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A colorimetric and ratiometric fluorescence probe for rapid detection of SO_2 derivatives bisulfite and sulfite

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ABSTRACT

As one of the main atmospheric pollutants, sulfur dioxide (SO_2) can be easily inhaled and turned into sulfite and bisulfite, which is harmful to both human health and ecological environment. Therefore, it is of significance to develop an effective method to detect the trace SO_2 derivatives—SO_3^{2-} and HSO_3^-. Herein, we synthesized a semi-cyanine-coumarin hybrid dye for detection of SO_3^{2-} and HSO_3^-. Based on the nucleophilic addition of HSO_3^-/SO_3^{2-} to the vinyl group, Probe 1 showed high response speed, selectivity, and sensitivity towards SO_3^{2-} and HSO_3^-. Upon addition of HSO_3^-/SO_3^{2-}, color obviously changes from blue to yellow which can be differentiated by naked eyes. Probe 1 displays colorimetric and ratiometric response toward HSO_3^- and SO_3^{2-}. The detection limit is as low as 27.6 nM and the signal-to-background ratio in fluorescence intensity can reach 35-folds. Moreover, Probe 1 showed high selectivity and anti-interference ability in the co-existence of the environmental and biologic species.

1. Introduction

As one of the main atmospheric pollutants, sulfur dioxide (SO_2) can be easily inhaled and turned into sulfite and bisulfite, which is harmful to human health, cause acid rain, damage aquatic and terrestrial ecosystems [1–7]. In an aqueous environment, SO_2 usually exists in the form of its derivatives—sulfite (SO_3^{2-}) and bisulfite (HSO_3^-), which usually stand for the activity or toxicity of SO_2 in solution [8]. Epidemiological studies have proved that long term SO_2 exposure or drinking the water containing its derivatives can induce some respiratory illnesses [9], lung cancer, cardiovascular diseases [10], and neurological disorders (migraine headaches, stroke and brain cancer) [11]. Toxicological studies further confirmed that the characteristics of voltage-gated sodium channels and potassium channels in rat hippocampal neurons could be influenced by SO_2 and its derivatives [12]. In addition, SO_2 and its derivatives could also affect thiol levels and redox balance in cells [13], which produce a neuronal insult [14]. Therefore, it is of significance to develop an effective method for detection of trace SO_2 derivatives [15–20].

Due to the advantages of non-invasiveness, high sensitivity, real-time spatial imaging, and ease of operation, fluorescent probes have become powerful tools for visualizing anions in environmental and biological systems [21,22]. So far, the fluorescence probes for detection of SO_2 derivatives are mainly based on nucleophilic reaction with aldehyde [23,24], SO_3^{2-}-mediated levulinate cleavage [25,26], Michael-type additions [27,28], and coordinative interactions [29]. Despite their utility, most of these fluorescent probes are still suffered from low selectivity in the presence of biothiols (Cys or Hcy), unsatisfactory detection limit and low response speed [25,30,31]. Moreover, some fluorescence probes are based on turn-on/turn-off response, which could influence their quantitative detection because of environmental effects [24,25,30]. Recently, ratiometric fluorescent probes for detection of SO_2 derivatives based on coumarin-hemicyanine dyes have received much research attention [15,32–34]. For instance, Hu et al. reported a twisted intramolecular charge transfer probe, which showed high response speed (less than 250 S) and low detection limit (3 nM) for detection of biological SO_2 derivatives [15]. Yu et al. explored a TCF-based probe with a very low detection limit

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(0.27 nM) for detection of SO_2 derivatives [33]. Yu et al. designed a mitochondria-targeted fluorescent probe for detecting the biological SO_2 derivatives, which showed high signal-to-background ratio, fast response time (less than 60 S), and low detection limit (0.15 μM) [34]. Therefore, it is of great theoretic and realistic significances to develop a new ratiometric fluorescence probe with high sensitivity, rapidly responsive speed, and high selectivity for sensing SO_2 derivatives.

It has been reported that HSO_3^- or SO_3^{2-} could be rapidly and quantitatively added to a,b-unsaturated compounds in aqueous solution [35]. Enlightened by this addition reaction, we hope that this reaction could be served as the foundation to design a novel fluorescence probe. Herein, we focused our attention on semicyanine-coumarin hybrid dyes because these dyes have typical donor-π-acceptor (D-π-A) structure, longer emission wavelength in the red (or NIR) region, and large Stokes shift from the ultrafast intramolecular charge transfer (ICT) [36–43]. In addition, this type of dyes is difficult to be inactivated in the presence of biothiols compared with other common Michael receptors [44]. Therefore, with all these considerations in mind, we designed a novel fluorescence probe (Probe 1) for detection of HSO_3^- or SO_3^{2-} on the basis of nucleophilic addition reaction, i.e., incorporating an electron-withdrawing unit of 1H-benzo[e]indolium through a vinylene bridge to the coumarin core. We hoped that HSO_3^- or SO_3^{2-} could break π-conjugation of coumarin-hemicyanine dyes in aqueous solution and thus block the ICT process. As a consequence, the two distinct emission peaks could be obtained after adding HSO_3^- or SO_3^{2-}. Fortunately, the experiment results indicated that the synthesized fluorescence probe showed high sensitivity, selectivity and response speed for the ratiometric detection of HSO_3^- or SO_3^{2-}.

2. Experimental

2.1. Synthesis

2.1.1. Synthesis of Compound 4

4-diethylamino salicyldehyde (5.79 g, 30 mmol) was dissolved in EtOH (30.0 mL), followed by addition of diethylmalonate (9.6 mL, 60 mmol) and piperidine (1 mL). After the mixture was refluxed for 12 h, the solvent was concentrated under vacuum, extracted with CH_2Cl_2, and washed with brine. Finally, the crude product was purified by column chromatography using Petroleum/Ethyl acetate (1:1, v/v) to give a yellow solid (6.53 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (s, 1H), 7.36 (d, J = 8 Hz, 1H), 6.60 (dd, J = 4 Hz, 1H), 6.45 (d, J = 4 Hz, 1H), 4.36 (m, J = 8 Hz, 2H), 3.45 (m, J = 8 Hz, 4H), 1.39 (t, J = 8 Hz, 3H), 1.23 (t, J = 8 Hz, 6H) (Fig. S1). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.24, 158.32, 152.86, 149.19, 131.03, 108.89, 107.65, 96.67, 61.12, 45.09, 14.38, 12.41 (Fig. S2).

2.1.2. Synthesis of Compound 3

Compound 4 (2.9 g, 10 mmol) was dissolved in 60 mL of 18% hydrochloric acid solution and refluxed for 8 h. After the mixture was cooled to room temperature, the pH value of the mixture was adjusted to 4.5 with 45% sodium hydroxide solution. The obtained yellow precipitate was filtrated, dried in vacuum, and purified by column chromatography to give Compound 3 (1.5 g, 68.7%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, J = 12 Hz, 1H), 7.25 (d, J = 8 Hz, 1H), 6.67 (dd, J = 4 Hz, 1H), 6.48 (d, J = 4 Hz, 1H), 6.04 (d, J = 8 Hz, 1H), 3.42 (m, J = 8 Hz, 4H), 1.21 (t, J = 8 Hz, 6H) (Fig. S3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.31, 156.73, 150.68, 143.74, 128.78, 109.11, 108.66, 108.25, 97.48, 44.78, 12.43 (Fig. S4).

2.1.3. Synthesis of Compound 2

$POCl_3$ (5 mL) was added dropwise to dry DMF (5 mL) at 0 °C. The mixture was stirred at 0 °C and room temperature for 30 min, respectively. Then, Compound 3 (1 g, 4.6 mmol) dissolved in DMF (3 mL) was added dropwise to the above solution. After the mixture was stirred at 60 °C for 3 h, it was poured into ice water. Finally, the precipitate was filtered, thoroughly washed with water, and dried in vacuum to obtain an orange solid (720 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.11 (S, 1H), 8.24 (S, 1H), 7.42 (d, J = 8 Hz, 1H), 6.66 (dd, J = 4 Hz, 1H), 6.48 (d, J = 4 Hz, 1H), 6.04 (d, J = 8 Hz, 1H), 3.49 (m, J = 8 Hz, 4H), 1.26 (t, J = 8 Hz, 6H) (Fig. S5). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.87, 161.87, 158.90, 153.50, 145.40, 132.53, 114.15, 110.24, 108.19, 97.08, 45.28, 12.44 (Fig. S6).

2.1.4. Synthesis of probe 1

Compound 2 (100 mg, 0.41 mmol), 1H-benzo[e]indolium (150 mg, 0.41 mmol) and NH_4OAc (77 mg, 1 mmol) were added to EtOH (10 mL). Then, the mixture was refluxed for 3 h to give a blue precipitate. Finally, the crude product was filtered, thoroughly washed with EtOH, and further dried in vacuum to attain a blue solid (105 mg, 42%), denoted as Probe 1. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.08 (s, 1H), 8.70 (d, J = 16 Hz, 1H), 8.24 (d, J = 8 Hz, 1H), 8.12 (t, J = 8 Hz, 2H), 8.06 (dd, J = 12 Hz, 2H), 7.74 (t, J = 8 Hz, 1H), 7.68 (t, J = 12 Hz, 1H), 7.64 (t, J = 8 Hz, 1H), 6.68 (dd, J = 8 Hz, 1H), 6.45 (d, J = 4 Hz, 1H), 4.94 (m, J = 8 Hz, 2H), 3.51 (m, J = 8 Hz, 4H), 2.13 (s, 6H), 1.68 (t, J = 8 Hz, 3H), 1.28 (t, J = 8 Hz, 6H). (Fig. S7). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 181.32, 161.13, 158.64, 154.40, 149.74, 138.09, 137.72, 131.55, 130.32, 128.52, 127.58, 127.08, 122.72, 112.55, 111.49, 110.93, 110.91, 108.26, 96.74, 53.43, 45.61, 43.08, 27.43, 14.28, 12.63 (Fig. S8). HRMS (ESI): calcd. For $[C_{31}H_{33}O_2N_2I\text{-}I]^+$ 465.2542; found 465.2542 (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 490 nm line of Xe lamp as excitation source at room temperature.

3. Result and discussion

3.1. Synthesis route

The synthetic route of Probe 1 is illustrated in Scheme 1. Firstly, Compound 4 was synthesized by the condensation reaction between 4-diethylamino salicyldehyde and diethylmalonate. Then, Compound 3 and Compound 2 were obtained by the decarboxylation and Vilsmeier-Haack reaction. Finally, Probe 1 was obtained by the condensation reaction in EtOH. The structures of Compound 4, Compound 3, and Compound 2, and Probe 1 were confirmed by NMR and HRMS spectroscopy (Supporting information, Figs. S1–S9).

3.2. Absorption and fluorescence spectra

Fig. 1 shows the time dependent absorption and fluorescence emission spectra of Probe 1 after adding HSO_3^- in DMF/PBS buffer solution (50/50, v/v, pH = 7.4, 20 mM). In absence of HSO_3^-, Probe 1 (10 μM) displays a strong absorption band at 588 nm, together with a low and broad band in the range of 350–470 nm (Fig. 1A). The former should be attributed to the conjugated D-π-A structure of Probe 1 (coumarin core: electron donor; 1H-benzo[e]indolium: electron acceptor), while the later should result from both benzo[e] indolium and coumarin structures. The fluorescence emission