Conformations and controlled manipulation of a long molecular wire on Cu(1 1 1)

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Received 21 January 2005; accepted for publication 7 April 2005
Available online 21 April 2005

Abstract

Low temperature scanning tunnelling microscopy is employed to investigate in detail the conformations of single Violet Lander molecules (C_{108}H_{104}) on Cu(1 1 1). The molecule consists of a long polyaromatic molecular board supported by four spacer legs. Several conformations, corresponding to different positions of the legs, are observed and characterised, showing that a much larger variety of conformations is possible compared with the other molecules of the Lander family. This is due to the longer central board and the consequently larger distance between the legs. Moreover, tip-induced conformational changes and molecular displacement are achieved in manipulation experiments.

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Keywords: Molecular wire; STM; Manipulation; Lander molecule

1. Introduction

The driving idea of developing electronic devices on the nanometer scale has focussed the attention on prototype nanomachines formed by one or few complex molecules and designed for a specific function [1,2]. A major contribution in this field was given by the use of scanning tunnelling microscopes (STM) in single atom and molecule manipulation experiments, in which the tip interacts directly with adsorbates and modifies them in a controlled way. This technique enables the organisation of well-defined atomic or molecular structures on a substrate, thus e.g. allowing the investigation of quantum corrals in particular conditions [3]. It serves also to reproduce the function of simple electronic devices. An atomic/molecular switch, e.g., was realised either by controlling the

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position of a single atom [4] or by acting on the conformation of a large molecule [5].

Their use as components in mechanical and electronic nanodevices requires that specific classes of molecules, each one suitable for a particular application, are synthesised. Landers are a family of organic molecules especially designed for its board to act as prototype for molecular wires. Their structure (see scheme in Fig. 1(a)) consists of a planar polyaromatic board, characterised by a small HOMO–LUMO separation, and of four side 3,5-(di-tert-butyl)-phenyl (TBP) groups. The latter ones can somehow rotate around their σ bonds and are meant to lift up the molecular wire board from the substrate when the molecule is adsorbed, thus keeping it partially electronically decoupled from the surface. A scheme of the possible orientations of the TBP legs with respect to the molecular body is reported in Fig. 1(b) and described in detail in the caption. The central board is projected beyond the spacers in both directions, which is useful to test the possibility of contacting the molecular wire with metallic steps or with each other. Several types of Landers have been synthesised. The simplest species, referred to as Single Landers (SL in the following), is now well known, while the more complex Reactive Landers (RL) are still under investigation. Both types adsorb

Fig. 1. Panel (a): Chemical structure of a Violet Lander (C$_{108}$H$_{104}$). The distance between back and front TBP groups and between TBP groups at the opposite sides of the body are indicated as $L$ and $W$, respectively. Panel (b): Degrees of freedom of the TBP legs with respect to the molecular body. After defining the reference axes so that the polyaromatic board lies in the XY plane and is aligned with the X direction, the position of each leg is determined by the angle $\phi$, corresponding to rotation in the XZ plane, and by the azimuth $\rho$ (rotation in the YZ plane). Some deformation of the legs, which is most probably present, is not taken into account in this simplified drawing. $\phi = 90^\circ$ corresponds to the gas-phase conformation of VL. Panel (c): typical STM image (37 Å × 41 Å, $V = 0.8$ V, $I = 2.0 \times 10^{-10}$ A) of a VL adsorbed in a Cu(111) terrace. The four lobes correspond to the TBP legs while the central board is decoupled from the substrate, and hence not imaged. The bar at the upper-left corner indicates its orientation.
on Cu surfaces in two different conformations, characterised by parallel or crossed legs [6], and can be easily STM manipulated.

We report here a low temperature STM investigation on the last molecule of the Lander family, the Violet Lander (VL), a scheme of which is reported in Fig. 1(a). It has a 25 Å long wire with a distance $L = 12.2$ Å between front and back TBP groups. Such structure guarantees the legs to be free to rotate independently, contrary to the case of the shorter SL, for which $L \approx 7$ Å and steric crowding hinders the independent movement of the legs. A previous investigation on Cu(100) at RT showed that VL molecules adsorb preferentially in the rectangular (parallel legs) conformation and tend to saturate steps before populating terrace sites [7]. On the nanopatterned O/Cu–Cu(110) surface, on the contrary, these molecules form long rows on the bare Cu(100) stripes and align themselves forming long wires. No strong interaction between adjacent molecules is however found [8]. We have deposited the VL on the Cu(111) surface for different sample temperatures ($T_{\text{dep}}$). We found that, in the low coverage limit, different adsorption sites are populated when $T_{\text{dep}} = 140$ K or $T_{\text{dep}} = 300$ K. Moreover, several conformations are present in both cases. For adsorption at terraces, conformational changes and/or displacement of the molecule can be induced by manipulation with the STM tip.

2. Experimental

Experiments were carried out in an ultra high vacuum (UHV) apparatus consisting of a preparation chamber, equipped with a tantalum Knudsen cell, a quartz microbalance and all other typical vacuum facilities, and a main chamber, hosting a home-made low temperature STM (LT-STM) described in detail elsewhere [9]. Before each experiment, the Cu(111) substrate is carefully prepared by several sputtering cycles followed by annealing to 750 K. VL are evaporated by resistively heating the home-built Knudsen cell to 660 K, while keeping the sample either at 300 K or at $T = 140$ K. An evaporation rate below $1 \times 10^{-6}$ ML/min (in ML of Cu(111)) is estimated from the very low coverage observed in STM images. After evaporation, the sample is cooled below 70 K and transferred into the LT-STM.

Images are acquired at a temperature between 7 and 8 K, in constant current mode and using typical voltages between 0.1 and 1.5 V and currents between 0.1 and 2.0 nA. The piezo constants were calibrated on the basis of the Cu lattice parameter, using images of the clean surface with atomic resolution. Lateral manipulations are performed either in a constant current [10] or in a constant height [11] mode.

3. Data presentation and discussion

A typical STM image for a VL adsorbed at a Cu(111) terrace is reported in Fig. 1(c): only four bright lobes appear in the STM images, each one corresponding to a TBP leg. Indeed the polyaromatic board is lifted from the surface by the TBP groups, so that its coupling with the surface itself is strongly weakened: hence the molecular body is not visible in STM images. In spite of that, it was demonstrated that the standing wave pattern observed for Lander molecules on Cu(111) is generated by the scattering of the 2D electron gas from the polyaromatic board—not from the legs—and therefore that the board is still electronically interacting with the metallic substrate [12]. The molecular body is oriented parallel to the long axis of the molecule. This information is not inferred directly from STM images. It is deduced from the structure of the molecule, for which the distance $L$ is larger than the width $W$, and confirmed by the analysis of the standing wave pattern produced by the molecule, which is sensitive to the board orientation [12]. Moreover, elastic-scattering quantum chemistry (ESQC) + molecular mechanics calculations performed for VL adsorbed on Cu(100) predict conformations in good agreement with the observed ones [13].

Fig. 2 shows different VL conformations observed upon deposition at $T = 140$ K. At this temperature diffusion is inhibited and the molecules are found mainly at terraces, with a random orientation with respect to the high symmetry directions. STM images are reported in the upper row.
Fig. 2. Row1: STM images of the different conformations of VL molecules adsorbed at terraces (50 Å × 50 Å, \( V = 0.8 \, V \), \( I = 2.0 \times 10^{-10} \, A \)). The bar in each panel and the arrow in (a1) indicate the orientation of the polyaromatic wire and the high symmetry \( \langle 111 \rangle \) direction, respectively. Row 2: height profiles of VL in the different conformations. They are recorded along lines parallel to the molecular body and in correspondence of the TBP legs, like the ones reported in panel (a1) as an example (continuous and dashed lines across the molecule). The relative position of the maxima, i.e. of the upper part of the TBP legs, gives information about the conformation of the molecule. Row 3: schematic drawing of the conformations reported in the upper panels, underlying the different orientations of the TBP groups with respect to the central board.
(1), while the central one shows the corresponding height profiles. We note that the quote H reported in the line scans refers to the apparent height of the TBP groups, and not to the board-surface distance. These height profiles give useful information on the relative position of the TBP legs for molecules in different conformations. Finally, the bottom row (3) contains schematic drawings of the VL conformations, as inferred from the information above. Panels (a) and (b) report the so-called parallel-legs and crossed-legs conformation, already well known from previous investigations on SL [6,14]. They correspond, respectively, to the case in which the TBP groups on one side of the central board rotate in the same direction and in the same/opposite direction with respect to those on the other side of the board. The fainter lobes visible in Fig. 2(b) correspond to the lower part of the legs and their orientation suggests that some lateral tilting towards the central wire has also occurred. These are the only conformations detected for SL and RL, due to the lowest mobility of TBP groups in that case. Panels (c) and (d) report two asymmetric conformations never observed before. The side groups are now oriented as in the corresponding schemes: in conformation (c) the front-left and back-right legs are parallel and rotated in the opposite direction with respect to the front-right and back-left ones. In (d), on the contrary, three legs are parallel and the fourth is tilted in the opposite direction. Some additional tilting towards the molecular body is also evident. The independent rotation of TBP groups on the same side of the molecular wire is a direct consequence of the particular design of VL; indeed the larger distance $L$ eliminates the steric hindrance between TBP groups present for SL and RL [6].

The interpretation of conformations (a)–(d) is confirmed by the result of ESQC calculations performed on Cu(100) [13]. Although the substrate is different, theoretical predictions fit quite well with the experimental data, thus suggesting that, in absence of defects, the substrate has not much influence on the final adsorption state. This hypothesis is supported by the behaviour of the SL, which causes different reconstructions on the substrate but does not show significant conformational changes when deposited on different Cu surfaces [6,14–16].

Panel (e) reports a further conformation, in which the upper lobes of the four TBP legs are close to each other while the lower ones are always visible in a more detached position with respect to the central axes of the molecule. We suggest that in such “8-lobes” conformation front and back legs are rotated in opposite direction and towards the central body, in such a way that their upper lobes almost touch each other. Although this conformation has no correspondence on the VL/Cu(100) system, it is the most frequently observed in our case, indicating that it should be energetically favoured on Cu(111) at $T_{\text{dep}} = 140$ K.

If VL molecules are deposited on Cu(111) at $T_{\text{dep}} = 300$ K, diffusion is activated and, in the low coverage limit, molecules populate only step sites. As it is evident from the STM images reported in the upper row of Fig. 3, the body of the molecule is still not imaged. From the position of the legs and from comparison with conformations at terrace sites we deduce, however, that the molecular body is always aligned with the step edge. Two conformations are observed for adsorption at steps, corresponding to parallel (a) and asymmetric legs (b), respectively. The former conformation is the most common, while the latter is observed only rarely.

The average apparent length ($L$), width ($W$) and height ($H$) of Violet Landers observed in the STM images on Cu(111) are summarised in Table 1 for the different conformations. We note that: (1) the statistic error associated to each value is much larger than the instrumental error of $0.5 \text{ Å}$ which affects the determination of each distance in single line scans. It is therefore not due to an instrumental effect; instead it reflects the spread of the data, which is indeed the maximum for the most asymmetric conformations. This indicates that the TBP groups can assume several intermediate positions although the same shape appears in STM images. (2) 66% of the molecules adsorb on terraces in conformation (e), suggesting that it is at least slightly energetically favoured when deposition occurs at $T_{\text{dep}} = 140$ K. At steps, on the contrary, the parallel-legs conformation is preferred. (3) Conformation (a) is the only one systematically observed in previous STM experiments on Cu(100). Form comparison of our results with the ones of Ref.
[7], it is evident that the average dimensions for molecules in such conformation are in good agreement. For all conformations, the average height between 3.7 and 4.0 Å is in accordance with what determined for VL/Cu(100) [7] and for SL (characterised by a shorter wire but the same legs) on different Cu surfaces [6,14].

From the apparent height of TBP groups of VL adsorbed on Cu(111), we can deduce that the molecular board is much closer to the surface that the 7 Å distance expected for the gas-phase conformation (φ = 90°). Moreover, STM images often show a non-alignment of the lower and upper lobes of TBP legs confirming that some deformation of the legs with respect to the gas phase occurs upon adsorption. Therefore, both rotation by an angle φ in the plane aligned with the molecular body (XZ referring to Fig. 1b) and rotation in the azimuthal plane (ρ) must have occurred. As in the case of SL, deformation is driven by attracting forces between the molecular board and the surface. Theoretical work, still in progress at the moment, indicates that such attraction is stronger than Van der Waals interaction, although the legs prevent the board to be fully chemisorbed. A simple geometrical model, considering only a rigid rotation of the TBP groups around their σ bonds and taking into account the estimated effective radius of rotation suggests that the legs should be tilted in a position close to φ = 20°. However such model, useful to give a first idea of the VL molecular conformations, is probably far from being
Table 1
Average dimensions of VL on Cu(111) as inferred from STM images

<table>
<thead>
<tr>
<th>Conformation</th>
<th>Population</th>
<th>( L ) (Max/min) Å</th>
<th>( W ) (Max/min) Å</th>
<th>( H ) (Max) Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) →→</td>
<td>17%</td>
<td>11.8 ± 2.3</td>
<td>7.9 ± 1.2</td>
<td>3.7 ± 0.3</td>
</tr>
<tr>
<td>→→</td>
<td>10.6 ± 2.2</td>
<td>6.9 ± 0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b) →→</td>
<td>3%</td>
<td>13.3 ± 1.5</td>
<td>7.1 ± 0.9</td>
<td>3.8 ± 0.2</td>
</tr>
<tr>
<td>←→</td>
<td>12.0 ± 1.8</td>
<td>6.9 ± 0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(c) →←</td>
<td>5%</td>
<td>16.9 ± 1.9</td>
<td>7.5 ± 0.6</td>
<td>3.9 ± 0.4</td>
</tr>
<tr>
<td>←→</td>
<td>10.3 ± 2.6</td>
<td>6.8 ± 0.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(d) →→</td>
<td>9%</td>
<td>14.8 ± 2.5</td>
<td>9.5 ± 2.1</td>
<td>4.0 ± 0.3</td>
</tr>
<tr>
<td>←→</td>
<td>9.6 ± 1.9</td>
<td>7.7 ± 1.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(e) →→</td>
<td>66%</td>
<td>10.9 ± 1.5</td>
<td>8.4 ± 1.0</td>
<td>3.7 ± 0.3</td>
</tr>
<tr>
<td>←→</td>
<td>9.7 ± 1.5</td>
<td>7.6 ± 0.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( L \) (up/down)

<table>
<thead>
<tr>
<th>Conformation</th>
<th>Population</th>
<th>( L ) (Max/min) Å</th>
<th>( W ) (Max/min) Å</th>
<th>( H ) (Max) Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) →→</td>
<td>92%</td>
<td>14.4 ± 1.6</td>
<td>8.5 ± 1.1</td>
<td>4.0 ± 0.3</td>
</tr>
<tr>
<td>→→</td>
<td>13.6 ± 1.5</td>
<td>7.9 ± 1.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b) →→ or →←</td>
<td>8%</td>
<td>9.5 ± 0.7</td>
<td>8.8 ± 0.4</td>
<td>3.9 ± 0.5</td>
</tr>
<tr>
<td>←→</td>
<td>15.8 ± 1.7</td>
<td>7.8 ± 0.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The upper table refers to molecules at terraces, the lower one to molecules at step sites; the conformations cited in column 1 are those marked with the corresponding letter in Figs. 2 and 3. Column 2 indicates the relative population, evaluated on a statistic of 125 molecules at terraces and 24 molecules at steps. Columns 3 and 4 report the distance between adjacent TBP groups, giving an estimate of the apparent length \( (L) \) and width \( (W) \) of the molecule; two values (Max/min) are reported for each parameter since the high mobility of the legs causes them to move independently, thus giving an asymmetric shape in the STM images. For molecules at steps, the two \( L \) values refer, on the contrary, to the distance between TBP legs at the upper or lower side of the step. The last column reports the apparent height of the molecule.

Fig. 4. Sequence of STM images \((V = 0.8 \text{ V}, I = 2.0 \times 10^{-10} \text{ A})\) recorded during lateral manipulation of a VL on Cu(111). The arrows indicate the tip path. The first step was done in constant current, the following ones in constant height manipulation mode. A schematic drawing of the corresponding conformation is reported in the inset of each panel.
Fig. 5. As Fig. 4, but only constant height manipulation was applied in this sequence. The molecule moves on the surface following the path evidenced in panel (g). The small circle in panel (b) shows the defect assumed as reference point to understand the molecule displacement. A schematic drawing of the conformation corresponding to each step is reported in the inset of each panel.
realistic. On Cu(100), it was indeed demonstrated by molecular mechanics calculations that both the $\phi$ and $\rho$ of the $\sigma$ bond connecting each TBP leg to the board must be taken into account [7].

Due to the presence of the four TBP legs lifting the conductive wire from the substrate, Lander molecules can be easily manipulated by the STM tip, thus changing their conformation and/or moving them from the initial adsorption site. Figs. 4 and 5 show two sequences recorded upon lateral manipulation of VL. Manipulation is performed both in constant current and in constant height mode, finding that the latter method is slightly more efficient. In Fig. 4 a molecule initially in the “8-lobes” conformation (a) switches to the asymmetric shape reported in Fig. 2(d1) following to a constant current manipulation in the direction indicated by the arrow. Further action of the tip, now in constant height mode, causes the molecule to change the relative position of its legs, reaching first (c) the mirror conformation of the one in panel (b), then the antiparallel legs conformation (d). Comparison with reference points located out of the image size (and hence not shown) indicate that in this sequence the molecule does not move significantly on the surface. The change of relative position with respect to the defect appearing in panel (b) is apparent, being due to a tip-induced displacement of the defect during subsequent scans. An example of a molecule running on the surface is provided by the sequence reported in Fig. 5. Taking as reference the small defect below the molecule, we see that, upon lateral manipulation in constant current mode, the molecule moves on the terrace, changing conformation and orientation several times and following a path of significant length with respect to the molecular dimensions (dotted line in panel (g)). In spite of their bigger size, VL molecules show the same attitude towards manipulation reported for the lighter molecules of the Lander family and increase therefore the length limit of molecular wires employed in such kind of experiments.

4. Conclusions

In conclusion, we have presented here a low temperature STM investigation on VL deposited on Cu(111). The main novelty of such long molecular wire with respect to the previous generation of molecules of Lander type is the large variety of conformational changes which are present upon adsorption and which can be induced by manipulation. We have indeed shown the existence of at least five conformations at terraces and two at steps. When adsorbed at terraces, the molecule can reversibly change its conformation and/or move on the surface according to manipulation by the STM tip. These results give further insight into the characterisation of molecules of the Lander family, which might open new perspectives in the build up of specifically designed molecules for molecular electronics.

References