Electronic Supplementary Information (ESI) for RSC Advances

Electronic Supplementary Information

A dual functional probe: sensitive fluorescence response to H_2S and colorimetric detection for SO_3^{2-}

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Abstract. This supplementary information provides all the additional information as mentioned in the text.

1. Synthesis

1.1. Synthesis of Compound 1

The solution of 2,3,3-Trimethylindolenine (160 mg, 1 mmol) and 1,3-propane sultone (150 mg, 1.2 mmol) in toluene (5 mL) was heated under reflux for 24 h. The resulting solution was cooled to room temperature and filtered. The filtered product was washed with diethyl ether and dried in vacuo to give compound **1** (250 mg, 89% yield) as a pink solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.09-8.07 (m, 1H), 7.86-7.84 (m, 1H), 7.67-7.62 (m, 2H), 4.69 (t, J = 7.7 Hz 2H), 2.86 (s, 3H), 2.66 (t, J = 6.5 Hz, 2H) 2.11-2.16 (m, 2H), 1.56 (s, 6H) ppm, ^{13}C NMR (125 MHz, DMSO): δ 197.04, 142.44, 141.70, 129.82, 129.44, 123.92, 115.95, 54.63, 47.87, 47.09, 44.47, 24.25, 22.55, 14.29 ppm.

1.2. Synthesis of Compound 2

N,N-Dimethylformamide (DMF, 4 mL) previously dissolved in CH_2Cl_2 (4 mL) was chilled in an ice bath. Phosphorus oxychloride (3.7 mL) dissolved in CH_2Cl_2 (3.5 mL) was then added dropwise. Afterward, cyclohexanone (1.0 g) was added. The solution was refluxed for 3 h, cooled, poured onto ice (20 g) and filtered. The filtered product was dried to give crude compound **2** (1.3 g, 73.9%). The crude compound **2** was used without further purification in the next reaction.

1.3. Synthesis of Compound 3

Compound **1** (281.1 mg, 1.0 mmol), sodium acetate (82 mg, 1.0 mmol) and compound **2** were (43 mg, 0.25 mmol) dissolved in acetic anhydride (6 mL) in a flask. The mixture was heated at 70 ºC with constant stirring. After 10 min, the other part compound **2** (43 mg, 0.25 mmol) was added into the reacting solution. 30-min later, the reaction mixture was cooled to room temperature and concentrated under vacuum. The resulting residue was finally purified by silica gel chromatography (CH_2Cl_2: CH_3OH = 5:1, *v/v*) to afford compound **3** as a deep green solid (310 mg, 80.8% yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.29 (d, J = 14.1, 2 H), 7.65 (d, J = 7.3 Hz, 2 H), 7.56 (d, J = 8.0 Hz, 2 H), 7.45 (dd, J = 11.8, 4.4 Hz, 2 H), 7.30 (t, J=7.5 Hz, 2H), 6.56 (d, J = 14.2 Hz, 2 H), 4.43-4.40 (m, 4H), 2.77 (t, J = 5.7 Hz, 4 H), 2.61 (t, J = 6.7 Hz, 4 H), 2.09-2.03 (m, 4H), 1.87-1.85 (m, 2H), 1.70 (s, 12H) ppm,

^{13}C NMR (125 MHz, DMSO-d_6): δ 172.74, 148.49, 143.70, 142.62, 141.65, 129.10, 127.10, 125.54, 122.92, 112.04, 102.48, 60.87, 49.43, 48.29, 43.39, 35.17, 28.02, 26.50, 23.96, 21.07, 19.11, 14.32 ppm.

1.4. Synthesis of Compound 4

Resorcinol (86.0 mg, 0.78 mmol) and triethylamine (0.3 mL) were placed in a flask containing DMF (2 mL), and the mixture was stirred at room temperature under N_2 atmosphere for 10 min. Compound **3** (216 mg, 0.31 mmol) in DMF (1.0 mL) was introduced to the mixture via a syringe, and the reaction mixture was heated at 50°C for 4 h. The solution was then removed under reduced pressure. The crude product was purified by silica gel flash chromatography (CH_2Cl_2: CH_3OH = 10:1, *v/v*) to give compound **4** as a blue-green solid (103 mg, 46.6% yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.55 (d, *J* = 14.8 Hz, 1H), 7.76 – 7.71 (m, 2H), 7.54 – 7.41 (m, 4H), 6.90 (d, *J* = 1.8 Hz, 1H), 6.83 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.74 (d, *J* = 14.8 Hz, 1H), 4.55 (t, 2H), 2.72 – 2.67 (m, 4H), 2.60 (t, J = 6.6 Hz, 2H), 2.08 (dt, *J* = 14.1, 7.0 Hz, 2H), 1.84 – 1.77 (m, 2H), 1.75 (s, 6H) ppm, ^{13}C NMR (125 MHz, DMSO-d_6): δ 177.27, 162.27, 161.27, 154,64, 145.21, 142.42, 142.00, 134.57, 129.68, 129.33, 127.11, 126.31, 123.17, 115.12, 114.87, 114.66, 113.44, 104.59, 102.44, 50.60, 48.07, 44.14, 28.87, 28.05, 24.32, 22.89, 20.59 ppm, MS (ESI, *m/z*) Calcd for $[C_{28}H_{29}NO_5S - H]^-$, 490.18, Found, 490.18.

2. Determination of Quantum Yields

The quantum yields for fluorescence were obtained by comparison of the integrated area of the corrected emission spectrum of the samples with that of a solution of rhodamine B standard ($\emptyset_s$ = 0.89 in ethanol).[S1] The quantum efficiency of probe **NIR-DNP** and compound **4** was measured in methanol. The quantum yields were calculated with the following equation:[S2]

$$\emptyset_u = \emptyset_s * (A_s/A_u) * (F_u/\,) *(\lambda_{exs}/\,\lambda_{exu}) * (n_u/n_s)^2 \qquad \text{(Eq. 1)}$$

where ∅ is the quantum yield, subscript *s* stands for the reference and *u* for the sample, *A* is the absorbance at the excitation wavelength, λ_{ex} is the excitation wavelength, *n* is the refractive index, and *F* is the emission integrated area.

Table S1. Fluorescence quantum yields of **NIR-DNP** and compound **4**

Series	Maximum absorption wavelength (nm)	Maximum absorption	Start (nm)	End (nm)	Integral area of discharge	Fluorescence quantum yield
Rhodamine B	545	0.011	505	700	16476.557	0.89
NIR-DNP	595	0.022	660	800	629.227	0.006
Compound **4**	665	0.031	660	800	5406.883	0.031

3. Sensing Property of Probe NIR-DNP for H_2S

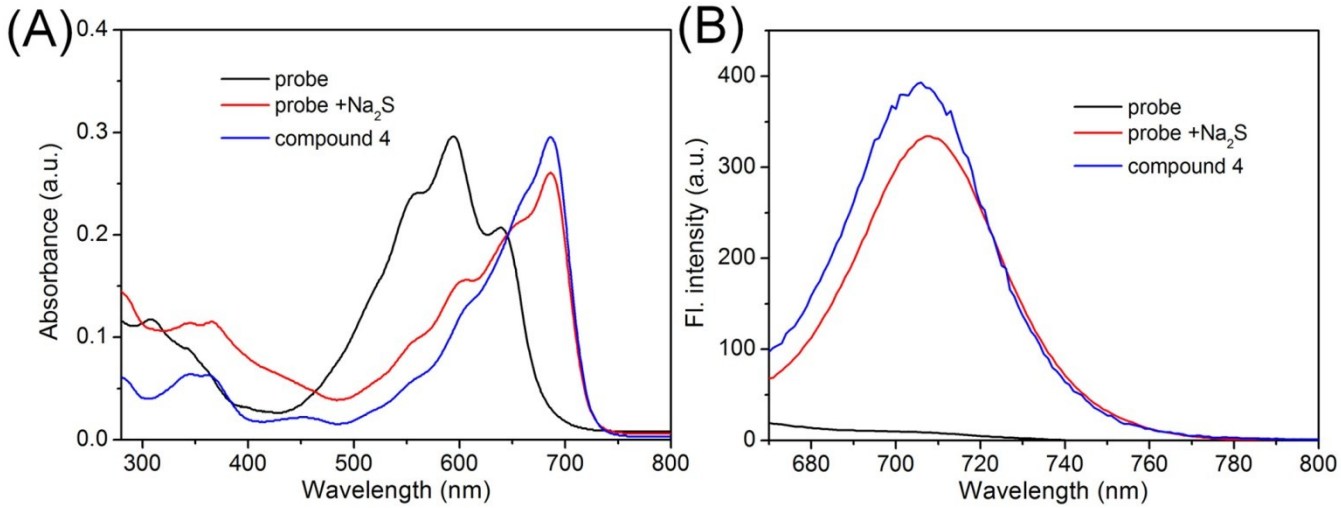


Fig. S1 (A) Absorption and (B) fluorescence emission spectra of compound **4** (10 μM, blue line) and probe **NIR-DNP** (10 μM), before (black line) and after reacted with Na_2S (500 μM, red line) in PBS (20 mM, pH 7.4) containing 10% DMSO (v/v).

In kinetic studies of the probe for H_2S detection, the apparent rate constant k_{obs} for the reaction of **NIR-DNP** with Na_2S was determined by fitting the fluorescence intensities to the pseudo-first-order equation:[S3]

$$ln[(F_{max} - F_t)/F_{max}] = -k_{obs}t \qquad \text{(Eq. 2)}$$

where F_t and F_{max} are respectively the fluorescence intensities at 707 nm at a time t and the maximum value obtained after the reaction completed.

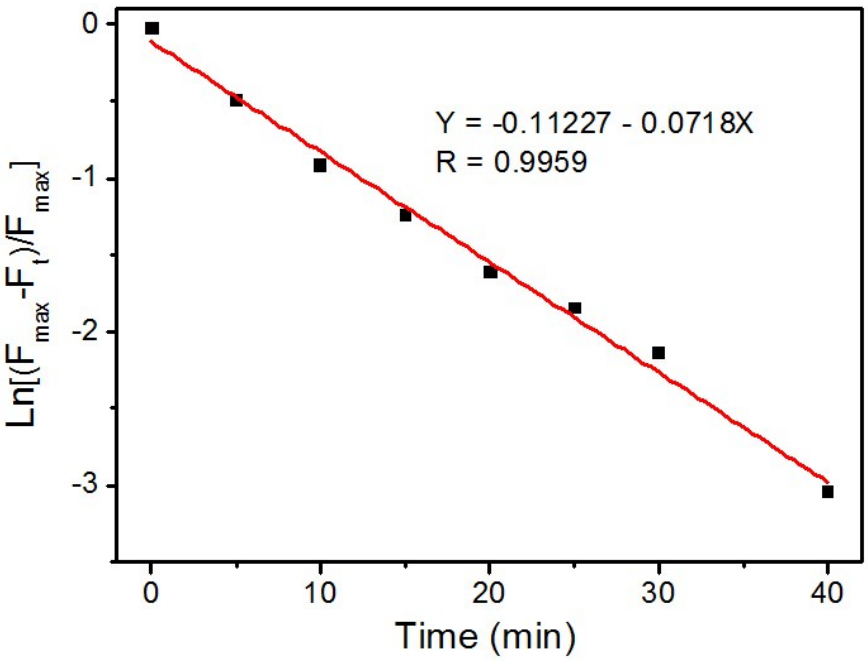


Fig. S2 The pseudo-first-order kinetic plot of the reaction of probe **NIR-DNP** (10 μM) with Na_2S (500 μM) in PBS (20 mM, pH 7.4) containing 10% DMSO (v/v).

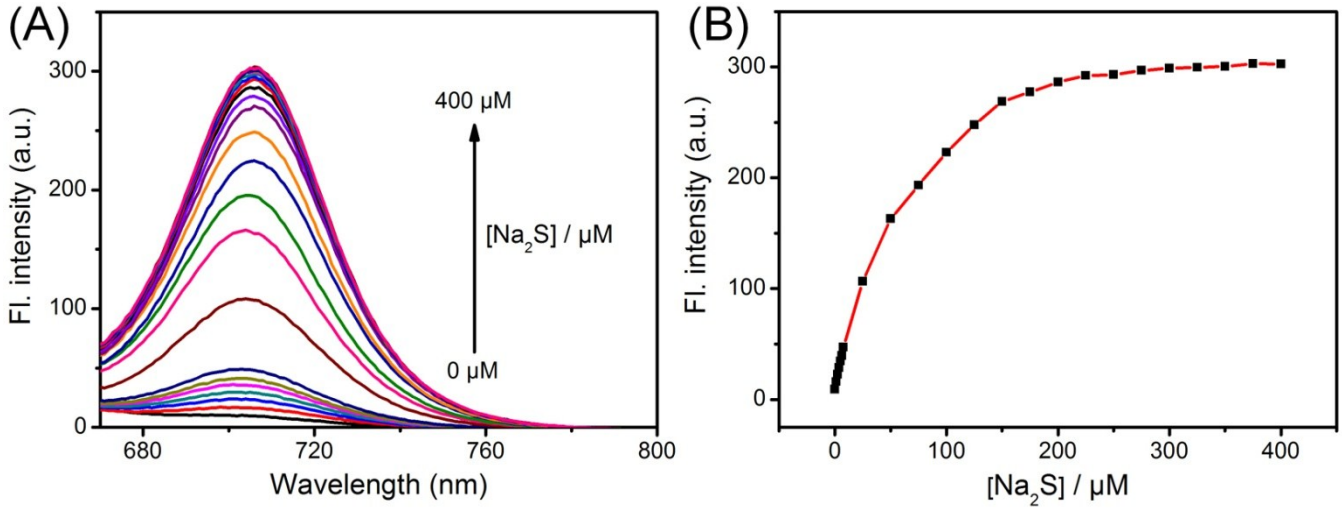


Fig. S3 (A) Fluorescence spectra of probe **NIR-DNP** (10 μM) upon addition of various concentrations of Na_2S (0-400 μM) in PBS (20 mM, pH 7.4) containing 10% DMSO (v/v). (B) Fluorescence intensity changes of probe **NIR-DNP** (10 μM) at 707 nm upon addition of various concentrations of Na_2S (0-400 μM).

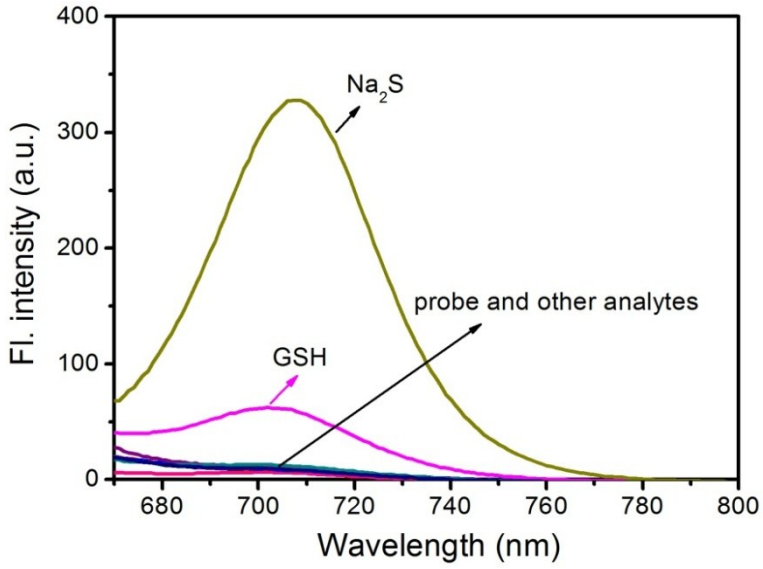


Fig. S4 Fluorescence spectra of **NIR-DNP** (10 μM) upon addition of various species (1 mM Cys, 5 mM GSH and 500 μM others) in PBS (20 mM, pH 7.4) containing 10% DMSO (v/v).

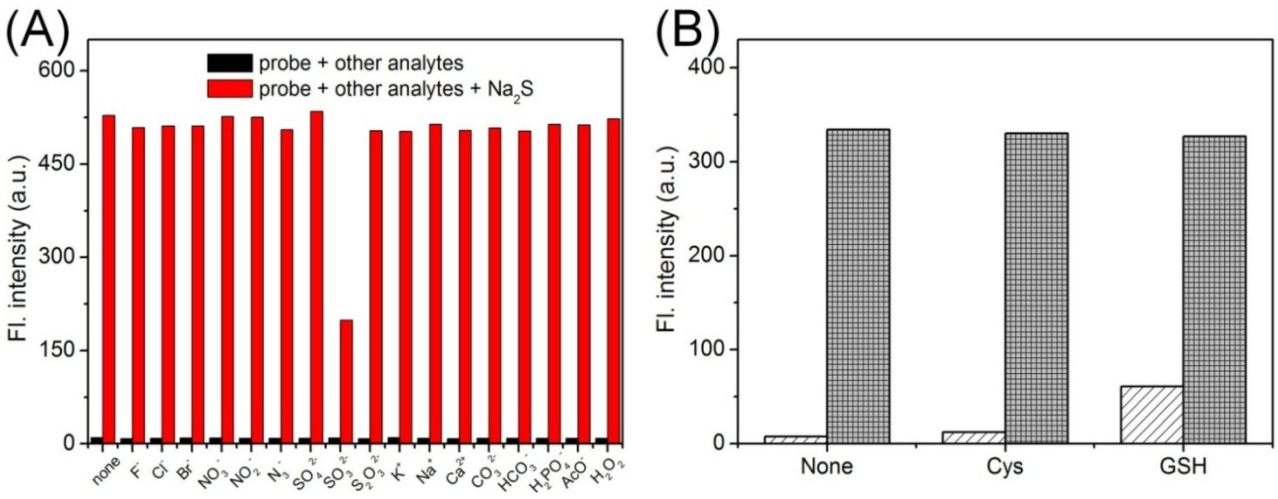


Fig. S5 (A) Fluorescence responses of probe **NIR-DNP** (20 μM) to Na_2S (100 μM) at 707 nm in the absence and presence of various analytes in PBS (20 mM, pH 7.4) containing 10% DMSO (v/v). Black columns: probe or probe treated with the marked analytes. Red columns: probe treated with the marked analytes followed by the addition of Na_2S (100 μM). (B) Fluorescence responses of probe **NIR-DNP** (10 μM) to Na_2S (500 μM) at 707 nm in the absence and presence of biothiols: Cys (1 mM) and GSH (5 mM) in PBS (20 mM, pH 7.4) containing 10% DMSO (v/v). Bar with oblique lines: probe **NIR-DNP** or probe **NIR-DNP** with biothiol (Cys or GSH). Bar with squares: probe **NIR-DNP** or probe **NIR-DNP** with biothiol (Cys or GSH) in the presence of Na_2S (500 μM).

4. Sensing Property of Probe NIR-DNP for SO_3^{2-}.

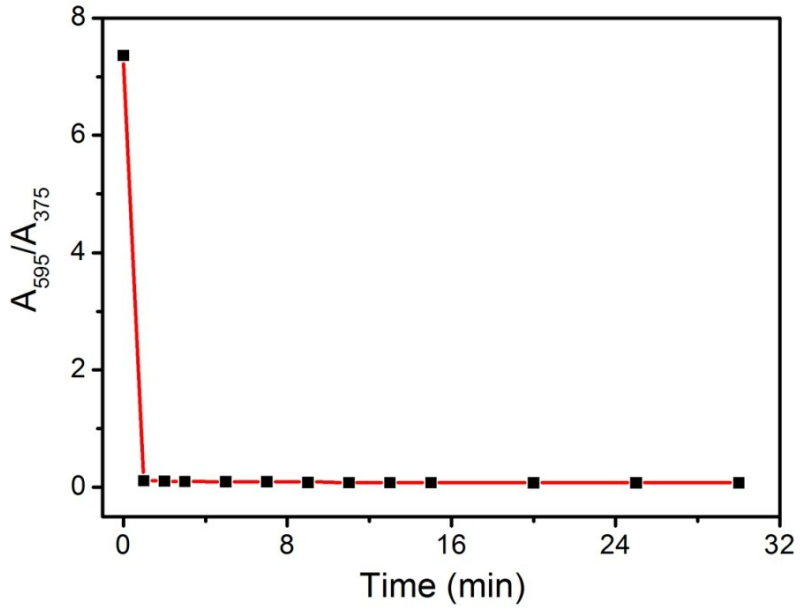


Fig. S6 The A_{595}/A_{375} ratio plot of probe **NIR-DNP** (10 μM) vs time in the presence SO_3^{2-} (500 μM) in PBS (20 mM, pH 7.4) containing 10% DMSO (v/v).

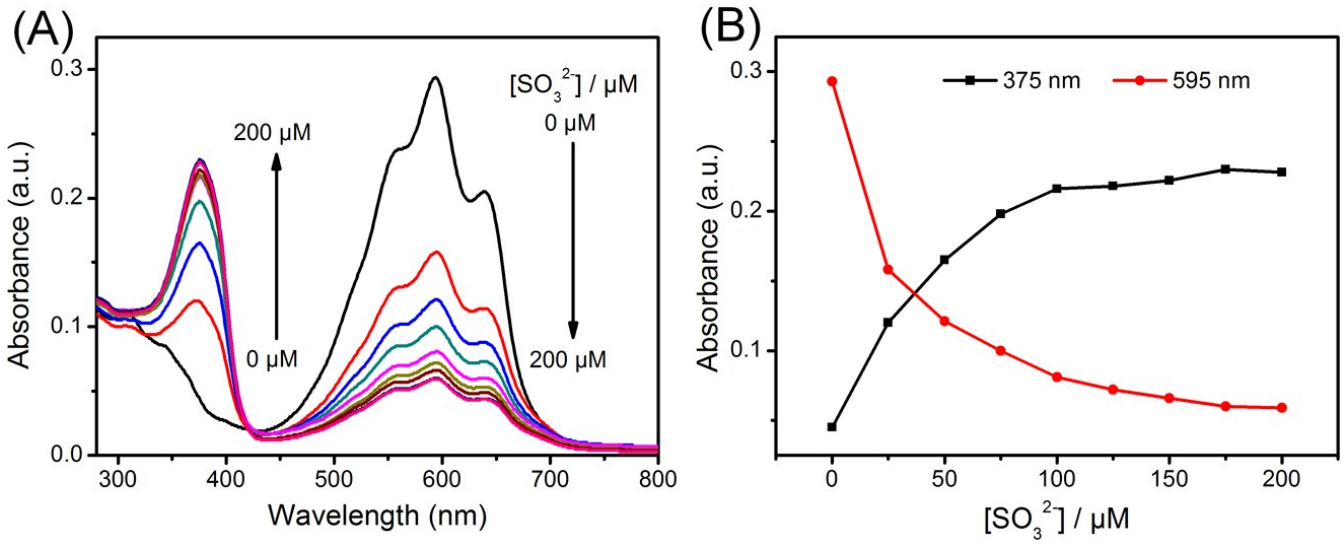


Fig. S7 (A) Absorption spectra of **NIR-DNP** (10 μM) upon addition of various concentrations of SO_3^{2-} (0-200 μM) in PBS (20 mM, pH 7.4) containing 10% DMSO (v/v). (B) Absorbance changes at 595 nm and 375 nm of NIR-DNP (10 μM) upon addition of various concentrations of SO_3^{2-} (0-200 μM) in PBS (20 mM, pH 7.4) containing 10% DMSO (v/v).

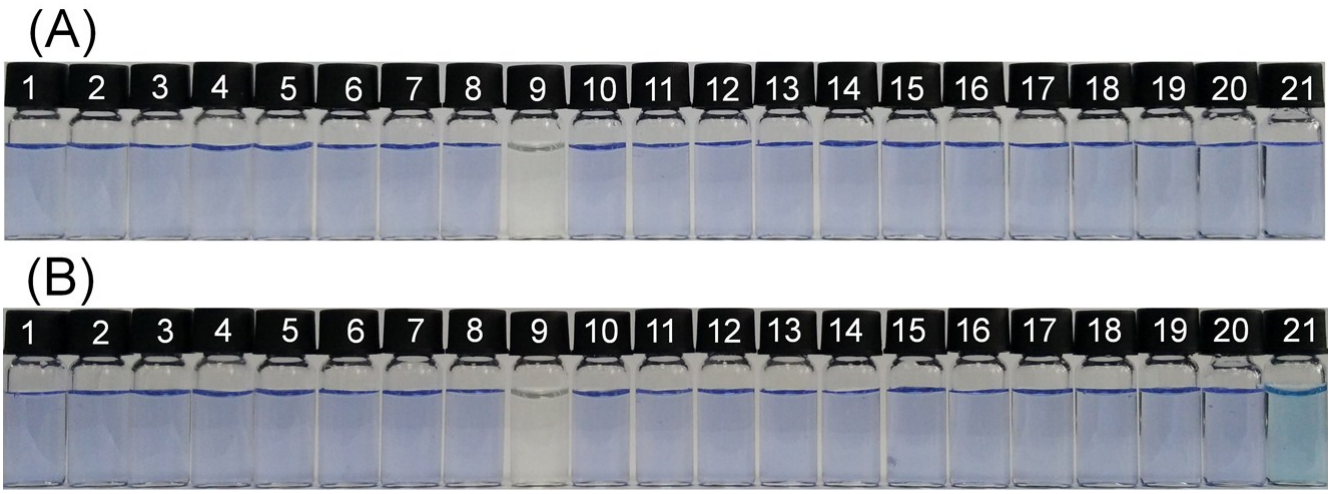


Fig. S8 Colour changes of probe **NIR-DNP (**10 μM**)** solutions under visible light after the addition various species for 3min (A) and 45 min (B): 1, probe alone, 2, F^-, 3, Cl^-, 4, Br^-, 5, NO_3^-, 6, NO_2^-, 7, N_3^-, 8, SO_4^{2-}, 9, SO_3^{2-}, 10, $S_2O_3^{2-}$, 11, K^+, 12, Na^+, 13, Ca^{2+}, 14, CO_3^{2-}, 15, HCO_3^-, 16, $H_2PO_4^-$, 17, AcO^-, 18, H_2O_2, 19, Cys, 20, GSH, 21, Na_2S (1 mM Cys, 5 mM GSH and 500 μM others).

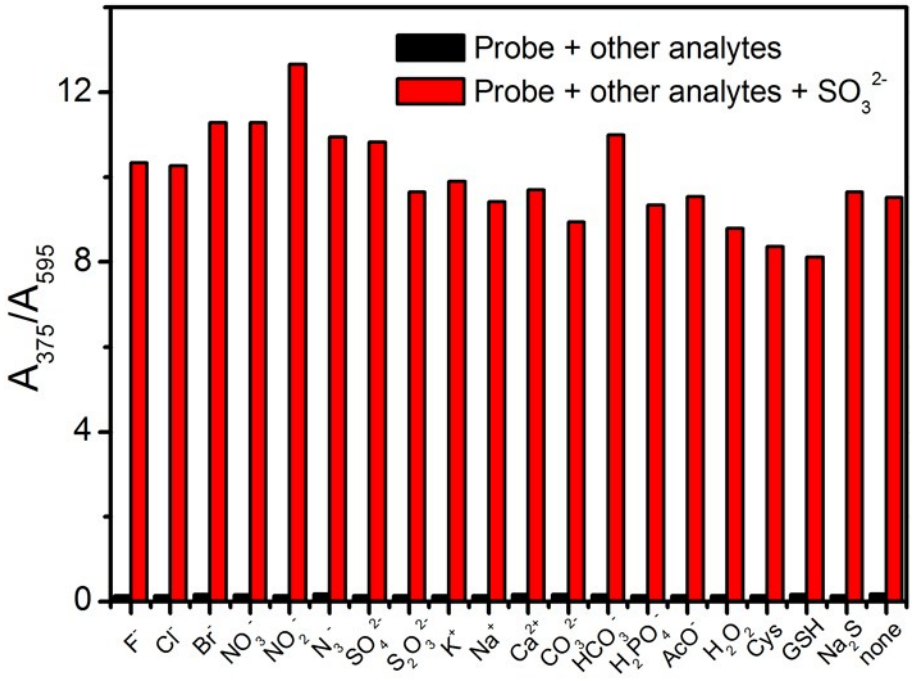


Fig. S9 Absorbance ratio (A_{375}/A_{595}) responses of **NIR-DNP** (10 μM) in PBS (20 mM, pH 7.4) containing 10% DMSO (v/v). Black bars: probe or probe treated with the marked analytes. Red bars: probe treated with the marked analytes followed by the addition 50 equiv. of SO_3^{2-}.

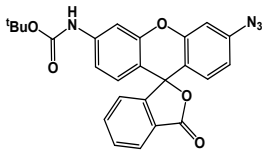
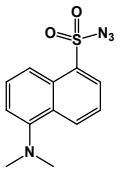
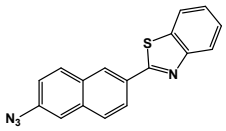
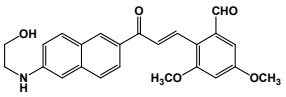
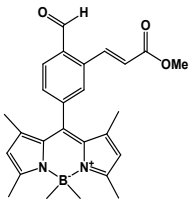
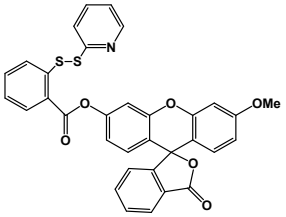
5. Calculation of the Detection Limit

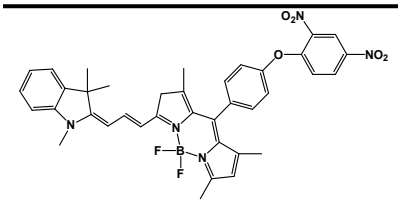
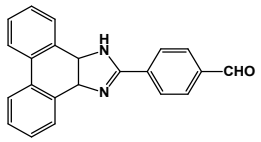
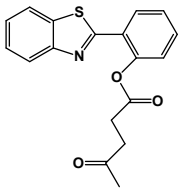
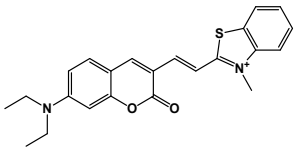
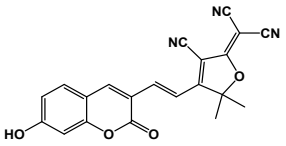
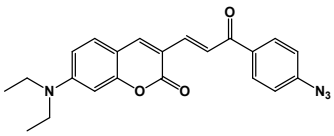
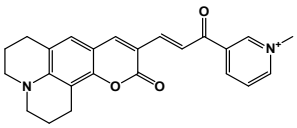
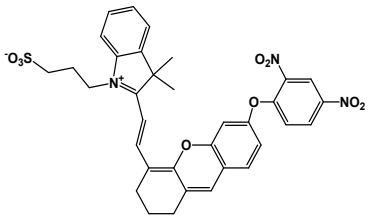
The detection limit was calculated with the following equation:

$$\text{Detection limit} = 3S_b/k \qquad \text{(Eq. 3)}$$

where S_b is the standard deviation of blank measurements, which was achieved by measuring the absorption or fluorescence spectrum of probe **NIR-DNP** ten times, and k is the slope of the fitted line.

Table S2. Comparison of probe NIR-DNP and the existed probes for H_2S and SO_3^{2-}

Probe	Analytes	$\lambda_{ex}/\lambda_{em}$ (nm)	Detection medium	Detection limit	Ref.
	H_2S	490/525	HEPES (pH 7.4), 0.2% DMF	5-10 μM	S4
	H_2S	340/535	PBS (pH 7.4), 0.5% Tween-20	1 μM	S5
	H_2S	360/480	HEPES (pH 7.4), 80% DMF	0.1 μM	S6
	H_2S	360/480	HEPES (pH 7.4), 1% CH_3CN	50 nM	S7
	H_2S	465/510	PBS (pH7.0), 1% DMSO	5 μM	S8
	H_2S	465/515	PBS (pH 7.4), 10% CH_3CN	1-10 μM	S9

	H_2S	650/708	PBS (pH 7.0), 20% ethanol, 3mM CTAB	0.1 μM	S10
	SO_3^{2-}	330/395	Na_2HPO_4-citric acid (pH 5.0), 30% DMF	2 μM	S11
	SO_3^{2-}	310/468	HEPES (pH 7.4), 30% CH_3CN	5 μM	S12
	SO_3^{2-}	445478	HEPES (pH 7.4), 30% DMF	0.38 μM	S13
	SO_3^{2-}	466/523	HEPES buffer (pH 7.4)	27 nM	S14
	Colorimetric: H_2S: orange to yellow; SO_3^{2-}: orange to colorless. Fluorescence: SO_3^{2-}: red to blue.	410/460 410/590	PBS (pH 7.4), 0.05% DMF 1mM CTAB	H_2S: no SO_3^{2-}: 0.1 μM	S15
	The same signal response with kinetic discrimination	450/515	PBS (pH 7.4), 0.3% DMF	H_2S: 0.27 μM SO_3^{2-}: 0.85 μM	S16
	Colorimetric: H_2S: purple to cyan; SO_3^{2-}: purple to colorless. Fluorescence: H_2S: no to NIR	650/707	PBS (pH 7.4), 10% DMSO	H_2S: 36.53 nM SO_3^{2-}:33.33 nM	This work

6. Data for Investigation of the Sensing Mechanisms.

6.1. Sensing Mechanism Studies of Probe NIR-DNP for H_2S

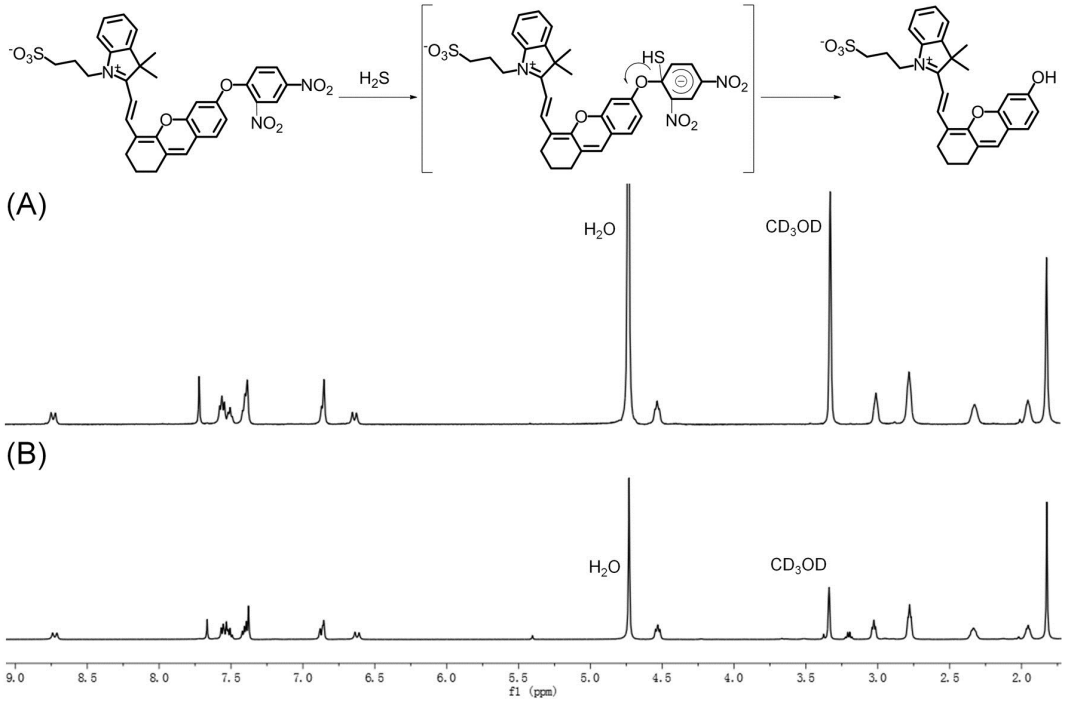


Fig. S10 (A) ^{1}H NMR spectrum of the isolated product after probe **NIR-DNP** was reacted with Na_2S. (B) ^{1}H NMR spectrum of compound **4**.

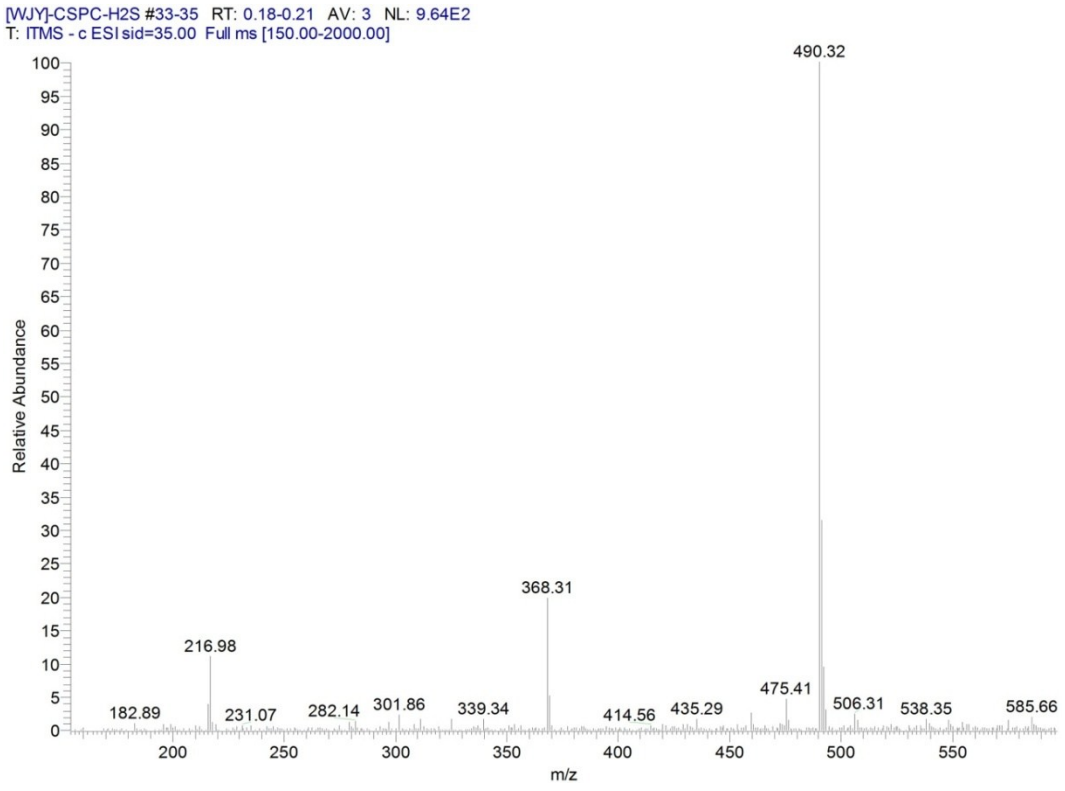


Fig. S11 ESI-MS of thiolysis product of **NIR-DNP** incubated with Na_2S.

6.2 Density Functional Theory Calculation

The ground state structures of compound **4** and **NIR-DNP** were optimized using DFT with B3LYP functional and 6–31 G basis set. The initial geometries of the compounds were generated by the Gauss View software. The excited state related calculations (UV–vis absorption) were carried out with the time dependent DFT (TDDFT) with the optimized structure of the ground (DFT/6–31 G). The emission of the fluorophores was calculated based on the optimized S1 excited state geometry. All of these calculations were performed with Gaussian 09 (Revision A.01).

Table S3. Selected electronic excitation energies (eV), oscillator strengths (*f*), main configurations, and CI Coefficients of the low-lying excited states of **NIR-DNP** and compound **4**. The data were calculated by TDDFT//B3LYP/6-31G based on the optimized ground state geometries.

Molecule	**Electronic transition**	**TDDFT/ B3LYP/6-31G SCRF=(Solvent=water)**				
		Energy[a] (eV)	**Wavelength** (nm)	***f***[b]	**Main configurations**[c]	**CI coefficients**[d]
NIR-DNP	S_0 -> S_1	1.9221 eV	645.04 nm	0.0359	HOMO→LOMO HOMO→LOMO + 1	0.64688 0.28021
	S_0 -> S_2	1.9952 eV	621.42 nm	0.0061	HOMO→LOMO HOMO→LOMO + 1	0.28122 0.64810
	S_0 -> S_3	2.3580 eV	525.80 nm	1.2732	HOMO→LOMO + 2	0.70560
	S_0 -> S_4	2.9578 eV	419.18 nm	0.0027	HOMO -1→LOMO HOMO -1→LOMO + 2	0.48388 0.50988
Compound 4	S_0 -> S_1	2.3137 eV	535.87 nm	1.2744	HOMO→LOMO	0.70895
	S_0 -> S_2	3.1010 eV	399.82 nm	0.0022	HOMO -1→LOMO	0.70514

[a]Only selected excited states were considered. [b]Oscillator strength. [c]only main configurations are presented. [d]The CI coefficients are in absolute values.

6.3 Sensing Mechanism Study of Probe NIR-DNP for SO_3^{2-}

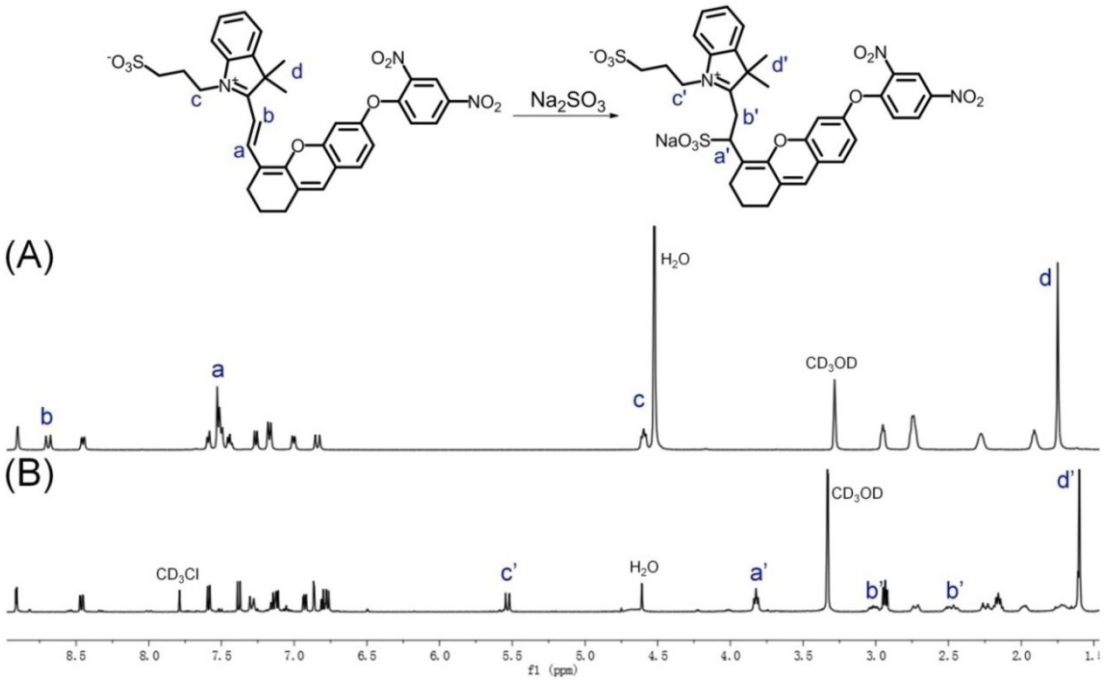


Fig. S12 (A) ^{1}H NMR spectrum of probe **NIR-DNP**. (B) ^{1}H NMR spectrum of probe **NIR-DNP** upon addition of Na_2SO_3 (1:2, n/n) in CD_3OD (with 10% D_2O, v/v).

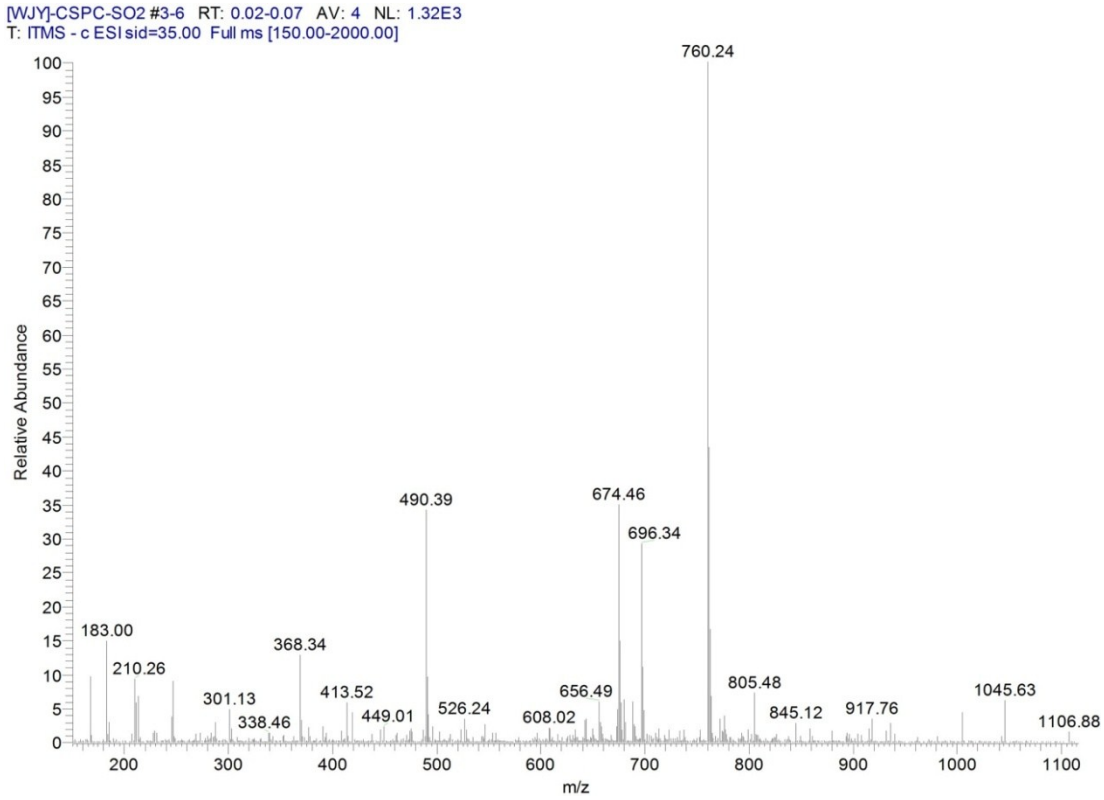


Fig. S13 ESI-MS of probe **NIR-DNP** treated with Na_2SO_3.

7. Effect of pH

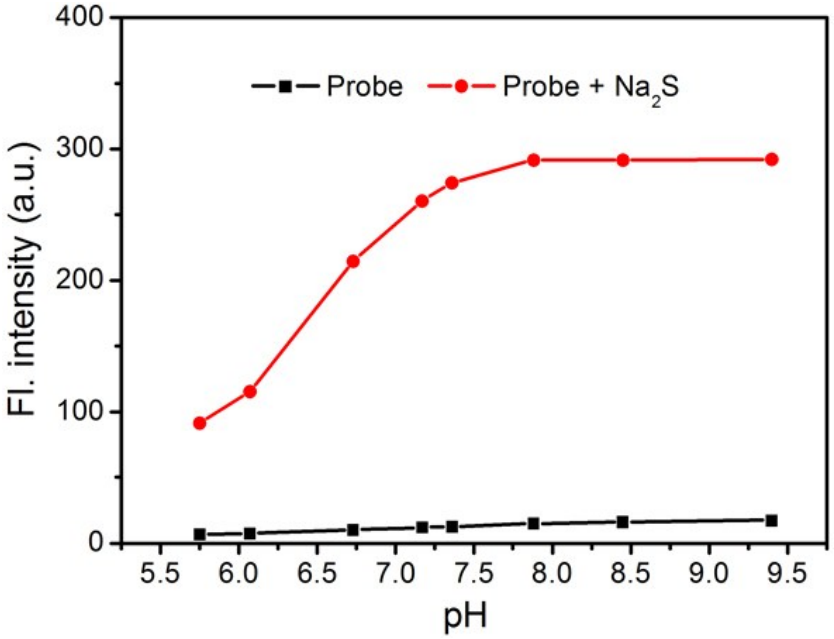


Fig. S14 The effect of pH on the fluorescence intensity of probe **NIR-DNP** (10 μM) in the absence (■) or presence (●) of Na_2S (500 μM).

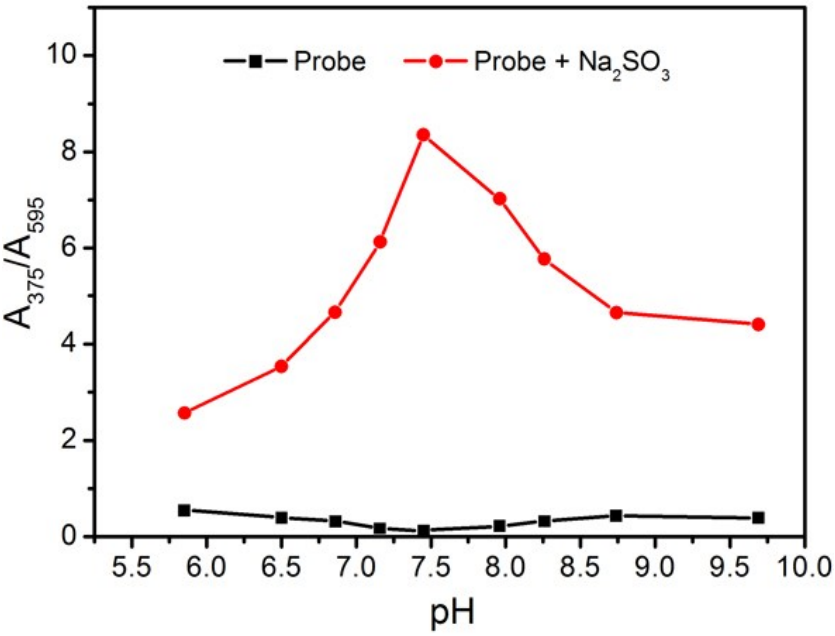


Fig. S15 The effect of pH on absorbance ratio of probe **NIR-DNP** (10 μM) in the absence (■) or presence (●) of Na_2SO_3 (500 μM).

7.1. Calculation of pKa Value.

The pKa value for compound **4** was estimated from the changes in the fluorescence intensity with

various pH values by using the relationship, log [(R_{max}–R)/(R–R_{min})] = pH–pKa.[S17] R is the ratio of emission intensity at two wavelengths. R_{max} and R_{min} are maximum and minimum limiting values of R, respectively. The pKa value (y-intercept) was derived from the plot of pH *v.s.* log [(R_{max}–R)/(R–R_{min})].

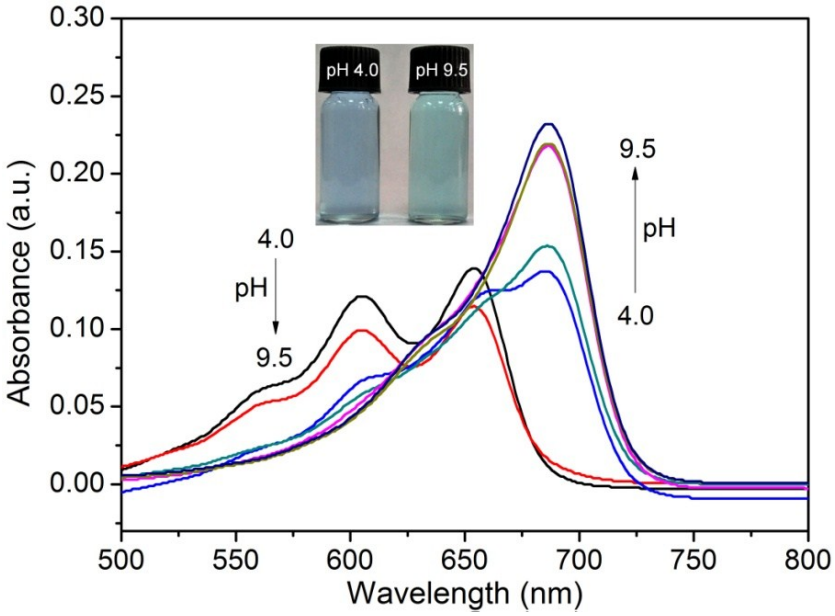


Fig. S16 Absorption spectra of compound **4** (5 μM) in PBS (20 mM) containing 10% DMSO (v/v) at different pH values (4.0, 5.05, 7.07, 7.4, 8.0, 9.0, 9.5). Inset: the change of solution color from pH 4.0 to pH 9.5.

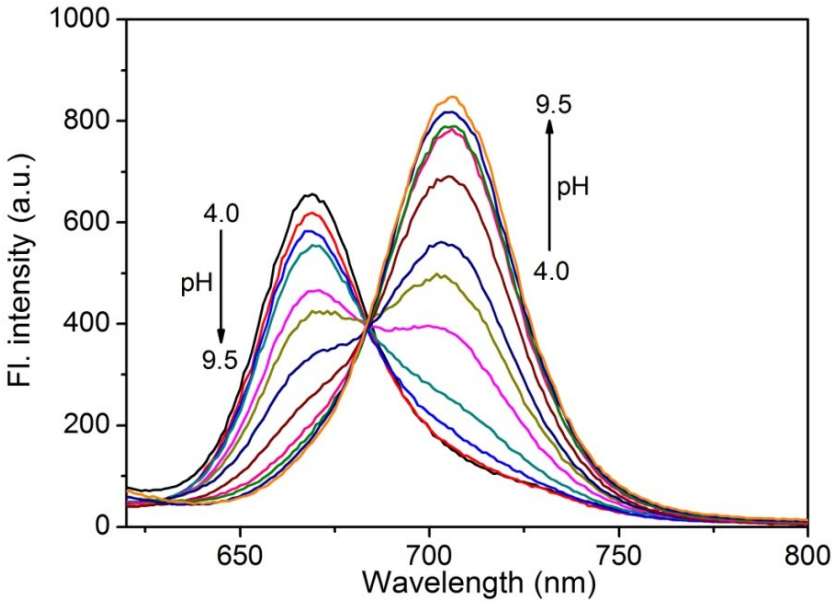


Fig. S17 Fluorescence emission spectra of compound **4** (5 μM) in PBS (20 mM) containing 10% DMSO (v/v) at different pH values (4.0, 5.0, 5.5, 5.95, 6.47, 6.75, 7.05, 7.5, 8.0, 8.25, 8.63, 9.5).

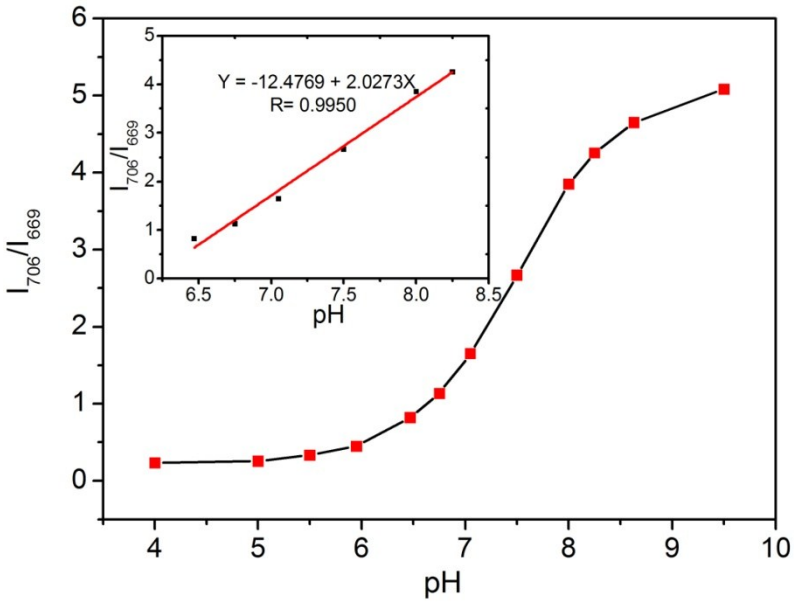


Fig. S18 Plots of I_{706}/I_{669} (ratio of the fluorescence intensity of compound **4** at λ = 706 nm and λ = 669 nm) versus pH for compound **4** (5 μM). Inset: the linear relationship between I_{706}/I_{669} and pH values in the range pH 6.47-8.25.

8. MTT Assay and Cell Imaging

U-251 cells were obtained from the Chinese Academy of Sciences (Shanghai, China) and routinely cultured with Dulbecco's modified Eagle's medium supplemented with 10% fetal bovine serum, 100 U/mL penicillin, and 100 μg/mL streptomycin at 37°C in 5% CO_2 atmosphere. The cytotoxicity of **NIR-DNP** and Cysteine (Cys) to U-251 cells was determined using MTT assay.

For example, U-251 cells were seeded in 96-well plates at a cell density of 5×10^4 cells/mL (200 μL/well). After 24 h incubation, cells were treated with different concentrations of **NIR-DNP** (0, 5, 10, 20, 40 and 80 μM) and continuously incubated at 37 °C for 24 h. After washing with PBS, cells were further cultured by both MTT solution (5 mg/mL, 50 μL/well) and supplemented cell culture medium (150 μL/well) for 4 h. After that, the supernatant was discarded and the resulting formazan crystals were dissolved in dimethyl sulfoxide (200 μL). The absorbance was measured using a microplate spectrophotometer (model 680, BIO-RAD) at 570 nm. Each experiment was repeated at least five times. Blank controls were run simultaneously during each experiment. The cytotoxicity assay of Cys to U-251 cells has the similar experiment method.

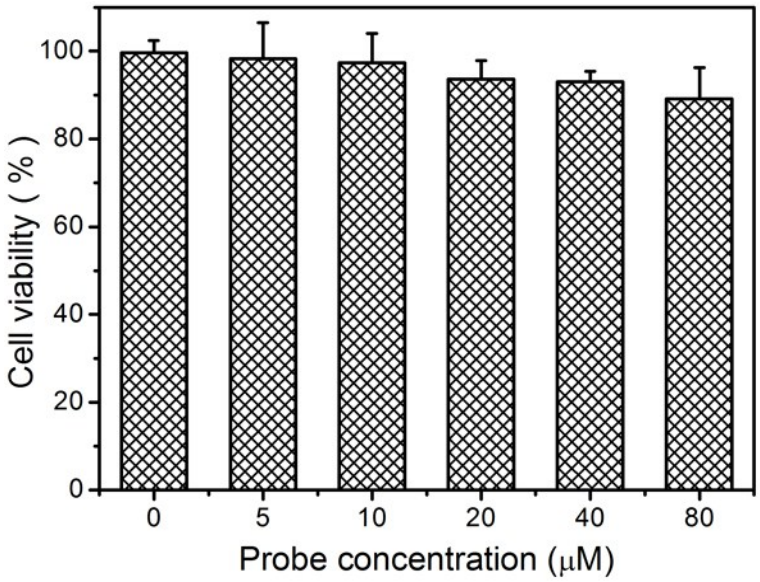


Fig. S19 Cytotoxicity assay of probe **NIR-DNP** for U-251 cell after 24-h culture.

As shown in Fig. S20, the percentage of viable U-251 cells after treatment with 0-500 μM of Cys for 1 h was over 90%, and the cell viabilities still remained above 80% after incubation with 500 μM of Cys for 5 h, which demonstrated that Cys did not show obvious cytotoxicity.

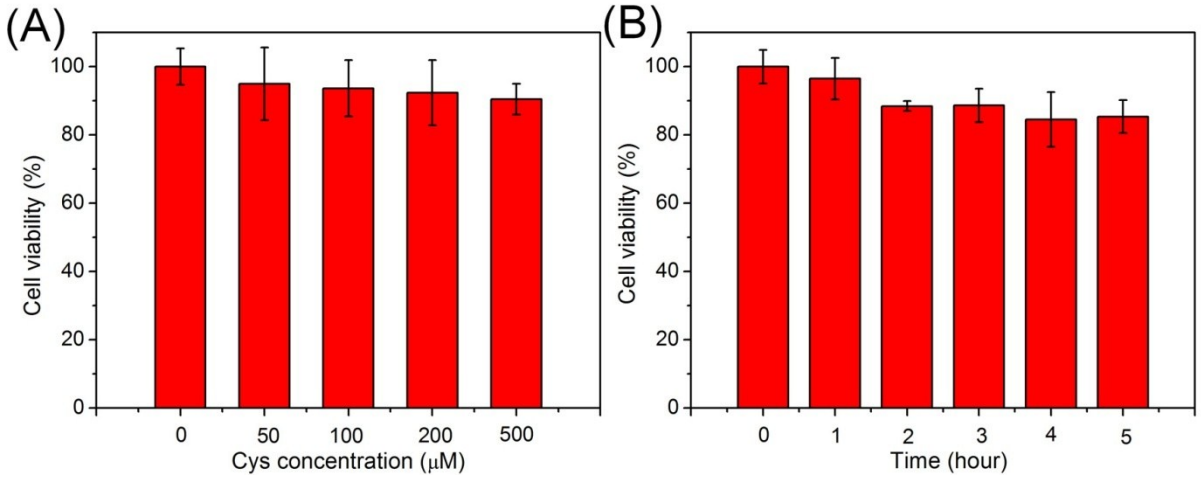


Fig. S20 (A) Cytotoxicity assay of Cys (0-500 μM) for U-251 cells after 1-h culture. (B) Cell viability of Cys (500 μM) at different times in U-251 cells.

Murine hepatocytes (Alpha mouse liver 12 cell line, AML12) were obtained from Chinese Academy of Sciences (Shanghai, China). AML12 hepatocytes were cultured in a medium comprised of 90% DMEM/F-12 medium (1:1, v:v) supplemented with 0.1% ITS Universal Culture Supplement (Corning),

40 ng/mL dexamethasone, 100 U/mL penicillin and 100 μg/mL streptomycin and 10% FBS. All cells were manipulated under sterile tissue culture hoods and maintained at 37°C in a humidified 5% CO_2 incubator. The cells were normally passaged at a ratio of 1:3 every three days to maintain them in the exponential growth phase. For living cell imaging, AML12 hepatocytes were re-seeded on 24-well plate at a density of 5 $\times 10^4$ cells/mL and cultured for 24 h. The cells were incubated with 50 μM probe **NIR-DNP** for 60 min at 37°C before being washed three times with PBS, and then treated with Na_2S (500 μM). After incubation for 60 min, cells were then rinsed with PBS for three times and imaged by an inverted fluorescence microscopy (Olympus CKX41, Japan). For endogenous H_2S imaging, cells were first incubated with thiols (Cysteine, 500 μM) for 60 min at 37 ºC. After washing, the cells were then incubated with **NIR-DNP** (50 μM) for another 60 min. The medium was replaced by PBS and cells were imaged immediately.

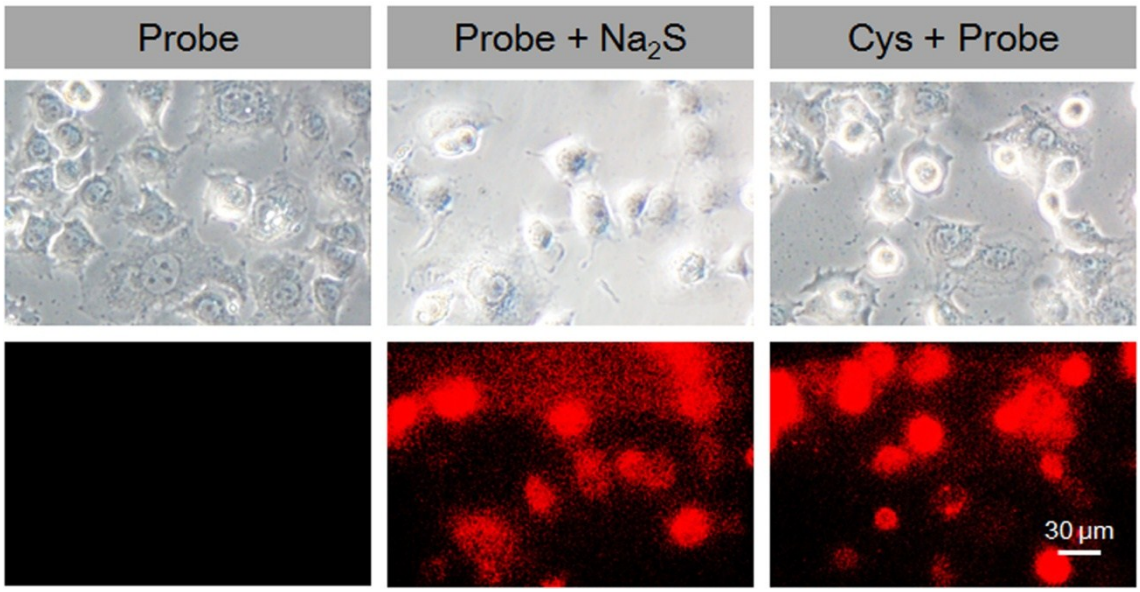


Fig. S21 Fluorescence images of probe **NIR-DNP** in AML12 hepatocytes. From left to right, cells were incubated with the probe **NIR-DNP** (50 μM) for 60 min; cells were first incubated with the probe **NIR-DNP** (50 μM) for 60 min, and then incubated with Na_2S (500 μM) for another 60 min; cells were first incubated with Cys (500 μM) for 60 min, and then incubated with the probe **NIR-DNP** (50 μM) for another 60 min. From top to bottom: bright-field images and fluorescence images, respectively.

9. ^{1}H NMR, ^{13}C NMR, FT-IR and High-resolution Mass Spectra of NIR-DNP

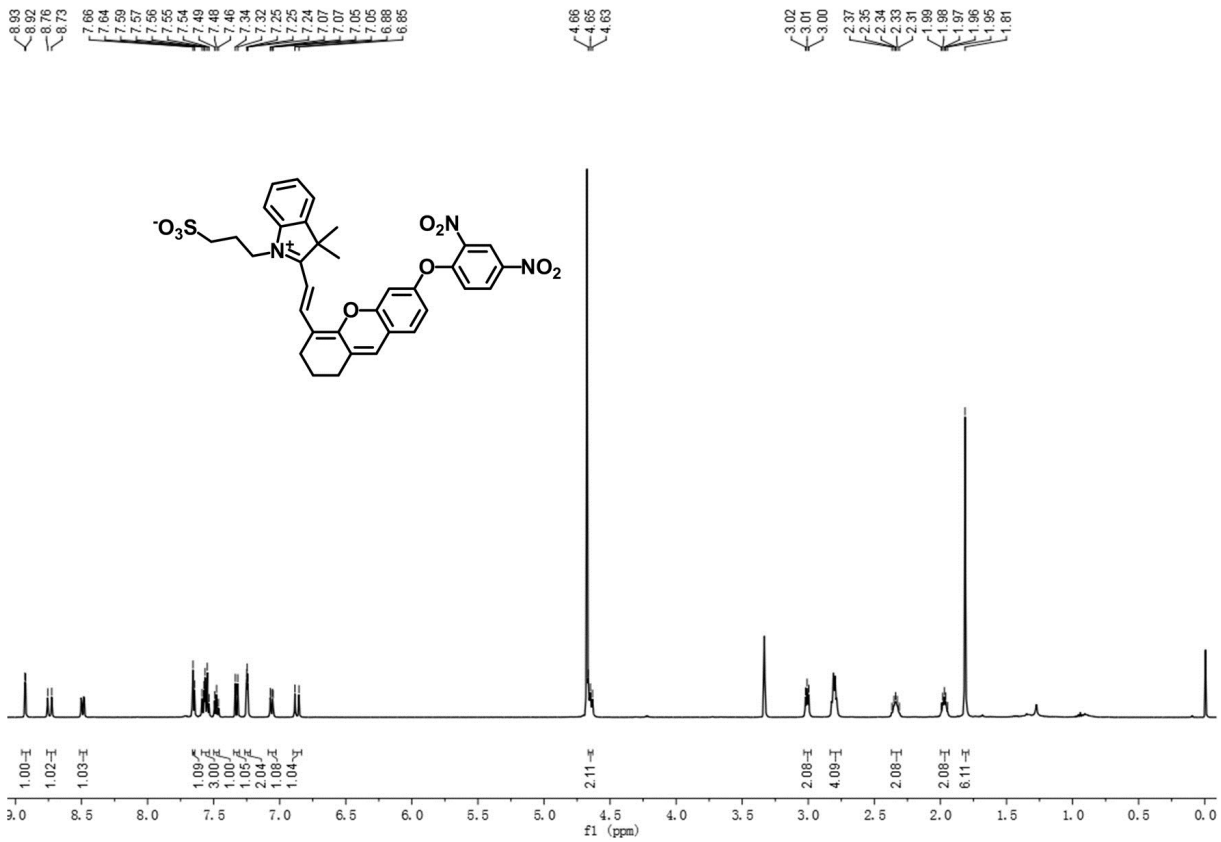


Fig. S22 ^{1}H NMR spectrum of **NIR-DNP** in $CDCl_3$ and CD_3OD.

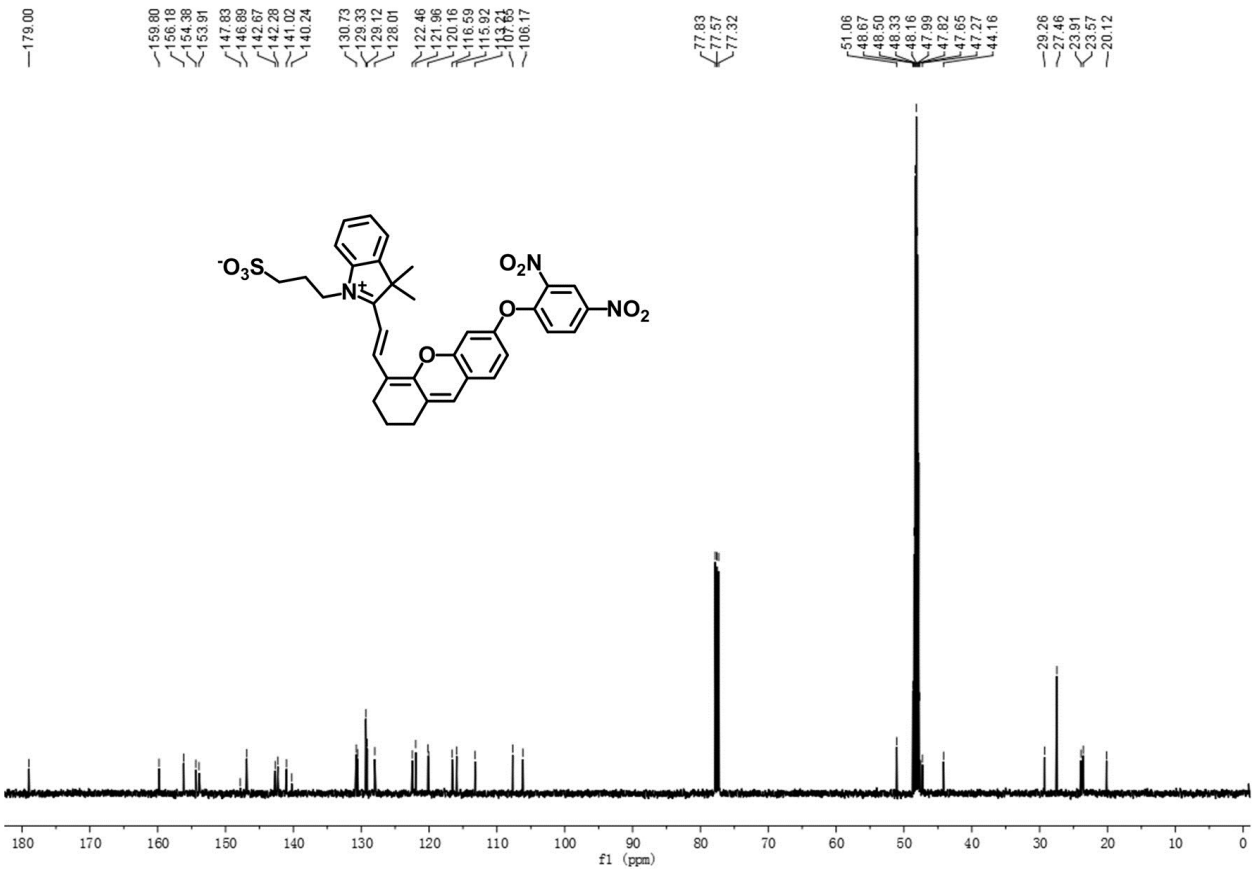


Fig. S23 ^{13}C NMR spectrum of **NIR-DNP** in $CDCl_3$ and CD_3OD.

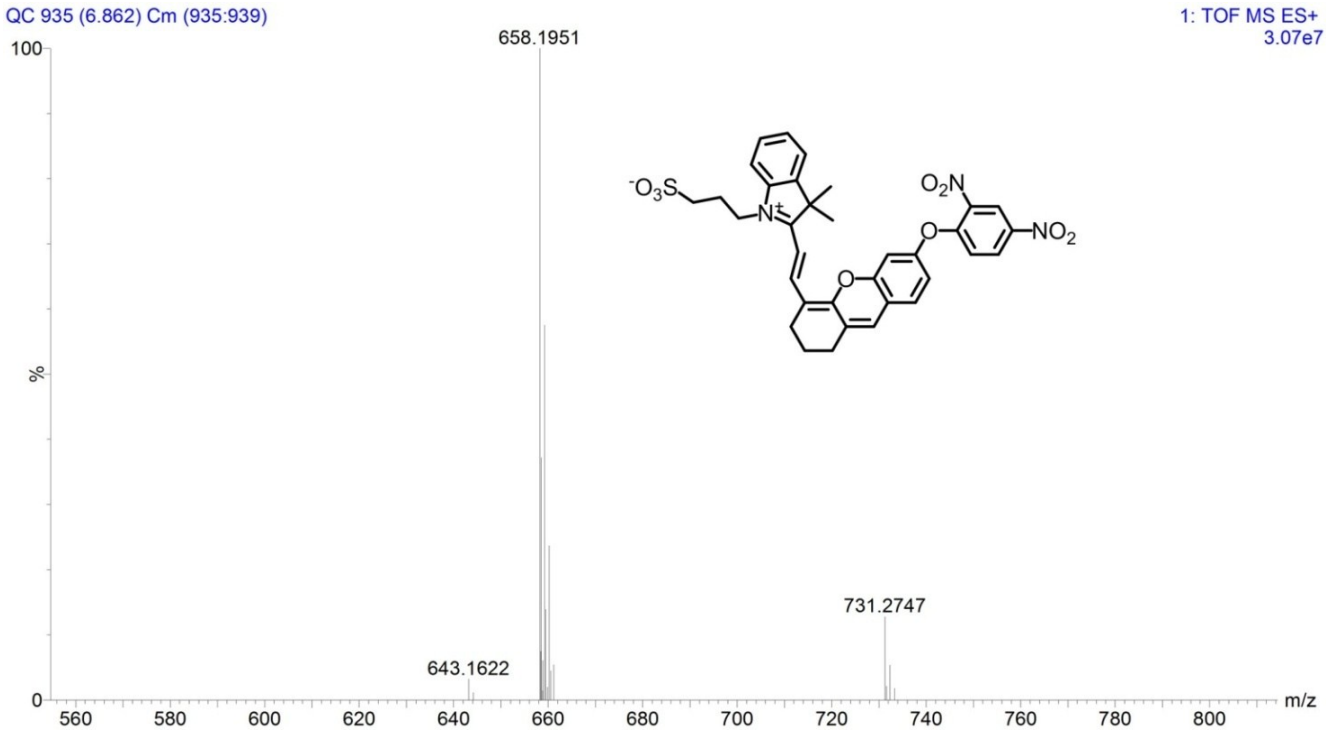


Fig. S24 HRMS of **NIR-DNP**.

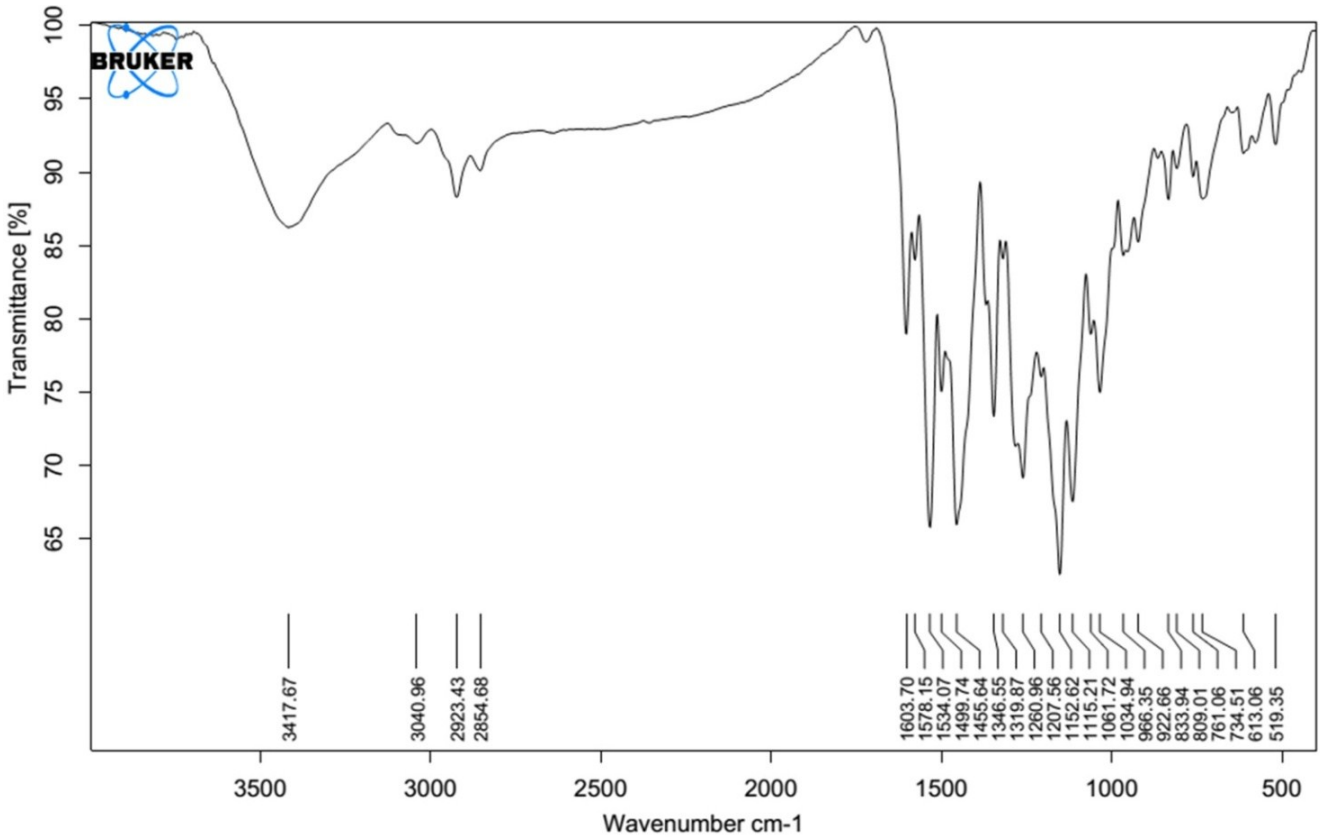


Fig. S25 FT-IR spectrum of **NIR-DNP**.

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