

Supporting :

**An anti-galvanic reduction single-molecule fluorescent probe for detection of
Cu(II)**

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Experimental

Materials.

Silver tetrafluoroborate (AgBF_4 , 99%), silver nitrate (99%), 2-methylpropane-2-thiol (99%), hydrazine hydrate (80%), were used as received from Aldrich. HPLC-grade methanol was purchased from Aldrich and used as received. Pure water was from Wahaha Co LTD., AgSBU^t was prepared by reacting equivalent amounts of AgNO_3 with HSBU^t in the presence of Et_3N .

Synthesis of $[\text{Ag}_{62}\text{S}_{13}(\text{SBU}^t)_{32}]^{4+}$ NCs

$[\text{Ag}_{62}\text{S}_{13}(\text{SBU}^t)_{32}]^{4+}$ NCs were synthesized referring to the reported method.¹ Briefly, AgSBU^t (39.8 mg, 0.202 mmol) was dispersed in 10 mL methanol under ultrasonication, then AgBF_4 (20.6 mg, 0.106 mmol) dissolved in 0.5 mL methanol was added. To the resulting solution 6 μL $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ (50% w/w in water) was added with stirring for 1 h in r. t.. The reaction mixture was kept at 60°C for another 20 h in the Schlenk flask. After cooled to room temperature, the red solution was filtered and the filtrate was dried by rotary evaporation. The obtained product was washed with hexane and re-dissolved in methanol. This process was repeated at least 5 times to completely remove the impurity.

Single-molecule imaging²

Monitoring of Fluorescence Signal Process under Zeiss LSM 710 Confocal Fluorescence Microscope. To immobilize and disperse the NCs, triethylene glycol (1 μL) was added into the solution of $[\text{Ag}_{62}\text{S}_{13}(\text{SBU}^t)_{32}]^{4+}$ NCs and $\text{Ag}_{62}\text{-Cu}^{2+}$ NCs (500 nM, 10 μL), then 1 μL of the mixture solution was dropped on the petri dishes and dried at r. t.. After the samples were dried, the fluorescence images were taken using a Plan-Apochromat 100x/1.40 Oil DIC M27 objective, recorded by using fast scanning, $\theta = 3.15 \mu\text{s}$ per pixel. Synthesis of $[\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2]^+$.

Characterization

The optical spectra of the $[\text{Ag}_{62}\text{S}_{13}(\text{SBU}^t)_{32}]^{4+}$ clusters (solvent: $\text{MeCN}:\text{H}_2\text{O}=1:1$) were measured on Hewlett-Packard (HP) Agilent 8453 diode array spectrophotometer at

room temperature. Fluorescence spectra were recorded on a FL-4500 spectrofluorometer. For the convenience of comparison, the excitation wavelength was set at 535 nm for all the cluster species in emission measurements. MALDI-TOF-MS were performed on a Bruker autoflex III time-of-flight (TOF) mass spectrometer. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenyldiene] malononitrile (DCTB) was used as the matrix for MALDI. TEM images were obtained by JEM 2100.

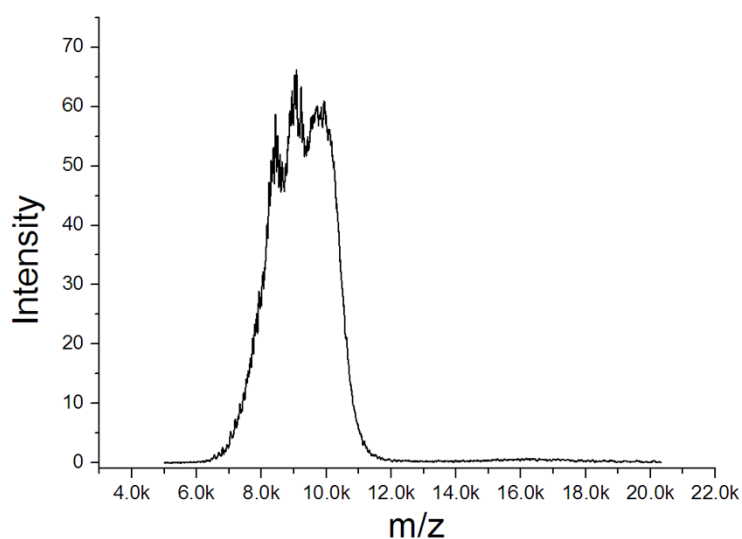


Figure S1 MALDI-TOF-MS of $[\text{Ag}_{62}\text{S}_{13}(\text{SBu}^{\text{t}})_{32}]^{4+}$.

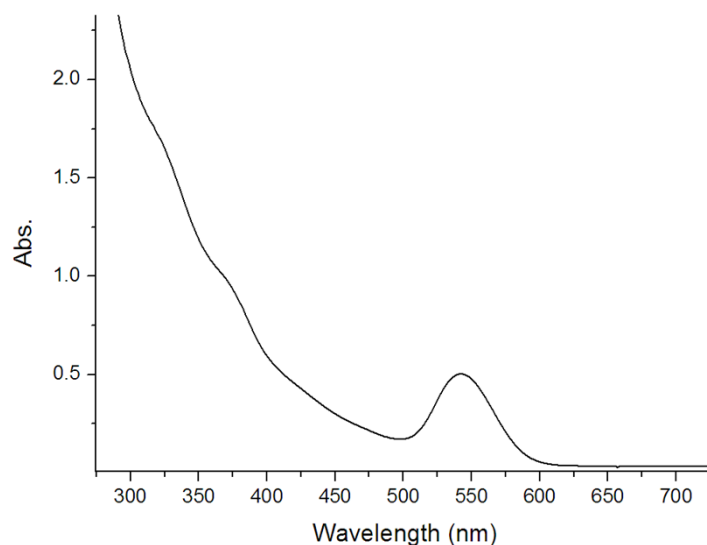


Figure S2 UV-Vis spectrum of $[\text{Ag}_{62}\text{S}_{13}(\text{SBu}^{\text{t}})_{32}]^{4+}$, measured in MeOH.

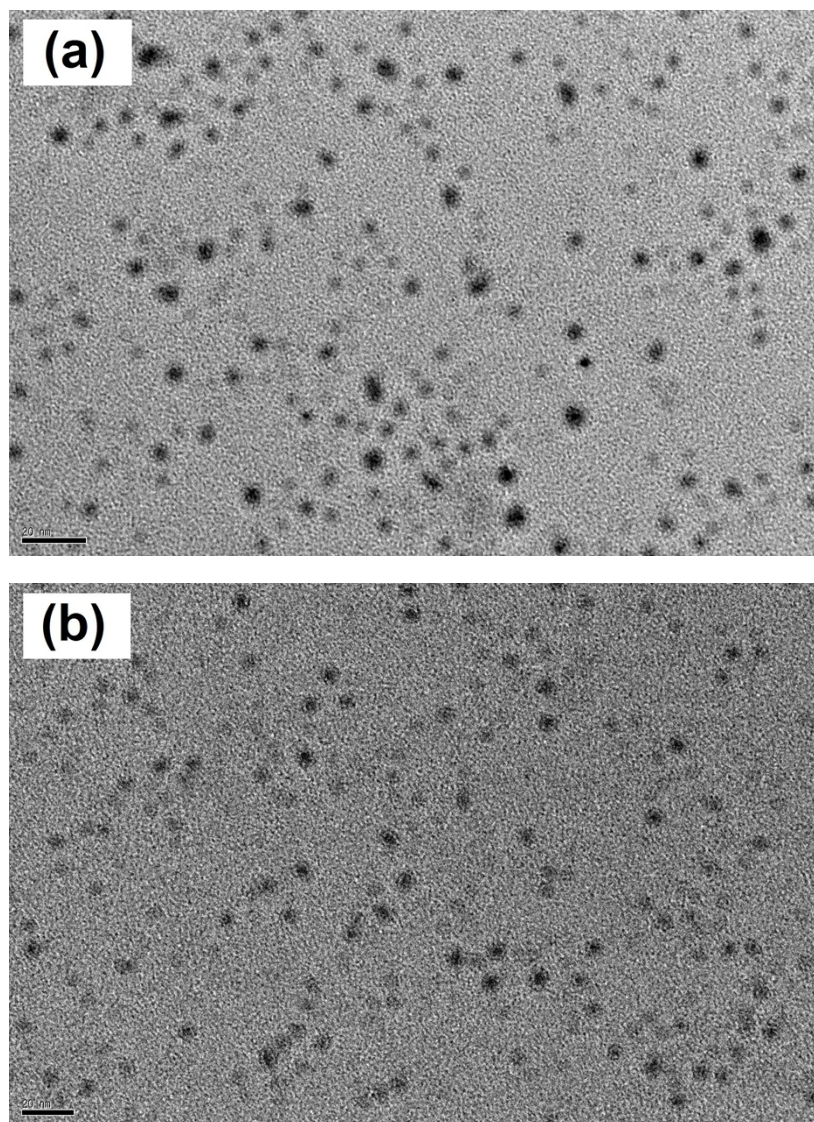


Figure S3 (a) Typical HRTEM image of initial $[\text{Ag}_{62}\text{S}_{13}(\text{SBu}^+)_{32}]^{4+}$. (b) After addition of 1equiv Cu^{2+} . The scale bar is 20 nm.

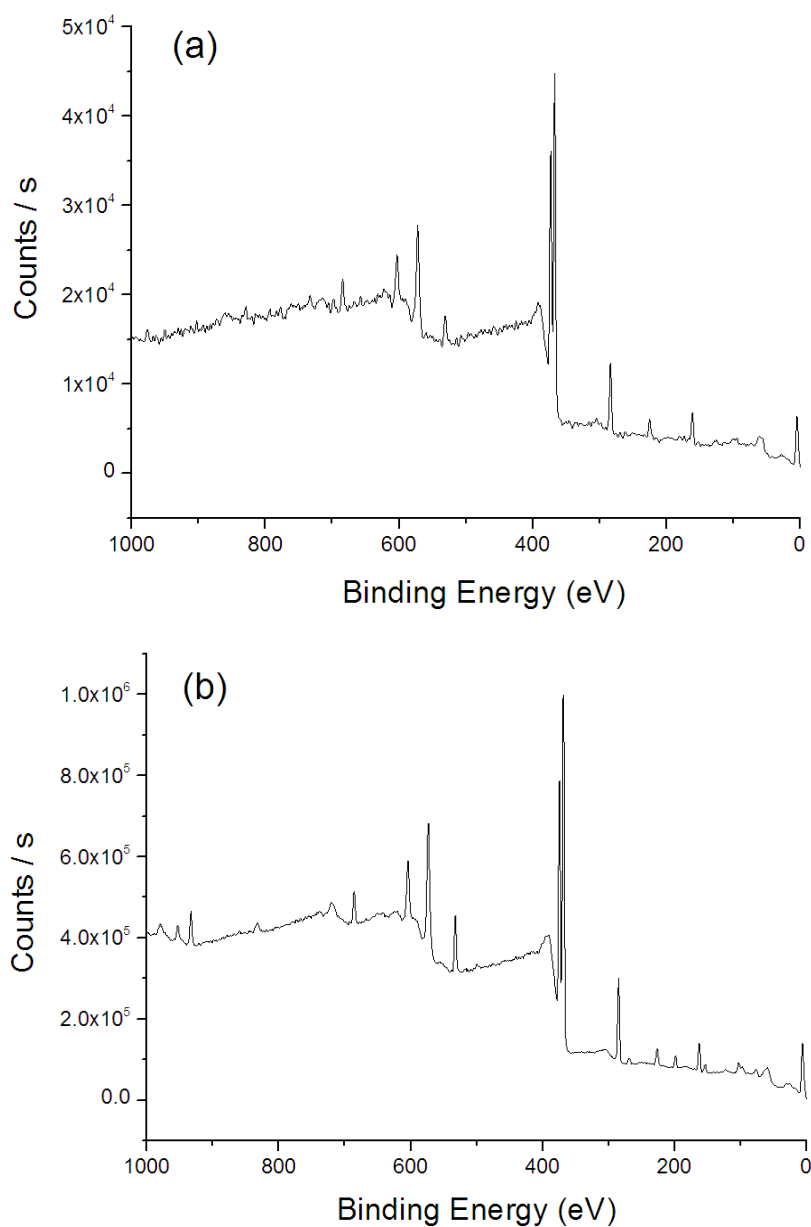


Figure S4 survey energy of (a) [Ag₆₂S₁₃(SBu^t)₃₂]⁴⁺ NCs, (b) [Ag₆₂S₁₃(SBu^t)₃₂]⁴⁺ NCs after addition of 1 equiv Cu(II).

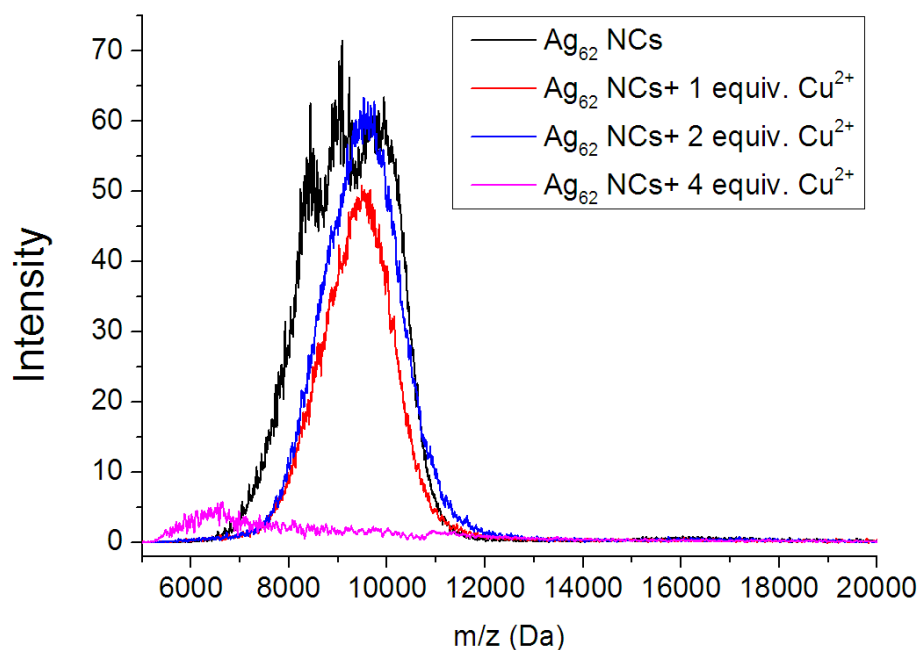


Figure S5 MALDI-TOF mass spectra of the $[\text{Ag}_{62}\text{S}_{13}(\text{SBu}^t)_{32}]^{4+}$ NCs (black line) before and after addition of 1 equiv Cu^{2+} (red line), 2 equiv (blue line) and 4 equiv (Magenta line), respectively.

References

1. G. Li, Z. Lei, Q. -M. Wang, *J. Am. Chem. Soc.* **2012**, *132*, 17678.
2. W. Luo, K. He, T. Xia, X. Fang, *Anal. Bioanal. Chem.* **2013**, *405*, 43.