Electronic Supplementary Information

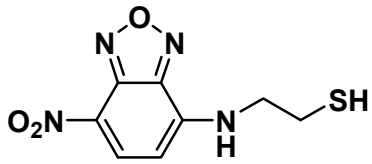
Fluorescent Sensors for Selective Detection of thiols: Expanding the Intramolecular Displacement Based Mechanism to New Chromophores

Li-Ya Niu,[a] Hai-Rong Zheng,[ab] Yu-Zhe Chen,[a] Li-Zhu Wu,[a] Chen-Ho Tung[a] and Qing-Zheng Yang*[a]

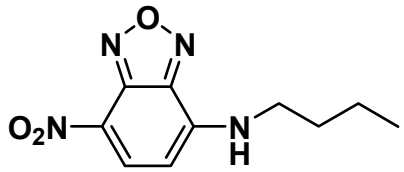
[a]Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, 100190, P. R. China

[b]University of Chinese Academy of Sciences, Beijing, 100049, P. R. China

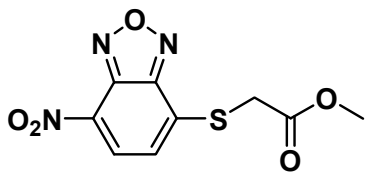
Synthesis



Synthesis of NBD-MEA. NBD-Cl (20 mg, 0.1 mmol) and cysteamine hydrochloride (57 mg, 0.5 mmol) was dissolved in 10 mL acetonitrile, and one drop of triethylamine was added. The reaction mixture was stirring at room temperature for 20 min, and then evaporated. The crude product was purified through column chromatography over silica (ethyl acetate/ petroleum ether = 1/4 as eluent) to give **NBD-MEA** as orange solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, 2H, J = 8.4 Hz), 6.57 (br, 1H), 6.24 (d, 2H, J = 8.4 Hz), 3.75 (m, 2H), 2.96 (m, 2H), 1.58 (t, 1H, J = 8.4 Hz). ESI-HRMS: calculated for $[M+H]^+$ 237.09822, found 237.09773.



Synthesis of NBD-N. NBD-Cl (20 mg, 0.1 mmol) was dissolved in 10 mL acetonitrile, and the solution was added 50 μL butylamine (37 mg, 0.5 mmol). The reaction mixture was stirred at room temperature for 2 h, and then evaporated. The crude product was purified through column chromatography over silica (ethyl acetate/ petroleum ether = 1/4 as eluent) to give NBD-N (21 mg, 91%) as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (d, 2H, J = 8.8 Hz), 6.25 (br, 1H), 6.18 (d, 2H, J = 8.8 Hz), 3.51 (q, 2H, J = 6.8 Hz), 1.81 (m, 2H), 1.52 (m, 2H), 1.02 (t, 6H, J = 7.2 Hz). ESI-HRMS: calculated for $[M+H]^+$ 241.03899, found 241.03829.



Synthesis of NBD-S. NBD-Cl (20 mg, 0.1 mmol) and methyl mercaptoacetate (27 μL,

0.3 mmol) was dissolved in 10 mL acetonitrile, and one drop of triethylamine was added. The reaction mixture was stirring at room temperature for 20 min, and then evaporated. The crude product was purified through column chromatography over silica (ethyl acetate/ petroleum ether = 1/9 as eluent) to give **NBD-S** as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (d, 2H, J = 7.6 Hz), 7.38 (d, 2H, J = 7.6 Hz), 4.10 (s, 3H), 3.80 (m, 3H). ESI-HRMS: calculated for $[M+H]^+$ 270.01792, found 270.01786. ESI-HRMS: calculated for $[M+H]^+$ 270.01792, found 270.01786.

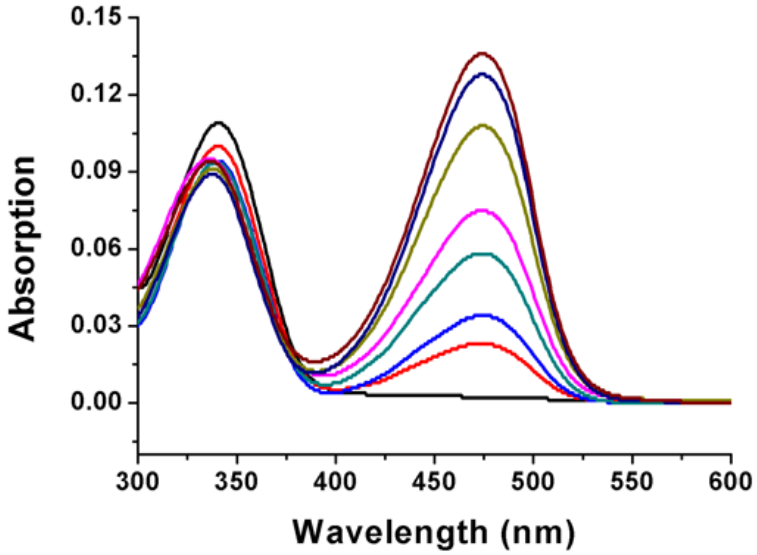


Fig. S1. Absorption spectral changes of NBD-Cl upon addition of the increasing concentrations of Cys (0, 10, 20, 40, 80, 100, 150, 200 μM). Each spectrum was recorded 2 min after Cys addition in acetonitrile/HEPES buffer (1:3, v/v, 20 mM, pH 7.4) at 37 °C.

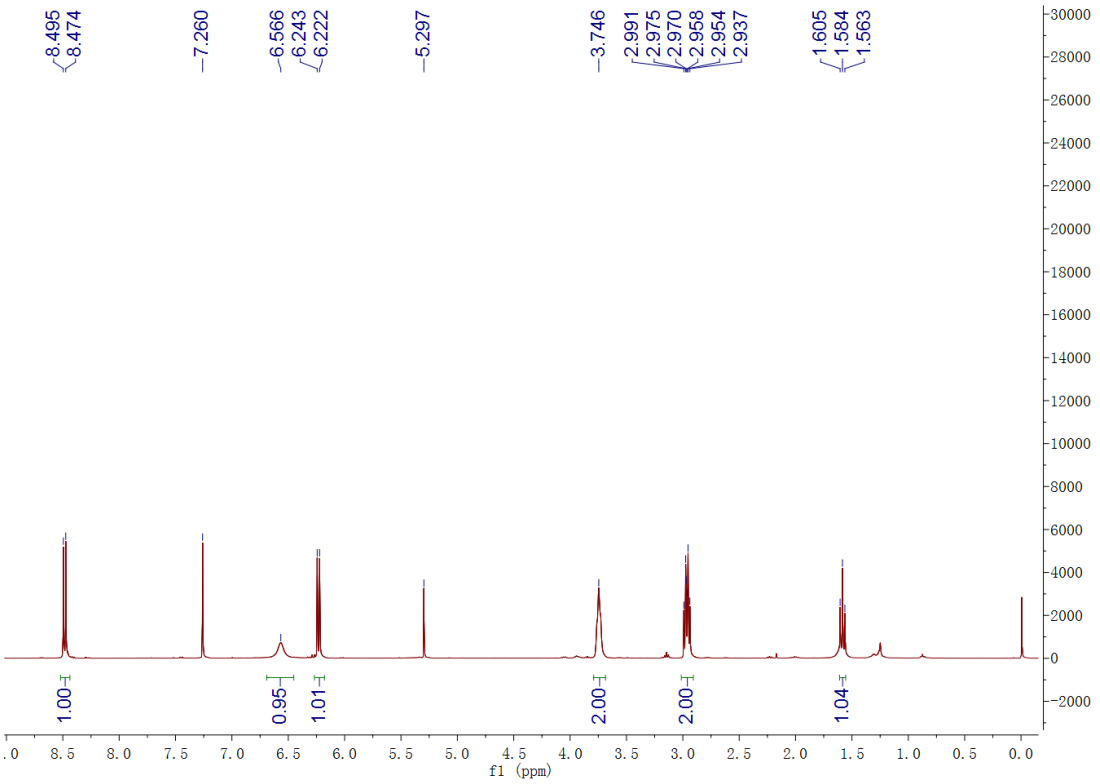


Fig. S2. ^{1}H NMR spectrum of **NBD-MEA.**

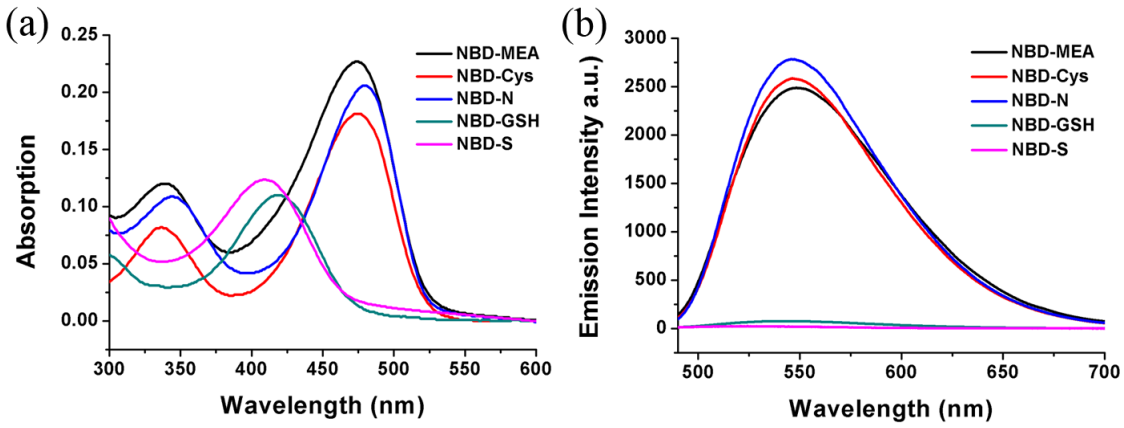


Fig. S3. (a) Asorption and (b) emission spectra of **NBD-MEA, NBD-Cys, NBD-N, NBD-GSH** and **NBD-S.**

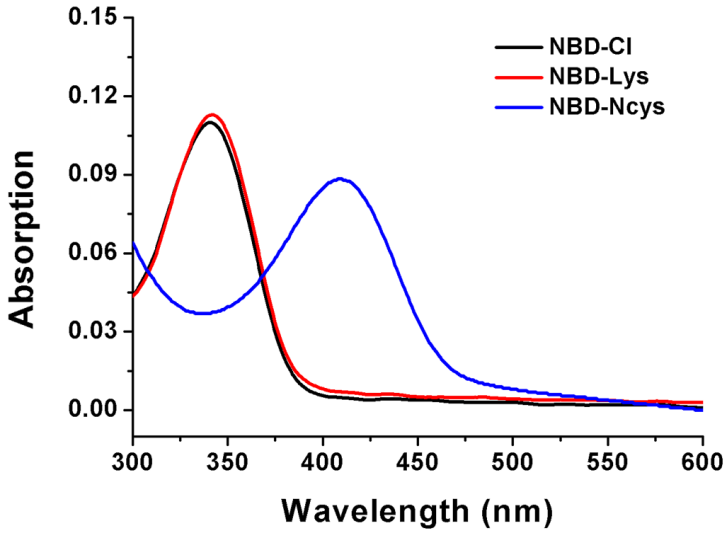


Fig. S4. Absorption spectra of NBD-Cl, NBD-Lys and NBD-Ncys. The spectra of NBD-Lys and NBD-Ncys were recorded after 30 min addition of Lys and N-acetylcysteine to NBD-Cl (10 μM) in acetonitrile/HEPES buffer (1:3, v/v, 20 mM, pH 7.4) at 37 °C.

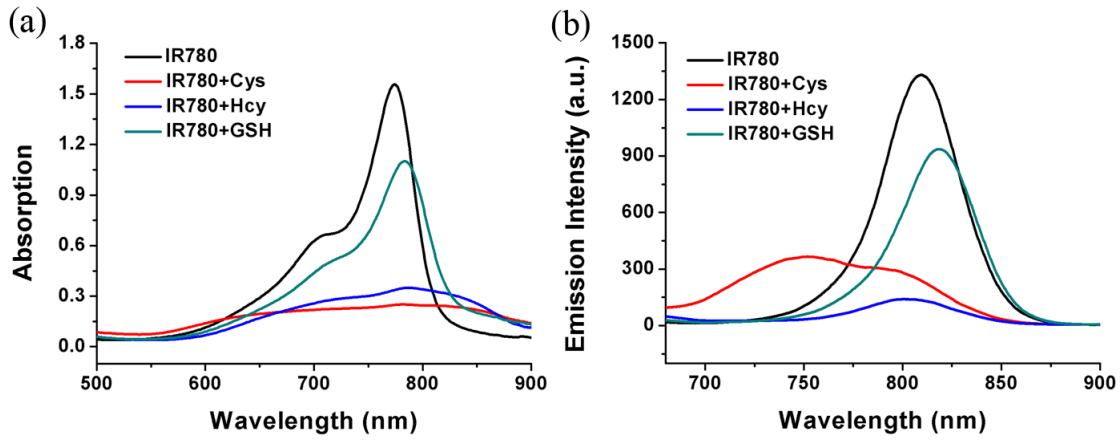


Fig. S5. (a) Absorption and (b) emission spectral of IR-780 (10 μM) in the presence of 100 equiv of Cys, Hcy and GSH in methanol/HEPES buffer (5:95, v/v, 20 mM, pH 7.4) at 37 °C. Each spectrum was recorded 60 min after addition. λ_{ex} = 650 nm.