Dyes and Pigments 123 (2015) 78–84

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

A colorimetric and ratiometric fluorescent probe with a large stokes shift for detection of hydrogen sulfide

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A R T I C L E I N F O

Article history:
Received 3 May 2015
Received in revised form
19 June 2015
Accepted 22 June 2015
Available online 18 July 2015

Keywords:
Fluorescence probe
Hydrogen sulfide
Stokes shift
Isophorone
Ratiometric detection
Selectivity

A B S T R A C T

Developing probes for selective and sensitive detection of hydrogen sulfide (H_2S) has received much research attention, because H_2S is an environmental toxin as well as an important signaling molecule to regulate physiological and pathological processes. In this work, a new colorimetric and ratiometric fluorescent probe (Probe 1) for H_2S detection was synthesized by employing dicyanoisophorone based fluorescence dye as a fluorophore and azide group as the response unit. The synthesized Probe 1 showed a long emission wavelength (λ_{em} = 643 nm) and large stokes shift ($\lambda_{em} - \lambda_{abs}$ = 163 nm). Based on the H_2S-induced reduction of azide group to amino group, Probe 1 showed high response speed, sensitivity, and selectivity toward HS^- under room temperature. Moreover, Probe 1 can ratiometrically respond to HS^- and the detection limit is as low as 0.13 μM. It was proved that Probe 1 is suitable for quantitatively detecting HS^- ions in river water samples. The numerous advantages of Probe 1 make it be potentially used for quantitative detection of H_2S in environment and living organisms.

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1. Introduction

As a member of the reactive sulfur species family, hydrogen sulfide (H_2S) has drawn much attention due to its effects on environmental toxins and poisons for centuries [1]. Usually, it is largely generated in coal and natural gas processing, petroleum industries, biogas production, automobile tail gas, and sewage treatment plants [2,3]. It can damage the human nerve and respiratory systems, causing people to lose consciousness or even die at very low concentrations (ppm levels) [4]. However, in biological systems, H_2S is usually produced from L-cysteine in reactions catalyzed by enzymes such as cystathionine β-synthase (CBS), cystathionine γ-lyase (CSE), and 3-mercaptopyruvate sulfur transferase (3MST), as well as from nonenzymatic processes [5]. Following nitric oxide (NO) and carbon monoxide (CO), H_2S has been considered to be the third gasotransmitter to regulate cardiovascular, neurona, immune, endocrine, and gastro-intestinal systems [6–8]. Many studies have shown that H_2S takes part in many physiological processes, such as angiogenesis [9], vasodilation [10], apoptosis [11], regulation of inflammation [12], and neuromodulation [13]. In addition, it also has been proved that abnormal H_2S production is linked to human diseases such as Alzheimer's disease [14], Down's syndrome [15], hypertension [10], and liver cirrhosis [16]. Therefore, the quantitative detection of H_2S is of great significance for both environmental and biological systems [17].

Considerable efforts have been devoted to exploring the effective strategies to measure H_2S [18]. Among these available methods, fluorescent imaging is considered to be one of the most promising approaches because of its sensitivity and simplicity [19,20]. So far, fluorescence probes for detection of H_2S are mainly based on three types of reactions [17]: (1) H_2S reductive reactions: reducing azides to amines, reducing nitro/azanol to amines, and reducing selenoxide to selenide [21–28]; (2) H_2S nucleophilic reactions: Michael addition reactions, dual nucleophilic reactions, double bond addition reactions, and thiolysis reactions [29–33]; (3) copper sulfide precipitation reaction [34–36].

Recently, colorimetric and ratiometric fluorescent probes have received extensive research attention, owing to their unique advantages such as low cost, simply pretreatment and naked-eye mode in a high-throughput fashion [37–42]. However, most H_2S

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http://dx.doi.org/10.1016/j.dyepig.2015.06.037
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probes still have the drawbacks of the single detection window and short excitation wavelengths [17]. So it is desirable to design some H_2S probes with double detection window and red/or NIR emission [43–47].

Dicyanoisophorone based fluorescent dyes are famous for their excellent properties in dye-sensitized solar cells [48,49] and organic nonlinear optical crystals [50,51] due to their typical donor-π-acceptor (D-π-A) structure, longer emission wavelength in the NIR region, and large Stokes shift from the ultrafast intramolecular charge transfer (ICT) [52]. However, to the best of our knowledge, dicyanoisophorone based fluorescent dyes have rarely been employed as fluorescence probes. Here, we designed a novel H_2S fluorescence probe (Probe 1) with double detection window and red emission by employing dicyanoisophorone based fluorescent dye as the fluorophore and azide group as the response unit (Scheme 1). As expected, H_2S can react with the azide group of Probe 1 and release the amino group. Probe 1 displayed high sensitivity and selectivity toward H_2S in red region.

2. Experimental

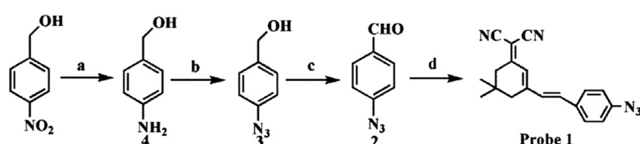
2.1. Synthesis

2.1.1. Synthesis of compound 4

4-Nitrobenzyl alcohol (3.80 g, 24.8 mmol) was dissolved in EtOH (30.0 mL), followed by addition of $FeCl_3$ (0.1 g) and activated carbon (0.5 g). After refluxed for 2 h, hydrazine hydrate (5.0 g, 100 mmol) was added dropwise to the above mixture at the same temperature. After being stirred for another 3 h, the mixture was filtered and the filter liquor was concentrated under vacuum. The obtained precipitation was purified by silica column chromatography using petroleum/ethyl acetate (2:1, v/v) to give a white solid (2.75 g, 90%). ^{1}H NMR (400 MHz, DMSO): δ = 6.95 (d, J = 8 Hz, 2H), 6.50 (d, J = 8 Hz, 2H), 4.92 (s, 2H), 4.79 (t, J = 8 Hz, 1H), 4.28 (d, J = 8 Hz, 2H) (Fig. S1). ^{13}C NMR (100 MHz, DMSO): δ = 145.97, 131.13, 128.78, 115.20, 65.16 (Fig. S2).

2.1.2. Synthesis of compound 3

2.15 g (17.5 mmol) of 4-aminobenzyl alcohol was added to 20 mL of 10% HCl aqueous solution at 0 °C, followed by addition of 1.45 g (21.0 mmol, 1.2 equiv) sodium nitrite dissolved in dry 10 mL CH_2Cl_2. After the mixture was stirred at 0 °C for 1 h, 4 mL of sodium azide (1.88 g, 28.9 mmol) aqueous solution was added drop-wise and stirred overnight. Then, the mixture was quenched with brine and extracted with ethyl acetate (100 mL × 3). The combined organic layer was dried over anhydrous sodium sulfate and concentrated in vacuum. Finally, the crude product was purified by flash chromatography (petroleum/ethyl acetate = 4:1) to give a yellow oil (2.21 g, 85%). ^{1}H NMR (400 MHz, DMSO): δ = 6.95 (d, J = 8 Hz, 2H), 6.50 (d, J = 8 Hz, 2H), 4.92 (s, 2H), 4.79 (t, J = 8 Hz, 1H), 4.28 (d, J = 8 Hz, 2H) (Fig. S3). ^{13}C NMR (100 MHz, DMSO): δ = 145.97, 131.13, 128.78, 115.20, 65.16 (Fig. S4)



Reagent and conditions: (a) hydrazine hydrate, $FeCl_3$, activated carbon, EtOH, 5 h, 90%. (b) sodium nitrite, sulfuric acid, then sodium azide, H_2O, 12 h, 85%. (c) pyridinium dichromate, CH_2Cl_2, 4 h, 83%. (d) piperidine, acetonitrile, 3 h, 48%.

Scheme 1. Synthetic route of Probe 1.

2.1.3. Synthesis of compound 2

Compound 3 (2.0 g, 13.4 mmol) was dissolved in CH_2Cl_2 (100 mL), followed by addition of pyridinium dichromate (6.06 g, 16.1 mmol). After the mixture solution was stirred at room temperature for 4 h, the reaction solution was filtered through 130 g of silica and the silica was washed with 1.5 L of CH_2Cl_2. Then, the filter solution was concentrated under vacuum and the crude product was purified by silica column chromatography using petroleum/ethyl acetate (5:1, v/v) to obtain a pale yellow oil (1.63 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.94 (s, 1H), 7.88 (d, J = 8 Hz, 2H), 7.15 (d, J = 12 Hz, 2H) (Fig. S5). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.58, 146.23, 133.21, 131.52, 119.46 (Fig. S6).

2.1.4. Synthesis of probe 1

Compound 2 (100 mg, 0.68 mmol), 2-(3,5,5-trimethyl-2-cyclohexen-1-ylidene)-Propanedinitrile (126 mg, 0.68 mmol), and piperidine (5 drops) were in sequence dissolved in acetonitrile (20 mL) and refluxed under N_2 for 3 h. Then, the mixture solution was concentrated under vacuum and the crude product was purified by silica column chromatography using petroleum/ethyl acetate (4:1, v/v) to give a yellow solid (102 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, J = 12 Hz, 2H), 7.05 (d, J = 8 Hz, 2H), 6.95 (t, J = 8 Hz, 2H), 6.84 (s, 1H), 2.60 (s, 2H), 2.46 (s, 2H), 1.08 (s, 6H) (Fig. S7). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.20, 153.68, 141.33, 132.53, 128.80, 123.61, 119.67, 113.51, 112.75, 78.69, 42.98, 39.19, 32.04, 28.03 (Fig. S8). HRMS (ESI): calcd. For $[C_{19}H_{17}N_5 + H]^+$ 314.1406; found 314.1404 (Fig. S9).

2.2. Characterization

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM400 NMR spectrometer with TMS as internal standard. HRMS was conducted on a Waters LCT Premier XE spectrometer. Absorption spectra were measured with a SHIMADZU UV-2450 spectrophotometer at room temperature. The fluorescence spectra were obtained on a SHIMADZU RF-5301PC fluorescence spectrophotometer by using 480 nm line of Xe lamp as excitation source at room temperature. HPLC analyses were performed on an InertSustain C18 column (5 μm, 4.6 mm × 250 mm) using a Shimadzu HPLC system that consists of two LC-20AD pumps and an SPD-M20A UV–vis detector at 450 nm with methanol (flow rate, 0.8 mL/min) and water (flow rate, 0.2 mL/min) as eluents.

2.3. Measurements of HS^- in river water samples

Two water samples were collected from Qing-Chun River of East China University of Science & Technology and Huang-Pu River of Shanghai, respectively. Before use, the water samples were filtered and the pH was adjusted with a PBS buffer (20 mM, pH 7.4). Then, the two samples were spiked with different concentrations of HS^- (5, 10, 20 μM). Prior to detection, they were further treated with Probe 1 to give the final mixtures (3.0 mL) containing Probe 1 (10 μM) and HS^- (5, 10, 20 μM). The fluorescence emission signals at 643 nm and 562 nm were measured with a SHIMADZU UV-2450 spectrophotometer.

3. Result and discussion

3.1. Synthesis route

The synthetic route of Probe 1 was illustrated in Scheme 1. Firstly, compound 4 was synthesized by reducing 4-nitrobenzyl alcohol in EtOH. Then, compounds 3 and 2 were obtained by diazotization and Sarrett oxidation, respectively. Finally, Probe 1 was prepared by the Knoevenagel condensation reaction in

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