



Cite this: *RSC Adv.*, 2023, **13**, 32137

Received 4th October 2023  
 Accepted 20th October 2023

DOI: 10.1039/d3ra06740h  
[rsc.li/rsc-advances](http://rsc.li/rsc-advances)

## A fluorous-tag-assisted fluorescent probe for simple and selective detection of hydrogen sulfide: application for turbid dyeing solutions<sup>†</sup>

Geonwoo Park,<sup>‡</sup> Mincheol Jang<sup>‡</sup> and Min Su Han<sup>‡</sup>  \*

Accurate hydrogen sulfide ( $H_2S$ ) detection has attracted much attention because its toxicity may affect aquatic environments and human health. However, recognizing  $H_2S$  levels by conventional fluorescent probes in turbid wastewater has been challenging because the opaque environment interferes with their photophysical properties. To overcome this limitation, a fluorous-tagging strategy can be used for the development of fluorescent sensors to detect  $H_2S$  in turbid solutions. The use of fluorescent probe assisted with fluorous-tag allowed for easy isolation of the probe using polytetrafluoroethylene (PTFE) material, while disturbing species were eliminated through a simple aqueous wash. This approach enabled the fluorescent probe to effectively quantify  $H_2S$ , even in opaque solutions containing organic dyes that could interfere with fluorescence emission.

### 1 Introduction

Hydrogen sulfide ( $H_2S$ ) is a toxic gas with a strong odor of rotten eggs that has been recognized as an endogenous gas-transmitter with nitric oxide (NO) and carbon monoxide (CO).<sup>1–4</sup> Sulfide compounds are commonly used and produced in industrial plants such as bleach in paper, printing, and dye production industries.<sup>5,6</sup> Especially,  $H_2S$  in wastewater can cause undesirable corosions of metals in aquatic environments such as rivers, resulting in harmful effects on physiological processes and life activities of human health.<sup>7,8</sup> Hence, the detection of  $H_2S$  in industrial wastewater has been widely recognized as an invaluable technique in recent decades.

Many approaches to detect  $H_2S$  using gas chromatography, colorimetry, and electrochemical method, have been suggested.<sup>9–11</sup> However, many of these approaches are often limited and avoided owing to their high costs, time-consuming procedures, and complex processes.<sup>12,13</sup> The fluorescent method for  $H_2S$  detection has gained significant attention owing to its high sensitivity, non-invasiveness, rapid response, and simplicity.<sup>14,15</sup> However, the application of the fluorescent method is limited for certain real samples in terms of interference because fluorescence is easily affected by the

environment of samples.<sup>16,17</sup> Hence, it is important to design the fluorescent probe so that it can effectively work regardless of interfering species. As representative examples, various research groups have introduced special functionalities to the fluorescent probe to enhance the probe's selectivity for target analyte or prevent the overlap of emission ranges with interfering fluorescence.<sup>18–21</sup> Nevertheless, the use of the fluorescent probes in deep-coloured solution, such as dyeing wastewater, remains challenging because the strong light scattering and light absorption induced by the turbid media can significantly attenuate the fluorescence intensity.<sup>22,23</sup> Therefore, a new alternative is required to develop a fluorescent probe that can accurately detect analytes independent of solution color and turbidity.

From this perspective, the fluorous-tagging strategy offers a solution by allowing for the easy and rapid isolation of the fluorescent probe, thereby minimizing interferences from other disturbing species.<sup>24</sup> A fluorous-tag is a simple and long per-fluoroalkyl chain moiety; thus, fluorous-tag-assisted substrates have strong, specific fluorous interaction with polytetrafluoroethylene (PTFE) materials, such as PTFE particles.<sup>25–27</sup> This specific affinity enables the fluorous-tagged substrates to be readily isolated using fluorous solid-phase extraction (F-SPE), eliminating the need for pre-filtration, column chromatography, recrystallization, and other troublesome purification procedures.<sup>27,28</sup> Despite these advantages, there have been few research applying the fluorous-tagging strategy in the field of chemosensors.<sup>29</sup> Therefore, a combination of fluorous-tag and fluorescent probe is expected to be an efficient new approach to the detection of targets in deep-coloured solutions.

In this study, a fluorous-tagged naphthalimide derivative, **F-Naph-N<sub>3</sub>** was used as a fluorescent probe for quantitatively

Department of Chemistry, Gwangju Institute of Science and Technology (GIST), 123 Cheomdangwagi-ro, Buk-gu, Gwangju 61005, Republic of Korea. E-mail: [happyhan@gist.ac.kr](mailto:happyhan@gist.ac.kr)

† Electronic supplementary information (ESI) available: Characterization data, photophysical properties, and experimental details for  $H_2S$  sensing in fluorescence spectrophotometer and imaging instrument. See DOI: <https://doi.org/10.1039/d3ra06740h>

‡ Geonwoo Park and Mincheol Jang contributed equally.



detecting  $\text{H}_2\text{S}$  (Scheme 1). It also showed good selectivity and competitive selectivity for  $\text{H}_2\text{S}$  in solution. Furthermore, this probe has highly hydrophobic and fluorophilic properties owing to the fluorous-tag, and it can thus be easily separated from commercially available PTFE materials through two simple steps: (1) spotting the sample on a PTFE membrane filter and (2) washing the membrane with deionized water (Scheme 1b). The sample solution containing **F-Naph-N<sub>3</sub>** and  $\text{H}_2\text{S}$  spotted on PTFE membrane filter exhibited intense fluorescence, allowing for quantification of the  $\text{H}_2\text{S}$  amount using imaging instrument. Finally, **F-Naph-N<sub>3</sub>** was successfully used as a sensor to detect  $\text{H}_2\text{S}$  in dye-containing opaque solutions, which is hard to achieve using conventional fluorescent probes and spectrometers.

## 2 Experimental

### 2.1 Materials and instruments

All chemical reagents were purchased from commercial suppliers (TCI, Sigma-Aldrich, Combi-blocks, DUKSAN and DAEJUNG). Except for 4-bromo-1,8-naphthalic anhydride, all reagents were used without any pre-purification. Polytetrafluoroethylene (PTFE) membrane filter was purchased from Advantec.

Proton nuclear magnetic resonance (400 MHz for  $^1\text{H}$  NMR), carbon NMR (100 MHz for  $^{13}\text{C}$  NMR), fluorine NMR (376 MHz for  $^{19}\text{F}$  NMR) spectra were obtained using a JEOL (400 MHz) NMR spectrometer. All UV/Vis spectra were recorded using an JASCO V-630 UV/Vis spectrometer, and all fluorescence spectra were measured using an Agilent Cary Eclipse fluorescence spectrometer. High-resolution mass spectra (HRMS) were obtained at Korea Basic Science Institute (Daegu, South Korea) using a JEOL KMS-700 MStation mass spectrometer with a standard electron ionization (EI $^+$ ) source or fast atom

bombardment (FAB $^+$ ) ion source. Melting points were measured using a BUCHI melting point M-565 apparatus. All Fluorescence images of PTFE membrane were visualized using a ChemiDoc MP imager (Bio-Rad) which was set as following – exposure time 0.01 s, excitation source: blue epi illumination, emission filter: 530/28 filter. Their fluorescence intensities were converted into green value (optical density) by using an Adobe Photoshop software.

### 2.2 Synthesis of **6** and **F-Naph-N<sub>3</sub>**

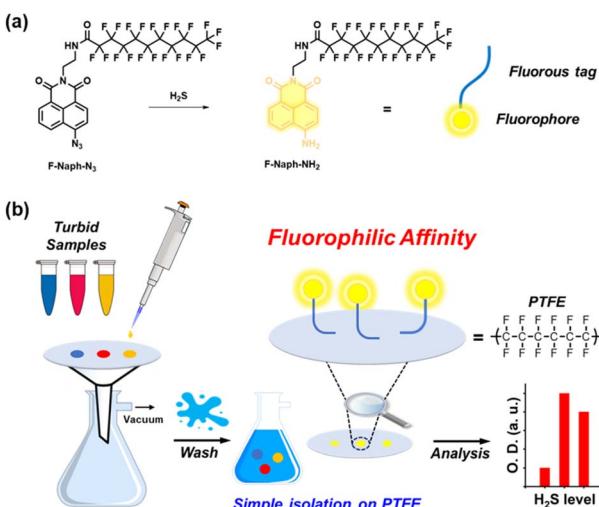
Heneicosafluoroundecanoic acid (1.35 g, 2.4 mmol), thionyl chloride (2.9 mL, 40.0 mmol), and pyridine (19.2  $\mu\text{L}$ , 0.24 mmol) were refluxed for 4 h. Thionyl chloride was removed under reduced pressure to give **6** as a white solid, and **6** was used in further reaction. To the next, **5** (0.42 g, 1.5 mmol) and triethylamine (0.25 g, 1.8 mmol) were dissolved in 24 mL of dry tetrahydrofuran (THF) and then **6** was added to the reaction mixture. The mixture was stirred for 24 h at room temperature. After the reaction, 100 mL of water was poured into the reaction mixture, and the precipitated solid was filtered. The residue was dissolved in DCM, washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , and the solvent was evaporated under reduced pressure. The collected solid was further purified by silica gel column chromatography (chloroform : methanol = 50 : 1 as an eluent) to afford **F-Naph-N<sub>3</sub>** (0.30 g, 24%) as a yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 8.66–8.68 (dd,  $J$  = 7.2, 1.2 Hz, 1H), 8.60–8.62 (d,  $J$  = 8.0 Hz, 1H), 8.48–8.50 (dd,  $J$  = 8.4, 1.2 Hz, 1H), 7.75–7.79 (dd,  $J$  = 8.4, 7.6 Hz, 1H), 7.51 (br s), 7.48–7.50 (d,  $J$  = 11.6 Hz, 1H), 4.48–4.51 (m, 2H), 3.77–3.81 (q,  $J$  = 4.8 Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 164.93, 164.47, 157.99, 144.37, 132.89, 132.43, 129.56, 129.32, 127.05, 124.47, 121.98, 118.15, 114.84, 40.70, 38.69 (carbon peak of fluorous-tag could not be observed due to low solubility and signal).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): -80.61, -119.64, -121.52, -121.70, -122.52, -122.58, -125.99. Melting point: 154–163 °C. HRMS (FAB $^+$ ):  $m/z$  calculated for  $\text{C}_{25}\text{H}_{11}\text{F}_{21}\text{N}_5\text{O}_3 + \text{H}^+ [\text{M} + \text{H}^+]$ : 828.0527, found: 828.0530.

### 2.3 General and pH dependence

All sample solutions (1.0 mL) were prepared in 1.5 mL Eppendorf tube. All fluorescence measurements were repeated three times at room temperature. To test the pH dependence of probe,  $\text{H}_2\text{S}$  (60  $\mu\text{M}$ ) was added to various buffer solutions (10 mM, pH 4.0–10.0) containing **F-Naph-N<sub>3</sub>** (20  $\mu\text{M}$ , 60% ACN). The fluorescence spectra were measured after 1 h.  $\lambda_{\text{ex}} = 418 \text{ nm}$ .  $\lambda_{\text{em}} = 530 \text{ nm}$ . Slit widths: 5 nm. The composition of buffer solution were as follows: pH 4.0–5.0 (sodium acetate), pH 6.0 (2-(*N*-morpholino)ethanesulfonic acid, MES), pH 7.0–8.0 (sodium phosphate), pH 9.0 (tris(hydroxymethyl)aminomethane, Tris), pH 10.0 (sodium bicarbonate).

### 2.4 Selectivity and competitive selectivity of **F-Naph-N<sub>3</sub>** toward $\text{H}_2\text{S}$ over other anions/biothiols

Various anions/biothiols (100  $\mu\text{M}$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{N}_3^-$ ,  $\text{SO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{HSO}_4^-$ ,  $\text{CN}^-$ /Cys, Hcy, and GSH) were added to sodium phosphate buffer



**Scheme 1** (a) Schematic of  $\text{H}_2\text{S}$  detection by **F-Naph-N<sub>3</sub>** based on naphthalimide fluorophore. (b) Graphical abstract illustrating the application of **F-Naph-N<sub>3</sub>** for  $\text{H}_2\text{S}$  detection in turbid dyeing samples by polytetrafluoroethylene (PTFE) membrane filter.



solution (SPB, 10 mM, pH 8.0) containing **F-Naph-N<sub>3</sub>** (20  $\mu$ M, 60% ACN). H<sub>2</sub>S (100  $\mu$ M) and same anions/biothiols (300  $\mu$ M) as in selectivity test were added to sodium phosphate buffer solution (SPB, 10 mM, pH 8.0) containing **F-Naph-N<sub>3</sub>** (20  $\mu$ M, 60% ACN). The fluorescence spectra were obtained after 1 h.  $\lambda_{\text{ex}} = 418$  nm.  $\lambda_{\text{em}} = 530$  nm. Slit widths: 5 nm.

## 2.5 Quenching effect by copper nitrate trihydrate

The different concentrations of H<sub>2</sub>S (20, 40, and 60  $\mu$ M) were added to sodium phosphate buffer solution (SPB, 10 mM, pH 8.0) containing **F-Naph-N<sub>3</sub>** (20  $\mu$ M, 60% ACN), and fluorescence intensity was measured for 1 h. Copper nitrate trihydrate (2 eq. of added H<sub>2</sub>S, 2 vol%) was then added to the solution, followed by additional measurement for 30 min.  $\lambda_{\text{ex}} = 418$  nm.  $\lambda_{\text{em}} = 530$  nm. Slit widths: 5 nm.

## 2.6 Practical application for dyeing samples

Alizarin red S (150  $\mu$ M), bromophenol blue (150  $\mu$ M), methyl orange (150  $\mu$ M), and their triple mixture (50 + 50 + 50  $\mu$ M) were prepared as opaque environments for the dyeing solutions. Each concentration of H<sub>2</sub>S (20, 40, and 60  $\mu$ M) was added to SPB (10 mM, pH 8.0) containing **F-Naph-N<sub>3</sub>** (20  $\mu$ M, 60% ACN) and organic dyes. After the incubation for 1 h, copper nitrate trihydrate (2 eq. of added H<sub>2</sub>S, 2% v/v) was added to the sample to quench the reaction. 5  $\mu$ L of sample was spotted onto PTFE membrane filter, and then water (80 mL  $\times$  2) was filtered to wash buffer, organic dyes, and other species, except for the probe. The wet PTFE membrane was dried up quickly by cool air-blowing. The fluorescence intensity was visualized using ChemiDoc MP imager (Bio-Rad) and then converted into optical density value using Adobe Photoshop software.

# 3 Results and discussions

## 3.1 Design and photophysical properties of probe

To design the fluorescent probe, a 1,8-naphthalimide scaffold was selected as a fluorophore because of its high quantum yield, good stability and solubility, low cost, and variable synthetic modification.<sup>30,31</sup> A 4-positioned azide in naphthalimide was set as detecting group, which can be selectively reduced to amine by H<sub>2</sub>S, thereby inducing fluorescence of probe. Finally, the  $-C_{10}F_{21}$  fluororous-tag was introduced through an *N*-(2-aminoethyl) acetamide moiety as a linker and **F-Naph-N<sub>3</sub>** was successfully synthesized (Scheme S1†). As shown in Scheme 1a, **F-Naph-N<sub>3</sub>** encountering H<sub>2</sub>S exhibited intense fluorescence turn-on upon conversion into **F-Naph-NH<sub>2</sub>**. To confirm the photophysical properties, the UV/Vis spectra of **F-Naph-N<sub>3</sub>** and **F-Naph-NH<sub>2</sub>** in acetonitrile (ACN) were investigated to verify their absorption properties. **F-Naph-N<sub>3</sub>** showed a maximum absorption peak at 365 nm while **F-Naph-NH<sub>2</sub>** showed a red-shifted absorption at 418 nm (Fig. S1†).

## 3.2 Screening experiments for optimization

Several screening experiments were conducted to optimize detection condition. First, solvent screening was examined and ACN was chosen because it had both appropriate solubilities to

highly hydrophobic **F-Naph-N<sub>3</sub>** and miscibility with H<sub>2</sub>O which accommodates buffer, H<sub>2</sub>S and quenching agent. Furthermore, the high volatility of ACN was suitable for application in F-SPE. Notably, ACN/H<sub>2</sub>O (v/v = 6 : 4) was determined to be the optimal solvent because the salt precipitated at an H<sub>2</sub>O ratio of less than 40%.

Next, the kinetics of **F-Naph-N<sub>3</sub>** with H<sub>2</sub>S were also studied.

Time-dependent fluorescence spectra were measured 2 h after the addition of various concentrations of H<sub>2</sub>S (Fig. 1b). Upon the addition of H<sub>2</sub>S, a gradual increase in the peak at 530 nm was observed over time. The fluorescence intensity enhancement was relatively moderate after 1 h for all H<sub>2</sub>S concentrations.

Moreover, the effects of the pH on the sensing reaction and fluorescence activity were also investigated. Fluorescence spectra of probe **F-Naph-N<sub>3</sub>** (20  $\mu$ M) were monitored in the presence and absence of H<sub>2</sub>S (3 eq.) at pH from 4.0 to 10.0 (Fig. 1c). The fluorescence intensity without H<sub>2</sub>S was negligible in all pH ranges, and despite the addition of H<sub>2</sub>S, the probe exhibited little fluorescence in the acidic pH range (pH < 7.0). The fluorescence sharply increased at a neutral pH and gradually increased as the pH increased. Hence, sodium phosphate buffer (SPB, pH 8.0) was selected as the optimized pH for experiment, which is close to physiological environment and provides sufficient fluorescence activity.

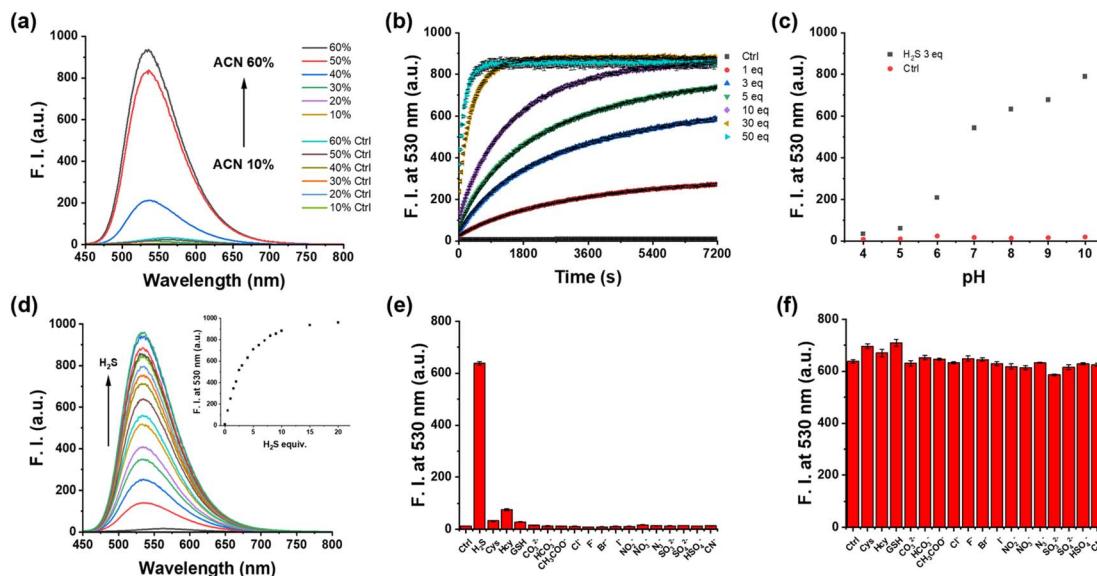
## 3.3 Sensitivity and selectivity of **F-Naph-N<sub>3</sub>** toward H<sub>2</sub>S

H<sub>2</sub>S titration experiments were conducted under optimized conditions to determine the sensing performance of **F-Naph-N<sub>3</sub>** for H<sub>2</sub>S. The probe (20  $\mu$ M) was incubated for 1 h in SPB (10 mM, pH 8.0) and ACN/H<sub>2</sub>O (v/v = 6 : 4) solutions after the addition of H<sub>2</sub>S, and the fluorescence spectra were measured (Fig. 1d). Before the addition of H<sub>2</sub>S, there was little fluorescence intensity; however, the peak at 530 nm was enhanced in proportion to the increasing H<sub>2</sub>S concentration. **F-Naph-N<sub>3</sub>** can detect H<sub>2</sub>S quantitatively with a detection limit as low as 0.28  $\mu$ M (Fig. S2†).

To examine the selectivity of **F-Naph-N<sub>3</sub>** for H<sub>2</sub>S among various interfering species, fluorescence spectra of the probe (20  $\mu$ M) were measured with 100  $\mu$ M of H<sub>2</sub>S and several biothiols (Cys, Hcy, and GSH) and various anions (CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, Cl<sup>-</sup>, F<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, N<sub>3</sub><sup>-</sup>, SO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, HSO<sub>4</sub><sup>-</sup> and CN<sup>-</sup>). Most analytes, except for H<sub>2</sub>S, rarely contribute to fluorescence enhancement (Fig. 1e). Furthermore, when **F-Naph-N<sub>3</sub>** (20  $\mu$ M) was treated with H<sub>2</sub>S (100  $\mu$ M) and same analytes (300  $\mu$ M) as in the previous test, the interference of other analytes on the sensing system was almost negligible (Fig. 1f). Both experiments demonstrate that **F-Naph-N<sub>3</sub>** affords good selectivity and competitive selectivity for H<sub>2</sub>S.

## 3.4 Fluorous solid-phase extraction using **F-Naph-N<sub>3</sub>**

Before applying **F-Naph-N<sub>3</sub>** in F-SPE, copper nitrate was introduced as a H<sub>2</sub>S scavenger after the incubation period to ensure that the probe no longer reacted with H<sub>2</sub>S and the fluorescence intensity did not increase during the following process. After adding H<sub>2</sub>S to the solution, the time-dependent fluorescence of

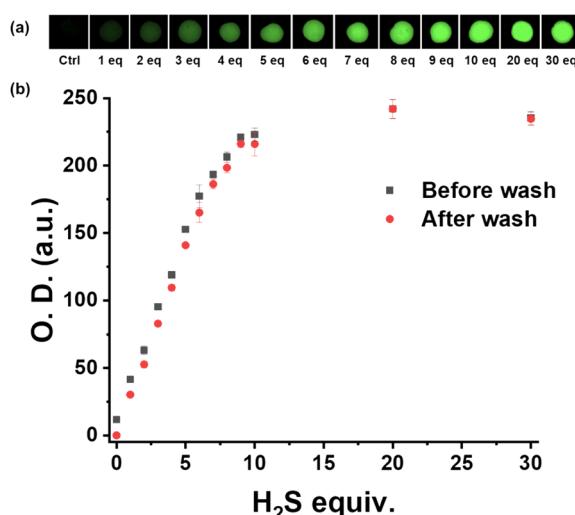


**Fig. 1** Fluorescence emission spectra of F-Naph-N<sub>3</sub> (20 μM) (a) with H<sub>2</sub>S (10 eq.) in different ratio of ACN/H<sub>2</sub>O solution (pH 8.0 sodium phosphate buffer (SPB) 10 mM) after 1 h [PMT: 580 V, slit: 5 nm] and (d) with various concentrations of H<sub>2</sub>S (0–400 μM) in ACN/H<sub>2</sub>O solution (v/v = 6 : 4, pH 8.0 SPB 10 mM) after 1 h. [PMT: 580 V, slit: 5 nm] (b) time-dependent fluorescent intensity of F-Naph-N<sub>3</sub> (20 μM) at 530 nm in the absence and presence of H<sub>2</sub>S in ACN/H<sub>2</sub>O solution (v/v = 6 : 4, pH 8.0 SPB 10 mM) after 1 h. [PMT: 580 V, slit: 5 nm] (c) the plot of fluorescence intensity at 530 nm of F-Naph-N<sub>3</sub> (20 μM) in the absence and presence of H<sub>2</sub>S (3 eq.) in ACN/H<sub>2</sub>O solution (v/v = 6 : 4, various pH range of buffer 10 mM) after 1 h. [PMT: 600 V, slit: 5 nm] (e) selectivity of F-Naph-N<sub>3</sub> (20 μM) in ACN/H<sub>2</sub>O solution (v/v = 6 : 4, pH 8.0 SPB 10 mM) in the presence of various analytes (100 μM) after 1 h: (1) control, (2) H<sub>2</sub>S, (3) Cys, (4) Hcy, (5) GSH, (6) CO<sub>3</sub><sup>2-</sup>, (7) HCO<sub>3</sub><sup>-</sup>, (8) CH<sub>3</sub>COO<sup>-</sup>, (9) Cl<sup>-</sup>, (10) F<sup>-</sup>, (11) Br<sup>-</sup>, (12) I<sup>-</sup>, (13) NO<sub>2</sub><sup>-</sup>, (14) NO<sub>3</sub><sup>-</sup>, (15) N<sub>3</sub><sup>-</sup>, (16) SO<sub>3</sub><sup>2-</sup>, (17) SO<sub>4</sub><sup>2-</sup>, (18) HSO<sub>4</sub><sup>-</sup>, (19) CN<sup>-</sup>. [PMT: 580 V, slit: 5 nm] (f) competitive selectivity of F-Naph-N<sub>3</sub> (20 μM) with H<sub>2</sub>S (100 μM) in ACN/H<sub>2</sub>O solution (v/v = 6 : 4, pH 8.0 SPB 10 mM) in the presence of various analytes (300 μM) after 1 h: same as in (e). [PMT: 580 V, slit: 5 nm],  $\lambda_{\text{ex}} = 418$  nm, at room temperature.

F-Naph-N<sub>3</sub> was measured for 1 h. Subsequently, copper(II) nitrate trihydrate, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O was added (2 eq. of added H<sub>2</sub>S, 2 vol%) to identify the quenching effect. As shown in Fig. S3,† the increase in fluorescence intensity instantly stopped and remained for an additional 30 min, confirming that copper nitrate can effectively quench the reaction by scavenging the remaining H<sub>2</sub>S.

Based on the results obtained in the solution state, F-Naph-N<sub>3</sub> was applied to F-SPE using a commercially available PTFE membrane filter. The sample was spotted onto the PTFE membrane and monitored using a hand-held UV lamp. Notably, the sample spots on the PTFE membrane filter induced strong fluorescence intensity, depending on the concentration of H<sub>2</sub>S (Fig. S4† and 2a). To further validate this trend, a titration experiment using F-SPE procedure with PTFE filter was conducted. ChemiDoc MP imager (Bio-Rad) was used to obtain the fluorescence image of the sample, and Adobe Photoshop was used to convert the fluorescence into an optical density value. The fluorescence intensity showed a good linear correlation with H<sub>2</sub>S even after two aqueous washes, showing the detection limit to be *ca.* 0.21 μM (Fig. 2b and S5†). According to the previously reported studies, fluorine atom basically disfavors other atoms due to its distinctive properties such as inert and amphiphobicity.<sup>32</sup> In addition, it results in that fluorous compounds, including fluorous-tagged substrates, generally favor fluorous phases instead of organic and aqueous phases, and various purification methods have been developed through

these phenomena using PTFE materials.<sup>25,26</sup> These imply that F-Naph-N<sub>3</sub> can be well absorbed on the PTFE material, and our result appropriately correlated the expected tendencies. As



**Fig. 2** (a) Fluorescence image of F-Naph-N<sub>3</sub> spotted on polytetrafluoroethylene (PTFE) membrane filter. (b) F-Naph-N<sub>3</sub> (20 μM) was spotted on PTFE membrane filter after 1 h incubation with the different concentration of H<sub>2</sub>S (0–600 μM) in an ACN/H<sub>2</sub>O solution (v/v = 6 : 4, pH 8.0 sodium phosphate buffer 10 mM), and the fluorescent intensity (optical density) of spots were measured before and after aqueous wash.



Table 1 Determination of H<sub>2</sub>S in dyes-containing samples<sup>a</sup>

Sample	Added H <sub>2</sub> S (μM)	Recovery <sup>c</sup> (%)	RSD (%)
Alizarin red S	20.0	107.8	13.1
	40.0	94.7	5.1
	60.0	97.8	14.1
Bromophenol blue	20.0	106.3	4.1
	40.0	99.6	10.1
	60.0	100	3.8
Methyl orange	20.0	109.2	2.1
	40.0	100.2	6.3
	60.0	101	7.4
Triple mixture <sup>b</sup>	20.0	111.3	10.9
	40.0	92.5	13.8
	60.0	97.5	9.5

<sup>a</sup> Condition: **F-Naph-N<sub>3</sub>** (20 μM) was spotted on PTFE membrane filter after 1 h incubation with the different concentration of H<sub>2</sub>S (20, 40, 60 μM) in an ACN/H<sub>2</sub>O solution (v/v = 6 : 4, pH 8.0 sodium phosphate buffer 10 mM) containing 150 μM of organic dyes, and then the fluorescent intensity (optical density) of spots were measured. <sup>b</sup> Triple mixture sample consisted of 50 μM of three dyes. <sup>c</sup> Recovery rate was calculated as follows: [(intensity at samples)/(intensity at standard curve)] × 100%.

a result, it was demonstrated that the fluorescence of the probe could be selectively measured after F-SPE, indicating its potential for independent detection in the presence of interfering species.

### 3.5 Application for turbid dyeing solutions

Because the probe was designed to quantitatively detect H<sub>2</sub>S in an opaque solution, F-SPE using **F-Naph-N<sub>3</sub>** was examined in four organic dye solutions with different concentrations of H<sub>2</sub>S. The fluorescence intensity of the probe was measured in 150 μM of each organic dye (Alizarin red S, Bromophenol blue, and Methyl orange), and their triple mixture (mixing three dyes of 50 μM) solutions. In Fig. S6,† the dashed line represents the standard values previously measured without any interfering species. As expected, the fluorescence of the dyeing solutions did not reach the standard value, indicating that their detection by fluorescence spectrometer is challenging due to the turbid environment. However, our fluorous-tagging strategy using **F-Naph-N<sub>3</sub>** successfully enabled the detection of H<sub>2</sub>S in the dyeing solution by effectively eliminating interfering organic dyes and other species through aqueous wash, as shown in Scheme 1b. Therefore, it was demonstrated that **F-Naph-N<sub>3</sub>** can effectively detect H<sub>2</sub>S levels in challenging turbid solutions (Table 1).

## 4 Conclusions

In summary, a fluorous-tag-assisted naphthalimide derivative, **F-Naph-N<sub>3</sub>** was developed as a fluorescent probe to detect H<sub>2</sub>S quantitatively. The interference effects of various anions and biothiols were almost negligible, indicating that **F-Naph-N<sub>3</sub>** has good selectivity for H<sub>2</sub>S in solution. Furthermore, it is noted that **F-Naph-N<sub>3</sub>** could be easily isolated on the PTFE filter, and the other species were eliminated by a simple aqueous wash. As

a result, the innovative fluorous-tagging strategy suggested in this work allows for accurate detection of H<sub>2</sub>S concentrations even in highly turbid and deep-coloured dyeing solution. This protocol successfully overcomes the limitations of fluorescent probes in challenging environments and provides potential application to extended range of real samples.

## Author contributions

Geonwoo Park: methodology, investigation, visualization, writing – original draft. Mincheol Jang: methodology, investigation, visualization, writing – original draft. Min Su Han: conceptualization, writing – review & editing, project administration.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (RS-2023-00247332 and RS-2023-00259685).

## References

- 1 L. Long, S. Cao, B. Jin, X. Yuan, Y. Han and K. Wang, *Food Anal. Methods*, 2019, **12**, 852–858.
- 2 Y. Chen, C. Zhu, Z. Yang, J. Chen, Y. He, Y. Jiao, W. He, L. Qiu, J. Cen and Z. Guo, *Angew. Chem.*, 2013, **52**, 1688–1691.
- 3 C. Szabó, *Nat. Rev. Drug Discovery*, 2007, **6**, 917–935.
- 4 Y. S. Kafuti, S. Zeng, X. Liu, J. Han, M. Qian, Q. Chen, J. Wang, X. Peng, J. Yoon and H. Li, *Chem. Commun.*, 2023, **59**, 2493–2496.
- 5 B. Yu, C. Chen, J. Ru, W. Luo and W. Liu, *Talanta*, 2018, **188**, 370–377.
- 6 R. G. Hendrickson, A. Chang and R. J. Hamilton, *Am. J. Ind. Med.*, 2004, **45**, 346–350.
- 7 S. Arsayiset and S. Teepoo, *Anal. Chim. Acta*, 2020, **1118**, 63–72.
- 8 Y. Feng, S. Hu, Y. Wang, X. Song, C. Cao, K. Wang, C. Jing, G. Zhang and W. Liu, *J. Hazard. Mater.*, 2021, **406**, 124523.
- 9 V. Vitvitsky and R. Banerjee, *Methods Enzymol.*, 2015, **554**, 111–123.
- 10 L. A. Montoya, T. F. Pearce, R. J. Hansen, L. N. Zakharov and M. D. Pluth, *J. Org. Chem.*, 2013, **78**, 6550–6557.
- 11 Y. Zhao, Y. Yang, L. Cui, F. Zheng and Q. Song, *Biosens. Bioelectron.*, 2018, **117**, 53–59.
- 12 Z. Xu, L. Xu, J. Zhou, Y. Xu, W. Zhu and X. Qian, *Chem. Commun.*, 2012, **48**, 10871–10873.
- 13 D. Gong, X. Zhu, Y. Tian, S.-C. Han, M. Deng, A. Iqbal, W. Liu, W. Qin and H. Guo, *Anal. Chem.*, 2017, **89**, 1801–1807.
- 14 B. Gu, W. Su, L. Huang, C. Wu, X. Duan, Y. Li, H. Xu, Z. Huang, H. Li and S. Yao, *Sens. Actuators, B*, 2018, **255**, 2347–2355.



15 S. Y. Park, S. A. Yoon, Y. Cha and M. H. Lee, *Coord. Chem. Rev.*, 2021, **428**, 213613.

16 T. Lu, Z. Lin, J. Ren, P. Yao, X. Wang, Z. Wang and Q. Zhang, *PLoS One*, 2016, **11**, e0149751.

17 L. C. Zanetti-Domingues, C. J. Tynan, D. J. Rolfe, D. T. Clarke and M. Martin-Fernandez, *PLoS One*, 2013, **8**, e74200.

18 T.-W. Wu, F.-H. Lee, R.-C. Gao, C. Y. Chew and K.-T. Tan, *Anal. Chem.*, 2016, **88**, 7873–7877.

19 Y.-S. Zeng, R.-C. Gao, T.-W. Wu, C. Cho and K.-T. Tan, *Bioconjugate Chem.*, 2016, **27**, 1872–1879.

20 S. Yoo and M. S. Han, *Chem. Commun.*, 2019, **55**, 14574–14577.

21 X. Zhao, W. Zheng, T. Qin, X. Du, Y. Lei, T. Lv, M. Zhou, Z. Xu, L. Wang, B. Liu and X. Peng, *Sens. Actuators, B*, 2022, **351**, 130980.

22 Y. Chen, Z.-P. Chen, J. Yang, J.-W. Jin, J. Zhang and R.-Q. Yu, *Anal. Chem.*, 2013, **85**, 2015–2020.

23 H. Yu, F. Qu, Z. Wu, J. He, H. Rong and H. Liang, *Water Res.*, 2020, **187**, 116452.

24 Q. Zhang, Z. Luo and D. P. Curran, *J. Org. Chem.*, 2000, **65**, 8866–8873.

25 Y. Feng, J. Wu, G. Chen and Y. Chai, *Org. Lett.*, 2020, **22**, 2564–2568.

26 L. Cai, Q. Chen, J. Guo, Z. Liang, D. Fu, L. Meng, J. Zeng and Q. Wan, *Chem. Sci.*, 2022, **13**, 8759–8765.

27 R. L. Nicholson, M. L. Ladlow and D. R. Spring, *Chem. Commun.*, 2007, **38**, 3906–3908.

28 D. P. Curran, S. Hadida and M. He, *J. Org. Chem.*, 1997, **62**, 6714–6715.

29 Y.-Y. Zhu, X.-D. Wu, M. Abed, S.-X. Gu and L. Pu, *Chem.-Eur. J.*, 2019, **25**, 7866–7873.

30 P. Xiao, J. Liu, Z. Wang, F. Tao, L. Yang, G. Yuan, W. Sun and X. Zhang, *Chem. Commun.*, 2021, **57**, 5012–5015.

31 H.-Q. Dong, T.-B. Wei, X.-Q. Ma, Q.-Y. Yang, Y.-F. Zhang, Y.-J. Sun, B.-B. Shi, H. Yao, Y.-M. Zhang and Q. Lin, *J. Mater. Chem. C*, 2020, **8**, 13501–13529.

32 M. Cametti, B. Crousse, P. Metrangolo, R. Milani and G. Resnati, *Chem. Soc. Rev.*, 2012, **41**, 31–42.

