

Electronic Supporting Information

Colorimetric sensor for highly sensitive and selective detection of copper ion

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1. Experimental

1.1 Synthesis of ketone-Cy¹

The aqueous sodium acetate (100 mg, 1.2 mmol) and solution of heptacyanine Cy.7.Cl (230 mg, 0.45 mmol)² were dissolved in anhydrous N, N-dimethylformamide (15 mL) and then heated at 90 °C for 6 hours under Ar atmosphere. Next, the solution was cooled to room temperature, and filtered, concentrated and evaporated under reduced pressure, followed by drying with a vacuum pump to give the red product. Then the ketone-Cy was purified with CH₂Cl₂/CH₃OH (8:2, v/v) by silica chromatography eluting.

1.2 Synthesis of Cy-NB¹

We dissolved heptacyanine Cy.7.Cl (100 mg, 0.19 mmol) and triethylamine (278 mL, 0.6 mmol) in anhydrous CH₂Cl₂ (15 mL) at 0 °C, then added the p-nitrobenzoyl chloride (10 mL) dropwise and kept stirring at 0 °C for 30 min. Then the mixture was warmed at room temperature and stirred overnight. For extraction operation, the solution was diluted with CH₂Cl₂ (30 mL), then the solvent was removed in vacuo to obtain a deep green crude mixture solid. Finally, Cy-NB was isolated by silica chromatography eluting with CH₂Cl₂/CH₃OH (8:2, v/v) as a green solid (40 mg, 38% yield).

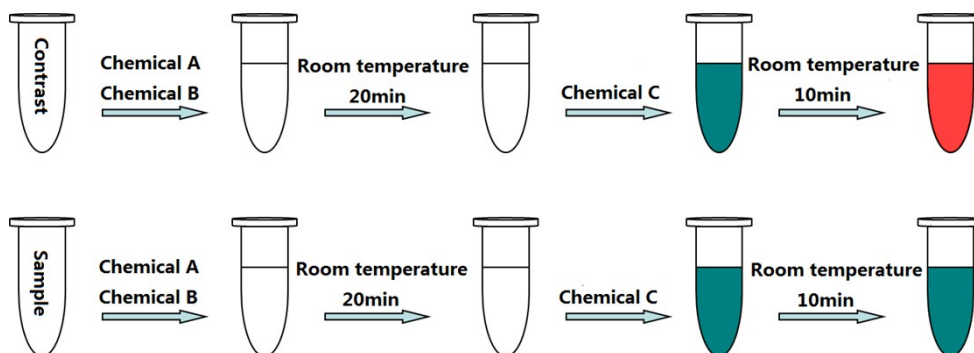


Fig. S1. Schematic diagram of the operation after the test sample, where Chemical A is 100 μL of PBS buffer solution in pH 7.4, Chemical B is 20 μL of 5 mM L-Cys solution and Chemical C is 10 μL of 50 μM probe Cy-NB dissolved in dimethylsulfoxide.

References

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- 2 R Wang, F Yu, L Chen, H Chen, L Wang and W Zhang. A highly selective turn-on near-infrared fluorescent probe for hydrogen sulfide detection and imaging in living cells, *Chem. Commun.*, 2012, 48(96), 11757–11759.

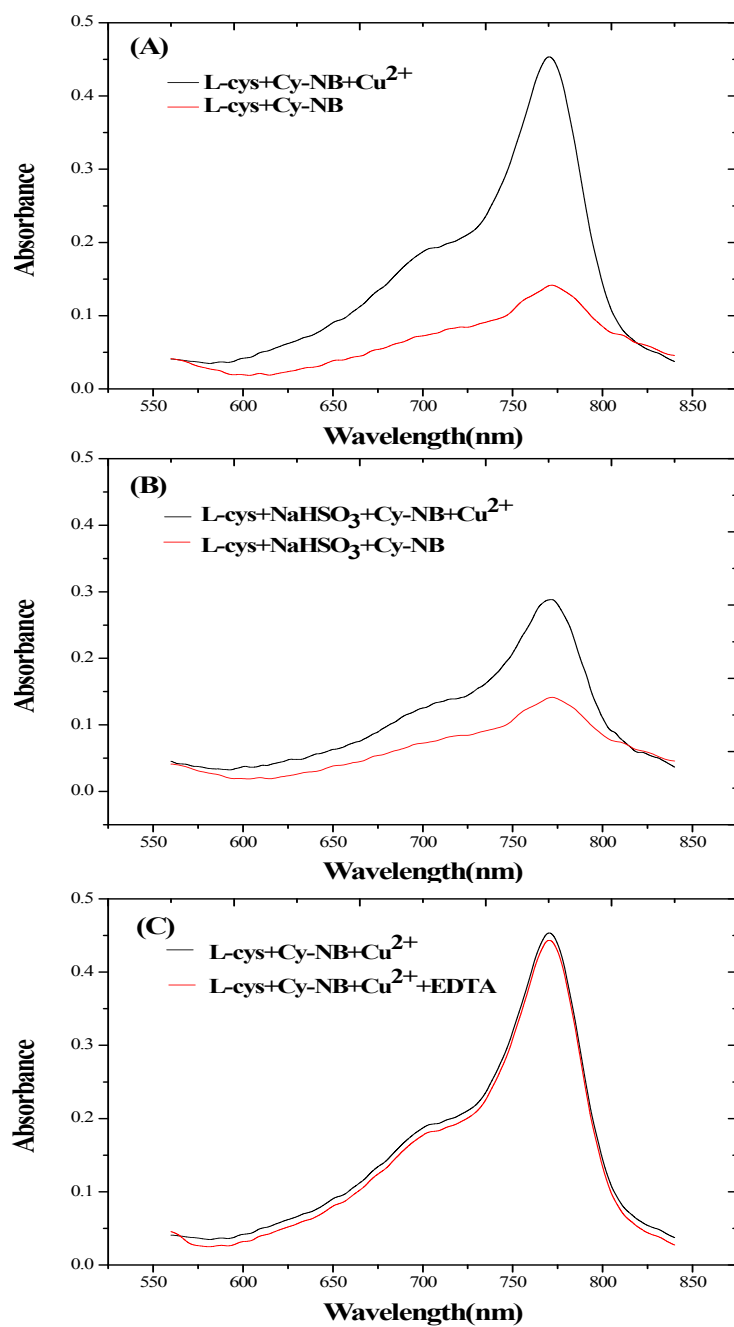


Fig. S2. Absorption spectra of Cy-NB which was generated by L-Cys and Cy-NB, (A) in the absence and presence of Cu²⁺, (B) in the absence and presence of Cu²⁺ after O₂ was consumed by 0.2 M NaHSO₃, and (C) in the absence and presence of 2 mM EDTA after L-Cys reacted with Cu²⁺.

2. LOD and LOQ calculation details

In our present study, LOD was calculated using the 3σ principle.^{3,4} Calculation is based on the signal response and standard deviation of the blank. The result presented in the content domain when y_D converted to concentration using the calibration function, $y_D = \bar{y}_B + 3\sigma_0$, where \bar{y}_B means the average value of the instrument blank response, and σ_0 means standard deviation of the blank^{3,4}. Herein, we detected 6 blank samples and attained the absorbance values of 0.143, 0.144, 0.143, 0.142, 0.142, 0.145. The absorbance mean value is 0.1432, and the σ_0 is 0.001068. So, a specific absorbance value ($0.1432 + 3 \times 0.001068 = 0.1464$) was obtained, and the corresponding concentration can be regarded as LOD. For clarity, the previous linear curve (Fig. 2B, inset) is enlarged within 0–30 nM as Fig. S3. As observed from the blue section, when the absorbance is 0.1464, the corresponding concentration of Cu^{2+} is 8.6 nM. Therefore, the LOD of 8.6 nM is attained.

LOQ is calculated using the 10σ principle.^{3,5} According to the red section of Fig. S3, when the absorbance is 0.1539, the concentration of Cu^{2+} is 27.2 nM. So, the LOQ of 27.2 nM is gained.

On the other hand, it has been pointed that the lower limit of the measuring interval can coincide with the LOQ which is higher than the LOD.^{6,7} So, the bottom concentration of the linear range could be set at 27.2 nM.

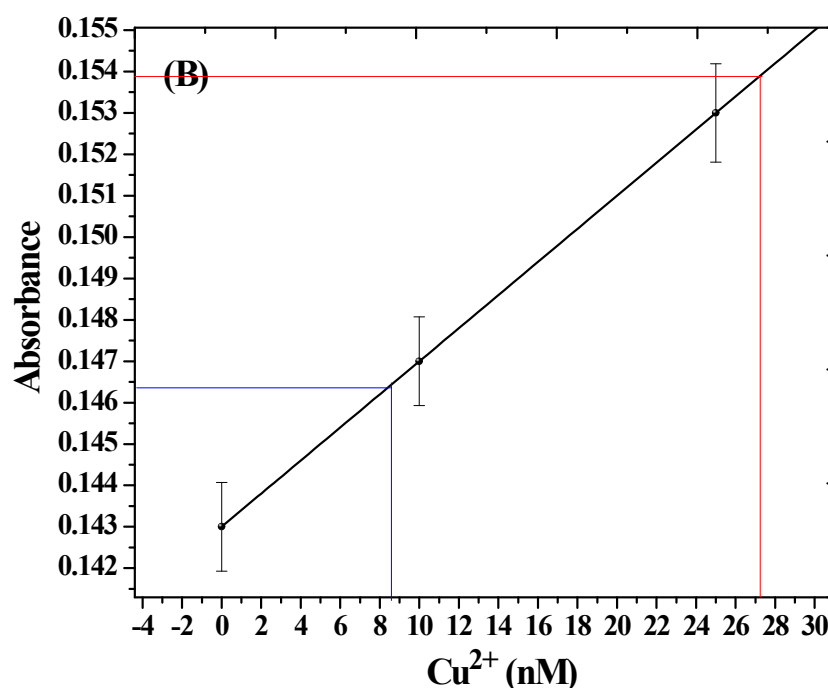


Fig. S3. Absorbance versus Cu^{2+} concentration within 0–30 nM.

Reference

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