

Supporting Information

Dispersion Stability, Ligand Structure and Conformation, and SERS Activities of 1-Alkanethiol Functionalized Gold and Silver Nanoparticles

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S1. pH change induced by C₂ binding to AgNPs and AuNPs.

The possible pH change induced by 1-AT binding to AuNPs and AgNPs was investigated using C₂ as the model 1-AT. 1.0 mL of 130.0 nM pre-concentrated AgNPs or AuNPs was mixed with 1.0 mL of ~ 2.0 mM C₂ in 50% aqueous ethanol (EtOH). The samples were centrifuged and the pH of the ligand binding solution was determined by measuring the pH of the supernatant. The initial pHs of the C₂, AgNP, and AuNP solutions were 5.6, 6.2, and 5.1 respectively.

Deprotonation was observed for C₂ adsorption onto AuNPs. The pH of ~ 2.0 mM C₂ in 50% aqueous ethanol changed from ~5.6 to 3.4 upon addition of AuNPs. However, there was no significant pH change when C₂ interacted with AgNPs. The pH of ~ 2.0 mM C₂ in 50% aqueous ethanol changed from ~5.6 to 5.4 upon addition of AgNPs. These pH measurements highlight the difference in the mechanism between 1-AT binding onto AgNPs and AuNPs in water. The 1-AT interaction with AuNPs involves the deprotonation of R-SH, while the 1-AT interaction with AgNPs is primarily due to the reaction of R-SH with Ag₂O formed on the AgNP surface.

S2. ICP-MS quantification of soluble gold and silver in AuNPs and AgNPs

A Perkin-Elmer Elan DRC II inductively coupled plasma mass spectrometer (ICP-MS) was used to quantify the amount of soluble free Ag or Au species in the supernatant of as-received AgNPs and AuNPs. After complete centrifugation removal of AgNPs (or AuNPs) from the as-received NPs, the concentration of silver or gold in the supernatant solution was analyzed

using ICP-MS with a cross-flow nebulizer and a spray chamber. The aerosol was carried by 0.9 L/min argon. The Ar gas flow for the plasma was 15 L/min. The rf power was set to 1100 W. A calibration curve for Ag ion (or Au ion) content from 0 to 40 $\mu\text{g/L}$ was established for ICP-MS analysis using a TraCERT 1000 mg/L Ag (or Au) standard of ICP quality from Sigma.

S3. TEM images of aged AgNP/1-AT.

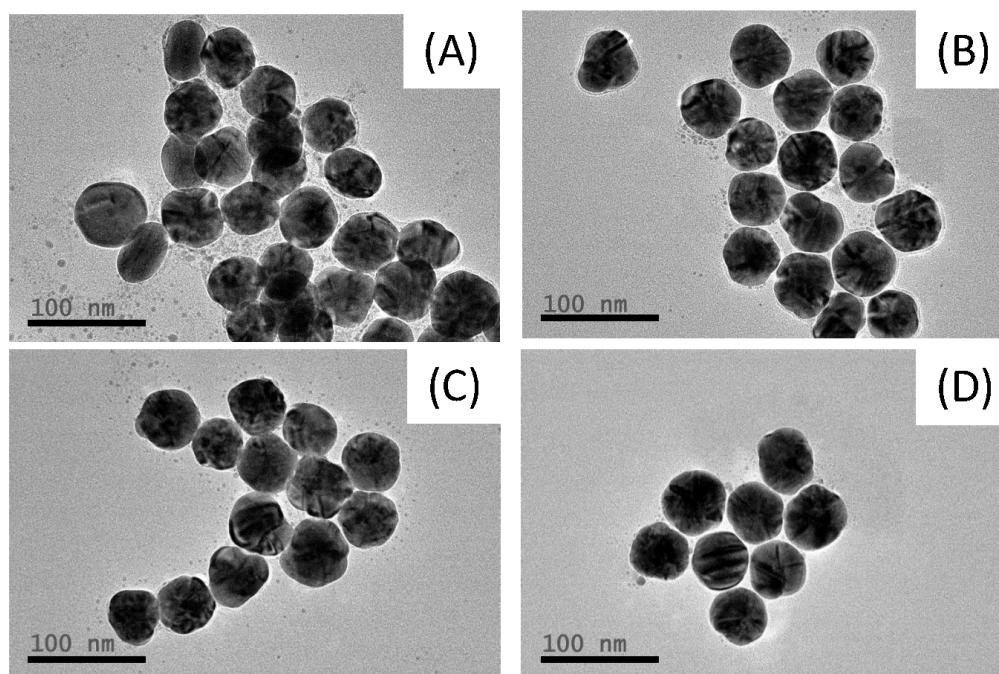


Figure S1. TEM images obtained with (A) one-day-aged $\text{C}_6/\text{AgNP}_{50\text{nm}}$ sample, (B) one-day-aged $\text{C}_{12}/\text{AgNP}_{50\text{nm}}$ sample, (C) six-day-aged $\text{C}_6/\text{AgNP}_{50\text{nm}}$ sample, and (D) six-day-aged $\text{C}_{12}/\text{AgNP}_{50\text{nm}}$ sample, respectively. The morphologies of the one-day-aged AgNP samples were very similar to their 6-day-aged counterparts.

S4. Representative Zoomed-in TEM images used for estimation of NP gap sizes.

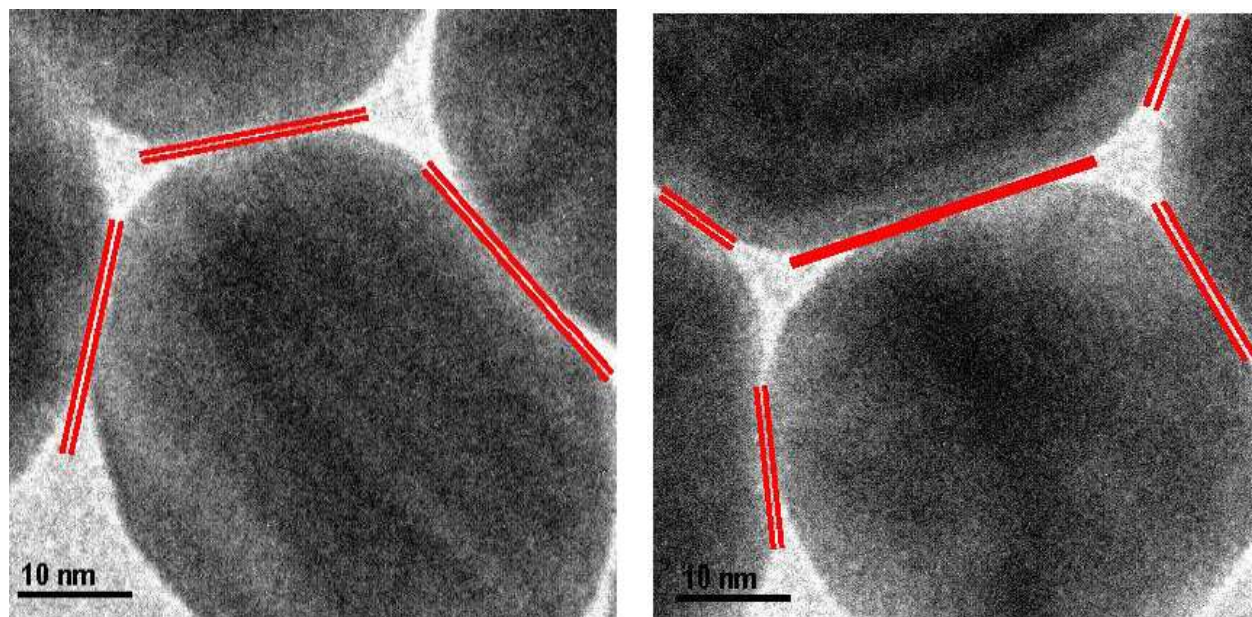


Figure S2. Example zoomed-in images used for estimation of the gap sizes between the neighboring NPs in a NP aggregate. These images were obtained by digital magnification of the TEM images obtained with C₁₂ functionalized 50 nm AgNPs.

S5. Time-dependent DLS of AgNP/C₁₂ and AuNP/C₁₂

Dynamic light scattering (DLS) measurements were performed using a DynaPro™ NanoStar system (Wyatt Technology, Santa Barbara, CA). DLS technique was used to measure the change in the hydrodynamic radii of the AgNP/C₁₂ (or AuNP/C₁₂) over time. There is no significant difference in the thickness of the C₁₂ overlayer on the one- and six-day aged C₁₂ functionalized NPs. DLS measurements further confirmed that 1-AT adsorption is mostly complete within the first 24 hrs of the sample incubation.

Table S1: DLS measurement of AgNP/C₁₂ and AuNP/C₁₂ samples over time. The error represents one standard derivation of five independent measurements.

Incubation time (Day)	0	1	6
Hydrodynamic diameter of AgNP/C ₁₂ (nm)	54.1 ± 0.7	63.5 ± 0.4	64.2 ± 0.7
Hydrodynamic diameter of AuNP/C ₁₂ (nm)	53.4 ± 1.0	63.2 ± 1.0	64.3 ± 1.6

S6. Concentration dependence of SERS spectra of C_{12} on $AgNP_{50nm}$ and $AuNP_{50nm}$

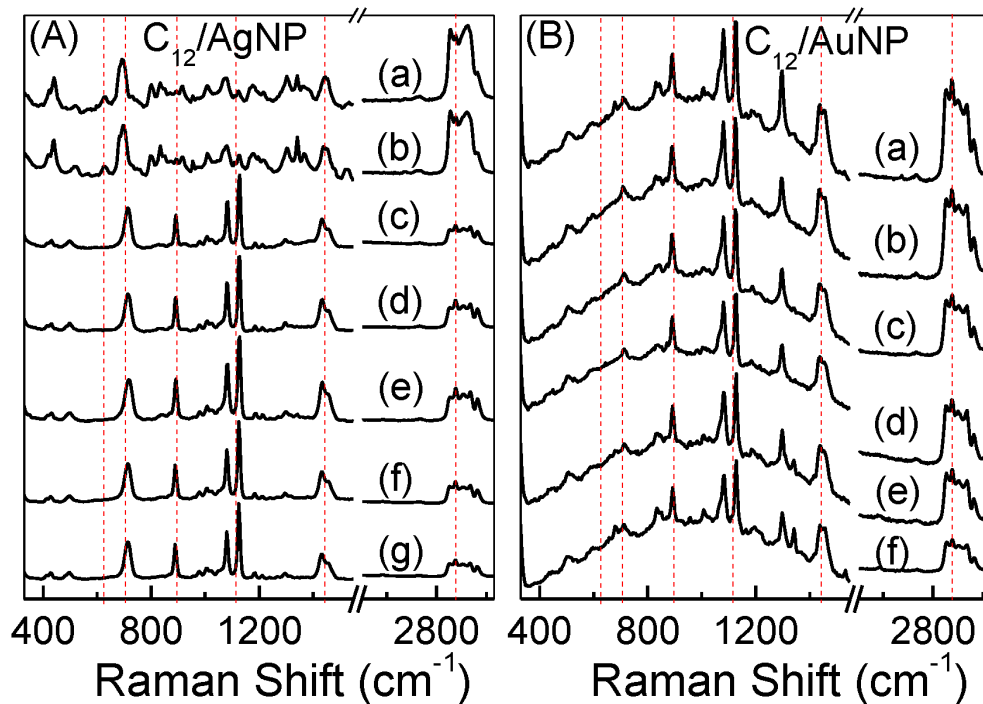


Figure S3. Concentration dependence of SERS spectra of C_{12} on (A) $AgNP_{50nm}$ and (B) $AuNP_{50nm}$. The nominal concentrations of both $AgNP_{50nm}$ and $AuNP_{50nm}$ are 20 pM, nominal concentrations of C_{12} in $AgNPs$ containing samples are a) 1.5 μM , (b) 2.5 μM , (c) 5.0 μM , (d) 10.0 μM , (e) 15.0 μM , (f) 25.0 μM , and (g) 50.0 μM , and nominal C_{12} concentrations in $AuNPs$ containing samples are a) 2.5 μM , (b) 5.0 μM , (c) 10.0 μM , (d) 15.0 μM , (e) 25.0 μM , and (f) 50.0 μM , respectively. The spectra were offset and scaled for clarity.

S7. Time-dependent SERS spectra of the C₆ on AgNPs and AuNPs

The possible time dependence of 1-AT conformation on AuNPs and AgNPs was investigated using C₆ as the model 1-AT. The SERS spectra obtained immediately after mixing C₆ with AgNPs or AuNPs are highly similar in their gauche and trans intensity ratios compared to those obtained with the three-day aged samples (Figure S3). This result strongly suggests that most of the 1-AT adsorption and 1-AT organization occurs within the first few minutes of 1-AT addition to NPs.

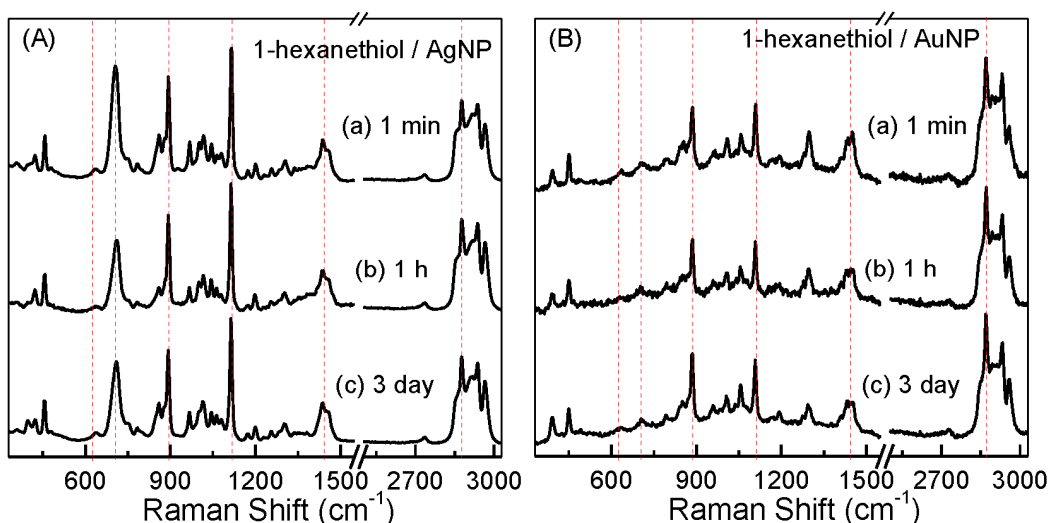


Figure S4. Time dependence of SERS spectra of 1-hexanethiol on (A) AgNP_{50 nm} and (B) AuNP_{50 nm}. SERS spectra were taken after (a) 1 min, (b) 1 h, and (c) 3 day sample incubation. The nominal concentrations of 1-AT and 50 nm NPs in the SERS samples are 50 μ M and 20 pM, respectively. The spectra were offset and scaled for clarity.

S8. SERS of C₂ and C₆ on 10, 30, and 50 nm AgNPs and AuNPs

Possible NP size dependence of 1-AT conformation on AuNPs and AgNPs was investigated using C₂ and C₆ as the model ligands. C₂ and C₆ SERS spectra obtained with the 50 nm NPs are similar to their 10 nm and 30 nm counterparts (Figure S4). This result indicates that the 1-AT crystallinity on AuNPs and AgNPs is mostly independent of the size of the NPs investigated.

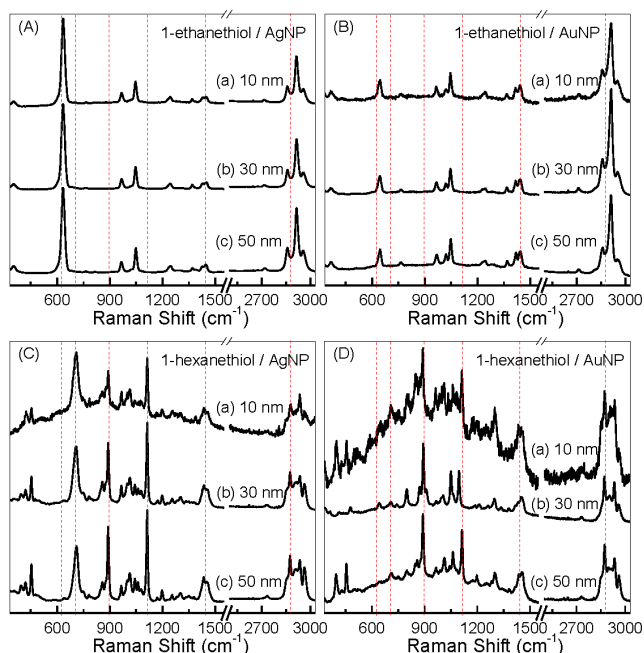


Figure S5. NP size dependence of SERS spectra of (A and B) 1-ethanethiol and (C and D) 1-hexanethiol on (A and C) AgNPs and (B and D) AuNPs. The nominal concentrations of 1-ethanethiol, 1-hexanethiol, 10 nm NPs, 30 nm NPs, and 50 nm NPs are 50 μ M, 50 μ M, 4 nM, 90 pM, and 20 pM, respectively. The spectra were offset and scaled for clarity.

S9. Representative in-situ TEM images of C₂ -, C₆-, and C₁₂- functionalized AuNPs

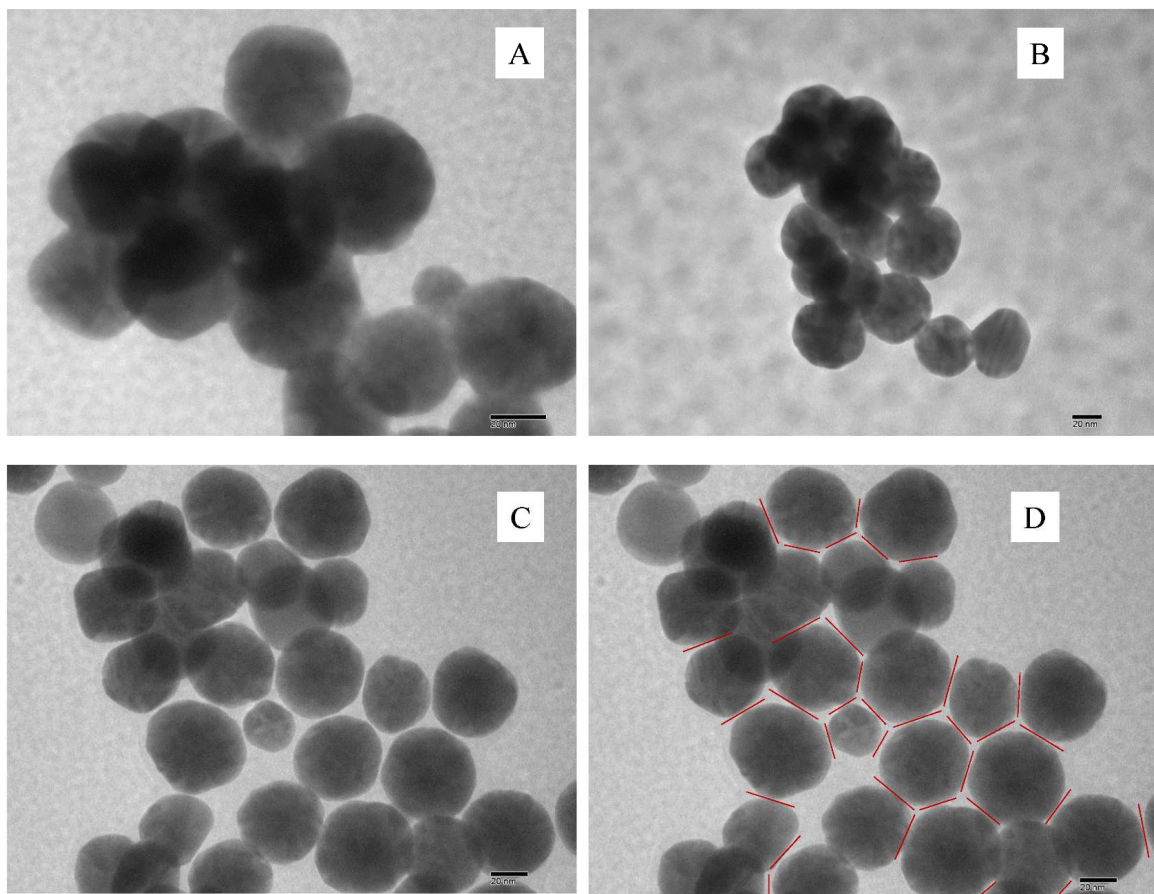


Figure S6: TEM image taken with in-situ (A) C₂-, (B) C₆-, and (C) C₁₂- functionalized AuNP aggregates. The nanoparticles were visually dried under ambient condition before transferred to a liquid sample holder. The internal pressure of the sample holder were kept at 1 atom during TEM measurement to keep the AuNP moisturized. There are no detectable gaps between adjacent NPs in C₂ and C₆- functionalized AuNPs. The average gap size between neighboring C₁₂-functionalized AuNPs is 1.8 ± 0.4 nm. The latter were estimated on the basis of 28 gaps highlighted in Figure 2(D). The scale bars represent 20 nm in all the images.

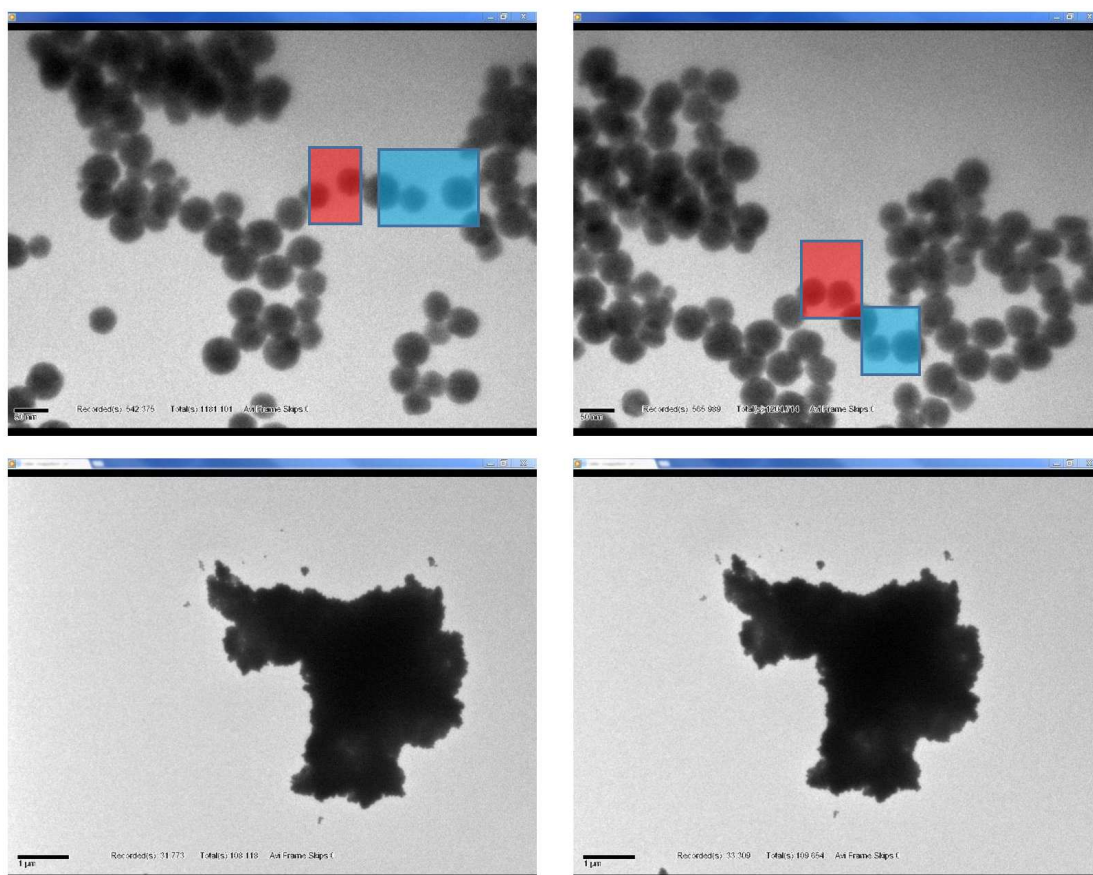


Figure S7: Snapshots from videos taken for (top row) a small and (bottom row) a large C₆-containing AuNP aggregate submerged in water, respectively. The small AuNP aggregates are mobile, but not the large one. Highlighted in the snapshot images in top row are the two pairs of initially separated particles joined together. The scale bar for the snapshot images in top and bottom row are 50 nm and 1 μm, respectively. Description of the experimental procedure for the in-situ TEM videos is available in the experimental section in the main text.