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高选择和高灵敏检测溶液和气相中硫化氢的新型萘酰亚胺类开启型荧光探针

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摘要 构建了一种用于硫化氢检测的新型萘酰亚胺类开启型荧光探针(**NPHQ**). 因硫化氢亲核效应促使 **NPHQ** 中萘醌结构离解, 导致探针分子中的光诱导电子转移(PET)效应消失和萘酰亚胺分子内电荷转移(ICT)效应恢复, 而呈现出强烈的荧光开启效应. **NPHQ** 荧光强度对 0～0.5 μmol/L 硫化氢呈线性增强, 检测限为 1.68 nmol/L. **NPHQ** 具备的高选择性、高灵敏度和荧光开启响应, 使其在溶液和气相中检测硫化氢, 具有较好的应用前景和价值.
关键词 硫化氢; 荧光探针; 开启型; 萘酰亚胺; 溶液和气相

A Novel Turn-On Fluorescent Probe Based on Naphthalimide for Highly Selective and Sensitive Detection of Hydrogen Sulfide in Solution and Gas

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Abstract A novel turn-on fluorescent probe (**NPHQ**) based on naphthalimide had been constructed to detect hydrogen sulfide. The nucleophilic effect of hydrogen sulfide induced the decomposition of naphthoquinone structure, which resulted in the disappearance of photo-induced electron transfer (PET) of **NPHQ** and recovery of intramolecular charge transfer (ICT) of naphthalimide. The fluorescence intensities of **NPHQ** showed a linear enhancement response to hydrogen sulfide in the concentration range of 0～0.5 μmol/L with limit of detection of 1.68 nmol/L. Moreover, **NPHQ** held promising application prospects for detecting hydrogen sulfide in solution and gas based on its high selectivity, sensitivity and specific turn-on emission.
Keywords hydrogen sulfide; fluorescence probe; turn-on; naphthalimide; solution and gas

1 Introduction

Hydrogen sulfide (H_2S) is a colorless, extremely poisonous gas with a rotten egg stench that may readily harm the human central nervous system and respiratory system.[1] H_2S has been found to be another endogenous gas signalling molecule[2] besides nitric oxide[3] and carbon monoxide,[4] and identified as an important multifunctional molecule that regulates different physiological systems. H_2S is widely known to be present in several tissues and organs of the body, and to be associated with a number of physiological processes[5] such as inflammation,[6] vasodilation,[7] myocardial contraction,[8] apoptosis,[9] insulin secretion,[10] nerve conduction[11] and regulation.[12] At the same time,

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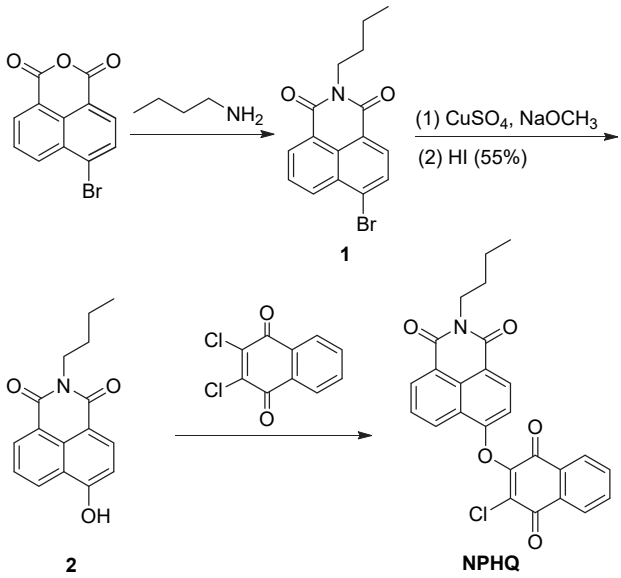
more and more reports confirm that once H_2S concentration exceeds its normal levels in human body, it can lead to a series of diseases such as arterial and pulmonary hypertension, diabetes, gastric mucosal damage, liver cirrhosis, alzheimer's disease, down's syndrome, and heart disease.[13] H_2S is released into the environment from both anthropogenic and natural sources, and a large portion of H_2S originates from industrial production, such as paper production, sulfide dyes, sewage treatment, gas manufacturing, natural gas purification and petroleum refining.[14] Given the impacts of H_2S on the environment and human health, the development of molecular probes for its early detection to ameliorate its terrible effects is of great scientific importance.

The detection of H_2S has been made easier in recent years with the development of a number of techniques,[15] including electrochemical analysis,[16] gas chromatography,[17] mass spectrometry,[18] and high performance liquid chromatography.[19] Yet, these procedures are difficult and time-consuming to carry out, and special equipments are required to meet the rapid, accurate and real-time detection of the objectives. In contrast, the fluorescence detection approach has garnered a lot of interest due to its straightforward operation, excellent selectivity, high sensitivity, and low cost.[20] Many fluorescent probes have been created and manufactured to detect H_2S. The detection principles mainly include reduction of azidoes,[21] reduction of nitro to amino groups,[22] copper sulfide precipitation,[23] nucleophilic substitution,[24] selenium-sulfur exchange reaction[25] and thiolysis reactions.[26] However, they also have some disadvantages such as low sensitivity and poor selectivity. More importantly, the long response time makes them difficult to accomplish rapid detection of H_2S in practical application (*e.g.* real-time detection of H_2S in oil production and processing).[27] Hence, it remains a challenge to design fluorescent probes with easy synthesis, high sensitivity, high selectivity, low limit of detection (LOD) and rapid response for detection of H_2S.

In this paper, a novel "turn-on" fluorescent probe (**NPHQ**) that could be used to detect H_2S was described. The synthesis pathway of **NPHQ** was displayed in Scheme 1. The structures of intermediates and **NPHQ** were confirmed on the basis of nuclear magnetic resonance spectroscopy (NMR) and high-resolution mass spectra (HRMS). The naphthalimide and its derivatives showed good photophysical properties, including the advantages of better photostability, visible excitation and emission, and a large stokes shift. Therefore, naphthalimide was used as the fluorophore.[28] When naphthoquinone was attached to the 4-position of 1,8-naphthalimide, the electron-rich nature of naphthoquinone gave rise to the photo-induced electron transfer (PET) effect,[29] rendering the molecule non-fluorescent. Aromatic nucleophilic substitution (S_NAr) reaction took place in the presence of H_2S, which resulted in the recovery of intramolecular charge transfer (ICT) of naphthalimide, and the fluorescence turned on selectively and sensitively. **NPHQ** had also been designed to be attached



Scheme 1 Synthetic route of **NPHQ**

to the filter paper to obtain the test strips, which was used to detect H_2S gas.

2 Results and discussion

2.1 Selectivity

Selectivity was one of the most crucial aspects of fluorescent probe in detection procedure. To assess the selectivity of **NPHQ**, fluorescence response of **NPHQ** (10 μmol/L) toward H_2S (100 μmol/L) and other interfering substances (100 μmol/L) including Mn^{2+}, Al^{3+}, Sn^{4+}, K^+, Cr^{3+}, Ca^{2+}, Zn^{2+}, Na^+, Ba^{2+}, Ce^{3+}, Mg^{2+}, I^-, $S_2O_5^{2-}$, HCO_3^-, MnO_4^-, HSO_3^-, SO_4^{2-}, $Cr_2O_7^{2-}$, $H_2PO_4^-$, CO_3^{2-}, Br^-, ClO_3^-, NO_2^-, ClO^-, H_2O_2, GSH, Cys, Hcy, DTT, *β*ME in dimethyl sulfoxide (DMSO)/H_2O (*V*/*V*=1/9) were recorded. The results were shown in Figure 1.

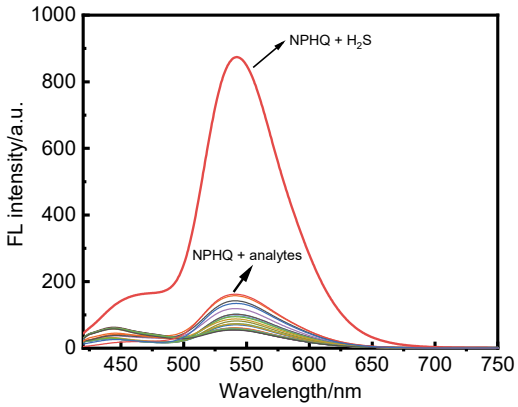


Figure 1 Fluorescence response of **NPHQ** (10 μmol/L) against different interfering analytes (100 μmol/L)

Weak fluorescence emission was observed at 542 nm for **NPHQ**, and a substantial fluorescence amplification (16-fold) was shown after the addition of H_2S, while there were no obviously fluorescence changes caused by the

addition of other cation, anion, biological thiols (*β*ME, DTT, GSH, Cys and Hcy) or reactive oxygen species (H_2O_2 and ClO^-). Among these analytes, the maximum fluorescence increasement was GSH (2.8-fold). This suggested that **NPHQ** exhibited high selectivity for H_2S, implying that **NPHQ** could specifically interact with H_2S and recognize it.

2.2 Concentration dependence

In order to investigate the recognition performance of **NPHQ** for H_2S, the detailed changes in optical spectra of **NPHQ** after addition of H_2S were shown in Figure 2. As shown in Figure 2a, a weakening of the ripple-like broad absorption band at 355 nm was observed for **NPHQ** (10 μmol/L), while a new absorption band at 360 nm was emerged. This phenomenon was due to the 4-position substitution of naphthoquinone by hydroxyl, which changed the electronic push-pull effect in the molecule, resulting in a small red shift in the absorption spectrum. **NPHQ** emitted a weak fluorescence at 542 nm. When 0.5 μmol/L H_2S was added, the fluorescence intensity of **NPHQ** was found to be greatly increased (16-fold), and a noticeable "turn-on" fluorescence was detected. Under irradiation of the 365 nm fluorescent lamp, the fluorescence colour of **NPHQ** changed from absent to light yellow (Figure 2a, inset). These apparent changes in UV-Vis and fluorescence spectra indicated that **NPHQ** could produce an obvious response to H_2S.

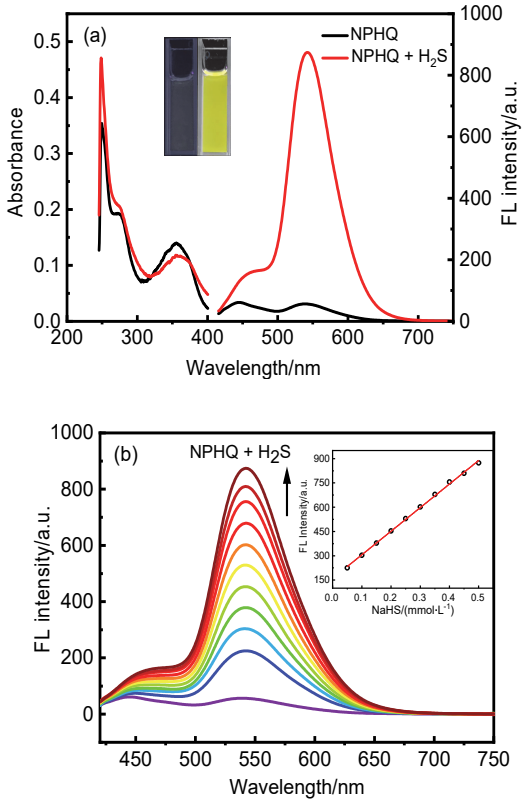


Figure 2 (a) Absorption and emission spectra of **NPHQ** (10 μmol/L) in DMSO/H_2O (V/V=1/9) solution in absence and presence of H_2S (100 μmol/L) (inset: the fluorescence color of **NPHQ** in absence and presence of H_2S under 365 nm fluorescent lamp); (b) fluorescence intensity changes of **NPHQ** (10 μmol/L) in DMSO/H_2O (V/V=1/9) solution with the addition of H_2S (0～0.5 μmol/L) (inset: linear relationship between the fluorescence intensity of **NPHQ** and the concentration of H_2S)

To test the sensitivity of **NPHQ** to H_2S, the fluorescence titration experiments were performed as shown in Figure 2b. It could be seen that **NPHQ** quickly responded to H_2S by the fluorescence signal at 542 nm. The intensity of maximum emission wavelength of **NPHQ** at 542 nm was weak, and gradually enhanced with the addition of H_2S, and reached peak when the amount of H_2S exceeded 0.5 μmol/L. More importantly, a satisfactory linear relationship (Y= 160.6271 + 1456.3507X, R^2 = 0.9984) was observed between the F_{542} of **NPHQ** and the concentration of H_2S, when the concentration of H_2S was in the range of 0～0.5 μmol/L. According to LOD=3σ/k,[30] the limit of detection was determined to be 1.68 nmol/L, indicating that **NPHQ** was highly sensitive to H_2S. Using quinine sulfate (0.1 mol/L) as reference, the fluorescence quantum yields of **NPHQ** before and after reacting with H_2S were 0.04 and 0.45, respectively.

2.3 Response time

The response time to the analytes was significant indicator to evaluate the performance of fluorescent probe. As a result, the time dependence between the fluorescence intensities of **NPHQ** at 542 nm and the adding time of H_2S were investigated. As shown in Figure S6, the fluorescence intensity of **NPHQ** was found to reach the maximum after the addition of H_2S for 10 s, indicating that **NPHQ** could rapidly identify H_2S by fluorescence, and could be used for real-time detection of H_2S.

2.4 Competitive experiment

Competitive experiments were performed on **NPHQ** (10 μmol/L) in DMSO/H_2O (V/V=1∶9) solution in order to investigate the selectivity of **NPHQ** for H_2S in complex environment. Various interfering species (100 μmol/L) including Mn^{2+}, Al^{3+}, Sn^{4+}, K^+, Cr^{3+}, Ca^{2+}, Zn^{2+}, Na^+, Ba^{2+}, Ce^{3+}, Mg^{2+}, I^-, $S_2O_5^{2-}$, HCO_3^-, MnO_4^-, HSO_3^-, SO_4^{2-}, $Cr_2O_7^{2-}$, $H_2PO_4^-$, CO_3^{2-}, Br^-, ClO_3^-, NO_2^-, ClO^-, H_2O_2, GSH, Cys, Hcy, DTT, *β*ME were discussed. In the existence of these interferents, the fluorescence intensities of **NPHQ** at 542 nm were illustrated in Figure 3. Obviously, weak fluorescence changes caused by competitive analytes while H_2S led to significant fluorescence enhancement. These results indicated that **NPHQ** was able to detect H_2S selectively in the existence of interferents.

2.5 Effect of pH

To explore the potential applicability of **NPHQ**, the pH effect was determined at various pH 1～14. The fluorescence intensities of **NPHQ** at 542 nm in absence and presence of H_2S kept constant at pH 1～9. When pH was in the range of 10～14, significant variation of the fluorescence intensities occurred. It could be seen that the fluorescence intensities gradually decreased in the presence of

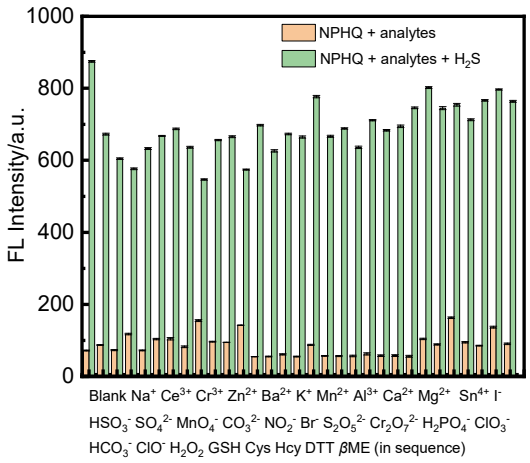


Figure 3 Fluorescence intensities of **NPHQ** (10 μmol/L) in the presence of 100 μmol/L interfering species including H_2S, Mn^{2+}, Al^{3+}, Sn^{4+}, K^+, Cr^{3+}, Ca^{2+}, Zn^{2+}, Na^+, Ba^{2+}, Ce^{3+}, Mg^{2+}, I^-, $S_2O_5^{2-}$, HCO_3^-, MnO_4^-, HSO_3^-, SO_4^{2-}, $Cr_2O_7^{2-}$, $H_2PO_4^-$, CO_3^{2-}, Br^-, ClO_3^-, NO_2^-, ClO^-, H_2O_2, GSH, Cys, Hcy, DTT and βME (λ_{ex}=390 nm)

H_2S, and the phenomena were just the opposite in the absence of H_2S. These results indicated that **NPHQ** could detect H_2S at pH from 1 to 9.

2.6 Response mechanism

The response mechanism of **NPHQ** for the detection of H_2S was provided in light of the variations in UV-Vis absorption and fluorescence emission spectra before and after injection of H_2S. As shown in Figure 4, upon reaction with H_2S, the naphthoquinone group of **NPHQ** was released to form 4-hydroxy-1,8-naphthalimide, which consequently led to the recovery of ICT effect in naphthalimide and exhibited "turn-on" fluorescence. Moreover, the fluorescence spectrum of compound **2** (10 μmol/L) was consistent with the fluorescence spectrum of **NPHQ** (10 μmol/L) reaction with H_2S. In order to prove above mechanism, **NPHQ** (100 mg), NaHS (188 mg) and hydrochloric acid solutions (pH=1, 50 μL) were added in DMSO/H_2O (V∶V=1∶9) solution. After reaction for 1 min, the mixture was separated and purified by column chromatography. It was found that the UV-Vis and fluorescence spectra of the product and compound **2** in the same concentration overlapped. The fluorophore structure was confirmed as 4-hydroxyl-1,8-naphthalimide by ^{1}H NMR, ^{13}C NMR and HRMS. The results clearly supported that H_2S could induce the decomposition of naphthoquinone structure, and 4-hydroxy-1,8-naphthalimide was formed. Consequently, the fluorescence turned on.

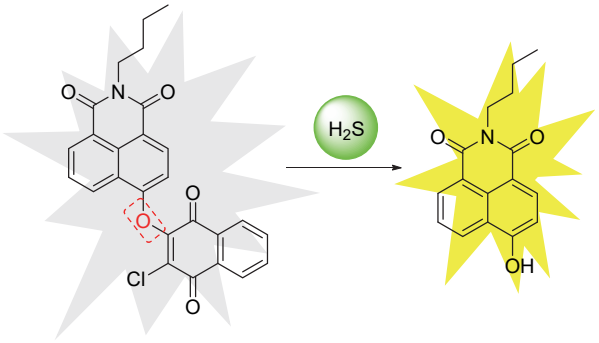


Figure 4 Proposed recognition mechanism of **NPHQ** to H_2S

2.7 Application

To evaluate the portable performance of **NPHQ** for the detection of H_2S gas, test strips were made by dipping the test paper into **NPHQ** solution (1 mmol/L). Test strips were placed into a centrifuge tube (10 mL) and then H_2S gas was added to reach different concentrations. As illustrated in Figure 5, the test strips showed significant yellow fluorescence changes under 365 nm portable fluorescent lamp, when they were exposed to an atmosphere of H_2S gas at 38～607 mg/m^3. The fluorescence intensities were observed to increase gradually with increased H_2S. These phenomena indicated that the test strips containing **NPHQ** could achieve real-time detection of H_2S gas qualitatively. **NPHQ**-based test strips showed great potential for future applications. The selectivity of the test strips in different gas (H_2, O_2, CO_2, SO_2) was further investigated. Only the test strips treated with H_2S gas showed an obvious yellow fluorescence, while the test strips treated with other gases showed no distinctive change. These phenomena made clear that the test strips were able to efficiently detect H_2S gas, indicating its potent practical application.

3 Conclusions

In conclusion, a novel fluorescent probe **NPHQ** based on naphthalimide was designed and synthesized. **NPHQ** was

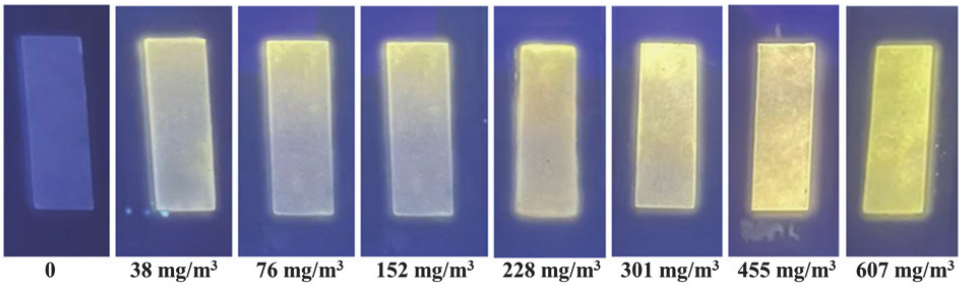


Figure 5 Test strips for detection of H_2S gas (0, 38, 76, 152, 228, 301, 455, 607 mg/m^3) under fluorescent lamp
λ_{ex}=365 nm. Pictures were taken after exposure to H_2S gas for 10 s

reactive fluorescent probe for detection of H_2S which used naphthoquinone as the receptor with relatively simple synthesis. **NPHQ** exhibited remarkable "turn-on" fluorescence response to H_2S, showing a rapid (within 10 s) and notable fluorescence enhancement (16-fold), and the LOD was 1.68 nmol/L. **NPHQ** had a relatively low LOD and response time for H_2S compared with those reported in literature.[31] **NPHQ** remained highly selective and sensitive to H_2S when coexisting with other interfering analytes. In addition, portable test strips could be easily prepared and their fluorescence changed selectively, rapidly and distinctly in the presence of H_2S gas (38～607 mg/m^3). This work provided a new method with high selectivity, sensitivity and potent practicability for detection of H_2S in solution and gas.

4 Experimental section

4.1 Materials and apparatus

4-Bromo-1,8-naphthalic anhydride, $NaOCH_3$, $CuSO_4$•$5H_2O$, butylamine, 55% HI, 2,3-dichloro-1,4-naphthoquinone and K_2CO_3 were purchased from Macklin. Gases including H_2S, CO_2, O_2, SO_2 and H_2 were purchased from Jingzhou Special Gases Co., Ltd. All of the reagents were analytical grade, bought from Sinopharm, and utilized without further purification. Flash column chromatography was performed using silica gel (200～300 mesh). The instrument used to obtain ^{1}H NMR and ^{13}C NMR spectra was a Bruker AVANCE III 600 MHz NMR spectrometer. Mass spectra of the new compounds were obtained using an Agilent Technologies 1290 Infinity mass spectrometer. Shimadzu UV-2450 spectrometer was used to gather UV-Vis spectra, and fluorescence spectra were collected on a Perkin Elmer LS55 spectrometer. pH measurements were carried out using a REX benchtop pH-3c.

4.2 Synthesis of NPHQ

6-Bromo-2-butyl-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (**1**): 4-Bromo-1,8-naphthalic anhydride (2.77 g, 10 mmol) and butylamine (0.80 g, 11 mmol) were dissolved in anhydrous EtOH (50 mL) with stirring and refluxing at 80 ℃ for 8 h. The solvent was removed under reduced pressure. The residue was dried after being washed with water, and purified by silica gel column chromatograph with CH_2Cl_2/PE (*V*/*V*=3/2) to give compound **1**[32] as white solid (2.83 g, yield 84%). m.p. 103.5～104.5 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 8.58 (d, *J*=7.9 Hz, 2H), 8.35 (d, *J*=7.8 Hz, 1H), 8.24 (d, *J*=7.8 Hz, 1H), 8.01 (d, *J*=7.9 Hz, 1H), 4.11～3.98 (m, 2H), 1.62 (t, *J*=7.5 Hz, 2H), 1.36 (dd, *J*=15.0, 7.5 Hz, 2H), 0.93 (t, *J*=7.4 Hz, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 163.11, 163.06, 132.8, 131.8, 131.6, 131.2, 130.0, 129.4, 129.1, 128.5, 123.0, 122.2, 39.9, 30.0, 20.2, 14.1.

2-Butyl-6-methoxy-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (**2**): Anhydrous CH_3OH (40 mL) was used to dissolve compound **1** (2.89 g, 10 mmol), $CuSO_4$•$5H_2O$ (0.25 g, 1 mmol) and $NaOCH_3$ (1.08 g, 20 mmol), and then the mixture was stirred and refluxed at 75 ℃ for 5 h. The solvent was removed under reduced pressure, and 40 mL of 1 mol/L HCl was added. The mixture was agitated for 0.5 h at 25 ℃. After the reaction was completed, the precipitate was obtained by filtration, and progressively dissolved in 55% HI (13 mL) with stirring and refluxing at 130 ℃ overnight. After cooling to room temperature, the crude product was filtered, washed with cold water (200 mL), and purified by silica gel column chromatography with PE/EtOAc (*V*/*V*=1/1) to obtain compound **2**[33] as yellow solid (1.55 g, yield 66%). m.p. 236～238 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 11.84 (s, 1H), 8.51 (dd, *J*=8.3, 1.1 Hz, 1H), 8.45 (dd, *J*=7.3, 1.1 Hz, 1H), 8.33 (d, *J*=8.2 Hz, 1H), 7.74 (dd, *J*=8.2, 7.4 Hz, 1H), 7.14 (d, *J*=8.2 Hz, 1H), 4.07～3.96 (m, 2H), 1.66～1.53 (m, 2H), 1.40～1.26 (m, 2H), 0.92 (t, *J*=7.4 Hz, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 168.46, 167.79, 165.06, 138.27, 135.83, 133.96, 133.62, 130.28, 127.18, 126.60, 117.46, 114.76, 44.03, 34.65, 24.76, 18.61.

2-Butyl-6-((3-chloro-1,4-dioxo-1,4-dihydronaphthalen-2-yl)oxy)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (**NPHQ**): K_2CO_3 (0.4 g, 2.9 mmol) was added to a solution of compound **2** (0.50 g, 2.9 mmol) in DMSO (20 mL) with stirring at 25 ℃ for 5 min, and then 2,3-dichloro-1,4-naphthoquinone (0.59 g, 2.6 mmol) was added to the mixture. After stirring for 12 h at 25 ℃, the mixture was poured into ice water, extracted with EtOAc (30 mL×3), and washed with saturated brine (60 mL). The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The crude product was further purified by silica gel column chromatography with CH_2Cl_2/MeOH (*V*/*V*=10/1) to obtain **NPHQ** as yellow solid (0.45 g, yield 53%). m.p. 226.2～228.1 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 8.69 (dd, *J*=8.3, 0.9 Hz, 1H), 8.61 (dd, *J*=7.3, 1.0 Hz, 1H), 8.35 (d, *J*=8.2 Hz, 1H), 8.18 (dd, *J*=7.7, 1.1 Hz, 1H), 8.03～7.94 (m, 3H), 7.93 (dd, *J*=7.5, 1.3 Hz, 1H), 7.60 (d, *J*=8.2 Hz, 1H), 4.24～3.91 (m, 2H), 1.72～1.56 (m, 2H), 1.36 (dd, *J*=15.0, 7.4 Hz, 2H), 0.93 (t, *J*=7.4 Hz, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 177.78, 163.89, 163.19, 157.11, 152.53, 135.31, 135.08, 132.49, 132.05, 131.01, 129.33, 128.36, 128.08, 127.29, 127.07, 122.84, 122.68, 118.05, 111.66, 30.14, 20.26, 14.21; HRMS (ESI$^+$) calcd for $C_{26}H_{19}ClNO_5$ [M+H]$^+$ 460.0952, found 460.0956.

4.3 Preparation of stock solutions

Stock solution of **NPHQ** (1 mmol/L) was prepared in DMSO medium. H_2S was achieved from sodium hydrosulfide (NaHS). The stock solution of NaHS (10 mmol/L) was prepared by dissolving it in ultrapure water. The other stock solutions of interfering species (Mn^{2+}, Al^{3+}, Sn^{4+}, K^+, Cr^{3+}, Ca^{2+}, Zn^{2+}, Na^+, Ba^{2+}, Ce^{3+}, Mg^{2+}, I^-, $S_2O_5^{2-}$, HCO_3^-, MnO_4^-, HSO_3^-, SO_4^{2-}, $Cr_2O_7^{2-}$, $H_2PO_4^-$, CO_3^{2-}, Br^-, ClO_3^-, NO_2^-, ClO^-, H_2O_2, GSH, Cys, Hcy, DTT and βME) (10 mmol/L) were prepared by dissolving corresponding compounds in ultrapure water. The corresponding solutions with different concentration were obtained by diluting stock solution in a certain proportion.

4.4 Determination of LOD

The LOD was calculated according to the formula

LOD＝3σ/k. In this formula, σ was the standard deviation of the blank which was obtained through 11 times tests of the probe in solution, and k was the slope of the intensity versus sample concentration. The coefficient was 3 according to the compendium of analytical nomenclature standard.

4.5 Preparation of test strips

The filter paper was cut into test strips (3 cm×1 cm), and then the test strips were placed into the prepared solution of **NPHQ** (1 mmol/L). Noticed that each test strips contained the same number of **NPHQ**.

Supporting Information The NMR and HRMS spectra of compounds **1**, **2** and **NPHQ**. Fluorescence intensity changes of **NPHQ** at 542 nm with the addition of H_2S (100 μmol/L) as time elapses. The pH-dependent (pH＝1～14) fluorescence intensities of **NPHQ** (10 mmol/L) in DMSO/H_2O (V/V＝1/9) in absence and presence of H_2S. The absorption and fluorescence spectra of compound **2** and the product of **NPHQ** reaction with H_2S. The fluorescence spectra of compound **2** and the solution of **NPHQ** reaction with H_2S. Test strips for the detection of other gases with the concentration of 607 mg/m^3, and the pictures were taken after exposure to gases for 5 min. Comparison of fluorescent probes for detection of H_2S. The Supporting Information is available free of charge via the internet at http://sioc-journal.cn/.

References

[1] (a) Zhang, X.; Bian, J. S. *ACS Chem. Neurosci*. **2014**, *5*, 876.
(b) Chen, C. Q.; Xin, H.; Zhu, Y. Z. *Acta Pharmacol. Sin.* **2007**, *28*, 1709.
(c) Panthi, S.; Manandhar, S.; Gautam, K. *Transl. Neurodegener.* **2018**, *7*, 1.
(d) Li, W.; Wang, L.; Yin, S.; Lai, H.; Yuan, L.; Zhang, X. *Chem. Sci*. **2020**, *11*, 7991.

[2] (a) Polhemus, D. J.; Lefer, D. J. *Circ. Res*. **2014**, *114*, 730.
(b) Yang, M.; Fan, J.; Du, J.; Peng, X. *Chem. Sci*. **2020**, *11*, 5127.

[3] Wu, L.; Wang, R. *Pharmacol. Rev*. **2005**, *57*, 585.

[4] Lamattina, L.; Garcia-Mata, C.; Graziano, M.; Pagnussat, G. *Annu. Rev. Plant Biol*. **2003**, *54*, 109.

[5] (a) Cirino, G.; Szabo, C.; Papapetropoulos, A. *Physiol. Rev.* **2023**, *103*, 31.
(b) Szabo, C. *Nat. Rev. Drug Discovery* **2007**, *6*, 917.

[6] Whiteman, M.; Winyard, P. G. *Expert. Rev. Clin. Pharmacol.* **2011**, *4*, 13.

[7] Li, Y.; Bai, J.; Yang, Y. H.; Hoshi, N.; Chen, D. B. *Antioxidants* **2020**, *9*. 1127.

[8] Kimura, H. *Antioxid. Redox Signaling* **2010**, *12*, 1111.

[9] Hu, X.; Chi, Q.; Wang, D.; Chi, X.; Teng, X.; Li, S. *Ecotoxicol. Environ. Saf.* **2018**, *164*, 201.

[10] Feliers, D.; Lee, H. J.; Kasinath, B. S. *Antioxid. Redox Signaling* **2016**, *25*, 720.

[11] Munaron, L.; Avanzato, D.; Moccia, F.; Mancardi, D. *Cell Calcium*. **2013**, *53*, 77.

[12] Roorda, M.; Miljkovic, J. L.; van Goor, H.; Henning, R. H.; Bouma, H. R. *Redox Biol*. **2021**, *43*, 101961.

[13] (a) Elrod, J. W.; Calvert, J. W.; Morrison, J.; Doeller, J. E.; Kraus, D. W.; Tao, L.; Jiao, X.; Scalia, R.; Kiss, L.; Szabo, C.; Kimura, H.; Chow, C. W.; Lefer, D. J. *Proc. Natl. Acad. Sci*. **2007**, *104*, 15560.
(b) Yang, G.; Wu, L.; Jiang, B.; Yang, W.; Qi, J.; Cao, K.; Meng, Q.; Mustafa, A. K.; Mu, W.; Zhang, S.; Snyder, S. H.; Wang, R. *Science* **2008**, *322*, 587.
(c) Linden, D. R. *Antioxid. Redox Signaling* **2014**, *20*, 818.
(d) Olson, K. R.; Donald, J. A. *Acta Histochem*. **2009**, *111*, 244.
(e) Bhatia, M.; Gaddam, R. R. *Antioxid. Redox Signaling* **2021**, *34*, 1368.
(f) Dilek, N.; Papapetropoulos, A.; Toli-ver-Kinsky, T.; Szabo, C. *Pharmacol. Res.* **2020**, *161*, 105119.

[14] Petruci, J. F.; Fortes, P. R.; Kokoric, V.; Wilk, A.; Raimundo, I. M. Jr.; Cardoso, A. A.; Mizaikoff, B. *Analyst* **2014**, *139*, 198.

[15] Choi, M. G.; Cha, S.; Lee, H.; Jeon, H. L.; Chang, S. K. *Chem. Commun.* **2009**, *47*, 7390.

[16] (a) Hammers, M. D.; Taormina, M. J.; Cerda, M. M.; Montoya, L. A.; Seidenkranz, D. T.; Parthasarathy, R.; Pluth, M. D. *J. Am. Chem. Soc*. **2015**, *137*, 10216.
(b) Lv, J.; Wang, F.; Qiang, J.; Ren, X.; Chen, Y.; Zhang, Z.; Wang, Y.; Zhang, W.; Chen, X. *Biosens. Bioelectron.* **2017**, *87*, 96.
(c) Jin, X.; Wu, S.; She, M.; Jia, Y.; Hao, L.; Yin, B.; Wang, L.; Obst, M.; Shen, Y.; Zhang, Y.; Li, J. *Anal. Chem*. **2016**, *88*, 11253.
(d) Wang, H.; Yang, D.; Tan, R.; Zhou, Z. J.; Xu, R.; Zhang, J. F.; Zhou, Y. *Sens. Actuators*, *B* **2017**, *247*, 883.

[17] Raymond, D. M.; Nilsson, B. L. *Chem. Soc. Rev*. **2018**, *47*, 3659.

[18] Gun, J.; Modestov, A. D.; Kamyshny, A.; Ryzkov, D.; Gitis, V.; Goifman, A.; Lev, O.; Hultsch, V.; Grischek, T.; Worch, E. *Microchim. Acta* **2004**, *146*, 229.

[19] (a) Wang, R.; Gu, X.; Li, Q.; Gao, J.; Shi, B.; Xu, G.; Zhu, T.; Tian, H.; Zhao, C. *J. Am. Chem. Soc.* **2020**, *142*, 15084.
(b) Qian, Y.; Karpus, J.; Kabil, O.; Zhang, S. Y.; Zhu, H. L.; Banerjee, R.; Zhao, J.; He, C. *Nat. Commun*. **2011**, *2*, 495.

[20] (a) Chen, Z.; Mu, X.; Han, Z.; Yang, S.; Zhang, C.; Guo, Z.; Bai, Y.; He, W. *J. Am. Chem. Soc.* **2019**, *141*, 17973.
(b) Ge, C.; Di, X.; Han, S.; Wang, M.; Qian, X.; Su, Z.; Liu, H. K.; Qian, Y. *Chem. Commun.* **2021**, *57*, 1931.
(c) Teng, Y.; Yang, H.; Li, X.; Wang, Y. C.; Yin, D. L.; Tian, Y. L. *Chin. J. Chem.* **2022**, *40*, 209.

[21] Wan, Q.; Song, Y.; Li, Z.; Gao, X.; Ma, H. *Chem. Commun.* **2013**, *49*, 502.

[22] (a) Xuan, W.; Pan, R.; Cao, Y.; Liu, K.; Wang, W. *Chem. Commun.* **2012**, *48*, 10669.
(b) Liu, C.; Pan, J.; Li, S.; Zhao, Y.; Wu, L. Y.; Berkman, C. E.; Whorton, A. R.; Xian, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 10327.

[23] (a) An, Y.; Wang, P.; Yue, Z. *Spectrochim. Acta*, *Part A* **2019**, *216*, 319.
(b) Sun, M.; Yu, H.; Li, H.; Xu, H.; Huang, D.; Wang, S. *Inorg. Chem*. **2015**, *54*, 3766.

[24] (a) Ren, X.; Wang, F.; Lv, J.; Wei, T.; Zhang, W.; Wang, Y.; Chen, X. *Dyes Pigm.* **2016**, *129*, 156.
(b) Li, X.; Wang, A.; Wang, J.; Lu, J. *Anal. Chem*. **2019**, *91*, 15703.
(c) Hu, Y.; Chen, Z. H.; Ma, L. L.; Zhang, Z. Y.; Zhang, H.; Yi, F. P.; Liu, C. X. *Tetrahedron* **2022**, *117*, 132837.

[25] Peng, B.; Zhang, C.; Marutani, E.; Pacheco, A.; Chen, W.; Ichinose, F.; Xian, M. *Org. Lett*. **2015**, *17*, 1541.

[26] Hong, J.; Feng, W.; Feng, G. *Sens. Actuators*, *B* **2018**, *262*, 837.

[27] (a) Kaushik, R.; Ghosh, A.; Singh, A.; Jose, D. A. *Anal. Chim. Acta* **2018**, *1040*, 177.
(b) Han, H. H.; Tian, H.; Zang, Y.; Sedgwick, A. C.; Li, J.; Sessler, J. L.; He, X. P.; James, T. D. *Chem. Soc. Rev*. **2021**, *50*, 9391.

[28] (a) Geraghty, C.; Wynne, C.; Elmes, R. B. P. *Coord. Chem. Rev.* **2021**, *437*, 213713.
(b) Zhou, W.; Liang, Q. X.; Wu, A. B.; Su, W. M.; Yu, W. C. *J. Appl. Polym. Sci.* **2023**, *140*, https://doi.org/10.1002/app.53727.
(c) Zhou, W.; Chen, Q.; Wu, A. B.; Zhang, Y.; Yu, W. C. *J. Chin. Chem. Soc.* **2020**, *67*, 1213.
(d) Shi, C. T.; Luo, J.; Wang, Y. C.; Ding, L.; Liang, Q.; Yang, Z.; Lu, J.; Wu, A. B. *Spectrochim. Acta*, *Part A* **2023**, *289*, 122245.
(e) Shi, C. T.; Yu, M.; Wu, A. B.; Luo, J. X.; Li, X. J.; Wang, N. C.; Shu, W. M.; Yu, W. C. *Chin. J. Org. Chem.* **2022**, *42*, 2806 (in Chinese).
(师春甜，余美，吴爱斌，罗江雄，黎小军，王宁晨，舒文明，余

维初, 有机化学, **2022**, *42*, 2806.)
(f) Shi, C. T.; Huang, Z. Y.; Wu, A. B.; Hu Y. X.; Wang, N. C., Zhang, Y.; Shu, W. M.; Yu, W. C. *RSC Adv.* **2021**, *11*, 29632.
(g) Ren, J. B.; Wang, L.; Guo, R.; Tang, Y. H.; Zhou, H. M.; Lin, W. Y. *Acta Chim. Sinica* **2021**, *79*, 87 (in Chinese).
(任江波, 王蕾, 郭锐, 唐永和, 周红梅, 林伟英, 化学学报, **2021**, *79*, 87.)

[29] (a) Lee, M. H.; Kim, J. S.; Sessler, J. L. *Chem. Soc. Rev*. **2015**, *44*, 4185.
(b) Goswami, S.; Sen, D.; Das, N. K. *Org. Lett*. **2010**, *12*, 856.

[30] Yang, L. L.; Tang, A. L.; Wang, P. Y.; Yang, S. *Org. Lett*. **2020**, *22*, 8234.

[31] (a) Ma, T.; Huo F.; Wen Y.; Glass T. E.; Yin C. *Spectrochim. Acta*, *Part A* **2019**, *214*, 355.
(b) Zhang, J.; Mu, S.; Wang, Y.; Li, S.; Shi, X.; Liu, X.; Zhang, H. *Anal. Chim*. *Acta* **2022**, *1195*, 339457.
(c) Ou, L.; Guo, R.; Lin, W. *Anal. Methods* **2021**, *13*, 1511.
(d) Zhang, C.; Zhang, L.; Li, Y.; Ren, Z.; Li, L.; Zhang, Y.; Li, Y.; Liu, C. *J. Mol. Struct*. **2022**, *1250*, 131777.
(e) Guo, M. Y.; Wang, W.; Ainiwaer, D.; Yang, Y. S.; Wang, B. Z.; Yang, J.; Zhu, H. L. *Talanta* **2022**, *237*, 122960.
(f) Du, Y.; Wang, H.; Zhang, T.; Wen, W.; Li, Z.; Bi, M.; Liu, J. *Spectrochim. Acta*, *Part A* **2022**, *265*, 120390.

[32] Choi, M. G.; Kim, N. Y.; Lee, Y. J.; Ahn, S.; Chang, S. K. *Chem. Commun.* **2019**, *55*, 11398.

[33] Shi, J.; Wang, Y.; Tang, X.; Liu, W.; Jiang, H.; Dou, W.; Liu, W. *Dyes Pigm.* **2014**, *100*, 255.

(Lu, Y.)

