Supporting Information for

The sphere-to-rod transition of squaraine-embedded micelles: a self-assembly platform displays a distinct response to cysteine and homocysteine

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Materials. Natural amino acids, Hcy, SDS and CTAB were purchased from Xiaan Wolsen Bio. Reagents Co. (Xiaan, China) and were used as received unless specifically noted. CBT and sodium salicylate were purchased from Aladdin (China). Cationic squaraine dye, **SQ**, was synthesized and purified as reported previously.[S1]

Measurements

Absorption and emission spectra were collected by using a Shimadzu 1750 UV-visible spectrometer and a RF-5301 fluorescence spectrometer (Japan), respectively. SEM images were observed at 75 K with a JSM-6701F scanning electron microscope.

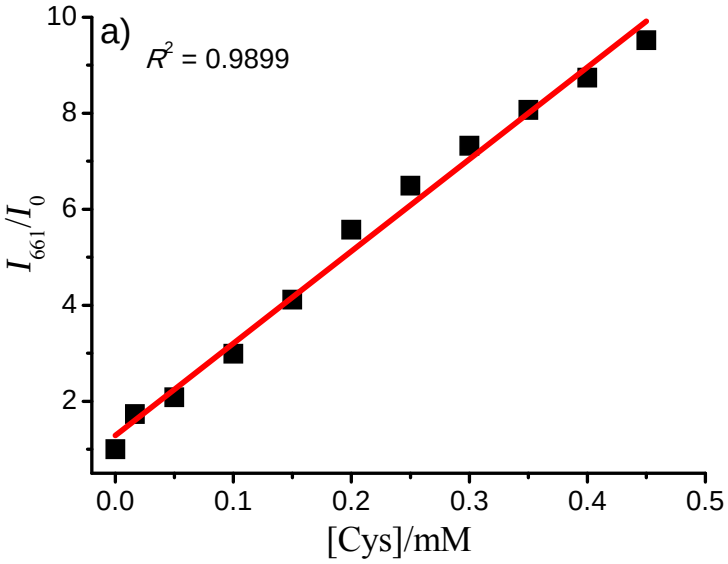
Sample Preparation and Titration. Stock solutions of CBT and Cys (or Hcy) were mixed at 25^0C with the 1:1 molar ratio of CBT to Cys (or Hcy) in aqueous solution for 3 min. Stock solution of **SQ** (5.0×10^{-4} M) was prepared in ethanol and diluted to 5.0×10^{-6} M for titration experiments. CBT-Cys or CBT-Hcy solutions were added to **SQ** solution, UV and fluorescence spectra were monitored within 1 min.

Preparation of human blood samples. The procedure for preparation of human blood samples is followed the reported literature.[S2] Human blood samples were collected from healthy volunteers treated in the local Medical Hospital. All samples were obtained by venipuncture and collected in heparinized vacutainer tubes. Then, a 200 μL aliquot of the blood was deproteinized by mixing immediately with 400 μL of cold 10% Cl_3CCOOH. After vortex mixing, the mixture was centrifuged at 8000 rpm for 10 min. A total of 400 μL of the supernatant was collected. The obtained supernatant was ready for assays.

S1. Y. Xu, Z. Li, A. Malkovskiy, S. Sun and Y. Pang, *J. Phys. Chem. B*, 2010, 114, 8574.
S2. D. Tian, Z. Qian, Y. Xia and C. Zhu, *Langmuir*, 2012, 28, 3945.

Table S1 Determination results of Cys in diluted human blood samples (*n*=3)

Entry	without spiking	0.21 mM Cys spiked	Recovery (%)
1	0.014±0.007	0.223±0.008	99.54±1.14
2	0.012±0.005	0.225±0.001	101.63±0.20
3	0.012±0.003	0.227±0.007	102.36±2.33



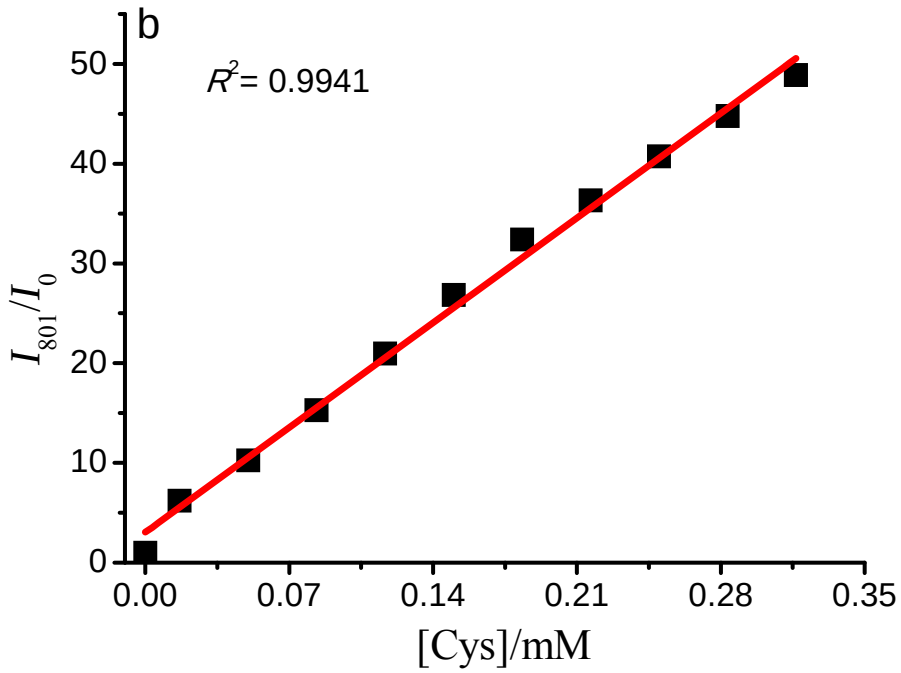


Fig. S1 The relative fluorescence change of **SQ** (5.0×10^{-6} M) at 661 (a) and 801 nm (b) in aqueous solution in the presence of CBT and CTAB (0.05% wt) with increasing concentrations of Cys as indicated (the molar ratio of CBT to Cys was fixed as 1:1. λ_{ex} = 600 nm).

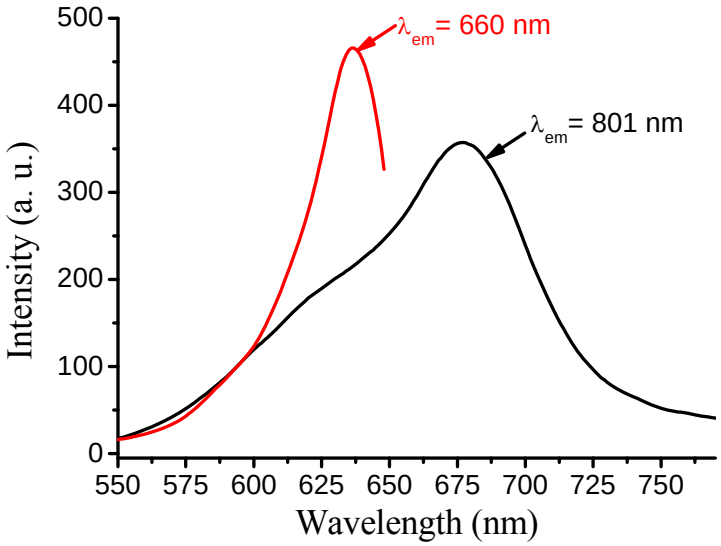


Fig. S2 Excitation spectra of **SQ** (5.0×10^{-6} M) in aqueous solution in the presence of CBT, CTAB (0.05% wt) upon addition of Cys, where [CBT] = [Cys] = 1.5×10^{-4} M and λ_{em} = 660 and 801nm respectively.

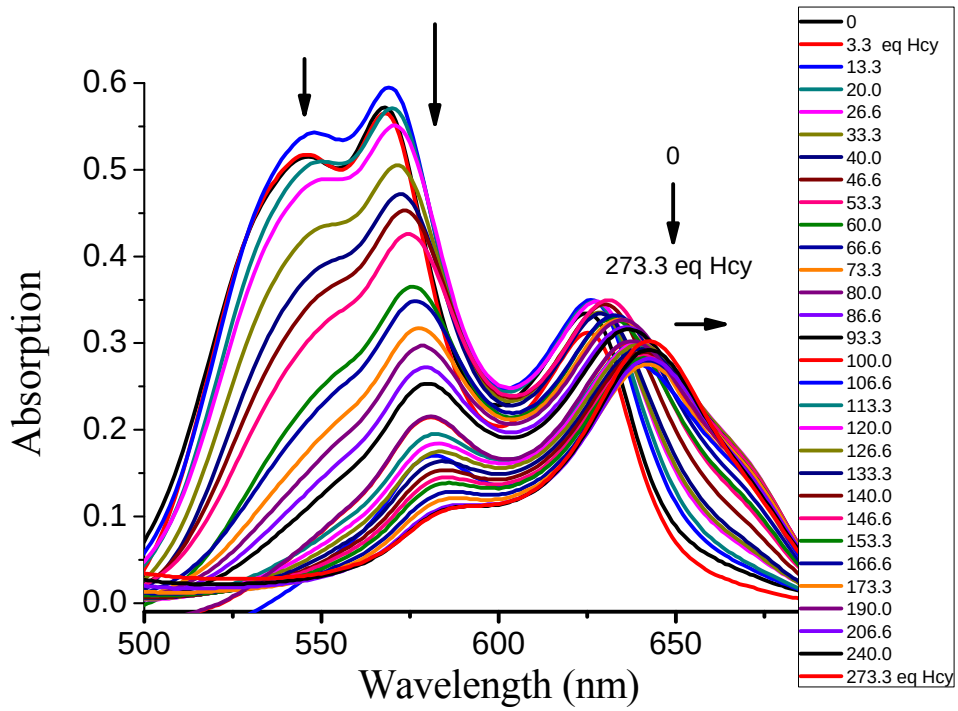


Fig. S3 Absorption spectra change of **SQ** (5.0×10^{-6} M) in aqueous solution containing CTAB (0.05% wt) with increasing concentrations of Hcy as indicated (the molar ratio of CBT to Hcy was fixed as 1:1).

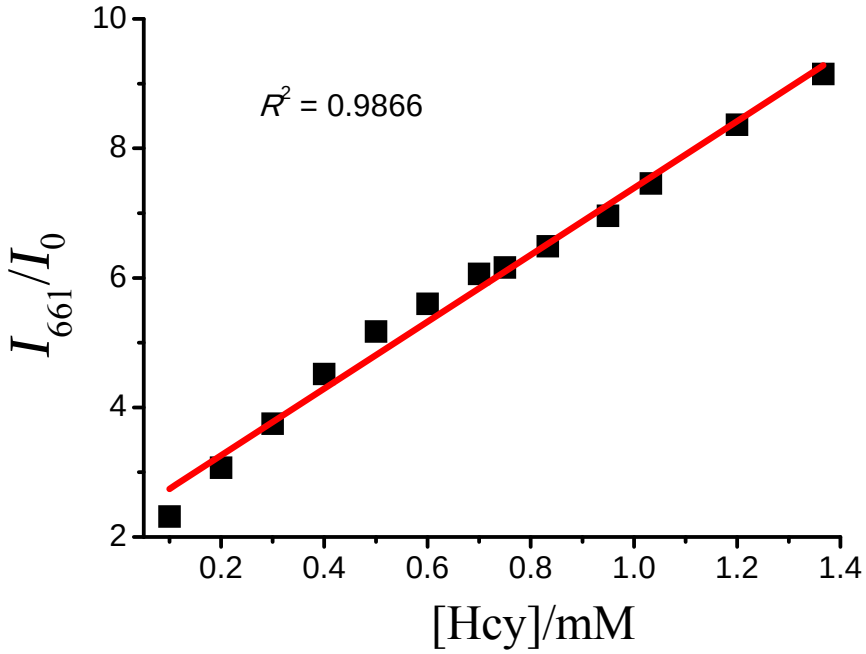


Fig. S4 The relative fluorescence change of **SQ** (5.0×10^{-6} M) at 661 nm in aqueous solution in the presence of CBT and CTAB (0.05% wt) with increasing concentrations of Hcy as indicated (the molar ratio of CBT to Hcy was fixed as 1:1. λ_{ex} = 600 nm).

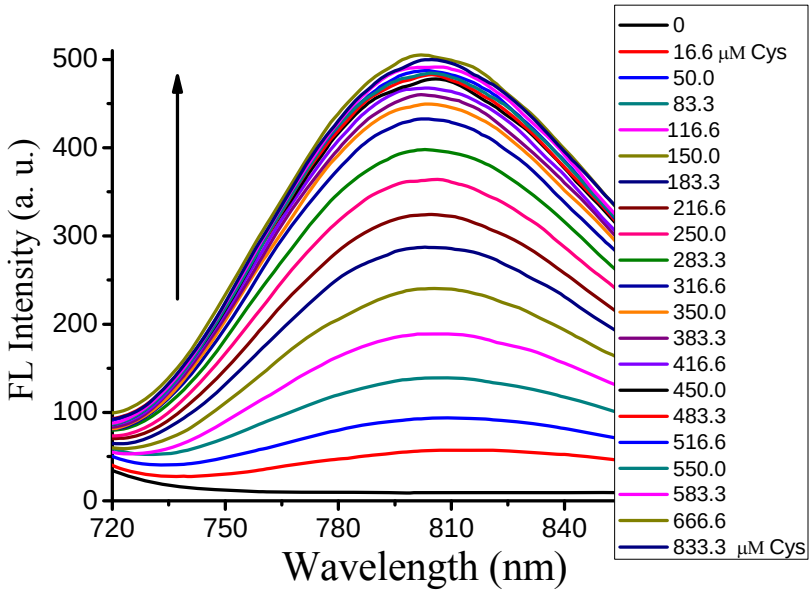


Fig. S5 Variation in the emission spectra of **SQ** (5.0×10^{-6} M) in aqueous solution containing CTAB (0.05% wt) with increasing concentrations of Cys as indicated (the molar ratio of CBT to Cys was fixed as 1:1 and λ_{ex} = 600 nm).

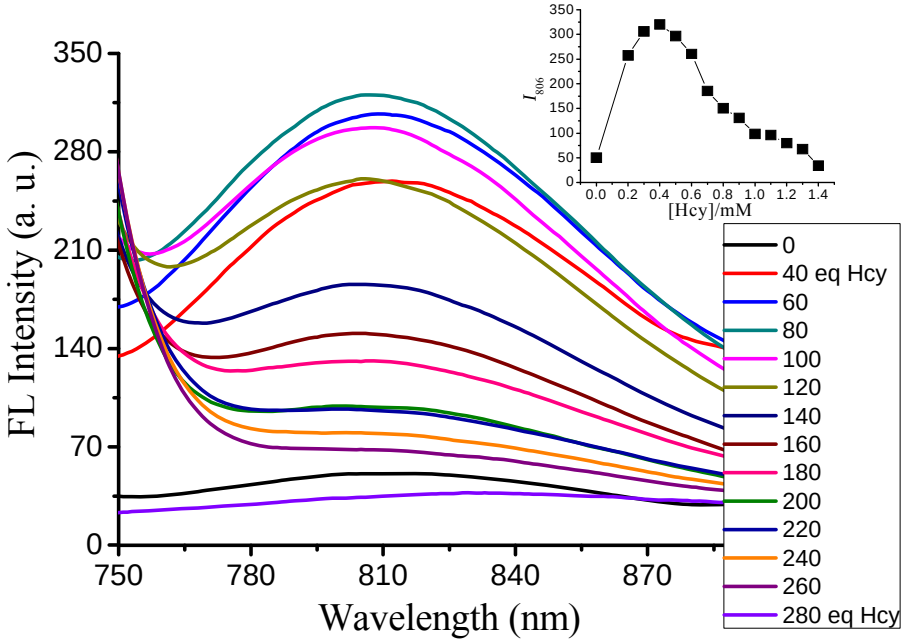


Fig. S6 Variation in the emission spectra of **SQ** (5.0×10^{-6} M) in aqueous solution containing CTAB (0.05% wt) with increasing concentrations of Hcy as indicated (the molar ratio of CBT to Hcy was fixed as 1:1 and λ_{ex} = 600 nm. Inset: the response of fluorescence intensity at 806 nm to the concentration of Hcy).

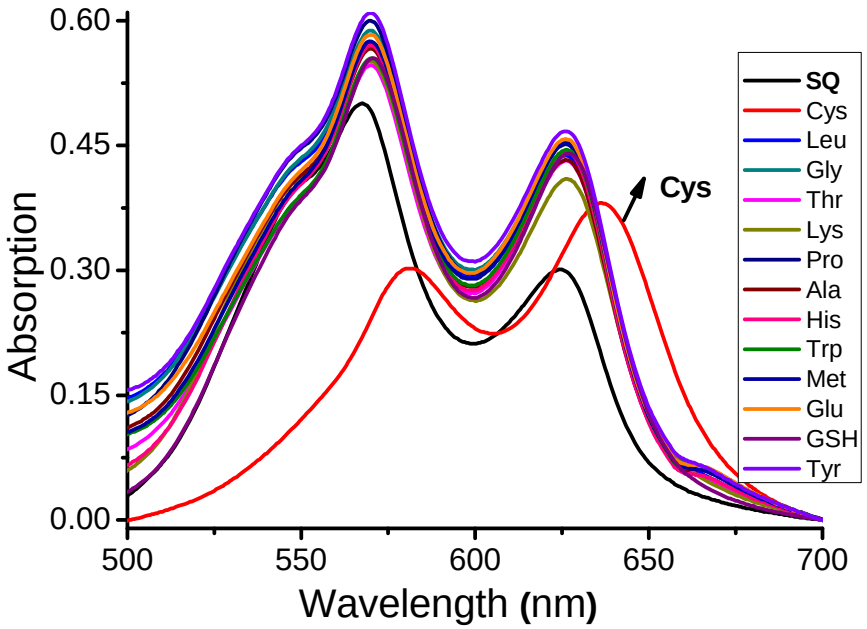


Fig. S7 Absorption spectra of **SQ** (5.0×10^{-6} M) alone and with various amino acids in aqueous solution in the presence of CBT and CTAB (0.05% wt), where [CBT] = [amino acids] = 4.5×10^{-4} M.

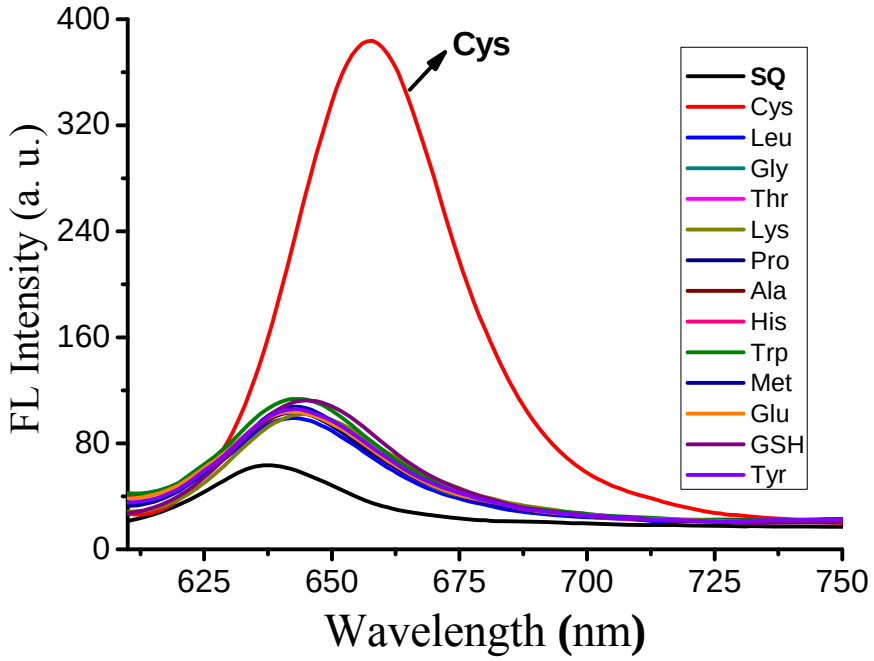


Fig. S8 Fluorescence spectra of **SQ** (5.0×10^{-6} M) alone and with various amino acids in aqueous solution in the presence of CBT and CTAB (0.05% wt), where [CBT] = [amino acids] = 4.5×10^{-4} M and λ_{ex} = 600 nm.

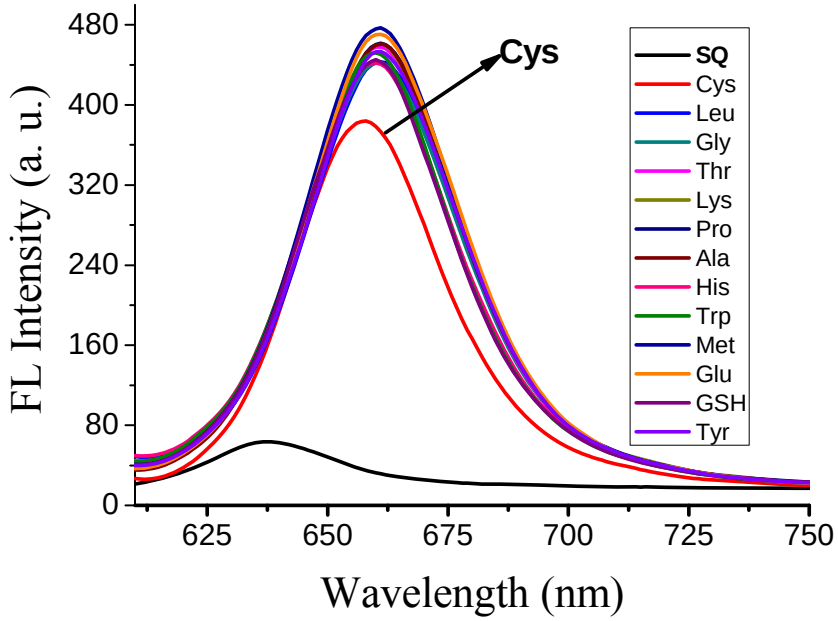


Fig. S9 Fluorescence spectra of **SQ** (5.0×10^{-6} M) with various amino acids and subsequent addition of Cys in aqueous solution in the presence of CBT and CTAB (0.05% wt), where [CBT] = [amino acids] = 4.5×10^{-4} M and λ_{ex} = 600 nm.

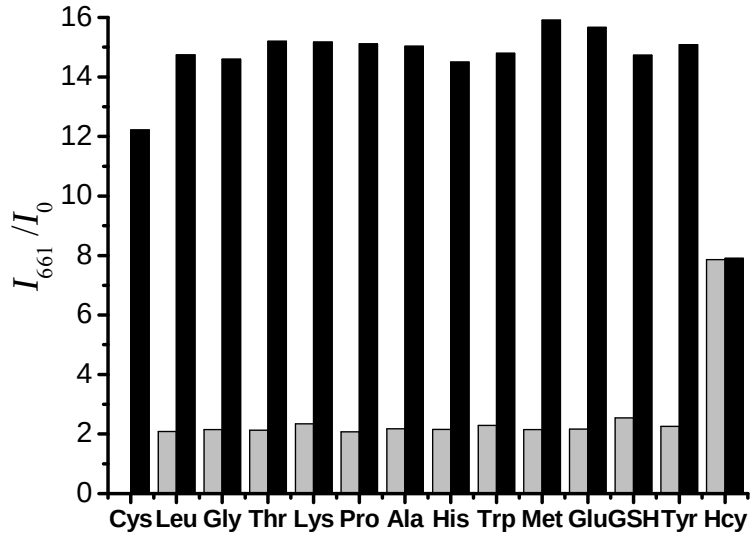


Fig. S10 Emission intensity change (I_{661}/I_0) of **SQ** (5.0×10^{-6} M) at 661 nm in aqueous solution containing CBT and CTAB (0.05% wt) in the presence of different amino acids with excitation wavelength at 600 nm (dark bar). Black bars represent the intensity with subsequent addition of Cys ([CBT] = [amino acids] = 4.5×10^{-4} M). I_0 indicates the fluorescence intensity of free amino acids, while I_{661} indicated the fluorescence intensity upon addition of amino acids.

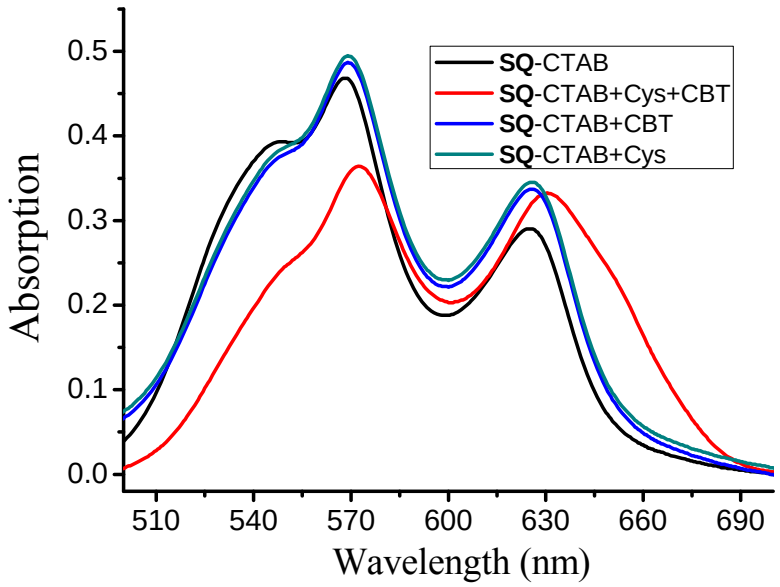


Fig. S11 Absorption spectra of **SQ** (5.0×10^{-6} M) in aqueous solution in the absence and the presence of CBT, CTAB (0.05% wt) and the mixture of CBT and Cys (CBT-Cys), where [CBT] = [Cys] = 1.5×10^{-4} M.

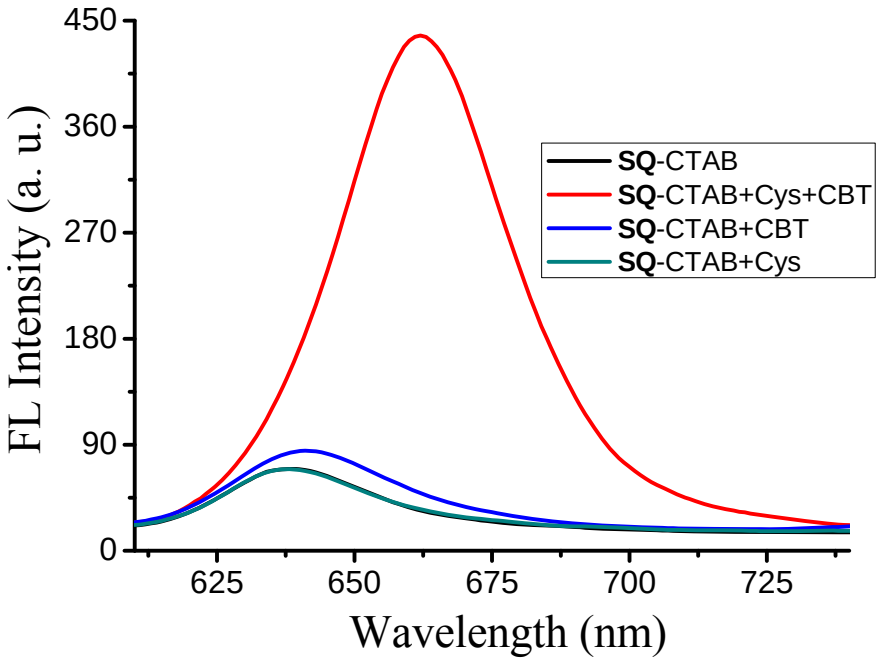


Fig. S12 Fluorescence spectra of **SQ** (5.0×10^{-6} M) in aqueous solution in the absence and the presence of CBT, CTAB (0.05% wt) and the mixture of CBT and Cys (CBT-Cys) ([CBT] = [Cys] = 1.5×10^{-4} M. Excitation wavelength at 600 nm).

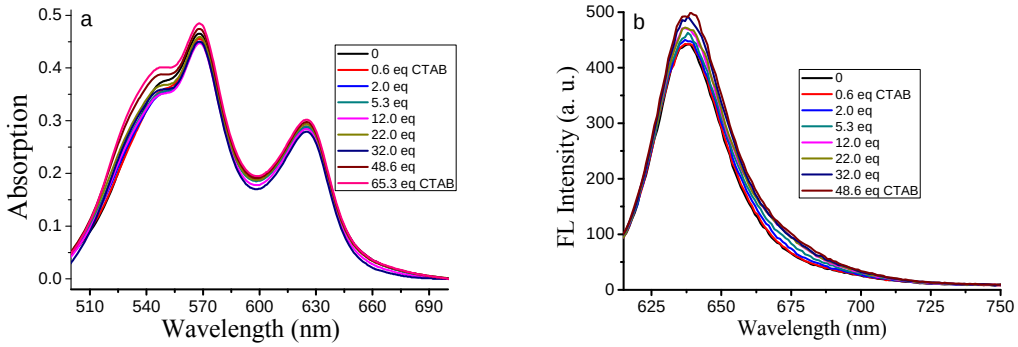


Fig. S13 Absorption (a) and fluorescent (b) spectra change of **SQ** (5.0×10^{-6} M) in aqueous solution upon addition of CTAB.

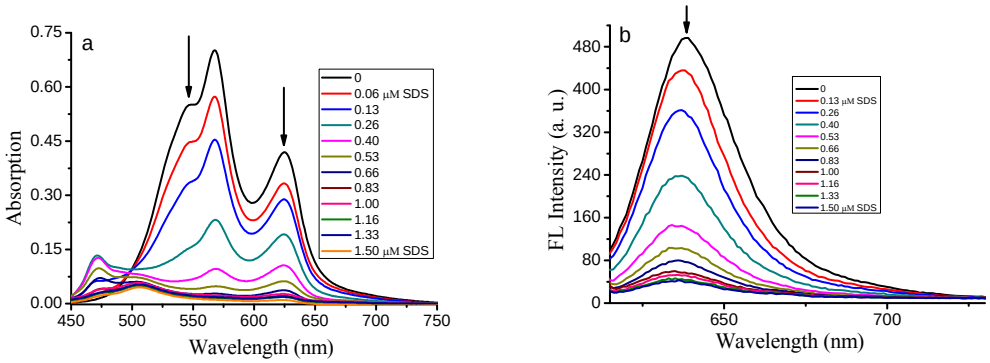


Fig. S14 Absorption (a) and fluorescent (b) spectra change of **SQ** (5.0×10^{-6} M) in aqueous solution upon addition of SDS.

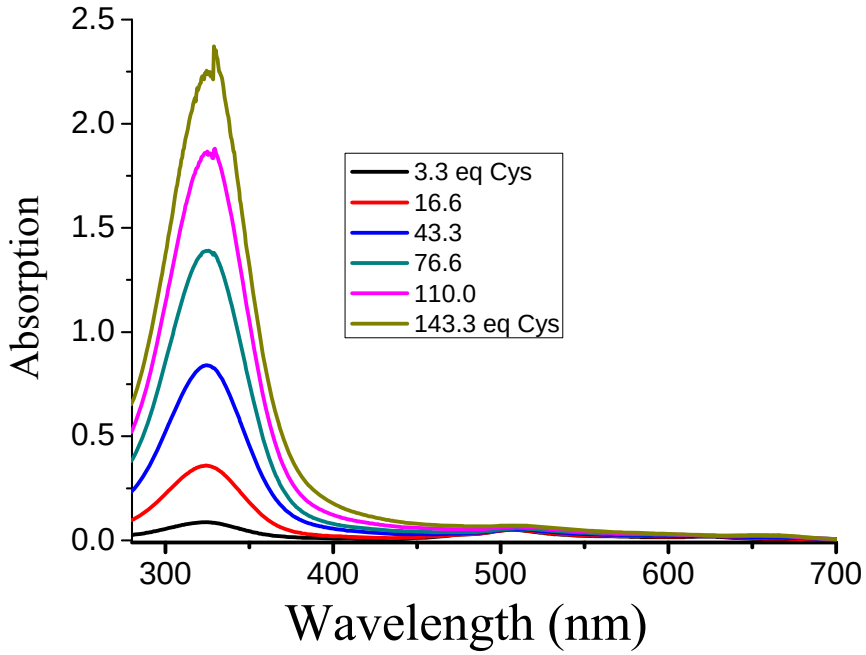


Fig. S15 Absorption spectra change of **SQ** (5.0×10^{-6} M) in aqueous solution containing SDS (1.5 μM) with increasing concentrations of Cys as indicated (the molar ratio of CBT to Cys was fixed as 1:1).

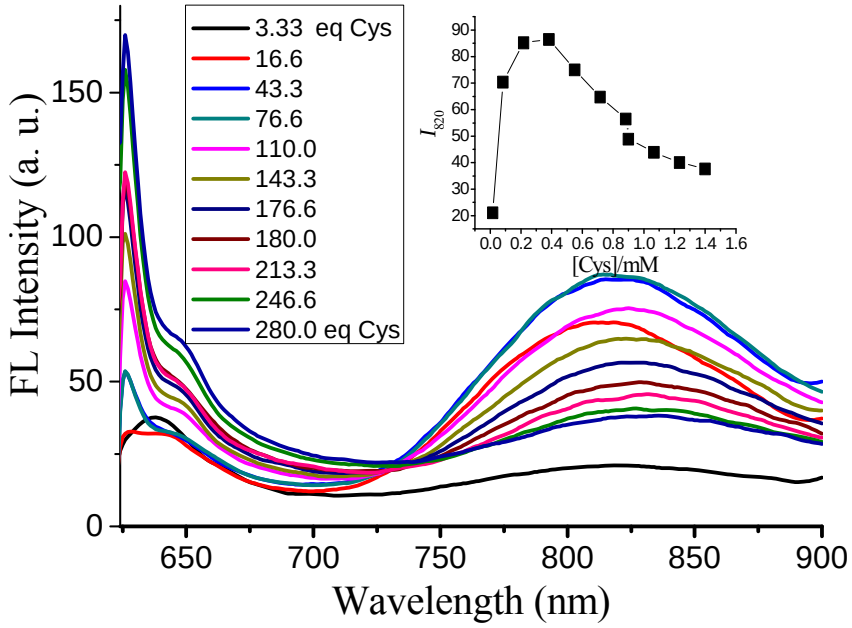


Fig. S16 Variation in the emission spectra of **SQ** (5.0×10^{-6} M) in aqueous solution containing SDS (1.5 μM) with increasing concentrations of Cys as indicated (the molar ratio of CBT to Cys was fixed as 1:1 and λ_{ex} = 600 nm. Inset: the response of fluorescence intensity at 820 nm to the concentration of Cys).

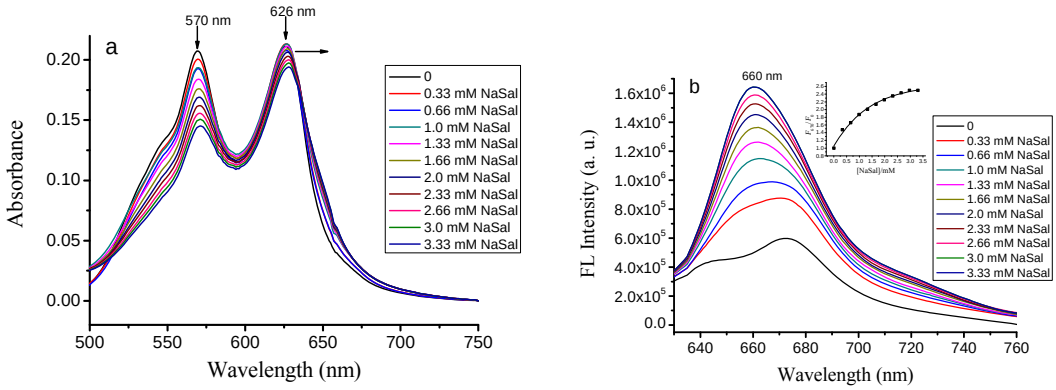


Fig. S17 Absorption (a) and fluorescence (b) change of **SQ** (5 μM) in aqueous upon addition of NaSal in the presence of 333 μM of CTAB.

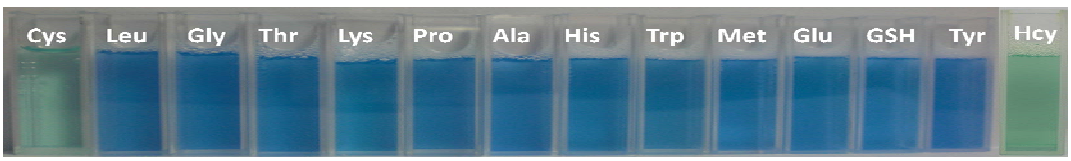


Fig. S18 Color change of **SQ** (5.0×10^{-6} M) with various amino acids and Hcy in aqueous solution in the presence of CBT and CTAB (0.05% wt), where [CBT] = [amino acids] = [Hcy] = 4.5×10^{-4} M.

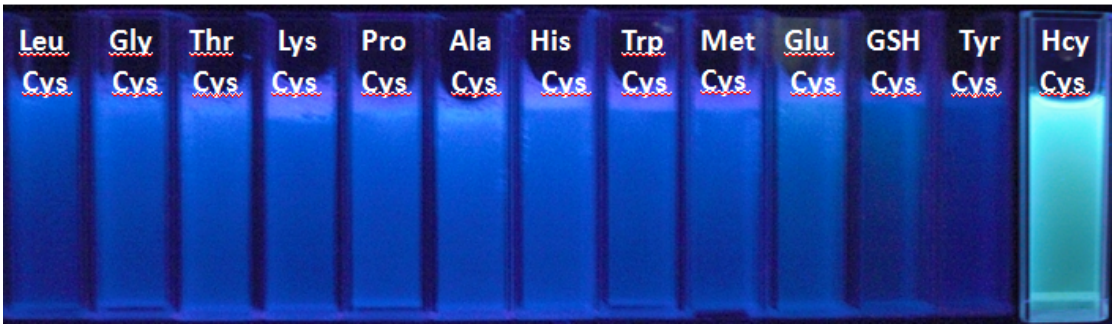


Fig. S19 Fluorescence change of **SQ** (5.0×10^{-6} M) with various amino acids and Hcy in aqueous solution in the presence of CBT, CTAB (0.05% wt) and Cys, where [CBT] = [amino acids] = [Hcy] = 4.5×10^{-4} M, excitation by hand-hold UV lamp.

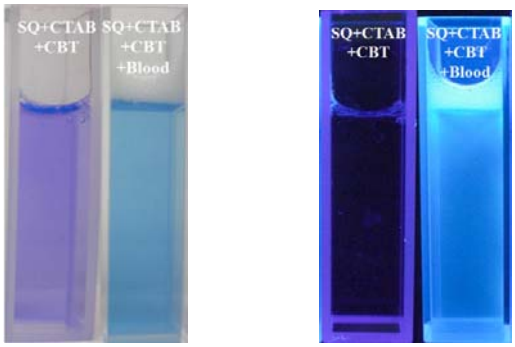


Fig. S20 Color (left) and fluorescence (right) change of **SQ** (5.0×10^{-6} M) before and after addition of human plasma in aqueous solution in the presence of CBT and CTAB (0.05% wt), where [CBT] = [amino acids] = [Hcy] = 4.5×10^{-4} M, excitation by hand-hold UV lamp.

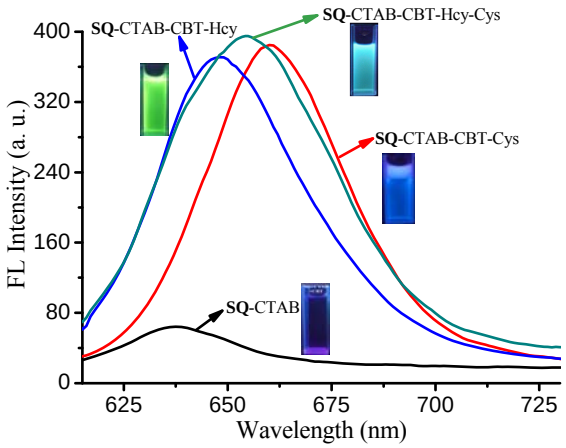


Fig. S21 Fluorescence spectra of **SQ** (5.0×10^{-6} M) in aqueous solution in the presence of CBT, CTAB (0.05% wt) upon addition of Cys, Hcy and mixture of them (1;1), where [CBT] = [Cys] = [Hcy] = 1.5×10^{-4} M and λ_{ex} = 600 nm. Inset: fluorescent images of solution excited by UV hand-hold lamp.

In the presence of both Cys and Hcy, the fluorescence spectrum of **SQ** solution is between that of Cys and Hcy.

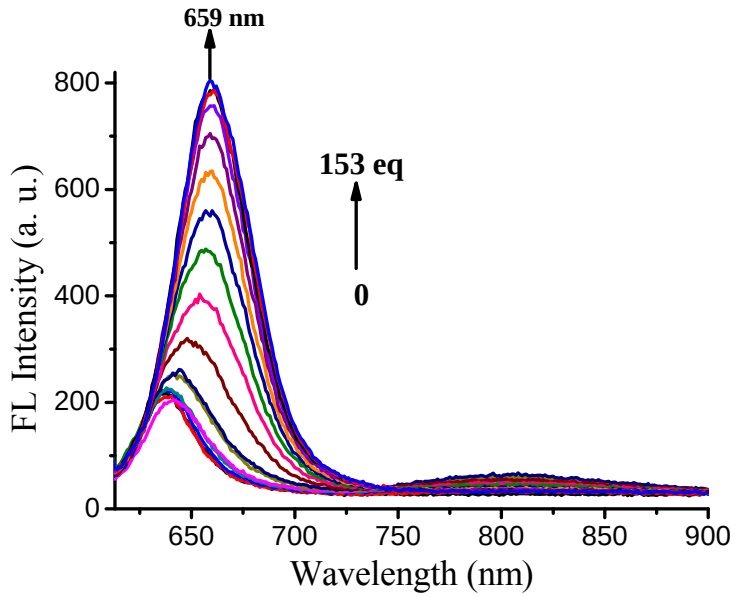


Fig. S22 Variation in the emission spectra of **SQ** (5.0×10^{-6} M) in aqueous solution containing CTAB (0.05% wt) and CBT with increasing equivalent of mixture (Cys and Hcy) as indicated (the molar ratio of [CBT]: [Cys]: [Hcy] = 2:1:1 and λ_{ex} = 600 nm).

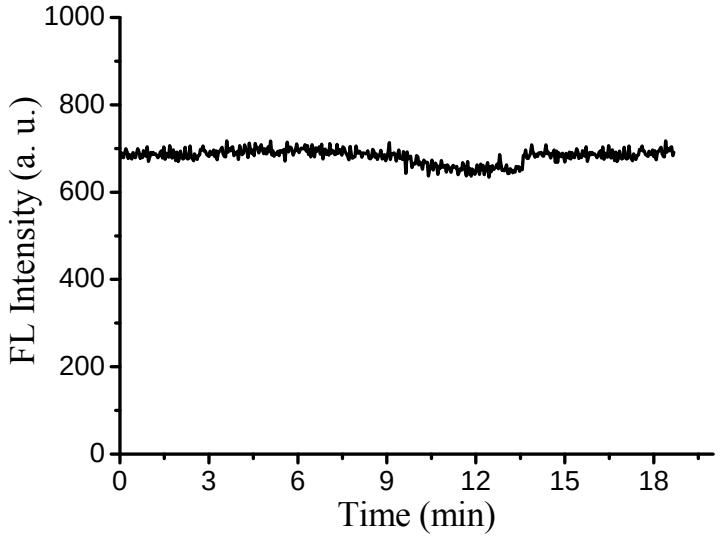


Fig. S23 The fluorescence intensity change of **SQ** (5 μM) at 661 nm in aqueous solution in the presence of luciferin derivatives (CBT and Cys) and CTAB (0.05% wt) with increasing reaction time as indicated, where [CBT] = [Cys] = 8.0×10^{-4} M (excitation wavelength at 600 nm).

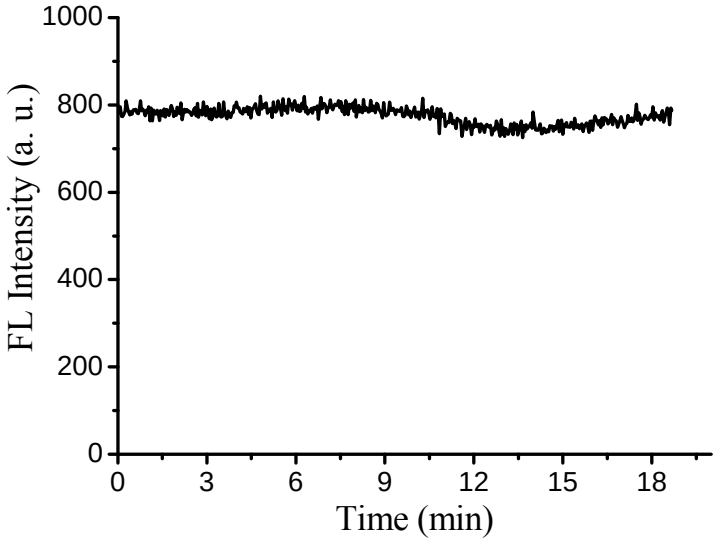


Fig. S24 The fluorescence intensity change of **SQ** (5 μM) at 648 nm in aqueous solution in the presence of luciferin derivatives (CBT and Hcy) and CTAB (0.05% wt) with increasing reaction time as indicated, where [CBT] = [Hcy] = 1.3×10^{-3} M (excitation wavelength at 600 nm).

The fluorescence changes at maximal intensity with increasing reaction time were investigated, which reflects the reaction kinetics of luciferin derivatives and CTAB. As shown in Fig. S23-24, these results indicated that their intermolecular equilibrium can level off very fast within 60 seconds.

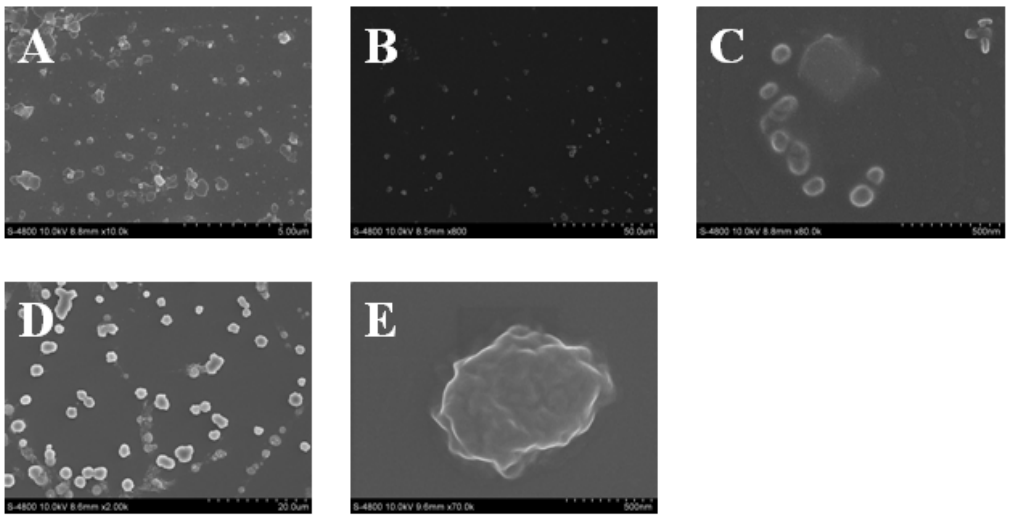


Fig. S25 SEM images of **SQ**-embedded CTAB micelles in the presence of CBT, where (A) without addition of amino acids, (B) after addition of Cys, (C) after addition of Hcy, (D) and (E) after addition of mixture of Cys and Hcy.

The micelles of **SQ**-embedded CTAB micelles are elliptic in the presence of both Cys and Hcy, which are between sphere- and rod-like micelles.

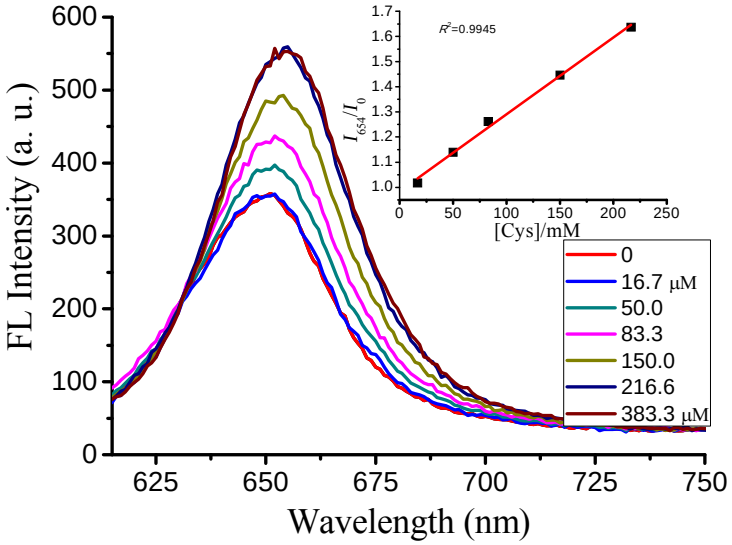


Fig. S26 Variation in the emission spectra of **SQ** (5.0×10^{-6} M) in human plasma containing CTAB (0.05% wt) and CBT with increasing concentrations of Cys as indicated (the molar ratio of CBT to Cys was fixed as 1:1 and λ_{ex} = 600 nm). Inset: the relative fluorescence change at 654 nm with increasing concentrations of Cys as indicated.