

Supporting Information

Prototypical Organic–Oxide Interface: Intramolecular Resolution of Sexiphenyl on In₂O₃(111)

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Deposition of 6P at room temperature

The deposition of 6P on the $\text{In}_2\text{O}_3(111)$ surface was inadvertently accompanied by some water co-dosing, in spite of a thorough degassing of the evaporant prior to the experiments. Moreover, $\text{In}_2\text{O}_3(111)$ is very reactive towards dissociative water adsorption at room temperature, and small amounts of water are already sufficient to saturate the surface.¹ Thus, the surface after 6P deposition was never completely free of OH groups, which is partially causing the disorder on the as-prepared surface. Figure S1 shows a preparation where the surface is almost fully covered by OH groups (giving rise to bright triangular and curved features in STM¹) in addition to the 6P.

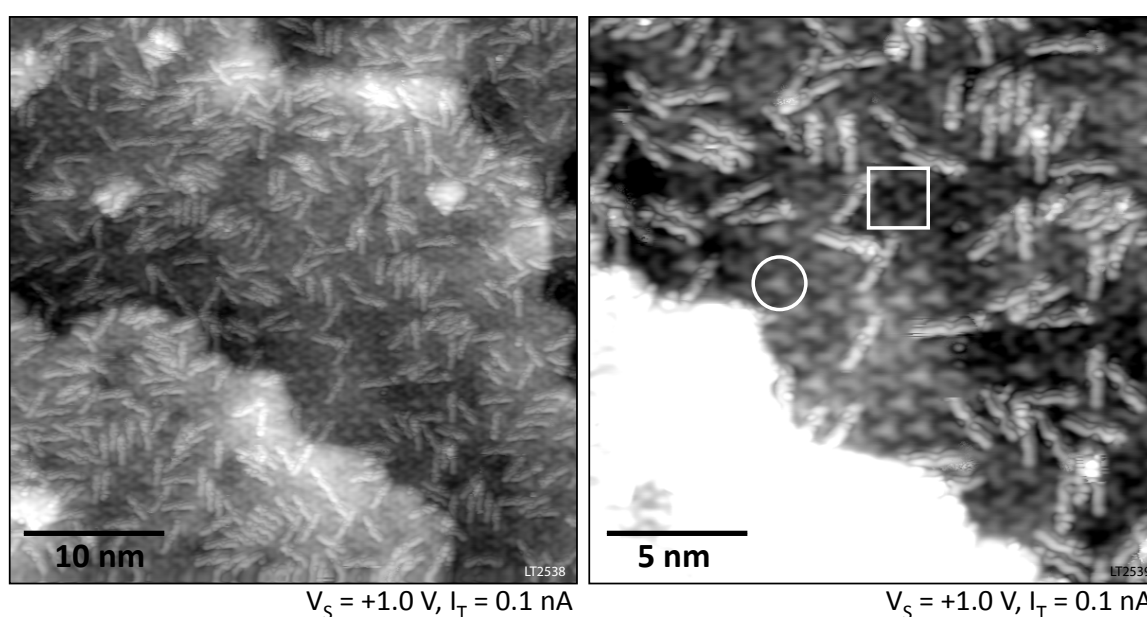


Figure S1: Deposition of 6P at room temperature without post-annealing. The surface is almost fully covered with OH groups from water dissociation resulting in bright triangles (white circle) and less bright curved objects (white square). The 6P molecules show only a weak preference for certain azimuthal orientations.

6P on Cu(100) imaged with a CO tip

6P on Cu(100) was used as a benchmark system to reproduce the expected²⁻⁴ AFM contrast of flat and planar organic molecules after picking up a CO molecule with the tip (see also ref 5). Here 6P was evaporated onto clean Cu(100) at room temperature, and CO was dosed into the STM/AFM at 5 K. The CO was picked up in the constant height AFM mode by scanning across the molecule, and manually moving the tip very close to the surface. Figure S2 shows images acquired with different oscillation parameters (a, b) and qPlus sensors (c). In all examples the hexagonal shape of the phenyl rings (including the C-C bonds linking the individual rings) are clearly distinguished.

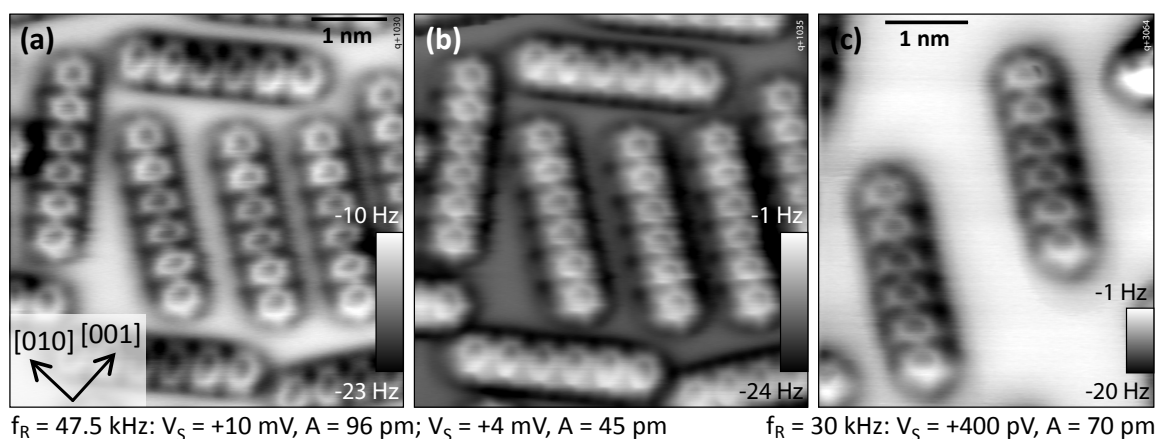


Figure S2: Constant-height non-contact AFM images of 6P on Cu(100) using a CO-functionalized tip. (a, b) The same region on the surface imaged with different oscillation parameters. (c) Image acquired with a different qPlus sensor. $T_{AFM} = 5$ K.

Appearance of the (2×1) structure in STM

The (2×1) structure shows weak resolution of the individual molecules when imaged with a tip prepared on a metal surface. In the most-common imaging contrast, Figures S3(a-e), the periodicity of the bright stripes is easily discerned, while the dark stripes show little contrast. Usually, a slight enhancement in the dark stripes is observed at bias voltages below +1 V. At bias voltages above +2 V, the tip starts to interact with the molecules (horizontal stripes in panels (d, e)) causing slight changes in the local contrast when subsequently imaged at lower voltages, although no molecules were apparently removed. In another frequently encountered contrast, each 6P of the bright stripes is represented by three distinct blobs, and the molecules of the dark stripes feature a zigzag shape (“W”-like), see Figure S3(f).

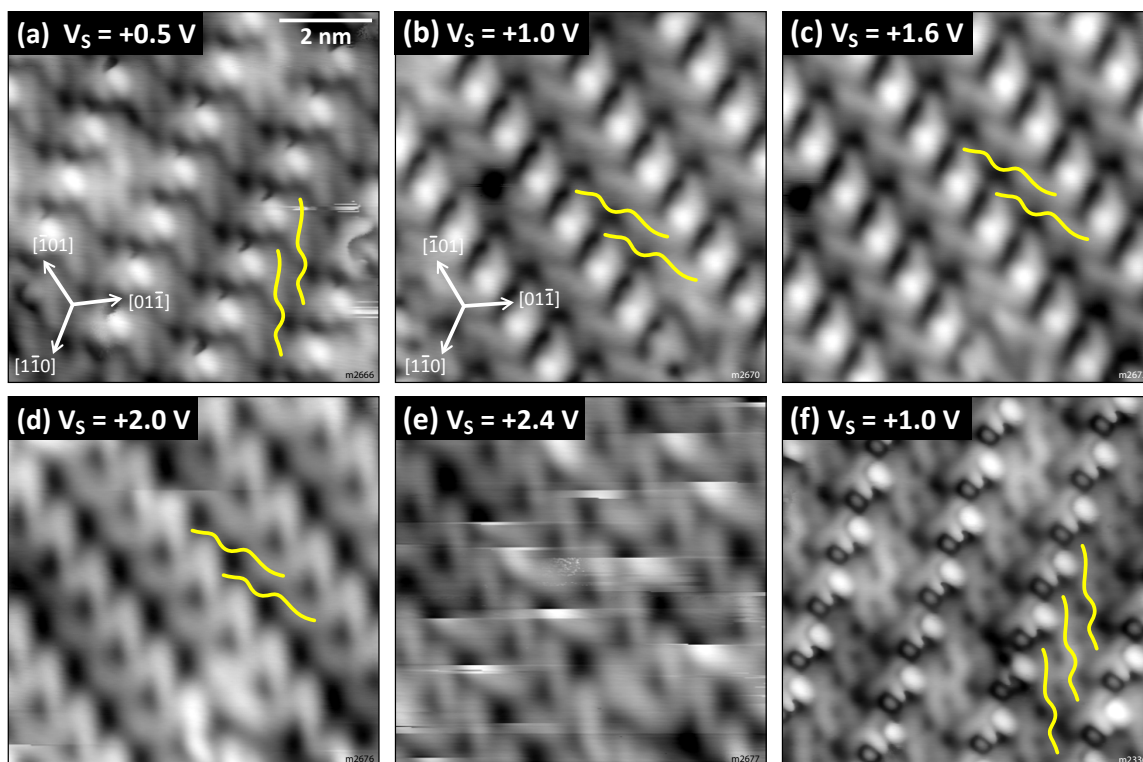


Figure S3: Bias dependence of the imaging contrasts on the (2×1) structure obtained with metallic tips. (a-d) Most common contrast, where the elongated, bright and featureless blobs appear instead of the 6P molecules of the bright stripes. The yellow curve taken from (f) marks the position of the dark 6P. Note the different domain in (a) with respect to (b-e). (f) Different imaging contrast where the molecules of the bright stripes show three distinct features and the zigzag motif (yellow curve) of the 6P in the dark stripes is clearly visible. The domain has the same orientation as in (a). All: $I_T = 0.1$ nA. $T_{STM} = 80$ K.

On surfaces with a high 6P density, such as in the (2×1) structure, a special tip termination can be reproducibly prepared by dipping the tip gently into the surface; likely this attaches a 6P molecule or a fragment to the tip. The contrast on the stripe structure becomes more distinct, and the individual molecules of both, the dark and the bright stripes, are easily discernible. Figures S4(a, b) display this new contrast at two different bias voltages. In the bright stripes, the region in-between the molecules becomes more intense in panel (b). In panel (c), with the slow scanning direction from top to bottom, the tip changed into a less-pronounced contrast at the position of the broken white line, and eventually lost resolution, similar to panel (d). The positions of the molecules are indicated throughout Figure S4 by black lines, the reference being the molecules of the dark stripes (white circle). The comparison shows that the bright stripes are formed mostly by the regions in-between the 6P molecules when imaged with the metallic tip. The elongated protrusions reflect neither the position of the molecules, nor their azimuthal angle with respect to the stripe direction.

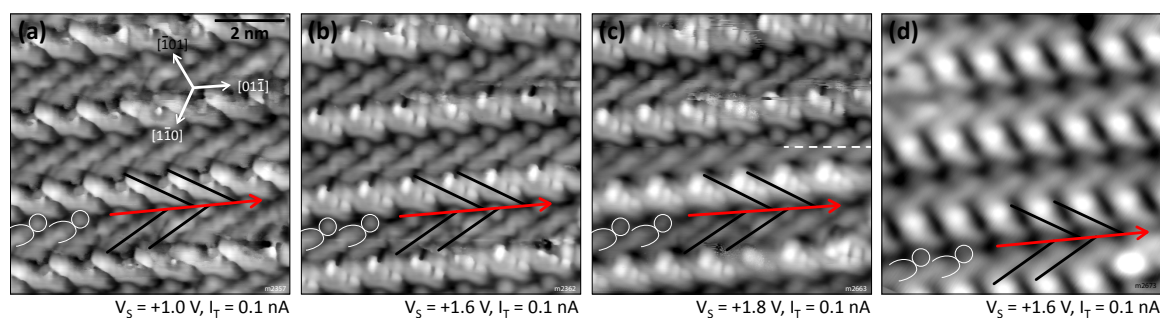


Figure S4: (a-c) Same area of the 6P (2×1) overlayer, scanned repeatedly with the STM. The tip switches from the “high resolution” mode to the contrast typically observed with metallic tips (d). Black lines indicate the position of the 6P within the bright stripes. $T_{\text{STM}} = 80$ K.

References

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