Supporting information for

A near-infrared and two-photon dual-mode fluorescent probe for colorimetric monitoring SO_2 *in vitro* and *in vivo*

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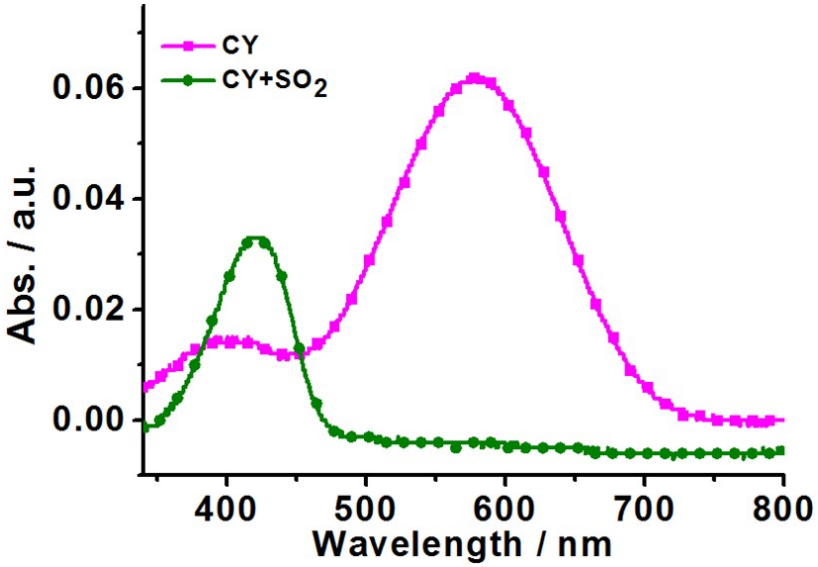

Fig. S1. The absorption spectra of fluorescent probe **CY** in the presence or absence of SO_2.

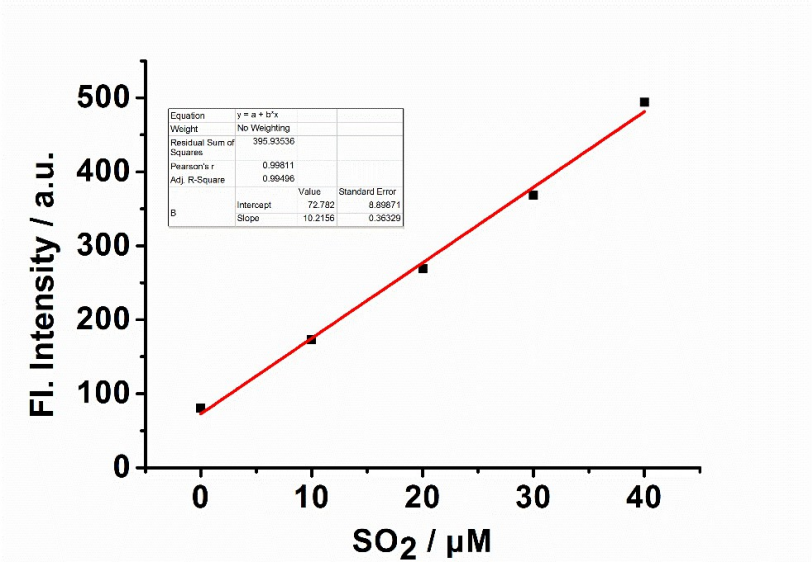

Fig. S2. Linear fit of the fluorescence intensity change at 500 nm with $NaHSO_3$ (0 – 40 μM) excited at 420 nm.

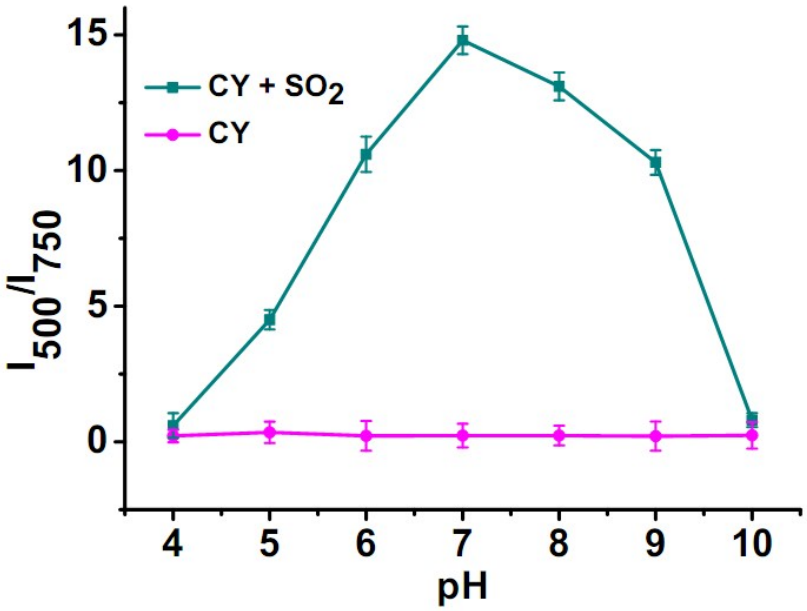

Fig. S3. The fluorescent intensities (I_{500}/I_{750}) of **CY** in the presence or absence of $NaHSO_3$ under various pH (pH = 4.0-10.0) conditions.

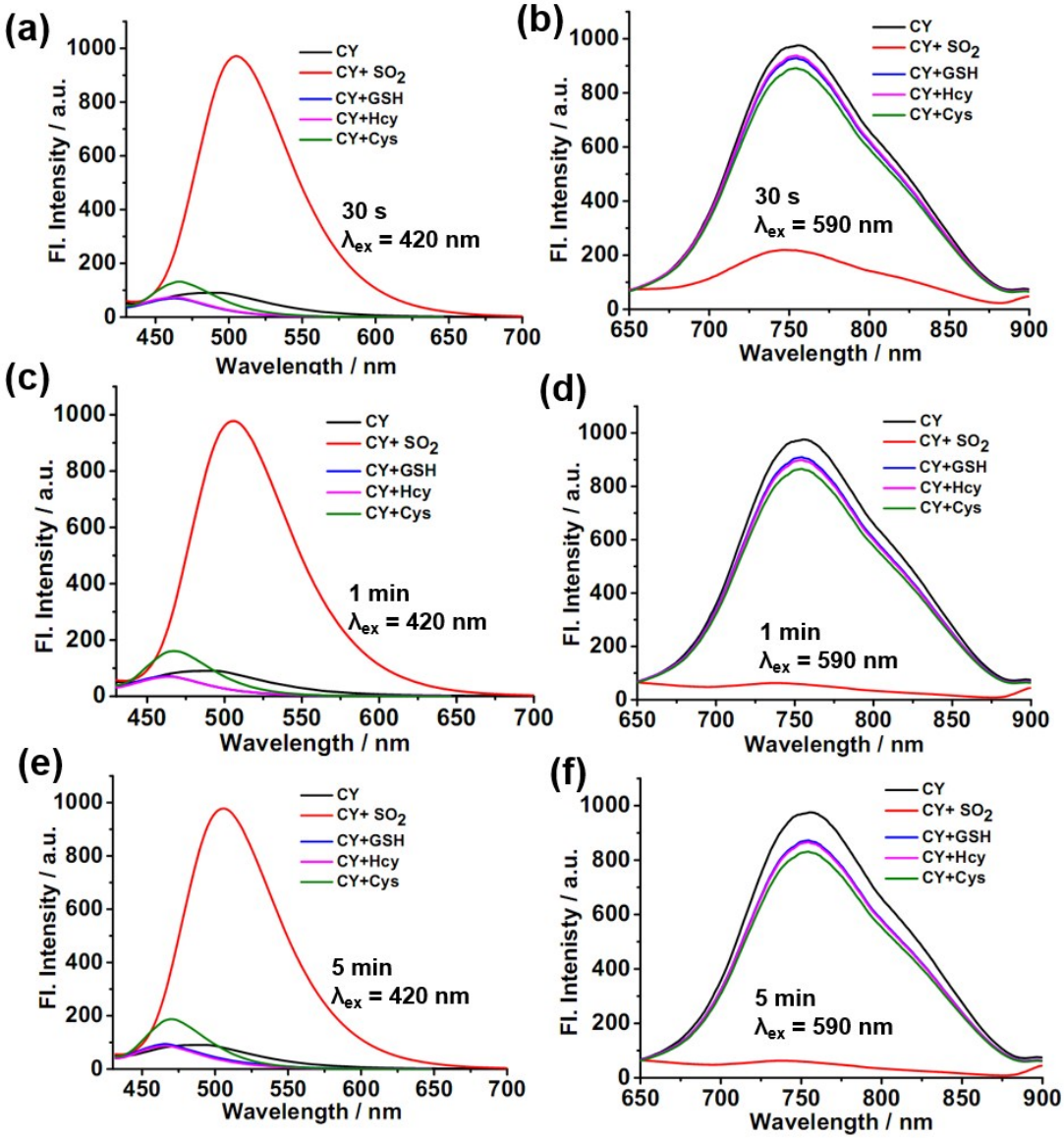

Fig. S4. The time-dependent fluorescent curves of **CY** in the presence or absence of $NaHSO_3$ (100 μM), GSH(100 μM), Cys(100 μM) and Hcy(100 μM) in Hepes buffers(pH 7.4, with 50% acetonitrile). (a,b) 10μM CY encountered with $NaHSO_3$, GSH, Cys and Hcy for 30s; (c,d) 10μM CY encountered with $NaHSO_3$, GSH, Cys and Hcy for 1 min; (e,f) 10μM CY encountered with $NaHSO_3$, GSH, Cys and Hcy for 5 min. λ_{ex}= 420 nm(slit (nm) 5/5), λ_{em} = 430 -700 nm and λ_{ex}= 590 nm(slit (nm) 10/10), λ_{em} = 650 -900 nm.

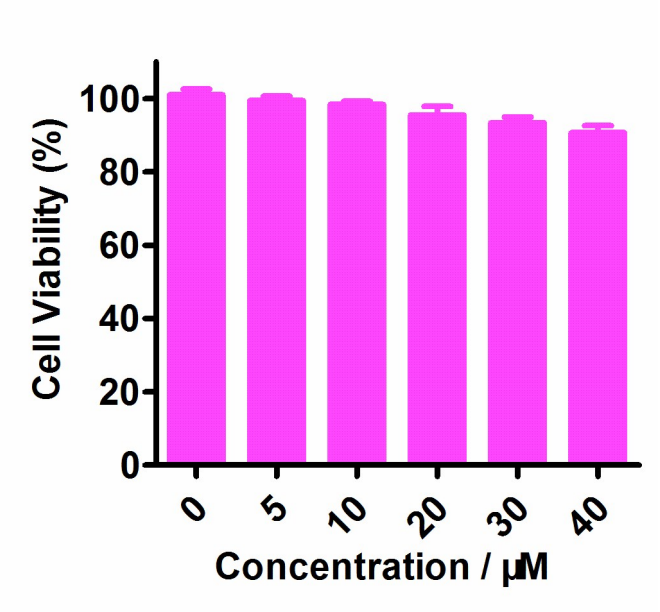

Fig. S5. Cell viability of HepG2 cells treated with different concentrations (0-40 μM) of **CY** for 24 h.

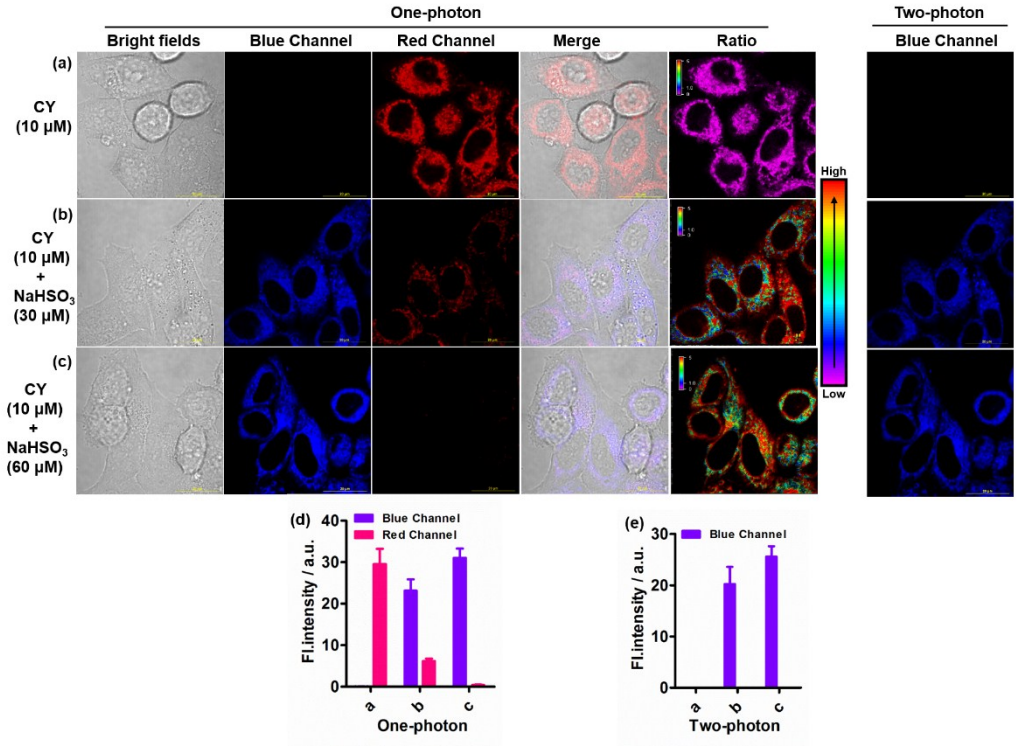

Fig. S6. NIR and two-photon images for detecting exogenous SO_2 in HepG2 cells with probe **CY**. (a) HepG2 cells incubated with 10 μM free **CY** for 30 min; (b) cells were firstly incubated with 10 μM **CY** for 30 min, and then treated with $NaHSO_3$ (30 μM) for another 30 min; (c) cells were incubated with 10 μM **CY** for 30 min and then

treated with $NaHSO_3$ (60 μM) for another 30 min; (d,e) quantified fluorescence intensities of groups a, b, c and d in Blue and Red channel respectively under one- and two-photon modes with Images J. software. Error bars represent standard deviation (±S.D.), n = 3, the statistical analysis was performed from three separate biological replicates. One-photon mode: Blue Channel: λ_{ex} = 404 nm, λ_{em} = 425-475 nm, Red Channel: λ_{ex} = 640 nm, λ_{em} = 663-738nm; two-photon mode: λ_{ex} = 800 nm, λ_{em} = 425-475 nm. Scale bar: 20 μm.

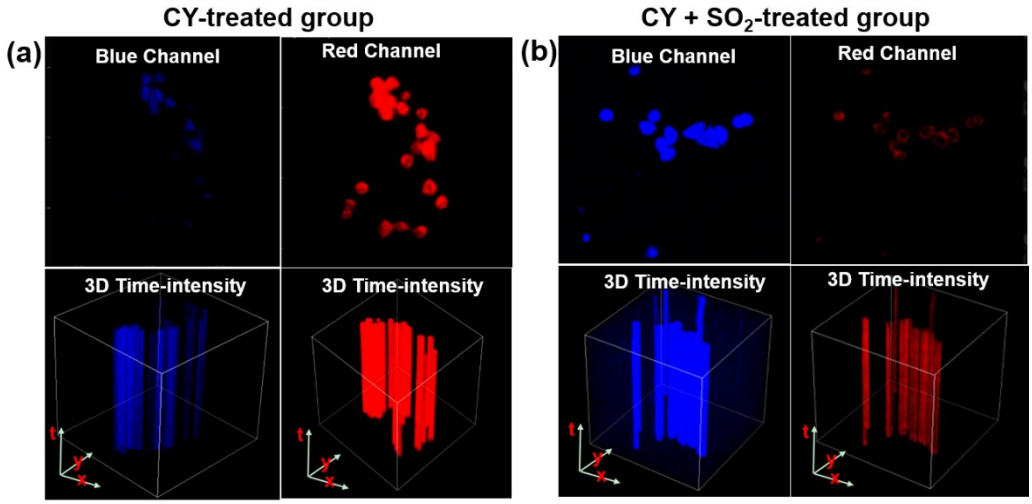

Fig. S7. Fluorescence images for detecting exogenous SO_2 in HepG2 cells with probe **CY** after continuous irradiation for 25 min. (a) HepG2 cells incubated with 10 μM free **CY** for 30 min, and then irradiation for 25 min; (b) cells were firstly incubated with 10 μM **CY** for 30 min, and then treated with $NaHSO_3$ (60 μM) for another 30 min, followed by irradiation for 25 min. Upper row of a and b: the representative images in blue and red channels at 12 min with irradiation; bottom row of a and b: 3D time-dependent fluorescence images after 30 min irradiation in blue and red channels respectively. Blue Channel: λ_{ex} = 404 nm, λ_{em} = 425-475 nm, Red Channel: λ_{ex} = 640 nm, λ_{em} = 663-738nm.

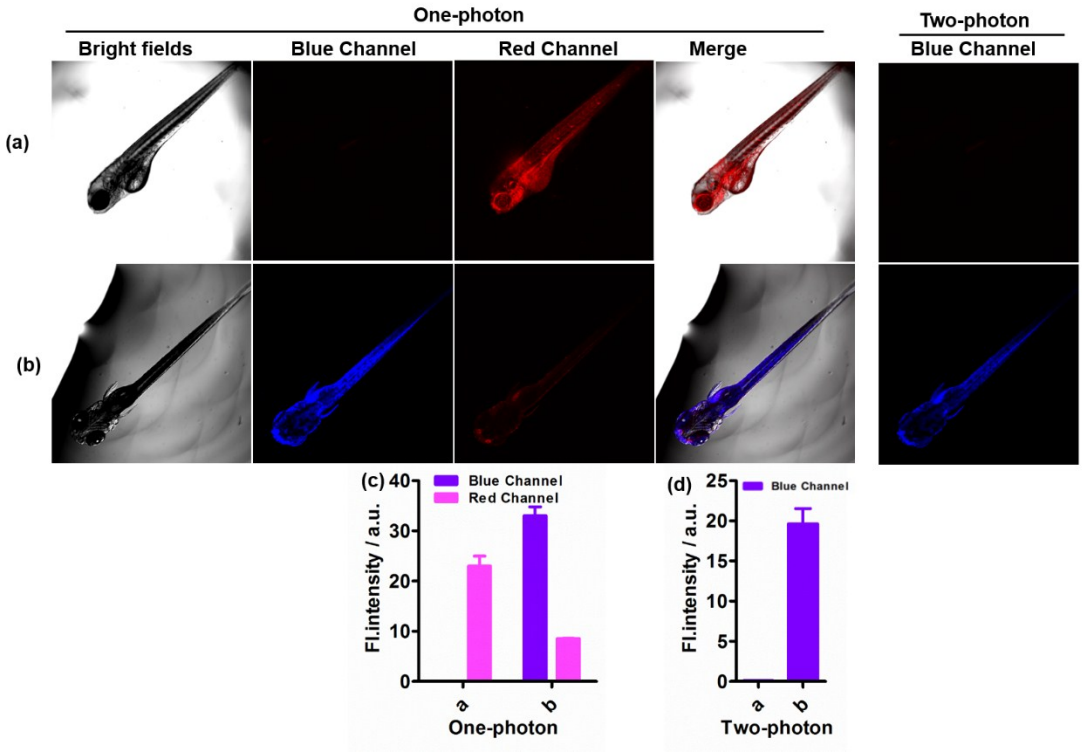

Fig. S8. NIR and two-photon fluorescence images for imaging SO_2 in zebrafish with 10 μM **CY**. (a) zebrafish were treated with free 10 μM **CY** for 30 min; (b) zebrafish were pre-treated with 10 μM **CY** for 30 min, and then treated with $NaHSO_3$ (30 μM) for another 30 min. (c) quantified fluorescence intensities of groups a and b Blue and Red channel respectively under one- and two-photon modes with Images J. software. Error bars represent standard deviation (±S.D.), n = 3, the statistical analysis was performed from three separate biological replicates. One-photon mode: Blue Channel: λ_{ex} = 404 nm, λ_{em} = 425-475 nm, Red Channel: λ_{ex} = 640 nm, λ_{em} = 663-738nm; two-photon mode: λ_{ex} = 800 nm, λ_{em} = 425-475 nm. Scale bar: 20 μm.

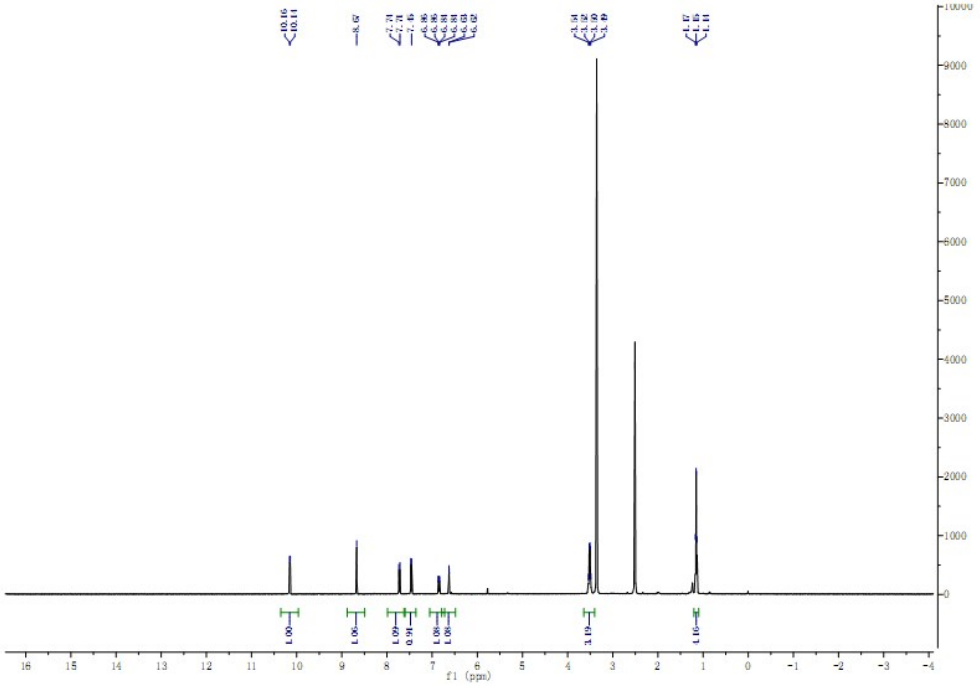

Fig. S9. [1]HNMR (100 MHz, DMSO-d_6) spectrum of compound **4**.

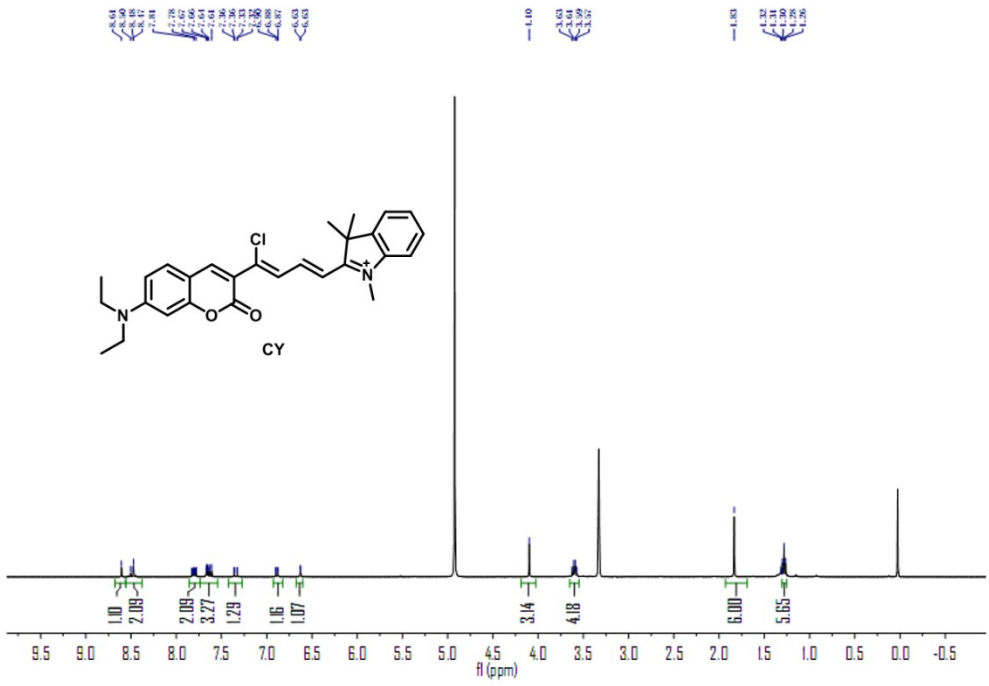

Fig. S10. [1]HNMR (100 MHz, CD_3OD) spectrum of **CY**.

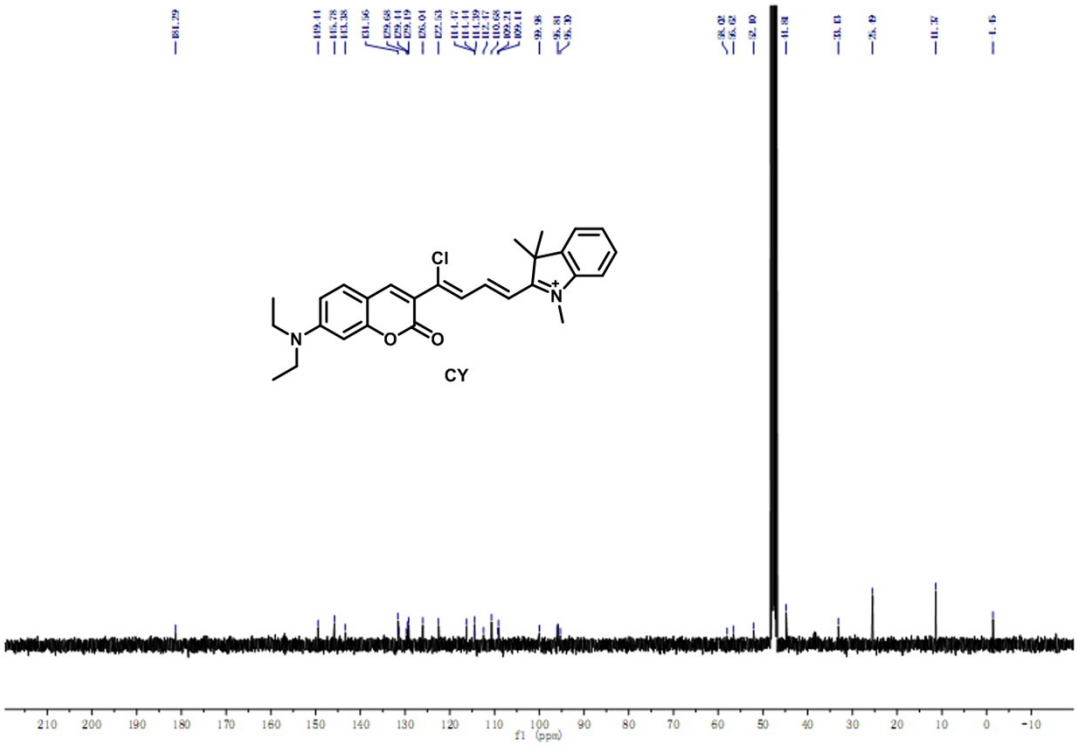

Fig. S11. ^{13}CNMR (100 MHz, CD_3OD) spectrum of **CY**.

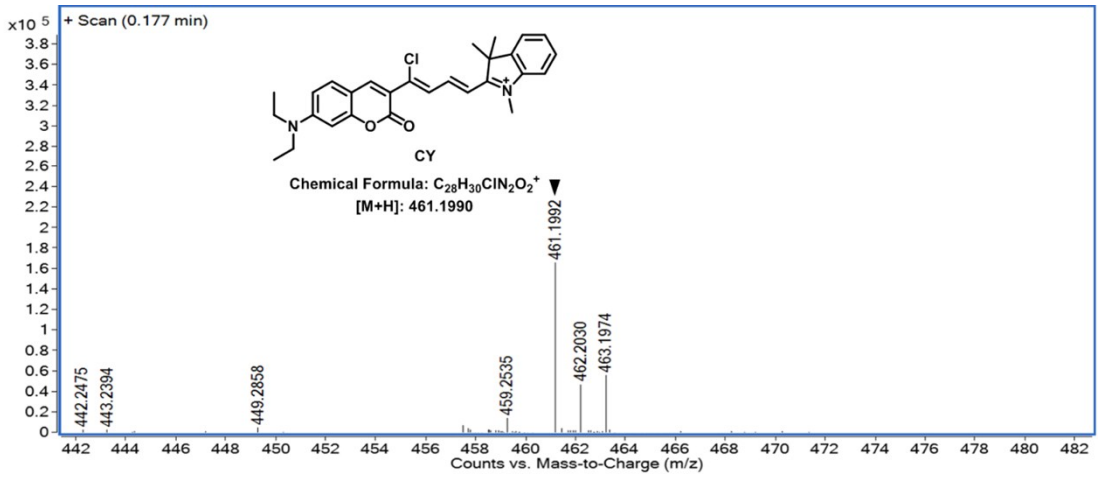

Fig. S12. HRMS spectrum of **CY**.