Supporting information for

Single Near-infrared Fluorescent Probe with High and Low Sensitivity Sites for Sensing Different Concentration Ranges of Biological Thiols with Distinct Modes of Fluorescence Signals

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Table of Contents

Pages

Materials and instruments. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Solvents used were purified by standard methods prior to use. Twice-distilled water was used throughout all experiments. Mass spectra were performed using an LCQ Advantage ion trap mass spectrometer from Thermo Finnigan or Agilent 1100 HPLC/MSD spectrometer. NMR spectra were recorded on an INOVA-400 spectrometer, using TMS as an internal standard. Electronic absorption spectra were obtained on a Labtech UV Power PC spectrometer. Photoluminescent spectra were recorded at 37˚C with a HITACHI F4600 fluorescence spectrophotometer. The fluorescence imaging of cells was performed with OLYMPUS FV1000 (TY1318) confocal microscopy. The *in vivo* (living mice) imaging was carried out using an IVIS Lumina XR (IS1241N6071) *in vivo* imaging system. TLC analysis was performed on silica gel plates and column chromatography was conducted over silica gel (mesh 200–300), both of which were obtained from the Qingdao Ocean Chemicals.

Determination of the fluorescence quantum yield[1-3]: Fluorescence quantum yields for **CHMC1, CHMC1-C, CHMC2, and CHMC2-C** were determined by using ICG (Φ_f = 0.13 in DMSO) as a fluorescence standard.[1] The quantum yield was calculated using the following equation:

$$\Phi_{F(X)} = \Phi_{F(S)} (A_S F_X / A_X F_S) (n_X / n_S)^2$$

Where Φ_F is the fluorescence quantum yield, A is the absorbance at the excitation wavelength, F is the area under the corrected emission curve, and n is the refractive index of the solvents used. Subscripts S and X refer to the standard and to the unknown, respectively.

Calculation of pK_a Values. pK_a values of **CHMC1** and **CHMC2** dye at acidic to near-neutral pH regions were calculated by regression analysis of the fluorescence data to fit equation (1)

$$pH - pK_a = \log (F_{max} - F)/(F - F_{min}) \qquad (1)$$

Where F is the area under the corrected emission curve, F_{max} and F_{min} are maximum and minimum limiting values of F, respectively.

Synthesis of compound CHMC1-C.

$POC1_3$ (2.0 mL) was added dropwisely by a separatory funnel to a flask containing DMF (5 mL) with stirring at 0 °C over 30 min. Compound **1** (350 mg) in DMF (0.2 ml) was added slowly with stirring and the mixture was heated for 5 h at 90 °C. Then the mixture was poured to ice water and the resulting precipitate was filtered off and washed with cold water (100 ml) to afford the orange solid **2**, which was utilized in the next reaction without purification again. Indolium salt (600 mg, 2 mmol) and 0.345 g (440 mg, 2 mmol) of the compound **2** were dissolved in 70 ml of a mixture of 1-butanol and benzene (7:3) in a flask equipped with a Dean-Stark trap. The mixture was heated at reflux with stirring and the water formed was collected in the trap. After 5 h, the reaction was cooled to room temperature, and the solvents were removed in vacuo. The red solid **CHMC1-C** was purified by column chromatography on silica gel flash chromatography using CH_2Cl_2/EtOH (50: 0 to 30: 1). ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.45 (d, *J* = 15.9 Hz, 1H), 7.93- 7.87 (m, 2H), 7.77 (d, *J* = 8.7 Hz, 1H), 7.67- 7.62 (m, 2H), 7.21 (d, *J* = 15.9 Hz, 1H), 7.03 (d, *J* = 2.3 Hz, 1H), 6.99 (dd, *J* = 8.7, 2.5 Hz, 1H), 4.11 (s, 3H), 3.86 (s, 3H), 2.99 (dd, *J* = 8.1, 5.7 Hz, 2H), 2.92 (dd, *J* = 8.2, 5.5 Hz, 2H), 1.76 (s, 6H). ^{13}C NMR (100 MHz, DMSO) δ 181.17, 162.35, 147.56, 143.57, 142.23, 142.08, 141.61, 130.01, 129.64, 129.38, 129.26, 125.00, 123.18, 115.50, 113.94, 113.86, 113.28, 55.97, 52.14, 34.73, 26.93, 26.36, 23.68. MS (ESI) m/z = 378.2 $[M]^+$; HRMS (ESI) Calcd for $C_{24}H_{25}ClNO^+$ ($[M]^+$): 378.1619, Found, 378.1617.

Synthesis of compound CHMC1.

To a solution of compound **CHMC1-C** (250mg, 0.5mmol) and BBr_3 (500 mg) in dry dichloromethane (5 ml) were stirred under ice bath for 12 h at N_2 atmosphere. After 12 h, the mixture was poured onto 100 g of crushed iced and mixed carefully, and then the aqueous phase was extracted with dichloromethane (3 × 100 mL). The organic layers were collected, dried over Na_2SO_4, and evaporated under reduced pressure. The red solid was purified by column chromatography on silica gel flash chromatography using CH_2Cl_2/EtOH (20:1). The desired product was obtained as a red solid. ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 10.54 (s, 1H), 8.44 (d, *J* = 15.8 Hz, 1H), 7.94-7.87 (m, 2H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.65-7.60 (m, 2H), 7.18 (d, *J* = 15.8 Hz, 1H), 6.85 -6.80 (m, 2H), 4.12 (s, 3H), 2.90 (s, 4H), 1.75 (s, 6H). ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 181.05, 161.53, 147.79, 143.51, 142.95, 142.24, 141.91, 129.70, 129.48,

129.36, 129.17, 123.64, 123.18, 115.42, 115.25, 114.81, 113.32, 52.03, 34.69, 26.96, 26.48, 23.73. MS (ESI) m/z = 364.2[M]$^+$; HRMS (ESI) Calcd for $C_{23}H_{23}ClNO^+$ ([M]$^+$): 364.1462, Found, 364.1461.

Synthesis of compound CHMC2-C.

$POC1_3$ (2.0 mL) was added dropwisely by a separatory funnel to a flask containing DMF (5 mL) with stirring at 0°C over 30 min. Compound **1** (350 mg) in DMF (0.2 ml) was added slowly with stirring and the mixture was heated for 5 h at 90 °C. Then the mixture was poured to ice water and the resulting precipitate was filtered off and washed with cold water (100 ml). Then orange solid **2** was afforded which was utilized in the next reaction without purification again. Benz[e]indolium salt (730 mg, 2 mmol) and 0.345 g (440 mg, 2 mmol) of the compound **2** were dissolved in 70 ml of a mixture of 1-butanol and benzene (7:3) in a flask equipped with a Dean-Stark trap. The mixture was heated at reflux with constant stirring and the water formed was collected in the trap. After 5 h, the reaction was cooled to room temperature, and the solvents were removed in vacuo. The red solid **CHMC2-C** was purified by column chromatography on silica gel flash chromatography using CH_2Cl_2/EtOH (50: 0 to 30: 1). ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.57 (d, *J* = 15.9 Hz, 1H), 8.46 (d, *J* = 8.4 Hz, 1H), 8.32 (d, *J* = 8.9 Hz, 1H), 8.23 (d, *J* = 8.1 Hz, 1H), 8.14 (d, *J* = 9.0 Hz, 1H), 7.79 (dd, *J* = 8.2, 3.7 Hz, 2H), 7.74 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 15.9 Hz, 1H), 7.05-6.98 (m, 2H), 4.80 (q, *J* = 6.9 Hz, 2H), 3.87 (s, 3H), 3.05- 2.91 (m, 4H), 2.01 (s, 6H), 1.52 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 181.19, 162.00, 146.86, 141.63, 141.26, 138.51, 138.19, 133.09, 131.12, 129.94, 129.75, 128.86, 128.38, 127.22, 126.65, 124.66, 123.02, 113.48, 113.06, 112.93, 112.31, 55.59, 53.46, 46.87, 42.45, 26.57, 25.99, 23.35, 13.69. MS (ESI) m/z = 442.2 [M]$^+$; HRMS (ESI) Calcd for $C_{29}H_{29}ClNO^+$ ([M]$^+$): 442.1923, Found, 442.1925.

Synthesis of compound CHMC2.

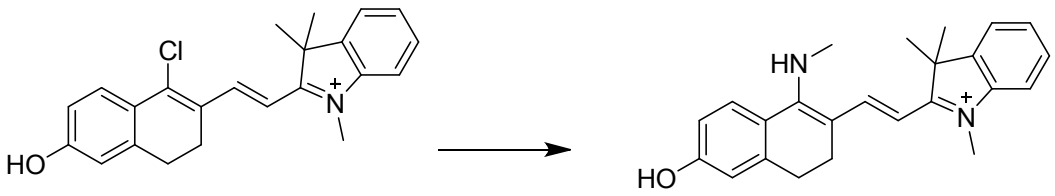
To a solution of compound **CHMC2-C** (569mg, 1mmol) and BBr_3 (600 mg) in dry dichloromethane (5 ml) were stirred under ice bath for 12 h at N_2 atmosphere. After 12 h, the mixture was poured onto 100 g of crushed iced and mixed carefully, and then the aqueous phase was extracted with dichloromethane (3 × 100 ml). The organic layers were collected, dried over Na_2SO_4, and evaporated under reduced pressure. The red solid was purified by column chromatography on silica gel flash chromatography

using CH_2Cl_2/EtOH (25:1). The desired product was obtained as a red solid. ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 10.57 (s, 1H), 8.58 (d, *J* = 15.8 Hz, 1H), 8.46 (d, *J* = 8.4 Hz, 1H), 8.31 (d, *J* = 9.0 Hz, 1H), 8.23 (d, *J* = 8.2 Hz, 1H), 8.14 (d, *J* = 9.0 Hz, 1H), 7.80 (t, *J* = 7.3 Hz, 1H), 7.76-7.68 (m, 2H), 7.21 (d, *J* = 15.9 Hz, 1H), 6.86 - 6.79 (m, 2H), 4.79 (q, *J* = 7.0 Hz, 2H), 2.94 (s, 4H), 2.00 (s, 6H), 1.57- 1.45 (m, 3H). ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 180.99, 161.13, 147.06, 142.50, 141.58, 138.31, 138.21, 133.01, 131.09, 129.94, 129.33, 128.88, 128.35, 127.13, 126.65, 123.29, 122.99, 114.86, 114.41, 113.03, 111.64, 53.34, 42.27, 26.56, 26.06, 23.32, 13.65. MS (ESI) m/z = 428.2$[M]^+$; HRMS (ESI) Calcd for $C_{28}H_{27}ClNO^+$ ($[M]^+$): 428.1775, Found, 428.1776.

Synthesis of compound CHMC-thiol.

A mixture of **CHMC**1 (490 mg, 1mmol) and 2,4-dinitrobenzene-1-sulfonyl chloride (530mg, 2mmol) in dry dichloromethane was stirred at room temperature for 5h at N_2 atmosphere under the basic conditions. Then, the solvent was evaporated under reduced pressure to give the crude product, which was purified by column chromatography on silica gel flash chromatography using CH_2Cl_2/EtOH (30:1). ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 9.15 (d, *J* = 2.0 Hz, 1H), 8.65 (dd, *J* = 8.7, 2.0 Hz, 1H), 8.55 (d, *J* = 1.9 Hz, 1H), 8.39 (s, 1H), 8.36 (s, 1H), 8.08 (d, *J* = 8.6 Hz, 1H), 7.95 (dd, *J* = 5.8, 2.9 Hz, 1H), 7.91-7.88 (m, 1H), 7.84 (d, *J* = 8.7 Hz, 1H), 7.68-7.66 (m, 1H), 7.35 (s, 1H), 7.20 (dd, *J* = 8.5, 1.8 Hz, 1H), 4.15 (s, 3H), 3.03-3.01 (m, 2H), 2.96-2.93 (m, 2H), 1.76 (s, 6H). ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 181.51, 151.85, 149.87, 148.35, 146.56, 143.82, 142.19, 141.62, 138.85, 133.85, 133.57, 131.78, 131.03, 128.87, 127.93, 125.91, 123.22, 121.56, 121.46, 120.89, 118.59, 116.34, 115.89, 56.72, 52.49, 35.07, 26.03, 23.39, 18.83. MS (ESI) m/z =594.1 $[M]^+$; HRMS (ESI) Calcd for $C_{29}H_{25}ClN_3O_7S^+$ ($[M]^+$): 594.1093, Found, 594.1096.

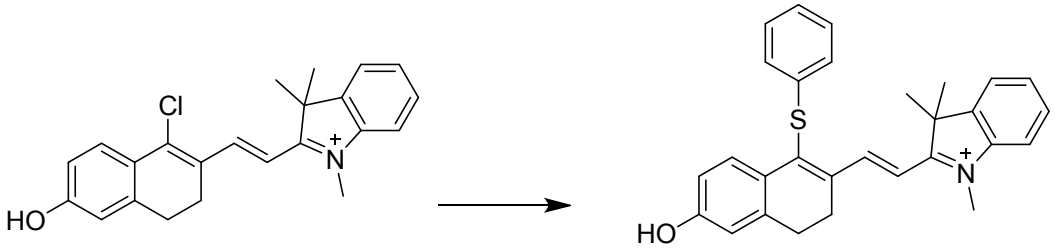
Synthesis of compound 5.



CHMC1 **5**

Compound **CHMC1** (49.1 mg, 0.1 mmol) and methylamine (15 mg, 0.5 mmol) were placed in a flask containing dry DMF (4.0 ml). After heating overnight at 90℃ under nitrogen, the solution was concentrated under reduced pressure. The resulting crude product was purified by silica gel flash chromatography using ethyl CH_2Cl_2/MeOH (30: 1) as eluent to give the compound **5** as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 9.32 (s, 1H), 7.92 (d, *J* = 107.6 Hz, 1H), 7.65 (s, 2H), 7.46 (s, 2H), 7.20 (s, 2H), 7.00 (d, *J* = 6.3 Hz, 1H), 6.84 (s, 1H), 4.24 (s, 3H), 3.56-3.59 (m, 2H), 2.61-2.64 (m, 2H), 1.65 (s, 3H), 0.89 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.19, 169.71, 168.92, 167.69, 164.44, 164.26, 163.38, 162.80, 160.46, 132.25, 130.88, 129.41, 128.79, 122.93, 122.45, 121.95, 120.40, 119.72, 115.57, 108.37, 93.54, 65.54, 30.53, 29.66, 28.80, 19.15. MS (ESI) m/z =359.1 $[M]^+$.

Synthesis of compound 6.



Compound **CHMC1** (49.1 mg, 0.1 mmol) and thiophenol (33 mg, 0.3 mmol) were placed in a flask containing dry DMF (4.0 ml), and then two drops of TEA was added. After heating overnight at 90℃ under nitrogen, the solution was concentrated under reduced pressure. The resulting crude product was purified by silica gel flash chromatography using ethyl CH_2Cl_2/MeOH (35: 1) as eluent to give the compound **6** as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, *J* = 15.5 Hz, 1H), 7.51 (d, *J* = 8.7 Hz, 1H), 7.43-7.39 (m, 3H), 7.20 (s, 1H), 7.15-7.00 (m, 6H), 6.88 (s, 1H), 6.65 (d, *J* = 6.9 Hz, 1H), 4.17 (s, 3H), 2.64-2.68 (m, 4H), 1.64 (s, 6H). ^{13}C NMR (100 MHz,

$CDCl_3$) δ 181.16, 162.00, 151.97, 149.64, 142.68, 142.16, 141.75, 138.79, 135.66, 132.28, 129.39, 128.79, 128.13, 126.58, 124.83, 122.33, 115.61, 115.29, 113.86, 110.99, 51.62, 35.07, 29.66, 27.66, 27.14, 25.56. MS (ESI) m/z =438.1 $[M]^+$

HeLa cell and MCF-7 cell Culture and Imaging Using CHMC-thiol.

HeLa cell or MCF-7 were seeded in a 12-well plate in Dulbecco's modified Eagle'smedium (DMEM) supplemented with 10% fetal bovine serum for 24 h. HeLa cell or MCF-7 cell were then incubated with or without N-ethylmaleimide (as a thiol blocking agent) in the culture medium for 30 min at 37 °C. After washing with PBS three times to remove the remaining N-ethylmaleimide, the cells were further incubated with the probe **CHMC-thiol** (5 μM) for 30 min at 37 °C. After washing the cells with PBS three times, the cells were imaged using OLYMPUS FV1000 (TY1318) confocal microscope with an excitation filter of 546 nm. For another control experiment, HeLa cell or MCF-7 cell were then incubated with or without Cys (100 μM) in the culture medium for 30 min at 37 °C. After washing with PBS three times to remove the remaining Cys, the cells were further incubated with the probe **CHMC-thiol** (5 μM) for 30 min at 37 °C. After washing the cells with PBS three times, the cells were imaged using OLYMPUS FV1000 (TY1318) confocal microscope with an excitation filter of 546 nm.

Fluorescent Imaging in Living Mice Using CHMC-thiol. The Kunming mice were divided into three groups. One group was given saline (100 μL) in the peritoneal cavity, followed by intraperitoneal （i.p.） injection with **CHMC-thiol** (20 μM, in 20 μL DMSO). The second group was given an i.p. injection of N-ethylmaleimide (1 mM, in 100 μL saline), and followed by i.p. injection with **CHMC-thiol** (20 μM, in 20 μL DMSO) as the negative control experiment. The third group was given an i.p. injection of Cys (100 μM, in 100 μL saline), and followed by i.p. injection with **CHMC-thiol** (20 μM, in 20 μL DMSO). The mice were anesthetized, and the abdominal fur was removed. After the probe injection, the mice were imaged using an IVIS Lumina XR (IS1241N6071) *in vivo* imaging system. With an excitation filter of 550 nm and the orange and red channels are corresponding to the emission windows of 580-640 nm, and 650-750 nm, respectively.

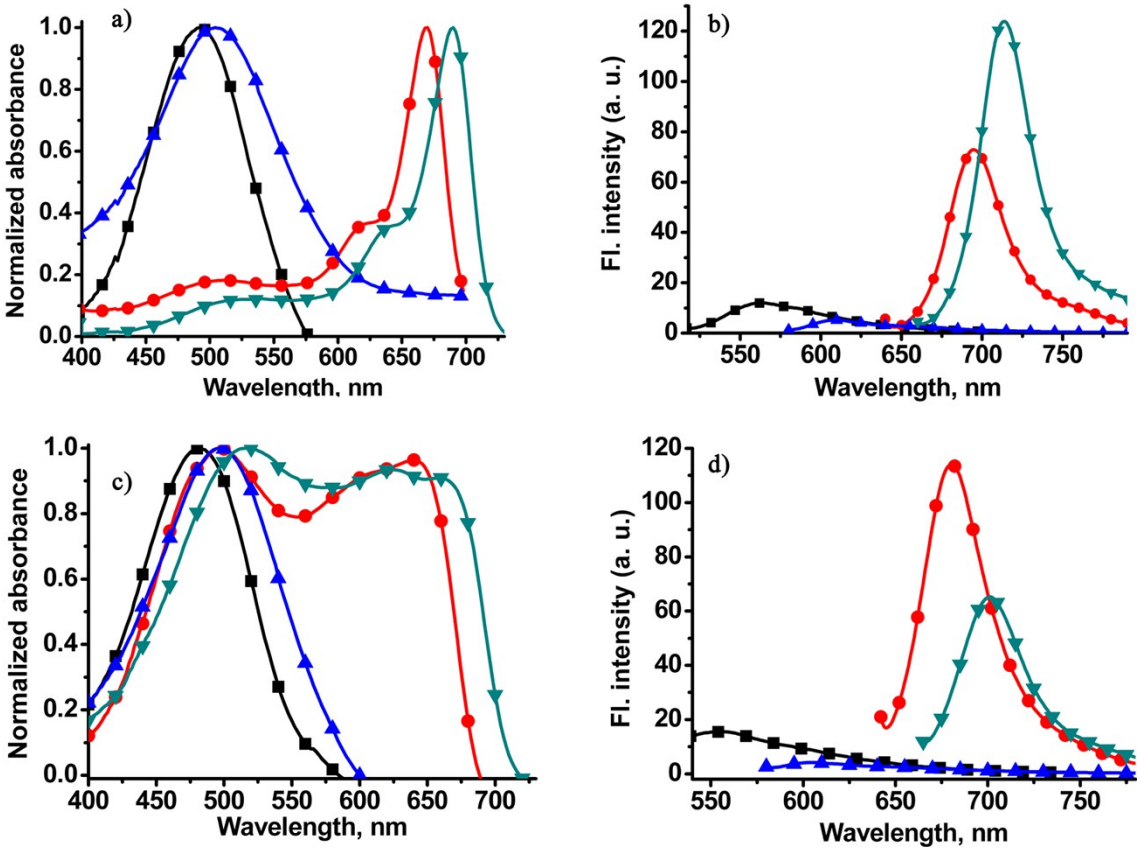


Figure S1. (a) The normalized absorption spectra of compounds **CHMC1** (●), **CHMC1-C** (■), **CHMC2** (▼) and **CHMC2-C** (▲) in EtOH; (b) The fluorescence emission spectra of compounds **CHMC1** (●), **CHMC1-C** (■), **CHMC2** (▼) and **CHMC2-C** (▲) in EtOH; (c) The normalized absorption spectra of compounds **CHMC1** (●), **CHMC1-C** (■), **CHMC2** (▼) and **CHMC2-C** (▲) in PBS; (d) The fluorescence emission spectra of compounds **CHMC1** (●), **CHMC1-C** (■), **CHMC2** (▼) and **CHMC2-C** (▲) in PBS.

Table S1. Photophysical Properties of **CHMC** dyes in EtOH.

Compound	λ_{max} (nm)	ε_{max} (10^5)	λ_{em} (nm)	Φ	Stokes Shift (nm)
CHMC1	670	1.42	695	0.08	25
CHMC1-C	494	0.18	564	0.02	70
CHMC2	690	1.48	714	0.06	24
CHMC2-C	506	0.36	610	0.01	104

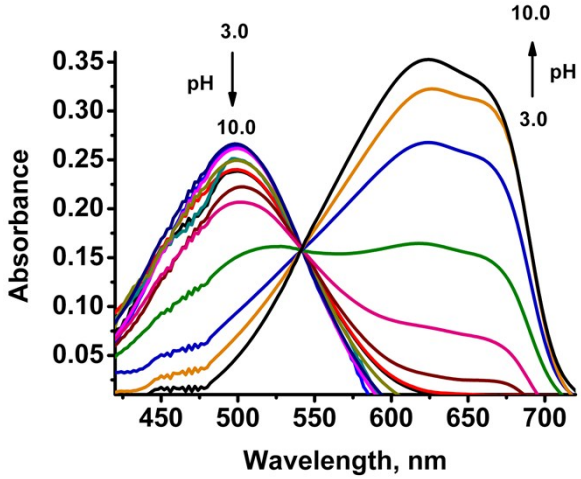


Figure S2. pH-dependence of the absorption spectra of compound **CHMC1** (5 μM) with the arrows indicating the change of the absorption intensities with pH enhancement from 3.0 to 10.0.

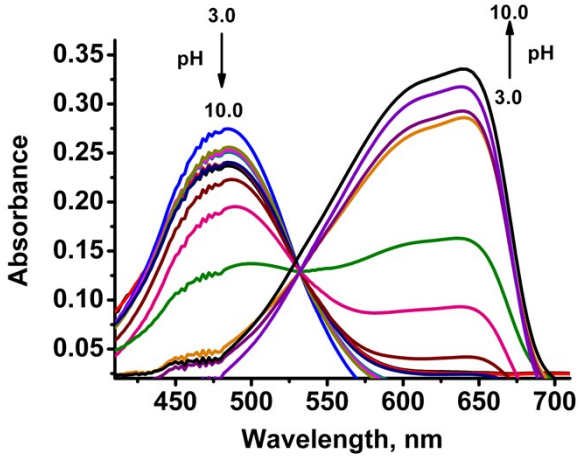


Figure S3. pH-dependence of the absorption spectra of compound **CHMC2** (5 μM) with the arrows indicating the change of the absorption intensities with pH enhancement from 3.0 to 10.0.

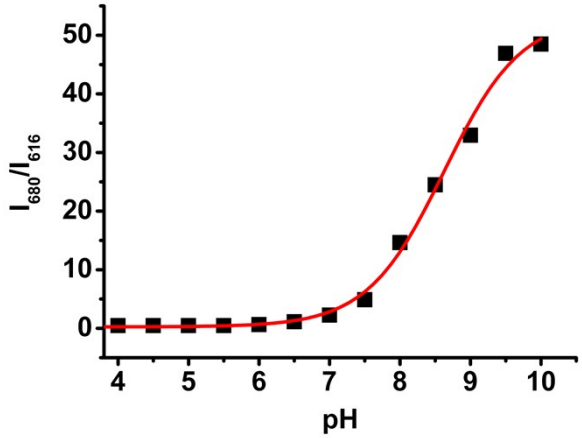


Figure S4. Sigmoidal fitting of the pH-dependent ratios of fluorescence intensity (I_{680}/I_{616}) of **CHMC1**.

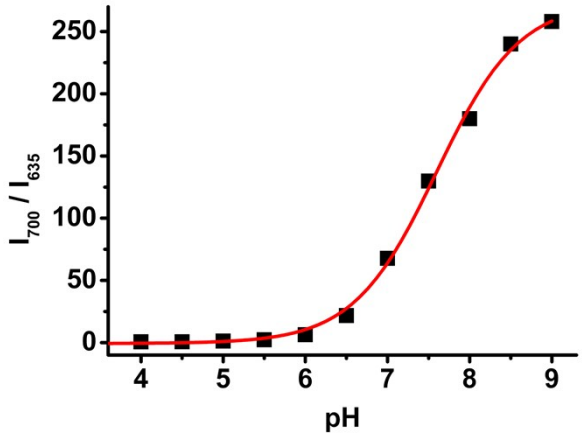


Figure S5. Sigmoidal fitting of the pH-dependent ratios of fluorescence intensity (I_{700}/I_{635}) of **CHMC2**.

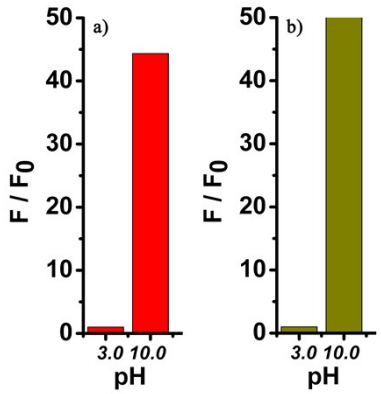


Figure S6. The fluorescence enhancement of **CHMC1** (a) and **CHMC2** (b) with pH increase from 3.0 to 10.0, excitation at 630 nm, emission at 680 and 700 nm, respectively. F/F_0 represented the enhancement of the fluorescence intensity.

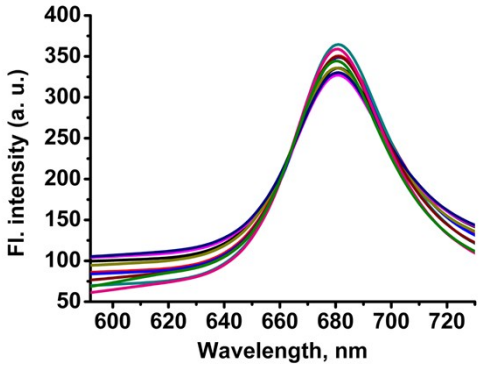


Figure S7. Fluorescence spectra of the **CHMC1** (5 μM) in PBS in the presence of low concentration range of Cys (0-35 μM).

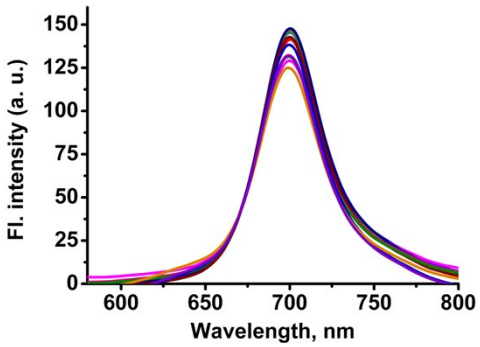


Figure S8. Fluorescence spectra of the **CHMC2** (5 μM) in PBS in the presence of low concentration range of Cys (0-35 μM).

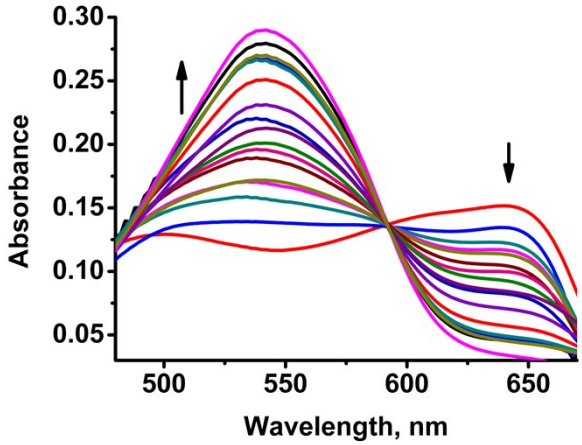


Figure S9. Absorption spectra of **CHMC1** (5 μM) in PBS in the presence of high concentration range of Cys (35-500 μM) of Cys.

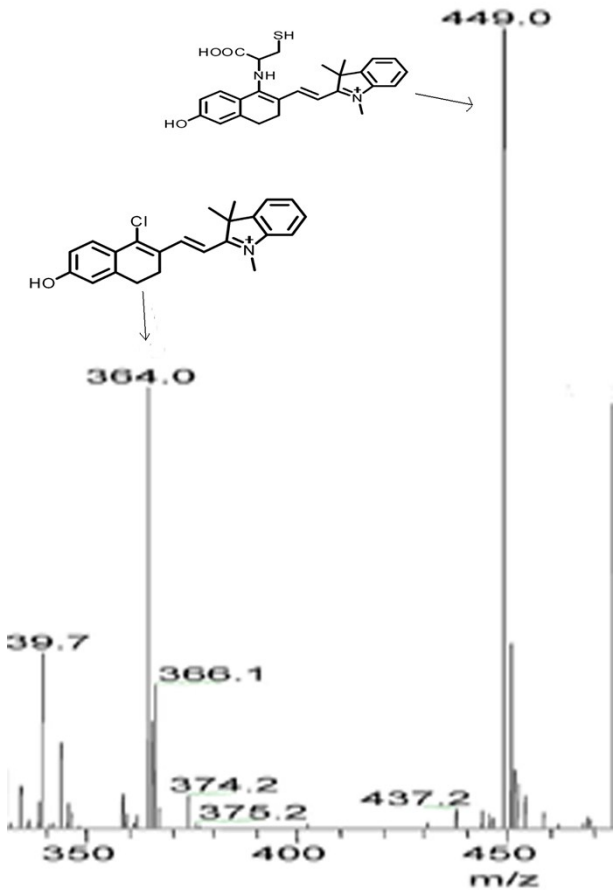


Figure S10. Mass spectrum (ESI) of the reaction mixture of the **CHMC1** with Cys.

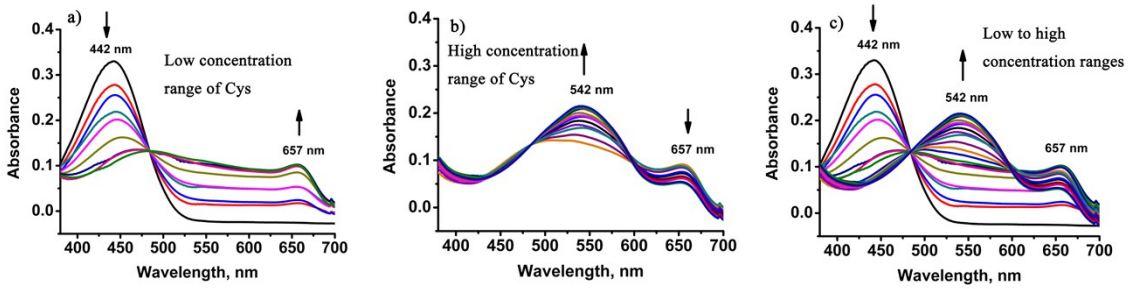


Figure S11. (a) Absorption spectra of the probe **CHMC-thiol** (5 μM) in the aqueous buffer in the presence of low concentration range of Cys (0-50 μM); (b) Absorption spectra of the probe **CHMC-thiol** (5 μM) in the aqueous buffer in the presence of high concentration range of Cys (50-500 μM); (c) Absorption spectra of the probe **CHMC-thiol** (5 μM) in the aqueous buffer in the presence of low to high concentration ranges of Cys (0-500 μM). All spectra were obtained after adding the analyte for 1 hour.

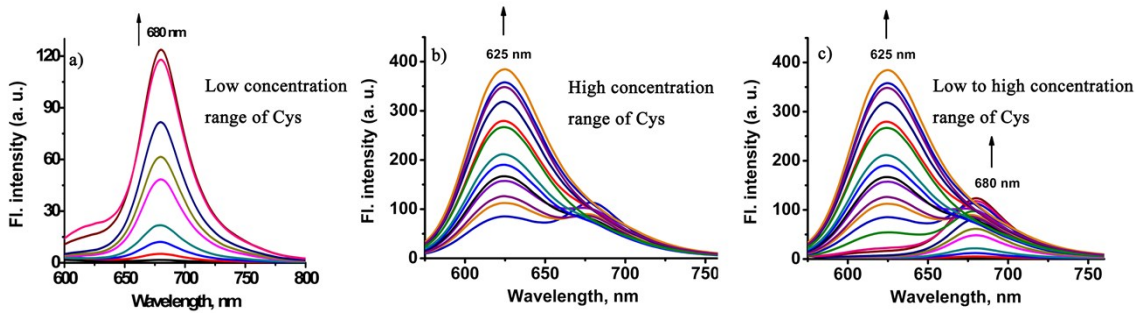


Figure S12. (a) Fluorescence spectra of the probe **CHMC-thiol** (10 μM) in the aqueous buffer in the presence of low concentration range of Cys (0-50 μM), excitation at 550 nm; (b) Fluorescence spectra of the probe **CHMC-thiol** (10 μM) in the aqueous buffer in the presence of high concentration range of Cys (50-500 μM), excitation at 550 nm; (c) Fluorescence spectra of the probe **CHMC-thiol** (10 μM) in the aqueous buffer in the presence of low to high concentration range s of Cys (0-500 μM), excitation at 550 nm.

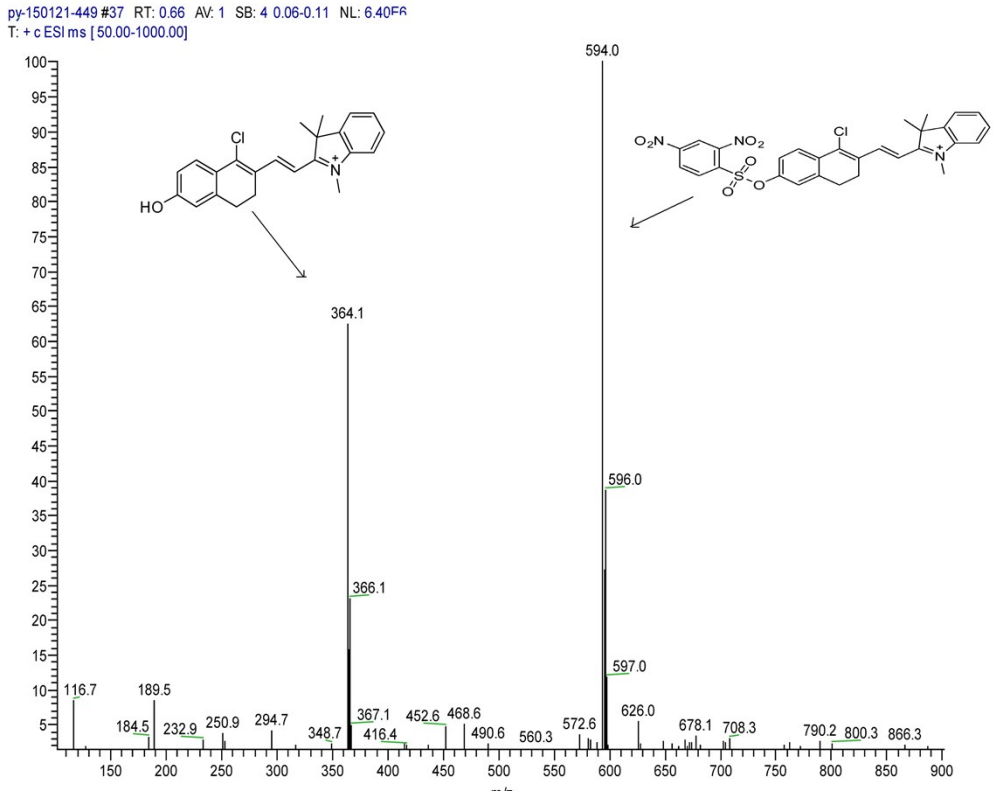


Figure S13. Mass spectrum (ESI) of the reaction mixture of probe **CHMC-thiol** with low concentration range of Cys.

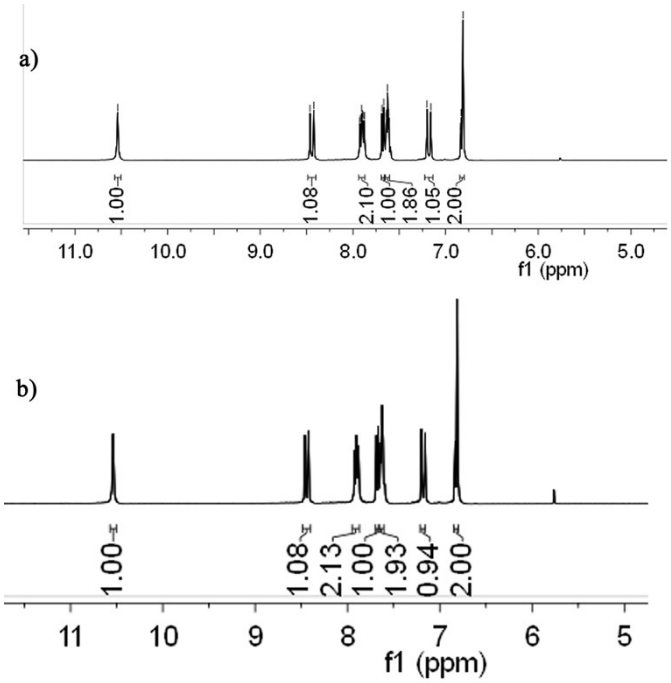


Figure S14. Partial ^{1}H NMR spectra of the compound **CHMC1** (a) and the isolated product of the probe **CHMC-thiol** with low concentration range of Cys (b).

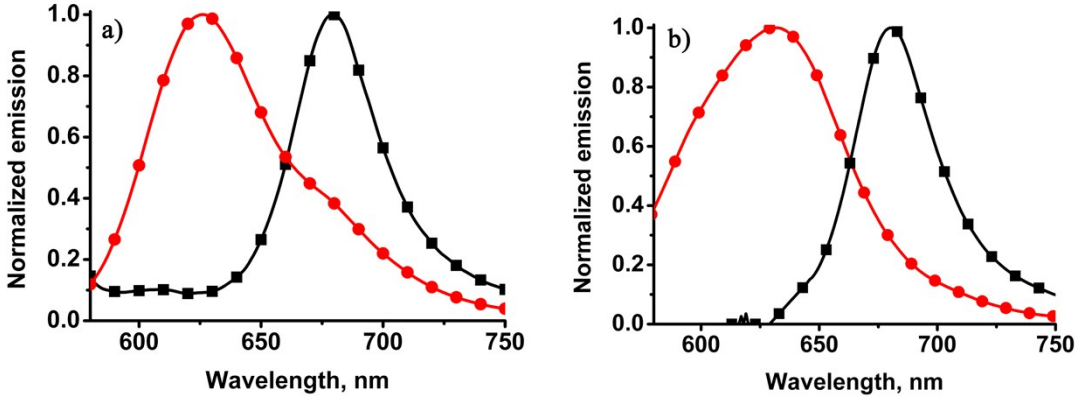


Figure S15. (a) Normalized emission of 5 μM probe **CHMC-thiol** reaction with low concentration range of Cys (■) and with high concentration range of Cys (●) in PBS; (b) Normalized emission of 5 μM compounds **CHMC1** (■) and compound **5** (●) in PBS.

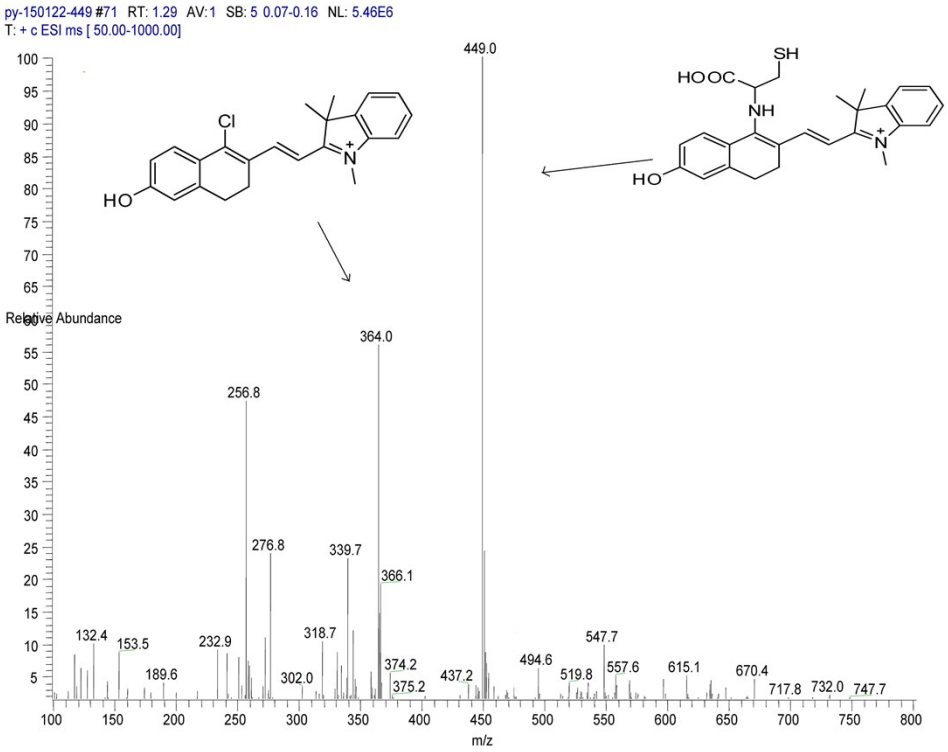


Figure S16. Mass spectrum (ESI) of the reaction mixture of the probe **CHMC-thiol** with high concentration range of Cys.

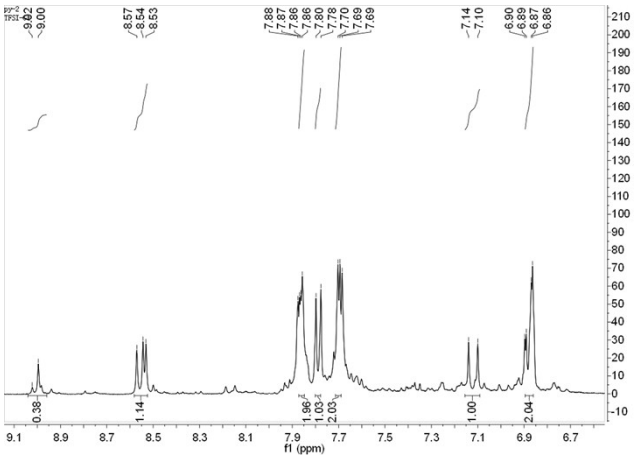


Figure S17. Partial ^{1}H NMR spectra of the probe **CHMC-thiol** with high concentration range of Cys.

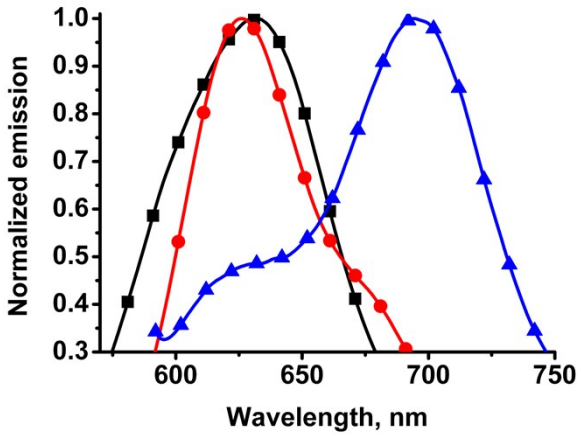


Figure S18. Normalized emission of compound **5** (■), compound **6** (▲), and 5 μM probe **CHMC-thiol** reaction with high concentration range of Cys (●) in PBS.

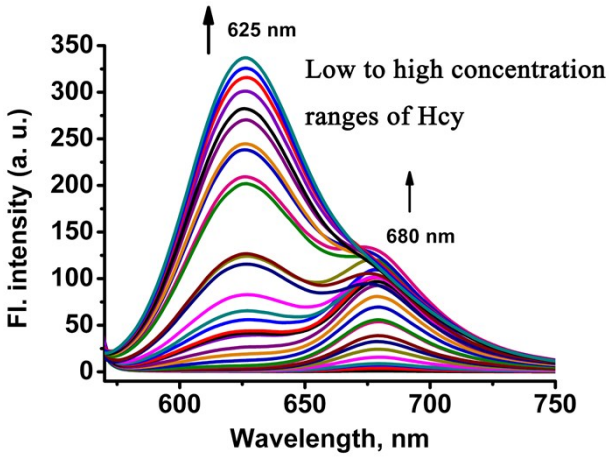
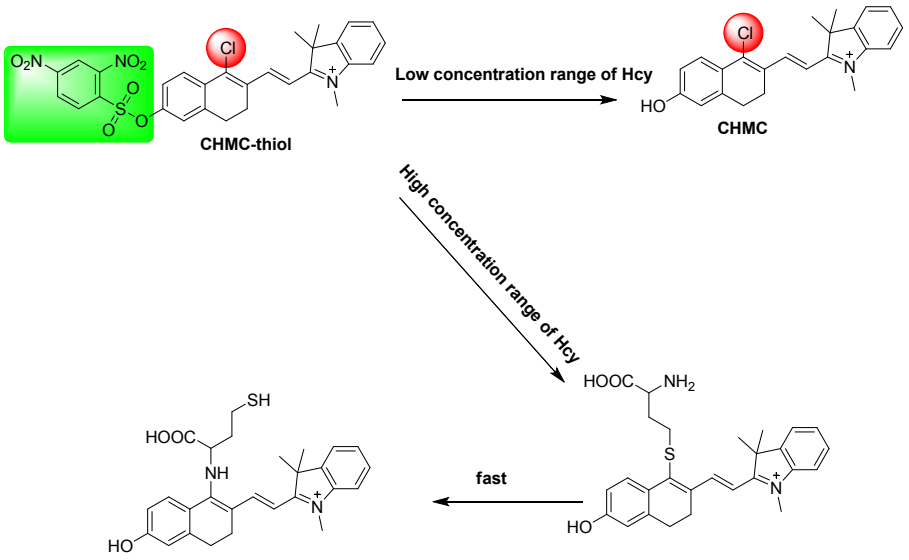


Figure S19. Fluorescence spectra of the probe **CHMC-thiol** (5 μM) in the aqueous buffer in the presence of low to high concentration ranges of Hcy (0-500 μM), excitation at 550 nm.



Scheme S1. The proposed reaction mechanism of **CHMC-thiol** with Hcy.

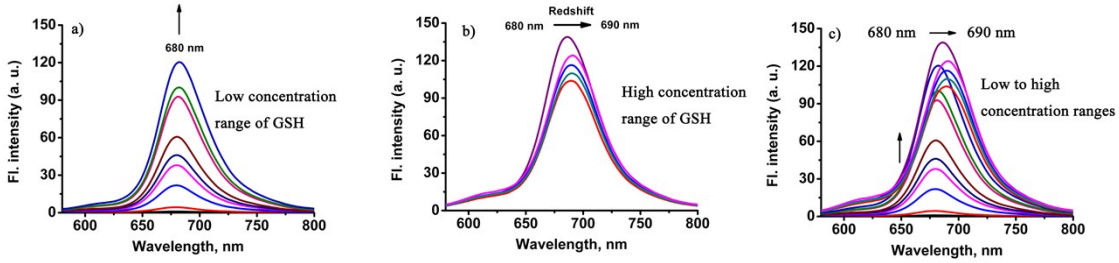
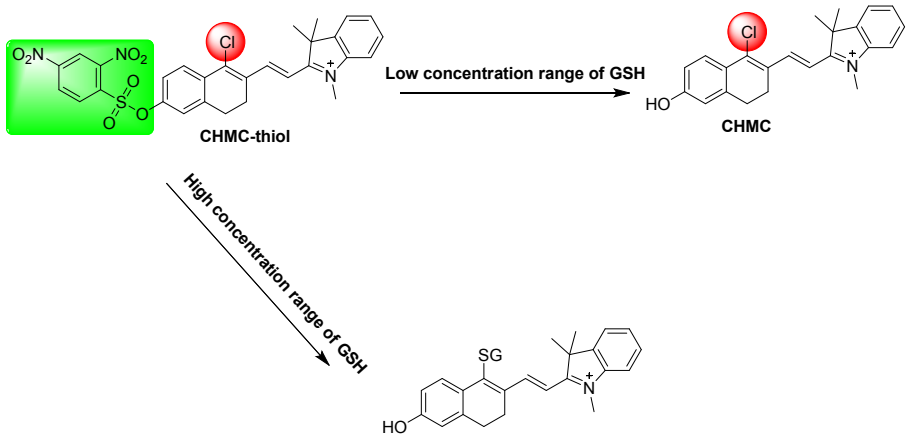


Figure S20. Fluorescence spectra of the probe **CHMC-thiol** (10 μM) in the aqueous buffer in the presence of low concentration range of GSH (0-50 μM), excitation at 550 nm; (b) Fluorescence spectra of the probe **CHMC-thiol** (10 μM) in the aqueous buffer in the presence of high concentration range of GSH (50-500 μM), excitation at 550 nm; (c) Fluorescence spectra of the probe **CHMC-thiol** (10 μM) in the aqueous buffer in the presence of low to high concentration ranges of GSH (0-500 μM), excitation at 550 nm.



Scheme S2. The proposed reaction mechanism of **CHMC-thiol** with GSH.

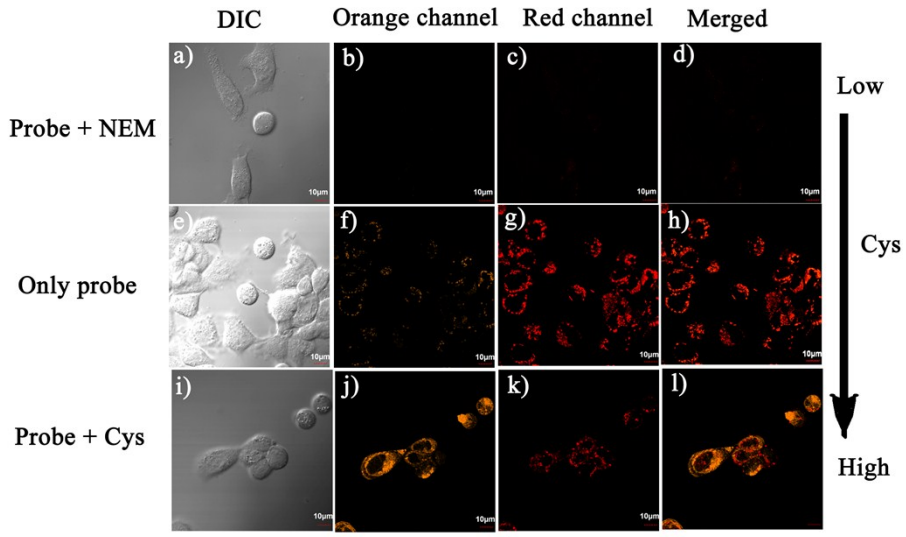


Figure S21. Brightfield and fluorescence images of MCF-7 cells stained with the probe **CHMC-thiol**: (a–d) Brightfield and fluorescence images of the cells incubated with N-ethylmaleimide (1 mM) for 30 min, and then co-incubated with **CHMC-thiol** (5 μM) for 30 min: (a) Brighfield image; (b) Fluorescence image from the orange channel; (c) Fluorescence image from the red channel, and (d) Overlay of (b) and (c); (e–h) Brightfield and fluorescence images of the cells only incubated with the probe (5 μM) for 30 min: (e) Brightfield image; (f) Fluorescence image from the orange channel; (g) Fluorescence image from the red channel; and (h) Overlay of (f) and (g); (i–l) Brightfield and fluorescence images of the cells incubated with Cys (100 μM) for 30 min, and then treated with the probe (5 μM) for another 30 min: (i) Brightfield

image; (j) Fluorescence image from the orange channel; (k) Fluorescence image from the red channel, and (l) Overlay of (j) and (k). The orange and red channels are corresponding to the emission windows of 580-640, and 650-750 nm, respectively. Scale bar =10 μm.

References

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2. D. Magde, G. E. Rojas and P. Seybold, *Photochem. Photobiol.*, 1999, **70**, 737.
3. D. Oushiki, H. Kojima, T. Terai, M. Arita, K. Hanaoka, Y. Urano and T. Nagano, *J. Am. Chem. Soc*., 2010, **132**, 2795.

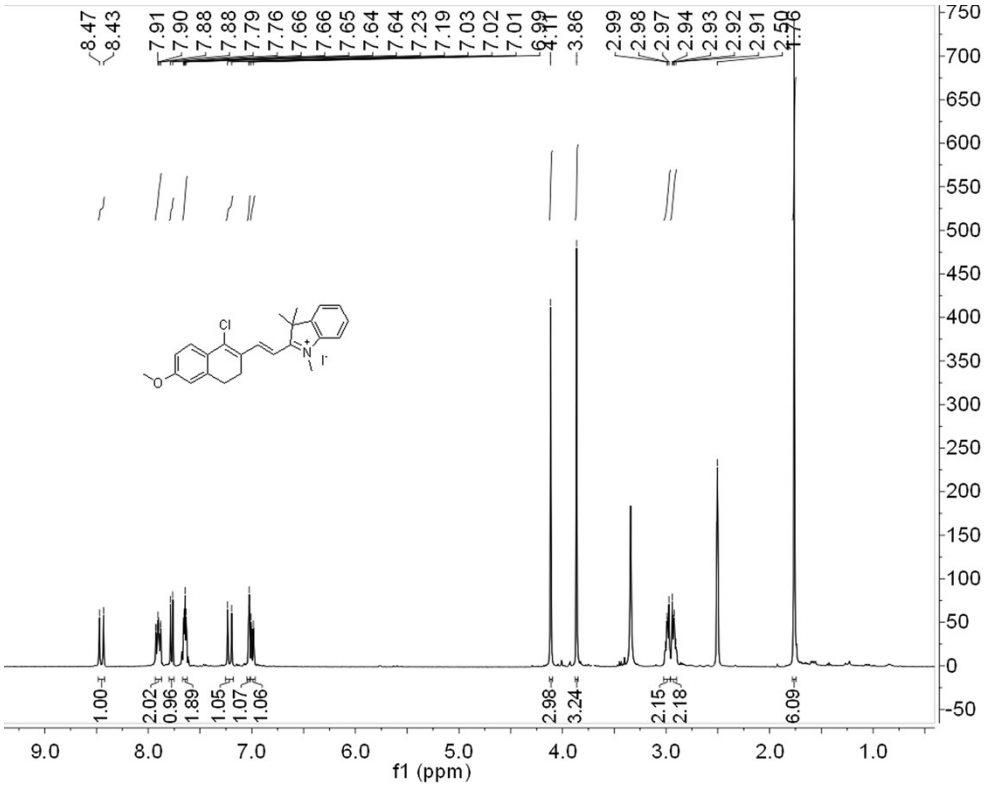

Figure S22. ^{1}H NMR spectrum of **CHMC1-C** ($(CD_3)_2SO$).

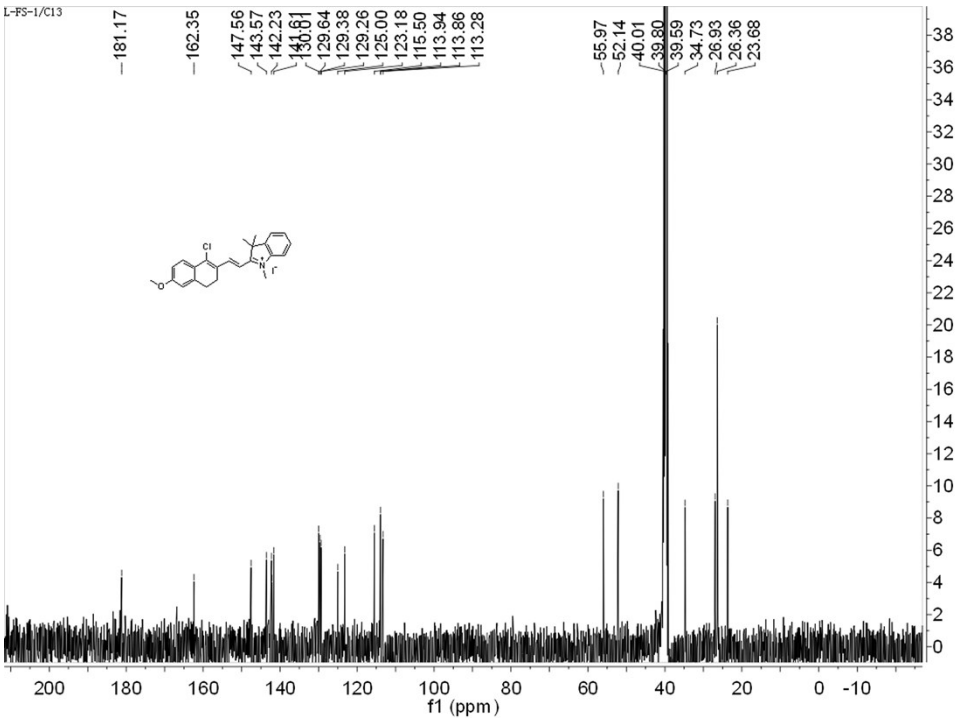

Figure S23. ^{13}C NMR spectrum of **CHMC1-C** ($(CD_3)_2SO$).

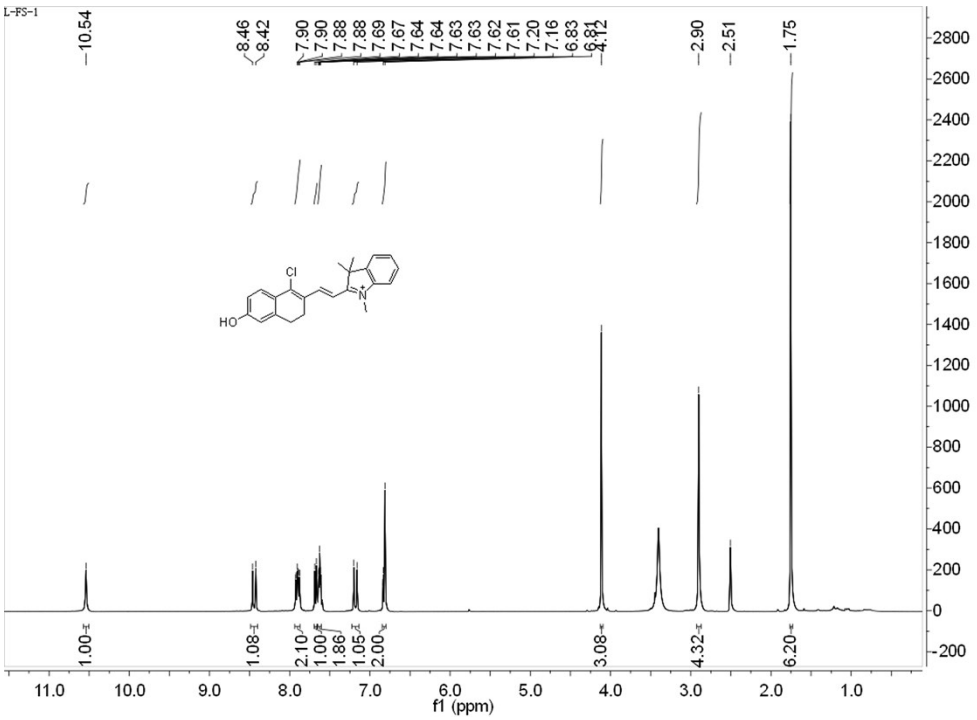

Figure S24. ^{1}H NMR spectrum of **CHMC1** ($(CD_3)_2SO$).

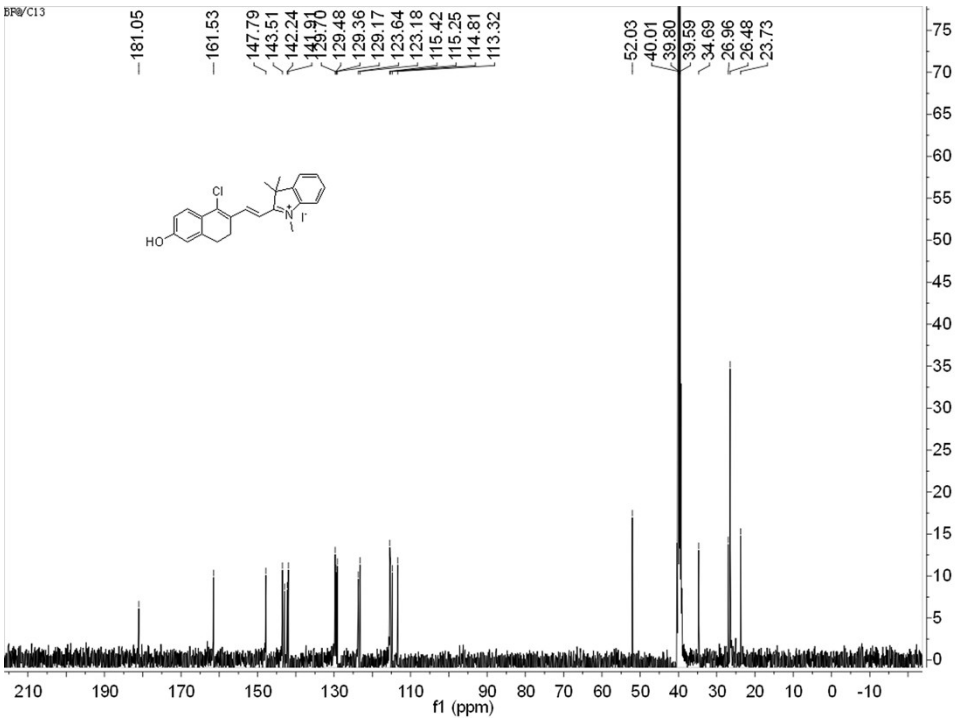

Figure S25. ^{13}C NMR spectrum of **CHMC1** ($(CD_3)_2SO$).

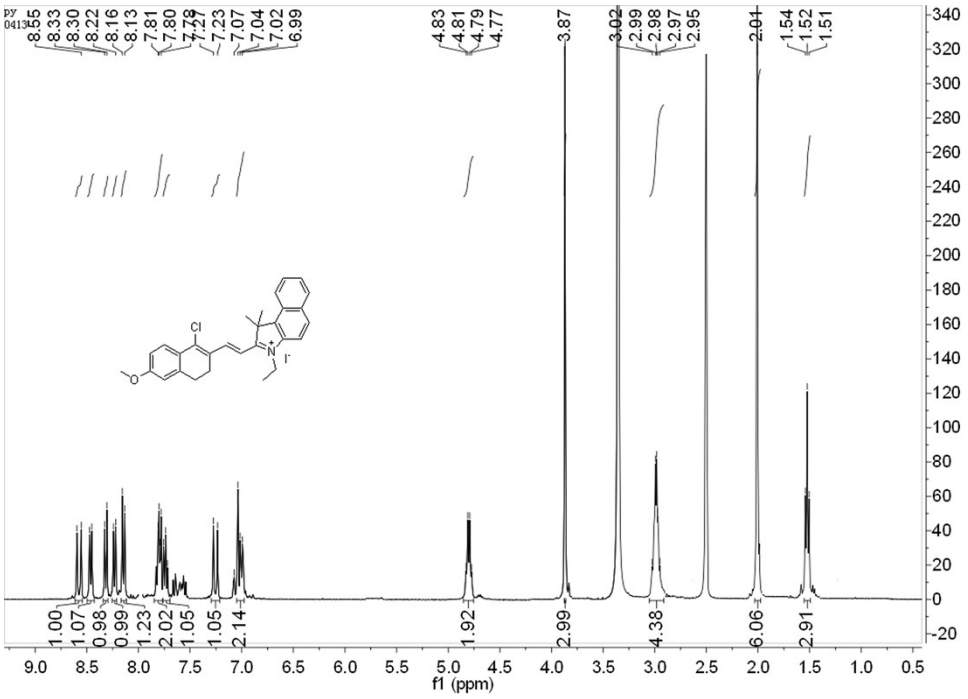

Figure S26. ^{1}H NMR spectrum of **CHMC2-C** ($(CD_3)_2SO$).

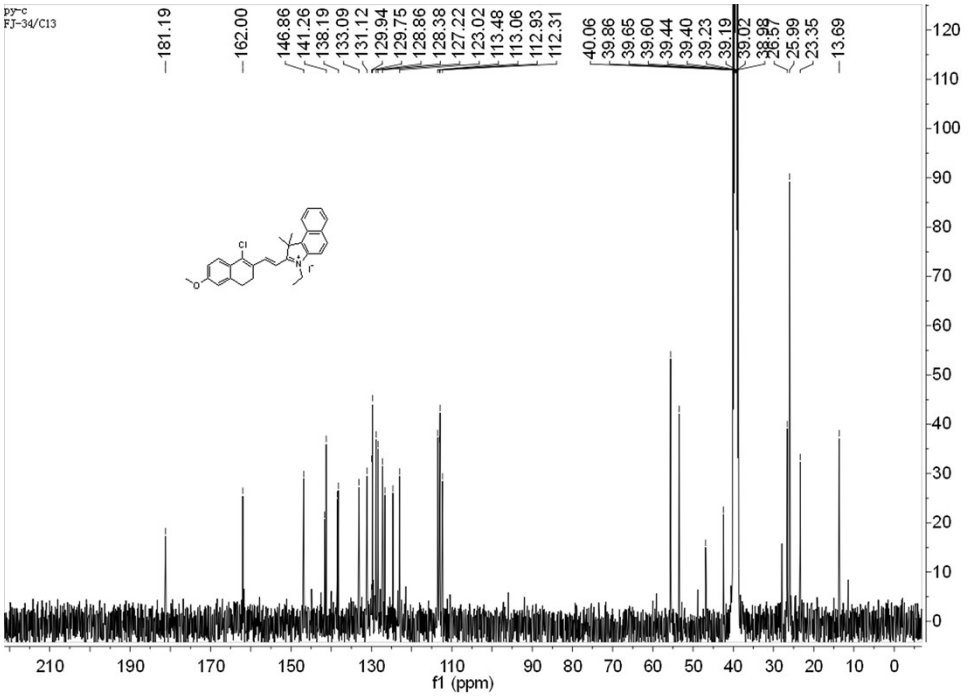

Figure S27. ^{13}C NMR spectrum of **CHMC2-C** ($(CD_3)_2SO$).

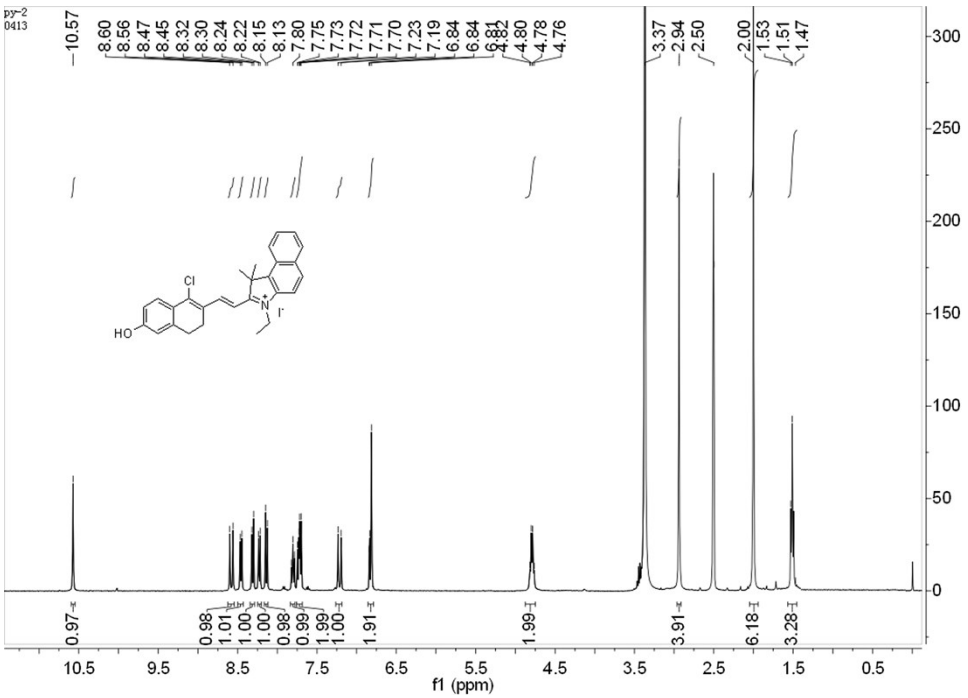

Figure S28. ^{1}H NMR spectrum of **CHMC2** ($(CD_3)_2SO$).

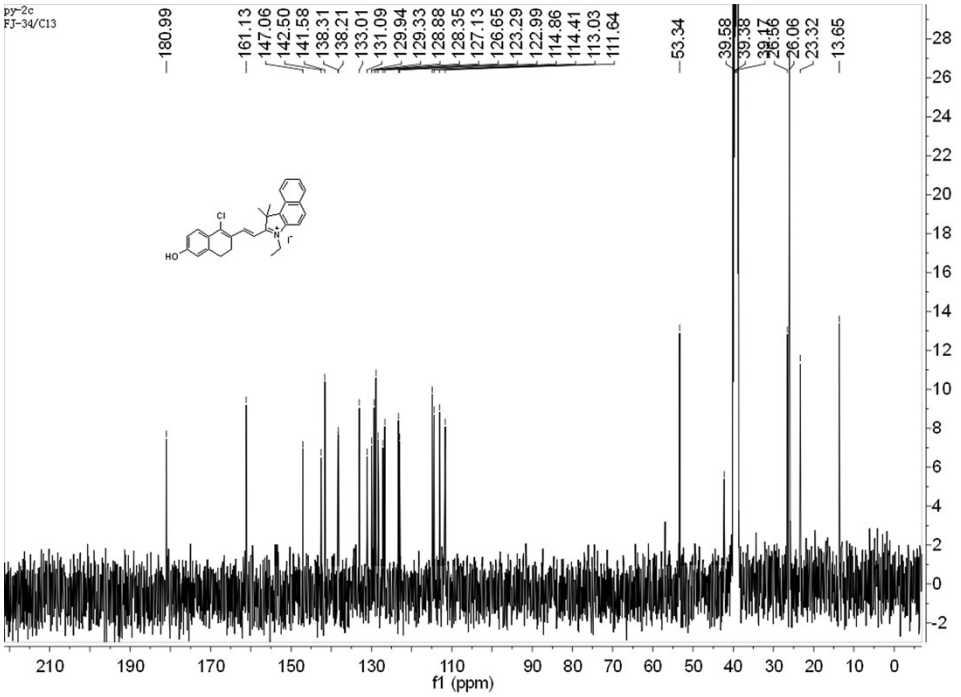

Figure S29. ^{13}C NMR spectrum of **CHMC2** ($(CD_3)_2SO$).

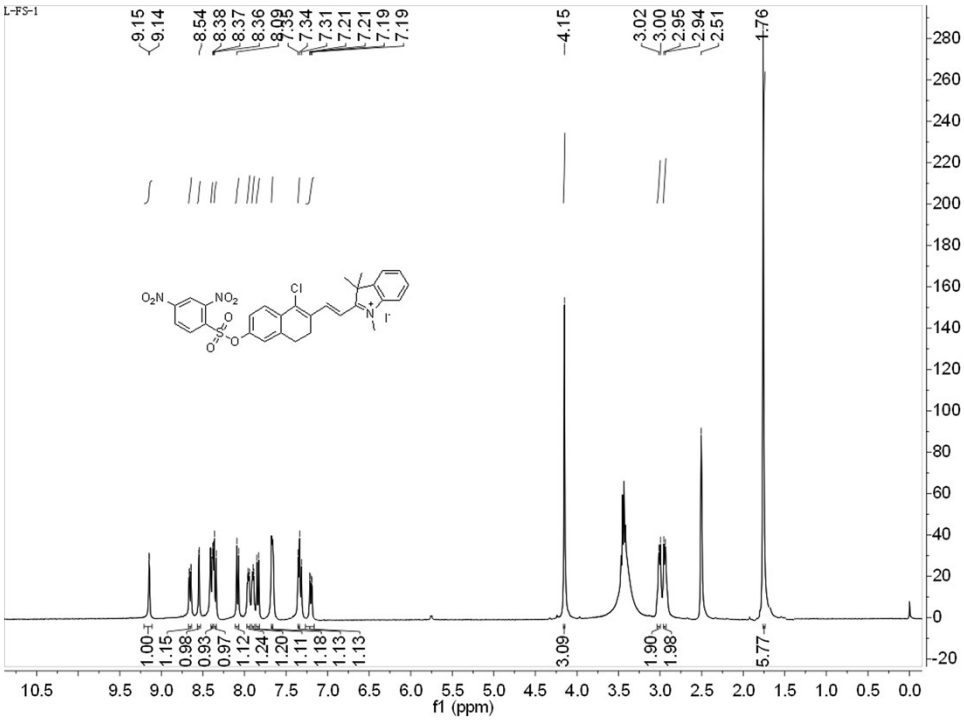

Figure S30. ^{1}H NMR spectrum of **CHMC-thiol** ($(CD_3)_2SO$).

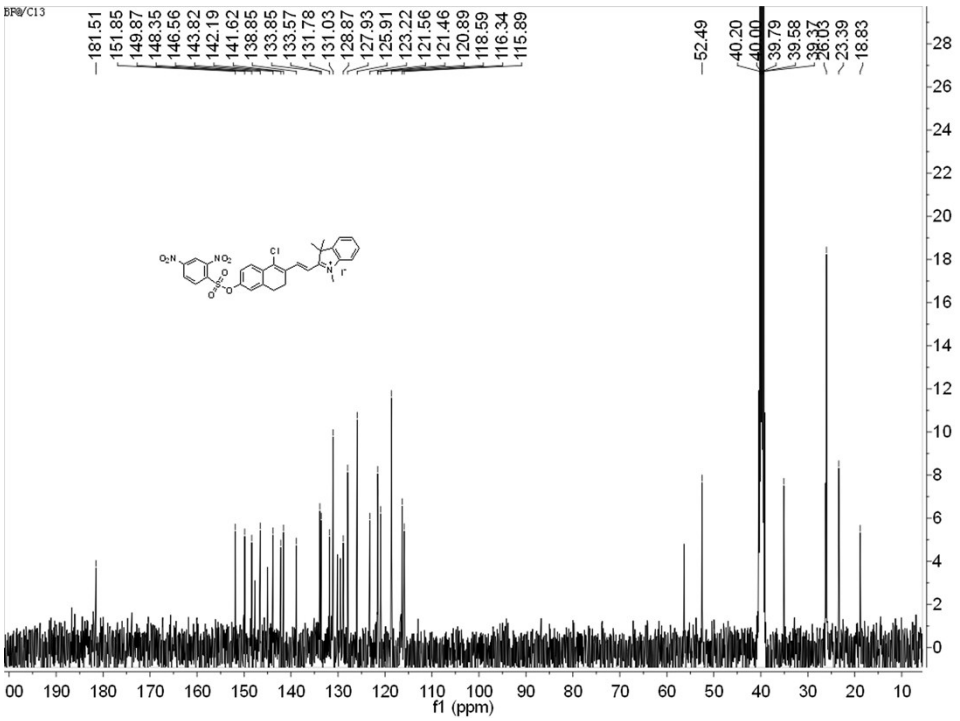

Figure S31. ^{13}C NMR spectrum of **CHMC-thiol** ($(CD_3)_2SO$).

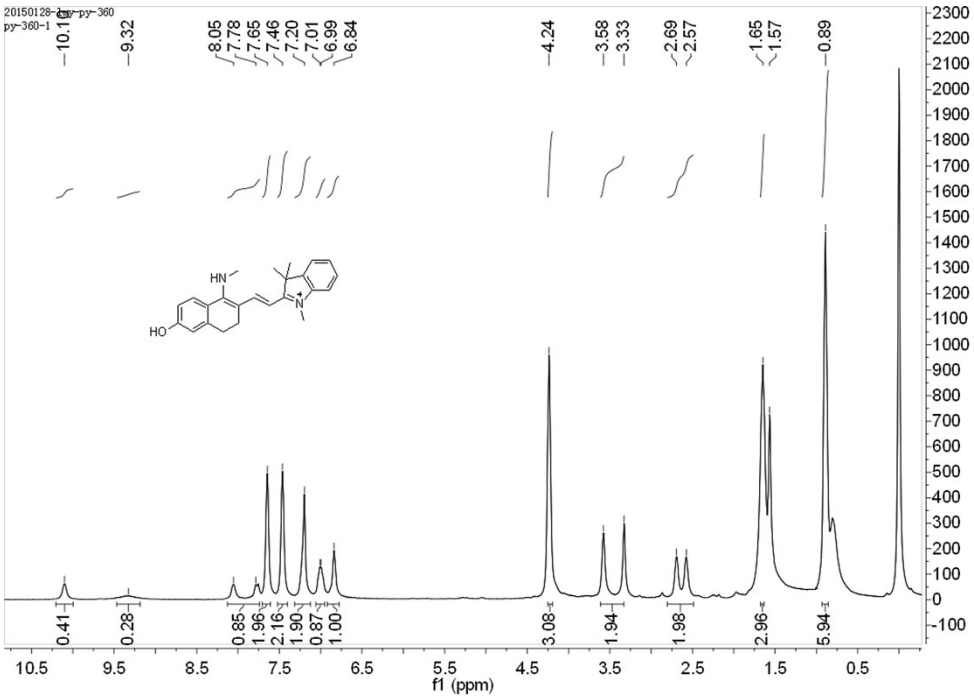

Figure S32. ^{1}H NMR spectrum of **5** ($CDCl_3$).

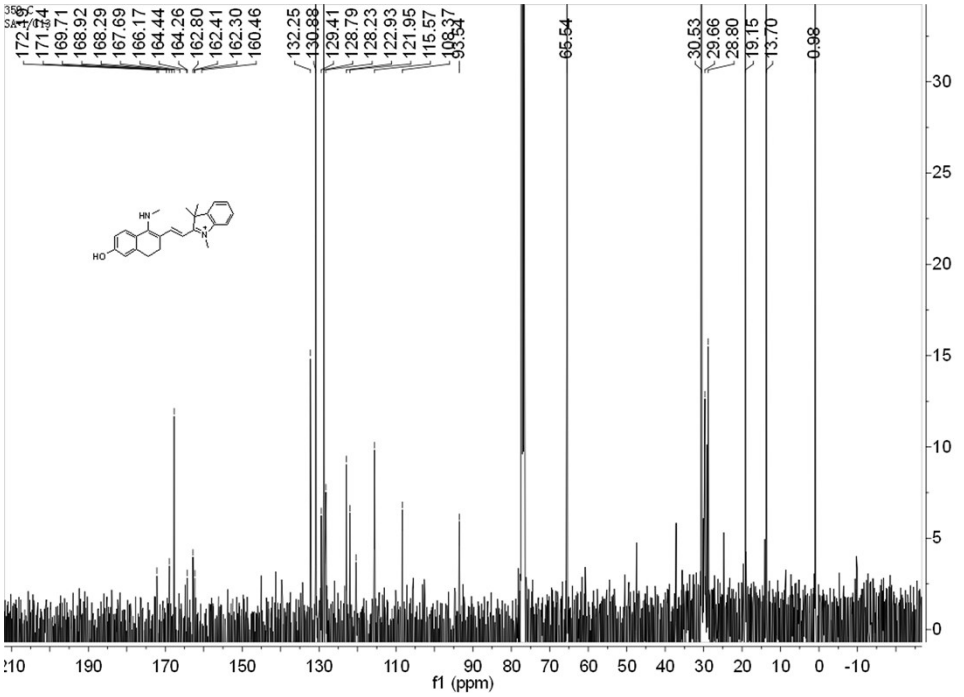

Figure S33. ^{13}C NMR spectrum of **5** ($CDCl_3$).

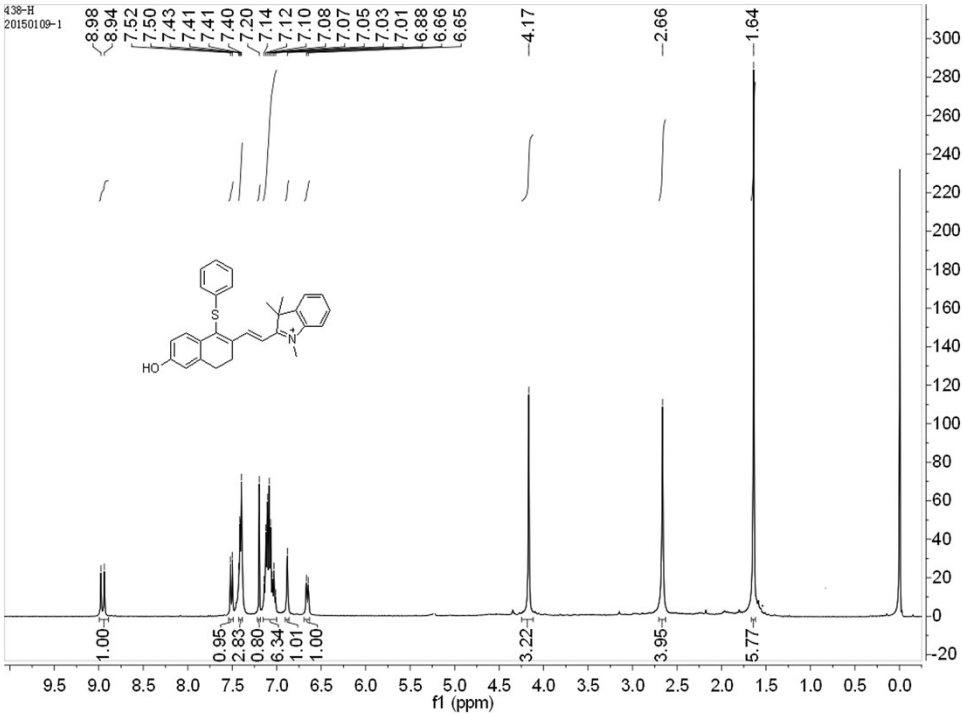

Figure S34. ^{1}H NMR spectrum of **6** ($CDCl_3$).

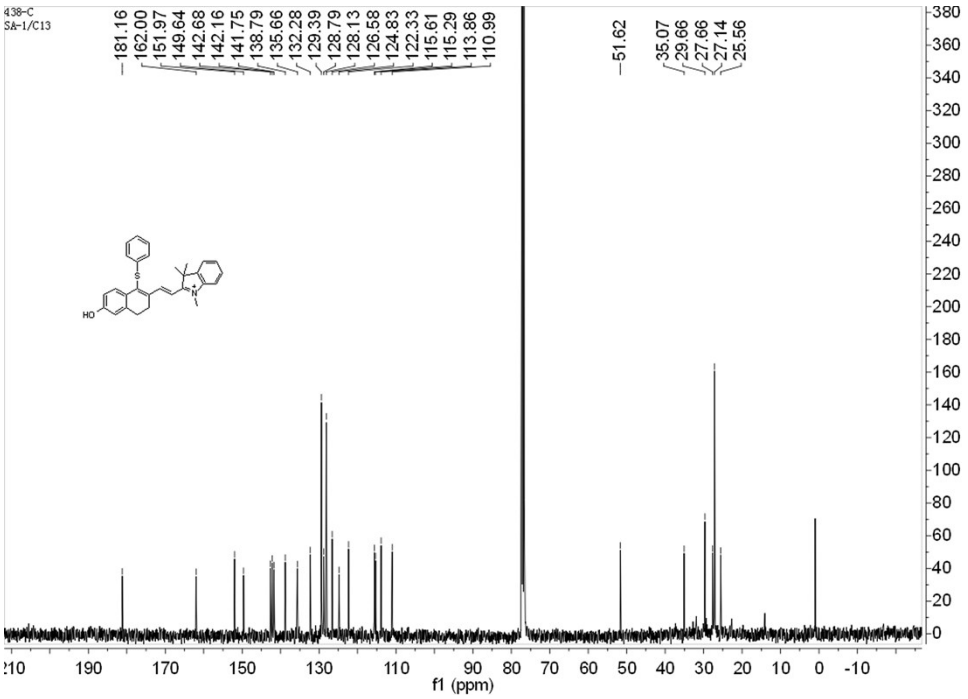

Figure S35. ^{13}C NMR spectrum of **6** ($CDCl_3$).