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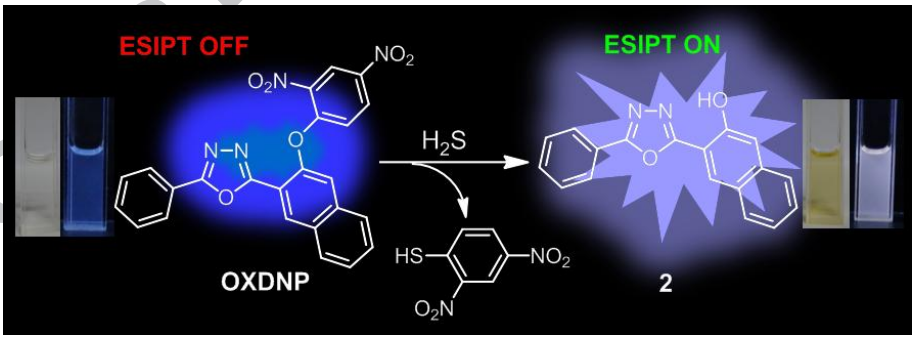
Graphical abstract

A new 2,5-diaryl-1,3,4-oxadiazole-based ratiometric fluorescent probe (**OXDNP**) for rapid and highly selective recognition of hydrogen sulfide has been developed.



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A 2,5-diaryl-1,3,4-oxadiazole-based fluorescent probe for rapid and highly selective recognition of hydrogen sulfide with a large Stokes shift through switching on ESIPT

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Abstract: A new 2,5-diaryl-1,3,4-oxadiazole derived ratiometric fluorescent probe (**OXDNP**) for hydrogen sulfide recognition has been developed. Probe **OXDNP** displays highly selective and sensitive detection to HS^- over other anions and thiol-containing amino acids in DMSO solution with fast response and a large Stokes shift. Through HS^- induced thiolysis of the dinitrophenyl ether, the excited state intramolecular proton transfer (ESIPT) featured precursor was released, which led to dual fluorescence emission "turn on" and ratiometric emission behavior of the sensing system. The pseudo-first-order reaction rate constant was calculated to be 1.234 s^{-1}. The HS^- recognition mechanism was proved by HPLC-MS and ^1H NMR comparison investigations.

Keywords: Hydrogen sulfide; Fluorescence probe; Ratiometric; ESIPT; 1,3,4-Oxadiazole

1. Introduction

Hydrogen sulfide (H_2S) is a inflammable colorless gas with a distinctive odor of rotten eggs, exposure to H_2S can elicit irritation of the eyes and infuriation in the respiratory tract.[1] Abnormal level in H_2S has also been recognized to be related with

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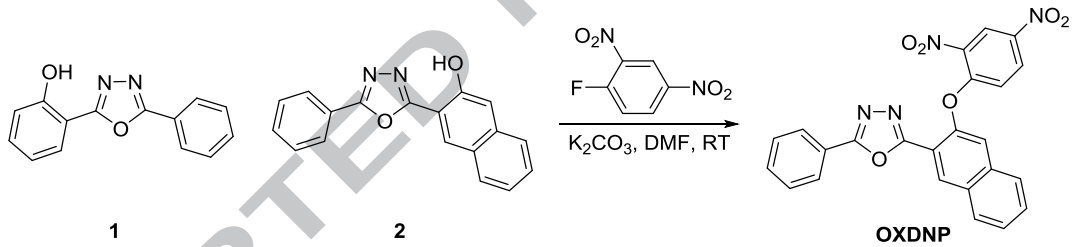
several diseases including Alzheimer's disease, Down's syndrome, diabetes, and liver cirrhosis.[2] On the other hand, H_2S plays paramount roles in a wide range of physiological processes,[3] such as vasodilation, neuromodulation, apoptosis, anti-inflammation, anti-oxidation, inhibition of insulin signaling.[4] Therefore, easy and convenient methods for H_2S detection are of importance for rapid assessment of this biologically and environmentally important species.

To date, various H_2S detection methods including polarography, electrochemical analysis, gas chromatography, colorimetry method as well as semiconductor-based transistors/resistors have been developed.[5] Among the methods, fluorescence detection of H_2S continuously attracted the attention of researchers due to the operational simplicity, real-time response and high sensitivity of fluorescence technique. Recently, several types of reaction-based fluorescent probes for H_2S detection have been reported, mainly including H_2S-triggered azide reduction,[6] nucleophilic addition,[7] H_2S induced metal ion displacement of Cu^{2+} or Zn^{2+} complexes,[8] and H_2S-induced cleavage of 2,4-dinitrophenyl ether.[9] Superior to the probes that depend on single emission intensity alteration, ratiometric fluorescent probes could monitor the sensing process at two emission wavelength and possess a distinct advantage of built-in correction, which can avoid various environmental effects and favorable to more accurate detection. Although a few ratiometric fluorescent probes for H_2S detection have been documented,[7d, 10] most of the probes suffered from a delayed response time (more than 20 min) except the works reported by Guo,[7c] Tang,[7d] Guo and He,[7e] and Goswami.[11] Therefore, development of new

fluorescent probes for H_2S recognition with ratiometric emission output and rapid response is still highly desirable.

Recent studies manifest that fluorophores with ESIPT characteristics are ideal candidates for constructing ratiometric fluorescent probes due to their dual emission bands and large Stokes shift. Besides the commonly used ESIPT featured fluorophores including 2-(2′-hydroxypehnyl)benzoxazole, 2-(2′-hydroxypehnyl)benzothiazole, 2-(2′-hydroxypehnyl)benzimidazole, and 3-hydroxyflavone, the ESIPT behavior of some 2,5-diaryl-1,3,4-oxadiazole compounds has also been investigated.[12] However, most of the reports on 2,5-diaryl-1,3,4-oxadiazole derivatives are mainly focused on the synthetic methods[13] and their application as ligands for organic light-emitting diode (OLED) materials,[14] taking the advantage of ESIPT characteristic of these fluorogens for metal ion or anion recognition are still rare,[15] partly due to the short emission wavelength of these fluorogens. For instance, 2-(5-phenyl-1,3,4-oxadiazol-2-yl)phenol (**1**) (Scheme 1), which displays ESIPT behavior, generally emits at a wavelength less than 500 nm.[15a, 16] A commonly employed method to obtain a long wavelength emission fluorogen is to expand the conjugation system of a certain fluorophore. Thus, it is reasonable to envision that further expand the conjugation effect of **1** may result in longer-wavelength emission while retain the ESIPT property. Our preliminary examination showed that compound **2**, which possesses a longer conjugation system than that of **1**, indeed exhibits dual emission in DMSO solution with a shorter-wavelength emission at 418 nm and a longer-wavelength emission at 556 nm.

Along with this line, we herein designed and synthesized a new 2,5-diaryl-1,3,4-oxadiazole derived fluorescent probe **OXDNP** by masking the phenolic hydroxyl group of **2** with 2,4-dinitrophenyl (DNP) group (Scheme 1). The incorporated H_2S reactive DNP ether moiety acts not only as a fluorescence quencher,[17] but also as a ESIPT inhibition group. We speculated that the H_2S induced nucleophilic cleavage of the ether bond in **OXDNP** can release free **2** and thereby restore the dual emission and large Stokes shift behavior of **2**, thus realizing a selectively fluorescence "turn on" recognition of H_2S. Subsequent investigations demonstrate that **OXDNP** indeed behaves highly selective and sensitive ratiometric recognition to H_2S with a fast response and a large Stokes shift in DMSO solution.



Scheme 1. The structure of model compound **1** and synthesis of probe **OXDNP**.

2. Results and discussion

Probe **OXDNP** was readily prepared by reaction of **2**[18] with 2,4-dinitrofluorobenzene in DMF as illustrated in Scheme 1, which was structurally characterized by ^{1}H NMR, ^{13}C NMR and HRMS analysis (see supplementary data). The fluorescence responses of **OXDNP** to different anions, thiol-containing amino acids were firstly evaluated (Fig. 1). As expected, probe **OXDNP** (10 μM) exhibits a weak emission band centered at 413 nm in DMSO (λ_{ex} = 334 nm), which is attributed to the photo-induced electron transfer (PET) process resulted from the DNP moiety.

Upon addition of HS^- (NaHS was used as H_2S source), dramatic emission enhancements of two bands at 418 nm and 556 nm were observed. The major emission band centered at 418 nm was attributed to the *enol* emission from **2**, and the emission band centered at 556 nm came from the H-transferred *Keto* tautomer emission, which results in a Stokes shift as large as 222 nm. Whereas, on individual addition of various anions including AcO^-, F^-, Br^-, Cl^-, CN^-, I^-, SCN^-, PO_4^{3-}, CO_3^{2-}, HCO_3^-, $H_2PO_4^-$, HPO_4^{2-}, NO_3^-, SO_4^{2-}, $P_2O_7^{4-}$, HSO_4^-, HSO_3^-, $S_2O_3^{2-}$ and thiol-containing amino acids (Cys, Hcy, GSH) to **OXDNP** solution, there was no significant fluorescence intensity variations was observed except that the fluorescence intensity was weakened in the presence of GSH. Similarly, UV-Vis spectra response of **OXDNP** to the tested analytes also revealed a selective response to HS^-. Addition of HS^- to **OXDNP** solution elicited a significant increase in absorption intensity at 473 nm (Fig. S1) accompanied with a color change from colorless to yellow. Other examined analytes only promoted minor absorption intensity alterations. The HS^- elicited color changes under UV light and daylight are naked eye observable (Fig. S2). These results demonstrate that probe **OXDNP** exhibits excellent selectivity to HS^- through fluorescence and colorimetry dual-channel responses.

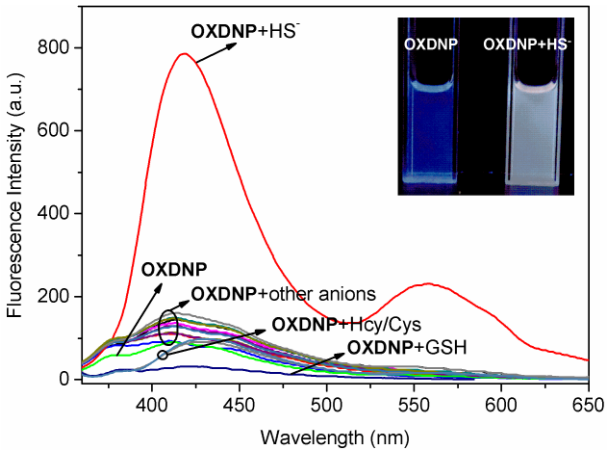


Figure 1. Fluorescence spectra changes of **OXDNP** in DMSO upon individual addition of 10.0 equiv. of different anions and thiols (Cys, Hcy, GSH). λ_{ex} = 334 nm. Inset: Fluorescence color changes of **OXDNP** solution before and after addition of HS^- under illumination at 365 nm with a portable UV lamp.

To obtain better insight into the sensing behavior of **OXDNP** to HS^-, fluorescence titration experiments were then conducted. As shown in figure 2, upon incremental addition of HS^- (0 to 10.0 equiv.) to **OXDNP** solution, gradual increase in fluorescence intensities at 418 nm and 556 nm were observed, this emission spectra change was terminated when 10 equiv. of HS^- was employed. Similarly, the UV-Vis spectra of **OXDNP** showed gradual increase in absorbance at 473 nm upon incremental addition of HS^- (Fig. S3). The emission intensity ratio of $I_{556\ nm}/I_{418\ nm}$ showed a good linearity between concentration ranges of HS^- from 2 μM to 20 μM (Fig. 2**,** inset). Based on the fluorescence titration profile, the detection limit of **OXDNP** for HS^- was estimated to be 2.0 μM (Fig. S4),[19] indicating that **OXDNP** is sensitive enough to detect HS^- concentration in DMSO system. Time-dependent fluorescence spectra changes reveal that 10 equiv. of HS^- is sufficient to complete the sensing reaction within a few seconds under the experimental conditions. Therefore,

the reaction kinetics of **OXDNP** in the presence of 10 equiv. of HS^- according to a pseudo-first-kinetic was investigated (Fig. 3) with the equation $I_t=I_{max}+A\times\exp(k\times t)$.[20] In the equation, I_t represents the fluorescence intensity (418 nm) of the test solution at time t, I_{max} represents the maximum fluorescence intensity (418 nm) of the test solution. The pseudo-first-order rate constant k was calculated to be 1.234 s^{-1}, indicative of the remarkable high sensitivity of **OXDNP** for H_2S detection.

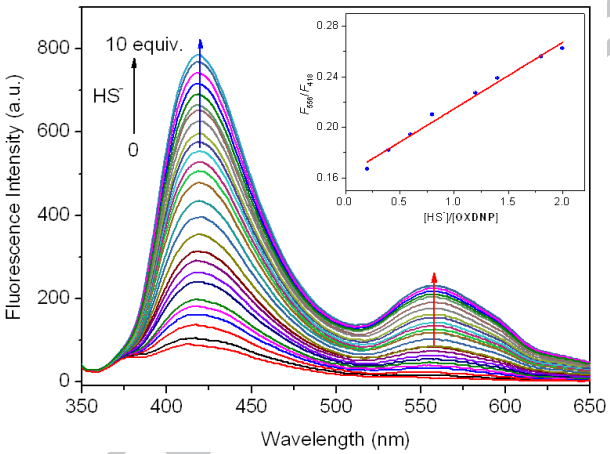


Figure 2. Fluorescence spectra changes of **OXDNP** (10 μM) in DMSO solution upon incremental addition of HS^- (0 to 10.0 equiv.). λ_{ex} = 334 nm. Inset: fluorescence intensity ratio of F_{556}/F_{418} as a function of HS^- amount.

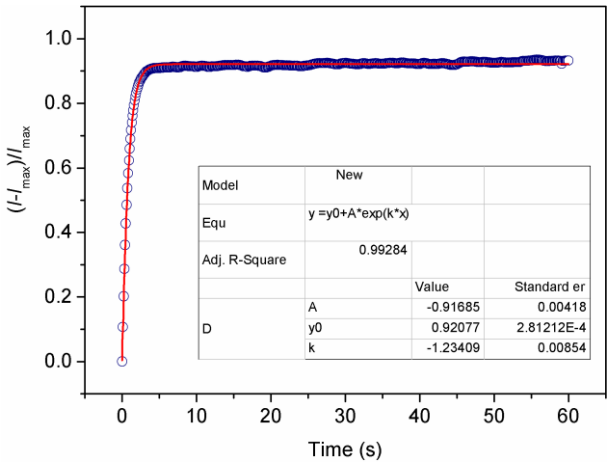


Figure 3. The kinetic study of the response of **OXDNP** (10 μM) to HS^- (10.0 equiv.) under pseudo-first-order conditions in DMSO.

To examine the interfering effects of the analytes as mentioned above on HS^- recognition, competition assays were subsequently carried out (Fig. 4). The results show that co-existence of the same concentration of other background analytes promoted no significant influence on HS^- detection, demonstrating the excellent anti-interference ability of **OXDNP** for HS^- recognition.

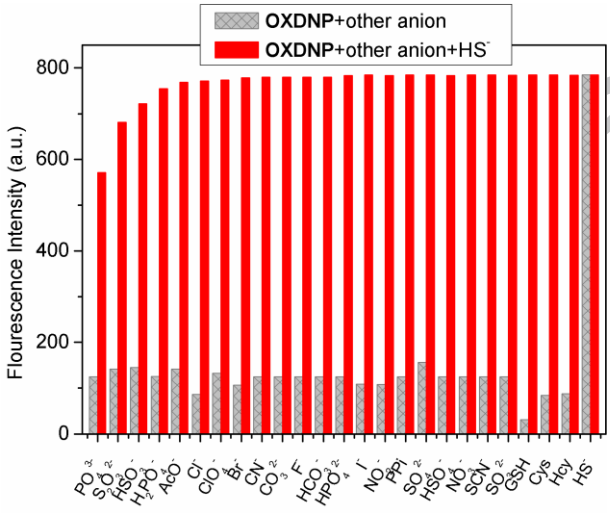


Figure 4. Fluorescence intensity (418 nm) changes of **OXDNP** (10 μM) in DMSO solution upon sequential addition of various background analytes (10.0 equiv.) and HS^- (10.0 equiv.). λ_{ex} = 334 nm.

It is noteworthy that the fluorescence spectrum of **OXDNP** in the presence of HS^- exhibits an almost identical emission pattern as that of free **2** (Fig. S5), suggesting that the speculated HS^--triggered thiolysis of dinitrophenyl ether happened and free **2** was released. To further corroborate this reaction process, HPLC-MS chromatograms of compound **2**, probe **OXDNP**, and the reaction mixture of **OXDNP** with HS^- were compared (Fig. S6). Probe **OXDNP** showed a single peak at retention time of 16.882 min with *m/z* = 445.0 ($[M+1]^+$) (Fig. S6a). Compound **2** and the reaction product of **OXDNP** with HS^- exhibited retention time of 26.171 min and 26.315 min respectively

with the same *m/z* value (289.0 ($[M+1]^+$) (Fig. S6b and 6c). These results reveal that HS^- can completely cleave the dinitrophenyl ether moiety and release **2**. Another solid evidence for this sensing mechanism comes from the ^1H NMR comparison studies (Fig. 5). Since the HS^- anion used in the experiments is the corresponding water solution, a mixed solvent of D_2O-DMSO-d_6 (5:95, v/v) was used when comparing the ^1H NMR spectra of **OXDNP**, **2** and **OXDNP**+HS^-. On addition of HS^- to **OXDNP** solution, a resemblant spectrum of **2** was observed from that of the mixture (Fig. 5c), unambiguously demonstrating that **2** was indeed reoccurred on treatment of **OXDNP** with HS^-. Based on the above investigation results, a reaction-based HS^- detection mechanism was illustrated in Scheme 2.

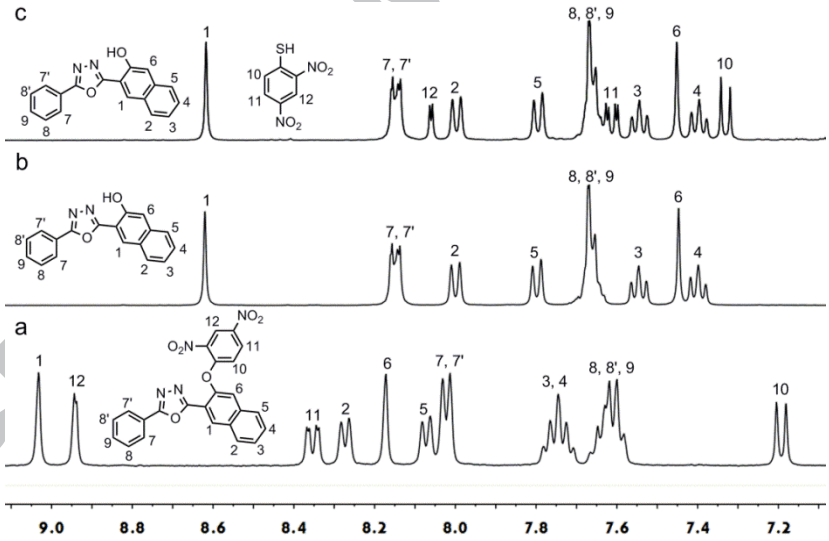
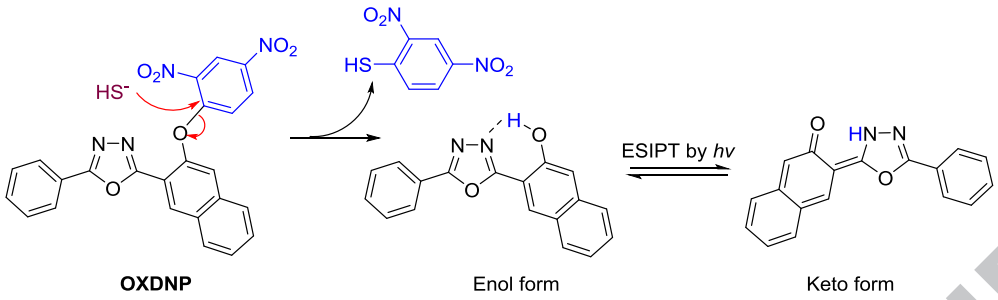


Figure 5. Partial ^1H NMR spectra of **OXDNP** (a), **2** (b) and **OXDNP**+HS^- (c) in DMSO-d_6/D_2O (95:5, v/v).



Scheme 2. The sensing mechanism of **OXDNP** for HS^-.

3. Conclusions

In summary, we have synthesized a new 2,5-diaryl-1,3,4-oxadiazole-based fluorescent probe **OXDNP** for hydrogen sulfide recognition. In DMSO solution, probe **OXDNP** displays highly selective and sensitive recognition toward HS^- over other examined anions as well as thiol-containing amino acids. The HS^- sensing mechanism, namely, HS^- triggered thiolysis reaction, was proved by HPLC-MS and ^1H NMR investigations. The HS^- recognition event is fast and can complete within a few seconds, which leads to releasing of the ESIPT featured precursor **2** and results in dual "turn on" ratiometric emission and a large Stokes shift. The pseudo-first-order reaction rate constant was estimated to be 1.234 S^{-1}. Therefore, through this "protection-deprotection" strategy, an effective fluorescent recognition of HS^- was achieved. The results of this work are believed to be instructive for the design of novel ESIPT featured 2,5-diaryl-1,3,4-oxadiazole-based fluorescent probes.

Acknowledgments

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LR2015001).

Supplementary data

Instrumental details, synthesis and characterization of **OXDNP**, and supplementary figures (Figure S1-S9).

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