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A simple pyrene-pyridinium-based fluorescent probe for colorimetric and ratiometric sensing of sulfite

Guanshu Xu, Huan Wu, Xingang Liu, Ruokun Feng, Zhanxiang Liu*

Department of Chemistry, Zhejiang University, Campus Xixi, Hangzhou 310007, PR China

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ABSTRACT

The fluorescent probe is constructed by incorporating an α, β-unsaturated pyridinium to a pyrene fluorophore. The chemodosimeter has shown a selective and sensitive response to sulfite anion over other various anions and biological thiol through a Michael addition of the sulfite to the alkene of the probe. Meanwhile, it can be easily observed that the color of the probe for sulfite changes from yellow to colorless by the naked eye, and from yellow to blue under UV lamp immediately after the sulfite is added.

1. Introduction

In the food industry, sulfite is commonly used as preservatives, anti-oxidants, bacteriostasis agents for food and beverages to prevent oxidation and bacterial growth, and to control fruit and vegetable degradation caused by enzymatic or nonenzymatic reactions. Sulfite can also maintain the stability and potency of some medications during production and storage [1]. Meanwhile, sulfites are also exploited as the additives to the drug epinephrine in order to prevent its oxidation to adrenochrome and resulting inactivation [2]. However, a certain concentration level of sulfite may cause adverse reactions and acute symptoms in people who are hypersensitive to them, and result in difficulty breathing, wheezing, hives, and gastrointestinal distress [3,4]. In fact, there is evidence that some people may be extremely sensitive to sulfite even at very low levels [5], and that bronchoconstriction can occur in many asthmatic patients [6]. On the other hand, a significant amount of harmful sulfur dioxide (SO_2) gas can dissolve in water and then is transformed into sulfite when the pH of the solution becomes neutral [7–9]. Sulfite contaminated waste water can seriously deplete the amount of oxygen in water to levels which are unsustainable to aquatic life forms.

As a result, the presence of sulfite in the environment has aroused great concern and the use of sulfite in food stuffs and in waste water is strictly regulated in many countries. Recognition of these potential adverse effects has stimulated considerable interest in the development of methods to detect and quantify sulfite contaminants. Therefore, it is very important to develop efficient methods for the detection and quantization of sulfite for food safety and quality control, clinical and environmental applications.

As a consequence of the concerns enumerated above, various conventional methods based on electrochemistry [10], spectrophotometry [11], chromatography [12], phosphorimetry [13], capillary electrophoresis [14], chemiluminescence [15], flow injection analysis [16] and enzymatic techniques [17] have been extensively used for the detection and quantification of sulfites. However, conventional methods for sulfite analyses usually require troublesome sample pretreatment and are either time-consuming or require sophisticated instrumentation unsuitable for routine analysis. For this reason, more convenient sensing systems for sulfite, such as optical sensors, have attracted much research interest.

As an alternative, fluorescence sensing is appealing because of its high sensitivity, excellent selectivity, and simplicity. Furthermore, fluorescence sensing is potentially applicable for bioimaging in living cells and offers temporal and spatial resolution [18]. Up to now, several fluorescent probes for sulfites have been designed on the basis of the selective deprotection of a levulinate group [19],

* Corresponding author.
E-mail address: liuzhanx@zju.edu.cn (Z. Liu).

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complexation with amines [20], selective nucleophilic reaction with aldehyde [21] and Michael-type additions [22,23]. However, most of these fluorescent probes respond to sulfites with changes only in fluorescent intensity or need a long response time (5 min–10 h), which limits their application. By contrast, ratiometric fluorescent probes allow the measurement of emission intensities at two different wavelengths, which should provide a built-in correction for environmental effects and can also increase the dynamic range of fluorescence measurements [24,25]. Therefore, the design of novel fluorescent probes with colorimetric and ratiometric responses to sulfite attracts our attention. The goal of the work reported herein is to develop a new simple colorimetric and ratiometric probe for sulfite that would allow us to more easily and accurately detect and quantitate this anionic species. On the other hand, pyrene has been demonstrated as the most effective fluorophores for the design of fluorescent chemosensors which exhibits very strong blue fluorescence with a high quantum efficiency and their chemical stabilities [26]. Therefore, we designed and synthesized the probe (Scheme 1) as a novel ratiometric fluorescent sulfite probe based on a pyrene-pyridinium platform.

2. Experimental

2.1. Chemicals and apparatus

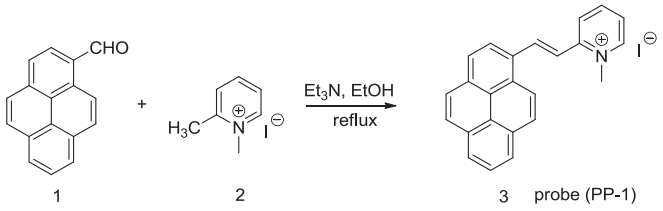
Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents were purified by standard methods. Twice-distilled water was used throughout all experiments. NMR spectra were recorded on a BRUKER 400 spectrometer, using TMS as an internal standard. All accurate mass spectrometric experiments were performed on a microTOF-Q II mass spectrometer (Bruker Daltonik, Germany). UV–Vis absorption spectra were measured using a Shimadzu UV-2450 spectrophotometer. Emission spectra were recorded at room temperature using a HITACHI F4600 fluorescence spectrophotometer with both the excitation and emission slit widths set at 5.0 nm. Column chromatography was conducted over silica gel (mesh 200–300), both of which were obtained from Qingdao Ocean Chemicals. The solutions of various testing species were prepared from Na_2SO_4, NaF, NaI, $Na_2S\cdot 9H_2O$, NaCl, NaBr, NaN_3, $NaNO_3$, $Na_2S_2O_3\cdot 5H_2O$, Na_2SO_3, CH_3COONa, NaSCN, Cys, in twice-distilled water.

2.2. Synthesis

The fluorescent probe for sensing sulfite was readily synthesized via a one step synthetic route. (Scheme 1). Pyrene-1-carbaldehyde **1** was first reacted with 1,2-dimethylpyridin-1-ium iodide **2** in anhydrous ethanol to afford the fluorescent probe *(E)*-*N*-methyl-2-(2-(pyren-1-yl)vinyl)pyridinium iodide (**PP-1**) **3** in 52% yield as shown in Scheme 1. The desired products were well characterized by standard NMR and mass spectrometry.

2.2.1. Synthesis of 2-methyl-N-methyl pyridinium iodide **2** [26b]

9.85 g (105.8 mmol) of 2-methylpyridine and 14.98 g (105.5 mmol) of iodomethane were dissolved in 20 mL of acetonitrile. The mixture was refluxed for 10 h. After cooling to room temperature, the mixture was concentrated under reduced pressure and then ethyl ether was added and stirred. The precipitate was filtered and washed twice with ethyl ether. 10.68 g of salts were resulted. The crude product was used directly without further purification.



Scheme 1. The preparation of the fluorescent probe (**PP-1**).

2.2.2. Synthesis of (E)-N-methyl-2-(2-(pyren-1-yl)vinyl)pyridinium iodide (**PP-1**) (**3**) [26].

0.30 g (1.3 mmol) pyrene-1-carbaldehyde and 0.24 g (1 mmol) 2-methyl-*N*-methyl pyridinium iodide were dissolved in 10 mL ethanol with three drops of triethyl amine. The mixture was refluxed for 12 h and then concentrated under reduced pressure. The precipitate was filtered and washed twice with ethyl ether. The crude product was chromatographed with dichloromethane/ethanol1and methanol. The pure product was obtained as an orange solid (0.23 g, 52%).

^{1}H NMR (DMSO-d^6, 400 MHz):δ: 9.06-9.02 (d, J = 16 Hz, 1H), 8.96-8.91 (m, 3H), 8.81-8.79 (d, 1H, J = 8 Hz), 8.60–8.56 (m, 1H), 8.45-8.39 (m, 4H), 8.33-8.27 (m, 2H), 8.17-8.14(m, 1h), 7.96 (m, 2H), 7.92-7.88 (d, J = 16 Hz, 1H), 4.49 (s, 3H); ^{13}C NMR (DMSO-d^6, 100 MHz) 152.70, 146.57, 144.68, 139.51, 133.01, 131.35, 130.73, 130.03, 129.39, 129.19, 127.87, 127.24, 126.85, 126.57, 126.12, 125.84, 125.69, 125.39, 124.57, 124.21, 123.52, 120.22, 46.65. HRMS (EI) *m/z* (%):320.1444 ([M–I]$^+$, 100). Anal. calcd for $C_{24}H_{18}N^+$ *m/z*: 320.1439.

3. Results and discussion

Subsequently, the sensing behavior of probe toward sulfite was investigated with absorption and fluorescence spectroscopy in phosphate buffer (pH 7.4, 30 mM, containing 30% ethanol as a cosolvent). As show in Fig. 1, the free probe **3** displays a strong absorption at around 390 nm. However, the introduction of increasing concentrations of sulfite to the solution of probe **3** (5×10^{-6} M) resulted in a gradual decrease of the absorption peak at 390 nm and a progressive increase of a new absorption band around 345 nm. After addition of 50 equiv. Na_2SO_3 to probe **3**, the color of the solution changed immediately from yellow to colorless under the visible light. Meanwhile, a well-defined isobesticpoint was observed at 351 nm, indicating the formation of a new species up on the mixture of probe **3** with sulfite.

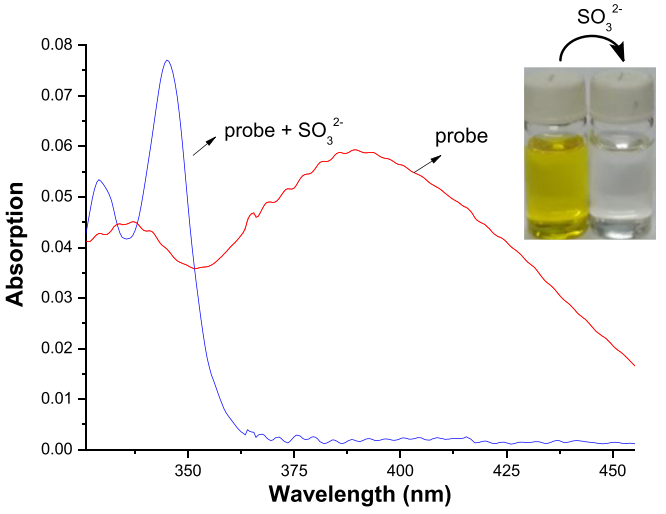


Fig. 1. Uv–vis spectral change in the presence of 50 equiv. of SO_3^{2-} to probe (5×10^{-6} M) in PBS (pH = 7.4, 30% EtOH, V:V). Insert: color change observed by the naked eye. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)