

Supporting Information For

Lighting Up Thiolated Au@Ag Nanoclusters via Aggregation-Induced Emission

*Xinyue Dou,[‡] Xun Yuan,[‡] Yong Yu, Zhentao Luo, Qiaofeng Yao, David Tai Leong, and Jianping
Xie^{*}*

Department of Chemical and Biomolecular Engineering, National University of Singapore, 4
Engineering Drive 4, 117576, Singapore

[‡] These two authors contributed equally to this work.

CORRESPONDING AUTHOR FOOTNOTE. * To whom the correspondence should be
addressed.

E-mail: chexiej@nus.edu.sg; Tel: +65 6516 1067

EXPERIMENTAL SECTION

1. Materials

All chemicals were used as received: hydrogen tetrachloroaurate(III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) from Alfa Aesar; silver nitrate (AgNO_3) and sodium hydroxide (NaOH) from Merck; L-cysteine (Cys), L-glutathione reduced (GSH), 2,5-dihydroxybenzoic acid (DHB) from Sigma-Aldrich. Ultrapure Millipore water (18.2 M Ω) was used throughout the study. All glassware and poly-tetrafluoroethylene-coated magnetic stir bars were cleaned with *aqua regia* and rinsed with copious water and ethanol before drying in the oven.

2. Instruments

UV-vis absorption and luminescence spectra were recorded on a Shimadzu UV-1800 spectrometer and a PerkinElmer LS55 fluorescence spectrometer, respectively. Luminescence lifetimes were analyzed by the time-correlated single-photon counting (TCSPC) on a Horiba Jobin Yvon Fluorolog-3 spectrofluorometer. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos AXIS Ultra^{DLD} spectrometer (Kratos Analytical Ltd). Transmission electron microscopy (TEM) was carried out on a JEOL JEM 2010 microscope operating at 200 kV. The size of the NCs was measured by matrix-assisted laser desorption ionization-time-of-flight (MALDI-TOF) mass spectrometry on a Bruker Daltonics Autoflex II TOF/TOF system. Saturated DHB solution was selected as the matrix for MALDI-TOF measurements. Dialysis tubing of 3000 Da molecular weight cut off (MWCO) was used for the purification of the NCs. The composition of the NCs was analyzed by inductively coupled plasma - mass spectroscopy (ICP-MS) on an Agilent 7500A. Native polyacrylamide gel electrophoresis (PAGE) was carried out on a Bio-Rad Mini-Protean Tetra Cell system. 30 and 4 wt% acrylamide monomers were prepared for resolving and stacking gels, respectively. Sample solutions were loaded in the stacking gel. The electrophoresis was allowed to run at 4 °C with a constant voltage of 170 V.

3. Synthesis of Highly Luminescent GSH-Protected Au@Ag NCs.

The parental $\text{Au}_{18}(\text{SG})_{14}$, $\text{Au}_{15}(\text{SG})_{13}$, and $\text{Au}_{25}(\text{SG})_{18}$ NCs were prepared by a reported carbon monoxide (CO)-reduction method.^{1, 2} The as-prepared Au NCs were then purified by dialysis for about 9 h. To synthesize Au@Ag NCs, an aqueous AgNO_3 solution (0.5 mL, 2 mM) was introduced to the purified parental Au_{18} NCs (5 mL, 0.8 mM) under a vigorous stirring condition (1000 rpm). The reaction was allowed to proceed for ~15 min, and the as-synthesized $\text{Au}_{18}@\text{Ag}$ NCs were collected for further characterizations.

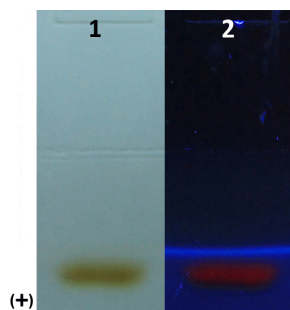


Figure S1. Digital photos of the PAGE gel of the as-synthesized luminescent Au₁₈@Ag NCs under visible (lane 1) and UV (lane 2) light.

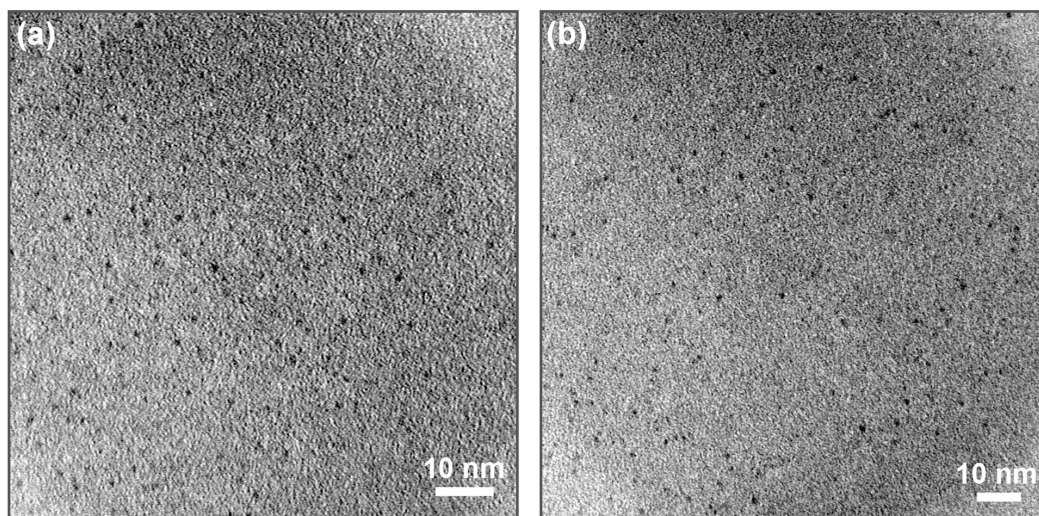


Figure S2. Representative TEM images of (a) the parental Au₁₈ NCs and (b) the as-synthesized luminescent Au₁₈@Ag NCs.

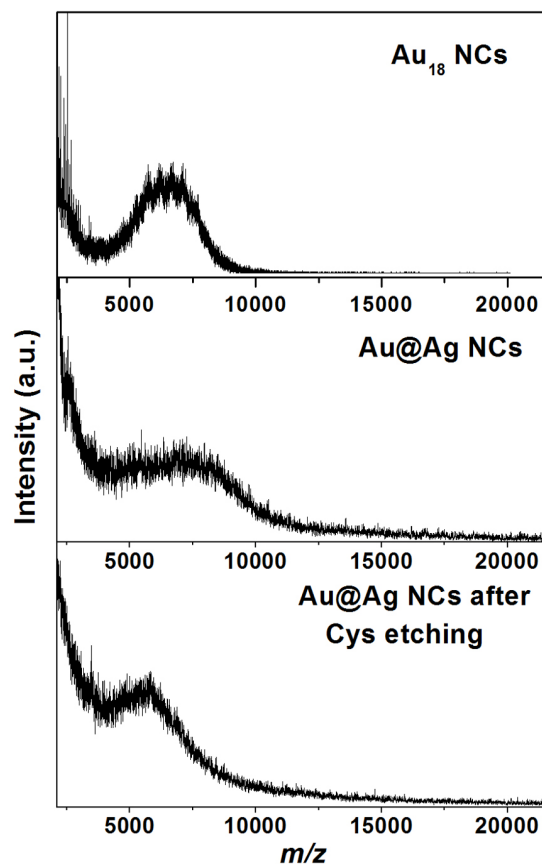


Figure S3. MALDI-TOF mass spectra of the parental Au_{18} NCs (top panel), as-synthesized luminescent $\text{Au}_{18}\text{@Ag}$ NCs (middle panel), and luminescent $\text{Au}_{18}\text{@Ag}$ NCs after the addition of a certain amount of Cys (bottom panel).

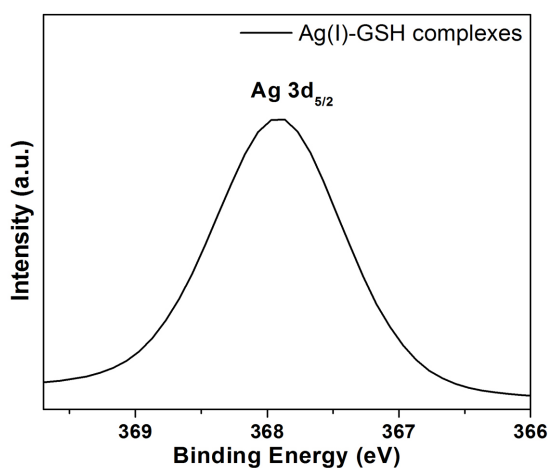


Figure S4. XPS spectrum of the Ag 3d species of the Ag(I)-GSH complexes.

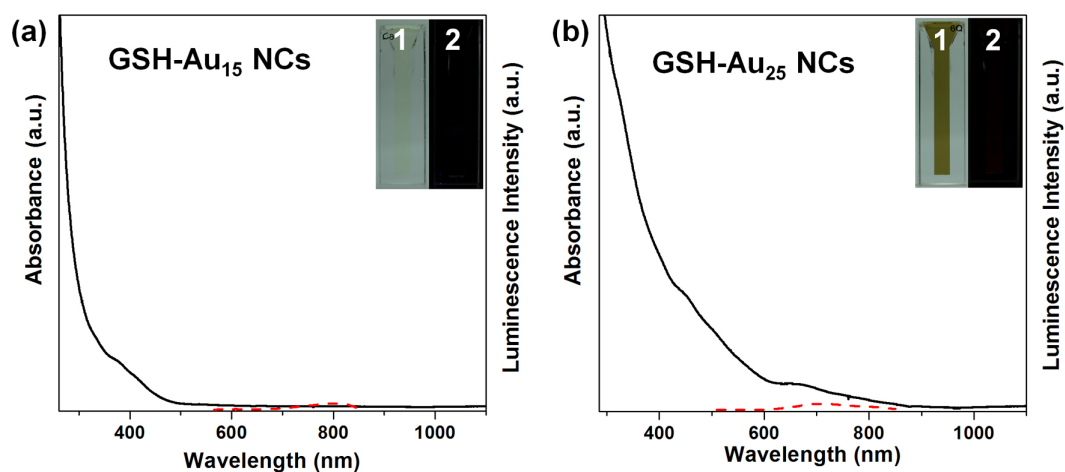


Figure S5. Optical absorption (solid lines), photoemission (dash lines) spectra, and digital photos (insets) of (a) the parental Au₁₅(SG)₁₃ NCs and (b) Au₂₅(SG)₁₈ NCs. Item 1 and 2 in the insets are taken under normal and UV light, respectively.

References

- 1 Y. Yu, Z. Luo, Y. Yu, J. Y. Lee and J. Xie, *ACS Nano*, 2012, **6**, 7920.
- 2 Y. Yu, X. Chen, Q. Yao, Y. Yu, N. Yan and J. Xie, *Chem. Mater.*, 2013, **25**, 946.