

Supporting Information:

Harnessing Interparticle *J*-Aggregate Induced Plasmonic Coupling for Surface-Enhanced Raman Scattering

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Experimental details

Chemicals. The chemicals included hydrogen tetrachloroaurate (HAuCl₄, 99%), sodium citrate (Cit, 99%), DL-homocysteine (Hcys 95%) and ethanol (EtOH, 99.9%). All chemicals were purchased from Sigma-Aldrich and used as received. Water was purified with a Millipore Milli-Q water system. Cyanine dye: 1,1'-Dibutyl-3,3,3',3'-tetramethylindocarbocyanine iodide (Tlc, (C₃₁H₄₁IN₂), ≥98.0%) is obtained from Changzhou Dongnan pengcheng Chemicals Co., Ltd. The chemicals included hydrogen tetrachloroaurate (HAuCl₄, 99%), sodium citrate (Cit, 99%). All chemicals were purchased from Sigma-Aldrich and used as received.

Synthesis. The synthesis of citrate-capped gold nanoparticles (Au_{13nm}) followed standard method,¹ which involved reduction of AuCl₄⁻ by citrate under boiling condition. Citrate acts as both reducing and capping agents. Gold nanoparticles of larger sizes (30-100 nm) were synthesized by seeded and aggregative growth method,² which involved reduction of AuCl₄⁻ by acrylate forming seeds and seeded growth at room temperature. Acrylate acts as both reducing and capping agents. The stock concentration of gold nanoparticles was determined according to the absorbance data and the average size of the particles. The molar absorptivity for these nanoparticles was determined at the surface plasmon resonance band maximum.^{2a}

Measurements. The interparticle *J*-aggregation induced assembly of Au_{nm} was carried out under ambient condition. UV-Visible (UV-Vis) spectra were acquired with a HP 8453 spectrophotometer over the range of 200-1100 nm. A quartz cuvette with a pathlength of 1.0 cm was utilized. Surface-enhanced Raman scattering (SERS) spectra were measured by an Advantage 200A Raman spectrometer (DeltaNu) and the data were collected from 200 to 3400 cm⁻¹. The laser power and wavelength were 5 mW and 632.8 nm, respectively.

Theoretical Simulation. The simulation of the surface plasmon resonance band and the electrical field was performed using MNPBEM toolbox,³ which involved setting up the nanoparticles' boundary conditions and the dielectric environment to calculate the optical absorption and the electrical field around the nanoparticles. Two models of dimer or trimer of Au NPs were used the theoretical simulations. The first is a simpler model of dimer which involves using two naked Au NPs with an Tlc-defined interparticle distance. This model was also used simulation of a trimer. The second is a "core-shell" model of dimer. This is an advanced model because it considers the adsorption of Tlc on Au NP to define a shell (1.5 nm) around the Au core with a shell refractive index (2.40) and an interparticle π-π stacking distance (0.4 nm)

Additional Data:

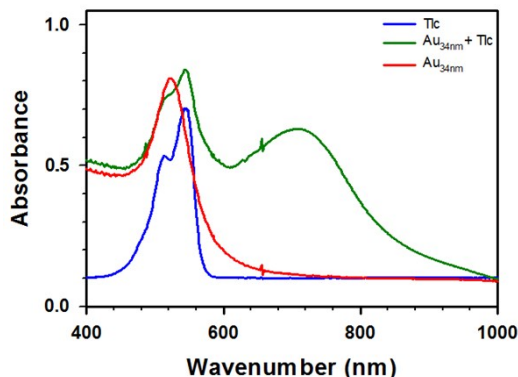


Fig. S1. UV-vis spectra for Tlc (blue), Au NPs (red), and Au NPs in the presence of Tlc (green). Tlc (blue, [Tlc] = 1.23 μM), Au_{34nm} (red, [Au_{34nm}] = 0.155 nM), and Au_{34nm} + Tlc (green, [Au_{34nm}] = 0.155 nM, [Tlc] = 0.176 μM).

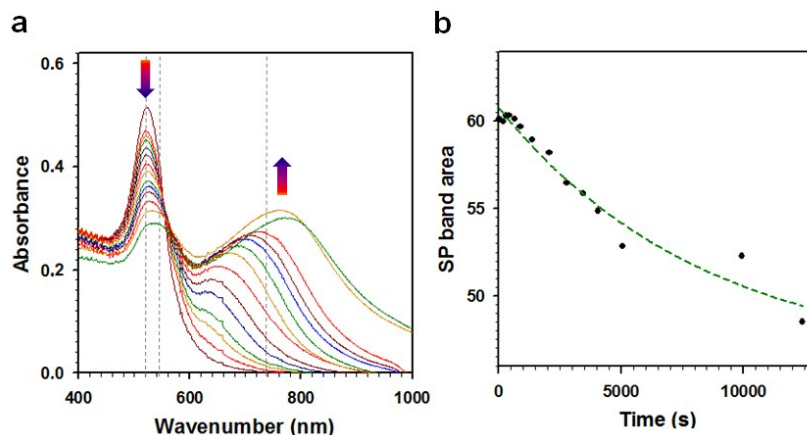


Fig. S2. UV-vis spectral evolution for an aqueous solution of Au NPs (34 nm) in the presence of Tlc. (a) UV-vis spectra at different times (from 0 to 1200 s). $[Au_{34nm}] = 8.9 \times 10^{-2}$ nM; $[Tlc] = 2.4 \times 10^{-2}$ μ M. (b) kinetic plot for the shorter-wavelength SP band; dotted line represent curve fitting by a 1st order reaction model ($y = A_1 + A_1' \times e^{-kt}$) which yields $A_1 = 46.05$, $A_1' = 14.75$, $k = 1.2 \times 10^{-4}$ s⁻¹.

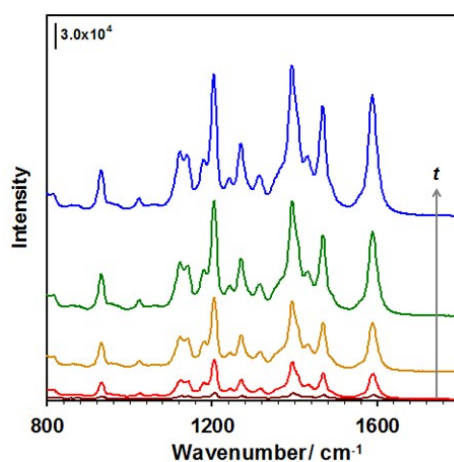


Fig. S3. SERS spectral evolution as a function of time for an aqueous solution of Au_{34nm} upon addition of Tlc. Time: 1~6000 s (from a to e). $[Au_{34nm}] = 0.089$ nM; $[Tlc] = 0.0238$ μ M. (Integration = counts/20s).

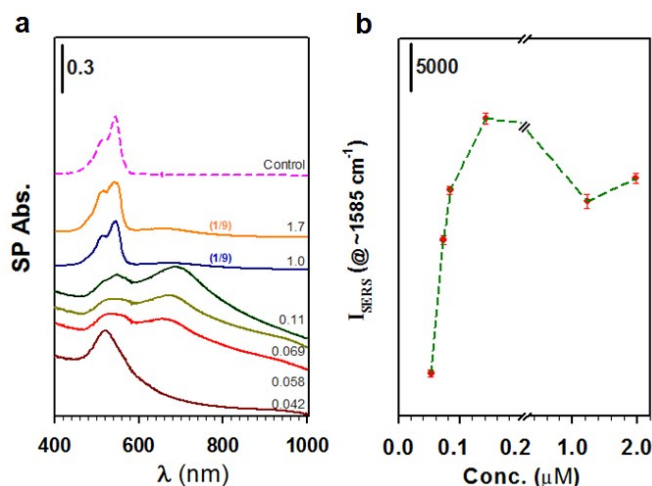


Fig. S4. (a) Spectrum for a solution of Au_{13nm} (2.5 nM) upon addition of Tlc (different concentration) in terms of the surface coverages (θ_T) on the gold NPs. Control: 0.31 μ M Tlc. (b) Kinetic plot of corresponding SERS peak intensity (I) at ~ 1585 cm⁻¹ vs. Tlc concentration. The surface coverage was estimated based on 3D model of Tlc and densely packed monolayer on gold nanoparticle surface. e.g., for Au_{13 nm}, surface area is $4\pi (6.5nm)^2 = 5.31 \times 10^{-12}$ cm²; For Tlc, which can be treated as a rectangular box with short side, long side, or flat orientation anchoring the surface. The long side is ~ 2.0 nm, the short side is ~ 1.4 nm, whereas the thickness is ~ 0.5 nm. For the short side orientation, the area is 0.70×10^{-14} cm² for per Tlc, yielding 5.31×10^{-12} cm² / 0.70×10^{-14} cm² = 759 Tlc/Au_{13 nm}. Similarly, 531 Tlc/Au_{13 nm} for short side orientation, and 190 Tlc/Au_{13 nm}

for flat orientation. The average of Tlc molecules on per Au_{13 nm} is ~493. Experimentally, for a solution of Au_{13 nm} (2.5 nM), the addition of 0.0528 μM Tlc would yield ~21 Tlc/Au_{13 nm}, which in terms of a surface coverage (θ_T) would be 21/493=0.042.

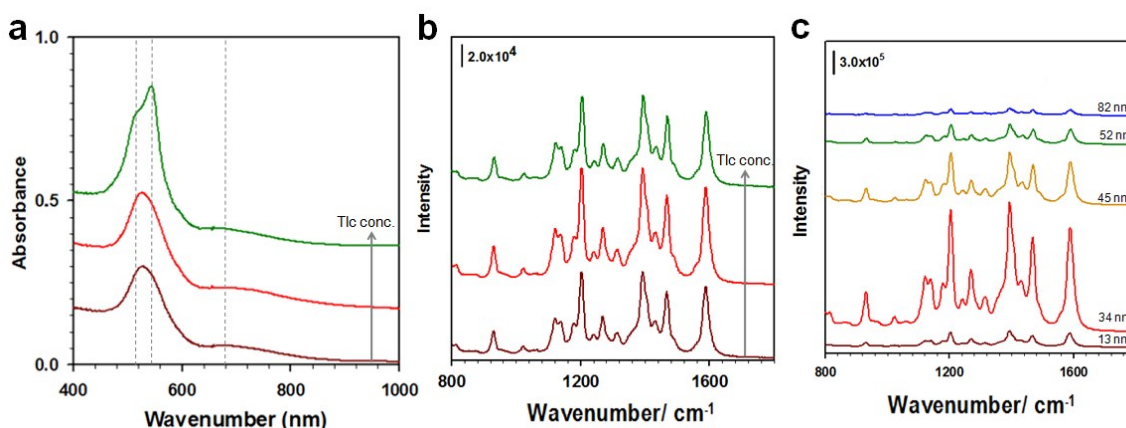


Fig. S5. UV-vis and SERS spectra for aqueous solutions of Au NPs in the presence of Tlc. (a) UV-Vis spectra and (b) SERS spectra for a solution of Au_{45nm} (0.0259 nM) upon addition of Tlc dyes in different concentrations: 0.0146 μM (i.e., $\theta_T = 0.10$), 0.0293 μM (i.e., $\theta_T = 0.20$), and 0.146 μM (i.e., $\theta_T = 1.0$). (c) SERS spectra for Au NPs with five different particle diameters (13 nm (2.5 nM, $\theta_T = 0.175$), 34 nm (0.089 nM, $\theta_T = 0.102$), 45 nm (0.0259 nM, $\theta_T = 0.998$), 52 nm (0.0242 nM, $\theta_T = 0.590$) and 82 nm (0.00718 nM, $\theta_T = 1.0$)).

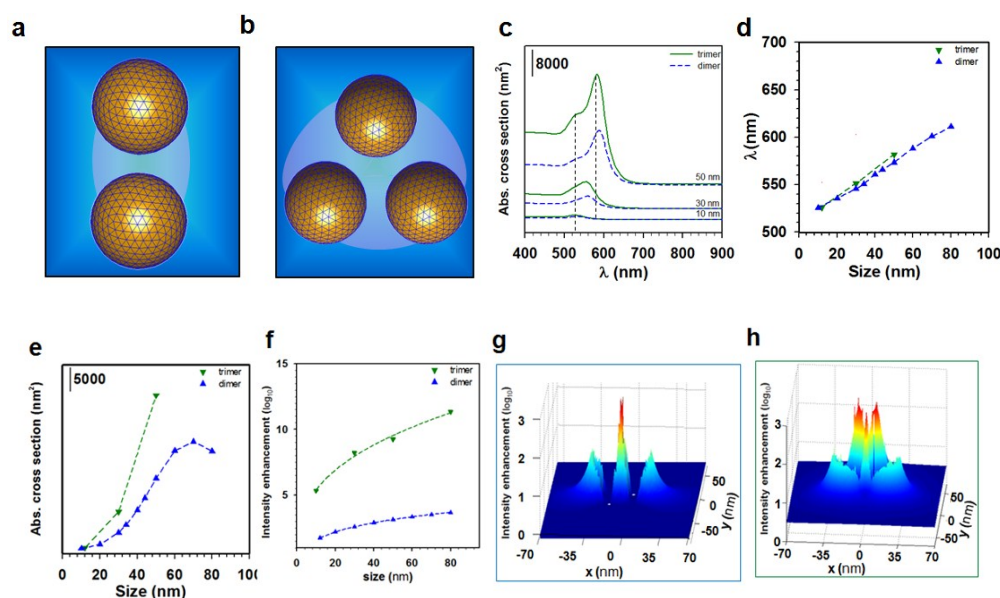


Fig. S6. Simulated optical absorbance cross sections and E-field enhancements upon interparticle plasmonic coupling. (a-b) simple dimer (a) and trimer (b) models of Au NPs (naked NPs with adsorbed Tlc defining the interparticle distance). (c) Simulated absorbance cross section for dimer and trimer of Au NPs of different sizes with interparticle distance defined by π - π stacking of Tlc (3.4 nm). (d) Wavelength (λ , nm) at SP band maximum vs. particle size for dimer and trimer. (e) absorbance (*Abs.*) cross section (nm²) vs. particle size for dimer and trimer. (f) E-field intensity enhancement (in common logarithm) vs. particle size for dimer and trimer (633 nm laser excitation). (g-h) An example of 3D contour plot for the E-field enhancement for Au_{30nm} dimer (g) and Au_{30nm} trimer (h).

References

1. I.-I. S. Lim, U. Chandrachud, L. Wang, S. Gal, and C. J. Zhong, *Anal. Chem.* 2008, **80**, 6038.
2. (a) P. N. Njoki, J. Luo, M. M. Kamundi, I.-I. S. Lim, and C. J. Zhong, *Langmuir*, 2010, **26**, 13622; (b) P. N. Njoki, I.-I. S. Lim, D. Mott, H.-Y. Park, B. Khan, S. Mishra, R. Sujakumar, J. Luo and C. J. Zhong, *J. Phys. Chem. C*, 2007, **111**, 14664.

3. (a) U. Hohenester, *Comput. Phys. Commun.*, 2014, **185**, 1177; (b) U. Hohenester and A. Trügler, *Comput. Phys. Commun.*, 2012, **183**, 370.