

SUPPORTING INFORMATION

Reactivity of $[\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}]^-$ Nanoparticles with Metal Ions

Jai-Pil Choi,[†] Christina A. Fields-Zinna, Rebecca L. Stiles,[‡] Ramjee Balasubramanian,[§] Alicia D. Douglas,[#] Matthew C. Crowe, and Royce W. Murray*

Kenan Laboratories of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599-3290

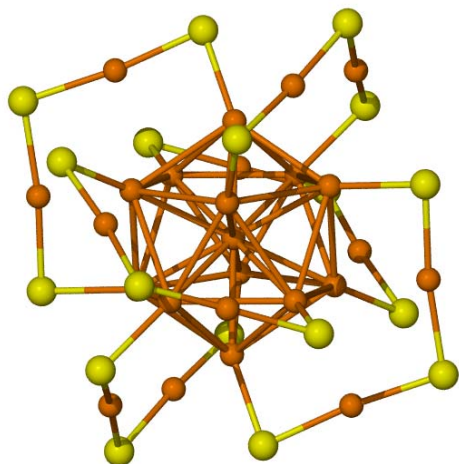


Figure S-1. Crystal structure of $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}$, where smaller orange balls are Au atoms, and larger yellow balls are sulfur atoms (the rest of ligand, $-\text{CH}_2\text{CH}_2\text{Ph}$, is not pictured). Image emphasizes the Au_2L_3 semi-rings. From Ref. 9.

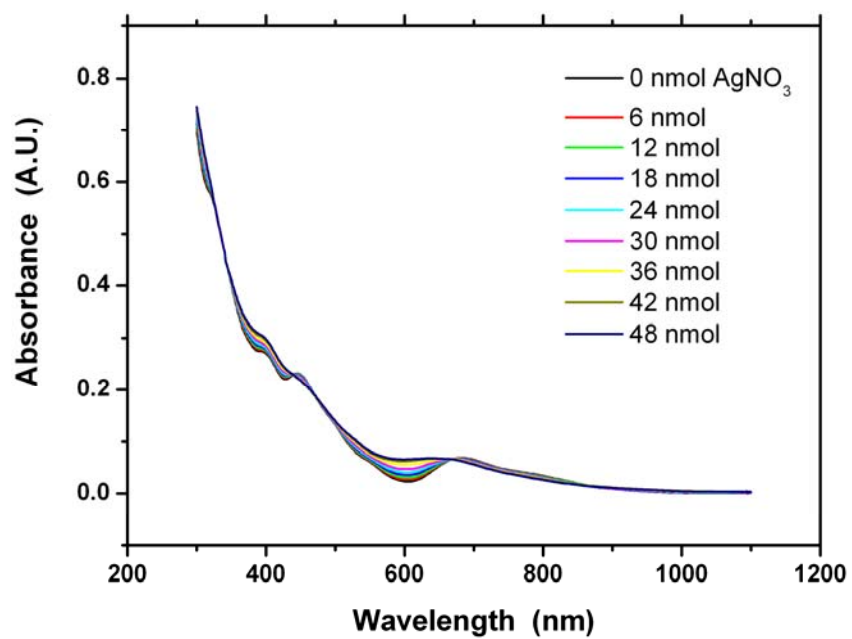


Figure S-2. Full-range (300 ~ 1100 nm) UV-Vis spectra of 46 nmole Au_{25}^- in CH_2Cl_2 titrated by Ag^+ (added as 10 mM AgNO_3 in acetonitrile).

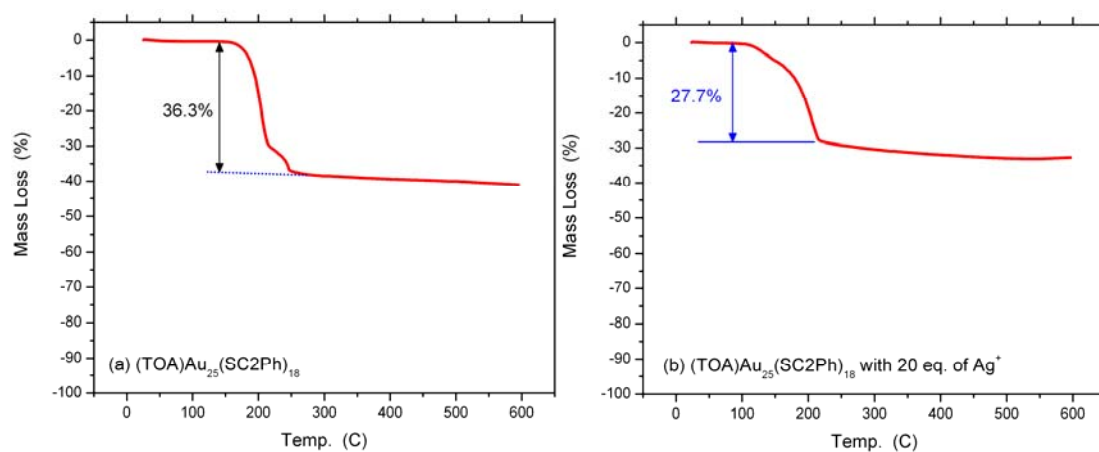


Figure S-3. Thermogravimetric analysis of (a) $(\text{Oct}_4\text{N}^+)[\text{Au}_{25}(\text{SC}_2\text{Ph})_{18}^-]$ and (b) after reaction with 20 equivalents of Ag^+ .

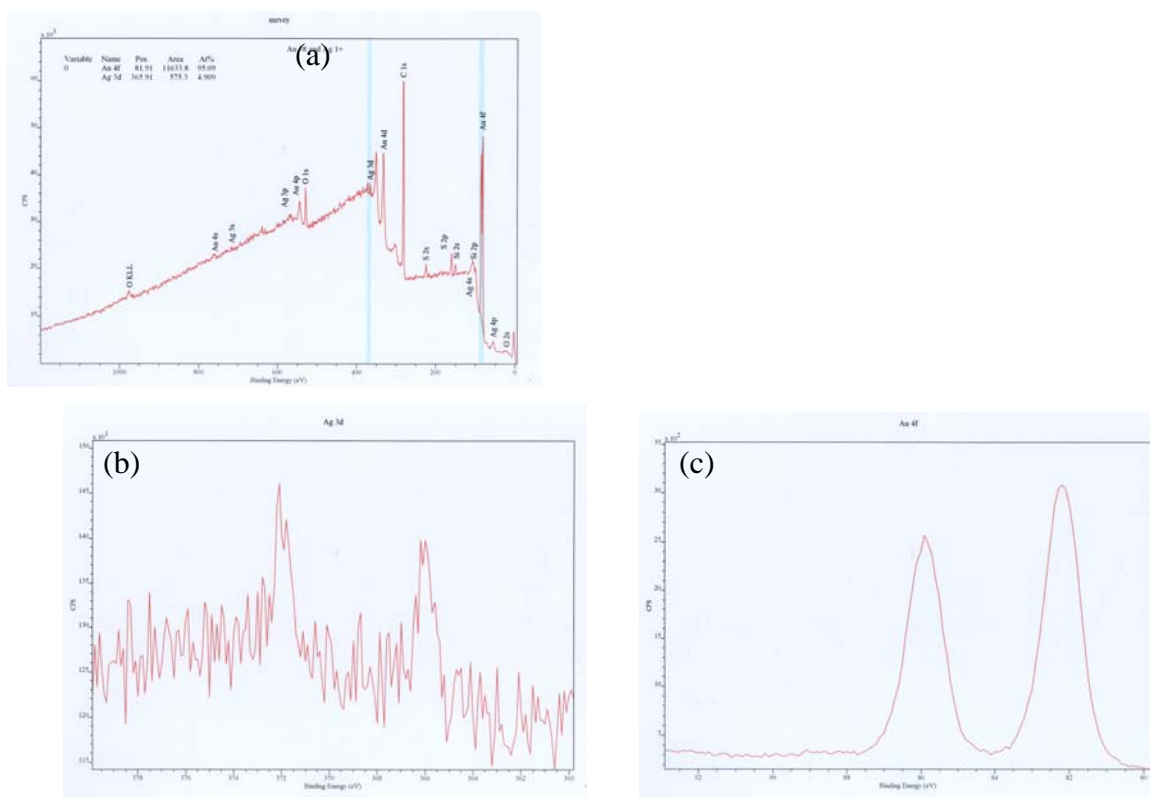


Figure S-4. X-ray photoelectron spectra of the Au_{25}^- nanoparticles after reaction with 20 equivalents of Ag^+ . After the reaction, the solvent was removed and the sample was washed with methanol to get rid of AgNO_3 residues. (a) survey scan, (b) 3d-Ag, and (c) 4f-Au.

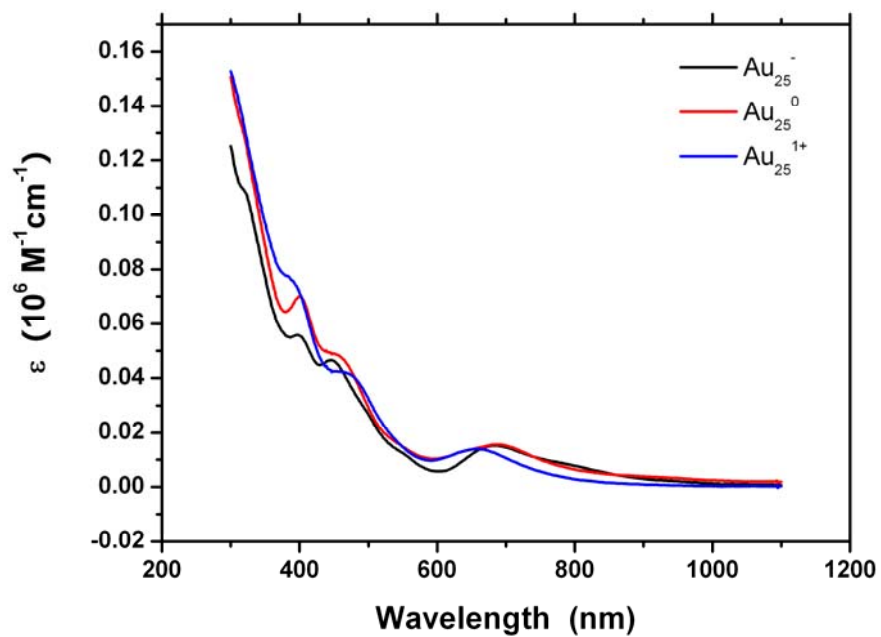


Figure S-5. UV-vis absorption spectra of Au_{25}^- , Au_{25}^0 , and Au_{25}^{1+} . Au_{25}^0 and Au_{25}^{1+} were prepared by chemically oxidizing Au_{25}^- with an aqueous $\text{Ce}(\text{SO}_4)_2$ solution. The charge states of Au_{25} were estimated by measuring the rest potentials (E_{REST}) of the oxidized Au_{25} solution, in reference to voltammetrically assessed formal potentials.

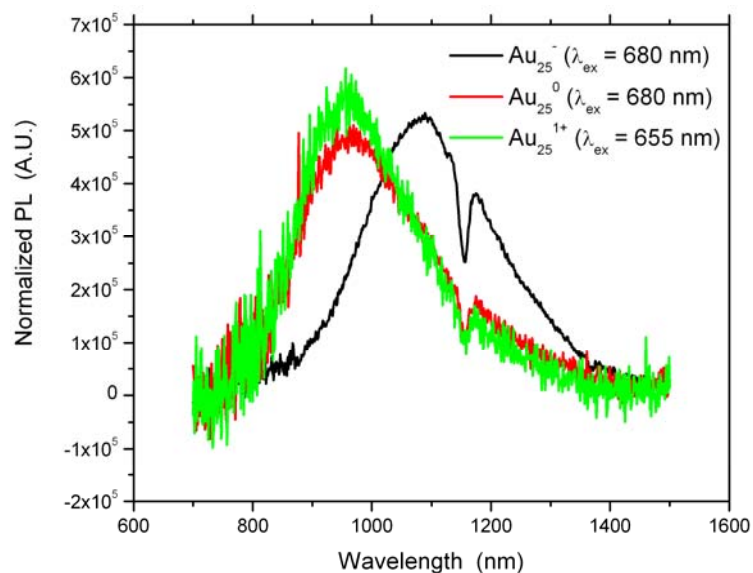


Figure S-6. Photoluminescence spectra of Au₂₅⁻, Au₂₅⁰, and Au₂₅¹⁺. Au₂₅⁰ and Au₂₅¹⁺ were prepared by chemically oxidizing Au₂₅⁻ with an aqueous Ce(SO₄)₂ solution. The charge states of Au₂₅ were estimated by measuring the rest potentials (E_{REST}) of the oxidized Au₂₅ solution.

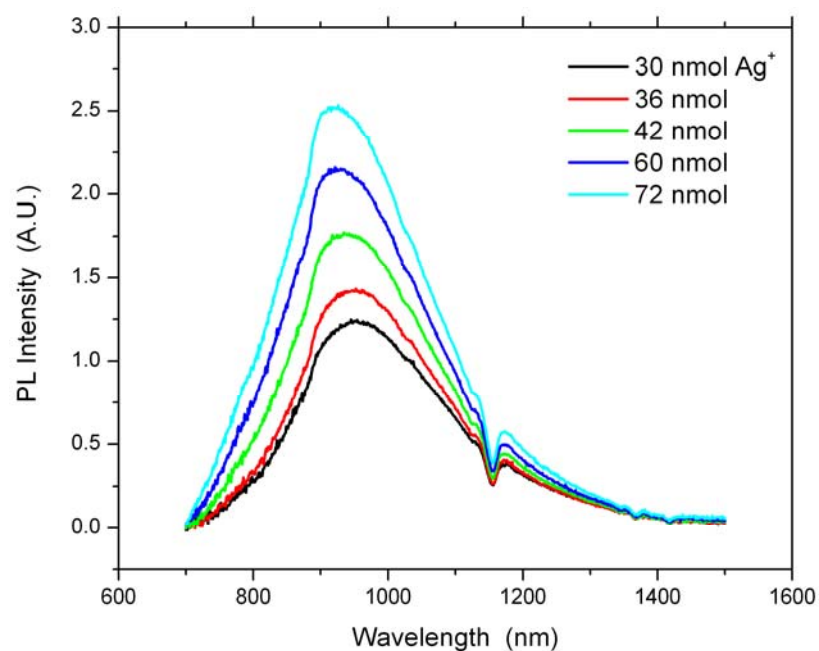


Figure S-7. Photoluminescence spectra of Au_{25}^- titrated by Ag^+ . $\lambda_{\text{EX}} = 400$ nm. 32.4 nmole Au_{25}^- MPCs in CH_2Cl_2 titrated with 30 ~ 72 nmole Ag^+ . Additions of smaller equivalents of Ag^+ are shown in the manuscript figure.

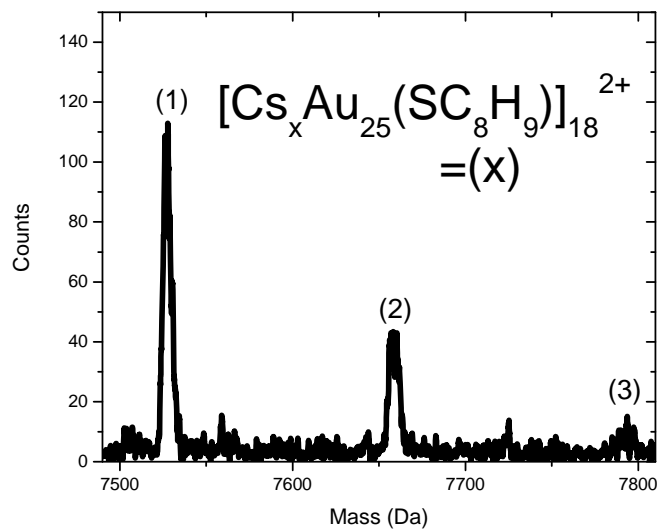


Figure S-8. Electrospray ionization (ESI) – TOF mass spectrum of Au_{25}^- obtained with 2.6 mg CsOAc (OAc = acetate) per mg MPCs in 70:30 methanol: CH_2Cl_2 . The numbers in parentheses represents the number of bound Cs^+ ions.

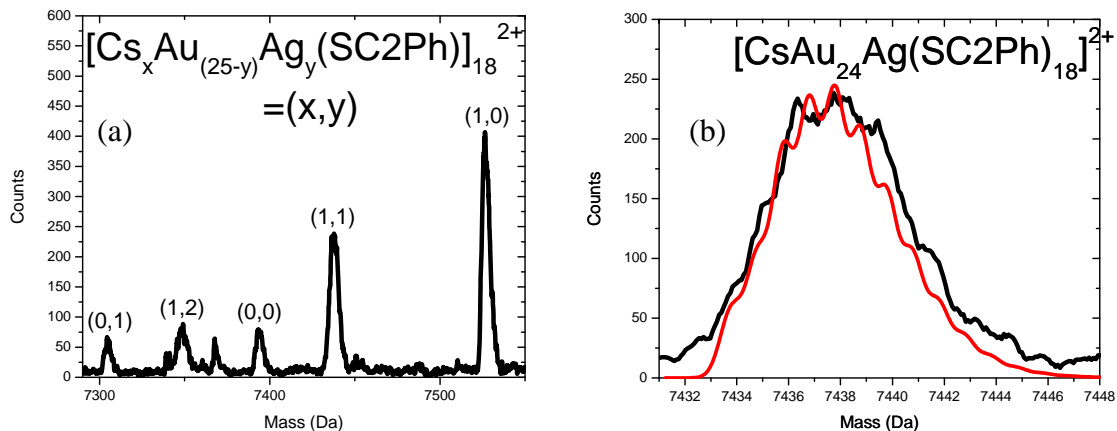


Figure S-9. (a) Electrospray ionization (ESI) – TOF mass spectrum of Au₂₅ with 1.5 equivalents of Ag⁺. 2.6 mg of CsOAc (OAc = acetate) per mg MPC was added to 70:30 methanol:CH₂Cl₂ to obtain the spectra. The numbers in parentheses correspond to x and y of MPC formula. (b) High-resolution analysis of $[\text{CsAu}_{24}\text{Ag}(\text{SC}_2\text{Ph})]^{2+}$; the red line is simulation. The sample was washed with MeOH to remove excess AgNO₃. Sample was run through ESI in a solution of 70:30 v:v methanol:CH₂Cl₂.

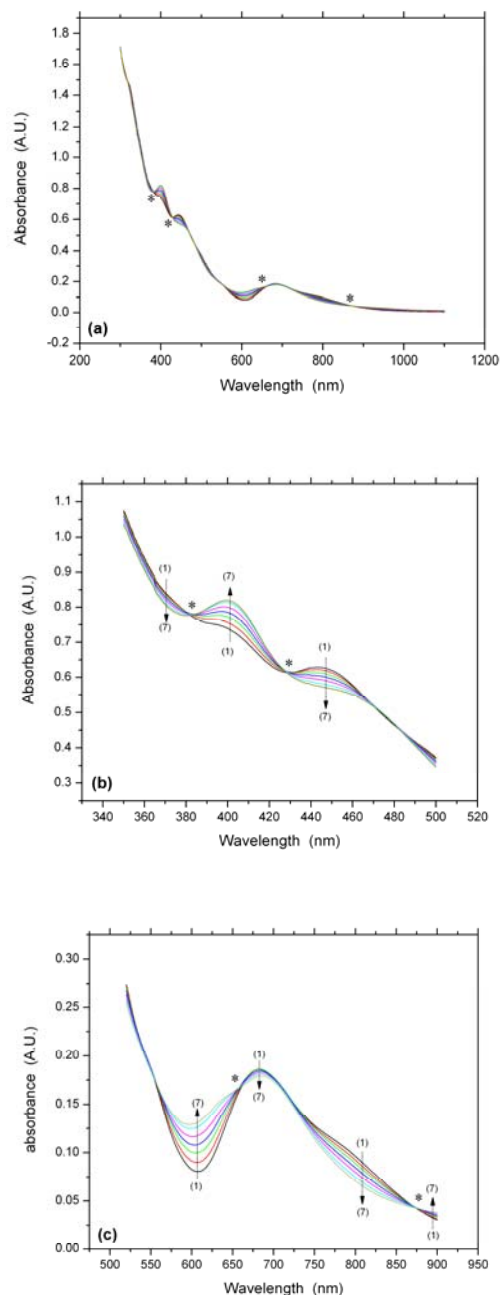


Figure S-10. UV-Vis absorption spectra of 29 μM Au_{25} MPCs in CH_2Cl_2 in the presence of Cu^{2+} , whose added concentrations are (1) 0 μM , (2) 2.3 μM , (3) 4.5 μM , (4) 6.8 μM , (5) 9.1 μM , (6) 11.3 μM , and (7) 13.6 μM . Isosbestic points are denoted as * at 383, 430, 660, and 875 nm. Cu^{2+} was added as small volumes of 6.8 mM CuCl_2 in CH_3CN .

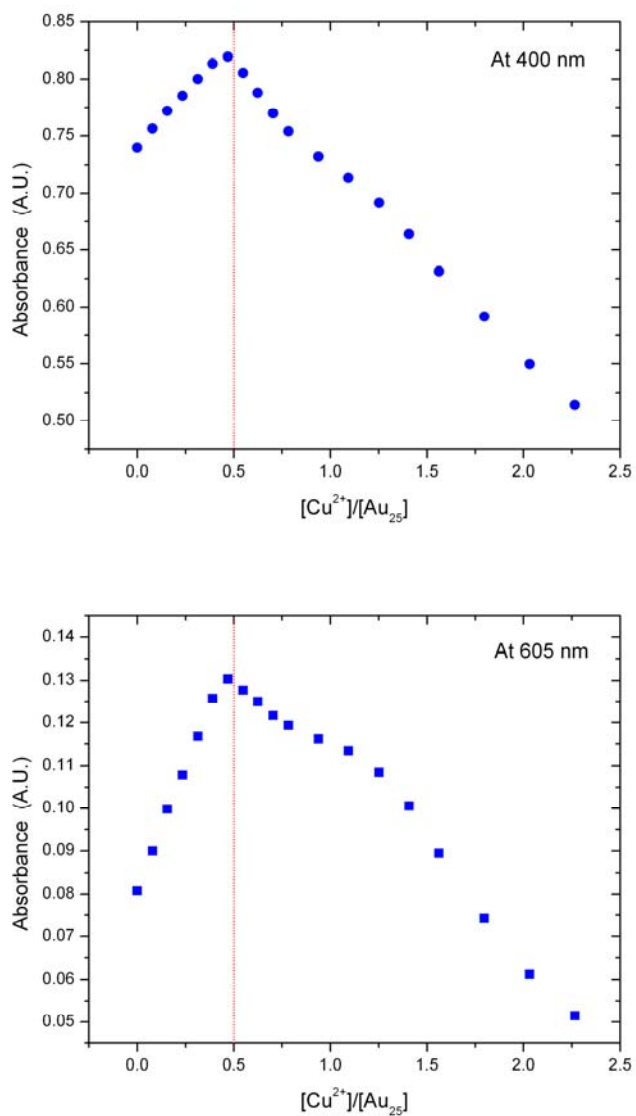


Figure S-11. Cu^{2+} titration plots of concentration ratio vs. absorbance at 400 nm and 605 nm. The initial concentration of Au_{25} MPCs in CH_2Cl_2 was 29 μM , and a 6.8 mM CuCl_2 stock solution prepared in CH_3CN was used for titration.

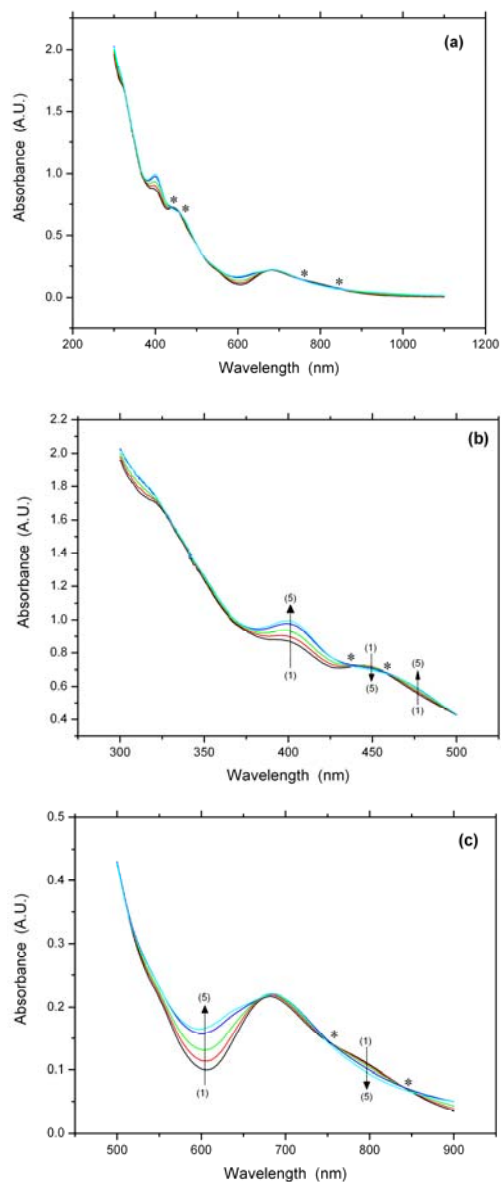
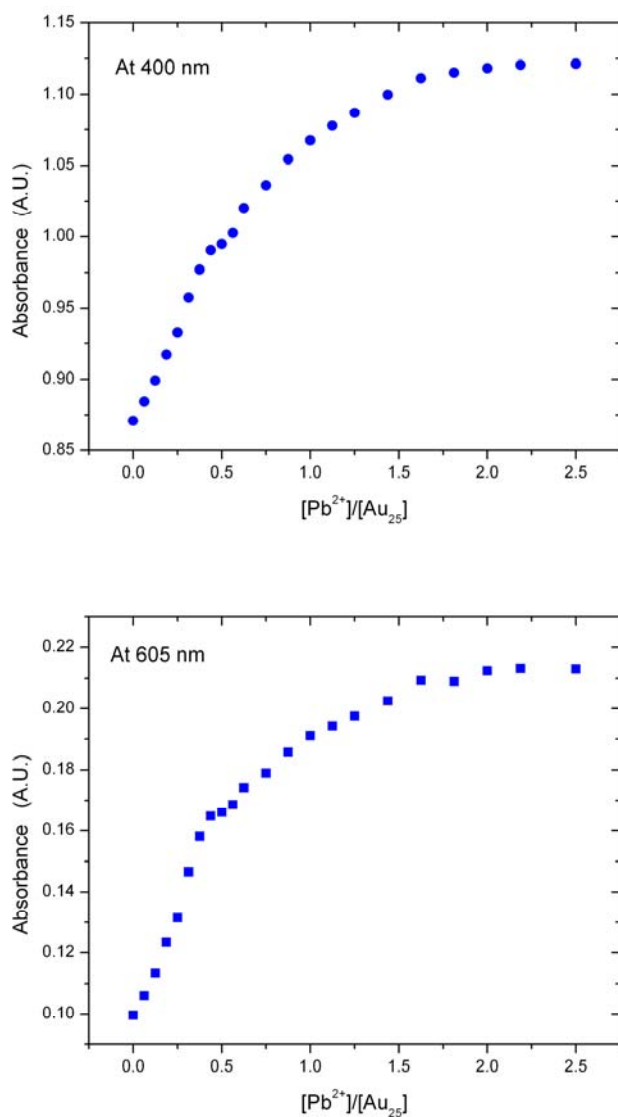


Figure S-12. UV-Vis absorption spectra of 32 μM Au_{25} MPCs in CH_2Cl_2 in the presence of Pb^{2+} , whose concentrations are (1) 0 μM , (2) 4 μM , (3) 8 μM , (4) 12 μM , and (5) 16 μM . Isosbestic points are denoted as * at 438, 458, 755, and 843 nm. For the titration of Pb^{2+} , 6.0 mM $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ in CH_3CN was used.



FigureS-13 Pb^{2+} titration plots of concentration ratio vs. absorbance at 400 nm and 605 nm. The initial concentration of Au_{25} MPCs in CH_2Cl_2 was $32\ \mu M$, and a $6.0\ mM\ Pb(ClO_4)_2 \cdot 3H_2O$ stock solution prepared in CH_3CN was used for titration.

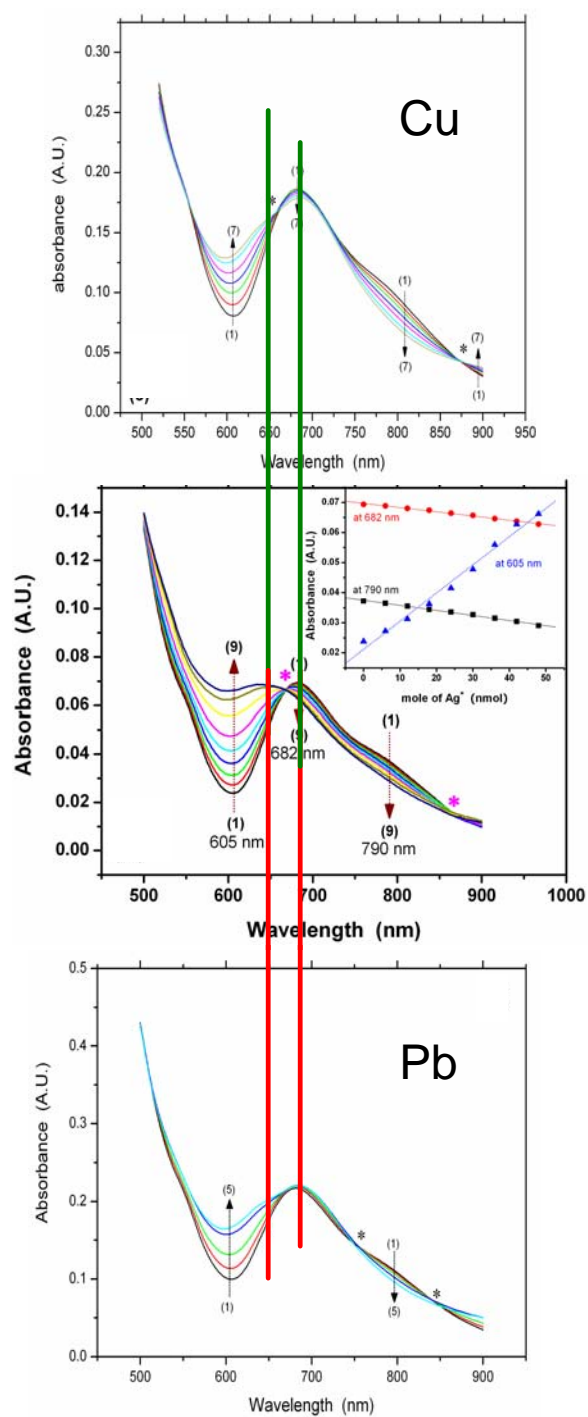


Figure S-14 Comparison of nanoparticle spectra produced by different metal ions. The vertical red bars guide the eye and show that spectra of solutions containing 1:1 Ag^+ and 0.5:1 Cu^{2+} and Pb^{2+} / nanoparticle mole ratio are subtly different.