

Assembling of Functional Cyclodextrin-decorated Upconversion Luminescence Nanoplatfom for Cysteine- sensing

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Experimental Section

Synthesis of RHO

Rhodamine B hydrazide (0.456 g, 1 mmol) was dissolved in ethanol solvent, excess amount of 40% oxaldehyde mixed with ethanol was added with stirring overnight at room temperature. Then plenty of saturated sodium chloride solution was added to precipitate the crude product. It was finally purified by flash column chromatography on silica gel with dichloromethane as eluent, affording 0.37 mg of compound RHO as a yellow solid (yield 73%). ¹H NMR (300 MHz, CDCl₃) δ 9.45 (d, J = 7.5 Hz, 1H), 8.03 (d, J = 0.8 Hz, 1H), 7.61–7.46 (m, 2H), 7.37 (d, J = 7.4 Hz, 1H), 7.11 (d, J = 0.5 Hz, 1H), 6.43 (dd, J = 17.0, 5.6 Hz, 4H), 6.25 (dd, J = 8.8, 2.4 Hz, 2H), 3.33 (q, J = 7.1 Hz, 8H), 1.17 (t, J = 7.1 Hz, 12H); ¹³C NMR (75 MHz, CDCl₃) δ 12.57, 44.46, 66.15, 98.40, 104.07, 108.40, 124.09, 126.82, 127.55, 128.62, 134.88, 141.60, 149.26, 152.70, 152.85, 165.82, 192.60.

Synthesis of β-NaYF₄: 20% Yb³⁺, 2% Er³⁺ nanoparticles

In a typical synthesis, YCl₃·6H₂O (0.78 mmol), YbCl₃·6H₂O (0.20 mmol) and ErCl₃·6H₂O (0.02 mmol) were added to a three-necked flask containing oleic acid (6 mL) and 1-octadecene (15 mL). The solution was heated to 160 °C under nitrogen atmosphere for half an hour to get a homogeneous solution and then cooled down to room temperature naturally. 10 mL methanol solution containing NH₄F (4 mmol) and NaOH (2.5 mmol) was added dropwise to the flask and stirred for 30 minutes. Then solution was heated slowly to 70 °C to thoroughly evaporate the methanol. Subsequently, degassed at 100 °C for 10 minutes, the solution was heated to 300 °C and maintained for 1 h under nitrogen protection. After the solution was cooled down to room temperature, nanoparticles were precipitated by adding ethanol, centrifuged and washed with ethanol for three times. The isolated nanoparticles were redispersed in cyclohexane for further experiments.

Preparation of α-CD-modified UCNPs

α-CD modified OA-UCNPs was carried out as follows: OA-UCNPs were dissolved

in hexane to form 0.5 mg/mL solution and then mixed with equal volume α -CD in water (5 mM) to form the inclusion complexes between OA and α -CD. After stirring for 20 h, the transparent hexane in upper layer was discarded, and the white suspension in water under layer was centrifuged and washed with water for three times. The collected modified UCNPs were re-dispersed in water for further use.

Characterization

The X-ray diffraction (XRD) measurements were performed on a Bruker D8 FOCUS diffractometer using a Cu target radiation source ($\lambda = 0.15418$ nm). The transmission electron microscopy (TEM) images were determined with a JEOL JEM-2010 transmission electron microscope. Dilute dispersions in cyclohexane were dropped on carbon formvar-coated copper grids and air dried before imaging. ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance 300 spectrometer using tetramethylsilane as the internal standard. Field-emission scanning electron microscopy (FE-SEM) images were measured on a Hitachi S-4800 microscope. Upconversion luminescence spectra measurements were acquired on a Hitachi F-4500 fluorescence spectrophotometer with the excitation of a 0-5 W adjustable CW 980 nm laser diode (Hi-Tech Optoelectronics Co., Ltd. China). UV-Vis absorption spectra were obtained on a Shi-madzu-UV-3101 scanning spectrophotometer. Mass spectrometry was performed on a Waters Quattro premier XE (WATERS, USA) with an electrospray ionization (ESI) source. Ionization was carried out in positive mode with a capillary voltage of 3000 V. Data were collected in centroid mode from m/z 100 to 2000. Emission lifetimes were measured at 540 nm (from Er^{3+}) with a Lecroy Wave Runner 6100 Digital Oscilloscope (1GHz) using a tunable laser as the excitation source (Continuum Sunlite OPO).

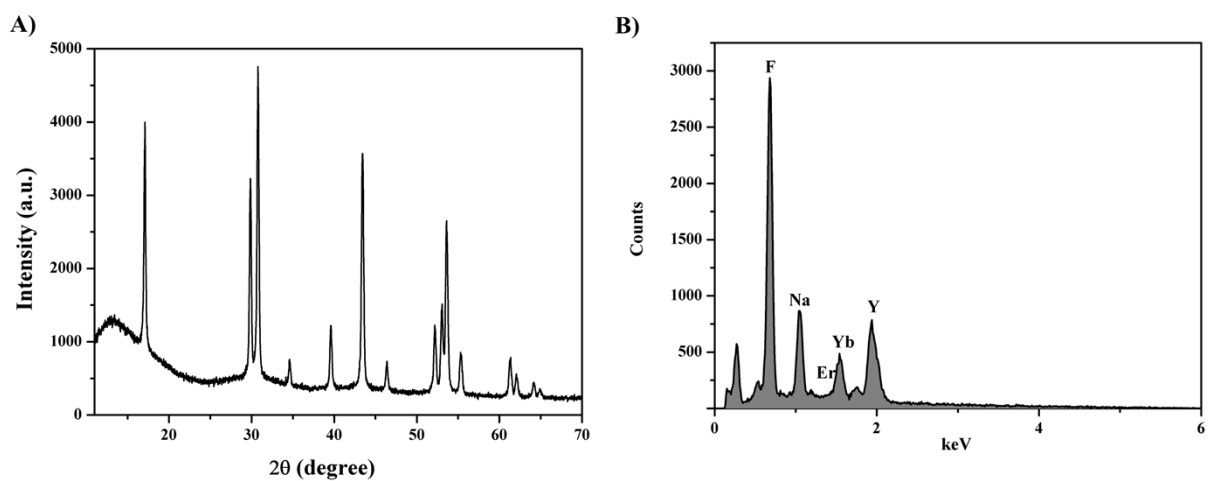


Fig. S1 XRD pattern(A) and EDX analysis(B) of $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$.

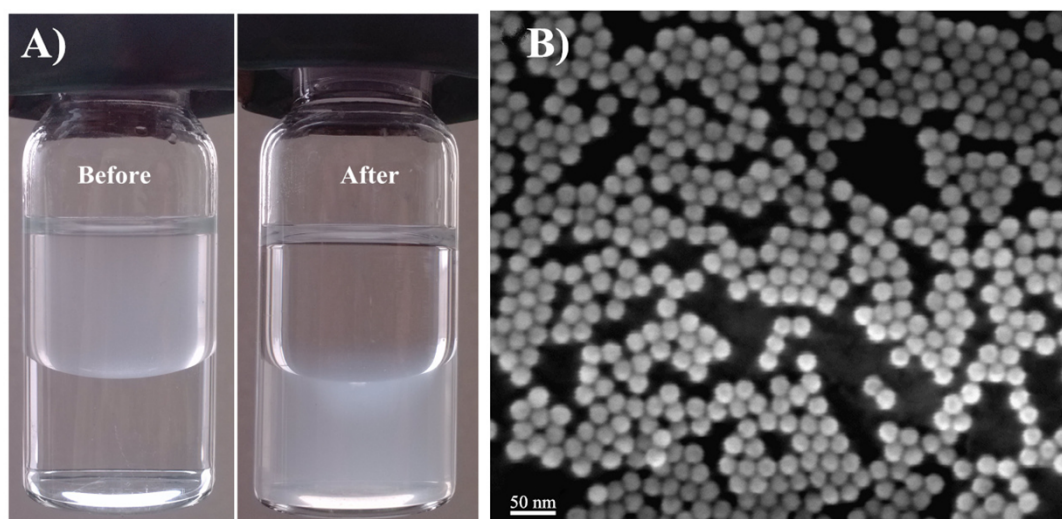


Fig. S2 Transformation of UCNPs dispersed in cyclohexane and water before and after modified by α -CD and the morphology of α -CD modified UCNPs by SEM

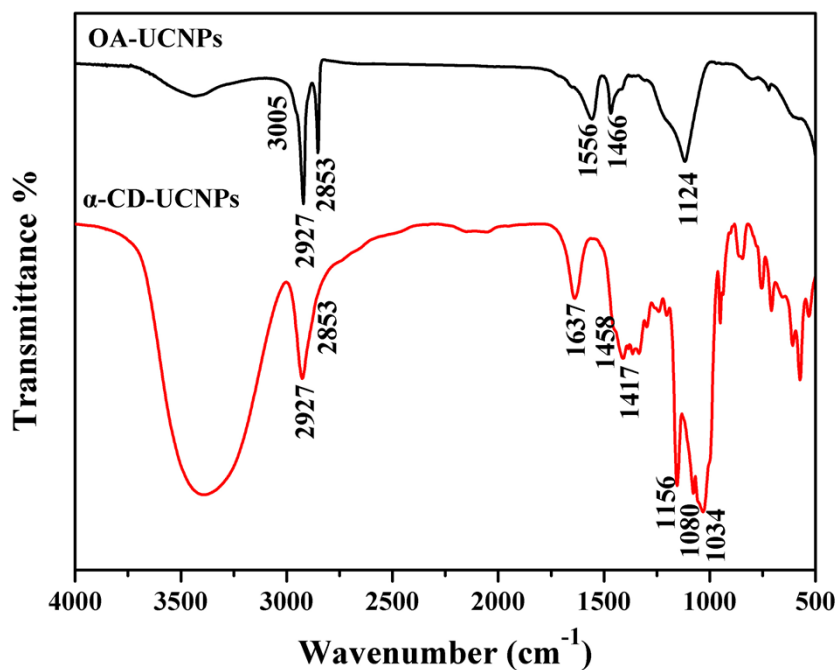


Fig. S3 FT-IR spectra of OA-UCNPs and α -CD-UCNPs.

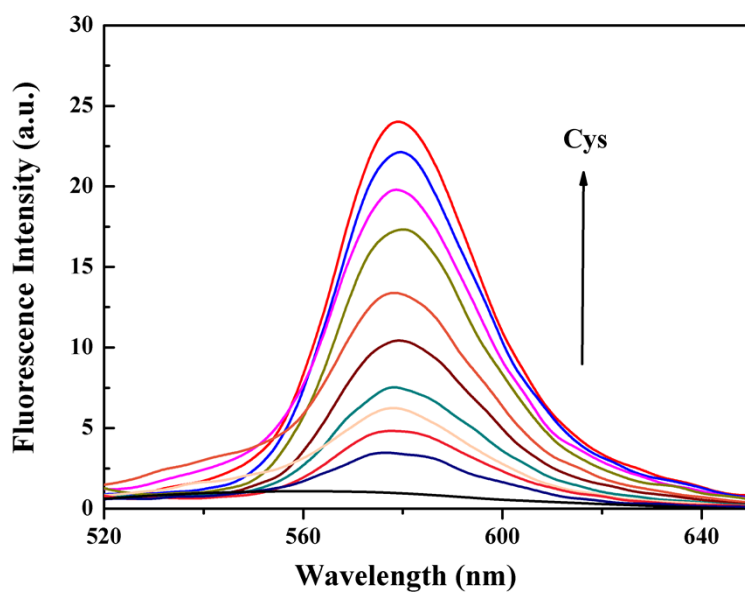


Fig. S4 The emission titration profile of RHO ($10 \mu\text{M}$) in the solution of ethanol/water (3:7, v/v) with gradually increasing amount of Cys (0-100 μM) (ex= 520 nm, slit: 5 nm/5 nm).

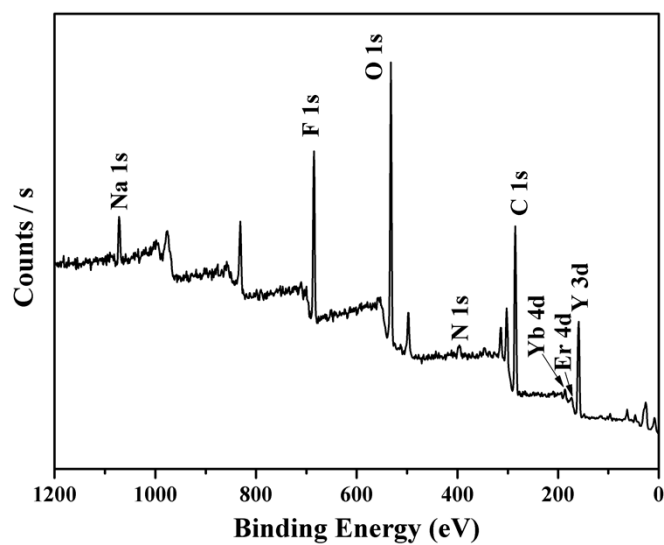


Fig. S5 XPS spectra of the as-prepared system, the peaks at 1072.6 eV, 284.5 eV, 532.3 eV, 158.4 eV, 685.1 eV, 396.1 eV, 186.4 eV and 173.2 eV were assigned to the binding energy of Na $1s$, C $1s$, O $1s$, Y $_{3d5/2}$, F $1s$, N $1s$, Yb $4d_{5/2}$ and Er $4d_{5/2}$.

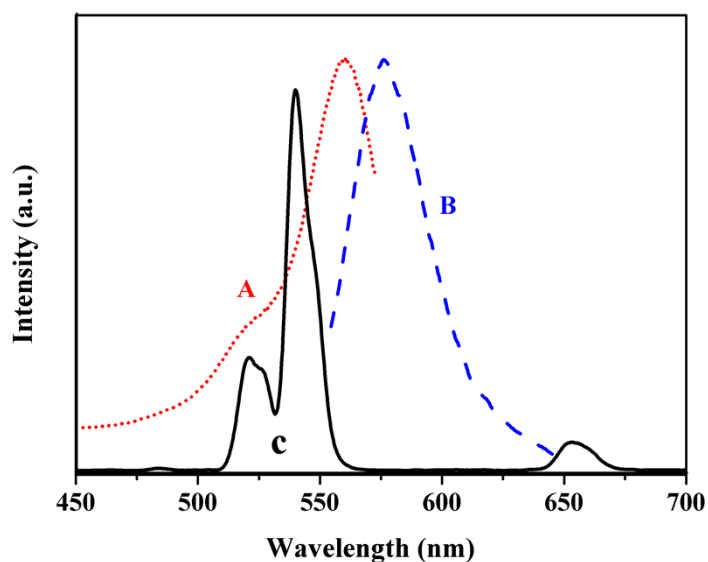


Fig. S6 The excitation (A, $\lambda_{em} = 578$ nm) and emission spectra (B, $\lambda_{ex} = 540$ nm) of RHO in the presence of Cys; UCL spectra of OA-UCNPs (C) under 980 nm excitation.

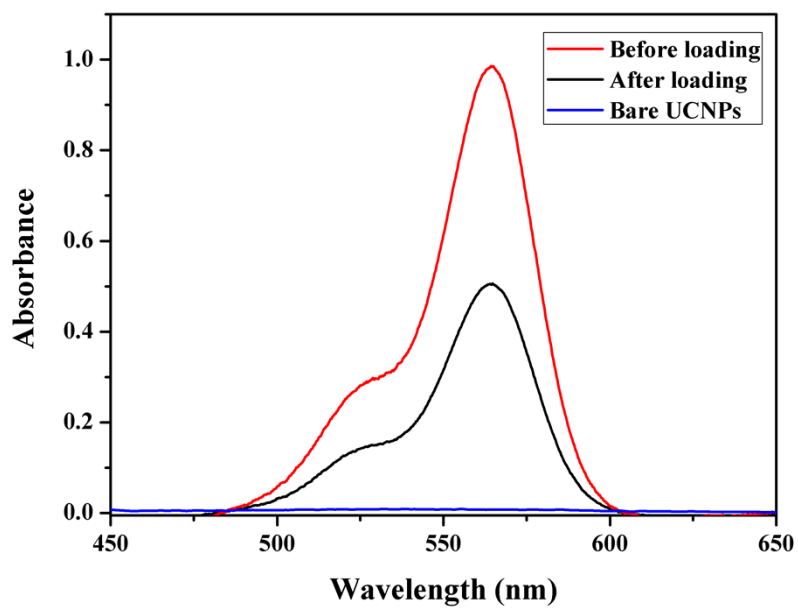


Fig. S7 The UV-vis absorbance spectra of bare UCNPs (blue curve), RHO before loading (red curve) and after loading (black curve) on to α -CD-UCNPs.

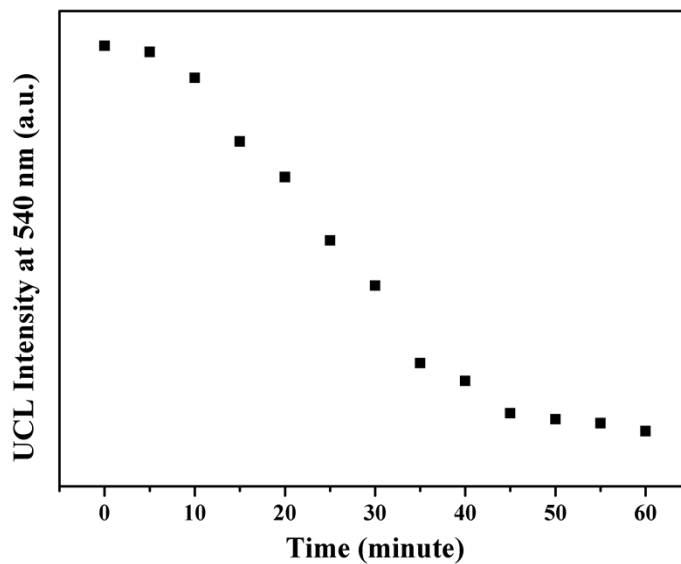


Fig. S8 The changes of UCL intensity at 540 nm along with different time after addition of 100 μ M Cys into the RHO functionalized UCNPs solution (0.5 mg/mL in PBS, pH=7.0)

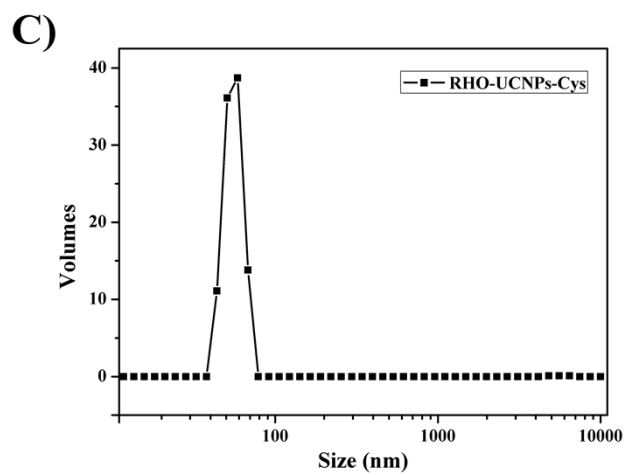
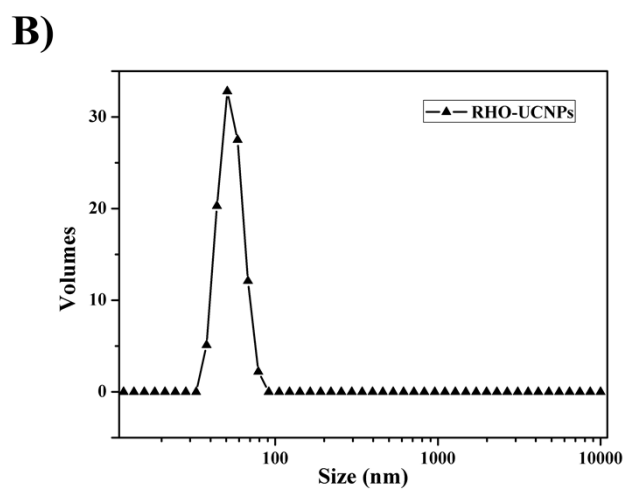
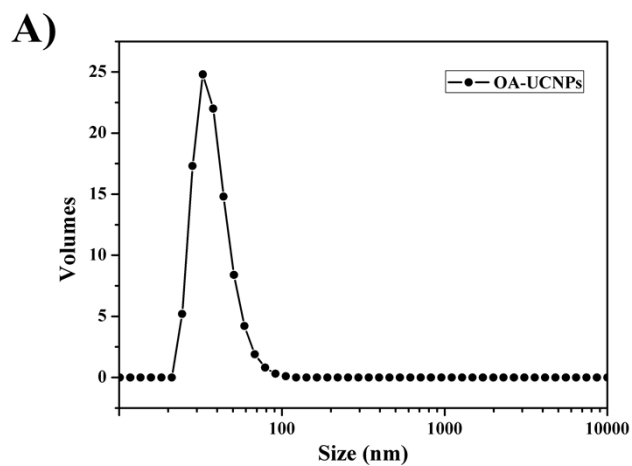


Fig. S9 DLS data of (A) OA-UCNPs, 32 nm; (B) RHO-UCNPs, 51 nm; (C) RHO-UCNPs-Cys, 58 nm

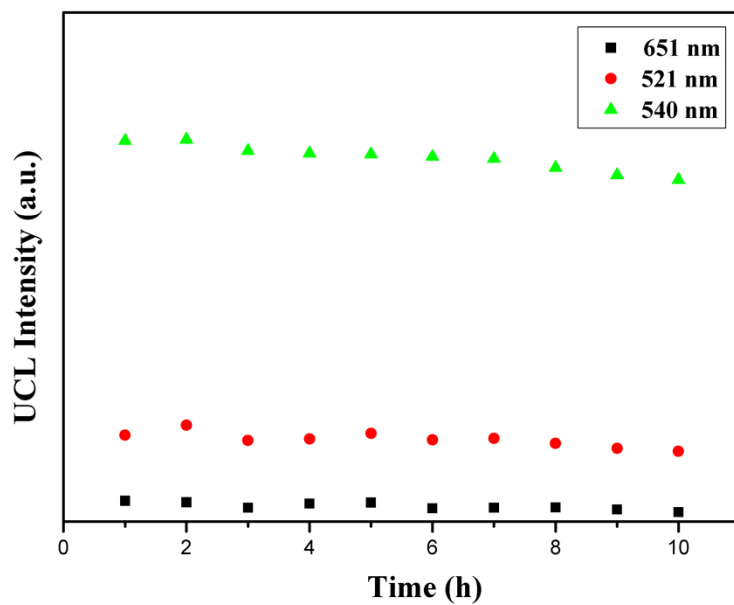


Fig. S10 The relative UCL intensity (peaking at 521 nm, 540 nm and 651 nm respectively) of the sensing system in the presence of Cys (100 μ M) for different times.

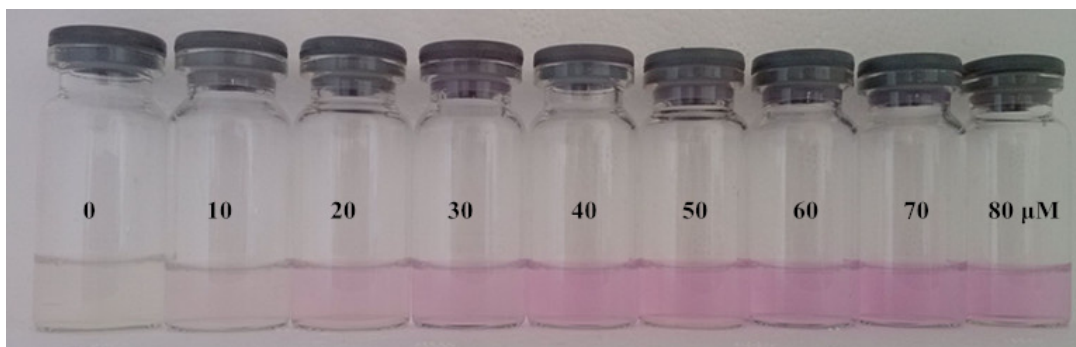


Fig. S11 Colour changes of the sensing system upon addition of increasing amount of Cys(0-80 μ M).

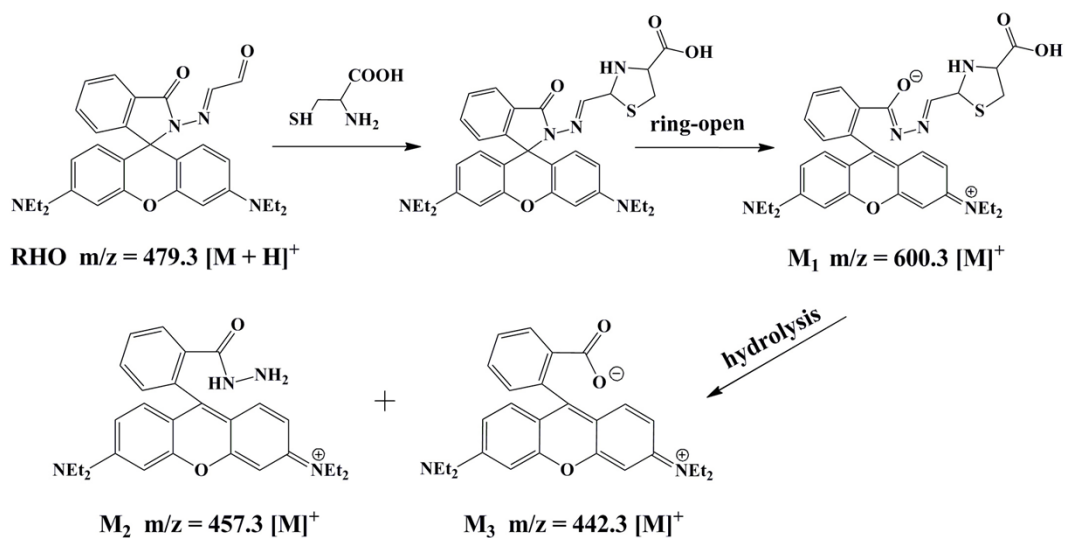


Fig. S12 Proposed sensing mechanism of Cys

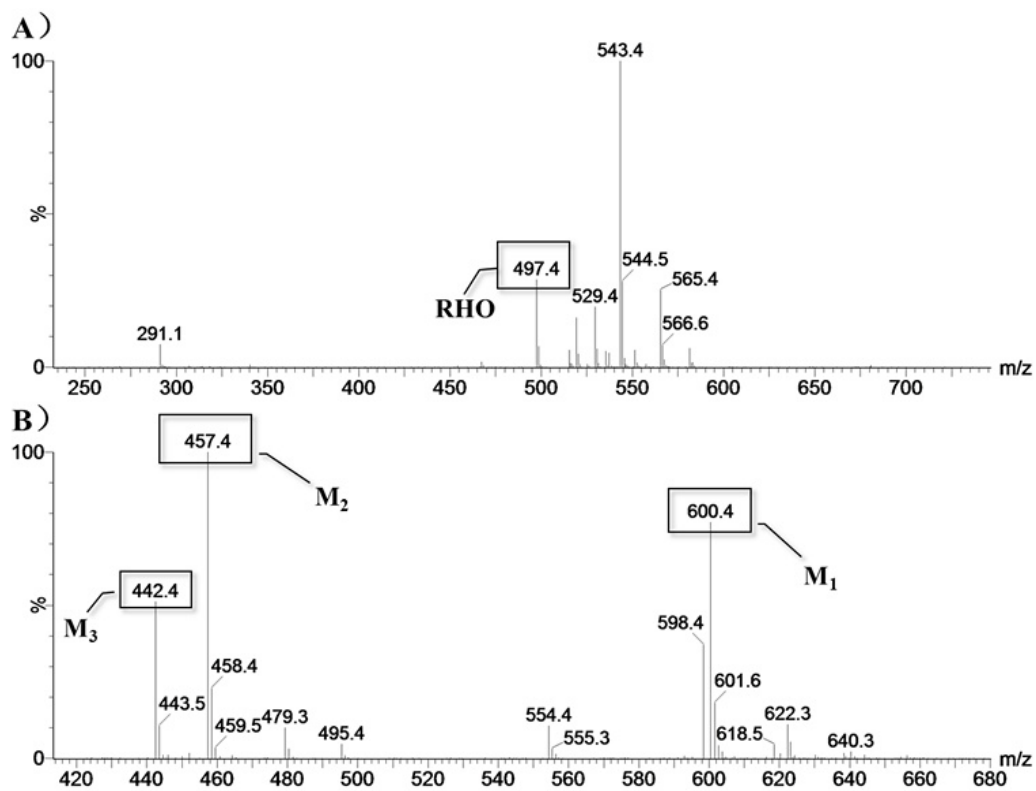


Fig. S13 ESI-MS of the product: reaction of RHO with Cys