Supporting Information

for

Tuning Chemical Interface Damping: Interfacial Electronic Effects of Adsorbate Molecules and Sharp Tips of Single Gold Bipyramids

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1. Chemicals and Materials

Unless stated otherwise, all chemicals were purchased from commercial suppliers and used as received. HAuCl\textsubscript{4} (>99.9%), AgNO\textsubscript{3} (>99%), poly (vinyl pyrrolidone) (PVP, MW = 55 000), cetyltrimethylammonium chloride (CTAC, solution in water, 25 wt. %), cetyltrimethylammonium bromide (CTAB, >99.0%), NaBH\textsubscript{4} (>98.0%), sodium citrate dihydrate (99%), and HCl (37%) were purchased from Aldrich and used as received. Ascorbic acid (AA, 99.5%) and ammonia (NH\textsubscript{3}, 28–30%) were obtained from DaeJung Chemicals & Metals Co. and Junsei, respectively. Other chemicals, unless specified, were of reagent grade, and highly purified water with a resistivity greater than 18.0 M\textOmega cm was used to prepare the aqueous solutions. Citrate-stabilized gold nanorods (AuNRs) used in this study were purchased from Nanopartz (Loveland, CO, USA). Gold bipyramids (AuBPs) used in this study were synthesized via a seed-mediated method described in the following.

2. Synthesis of AuBPs

Prior to the synthesis of AuBPs, small gold nanocrystal (AuNC) seeds were first prepared. For the preparation of the AuNC seed solution, 0.2 mL of HAuCl\textsubscript{4} (10 mM), 0.5 mL of sodium citrate dihydrate (10 mM), and 0.3 mL of NaBH\textsubscript{4} (10 mM) were injected sequentially into 18.95 mL of highly purified water with vigorous stirring, and the solution was kept then for 2 h. This solution was used as an AuNC seed solution without additional treatments. For a typical synthesis of AuBPs, 0.5 mL of HAuCl\textsubscript{4} (10 mM), 0.1 mL of AgNO\textsubscript{3} (10 mM), 0.2 mL of HCl (1 M), 0.08 mL of AA (100 mM), and 0.1 mL of Au NC seeds solution were injected sequentially into a 10 mL aqueous solution of CTAB (100 mM). The solution was incubated in a water bath at 30 °C for 2 h. The solution was kept overnight at room temperature. The final solution contained both AuBPs and Au spheres.
3. Purification of AuBPs

First, Ag was grown on the AuBPs and spheres to separate the AuBPs from spherical Au NCs. The prepared AuBPs and sphere suspension (10 mL) was centrifuged at 7500 rpm for 15 min. The precipitate was redispersed into a 7.5 mL aqueous solution of CTAC (80 mM), and 3.6 mL of AgNO₃ (10 mM) and 1.8 mL of AA (100 mM) were then added sequentially by gently stirring for 5 s. The solution was kept in a water bath at 65 °C for 4 h. The resulting Au–Ag nanoparticle (NP) solution was centrifuged at 6000 rpm for 10 min, and the resulting precipitate was redispersed into 6 mL of an aqueous solution of CTAB (50 mM). The solution was kept in a water bath at 30 °C for 1 h to exclusively settle the Ag–Au bipyramids. Subsequently, the supernatant was discarded and the precipitate was redispersed in a 5 mL aqueous solution of CTAB (50 mM). Finally, to etch the grown Ag on the Au bipyramids, 0.1 mL of NH₃ (28–30 wt. %) and 0.07 mL of H₂O₂ were injected. The solution was kept at room temperature for 1 h. The solution was then centrifuged at 6000 rpm for 10 min and washed with highly purified water.

4. Characterization of AuBPs and AuNRs

Structural characterizations of synthesized AuBPs and AuNRs were carried out using a transmission electron microscope (TEM) (H-8100, Hitachi, Japan) and a scanning electron microscope (SEM) (JSM6500F, JEOL, Japan). Furthermore, the heterogeneous LSPR ensemble absorption spectra of AuBPs and AuNRs dispersed in water were recorded with a Varian Carry 300 UV-Vis spectrometer (Agilent Technology, USA).

More Discussion: In the present study, the AuBPs with high mono-dispersity used for the CID investigations were synthesized using a seed-mediated method (Figures S1 and S2)¹⁻³. Figure S3 presents the 3D structure of a AuBP synthesized in this study as a function of the rotational angle. The rod-like anisotropic shape of AuNRs are clearly observed by transmission electron
microscopy (TEM) (Figure S4). From two corresponding batches of AuBPs and AuNRs, their mean sizes were determined to be 24.7 nm × 76.1 nm and 25.3 nm × 75.1 nm, respectively (Figures S5 and S6). With respect to these sizes, the two samples have similar aspect ratios (ARs): 3.08 for AuBPs and 2.97 for AuNRs. Figure 1C shows the ensemble extinction spectrum for the AuBPs (red-curve) overlaid on top of the AuNRs (orange-curve), including the high-energy (smaller wavelength) transverse peaks (AuBP/AuNR: 521 nm/522 nm) and low-energy (higher wavelength) longitudinal peaks (AuBP/AuNR: 726 nm/714 nm). The similarities between the AR of the AuBPs and AuNRs indicate that their longitudinal resonance modes are similar and away from the inter-band electronic transitions onset (517 nm/ 2.4 eV)\(^4\). This helps reduce the effect of frequency-dependent changes in the LSPR linewidth (or FWHM)\(^5\). Accordingly, because the transverse peaks are observed sporadically for single particle scattering spectra, the only effects observed in the longitudinal modes of LSPR scattering spectra are related to the shape of the Au nanoparticles, including the sharp tips of AuBPs. From the normalized extinction spectra of AuBPs (red-curve) and AuNRs (orange-curve), as shown in Figure 1C, three distinctive spectral characteristics were observed relative to the shape of each nanoparticle sample. The maximum extinction of longitudinal peak of AuBPs was redshifted towards lower energies (or higher wavelengths). In addition, the FWHM was broadened and the absorption intensity was decreased slightly. Although two samples with similar ARs were used in the same local refractive index environment, their extinction spectra were modified significantly. The differences observed on the spectrum might be due to the sharp tips of AuBPs. On the other hand, although the samples of AuBPs and AuNRs have high mono-dispersity, these effects might also be caused by the slight heterogeneity (distribution of size or shape) of the individual particles within the ensemble samples\(^6\). Studies have shown that heterogeneity in the size of the nanoparticles induces a redshift\(^8\).
5. Fabrication of a Flow Cell

We fabricated a flow cell using parafilm as a spacer between two coverslips #1 (24 mm × 60 mm). Three channels were cut into the parafilm and six holes were cut into one of the coverslips by using a commercially available CO₂-laser cutter system. The parafilm and coverslips were overlaid so that the holes in one of the coverslips matched with the ends of the channels in the parafilm. The flow cell was placed on a heating plate at 120 °C for a few seconds so that the parafilm melted and the flow cell became airtight.

6. Sample Preparation for Single Particle Study

The samples for single particles studies were prepared as follows. The colloid solution was first diluted to the appropriate concentration with pure water. The diluted solution was then sonicated for 10 min at room temperature. The samples were prepared by spin casting on pre-cleaned SO₂ glass slides. Subsequently, a 22 mm × 22 mm No. 1.5 coverslip (Corning. NY) was placed on the glass slide. Although AuBPs and AuNRs in the water refractive index samples were used directly, to obtain the air and oil refractive indices, the samples were dried at room temperature, which permitted a change from the air refractive index medium to oil. Throughout all the experiments, the concentration of AuBPs and AuNRs on the glass slide surface was controlled to be approximately 1 μm⁻² to facilitate single particle characterization and minimize inter-particle LSPR coupling, resulting in spectral shifts.

7. Single Particle Microscopy and Spectroscopy

In a home-built system, dark-field (DF) microscopy imaging was carried out under a Nikon inverted microscope (ECLIPSE Ti-U). In DF mode, the microscope utilized a Nikon Plan Fluor 100x 0.5-1.3 oil iris objective and a Nikon DF condenser. An Andor iXonEM+ CCD camera (iXon Ultra 897) was employed to record DF images of AuBPs and AuNRs. The collected images were
analyzed with the ImageJ software (https://imagej.nih.gov/ij/download.html, NIH). Furthermore, DF scattering spectra were acquired with an Andor spectrophotometer (SHAMROCK 303i, SR-303i-A) connected with an Andor CCD camera (Newton DU920P-OE). When obtaining a spectrum, the scanning stage moved the sample to the desired location so that only scattered light from the selected location was collected by the objective. The scattered light was directed to the entrance of the spectrophotometer, dispersed by a grating (300 l/mm, center wavelength of 700 nm), and detected by the Andor Newton CCD camera. The background was measured at a region without any particles. Data analysis was performed with specially designed Matlab programs.

8. Correlation Study between SEM and Optical Microscopy

In this study, we correlated SEM images with optical images and spectra of single Au nanoparticles (AuBPs, AuNRs, Figures S9 and S10). After cleaning glass slides, a gold pattern was created by evaporating a 5 nm Ti layer followed by a 20 nm Au layer through an indexed copper Transmission Electron Microscopy (TEM) grid (Ted Pella) placed on the cleaned glasses (Figure S10). This pattern aided in locating the same particles in SEM and optical microscopy as clearly demonstrated in the overlaid SEM and DF image (Figure S9). First, we took SEM images of single Au nanoparticles well separated on a glass slide. We then obtained DF scattering images and spectra of same Au nanoparticles under DF microscopy and spectroscopy.

9. Thiol Binding Experiments under DF Single Particle Spectroscopy

Single particle scattering spectra of Au nanoparticles were obtained at the start of the experiment for reference. Then, an ethanolic 1-mM thiol solution was introduced through the flow cell while continuously taking single particle spectra of the same Au nanoparticles (AuBPs and
AuNRs) for a period of 60 min. It should be noted that thiol (-SH) group has a strong affinity for gold.

10. Langmuir Adsorption Isotherm

In this study, to compare quantitatively the amount of CID when introducing various thiol molecules, it was necessary to establish whether a comparable, if not complete, coverage of adsorbed thiol molecules had been achieved.\(^5\) Therefore, a time evolution typical for a Langmuir adsorption isotherm was employed, i.e., \(\theta = 1 - \exp(-k_L \cdot c \cdot t)\), where the coverage \(\theta\) depends on the time \(t\), thiol concentration \(c\), and Langmuir adsorption constant \(k_L\). As the thiol concentration was constant (1 mM in this study), the adsorption constant was simplified to \(k = k_L \cdot c\) and the LSPR linewidth broadening due to thiol adsorption was fitted with \(\Delta \Gamma(t) = \Delta \Gamma_{CID}[1 - \exp(-kt)]\).\(^5\) This Langmuir adsorption model led to the equilibrium value of CID, \(\Delta \Gamma_{CID}\), for AuBPs (or AuNRs) at complete thiol adsorption. These \(\Delta \Gamma_{CID}\) values compare well with the LSPR linewidth broadening measured for individual nanoparticles after 60 min of thiol binding.

11. Raman Instrumentation

A home-made Raman spectroscopic system with a 785-nm diode laser was used for SERS measurements. The laser power was set to be 60 mW. However, the real laser intensity that arrived on the stage was the half of the initial power due to the loss by the path and mirrors. The monochromator with the spectral resolution of 0.1 nm was used with 600 l/mm grating and the slit width was set to be 100 μm. The Raman spectra were collected by using 40 × objective lens with a numerical aperture (NA) of 0.75. The Andor CCD camera (Newton Du9209-OE) was used as a detector and the Andor spectrometer (SHAMROCK 303i, SR-3031-A) transmits the electric data as the spectrum. All the Raman spectra were analyzed with the Matlab program.
12. Real-time Raman Measurements with Gold Bipyramids

For real-time SERS sample preparation, 100 µL of AuBPs was transferred into tube and centrifugated at 2,400 rpm for 30 min for removing surfactant, CTAB. The washed AuBPs sample was dispersed in ethanol and were sonicated for a few seconds for enough dispersion. As soon as adding the probe molecules solutions with each concentration to rinsed AuBPs solution, the prepared samples were put into the capillary tube with the size of 0.25-mm wall thickness and 100-mm length. As soon as mixing two solutions, it was measured within capillary tube, and both ends of capillary tube were sealed for preventing the loss of solvent, ethanol, due to evaporation. This Raman measurement was repeated every 3 minutes until the Raman signal was saturated.

More Discussion: 4-Thiophenoles with a benzene ring (p-ATP and p-NTP) are adsorbed effectively on the surfaces of AuBPs with sharp-tips according to real-time surface-enhanced Raman spectroscopy (SERS) (Figure S25). The experimental setup for Raman spectroscopy is provided in Figure S23. SERS was used in this study for three reasons. First, Raman spectroscopy is a powerful tool for obtaining chemical information on Raman probe molecules. Second, p-ATP and p-NTP with a benzene ring offer high SERS signals compared to 1-alkanethiol. Finally, the adsorption of 4-thiophenols on the nanoparticle surfaces over time can be confirmed through characteristic Raman peaks. As shown in Figure S25, the Raman intensity and peak at 1357 cm\textsuperscript{-1} assigned to NO\textsubscript{2} vibrations increased gradually with time after introducing the thiol solution (p-NTP, 1 mM), and after 60 minutes of thiol binding on the AuBP surfaces, the enhanced signals of the peak at 1357 cm\textsuperscript{-1} became saturated for p-NTP (1 mM). This indicates that p-NTP molecules are adsorbed effectively on the AuBP surfaces over time and are densely packed on the particle surfaces after 1 hr. As a control, no increase in the SERS signal of p-NTP was observed without AuBP substrates (Figure S26). Therefore, the time-dependent effective
adsorption of 4-thiophenols on the AuBP surfaces was confirmed, which is consistent with the single particle measurements in Figures 4 and S22.

13. SERS Study on the Isomeric Steric Effects (ortho, meta, and para groups)

To further support the time-dependent effective binding of the three isomeric steric positons of the additional functional groups on the AuBP surfaces, real-time SERS measurements were carried out with ATP (1 mM) having three isomeric positions (ortho-, meta- and para-) in the presence of AuBPs within a capillary tube measured every 3 minutes under 785-nm laser illumination. The Raman signals at the peak of 1100 cm\(^{-1}\) assigned to C-S vibrations increased gradually with time for all three isomeric positions of ATP (Figures S30 and S31). Furthermore, after 60 minutes of thiol binding on the AuBP surfaces, the enhanced signals of the peak 1100 cm\(^{-1}\) were saturated for all three isomeric positions (Figure S31). The results suggest that all of the ATP molecules with different steric effects are bound effectively to the AuBP surfaces over time and are densely packed on the surfaces after 60 minutes. Furthermore, for ATP with the ortho- and meta-positions having a similar steric effect, ortho-ATP produced stronger Raman signals than m-ATP under the same experimental conditions. Therefore, depending on the location of the EDG (ortho, meta, or para directors), the CID effect induced by benzene rings with EDG should be considered as induced by sulfur atoms bound to the surface of the nanoparticles and weakened by the promotion of electron back transfer by EDG.

14. Defocused Orientation and Position Imaging Technique

Anisotropic AuBPs that are much smaller than the wavelength of incident light can be considered electric point dipoles. According to an electrostatic approximation, plasmon oscillations from anisotropic AuBR can be simplified as three-perpendicular independent dipoles along the three axes (Figure S17A). Oscillation along the long principal axis (a-axis) is defined as
a longitudinal mode and the other perpendicular oscillations are defined as transverse modes vibrating along the short axes (b and c axes). $E_a$ indicates the scattering electric field of the AuBP along the main long axis, while $E_b$ and $E_c$ are the scattering electric fields along the short transverse axes, b and c. The overall scattering electrical field from a AuBP can be quantified through a linear superposition of three independent scattering electric fields associated with three mutually orthogonal dipoles, as shown in the following equation:

$$E_{\text{(scat)}} = \sum_{a,b,c} E_{\text{(scat)j}} = E_{\text{(scat)a}} + E_{\text{(scat)b}} + E_{\text{(scat)c}}$$

However, $E_a$, the scattering electric field of the AuBP along the main long axis (or the longitudinal dipole) is much more dominant than the two transverse dipoles. Therefore, a AuBP behaves as a single dipole character.

Defocused orientation and position imaging (DOPI) technique\textsuperscript{1-3} is a direct and simple method with the capability of visualizing and determining three-dimensional (3D) dipole orientation of anisotropic single AuBPs. The core idea is that the direct detection of the spatial distribution of the scattered or emitted field of single dipoles becomes possible when the imaging system is defocused deliberately by $\sim$1 μm.

15. Simulation of Scattering Image Patterns of AuBPs

We used the simulation program developed by Enderlein and Böhmer.\textsuperscript{9} The program is designed to calculate the characteristic intensity distribution from an emitter with three perpendicular emission dipoles of different emission strength. It has been widely used to determine the spatial orientation of single dye molecules.\textsuperscript{9-10} The simulation program is a special Matlab based utility with a graphics user interface (GUI) for easy calculation. This program allows us to calculate exactly the defocused (or focused) images of single molecules. For using the GUI,
one should download the files from the website (http://www.joerg-enderlein.de/imagingOfSingleMolecules.html).

The parameters that can be input are: the numerical aperture of the objective lens, magnification of imaging, extent of defocusing (or defocusing distance in micrometers), $\kappa$ and $R$. For defining the emission strength ratios of the three independent dipoles (Figure S17A), we input the parameter $\kappa$ and $R$ into the program. The ratio $\kappa$ defines the ratio of the emission strength of the b- to the c-dipole (transverse dipoles, Figure S17) as shown below.

$$ I_b / I_c = (1 - \kappa) / (1 + \kappa) $$

In addition, the ratio $R$ defines the emission strength of the a-dipole (or longitudinal dipole) to the combined b and c dipoles (or transverse dipoles) as shown below.

$$ R \times I_a + (1 - R) \times (I_b + I_c) $$

When $R$ is 1, we only have the contribution from a-dipole (longitudinal dipole) to the image patterns. In the present study, we used a $R$ value of 1 to simulate the scattering patterns of single dipoles generated on the AuBP surface at different LSPR excitation wavelengths.

16. Multiple Orientation Effect of Single AuBPs

In CID studies using single AuBPs with sharp tips, their orientations on a glass slide could also affect the experimental results. Therefore, this study investigated the three-dimensional (3D) spatial orientations of single AuBPs (approximately 100 particles) cast on a glass slide through DF scattering imaging, as shown in Figures S16-S19. When the DF images were defocused, certain patterns could be observed like a donut-shape, indicating the orientation (or spatial field distribution) of a particle by the brightness (Figures S16 and S18). To increase the degree of confidence, a simulation was performed, which produced results consistent with the experimental
results (Figure S18). From the defocused DF imaging method, the average polar angle, $\theta$, of AuBPs, as defined in Figure S17A, was approximately 65.9° (Figure S19B). Therefore, they showed almost equal orientation tendency, meaning no effect of orientation for the CID experiment of AuBPs while focusing only on the chemical effect.
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Supporting Figures

Figure S1. SEM image to show AuBPs synthesized with high monodispersity in this study.
Figure S2. (A) TEM image of AuBPs synthesized in this study. The average diameter and length are 26 nm and 76 nm, respectively. (B) Enlarged TEM image of single AuBP with sharp tips.
Figure S3. Schematic diagram to show 3D structure of AuBP synthesized in this study at different rotational angles.
Figure S4. TEM image of AuNRs purchased from Nanopartz
Figure S5. Histograms to show the average length (A) and width (B) of single AuBPs used in this study. A red-curve shows a Gaussian fit to the experimental data, yielding the mean length and width.
Figure S6. Histograms to show the average length (A) and width (B) of single AuNRs used in this study. A red-curve shows a Gaussian fit to the experimental data, yielding the mean length and width.
**Figure S7.** A photograph to show the experimental setup for single particle microscopy and spectroscopy.
Figure S8. Schematic diagram to show the working principle of scattering-based DF microscopy and spectroscopy for single Au nanoparticles.
Figure S9. Overlaid SEM and DF scattering images of same AuNRs in this correlation study.
Figure S10. (A-D) SEM images of AuNRs in same region and deposited on a slide with gold pattern. The gold pattern allowed to locate same Au nanoparticles (AuBPs, AuNRs) under optical microscopy.
Figure S11. Single particle scattering spectra of AuBPs in water. The ensemble spectrum of AuBPs dispersed in water is overlaid with single particle spectra for comparison.
Figure S12. Single particle scattering spectra of AuNRs in water. The ensemble spectrum of AuNRs dispersed in water is overlaid with single particle spectra for comparison.
Figure S13. Overlaid DF scattering spectra of a single AuBP1 and AuNR1 in Figure 2. The normalized scattering spectra are presented in eV.
Figure S14. (A) Histogram to show the distribution of DF scattering intensity measured from single AuBPs. (B) Histogram to show the distribution of DF scattering intensity obtained from single AuNRs. In this study, DF scattering imaging was performed to obtain the intensity histogram for each sample (AuBPs or AuNRs) measured under the same experimental condition.
Figure S15. Single particle scattering spectrum of AuBP1 fitted using a Lorentzian function to extract the homogeneous LSPR linewidth. The DF scattering spectrum of AuBP1 is presented in eV.
Figure S16. (A) Defocused scattering image of anisotropic single AuBPs with sharp tips. (B) Enlarged defocused scattering image patterns of single AuBPs in (A). A donut-shaped image pattern is observed for AuBPs, and we can extract 3D spatial orientations of single AuBPs from their characteristic donut-shaped scattering patterns.
Figure S17. (A) Schematic depicting three-perpendicular dipoles along the three axes. $E_a$ denotes the scattering electric-field of the AuBP along the main long axis. Definitions of the polar angle $\theta$ and the azimuthal angle $\phi$ of a AuBP in 3D space are also shown. (B) Schematic of AuBPs to produce characteristic doughnut-shaped scattering patterns depending on their spatial orientations in 3D space.
**Figure S18.** The measured and best-matched simulation patterns from randomly selected AuBPs (Figure S16) in different orientations on a glass slide. The measured defocused patterns (A–D) are obtained at the defocusing distance of ~1 μm. It is shown that the measured patterns (A–D) match well with the simulated patterns (E–H).
Figure S19. (A) Schematic depicting the polar angle $\theta$ of a AuBP deposited on a glass slide. (B) A histogram to show the measured polar angle $\theta$ of single AuBPs in Figure S16, and a mean of polar angle for 30 AuBPs was determined to be $65.9^\circ$. The polar angle of AuBPs was determined through the pattern match analysis.
**Figure S20.** Chemical interfacial damping of single AuBPs with thiol molecules. (A) Single particle scattering spectra of AuBP recorded in ethanol before adding a drop of 1-decanethiol (grey-curve) and 10 minutes after adding an ethanolic solution of 1-decanethiol through a home-built flow cell (red-curve). (B) Single particle scattering spectra normalized to better compare the LSPR wavelength shift as well as the LSPR linewidth broadening.
Figure S21. Adsorbate molecules used in this study. The thiophenol has various additional functional groups with different ortho-, meta-, para-positions on the benzene ring.  

(A) ortho-aminothiophenol (B) meta-aminothiophenol (C) para-aminothiophenol (D) ortho-trifluoromethylthiophenol (E) meta-trifluoromethylthiophenol (F) para-trifluoromethylthiophenol (G) para-hydroxythiophenol (H) para-nitrothiophenol
Figure S22. Effects of thiolated benzene rings with additional functional groups with different electronic potential on CID for AuBPs and AuNRs. (A) Illustration of binding thiolated benzene rings with additional functional groups (4-amino and 4-nitro) on the surfaces of AuBPs (top) and AuNRs (bottom). (B) Time dependence of thiol adsorption observed via LSPR linewidth (or FWHM) broadening for single AuBPs (left) and single AuNRs (right) for each sample (p-ATP and p-NTP). The scattering spectra of 20 single gold nanoparticles (AuBPs, AuNRs) were obtained repeatedly from each sample for a period of approximately 60 min and the LSPR linewidth $\Delta \Gamma$ was extracted with respect to the starting value. The fitted curves are shown as black. (C) The shift of homogeneous LSPR linewidth induced by p-ATP and p-NTP with different electronic effects for both single AuBPs (blue-curve) and single AuNRs (red-curve).
**Figure S23.** A photograph to show inverted microscope equipped with Raman spectroscopy with 785-nm diode laser, mirrors, and spectrograph with CCD camera.
**Figure S24.** Schematic diagram to depict the Raman measurement of thiophenols (ATP, NTP) in the presence of AuBPs within a capillary tube under 785-nm laser illumination. The corresponding Raman signal from the sample is collected by an objective lens.
Figure S25. Raman measurements to demonstrate the effective adsorption of thiolated benzene rings on the AuBP surfaces. (A) Real-time surface-enhanced Raman spectra of p-NTP (1 mM) in the presence of AuBPs within a capillary tube measured every 3 minutes under 785-nm laser illumination. Raman peak at 1357 cm\(^{-1}\) assigned to NO\(_2\) vibration is increased gradually as a function of time. (B) Corresponding change in the Raman intensity at 1357 cm\(^{-1}\) is plotted, and p-NTP molecules are effectively adsorbed and densely packed on the particle surfaces after 1 hr.
Figure S26. Real-time surface-enhanced Raman spectra of p-NTP (1 mM) in the absence of AuBPs within a capillary tube measured every 3 minutes under 785-nm laser illumination.
**Figure S27.** The corresponding shift of the LSPR wavelength induced by para-aminothiophenol (p-ATP) and para-nitrothiophenol (p-NTP) as compared to the LSPR linewidth shift in Figure S22.
Figure S28. Comparison of the FWHM values (meV) for the two cases (without citrate, with citrate). In this study, the capping reagent present on the surface of the AuBPs was removed by performing oxygen plasma treatment for 20 s. Two samples were measured in water under single particle DF scattering microscopy and spectroscopy. We measured 30 nanoparticles for each sample to compare the FWHM values.
Figure S29. Illustration of ortho-, meta- and para-thiolated isomers of benzene ring binding to single AuBPs. AG stands for additional functional group.
Figure S30. Real-time surface-enhanced Raman measurements with ATP (1 mM) having three isomeric positions of (A) ortho-, (B) meta-, and (C) para- in the presence of AuBPs within a capillary tube measured every 3 minutes under 785-nm laser illumination.
**Figure S31.** Changes in the Raman intensity at the peak of 1100 cm$^{-1}$ assigned to C-S vibration for ATP (1 mM) with three isomeric positions of (A) ortho-, (B) meta-, and (C) para- as a function of time. After 60 minutes of thiol binding on the AuBP surfaces, the enhanced signals of the peak 1100 cm$^{-1}$ were saturated for all of three isomeric positions.