Simple NIR-Emitting ESIPT Fluorescent Probe for Thiophenol with a Remarkable Stokes Shift and Its Application

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1. INTRODUCTION

Thiophenol plays important roles in pharmaceutical industries and manufacturing agrochemical.1−5 However, the potential hazards of thiophenol to the biological and ecological environments cannot be non-negligible due to its high toxicity. For instance, the LC₅₀ of thiophenol for fish is in the range of 0.01−0.4 mM.4 The LD₅₀ of thiophenol is 25 mg/kg for mice, 24 mg/kg for birds,7 and 46 mg/kg for rats.6 Moreover, thiophenol can be absorbed by skin contact and inhalation, which can result in many diseases including muscular weakness, central nerve injury, nausea, coma, vomiting, shortness of breath, and even death.7,8 For this reason, thiophenol is recognized by the USEPA as a prioritized pollutant.9−11 Hence, it is of great significance to develop effective methods for monitoring thiophenol in the environment and biological systems.

The traditional methods, such as high-performance liquid chromatography (HPLC),16 gas chromatography−mass spectrometry (GC−MS),11 and UV,12 have been established for thiophenol detection in the environment. Although these methods have displayed good reproducibility and accuracy toward thiophenol, they are unsuitable for detection of thiophenol in living samples owing to the needs of high cell or tissue destruction. By contrast, fluorescent-based probes have great potential applications in both environmental and biological systems because of their high sensitivity, simplicity, lower detection limits, and nondestructive detection.13−20 However, development of fluorescent probes for thiophenol is extremely challenging to differentiate thiophenol from thiols due to similar chemical properties between thiophenol and thiols. Fortunately, since the pioneer work of distinguishing thiophenol and thiols from Wang,21 a number of probes have been developed based 2,4-dinitrobenzenesulfonate and dinitrophenyl ether recognition groups.22−43 Although those probes worked well, many limitations in practical use remain to be overcome. For example, some probes could suffer from slow response (>10 min) or need of surfactants to accelerate the reactions, which was a disadvantage for real-time detection. Some probes might be subject to a small Stokes shift (<100 nm), which was defects for sensitivity determination and bioimaging due to the self-absorption interference. Furthermore, most of the reported thiophenol fluorescent probes emitted in the short-wavelength region (in blue or yellow emission), which was capable of limitations in biological imaging due to the interference by background autofluorescence of living cells and organisms. Near-infrared (NIR) fluorescent probes with long-wavelength emissions are ideal tools for overcoming the above-mentioned problems, which has unique advantages including minimum interference of the background, decreased photodamage to biological samples, and deep tissue penetration.44−46 Meanwhile, the fluorescent probes with large Stokes shift can reduce the interferences induced by autofluorescence or self-absorption and then improve the detection accuracy and sensitivity due to the major shifts separated emission and excitation bands, which is suitable for fluorescence imaging.47−57 Based on the current studies, only few probes for thiophenol detection having all the above-mentioned merits have been reported. Therefore,
development of fast-responding, excellent selectivity, and NIR fluorescent probes with large Stokes shift for monitoring thiophenol are still highly demanded.

Based on these analyses, a novel NIR and ESIPT fluorescent probe (2E,4E)-5-(4-(dimethylamino)phenyl)-1-(2-(2,4-dinitrophenoxymethyl)phenyl)penta-2,4-dien-1-one (DAPH-DNP) was designed and synthesized for the selective and real-time detection of thiophenol, in which a 2,4-dinitrophenyl (DNP) group was used as a thiophenol recognition unit and (2E,4E)-5-(4-(dimethylamino)phenyl)-1-(2-hydroxyphenyl)penta-2,4-dien-1-one (DAPH) was utilized as a fluorophore (Scheme 1).

Scheme 1. Proposed Mechanism of the Detection of Thiophenol by DAPH-DNP

The DAPH dye with an electron-donor group N,N-dimethylamino and o-hydroxyacetophenone was selected as a fluorescent signaling unit due to its salient characteristics including large Stokes shift, emission in the NIR region, ESIPT properties, and easy synthetic modification. In the probe DAPH-DNP, 2,4-dinitrophenyl group was attached to the hydroxyl site, which resulted in fluorescence quenching due to the hampering of the ESIPT process. However, the nucleophilic substitution of dinitrophenyl ether mediated by thiophenol would release the hydroxyl group and thus ESIPT process produced by formed the intramolecular hydrogen bonds between carbonyl oxygen and the hydroxyl group, accompanied with the strong electron-donating group N,N-dimethylamino, the probe DAPH-DNP generated NIR fluorescence emission. Indeed, the NIR probe showed excellent sensitivity, good selectivity, fast response rate, and large Stokes shift for thiophenol detection. More importantly, the probe DAPH-DNP was successfully used for thiophenol detection in water samples and living cells, which suggested its practical application in environment and biology. To the best of our knowledge, no NIR and ESIPT fluorescent probe for thiophenol has been reported.

2. RESULTS AND DISCUSSION

2.1. Sensing Properties of DAPH-DNP for PhSH. To verify whether DAPH-DNP has sensing ability for PhSH, spectral properties of DAPH-DNP before and after the addition of thiophenol were tested in phosphate-buffered saline (PBS) solution (50 mM, pH 7.4, with 10% N,N-dimethylformamide (DMF)). As shown in Figure 1, the probe DAPH-DNP itself exhibited a maximal absorption peak at 447 nm. When thiophenol was added to the solution of DAPH-DNP, the absorption band at 447 nm disappeared. At the same time, a new peak at 462 nm appeared. As a result, it implicated that thiophenol can result in a structural change in DAPH-DNP.

Figure 1. UV–vis absorption spectrum of DAPH-DNP in the absence (a) or presence (b) of thiophenol in PBS solution (50 mM, pH 7.4, with 10% DMF).

For the purpose to gain further insight into DAPH-DNP for detecting thiophenol, the fluorescence response of DAPH-DNP toward thiophenol was examined in PBS solution (50 mM, pH 7.4, with 10% DMF). As shown in Figure 2, the emission intensity of DAPH-DNP was negligible in the buffer solution, which was attributed to the protection of phenol with the 2,4-dinitrophenyl group. When thiophenol was added, an obvious fluorescence emission band was observed at 654 nm. With continued addition thiophenol, the normalized fluorescence intensity of DAPH-DNP system at 654 nm was gradually enhanced. This result, mainly owing to the cleavage reaction of thiophenol, released the phenol and ESIPT process appeared. Moreover, a good linear relationship between the concentration of thiophenol (0–80 μM) and the normalized fluorescence intensity at 654 nm was acquired. Simultaneously, the normalized fluorescence intensity of the DAPH-DNP solution increased up to 27-fold when the concentration of thiophenol was 80 μM. The limit of detection was calculated to be 3.8 × 10^{-8}, which showed that DAPH-DNP had high sensitivity for thiophenol. Therefore, DAPH-DNP can be used for quantitatively monitoring thiophenol.

2.2. Selectivity and Competition. Selectivity is an important parameter to evaluate the performance of a new probe. To demonstrate the selectivity of DAPH-DNP, we investigated the fluorescent response of DAPH-DNP toward relevant species such as (PhSH, p-CH3O-PhSH, p-NH2-PhSH, p-CH2-PhSH, phenol, aniline, Gly, Hcy, Cys, GSH, NaClO, NaHS, H2O2, KSCN, NaNO2, NaBr, KI, NaHSO3, NaI).

Figure 2. (a) Fluorescence emission spectra of DAPH-DNP (10 μM) in the presence of different concentrations of thiophenol in PBS solution (50 mM, pH 7.4, with 10% DMF). (b) Linear correlation between the normalized fluorescence intensity at 654 nm and thiophenol concentration. λex = 462 nm.
shown in Figure 3a, the introduction of thiophenol leads to a remarkable fluorescence enhancement at 654 nm, whereas negligible fluorescence was observed after incubation with other relevant species. These results indicated that DAPH-DNP can selectively for recognition.

| Probe | $\lambda_{ex}/\lambda_{em}$ (nm) | Response time | Detection limit | Linear range | Ref. |
|-------|-------------------------------|--------------|----------------|--------------|------|
| ![Probe Image 1] | 500/610 | 2 min | 8.1 nM | 0-10 μM | [49] |
| ![Probe Image 2] | 490/510 | 20 min | 26.01 nM | 1-5 μM | [50] |
| ![Probe Image 3] | 420/492 | 30 min | 33 nM | 0-20 μM | [51] |
| ![Probe Image 4] | 395/462 | 15 min | 30 nM | 0-30 μM | [52] |
| ![Probe Image 5] | 488/590 | 5 min | 36 nM | 0-20 μM | [53] |
| ![Probe Image 6] | 420/550 | 60 min | 79 nM | 0-5 μM | [54] |
| ![Probe Image 7] | 484/623 | 30 min | 2.9 nM | 0-10 μM | [55] |
| ![Probe Image 8] | 503/606 | 2 min | 8.2 nM | 0-20 μM | [56] |
| ![Probe Image 9] | 350/580 | 30 s | 7.26 nM | 0-10 μM | [57] |
| ![Probe Image 10] | 462/654 | 6 min | 38 nM | 0-80 μM | This work |

Table 1. Comparison of DAPH-DNP with Other Probes for Thiophenol

To study the anti-interference performance of DAPH-DNP as a thiophenol selective probe, DAPH-DNP to thiophenol was carried out with the coexistence of different individual species. As shown in Figure 3b, the fluorescence intensity of DAPH-DNP solution at 654 nm had no obviously identical to
that in the case of thiophenol alone by coexisting thiophenol and other species. The combined results suggested that DAPH-DNP possesses strong anti-interference ability for the detection of thiophenol.

2.3. Effect of pH on DAPH-DNP. The effects of pH on the emission profile of DAPH-DNP were further investigated in the presence and absence of thiophenol. As shown in Figure 4, the normalized emission intensity of the DAPH-DNP solution at 654 nm displayed negligible changes over a wide pH range from 1.0 to 12.0, which indicated that DAPH-DNP was not affected by the pH value. However, the normalized fluorescence intensity of DAPH-DNP system at 654 nm displayed enhancement at pH between 4.0 and 7.0 in the presence of thiophenol, exhibited the maximum normalized fluorescence intensity at pH 7.0, and remained unchanged at pH >7.0. This result, mainly due to the nucleophilic substitution reaction of thiophenol with dinitrophenyl ether, does not occur under strong acidic conditions. A physiological pH of 7.4 implies that DAPH-DNP has potential application in biological systems.

2.4. Response Time of DAPH-DNP to PhSH. The time-dependent fluorescence intensities of DAPH-DNP were also determined before and after the addition of thiophenol. As shown in Figure 5, in the absence of thiophenol, the fluorescence intensity of the DAPH-DNP solution at 654 nm did not change with the increase of time, indicating that DAPH-DNP was stable. By contrast, with the introduction of thiophenol, the DAPH-DNP solution at 654 nm exhibited a fluorescence enhancement with time and became constant after about 6 min. The rapid response explained that DAPH-DNP can monitor thiophenol in real time.

2.5. Mechanism Study. It is known that dinitrophenyl ether can convert to phenol by a thiophenol-triggered nucleophilic substitution reaction. To confirm the mechanism of sensitivity of DAPH-DNP for thiophenol, the reaction product of DAPH-DNP with thiophenol was obtained and subjected to 1H NMR. As shown in Figure S1, DAPH-DNP displayed three proton signals at 8.80, 8.24, and 7.19 ppm, which were attributable to the dinitrophenyl group. Those proton signals in DAPH-DNP disappeared, and a new peak of phenol (13.16 ppm) appeared in the presence of thiophenol (Figure S4), indicating that thiophenol caused the removal of dinitrophenyl group and the release of DAPH. After the addition of thiophenol, the high-resolution mass spectrometry (HRMS) spectrum showed a peak at m/z = 294.1493 (Figure S5), corresponding to DAPH (calcd C19H19NO2 [M + H]+, 294.1497). The data supported the responding mechanism as displayed in Scheme 1.

2.6. Application of DAPH-DNP in Water Samples. Considering the potential pollution of thiophenol to the environment, we employed DAPH-DNP to monitor thiophenol in the water samples from Yuanjiang River and tap water in Changde city to investigate its practicability in environmental science. As shown in Table S1, there was a good recovery of thiophenol in the range from 97.0 to 103% in the water sample, indicating that DAPH-DNP is suitable for the detection of thiophenol in real samples.

2.7. Imaging in Living Cells. The cytotoxicity of DAPH-DNP was investigated by the MTT assay (Figure S7). The results displayed that DAPH-DNP showed little cytotoxicity for cells. To further investigate the potential utility of DAPH-DNP, the experiments of imaging thiophenol in living cells were carried out. As shown in Figure 6, when HeLa cells were incubated with DAPH-DNP for 0.5 h, washing with PBS showed no fluorescence. However, the HeLa cells, which were preloaded with DAPH-DNP, washed with PBS, and incubated with thiophenol for 0.5 h, showed remarkable red fluorescence. These results suggested that DAPH-DNP can be used for imaging thiophenol in living cells.

3. CONCLUSIONS

In summary, we have synthesized a new NIR fluorescent probe DAPH-DNP for detecting thiophenol via the ESIPt mechanism. The probe exhibits high selectivity and sensitivity, rapid response, remarkable large Stokes shift, and NIR fluorescence recognition for thiophenol. In practical
applications, the probe can detect thiophenol in water samples with good recoveries. Importantly, the probe is successfully applied to image thiophenol in living cells. Taken together, the probe is promising for the detection of thiophenol in environmental and biological systems.

4. EXPERIMENTAL SECTION

4.1. Materials and Instruments. 2-Hydroxyacetophenone, cinnamaldehyde, and 1-fluoro-2,4-dinitrobenzene were obtained from Energy Chemical, China. All the other chemical reagents were commercially available. 1H NMR and 13C NMR spectra were recorded on a Bruker AVB-500 spectrometer. HRMS analysis was performed on an Agilent 6530 Accurate-Mass Q-TOF system. Fluorescence spectra were recorded on a Bruker AVB-500 spectrometer.

4.2. Preparation of DAPH-DNP. The DAPH compound was synthesized according to the reported literature. DAPH (0.293 mg, 1 mmol), 1-fluoro-2,4-dinitrobenzene (0.223 mg, 1.2 mmol), and K2CO3 (0.166 mg, 1.2 mmol) were dissolved in DMF (5 mL). The mixture was stirred overnight at room temperature (RT), poured into water (10 mL), and extracted with EtOAc (2 × 50 mL). The organic phase was evaporated to dryness, and the residue was dissolved in DMF. The above stock solutions were used as testing solutions.

4.3. Spectroscopic Measurements. The probe DAPH-DNP stock solution was prepared (1.0 × 10⁻³ mol/L) in DMF. The above stock solutions were used as testing solutions. All the above solutions were diluted and then incubated with an appropriate volume of 50 mM PBS buffered solution and a certain amount of PhSH. The testing solutions were measured by fluorescence spectrometer.

4.4. Thiophenol Detection in Real Samples. The crude water samples (Yuanjiang River and tap water in Changde city) were passed through a microfiltration membrane before the test. The water samples containing probe DAPH-DNP (10 μM) and thiophenols (0, 5, 10, and 20 μM) were measured used fluorescent spectrometer.

4.5. Cell Imaging. The HeLa cells were seeded in a 96-well plate and allowed to attach to the culture medium at 37 °C for 24 h. Then, the cells interacted with probe DAPH-DNP (10 μM) for 0.5 h. After washing with PBS, the cells were pretreated with thiophenol and further incubated for 0.5 h at 37 °C. The HeLa cells were washed with PBS and imaged. As control experiments, the HeLa cells were incubated with probe DAPH-DNP (10 μM), washed with PBS, and imaged.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00389.

Spectroscopic data and NMR and MS spectra (PDF)

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