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Morphology-Preserved Alloying in Anisotropic Gold Nanoparticles Using Atomically Precise Nanoclusters

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Abstract: Noble metal nanoparticles (NPs) exhibit superior plasmonic, catalytic, electronic, and magnetic properties upon alloying with a second metal. However, the synthesis of bimetallic alloy NPs of non-spherical morphologies presents a challenge due to the necessity of concurrently modulating the nucleation and growth kinetics of various metallic constituents. In this study, a simple solution-phase reaction between a phosphine-protected copper nanocluster (NC), namely $[Cu_{18}(DPPE)_6H_{16}]^{2+}$ [DPPE = 1,2-bis(diphenylphosphino)ethane] (abbreviated as Cu_{18}) and gold nanotriangles (AuNTs) is reported as a straightforward strategy to obtain gold-copper alloy nanotriangles (AuCuNTs) while keeping their sizes and sharp edges intact. Extending this protocol to gold nanorods (AuNRs) and nanocubes (AuNCbs), demonstrates its generality for creating anisotropic Au–Cu alloy NPs. Auger spectroscopic analyses confirm that Cu(0) is the predominant Cu species in the AuCuNTs, indicating that oxidation of Cu in the resulting nanostructures is prevented. A further interaction of AuCuNTs with $[Ag_{25}(DMBT)_{18}]^-$ [DMBT = 2,4-dimethylbenzenethiol] (abbreviated as Ag_{25}) has yielded AuCuAgNTs, offering a facile synthetic route to trimetallic anisotropic NPs. Thus, the current study corroborates atomically precise metal NCs as versatile precursors for tuning the composition of plasmonic anisotropic NPs to meet diverse technological and industrial needs.

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Experimental procedures:

Chemicals. Tetrachloroauric acid trihydrate ($HAuCl_4$, $3H_2O$), hexadecyltrimethylammonium chloride (CTAC), hexadecyltrimethylammonium bromide (CTAB), sodium borohydride ($NaBH_4$), 2,4-dimethylbenzenethiol (DMBT), 1,2-bis(dipehnylphosphino)ethane (DPPE), sodium iodide (NaI) and ascorbic acid (AA) were purchased from Sigma Aldrich. Silver nitrate ($AgNO_3$) and sodium hydroxide (NaOH) pellets were procured from Rankem, India. All organic solvents, including dimethylformamide (DMF), dichloromethane (DCM) and methanol (MeOH) were purchased from Rankem chemicals in analytical grade quality. These chemicals were utilized without further purification. Glassware was thoroughly cleansed using aqua regia, followed by extensive rinsing with distilled water and subsequent drying under ambient conditions prior to their application.

Synthesis of gold nanotriangles. Trigonal planar nanoparticles with high size and shape monodispersity were synthesized following a method previously reported.[1] The first step of the synthesis was seed preparation, where 4.7 mL 100 mM CTAC was taken in a 20 mL glass vessel. Under mild stirring, 25 μL of 10 mM $HAuCl_4$ was mixed to it followed by the rapid injection of 300 μL 10 mM freshly prepared (in ice-cold water) $NaBH_4$. Vigorous stirring continued for 2 min after the addition of $NaBH_4$ to facilitate the release of hydrogen gas generated in the medium. After this, the brown-colored seed solution was kept undisturbed for 2 hours. Two separate growth solutions were then prepared.

Growth solution I, i.e., G-I. To 1.6 mL of 100 mM CTAC, 8 mL of water, 40 μL of 10 mM $HAuCl_4$, and 15 μL of 10 mM NaI were sequentially added by mild manual mixing.
Growth solution II, i.e., G-II. To 40 mL of 50 mM CTAC, 500 μL of 10 mM $HAuCl_4$ and 300 μL of 10 mM NaI were added, following the same procedure as for **G-I**. The seed solution was subsequently diluted 10 times using 100 mM CTAC. 40 μL and 400 μL of 100 mM AA were added in single shots to **G-I** and **II**, respectively. Immediately after this, 100 μL of the diluted seed was added to **G-I** under gentle manual mixing. Within 1 s of mixing, as the color of the **G-I** turned pink, 3.2 mL of it was transferred to the **G-II**. This was mixed in a similar fashion for 10 s. Within 10 min, the **G-II** turned blue in color.

Purification of AuNTs. As-synthesized AuNTs contained a proportion of gold nanoparticles of non-targeted shapes. To eliminate them, the flocculation method suggested by Scarabelli *et al.* was employed.[1] The synthesized AuNTs were dispersed in 175 mM CTAC by adding a suitable amount of aqueous CTAC stock solution (25 wt%) into growth solution II. The mixture was kept undisturbed for 2 hours at room temperature. As a result of this, AuNTs with high size and shape monodispersities were selectively precipitated, leaving the undesired particles in the supernatant. The supernatant was subsequently decanted, and the sediment was dispersed in DI water with mild sonication, yielding a greenish-blue dispersion. These purified AuNTs were centrifuged twice at 6000 rpm for 5 min and redispersed in DI water before use.

Synthesis of Cu_{18}. The synthesis followed an established procedure[2] with certain modifications. In a Schlenk tube under vacuum, 100 mg copper iodide and 120 mg bis(diphenylphosphino)ethane was taken. 15 mL Acetonitrile was added to it with stirring. After 30 minutes, solid sodium borohydride (180 mg) was added and the reaction mixture was continuously stirred for 4 hours at room temperature. The resulting precipitate was centrifuged and rinsed with DI water to remove unreacted $NaBH_4$, if any. The product was extracted with DCM, filtered and finally dispersed in DMF.

Synthesis of gold nanorods. AuNRs were synthesized following the method described by Samal *et al.*[3] Precisely, 1 mL of 10 mM $HAuCl_4$ was added to 20 mL of 100 mM CTAB with mild stirring. Subsequently, 130 μL of 10 mM $AgNO_3$ and 140 μL of 100 mM AA were added in sequence. Following these additions, 200 μL of 1.67 mM $NaBH_4$ (freshly prepared using cold DI water) was added and the stirring was stopped immediately. The solution was kept undisturbed for at least four hours. Before any further treatment, the AuNR was centrifuged (at 13000 rpm for 15 min, twice), the supernatant containing excess CTAB was discarded, and the precipitated AuNRs were redispersed in DI water.

Synthesis of gold nanocubes (AuNCbs). The synthesis of AuNCbs was executed following a 3 step synthetic protocol proposed by Nam group.[4]

Seed solution: 9.75 mL 100 mM CTAB solution was prepared in a glass vial, to which 250 µL of 10 mM $HAuCl_4$ was added under moderate stirring. Then 600 µL of 10 mM $NaBH_4$ (freshly prepared in ice-cold DI water) was quickly added to the brownish-yellow solution. Stirring was continued for an additional 3 min before the seed was allowed to age at room temperature (27 °C for 3 hours).

Growth solution I. In a separate 10 mL vial, 2 mL of 200 mM CTAC, 1.5 mL of 100 mM AA, and 50 µL of the previously prepared seed solution were mixed sequentially with moderate stirring. The stirring speed was then fixed at 300 rpm, and 2 mL of 0.5 mM $HAuCl_4$ was injected in one shot. Mixing was continued for 15 min at room temperature, followed by centrifugation twice at 13000 rpm for 30 min. Each time the supernatant was decanted to remove unreacted chemicals. The pellet was resuspended in 1 mL DI water and, 1 mL of 20 mM CTAC after the first and second wash, respectively.

Growth solution II. For the final growth solution, in a 20 mL glass vial, 6 mL of 100 mM CTAC was mixed with 30 µL of 13 mM aqueous NaBr solution. The concentration of growth solution I was adjusted such that the optical density (O.D.) was 2; and 6 µL of it was added subsequently. To this, 390 µL of 10 mM AA was added, with thorough mixing at a constant 500 rpm. Finally, 6 mL of 0.5 mM $HAuCl_4$ was added to the vial in a single step, and the mixing continued for 25 min. The final growth solution was centrifuged at 7000 rpm for 12 min followed by resuspension in DI water, twice.

Reaction between AuNT and Cu_{18}. A 2 mL aqueous dispersion of clean AuNTs, exhibiting O.D. ~1 at 640 nm (LSPR peak position), was centrifuged, and redispersed in the same volume of DMF. This suspension was transferred to a 5 mL glass vial. For a typical reaction, the freshly synthesized Cu_{18} NC (concentration 135 mg/mL) was diluted 100 times using DMF, and 20 µL of this Cu_{18} NC was added to the AuNTs under moderate stirring. The stirring continued for at least 3 hours, after which the reaction mixture was centrifuged at 6000 rpm. The pallet was redispersed in either DMF or DI water and used for further experiments or investigation.

Instrumentation:

Absorption spectra in solution were recorded in standard cuvettes using a PerkinElmer Lambda 365 spectrometer in the wavelength range of 200- 800 nm. Mass spectra of all the clusters were measured using the Waters Synapt G2Si High-Definition Mass Spectrometer. XPS Measurements were done using an ESCA Probe TPD spectrometer of Omicron Nanotechnology. Polychromatic Al Kα was used as the X-ray source (hν = 1486.6 eV). The concentration of Au in the reaction mixture was detected using PerkinElmer NexION 300X ICPMS with appropriate standards. XRD patterns were obtained using a Bruker AXS D8 Discover diffractometer with Cu Kα radiation (λ = 1.54 Å). The samples underwent scanning from 5° to 90° in the 2θ range, and the resulting peaks were compared with the Joint Committee on Powder Diffraction Standards (JCPDS) database. Morphology and elemental analyses of AuCuNCbs and AuCuNRs were performed using Verios G4 UC, FEI scanning electron microscope. All TEM images were collected using a JEOL 3010 high-resolution TEM operated at 200 kV. A Gatan multistage CCD camera was used to record the image. The STEM imaging was performed using a JEOL JEM-2800 high throughput electron microscope operated at 200 kV with simultaneous bright field (BF) and dark field (DF) STEM imaging. All electron microscopy samples were prepared by dropcasting 10 µL of sample on 300 mesh Ni grids with ultrathin carbon support film.

Supplementary Figures

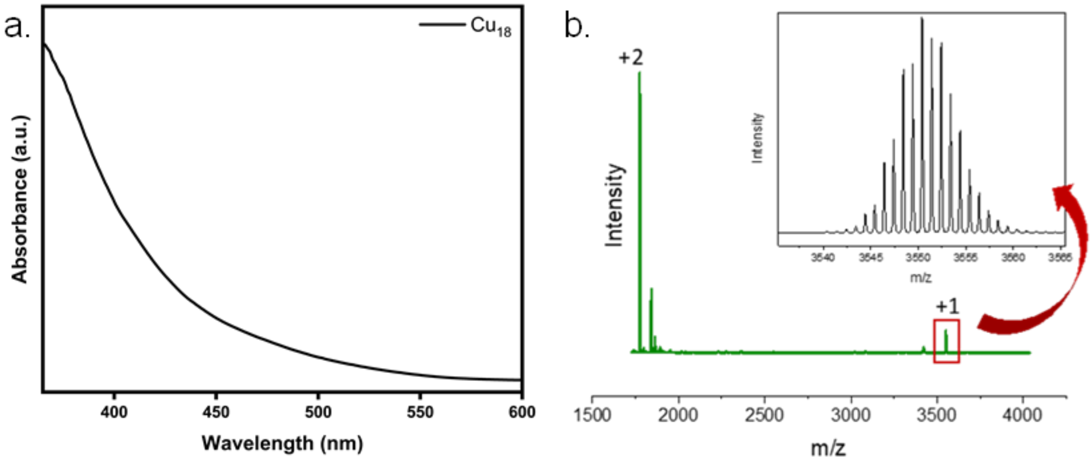


Figure S1. Characterization of Cu_{18} NC. a. UV-vis spectrum of Cu_{18}. b. ESI-MS of Cu_{18} showing molecular ion peak at m/z 3552 and +2 charge state at m/z 1775. The inset shows the distribution of the former peak.

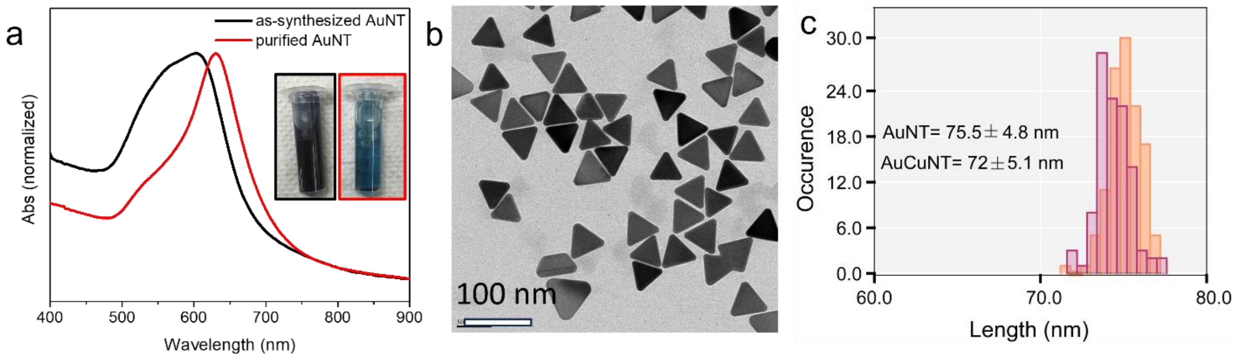
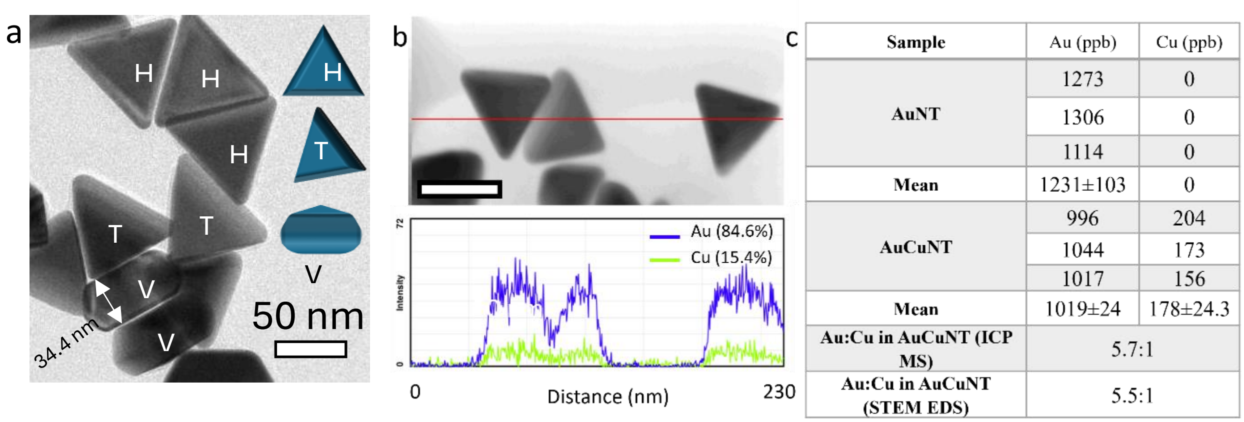


Figure S2. Characterization of AuNTs. (a) UV vis absorption spectra before and after purification by the flocculation method (inset shows the change in color of the dispersion), (b) TEM image of the purified AuNTs, (c) size distribution of AuNT and AuCuNTs (125 particles each).



Sample	Au (ppb)	Cu (ppb)
AuNT	1273	0
	1306	0
	1114	0
Mean	1231±103	0
AuCuNT	996	204
	1044	173
	1017	156
Mean	1019±24	178±24.3
Au:Cu in AuCuNT (ICP MS)	5.7:1	
Au:Cu in AuCuNT (STEM EDS)	5.5:1	

Figure S3. (a) TEM image of AuCuNTs including horizontal (H), tilted (T), and vertical (V) orientations of the NTs. Inset shows the cartoon representation of these orientations. (b) Bright field STEM image of three additional AuCuNTs and respective EDS line scans showing uniformity of Cu content in each AuCuNT, (c) ICP MS of parent AuNTs and AuCuNTs showing Au:Cu = 5.7:1. Three separate analyses were done to take an average.

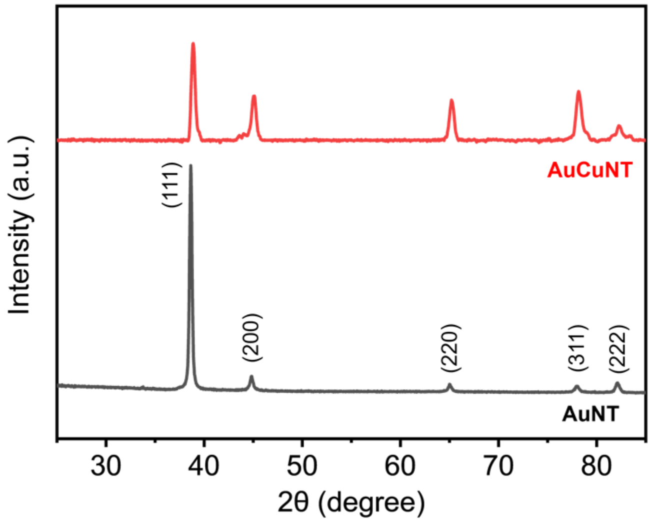


Figure S4. Powder XRD patterns of AuNT and AuCuNT. All the peaks are preserved but shifted upon alloying. No new peaks appeared, which indicates the absence of copper oxide layers in AuCuNTs.

Table S1. The concentration of Au found in the supernatant at different molar ratios of Cu_{18} to AuNT.

O.D. of AuNTs at λ_{max}	1	1	1	1	1
[Cu_{18}] (mg/mL)	0	0.24	1.21	2.42	12.1
[Au(I)] in supernatant (ppb)	96	104	576	776	996
	85	153	617	786	795
	77	158	748	545	642
Average [Au(I)]	86±7.8	138±24	647±73	702±111	811±145

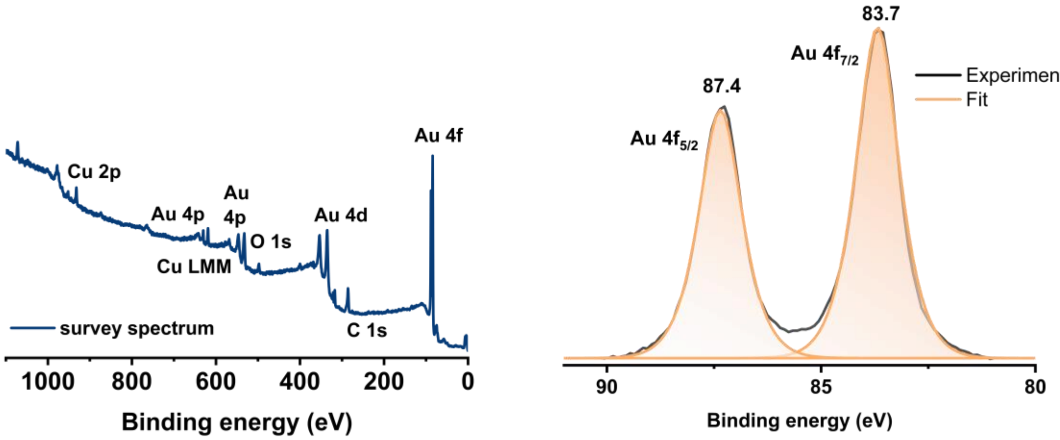


Figure. S5. XPS spectra of AuCuNT: (a) the survey spectrum, b) Au 4f X-ray photoelectron spectrum of AuCuNT.

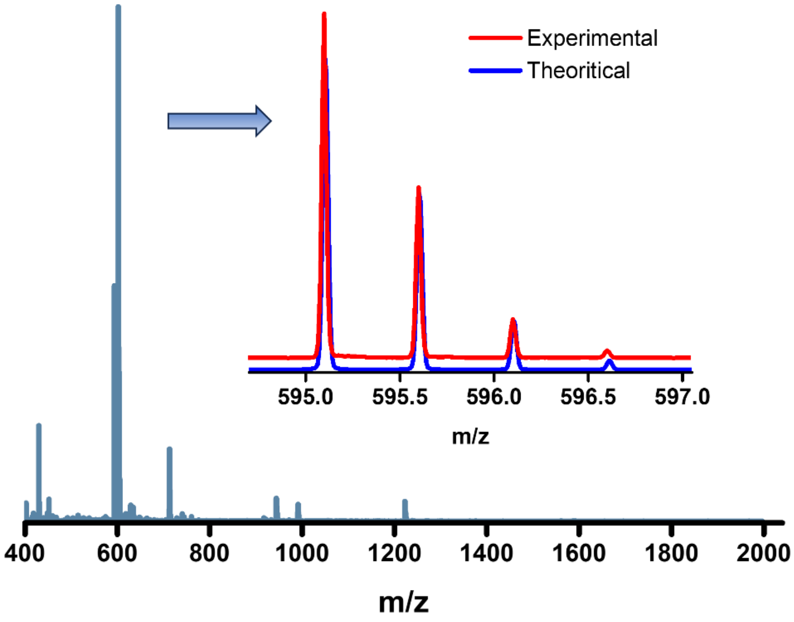


Figure S6. ESI-MS of the supernatant obtained by centrifuging the reaction product. The inset shows the exact matching of the isotopic distribution of the experimental and theoretical spectra of the species $[Au_2(DPPE)_2]^{2+}$ at m/z 595.

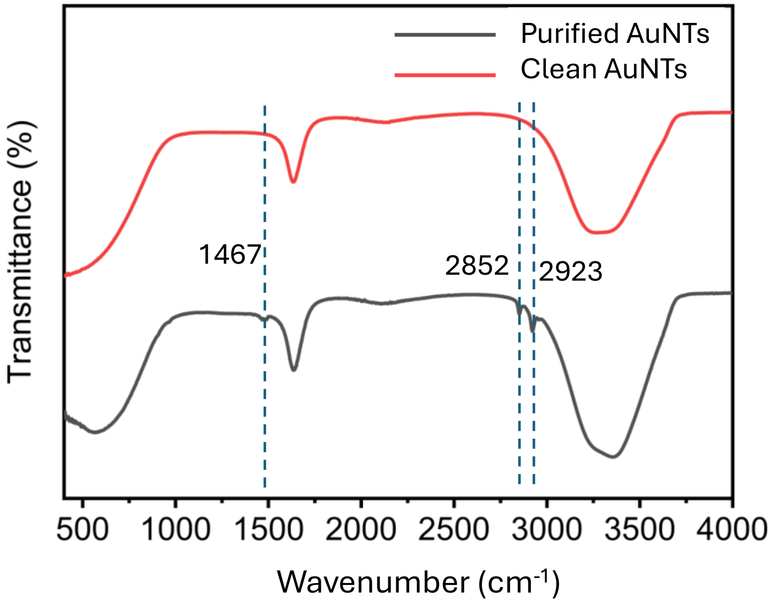


Figure S7. FT-IR spectra of purified AuNTs showing characteristic peaks of CTAC (peaks at 2923 and 2852 cm $^{-1}$ due to the $-CH_2$ stretching of the CTAC chain, at 1467 cm^{-1} results from the deformation vibrations of $-CH_3$ and $-CH_2$ groups),[5] that was absent in clean AuNTs.

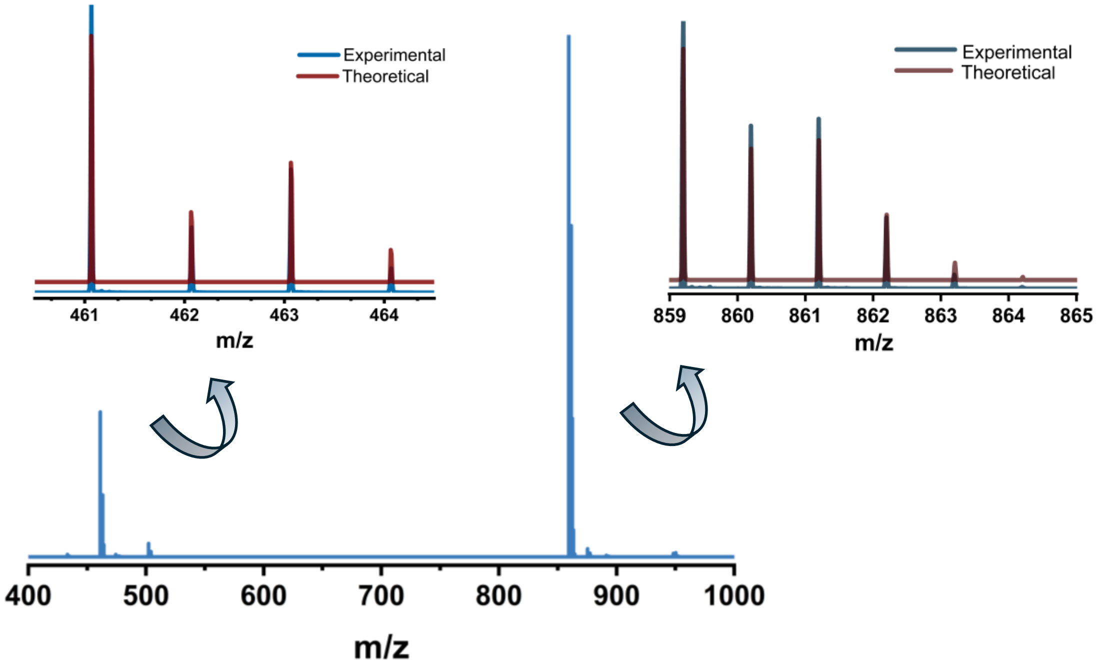


Figure S8. ESI-MS of Cu_{18} in DMF shows peaks at m/z 462 and 860 for $[Cu(DPPE)]^+$ and $[Cu(DPPE)_2]^+$, respectively. Inset shows the isotopic distribution of the peaks with a theoretical match.

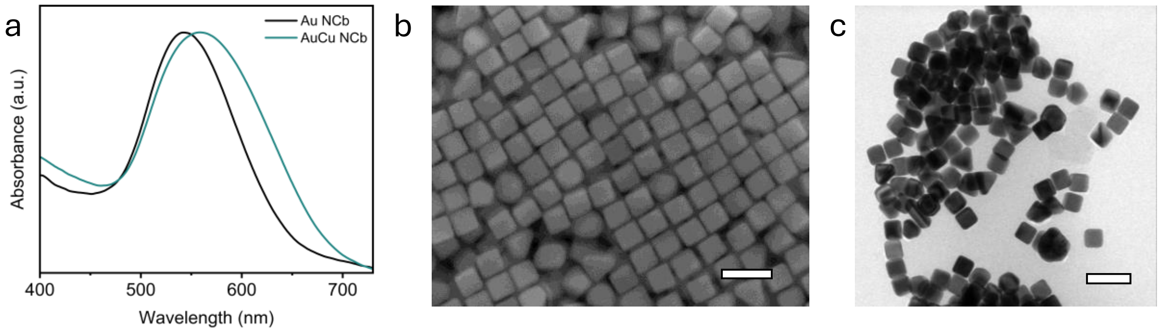


Figure S9. Characterization of AuNCbs: (a) Comparative UV vis absorption spectra of AuNCb and AuCuNCbs showing red shift and broadening of the SPR peak at 540 nm, (b) SEM and (c) TEM image of parent AuNCbs, scale bar 100 nm.

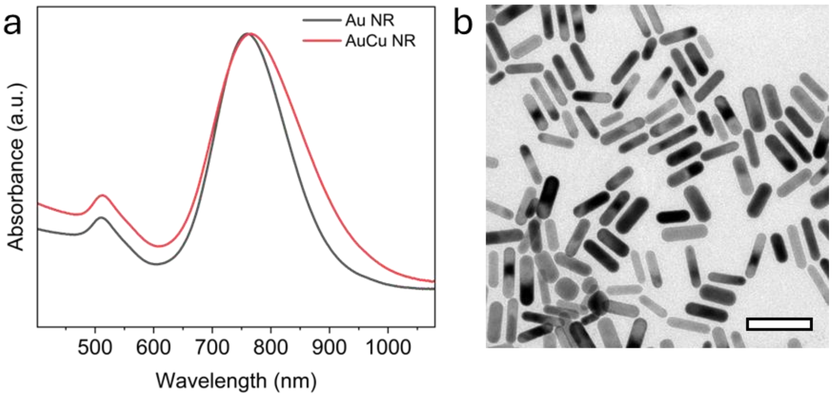


Figure S10. Characterization of AuNRs: (a) Comparative UV vis absorption spectra of AuNR and AuCuNR showing slight red shift and broadening of the SPR peak at 760 nm, (b) TEM image of parent AuNRs, scale bar 50 nm.

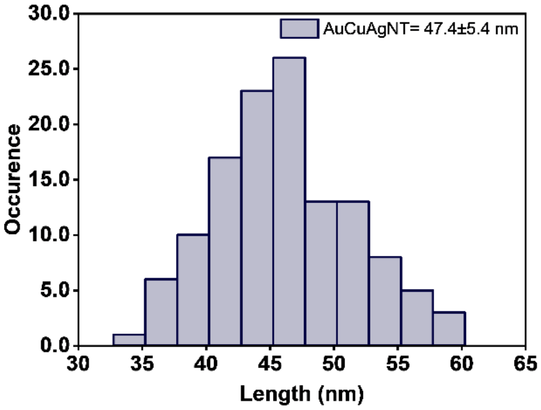


Figure S11. Size distribution of AuCuAgNTs (125 particles).

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