Electronic Supplementary Information (ESI)

Tuning the Selectivity of Amino Acids Recognition with Dynamic Covalent Bond Constrained Fluorophores in Aqueous Media

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1. General Methods

^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker Biospin avance III spectrometer. Deuterated reagents for characterization and *in situ* reactions were purchased from Sigma-Aldrich Chemical Co. and Cambridge Isotope Laboratories, Inc. (purity ≥ 99.9%). The chemical shifts (δ) for ^{1}H NMR spectra, given in ppm, are referenced to the residual proton signal of the deuterated solvent. Mass spectra were recorded on a Bruker IMPACT-II spectrometer. pH was measured using a Sartorius PB-10 pH meter. All other reagents were obtained from commercial sources and were used without further purification, unless indicated otherwise.

Synthesis of dynamic covalent fluorescent switches. Fluorescent switches **A1**-**A5** were synthesized from corresponding aromatic amines and 2-formylbenzenesulfonyl chloride using the previously reported method.[S1] Aromatic amines 2-aminoanthracene and 7-amino-4-methylcoumarin were obtained from commercial sources for the preparation of probes **A1** and **A3**, respectively. Other fluorescent aromatic amines, including 3-amino-7-(diethylamino)-2*H*-chromen-2-one,[S2] 6-amino-2-(2-methoxyethyl)-1*H*-benzo[de]isoquinoline-1,3(2*H*)-dione,[S3] and (*E*)-2-(2-(4-aminostyryl)-4*H*-chromen-4-ylidene)malononitrile[S4] were prepared according to the literature method for the synthesis of **A2**, **A4**, and **A5**, respectively.

Dynamic covalent reactions. Dynamic covalent reactions (DCRs) were performed *in situ* in 50 mM phosphate buffer (PB buffer) prepared by D_2O at room temperature without isolation and purification. Probe **A4** (5 mM) and amines (1-$BuNH_2$ or amino acids, 3.0 equiv.) were dissolved in deuterated PB buffer, respectively, and the desired pH was adjusted with concentrated NaOH or HCl solution. The components were mixed under the same pH and stirred at room temperature until the equilibrium was reached for ^{1}H NMR characterization. For redox-responsive switch sodium perborate ($NaBO_3$•$2H_2O$) or tris(2-carboxyethyl)phosphine hydrochloride (TCEP) was added as solids, and the pH was adjusted back to 7.4.

Fluorescence experiments in aqueous solution. Fluorescence spectra in solution were

recorded on a microplate reader (BioTek SYNERGY H4) at a concentration of 50 μM of each probe in a mixed solvent of DMSO and 50 mM PB buffer (5:95 for **A2**, **A3**, and **A4**; and 40:60 for **A1** and **A5**, v/v). Stock solutions of components were prepared. For pH titration, probes **A1**-**A5** were dissolved in DMSO and diluted with PB buffer, and the desired pH was adjusted with concentrated NaOH or HCl solution. The apparent pK_a values of **A1**-**A5** were calculated from modified Henderson Hasselbuck equation.[S5-S6] The plot (see Fig. S1-S10) of fluorescence intensity of probes **A1**-**A5** against pH displays a sigmoid function. The pK_a value was determined by fitting the fluorescent data at different pH according to the following equation:

$$\log\left(\frac{F_{max}-F}{F-F_{min}}\right) = \mathrm{p}K_a - \mathrm{pH}$$

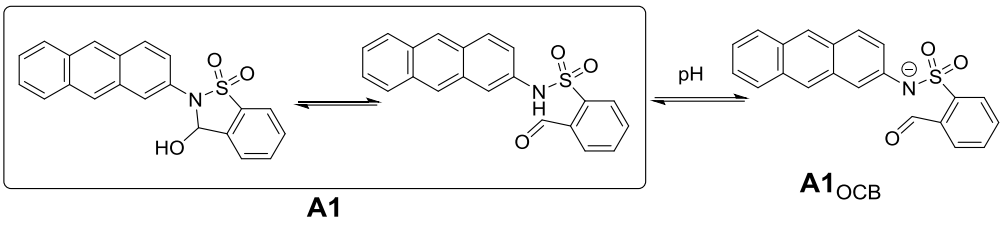
where F_{max} and F_{min} refer to the maximum and minimum values of fluorescence intensity during the variation of pH values and pK_a is the corresponding acidic dissociation constant.

For fluorescent detection of amines (1-BuNH_2 or amino acids), corresponding amines were dissolved in PB buffer, and the desired pH was adjusted. The solutions of probes and amines were then mixed under the same pH. The spectra were recorded after the equilibrium was reached. For NMR and fluorescence analysis, please see specific conditions in figure captions of the main text or supporting information if necessary. The limit of detection (LOD) was calculated by following equation:[S7-S8]

$$\mathrm{LOD} = \frac{3\sigma}{S_0}$$

where σ is the standard deviation of the normalized fluorescence intensity of the probe without amino acid, and S_0 is the slope of the linear regression fit.

2. Fluorescence Responses in pH Titration Studies



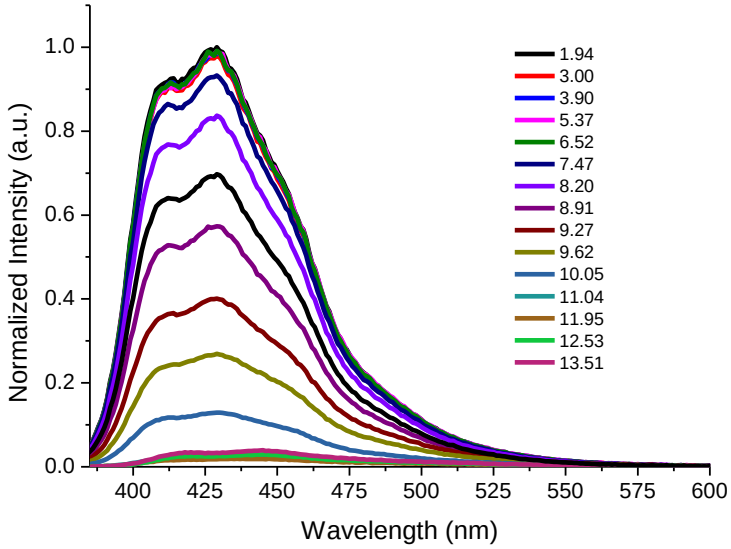


Figure S1. Fluorescent spectra of pH titration of **A1** (50 μM, λ_{ex} = 358 nm). Solvent: (DMSO/PB buffer = 40:60, v/v).

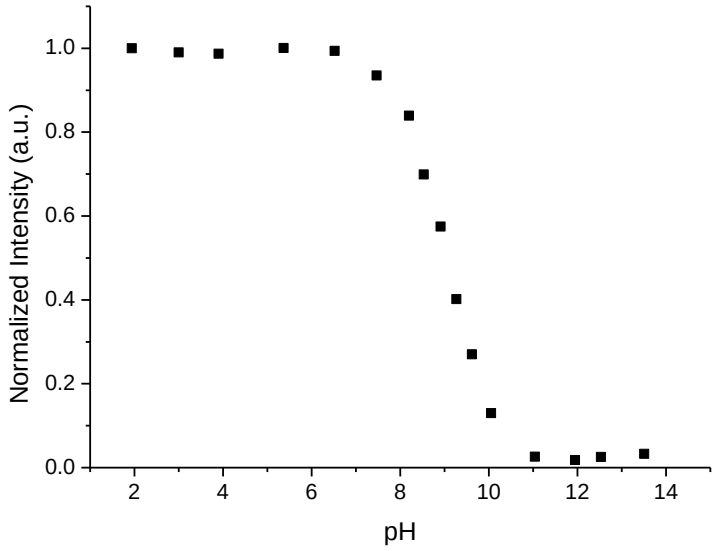
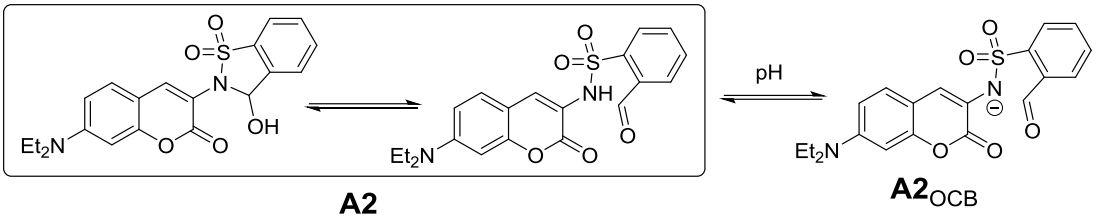


Figure S2. Fluorescence titration curve of **A1** at 429 nm.



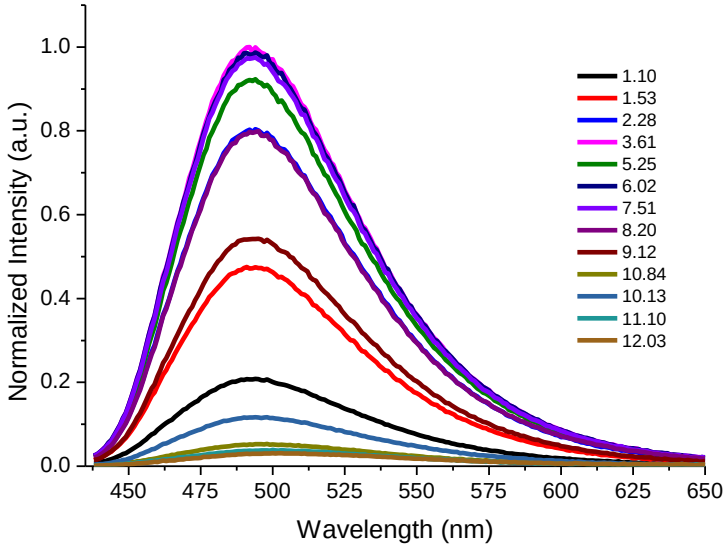


Figure S3. Fluorescent spectra of pH titration of **A2** (50 μM, λ_{ex} = 380 nm). Solvent: (DMSO/PB buffer = 5:95, v/v).

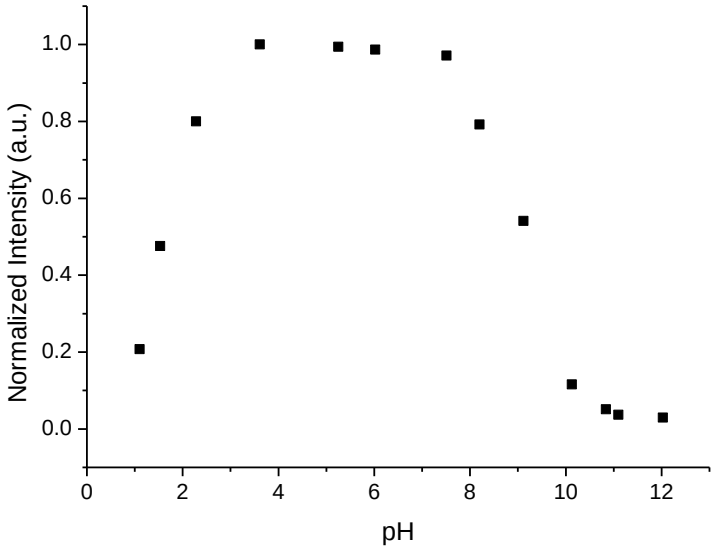
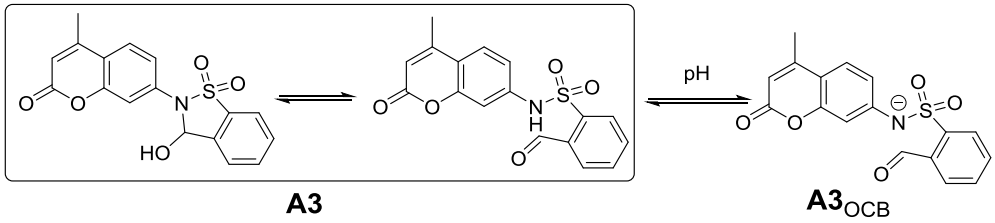


Figure S4. Fluorescence titration curve of **A2** at 493 nm.



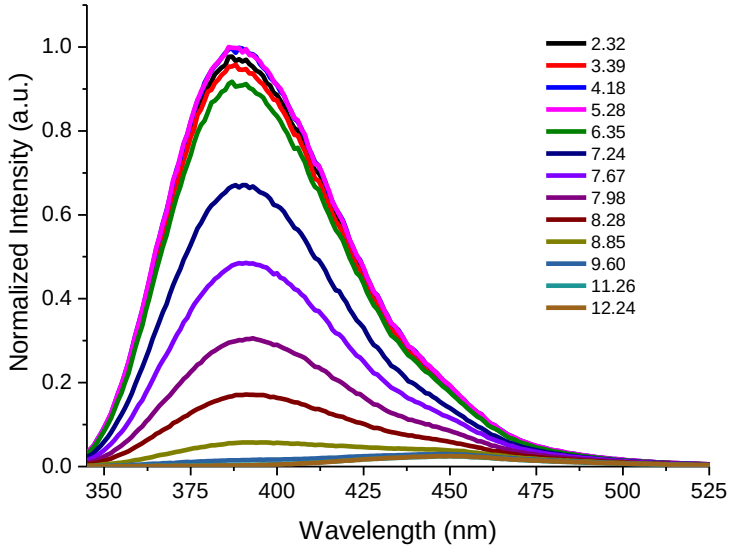


Figure S5. Fluorescent spectra of pH titration of **A3** (50 μM, λ_{ex} = 324 nm). Solvent: (DMSO/PB buffer = 5:95, v/v).

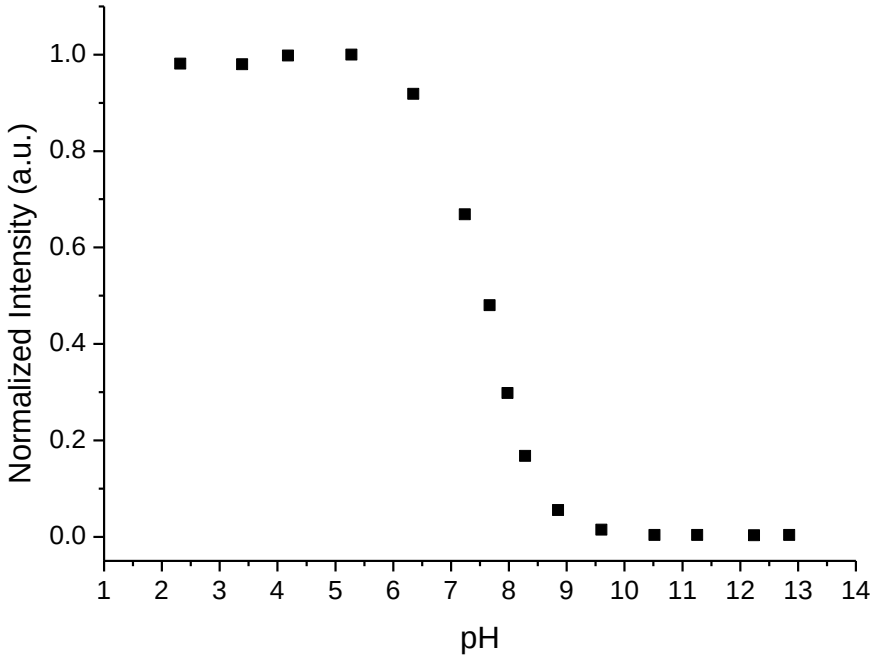
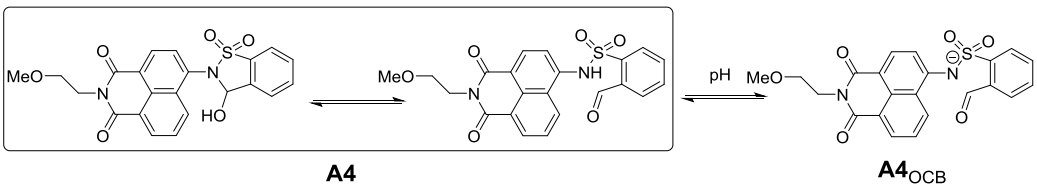


Figure S6. Fluorescence titration curve of **A3** at 393 nm.



A4 **$A4_{OCB}$**

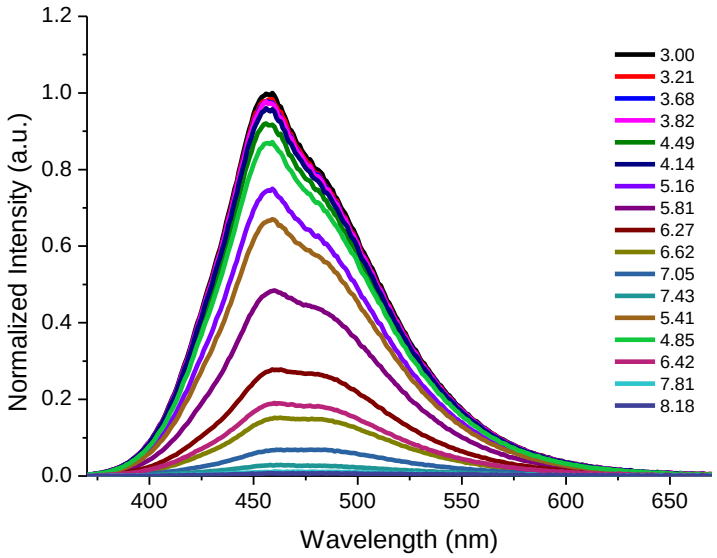


Figure S7. Fluorescent spectra of pH titration of **A4** (50 μM, λ_{ex} = 344 nm). Solvent: (DMSO/PB buffer = 5:95, v/v).

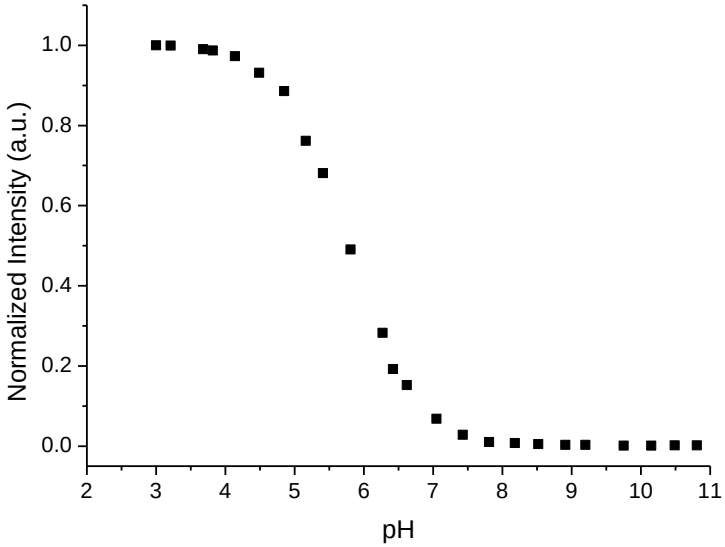
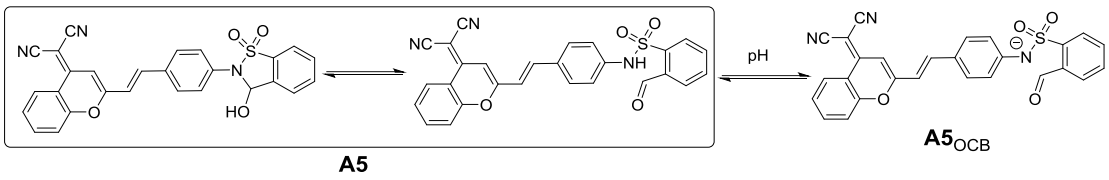


Figure S8. Fluorescence titration curve of **A4** at 459 nm.



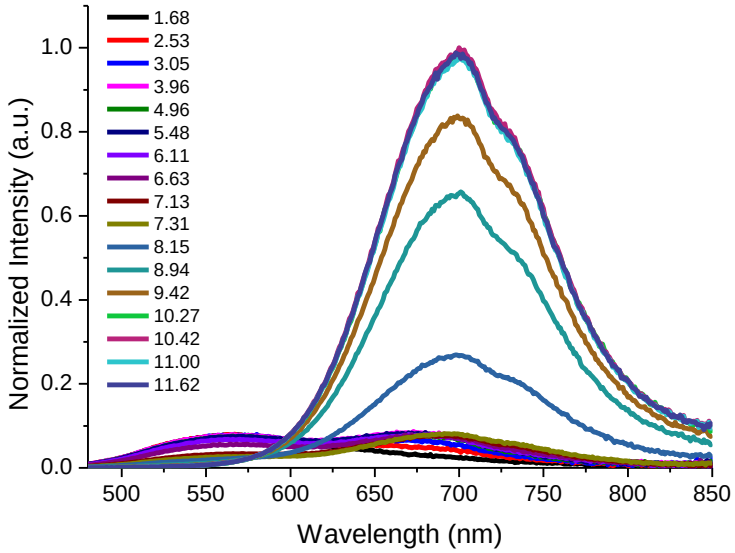


Figure S9. Fluorescent spectra of pH titration of **A5** (50 μM, λ_{ex} = 450 nm). Solvent: (DMSO/PB buffer = 40:60, v/v).

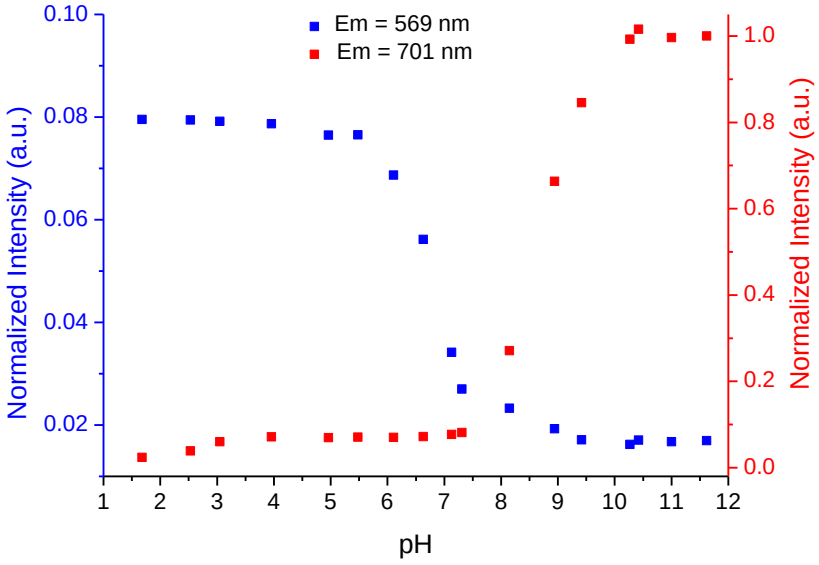


Figure S10. Fluorescence titration curve of **A5** at 701 nm and 569 nm.

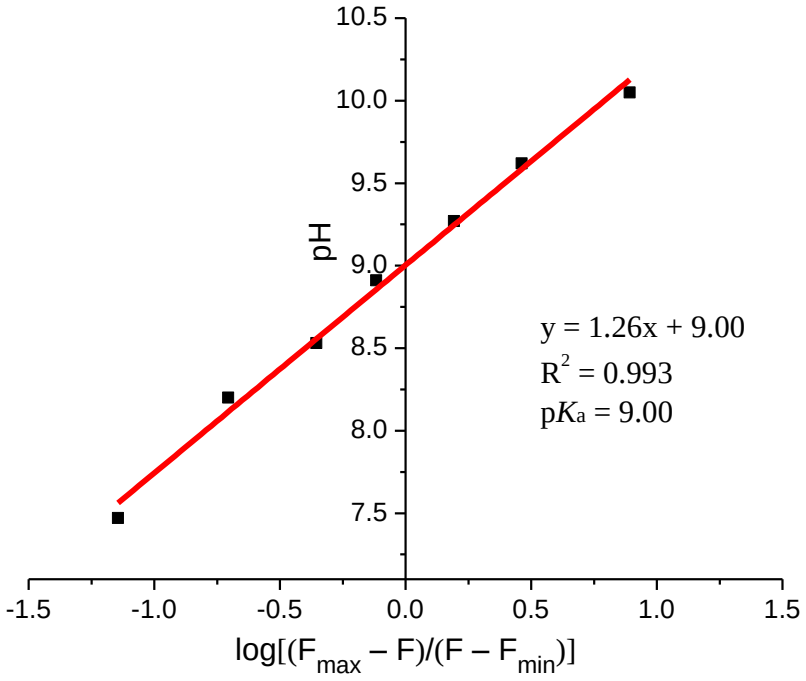


Figure S11. Linear fitting of fluorescence titration data of **A1** (Fig. S2) for pK_a determination.

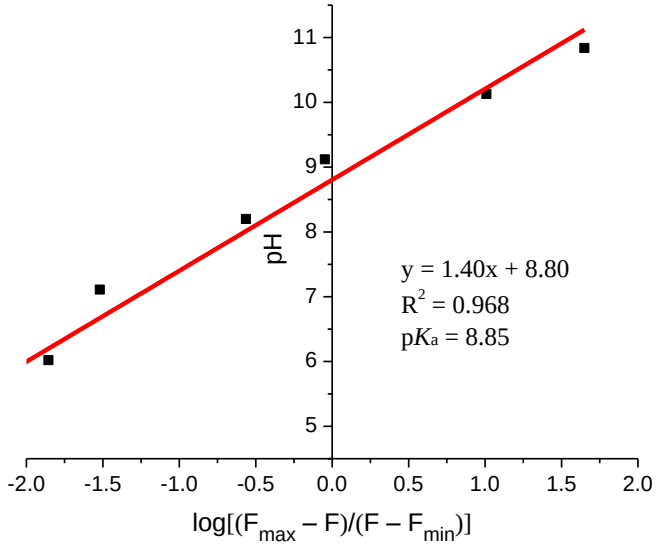


Figure S12 Linear fitting of fluorescence titration data of **A2** (Fig. S4) for pK_a determination.

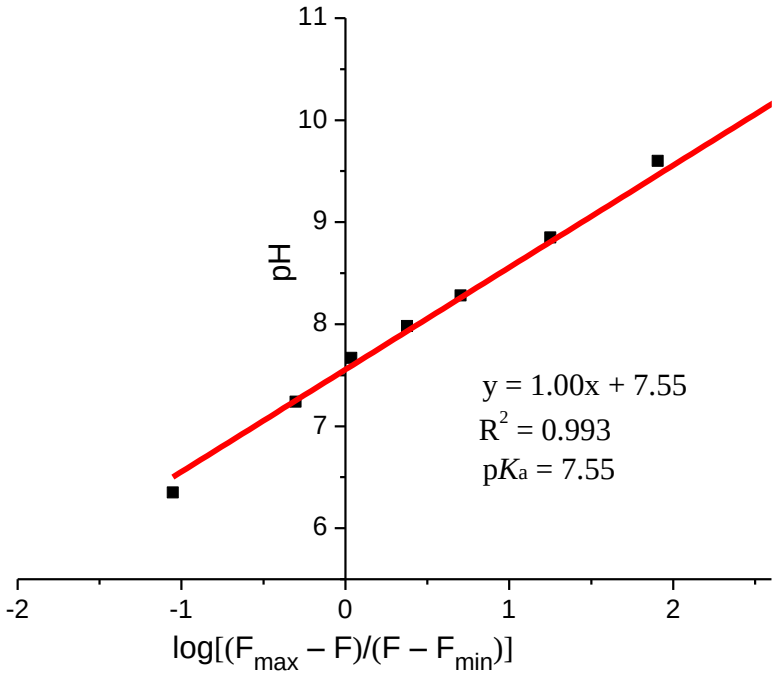


Figure S13. Linear fitting of fluorescence titration data of **A3** (Fig. S6) for pK_a determination.

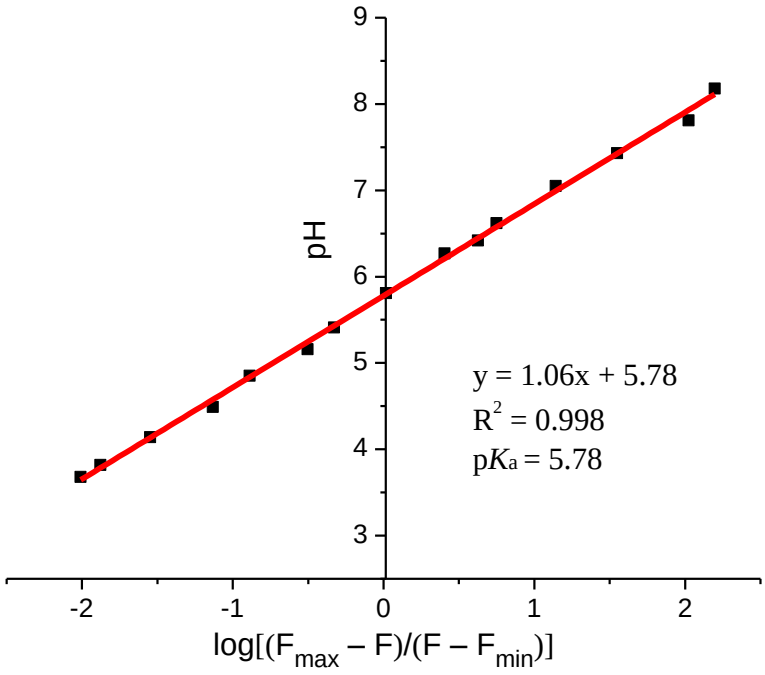


Figure S14. Linear fitting of fluorescence titration data of **A4** (Fig. S8) for pK_a determination.

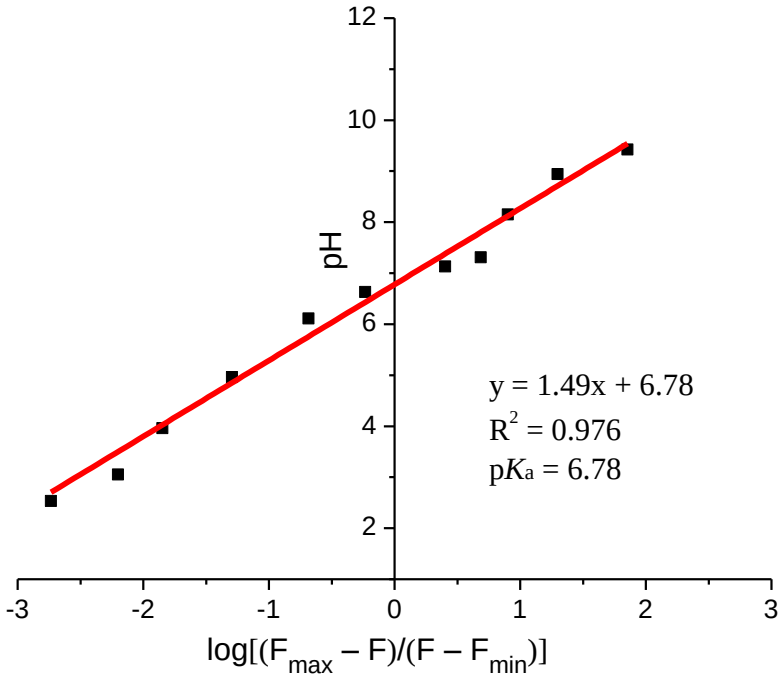


Figure S15. Linear fitting of fluorescence titration data of **A5** (569 nm in Fig. S10) for pK_a determination.

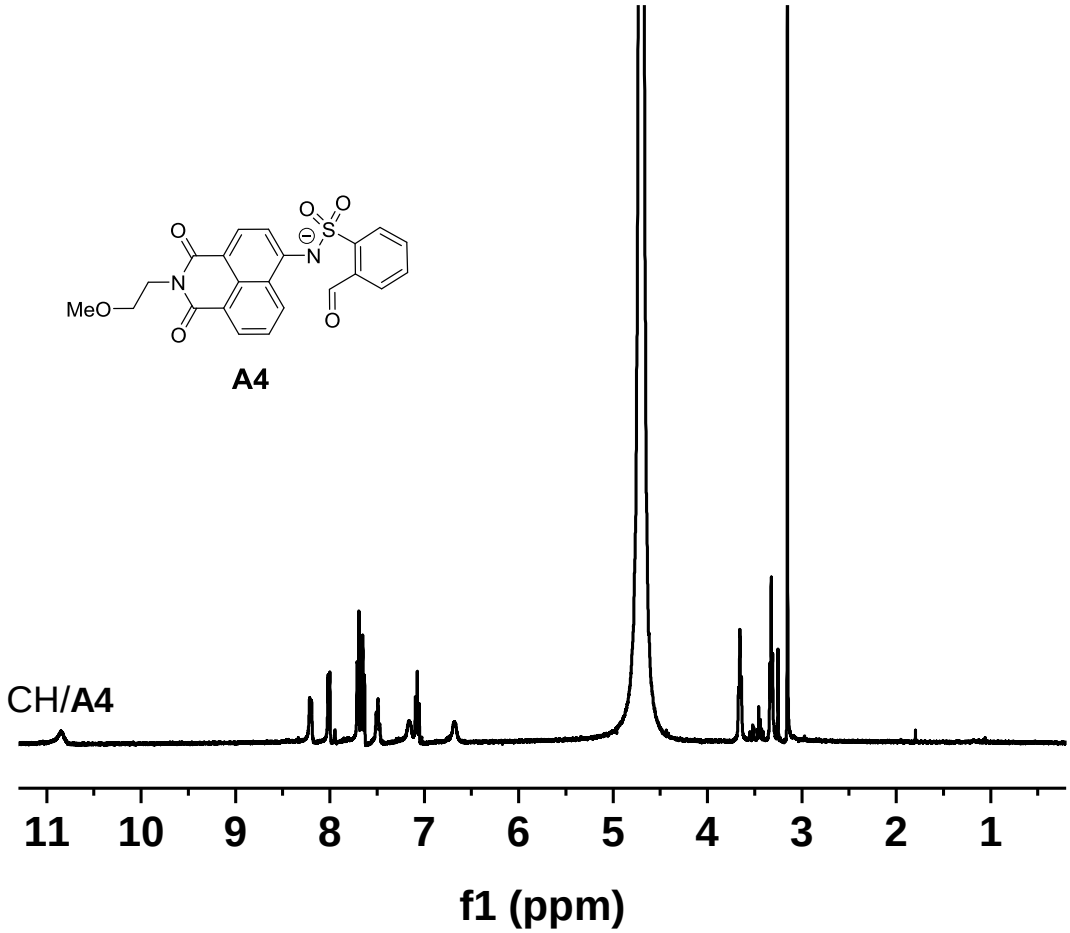


Figure S16. ^{1}H NMR spectrum of **A4** at pH 7.4 in PB D_2O buffer.

3. Recognition of Amino Acids in Aqueous Solution

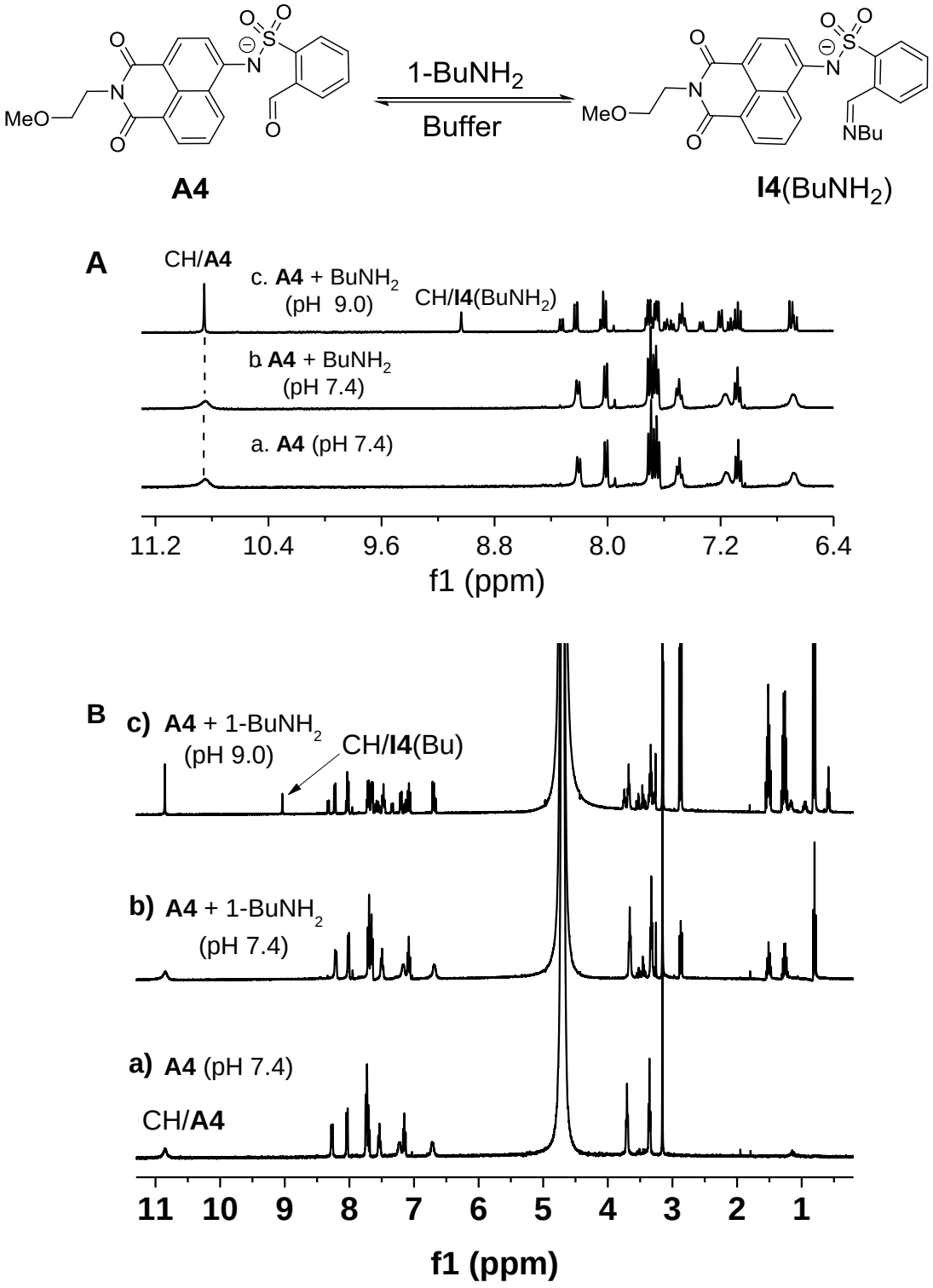


Figure S17. Partial (A) and full (B) ^{1}H NMR spectra of **A4** at pH 7.4 (a), and its reaction with 1-butylamine (3.0 equiv.) at pH 7.4 (b), or pH 9.0 (c) in PB D_2O buffer. This figure shows full NMR spectra of Figure 3A in the main text.

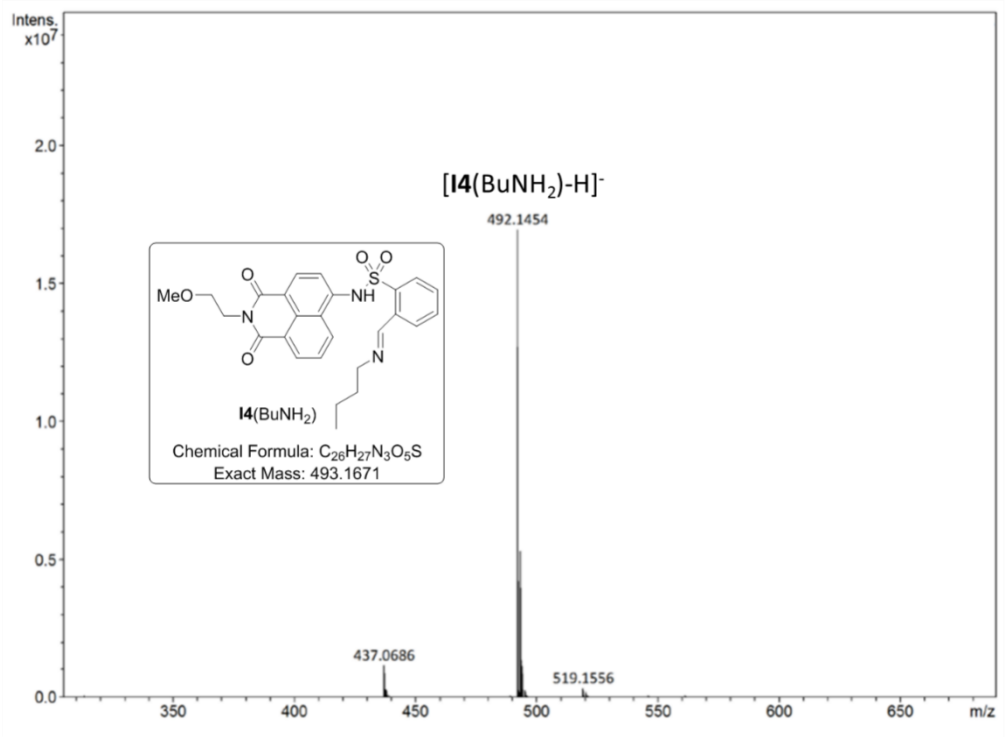


Figure S18. ESI mass spectrum of the reaction of **A4** and 1-butylamine in buffer at pH 7.4.

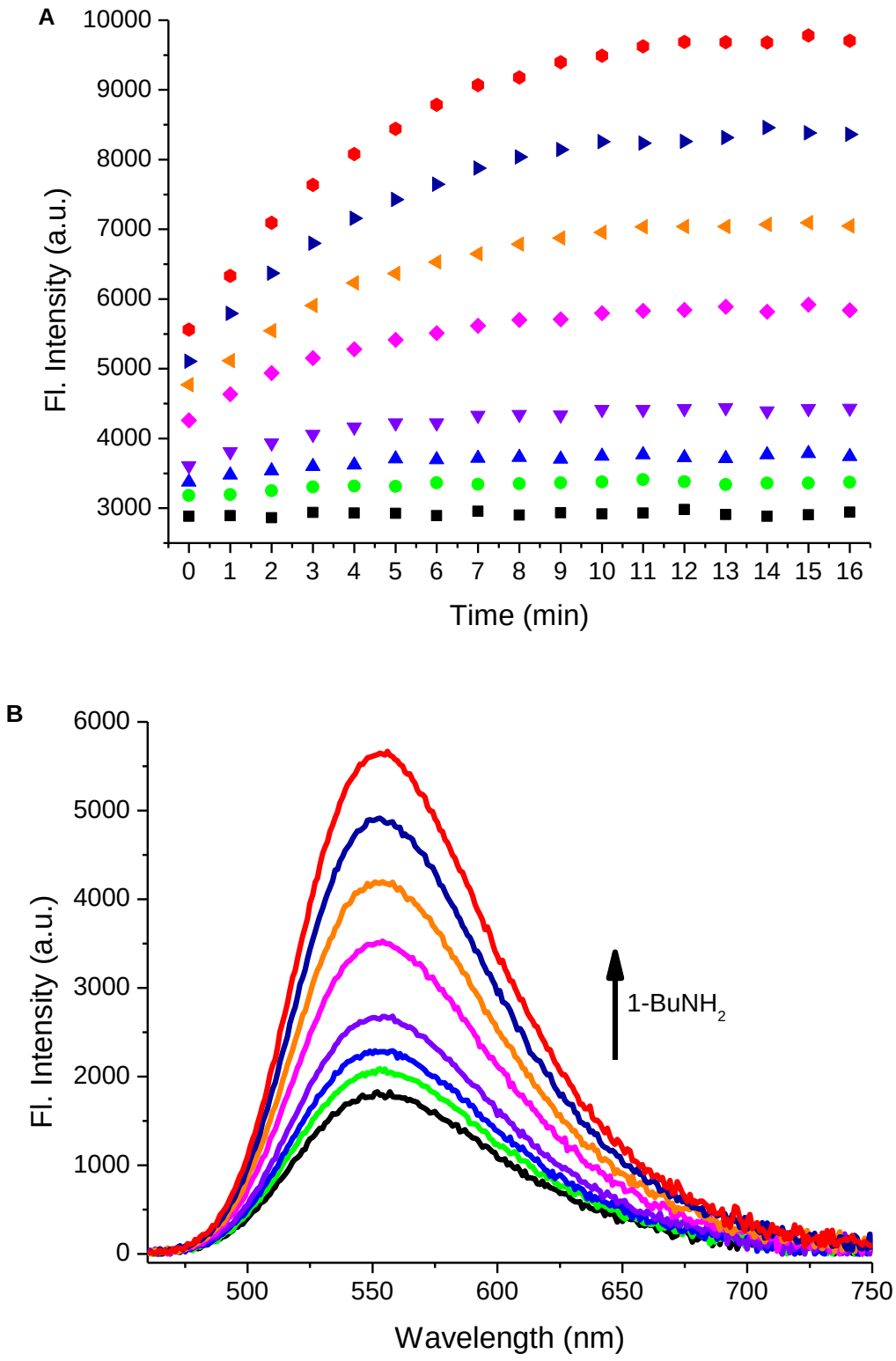


Figure S19. (A) Time-dependent fluorescence traces at 557 nm after addition of various concentrations of 1-butylamine (0.0, 1.0, 2.5, 5, 10, 20, 30, 40, 50 equiv. respectively) to **A4** (50 μM, λ_{ex} = 446 nm) at pH 9.0. (B) Fluorescence spectra of (A) at equilibrium. Solvent: (DMSO/PB buffer = 5:95, v/v).

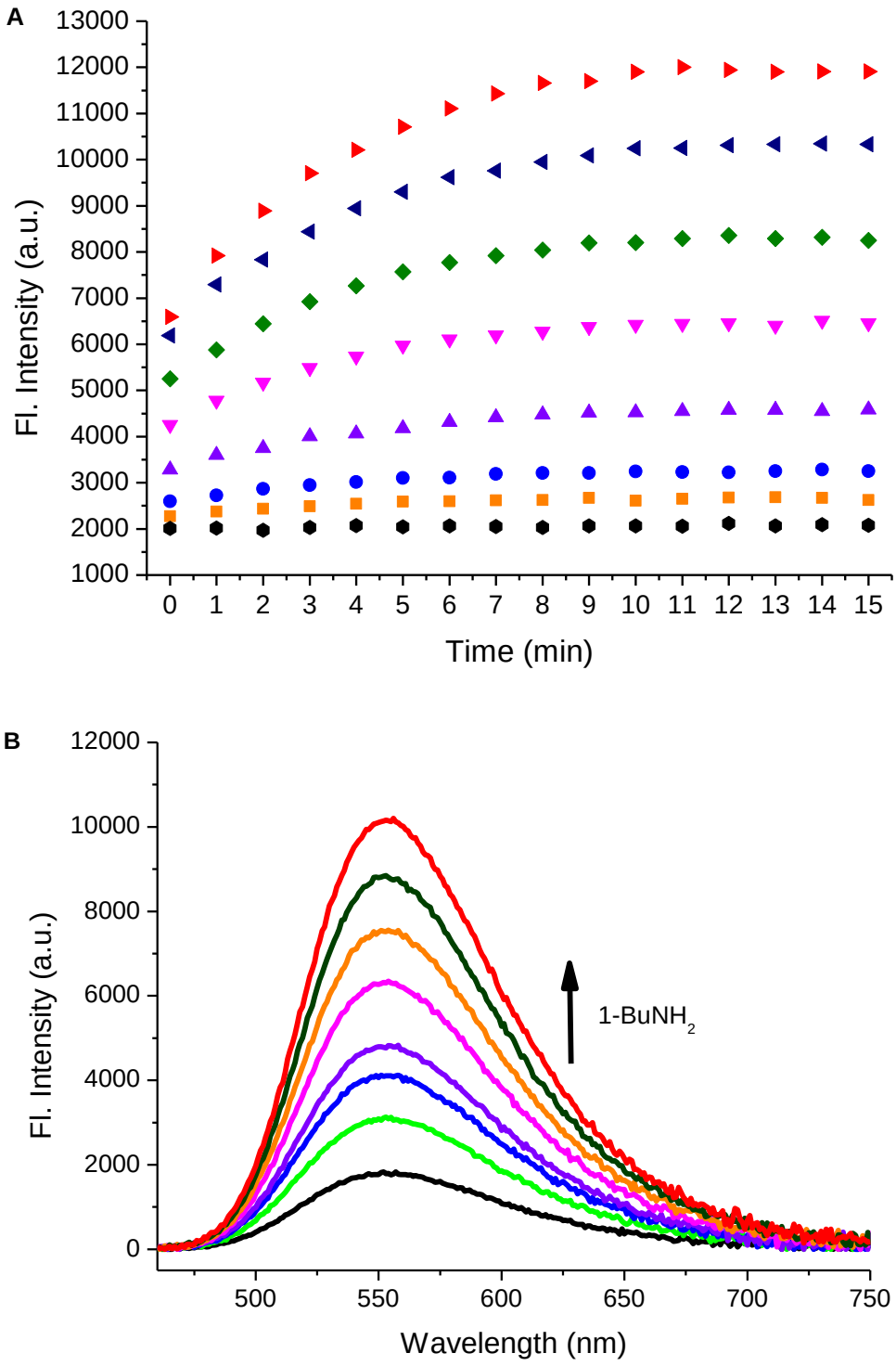


Figure S20. (A) Time-dependent fluorescence traces at 557 nm after addition of various concentrations of 1-butylamine [0.0, 1.0, 2.5, 5, 10, 20, 30, 40, 50 equiv. respectively] to **A4** (50 μM, λ_{ex} = 446 nm) at pH 9.5. (B) Fluorescence spectra of (A) at equilibrium. Solvent: (DMSO/PB buffer = 5:95, v/v).

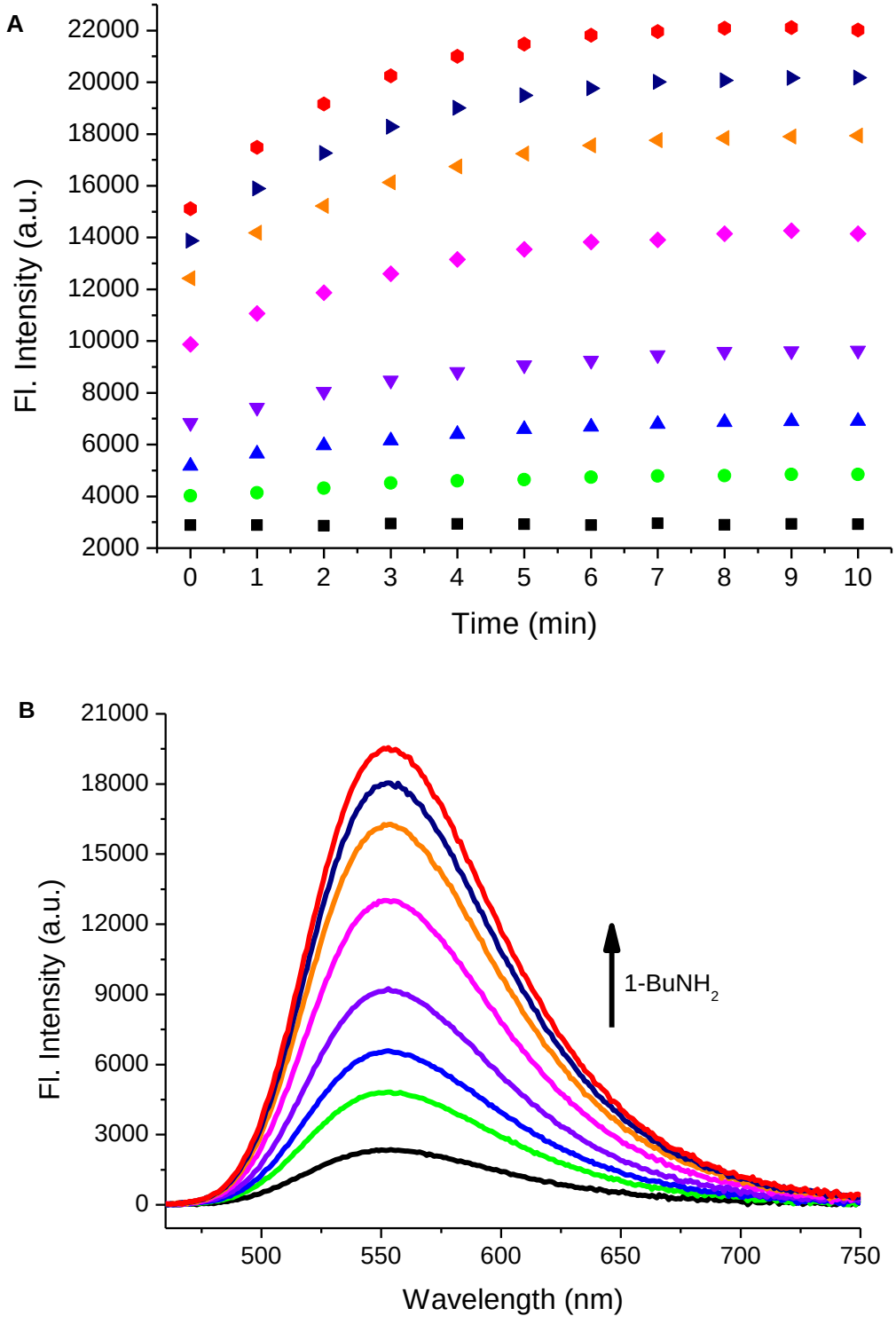


Figure S21. (A) Time-dependent fluorescence traces at 557 nm after addition of various concentrations of 1-butylamine [0.0, 1.0, 2.5, 5, 10, 20, 30, 40, 50 equiv. respectively] to **A4** (50 μM, λ_{ex} = 446 nm) at pH 10. (B) Fluorescence spectra of (A) at equilibrium. Solvent: (DMSO/PB buffer = 5:95, v/v).

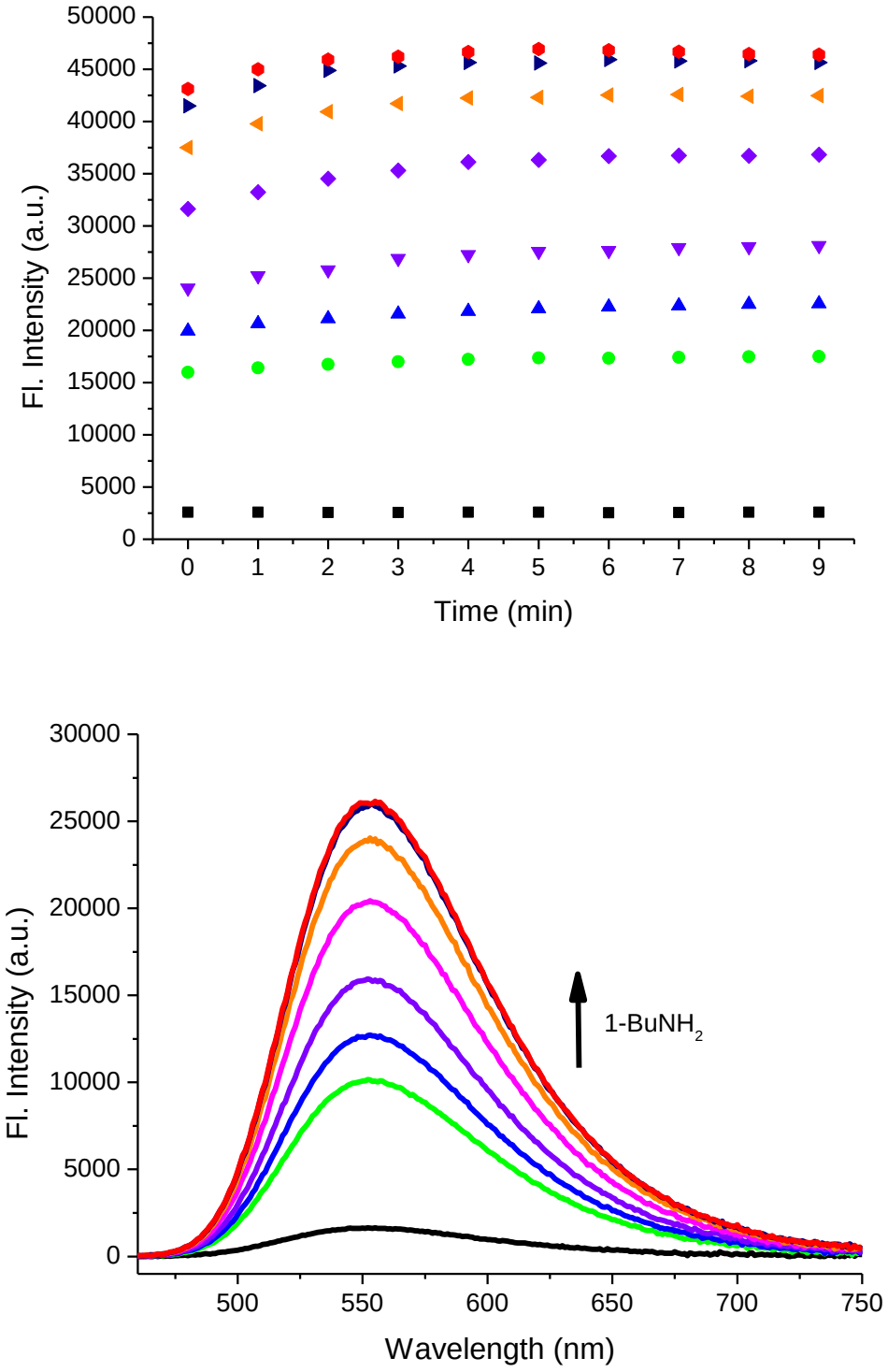


Figure S22. (A) Time-dependent fluorescence traces at 557 nm after addition of various concentrations of 1-butylamine [0.0, 1.0, 2.5, 5, 10, 20, 30, 40, 50 equiv. respectively] to **A4** at (50 μM, λ_{ex} = 446 nm) at pH 10.5. (B) Fluorescence spectra of (A) at equilibrium. Solvent: (DMSO/PB buffer = 5:95, v/v).

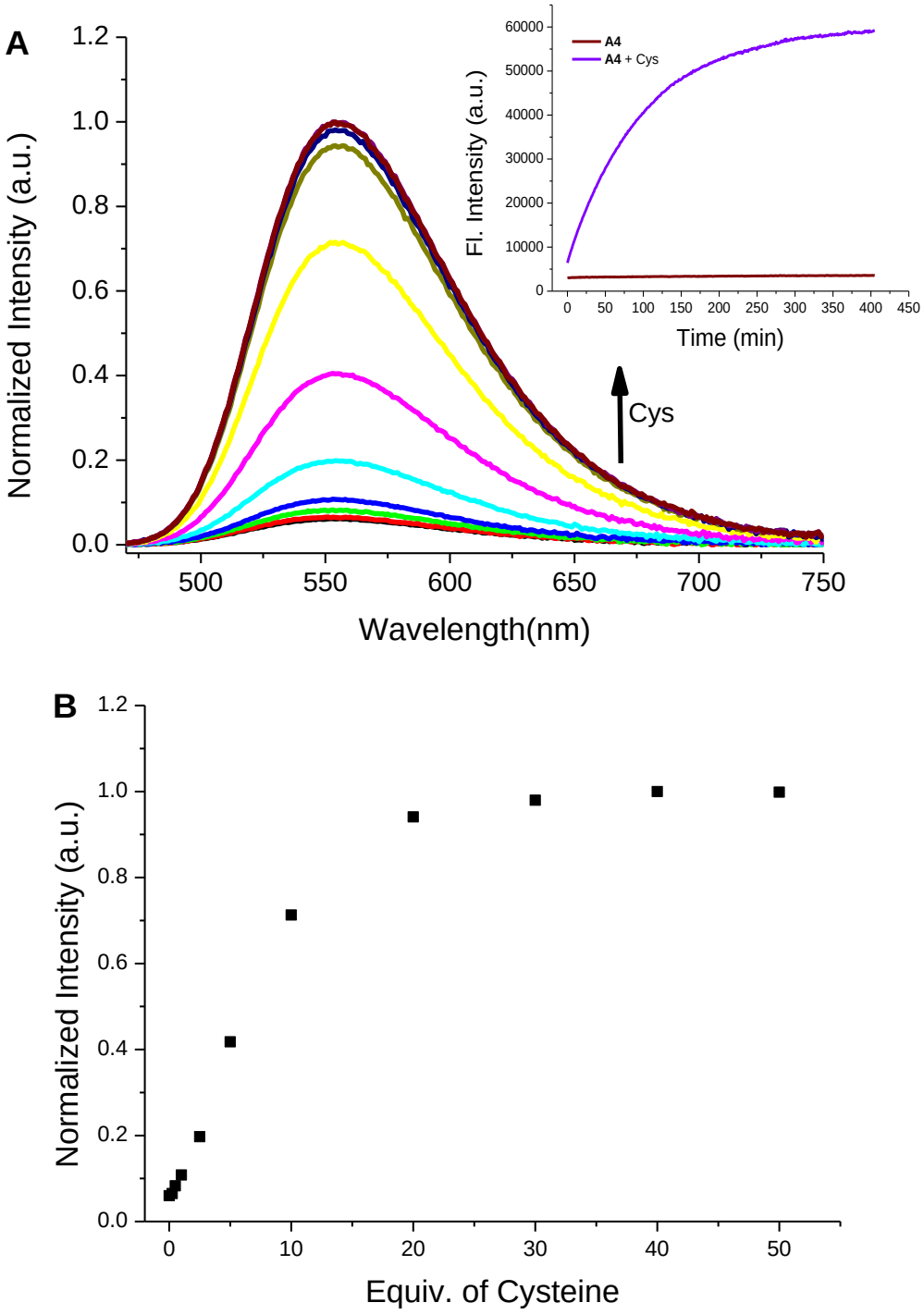


Figure S23. (A) Fluorescence spectra of the reaction of **A4** (50 μM, λ_{ex} = 446 nm) and cysteine (0 - 50.0 equiv) at pH 7.4. Solvent: (DMSO/PB buffer = 5:95, v/v). Inset: Time-dependent fluorescence traces at 557 nm of **A4** (50 μM) after addition of Cys (50.0 equiv.). (B) The titration curve at 557 nm.

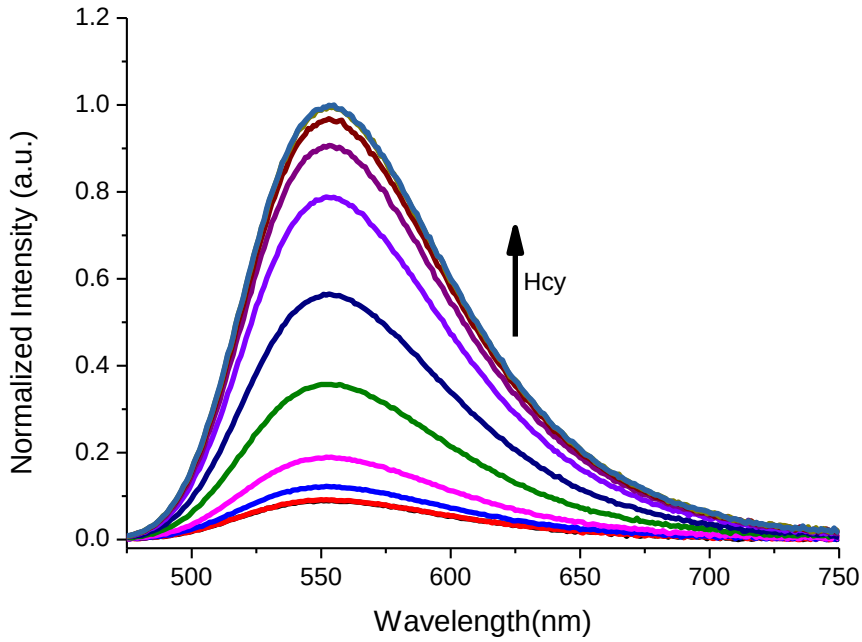


Figure S24. Fluorescence spectra of the reaction of **A4** (50 μM, λ_{ex} = 446 nm) with homocysteine (0 - 50.0 equiv) at pH 7.4. Solvent: (DMSO/PB buffer = 5:95, v/v)

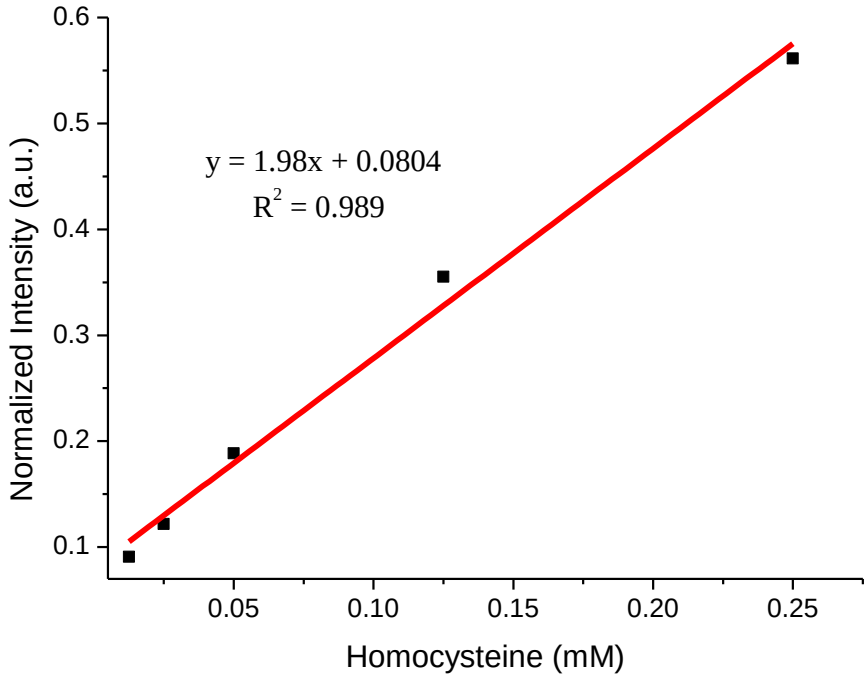


Figure S25. Linear range of fluorescence response for **A4** towards varied concentration of homocysteine at 459 nm (λ_{ex} = 344 nm). The limit of detection is 1.79 μM for homocysteine.

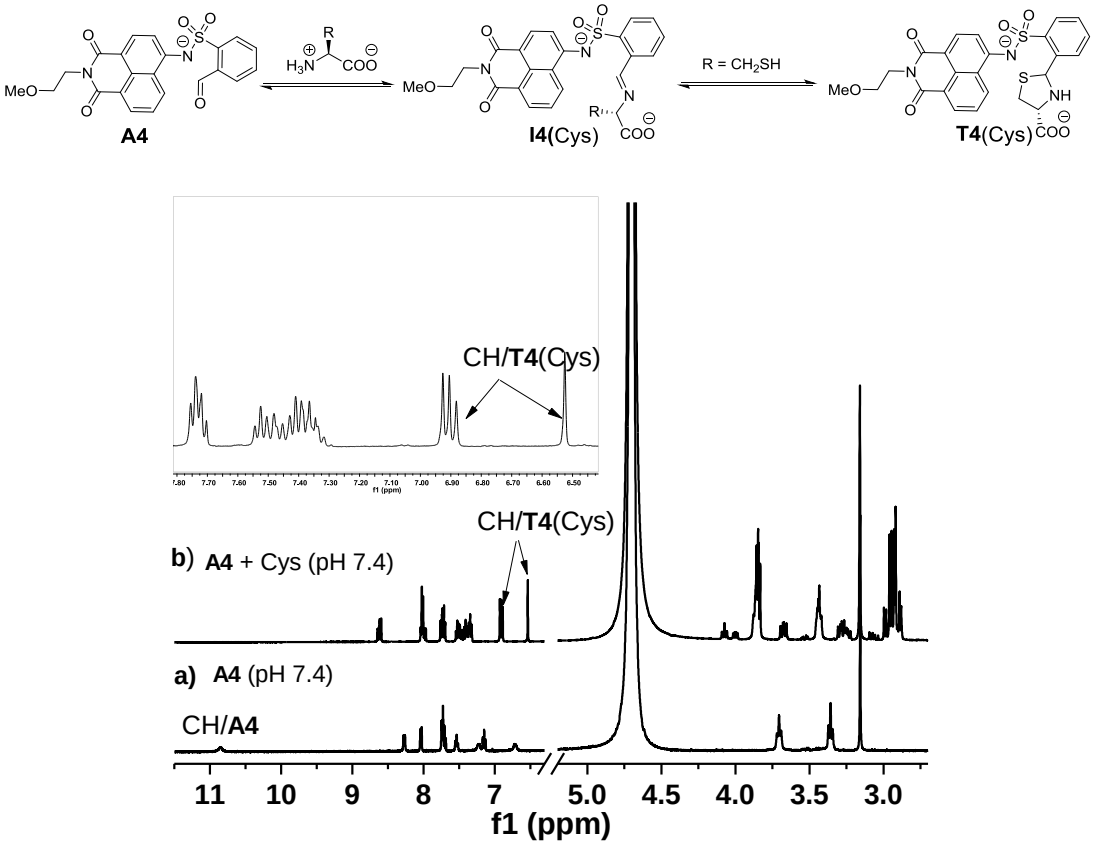


Figure S26. ^{1}H NMR spectra of **A4** at pH 7.4 (a), and its reaction with cysteine (3.0 equiv.) at pH 7.4 (b) in PB D_2O buffer.

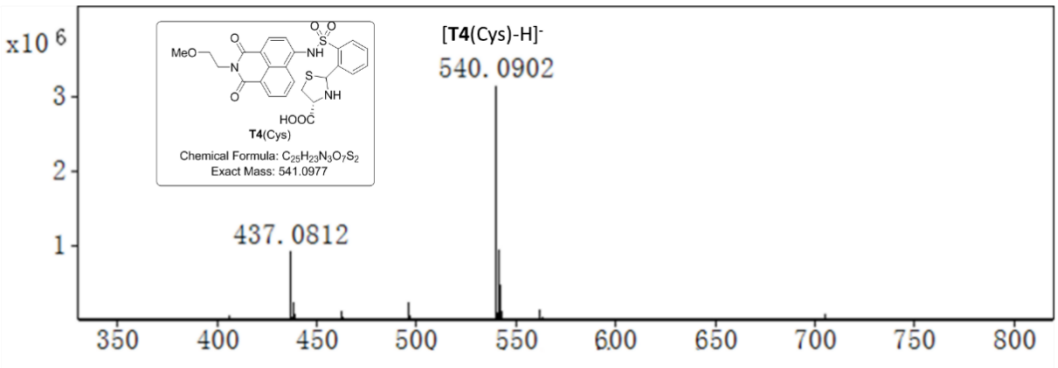


Figure S27. ESI-mass spectrum of the reaction of **A4** with cysteine in buffer at pH 7.4.

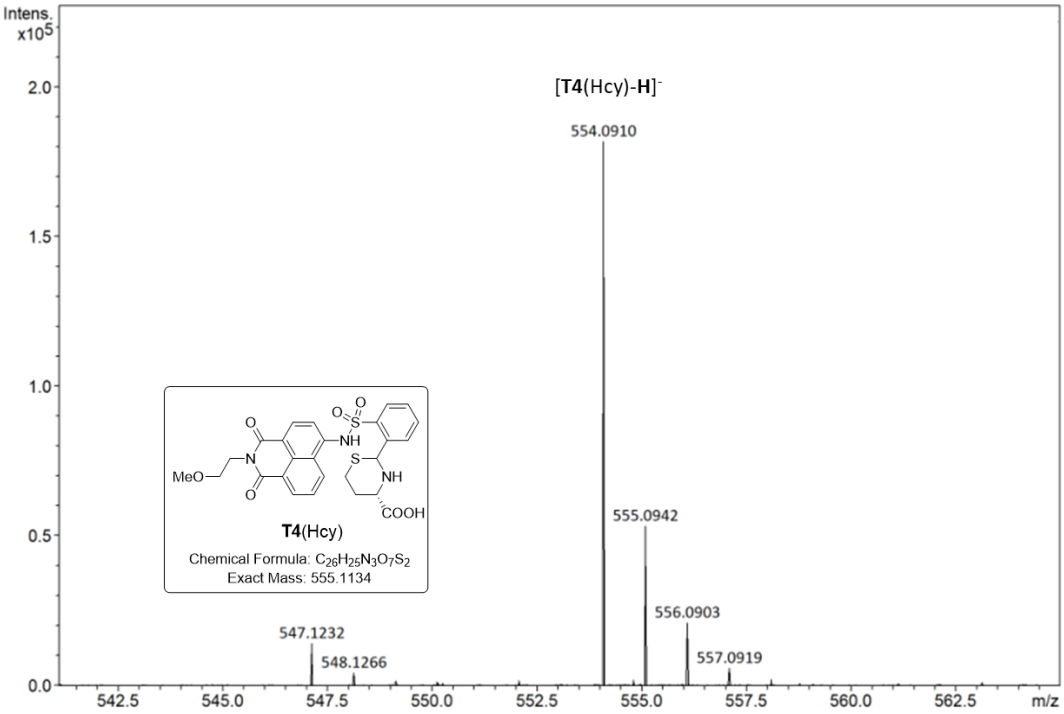


Figure S28. ESI mass spectrum of the reaction of **A4** and Hcy in buffer at pH 7.4.

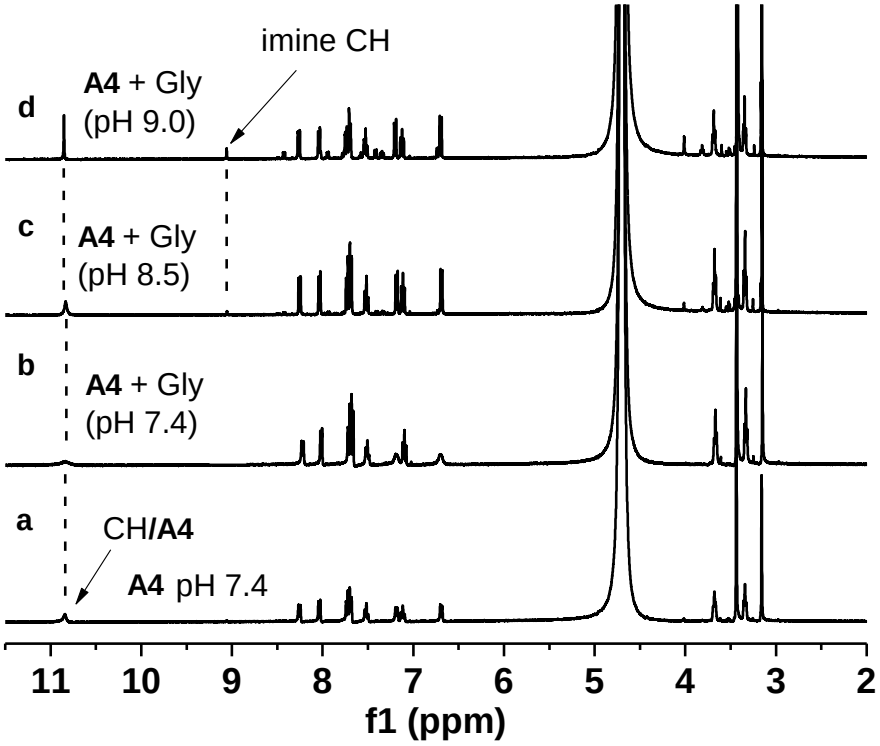


Figure S29. ^{1}H NMR spectra of **A4** at pH 7.4 (a), and its reaction with glycine (3.0 equiv.) at pH 7.4 (b), pH 8.5 (c), or pH 9.0 (d) in PB D_2O buffer.

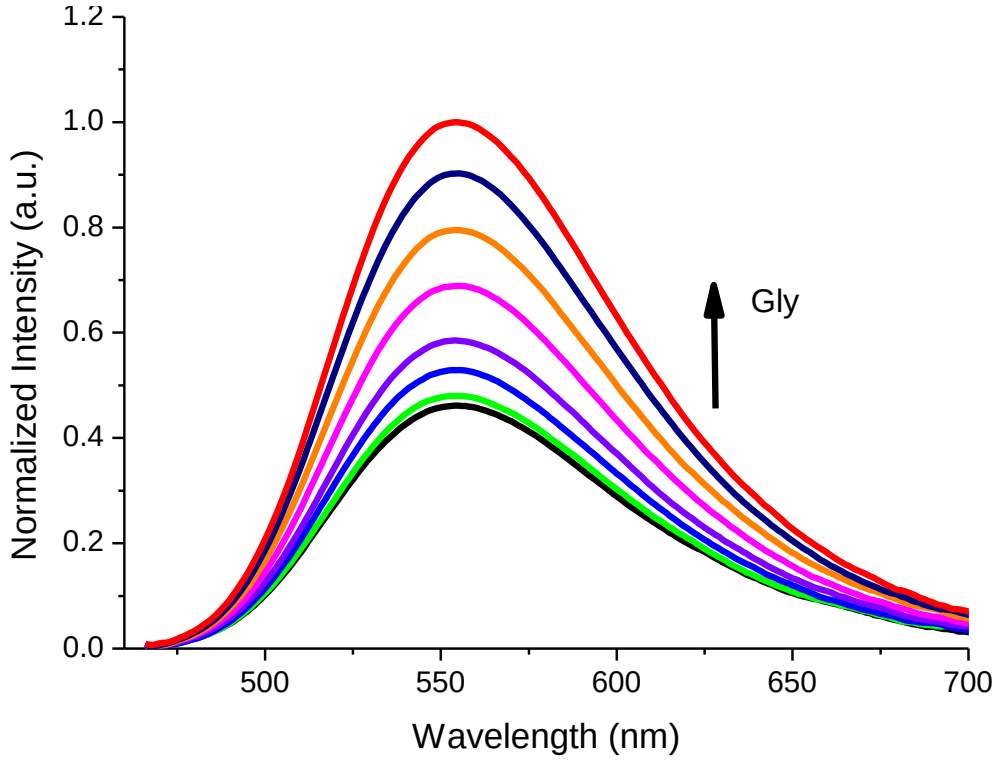


Figure S30. Fluorescence spectra of the reaction of **A4** (50 μM, λ_{ex} = 446 nm) and glycine (0, 2.5, 5.0 10.0, 20.0, 30.0, 40.0, 50.0 equiv.) at pH 9.0. Solvent: (DMSO/PB buffer = 5:95, v/v).

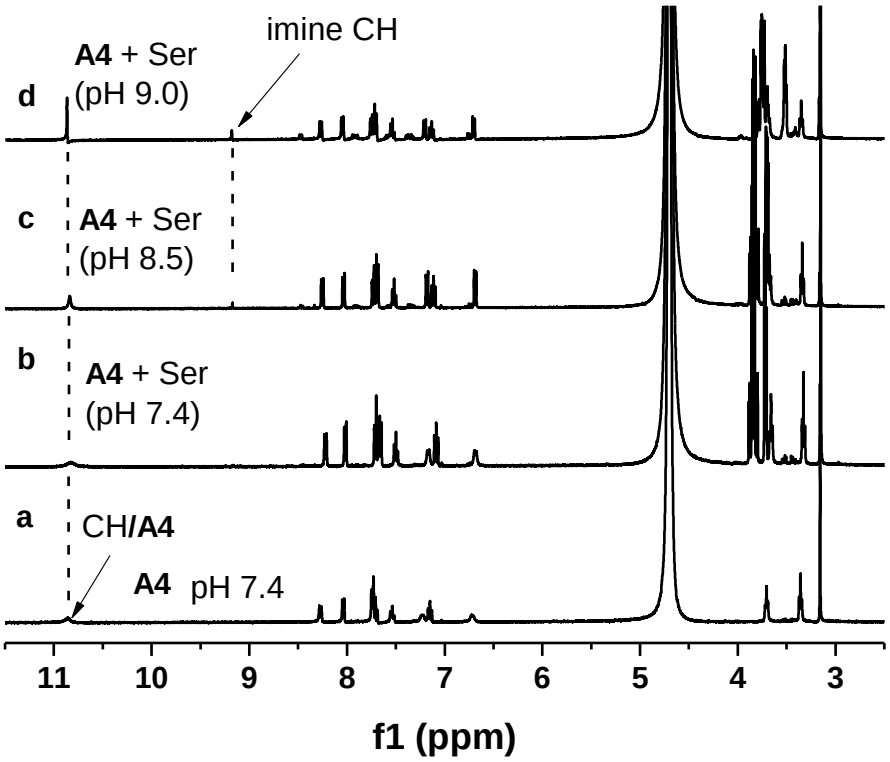


Figure S31. ^{1}H NMR spectra of **A4** at pH 7.4 (a), and its reaction with serine (3.0 equiv.) at pH 7.4 (b), pH 8.5 (c), or pH 9.0 (d) in PB D_2O buffer.

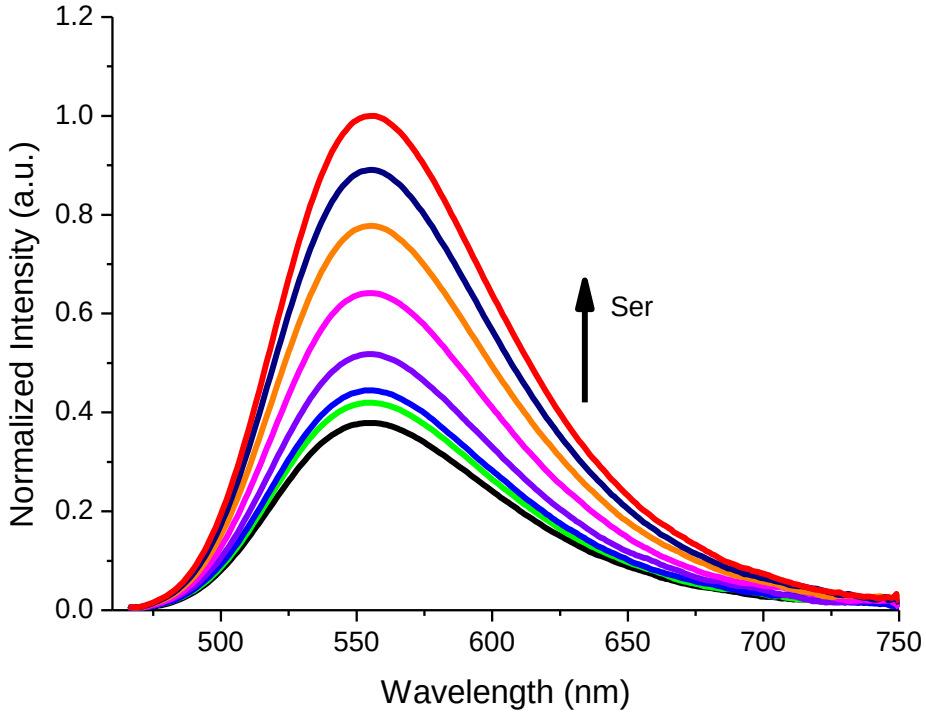


Figure S32. Fluorescence spectra of the reaction of **A4** (50 μM, λ_{ex} = 446 nm) and serine (0, 2.5, 5.0 10.0, 20.0, 30.0, 40.0, 50.0 equiv.) at pH 9.0. Solvent: (DMSO/PB buffer = 5:95, v/v).

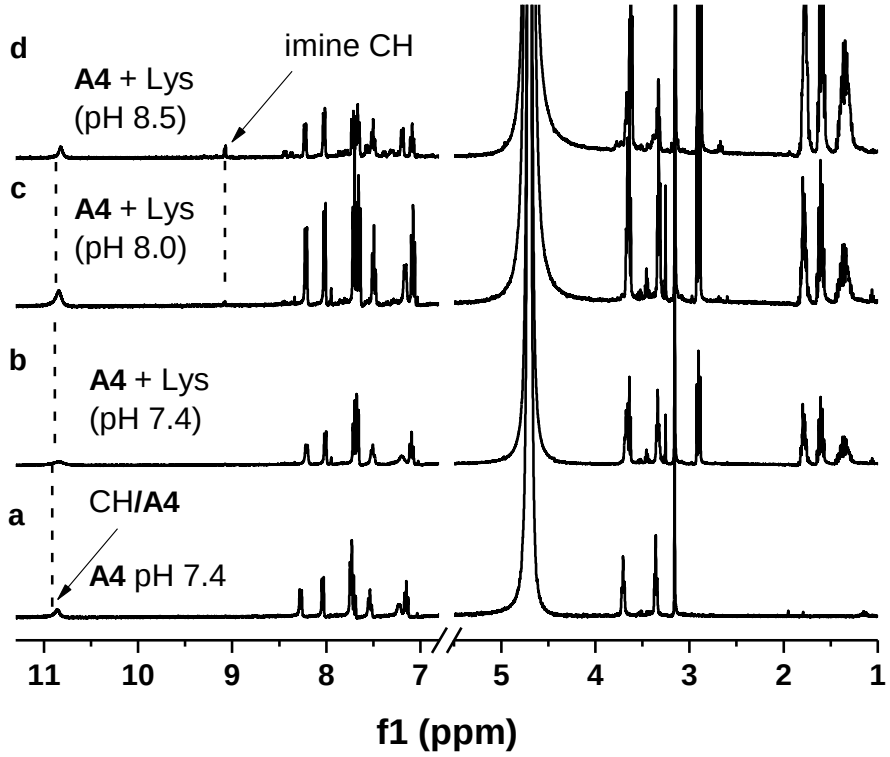


Figure S33. ^{1}H NMR spectra of **A4** at pH 7.4 (a), and its reaction with lysine (3.0 equiv.) at pH 7.4 (b), pH 8.0 (c), or pH 8.5 (d) in PB D_2O buffer.

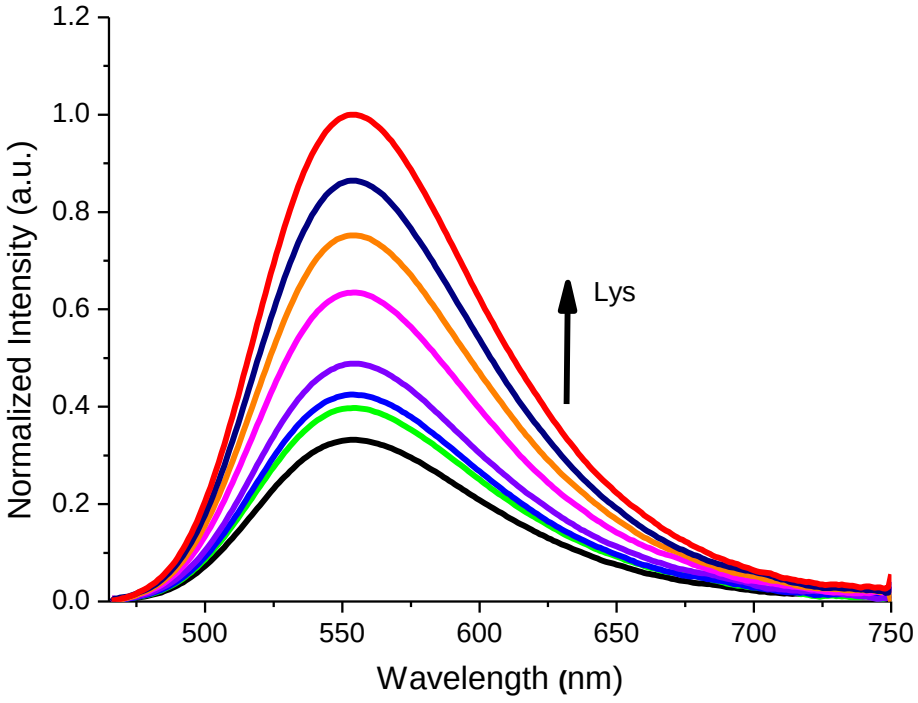


Figure S34. Fluorescence spectra of the reaction of **A4** (50 μM, λ_{ex} = 446 nm) and lysine (0, 2.5, 5.0 10.0, 20.0, 30.0, 40.0, 50.0 equiv.) at pH 8.0. Solvent: (DMSO/PB buffer = 5:95, v/v).

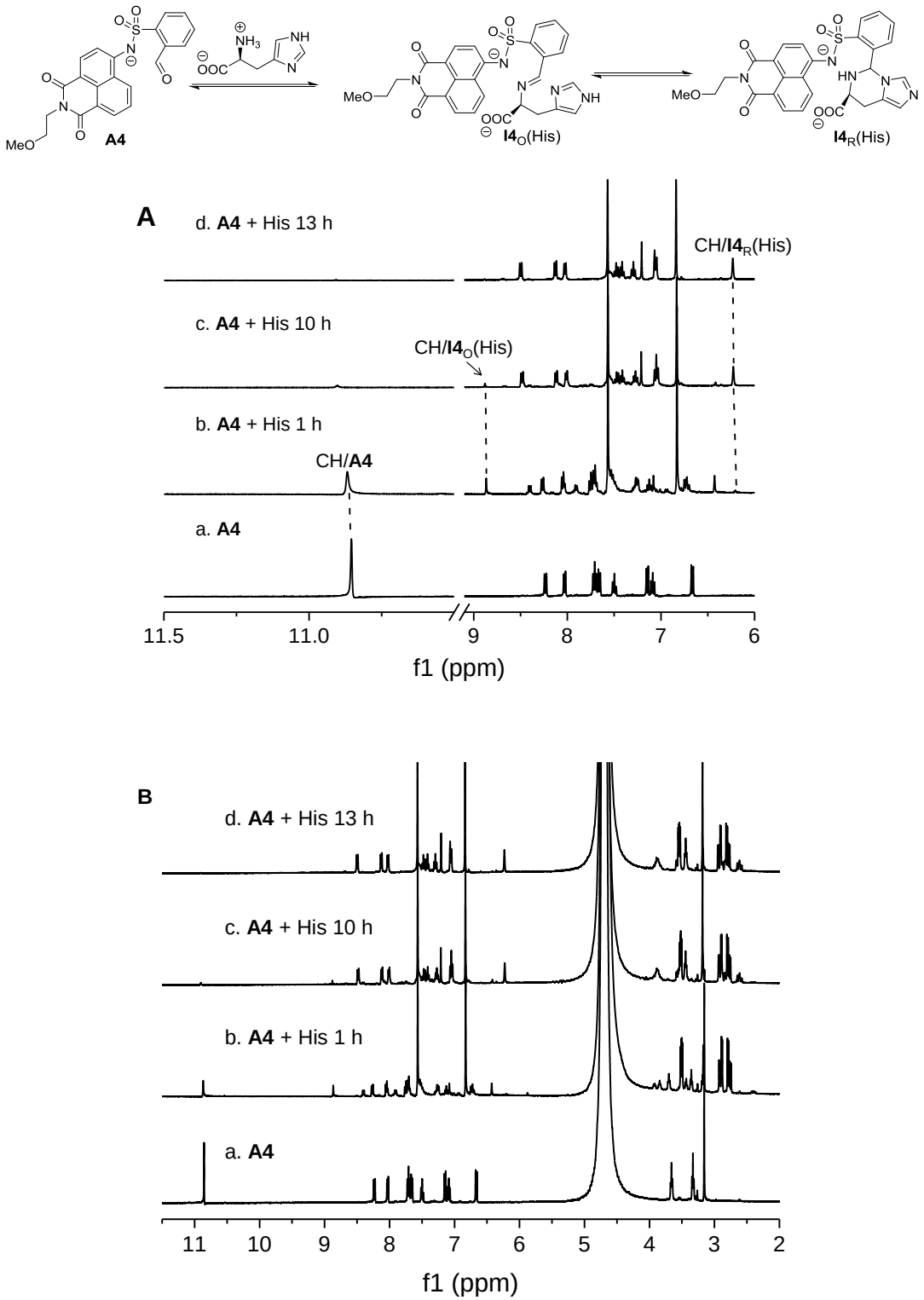


Figure S35. Partial and full ^{1}H NMR spectra of **A4** at pH 10 (a), and its reaction with histidine (3.0 equiv.) for 1 h (b), 10 h (c), and 13 h (d) in PB D_2O buffer at pH 10.

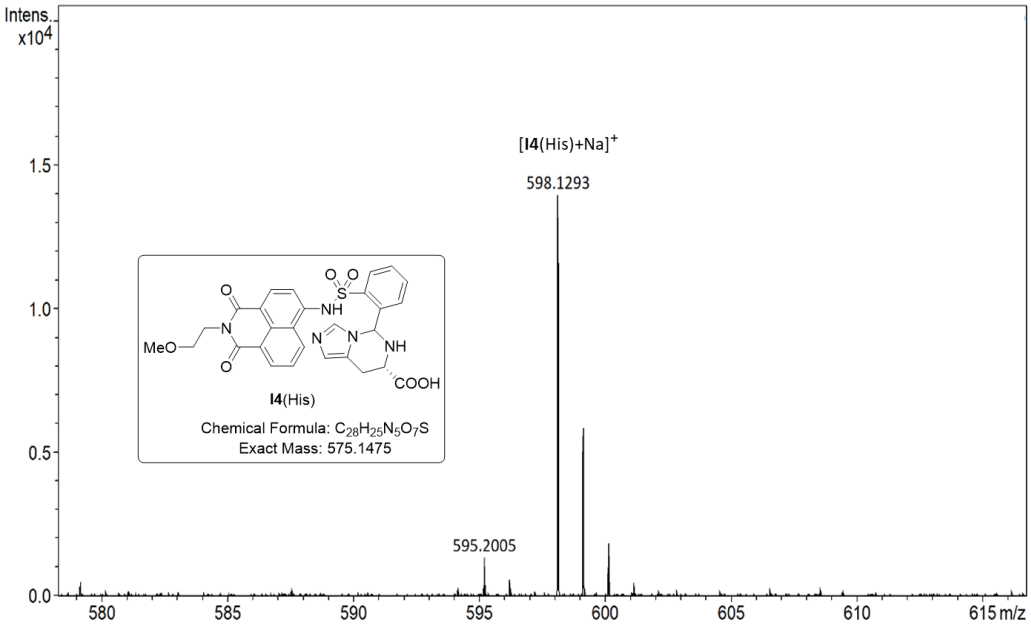


Figure S36. ESI mass spectrum of the reaction of **A4** and His in buffer at pH 10.

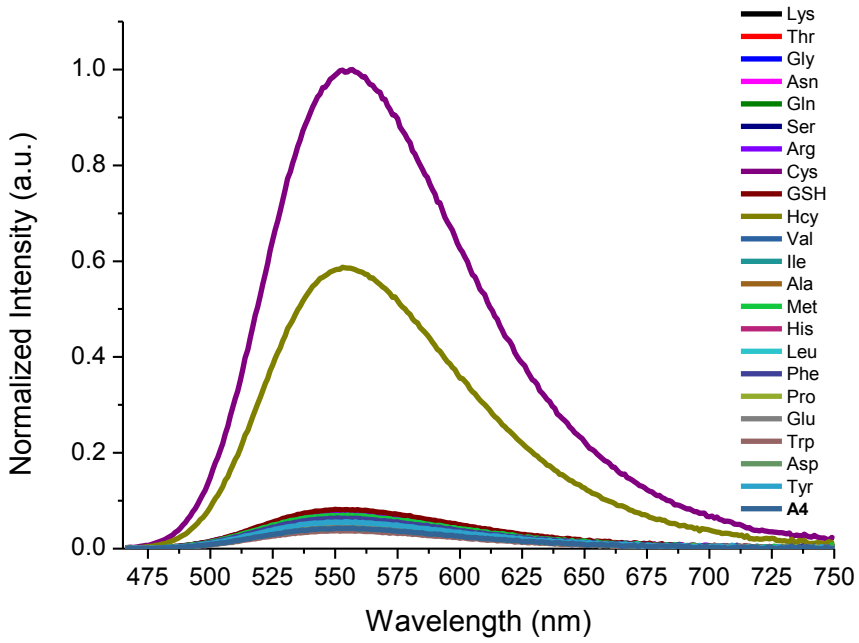


Figure S37. Fluorescence spectra of the reaction of **A4** (50 μM, λ_{ex} = 446 nm) with various amino acids (50 equiv) at pH 7.4. Solvent: DMSO/buffer = 5:95, v/v.

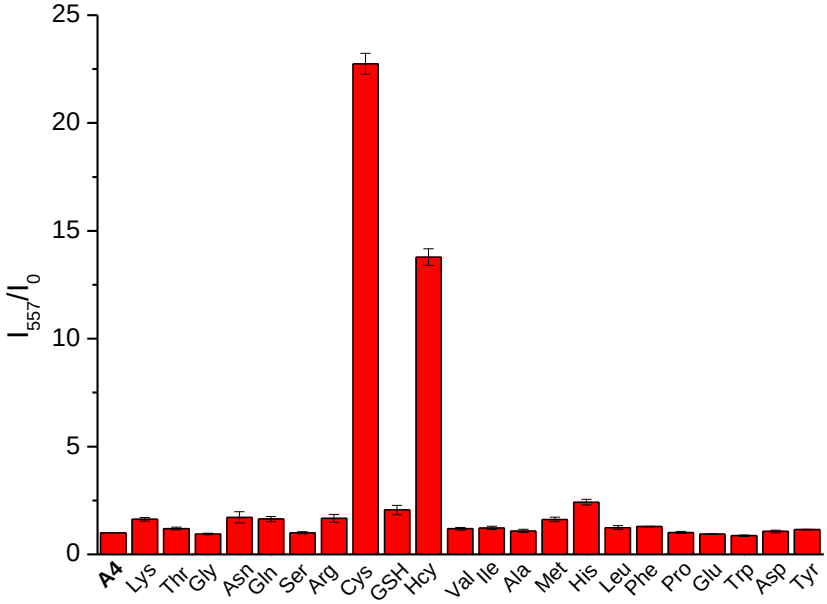


Figure S38. Fluorescencere response (I_{557}/I_0) of **A4** (50 μM, λ_{ex} = 418 nm) toward various amino acids (50 equiv) at pH 7.4 (λ_{ex} = 446 nm). Solvent: DMSO/buffer = 5:95, v/v. I_0: Fluorescence intensity of **A4** at 557 nm in the absence of amino acids.

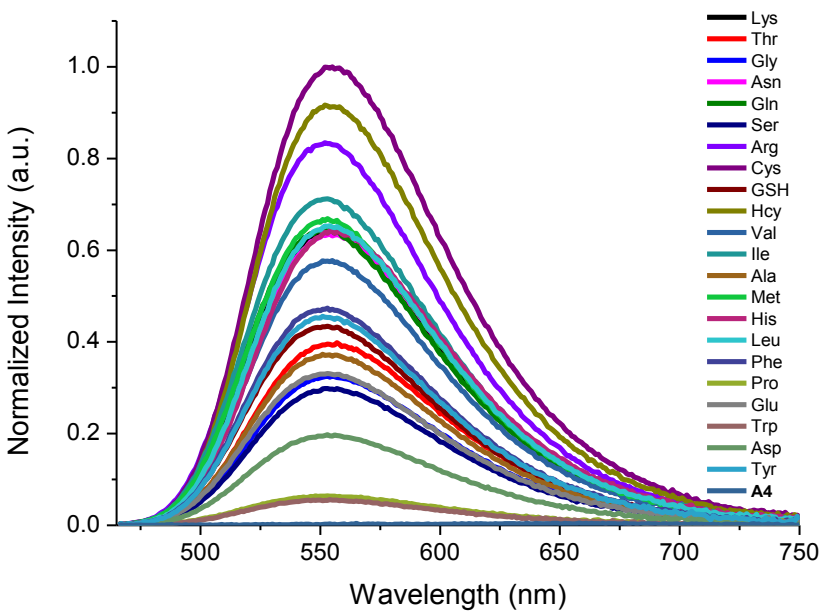


Figure S39. Fluorescence spectra of the reaction of **A4** (50 μM, λ_{ex} = 446 nm) with various amino acids (50 equiv) at pH 10. Solvent: DMSO/buffer = 5:95, v/v.

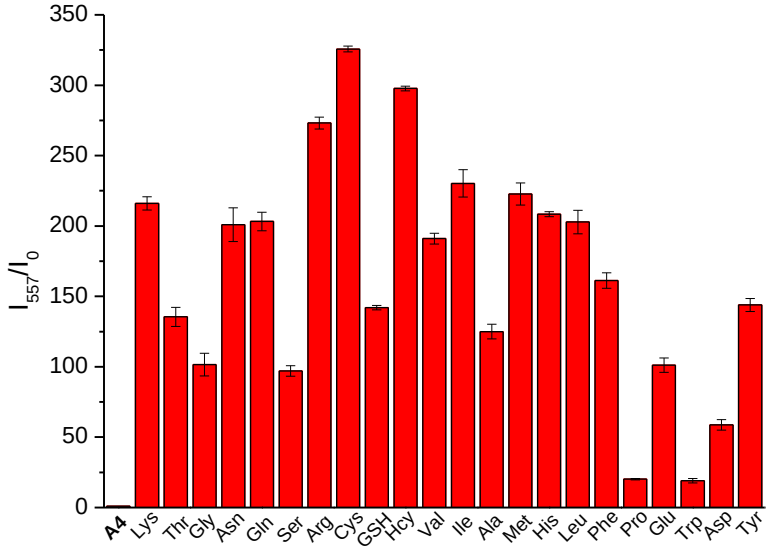


Figure S40. Fluorescencere response (I_{557}/I_0) of **A4** (50 μM, λ_{ex} = 446 nm) toward various amino acids (50 equiv) at pH 10. Solvent: DMSO/buffer = 5:95, v/v. I_0: Fluorescence intensity of **A4** at 557 nm in the absence of amino acids.

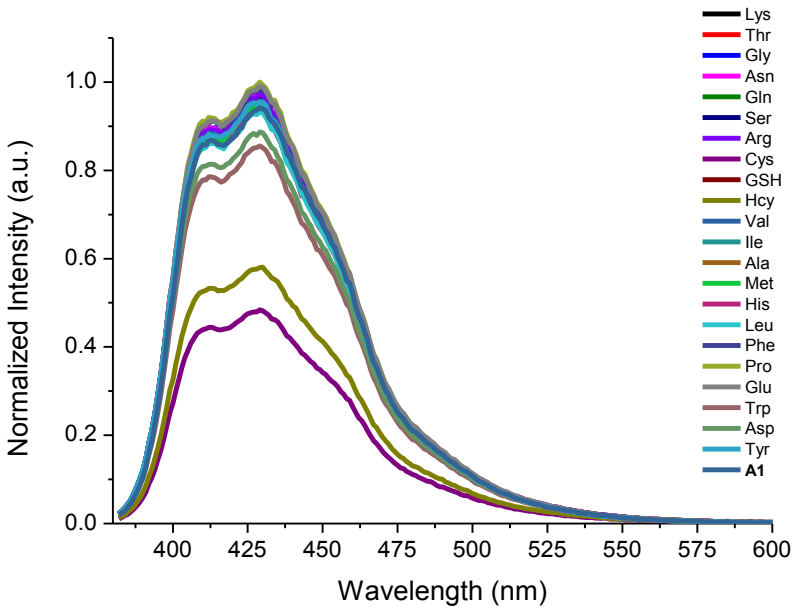


Figure S41. Fluorescence spectra of the reaction of **A1** (50 μM, λ_{ex} = 358 nm) with various amino acids (50 equiv) at pH 7.4. Solvent: DMSO/buffer = 40:60, v/v.

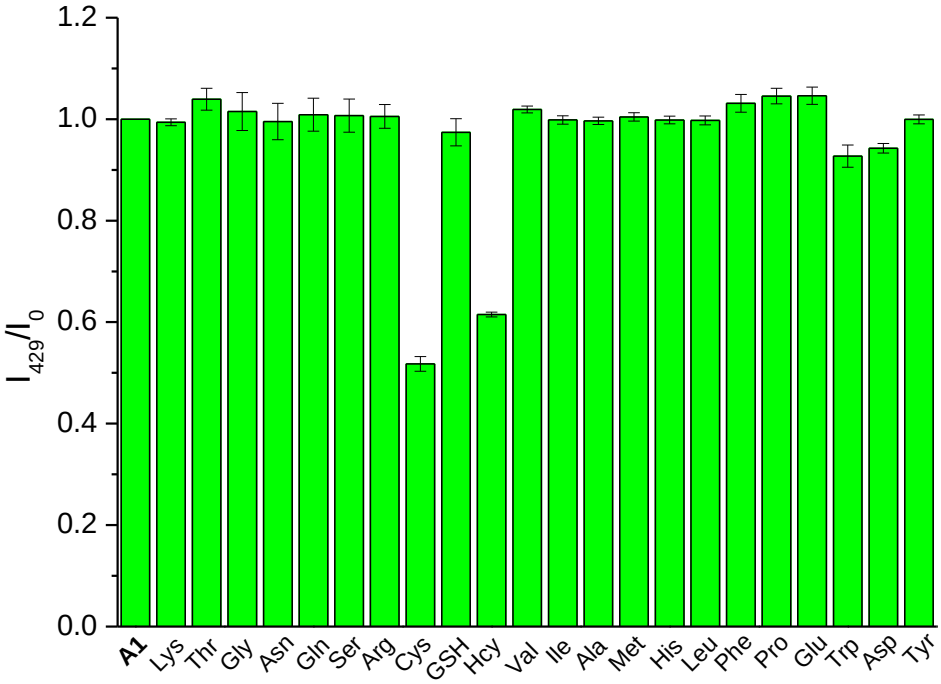


Figure S42. Fluorescencere response (I_{429}/I_0) of **A1** (50 μM, λ_{ex} = 358 nm) toward various amino acids (50 equiv) at pH 7.4 (λ_{ex} = 358 nm). Solvent: DMSO/buffer = 40:60, v/v. I_0: Fluorescence intensity of **A1** at 429 nm in the absence of amino acids.

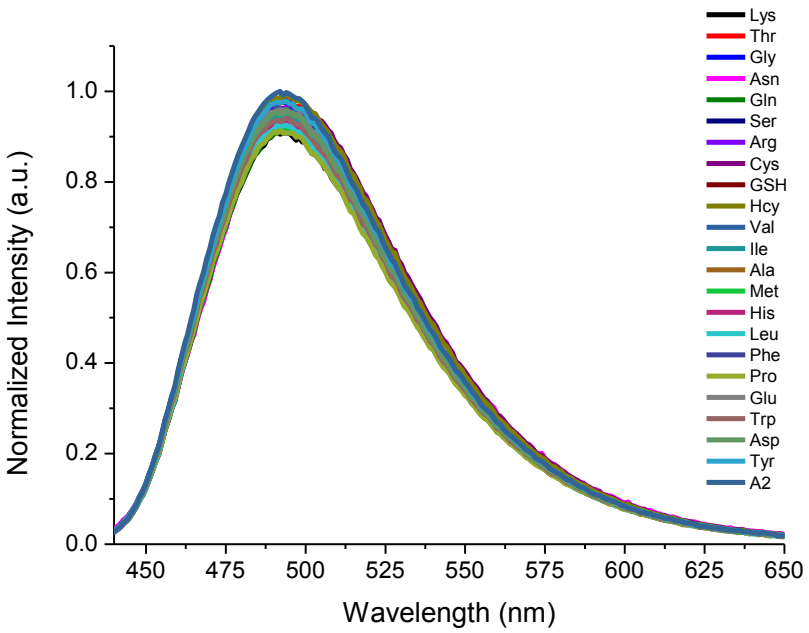


Figure S43. Fluorescence spectra of the reaction of **A2** (50 μM, λ_{ex} = 418 nm) with various amino acids (50 equiv) at pH 7.4. Solvent: DMSO/buffer = 5:95, v/v.

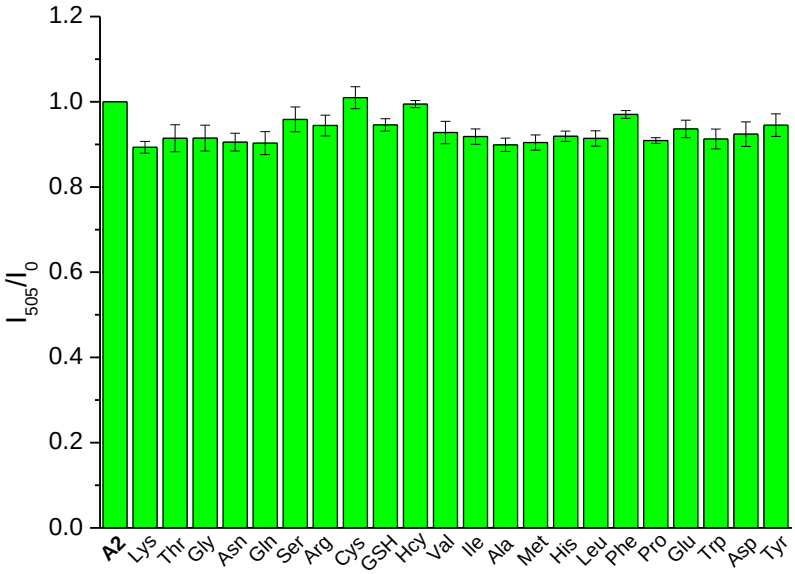


Figure S44. Fluorescencere response (I_{505}/I_0) of **A2** (50 μM, λ_{ex} = 418 nm) toward various amino acids (50 equiv) at pH 7.4 (λ_{ex} = 418 nm). Solvent: DMSO/buffer = 5:95, v/v. I_0: Fluorescence intensity of **A2** at 505 nm in the absence of amino acids.

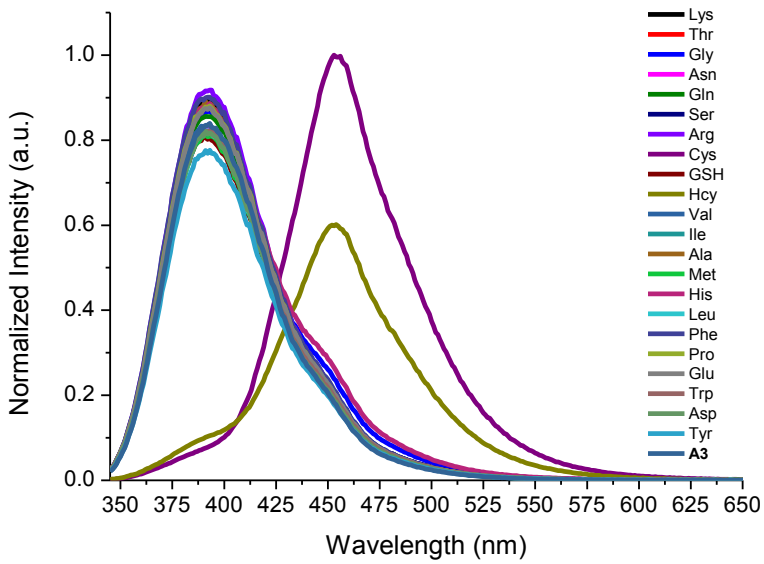


Figure S45. Fluorescence spectra of the reaction of **A3** (50 μM, λ_{ex} = 324 nm) with various amino acids (50 equiv) at pH 7.4. Solvent: DMSO/buffer = 5:95, v/v.

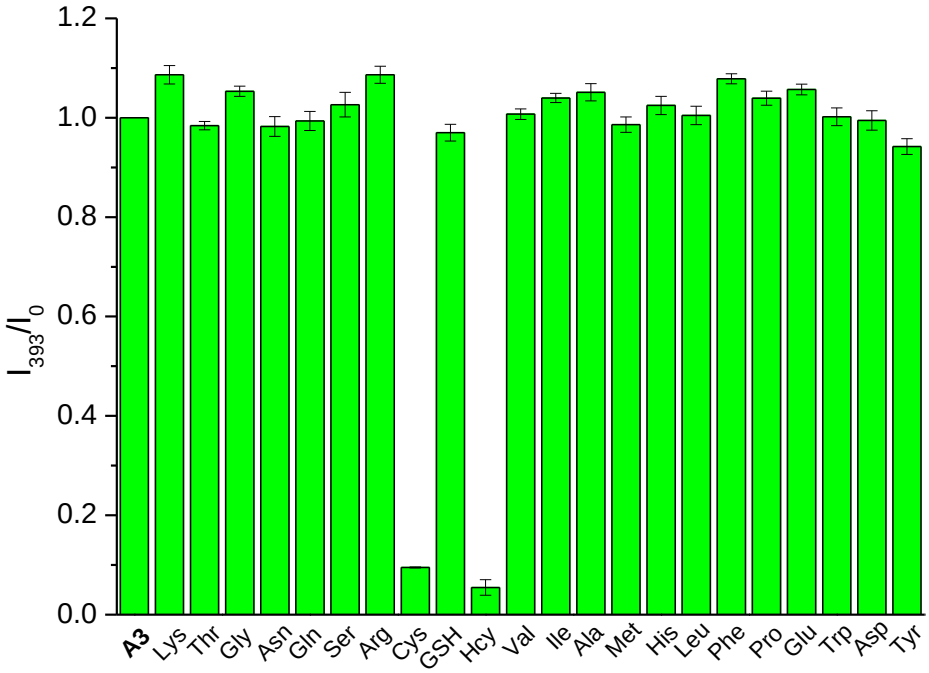


Figure S46. Fluorescencere response (I_{393}/I_0) of **A3** (50 μM, λ_{ex} = 324 nm) toward various amino acids (50 equiv) at pH 7.4 (λ_{ex} = 324 nm). Solvent: DMSO/buffer = 5:95, v/v. I_0: Fluorescence intensity of **A3** at 393 nm in the absence of amino acids.

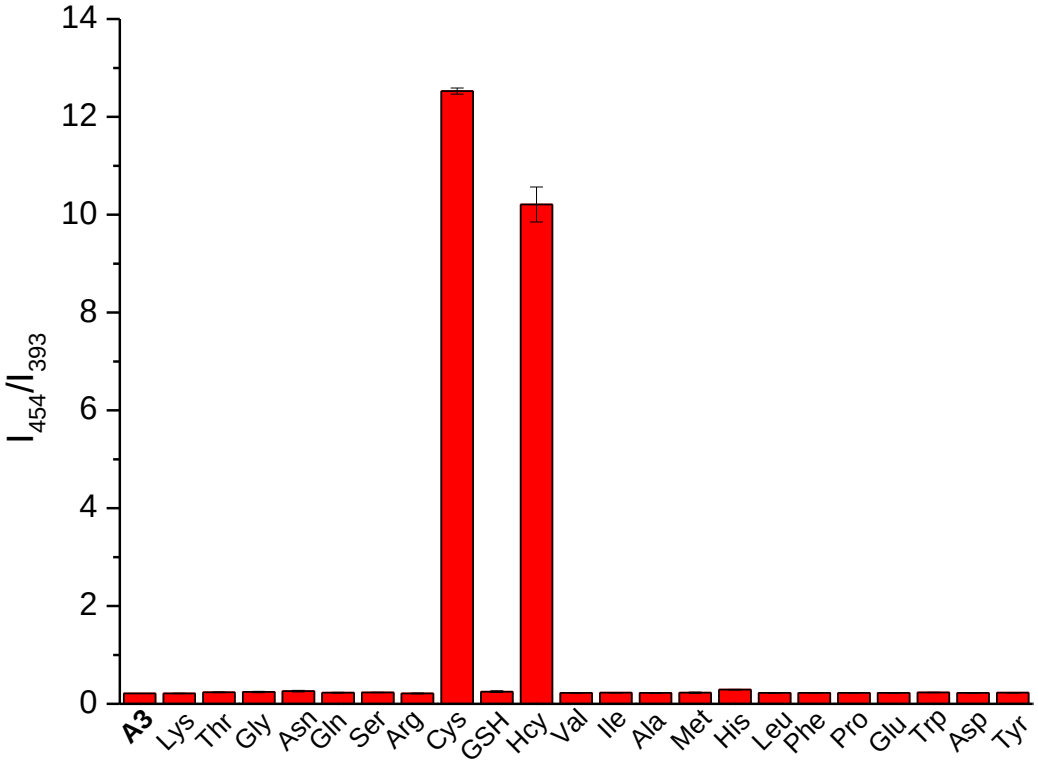


Figure S47. Fluorescence responses (I_{454}/I_{393}) of **A3** (50 μM, λ_{ex} = 324 nm) toward various amino acids at pH 7.4 (λ_{ex} = 324 nm). Solvent: DMSO/buffer = 5:95, v/v.

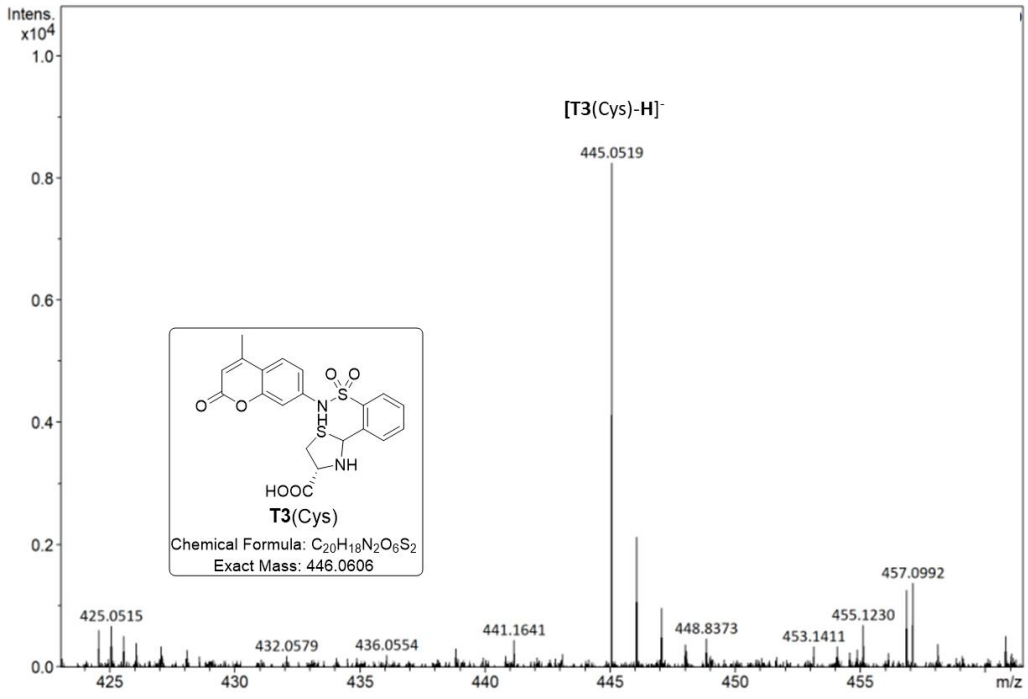


Figure S48. ESI mass spectrum of the reaction of **A3** and Cys in buffer at pH 7.4.

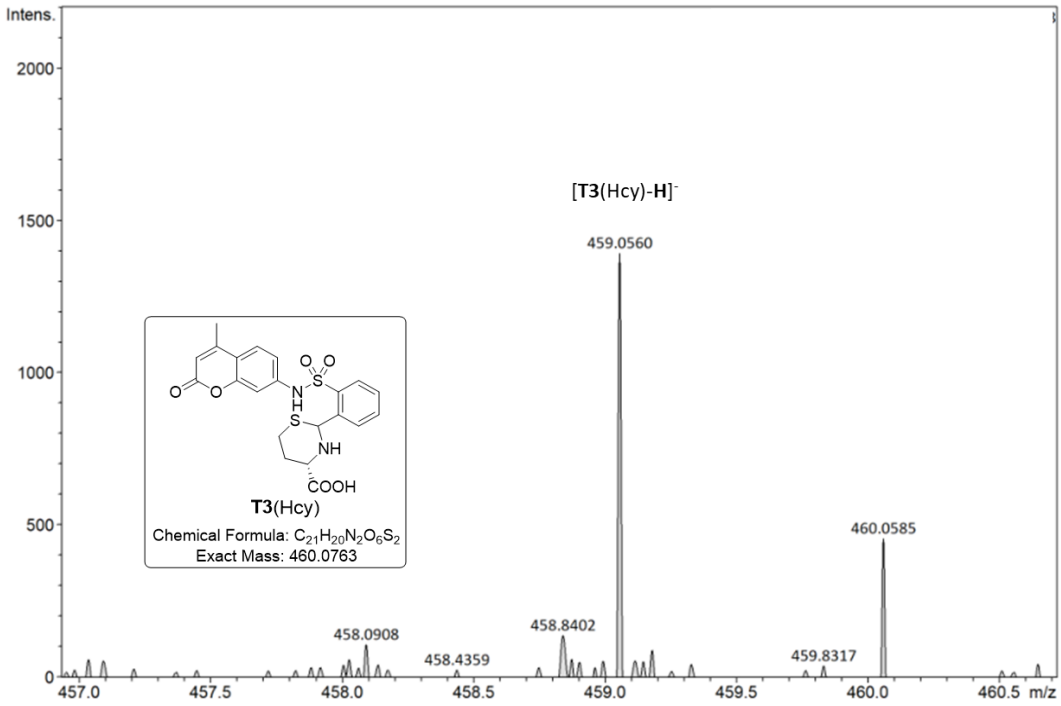


Figure S49. ESI mass spectrum of the reaction of **A3** and Hcy in buffer at pH 7.4.

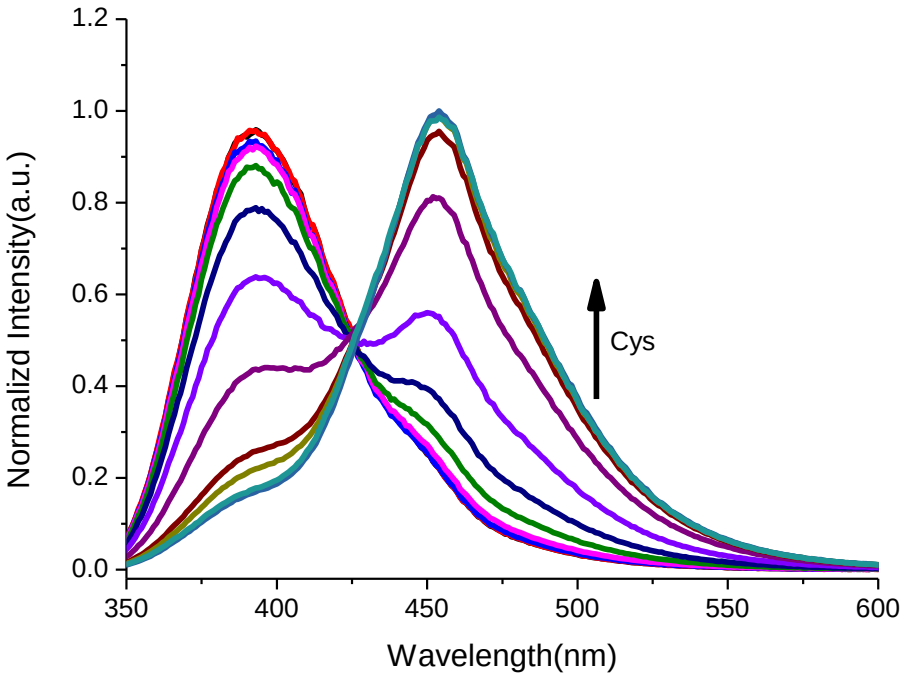


Figure S50. Fluorescence spectra of the reaction of **A3** (50 μM, λ_{ex} = 324 nm) and cysteine (0 - 50.0 equiv) at pH 7.4. Solvent: (DMSO/PB buffer = 5:95, v/v).

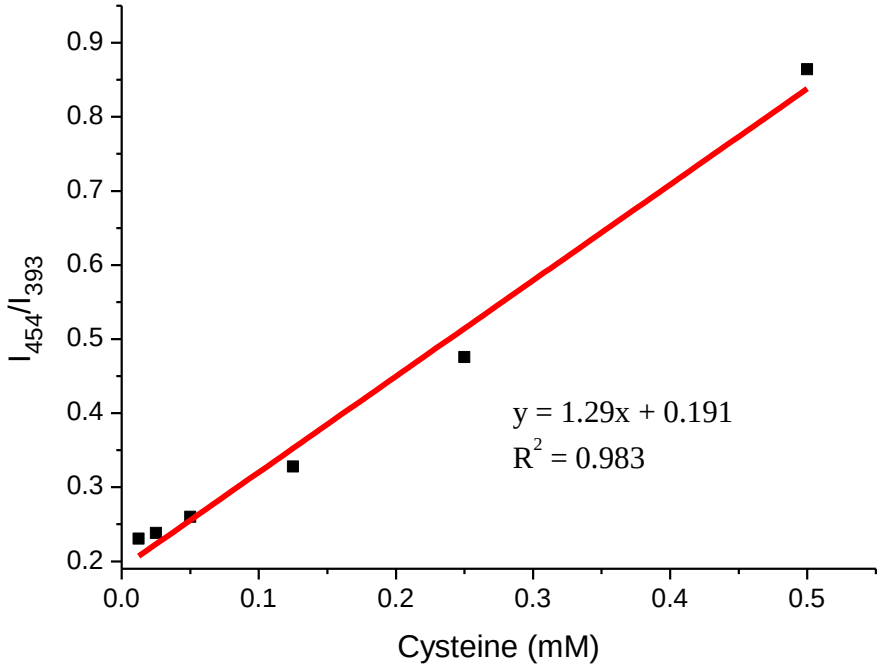


Figure S51. Linear range of fluorescence response for **A3** towards varied concentration of cysteine (I_{454}/I_{393}, λ_{ex} = 324 nm). The limit of detection is 4.03 μM for cysteine.

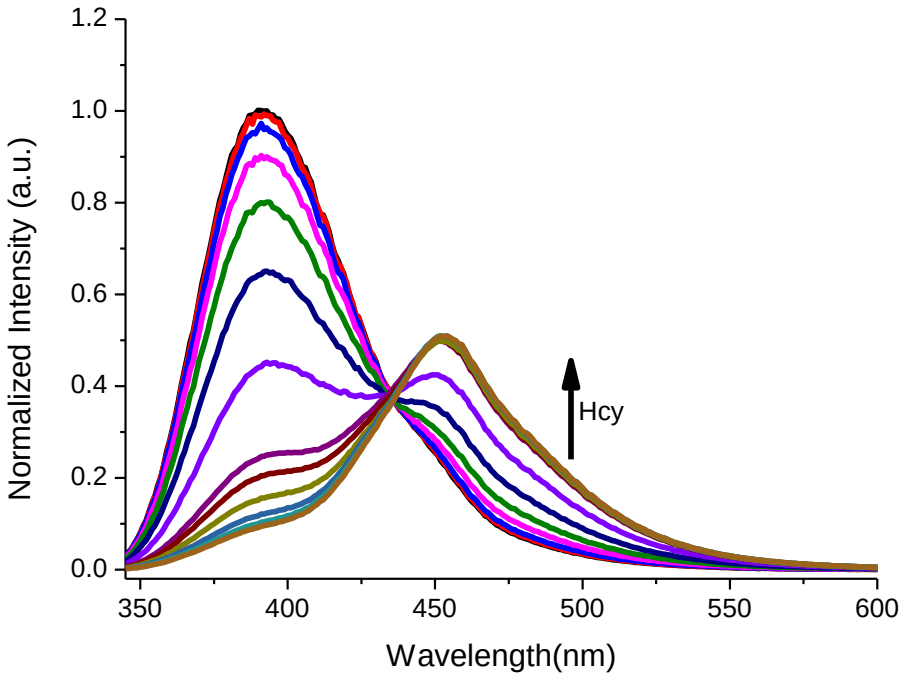


Figure S52. Fluorescence spectra of the reaction of **A3** (50 μM, λ_{ex} = 324 nm) and homocysteine (0 - 50.0 equiv) at pH 7.4. Solvent: (DMSO/PB buffer = 5:95, v/v).

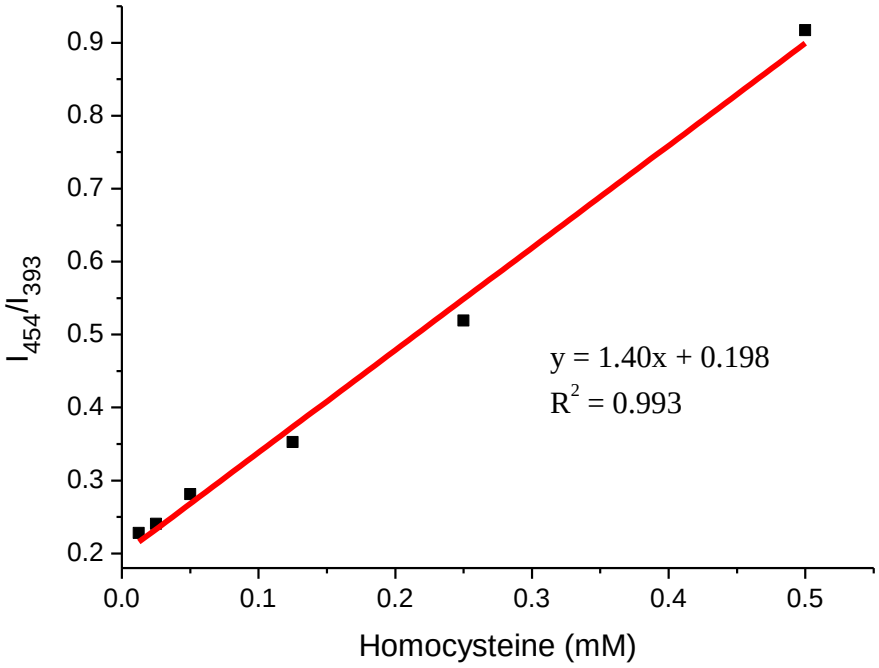


Figure S53. Linear range of fluorescence response for **A3** towards varied concentration of homocysteine (I_{454}/I_{393}, λ_{ex} = 324 nm). The limit of detection is 3.53 μM for homocysteine.

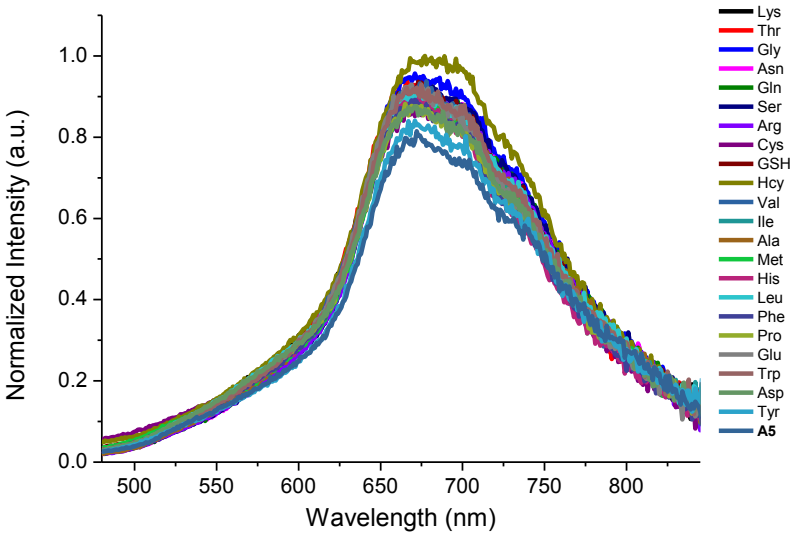


Figure S54. Fluorescence spectra of the reaction of **A5** (50 μM, λ_{ex} = 450 nm) with various amino acids (50 equiv) at pH 7.4. Solvent: DMSO/buffer = 40:60, v/v.

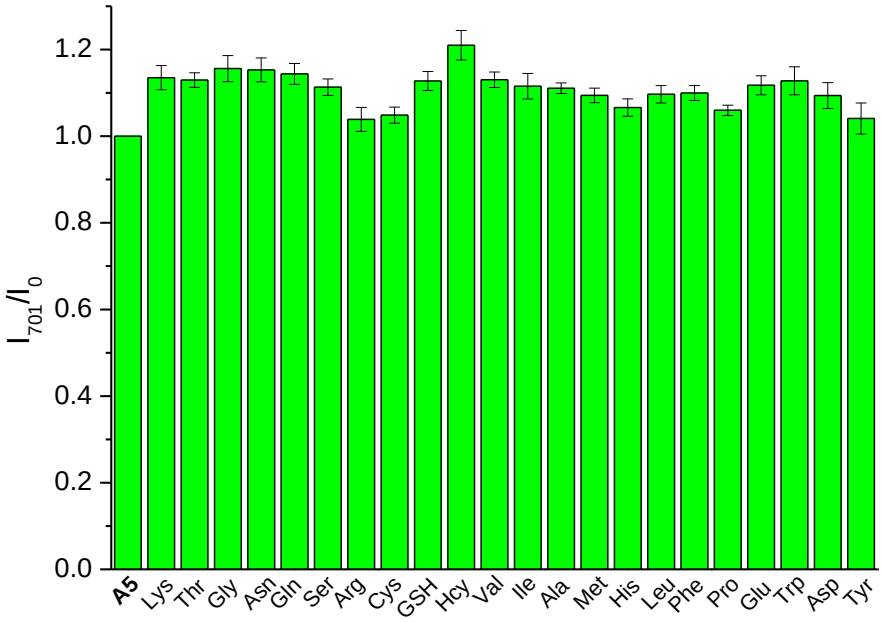


Figure S55. Fluorescencere response (I_{701}/I_0) of **A5** (50 μM, λ_{ex} = 450 nm) toward various amino acids (50 equiv) at pH 7.4 (λ_{ex} = 450 nm). Solvent: DMSO/buffer = 40:60, v/v. I_0: Fluorescence intensity of **A5** at 701 nm in the absence of amino acids.

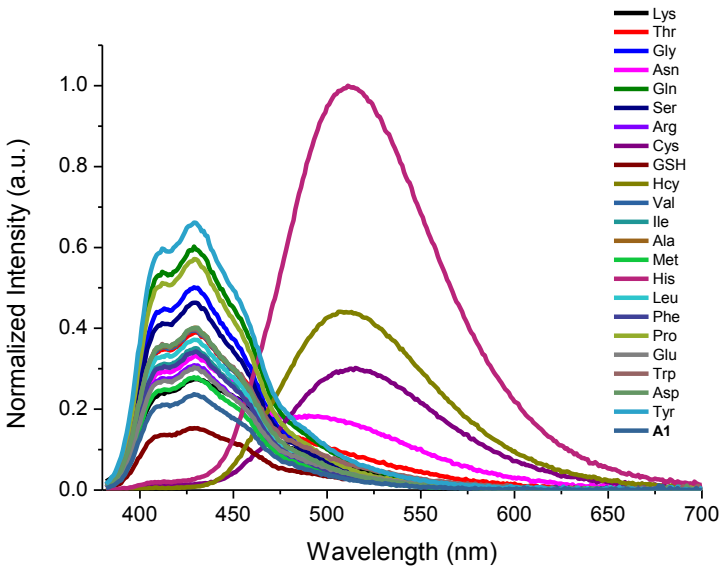


Figure S56. Fluorescence spectra of the reaction of **A1** (50 μM, λ_{ex} = 358 nm) with various amino acids (50 equiv) at pH 10. Solvent: DMSO/buffer = 40:60, v/v.

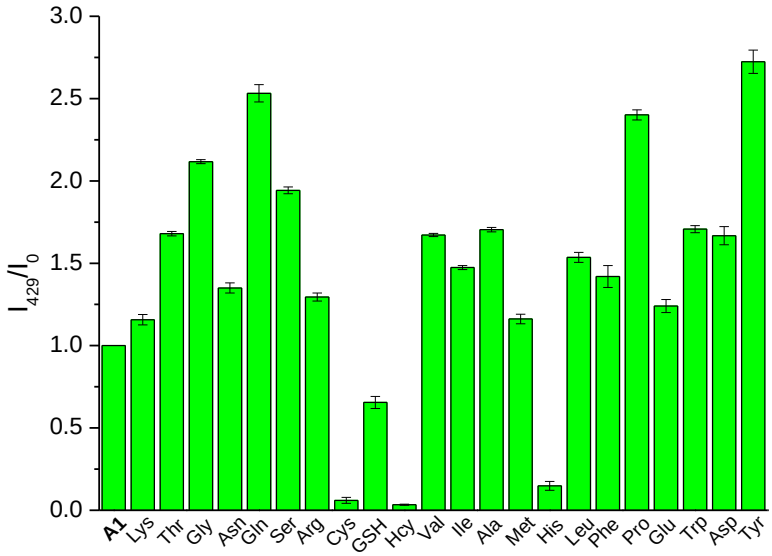


Figure S57. Fluorescencere response (I_{429}/I_0) of **A1** (50 μM, λ_{ex} = 358 nm) toward various amino acids at pH 10. Solvent: DMSO/buffer = 40:60, v/v. I_0: Fluorescence intensity of **A1** at 429 nm in the absence of amino acids.

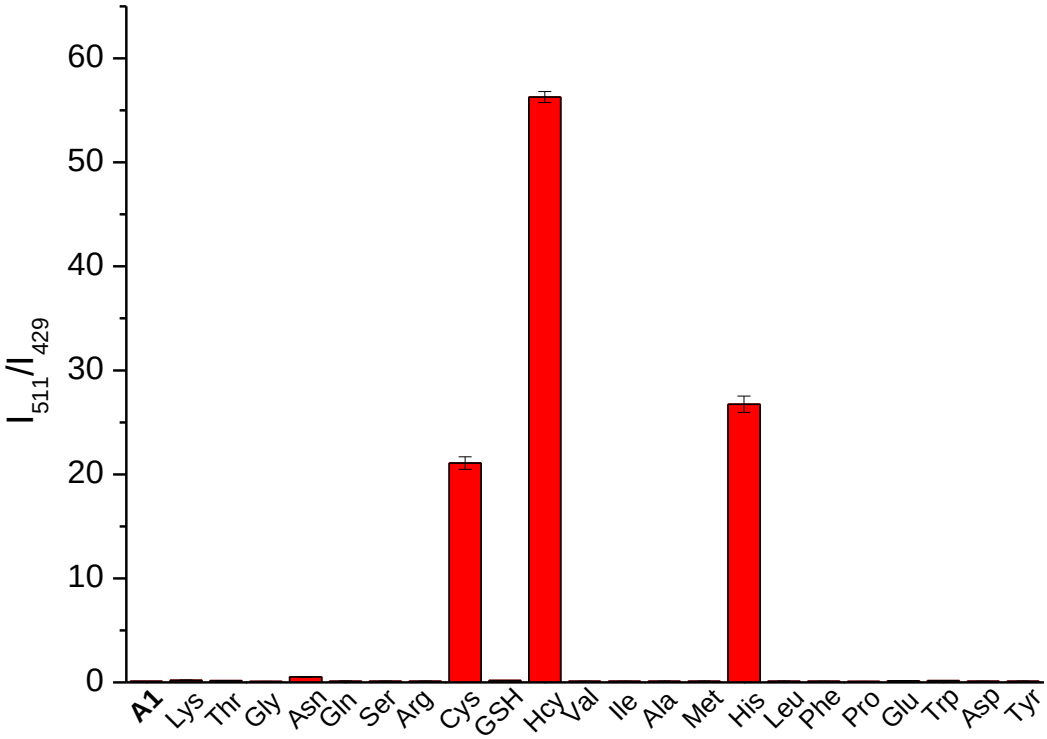


Figure S58. Fluorescencere response (I_{511}/I_{429}) of **A1** (50 μM, λ_{ex} = 358 nm) toward various amino acids at pH 10. Solvent: DMSO/buffer = 40:60, v/v.

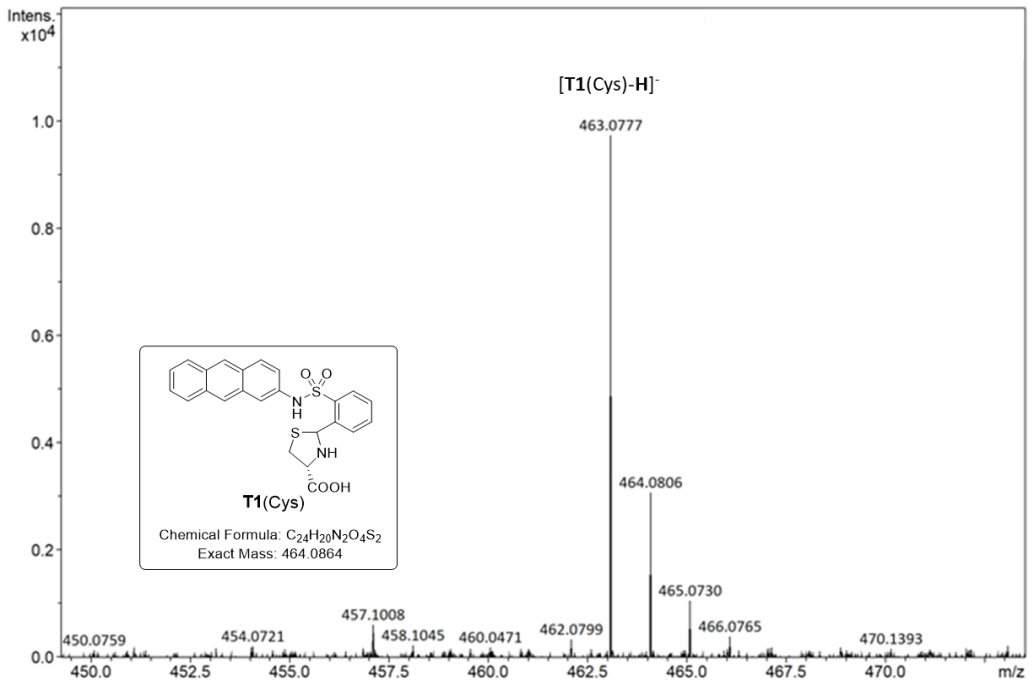


Figure S59. ESI mass spectrum of the reaction of **A1** and Cys in buffer at pH 10.

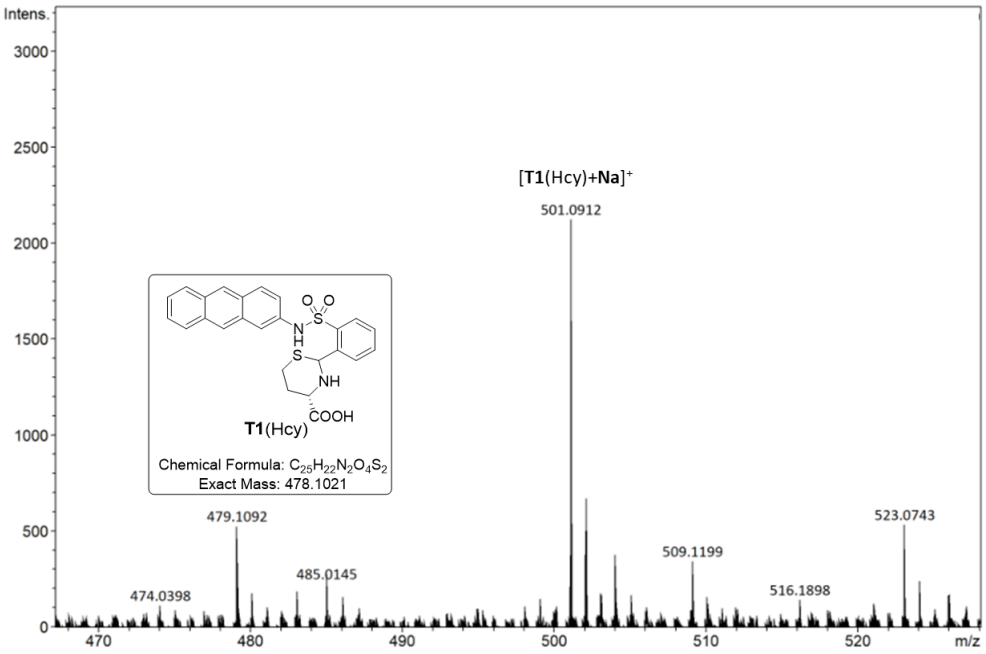


Figure S60. ESI mass spectrum of the reaction of **A1** and Hcy in buffer at pH 10.

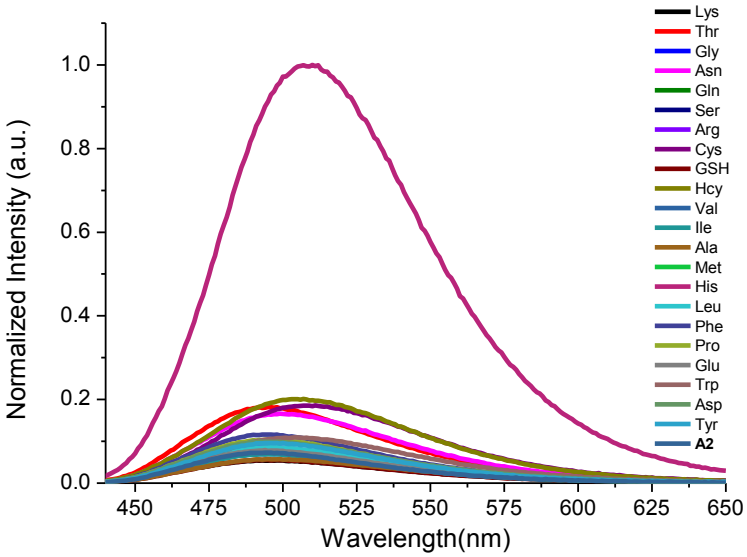


Figure S61. Fluorescence spectra of the reaction of **A2** (50 μM, λ_{ex} = 418 nm) with various amino acids (50 equiv) at pH 10. Solvent: DMSO/buffer = 5:95, v/v.

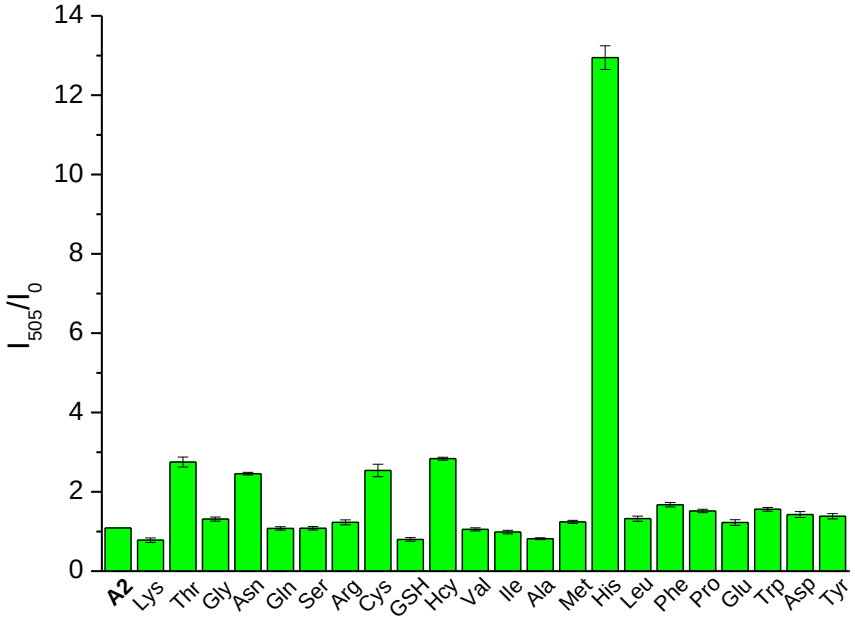


Figure S62. Fluorescencere response (I_{505}/I_0) of **A2** (50 μM, λ_{ex} = 418 nm) toward various amino acids (50 equiv) at pH 10 (λ_{ex} = 418 nm). Solvent: DMSO/buffer = 5:95, v/v. I_0: Fluorescence intensity of **A2** at 505 nm in the absence of amino acids.

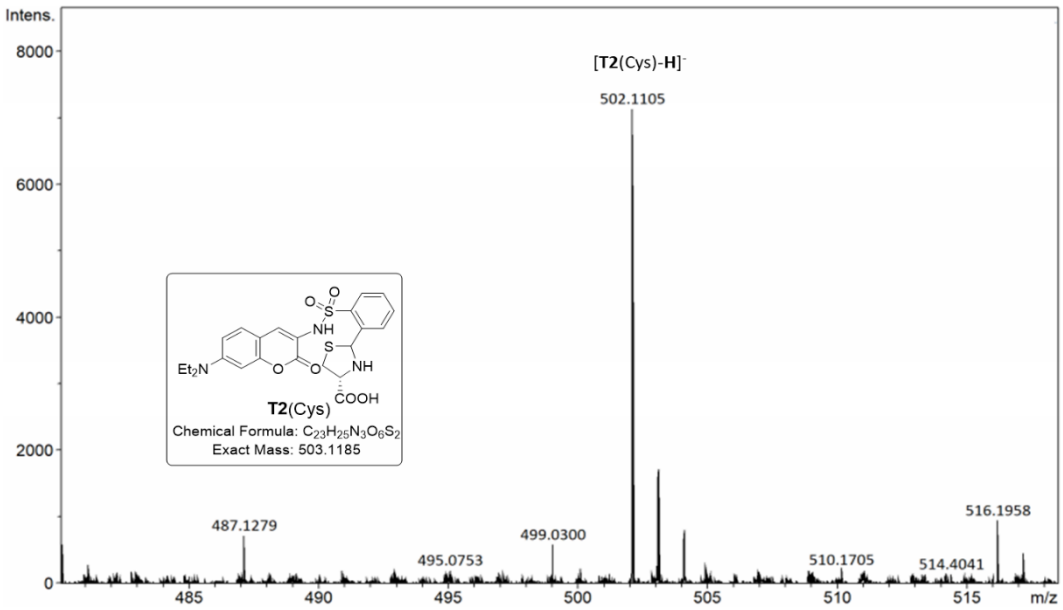


Figure S63. ESI mass spectrum of the reaction of **A2** and Cys in buffer at pH 10.

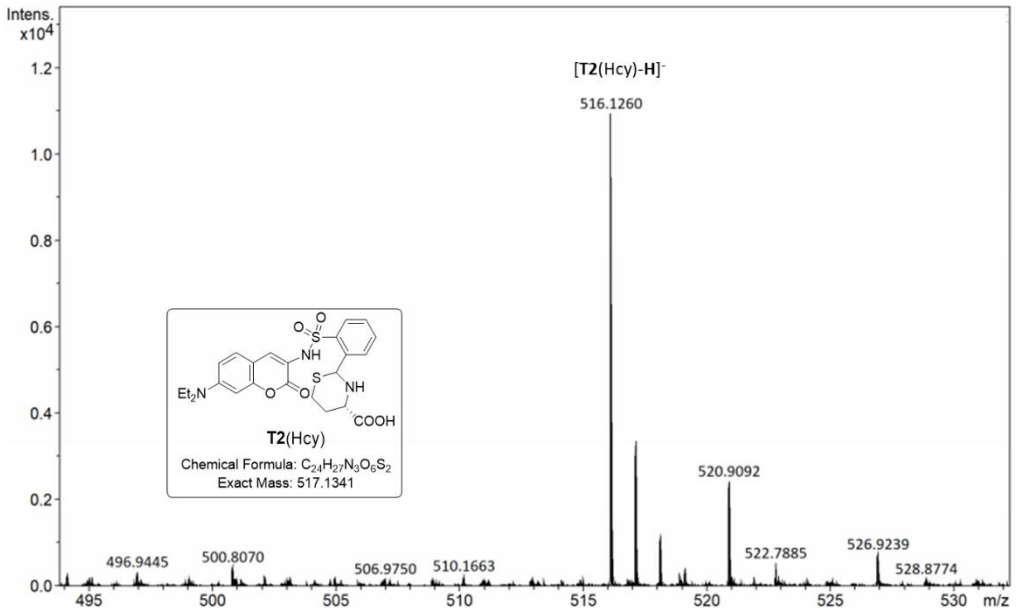


Figure S64. ESI mass spectrum of the reaction of **A2** and Hcy in buffer at pH 10.

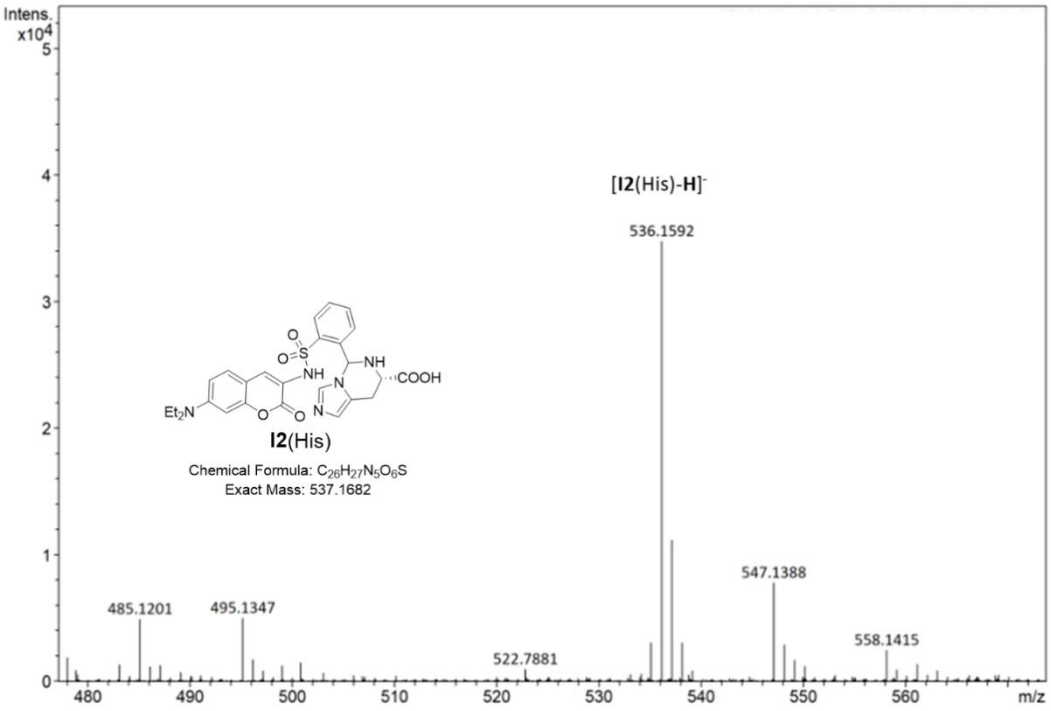


Figure S65. ESI mass spectrum of the reaction of **A2** and His in buffer at pH 10.

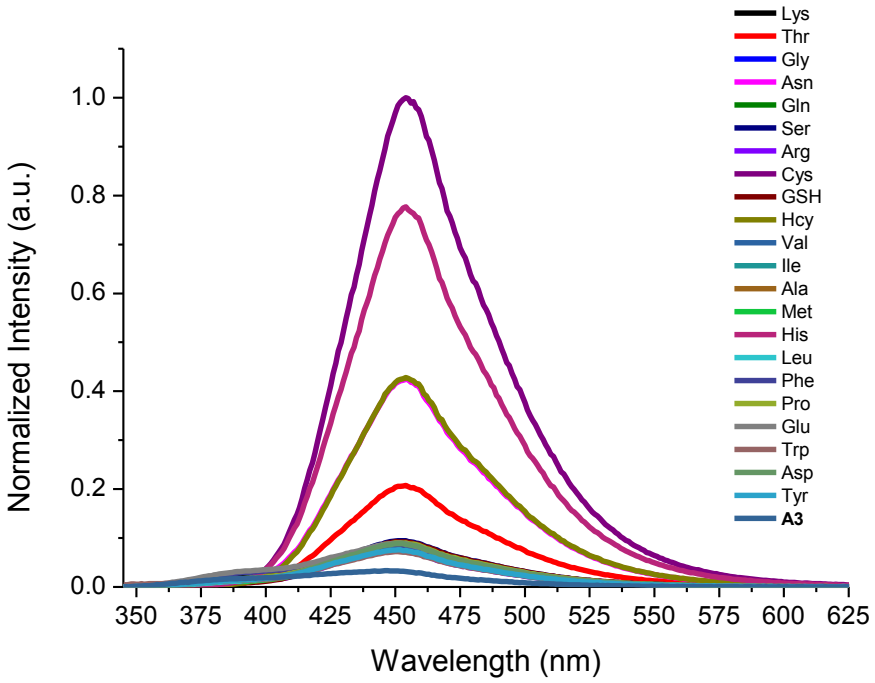


Figure S66. Fluorescence spectra of the reaction of **A3** (50 μM, λ_{ex} = 324 nm) with various amino acids (50 equiv) at pH 10. Solvent: DMSO/buffer = 5:95, v/v.

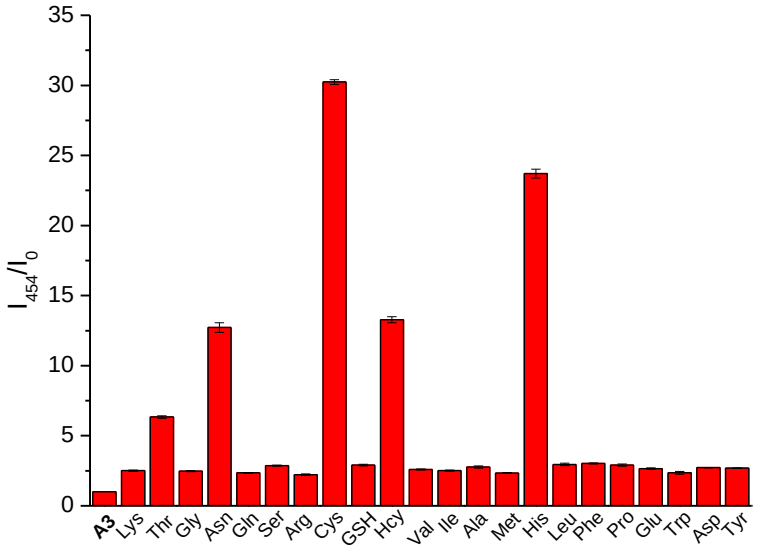


Figure S67. Fluorescencere response (I_{454}/I_0) of **A3** (50 μM, λ_{ex} = 324 nm) toward various amino acids (50 equiv) at pH 10 (λ_{ex} = 324 nm). Solvent: DMSO/Buffer = 5:95, v/v. I_0: Fluorescence intensity of **A3** at 454 nm in the absence of amino acids.

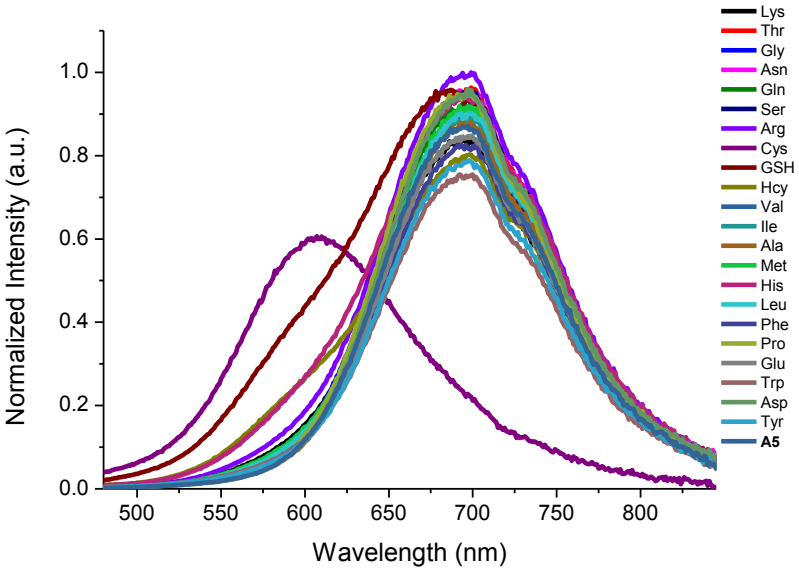


Figure S68. Fluorescence spectra of the reaction of **A5** (50 μM, λ_{ex} = 450 nm) with various amino acids (50 equiv) at pH 10. Solvent: DMSO/buffer = 40:60, v/v.

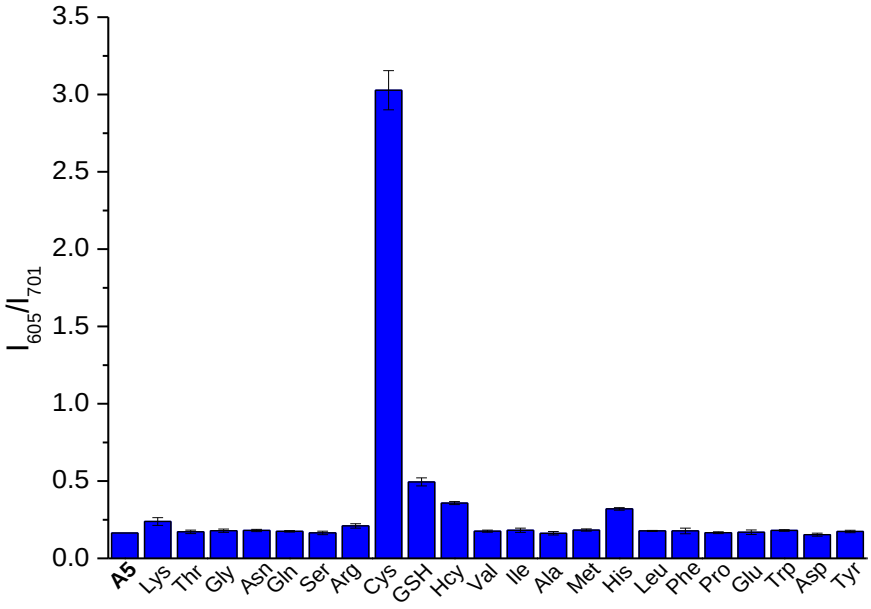


Figure S69. Fluorescencere response (I_{605}/I_{701}) of **A5** (50 μM, λ_{ex} = 450 nm) toward various amino acids (50 equiv) at pH 10 (λ_{ex} = 450 nm). Solvent: DMSO/buffer = 40:60, v/v.

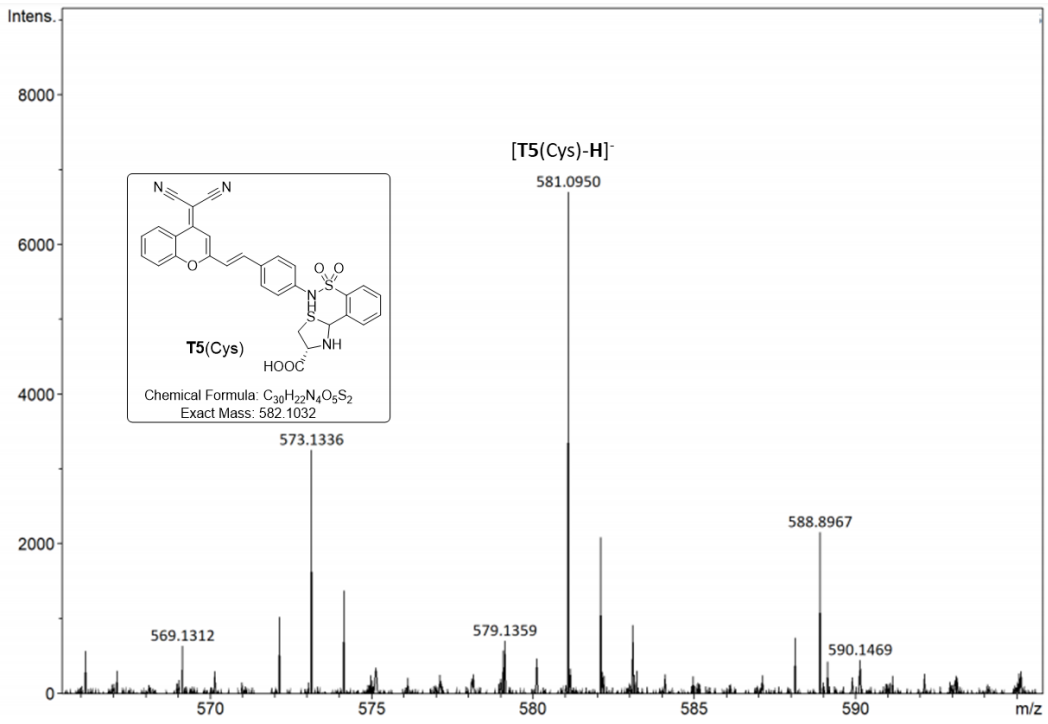


Figure S70. ESI mass spectrum of the reaction of **A5** and Cys in buffer at pH 10.

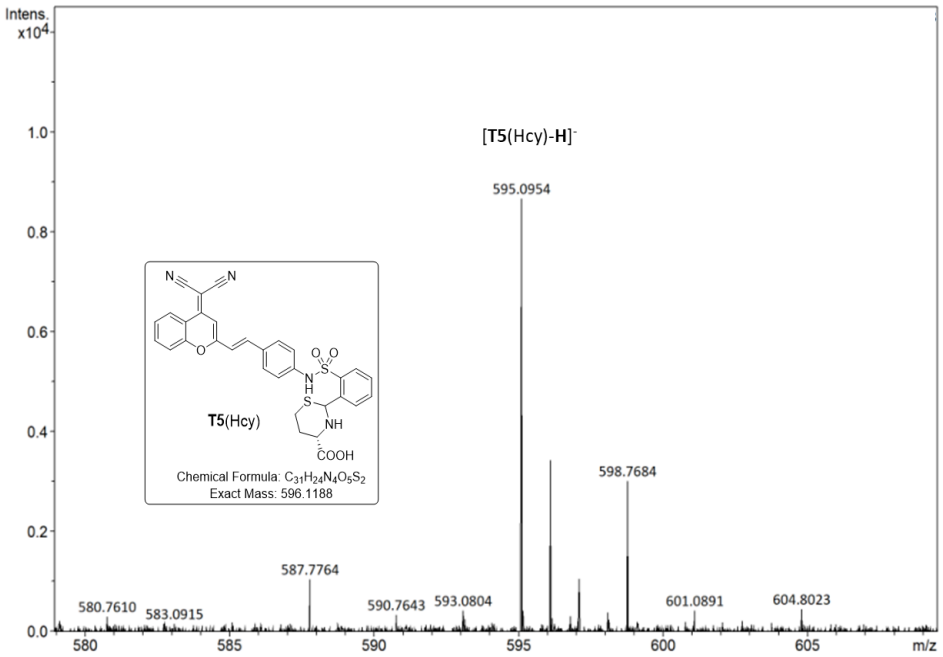


Figure S71. ESI mass spectrum of the reaction of **A5** and Hcy in buffer at pH 10.

4. Switchable Dynamic Covalent Networks

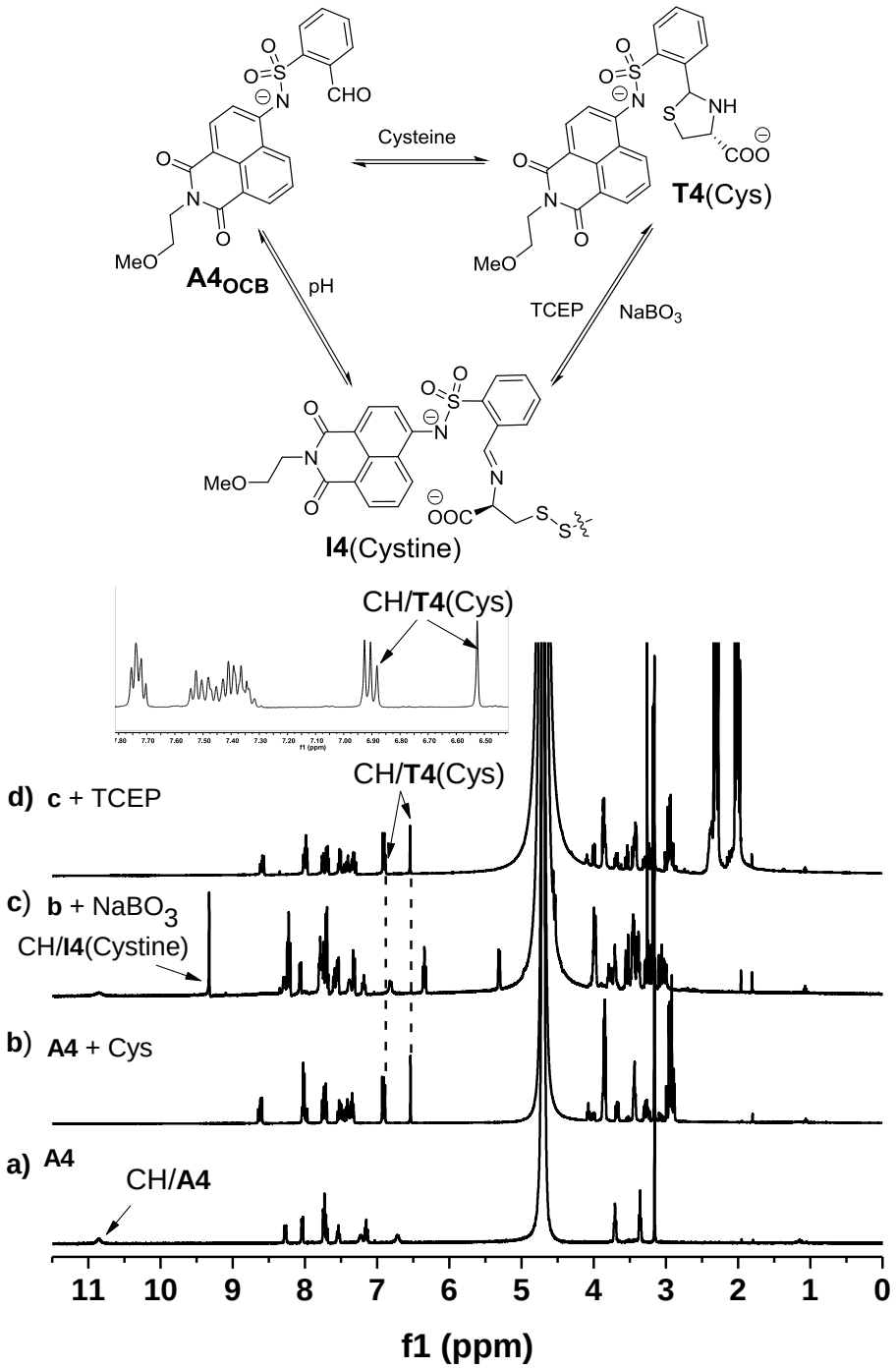


Figure S72. Stimuli-responsive switch between assemblies incorporating **A4** and cysteine. (a) ^{1}H NMR spectrum of **A4** in D_2O PB buffer; (b) the reaction of **A4** with cysteine (3.0 equiv.); (c) the addition of $NaBO_3$ (3.0 equiv.) into panel b; (d) the addition of TCEP (3.0 equiv.) into panel c. This figure shows the details and full spectra of Figure 6C in the main text.

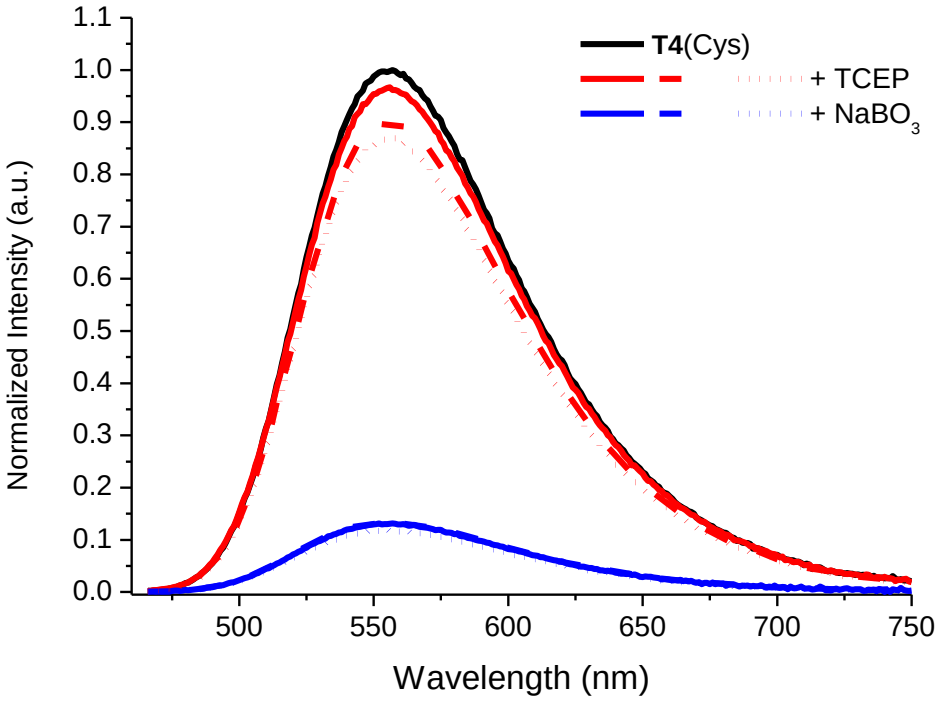


Figure S73. Fluorescence spectra of **T4**(Cys) created by the reaction of **A4** (50 μM, λ_{ex} = 446 nm) with cysteine, and the change upon consecutive addition of $NaBO_3$ followed by TCEP in buffer. This figure shows the spectra of Figure 6D in the main text.

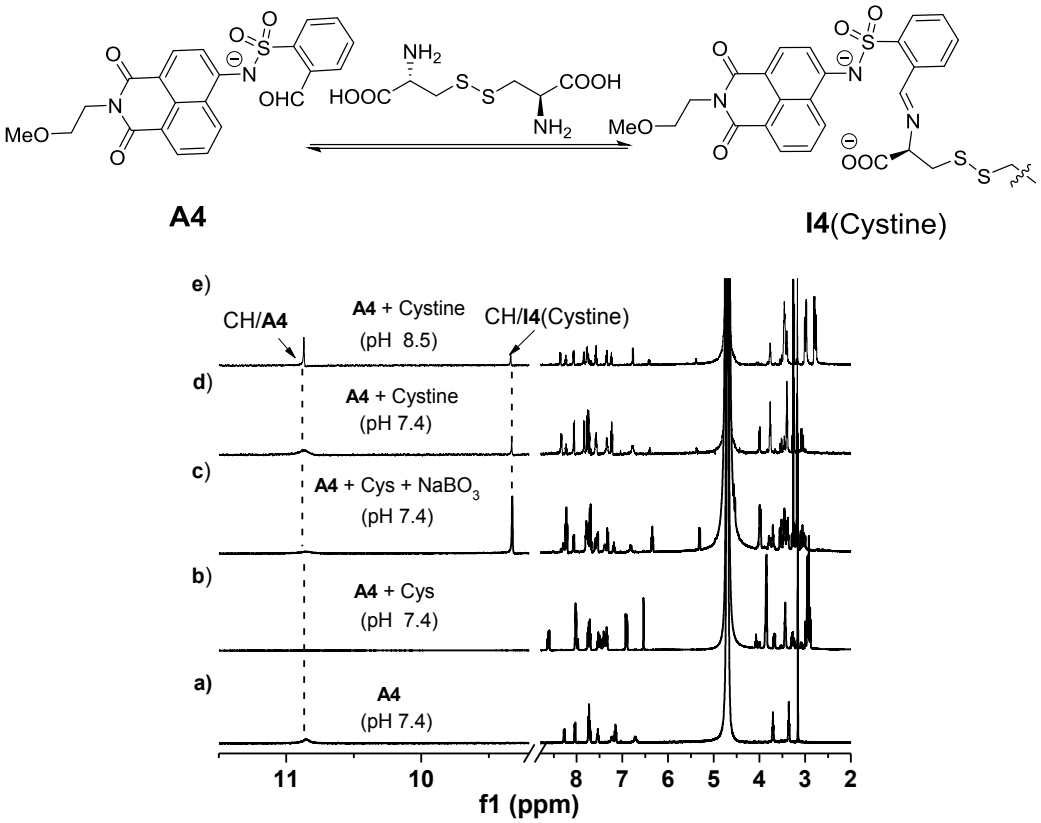


Figure S74. The control experiment of **A4** and cystine in D_2O PB buffer. (a) ^1H NMR spectrum of **A4** at pH 7.4; (b) the reaction of **A4** with cysteine (3.0 equiv.) at pH 7.4; (c) the addition of $NaBO_3$ (3.0 equiv.) into panel b at pH 7.4; (d, e) the reaction of **A4** with cystine (3.0 equiv.) at pH 7.4 or pH 8.5.

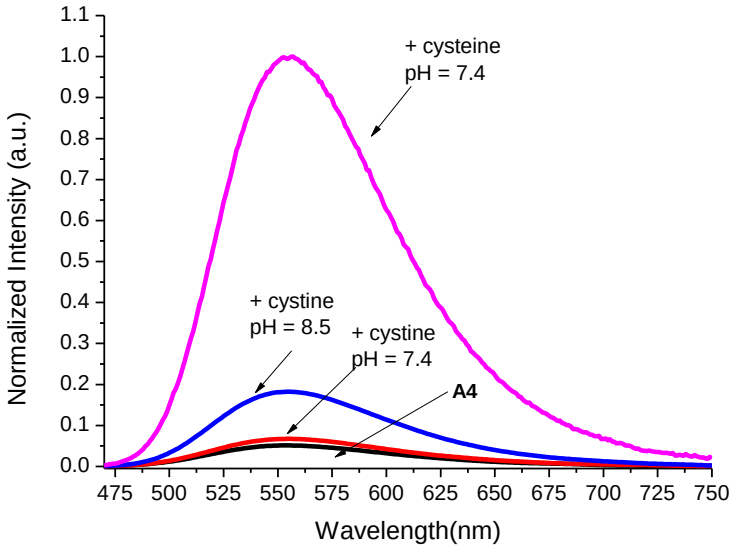


Figure S75. Fluorescence spectra of the reaction of **A4** (50 μM, λ_{ex} = 446 nm) and cystine (50.0 equiv.) at pH 7.4 or 8.5. Solvent: DMSO/buffer = 5:95, v/v.

5. References

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