

Electronic Supplementary Information

An effective signal enhancement strategy for sensing cysteine based on aluminium-initiated emission

Wu Zou^a, Xuejiao Chen^a, Cheng Huan^b, Tingting Gu^a, Jiaoyun Xia^a and Fuchun Gong^{a*}

^aCollege of Chemistry and Biologic Engineering, Changsha University of Science and
Technology, Changsha, 410114, China

^bHunan Institute of Animal and Veterinary Science, Changsha, 410131, China

* Corresponding author: Fuchun Gong

Tel.: +86-731- 85258733

Fax.: +86-731-85258733

E. mail : gongfc139@163.com

gongfc@csust.edu.cn

Section 1. Synthesis of S-DPM

Fig. S1. ^1H NMR of S-DPM reacted with Cys

Fig. S2. Plot of the fluorescence intensities as a function of Cys concentration.

Fig. S3. Optimization of sensing for Cys

Table S1. Determination of the fluorescence quantum yield of DPM, S-DPM and DPM-Al^{3+}

References

Section 1. Synthesis of S-DPM

1.1. Synthesis of 2'-hydroxychalcone

An appropriate amount of benzaldehyde (2.12 g, 20 mmol) and 2'-hydroxyacetophenone (2.72 g, 20 mmol) were put in 35 mL EtOH with stirring until complete dissolution. Then, 5.6 g potassium hydroxide(100 mmol) was added. The reaction mixture was stirred at room temperature for 12 h. After that, the reaction mixture was poured into a 100 mL ice water, acidified with cold 18%HCl (pH = 4), extracted with ethylacetate (3×80 mL). The organic layer was washed with water and brine, followed by drying over anhydrous Na₂SO₄ and then the solvent was evaporated. The residues was purified by column chromatography on a silica gel column (*n*-hexane: ethylacetate, 7:3). The organic solvents were removed by evaporation to give a faint yellow solid 3.24 g (67.5%). IR (KBr) ν_{\max} (cm⁻¹): 3400 (b, OH), 3058.89, 2925.88, 1658.67 (C=O), 1602.74, 1564.16, 1488.94 (C=C), 1217.00 (C-O). ¹H-NMR (400 MHz, DMSO-d₆): δ H (ppm): 11.50 (1H, s, C2'-OH), 8.25 (d, 1H, H-6, J = 7.32 Hz), 8.06 (d, 1H, H- β , vinylic, J = 15.60 Hz), 7.95 (d, 2H, H-2', H-6', J = 8.72 Hz), 7.82 (d, 1H, H- α , vinylic, J = 16.00 Hz), 7.56 (m, 3H, H-3, H-4, H-5), 7.00 (d, 2H, H-3', H-5', J = 8.28 Hz). ¹³C-NMR (75MHz, DMSO-d₆): δ C (ppm): 193.50, 161.90, 143.28, 136.45, 135.49, 133.43, 130.96, 130.87, 129.03, 122.51, 120.71, 119.20, 117.75. QTOF-MSES⁺: [M⁺]⁺(in ESI) = 224.25 (100%); Analysis calculated for C₁₅H₁₂O₂: C, 80.20%; H, 6.68%; Found: C, 80.16%; H, 6.70%.

1.2. Synthesis of 2'-hydroxyldihydropyrimidobenzimidazole (DPM)

DPM was prepared according to ref.[1] with a minor modification. An

appropriate amount of 2'-hydroxychalcone (2.24 g, 10.0 mmol) and 2-aminobenzimidazole (1.33 g, 10.0 mmol) were stirred in ethanol (50 mL). After dissolution, 5.6 g potassium hydroxide (250.0 mmol) was added to it. The reaction mixture was heated in an oil bath at 76 °C for 6h. After cooling to room temperature, the pH of the reaction mixture was adjusted to 7 by the addition of concd. HCl. After removal of organic solvents, the resulting brown residue was dissolved in ethyl acetate, and the solution was washed with brine. After evaporation of organic layers, the residue was dissolved in a minimal amount of CH₂Cl₂ and charged onto a silica gel column packed with CH₂Cl₂. The column was eluted stepwise with ethyl acetate-petroleum ether (7:3). The organic solvents were removed by evaporation to give a faint brown solid 1.74 g(52.6%). DPM: brown crystals mp:122~123 °C. IR (KBr) ν_{\max} (cm⁻¹)3580, 3410 (b,OH), 3376, 3318,(C=N) 2180, 2240, 2838, 2256(C=N), 1673, 1576, 1511, 1489(C=C), 1369, 1315, 1259(C-O), 1225, 1174, 1116, 1077, 1035, 1009, 853, 839, 810, 789, 748, 726(C-H). ¹HNMR δ : 8.01 (s, 2H), 7.57–7.31 (m, 6H), 5.88 (s, 2H), 3.88 (ddd, J = 13.9, 9.4, 6.1 Hz, 2H), 2.87–2.70 (m, 1H), 1.67–1.43 (m, 2H), 1.30 (dt, J = 14.7, 7.3 Hz, 3H), 0.87 (t, J = 7.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 118.1, 120.3, 121.7, 123.9, 124.8, 125.6, 127.9, 129.1, 129.3, 130.2, 131.2, 131.8, 136.6, 157.2, 154.6, 178.5. MS (ESI): m/z 362.42 [M⁺Na]⁺. Analysis calculated for C₂₂H₁₇N₃O(339.42):C, 77.80%; H, 5.00%; N, 12.37%. Found: C, 77.81%; H, 5.07%; N, 12.35%.

1.3. Synthesis of S-DPM

2-(2'-oxo-(2,4-dinitrobenzenesulfonyl)-phenyl)-3,4-dihydro-4-(phenyl)-

pyrimido[1,2-a]-benzimidazole(S-DPM) was synthesized according to previous typical literature[2] with minor modifications. 2,4-dinitrobenzenesulfonyl chloride (2.67 g, 10mmol) was added to a mixture of compound 2 and Et₃N (20 mmol) in dichloromethane(80 mL). The resulting solution was stirred for 4 h at room temperature. After completion of the reaction, the mixture was washed with brine (25 mL×3) and the organic layer was dried over MgSO₄. After filtered, the solvent was evaporated under reduced pressure. The residues was purified by column chromatography on silica gel with 5:2 petroleum ether:ethyl acetate (v/v) to afford probe S-DPM(2.8 g, 75.1%) as a pale yellow solid. M.P. 162–164 °C; IR (KBr, cm⁻¹): 3301, 3023, 2896, 1669, 1579; ¹H NMR (300 MHz, DMSO-d₆): δ 3.08 (dd, 1H, J = 6.3, 17.4 Hz, CH₂), 3.90 (dd, 1H, J = 8.4, 8.7 Hz, CH₂), 5.45 (dd, 1H, J = 6.3, 8.9 Hz, 5-H of pyrimidine), 6.70 (t, 1H, J = 7.2 Hz, Ar-H), 6.98 (d, 2H, J = 7.8 Hz, Ar-H), 7.15 (dd, 2H, J = 7.5, 8.7 Hz, Ar-H), 7.69–7.76(m, 4H, Ar-H), 7.41–7.67 (m, 6H, Ar-H); ¹³CNMR (75 MHz, DMSO-d₆): 163.1, 146.9, 144.3, 142.6, 139.4, 131.7, 128.9, 128.8, 127.4, 127.3, 127.1, 126.4, 125.8, 119.2, 118.4, 112.8, 63.1, 43.1; HRMS: calcd for [M + H]⁺ C₃₀H₂₅N₅SO₇: 573.12; found: 573.05. Analysis calculated for C₃₀H₂₅N₅S O₇: C, 62.93%; H, 4.41%; N, 12.21%, O, 16.78%. Found: C, 62.94%; H, 4.37%; N, 12.22%, O, 16.75%.

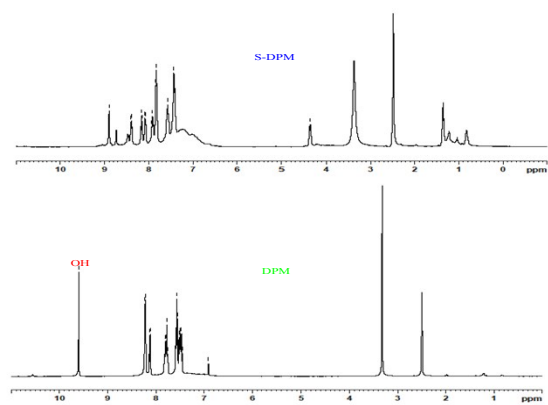


Fig. S1 ^1H NMR of S-DPM reacted with Cys

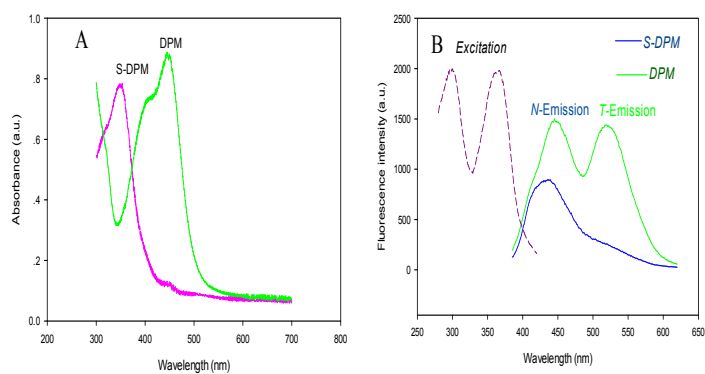


Fig. S2 UV-vis spectra (A) and fluorescence spectra changes (B) of 30 μ M DPM and S-DPM in ethanol-HEPES solutions (pH 7.4, 2:3, v/v). Excitation wavelength is 365 nm.

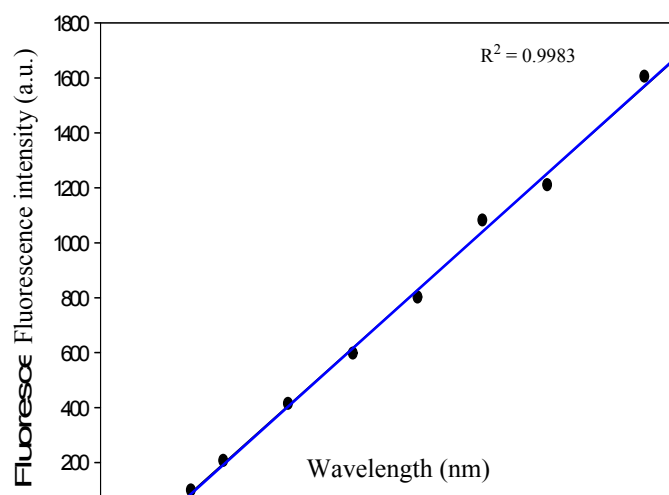


Fig. S3 Linear relationship between the fluorescence emission peaking at 521 (under 365 nm excitation) of S-DPM and Cys concentrations in the range of 1-150 μM at pH 7.4.

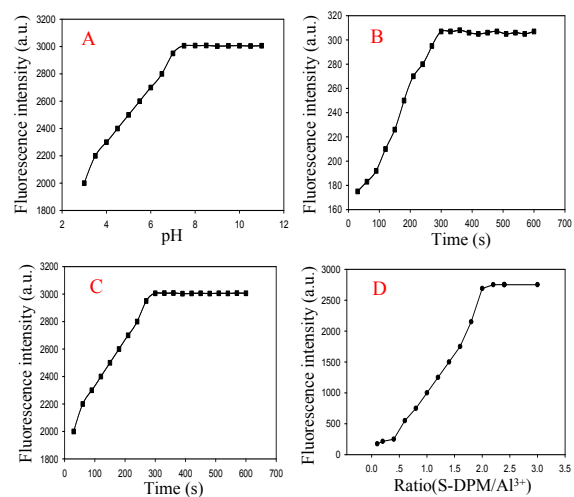


Fig. S4 (A) Fluorescence responses of the S-DPM at different pH values. (B) Recovery time of S-DPM with the addition of Cys. (C) The time of fluorescence enhancement of S-DPM after adding a 25 μM Al^{3+} solution. (D) The ratio of S-DPM to Al^{3+} .

Table S1 Determination of the fluorescence quantum yield(FQY) of DPM, S-DPM and DPM-Al³⁺

Sample	Solvent	FQY
DPM	ethanol-	0.173
S-DPM	ethanol-	0.006
DPM-Al ³⁺	ethanol-	0.865

Absorbance in the 1 cm fluorescence cuvette were kept under 0.1 at the excitation wavelength of 360 nm. The analytes quinine sulfate, DPM, S-DPM and DPM-Al³⁺ were dissolved in the ethanol-HEPES solutions (10 mM, pH 7.4, v/v = 2:3). The ESIPT emission of DPM was used to estimate its FQY.

References

- (1) Mohamed, A.M.; Eee, E.M.K.; Fathy, A.A. *J. Indian. Chem. Soc.* **1987**, *64*, 753-755.
- (2) Majumdar, P.; Zhao, J.Z. *J. Phys. Chem. B.* **2015**, *119*, 2384-2394.