

Electronic Supplementary Information

A sensitivity tuneable tetraphenylethene-based fluorescent probe for directly indicating the concentration of hydrogen sulfide

Yunbo Cai,^a Lingzhi Li,^a Zongtan Wang,^a Jing Zhi Sun,^a Anjun Qin,^{*ab} and Ben Zhong Tang^{*abc}

^a MOE Key Laboratory of Macromolecule Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China. E-mail: qinaj@zju.edu.cn (A.J.Q.), tangbenz@ust.hk (B.Z.T.)

^b Guangdong Innovative Research Team, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China.

^c Department of Chemistry, Institute for Advanced Study, Institute of Molecular Functional Materials, and State Key Laboratory of Molecular Neuroscience, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong China.

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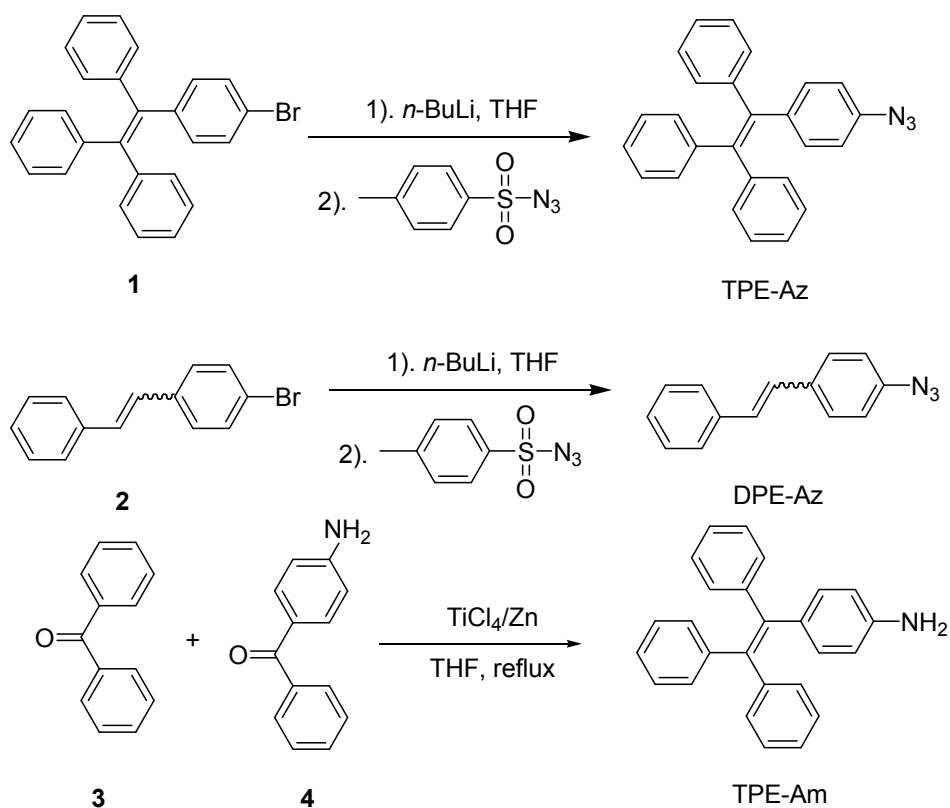
Experimental section

1. Materials and Instruments.

4-Aminobenzophenone, titanium tetrachloride and 4-bromobenzophenone were purchased from Alfa Aesar. 2-Bromobenzaldehyde and *n*-BuLi were purchased from Acros. Benzaldehyde was purchased from J&K. Other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. Tetrahydrofuran (THF) was distilled under normal pressure from sodium benzophenone ketyl under nitrogen immediately prior to use.

^1H and ^{13}C NMR spectra were measured on a Mercury plus 400MHz NMR spectrometer in CDCl_3 or DMSO-d_6 using tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. FT-IR spectra were recorded on a Bruker Vector 22 spectrometer. UV-vis absorption spectra were obtained on a Varian CARY 100 Bio UV/Visible spectrophotometer. Photoluminescence spectra were recorded on a Shimadzu RF-5301PC Spectrofluorophotometer. Elemental analysis was performed on a ThermoFinnigan Flash EA1112 apparatus.

2. Synthesis of probes.



Synthesis of 1-(4-azidophenyl)-1,2,2-triphenylethene (TPE-Az). Into a 250 mL round-bottom flask was placed 1-(4-Bromophenyl)-1,2,2-triphenylethene (**1**, 617 mg, 1.5 mmol). The flask was evacuated under vacuum and re-filled with dry nitrogen three times. After THF (50 mL) was added, the solution was cooled down to $-78\text{ }^{\circ}\text{C}$, into which *n*-BuLi (1.13 mL, 1.8 mmol, 1.6 M in hexane) was added dropwise. The mixture was kept at $-78\text{ }^{\circ}\text{C}$ for 2 h and then 355 mg (1.8 mmol) of 4-methylbenzenesulfonyl azide dissolved in 10 mL of THF was added dropwise. After reacted at $-78\text{ }^{\circ}\text{C}$ for 1 h, the mixture was warmed slowly to room temperature and stirred overnight. Afterward, saturated NH_4Cl solution (60 mL) was added to quench the reaction, and THF was evaporated. Then, dichloromethane (DCM) was added to extract the product three times. The organic layer was combined and washed with water and brine and dried over MgSO_4 . After filtration and solvent evaporation, the crude product was purified by a silica gel column chromatography using petroleum ether as eluent. Pale yellow solid of TPE-Az was obtained in 92.3% yield (517 mg). IR (KBr), ν (cm^{-1}): 3083, 2124, 1498, 1287, 823, 755, 695. ^1H NMR (400MHz, DMSO-d_6), δ (TMS, ppm): 7.10-7.14(m, 9H), 6.96-7.00(m, 8H), 6.89(d, 2H). ^{13}C

NMR (400MHz, DMSO- d_6), δ (TMS, ppm): 143.5, 143.4, 141.3, 140.5, 140.1, 137.9, 132.8, 131.1, 128.3, 127.1. Anal. Calcd for $C_{26}H_{19}N_3$: C, 83.62; H, 5.13; N, 11.25; Found: C, 83.85; H, 5.11; N, 10.99.

Synthesis of 1-azido-4-styrylbenzene (DPE-Az). Into a 250 mL round-bottom flask was placed 1-bromo-4-styrylbenzene (**2**, 800 mg, 3.1 mmol). The flask was evacuated under vacuum and re-filled with dry nitrogen three times. After THF (50 mL) was added, the solution was cooled down to -78 °C, into which *n*-BuLi (2.3 mL, 3.7 mmol, 1.6 M in hexane) was added dropwise. The mixture was kept at -78 °C for 2 h and then 730 mg (3.7 mmol) of 4-methylbenzenesulfonyl azide dissolved in 10 mL of THF was added dropwise. After reacting at -78 °C for 1 h, the mixture was warmed slowly to room temperature and stirred overnight. Afterward, saturated NH_4Cl solution (60 mL) was added to quench the reaction, and THF was evaporated. Then, DCM was added to extract the product three times. The organic layer was combined and washed with water and brine and dried over $MgSO_4$. After filtration and solvent evaporation, the crude product was purified by a silica gel column chromatography using petroleum ether as eluent. Pale yellow solid of TPEN3 was obtained in 92.1% yield (632 mg). IR(KBr), ν (cm^{-1}): 3025, 2114, 1596, 1505, 1294, 963, 817, 530. 1H NMR(400MHz, DMSO- d_6), δ (TMS, ppm): 7.64-7.66 (d, 2H), 7.58-7.60 (d, 2H), 7.36-7.40 (t, 2H), 7.24-7.29 (t, 3H), 7.11-7.13 (d, 2H). ^{13}C NMR (400MHz, DMSO- d_6), δ (TMS, ppm): 138.8, 137.4, 134.6, 129.2, 128.7, 128.5, 128.1, 127.9, 126.9, 119.9. Anal. Calcd for $C_{14}H_{11}N_3$: C, 76.00; H, 5.01; N, 18.99; Found: C, 76.02; H, 4.89; N, 18.87.

Synthesis of 1-(4-aminophenyl)-1,2,2-triphenylethene (TPE-Am). Under an N_2 atmosphere, a two-necked flask equipped with a magnetic stir was charged with zinc powder (9.6 g, 144mmol) and 60 mL THF. The mixture was cooled to 0--5 °C, and $TiCl_4$ (7.8 mL, 72 mmol) was slowly added by a syringe with the temperature kept under 10 °C. The suspending mixture was warmed to room temperature and stirred for 0.5 h, then heated at reflux for 2.5 h. The mixture was again cooled to 0--5 °C, charged with pyridine (6 mL, 36 mmol) and stirred for 10 min. The solution of benzophenone (**3**, 3.15 g, 17.28 mmol) and 4-aminobenzophenone (**4**, 2.84 g,

14.4mmol) in 15 mL THF was added slowly. After addition, the reaction mixture was heated at reflux until the reactants were consumed (monitored by TLC). The reaction was quenched by Na₂CO₃ solution and extracted with DCM. The organic layer was combined and concentrated. The crude product was purified by a silica gel column chromatography using petroleum ether/ethyl acetate as eluent. Pale yellow solid of TPE-Am was obtained in 51.2% yield (2.56 g). IR (KBr), ν (cm⁻¹): 3385, 3044, 1617, 1513, 1277, 820, 739, 698. ¹H NMR (400MHz, DMSO-*d*₆), δ (TMS, ppm): 6.97-7.11 (m, 17H), 6.80 (d, 2H), 6.43 (d, 2H). ¹³C NMR (400MHz, DMSO-*d*₆), δ (TMS, ppm): 144.2, 144.1, 144.0, 140.8, 139.4, 134.5, 132.5, 131.4, 127.5, 126.3, 126.0, 114.6. Anal. Calcd for C₂₆H₂₁N: C, 89.88; H, 6.09; N, 4.03; Found: C, 90.09; H, 6.09; N, 3.97.

3. Fluorescence responses of the probes on H₂S.

Time-dependent experiments. The solution of TPE-Az in DMSO (50 μ M, 2 mL) were added NaHS solution (10⁻² M, 50 μ L) and incubated for 0.5 -10 min. Then the solutions were diluted with 8 mL HEPES buffer (10 mM, pH 7.4) and the photoluminescence (PL) spectra were measured.

Selectivity. The solutions of TPE-Az in DMSO (50 μ M, 2 mL) were added NaHS (10⁻² M, 50 μ L) and other competitive species (10⁻² M, 50 μ L) in water and incubated for 5 min. Then the solutions were diluted with 8 mL HEPES buffer (10 mM, pH 7.4) and the PL spectra were measured.

4. Tunable sensitivity of TPE-Az.

The solutions of TPE-Az (2 mL) were added NaHS in water and incubated for 5 min. Then the solutions were diluted with 8 mL HEPES buffer (10 mM, pH 7.4). Afterward, the PL spectra were measured. To make the data more accurate, the measurements were repeated for three times. The final concentration of TPE-Az was 10, 20 and 50 μ M, and the final concentration of NaHS was 0.2-5 equivalent of TPE-Az.

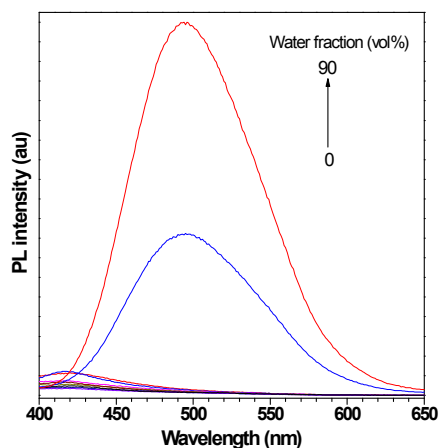


Fig. S1. PL spectra of TPE-Am in the DMSO/water mixtures with different water fractions. $\lambda_{\text{ex}} = 340$ nm.

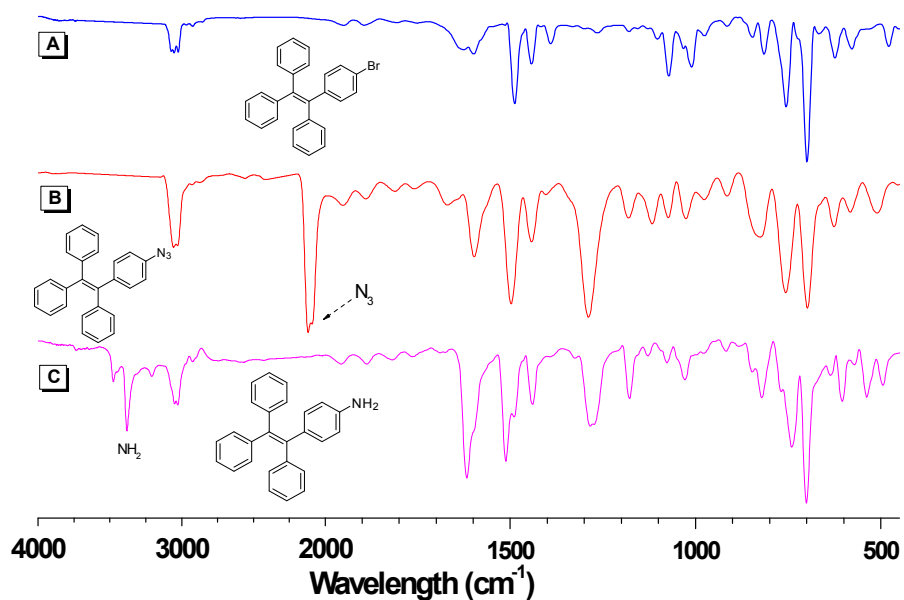


Fig. S2. IR spectra of (A) **1**, (B) TPE-Az, and (C) TPE-Am.

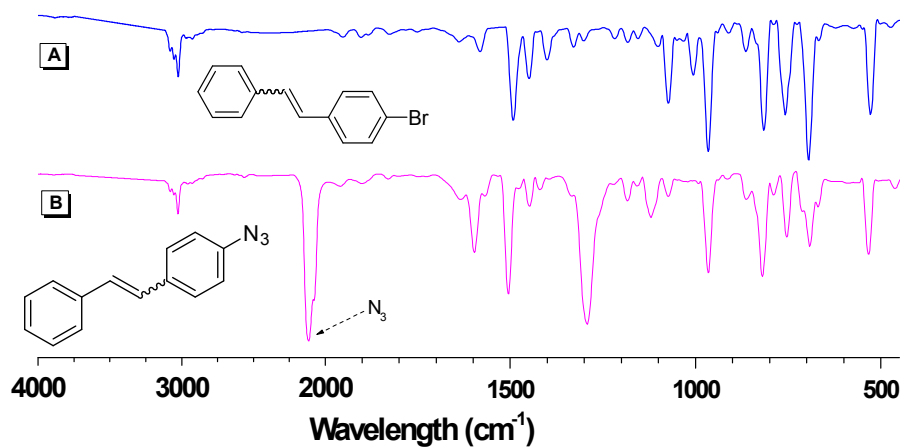


Fig. S3 IR spectra of (A) **2** and (B) DPE-Az.

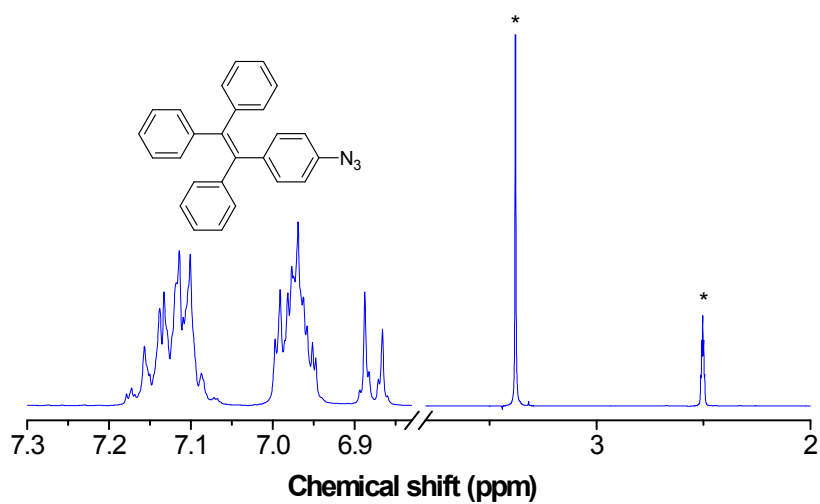


Fig. S4 ^1H NMR spectrum of TPE-Az in $\text{DMSO-}d_6$. The solvent peaks are marked with asterisks.

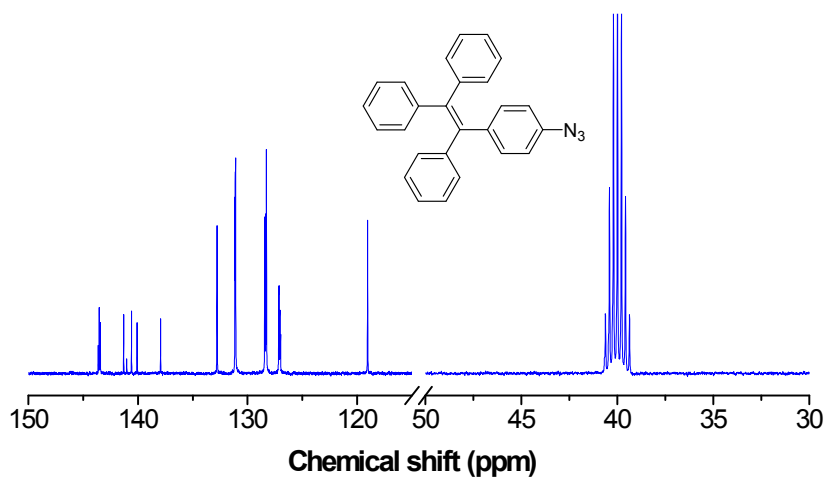


Fig. S5 ^{13}C NMR spectrum of TPE-Az in $\text{DMSO-}d_6$.

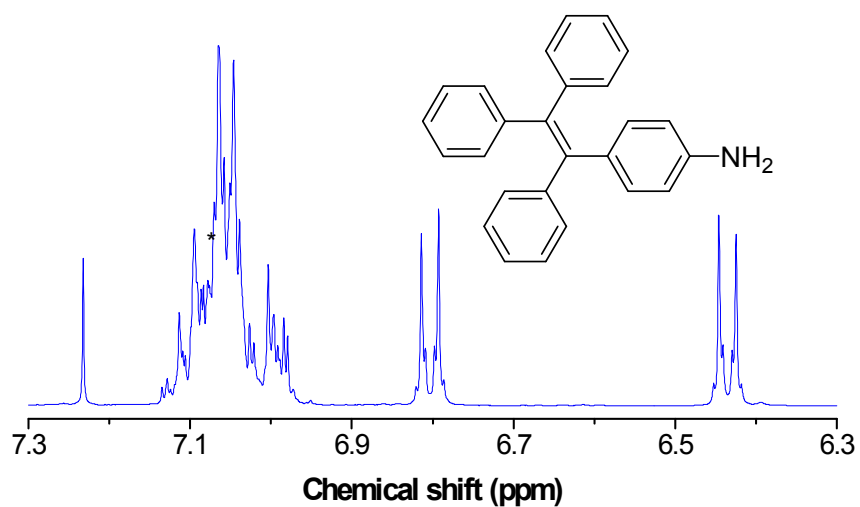


Fig. S6 ^1H NMR spectrum of TPE-Am in CDCl_3 . The solvent peaks are marked with asterisks.

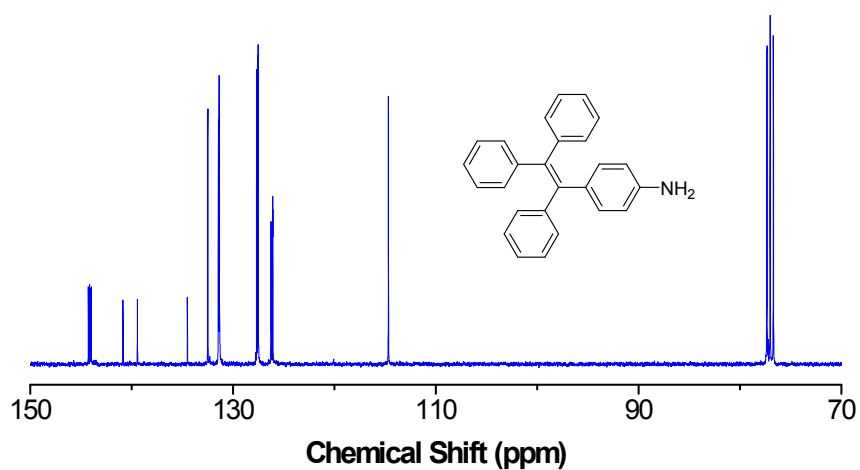


Fig. S7 ^{13}C NMR spectrum of TPE-Am in CDCl_3 .

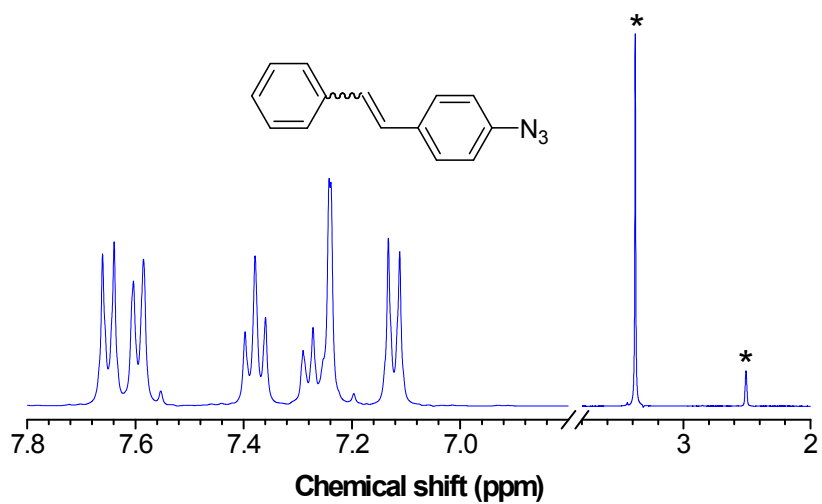


Fig. S8 ^1H NMR spectrum of DPE-Az in $\text{DMSO-}d_6$. The solvent peaks are marked with asterisks.

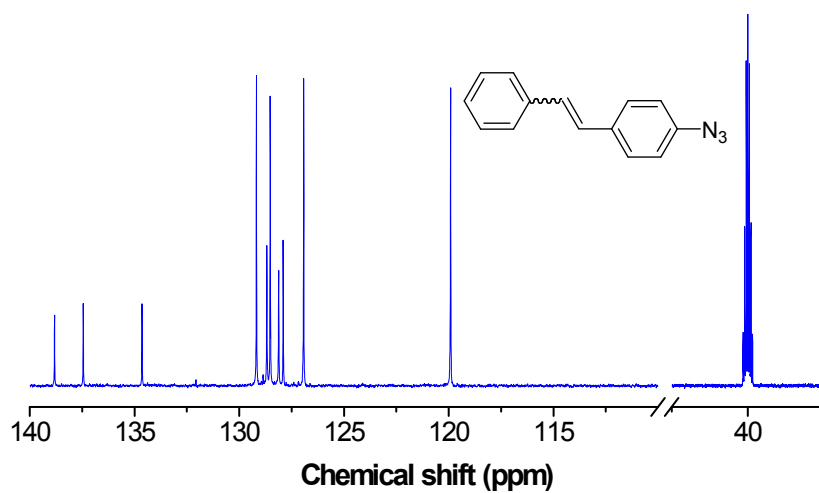


Fig. S9 ^{13}C NMR spectra of DPE-Az in $\text{DMSO-}d_6$.

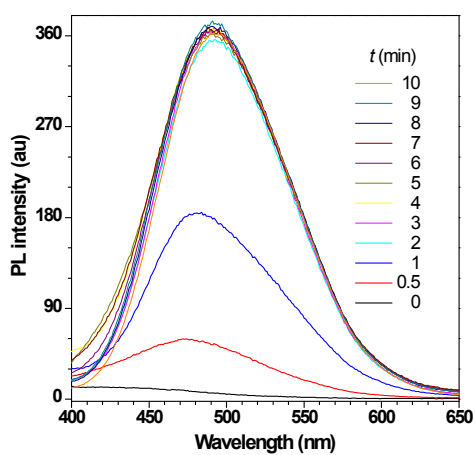


Fig. S10. Time-dependent PL changes of TPE-Az upon addition of H_2S in DMSO/HEPES buffer mixtures with buffer fraction of 80%. Concentration of TPE-Az: $10\ \mu\text{M}$. $\lambda_{\text{ex}} = 340\ \text{nm}$.

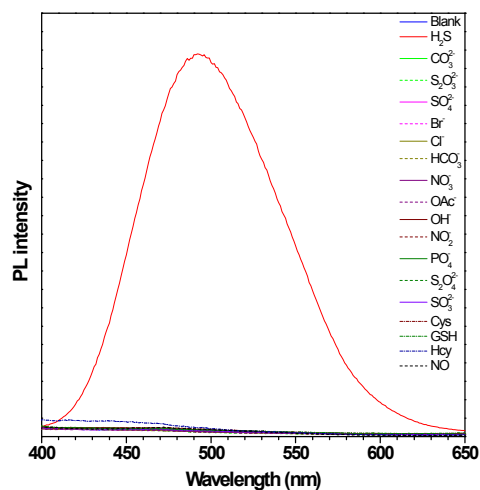


Fig. S11. PL spectra of TPE-Az incubated with analytes for 5 min in DMSO/HEPES buffer mixtures with buffer fraction of 80%. Concentration of TPE-Az: 10 μM , analytes: 1 mM for Cys, 5 mM for GSH and 50 μM for others. $\lambda_{\text{ex}} = 340 \text{ nm}$.

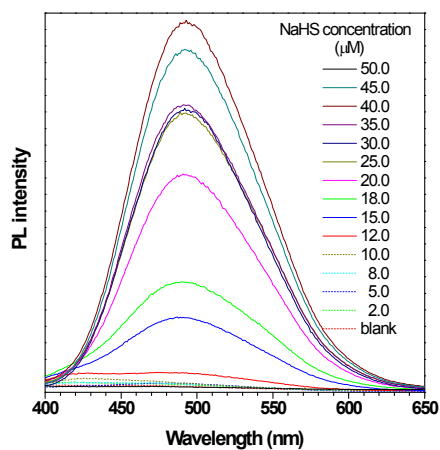


Fig. S12. PL spectra of TPE-Az in the presence of different amounts of NaHS in DMSO/HEPES buffer mixtures with buffer fraction of 80%. Concentration: 10 μM , $\lambda_{\text{ex}} = 340 \text{ nm}$.

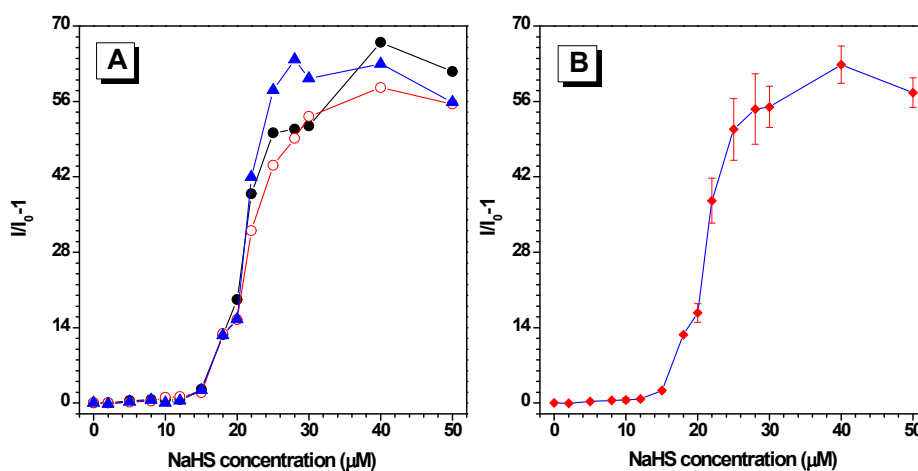


Fig. S13. (A) Relative and (B) averaged PL intensity of TPE-Az vs. NaHS concentration in DMSO/HEPES buffer mixtures with buffer fraction of 80%. Concentration of TPE-Az: 10 μM .

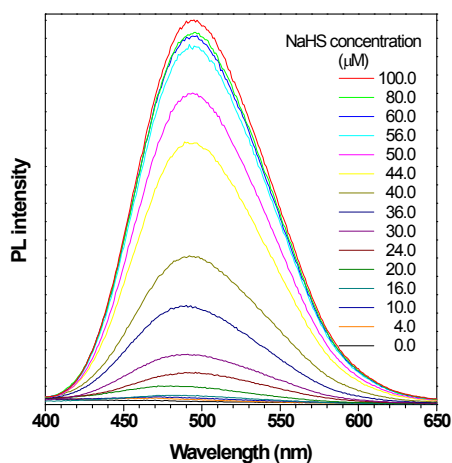


Fig. S14. PL spectra of TPE-Az in the presence of different amounts of NaHS in DMSO/HEPES buffer mixtures with buffer fraction of 80%. Concentration: 20 μM , $\lambda_{\text{ex}} = 340 \text{ nm}$.

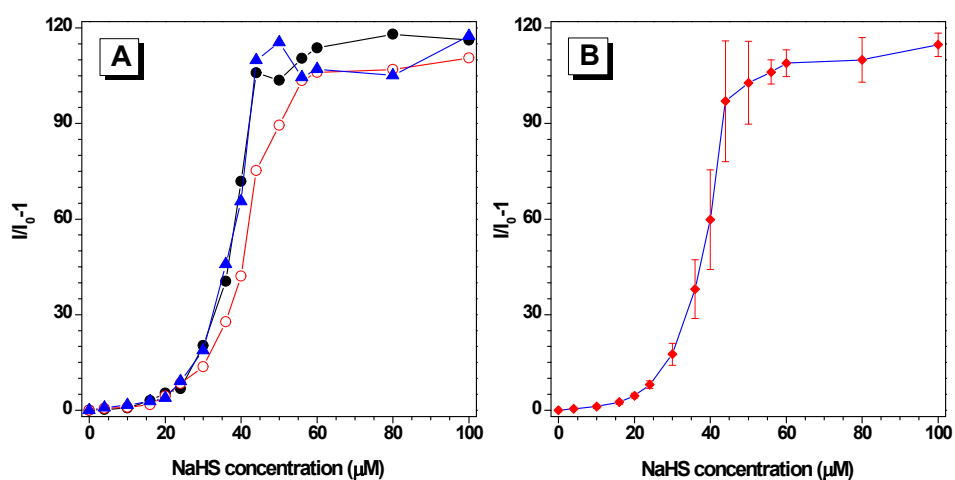


Fig. S15. (A) Relative and (B) averaged PL intensity of TPE-Az vs. NaHS concentration in DMSO/HEPES buffer mixtures with buffer fraction of 80%. Concentration of TPE-Az: 20 μM .

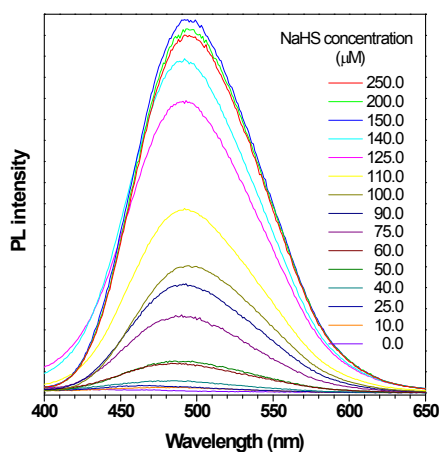


Fig. S16. PL spectra of TPE-Az in the presence of different amounts of NaHS in DMSO/HEPES buffer mixtures with buffer fraction of 80%. Concentration: 50 μM , $\lambda_{\text{ex}} = 340 \text{ nm}$.

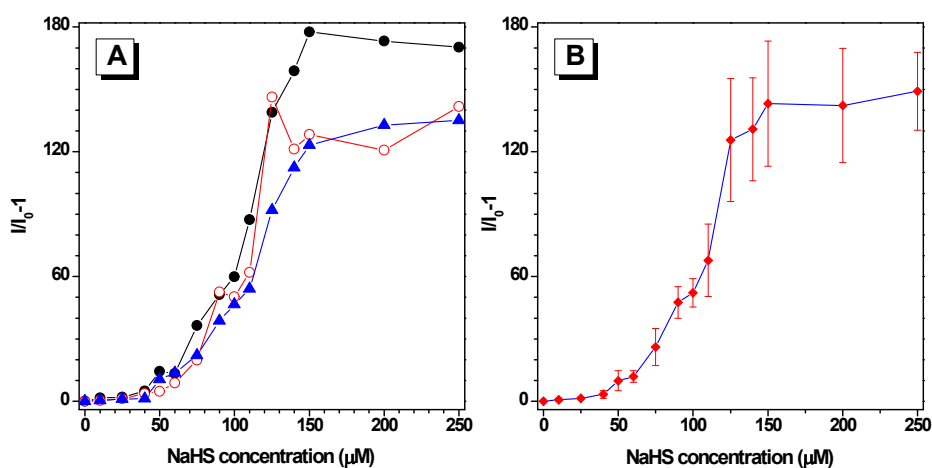


Fig. S17. (A) Relative and (B) averaged PL intensity of TPE-Az vs. NaHS concentration in DMSO/HEPES buffer mixtures with buffer fraction of 80%. Concentration of TPE-Az: 50 μM.

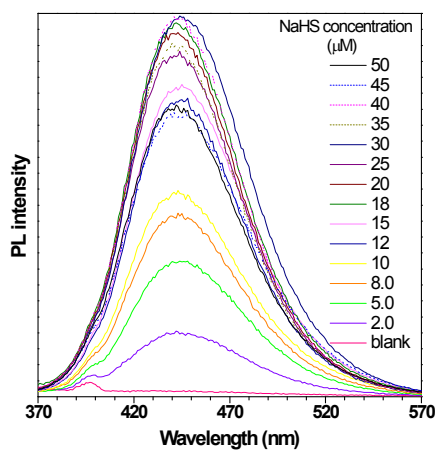


Fig. S18. PL spectra of DPE-Az in the presence of different amounts of NaHS in DMSO/HEPES buffer mixtures with buffer fraction of 80%. Concentration of DPE-Az: 10 μM. $\lambda_{\text{ex}} = 348 \text{ nm}$.

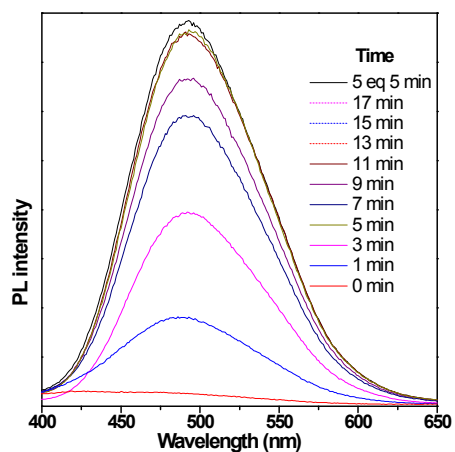


Fig. S21. Time-dependent PL changes of TPE-Az upon addition of 2 equivalents of H_2S in DMSO/HEPES buffer mixtures with buffer fraction of 80%. Concentration of TPE-Az: $10 \mu\text{M}$. $\lambda_{\text{ex}} = 340 \text{ nm}$.