Supplementary Material (ESI) for New Journal of Chemistry
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Electronic Supplementary Information (ESI)

A Bodipy-based Derivative for Selective Fluorescence Sensing of Homocysteine and Cysteine

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Contents of ESI

Instruments and reagents

Melting points were determined on a PHMKG 05 (Germany) apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were measured on a Varian INOVA 400 M spectrometer. NICOLET IS10 FT-IR spectrometer was used for recording IR spectra using KBr pellets in a wide spectral range, *i.e.* 4000-400 cm^{-1}. ESI mass spectra were recorded out on an Agilent 1100 series LC/MSO Trap of MS spectrometer. UV-visible spectral studies were performed on a Perkin Elmer Lambda-35 UV-visible double beam spectrophotometer using standard 1.00 cm quartz cells. Solution fluorescence spectra were measured on a Perkin Elmer LS 55 instrument. Amino acids and GSH were purchased from Sigma. CH_3CN was used the chromatographically pure. The other reagents and solvents were of analytical grade and used without further purification.

Spectra data of 1 and 2

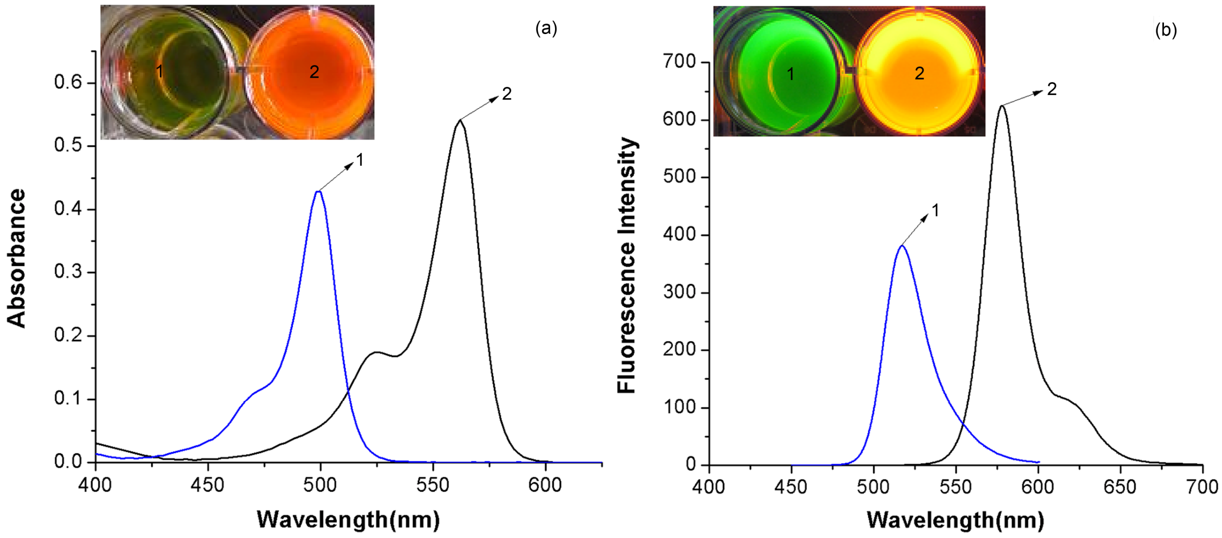


Fig. S1 Absorbance spectra (a) and emission spectra (b) of compounds **1** and **2** in CH_3CN (5 μM, respectively). Inset: (a) photographs of **1** and **2** (0.5 mM); (b) emission photographs of **1** and **2** (0.5 mM).

In absolute acetonitrile, the maximum absorbance of compound **1** is at 499nm with an extinction coefficient of 8.57×10^4 mol^{-1} L cm^{-1}. Since the π-π conjugate system of **2** is larger, the maximum absorbance of **2** red shifts to 562 nm with an extinction coefficient of 1.08×10^5 mol^{-1} L cm^{-1}. The emission wavelengths of compound **1** and **2** are at 518 nm (λ_{ex} = 498 nm) and 578 nm (λ_{ex} = 557 nm), respectively. The emission bandwidths are narrow, thus avoid the interference of other fluorescent compounds. The quantum yield of **1** is 0.26, which was determined by using fluorescein isothiocyanate as the standard in a 0.1 M NaOH solution (φ=0.90)[1]; The quantum yield of **2** is 0.80, determined by using Rhodamine B as the standard in ethanol solution (φ=0.49)[2].

Titration experiments

Benesi-Hildebrand analysis: [3]

$$\frac{1}{I_0 - I} = \frac{1}{I_0 - I'} + \frac{1}{K_a \left(I_0 - I'\right)\left[object\right]}$$

where, K_a, I_0, I and I' are the binding constant, the observed fluorescence intensity in the absence of object, the observed fluorescence intensity in the presence of object and the fluorescence intensity of the probe-object complex, respectively.

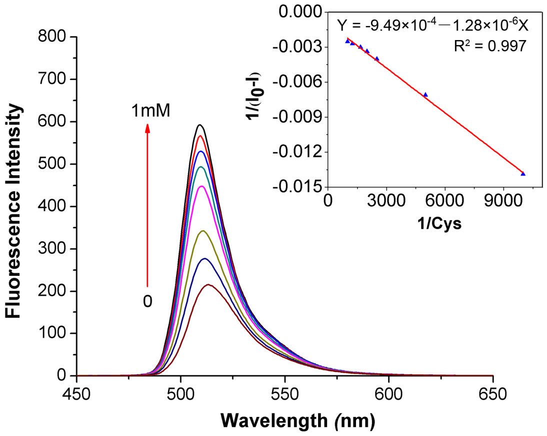


Fig. S2 Emission spectra (λ_{ex} = 498 nm) of compound **1** (1×10^{-6} M) upon the addition of increasing concentration (0, 0.1, 0.2, 0.4, 0.5, 0.6, 0.8, 1 mM) of Cys in CH_3CN/H_2O (v/v, 3 : 2) at pH 7.4 buffered with 0.1 M HEPES at ambient temperature. (Inset: the Benesi- Hildebrand plot of **1** with Cys, in which the fluorescence intensity (1/(Io-I)) at 509 nm is plotted against the concentration of 1/Cys)

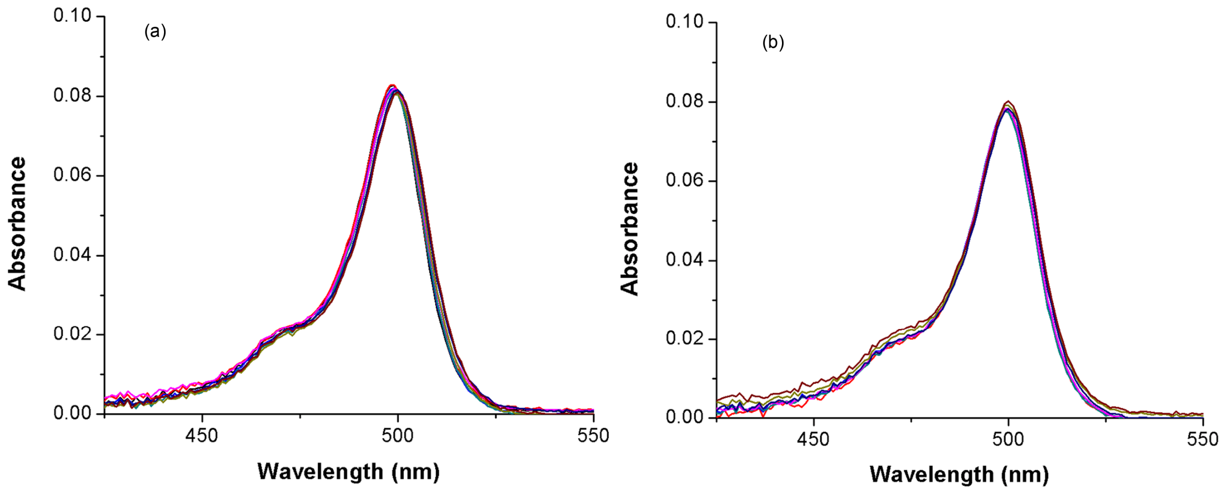


Fig. S3 Absorbance spectra of compound **1** (1×10^{-6} M) upon the addition of increasing concentrations (0, 0.1, 0.2, 0.4, 0.5, 0.6, 0.8, 1 mM) of Hcy (a) and Cys (b) in a 0.1 M HEPES buffer of pH 7.4/CH_3CN (v/v, 2 : 3) at ambient temperature, respectively.

Modelling molecular configuration

The modelling work was performed using the Chemoffice 2004 software package. The two-dimensional (2D) structures were sketched using the Chem Draw Ultra version 8.0, cleaned copy and pasted into the Chem3D ultra version 8.0. In order to model, molecular mechanical and semi-empirical theories were used. The resulting three-dimensional (3D) structures were optimized by the molecular mechanics minimization using a MM2 force field, and the further run of MOPAC using the Austin Model-1 (AM1) Hamiltonian method.[4]

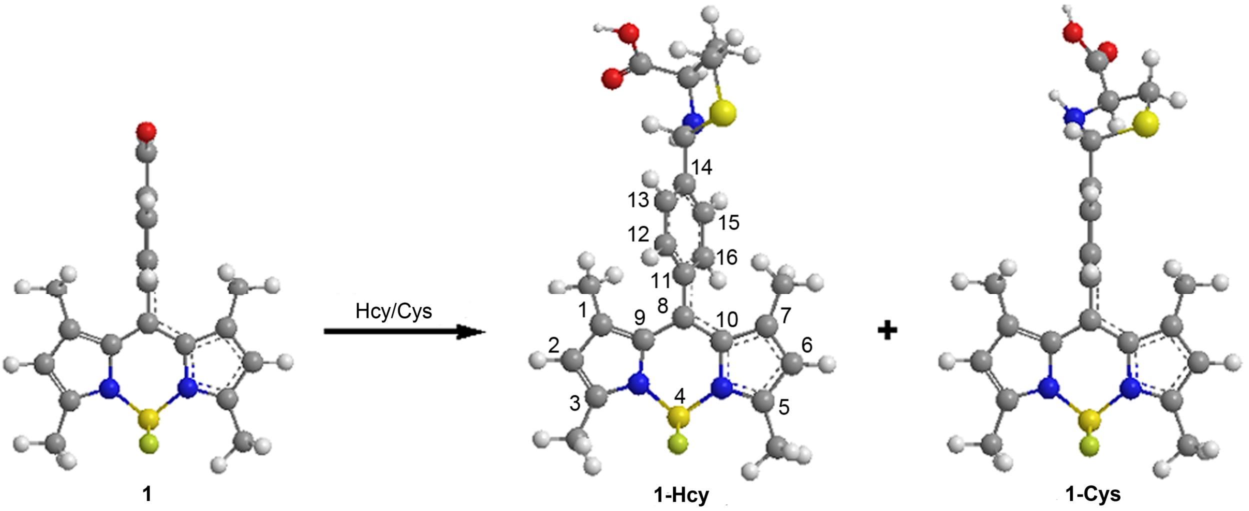
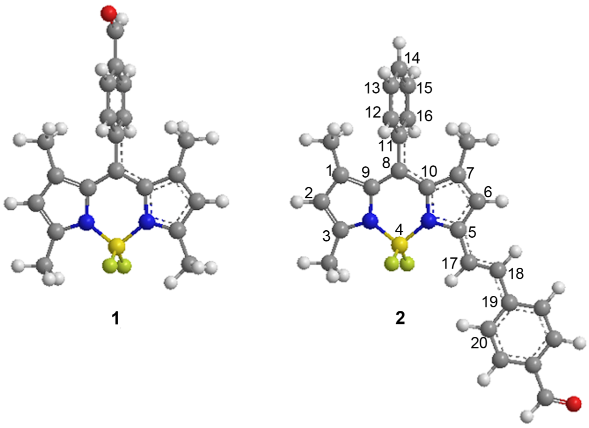


Fig. S4 Calculated structures of compound **1** and its reaction products **1'.**

Table S1 Selected calculated structural data for **1** and **1’**.

Parameters[a]	**1**	**1-Hcy**	**1-Cys**
C(8)-C(11) (Å)	1.4715	1.4655	1.4705
C(9)-C(8)-C(11)-C(12) (°)	90.2	66.6	90.1
C(10)-C(8)-C(11)-C(16) (°)	90.2	66.6	89.9
C(1)-C(9)-C(8)-C(11) (°)	-0.1	2.5	-0.4
C(7)-C(10)-C(8)-C(11) (°)	0.1	10.9	0.6
C(1)-C(9)-C(8)-C(10) (°)	179.8	-178.4	179.6
C(9)-C(8)-C(10)-C(7) (°)	-179.9	-168.2	-179.5

[a] Atom numbering scheme shown in Fig. S4



1 **2**

Fig. S5 Calculated structures of compounds **1** and **2.**

Table S2 Selected calculated structural data for **1** and **2**.

Parameters[a]	**1**	**2**
C(9)-C(8)-C(11)-C(12) (°)	90.2	90.2
C(1)-C(9)-C(8)-C(10) (°)	179.8	-179.8
C(9)-C(8)-C(10)-C(7) (°)	-179.9	179.6
C(6)-C(5)-C(17)-C(18) (°)	-	2.8
C(5)-C(17)-C(18)-C(19) (°)	-	179.9
C(17)-C(18)-C(19)-C(20) (°)	-	-17.4

[a] Atom numbering scheme shown in Fig. S5.

References

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