

Supporting information:

Metal Exchange Method for Thiolate-protected Tri-metal $M_1Ag_xAu_{24-x}(SR)_{18}^0$ ($M=Cd/Hg$) Nanoclusters

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Experimental methods

Chemicals

Unless specified, reagents were purchased from ACROS Organics or Sigma-Aldrich and used without further purification. Tetrachloroauric(III) acid ($HAuCl_4 \cdot 3H_2O$, >99.99% metals basis), $AgNO_3$ (99.85%), $CdCl_2$ (99%), $HgCl_2$ (99%), $NaBH_4$ (>98%) and tetraoctylammonium bromide (TOAB) were received from ACROS Organic. Toluene (HPLC grade, $\geq 99.9\%$, Sigma-Aldrich), Ethanol (HPLC grade, $\geq 99.9\%$) and Methanol (HPLC grade, $\geq 99.9\%$) were from Sigma-Aldrich. Pure water was ordered from Wahaha Co LTD.

Synthesis of Ag^+SR , $Cd^{II}(SR)_2$ and $Hg^{II}(SR)_2$ complex

1 mL aqueous solution of metal salts ($AgNO_3$, $CdCl_2$, $HgCl_2$, concentration was set as 0.21 mM) was mixed with 5 mL ethanol. Another 7 mL ethanol solution containing 0.6 mL PhC_2H_4SH and 2 mL triethylamine was added to the first made metal salt solution under vigorous stirring. After 30 mins of stirring, the contents were taken to centrifuge. The precipitate was washed at least 3 times with ethanol to remove the excess thiol and then dried under vacuum. The white powder thiolate-metal complex was obtained.

Synthesis of $Au_{25}(SC_2H_4Ph)_{18}^- TOA^+$ nanocluster

The synthesis steps were similar to a previously reported process. In a standard synthesis for homogold $Au_{25}(SR)_{18}^-$ nanoclusters, $HAuCl_4 \cdot 3H_2O$ (0.2 g/mL, 0.4 mL) was dissolved in 5 mL pure water, and TOAB (0.254 g, 0.47 mmol) was dissolved in 10 mL toluene. The two solutions were mixed in a 25 mL round bottom flask. After ~15 min stirring (~1200 rpm), the aqueous solution turned colorless and then removed. The toluene solution of Au(III) was cooled down to 0 °C in an ice bath over a period of 30 mins. $PhCH_2CH_2SH$ (0.17 mL, ~3 equivalents per the moles of gold) was later added to the toluene solution under a slow stirring speed ~30 rpm. After the solution turned to clear (~1 hr), the stirring speed was increased to fast stirring (~1200 rpm). At the same time, a cooled aqueous solution contained 0.155 g $NaBH_4$ (4 mmol) was quickly added to the above solution to initiate the reaction. The reaction was allowed to proceed overnight. After that, the aqueous layer (at the bottom of the flask) was removed, and the toluene solution was dried via rotavaporation. Methanol (~20 mL) was added to remove the by-products and this wash/centrifugation cycle was repeated at least 3 times. Then acetonitrile (10 mL) was used to extract pure $Au_{25}(SC_2H_4Ph)_{18}^- TOA^+$ NCs.

Synthesis of $Ag_xAu_{25-x}(SR)_{18}^-$ nanoclusters by using Metal Exchange method

10 mg $Au_{25}(SC_2H_4Ph)_{18}^-$ nanocluster was dissolved in 10 mL toluene, then 10 mg Ag^+SR complex (powder) was added to the solution. The reaction was allowed to proceed for 6hr at room temperature. The product was first centrifuged to remove the unreacted Ag^+SR complex and other by-product, then extracted with acetonitrile and then evaporated to dryness.

Synthesis of $Cd_1Ag_xAu_{24-x}(SR)_{18}^0$ nanoclusters by using Metal Exchange method

10 mg $Ag_xAu_{25-x}(SR)_{18}^-$ nanocluster was dissolved in 10 mL toluene, then 10 mg $Cd^{II}SR$ complex (powder) was added to the solution. The reaction was allowed to proceed for 24hr at 40 °C. The product was first centrifuged to remove the unreacted $Cd^{II}SR$ complex and other by-product, then extracted by a mixed CH_2Cl_2 /acetonitrile solution and evaporated to dryness.

Synthesis of $\text{Hg}_1\text{Ag}_x\text{Au}_{24-x}(\text{SR})_{18}^0$ nanoclusters by using Metal Exchange method

The synthesis of Hg doped tri-metal nanocluster is similar to Cd doped one, the major different is the temperature and reaction time. 10 mg $\text{Ag}_x\text{Au}_{25-x}(\text{SR})_{18}^-$ nanocluster was dissolved in 10 mL toluene, then 10 mg $\text{Hg}^{\text{II}}\text{SR}$ complex (powder) was added to the solution under room temperature. The reaction time is quite short, 30 seconds was enough to transfer all bi-metallic nanoclusters to Hg doped tri-metallic nanoclusters.

Characterization

UV-Vis absorption spectra were obtained using an Agilent 8453 instrument, and solution samples were prepared using toluene as the solvent. ESI-TOF-MS was recorded using a Waters Q-TOF mass spectrometer equipped with Z-spray source. The source temperature was kept at 70 °C. The sample was directly infused into the chamber at 5 $\mu\text{L}/\text{min}$. The spray voltage was kept at 2.20 kV and the cone voltage at 60 V. To prepare the ESI sample, clusters were dissolved in toluene (1 mg/mL) and diluted (v/v=1:2) by dry methanol containing 5 mM CsOAc to ionize the clusters by forming Cs^+ -cluster adducts. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB 250.

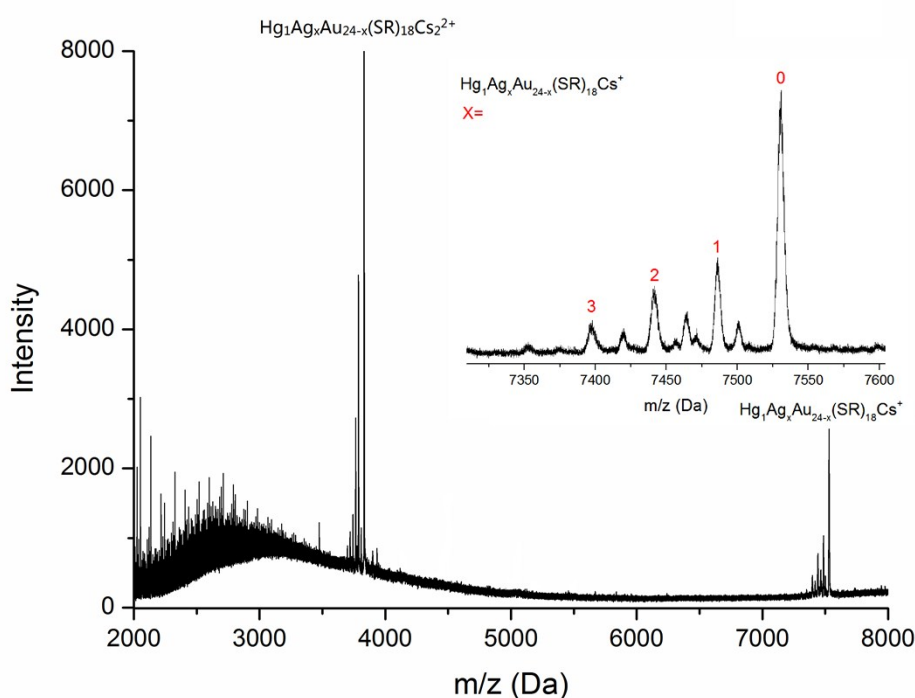


Figure S1. Positive mode ESI-MS spectrum of Hg doped tri-metallic $\text{Hg}_1\text{Ag}_x\text{Au}_{24-x}(\text{SR})_{18}^0$ nanoclusters.

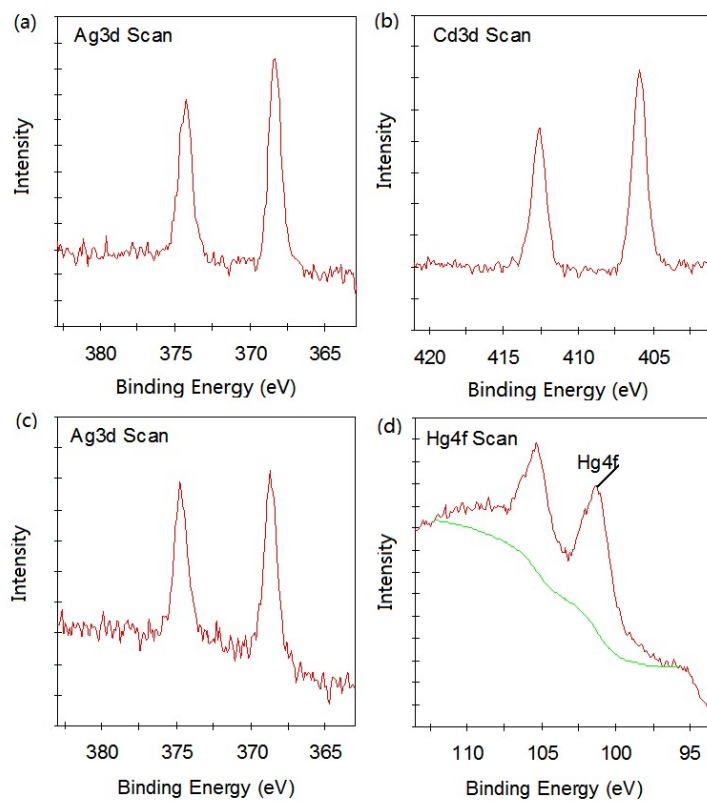


Figure S2. XPS spectra of (a) Ag 3d in $\text{Cd}_1\text{Ag}_x\text{Au}_{24-x}(\text{SR})_{18}^0$; (b) Cd 3d in $\text{Cd}_1\text{Ag}_x\text{Au}_{24-x}(\text{SR})_{18}^0$; (c) Ag 3d in $\text{Hg}_1\text{Ag}_x\text{Au}_{24-x}(\text{SR})_{18}^0$; (d) Hg 4f in $\text{Hg}_1\text{Ag}_x\text{Au}_{24-x}(\text{SR})_{18}^0$. $\text{R}=\text{C}_2\text{H}_4\text{Ph}$.