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Reaction-based fluorescent probe for detecting of sulfur dioxide derivatives and hydrazine *via* distinct emission signals

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ABSTRACT

Recently, the construction of multiple analytes responsive fluorescent probes with distinct emission signals has attracted widely attention. Thus, we have designed and synthesized a new fluorescent probe, 2-(2-hydroxyphenyl)benzothiazole dye skeleton (**HBT-1**), for the detection of sulfur dioxide and hydrazine. Significant fluorescence enhancements in two distinct emission bands (λ_{em} = 464 nm and 498 nm) were generated when **HBT-1** reacted with sulfur dioxide derivatives or hydrazine, respectively. Furthermore, the probe **HBT-1** response can be saturated surpurisingly at the low concentration (100 μM), shorter reaction time for sulfur dioxide derivatives, while a longer reaction time and greater concentration (400 μM) for hydrazine. In other words, the probe **HBT-1** can detect sulfur dioxide derivatives without hydrazine interference at low analyte concentrations.

Introduction

Sulfur dioxide derivatives (sulfite and bisulfite) and hydrazine are widely used as raw materials in various chemical industries. However, environment pollution was always caused by their use and disposal in the whole chemical industrial process. In general, sulfur dioxides is endogenously produced from sulfur-containing amino acids in bio-systems, and is recognized as a new gaseous transmitter on account of its particular function in many physiological processes [1]. Many types of diseases are associated with its abnormal levels [2]. Moreover, hydrazine also causes inreversible damages to cells, tissues and organs due to it is readily penetrated and absorbed by the body's mouth and skin [3]. Thus, considerable attention has been focused on the development of reliable and real-time analytical methods for the determination of sulfur dioxide derivatives and hydrazine.

In the past few years, the development of small-molecule fluorescent probes for detecting neutral and ionic species in the environment and bio-system has attracted increasing attention owing to their simplicity, low cost, high sensitivity as well as selectivity, and real-time detection [4]. So far, a large number of fluorescent probes have been developed for monitoring sulfur dioxide derivatives [5] or hydrazine [6], based on chemical reactions. These fluorescence probes have good selectivity and sensitivity in aqueous solution and bio-samples, but most of them are only capable of detecting a single analyte. Till today, the development of fluorescent probes with a distinct fluorescence response towards sulfur dioxide derivatives and hydrazine still remains challenging. Thus, it is necessary to construct multiple analytes responsive fluorescent probes with distinct emission signals.

2-(2-Hydroxyphenyl)benzothiazole was chosen as a fluorophore with excellent spectral properties, and extensively used in the design of fluorescent probes [7]. Here, we synthesized a novel fluorescent probe (**HBT-1**) for the detection of differential analytes, sulfur dioxide derivatives and hydrazine, based on the chemical reaction between the probe and analytes, as well as the different fluorescence signals of the corresponding product (Scheme 1). It has been speculated that the fluorescence of the probe (**HBT-1**) could be quenched because of the intramolecular charge-transfer (ICT) effect [8]. There is a significant change in the fluorescence signals when the **HBT-1** has been added into the sulfur dioxide derivatives or hydrazine, as **HBT-1** has been subsequently converted into **HBT-S or HBT-N**.

Results and discussion

The probe **HBT-1** was readily prepared by condensation reaction between compound **1** and malononitrile (see experiment

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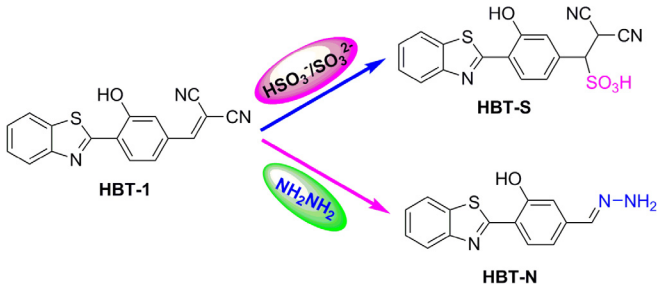

Scheme 1. Reaction between probe HBT-1 and sulfur dioxide derivatives or hydrazine.

section), and characterized by the standard NMR spectra and mass spectra (Fig. S1–3).

With **HBT-1** in hand, its optical properties has been tested in the presence of $NaHSO_3$ and NH_2NH_2 at ambient temperature, respectively. The free probe **HBT-1** (10 μM) exhibited a maximal absorption band at around 330 nm in pH 7.4, 10 mM PBS buffer-DMSO (8:2, v/v) (Fig. S4). The UV–vis spectrum of probe **HBT-1** had obviously changed, after reacting with 100 μM $NaHSO_3$ or 700 μM NH_2NH_2, respectively. The maximum absorption increased at around 300–450 nm prominently (Fig. S4). The time dependent of the fluorescence spectra of probe **HBT-1** has also been studied in the presence of $NaHSO_3$ and NH_2NH_2. Firstly, upon treatment with $NaHSO_3$, the emission fluorescence intensity (@ 464 nm) of the sensing system increased dramatically in 7 min and reached a steady state as the increment of reaction time. In the absence of $NaHSO_3$, the fluorescence background remained unchanged under identical conditions (Fig. 1a). Concomitantly, upon treatment with NH_2NH_2, the fluorescence intensity (@498 nm) increased as the increment of reaction time, then almost levels off after 40 min (Fig. 1b). In the absence of NH_2NH_2, the fluorescence background remained a slight increase under identical conditions (Fig. S5). Because the probe has some decomposition over time. In addition, we also discussed the time relationship between the low concentration of $NaHSO_3$ (40 μM), NH_2NH_2 (200 μM) and the probe **HBT-1**. As shown in Fig. S6, The emission intensity of **HBT-1** at 464 nm increased gradually after addition of $NaHSO_3$ and reached a plateau approximately 7 min. However, after treatment with NH_2NH_2 (200 μM), a rapidly increase in the fluorescence intensity was observed at approximately 50 min, as the reaction time increases, the fluorescence of the probe increases slowly in 100 min. These results indicated that the reaction time of the probe **HBT-1** with $NaHSO_3$ is shorter than that of NH_2NH_2.

Subsequently, the fluorescence changes of the probe **HBT-1** were investigated in 10 mM PBS buffer-DMSO (8:2, v/v) at pH of 7.4, with the titration of $NaHSO_3$ or NH_2NH_2. As shown in Fig. 2a, the blank solution of **HBT-1** is very weak red fluorescence due to the fluorescence quenching in the strong ICT process. However, upon treatment with $NaHSO_3$, a 40-fold enhancement in fluorescence intensity was observed at around 464 nm when the concentration of $NaHSO_3$ reached 10 equiv. Notably, it can be seen in Fig. 2b, different emission signals were also observed for NH_2NH_2, which generated slight red-shifted fluorescence signals (@498 nm) as the increased concentration of NH_2NH_2. A maximal fluorescence enhancement (10-fold) was obtained when the concentration of NH_2NH_2 reached 40 equiv. The detection limits for **HBT-1** were calculated to be 6.3×10^{-7} M and 1.7×10^{-5} M using LOD = 3 σ/k (LOD-limit of detection; σ-the standard deviation of blank measurements; k-the slope of the calibration curve) (Fig. S7), respectively. It indicates that the probe **HBT-1** are highly sensitive to $NaHSO_3$ and NH_2NH_2. For verifying the above sensing mechanism, the product of **HBT-1** + $NaHSO_3$ and **HBT-1** + NH_2NH_2

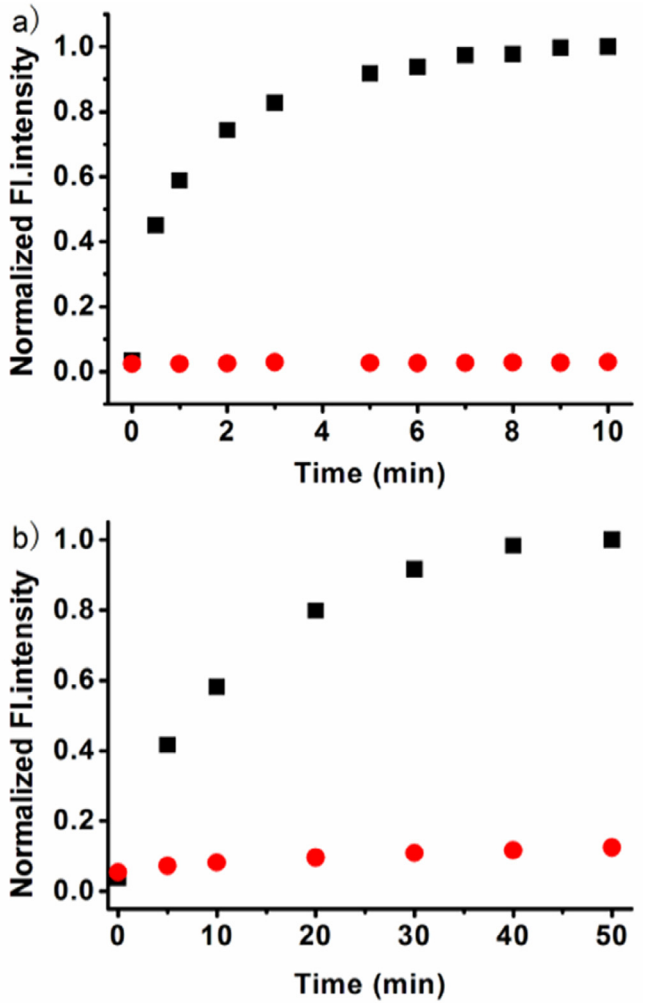

Fig. 1. The fluorescence spectra of **HBT-1** (10 μM) after the addition of $NaHSO_3$ (a) (100 μM) and NH_2NH_2 (b) (700 μM) during different times in pH 7.4 PBS buffer-DMSO (8:2, v/v) at room temperature.

have been studied by mass spectrometry. An apparent peak was observed at m/z 386.5 in the addition product [**HBT-S**+H]$^+$ in the mass spectrometry. Similarly, the m/z peak 269.7 of the addition product [**HBT-N**+H]$^+$ can also be observed in the mass spectrometry (Fig. S8). Based on the previous reported mechanism [5l,m,6a,b].

To gain insight into the probing mechanism, computations on the probe **HBT-1** before and after combination with $NaHSO_3$ and NH_2NH_2 were performed by density functional theory (DFT) [9]. According to the calculation results (Fig. 3), for probe **HBT-1**, the electron of the HOMO are mainly distributed on the dicyanovinyl unit and the hydroxyl-substituted benzene ring, whereas the LUMO is basically localized the 2-(2-hydroxyphenyl)-benzothiazole unit, it clearly indicates the ICT character. However, electrons are mainly localized on the 2-(2-hydroxyphenyl)benzothiazole unit for **HBT-S**, otherwise its on the whole molecule at both the ground and excited states for **HBT-N**. It is worth mentioning that the energy gaps between HOMO and LUMO increased from **HBT-1** (3.18 eV) to its reaction product of **HBT-S** (4.29 eV) and **HBT-N** (3.92 eV). The results indicate that the ICT effect is weak and a blue shift in the fluorescence emission spectra.

To investigate the selectivity, the probe **HBT-1** was treated with various analytes, sulfite, bisulfite or NH_2NH_2 in pH 7.4, 10 mM PBS buffer-DMSO (8:2, v/v). As shown in Fig. 4a, the addition of the