Electronic Supplementary Information

A "turn-on" fluorescent probe for specially recognize on intracellular GSH and its application in bioimaging

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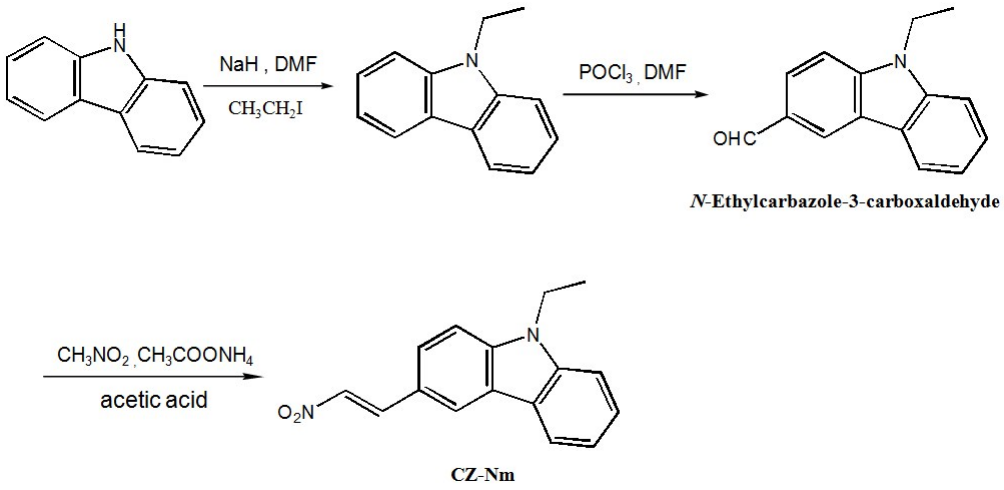
1. Synthesis



Scheme S1. Synthesis of CZ-Nm.

Synthesis of N-Ethylcarbazole and N-Ethylcarbazole-3-carboxaldehyde

N-Ethylcarbazole was synthesized according to the literature procedure.[1] N-Ethylcarbazole-3-carboxaldehyde was synthesized from N-Ethylcarbazole by using well known Vismeier Haack's formylation reaction.[2]

N-Ethylcarbazole: To a stirred solution of carbazole (1.00 g, 6.00 mmol) in dry DMF (20.0 mL), NaH (0.35 g, 60% suspension in mineral oil, 7.20 mmol) was added portionwise under nitrogen atmosphere at 0 ^oC. The reaction mixture was then warmed to room temperature and stirred for 30 min. After cooling to 0 ^oC, EtI (0.50 mL, 8.00 mmol) was added dropwise to the reaction mixture. The reaction mixture was warmed to room temperature and stirred overnight. Water was added and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, and chromatography on silica gel using DCM/PE (v/v, 1:5) as the eluent afforded a colorless solid (0.98 g, 83% yield).

N-Ethylcarbazole-3-carboxaldehyde: A solution of N-Ethylcarbazole (1.60 g, 8.20 mmol) in DMF (15 mL) was treated with $POCl_3$ (0.75 mL) under N_2 and the reaction mixture was warmed at 125 °C for 1 h. Then the dark brown solution was poured into a 20% aqueous solution of NaOAc (60 mL) and extracted with CH_2Cl_2 at the room temperature. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using DCM/PE (v/v, 1:10) as the eluent afforded a faint yellow solid (1.37 g, 75% yield).

Reference

1. B. P. Bandgar, L. K. Adsul, H. V. Chavan, S. S. Jalde, S. N. Shringare, R. Shaikh, R. J. Meshram, R. N. Gacche, V. Masand, Bioorg. Med. Chem. Lett., 2012, 22, 5839-5844.
2. J. S. Stover, J. Shi, W. Jin, P. K. Vogt and D. L. Boger, *J. Am. Chem. Soc.*, 2009, 131, 3342-3348.

2. Supplementary Data

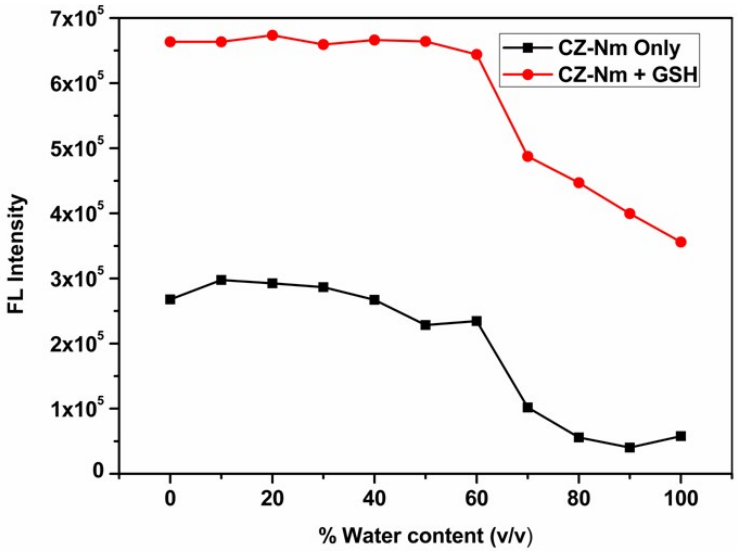


Fig. S1. Effect of fraction of water on the interaction of probe CZ-Nm (10 μM) with GSH (500 equiv) in PBS buffer-DMF (0.1 M, pH 7.4, v/v, 4:1) solution (λ_{ex}=360 nm).

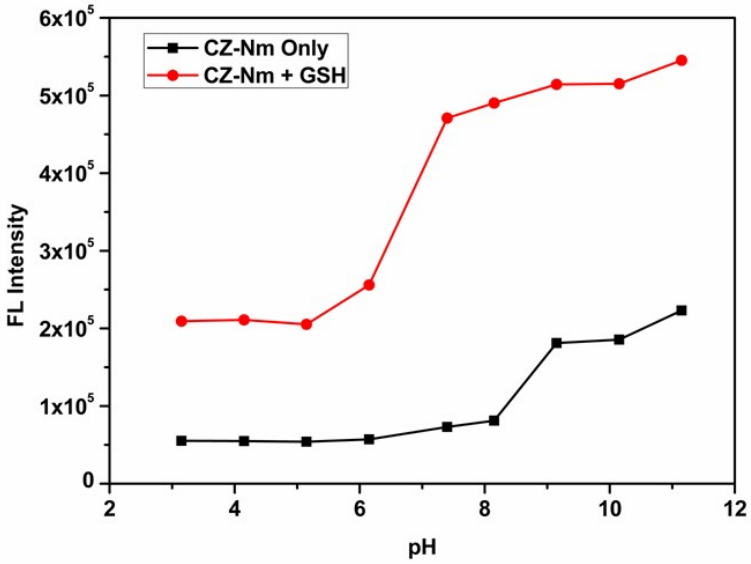


Fig. S2. Effect of pH on the interaction of probe CZ-Nm (10 μM) with GSH (500 equiv) in PBS buffer-DMF (0.1 M, pH 7.4, v/v, 4:1) solution (λ_{ex}=360 nm).

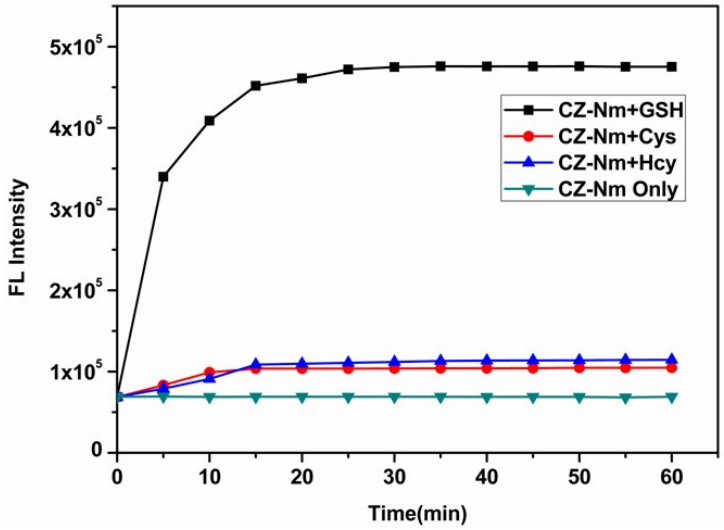


Fig. S3. Time-dependent fluorescence intensity of probe CZ-Nm (10 μM) at 420 nm in the presence of 500 equiv GSH, Cys and Hcy.

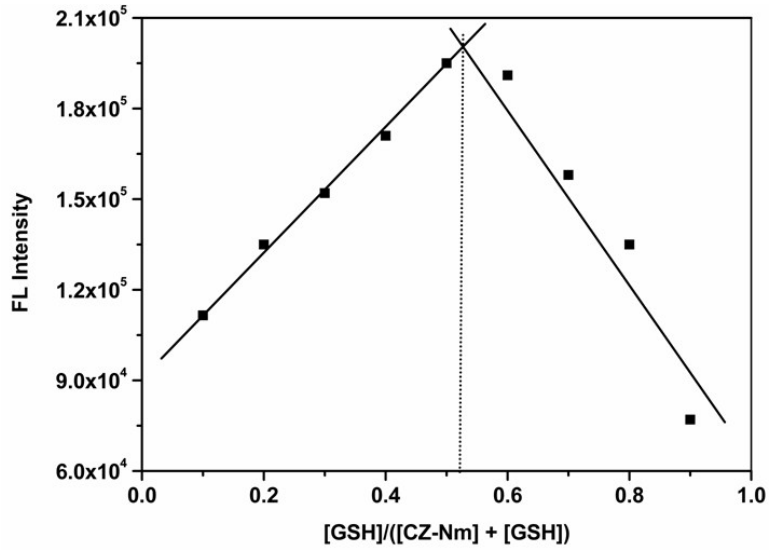


Fig. S4. Job's plot of the reaction between CZ-Nm and GSH in PBS buffer-DMF (0.1 M, pH 7.4, v/v, 4:1). Total concentration of CZ-Nm and GSH was kept constant at 20.0 μM.

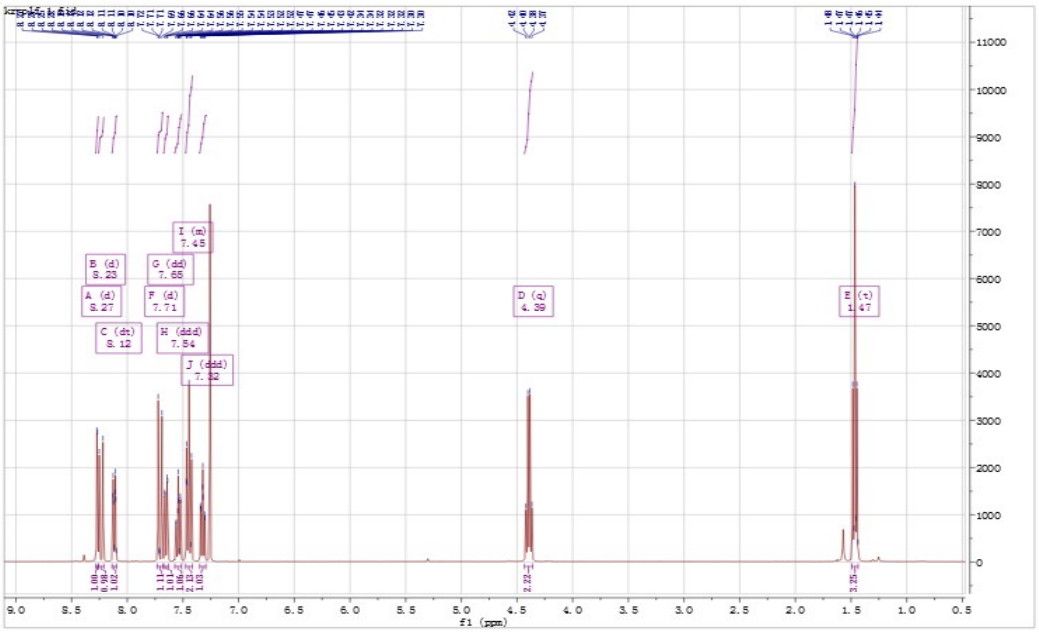


Fig. S5. ^{1}H NMR of CZ-Nm. ($CDCl_3$)

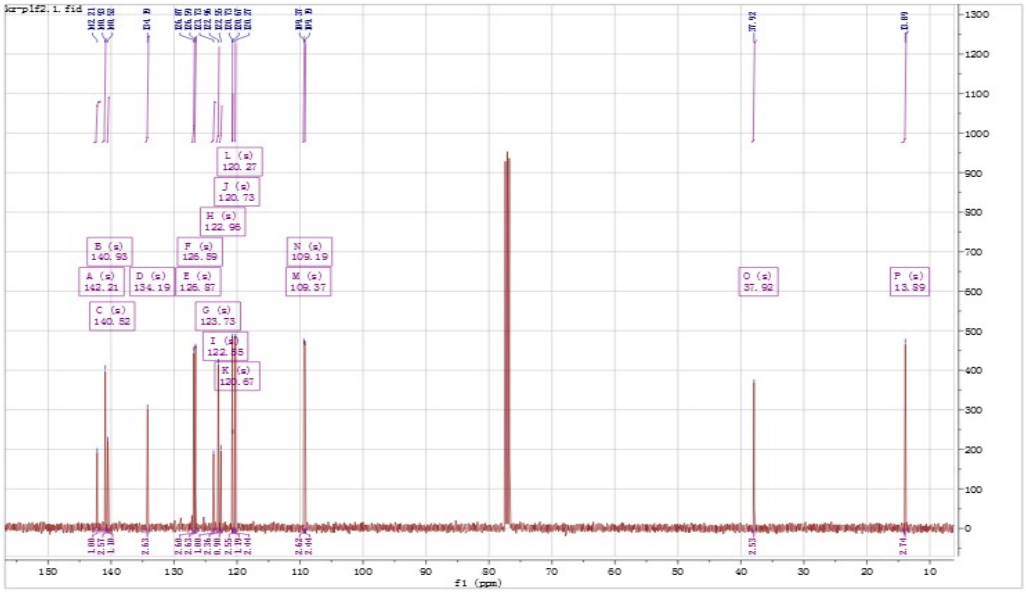


Fig. S6. ^{13}C NMR of CZ-Nm. ($CDCl_3$)