

Supporting information for

“Clicked” Plasmonic Core-Satellites: Covalently Assembled Gold Nanoparticles

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Materials

All materials were used as received without any further purification. Cetyltrimethylammonium bromide (CTAB), gold chloride (HAuCl₄·4H₂O), sodium borohydride (NaBH₄), ascorbic acid, p-aminothiophenol (p-ATP), N,N'-Carbonyldiimidazole (CDI), Heptynoic acid, 1,2-bis(11-azidoundecyl)disulfane, d₆-dimethyl sulfoxide (d₆-DMSO), dimethylformamide (DMF) and tetrahydrofuran (THF) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Cetyltrimethylammonium chloride (CTAC) was obtained from TCI (Portland, OR, USA). Formvar/carbon coated copper TEM grids were acquired from Ted Pella (Redding, CA, USA). Nanopure water (>18.0 MΩ-cm) was used for all experiments.

Methods

Gold nanostructures synthesis

Gold nanoparticles

Gold nanoparticles were synthesized in three steps. In the first step, seed solution was prepared by vigorous mixing of 5 ml of aqueous CTAC solution (0.2 M), 4.5 ml of nanopure water and 515 μl of HAuCl₄ (4.86 mM) with 450 μl of ice-cold NaBH₄ solution. The seed solution was aged for 1 hr at 30°C in a hot bath. In the second step, the growth solution was prepared by mixing 4.5 ml of nanopure water, 5 ml of aqueous CTAC solution (0.2 M), 515 μl of HAuCl₄

(4.86 mM), and 75 μ l of ascorbic acid (0.04 M). To this colorless solution, 25 μ l of seed solution was added with vigorous stirring and kept undisturbed for two days to obtain highly uniform spherical nanoparticles with LSPR at 521 nm. The size of the nanoparticles obtained at this stage was 20 nm. In the final step, to obtain the 70 nm spherical nanoparticles growth solution was prepared similar to second step but 10 μ l of as synthesized 20 nm nanoparticles were used as a seed. The size and morphology of the nanoparticles were characterized in TEM (Figure 1).

Synthesis of N-(4-mercaptophenyl)hept-6-ynamide

5 ml of heptynoic acid (1 mmol) in THF was added to 10 ml of round bottom flask and was put to magnetic stirring. The reaction mixture was activated with 2 mmol of N,N'-carbonyldiimidazole for 2 hours under a blanket of nitrogen at 80 °C. To this reaction mixture, 1 mmol of p-aminothiophenol was added and the reaction was continued for 24 hours. THF was evaporated and the final compound was dissolved in ethyl acetate. The solution was washed several times with Nanopure water to remove the byproducts and the final product, N-(4-mercaptophenyl)hept-6-ynamide, was analyzed and confirmed using ¹H-NMR.

Modification of core and satellites with 1,2-bis(11-azidoundecyl)disulfane and N-(4-mercaptophenyl)hept-6-ynamide, respectively:

1 ml of 1,2-bis(11-azidoundecyl)disulfane (10 μ mol) and N-(4-mercaptophenyl)hept-6-ynamide (10 μ mol) in DMF were prepared in separate 2 ml glass vials. Then, 1 ml of cores (5 nM) and 1 ml of satellites (10 nM) in water were added to 1 ml of 1,2-bis(11-azidoundecyl)disulfane and 1ml of N-(4-mercaptophenyl)hept-6-ynamide, respectively. The reaction mixture was sonicated for 15 minutes and kept under stirring for 4 hours at 80 °C to replace the CTAB on gold nanoparticles with corresponding Click linker molecules. Then the final reaction mixture was dialyzed for 6 hrs in Nanopure water to replace mixture of DMF and water with water. The

success of the surface modification was confirmed by 2 nm red-shift in localized surface plasmon resonance wavelength due to the change in refractive index.

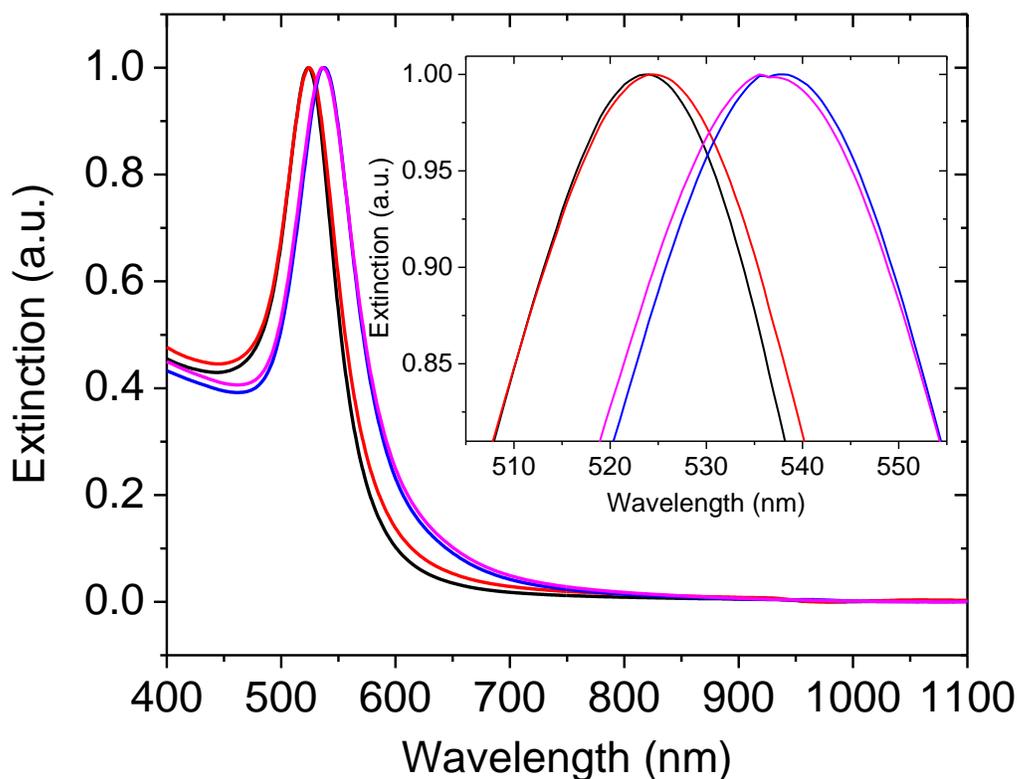


Figure S 1. UV-Vis extinction spectra of core (pink), satellites (black), azide linker-modified cores (blue) and alkyl linker-modified satellites (red). The successful functionalization of satellites and cores with respective linkers is indicated by 1-2 nm red shift in both cases.

Click reaction

500 μ l of N-(4-mercaptophenyl)hept-6-ynamide modified cores (5 nM) was mixed with 500 μ l of 5-azido-N-(4-mercaptophenyl)pentanamide modified satellites (10 nM) in a 2 ml eppendroff tube. To initiate the Click the reaction, 10 μ l of CuSO_4 (10 μ M) and 10 μ l of sodium ascorbate (10 μ M) were added to the previous mixture under continuous stirring at 600 rpm. The reaction

mixture left undisturbed overnight to completely append the satellites to cores through Click linkage. The unbound satellite nanoparticles were removed by centrifuging at 5000 rpm for 10 minutes and dispersed in nanopure water for further characterization. The resultant nanoparticles clusters were characterized with UV-Vis, Dynamic light scattering (DLS), Raman spectroscopy and Transmission electron microscopy (TEM).

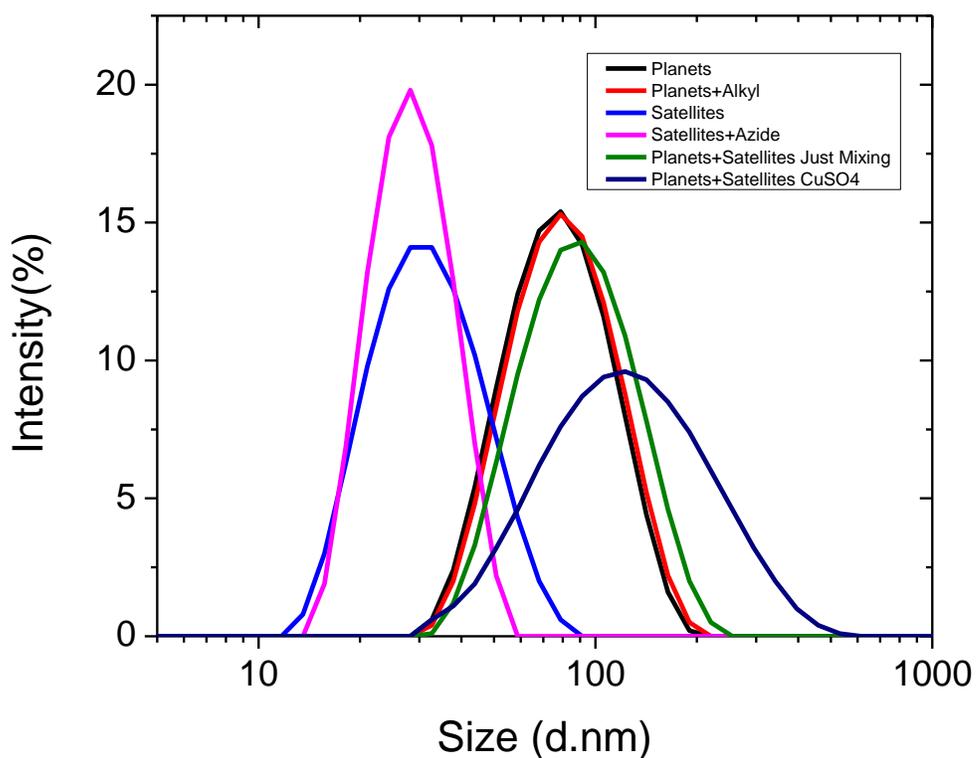


Figure S 2. Dynamic light scattering experiments clearly differentiate between successful core-satellite assembly (dark blue) and uncontrolled mixing (green).

¹H-NMR

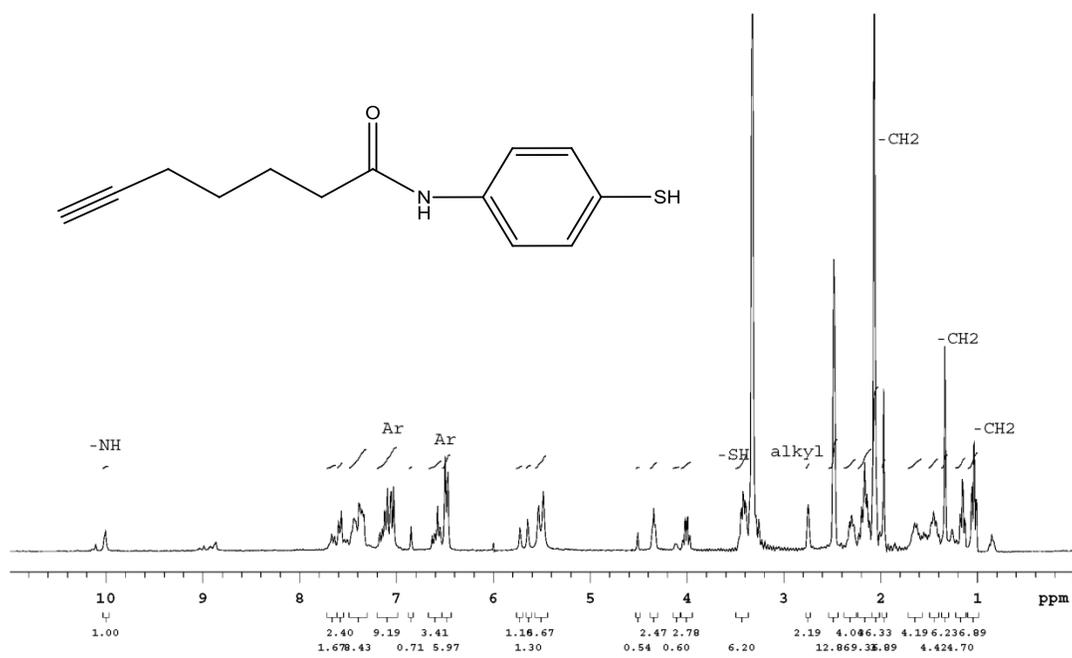


Figure S 3. ¹H-NMR spectra of N-(4-mercaptophenyl)hept-6-ynamide, a custom-made molecules with in-built Raman reporter and alkyl terminal for Click reaction.

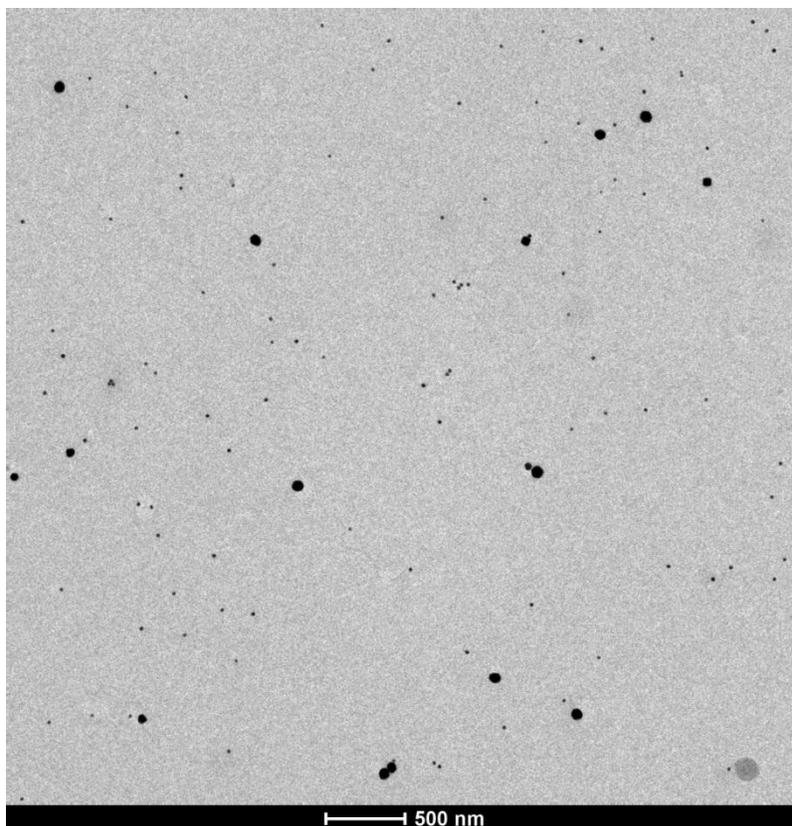


Figure S4. TEM image shows the uncontrolled mixing of non-functionalized cores and satellites showing the randomly distributed cores and satellites on TEM grid and no signs of core-satellite clusters.