

Supporting information

for

Binding group for Highly Ordered SAMs Formation: Carboxylic *versus* Thiol

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Sample preparation

All solvents were obtained from commercial sources. *n*-hexadecane (99.9%), tetrahydrofuran and absolute ethanol (99.8%) were obtained from Acros Organics, Sigma Aldrich and POCH, respectively. Reagents were used as received without further purification.

The hybrid aromatic-aliphatic molecules of the BP2SH ($\text{CH}_3\text{-(C}_6\text{H}_4)_2\text{-(CH}_2)_2\text{-SH}$) were synthesized according to the methodology described in details elsewhere.¹ The BP2COOH molecules ($\text{C}_6\text{H}_5\text{-C}_6\text{H}_4\text{-(CH}_2)_2\text{-COOH}$, 98%) was purchased from Alfa Aesar and used without further purification.

For the STM measurements the Ag(111) substrates were prepared by evaporation of ca. 150 nm of silver (rate = 1.7 nm/s, temp. ~260°C) on mica substrates. For the XPS and the IRRAS analysis the Ag(111) substrates were prepared by evaporation of ca. 150 nm of silver (rate = 1.7 nm/s, room temp.) onto polished single-crystal silicon (100) wafers (ITME, Warsaw) primed with a 5 nm chromium to improve the adhesion.

To form BP2S/Ag SAMs, freshly prepared Ag(111) substrate was immersed for 24 hours at room temperature or 60 °C in 1 mM ethanolic solution of BP2SH molecule. For the BP2COO/Ag SAMs formation the Ag(111) substrate was immersed by 5 minutes at room temperature in 1mM *n*-hexadecane and

tetrahydrofuran (1:1) solution of the BP2COOH molecules. Immediately before analysis, the samples were removed from the solution, rinsed with pure solution, and dried under nitrogen.

STM measurements

STM measurements were carried out in air at room temperature using a low current NanoScope® MultiMode 8 microscope from Bruker. In all cases, the tips were prepared mechanically by cutting a 0.25 mm Pt/Ir alloy (8:2, Goodfellow) wire. The data were collected in constant current mode using tunnelling currents in the range of 2-35 pA and a sample bias between 0.2-1 V (tip positive).

IRRAS measurements

IR reflection absorption spectroscopy measurements were performed with a dry-air-purged Thermo Scientific FTIR spectrometer model Nicolet 6700 equipped with a liquid nitrogen-cooled MCT detector. All spectra were taken using p-polarized light incident at a fixed angle of 80° with respect to the surface normal. Spectra were measured at a resolution of 2 cm⁻¹ and are reported in absorbance units $A = -\log R/R_0$, where R is the reflectivity of the substrate with the monolayer and R₀ is the reflectivity of the reference. Substrates covered with a perdeuterated hexadecanethiolate SAM were used as a reference.

XPS measurements

X-ray photoelectron spectroscopy (XPS) measurements were performed with a photoelectron spectrometer equipped with a hemispherical analyser VG SCIENTA R3000. The spectra were taken using a monochromatized aluminum source Al K α (E= 1486.6 eV), MX-650 VG Scienta. The base pressure in the analytical chamber was 5·10⁻⁹ mbar. The spectra acquisition was carried out in normal emission geometry with analyser energy resolution of 0.15 eV. The inelastic background was subtracted using the Shirley method and the photoemission peaks were fit using convolution of the Gaussian and Lorentzian functions with adjustable weights.

Comment on the area per molecule measured for the BP2S/Ag SAMs.

Former spectroscopic study for the BP_nS/Au homolog series (n =1-6) demonstrated an odd-even effect in the orientation of the biphenyl moieties with a more upright orientation for the odd-numbered members of series.¹ It was also shown in this study¹ that upon changing the substrate to Ag a similar but reversed odd-even effect is observed with a more upright orientation for the even-numbered members of the BP_nS/Ag series. Later STM

analysis,^{2,3} performed only for the BPnS/Au series, demonstrated that this odd-even effect is also visible in the 2D structure of these SAMs correlating more upright orientation of the biphenyl group for odd-numbered members of the series with a smaller area per molecule $\sim 0.216 \text{ nm}^2$. Assuming that this structural effect observed in the STM analysis for the Au substrate is exactly reversed for the Ag substrate one could expect same or very similar area per molecule for the BP2S/Ag and the odd-numbered members of the BPnS/Au series such as the BP3S/Au i.e. $\sim 0.216 \text{ nm}^2$. Our measurements show that this is not the case and much larger area per molecule of ($\sim 0.288 \text{ nm}^2$) is observed for the BP2S/Ag. We would like to point, however, that analyzed here BP2S/Ag is also different from the BP3S/Au concerning its formation process. In contrast to the BP3S/Au, the BP2S/Ag does not form 2D ordered SAMs when prepared at room-temperature, and importantly, this is the case despite theoretically predicted⁴ lower corrugation of the thiol-metal potential energy hypersurface for the Ag substrate compared to the Au which should promote mobility of molecules on the surface and thus organization of the respective 2D structure. Moreover, as documented by the current STM data, to form 2D ordered structures of the BP2S/Ag having domains size similar to the BP3S/Au one has to increase formation temperature up to $60 \text{ }^\circ\text{C}$. Therefore, current experiments show that (i) changing the substrate from the Au(111) to the Ag(111) does not reverse the odd-even effect in a fully symmetric way, and (ii) theoretically predicted lower corrugation of the thiol-metal potential energy hypersurface for the Ag(111) compared to the Au(111) seems to be questionable for SAMs analyzed here.

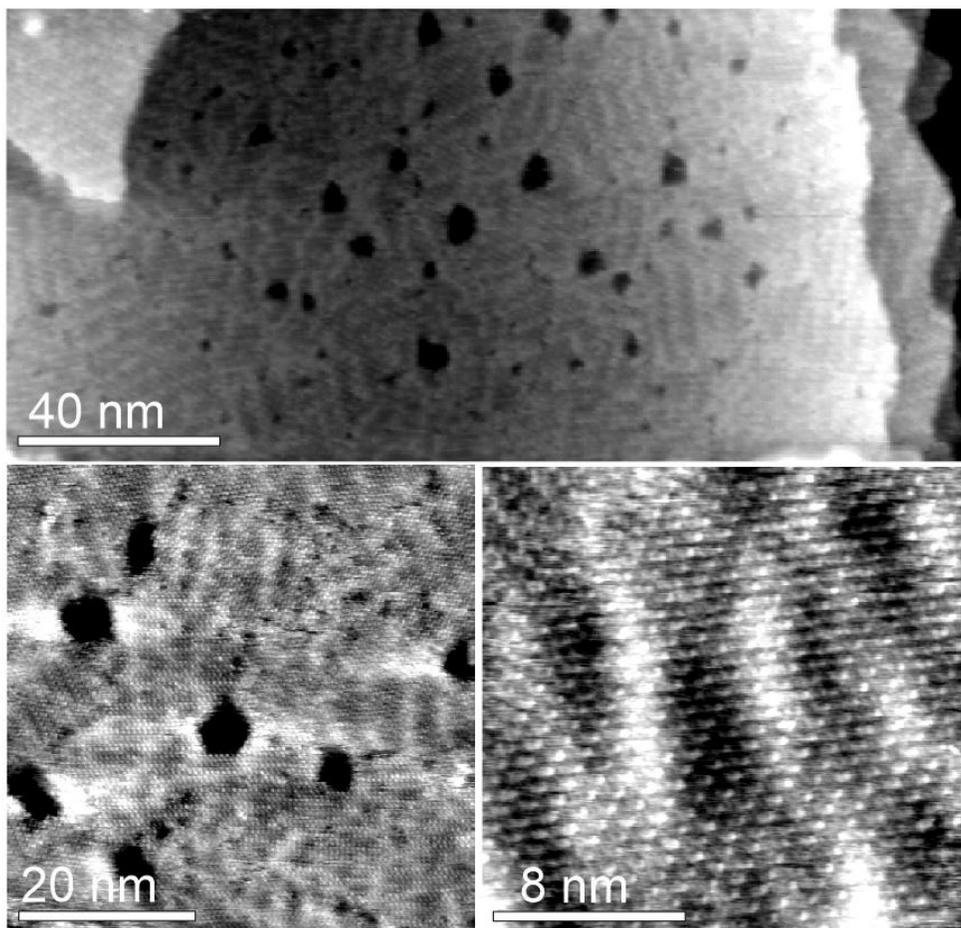


Figure S1

Overview of STM data for the BP2COO/Ag(111) sample stored for 95 days in the air. The structural analysis reveals the same features as observed for the freshly prepared sample i.e. pattern of dark stripes which is superimposed on the undisturbed molecular lattice (see Figure 2 in the paper). The lack of evidences for the film structure destruction indicates that this type of SAMs remains unaffected by the long term exposition to the ambient conditions.

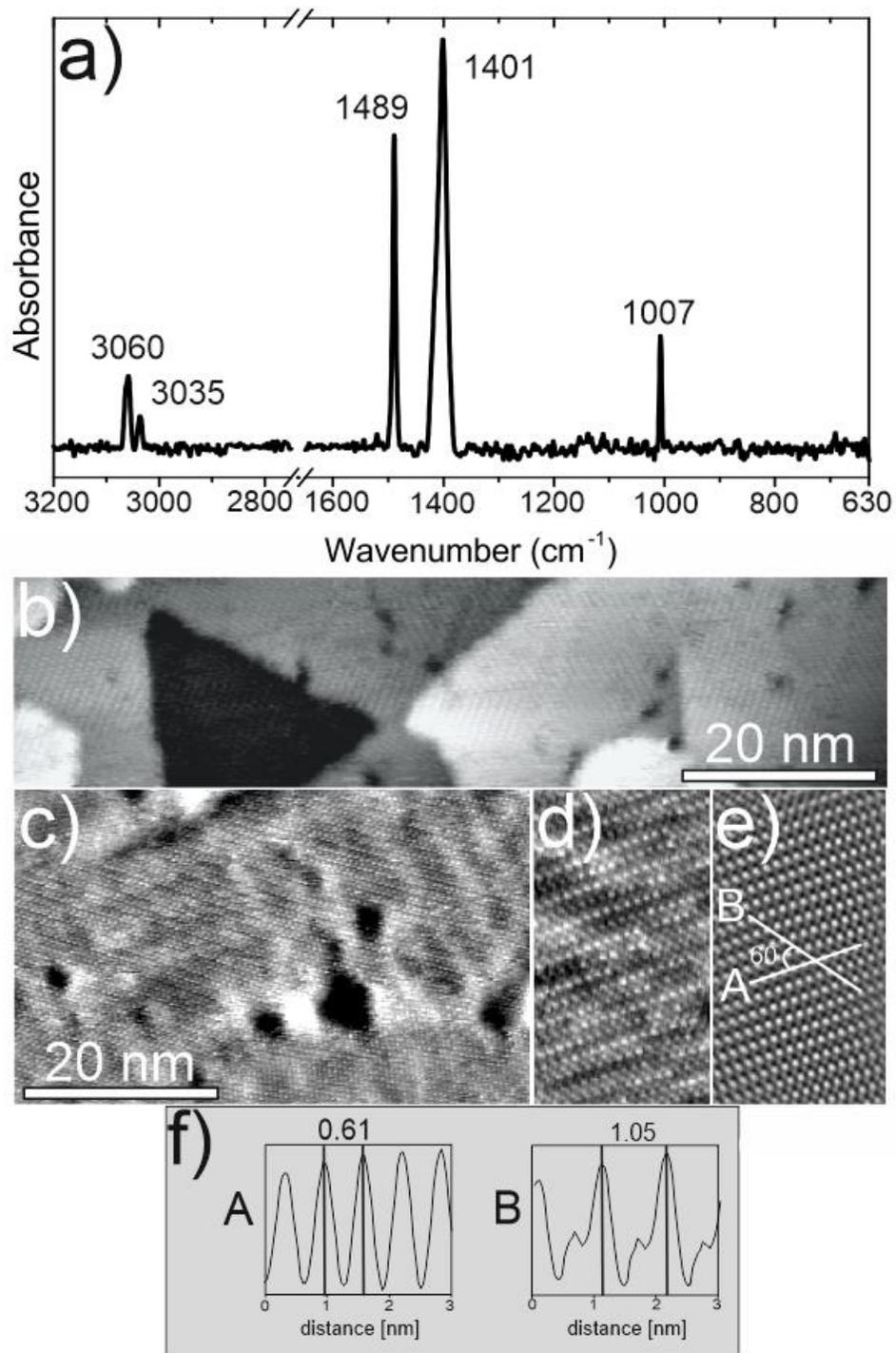


Figure S2

Overview of IRRAS and STM data for the BP2COO/Ag SAMs prepared at room temperature by 5 min. incubation in 1mM ethanol solution. The data show no systematic difference to the formation of this film from 1 mM THF/hexadecane (1:1) solution as discussed in the paper . In (a) IRRAS spectra for comparing with Figure 1a. In (b) – (f) overview of STM data analysis for comparing with Figure 3.

References

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