Supporting Information

Ultra-small water-soluble fluorescent copper nanoclusters for p-

nitrophenol detection

Mayowa Oyebanji^a, Ling Chen^a, Ruru Qian^a, Mengyuan Tu^a, Qiangli Zhang^a, Xuejiao Yang^a, Haizhu Yu^{a*}, Manzhou Zhu^a ^aDepartment of Chemistry and Centre for Atomic Engineering of Advanced Materials, Key Laboratory of Structure and Functional Regulation of Hybrid Materials of Physical Science and Information Technology and Anhui Province Key Laboratory of Chemistry for Inorganic/Organic Hybrid Functionalized Materials, Anhui University, Hefei 230601, China.

* Corresponding author: Prof. Haizhu Yu (E-mail: yuhaizhu@ahu.edu.cn)_

List of Contents

- 1. Synthesis optimization for Cu-SG NCs.
- 2. Time-dependent fluorescence response of Cu-SG NCs to p-NP.
- 3. HRTEM of Cu-SG NCs and Cu-SG NCs with p-NP.
- 4. EDS analysis of Cu-SG NCs.
- 5. XPS analysis of Cu-SG NCs.
- 6. ESI-MS of the Cu-SG NCs.
- 7. Ligand effect on the Cu NCs fluorescence and selective p-NP detection.
- 8. Comparison of glutathione protected copper nanoclusters for p-NP detection.



Fig. S1. The one-factor-at-a time tests on fluorescence intensity dependencies on pH value (A), reaction time (B), temperature (C), and optimal excitation wavelength (D) for Cu-SG NCs.



Fig. S2. Time-dependent fluorescence response of Cu-SG NCs to 80 µM p-NP.



Fig. S3. (A) HRTEM images of Cu-SG NCs (inset: size distribution histogram). (B) HRTEM images of Cu-SG NCs with p-NP (0.5 mM) (inset: size distribution histogram).



Fig. S4. (A) EDS spectra of Cu-SG NCs. (B) EDS elemental mapping images of C, N, O, S, and Cu for Cu-SG NCs.



Fig. S5. (A) XPS spectra of the Cu-SG NCs. (B) High resolution XPS spectra of S2p.



Fig. S6. ESI-MS of the as-synthesized Cu-SG NCs (inset: zoom-in spectra peaks of $[Cu_{14}(SG)_{12}+(x+2)Na-(x+1)H]^{3+}$, x = 1-3. top inset is the correlation between experimental and theoretical isotopic pattern of $[Cu_{14}(SG)_{12}+3Na-2H]^{3+}$, x = 1).



Fig. S7. (A) The UV-vis absorption spectra of Cu-SG NCs, Cu-MSA NCs, and Cu-Capt NCs. (B) The luminescence spectra of Cu-SG NCs, Cu-MSA NCs, and Cu-Capt NCs. (C) The DLS of Cu-SG NCs, Cu-MSA NCs, and Cu-Capt NCs. (D) The luminescence of Cu-MSA NCs and its mixture with p-NP (0.1 mM), and Cu-Capt NCs and its mixture with p-NP (0.1 mM).

Glutathione protected copper nanoclusters	Synthesis	Average Size (nm)	Buffer requirement	Detection range (µM)	Detection limit (µM)	Ref.
GSH-Cu nanoclusters	65 °C, 4 hrs.	3.5	Yes	0.1–300	0.02	1
GSH-Cu nanoclusters	37 °C, 3 hrs.	3.0	Yes	0.5–2500	0.17	2
Cu-SG nanoclusters	40 °C, 40 mins.	0.7	No	0.04–2000	0.03	this work.

Table S1. Comparison of glutathione protected copper nanoclusters for p-NP detection.

References

1 H.-B. Wang, B.-B. Tao, N.-N. Wu, H.-D. Zhang and Y.-M. Liu, Spectrochim. Acta. A. Mol. *Biomol. Spectrosc.*, 2022, **271**, 120948. 2 Q. Zhang, H. Mei, W. Zhou and X. Wang, *Microchem. J.*, 2021, **162**, 105842.