Electronic Supplementary Information

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

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S3 Instruments and Quantum yield calculation
S4 Synthetic routes
S5 $^1$H NMR spectrum of compound 2 (15-0 ppm)
S6 $^{13}$C NMR spectrum of compound 2
S7 $^1$H NMR spectrum of compound 2 (expanded)
S8 Mass spectrum of compound 2
S9 UV-vis spectra of compound 2 in the presence of H$_2$S and different analyte in H$_2$O/CH$_3$CN (99.5:0.5, v/v) buffered with HEPES; pH = 7.4.
S10 Mass spectrum of product 3
S11 The blue shift of fluorescence emission band.
S12 Temperature dependent fluorescence studies
S13 Competitive fluorescence selectivity of compound 2
S14  Calculations for detection limit and detection limit of \( \text{H}_2\text{S} \)

S15  Procedure for test-strips studies
**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°C. 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. ¹H spectra were recorded on a JEOL-FT NMR-AL 300 MHz spectrophotometer using CDCl₃ 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 yields¹ were determined by using optically matching solution of diphenyl anthracene (Φᵣ = 0.9 in cyclohexane) as standard at an excitation wavelength of 373 nm and quantum yield is calculated using the equation:

\[
Φₛ = Φᵣ \times \frac{10^{-Aᵣ}}{10^{-Aₛ}} \times \frac{Nₛ^2}{Nᵣ^2} \times \frac{Dₛ}{Dᵣ}
\]

Φₛ and Φᵣ are the radiative quantum yields of sample and the reference respectively, Aₛ and Aᵣ are the absorbance of the sample and the reference respectively, Dₛ and Dᵣ the respective areas of emission for sample and reference. Lₛ and Lᵣ are the lengths of the absorption cells of sample and reference respectively. Nₛ and Nᵣ are the refractive indices of the sample and reference solutions (pure solvents were assumed respectively).

Synthesis

Compounds 1 and 2 were synthesized according to previously reported procedures.

\[ \text{Scheme 1 Synthesis of compound 2.} \]
$^1$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$_2$S and different analyte in H$_2$O/CH$_3$CN (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$_2$S (25 µM); (B) other analytes (25 µM each) in H$_2$O:CH$_3$CN (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 H2S.
Temperature dependent fluorescence studies

Figure S12. Fluorescence response of 2 (5 µM) in H$_2$O:CH$_3$CN (99.5:0.5, v/v) buffered with HEPES in different temperature (°C) value ($\lambda_{ex}$= 320 nm) to addition of 30 µM H$_2$S at pH = 7.4. Red bars indicate the presence of H$_2$S and blue bars represent only free ligand 2. Data were given after incubation with H$_2$S after 15 minutes.
Competitive fluorescence selectivity of compound 2

Figure S13. Competitive fluorescence selectivity of 2 (5 μM) towards H$_2$S (30 μM) in H$_2$O:CH$_3$CN (99.5:0.5, v/v) buffered with HEPES, pH = 7.4; $\lambda_{ex} = 320$ nm in the presence of other analyte (30 μM each). Bars represent the emission intensity ratio ($I/I_0$) ($I_0 =$ initial fluorescence intensity at 462 nm; $I =$ final fluorescence intensity at 462 nm after the addition of other analyte. 1, H$_2$S; 2, Cys; 3, H$_2$O$_2$; 4, ClO$^-$; 5, TBHP; 6, F$^-$; 7, Br$^-$; 8, I$^-$; 9, N$_3$$^-$; 10, CN$^-$; 11, AcO$^-$ and 12, S$_2$O$_3^{2-}$; 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 H₂S

Figure S14. Figure showing the fluorescence intensity at 462 nm as a function of H₂S concentration. To determine the detection limit, fluorescence titration of compound 2 (5 µM) with H₂S was carried and the fluorescence intensity as a function of H₂S 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.

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

\[ = 10 \times 10^{-7} \text{ M} \]
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$_2$S ($10^{-4}$ M in distilled water) poured on the test-strip. After 20 minutes the photograph of the test-strip was taken under UV-lamp.