Adsorption behavior of Lander molecules on Cu(110) studied by scanning tunneling microscopy

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The adsorption of a large organic molecule, named Lander, has been studied on a Cu(110) substrate by scanning tunneling microscopy (STM). At low temperatures three different conformations of the molecule are observed on the flat surface terraces. At room temperature the Lander molecules are highly mobile and anchor preferentially to step edges. There the molecules cause a rearrangement of the Cu step atoms leading to the formation of Cu nanostructures that are adapted to the dimension of the molecule, as revealed directly by STM manipulation experiments. Upon annealing to 500 K the molecules order at higher coverages partially into small domains. In all cases the exact adsorption conformation of the molecules was identified through an interplay with elastic scattering quantum chemistry calculations. © *2002 American Institute of Physics.*
[DOI: 10.1063/1.1498475]

I. INTRODUCTION

The interaction between large organic molecules and metal surfaces has recently been studied extensively, both from a fundamental point of view[1–5] and because of prospective applications in molecular electronics and nanomechanical devices.[6–11] Ideally, to create functional monomolecular or hybrid-molecular devices, it is necessary to develop an architecture for the interconnection of individual molecules, molecular devices and wires, in a planar conformation and with atomic precision.[7]

When large molecules adsorb on metal surfaces the molecule–substrate interaction may be quite complex and one cannot *a priori* transfer certain molecular functionalities, designed for molecules in the gas phase, to a situation where molecules are adsorbed on surfaces. The surface may undergo a restructuring process in order to accommodate the molecule[12–14] and conformational changes may occur within individual molecules;[15–17] both aspects will be addressed in this paper.

The exact adsorption conformation may play an important role when for example measuring the conductance through a single molecule.[18] It is thus necessary to have in-

formation on the detailed bonding geometry of the molecules on the surface and on the interactions that induce molecular anchoring on the substrate at hand. Molecular conformations have, however, not been investigated intensively so far for complex molecules.[15–17]

A prototype of a molecule in the area of molecular electronics, designed to act as a molecular wire, typically consists of a central aromatic π board which is separated from the surface and surrounding molecules by spacer groups.[7] The size of the molecules and the flexibility of their spacer legs may give rise to different conformations upon adsorption.[16,17]

We have studied a large organic molecule, referred to as Lander, on a Cu(110) substrate. The conductance through the molecule has previously been studied on a Cu surface.[18] The adsorption and ordering of Lander molecules was investigated by scanning tunneling microscopy (STM) imaging and manipulation. From an interplay with theoretical elastic scattering quantum chemistry (ESQC) calculations[19,20] we determine three different molecular conformations on flat Cu(110) terraces. Each can be associated with a distortion of the molecular conformation similar to the gas phase conformations of the molecule.

At room temperature (RT) the molecules diffuse readily across the surface and the adsorption of molecules at step edges is accompanied by the formation of Cu nanostructures

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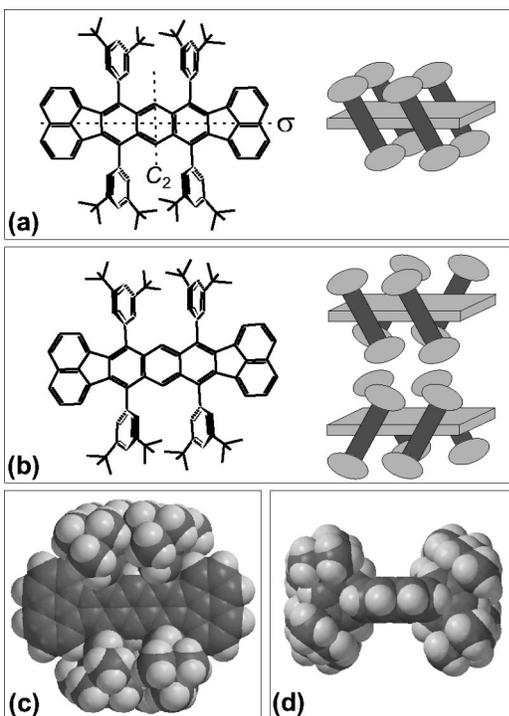[a)]Author to whom correspondence should be addressed. Electronic mail: fbe@phys.au.dk

FIG. 1. Molecular structure of the Lander molecule ($C_{90}H_{98}$) consisting of a central polyaromatic board (terminated by two fluoranthene groups) and four spacer legs (3,5-di-*tert*-butylphenyl substituents). (a) Achiral form with C_{2h} symmetry: eclipsed conformation of legs on opposite sides of the board as better seen from the schematic drawing. The symmetry elements (rotation and mirror axes) are indicated. (b) Chiral form with C_2 symmetry: staggered conformation of legs on opposite sides of the board, which results in two enantiomers (indicated in the schematic drawing). The rotation axis runs perpendicular to the paper plane through the center of the molecule. Space-filling model of a chiral form: (c) top view and (d) side view (along the board) showing how the spacer legs separate the central board form the surface.

to which the molecules anchor. The dimensions of these nanostructures fit exactly the distances between the spacer legs of the molecule. From a comparison of experimental and calculated STM images we can obtain information on the exact conformation of the molecules on the nanostructure. From these and similar previous studies[12,13] we can conclude that the molecular bonding and ordering is controlled by a subtle balance between intermolecular forces and molecule–substrate interactions. Often the latter is strong enough to induce surface restructuring processes and therefore one cannot simply consider the surface as a static checkerboard for molecular adsorption.

II. THE LANDER MOLECULE

The investigated Lander molecule ($C_{90}H_{98}$), shown in Fig. 1, is about 17 Å long and 15 Å wide and consists of a central polyaromatic unit (4.5 Å wide), which is surrounded by four "spacer legs." These legs are designed in such a way as to elevate the central part of the molecule by a nominal distance of 5 Å above the substrate upon adsorption [assuming an unperturbed conformation as in the gas phase, see Fig. 1(d)]. This separation should then electrically isolate the

board from the surface, so that the Lander board may ideally act as a molecular wire even when adsorbed on a metallic support.

In the gas phase the molecule can adopt different minimum-energy conformations, because the spacer groups are to some extent rotatable around the σ bond connecting them to the center board. The preferred conformation is attained by a rotation of the spacer legs out of the right-angled orientation to the board plane, which approaches the aromatic benzene units to the spacer groups and leads to preferable π–π stacking.

The two spacer groups on each side of the center board can both be tilted to the left or right out of the right-angled orientation. Hence there are three minimum energy conformations: an achiral form with C_{2h} symmetry ["eclipsed" conformation of legs on opposite sides of the board—Fig. 1(a)] and two enantiomorphic chiral forms with C_2 symmetry ["staggered" conformation of legs on opposite sides of the board—Fig. 1(b)].

III. MOLECULAR CONFORMATIONS ON FLAT TERRACES

The molecules were deposited from a glass crucible (heated to 550 K) under ultrahigh vacuum (UHV) conditions onto a clean Cu(110) surface. The molecular powder was thoroughly degassed prior to use at 500 K in UHV. The molecular coverage on the surface was varied by keeping the crucible temperature constant and changing the exposure time (5–1200 s). The absolute coverage was determined directly by STM. The adsorption of the molecules on Cu(110) was studied by means of a variable-temperature STM setup.[21,22]

At low temperatures (100 K) and low coverage we observe single molecules adsorbed on Cu terraces. High-resolution STM images reveal Lander molecules as four lobes with an (voltage-independent) apparent height of 4.5 $\pm$ 0.2 Å [Figs. 2(a) and 2(c)]. These lobes correspond to tunneling paths through the spacer legs of the molecule, evidenced from ESQC calculations[19,20] as will be discussed below. We observe that the molecules are arranged in three ways (Fig. 3): two rhomboidal shapes that are mirror symmetric to each other and one rectangular shape.[23] This suggests that a correlation exists between the molecular conformations on the surface and the minimum-energy conformations in the gas phase, which were discussed in the preceding section. The two chiral (eclipsed) conformations correspond to rhomboidal shapes in the STM images and the achiral (staggered) conformation corresponds to rectangular shapes in the STM images.

The two lobes have a peak-to-peak distance along the close-packed Cu direction of 5.8 $\pm$ 1.1 Å in all conformations. This value is in fairly good agreement with the distance between spacer groups attached to the same side of the board (5 Å) as expected from the gas-phase molecular model (Fig. 1). In the rhomboidal conformations the two groups of lobes along the close-packed direction are displaced in total by 3.1 $\pm$ 1.2 Å out of the rectangular arrangement, again in agreement with the gas-phase molecular model (around 2.5 Å). The lobe distance perpendicular to the close-packed di-
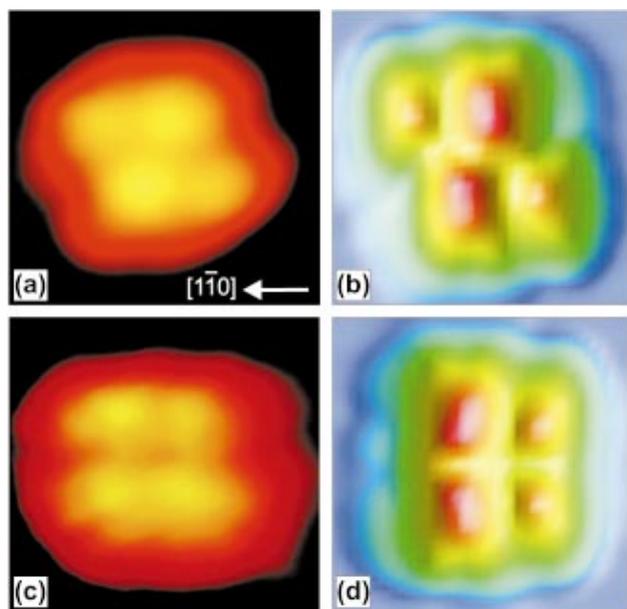
FIG. 2. (Color) STM image of a Lander molecule on Cu(110) at 100 K (20×20 Å^2, $V = -1000$ mV, $I = -0.21$ nA) with (a) rhomboidal shape and (c) rectangular shape. (b) and (d) ESQC-calculated STM images of the rhomboidal (chiral) and rectangular (achiral) Lander molecules, respectively, using the same tunneling parameters as in the experiments. The aromatic board of the Lander molecules is parallel to the close-packed Cu direction indicated in the image.

rection, however, is 6.8 ± 1.9 Å, which is much less than expected from spacer group distances in the gas-phase model (around 10 Å). This implies a significant distortion of the legs.

Detailed information on the adsorption conformations of the Lander were extracted by comparison of the experimental data with simulated STM images computed via the ESQC approach.[19,20] The ESQC routine was used together with standard molecular-mechanics calculations (MM2 routine with a generalized potential for surface metal atoms) to optimize the conformations of the Lander molecules on the Cu(110) surface. Our ESQC calculations are based on the calculation of the full scattering matrix of the STM tunnel junction.[19,20] The junction fully takes into account the Cu surface, the adsorbed molecule and the tip apex. The electronic interactions inside the junction are calculated using a semiempirical extended Hückel approximation. The success of the ESQC method has previously been demonstrated.[16–18,24]

In Figs. 2(b) and 2(d) we present calculated STM images of an isolated molecule with rhomboidal and rectangular conformation on a flat Cu(110) terrace, respectively, using tunneling parameters identical to the experimental ones. The agreement with experiment is very good (allowing for the fact that the tip used in the simulations is atomically sharp, thereby reducing tip-convolution effects that are observed experimentally). The calculations reproduce the rhomboidal and rectangular arrangement of the four lobes associated with tunnel channels through the four spacer legs. The molecular orbitals of the board do not contribute to the image contrast, in agreement with the experimental findings.

Notice that for both the rhomboidal and the rectangular

conformation two of the lobes are dimmer than the other two. From ESQC calculations we infer that the two dimmer lobes are each due to a simple tunneling path through one leg only. The two brighter lobes, on the other hand, are due to a more complete tunneling path formed by a combination of tunneling channels through the upper part of one leg and the lower part of the neighboring leg on the same side of the board [compare Figs. 1(a) and 1(b)].

The fact that the distance between lobes in the STM images (6.8 Å) is shorter than expected from the gas-phase model (10 Å) is clarified by ESQC calculations. A strong attraction of the π system of the board towards the metal surface (which was also found for similar molecules[17]) introduces a severe constraint on the legs, which leads to an out-of-plane distortion of each leg-board σ bond. In turn, this has the effect of approaching opposite spacer groups. The calculations also confirm that Lander molecules adsorb with the axis of the board parallel to the close-packed Cu direction. We hence conclude that the three different molecular shapes observed in the STM images correspond to the three possible geometrical conformations of the molecule on the surface (as shown in Fig. 1).

A molecule's conformation sometimes changes during STM imaging at RT, as shown in Fig. 3. In this case the center molecule switches from a rhomboidal conformation to a rectangular shape. The molecule in the lower-right corner, which initially has a rhomboidal conformation in (a), changes its appearance repeatedly during the imaging process in (b), as indicated by the stripes observed through the molecule. The dominant shape is the rhomboidal conformation enantiomorph to the one in (a). A switch in conformation may also occur when a manipulation process at reduced tunneling resistance is performed (which leads to a lateral manipulation). Both observations confirm that the different conformations belong to the same molecule.

IV. MOLECULAR CONFORMATIONS AT STEP EDGES

At RT the Lander molecules are at low coverages found to be very mobile on the Cu(110) surface and diffuse readily to step edges, as observed for similar molecules on the same surface.[25] In an earlier study we demonstrated that the anchoring of Lander molecules to a Cu step edge is caused by a strong interaction between the molecule's π system and the surface, which causes the mobile Cu kink atoms to arrange in nanostructures underneath the aromatic board of the Lander (Fig. 4).[26] The molecules thus act as a template, accommodating Cu atoms at a step edge. These Cu nanostructures are unravelled by low-temperature STM manipulation experiments.

The Cu nanostructure has a width of 7.5 ± 0.5 Å (corresponding to two neighboring close-packed Cu rows) and a length of 18.5 ± 3.5 Å (corresponding to about seven atoms per row).[26] For comparison, the aromatic board of the Lander has very similar dimensions, being 17 Å long and 5.8 Å wide. This clearly demonstrates how the dimensions of the Cu nanostructure are adapted to the molecular structure [see Fig. 4(c)].

It has been demonstrated theoretically and experimentally that the anchoring to the nanostructure at step edges
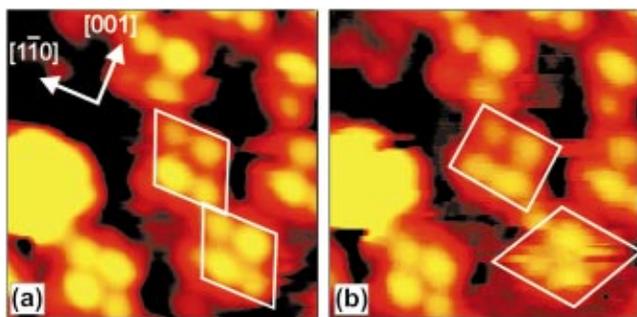
FIG. 3. (Color) STM images of Lander molecules revealing conformational changes (50×50 Å^2, $V = -1000$ mV, $I = -0.25$ nA). (a) The center and lower-right molecule show the same rhomboidal shape. (b) The center molecule changed to the rectangular shape, while the lower-right molecule reveals a fluctuating conformation while imaging, with a dominating rhomboidal shape mirror symmetric to the original shape.
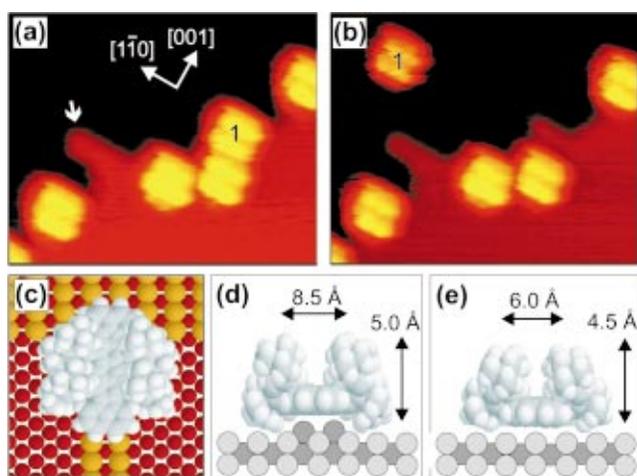

FIG. 4. (Color) (a) Before manipulating the Lander molecule labeled "1" from a Cu(110) step edge (136×112 Å^2, $V = -1768$ mV, $I = -0.37$ nA, $T = 95$ K). A nanostructure from a previous manipulation experiment is visible and indicated by an arrow. (b) After the manipulation of the molecule along the [$1\bar{1}0$] direction the nanostructure underneath becomes visible (tunneling parameters for manipulation; $V = -55$ mV, $I = -1.05$ nA). (c) Model of the Lander on the nanostructure, showing that the board is parallel to the nanostructure. For clarity, the length of the nanostructure is extended beyond the molecule. Cross-sectional side view of the Lander (d) on a nanostructure and (e) on a flat terrace. The distance between and height of the spacer groups (from calculated STM images) are stated.
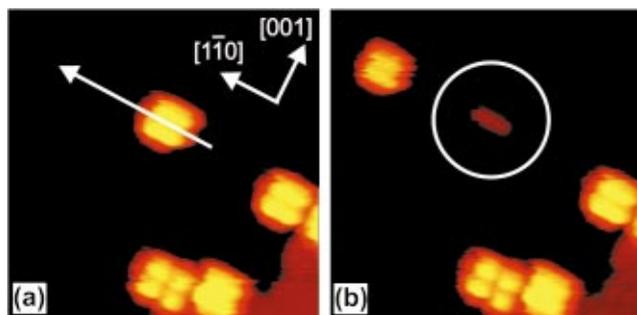

FIG. 5. (Color) Manipulation sequence of a Lander molecule on a Cu(110) terrace at 95 K after RT deposition (150×150 Å^2 $V = -1769$ mV, $I = -0.28$ nA). (a) Before manipulation. The arrow marks the manipulation direction. (b) After manipulation (tunneling parameters for manipulation, $V = -11$ mV, $I = -3.1$ nA). The circle marks the Cu rows that are visible where the molecule was adsorbed before.
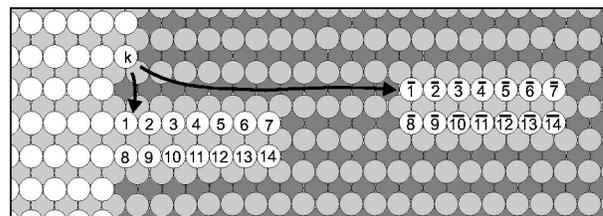

FIG. 6. Labelling of atoms in a nanostructure attached to a step (1–14) and on the terrace ($\bar{1}$–$\overline{14}$) referring to Table I. k marks a kink atom.

also causes conformational changes of the molecule compared to adsorption on a flat terrace.[26] The Lander adsorption on a Cu nanostructure at a step edge leads to a significantly different height (5.0 Å) and width (8.3 Å) between the spacer legs [Fig. 4(d)] as compared to the dimensions on the flat terraces [4.5 and 6.3 Å, respectively, see Fig. 4(e)]. According to ESQC calculations this is due to a more vertical conformation of the legs when adsorbed on the nanostructure [the reduced height on the terrace is clearly visible in Fig. 4(b)]. The reason is the almost restored planarity of the σ bonds between the spacer legs and the aromatic board when the molecule adsorbs on the Cu nanostructure, whereas the spacer legs are distorted significantly more when the molecule adsorbs on a flat terrace in order to achieve a comparable interaction between the π system and the Cu surface.[26]

While the manipulation of molecules at steps always revealed a restructured step (nanostructure), the manipulation of molecules on Cu terraces usually did not reveal any surface restructuring. In rare cases it was, however, possible to observe a nanostructure underneath molecules adsorbed on a flat terrace as well (Fig. 5). The dimensions of these nanostructures are consistent with the nanostructures at step edges.

Upon adsorption of the molecules at low temperatures (<150 K), no nanostructures are found underneath the molecules—neither on flat terraces nor at step edges. At these low temperatures, the mobility of Cu kink atoms at step edges is not high enough for the nanostructure to form. We can thus conclude that the process of step restructuring is thermally activated.

On a terrace the nanostructure formation at RT may be initiated when a molecule meets a Cu adatom and subsequently more adatoms are captured to build up the structure. The low concentration of Cu adatoms at RT is the main reason for Cu nanostructures only seldom being observed on terraces. Another reason stems from the energetics involved in forming the Cu nanostructure, which can be understood within a very simple model presented in the following.

TABLE I. Formation energies $\triangle E_i$ of the atoms in nanostructure at a step and on a terrace out of kink atoms on Cu(110) in eV obtained successively corresponding to their label numbers (Fig. 6) by means of EMT via Eq. (1).

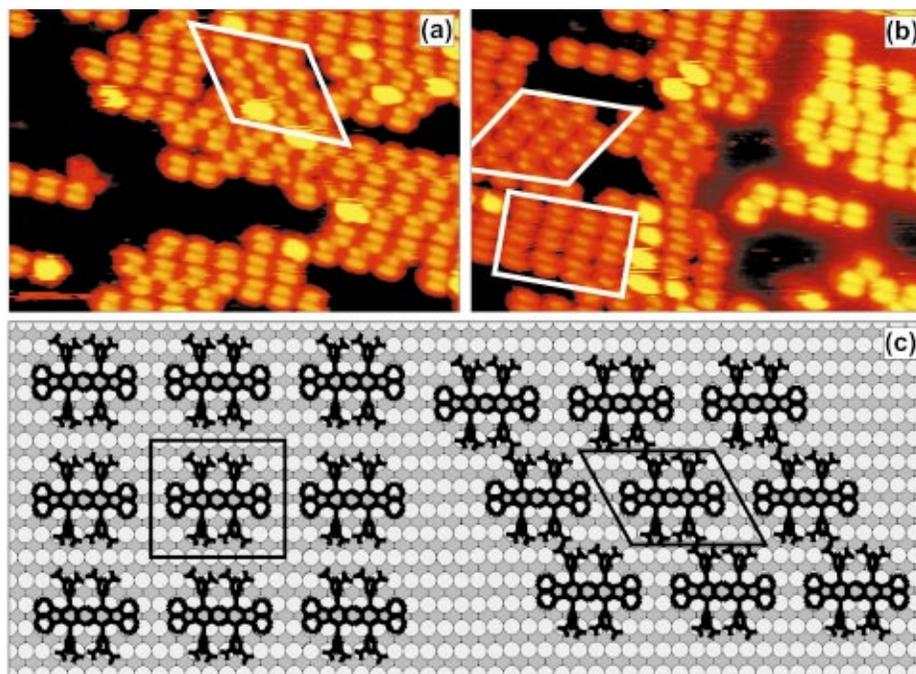| Atom label i	At step			On terrace		
	1–7	8–14	$\bar{1}$	$\bar{2}$–$\bar{7}$	$\bar{8}$	$\bar{9}$–$\overline{14}$
$\triangle E_i$	0.04	0.0	0.28	0.04	0.24	0.0
$\Sigma_1^{14} \Delta E_i$		0.28			0.75	

FIG. 7. (Color) Higher coverages of Lander molecules with partial ordering at RT after annealing to 500 K (300×200 Å^2, $V = -1071$ mV, $I = -0.32$ nA). (a) A domain of rhomboidally shaped molecules. (b) Domains of rhomboidally shaped molecules and rectangularly shaped molecules. Note a step edge running vertically through the center of the image, hence the molecules on the right-hand side are imaged brighter. (c) Ball model of the double row structure. Molecules are shown in black and the unit cells of the rectangular $p(8 \times 5)$ and the rhomboidal $\binom{34}{80}$ structure are indicated.

In general, the adsorption of molecules will induce a restructuring of the surface only if the gain in the adsorption energy ΔE_{ad} of the molecules on the disrupted surface, as compared to the virgin surface, is sufficiently high to balance the energy ΔE_{metal} required to break the metal bonds and form the Cu nanostructure, i.e., the energy difference between the restructured and the virgin *clean* surface. A lower bound for ΔE_{ad} of the Lander molecules can be estimated from ΔE_{metal} involved in forming the Cu nanostructures.

Within the approximative effective medium theory (EMT) approach,[27,28] the energy E_i of an atom in an fcc structure is a simple function of the nearest-neighbor (NN) and next-nearest-neighbor (NNN) coordination numbers, (N_1 and N_2, respectively). For Cu atoms in the topmost surface layers we have

$$E_i(N_1, N_2) \simeq V_2(12 - N_1) + \tfrac{1}{2}V_3(12 - N_1)^2$$
$$+ V_2'(6 - N_2). \tag{1}$$

Using the relevant parameters for Cu,[29] we calculate the energies E_i for every atom which changes its coordination number when being expelled from the close-packed Cu rows.

The energy necessary to move a kink atom (k) to a position i in the nanostructure is calculated successively by means of Eq. (1). The labelling of the atoms in the following refer to Fig. 6, and the results are presented in Table I. Overall the creation of a nanostructure at a step requires an energy of 0.28 eV.[30] The situation is quite different for a nanostructure on a terrace due to the reduced number of nearest neighbors of the terrace atoms ($\bar{1}$) and ($\bar{8}$) compared to the step atoms (1) and (8).[31] In our model, the formation of a terrace nanostructure requires an overall energy of 0.75 eV, which represents a lower bound for the adsorption energy. The

lower value for the nanostructure formation at a step leads to a much higher energy gain, and partly explains the dominance of step nanostructures.[32]

The driving force for the restructuring is the increase in adsorption energy on the nanostructure. This is partly due to the increased interaction of the aromatic π system of the Lander board with the surface, because of their closer proximity. Additionally, the nanostructure contains low-coordinated Cu atoms that are highly reactive. ESQC calculations showed that on a plane surface such an interaction is only possible because of severe spacer group deformations [Fig. 4(d)]. Adsorption on a nanostructure is hence accompanied by a strain release in the σ bonds of the spacer groups to the aromatic board [Fig. 4(e)], which is the second contribution to the energy gain.

V. MOLECULAR STRUCTURES AT HIGH COVERAGE

When a higher coverage of molecules is adsorbed at RT, no clear indication for spontaneous large-scale ordering is found, except that all molecules have a tendency to form short one-dimensional chains [Figs. 7(a) and 7(b)] aligned along the close-packed [$1\bar{1}0$] direction of the Cu(110) substrate. The attractive interaction between molecules within these chains is most likely due to van der Waals forces. A partial ordering is observed, if a RT-deposited film is annealed to around 500 K (or likewise, if the molecules are deposited onto a sample kept at elevated temperatures). In this case three possible structures are found, which reflect the rhomboidal and rectangular adsorption geometries of the single molecules described above (Fig. 7).

In all three domains the molecules are again aligned in rows along the [$1\bar{1}0$] direction, with a molecule–molecule

distance of around 20 ± 2 Å, corresponding to a simple van der Waals bonding distance of the molecules [see Fig. 7(c)]. As revealed in Figs. 7(a) and 7(b), rows of chiral, rhomboidal molecules order into chiral domains that reflect the C_2 symmetry of the molecule. Equivalently, the achiral molecules form achiral, rectangular domains [Fig. 7(b)]. Figure 7(c) shows a model of the domain structures with the commensurable superstructure of the molecules. The rectangular $p(8 \times 5)$ and rhomboidal $\left(\begin{smallmatrix} 3 & \pm 4 \\ 8 & 0 \end{smallmatrix}\right)$ structures are sketched.

We can only speculate about the origin of the different domain structures. A closer packing of the rhomboidal molecules perpendicular to the close-packed Cu rows may be due to the orientation of spacer groups of neighboring Lander molecules, pointing in opposite directions. This leads to a staggered approach and avoids steric hindrance between the bulky *tert*-butyl parts of adjacent spacer groups.

It is somewhat surprising that Lander molecules do not form extended, ordered domains on the Cu(110) surface, while they do so on the less corrugated Cu(001) surface.[33] In this case, chains of rhomboidal molecules form even at low coverages along specific crystal directions of the Cu(001) surface, which build up into extended domains close to monolayer coverage.

VI. CONCLUSIONS

We have studied the adsorption of the Lander molecule on Cu(110). Three different conformations of the molecules are found, all with the aromatic board parallel to the substrate and oriented along the Cu $[1\bar{1}0]$ direction. The observed conformations were correlated with the exact orientation of the spacer groups on the surface through an interplay with theoretical ESQC calculations. The Lander molecules mainly display local, one-dimensional ordering and small domains are formed only after annealing at 500 K, which reflect the symmetry of the comprising molecule conformations.

By STM manipulation we have shown that Lander molecules locally restructure monatomic steps into characteristic nanostructures, which are two atomic rows wide and approximately seven atoms long. The molecules act as templates in the formation of nanostructures on the Cu(110) surface. As in the case of HtBDC molecules on the same surface,[12,13] there is a strong interaction between the molecule's aromatic π system and the substrate. This is stressed by the fact that the bond of the spacer groups to the aromatic board is severely bent to enable the approach of the aromatic board to the substrate.

The results confirm that large, flexible molecules can adopt several different adsorption conformations on metal surfaces that involve unexpected restructuring processes on the surface. This emphasizes the importance of manipulation experiments to investigate the adsorption of large molecules on surfaces, and also suggests that surface restructuring processes are substantially more common than generally believed for the adsorption of large molecules.

Finally, the separation of a potentially strongly bonding molecular part (π system) from metal surfaces seems generally to be a driving force for a restructuring of the metal surface in order to maximize the adsorption energy. These and previous results[12,13] point to the possibility of custom designing molecules with specific properties that will induce desired surface structures.

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[29] $V_2 = 0.109$ eV and $V_2' = 0.0246$ eV for the effective NN and NNN pair interactions, respectively, and $V_3 = 0.0023$ eV for the effective NN three-body interaction for Cu (Ref. 27).

[30] For the nanostructure at the step it is only the build-up of the first row $(1-7)$ which costs energy (0.04 eV per atom mainly due to NNN changes), while the second row basically does not lead to energy changes compared to the kink-site adsorption site.

[31] This implies that moving kink atoms (k) to the positions ($\bar{1}$) and ($\bar{8}$) requires a large formation energy of 0.28 and 0.24 eV, respectively, while the other atoms ($\bar{2}$–$\bar{7}$) and ($\bar{9}$–$\bar{14}$) encounter the same energetic situation as the equivalent atoms in the nanostructure at steps (2–7) and (9–14).

[32] It is also more likely to grow a nanostructure at a step, since the supply of Cu atoms is much larger than on a terrace, where only diffusing adatoms are available.

[33] J. Kuntze and R. Berndt (private communication).