

Supplementary data for

A dansyl-based fluorescent probe for the highly selective detection of cysteine based on d-PeT switching mechanism

Yudong Xiao², Yujin Guo¹, Ruili Dang¹, Xin Yan³, Pengfei Xu^{1,*} and Pei Jiang^{1,*}

¹ Institute of Clinical Pharmacy & Pharmacology, Jining First People's Hospital, Jining Medical University, Jining 272000, China;

² Department of Radiology, the Second Xiangya Hospital of Central South University, Changsha 410010, China;

³ Research Center for Drug Discovery, School of Pharmaceutical Sciences, Sun Yat-sen University, 132 East Circle at University City, Guangzhou, 510006, China.

* Co-correspondence: pengfeixucs@outlook.com (P. X.) Tel.: +86 537 2106207, Fax: +86 537 2106207; jiangpeicsu@sina.com (P. J.) Tel.: +86 537 2106208, Fax: +86 537 2106208.

1. Materials and Methods

All chemical reagents and solvents were analytical grade and purchased from commercial suppliers. ^1H NMR spectra were recorded on a 400 MHz Varian Unity Inova NMR spectrophotometer. ^{13}C NMR spectra were recorded on the same instrument (100 MHz) with total proton decoupling. Mass spectra were recorded with Thermo Scientific Orbitrap Velos Pro MS spectrometer. UV-Vis absorption spectra were measured with a Shimadzu UV-2450 UV-visible spectrophotometer. Fluorescence spectra were recorded on Hitachi F-7000 spectrofluorometer. All UV/Vis and fluorescence titration experiments were performed using 10 μM of DN-C in a mixed buffer solution of CH_3CN : PBS (50:50, v/v, pH=7.4, 10 mM) with varying concentrations of analytes at room temperature.

Synthesis of compound DN: To a solution of 3-aminophenol (321 mg, 3.0 mmol) in anhydrous acetonitrile (10 mL) was added dansyl chloride (269 mg, 1.0 mmol). The mixture was stirred at room temperature for 2 h. After evaporation of solvent under reduced pressure, the crude product was purified by silica gel chromatography to afford DN (263 mg, yield 77 %).

Synthesis of compound DN-C: A mixture of compound DN (342 mg, 1.0 mmol), acryloyl chloride (180 mg, 2.0 mmol) and Ethyldiisopropylamine (260 mg, 2.0 mmol) in 20 ml anhydrous acetonitrile was reflux at 100 $^\circ\text{C}$ for 24 hrs. After completion of the reaction, the reaction mixture was concentrated under reduced pressure. The crude product was purified by silica gel chromatography to give target product (344 mg, 87%). ^1H NMR (400 MHz, CDCl_3): δ 8.57 (d, J= 8.4 Hz 1H), 8.32 (d, J= 8.4 Hz 1H), 8.24 (m, 2H), 7.48 (t, J= 8.0 Hz 1H), 7.28 (t, J= 8.0 Hz 1H), 7.20 (d, J= 7.2 Hz 1H), 6.78 (m, 2H), 6.65 (d, J= 9.2 Hz 1H), 6.31 (d, J = 17.2Hz, 1H), 6.15-6.08 (dd, J = 17.2, 10.4 Hz, 1H), 5.70 (d, J = 10.4 Hz, 1H), 2.88 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 162.96, 152.26, 152.18, 138.79, 133.17, 132.29, 132.11, 131.47, 130.16, 129.77, 129.56, 128.91, 128.47, 123.36, 117.88, 115.23, 115.39, 112.67, 106.75, 45.78. MS (ESI, m/z) Calcd for $[\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_4\text{S}+\text{H}]^+$: 397.46 found: 397.25 .

2. UV-vis spectra of DN-C upon addition of Cys.

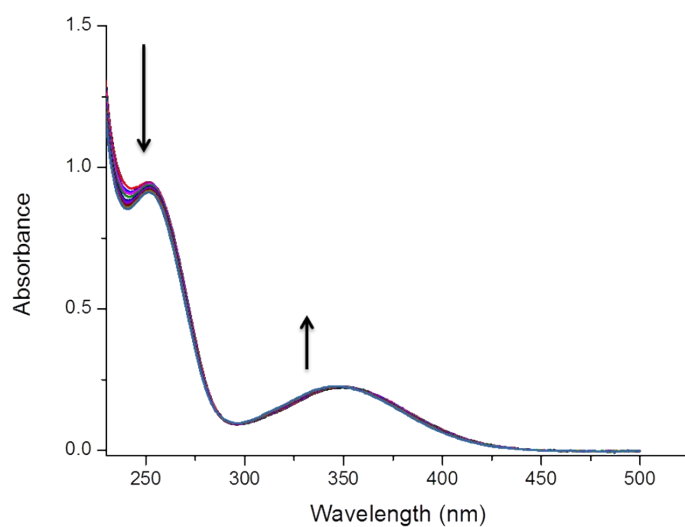


Figure S1. UV-vis spectra of **DN-S** (10.0 μM) a mixed buffer solution of CH_3CN : PBS (50:50, v/v, pH=7.4, 10 mM) upon addition of Cys (0-100 μM).

3. Effect of pH.

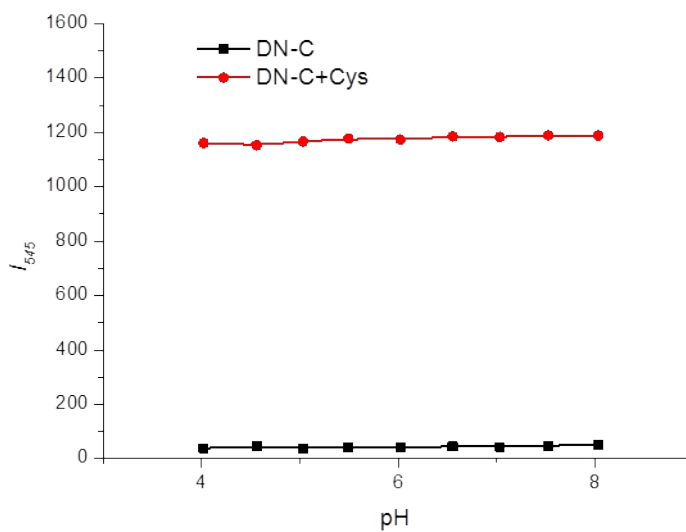


Figure S2. pH effect on the $I_{545 \text{ nm}}$ of **DN-C** (10 μM) in the absence and presence of Cys (100 μM).

4. Density functional theory (DFT) optimized structure of DN-C.

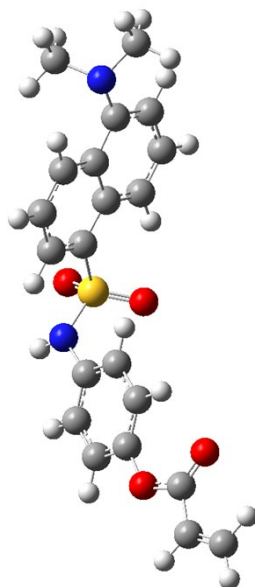


Figure S3. Density functional theory (DFT) optimized structure of **DN-C**. In the ball-and-stick model, carbon, oxygen, sulfur and nitrogen atoms are colored in gray, red, yellow and blue, respectively.

5. Fluorescence quantum yield of DN and DN-C in acetonitrile.

Table S1

	Φ_{fl}
DN	0.41
DN-C	0.09

The fluorescence quantum yield was determined with fluorescein in 0.1 N H₂SO₄ aq. ($\Phi_{fl} = 0.55$) as a standard.

6. The plausible mechanism for detection of Cys.

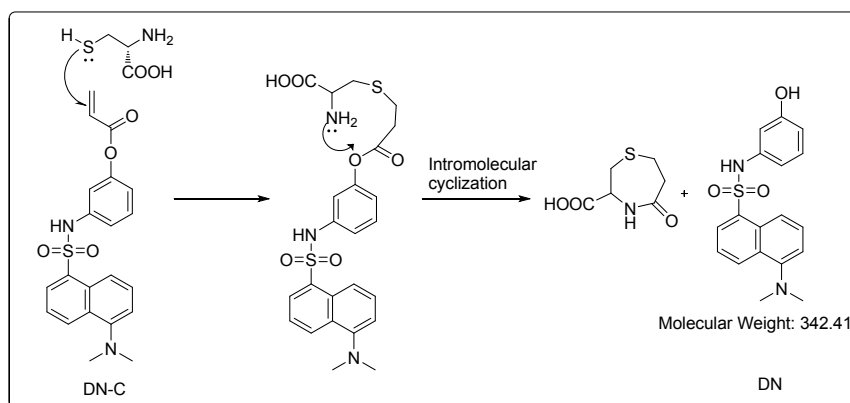


Figure S4. The proposed mechanism for detection of Cys.