (V/V = 3 : 7, 50 mM, pH 7.4) solution.  $\lambda_{ex} = 454$  nm.



Fig. S10. HRMS spectrum of the reaction between Probe 1 and PhSH.



**Fig. S11.** Effect of pH on the fluorescence intensity at 613 nm of Probe 1 (10  $\mu$ M) in DMSO–HEPES (V/V = 3 : 7, 50 mM, pH 7.4) solution with (•) and without (•) PhSH (20  $\mu$ M).  $\lambda_{ex} = 454$  nm.