

Electronic Supplementary Information (ESI) for

Discriminative Fluorescence Detection of Cysteine, Homocysteine and Glutathione via Reaction-Dependent Aggregation of Fluorophore-Analyte Adducts

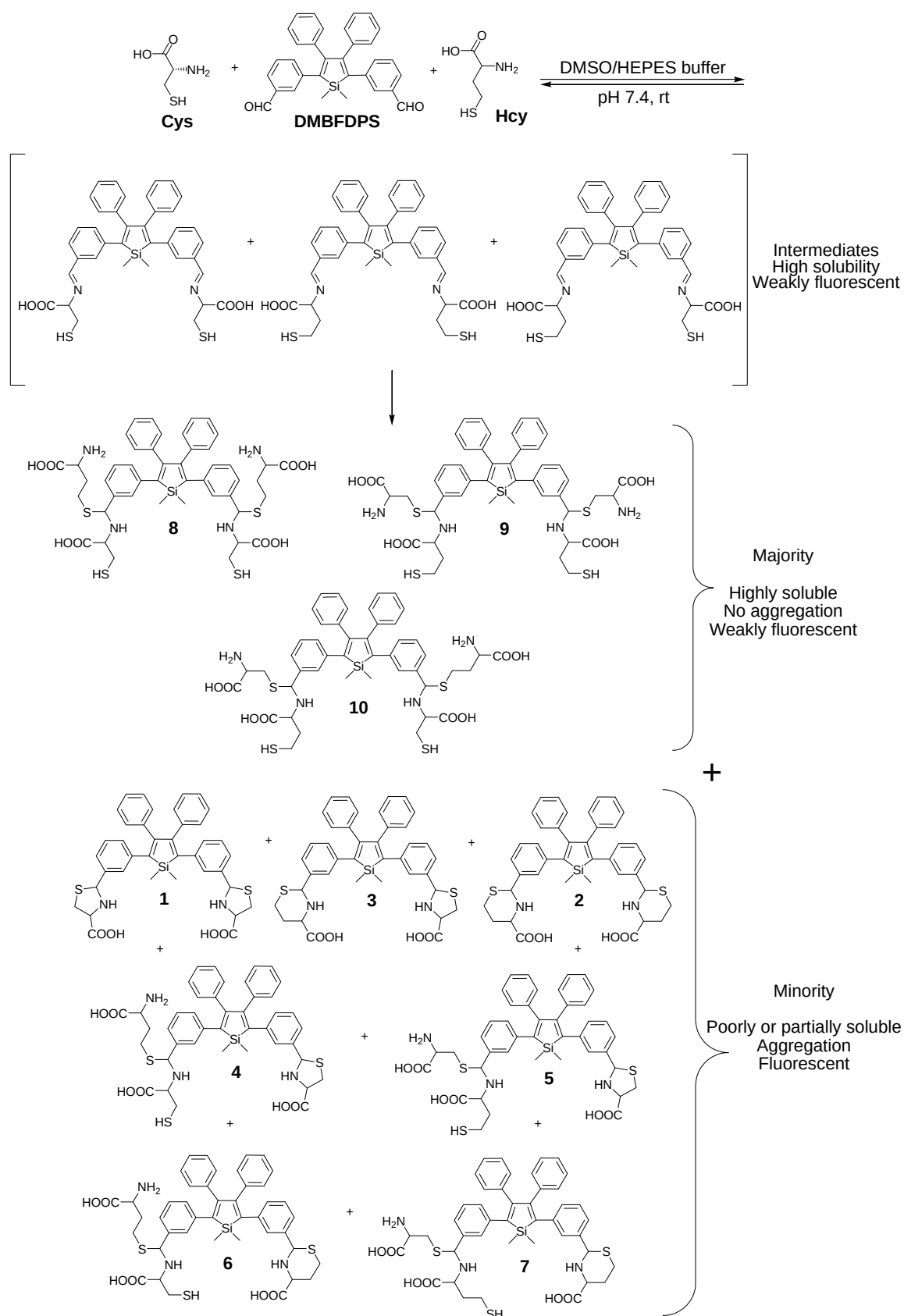
Ju Mei,^a Jiaqi Tong,^a Jian Wang,^a Anjun Qin,^a Jing Zhi Sun,^{*,a} and Ben Zhong Tang^{*,a,b}

^a MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, PR China;

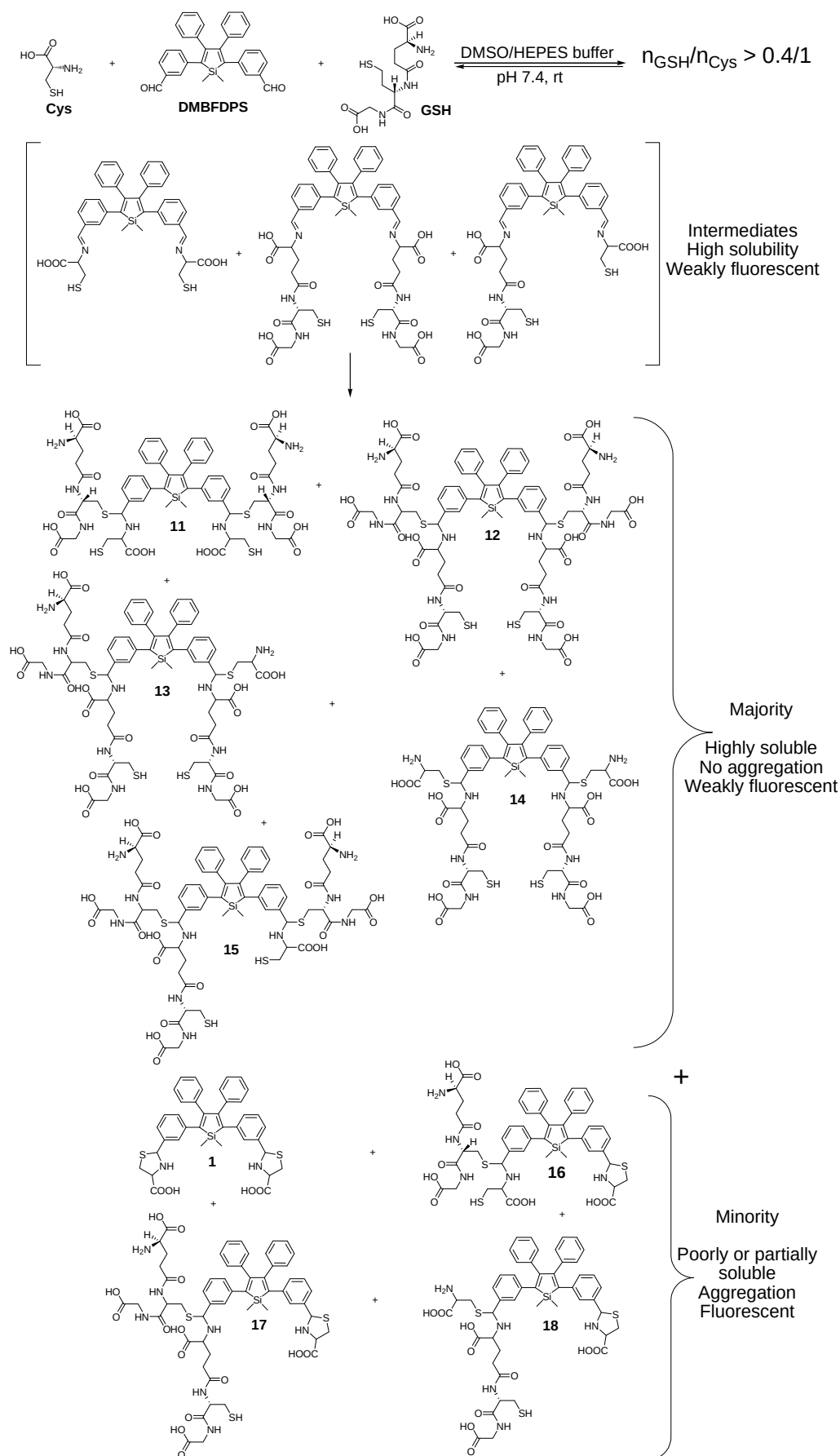
^b Department of Chemistry, Institute for Advanced Study, Institute of Molecular Functional Materials, State Key Laboratory of Molecular Neuroscience, and Division of Biomedical Engineering, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, PR China.

Table of Contents

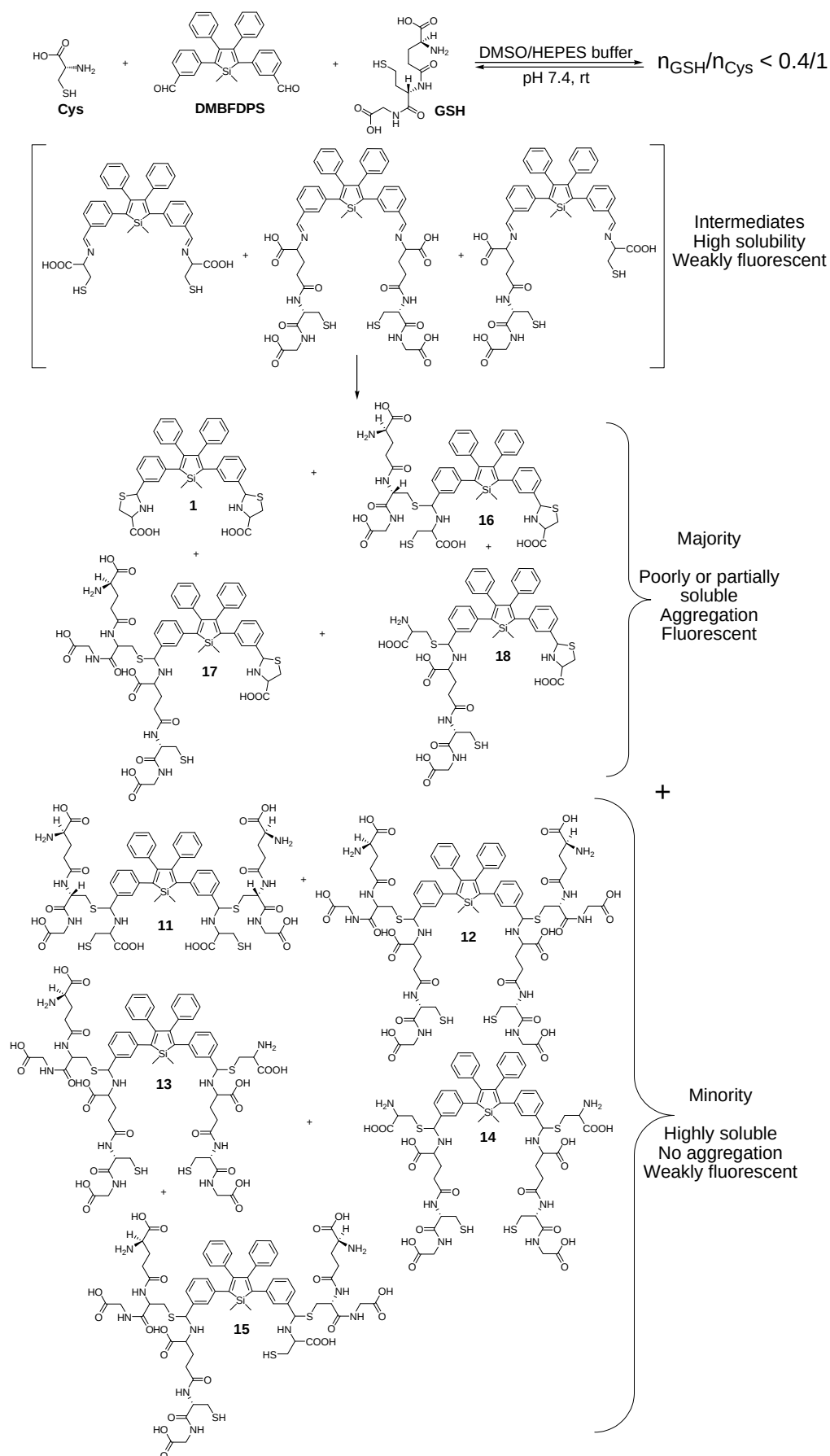
Scheme S1. Reactions of DMBFDPS in the co-existence of Cys and Hcy.	(2)
Scheme S2. Reactions of DMBFDPS in the co-existence of Cys and GSH (when GSH/Cys>0.4/1)	(3)
Scheme S3. Reactions of DMBFDPS in the co-existence of Cys and GSH (when GSH/Cys<0.4/1).	(4)
Scheme S4. Reactions of DMBFDPS in the co-existence of Cys and N-acetyl-Cys	(5)
Fig. S1. AIE property of DMBFDPS.	(6)
Fig. S2. ¹ H NMR spectra of DMBFDPS and the resultant of DMBFDPS reacted with Cys in <i>d</i> ₆ -acetone. The solvent peaks are marked with asterisks.	(7)
Fig. S3. FTIR spectra of DMBFDPS and the resultant thiazolidine derivatives.	(8)
Fig. S4. FL spectra of DMBFDPS and Cys in the mixture of DMSO and 10 mM HEPES buffer with different Cys concentrations.	(9)
Fig. S5. a) UV-vis spectra of DMBFDPS and Cys in the mixture of DMSO and HEPES buffer with different Cys concentrations. b) Enhancement of FL intensity and shift of FL peak versus Cys concentration.	(10)
Fig. S6. UV and plots of fluorescence enhancement and wavelength shift versus Cys concentrations.	(11)
Fig. S7. FL spectra of DMBFDPS with different amino acid, protected Cys and glucose.	(12)
Fig. S8. PL spectra of DMBFDPS with Cys in the presence of different amino acids, protected Cys and glucose.	(13)
Fig. S9. Photographs of DMBFDPS with Cys in the presence of different amino acids, protected Cys and glucose.	(13)
Fig. S10. ¹ H NMR spectra of the resultants of probe reacting with Cys and GSH.	(14)
Fig. S11. FTIR spectra of the resultants of probe reacting with Cys and GSH.	(15)
Fig. S12. FL spectra of the reverse detection of GSH in the presence of Cys.	(16)
Fig. S13. Photographs of reverse detection of GSH in the presence of Cys.	(16)
Fig. S14. UV-vis spectra of the spiked Cys detection in deproteinized human plasma.	(17)



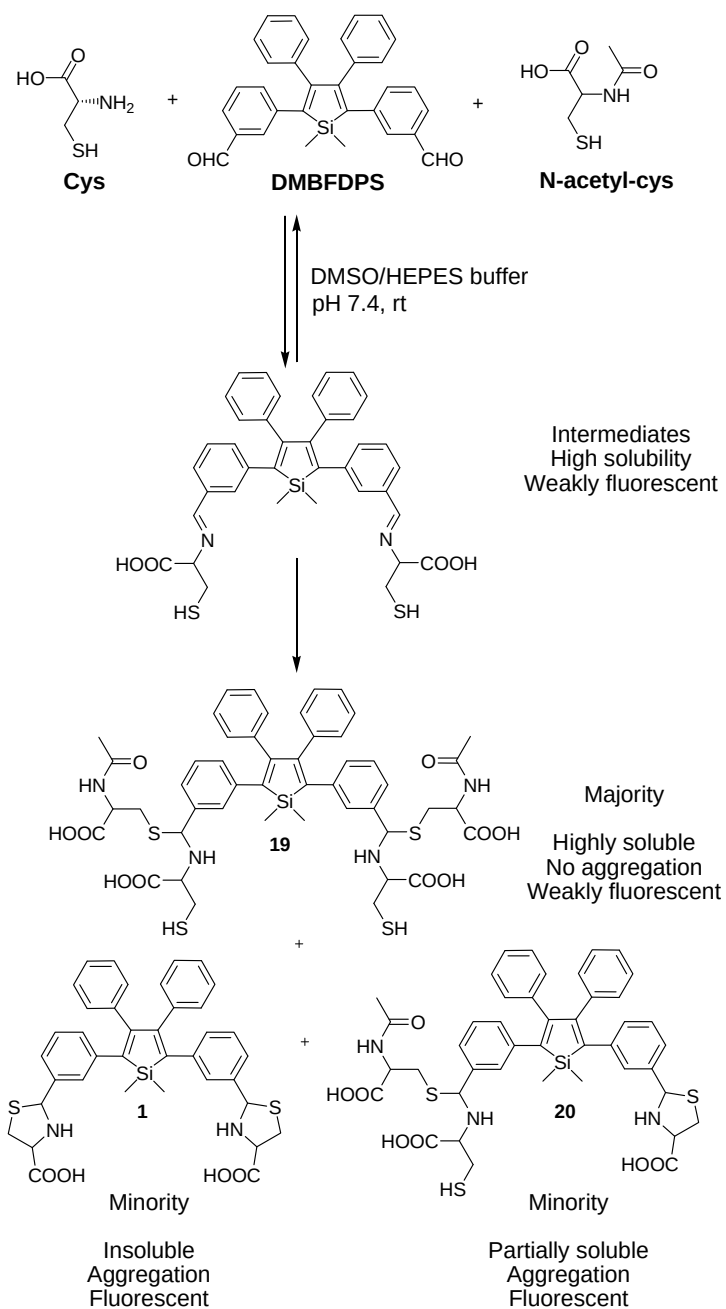
Scheme S1 Reactions of DMBFDPS in the co-existence of Cys and Hcy.



Scheme S2 Reactions of DMBFDPS in the co-existence of Cys and GSH (when GSH/Cys>0.4/1).



Scheme S3 Reactions of DMBFDPS in the co-existence of Cys and GSH (when $\text{GSH}/\text{Cys} < 0.4/1$).



Scheme S4 Reactions of DMBFDPS in the co-existence of Cys and N-acetyl-Cys.

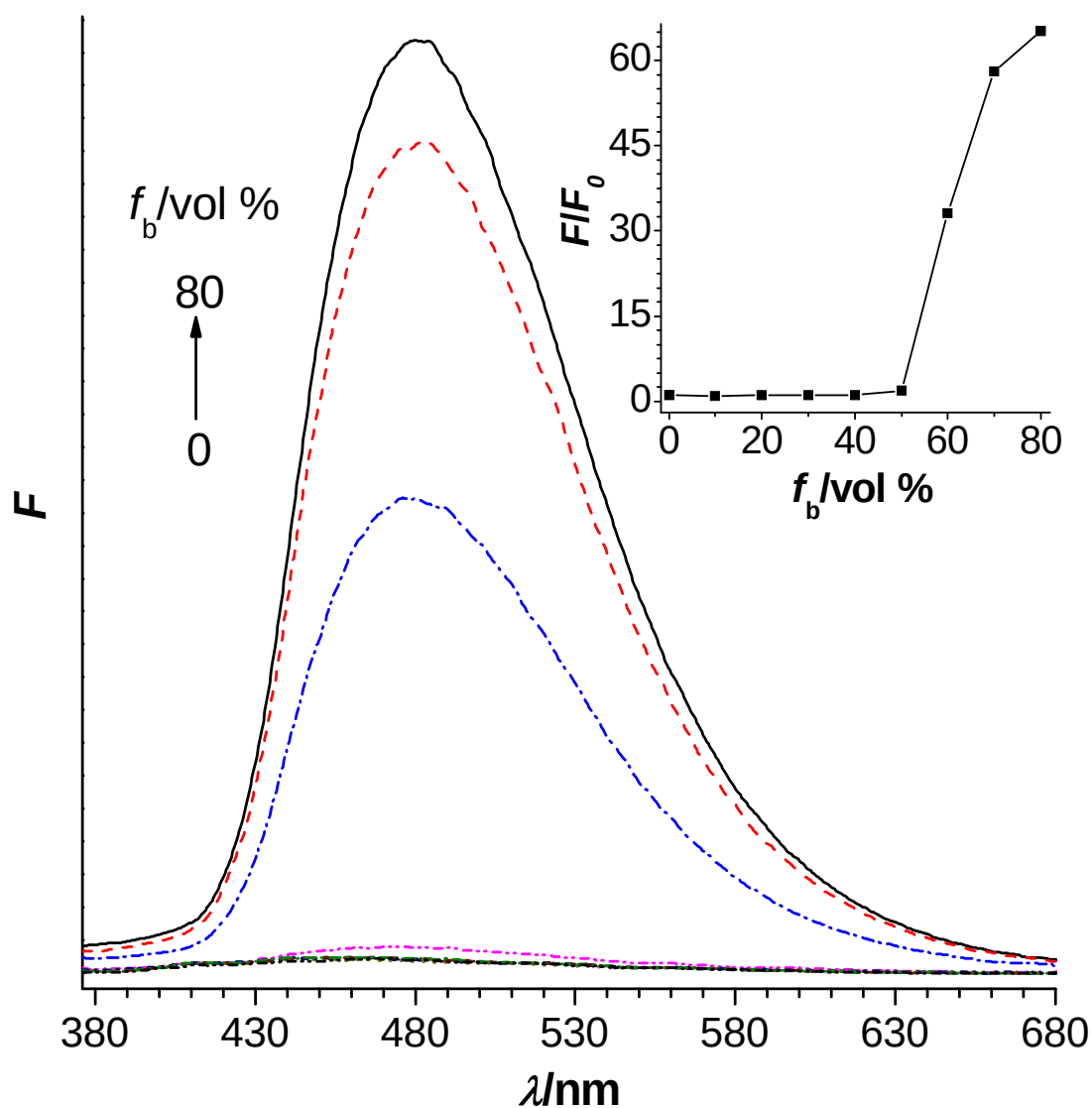


Fig. S1 FL spectra of DMBFDPS in the mixture of chromatographically pure DMSO and 10 mM HEPES buffer solution (pH 7.4) with different buffer solution fractions (f_b , in volume), concentration = 25 μM , $\lambda_{\text{ex}} = 356$ nm, F = FL intensity. Inset: Plots of F/F_0-1 versus f_b of DMBFDPS in the DMSO/buffer mixture. F_p = peak FL intensity and $F_{p,0}$ = peak FL intensity at $f_b = 0$.

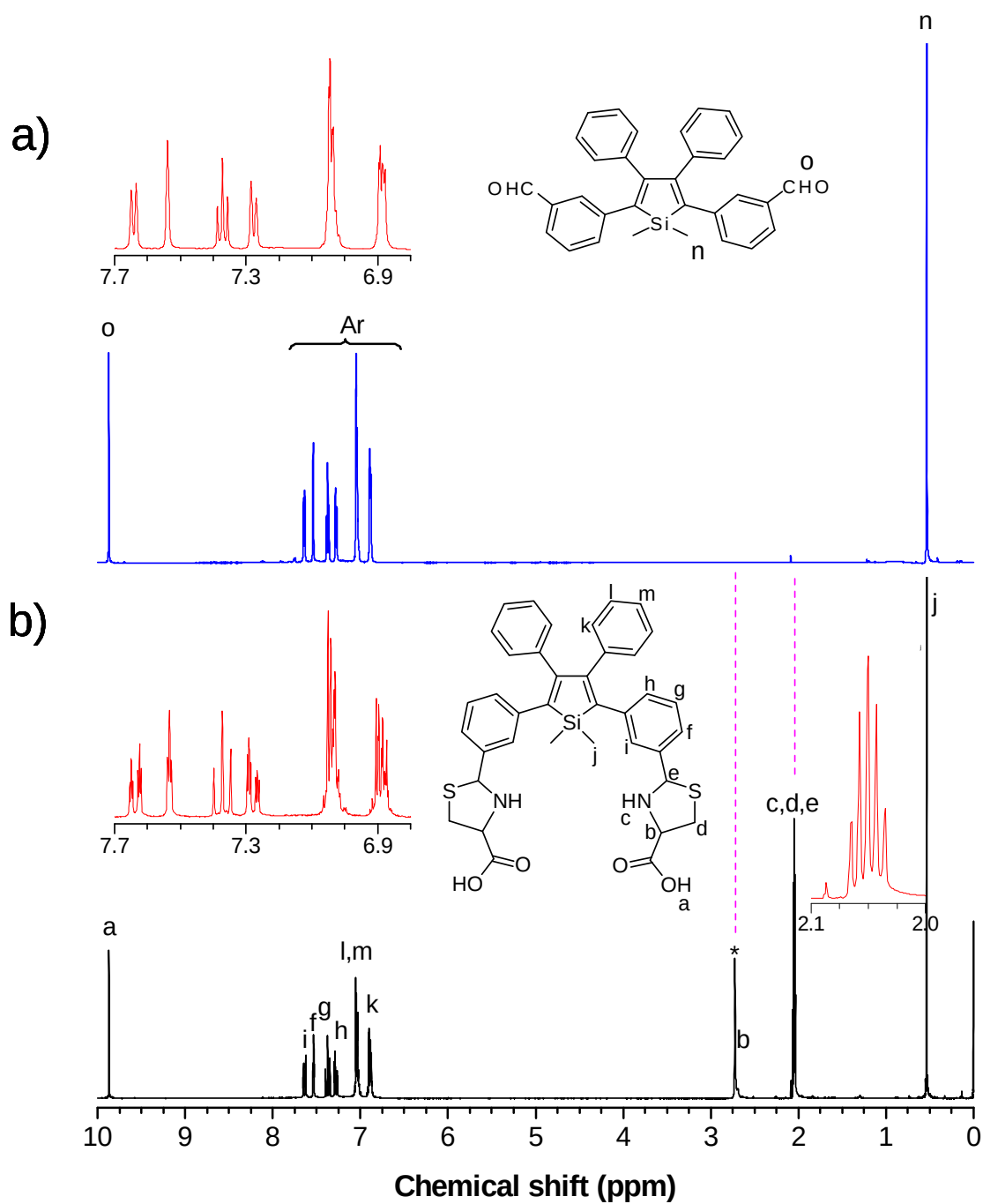


Fig. S2 ^1H NMR of DMBFDPS and the resultant of DMBFDPS with Cys in d_6 -acetone. The solvent peaks were marked with asterisks.

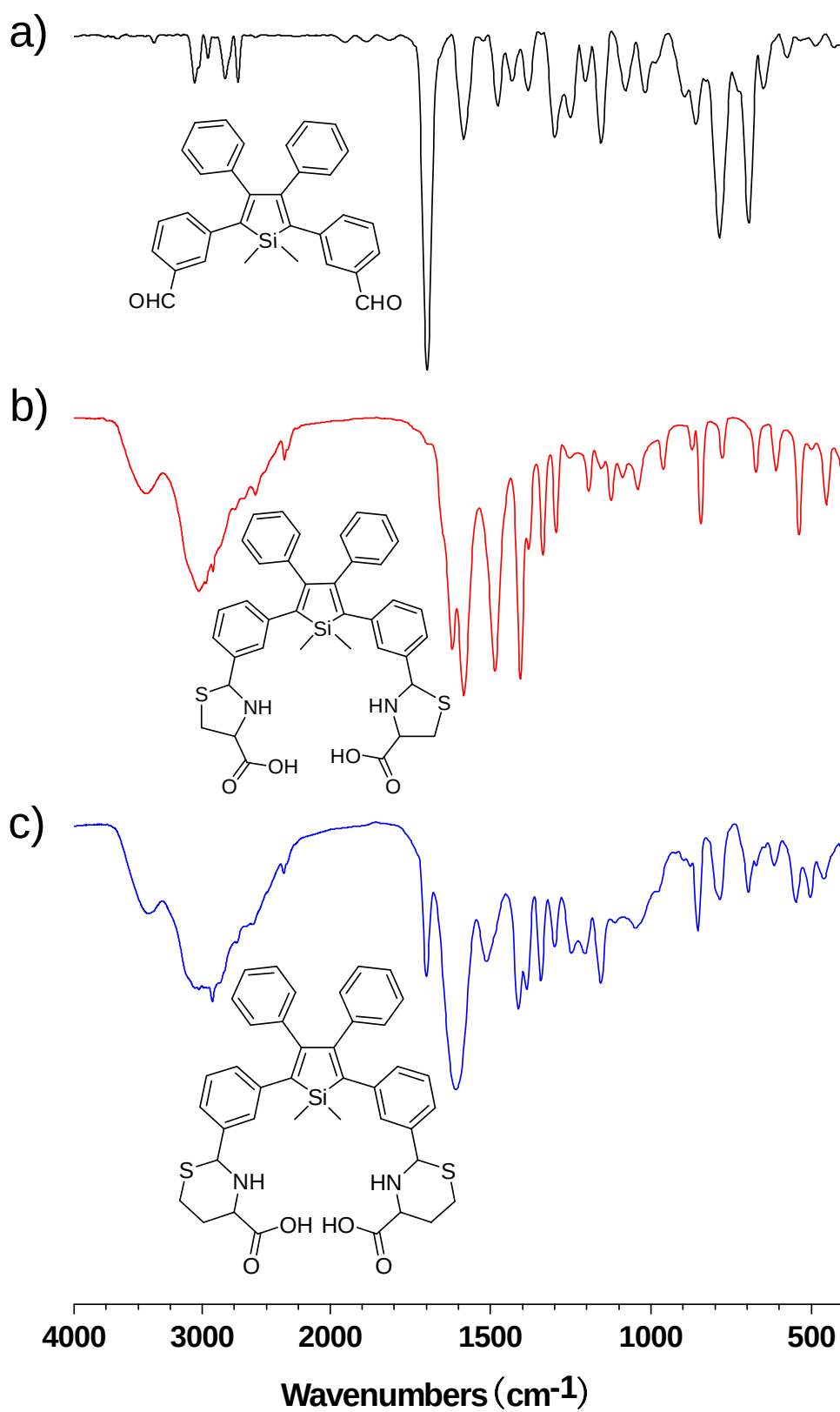


Fig. S3 FTIR spectra of DMBFDPS and the reaction resultant with Cys or Hcy.

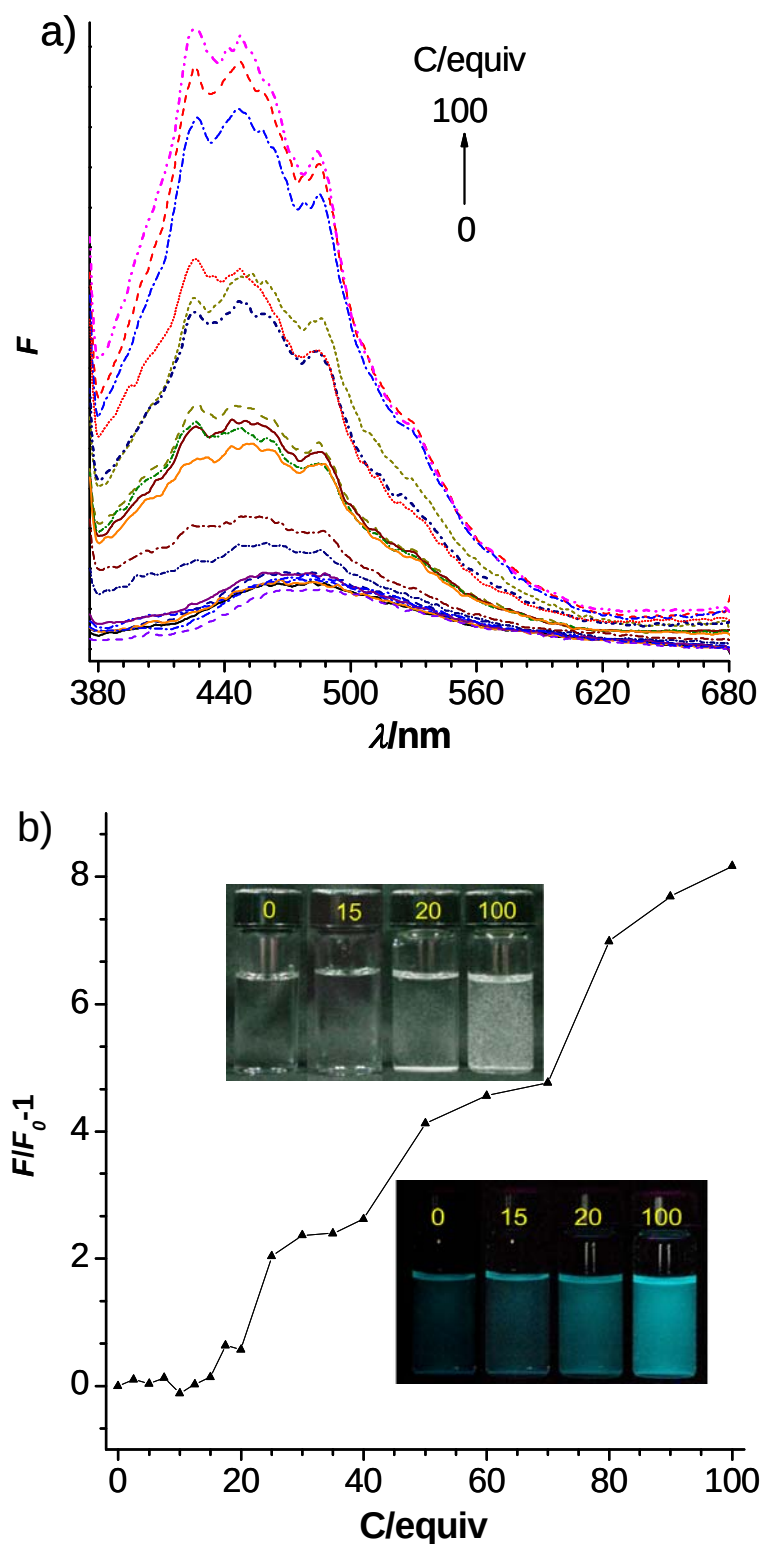


Fig. S4 a) FL spectra of DMBFDPS and Cys in the mixture of chromatographically pure DMSO and 10 mM HEPES buffer (6/4 in volume, pH 7.4) with different Cys concentrations. [DMBFDPS] = 25 μM , $\lambda_{\text{ex}} = 356 \text{ nm}$. b) Plot of FL enhancement versus Cys concentration. All were measured at rt 60 min later. Inset: Photos of DMBFDPS and Cys in the above mixture with different Cys concentrations (equiv) taken under ambient light (upper) and UV-lamp (bottom, $\lambda_{\text{ex}} = 365 \text{ nm}$).

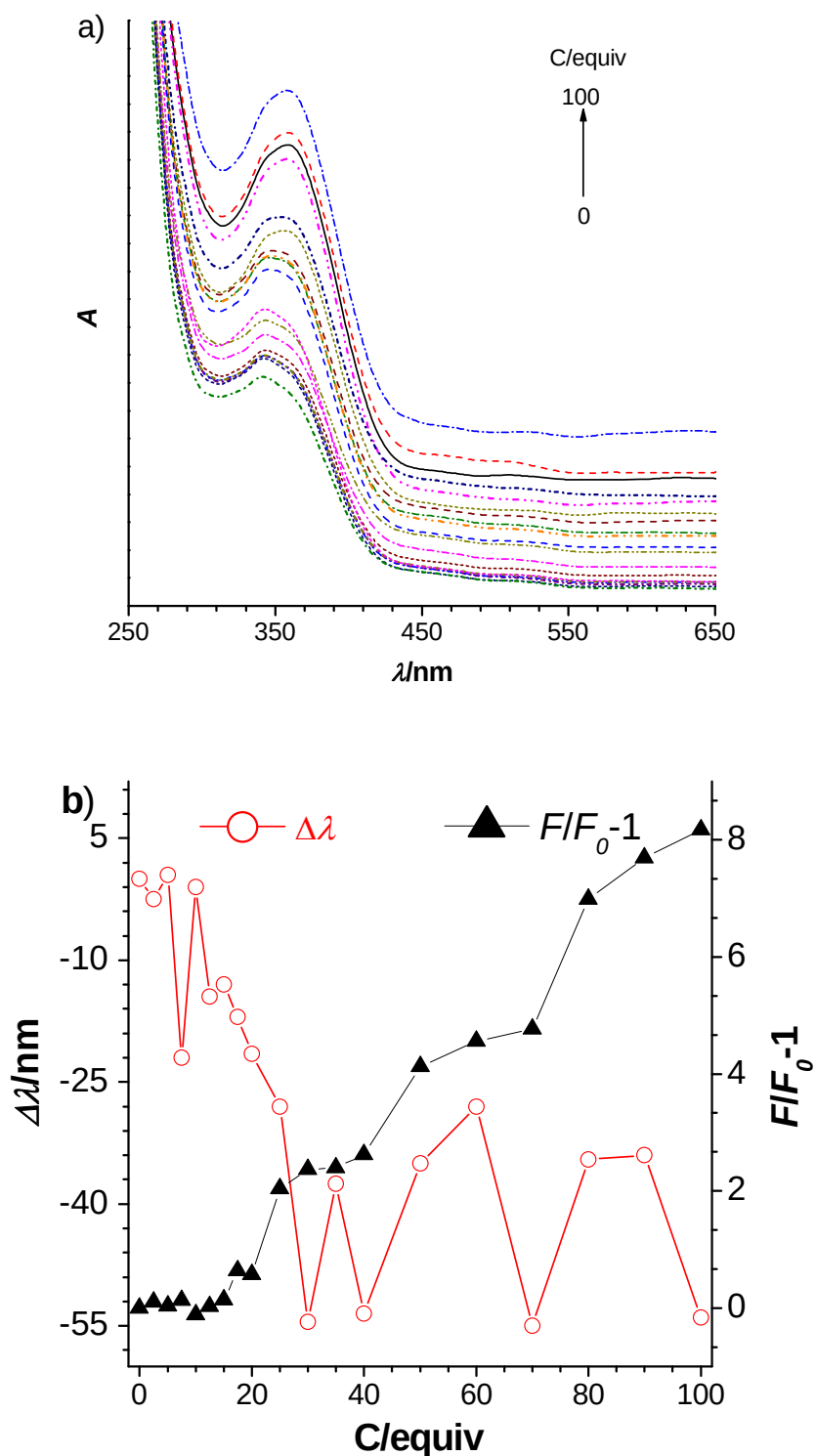


Fig. S5 a) UV-vis spectra of DMBFDPS and Cys in the mixture of chromatographically pure DMSO and 10 mM HEPES buffer (6/4 in volume, pH 7.4) with different Cys concentrations, [DMBFDPS] = 25 μM . b) The corresponding FL plot (enhancement of FL intensity and shift of FL peak versus Cys concentration) of the above mentioned mixtures, $\Delta\lambda$ for wavelength shift, F for peak FL intensity and F_0 for the peak FL intensity of DMBFDPS at [Cys] = 0. All measurements were carried out at rt 60 min later.

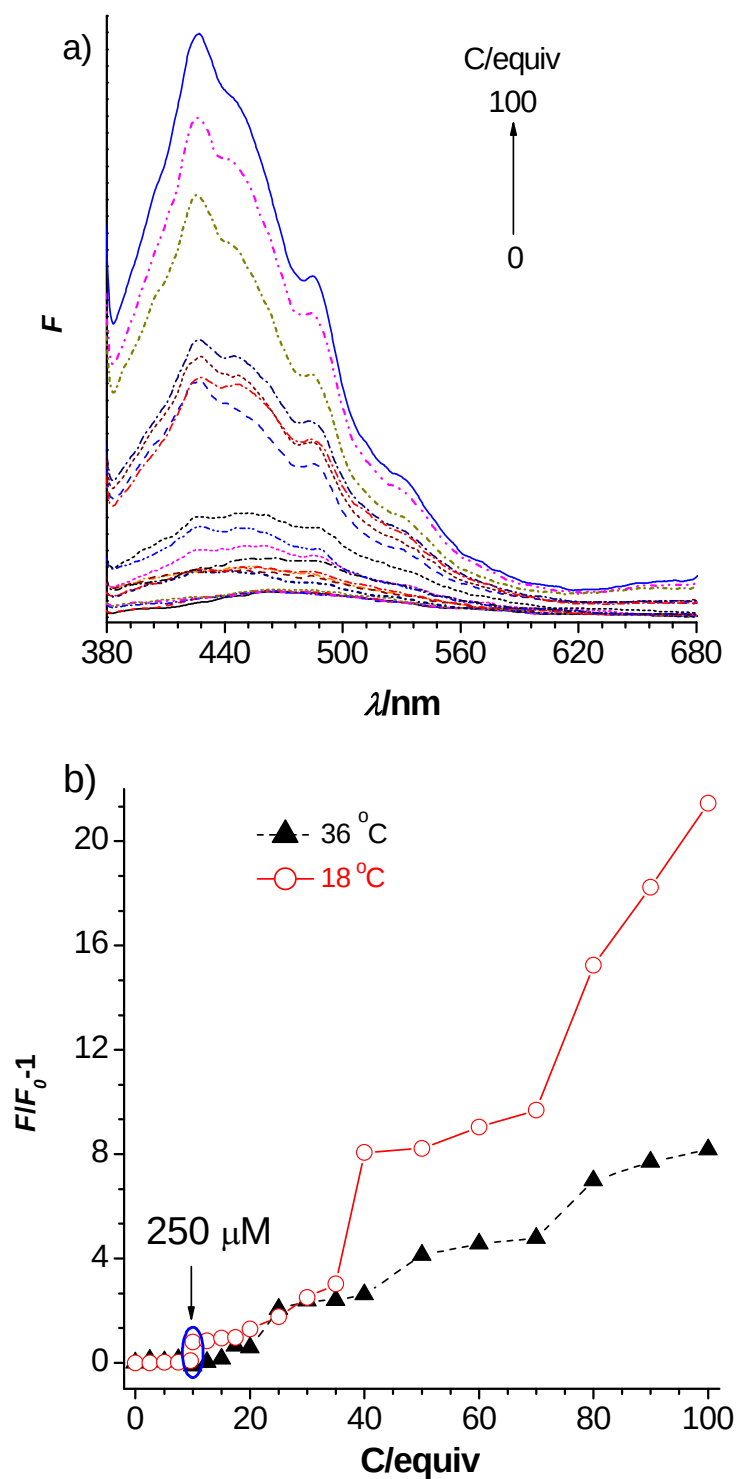


Fig. S6 a) FL spectra of DMBFDPS and Cys in the mixture of chromatographically pure DMSO and 10 mM HEPES buffer (6/4 in volume, pH 7.4) with different Cys concentrations detected at 18 °C. [DMBFDPS] = 25 μM , λ_{ex} = 356 nm. b) Plots of FL enhancement versus the Cys concentration. The measurements were taken at 18 °C (red circle) and 36 °C (black triangle) 60 min later.

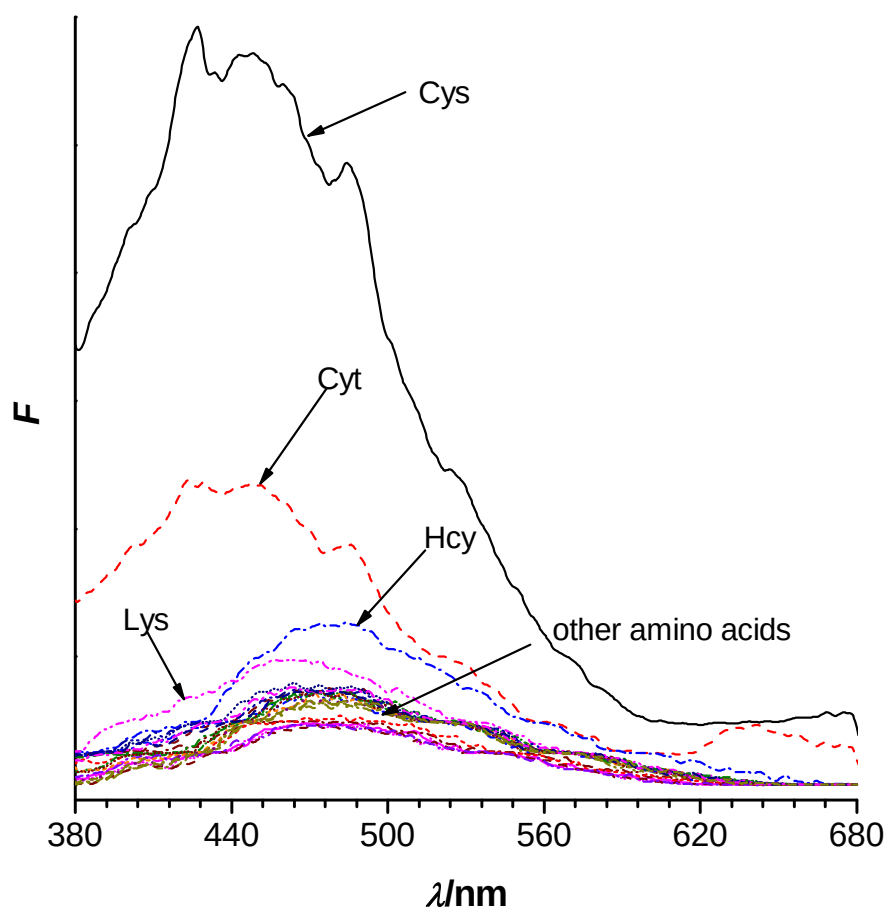


Fig. S7 FL spectra of DMBFDPS with different analytes (Ala, Arg, Asp, Glu, Gly, His, Ile, Leu, Lys, Met, Phe, Ser, Thr, Tyr, Val, Pro, Hcy, Pgl, GSH, Cya, Cyt, and Glucose) in the mixture of chromatographically pure DMSO and 10 mM HEPES buffer (6/4 in volume, pH 7.4), [DMBFDPS] = 25 μ M, [analyte] = 2.5 mM, λ_{ex} = 356 nm. All measurements were conducted at rt 60 min later.

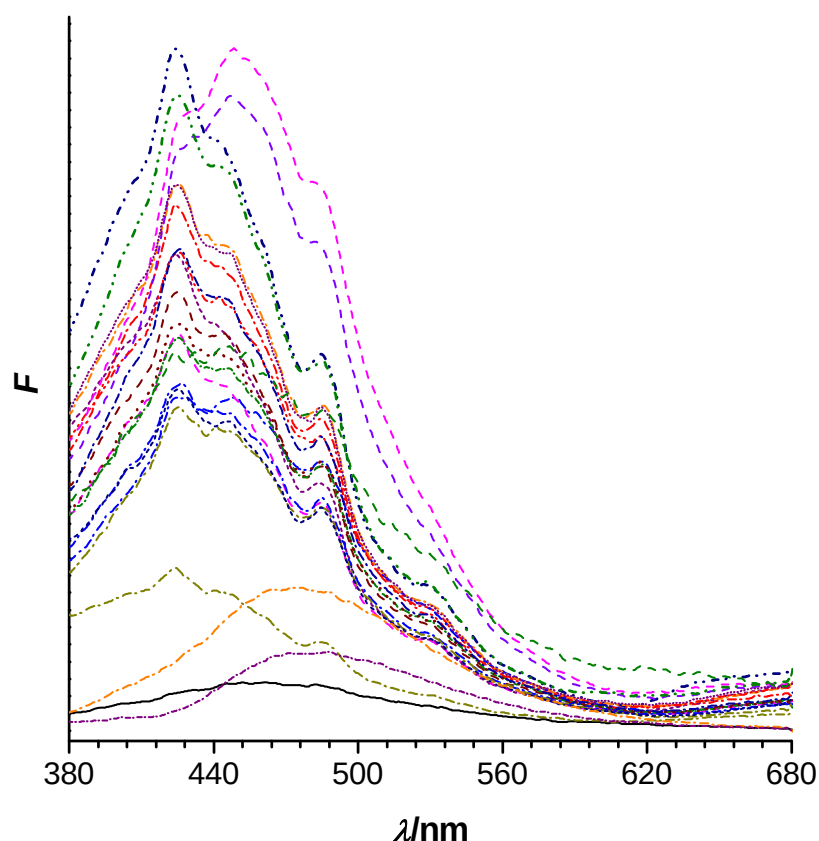


Fig. S8 FL spectra of DMBFDPS with Cys in the presence of different analytes (Ala, Arg, Asp, Glu, Gly, His, Ile, Leu, Lys, Met, Phe, Ser, Thr, Tyr, Val, Pro, Hcy, Pgl, GSH, Cya, Cyt, and Glucose) in the mixture of chromatographically pure DMSO and 10 mM HEPES buffer (6/4 in volume, pH 7.4), [DMBFDPS] = 25 μ M, [analyte] = 2.5 mM. All were measured at rt 60 min later.

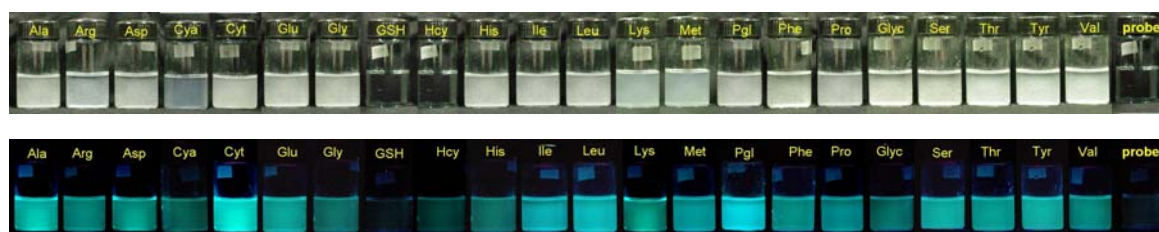


Fig. S9 Photographs of DMBFDPS with Cys in the presence of different analytes (Ala, Arg, Asp, Glu, Gly, His, Ile, Leu, Lys, Met, Phe, Ser, Thr, Tyr, Val, Pro, Hcy, Pgl, GSH, Cya, Cyt, and Glucose) in the mixture of chromatographically pure DMSO and 10 mM HEPES buffer (6/4 in volume, pH 7.4), [probe] = 25 μ M, [analyte] = 2.5 mM. The photographs in upper and bottom row were taken under ambient and UV-light (λ_{ex} = 365 nm), respectively. Probe = DMBFDPS.

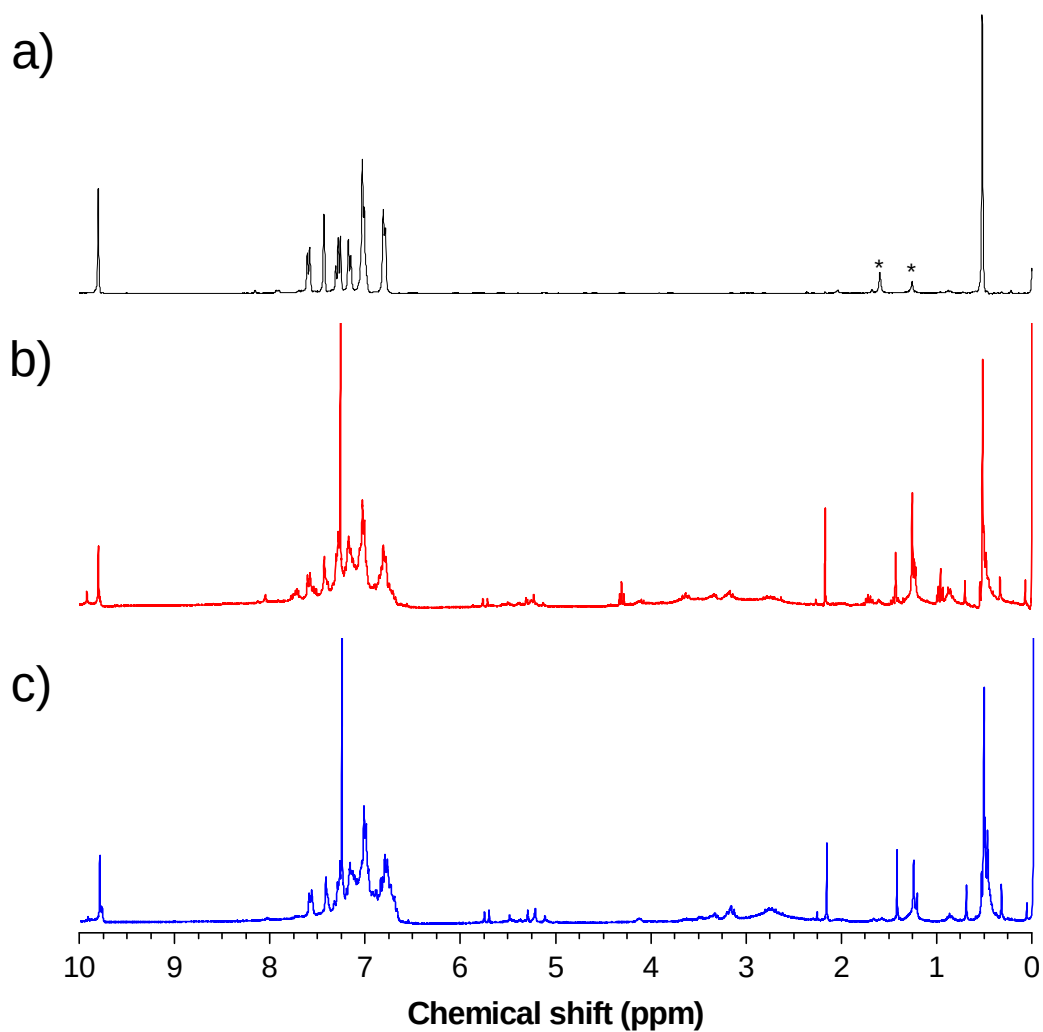


Fig. S10 ^1H NMR of (a) DMBFDPS and the resultant of (b) DMBFDPS with Cys+GSH and (c) DMBFDPS with Cys+Cya in CDCl_3 . The solvent peaks were marked with asterisks.

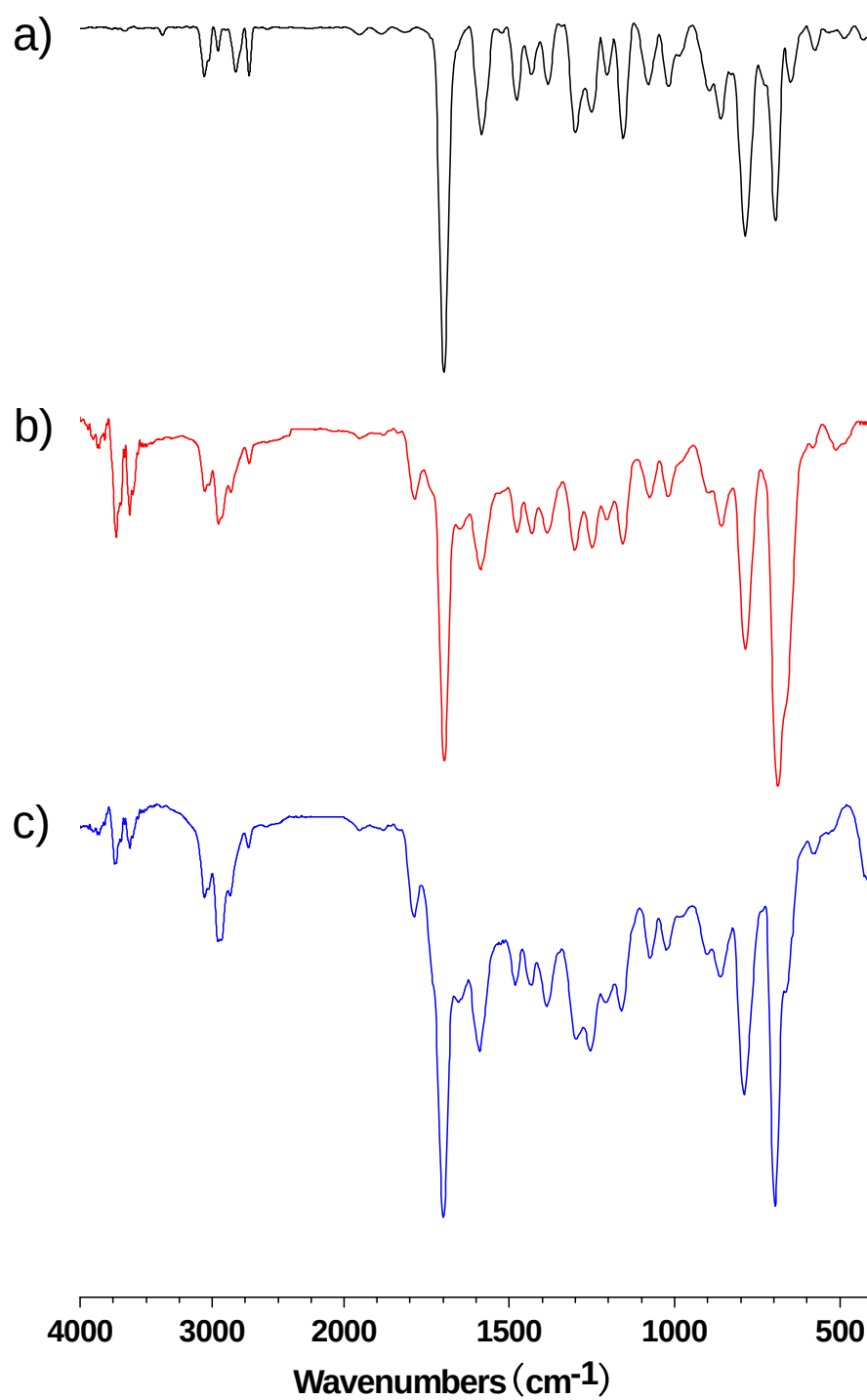


Fig. S11 FTIR spectra of DMBFDPS and the reaction resultant with Cys+GSH or Cys+Cya.

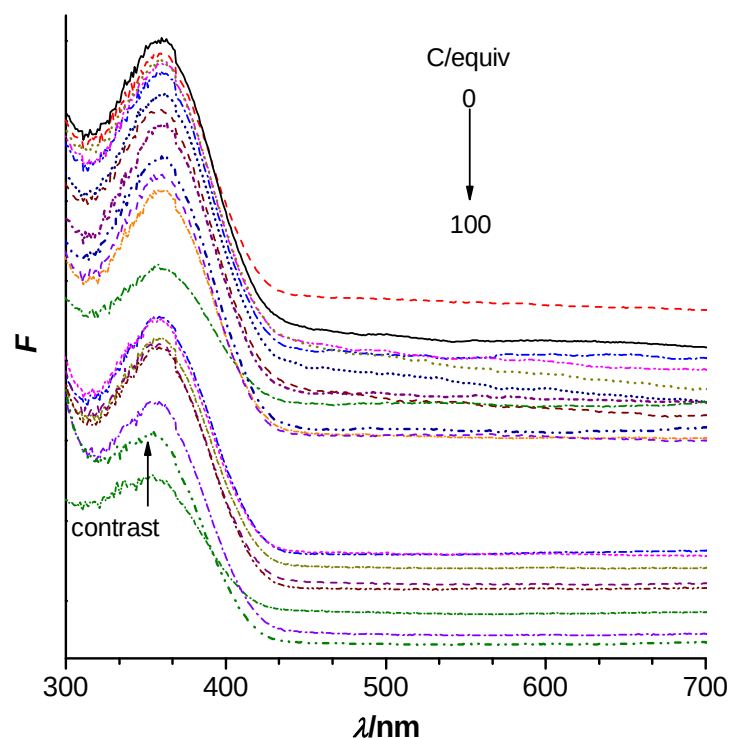


Fig. S12 The FL spectra of DMBFDPS and Cys in the presence of GSH in the mixture of chromatographically pure DMSO and 10 mM HEPES buffer (6/4 in volume, pH 7.4) with different concentrations of GSH, [DMBFDPS] = 25 μ M, [Cys] = 2.5 mM. All were measured at rt 60 min later.

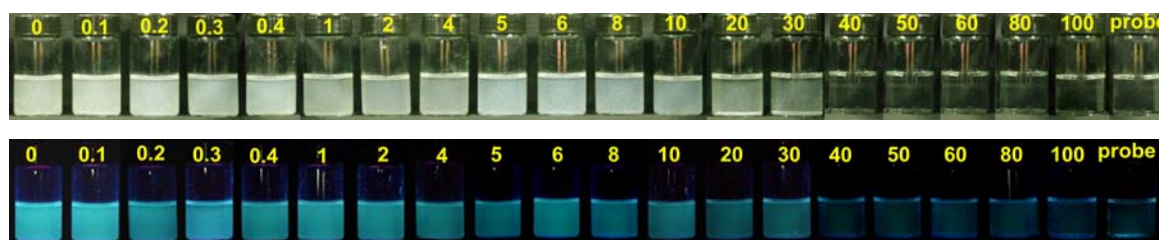


Fig. S13 Photographs of DMBFDPS and Cys in the presence of GSH in the mixture of chromatographically pure DMSO and 10 mM HEPES buffer (6/4 in volume, pH 7.4) with different concentrations of GSH (equiv), [DMBFDPS] = 25 μ M, [Cys] = 2.5 mM. Upper row is taken under ambient light and the bottom row is under UV-lamp (λ_{ex} = 365 nm).

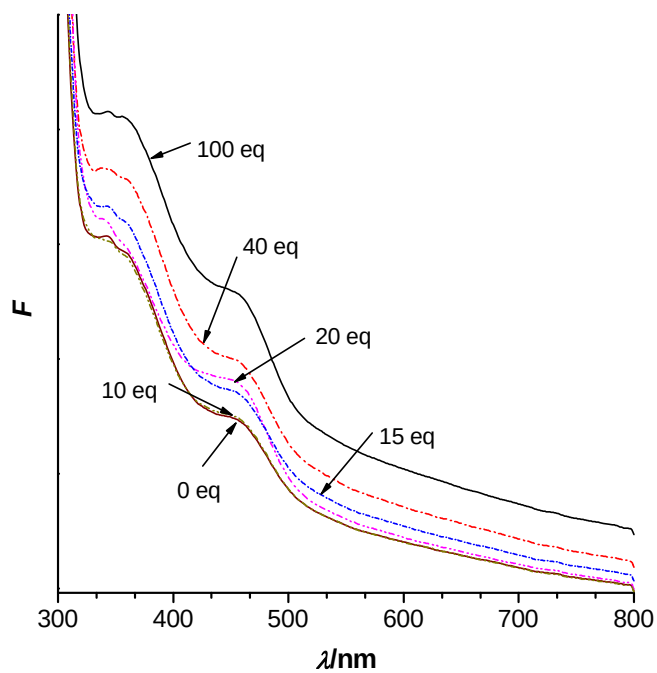


Fig. S14 UV-vis spectra of DMBFDPS with Cys in the mixture of chromatographically pure DMSO and deproteinized human plasma (6/4 in volume, pH 7.4) with different concentrations of Cys (equiv), [DMBFDPS] = 25 μ M. All spectra were measured at rt 3 hrs later.