Supporting Information

A Real-Time Colorimetric and Ratiometric Fluorescent Probe for Sulfite

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1. Quantum Yields.
Quantum yields were determined using fluorescein as a standard according to the published method. The quantum yield was calculated according to the equation: \( \Phi_{\text{sample}} = \Phi_{\text{standard}} \times \left( \frac{I_{\text{sample}}}{I_{\text{standard}}} \right) \times \left( \frac{A_{\text{sample}}}{A_{\text{standard}}} \right) \); where \( \Phi \) is the quantum yield, \( \Phi_{\text{standard}} = 0.85 \) in 0.1 M NaOH; \( I_{\text{sample}} \) and \( I_{\text{standard}} \) are the integrated fluorescence intensities of the sample and the standard, \( A_{\text{sample}} \) and \( A_{\text{standard}} \) are the optical densities, at the excitation wavelength, of the sample and the standard, respectively.

Quantum yield of Probe 1: \( \Phi = 0.028 \). Quantum yield of Probe 2: \( \Phi = 0.089 \). After the complete reaction with sulfite, the Quantum yield of Probe 1: \( \Phi = 0.006 \).

2. Detection limit.
The detection limit was calculated based on the fluorescence titration. Probe 1 was employed at 10 \( \mu \)M and the slit was adjusted to 5 nm/5 nm. To determine the S/N ratio, the emission intensity of Probe 1 without \( \text{Na}_2\text{SO}_3 \) was measured by 10 times and the standard deviation of blank measurements was determined. Under the present conditions, a good linear relationship between the fluorescence intensity and the \( \text{Na}_2\text{S} \) concentration could be obtained in the 0 – 200 \( \mu \)M (\( R = 0.997 \)), as shown in Fig. S1. The detection limit is then calculated with the equation: detection limit = \( 3\sigma_b \)/m, where \( \sigma_b \) is the standard deviation of blank measurements, \( m \) is the slope between intensity versus sample concentration. The detection limit was measured to be 58 \( \mu \)M at S/N = 3 (signal-to-noise ratio of 3:1).

3. The linear relationship of the fluorescent signal ratio to the concentration of sulfite

Fig. S1
A) Fluorescence response of Probe 1 (10 \( \mu \)M) to \( \text{SO}_3^{2-} \) (0, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 200\( \mu \)M, 0-20 eq) (\( \lambda_{\text{ex}} = 446 \) nm. Slit: 5 nm/5 nm, \( \lambda_{\text{scan}} = 460 \) – 700 nm ) in DMF:buffer = 2:8.
B) Fluorescence intensity ratio at 480 nm and 578 nm (\( I_{480}/I_{578} \)) of Probe 1 (10 \( \mu \)M) upon addition of \( \text{SO}_3^{2-} \) (0–200 \( \mu \)M, 0-20 eq) (\( \lambda_{\text{ex}} = 446 \) nm. Slit: 5 nm/5 nm) in DMF:buffer = 2:8.
**Fig. S2** Fluorescence intensity ratio at 501 nm and 625 nm ($I_{501}/I_{625}$) of Probe 2 (10 µM) upon addition of $SO_3^{2-}$ (0–2000 µM, 0–200 eq) ($\lambda_{ex} = 468$ nm, Slit: 3 nm/3 nm) in DMF: buffer = 5:5.

4. The fluorescent emission spectrum of probe 1 with $S_2O_4^{2-}$ and $S_2O_5^{2-}$
$^1$H NMR and $^{13}$C NMR spectrums.
ESI-MS and HRMS
$^1$H-$^1$H COSY spectrums of probe 1 and probe 2