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Cascade reaction-based rapid and ratiometric detection of H_2S/S^{2-} in the presence of bio-thiols with live cell imaging: demasking of ESIPT approach†

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For the rapid, ratiometric, fluorogenic and "naked eye" detection of H_2S/S^{2-}, a pro-excited state intramolecular proton transfer (ESIPT)-based receptor, 2-formyl-benzoic acid 2-benzothiazol-2-yl-phenyl ester (FBBP) has been designed. In the presence of H_2S/S^{2-} in preference to other common species, 2-(2-hydroxyphenyl)benzothiazole, a well known ESIPT-containing agent, is recovered from FBBP. Thus, H_2S/S^{2-} can be detected *in vitro* and *in vivo* by such a simple, easy-to-synthesise, practical ratiometric sensor.

Introduction

After nitrogen oxide and carbon monoxide, hydrogen sulfide (H_2S) has recently become known as the third of the principal gasotransmitters for regulating cardiovascular, neuronal, immune, endocrine and gastrointestinal systems.[1] H_2S is created endogenously from sulfur-containing molecules by the enzymes cystathionine β-synthase, cystathionine γ-lyase, and 3-mercaptopyruvate sulfurtransferase in the cytosols and mitochondria of mammalian cells.[2] Endogenous levels of H_2S play an important role in a vast number of physiological and pathological processes, such as regulation of vascular function and protection of cells from oxidative stress and vascular injury.[3] Thus, abnormal levels of H_2S are related to a series of diseases, such as diabetes, hypertension, stroke, Alzheimer's, Down's syndrome and cirrhosis of the liver.[4]

Therefore, visualization of the distribution and concentration of H_2S in living systems would be very significant and helpful in clarifying the biological roles of H_2S. Compared with reported methods such as colorimetric,[5] electrochemical analysis,[6] and gas chromatography,[7] small molecule fluorescent probes present high sensitivity, real-time imaging, and high spatiotemporal resolution and have excellent potential to be useful tools.

Alternatively, ratiometric fluorescent chemosensors are of particular interest because of their simplicity.[8] In particular, ratiometric sensing provides a way of avoiding any misinterpretation of analyte-induced fluorescence quenching or enhancement because of photobleaching, sensor concentration, and medium effects.[9] A ratiometric method measuring the ratio of fluorescence intensities at two wavelengths provides an alternative approach. However, up to now, only a limited number of ratiometric fluorescence probes for H_2S have been reported in the literature.[10]

Based on the H_2S-mediated reduction of azide (or nitro or hydroxyamine) to amine,[11] some groups have recently made great progress in the recognition of H_2S *in vitro* and *in vivo*. An H_2S-mediated nucleophilic addition reaction,[12] or a displacement strategy based on copper sulfide precipitation,[13] has also proved to be a convenient approach for this purpose. Yet, one of the factors limiting the extensive use of many probes is the multi-step synthesis required to obtain the receptor. Furthermore, most of the free fluorescent probes for H_2S have relatively low intensity with a "turn on" approach, which is a great barrier for real-time applications. Therefore, it is still necessary to devise simple fluorescent H_2S probes with a large rapid ratiometric response, which can be used for H_2S detection under physiological conditions.

However, because of their intrinsic properties, notably an ultra-fast reaction rate and an exceptionally large fluorescence Stokes shift,[14] great interest has been shown in excited state intramolecular proton transfer (ESIPT) compounds. Upon irradiation, 2-(2-hydroxyphenyl)benzothiazole (HBT) and its derivatives generate the ESIPT tautomers (the keto forms), which show fluorescence more strongly at longer wavelengths compared to the phenol forms. In recent times, researchers have also devised anion and cation sensors using the ESIPT method, with HBT as an ideal moiety for this purpose.[15] We also chose the well-characterised HBT as an ESIPT-containing moiety to construct a real-time probe for H_2S detection.

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Thus, in this paper, a new cascade reaction (nucleophilic addition, cyclisation and elimination)-based fluorogenic reactive probe, FBBP, is reported, which can be used to detect H_2S with a rapid response.

Experimental results and explanation

General

The chemicals and solvents were purchased from Sigma-Aldrich Chemicals and were used without further purification. Melting points were determined using a hot-plate melting point apparatus with an open-mouth capillary and were uncorrected. Proton nuclear magnetic resonance (^{1}H-NMR) and ^{13}C-NMR spectra were recorded on 500 MHz and 100 MHz instruments, respectively. For NMR spectra, deuterated chloroform ($CDCl_3$) was used as solvent with trimethyl siloxane as an internal standard. Chemical shifts are expressed in δ units and ^{1}H–^{1}H coupling constants in Hz. Fluorescence experiments were performed using a PTI fluorescence spectrophotometer, and using a fluorescence cell with a 10 mm path. The live cell imaging was carried out using a Leica DM2500 fluorescence microscope.

Experimental procedure

Synthesis of 2-formyl-benzoic acid 2-benzothiazol-2-yl-phenyl ester (FBBP). 2-Formyl benzoic acid (300 mg, 2 mmol) in dichloromethane (DCM) (10 ml) was taken in to a 100 ml round bottomed flask fitted with a dropping funnel. Oxalyl chloride (0.6 ml) was added into this solution, followed by 1 drop of dimethylformamide (DMF). Next, the whole solution was stirred for 4 hours at room temperature in a nitrogen atmosphere. The solvent was evaporated under vacuum to give 2-formyl benzoyl chloride. Next, crude 2-formyl benzoyl chloride was dissolved in dry DCM (10 ml) and a solution of HBT (550 mg, 2 mmol) in dry DCM (50 ml DCM mixed with a catalytic amount of triethyl amine) was added to it. The reaction mixture was stirred overnight. After completion of the reaction, the mixture was washed with water and the organic part was collected and dried over sodium sulfate (Na_2SO_4). This residue was dried under vacuum and purified by column chromatography using silica gel (100–200 mesh size) and 10–50% ethyl acetate in petroleum ether as eluent to give a white solid product (300 mg, 35%).

^{1}H-NMR (500 MHz, $CDCl_3$). δ 8.53 (d, 1H, $J = 5.5$), δ 8.49 (s, 1H), δ 8.12 (d, 1H, $J = 5$), δ 8.01 (d, 1H, $J = 10$), δ 7.93 (d, 1H, $J = 10$), δ 7.75 (q, 1H, $J = 10$), δ 7.71 (q, 1H, $J = 10$), δ 7.62 (m, 1H, $J = 4.3$), δ 7.5 (t, 1H, $J = 5.5$), δ 7.49 (t, 1H, $J = 7.5$), δ 7.35 (m, 1H, $J = 10$), δ 7.25 (s, 1H), δ 7.05 (s, 1H), δ 6.88 (s, 1H).

^{13}C-NMR (100 MHz, $CDCl_3$). 161.07, 155.83, 152.85, 150.89, 141.98, 139.75, 135.68, 132.71, 131.48, 129.17, 127.62, 126.75, 125.91, 123.64, 122.43, 122.30, 121.70, 118.03.

Electrospray ionisation-mass spectrometry (ESI-MS). 359.06 (m/z, 100%).

Fluorescence study

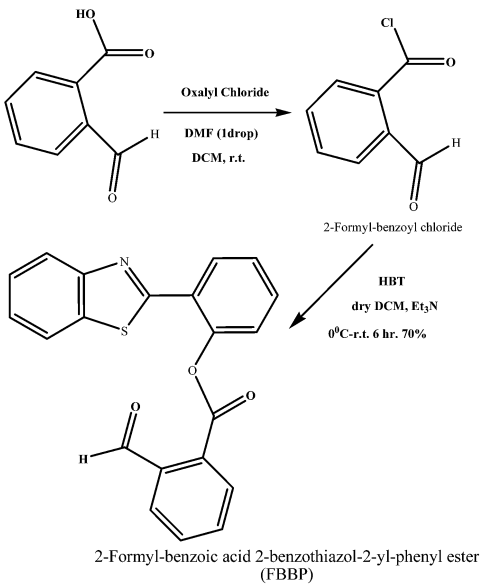
General method of fluorescence titrations. For fluorescence titrations, a stock solution of the sensor was prepared ($c = 1 \times 10^{-5}$ M l^{-1}) in acetonitrile–water ($CH_3CN : H_2O$) (2 : 8, v/v) at pH 7.4 using 10 mM HEPES buffer. The solution of the guest anion was prepared (2×10^{-5} M l^{-1}) in H_2O at pH 7.4 using 10 mM HEPES buffer. The original volume of the receptor solution was 2 ml. Solutions of the sensor at various concentrations and of increasing concentrations of cations, anions and amine-containing compounds were prepared separately. The spectra of these solutions were recorded using fluorescence methods.

Results and discussion

The synthesis of the sensor is shown in Scheme 1 (details of the procedure and spectra are given in the electronic ESI†).

It is well known that HBT and its derivatives produce the ESIPT tautomers (the keto forms), which show fluorescence more powerfully at longer wavelengths compared to the phenol forms upon irradiation. The enol isomer, which is lower in energy than the keto isomer in the electronic ground state, undergoes the proton transfer reaction upon excitation to the excited state. As shown in Fig. 1, FBBP itself exhibits emission at 359 nm (excitation at 310 nm). With the addition of only 0.5 μM of S^{2-}, the emission at 359 nm decreased, followed by a new peak appearing at 462 nm. This indicated that the chemical reaction between sulfide ions and the receptor (FBBP) started at this minimum concentration and thus the ESIPT properties of HBT were demasked (Scheme 2).

Accordingly, a color change from colorless to blue, as well as an emission with a well-defined iso-emissive point at 417 nm, was observed. Essentially, these changes in the fluorescence spectrum stopped and the ratio of the emission intensities at 359 nm and 462 nm (I_{462}/I_{359}) became constant when the amount of S^{2-} added reached 1.2 equiv. It is noteworthy that the difference in the two emission wavelengths is very large (emission shift: $\Delta F = 103$ nm), which not only contributes to the accurate measurement of the intensities of the two emission



Scheme 1 Outline of the synthesis of the receptor, FBBP.

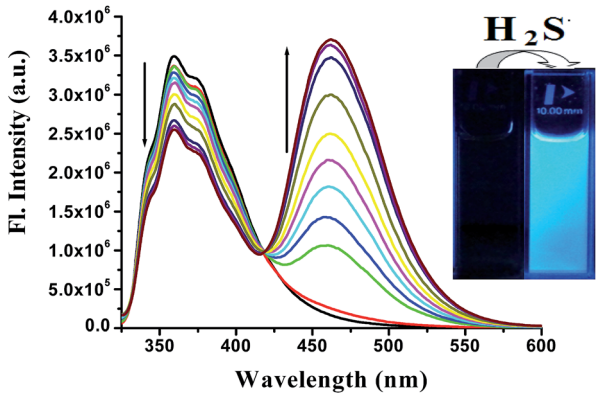
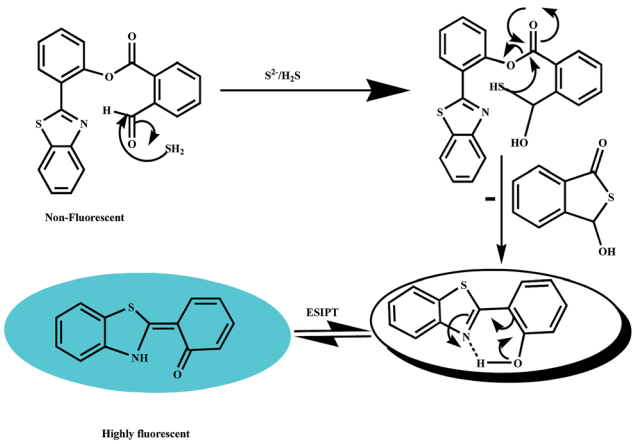


Fig. 1 Fluorescence titration spectra of FBBP ($c = 1.0 \times 10^{-5}$ M) in the presence of sodium sulfide (Na_2S; $c = 2.0 \times 10^{-5}$ M) at pH 7.5 in $CH_3CN : H_2O = 2 : 8$ (v/v). The inset shows the visual color change of FBBP with the addition of 5 equivalents of Na_2S under ultraviolet (UV) light.



Scheme 2 The reaction scheme of FBBP with S^{2-}.

peaks, but also results in a huge ratiometric value. In fact, in the presence of 1.2 equiv. of S^{2-}, an approximate 30-fold enhancement in the ratiometric value (I_{462}/I_{359} from 0.04 to 1.45) is achieved compared to that obtained with the sulfide-free solution (Fig. 1).

To evaluate the selective nature of H_2S/S^{2-} towards FBBP, spectral emission changes upon addition of 5 equivalents of common interfering species, *i.e.*, cysteine (Cys), glutathione (GSH), hydrogen peroxide (H_2O_2), fluoride (F^-), cyanide (CN^-), azide (N_3^-), hypochlorite (OCl^-), hydroxyl radical ($OH^\bullet$), thiocyanide (SCN^-), sulfite (SO_3^{2-}), hydrogen sulfite (HSO_3^-), thiosulfate ($S_2O_3^{2-}$) and ascorbic acid, were studied. As shown in Fig. 2, in most of these cases, no change in emission intensity ratio (I_{462}/I_{359}) was noted. The selectivity observed by emission monitoring matched, when FBBP was employed as a colorimetric sensor for the detection of sulfide ions. In contrast, a visual color change from colorless to bright blue was observed (under UV light) and was associated with the reaction of FBBP with sulfide ions.

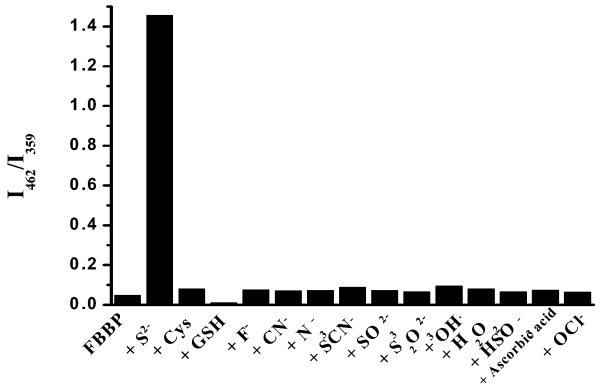


Fig. 2 The bar plot of the ratiometric response of FBBP in the presence of all the tested anions (5 equiv., except for S^{2-}, which was 1.2 equiv.).

The selectivity of the FBBP probe was also checked by quantitatively recording the fluorescence intensity of FBBP in the presence of an excess of 10 times the concentration of different types of interfering species (Fig. S3, ESI†). Most of the other species exhibited no effect on the FBBP detection of S^{2-}. Thus, these results demonstrated that FBBP has a sensitive response towards S^{2-}.

No significant color change was promoted by the addition of other anions under UV light. From the titration data (Fig. 3), it is clear that a concentration of 1.5 μM S^{2-} is enough for the ratiometric response using this unique probe. Under these conditions, the changes in the intensity of the two peaks (*i.e.*, I_{462} and I_{359}) produced an excellent linear function with respect to the concentration of sulfide between 3 and 12 μM (Fig. 4).

The detection limit for S^{2-} was determined to be 0.51 μM using the probe, *i.e.*, FBBP based on $K \times Sb1/S$, where Sb1 is the standard deviation and S is the slope of the calibration curve (see ESI†).

Using time-dependent fluorescence spectra, it was shown that the reaction was completed within approximately 3 min, with a rate constant of 1.9×10^{-2} s^{-1}, which strongly supports the high reactivity of the probe (Fig. S2, ESI†).

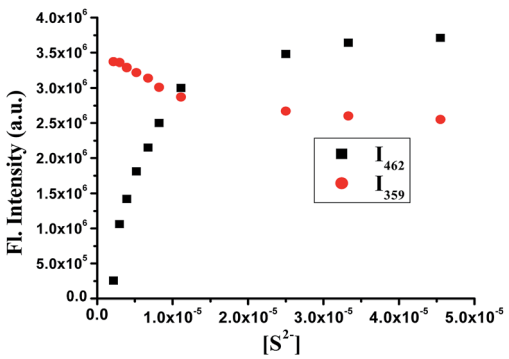


Fig. 3 Plot of $[S^{2-}]$ *versus* fluorescence intensity of FBBP at two different wavelengths, *i.e.*, at 462 and 359 nm ($\lambda_{ex} = 310$ nm).

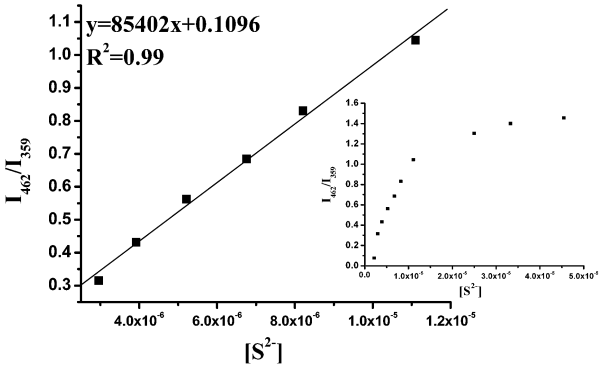


Fig. 4 Emission intensity ratio of FBBP *versus* $[S^{2-}]$ between 3 to 12 μM of $[S^{2-}]$ and the overall change of intensity ratio *versus* $[S^{2-}]$ (inset).

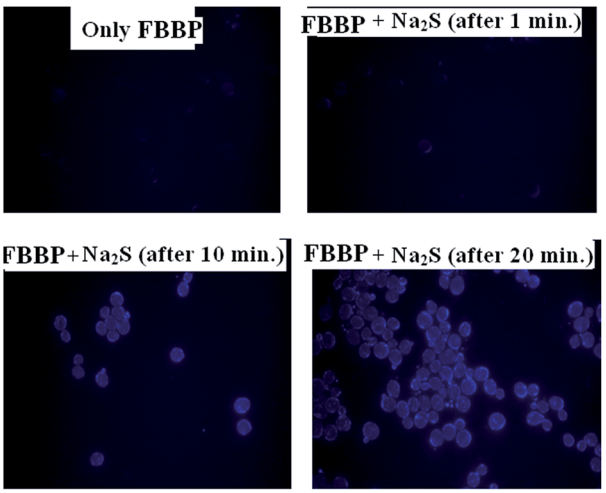


Fig. 5 Fluoresence image of a yeast cell treated with FBBP alone, and with FBBP with the addition of Na_2S (at time intervals of 1 min, 10 min and 20 min).

Predicted chemical mechanism for H_2S detection

It was envisaged that the observed change in presence of sulfide may arise from the HBT moiety which is released from FBBP with a cascade type of reaction between S^{2-} and the reactive probe, *i.e.*, FBBP. The formation of HBT from FBBP was confirmed by its ^{1}H-NMR structure. The characteristic aldehyde proton of FBBP disappeared with the appearance of a new phenolic proton peak of HBT when 1 equivalent of Na_2S solution was added to the solution of FBBP. The mass spectrum (ESI-MS) of the product after mixing with Na_2S shows a peak at *m*/*z* 227.04, which is possibly HBT, and at *m*/*z* 166.0, which is possibly a side product, which also proves a cascade-based reaction of S^{2-} towards FBBP, *m*/*z* 359.06 (see ESI†).

Detection of H_2S in living cells

It was then decided to examine whether FBBP could sense H_2S in living cells. Yeast (*Saccharomyces cerevisiae*) cells were grown in 5 ml of YPD broth (1% yeast extract, 2% peptone and 2% dextrose) overnight at 30 °C. Next day, a fresh 30 ml of YPD broth was inoculated with a sample from the overnight culture and grown till mid log phase (0.6–1.0 OD at 600 nm). FBBP (50 μM) was added to the culture and cells were grown for up to three hours. A portion (1 ml) of the cell culture was harvested and washed with phosphate-buffered saline. Finally the cell pellet was dissolved in 500 μl of ultrapure water (Sartorius Milli-Q) supplemented with 50 μM of Na_2S. Then imaging was carried out using a Leica DM2500 fluorescence microscope.

It can be seen that, after 30 min incubation with Na_2S solution, there was a higher fluorescence turn-on (Fig. 5). These experiments indicate that FBBP can be used to detect H_2S in living cells. The MTT assay for the probe, *i.e.*, FBBP, was conducted, and the results showed that the receptor could be used safely at a concentration of 50 μM (Fig. S24, ESI†).

Conclusion

In conclusion, a simple receptor (FBBP) has been designed and synthesized for the selective, sensitive and ratiometric rapid response towards sulfide with a chemodosimetric approach in aqueous media. From the spectral data, it is clear that the sensor can be used practically to detect H_2S/S^{2-} quantitatively with a high selectivity over other anions. The ESIPT-based sensing phenomenon is also useful for live cell imaging of H_2S/S^{2-}.

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