Supporting information: The structural order of the molecular adlayer impacts the stability of nanoparticle-on-mirror plasmonic cavities

Aqeel Ahmed,† Karla Banjac,‡ Sachin S. Verlekar,† Fernando P. Cometto,‡¶
Magalí Lingenfelder,* † and Christophe Galland,* †

†Laboratory of Quantum and Nano-Optics and Institute of Physics, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland.
‡Max Planck-EPFL Laboratory for Molecular Nanoscience and Institute of Physics, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland.
¶Departamento de Fisicoquímica, Instituto de Investigaciones en Fisicoquímica de Córdoba, INFIQC–CONICET, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, X5000HUA Córdoba, Argentina.

E-mail: magali.lingenfelder@epfl.ch; chris.galland@epfl.ch
SI 1: BPhT SAM heterogeneity on S24: Co-existence of different BPhT SAM structural phases along the neighbouring Au crystalline facets

Figure S1: STM characterization of the BPhT SAM molecular ordering on S24. (a) Large-scale STM image showing different BPhT phases on three adjacent Au facets. (b) Zoom-in STM image of the upper facet shown in (a). No periodic arrangement, visible on STM images as the regular patterns, suggests that the degree of the molecular ordering is lower than for phase shown in (c). (c) Zoom-in STM image of the lower facet shown in (a). The presence of the curved terraces (lateral size $> 10$ nm) and dark, Au vacancy islands (pits) randomly distributed along them are morphological features characteristic for the surface reconstruction that proceeds parallel to the SAM re-organization. $^1$ All images were obtained at the air/solid interface. Scanning parameters: $V_{bias} = -200$ mV, $I = 338.2$ pA

STM images in Figure S1(a) show significant differences between the two upper facets and the lower facet. Two upper facets appear nanostructured due to a few angstrom-large protrusions; yet, no periodic arrangement is observed. The lower facet appears nanostructured due to the curved terraces (lateral size $> 10$ nm) and dark, round features (i.e., pits formed
upon reconstruction). These differences in the appearance of the crystalline facets imply that different SAM phases co-exist along S24. Heterogeneities in BPhT SAM ordering on the samples prepared upon prolonged incubation in ethanoic solutions is in agreement with earlier reports.\textsuperscript{1,2} We speculate that BPhT SAMs on adjacent Au facets are in densely-packed phases with the small tilt angles between the principal molecular axis and the surface normal, as expected for SAMs prepared upon long immersion.\textsuperscript{1} Also, we take this opportunity to remind the reader that the template stripped Au (i.e., the mirror in NPoM) is a polycrystalline surface with mostly (111) crystalline facets - it contains (100) and (110) facets and it is not atomically flat. Each of these facets might have a different SAM structure (in term of the molecular configuration); domains with weakly adsorbed double layers or even multilayer structures are also possible, as recently reported for similar system.\textsuperscript{3} The direct consequence of the heterogeneities in S24 BPhT SAM ordering is evident in DF measurement in Figure 1(f) and 2(c, d) in the main text. Each NPoM on S24, prepared upon drop-casting NPs on the S24 BPhT SAM-functionalized mirror (shown here), has a different gap height, as evident from the large deviations in the peak position of the dipole mode.
Figure S2: (a) STM image of S24 showing Au islands formed upon surface reconstruction. The apparent height and width of islands are \( \approx 2.4 \text{ Å} \) and \( \approx 5 \text{ nm} \) respectively, as shown in height profiles in (b). Note that the herringbone pattern of the BPhT SAM is visible on the islands’ tops: this suggests that these islands are formed upon motion of the thiolate-Au adatom moieties. The formation of these islands is closely related to the formation of the vacancy depressions shown in Figure S1. This image was obtained at the nonanoic acid/solid interface. Scanning parameters: \( V_{\text{bias}} = -200 \text{ mV} \), \( I = 338.2 \text{ pA} \).
SI 3: Molecular ordering on the S24 reconstructed facets

Figure S3: (a) STM topography and current images showing the same Au terraces on S24. Note the herringbone pattern extending over the terraces. This suggests that the SAM domains are not confined by the step edges of the terraces (or the small islands shown in Figure S2). Single SAM domain extends over, at least, 10 nm; however, multiple SAM domains are present along the single Au crystalline domain regardless of its orientation or lateral size. (b) STM topography and current images showing two domains rotated by $\approx 120^\circ$. Both herringbone pattern and rotational domains under $\approx 120^\circ$ are characteristic for $(2\sqrt{3}x\sqrt{3})$.

Figure S4: Herringbone pattern of BPhT SAM on S24 together with the superimposed lattice and the $(2\sqrt{3}x\sqrt{3})$ unit cell.
SI 4: Regions with densely packed SAM on S2

Figure S5: STM topography image showing the domains with densely packed BPhT SAM on S2. Scanning parameters: \( V_{bias} = -573 \text{ mV} \), \( I = 494 \text{ pA} \).

SI 5: Characterization of the BPhT SAM molecular ordering in S2 and S24 based on electrochemical and STM characterization

Table S1: Position, full-width at half-maximum (FWHM), and charge density \( Q \) of the peaks in the voltammograms of Figure 1(a) in the main text

| Properties                              | S2   | S24  |
|-----------------------------------------|------|------|
| Potential versus Ag/AgCl (V)            | -0.85| -0.88|
| FWHM (V)                                | 0.07 | 0.08 |
| \( Q \) (\( \mu \text{C/cm}^2 \))       | 65   | 72   |

The parameters for the reductive desorption peaks shown in Figure 1(a) in the main text are listed in Table S1. The main differences in the integrated charge density – being 65.2 \( \mu \text{C/cm}^2 \) for S2 and 72.4 \( \mu \text{C/cm}^2 \) for S24 – imply on the less dense BPhT SAM layer on S2 comparing to the BPhT SAM layer on S24, further supporting discussion in the
main text. Even though these estimates on integrated charge are not directly comparable to the literature on electrochemical characterization of aromatic thiol SAMs\textsuperscript{4,5} because the glass/Cr/Au (mirror) used in this work were not flame annealed, formation of the less dense phase on S2 is in agreement with literature on characterization of similar systems prepared upon immersion in thiol solutions\textsuperscript{1,2} or evaporation.\textsuperscript{6}

Interpretation of reductive desorption, disclosing differences in the BPhT SAM ordering on global scale, is not straight forward due to the fact that several BPhT SAM phases co-exist on the neighbouring crystalline facets (see section SI 1). BPhT SAM heterogeneity is especially important for interpretation of the optical measurements on single NPoM revealing large deviations in the $l_1$ peak, mostly likely due to the differences in SAM (gap) heights for each NPoM. We thus evaluate the molecular ordering on S24 and S2 from STM images revealing the presence of the highly ordered BPhT SAMs across several hundred nanometers over the single crystalline facet on S24 and confined to the domains with the lateral dimensions < 10 nm on S2 together with disordered BPhT SAM on S2.

The distances between protrusions on S24, as-measured from the height profiles superimposed on the molecular rows in Figure 1 in the main text, are $8.9 \pm 0.9 \, \text{Å}$ along the single row and $4.2 \pm 1.0 \, \text{Å}$ across two rows implying on the square lattice close to the $(2\sqrt{3} \times \sqrt{3})$ structure (Figure S4). This finding is in excellent agreement with the paper by Azzam \textit{et al.}\textsuperscript{1} and Leung \textit{et al.}\textsuperscript{2} reporting on formation of SAMs with $(2\sqrt{3} \times \sqrt{3})$ structure and small domains upon long immersion in ethanolic solutions at room temperature. The phase with $(2\sqrt{3} \times \sqrt{3})$ structure, denoted as $\epsilon$ phase by Azzam \textit{et al.},\textsuperscript{1} is characterized by a tilt angle between the molecular axis and the surface normal $< 20^\circ$\textsuperscript{2,7} and islands formed upon surface reconstruction (Figure S2).

Highly ordered BPhT SAMs domains on S2, having lateral size < 10 nm, co-exists with disordered phase shown in Figure 1 (c) in the main text. Interestingly, poor resolution of the disordered phase is in full agreement with references\textsuperscript{1,2} reporting on poor quality of STM images of the BPhT adlayers.
Figure S6: Dark field (DF) and Raman setup used for optical characterization.
SI 7: Change in dark field (DF) with constant laser power

Figure S7: Peak wavelength and peak intensity of the dipole mode as a function of multiple exposures at constant laser power. The duration of exposure was limited to 5 minutes for each measurement. The red (blue) shaded region represents the standard deviation centered at the mean extracted by analyzing multiple NPoMs prepared with 24hr (2hr) incubation. (a,b) Constant power exposure with laser wavelength at 710 nm. (c,d) Constant power exposure with laser wavelength at 760 nm. Please note that the y-axis in (c) calculated by subtracting the laser wavelength from the peak position of the dipole mode. (e,f) Constant power exposure with laser wavelength at 632 nm. In all the experiments S24 NPoMs shows a red shift of the dipole peak along with a significant decrease in peak height. On the other hand S2 NPoMs show meagre changes in the position and peak height of the dipole mode. During the exposure at 632 nm both S2 and S24 show a much larger change in the peak position and intensity than observed for exposure with 710 and 760 nm. This could be the result of increased absorption of AuNS leading to significantly large temperature within the gap and hence prompting a faster molecular reorientation in S2 and S24.
Figure S8: (a-e) Complete evolution of the DF spectra as the power of the exposure laser is increased. The spectral position of the dipole mode is shown by dot-dash line until the modes can be distinctly identified (green dot). The spectra at the first (red line) and last dot (green line) are shown in the figure below each contour plot. The fusion of the AuNP and the gold substrate underneath at high laser intensities can also be seen by the emergence on charge transfer plasmon (CTP) indicated by black dashed line. The plots (a-e) correspond to NPoMs consist of single AuNPs (p2-p10), as shown by the SEM images in (f), placed on high incubation time SAM.
Figure S9: (a-e) Complete evolution of the DF spectra as the power of the exposure laser is increased. The spectral position of the dipole mode is shown by dot-dash line until the modes can be distinctly identified (green dot). The spectra at the first (blue line) and last dot (green line) are shown in the figure below each contour plot. The fusion of the AuNP and the gold substrate underneath at high laser intensities can also be seen by the emergence on charge transfer plasmon (CTP) indicated by black dashed line. The plots (a-e) correspond to NPoMs consist of single AuNPs (p9-p13), as shown by the SEM images in (f), placed on low incubation time SAM.
SI 10: Temperature extraction by anti-Stokes background

Figure S10: Electronic Raman temperature calculated by fitting the anti-Stokes background of multiple NPoMs with two exponentials. The large variations in temperature at power below 10 µW can be ignored due to poor signal to noise ratio. The initial temperature for NPoMs with low incubation time SAM was found to lower than those prepared with higher incubation time. Hence, the heat present within the nanogap could explain the molecular re-orientation and decrease in gap height.
SI 11: Raman spectra S2 and S24

Figure S11: Anti-Stokes (a) and Stokes (b) spectra acquired on S2 (blue) and S24 (red) with laser wavelength at 710 nm and power 6 µW and 8 µW respectively. The signature Raman peaks of BPhT (1: 1079 cm\(^{-1}\), 2: 1281 cm\(^{-1}\), 3: 1586 cm\(^{-1}\)) are clearly visible in the Stokes sideband. The corresponding DF spectra for S2 (yellow) and S24 (purple) are also overlaid as dotted lines. The Raman signal is greatly influenced by the position of the plasmonic resonance. (c-f) Time series of anti-Stokes and Stokes spectra collected at different laser powers. The dashed white lines represent the change between laser powers. The color scale represents the signal recorded on the CCD as counts s\(^{-1}\) µW\(^{-1}\). (c-d) show anti-Stokes and Stokes corresponding to the S24 DF spectra in Figure 2(a) in the main text. (e-f) show anti-Stokes and Stokes corresponding to the S2 DF spectra in Figure 2(b) in the main text.
SI 12: Evolution of higher order dipole mode

Figure S12: (a) The evolution of DF spectra on S24 as the laser power is increased. The red dot indicate the evolution of the bonding dipolar mode \( l_1 \) however after 99\( \mu \)W is it not possible to identify \( l_1 \). (b) Comparing the first (red) and the last (green) DF spectra show a redshift and decrease in the peak intensity of \( l_1 \). The higher order dipole mode \( l_2 \) also redshifts but shows an increase in its intensity marked by blue dashed arrow.

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