 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

<table>
<thead>
<tr>
<th>Section</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Materials and instruments</td>
<td>3</td>
</tr>
<tr>
<td>Determination of the fluorescence quantum yield</td>
<td>3</td>
</tr>
<tr>
<td>Calculation of pKa Values</td>
<td>3</td>
</tr>
<tr>
<td>Synthesis</td>
<td>4-8</td>
</tr>
<tr>
<td>Cell Culture and Imaging</td>
<td>8</td>
</tr>
<tr>
<td>Fluorescent Imaging in Living Mice</td>
<td>8</td>
</tr>
<tr>
<td>Figures S2-3</td>
<td>10</td>
</tr>
<tr>
<td>Figures S4-5</td>
<td>11</td>
</tr>
<tr>
<td>Figures S6-7</td>
<td>12</td>
</tr>
<tr>
<td>Figures S8-9</td>
<td>13</td>
</tr>
<tr>
<td>Figures S10-11</td>
<td>14</td>
</tr>
<tr>
<td>Figures S12-13</td>
<td>15</td>
</tr>
<tr>
<td>Figures S14-19</td>
<td>16-18</td>
</tr>
<tr>
<td>Scheme S1</td>
<td>19</td>
</tr>
<tr>
<td>Figure S20</td>
<td>19</td>
</tr>
<tr>
<td>Scheme S2</td>
<td>20</td>
</tr>
<tr>
<td>References</td>
<td>21</td>
</tr>
<tr>
<td>Figures S22-35</td>
<td>21-28</td>
</tr>
</tbody>
</table>
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: Fluorescence quantum yields for CHMC1, CHMC1-C, CHMC2, and CHMC2-C were determined by using ICG (Φf = 0.13 in DMSO) as a fluorescence standard. The quantum yield was calculated using the following equation:

\[ \Phi_{F(X)} = \Phi_{F(S)} \left( \frac{A_X F_X}{A_S F_S} \right) \left( \frac{n_X}{n_S} \right)^2 \]

Where \( \Phi_F \) 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)

\[ \text{pH} - pK_a = \log \left( \frac{F_{\text{max}} - F}{F - F_{\text{min}}} \right) \]

Where \( F \) is the area under the corrected emission curve, \( F_{\text{max}} \) and \( F_{\text{min}} \) are maximum and minimum limiting values of \( F \), respectively.
Synthesis of compound CHMC1-C.

POC1₃ (2.0 mL) was added dropwise 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 CH₂Cl₂/EtOH (50: 0 to 30: 1). ¹H NMR (400 MHz, (CD₃)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). ¹³C 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 C₂₄H₂₅ClNO⁺ ([M]+): 378.1619, Found, 378.1617.

Synthesis of compound CHMC1.

To a solution of compound CHMC1-C (250mg, 0.5mmol) and BBr₃ (500 mg) in dry dichloromethane (5 ml) were stirred under ice bath for 12 h at N₂ 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 Na₂SO₄, and evaporated under reduced pressure. The red solid was purified by column chromatography on silica gel flash chromatography using CH₂Cl₂/EtOH (20:1). The desired product was obtained as a red solid. ¹H NMR (400 MHz, (CD₃)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). ¹³C NMR (100 MHz, (CD₃)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, 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.**

POC\textsubscript{13} (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\textsubscript{2}Cl\textsubscript{2}/EtOH (50: 0 to 30: 1). ¹H NMR (400 MHz, (CD\textsubscript{3})\textsubscript{2}SO) 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). ¹³C NMR (100 MHz, (CD\textsubscript{3})\textsubscript{2}SO) 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\textsubscript{29}H\textsubscript{29}ClNO + ([M]+): 442.1923, Found, 442.1925.

**Synthesis of compound CHMC2.**

To a solution of compound **CHMC2-C** (569 mg, 1 mmol) and BBr\textsubscript{3} (600 mg) in dry dichloromethane (5 ml) were stirred under ice bath for 12 h at N\textsubscript{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\textsubscript{2}SO\textsubscript{4}, and evaporated under reduced pressure. The red solid was purified by column chromatography on silica gel flash chromatography.
using CH₂Cl₂/EtOH (25:1). The desired product was obtained as a red solid. ¹H NMR (400 MHz, (CD₃)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). ¹³C NMR (100 MHz, (CD₃)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 C₂₈H₂₇ClNO + ([M]+): 428.1775, Found, 428.1776.

**Synthesis of compound CHMC-thiol.**

A mixture of CHMC₁ (490 mg, 1mmol) and 2,4-dinitrobenzene-1-sulfonyl chloride (530mg, 2mmol) in dry dichloromethane was stirred at room temperature for 5h at N₂ 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 CH₂Cl₂/EtOH (30:1). ¹H NMR (400 MHz, (CD₃)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). ¹³C NMR (100 MHz, (CD₃)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 C₂₉H₂₅ClN₃O₇S ([M]+): 594.1093, Found, 594.1096.

**Synthesis of compound 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°C under nitrogen, the solution was concentrated under reduced pressure. The resulting crude product was purified by silica gel flash chromatography using ethyl CH₂Cl₂/MeOH (30: 1) as eluent to give the compound 5 as a red solid. ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (100 MHz, CDCl₃) 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.**

![Synthesis of compound 6.](image)

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°C under nitrogen, the solution was concentrated under reduced pressure. The resulting crude product was purified by silica gel flash chromatography using ethyl CH₂Cl₂/MeOH (35: 1) as eluent to give the compound 6 as a red solid. ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (100 MHz,
S8

CDCl3) 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’s medium (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.

<table>
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<th>Compound</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon_{\text{max}}$ ($10^5$)</th>
<th>$\lambda_{\text{em}}$ (nm)</th>
<th>$\Phi$</th>
<th>Stokes Shift (nm)</th>
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<td>CHMC1</td>
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<td>1.42</td>
<td>695</td>
<td>0.08</td>
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<td>CHMC1-C</td>
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<td>564</td>
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<tr>
<td>CHMC2</td>
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<td>1.48</td>
<td>714</td>
<td>0.06</td>
<td>24</td>
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<tr>
<td>CHMC2-C</td>
<td>506</td>
<td>0.36</td>
<td>610</td>
<td>0.01</td>
<td>104</td>
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</tbody>
</table>
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 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) Brightfield 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


Figure S22. $^1$H NMR spectrum of CHMC1-C ((CD$_3$)$_2$SO).
Figure S23. $^{13}$C NMR spectrum of CHMC1-C ((CD$_3$)$_2$SO).

Figure S24. $^1$H NMR spectrum of CHMC1 ((CD$_3$)$_2$SO).
Figure S25. $^{13}$C NMR spectrum of CHMC1 ((CD$_3$)$_2$SO).

Figure S26. $^1$H NMR spectrum of CHMC2-C ((CD$_3$)$_2$SO).
Figure S27. $^{13}$C NMR spectrum of CHMC2-C ((CD$_3$)$_2$SO).

Figure S28. $^1$H NMR spectrum of CHMC2 ((CD$_3$)$_2$SO).
Figure S29. $^{13}$C NMR spectrum of CHMC2 ((CD$_3$)$_2$SO).

Figure S30. $^1$H NMR spectrum of CHMC-thiol ((CD$_3$)$_2$SO).
Figure S31. $^{13}$C NMR spectrum of CHMC-thiol ((CD$_3$)$_2$SO).

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$_3$).