Electronic Supplementary Information

d-PET coupled ESIPT phenomenon for fluorescent turn-on detection of hydrogen sulfide

Shahi Imam Reja, Naresh Kumar, Roopali Sachdeva, Vandana Bhalla and Manoj Kumar,*

Department of Chemistry, UGC Sponsored Centre for Advanced Studies-1, Guru Nanak Dev University, Amritsar, Punjab, India.
Fax: +91 (0)183 2258820; Tel: +91 (0)183 2258802 9x3205;
E-mail: mksharmaa@yahoo.co.in

Instruments and quantum yield calculation

All reagents were purchased from Aldrich and were used without further purification. Acetonitrile (AR grade) was used to perform analytical studies. UV-vis spectra were recorded on a SHIMADZU UV-2450 spectrophotometer, with a quartz cuvette (path length 1 cm). The cell holder was thermostatted at 25^0C. The fluorescence spectra were recorded with a SHIMADZU 5301 PC spectrofluorimeter. Elemental analysis was done using a Flash EA 1112 CHNS/O analyzer from Thermo Electron Corporation. ^{1}H spectra were recorded on a JEOL-FT NMR-AL 300 MHz spectrophotometer using $CDCl_3$ as solvent and tetramethylsilane as the internal standard. Data are reported as follows: chemical shift in ppm (*d*), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad singlet), coupling constants *J* (Hz), integration and interpretation. Fluorescence quantum yields[1] were determined by using optically matching solution of diphenyl anthracene (Φ_{fr} = 0.9 in cyclohexane) as standard at an excitation wavelength of 373 nm and quantum yield is calculated using the equation:

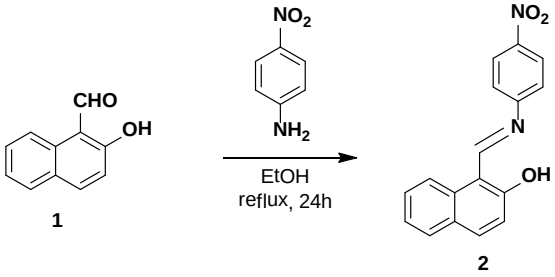
$$\Phi_{fs} = \Phi_{fr} \times \frac{1\text{-}10^{-ArLr}}{1\text{-}10^{-AsLs}} \times \frac{N_s^2}{N_r^2} \times \frac{D_s}{D_r}$$

Φ_{fs} and Φ_{fr} are the radiative quantum yields of sample and the reference respectively, A_s and A_r are the absorbance of the sample and the reference respectively, D_s and D_s the respective areas of emission for sample and reference. L_s and L_r are the lengths of the absorption cells of sample and reference respectively. N_s and N_r are the refractive indices of the sample and reference solutions (pure solvents were assumed respectively).

[1] Deams, J. N.; Grosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.

Synthesis

Compounds **1**[2] and **2**[3] were synthesized according to previously reported procedures.

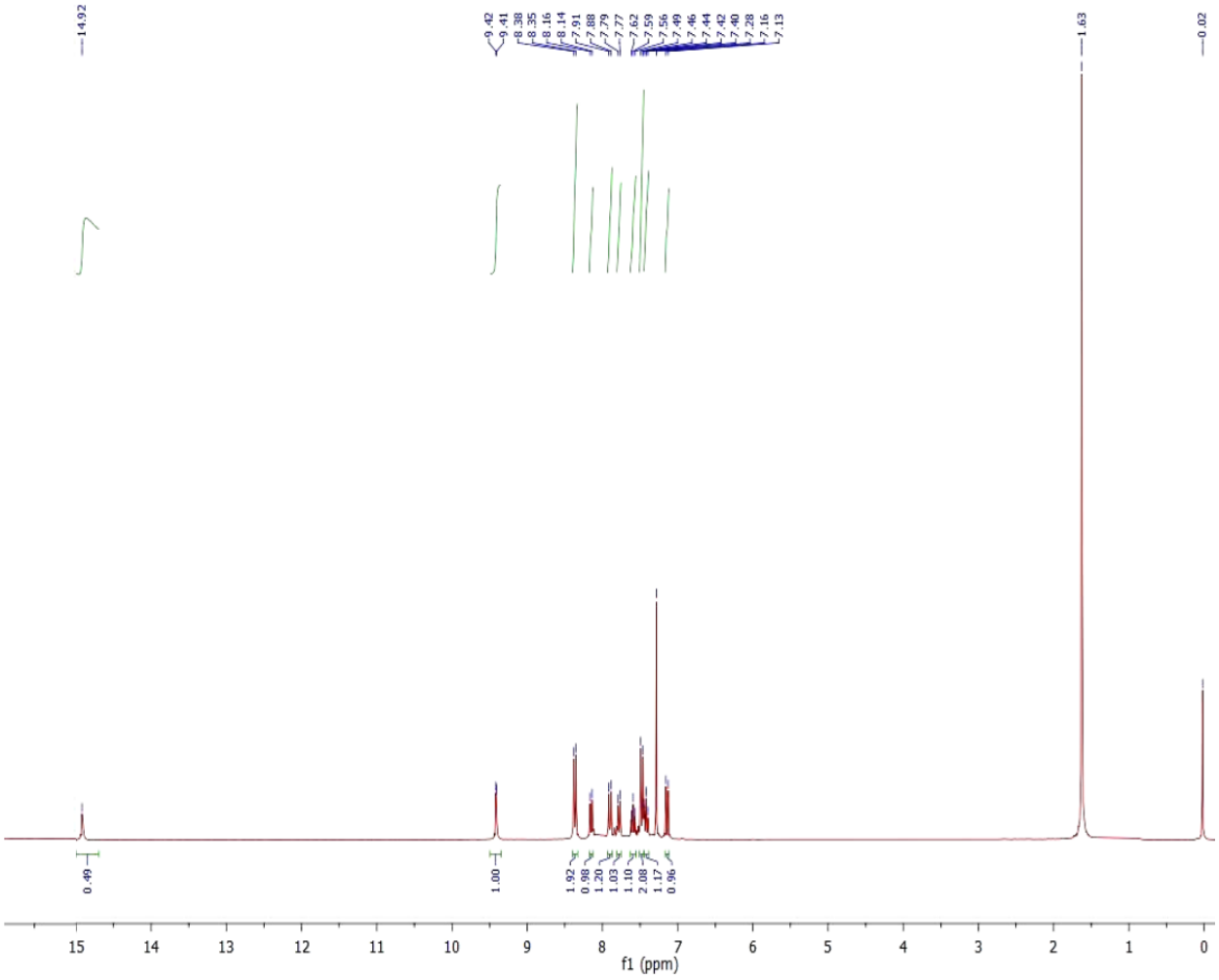


Scheme 1 Synthesis of compound **2**.

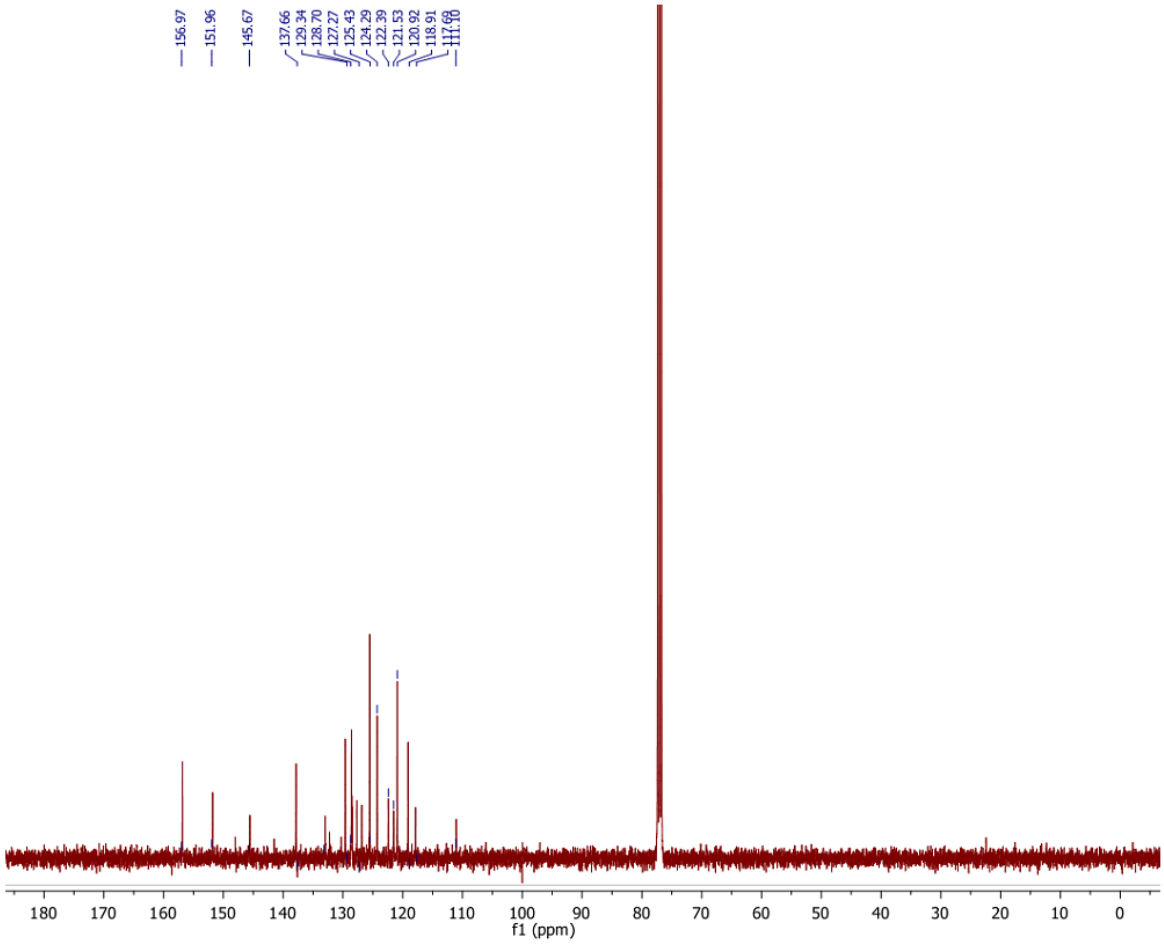
[2] Mehta, B. H.; Shaikh, J. A. *J. Indian Chem. Soc*., **2009**, *86*, 624.

[3] Antonov, L.; Fabian, W. M. F.; Nedeltcheva, D.; Kamounah, F. S. *J. Chem. Soc*., *Perkin Trans. 2*, **2000**, 1173.

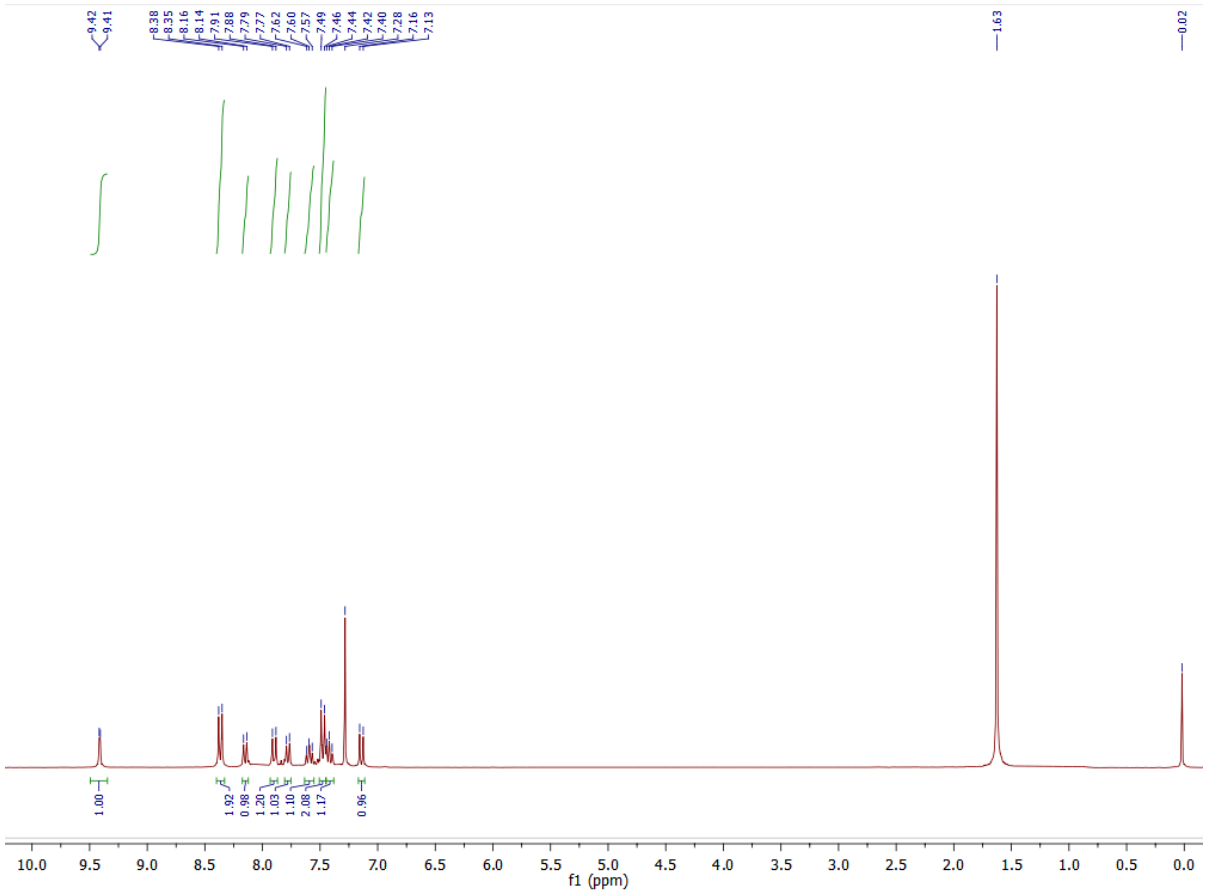
^{1}H NMR spectra of compound 2



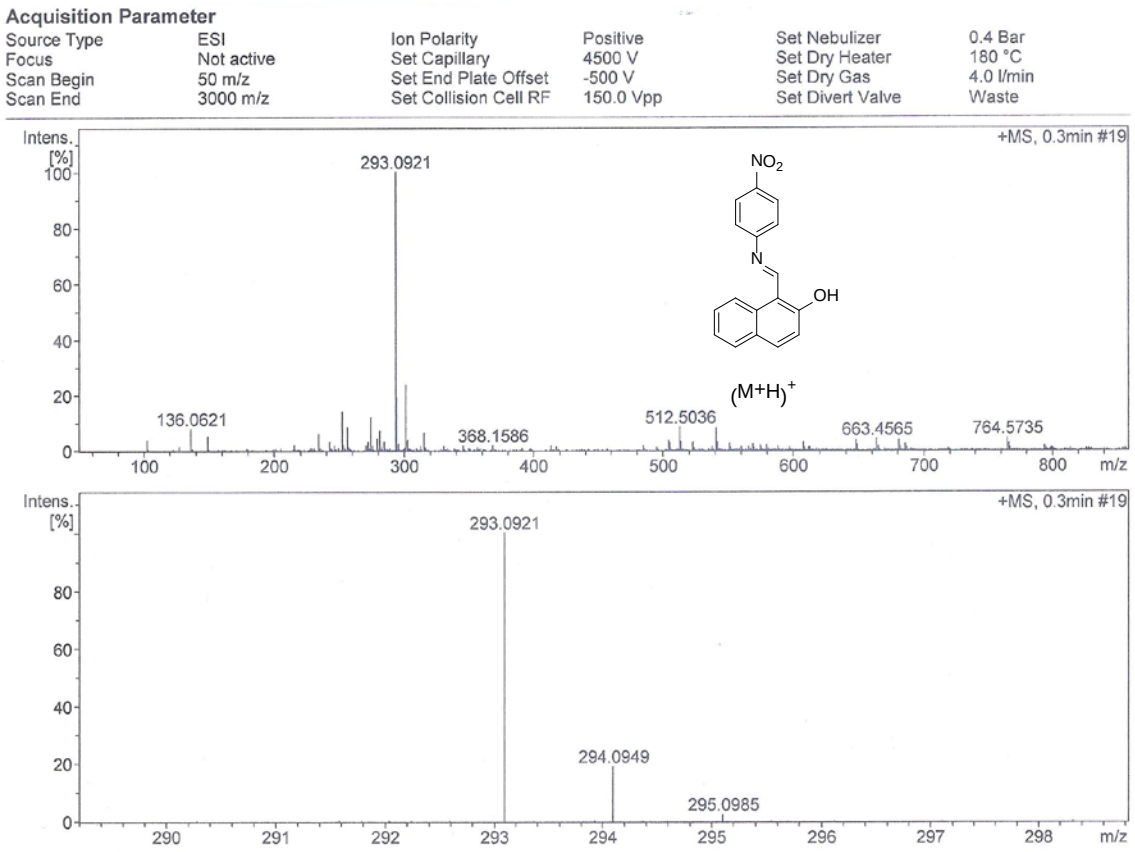
^{13}C NMR of compound 2



^{1}H NMR spectra of compound 2 (expanded)



Mass spectrum of compound 2



UV-vis spectra of compound 2 in the presence of H_2S and different analyte in H_2O/CH_3CN (99.5:0.5, v/v) buffered with HEPES; pH = 7.4.

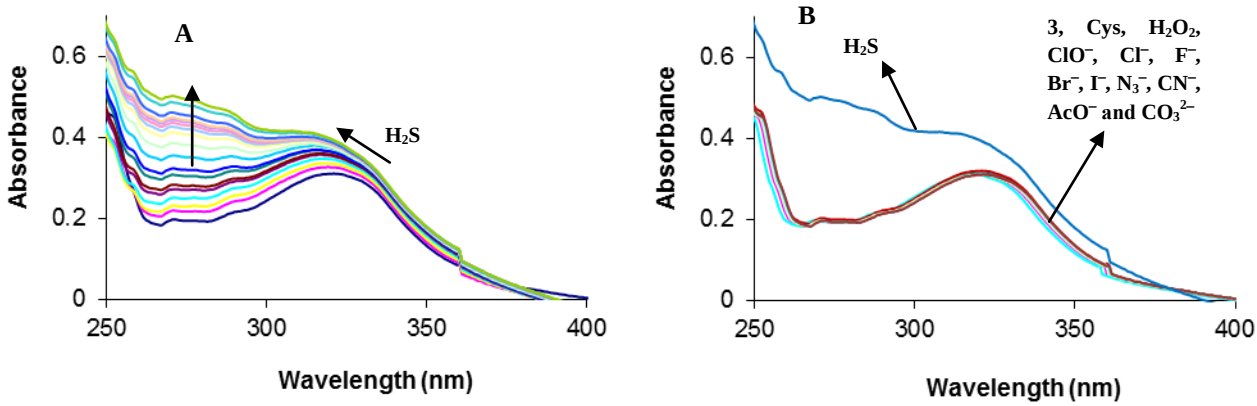
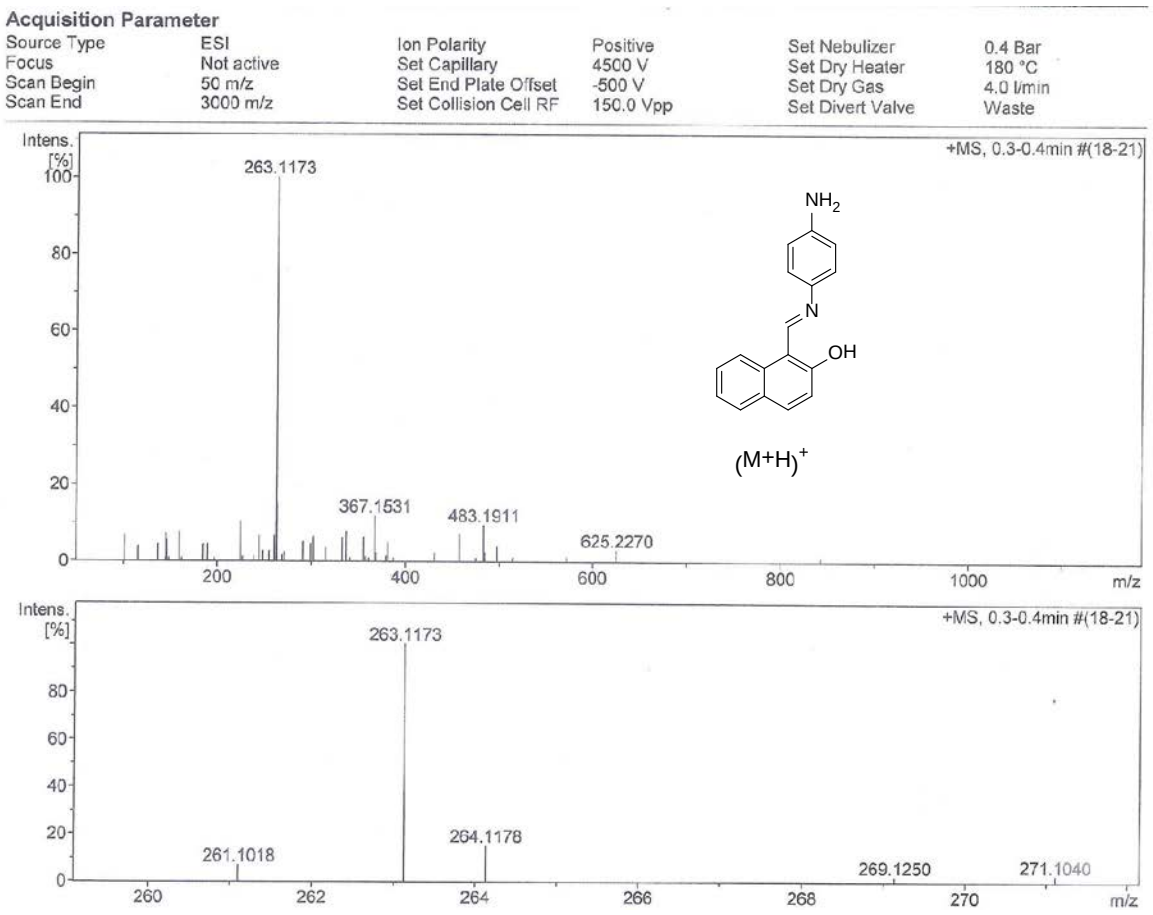


Figure S9. UV/vis spectra of receptor **3** (5 μM) in the presence of (A) H_2S (25 μM); (B) other analytes (25 μM each) in H_2O:CH_3CN (99.5:0.5, v/v) buffered with HEPES, pH = 7.4.

Mass spectrum of product 3



The blue shifting of the fluorescence emission band

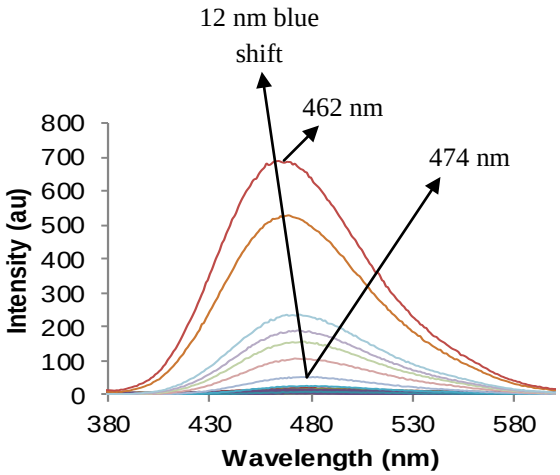


Figure S11. Blue shifted fluorescence emission spectrum of receptor **2** after addition of H_2S.

Temperature dependent fluorescence studies

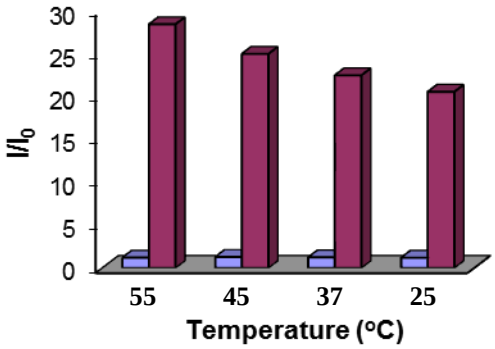


Figure S12. Fluorescence response of **2** (5 μM) in H_2O:CH_3CN (99.5:0.5, v/v) buffered with HEPES in different temperature (^{0}C) value (λ_{ex}= 320 nm) to addition of 30 μM H_2S at pH = 7.4. Red bars indicate the presence of H_2S and blue bars represent only free ligand **2.** Data were given after incubation with H_2S after 15 minutes.

Competitive fluorescence selectivity of compound 2

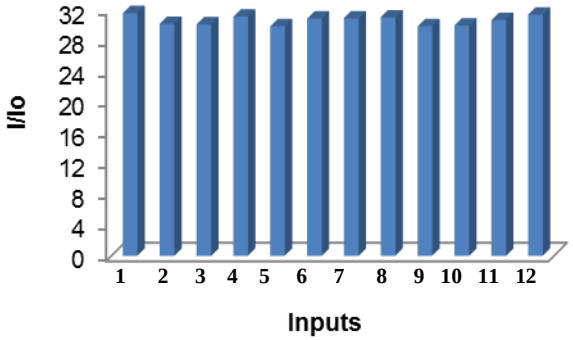


Figure S13. Competitive fluorescence selectivity of **2** (5 μM) towards H_2S (30 μM) in H_2O:CH_3CN (99.5:0.5, v/v) buffered with HEPES, pH = 7.4; λ_{ex} = 320 nm in the presence of other analyte (30 μM each). Bars represent the emission intensity ratio (I/I_o) (I_o = initial fluorescence intensity at 462 nm; I = final fluorescence intensity at 462 nm after the addition of other analyte. 1, H_2S; 2, Cys; 3, H_2O_2; 4, ClO^-; 5, TBHP; 6, F^-; 7, Br^-; 8, I^-; 9, N_3^-; 10, CN^-; 11, AcO^- and 12, $S_2O_3^{2-}$; Data were given after the incubation period of 20 minutes with appropriate analytes. Note: We are used main interfering analyte for competitive study.

Detection limit compound 2 towards H_2S

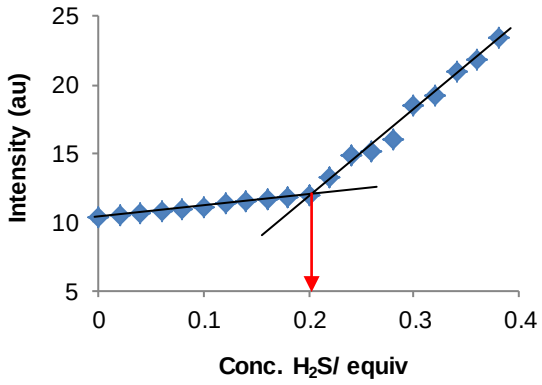


Figure S14. Figure showing the fluorescence intensity at 462 nm as a function of H_2S concentration. To determine the detection limit, fluorescence titration of compound **2** (5 μM) with H_2S was carried and the fluorescence intensity as a function of H_2S added was then plotted. From this graph the equivalents used at which there was a sharp change in the fluorescence intensity multiplied with the concentration of receptor **2** gave the detection limit.

$$\text{DL (detection limit)} = 5 \times 10^{-6} \times 0.2 = 10 \times 10^{-7}$$

$$= 10 \times 10^{-7}\ \text{M}$$

Preparation of test-strips:

We used pre-coated thin layer chromatography plate as a test-strip. At first we dipped the test-strip into the solution of compound 2 (10^{-3} M) in acetonitrile and then we took the photograph of the TLC strips under UV-lamp. The saturated solution of H_2S (10^{-4} M in distilled water) poured on the test-strip. After 20 minutes the photograph of the test-strip was taken under UV-lamp.