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ARTICLE TYPE

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

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For rapid, ratiometric, fluorogenic and "naked eye" detection of H_2S/S^{2-}, a pro-ESIPT based receptor, 2-formyl-benzoic acid 2-benzothiazol-2-yl-phenyl ester (FBBP) is designed. In presence of H_2S/S^{2-} over other common spcies, HBT, a well known ESIPT containing agent is recovered from FBBP. Thus we can detect H_2S/S^{2-} in vitro and in vivo by such a simple, easy-to-synthesise practical ratiometric sensor.

Introduction:

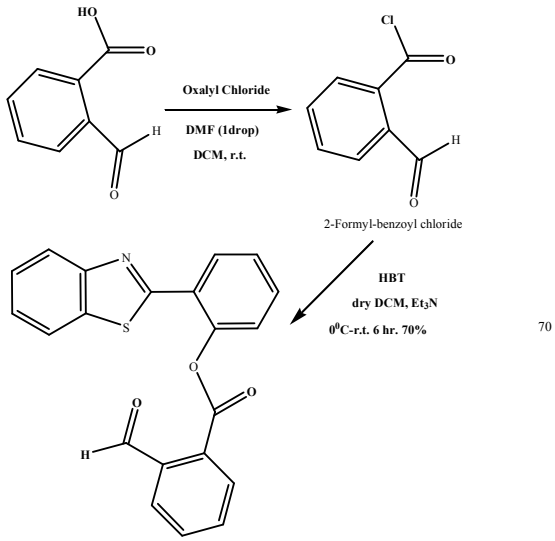
After NO and CO, H_2S is recently known as the third mainly important gasotransmitter for regulating cardiovascular, neuronal, immune, endocrine and gastrointestinal systems.[1] H_2S is created endogenously by enzymes of cystathionine b-synthase (CBS), cystathionine g-lyase (CSE), and 3-mercaptopyruvate sulfur transferase (3MST) in the cytosols and mitochondria of mammalian cells from sulfur-containing molecules.[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 the vascular injury.[3] Thus abnormal levels of H_2S are related with a series of diseases, such as diabetes, hypertension, stroke, Alzheimer's, Down's syndrome and liver cirrhosis.[4]

Thus, visualization of the distribution and concentration of H_2S in living systems would be very significant and helpful to clarify 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, high spatiotemporal resolution and have excellent potential to be useful tools.

Alternatively, ratiometric fluorescent chemosensors are of particular interest due to its simplicity.[8] In particular, ratiometric sensing provides a way of avoiding any misinterpretation of analyte-induced fluorescence quenching or enhancement due to photo bleaching, 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, hydroxyamine) to amine,[11] recently some groups have explored huge progress in the recognition of H_2S in vitro and in vivo. H_2S-mediated nucleophilic addition reaction[12] or displacement strategy based on copper sulfide precipitation [13] is also proved to be a convenient method for this purpose. Yet, one of the factors limiting the extensive use of lots of probes is the multi step synthesis to get 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. Thereby, it is still necessary to think up simple fluorescent H_2S probes with large rapid ratiometric response, which can be used for H_2S detection at physiological conditions.

Scheme 1: Synthetic outline of the receptor, FBBP.



2-Formyl-benzoic acid 2-benzothiazol-2-yl-phenyl ester (FBBP)

On the other hand, due to their inner properties similar to ultra-fast reaction rate and exceptionally huge fluorescence Stokes shift,[14] ESIPT (Exited state intramoleculer proton transfer) compounds have also drawn a lot of implication. Upon irradiation, 2-(2-hydroxyphenyl)benzothiazole (HBT) and its derivatives, generate the excited-state intramolecular proton transfer (ESIPT) tautomers (the keto forms), which show fluorescence more strongly at longer wavelength compared to the phenol forms. In recent times, researchers also planned anion and cation sensors with ESIPT method, taking (HBT) as an ideal moiety for this purpose.[15] We also choose well charecterised HBT as an ESIPT containing

moiety to construct a real time probe for H_2S detection.

Thus, we herein report a new cascade reaction (nucleophilic addition, cyclisation and elimination) based fluorogenic reactive probe, 2-formyl-benzoic acid 2-benzothiazol-2-yl-phenyl ester (FBBP) towards H_2S with a rapid response.

Experimental Result and explanation:

General:

The chemicals and solvents were purchased from Sigma-Aldrich Chemicals Private Limited and were used without further purification. Melting points were determined on a hot-plate melting point apparatus in an open-mouth capillary and were uncorrected. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on 500 MHz and 100 MHz instruments respectively. For NMR spectra, $CDCl_3$ was used as solvent with TMS as an internal standard. Chemical shifts are expressed in δ□□ units and ^{1}H–^{1}H coupling constants in Hz. Fluorescence experiment was done using PTI fluorescence spectrophotometer with a fluorescence cell of 10 mm path. The live-cell imaging was carried out by using 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 DCM (10ml) was taken in a 100ml round bottom flask fitted with dropping funnel. Oxalyl chloride (0.6ml) was added into this solution following 1 drop of DMF. Next, the whole solution was allowed to stir for 4 hours at room temperature in nitrogen atmosphere. The solvent was evaporated in vacuum to give 2-formyl benzoyl chloride. Next, crude 2-formyl benzoyl chloride was dissolved in dry DCM (10ml) and a solution of 2-(benzo[d]thiazol-2-yl) phenol (HBT; 550 mg, 2mmol) in dry DCM (50 ml DCM mixed with catalytic amount of triethyl amine) is added to it. The reaction mixture was stirred over night. After completion of the reaction, the mixture was washed with water and the organic part was collected and dried over 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 pet 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.

ESI MS: 359.06 (m/z, 100%).

Fluorescence Study:

General method of fluorescence titrations:

For fluorescence titrations, stock solution of the sensor was prepared (c = 1 x 10^{-5} ML^{-1}) in CH_3CN: H_2O (2:8, v/v) at pH 7.4 by using 10 mM HEPES buffer. The solution of the guest anion was prepared (2 x 10^{-5} ML^{-1}) in H_2O at pH 7.4 by using 10 mM HEPES buffer. The original volume of the receptor solution is 2 ml. Solutions of the sensor of various concentrations and increasing concentrations of cations, anions and amine containing compounds were prepared separately. The spectra of these solutions were recorded by means of fluorescence methods.

Result and discussion:

The synthesis of the sensor is shown in Scheme 1 (details of the procedure and spectra given in supporting information†).

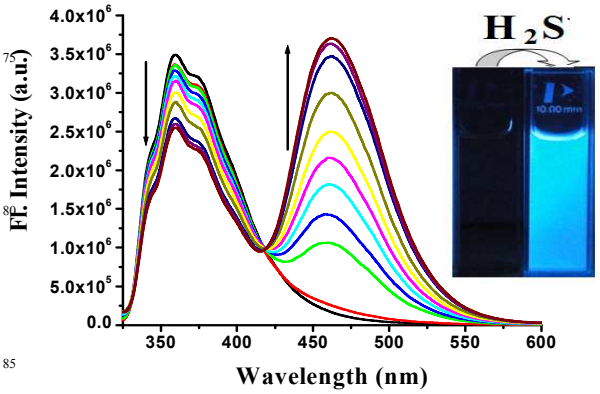


Figure 1: Fluorescence titration spectra of FBBP (c = 1.0 x 10^{-5} M) in presence of Na_2S (c = 2.0 x 10^{-5} M) at pH 7.5 in CH_3CN:H_2O = 2:8 (v/v) with the visual color change of FBBP with addition of 5 equivalent of Na_2S under UV light.

It is well known that, HBT and its derivatives produce the excited-state intramolecular proton transfer (ESIPT) tautomers (the keto forms), which show fluorescence more powerfully at longer wavelength 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 Figure 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 the chemical reaction between sulphide and the receptor (FBBP) started at this minimum concentration and thus the ESIPT properties of HBT was demasked.

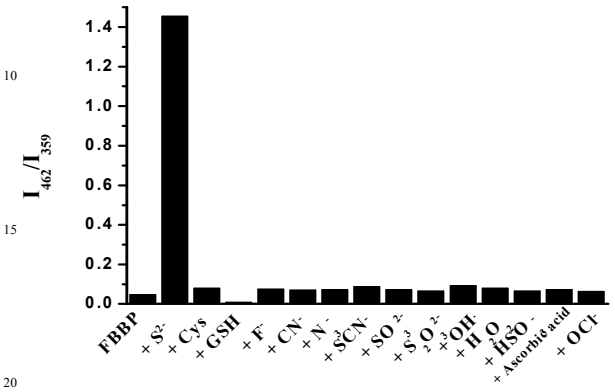


Figure 2: The bar plot of ratiometric response of FBBP in presence of all the tested anions (5 equiv. except S^{2-}, 1.2 equiv.).

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: ΔF = 103 nm), which not only contributes to the accurate measurement of the intensities of the two emission peaks, but also results in a huge ratiometric value. In fact, in the presence of 1.2 equiv. of S^{2-}, a ca. 30-fold enhancement in the ratiometric value (I_{462}/I_{359}, from 0.04 to 1.45) is achieved with respect to the sulphide-free solution (Fig. 1).

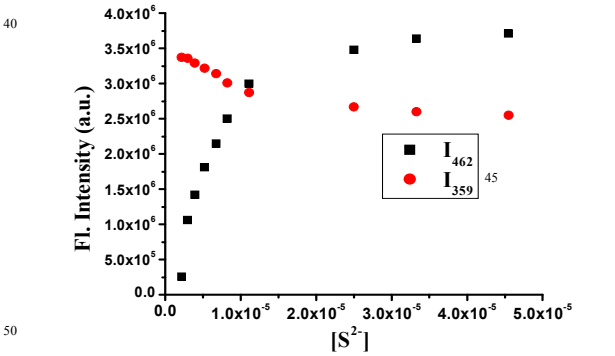


Figure 3: Plot of $[S^{2-}]$ vs. Fl. Intensity of FBBP at two different wave lengths i.e. at 462 and 359 nm (λ_{ex} = 310nm).

To evaluate the selective nature of H_2S/S^{2-} towards FBBP, emission spectral changes upon addition of 5 equivalent of common interfering species i.e., cysteine, glutathione, hydrogen peroxide, fluride, cyanide, azide, hypochlorite, hydroxyl radical, thiocyanide, sulphite, hydrozen sulphite, bi sulphite and ascorbic acid were studied. As shown in Figure 2, in most of these cases, no change in emission intensity ratio (I_{462}/I_{359}) was noticed. The selectivity observed by emission monitoring matched, when FBBP was employed as a colormetric sensor for sulphide ion. In contrast a visual color change from colorless to bright blue was observed (under UV-light) associated with the reaction of FBBP with sulphide ion.

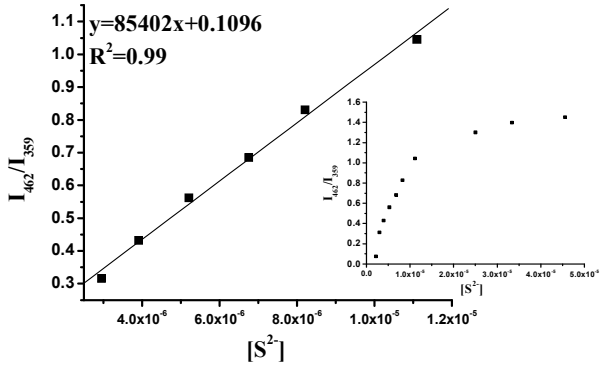
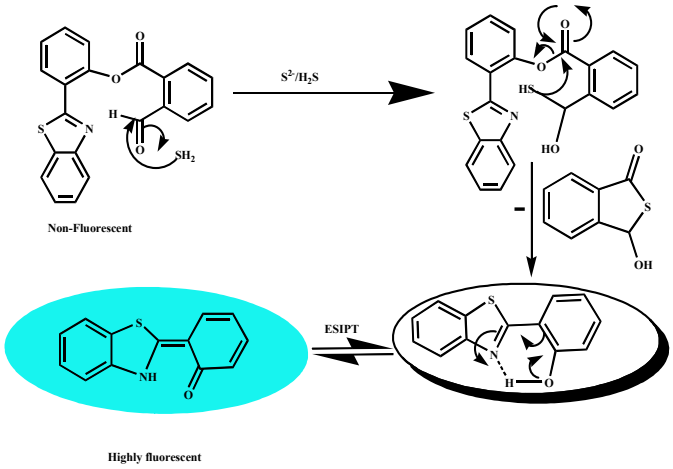


Figure 4: Emission intensity ratio of **FBBP** vs. $[S^{2-}]$ between 3 to 12 μM of $[S^{2-}]$ and the overall change of intensity ratio vs. $[S^{2-}]$ (inset).

The selectivity of the probe FBBP was also checked by quantitatively recording the fluorescence intensity of FBBP in the presence of 10 times excess of different types of interfering species (Figure S3:supporting information†). Most of other species exhibited no effect on FBBP detection of S^{2-}. Thus, these results demonstrated that FBBP had sensitive response toward S^{2-}.



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

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

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

In the time dependent fluorescence spectra, we see the reaction is completed within approximately 3 min with a rate constant of 1.9 x 10^{-2} sec^{-1}, which strongly supports the high reactivity of the probe (Fig. S2: supporting information†).

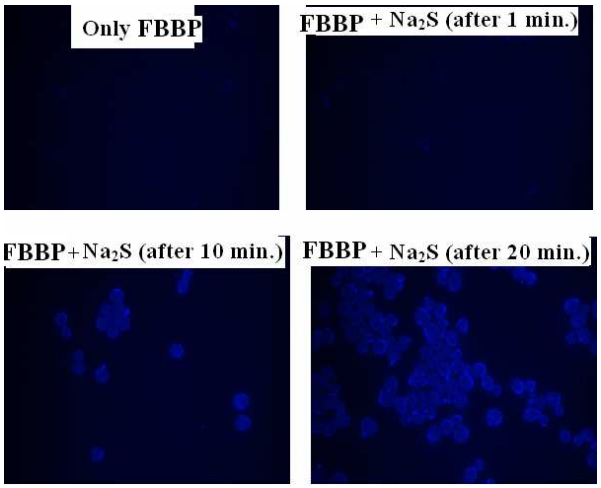


Figure 5: Fluoresence image of yeast cell treated with only FBBP and FBBP with addition of Na_2S (with a time interval of 1min., 10 min. and 20 min.

Predicted chemical mechanism for H_2S detection:

We envisaged that the observed change in presence of sulphide may arise from 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 the ^{1}H-NMR structure. The characteristic aldehyde proton of FBBP disappeared with appearance of a new phenolic proton peak of HBT when 1 equivalent of Na_2S solution is added to the solution of FBBP. The mass spectrum (ESI MS) of the product after mixing with Na_2S shows the peak at m/z 227.04 possibly for HBT & at m/z 166.0 possibly for the side product, which also proves a cascade based reaction of S^{2-} towards FBBP, m/z 359.06 (Supporting information†).

Detection of H_2S in living cells:

We then sought to examine whether FBBP can sense H_2S in living cells. Yeast (*Saccharomyces cerevisiae*) cells were grown in 5ml YPD broth (1% Yeast extract, 2% peptone and 2% dextrose) overnight at 30°C. Next day fresh 30ml YPD was inoculated from overnight culture and grown till mid log phase (0.6-1.0 OD at 600nm). 50 μM of FBBP was added to the culture and cells were grown up to 3 hour. 1ml of cell is harvested and washed with 1Xphosphate buffer saline (PBS). Finally the cell pellet was dissolved in 500 μL of ultrapure water (Sartorius Mili-Q) supplemented with 50μM of Na_2S. Then imaging was carried out by using Leica-DM2500 fluorescence microscope.

Wecan see that, after 30 min incubation with Na_2S solution, a higher turn-on fluorescence response can be observed (Fig. 5). These experiments indicate FBBP can be used to detect H_2S in living cells. The MTT assay for probe i.e. FBBP was conducted, and the results showed that the receptor can used with a concentration at 50 μM safely (Fig. S24: supporting information).

Conclusion:

In conclusion, we have designed and synthesized a simple receptor (FBBP) for selective, sensitive and ratiometric rapid response towards sulphide with a chemodosimetric approch in aqueous media. From the spectral data, it is clear that 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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Notes and references

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† Electronic Supplementary Information (ESI) available: [details of synthetic procedure and spectral data available]. See DOI: 10.1039/b000000x/

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