

Nanostructuring Cu Surfaces Using Custom-Designed Molecular Molds

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ABSTRACT

By means of STM imaging and manipulation, we show that violet Lander (VL) molecules ($C_{108}H_{104}$) act as nanoscale templates at the Cu(110) step edges, creating nanostructures to which the VLs are anchored. These nanostructures are longer and sometimes wider than those created by the related single Lander (SL) molecules due to the slightly different shape and size of the VL molecules. These results illustrate the possibility of controlling the formation of nanostructures on a surface on the atomic scale by means of a rational molecular design.

The interaction between large organic molecules and metal surfaces has recently been the subject of extensive investigations. The interest in these systems stems, on one hand, from the desire to understand elementary surface processes such as adsorption and diffusion,^{1–5} and on the other hand, from the potential perspective of novel applications in molecular electronics and nanomechanical devices.^{6–12} To create functional molecular devices, it is necessary to develop an architecture for their interconnection in a planar conformation and with atomic precision.⁶ When large molecules adsorb on metal surfaces, the molecule–substrate interaction may be quite complex, and molecular functionalities and conformations designed for molecules in the gas-phase cannot be transferred a priori to a situation where molecules are adsorbed on surfaces. For example, the surface may undergo a restructuring process in order to accommodate the molecule.^{4,5,7,8,13,14} Whereas the reconstructions induced by simpler adsorbates depend exclusively on their chemical nature, in the case of large organic molecules also the shape of the molecule comes into play. For instance, the molecular conformation has proven to play an important role in the chiral reconstruction induced by HtBDC on Cu(110), arising from the chirality of the lowest energy conformation of the molecule,^{3,4} or in the reshaping of the step edge induced by the molecule known as single Lander (SL).^{7,8}

Synthetic organic chemistry permits a very flexible molecular design. For example, different related molecules can

be synthesized so as to preserve the main design features of a given molecular species yet allow the modification of some architectural details, such as the distance or the angles between the functional groups. The surface reconstructions induced by these modified species should therefore open a new paradigm in the control of surface morphology at the atomic scale.

In this letter we investigate the rearrangement induced at the step edges of a Cu(110) surface by an organic molecule named violet Lander¹⁵ (VL, $C_{108}H_{104}$) and compare it with the reconstruction induced by the related single Lander molecule, which was shown before to act as a template for the fabrication of nanostructures at the Cu(110) step edges.^{7,8} Both molecules consist of a polyaromatic board with four Tbp (3,5-di-*tert*-butyl-phenyl) substituents that lift the molecular board above the surface and, therefore, act as “spacer legs”.^{7,15} The difference between the two species is the geometry of the board, being longer in the VL (2.5 nm) than in the SL (1.7 nm) and having a different distribution of phenyl rings with respect to their symmetry axis σ (see Figure 1a and b). Here we show that, similar to the case of the SL, the VL exploits its peculiar shape to trap diffusing Cu adatoms at the step edge, leading to the creation of nanostructures that protrude from the step edge. The molecules accommodate their board on the nanostructure, while the legs rest on the lower terrace. The details, however, of the nanostructure induced by the two molecules differ: the structure induced underneath the VL is longer, and sometimes also wider, than the corresponding structures created by the SL. Comparison with theoretical calculations allows us to trace the origin of these differences back to the different molecule–substrate interactions arising from the different

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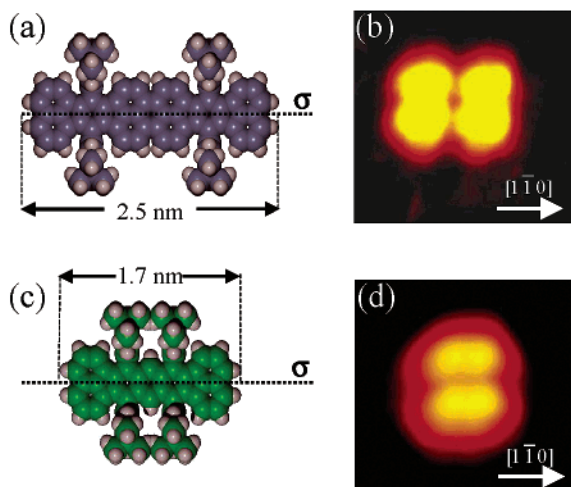


Figure 1. (a) Space-fill model of the violet Lander (VL) molecule ($C_{108}H_{104}$). The VL consists of a polyaromatic board and four di-tert-butyl-phenyl groups (spacer legs) sigma bonded to the board. (b) Typical STM image of a VL deposited on Cu(110). According to ESQC calculations, only the spacer legs contribute significantly to the tunneling intensity and, hence, the molecules are imaged with STM as four bright lobes. For comparison, the space-fill model (c) and STM image (d) of the single Lander molecule ($C_{90}H_{98}$) are included. The only difference between these molecules is the π -board, being about 0.8 nm longer in the case of the VL than in the SL and presenting a different distribution of benzene-like rings with respect to the symmetry axis σ .

geometry of the molecular board. This result demonstrates that the geometry of surface nanostructures induced by large organic molecules can be controlled by appropriately designing the molecular shape.

The experiments were performed in an ultrahigh vacuum chamber (base pressure $< 10^{-10}$ Torr), which hosts an Aarhus-type,¹⁶ variable-temperature (100–400 K) STM. The Cu(110) crystal was cleaned using standard sputtering–annealing procedures. Violet Lander molecules were evaporated from a glass crucible kept at 550 K, yielding evaporation rates of 0.001 ML/s, while the substrate was kept at room temperature (RT). The background pressure during deposition remained below 1×10^{-9} mbar. Contrary to SL molecules, VL molecules are not mobile on Cu(110) at room temperature. To promote surface diffusion and thus the anchoring of VL molecules to monatomic step edges, the Cu crystal was annealed to 475 K for 10 min after depositing the molecules.

The surface was subsequently cooled to about 220 K, and under these conditions the STM was used to manipulate individual molecules, enabling the selective displacement of the VLs anchored to Cu step edges. The manipulation is obtained by reducing the resistance in the STM tunneling junction by about 2 orders of magnitude, from 5 G Ω to about 0.05 G Ω , by either increasing the tunneling current or reducing the tunneling voltage, or both. This corresponds to approaching the tip about 0.2 nm to the surface. To control the tip's position accurately, we use a software option dedicated to manipulation experiments. This allows us to manipulate individual molecules one at a time along a predefined path, leaving the rest of the scan area unperturbed.

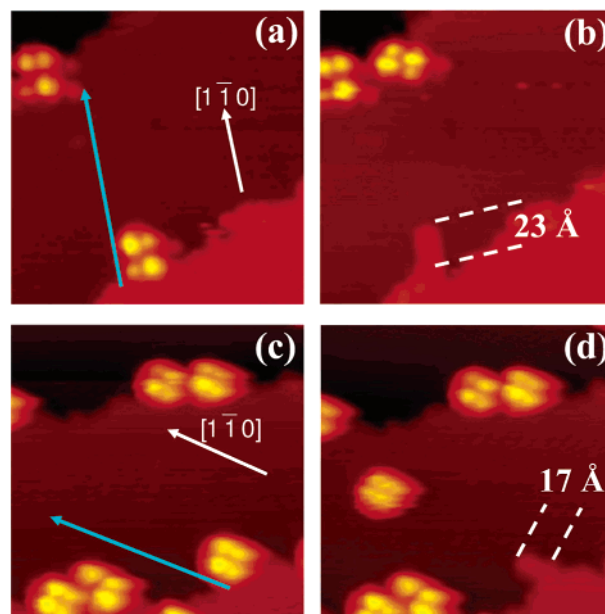


Figure 2. STM images (14.5×14.5 nm²) showing the manipulation sequences for the extraction of a violet Lander (a,b) and a single Lander (c,d) molecule from the step edge. The blue arrow marks the direction of the manipulation process as well as the particular molecule that is being manipulated. In both cases, the manipulation process reveals a protrusion of the upper terrace into the lower terrace on top of which the molecules were previously anchored. The length of the restructured step edge is longer in the case of the VL, consistent with the longer board of this molecule.

A manipulation sequence is shown in Figure 2a and b. Similar to the case of SL molecules, we observe that VLs induce a restructuring of the step edge, where a protrusion can be found at the position of the molecule before the manipulation. As in the SL case, the formation of the nanostructure and the anchoring of the VL to it occur along with a change in the molecular conformation that can be easily recognized in the STM images as a decrease in the overall height of the molecule and in the distance between the bumps at both sides of the board. We can, therefore, conclude that the VL and the SL act on Cu(110) step edges in the same manner. Nevertheless, a closer inspection of the STM images reveals that the size of the nanostructures induced by the two molecules is different. The nanostructures created by the SL are 7 ± 1 Cu atoms long and 2 Cu atoms wide.^{7,8} The VL, on the other hand, gives rise to structures 9 ± 1 Cu atoms long (see Figure 2) and their width is either 2 Cu atoms wide (70%), or 3 Cu atoms wide (30%, see Figure 3).

In the case of the SL, molecular mechanics (MM2) calculations showed that the creation of the discussed nanostructures is an energetically favorable process due to contributions from two different effects: (a) a decrease of the distance between the board and the substrate when the molecules are anchored to the nanostructure at the step edge, which leads to an increase in the electronic interactions between the π electrons of the central Lander board and the metallic surface, and (b) a relaxation of the bending angle between the board and the legs that partially releases the stress energy in the σ -bond.^{7,8} The roles of each one of these

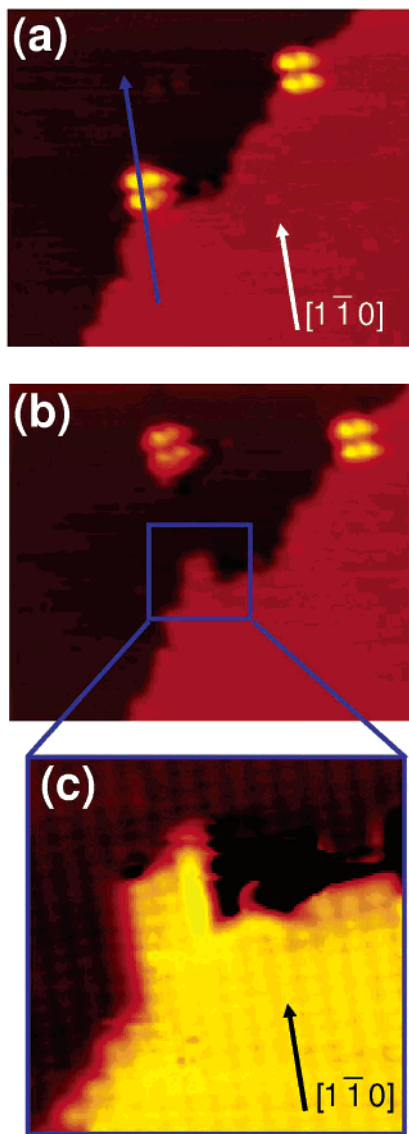


Figure 3. Manipulation sequence revealing a three-row structure underneath a VL molecule. Panels (a) and (b) are $23.5 \times 19.5 \text{ nm}^2$ STM images before (a) and after (b) the manipulation. Panel (c) shows an atomic-resolution $5 \times 5 \text{ nm}^2$ STM image that demonstrates the existence of three-row nanostructures.

contributions can be understood as follows. In the gas phase, the conformations of both molecules are characterized by bending angles of 90° , corresponding to a nonstressed σ -bond between the legs and the molecular board. Upon adsorption on the flat Cu(110) surface, the attractive interaction between the π -system in the molecular board and the metallic surface is known to force a conformational change, bending the legs out of the 90° gas-phase angle in order to approach the board to the surface, thereby introducing a considerable amount of stress in the σ -bond.^{7,8} Therefore, if the conformation of the adsorbed molecules is so that the angle between the legs and the board plane is close to 90° , a considerable release of the stress energy in the σ -bond will occur. This was proven to stabilize the formation of the nanostructures at the step edge created by the SL molecules.^{7,8}

If the length of the nanostructure were shorter than the length of the molecular board, part of the board would be

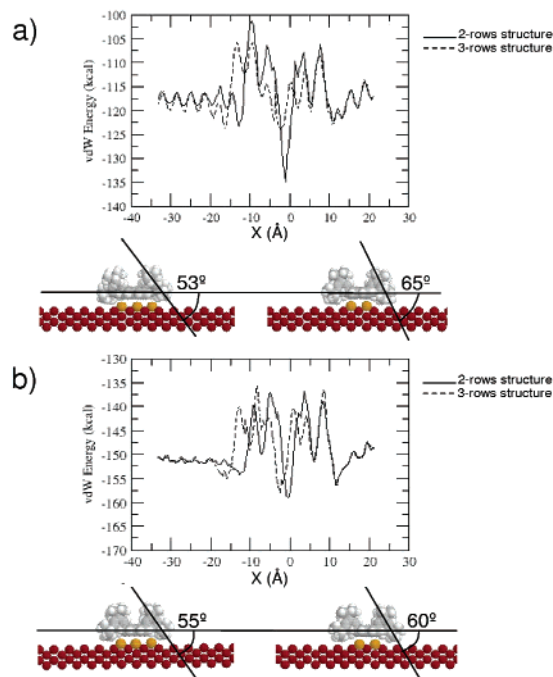


Figure 4. Energy vs lateral position with respect to a two-row (solid line) and three-row (dashed line) wide structure for the SL (a) and VL (b). While the adsorption energy of the VL is approximately the same for both kinds of structures, the SL exhibits a strong preference to form two-row structures.

placed beyond the end of the nanostructure and would thus be far away from the surface, decreasing the attractive interaction (a). On the other hand, the length does not affect the bending of the σ -bonds between the board and the legs (b). The most energetically favorable situation is therefore that in which the length of the nanostructure and the length of the molecular board are equal, which explains the longer nanostructures found in the VL case as compared to the SL case.

The discussion of the nanostructure's width is, however, not as straightforward, since increasing the width may lead to an increase in the attractive interaction between the board and the surface (a), but it may also force the legs to spread further, increasing the stress energy of the σ -bond (b). In Figure 4, we show the energy of the molecules as a function of their lateral position with respect to a nanostructure two Cu rows in width (solid line) and three rows in width (dashed line), respectively, calculated by means of an MM2 molecular mechanics routine. For both the SL and the VL, the preferential adsorption configuration on flat terraces is such that the axis of the molecules lies on top of a close-packed atomic row. When adsorbed on top of the nanostructure at the step edge, however, the adsorption site changes in the case of the SL: an adsorption of the SL on top of a two-row structure on the Cu(110) surface is favored by about 10.6 kcal/mol ($\approx 0.43 \text{ eV}$), when compared to the adsorption on top of a three-row structure. The formation energy of the nanostructure is the same, according to effective medium theory (EMT) calculations,⁸ when up to second-nearest neighbors are taken into account. Hence, SL molecules systematically form two-row-wide nanostructures because it

is energetically favorable. In the case of the VL, however, the energy difference is quite small (about 1.01 kcal/mol = 0.04 eV), which explains why the VL induces both two-row and three-row wide structures.

The ball models in Figure 4 show a front view of the SL and the VL molecules when resting on top of a two- and three-row structure, respectively. Whereas for the SL the angle between the legs and the board plane changes from 53° to 65° when the width of the nanostructure is increased from 2 to 3 atomic rows, it changes by only 5° in the case of the VL. This can be related to the different flexibility of the legs for the two types of Lander molecules: while the legs in the SL are very close to each other, thus preventing them from moving independently, in the VL they are farther apart, enabling the legs to bend and twist more independently.

As discussed above, the release of stress energy in the σ -bonds is one of the factors determining the stability of the nanostructures at the step edge. We can, thus, correlate the large energy difference between a SL adsorbed on top of a two- and a three-row structure to the large change in the bending angle of the sigma bonds adsorbed molecular conformation. The VL presents very similar angles for the adsorption on top of a two- and a three-row structure, and so the energy associated with the stress of the σ -bond does not change appreciably. Since the difference in molecular conformation is related to the different flexibility of the legs, and, as discussed above, the flexibility of the legs is a result of the molecular architecture, we can conclude that *the different molecular architecture of the SL and the VL is responsible for the differences in the size of the nanostructures they create.*

In conclusion, we have shown that, similar to SL molecules, VL molecules induce a reconstruction at the step edge of a Cu(110) surface. The nanostructures created by SL and VL molecules are similar in nature and originate from the same peculiar shape of the Lander molecules, i.e., both molecules act as nanoscale templates for the fabrication of nanostructures. The structure induced by the VL is, however, systematically longer and often wider (in 30% of the cases observed) than the one induced by the SL. We have shown that these differences arise from subtle differences in the molecular architecture between the VL and the SL. This result demonstrates that the reconstruction induced by large organic molecules can be fine-tuned by means of a rational design of the molecular shape. This possibility points to new opportunities of inducing predefined patterns on a metal surface at the atomic scale.

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