Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

ELECTRONIC SUPPLEMENTARY INFORMATION

Doping Au_{25} nanoparticles using utrasmall silver or copper nanoparticles as the metal source

Nan Xia, Zhikun Wu*

Key Laboratory of Materials Physics, Anhui Key Laboratory of Nanomaterials and Nanostructures, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, China.
E-mail: zkwu@issp.ac.cn

1. Experimental Section

Chemicals

All of the chemicals were commercially obtained and used without further purification. Captopril was purchased from Sangon Biotech. Tetrachloroauric(III) acid ($HAuCl_4{\cdot}4H_2O$, 99.7%) was purchased from Institute of Metal Research, CAS. Tetraoctylammonium bromide (TOABr, 98.0%), 2,4-Dimethylbenzenethiol and Sodium borohydride ($NaBH_4$, 99.0%) was obtained from Aladdin. 2-Phenylethanethiol (PhC_2H_4SH, 99.0%) was purchased from J&K Scientific Ltd. Silver nitrate ($AgNO_3$, 99.8%) were purchased from Shanghai chemical reagent co., Ltd. Copper nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$) was purchased from Sinopharm chemical reagent co., Ltd. α-Cyano-4-hydroxycinnamic acid (CHCA) was purchased from Sigma-Aldrich. Deionized water used in this study (resistivity of ~18 MΩ cm) was produced from a Milli-Q NANO pure water system.

Synthesis of $Au_{25}(Capt)_{18}$ was referred to Jin's work.[1]

Synthesis of $Ag_{30}(Capt)_{18}$ was referred to our previous work.[2]

Synthesis of $Au_{20}Ag_5(Capt)_{18}$

$Au_{25}(Capt)_{18}$ (15 mg, 0.0016 mmol) was dissolved in 2 ml methanol. Then 425 μl freshly made methanol solution of $Ag_{30}(Capt)_{18}$ (2 mg in 2 ml methanol) was added to the Au_{25} solution. The mixture was kept at 70°C for 2h under vigorous stirring. After that, the mixture was left in room temperature for another 3 days or more until the color of the solution became brownish red. Then the reaction mixture was centrifuged to remove the byproduct. The supernatant was collected and precipitated by adding excess acetone. The raw product was washed by acetone for 3~5 times and finally dried under vacuum. Further purification was performed using PAGE.

Synthesis of AgNPs protected by captopril

$AgNO_3$ (84.6 mg, 0.5 mmol) was dissolved in 25 ml deionized water, and captopril (141 mg, 0.65 mmol) was added, forming a green-yellow solution (pH ~1). The solution was cooled to ~$0^{o}C$ in an ice bath. After 30 min., a freshly made 5 ml aqueous solution of $NaBH_4$ (190 mg, 5.0 mmol) was added dropwise. The reaction was allowed to proceed for 2h. The particles were precipitated out by 3-fold ethanol and further recrystallized from methanol/acetone mixture.

Synthesis of AuAg alloy clusters using AgNPs

$Au_{25}(Capt)_{18}$ (15 mg, 0.0016 mmol) was dissolved in 2 ml methanol. Then freshly made methanol solution of AgNPs (1.5 mg in 1 ml methanol) was added to the Au_{25} solution. The mixture was kept at $70^{o}C$ for 2h under vigorous stirring. After that, the reaction mixture was centrifuged to remove the byproduct. The supernatant was collected and precipitated by adding excess acetone. The raw product was washed by acetone for 3~5 times and finally dried under vacuum. Further purification was performed using PAGE.

Synthesis of Au_{25} and Ag_{25} clusters protected by 2,4-dimethylbenzenethiol (DMBT) was referred to Bakr's work.[3]

Synthesis of AuAg alloy clusters protected by DMBT

Au_{25} (7.4 mg, 0.001 mmol) was dissolved in 1 ml toluene. Then Ag_{25} (1.3 mg in 0.5 ml toluene) was added to the Au_{25} solution. The mixture was kept at ambient temperature for 1h under vigorous stirring. Then the reaction mixture was precipitated by adding excess petroleum ether. The raw product was washed by petroleum ether for 3~5 times and finally dried under vacuum. Further purification was performed using TLC.

Synthesis of $Ag_{152}(PET)_{60}$ was referred to Pradeep's work.[4]

Synthesis of AuAg alloy clusters protected by PET

$Au_{25}(PET)_{18}$ (15 mg, 0.002 mmol) was dissolved in 2 ml toluene. Then freshly-made toluene solution of $Ag_{152}(PET)_{60}$ (2 mg in 0.5 ml toluene) was added to the Au_{25} solution. The mixture was kept at $80^{o}C$ for 2h under vigorous stirring. Then the reaction mixture was precipitated by adding excess petroleum ether. The raw product was washed by petroleum ether for 3~5 times and finally dried under vacuum. Further purification was performed using TLC.

Synthesis of Cu nanoparticles protected by captopril

Cu nanoparticles were prepared in reference to a previous method.[2] In a typical experiment, $Cu(NO_3)_2{\cdot}3H_2O$ (60 mg, 0.25 mmol) was dissolved in 25 ml deionized water, and captopril (163 mg, 0.75 mmol) was added, forming a green-yellow suspension. Then, NaOH was used to adjust the pH value to ~11. The solution was cooled to ~$0^{o}C$ in an ice bath. After 30 min., a freshly made 5 ml aqueous solution of $NaBH_4$ (94 mg, 2.5 mmol) was added dropwise. The reaction was allowed to proceed for 24h. The Cu nanoparticles were stored in the above reaction solution at $4^{o}C$ due to its instability. When used, the clusters were precipitated by 3-fold ethanol and further recrystallized from methanol/acetone mixture.

Synthesis of AuCu alloy clusters protected by captopril

$Au_{25}(Capt)_{18}$ (15 mg, 0.0016 mmol) was dissolved in 2 ml methanol. Then 750 µl freshly made methanol solution of $Cu_x(Capt)_y$ (6.8 mg in 2.5 ml methanol) was added to the Au_{25} solution. The mixture was kept at 70^oC for 2h under vigorous stirring. Then the reaction mixture was centrifuged to remove the byproduct. The supernatant was collected and precipitated by adding excess acetone. The raw product was washed by acetone for 3~5 times and finally dried under vacuum. Further purification was performed using PAGE.

Purification by polyacrylamide gel electrophoresis (PAGE)

Acrylamide gels (20% monomer and 5% crosslinker) in a tris(hydroxymethyl)aminomethane base buffer of pH ~8 was used for separation. The dried samples were dissolved in ~250 µl 10 vol% glycerol and were loaded onto a 1.5 mm gel. The electrophoresis was allowed to run for 2~4 h at a constant voltage of 110 V at room temperature. The bands containing differently sized clusters were individually cut, crushed, and incubated in ultrapure water to allow the products in the gels to diffuse out. The resulting solutions were filtered by a filter (0.22 µm pore size) to remove the gel lumps. The purified clusters are precipitated from the collected solution by acetone and finally dried under vacuum.

Characterization

UV/vis absorption spectra of the clusters were recorded at room temperature on a UV/Vis/NIR spectrophotometer (Shimadzu, UV2600). Fluorescence spectra were recorded on a Fluoromax-4 spectrofluorometer (HORIBA Jobin Yvon). The photobleaching study was also conducted on the Fluoromax-4 spectrofluorometer by monitoring the maximum emission intensity change after continuous exciting for 30 min. Ex/Em: 470/686 nm ($Au_{20}Ag_5(Capt)_{18}$); 346/460 nm (Hoechst 33342); 500/526 nm (Acridine orange). Matrix-assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF-MS) was performed on an autoflex Speed TOF/TOF mass spectrometer (Bruker). CHCA was used as the matrix for water-soluble clusters. X-ray Photoelectron Spectroscopy (XPS) measurements were performed on an ESCALAB 250Xi XPS spectrometer (ThermoScientific, America), using a monochromatized Al Kα source and equipped with an Ar+ ion sputtering gun. Thermal gravimetric analysis (TGA) were carried out with a TG/DTA 6300 analyzer (Seiko Instruments, Inc.), at a heating rate of 10 °C min^{-1} in N_2 atmosphere (flow rate ~50 mL min^{-1}). ICP-AES measurements were conducted on Inductively Coupled Plasma Optical Emission Spectrometer (iCAP 6300 ICP, Thermo Scientific).

2. Supporting Figures

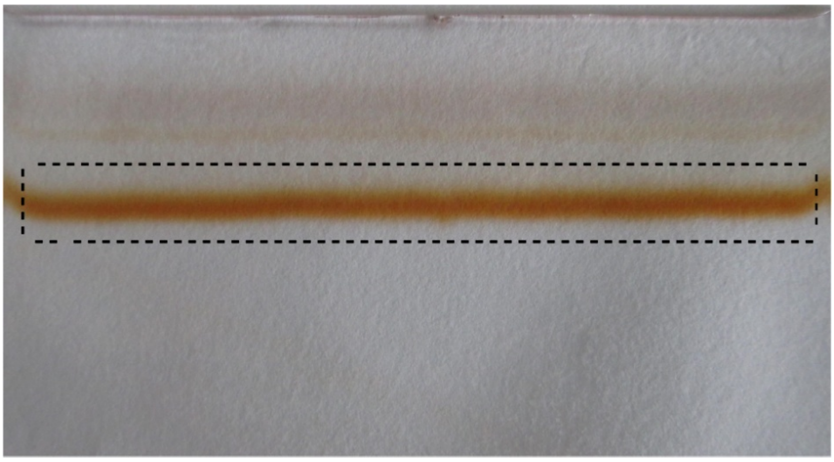

Fig. S1 PAGE of the crude product of the reaction between $Au_{25}(Capt)_{18}$ and $Ag_{30}(Capt)_{18}$. The band circled by dashed frame is the main product.

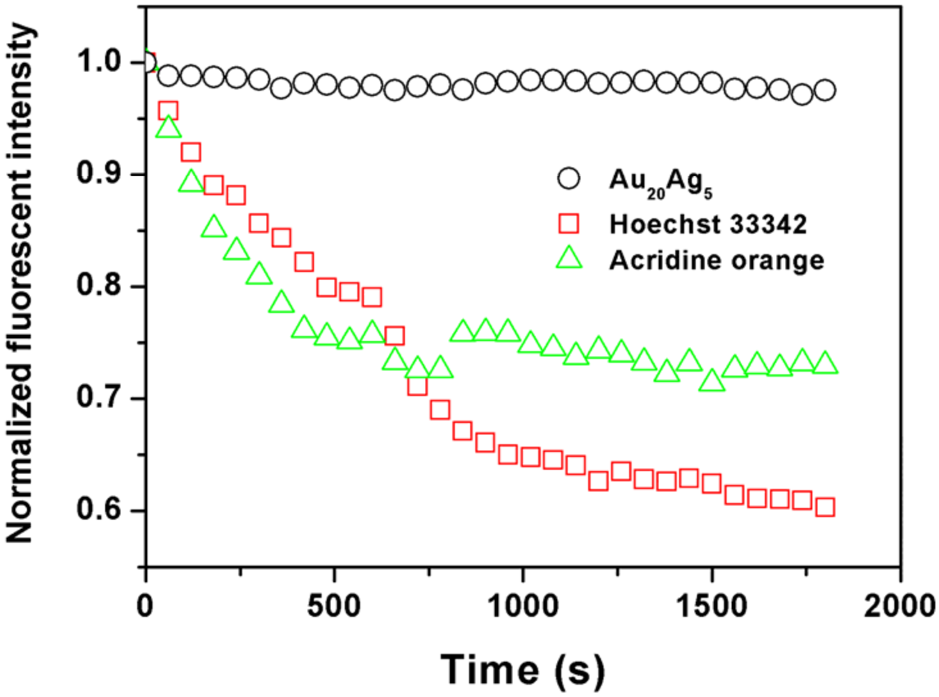

Fig. S2 Photo-bleaching stability comparison among $Au_{20}Ag_5(Capt)_{18}$, Hoechst 33342 and Acridine orange.

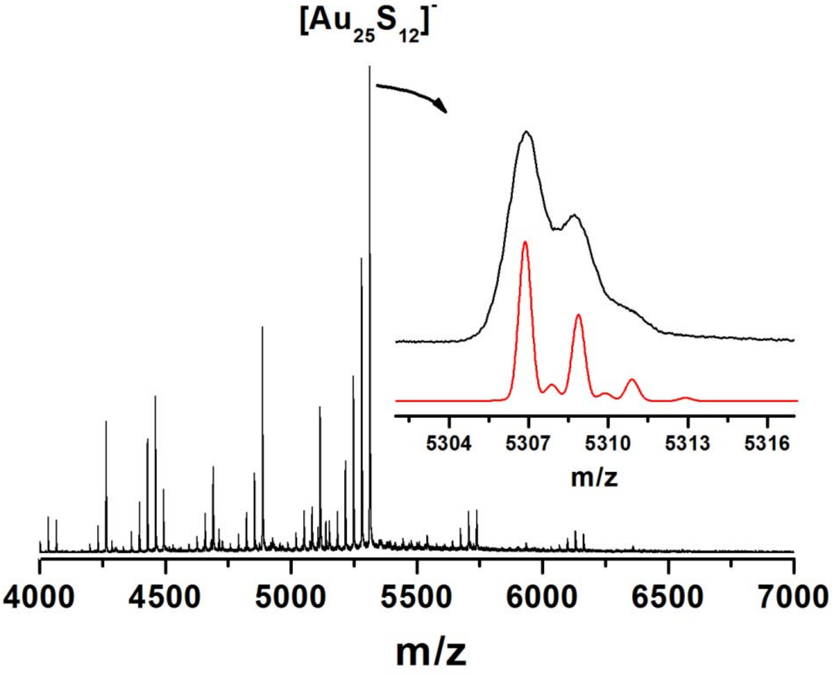

Fig. S3 MALDI-TOF mass spectrum of $Au_{25}(Capt)_{18}$ (acquired in negative ionization mode). Inset is the comparison of experimental and simulated isotope patterns of $[Au_{25}S_{12}]^-$.

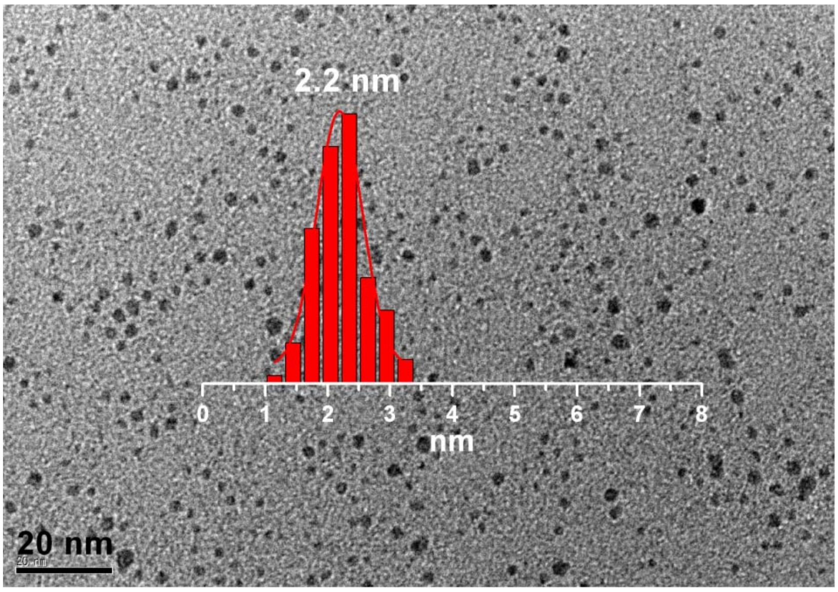

Fig. S4 TEM image of Ag nanoparticles protected by captopril.

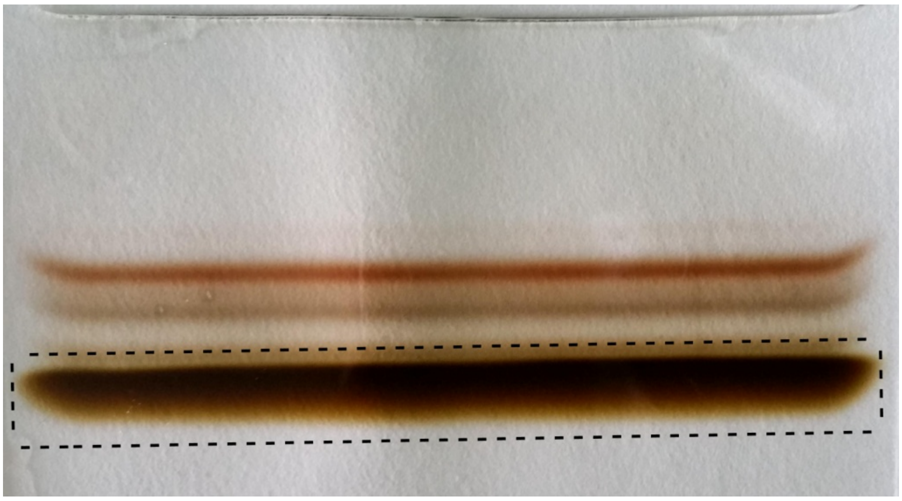

Fig. S5 PAGE of the crude product of the reaction between $Au_{25}(Capt)_{18}$ and ~2.2 nm Ag nanoparticles. The band circled by dashed frame is the main product.

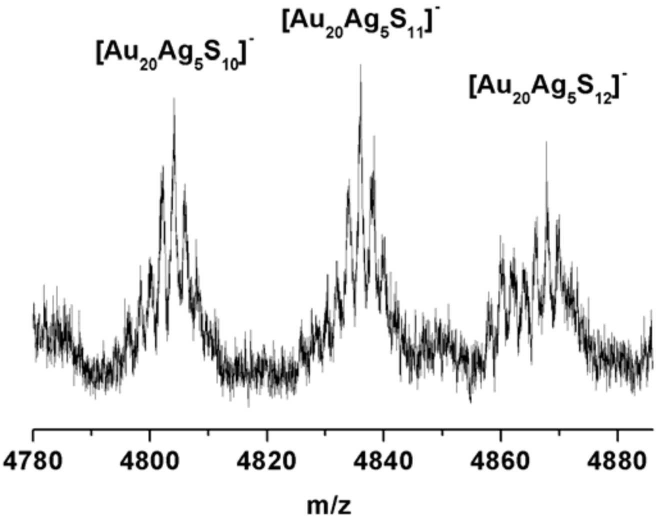

Fig. S6 The further enlarged mass spectrum showing the coexistence of $[Au_{20}Ag_5S_{10}]^-$, $[Au_{20}Ag_5S_{11}]^-$ and $[Au_{20}Ag_5S_{12}]^-$.

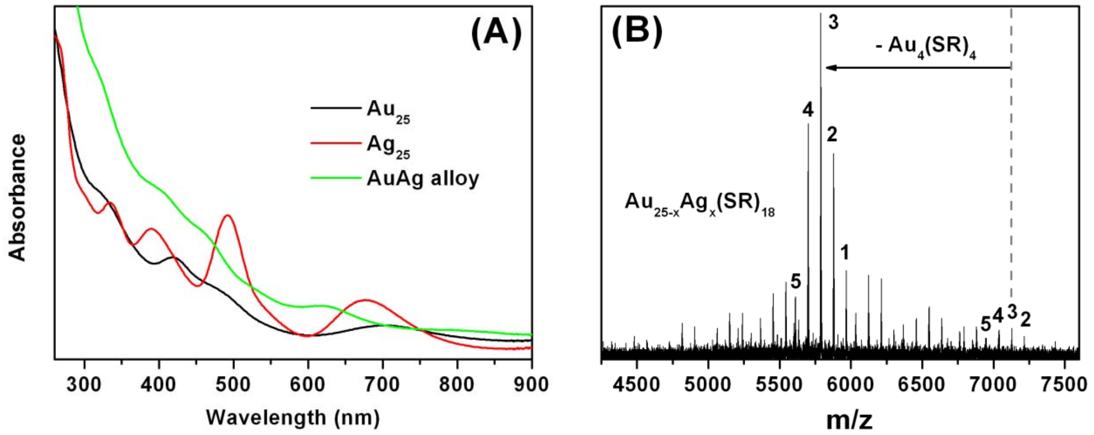

Fig. S7 (A) UV/vis/NIR absorption spectra of $Au_{25}(SR)_{18}$ (black line), $Ag_{25}(SR)_{18}$ (red line) and the purified alloy nanoparticles (green line). SR: 2,4-dimethylbenzenethiol. (B) MALDI mass spectrum of the purified alloy nanoparticles in positive ionization mode.

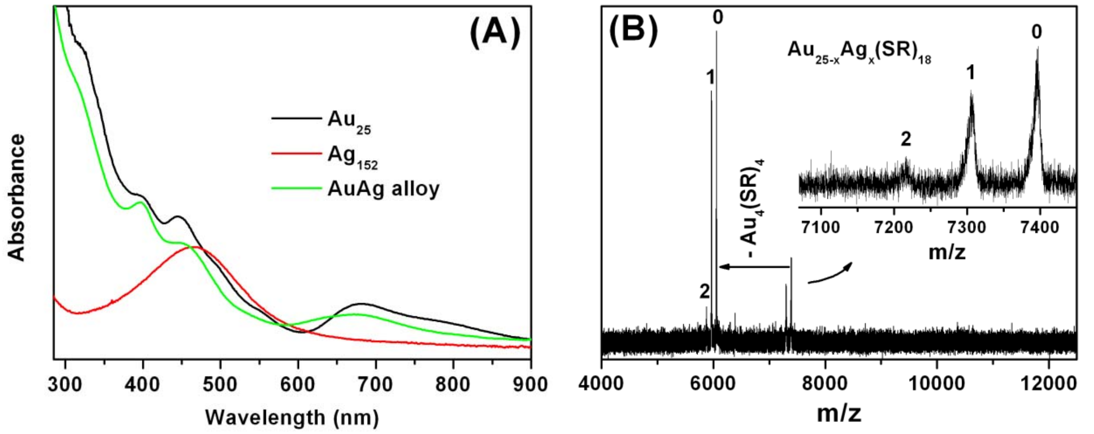

Fig. S8 (A) UV/vis/NIR absorption spectra of $Au_{25}(SR)_{18}$ (black line), $Ag_{152}(SR)_{60}$ (red line) and the purified alloy nanoparticles (green line). SR: phenylethanethiol. (B) MALDI mass spectrum of the purified alloy nanoparticles in positive ionization mode.

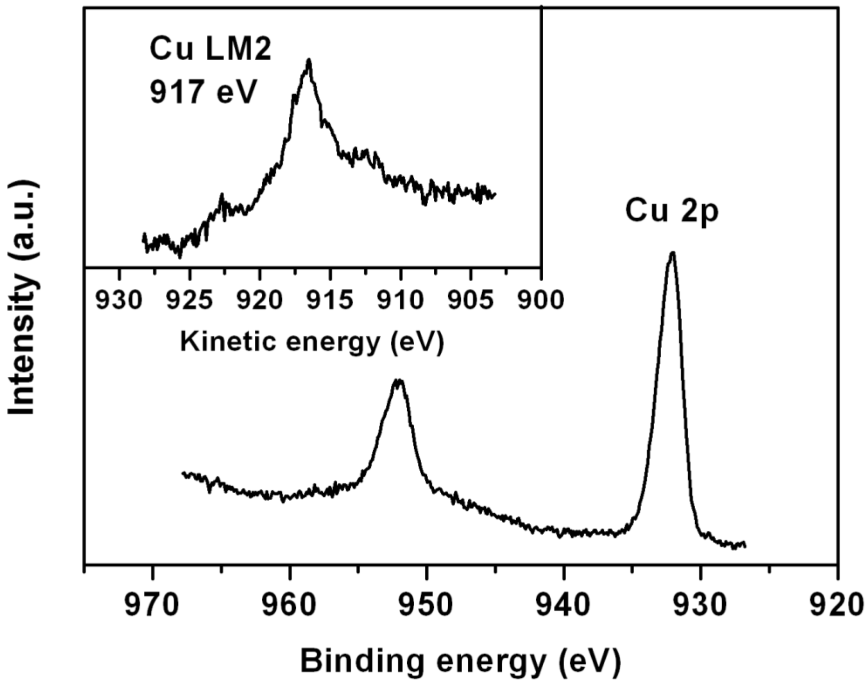

Fig. S9 XPS of Cu nanoparticles (Cu 2p scan). The inset shows Cu LM2 XAES spectrum.

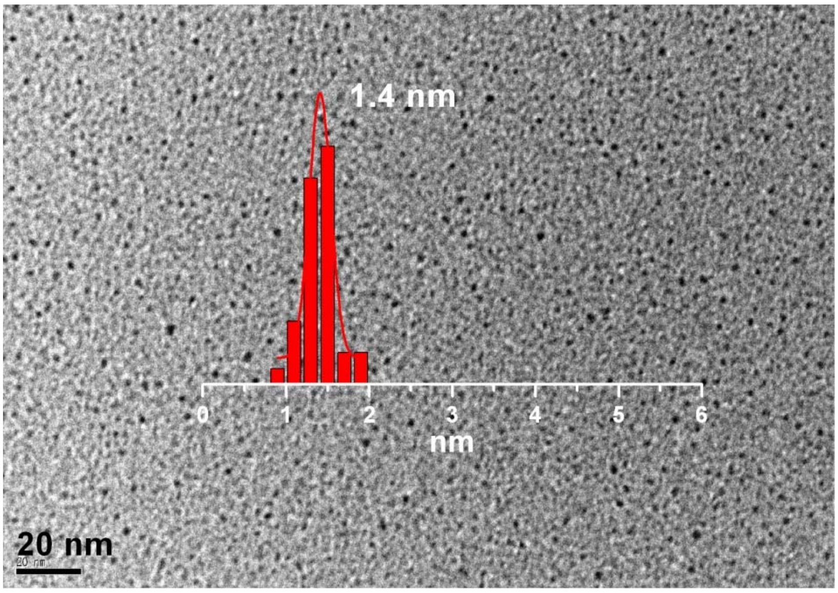

Fig. S10 TEM image of Cu nanoparticles protected by captopril.

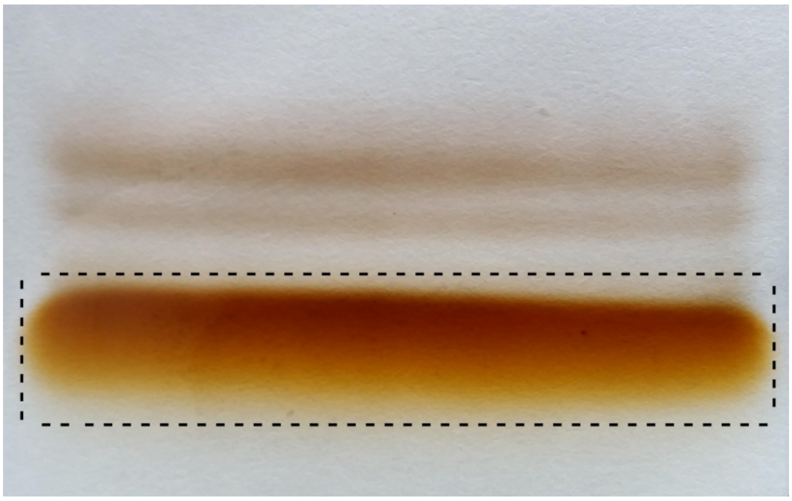

Fig. S11 PAGE of the crude product of the reaction between $Au_{25}(Capt)_{18}$ and Cu nanoparticles. The band circled by dashed frame is the main product.

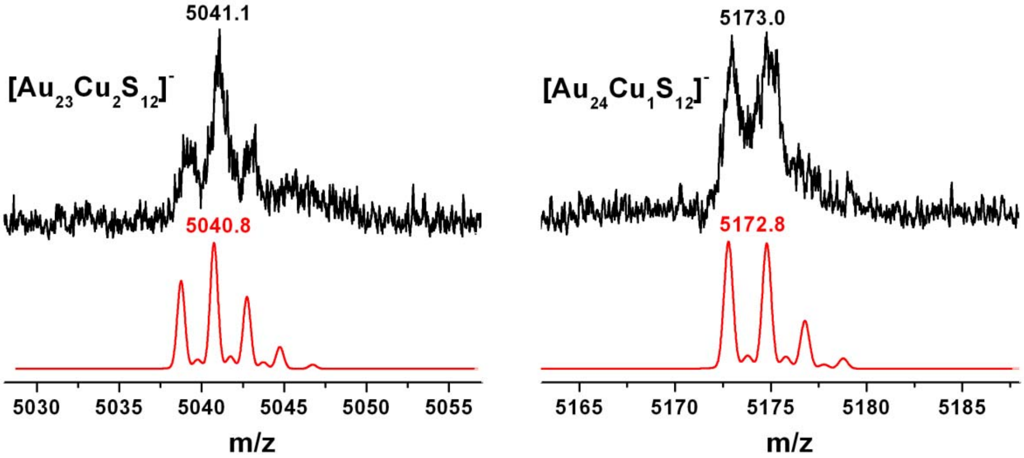

Fig. S12 Experimental (black line) and simulated (red line) isotope patterns of selected Au-Cu alloy nanoparticles ions.

References

[1] S. Kumar and R. Jin, *Nanoscale*, 2012, **4**, 4222-4227.

[2] N. Xia, J. Yang and Z. Wu, *Nanoscale*, 2015, **7**, 10013-10020.

[3] C. P. Joshi, M. S. Bootharaju, M. J. Alhilaly and O. M. Bakr, *J. Am. Chem. Soc.*, 2015, **137**, 11578-11581.

[4] I. Chakraborty, A. Govindarajan, J. Erusappan, A. Ghosh, T. Pradeep, B. Yoon, R. L. Whetten and U. Landman, *Nano Lett.*, 2012, **12**, 5861-5866.