Supporting Information

The role of surface defects on large organic molecule adsorption: Substrate configuration effects

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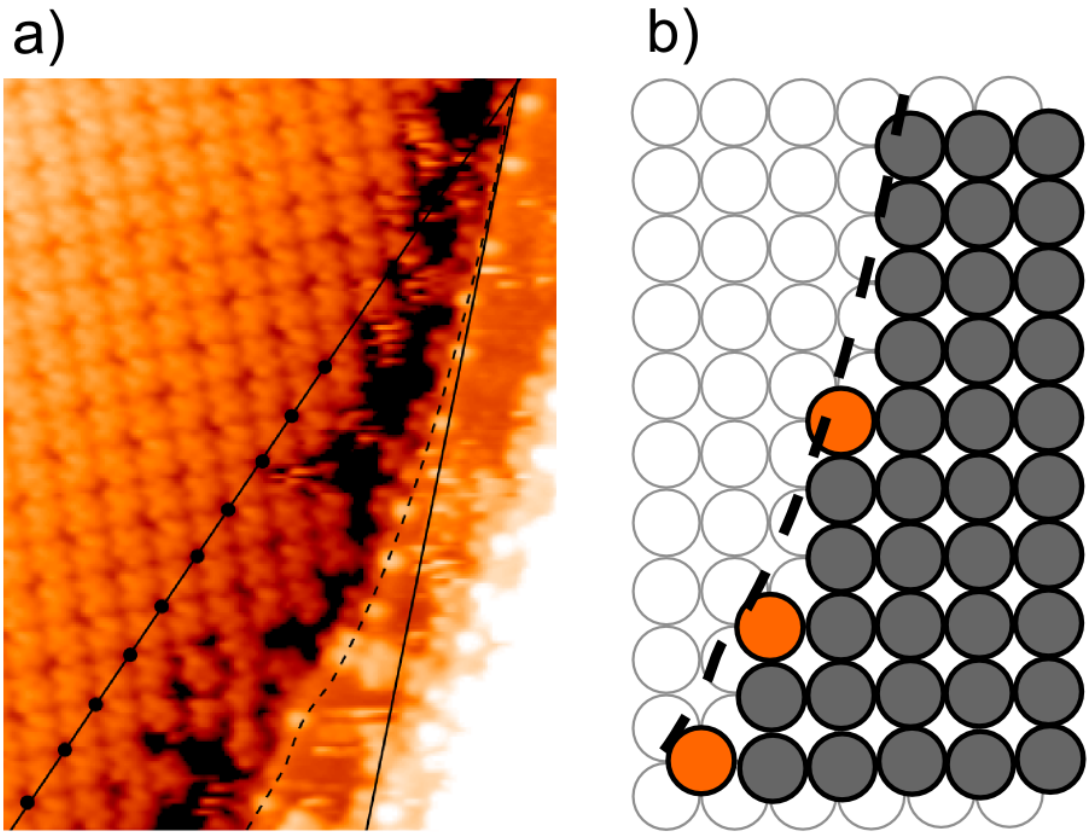

Figure S1

a) Ordered region (continuous line, left hand side) and approximate progression of the step (dashed line, middle). The continuous line on the right hand side is a tangent to the dashed line to guide the eye. b) Atomic model of the Ag atoms at the step (not drawn to scale). The kink atoms, which are a direct consequence of bent steps are coloured orange.

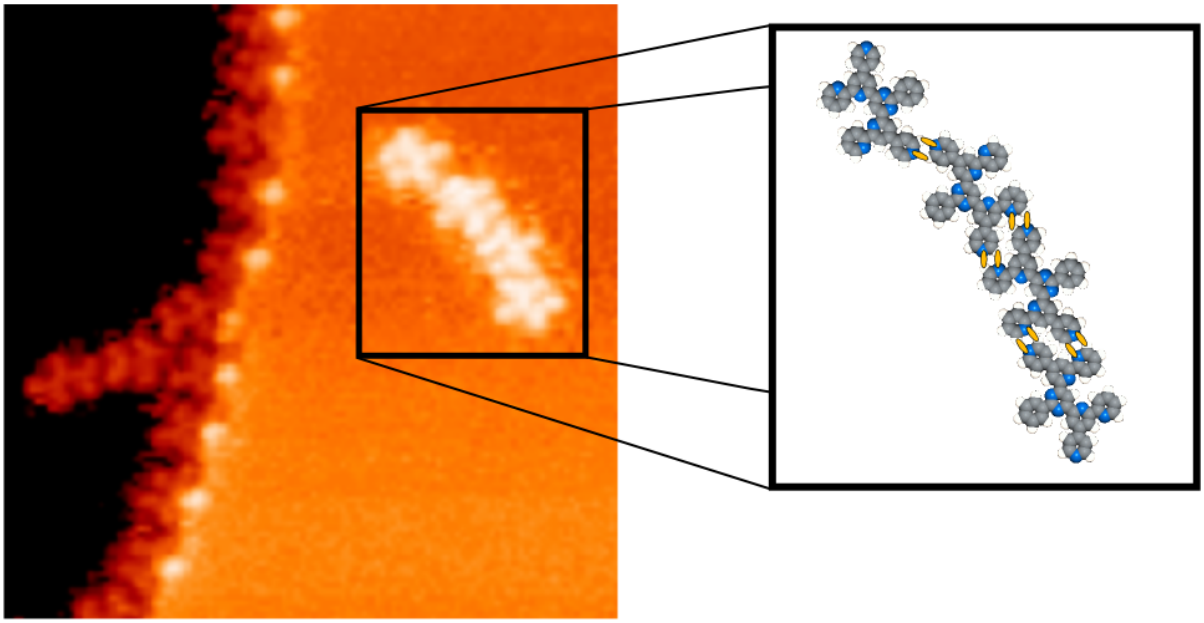

Figure S2

STM image of a molecular 1D chain (left hand side) and corresponding model (right hand side). The C-H···N interactions between the adsorbates are marked in orange.

Methods

Periodic DFT calculations were performed using the Vienna ab initio simulation package (VASP).[1] In order to account for electron-ion interactions, the projector augmented wave (PAW) method[2;3] was used. The electronic one-particle wave functions were expanded in a plane wave basis set up to an energy cut-off of 400 eV. Electron-electron exchange and correlation interactions have been described within the generalized gradient approximation (GGA) by employing the Perdew, Burke and Ernzerhof (PBE) functional.[4]

The metal surfaces were modeled by a slab consisting of five atomic layers that were separated by a vacuum region of about 20 Å. A (3x3) and a (3x1) unit cell of the overlayer structure on Ag(100) and Ag(711) respectively, was assumed to model the adsorption of molecules at low coverages. Adsorption on the kinked surface was modeled by a (18 3 -2) surface within a (1x1) surface unit cell. In case of Ag(18 3 -2) the natural unit cell of the surface is used, as it is already large enough to minimize lateral interactions between neighbouring molecules. The geometry of the adsorption complex was optimized by relaxing all atoms of the adsorbate and the metal atoms of two uppermost

layers of the surface. The layer spacing of the lower layers were taken from the theoretical lattice parameters calculated for bulk silver (4.167 Å). A 4x4x1 Monkhorst-Pack k point mesh with a Methfessel-Paxton smearing of 0.1 eV was used for the integration over the first Brillouin zone. Isolated molecules in the gas phase were treated employing a large cell (20 Å x 21 Å x 22 Å), the Γ-point only and a Gaussian smearing of 0.1 eV. Dispersion effects that are missing in current DFT-functionals were accounted for according to Grimme's correction scheme of 2010 (DFT-D3).[5] The screening of the metal, which is rather problematic in such approaches, was approximated by including only the uppermost layer of the metal in the evaluation of the dispersion energy, as suggested in Ref.[6].

The adsorption energy is defined as $E_{ad} = E_{tot} - E_{surf} - E_{mol}$, where E_{tot}, E_{surf} and E_{mol} are the total energy of the relaxed adsorption complex, the energy of the clean surface and the energy of the isolated molecule, respectively.

References

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