Supporting information

$Au_{144-x}Cu_x(SC_6H_{13})_{60}$ Nanomolecules: Effect of Cu incorporation on the composition and plasmon-like peak emergence in optical spectra

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Content:

Materials and method

Chemicals: phenylethanemercaptan (SAFC, ≥ 99%),1-hexanethiol (ALDRICH, 95%), sodium borohydride (Acros, 99%), ethanol (Acros, 99.5%), trans-2[3[(4tertbutyl)-2-methyl-2-propenylidene]malonoitrile (DCTB matrix) (Fluka ≥ 99%) were purchased from Aldrich. Other solvents such as methanol, toluene, acetonitrile, and acetone were used from fisher as received.

Equipment: ESI-MS (Electrospray Ionization- mass spectrometry) spectra were acquired on Waters SYNAPT HDMS instrument. MALDI-TOF (Matrix assisted laser desorption ionization time-of-flight) mass spectra were obtained on a Bruker Autoflex 1 mass spectrometer in linear positive mode using nitrogen laser (337 nm) with DCTB as the matrix. Ultra violet-visible absorption spectra were recorded in THF on a Shimadzu UV-1601 instrument.

Method

$Au_{144-x}Cu_x(SR)_{60}$ nanoalloy were synthesized using different Au:Cu incoming molar ratio starting from 1:0, 1:0.025, 1:0.10, 1:0.30 and 1:0.50. For example following procedure was used to synthesis Au:Cu-1:0.025 ratio. Initially, 0.00432 g (0.026 mmol) of $CuCl_2{\cdot}2H_2O$ was dissolved in Ethyl alcohol (5 mL, absolute 99.5%). Tetraoctylammonium bromide (0.2346 g, 0.468 mmol was dissolved in Ethyl alcohol (15 mL, absolute 99.5%). $HAuCl_4{\cdot}3H_2O$ (0.0512 g, 0.13 mmol)) was dissolved in Ethyl alcohol(5 mL, absolute 95%) Then reagents transferred into a 100 mL round bottom flask under fast stirring (~700 rpm). After 30 minutes, 1-hexanethiol (0.468 mmol /0.05757 mL) of was added under continuous stirring at ~700 rpm. The reaction mixture turned colorless after ~10 minutes. After 1 hour, $NaBH_4$ (0.3783 g, 10 mmol) was dissolved in 10 mL of Ethyl alcohol (absolute 95%) was added into the reaction mixture. The reaction was stopped after 2 hours. The reaction was stopped after 2 hours. Then excess thiols and other byproducts were removed thorough methanol wash (3 times). Then final product was extracted by THF. Further etching and solvent fractionation were done in order to isolate $Au_{144-x}Cu_x(SR)_{60}$ nanomolecules in pure form.

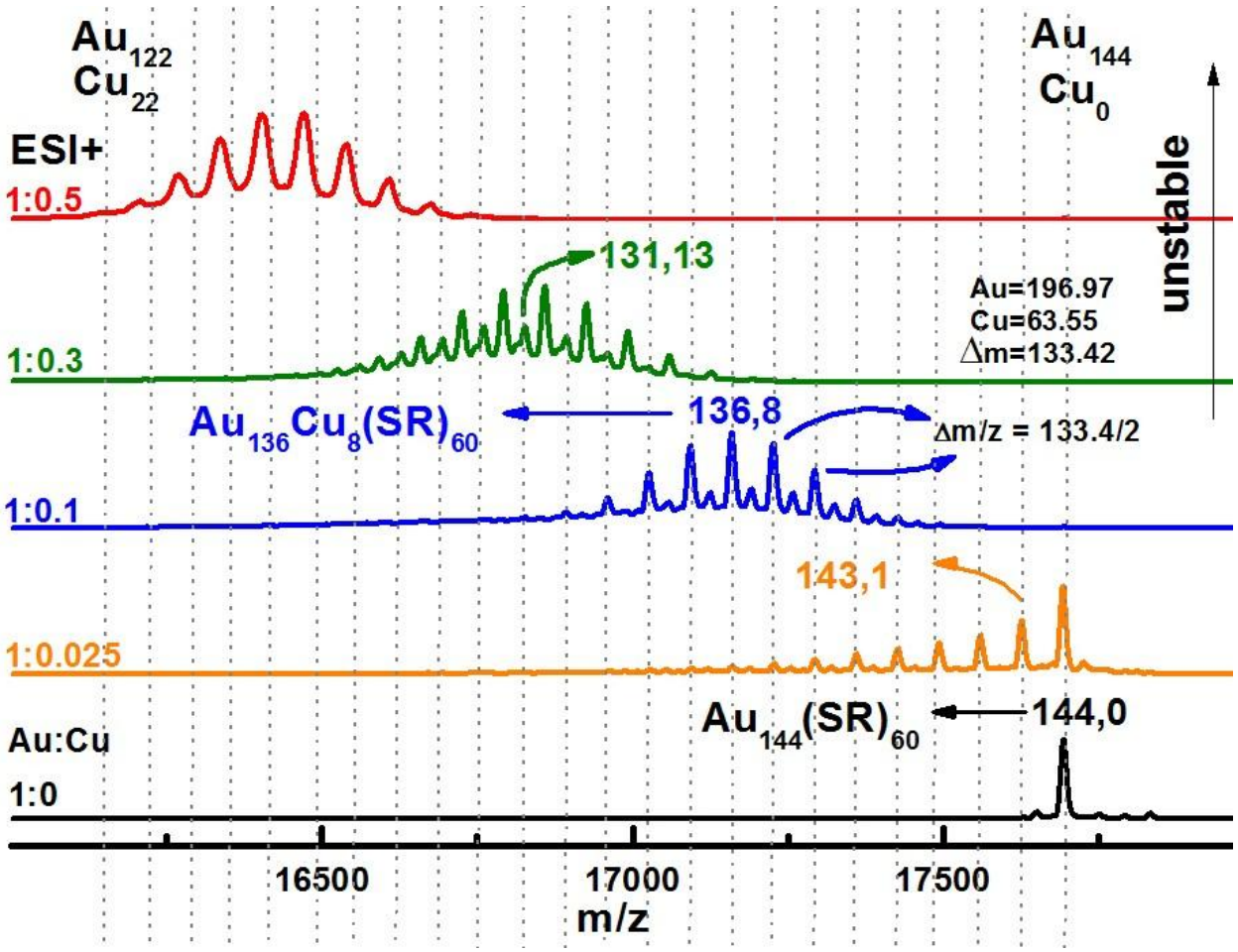

Figure S1. Expanded ESI (2-) mass spectra of $Au_{144-x}Cu_x(SC_6H_{13})_{60}$ nanomolecules for Au:Cu precursor ratios of 1:0 (black), 1:0.025 (orange), 1:0.1 (blue), 1:0.3 (green), and 1:0.5 (red) in the starting material. The mass difference between the peaks in nanoalloys match to the Au (196.97 Da) and Cu (63.55 Da) mass difference, Δm = 67 Da. Average number of Au and Cu atoms is denoted above each peak distribution.

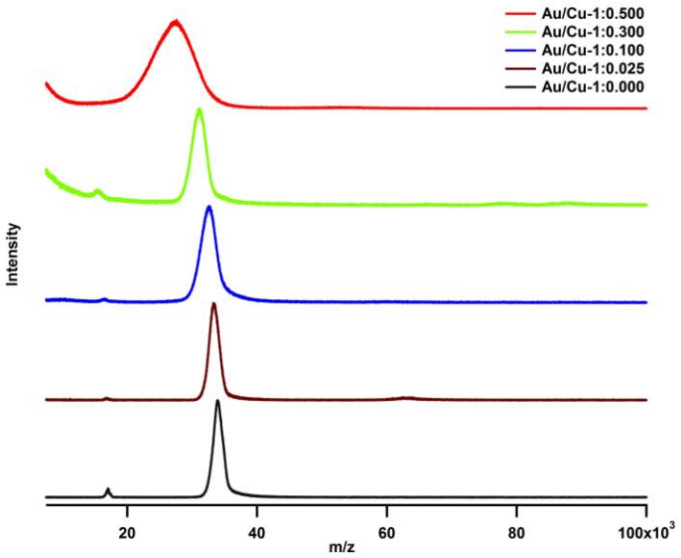

Figure S2. Expanded MALDI TOF-MS (negative mode) of $Au_{144-x}Cu_x$ $(SC_6H_{13})_{60}$ nanomolecules for Au:Cu precursor ratios of 1:0 (black), 1:0.025 (orange), 1:0.1 (blue), 1:0.3 (green), and 1:0.5 (red) in the starting material. Peak shift to the low mass region denoted the incorporation of Cu into the $Au_{144}(SR)_{60}$ structure. (Au_{144} peak is around 36 kDa. Note the absence of larger plamonic nanoparticles in the 50 – 100 kDa mass region).

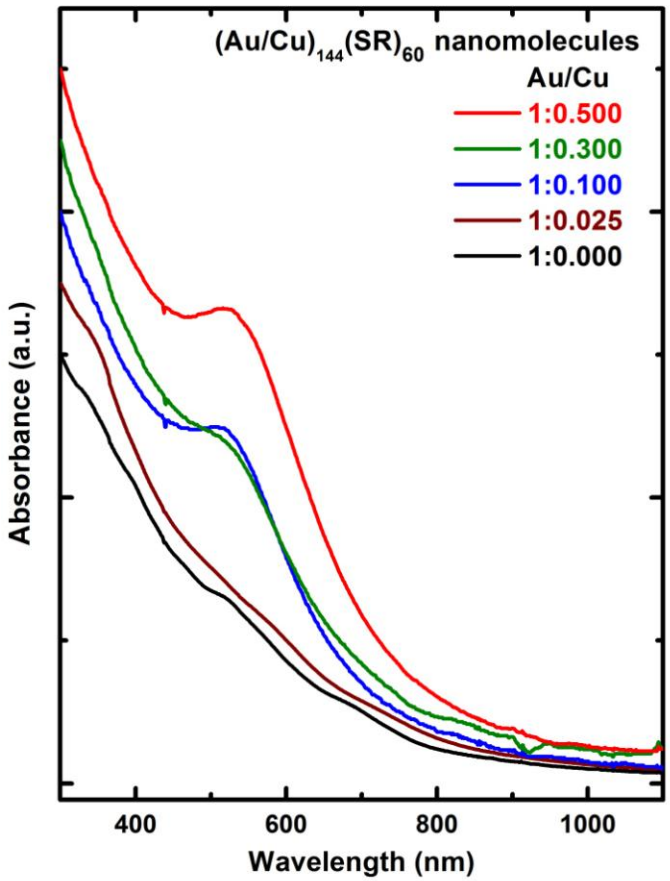

Figure S3. UV-visible spectra of the $Au_{144-x}Cu_x(SC_6H_{13})_{60}$ nanomolecules synthesized using different Au:Cu ratios of 1:0 (black), 1:0.025 (brown), 1:0.1 (blue), 1:0.3 (green), and 1:0.5 (red) in the starting material. Samples were dissolving in THF. (Figure S2 shows the absence of larger plasmonic nanoparticles, therefore we conclude that plasmon-like peak emerges in the 144-atom Au nanomolecule due to the incorporation of Cu atoms).

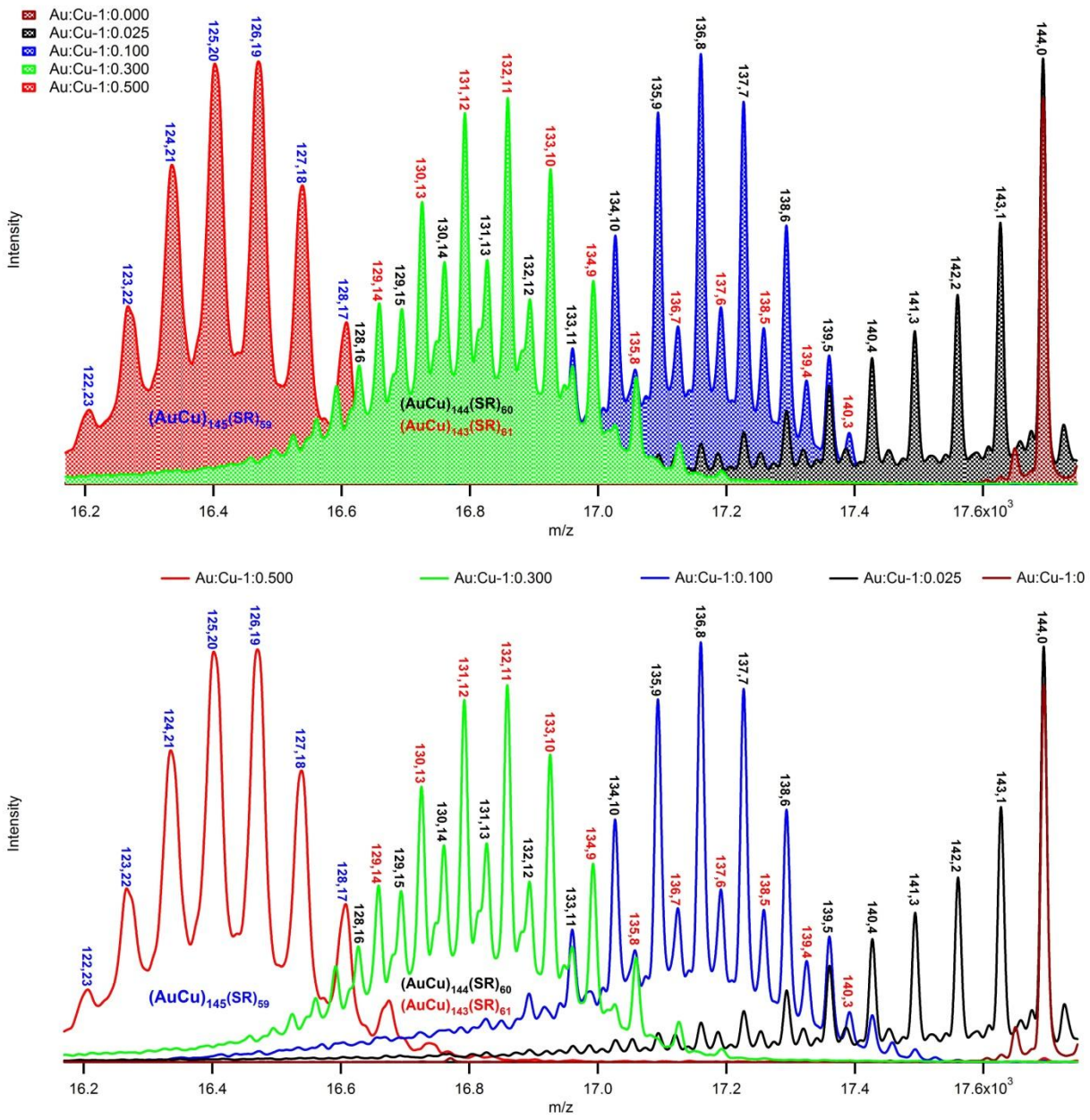

Figure S4. Expanded ESI-MS spectra of samples obtained with different Au: Cu precursor ratios. It is to be noted that along with $Au_{144-x}Cu_x(SR)_{60}$ metal atom nanomolecule, two other composition with $Au_{143-x}Cu_x(SR)_{61}$ and $Au_{145-x}Cu_x(SR)_{59}$ metal atoms have been observed depend on Au:Cu incoming molar ratio. Using Au: Cu precursor ratio of 1: 0.025, a maximum of 8 copper atom incorporations. Upon increasing the ratio to 1: 0.1, a maximum of 12 copper atom incorporations into 144 metal atom core was observed. However, peaks corresponding to 143 metal atoms were also observed, with a maximum of 8 copper atom incorporations. When the ratio was increased to 1:0.3, 143 total metal atom species were dominant, with maximum of 16 copper atom incorporations. The signal to noise ratio is atleast 10:1, but exceeds 100 for most peaks.