Electronic Supplementary Information

Synthesis of fluorescent phenylethanethiolated gold nanoclusters via pseudo-AGR method

ChuanhaoYao,[‡,a] ShuboTian,[‡,a] LingwenLiao,[a] Xinfeng Liu,[b] Nan Xia,[a] Nan Yan, [a] Zibao Gan, [a] and Zhikun Wu*[,a]

[a]Key Laboratory of Materials Physics, Anhui Key Laboratory of Nanomaterials and Nanostructures,Institute of Solid State Physics, Chinese Academy of Sciences, Hefei, 230031, China.
[b]National Center for Nanoscience and Technology, Chinese Academy of Sciences, Beijing, 100190, China
Email: zkwu@issp.ac.cn

1. Experimental Methods

Chemicals. All chemicals are commercially available and used as received. 2-Phenylethanethiol (PhC_2H_4SH, 99.0%) was purchased from Sigma-Aldrich. Tetrachloroauric(III) acid ($HAuCl_4·4H_2O$, 99.7%), tetrahydrofuran (THF, 99.0%), acetonitrile (CH_3CN, 99.0%), methanol (CH_3OH, 99.5%), DMSO (99.0%), dichloromethane (CH_2Cl_2, 99.0%), petroleum ether (AR) and toluene (99.5%) were purchased from Sinopharm chemical reagent co., ltd.

Synthesis of anion $Au_{25}(PET)_{18}$, $Au_{38}(PET)_{24}$ and $Au_{144}(PET)_{60}$ was referred to the previous work.[1-3]

Synthesis of Au-SC_2H_4Ph complex. $HAuCl_4·4H_2O$ was dissolved in CH_3CN and subsequently, 3 equivalents of PhC_2H_4SH was added. The reaction was proceeded for 2hrs under vigorous stirring and a colorless solution was attained indicating that the Au-SC_2H_4Ph complex was formed.[4]

Reaction of anion $Au_{25}(PET)_{18}$ with $AuCl_4^-$ ions or Au-SC_2H_4Ph complex. Excessive $AuCl_4^-$ ions or Au-SC_2H_4Ph complex (100 equivalents of $Au_{25}(SC_2H_4Ph)_{18}$) was dissolved in CH_3CN and then added into a toluene solution of $Au_{25}(SC_2H_4Ph)_{18}$. After addition of excessive $AuCl_4^-$ ions to $Au_{25}(SC_2H_4Ph)_{18}$, the color of solution rapidly turns from orange to gray and then to yellow. While in the process of reaction between $Au_{25}(SC_2H_4Ph)_{18}$ and Au-SC_2H_4Phcomplex, no remarkable color change was observed. The reaction proceeded for ~ 24 hrs at room temperature, and terminated by the addition of a large amount of petroleum ether. The precipitates were collected by

centrifugation and washed with CH_3OH for three times. After dried in vacuum, the precipitates were dissolved in dichloromethane (Of note, theprecipitates from reaction of $Au_{25}(PET)_{18}$ with $AuCl_4^-$ can not dissolved in dichloromethane) and subject subsequent separation and purification by thin-layer chromatography (TLC). The purified product was utilized for further Characterizations.

Characterizations. Electrospray ionization (ESI) mass spectra were recorded on a Waters Q-TOF mass spectrometer equipped with Z-spray source and the source temperature kept at 70 ^oC. To prepare the ESI sample, $Au_{24}(SC_2H_4Ph)_{20}$ was dissolved in toluene (~ 0.5 mg/mL) and diluted (1:1v/v) with ethanol solution containing 0.5 mM CsOAc. The sample was directly infused into the chamber at 5 μL/min. The spray voltage was 2.20 kV and the cone voltage was kept at 60 V. The UV/vis/NIR absorption was measured on a UV-2600 spectrophotometer (Shimadzu, Japan) at room temperature. Thermal gravimetric analysis (TGA) (~ 2 mg sample used) was conducted in a N_2 atmosphere (flow rate ~ 50 mL/min) on a TG/DTA 6300 analyzer (Seiko Instruments, Inc), and the heating rate was 10 ^oC/min. Fluorescence spectra were recorded on a Fluoromax-4 spectrofluorometer (HORIBA JobinYvon), and the excitation wavelength was kept at 440nm with slit of 20 nm. Fluorescent lifetimes were measured on a LifeSpec-Red Picosecond Lifetime Spectrometer (Edinburgh Instruments). Transmission electron microscopy (TEM) images for samples were taken by JEOL2010. The operating voltage on the microscope was 200 kV. The TLC plates were eluted with dichloromethane/petroleum ether mixture (1/2, v/v) at room temperature under Air atmosphere. Matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) was performed on an autoflex Speed TOF/TOF mass spectrometer (Bruker) in positive mode using Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-pro-penylidene] malononitrile (DCTB) as the matrix.

References

1. Z. Wu, J. Suhan and R. Jin, *J. Mater. Chem.,* 2009, **19**, 622.

2. H. Qian, W. Eckenhoff, Y. Zhu, T. Pintauer and R. Jin,*J. Am. Chem. Soc.*,2010, **132**, 8280.

3. H. Qian and R. Jin, *Chem. Mater.,* 2011, **23**, 2209.

4. M. Zhu, E. Lanni, N. Garg, M. E. Bier and R. Jin, *J. Am. Chem. Soc.*, 2008, **130**, 1138.

2. Supporting Figures

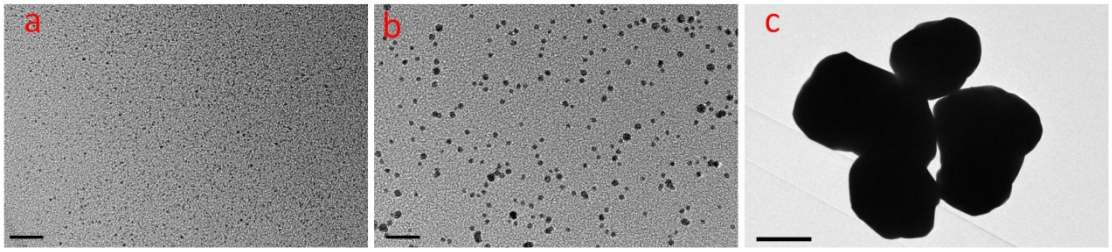

Fig. S1 TEM monitors the process of reaction between $Au_{25}(SC_2H_4Ph)_{18}$ and $AuCl_4^-$. (a): 0h; (b): 2h and (c) the final as-obtained solid. Scale bar for (a) and (b): 20 nm; Scale bar for (c): 200 nm.

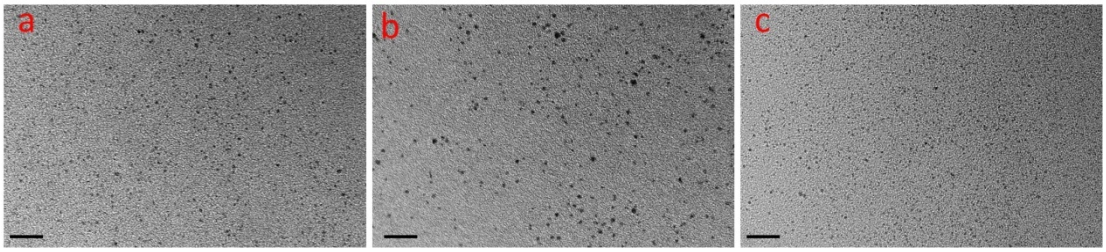

Fig. S2 TEM monitors the process of reaction between $Au_{25}(SC_2H_4Ph)_{18}$ and Au-PET complex. (a): 0h, (b):12h and (c): the final as-obtained Au_{24}. Scale bar: 20 nm.

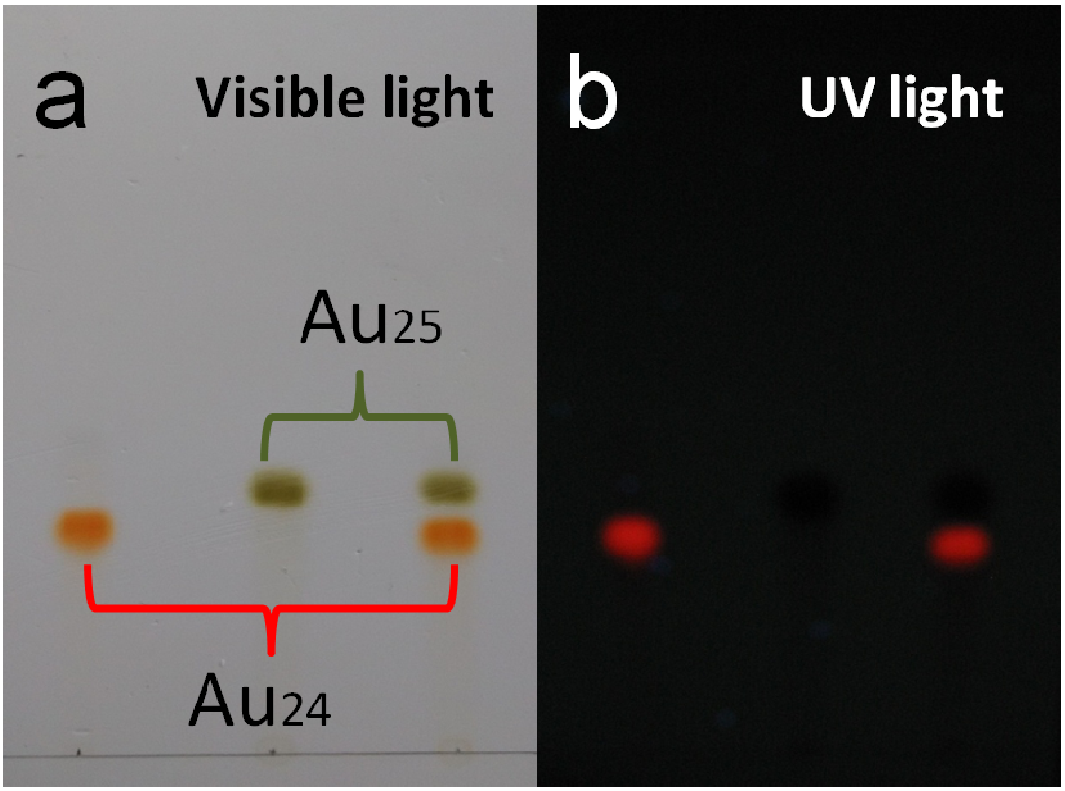

Fig. S3 Thin-layer chromatography (TLC) of the as-prepared nanoclusters and Au_{25} (Au_{24}, red and Au_{25}, dark yellow). The photos were taken under visible (left) and UV light (right), respectively.

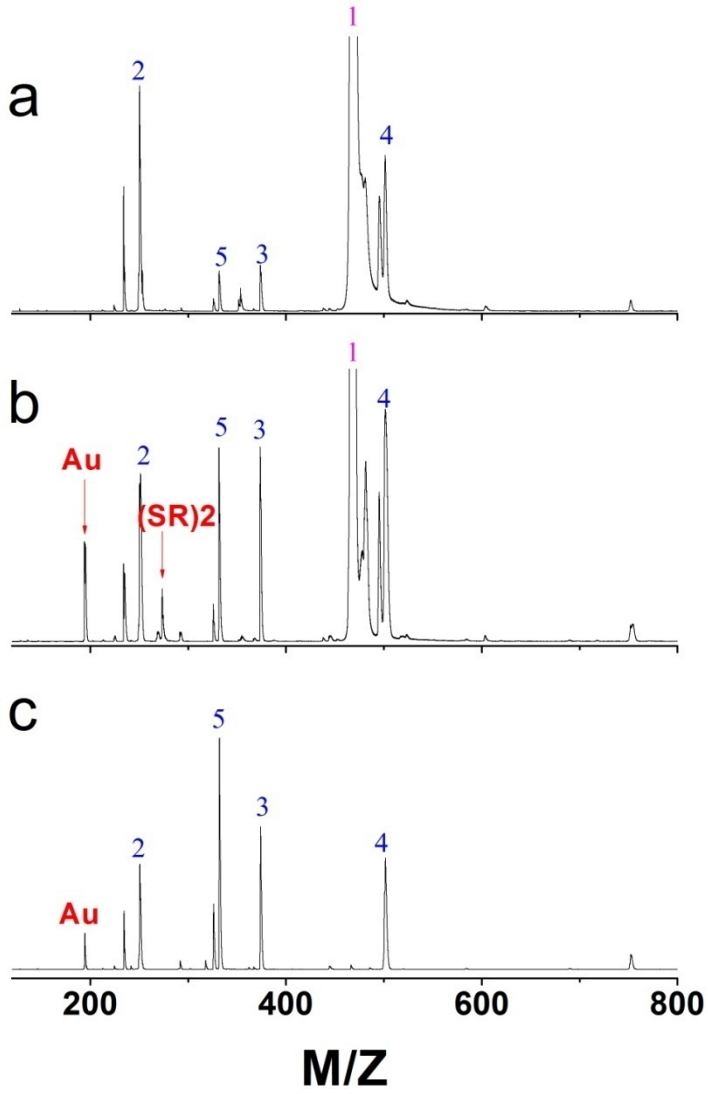

Fig. S4 Low M/Z range MALDI-MS spectra of Au_{25}, intermediate product (2h), and Au_{24}. The assignments for peaks 1-5: 1, $[TOA]^+$; 2, $[DCTB]^+$; 3, $[(DCTB)_3]^{2+}$; 4, $[(DCTB)_2]^+$; 5, $[Au(SC_2H_4Ph)]^+$.

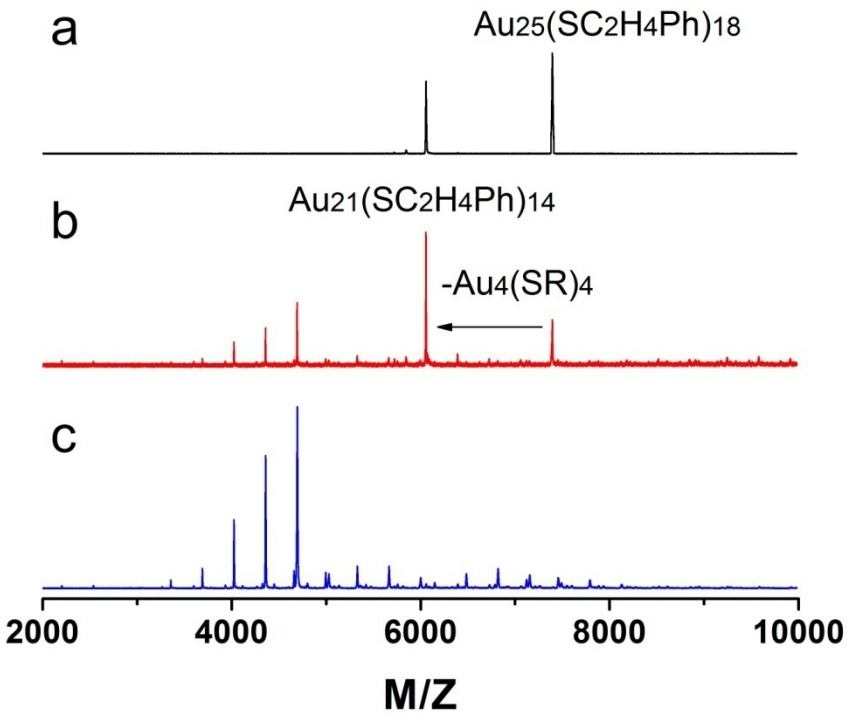

Fig. S5 High M/Z range MALDI-MS spectra of Au_{25}, intermediate product (2h), and Au_{24}.

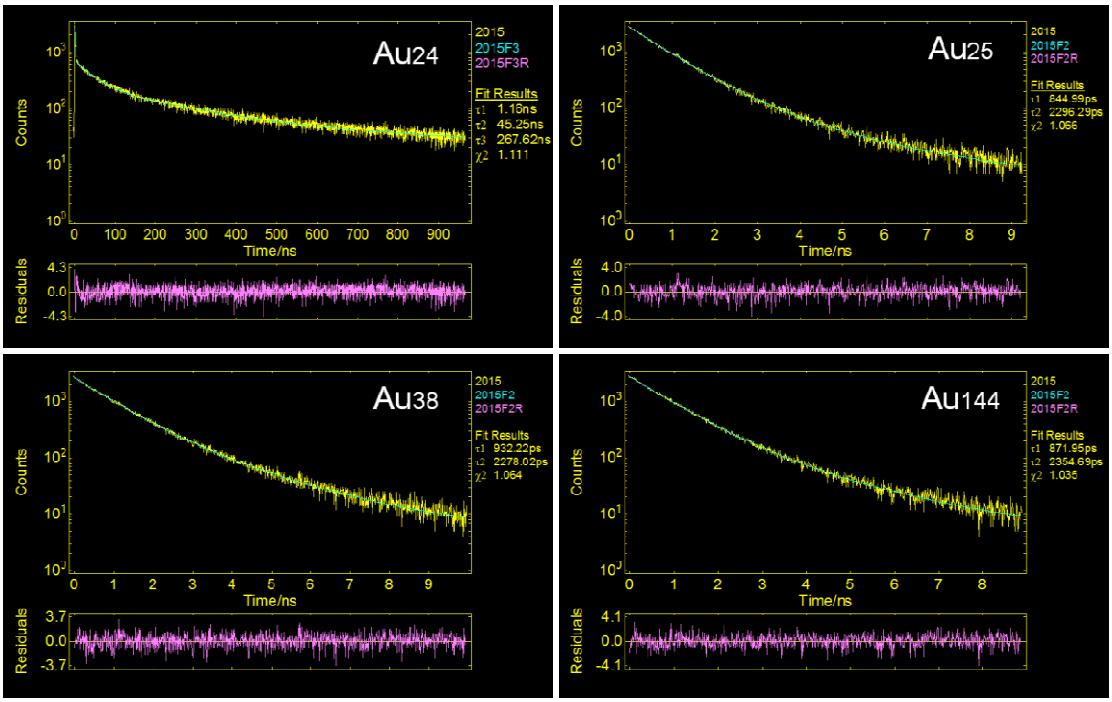

Fig. S6 Fluorescence decay profiles of Au_{24}, Au_{25}, Au_{38} and Au_{144} nanoclusters (The green curve in each figure is an exponential fit to the decay, and the violet curve shows the residuals of fitting).

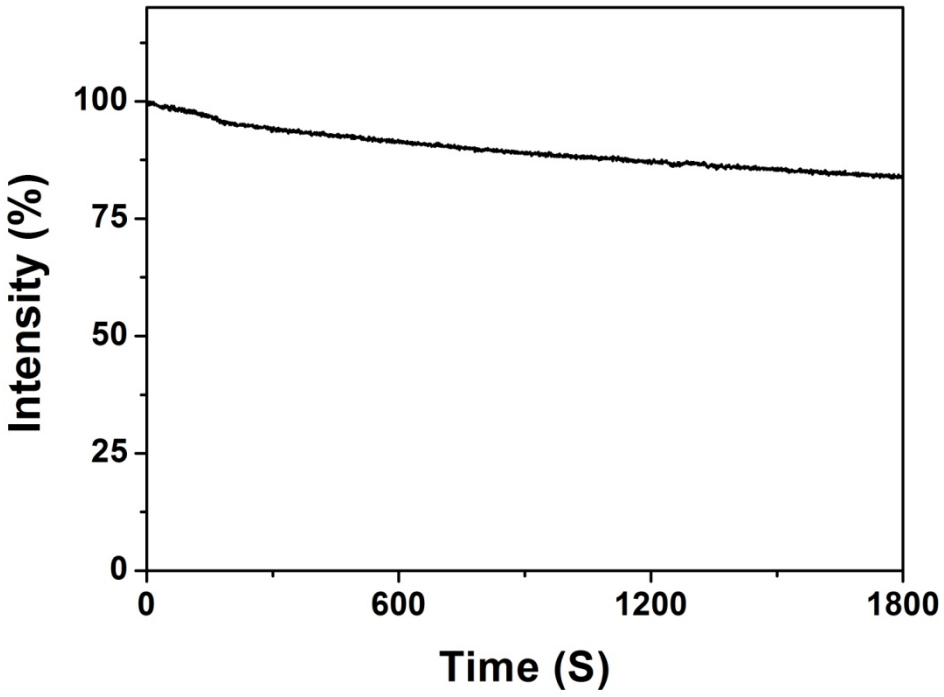

Fig. S7 Photobleaching curve of $Au_{24}(SC_2H_4Ph)_{20}$ nanocluster.