

**Supporting Information: Measuring binding kinetics of aromatic
thiolated molecules with nanoparticles *via* surface-enhanced Raman
spectroscopy**

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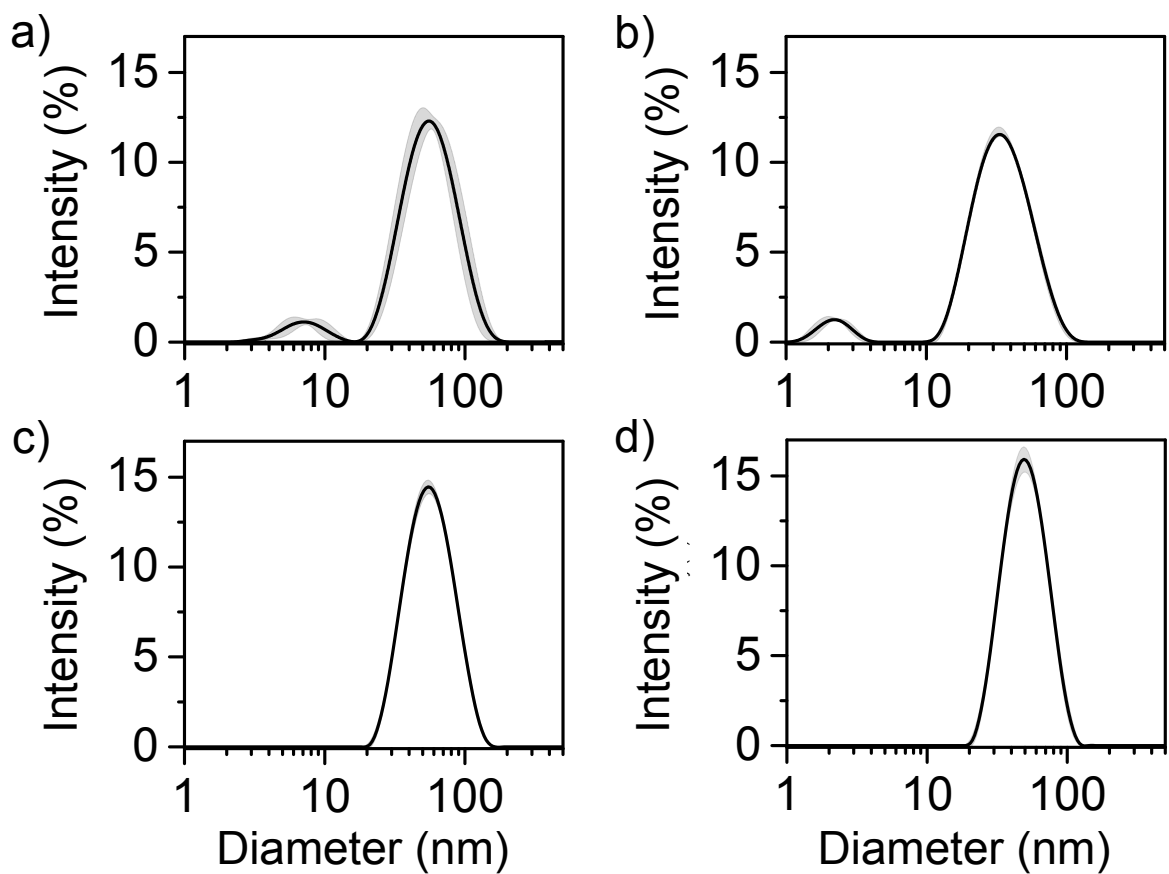


Figure S1. Dynamic light scattering (DLS) of (a) citrate-stabilized gold nanoparticles, (b) gold nanoparticles with DTNB stored for 2 weeks at room temperature, (c) gold nanoparticles stabilized with CTAB, and (d) gold nanoparticles replaced with 4-ATP and stored for 2 weeks at room temperature. Shaded area corresponds to the standard deviation of the measurements.

| DTNB (10 mM) | k_{obs} (min⁻¹) | A (a.u.) |
|-------------------------------------|---|---------------------------------------|
| 25 μL | 0.0117 | 1.10×10^5 |
| 50 μL | 0.00725 | 7.56×10^4 |
| 100 μL | 0.0141 | 1.46×10^5 |
| 200 μL | 0.0129 | 1.87×10^5 |
| Mean | 0.011 ± 0.003 | $1.3 \times 10^5 \pm 0.5 \times 10^5$ |

Table S1. First-order Langmuir adsorption model fit to the Raman band corresponding to the vibrational stretching mode $\nu(\text{NO}_2)$ at $1,340 \text{ cm}^{-1}$. Measurements were performed in a fused silica cuvette with 2 mL of nanoparticle solution and a concentration of 9.4 nM.

| 4-ATP (10 mM) | k_{obs} (min⁻¹) | A (a.u.) |
|-------------------------------------|---|---------------------------------------|
| 25 μL | 0.0100 | 3.78×10^5 |
| 50 μL | 0.0131 | 3.43×10^5 |
| 100 μL | 0.0125 | 3.78×10^5 |
| 200 μL | 0.0109 | 3.80×10^5 |
| Mean | 0.012 ± 0.002 | $3.7 \times 10^5 \pm 0.2 \times 10^5$ |

Table S2. First-order Langmuir adsorption model fit to the Raman band corresponding to the vibrational stretching mode $\nu(\text{C-C})$ at $1,594 \text{ cm}^{-1}$. Measurements were performed in a fused silica cuvette with 2 mL of nanoparticle solution and a concentration of 3.0 nM.

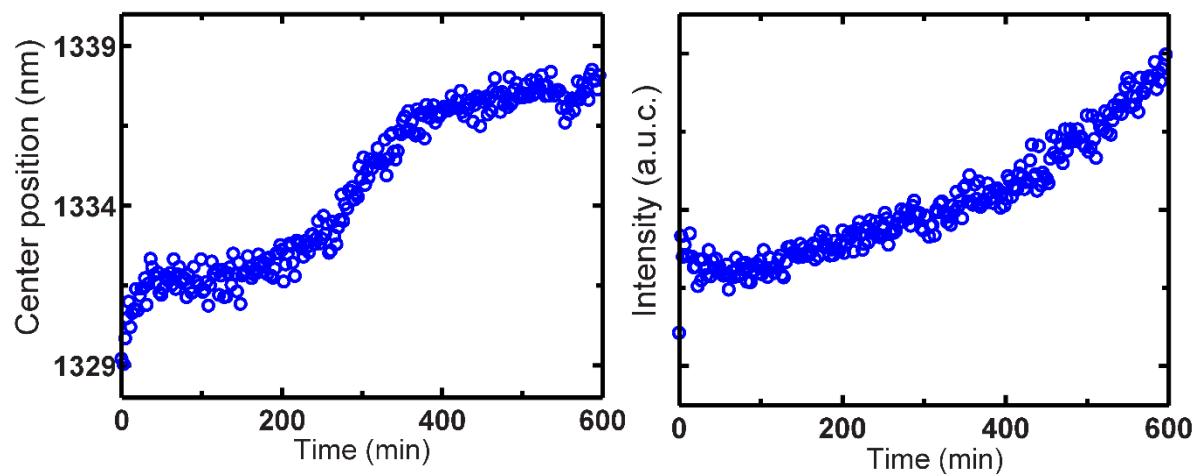


Figure S2. Kinetic data of DTNB (10 mM) added to a gold substrate. The substrate was cleaned with 3:1 concentrated H_2SO_4 to 30% H_2O_2 before addition. We see that even after 600 minutes of acquisition time, the intensity (evaluated at $\nu(\text{NO}_2)$) is still growing.

We found that it was necessary to perform additional steps on CTAB-stabilized gold nanorods in order to have successful ligand exchange occur. In order for successful ligand exchange to occur on gold nanorods, it was necessary to remove additional CTAB using an iterative process of washing the nanorods in chloroform, adding polystyrene sulfonate (PSS), and centrifugation (see Experimental Methods). Nonetheless, we not unable to completely remove all CTAB, as shown in the SERS spectra of the PSS-coated nanorods (Figure S3).

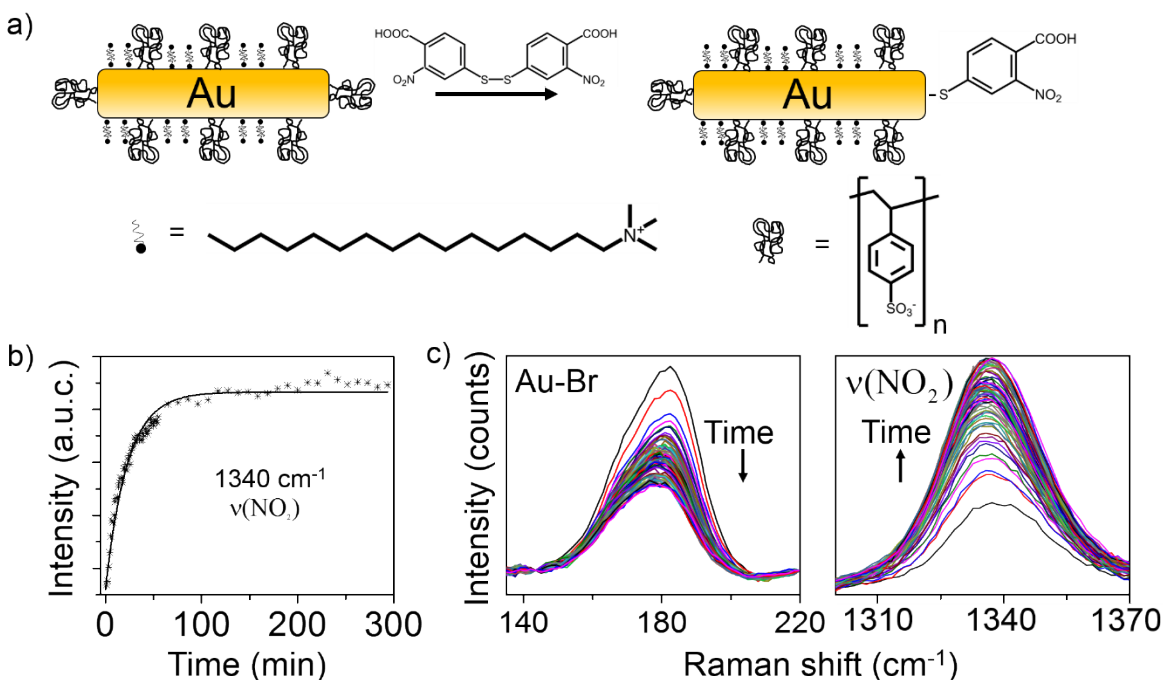


Figure S3. (a) Schematic of ligand exchange of CTAB and polystyrene sulfonate (PSS) with TNB on gold nanorods. (b) First-order Langmuir adsorption model fit to the $\nu(\text{NO}_2)$ mode. (c) Decay of the $\nu(\text{Au-Br})$ mode (left) and growth of the $\nu(\text{NO}_2)$ mode (right) during ligand exchange. The excitation wavelength was 785 nm.

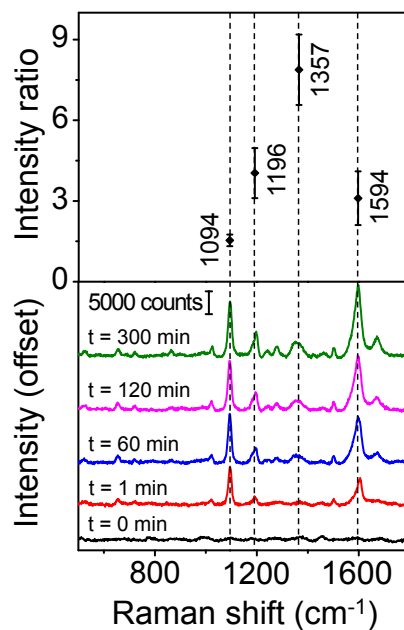


Figure S4. Kinetic SERS spectra of the exchange of 4-ATP (25 μL of 10 mM 4-ATP added to 2.0 mL of 3.0 nM gold nanoparticles) with CTAB on gold nanoparticles. The excitation wavelength was $\lambda_{\text{ex}} = 633$ nm with a 15 second integration time. An intensity ratio (area at $t = 1$ min to steady-state final area) was calculated to illustrate the growth of active vibrational modes (top). Error bars correspond to a 95% confidence interval.

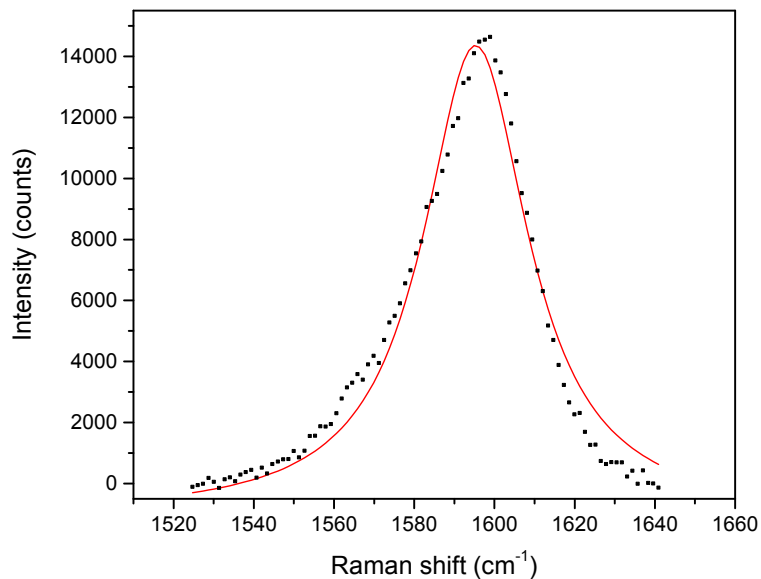


Figure S5. Example fit of Raman band near 1,600 cm^{-1} (4-ATP) to a Lorentzian distribution. For quantitative analysis of peak shifting and FWHM, Raman bands of interest were fit to a Lorentzian distribution of the form:

$$y = y_0 + \frac{2A}{\pi} \frac{w}{4(x - x_c)^2 + w^2} \quad \backslash * \text{MERGEFORMAT [1]}$$

where A is the area of the distribution, w is the full-width at half-maximum (FWHM), x_c is the center, and y_0 is the y-offset.

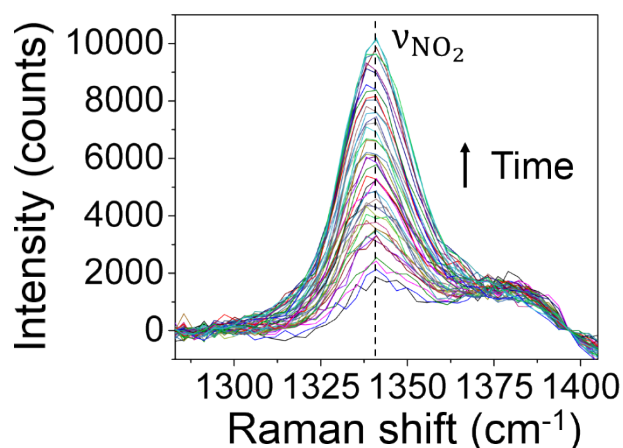


Figure S6. Ligand exchange of citrate-stabilized nanoparticles (9.4 nM) with TNB (30 μL). Time evolution of the band from $t = 0$ min to $t = 100$ min ($\lambda_{\text{ex}} = 633$ nm, 15 second integration time).

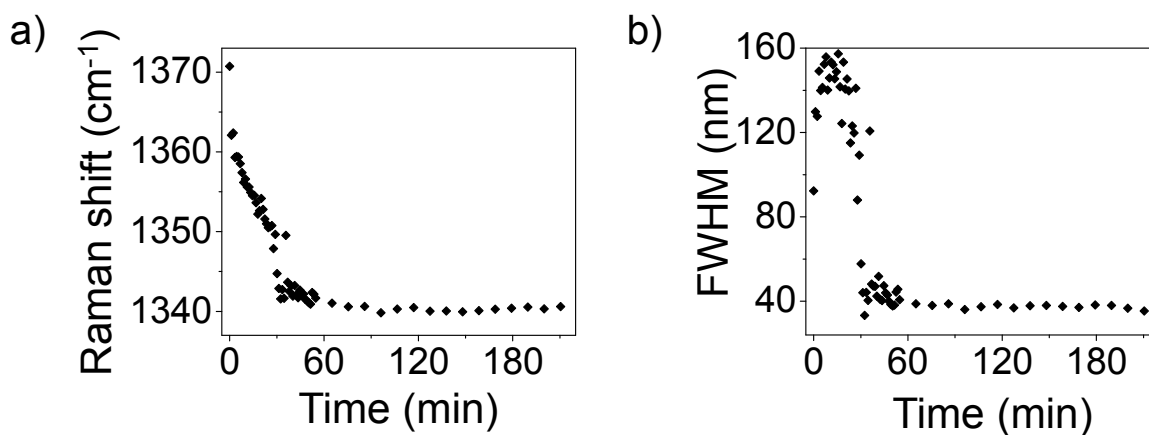


Figure S7. Representative results of fitting experimental SERS data to a Lorentzian distribution for the ligand exchange of citrate. (a) Time-dependent change in the centered Raman shift during the chemisorption process. (b) Time-dependent change in the FWHM of the $\nu(\text{NO}_2)$ mode. Note that $\lambda_{\text{ex}} = 633$ nm and 25 μL of 10 mM DTNB was added to a 2.0 mL solution of 9.4 nM citrate-stabilized gold nanoparticles.