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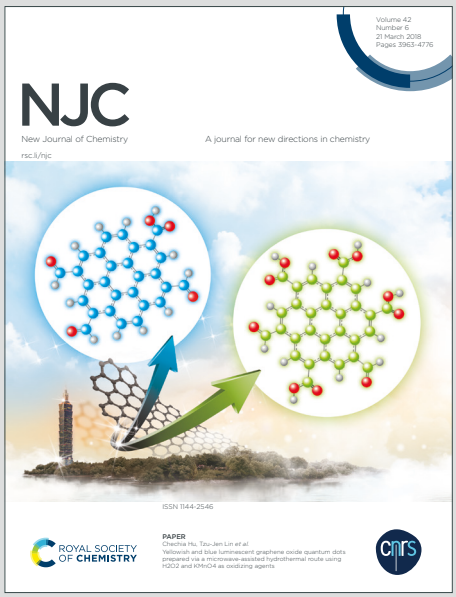

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ROYAL SOCIETY OF CHEMISTRY View Article Online
DOI: 10.1039/C9NJ03020D

ARTICLE

Construction of an effective far-red fluorescent and colorimetric platform containing a merocyanine core for specific and visual detection of thiophenol in both aqueous medium and living cells

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Thiophenol (PhSH) is toxic to environment and biological system although it is an indispensable material in synthetic processes of chemical products. In this work, we design and synthesize a malonitrile-based colorimetric and deep-red emission fluorescent dosimeter specifically for thiophenol detection by switching on the intramolecular charge transfer process. The 2,4-dinitrobenzene moiety in the probe can be cleaved off by thiophenol, which leads to a strong deep-red fluorescence increase at 645 nm (50-fold) with a low detect limit of 9 nM. The maximum plateau of emission intensity was reached in about 30 min since addition of thiophenol. Simultaneously, the presence of thiophenol can result in a prominent colorimetric change from orange to blue. Furthermore, the dosimeter can quantitatively sense thiophenol sparked in water samples and successfully visualize thiophenol in living SH-SY5Y cells.

1. Introduction

It is well known that thiophenol is highly toxic to organisms and extremely detrimental to environment although they are extensively used in organic synthesis as an indispensable raw material for preparing various agrochemicals, pharmaceuticals and others.[1-3] Due to high toxicity and carcinogenicity, trace inhalation or dermal contact with thiophenol might damage the central nervous system and cause several disorders, including but not limited to respiratory disease, headache, nausea, vomit, muscular weakness, etc.[4] Furthermore, reactive superoxide radicals as well as hydrogen peroxide probably could be generated through oxidation from thiophenol to disulphide, which might cause severe oxidative damage to erythrocyte cells.[5] It is reported that the thiophenol concentration from 0.01 to 0.4 mM to fish and from 2.15 to 46.2 mg/kg in mouse was reported as the median lethal dose,[6, 7] so that thiophenol is regarded as one of the top pollutants. Apparently, it is of a high demand to develop specifically sensing methods for thiophenol in environment and biology.

In this end, compared with traditional methods including electrochemistry and UV-vis spectrometry, small-molecule based fluorescence imaging has been attracting more and more attention due to their simplicity, easy operation, on-spot detection, low cost, non-destruction, and high spatiotemporality.[8-16] Since the pioneering work by Wang,[17] considerable amount of effort has been spent to construction of fluorescent probes sensing thiophenol, which usually contain a recognition unit such as benzenesulfonyl or phenol tailed by two nitro groups.[18-29] The strong nucleophilic attack of thiolate anions can readily cleave off the protected groups and finally release fluorescence through modulation of electron processes.[30-40] Moreover, as we know, far-red/near-infrared fluorescent dyes have many advantages such deep tissue penetration, low photodamage and photobleaching to biology and low interference from background.[41-43] It is to be noted that there have been only a few of thiophenol probes showing far-red fluorescence or even near-infrared emission (NIR) in literatures.[44-50] In 2014, Feng's group reported a thiophenol probe emitting fluorescence at 720 nm containing dicyanomethylene-4H-benzopyran core with a limit of detection (LOD) of 0.15 μM in PBS buffer-DMSO (7:3, v/v).[47] In 2017, a fluorescent probe with emission at 623 nm for thiophenol was developed by conjunction of coumarin anchored by phenothiazine with a LOD of 2.9 nM in PBS buffer assisted with CTAB (1mM).[48] Zhu's group developed another NIR fluorescent probe as a dicyanoisophorone derivative for thiophenol with the detection limit of 0.42 μM in PBS buffer-DMSO (1:1, v/v).[49] Recently, Song's group successfully discriminatorily detected thiophenol, hydrogen sulfide and mercapto amino acids with one fluorescent probe in a triple-emission mode.[50] Notably, these excellent probes still have some drawbacks such as use of highly proportional organic solvent, assistance of CTAB, or high detection limits. Especially, lack of far-red/NIR fluorophores extremely encumbered further development of performance-perfect probes and potential application in biology.

As we know, a practical way to construct the far-red/NIR fluorophores is introduction of suitable electron-withdrawing groups (EWGs) which can effectively modulate charge/electron

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Electronic Supplementary Information (ESI) available: [NMR spectra of the compounds, MS and chromatograms of the reaction systems, supplementary fluorescent spectra, cytotoxicity assay]. See DOI: 10.1039/x0xx00000x

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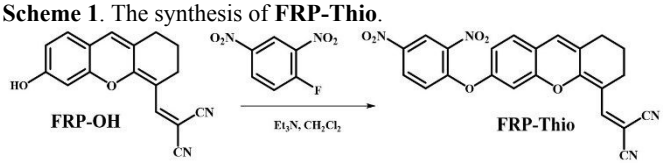
DOI: 10.1039/C9NJ03405F

transfer processes of targeted probes.[51-53] Furthermore, besides the shift of excitation/emission wavelength to the NIR range, this kind of EWGs also improves their sensitivity or selectivity toward analytes in biology. With this thought, we envisioned that a simple malonitrile group could substantially ameliorate chemical and/or photophysical properties of probes. Therefore, in this study, we developed a thiophenol fluorescent probe (**FRP-Thio**) as a merocyanine derivative tailed by malonitrile with the 2,4-dinitrophenol group. The probe showed a colorimetric change and also far-red emission (50-fold increase) by selectively and sensitively detecting thiophenol with a LOD of 9 nM. Benefited by the malonitrile group extending a π-conjugation, the emission wavelength of **FRP-Thio** was moved into the far-red fluorescence range. In addition, **FRP-Thio** could successfully visualize thiophenol in aqueous solution and living SH-SY5Y cells.

Scheme 1. The synthesis of **FRP-Thio**.



2. Experimental

2.1. Synthesis of FRP-Thio

FRP-OH (0.14 g, 0.5 mmol) was dissolved in 20 mL of MeCN and refluxed after addition of K_2CO_3 (0.09 g, 0.6 mmol) as well as 1-fluoro-2,4-dinitrobenzene (0.112 g, 0.6 mmol) with stirring overnight. The title compound **FRP-Thio** as a red solid was purified by flash chromatography using ethyl acetate/petroleum ether (1/1, v/v) (0.13 g， 58%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.94 (d, J = 2.8 Hz, 1H), 8.52 (dd, J = 9.2, 2.8 Hz, 1H), 8.23 (s, 1H), 7.62 (d, J = 8.5 Hz, 1H), 7.49 – 7.47 (m, 1H), 7.45 (d, J = 9.2 Hz, 1H), 7.37 (s, 1H), 7.18 (dd, J = 8.5, 2.4 Hz, 1H), 2.75 (t, J = 6.0 Hz, 2H), 2.65 (t, J = 6.1 Hz, 2H), 1.77 (p, J = 6.1 Hz, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 158.37, 156.38, 153.92, 153.51, 151.16, 142.86, 140.55, 130.76, 130.21, 129.67, 129.04, 122.38, 121.67, 119.27, 117.50, 116.91, 116.09, 110.63, 107.64, 70.17, 28.63, 24.64, 20.32. HRMS [$C_{23}H_{14}N_4O_6$+H^+] m/z: calcd. 443.0991, found 443.0979.

2.2. Fluorescent imaging in SH-SY5Y cells

SH-SY5Y cells were grown in DMEM containing 10% fetal bovine serum as well as 1% penicillin and streptomycin. SH-SY5Y cells adhered for 24 h before subsequent experiments. Two groups of cell experiments were set up. In a control group, SH-SY5Y cells were only pretreated with 10 μM **FRP-Thio** for 30 min. In the second group, SH-SY5Y cells were first incubated with 100 μM thiophenol and then further with10 μM **FRP-Thio** in turn.

3. Results and discussion

3.1. Design and synthesis of FRP-Thio

As mentioned before, the suitable tailing group in a push-pull system could modulate the emission wavelengths of targeted probes, and also significantly improve their selectivity and sensitivity. Additionally, many studies confirmed that the nucleophilicity of thiophenol could easily break down an ether bond between the 2,4-dinotrophenyl group and the fluorophore.[54,55] With this thought in mind, as displayed in Scheme 1, a deep-red fluorescent **FRP-Thio** for PhSH was synthesized in the presence of triethylamine in CH_2Cl_2 through linking the 2,4-dinotrophenyl unit and the fluorophore **FRP-OH**. This fluorophore tethered by the strong electron-withdrawing cyano groups emits the deep-red fluorescence due to the excellent intramolecular charge transfer process (ICT). Therefore, the presence of thiophenol could effectively cut off the ether bond, which finally released the fluorophore **FRP-OH** and led to a dramatic fluorescent enhancement. **FRP-Thio** was characterized by ^{1}H NMR, ^{13}C NMR as well as HRMS. (Fig. S1-S3).

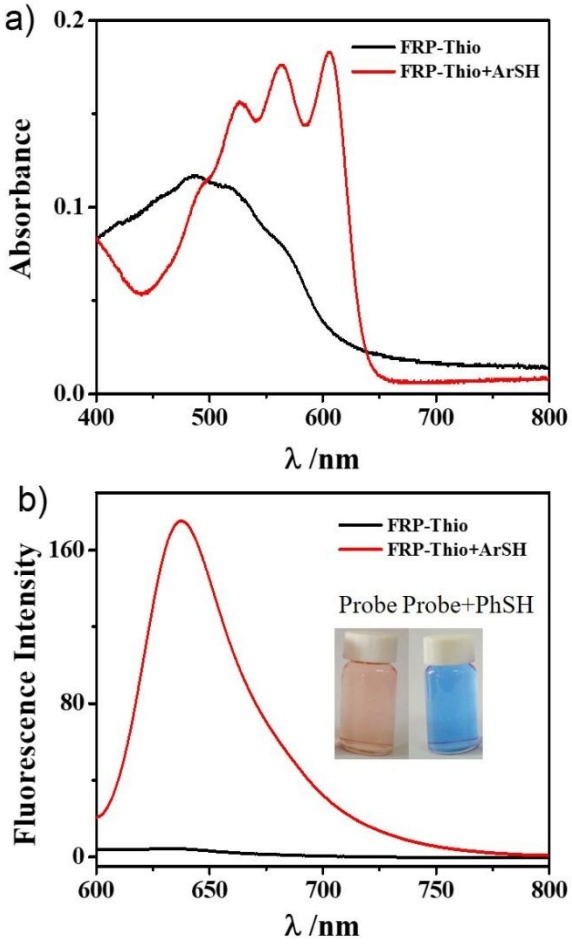


Fig. 1. UV-vis absorption (a), fluorescence (b) and color (Inset of b) changes of **FRP-Thio** (10 μM) in the absence and presence of thiophenol (200 μM) in DMF-H_2O (2/8, v/v, 20 mM PBS buffer, pH 7.4; $\lambda_{ex/em}$ = 560/645 nm).

3.2. UV-Vis absorption and fluorescence spectra

We firstly checked both the absorption and fluorescence spectra of **FRP-Thio** probe (10 μM) were performed in 20% DMF aqueous solution (v/v, 20 mM PBS buffer, pH 7.4) with or without thiophenol. As Fig. 1a demonstrated, free **FRP-Thio** exhibited only a broad absorption band at around 500 nm. However, Addition of thiophenol (20 equiv) into the probe solution led to three strong

absorption peaks at 528, 560, and 605 nm. As shown in Fig. 1b, the free probe is nonfluorescent. However, addition of thiophenol resulted in a distinct far-red fluorescence enhancement at 645 nm. Furthermore, the probe **FRP-Thio** displayed remarkable colorimetric responses from orange to blue-green with gradual addition of thiophenol under natural light (Inset of Fig. 1b). These outstanding changes of color and spectra indicate **FRP-Thio** can be a promising tool for thiophenol by naked eyes even without any instruments under physiological conditions.

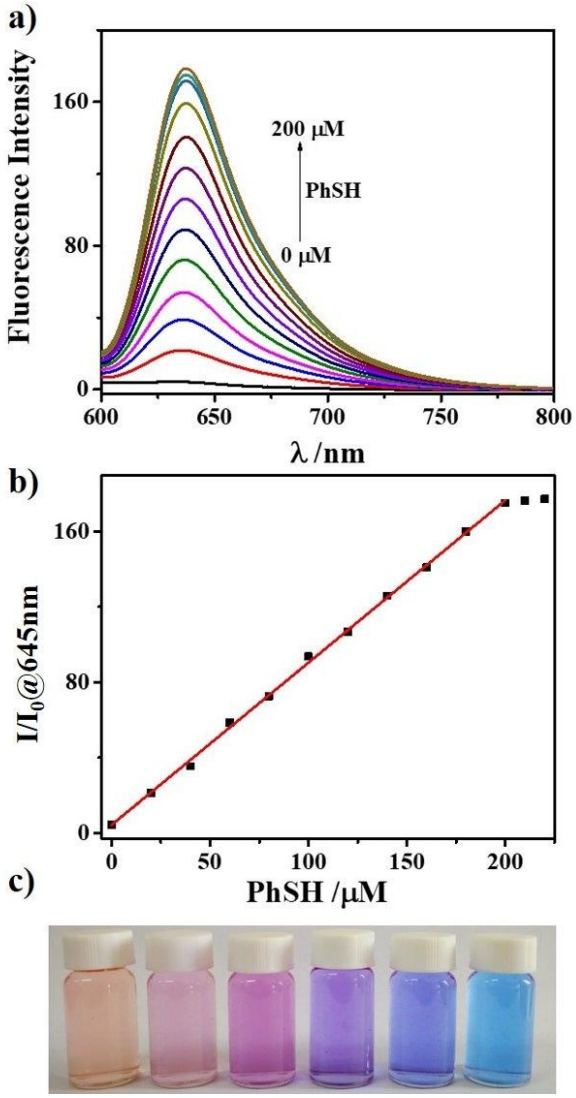


Fig. 2. (a) Fluorescence spectral changes at 645 nm of **FRP-Thio** (10 μM) upon addition of thiophenol (0-20 equiv) excited at 560 nm. Each spectrum was recorded at 30 min after addition of thiophenol. (b) The linear relationship between emission intensity at 645 nm and PhSH concentration. (c) Color change of **FRP-Thio** (10 μM) upon addition of thiophenol at different concentration (0, 40, 80, 120, 160, 200 μM) under natural light.

The subsequent titration experiments were performed to disclose the relationship between the probe (10 μM) toward thiophenol at different concentration in 20% DMF PBS buffer (20 mM, pH 7.4). As displayed in Fig. 2a, free **FRP-Thio** did not emit any obvious fluorescence. As expected, addition of thiophenol led to a remarkable enhancement of fluorescence enhancement at 645 nm excited at 560 nm. Apparently, this enhancement of emission intensity was reasonably attributed to the release of the fluorophore emitting at 645 nm. With gradual addition of thiophenol, the emission at 645 nm sharply rose and finally reached a maximum plateau with thiophenol (20 equiv). Additionally, the fluorescence intensities at 645 nm was perfectly proportional to thiophenol concentration (Fig. 2b). The LOD of 9.0 nM of **FRP-Thio** for thiophenol is estimated. Gradual addition of thiophenol (0, 40, 80, 120, 160, 200 μM) induced the distinctly colorimetric change as shown in Fig. 2c. Therefore, we can conclude that **FRP-Thio** can specifically detect thiophenol by spectroscopic or/and colorimetric methodology.

Response time is an important parameter for reaction-based probes. The kinetic profile of **FRP-Thio** (10 μM) reacting with thiophenol (200 μM) in 20% DMF PBS buffer (20 mM, pH 7.4) were investigated to determine the response time. The fluorescence at 645 nm increased with addition of thiophenol (200 μM) at first (Fig. S4). In about 30 minutes, it reached the maximum plateau. Moreover, Addition of thiophenol (100 μM) did not prolong the formation time of the maximum fluorescence intensity. No difference of equilibrium time for two different concentrations testified that the response time of **FRP-Thio** is not affected by the concentration of thiophenol. There is no obvious decay of emission intensity in the subsequent another 30 min. Hence, all these experiments support that **FRP-Thio** can reliably and rapidly detect thiophenol.

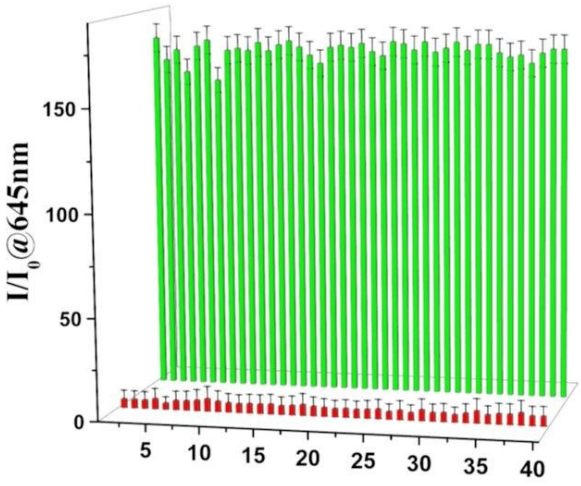


Fig. 3. Fluorescence responses at 645 nm of **FRP-Thio** (10 μM) with 500 μM relevant species (1. Blank, 2. K^+, 3. Na^+, 4. Al^{3+}, 5. Mg^{2+}, 6. Zn^{2+}, 7. Ba^{2+}, 8. Cu^{2+}, 9. Fe^{2+}, 10. Mn^{2+}, 11. Cd^{2+}, 12. Ca^{2+}, 13. F^-, 14. Cl^-, 15. SO_4^{2-}, 16. SO_3^{2-}, 17. AcO^-, 18. ClO^-, 19. H_2O_2, 20. Asp, 21. Try, 22. Gly, 23. Val, 24. Ile, 25. Glu, 26. Arp, 27. Leu, 28. Ala, 29. His, 30. Lys, 31. Met, 32. Phe, 33. Tyr, 34. Ser, 35. Pro, 36. Thr, 37. H_2S, 38. Hcy, 39. Cys, 40. GSH) as red bars or with following addition of 30 equiv of thiophenol (green bars) excited at 560 nm.

3.3. Selectivity and anti-interference studies

To further evaluate the specificity, the competing experiments in 20% DMF PBS buffer (20 mM, pH 7.4) were investigated by

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monitoring the fluorescence response of **FRP-Thio** (10 μM) with various interfering analytes. As displayed in Fig. 3, biothiols (Cys, Hcy, GSH) as well as other amino acid such as Asp, Try, Gly, Val, Ile, Glu, Arp, Leu, Ala, His, Lys, Met, Phe, Tyr, Ser, Pro, Thr and H_2S did not trigger any notable fluorescent enhancement even with addition of other analytes (500 μM). Furthermore, the same phenomena of **FRP-Thio** were observed in the presence of the related reactive oxygen species (ClO^- and H_2O_2; 50.0 equiv) and common cations and anions (K^+, Na^+, Cu^{2+}, Fe^{2+}, Al^{3+}, Ba^{2+}, Mn^{2+}, Cd^{2+}, Ca^{2+}, Mg^{2+}, Zn^{2+}, F^-, Cl^-, SO_4^{2-}, SO_3^{2-}, AcO^-; 50.0 equiv). In contrast, the following addition of thiophenol to **FRP-Thio** with the abovementioned competing species induced an outstanding fluorescence enhancement at 645 nm as well as significant color change from pink to blue (Fig. S5). These results evidenced that **FRP-Thio** owns the excellent specificity toward thiophenol over other competing species.

3.4. pH effect studies

In order to extend further environmental or biological application, the fluorescence changes (Fig. S6) of **FRP-Thio** in DMF-H_2O (2/8, v/v) were investigated at different pH values with or without thiophenol. **FRP-Thio** without thiophenol did not display obvious fluorescence change in the wide pH range of 2.0-11.0. Thiophenol resulted in a gradual fluorescence enhancement of **FRP-Thio** since pH 2.0; the maximum emission intensity appeared at around pH 8.0. By contraries, the emission at 645 nm slightly descended from pH 8.0 to 11.0. These studies implied that **FRP-Thio** is a promising tool for thiophenol in a pH range of 5-11.

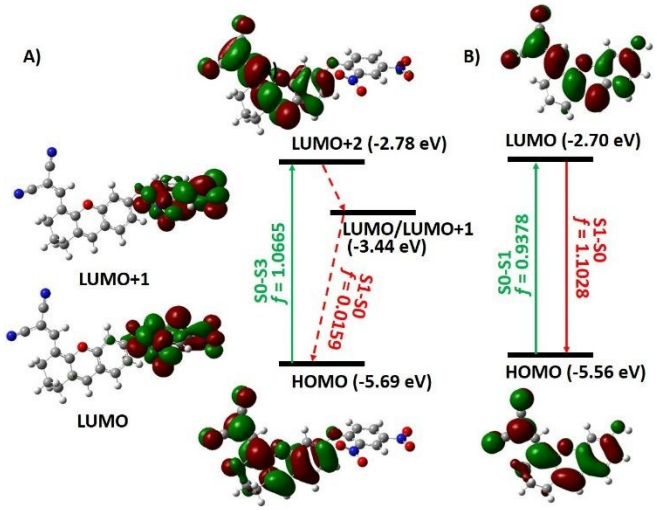

Fig. 4. Optimized structures and frontier molecular orbitals of **FRP-Thio** (a) and **FRP-OH** (b). Calculations were performed at the B3LYP/6-311G(d,p) level.

3.5. Mechanism study

Scheme 2. The proposed mechanism of **FRP-Thio** toward PhSH.

The electron-withdrawing groups have been extensively tethered in order to modulate the fluorescence spectra of probes. Therefore, as shown in Scheme 1, the cleavage of the 2,4-dinitrophenyl group of the probe was trigged by thiophenyl, which released the far-red emission fluorophore with malonitrile. This plausible recognition mechanism was in a good accordance with the spectroscopic data of the probe. first, we investigated the HRMS spectra of the probe in the presence or absence of thiophenol. Fig. S7 showed that the peak (m/z = 275.08271) could be reasonably attributed to the species ([**FRP-OH**-H^+]: calcd. 275.08205) besides the peak (m/z = 441.8429) assigned to the probe ([**FRP-Thio**-H^+]: calcd. 441.08350). These data definitely verified the abovementioned recognition mechanism in Scheme 1.

In order to further elucidate this mechanism of off-on fluorescence of **FRP-Thio** in the presence of thiophenol, the theoretical calculations including density functional theory (DFT) and time-dependent DFT (TDDFT) were conducted using Gaussian 09. The geometries of **FRP-Thio** and **FRP-OH** (Fig. 4a) were optimized at the B3LYP/6-311G(d,p) level, based on which, the electronic transitions energies of the probe and fluorophore were obtained from TD-DFT using the SMD solvation model (solvent = H_2O). Apparently, the allowed electron transition of **FRP-Thio** is reasonably assigned to S0→S3 (oscillator strength, f = 1.0665), which is characterized as the HOMO→LUMO+2 transition with 0.69871 of configuration interaction (CI). As shown in Fig. 4a, both HOMO and LUMO+2 mainly locate on the whole fluorophore while both LUMO and LUMO+1 spread around the receptor. Although there is no redistribution of the electronic density on HOMO and LUMO+2, the electron on LUMO+2 still can be retransferred back to LUMO+1 and subsequently to LUMO by means of internal conversion. It is to be mentioned that S1 is a dark state, confirming the electron transition from LUMO to HOMO is a non-radiative decay process (S1→S0, f = 0.0159). This is in agreement with quenching of the fluorescence of the probe. The allowed electron transition of the fluorophore is attributed to S0-S1 (f = 0.9378) which is mainly composed of the HOMO-LUMO with 0.70743 of CI. As demonstrated in Fig. 4b, the electronic density of both HOMO and LUMO are delocalized on the whole fluorophore. There is no redistribution observed of electron density on both LUMO and HOMO which makes up of the S1 state with 0.70743 of CI. The allowed S1→S0 (f = 1.1028) corresponds a typical intramolecular charge transfer (ICT) process leading to the strong fluorescence of **FRP-Thio** after reacting with thiophenol. Therefore, the theoretical calculations are in accordance with the experimental results.

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DOI: 10.1039/C9NJ03030D

Table 1. Determination of PhSH in water

Sample	PhSH spiked/μM	PhSH recovered/μM	Recovery/%
Jiazi Lake	0	Not detected	
	5	4.69	94
	10	9.73	97
	20	21.16	106
	30	29.34	98
Tab Water	0	Not detected	
	5	4.77	95
	10	10.27	102
	20	19.87	99
	30	29.53	98

3.6. Sensing thiophenol sparked in water samples and visualizing in living SH-SY5Y cells

Subsequently, we accessed whether **FRP-Thio** is feasible to the thiophenol spiked in real water samples. The water samples from Jiazi River and tap water were spiked with thiophenol and then treated with the probe in DMF which contained 10 μM probe as well as thiophenol with different concentration (5, 10, 20, 40 μM). The fluorescence was recorded after the solutions were incubated for 1h at room temperature. As shown in Table 1, it demonstrated satisfactory recovery values, which testified the quantitative detection application.

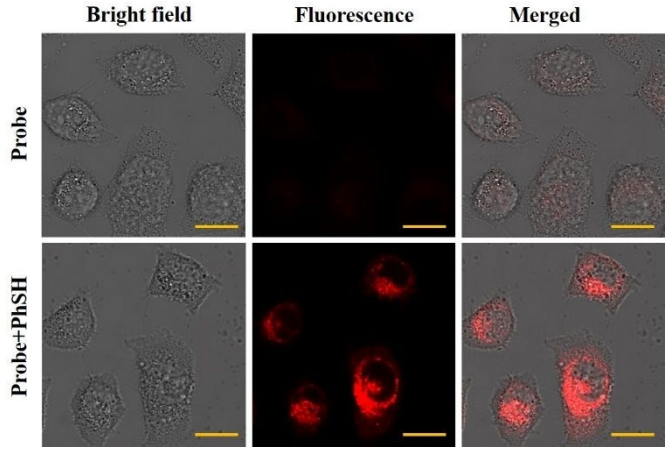

Fig. 5. Confocal fluorescence images of SH-SY5Y cells treated with **FRP-Thio** (10 μM) with or without of thiophenol (100 μM). (a) Bright field image of SH-SY5Y cells with **FRP-Thio**. (b) Bright field image of (a). (c) Merging of (a) and (b). (d) Bright field image of SH-SY5Y cells with **FRP-Thio** with addition of thiophenol. (e) Image of (d). (f) Merging of (d) and (e). Scale bar: 25 μm.

To check whether **FRP-Thio** is applicable in biological system, intracellular experiments of the probe toward thiophenol have been carried out. At first, the MTT assay for cytotoxicity of the probe using standard cell viability protocols were shown in Fig. S8. There was no obvious influence to cells even with a high concentration of the probe (20 μM) with a long incubation time of 24 h. Inspired by the low cytotoxicity, the probe was used to visualize thiophenol in living SH-SY5Y cells on a LSM710 confocal microscope. SH-SY5Y cells were pretreated with 10 μM **FRP-Thio** for half hour. The residual probe was washed off by PBS before imaging. There was no any obvious red emission signal detected excited at 560 nm (Fig. 5a-c). However, SH-SY5Y cells displayed red fluorescence when incubation with 10 μM **FRP-Thio** and then 100 μM thiophenol under excitation at 560 nm (Fig. 5d and e). The overlap image in bright field showed the good morphology of the cells which further demonstrated the low cytotoxicity and cell death (Fig. 5f). Therefore, these results fully supported that **FRP-Thio** is a promising turn-on florescent probe for quantitively thiophenol detection in real water sample and visualizing thiophenol in living SH-SY5Y cells.

4. Conclusions

In conclusion, we synthesized a colorimetric and far-red emission fluorescent probe (**FRP-Thio**) as a merocyanine derivative for specifically detecting thiophenol. The probe could specifically respond to thiophenol over aliphatic thiols by showing the far-red fluorescence enhancement at 645 nm as well as a remarkable colorimetric change from orange to blue-green. The probe also demonstrated a LOD of 9 nM with a 30 min response time toward thiophenol. Moreover, visualization of thiophenol in living cells was also successfully achieved.

Supporting Information

NMR spectra of the compounds, MS and chromatograms of the reaction systems, supplementary fluorescent spectra, cytotoxicity assay (PDF)

Acknowledgments

We thank for the supporting from Natural Science Foundation of China (grant No. 21101074), Shandong Provincial Natural Science Foundation of China (grant No. ZR2019MB040), the Young Taishan Scholars Program (tsqn201812080), the technology Foundation of University of Jinan (Grant No. XKY1823).

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View Article Online
DOI: 10.1039/C9NJ03020D

Thiophenol is toxic to environment and biological systems although it is an indispensable material of chemical products.