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Controlled manipulation of a single molecular wire along a copper atomic nanostructure

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Different stable conformations of a molecular wire along a short copper nanostructure are studied by means of low temperature scanning tunneling microscopy (STM) and controlled manipulations, with the aim of investigating the electronic contact of a single molecule to a metallic pad. The molecular wire is the so-called Lander molecule, a conjugated wire group supported by four legs. Independent of its position along the copper nanostructure, the central molecular wire is always in electronic interaction with the atomic wire underneath. This effect becomes visible in the STM images depending on the orientation of the legs. By STM manipulation, the molecular wire can be precisely positioned in an electronic contact conformation at the end of the atomic wire.

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I. INTRODUCTION

The continuing miniaturization of electronic devices is leading to an increasing interest in the application of single molecules in nanoelectronics.[1,2,3,4] Large organic molecules can now be designed to act as molecular wires,[5] molecular devices,[3] or intramolecular electronic circuits.[6] In order to work at a single molecule level, an operating molecular device requires an ultraclean and atomically well ordered environment. When adsorbed on a surface, the conformation of the molecule must be determined precisely. Its electronic interactions with the contact pads have to be investigated with atomic precision to avoid the random behavior of the devices observed recently.[7] In this context, low temperature scanning tunneling microscopy (LT-STM) is a fundamental technique to study different molecular conformations and to manipulate[8,9,10,11] single molecules, bringing them in electronic interaction with atomically ordered nanoelectrodes.[12] In the last years, various organic molecules have been imaged and manipulated on metal surfaces by LT-STM.[13,14]

The Lander molecule series[15] was designed to have a central conjugated polyaromatic molecular wire separated from a metallic surface by four lateral 3,5-di-*tert*-butyl-phenyl groups [Fig. 1(a)]. This allows to manipulate the molecule with the tip of a LT-STM and to decouple the wire part of the Lander from the metallic surface. More important, the height of the molecular wire on the surface is about 0.4 nm,[16] and is therefore well suited to interact electronically with a metallic pad that is one or two atomic layers high. In a recent work, the first member of the Lander series, the so-called single Lander molecule ($C_{90}H_{98}$), has been reversibly contacted to a monoatomic step edge of a Cu(111) surface by LT-STM manipulation.[12] The possibility of bridging a spatial gap between two chains of gold atoms with a single organic molecule and the such created electronic contact between the molecule and the metal atoms have been studied lately.[17]

Another interesting property of this single Lander is its ability to stabilize a short Cu atomic wire of toothlike shape at the edge of a Cu(110) atomic step.[18,19] The capability of the Lander molecule to reconstruct areas on the substrate has also been observed on the Cu(211) surface.[20] In the present case on Cu(110), the molecule acts as a template, fitting exactly the width of a double Cu atomic row on the Cu(110) surface. At low temperatures, this short Cu wire acts as a sliding ‘‘rail’’ for the Lander molecule. By moving the molecule precisely to the end of such a nanostructure, we can obtain a model geometry where one end of the central molecular wire is electronically connected to the metallic atomic wire. This represents a further step towards a complete atomically ordered interconnection between a molecular wire and a metallic pad. Furthermore, the molecule is self-fabricating its contacting pad. In this work, we present a detailed study of lateral manipulation of the Lander molecule along an atomic wire on Cu(110) performed with the STM tip. Molecular motion along the copper double rows is investigated by ‘‘snapshots’’ of intermediate positions. Rotation of the legs without any translation of the central board and lateral motion of the whole molecule can be independently induced by the STM tip. Moreover, the electronic interaction between the central wire and the copper nanostructure is investigated, in particular when the Lander is in a wire-end contact conformation.

II. EXPERIMENT

Experiments were performed in an ultra-high-vacuum chamber with a base pressure of 10^{-10} mbar equipped with low temperature STM, described in detail elsewhere.[21] The bare Cu(110) sample was cleaned by repeated cycles of Ne ion sputtering and annealing at 770 K. Small amounts of Lander molecules (≈ 0.01 monolayers as determined by STM) were deposited with a rate of about 1000 min/ML onto the substrate, kept at room temperature. The temperature of the evaporator, a home-built Knudsen cell, was about 620 K and controlled by a thermocouple. Subsequently, the sample was annealed to 370 K in order to enable the formation of Cu atomic wires by the molecules. All STM images were taken in the constant-current mode at temperatures between 7 and 8 K, at a bias voltage between 1.0 and 1.5 V with respect to the tip and with a tunneling current between 0.2 and 0.5 nA. No significant changes have been observed in the STM images by varying these two parameters. The manipulation ex-

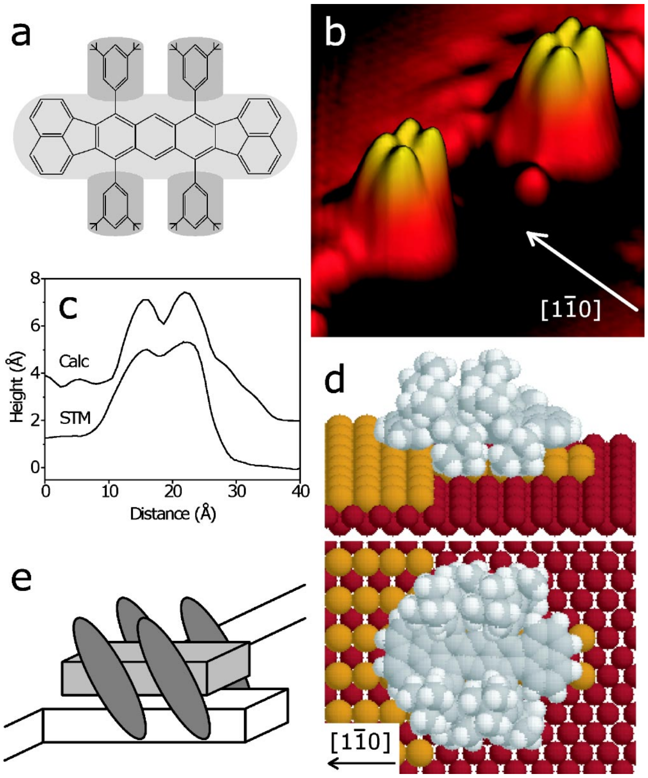

FIG. 1. (Color online) (a) Chemical structure of the Lander molecule with the polyaromatic board indicated in light gray and the four butyl-phenyl groups ("legs") in dark gray. (b) Three dimensional view of an experimental STM image of two Lander molecules adsorbed at a Cu(110) step edge. (c) Calculated (Calc) and experimental (STM) height profiles in the [$1\bar{1}0$] direction across a pair of "legs." (Calc) is shifted upwards by 2 Å for a better visibility. (d) Molecular model of the adsorption conformation after performing a complete conformation refinement by comparing experimental and calculated images scan by scan. (e) Schematic model of the adsorption conformation.

periments were performed either in constant-current[9] or in constant-height mode[22] using tunneling resistances between 50 and 200 kΩ.

III. CONFORMATION OF THE MOLECULE ALONG THE COPPER ATOMIC WIRE

The formation of a Cu tooth on the Cu(110) surface induced by Lander molecules has been reported recently.[18,19] In the present study we investigate the different conformations of the Lander on the rearranged atomic double rows in detail. Figure 1(b) shows a STM image of two Lander molecules adsorbed at a step edge in the most frequently observed conformation.

The conformation of the adsorbed molecules is obtained by a combination of the elastic-scattering quantum chemistry (ESQC) STM image calculation technique[23] with a molecular mechanics optimization of the geometry of the molecule on the substrate. The characteristic appearance of the Lander molecule in STM images consists of four lobes, accounting for the legs, while the central wire appears in a first analysis not visible as it is elevated from the substrate by the legs.[12,16,19] As presented in Fig. 1(b) and in the height profiles (c), the two lobes close to the step edge appear slightly lower than the other two. Their apparent heights are 4.2 ±0.2 and 4.5±0.2 Å, respectively, as determined from a large number of STM images. Note that these values are smaller than the real heights of the molecular legs, which are about 11 Å as obtained from calculations. This conformation has been reproduced theoretically and corresponds to the lowest energy conformation[18] of the molecule. The central molecular wire is perpendicular to the Cu(110) step edge and all four legs are rotated in the direction of the upper terrace [so-called parallel conformation, schematically shown in Fig. 1(d)]. It is important to note that two legs appear higher because they partially overlap the neighbor legs, thus producing an increased tunneling current. The distance between the two lobes on one side of the board is 6.4±0.2 Å and their distance across the board is 8.2±0.2 Å, in good agreement with previous investigations.[18] All four legs appear higher on the Cu wire than on the terrace (where they measure 3.2±0.2 and 4.0±0.2 Å, respectively), because on the nanostructure the distortion of the σ-bonds attaching the legs to the central molecular wire is smaller than on a free terrace.

IV. CONFORMATIONAL CHANGES INDUCED BY LATERAL MANIPULATION

In order to control the conformational changes of the Lander on the copper atomic wire, we have performed lateral manipulation with the STM tip. When the tip is moved just a short path across the molecule at a tunnel resistance of about 100 kΩ, only the orientation of the legs changes. This kind of manipulation is similar to the one performed on single Porphyrin-based Cu-TBPP molecules on Cu(211), realizing the principle of a conformational molecular switch.[24] As will be discussed in Sec. V, a lateral displacement of the entire molecule along the tooth can be obtained for a longer path and a lower tunnel resistance, up to a total removal of the molecule from the tooth.[18,19]

The possibility to switch between different leg orientations by STM manipulation is of fundamental importance in the present experiment, because, as we will see in the following, only some legs orientations allow the imaging of the interaction between a molecular wire end and the Cu atomic nanostructure.

The results of a series of STM leg manipulations with no displacement of the central wire are presented in Fig. 2. The changes in the orientation of the butyl-phenyl groups from Fig. 2(a) to Fig. 2(c) are clearly visible. This gentle manipulation permits to explore the two possible crossed-legs conformations [Figs. 2(a) and 2(c)] and the parallel legs conformation [Fig. 2(b)] of this molecule. The molecular model of each conformation is shown for comparison. Note that the present parallel legs conformation is different from the initial position in Fig. 1(b): The legs are now rotated towards the lower terrace and the two lobes close to the step edge appear higher than the other two.

For a better understanding of the leg-induced conformational changes, the apparent lateral displacements of the

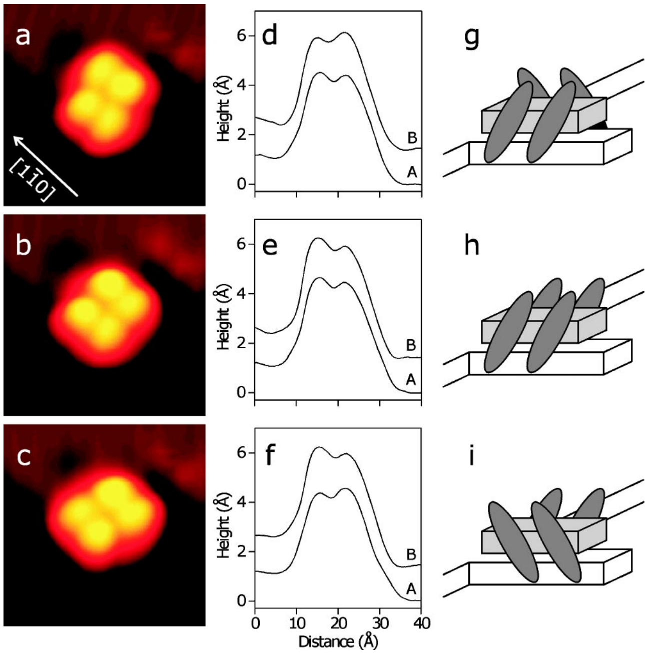

FIG. 2. (Color online) Manipulation series of a Lander molecule adsorbed on a wire. (a)–(c) STM images (45×45 Å^2) of different conformations. The corresponding line scans across the legs in the $[1\bar{1}0]$ direction are plotted in (d)–(f) (line scans *A* across the ‘‘lower’’ pairs of legs and *B*, shifted vertically by 1.5 Å for clarity, across the ‘‘upper’’ ones in the STM images). (g)–(i) show schematic models of the molecular conformations obtained after a conformation refinement.

single lobes during a full series of seven successive leg manipulations are plotted in Fig. 3. These lateral displacements are measured from STM images parallel to the central wire after selecting on the surface two fixed reference points [see the scheme in Fig. 3(b)]. The position of the legs in Fig. 2(b) serves as a reference and corresponds to the central conformation IV. The curve is nearly periodic: in the even steps all distances are close to zero while in the odd steps two distances increase to about 2 Å and the other two remain fixed. The molecule flaps reversibly back and forth between the parallel conformation of Fig. 2(b) and one of the two crossed legs conformations [Figs. 2(a) and 2(c)]. It is important to note that the position of two legs and therefore of the central board is always constant during these conformational changes, showing that the tip induces only a simple rotation of the legs without any translation of the whole molecule. Due to the strong steric coupling between the butyl-phenyl groups on the same side of the central wire, it is not possible to induce the rotation of one leg alone, as it was done for example with a Cu-TBPP molecule.[24]

V. STM MANIPULATION ALONG THE Cu ATOMIC WIRE

To move a Lander at the end of its Cu atomic wire, the whole molecule is manipulated along the copper atomic wire with the STM tip. In this case, the height of the tip above the surface is decreased during the manipulation and we work at a tunneling resistance of about 50 kΩ. The molecule maintains its original board orientation during the whole manipulation process until the end of the wire. Upon a lateral manipulation of the Lander molecule, the smallest manipulation length is found to be (4.5 Å ± 0.5) Å. According to the discussion in Sec. III this length reflects a combination of two effects: A rotation of the legs during the manipulation accounting for an apparent 2.1 Å shift of the molecule (see Fig. 3) and the size of the surface copper lattice constant imposing a minimum translation distance of 2.5 Å for the full molecule.

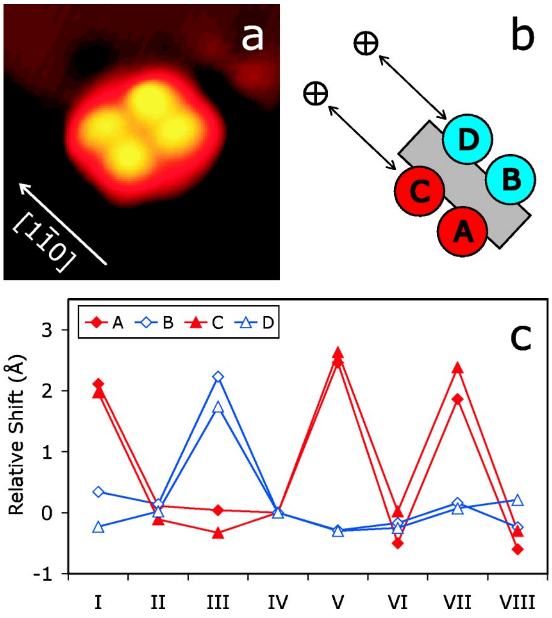

FIG. 3. (Color online) Lateral shift of the four lobes of the Lander molecule during a manipulation series. (a) STM image of the initial position (45×45 Å^2). (b) Schematic view of the Lander molecule—where *A*–*D* denote the four lobes—and two reference points (crossed circles) on the surface, to which the distance from the legs is measured. The position of the legs is determined from linescans across the legs in $[1\bar{1}0]$ direction, i.e., parallel to the two arrows. (c) Relative shift of the molecular legs *A*–*D* during the series where the roman numbers on the *x* axis denote the different steps [I reflects the initial position shown in (a), and III, IV, and V correspond to the images in Figs. 2(a), 2(b), and 2(c) respectively].

The potential energy of the molecule along the copper nanostructure is calculated starting with a molecule positioned on a terrace, away from the Cu(110) step edge. A molecular mechanics program (MM2) is used, minimizing the conformation of the molecule every 0.1 Å while moving in the $[\bar{1}10]$ direction, i.e., towards the lower terrace. A generalized potential is included in MM2 for the molecule-surface atom interactions. Since a Lander molecule can be considered physisorbed on the surface, this calculation method comprehends the most important features of the mechanical behavior of the molecule when manipulated along its Cu wire. Three characteristic regions are obtained in the curves in Fig. 4. On the upper terrace, the diffusion barrier is less than 5 kcal/mol (0.25 eV), which enables STM manipulation at low temperature. The same diffusion barrier is obtained for the molecule on the lower terrace. Between those two flat potential energy regions, the central potential

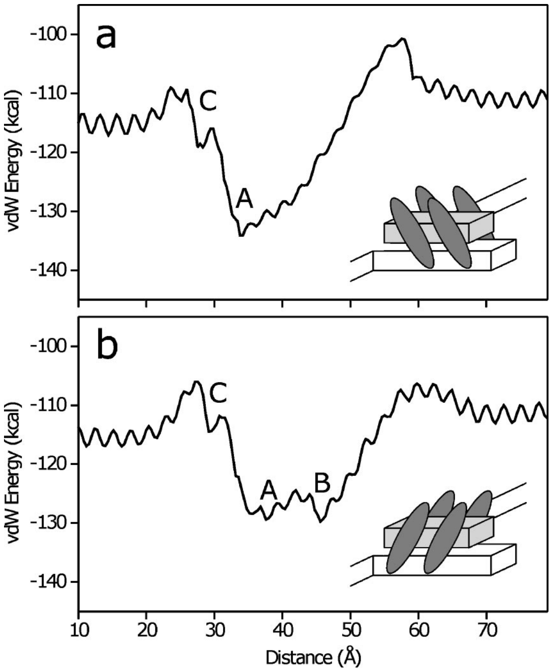

FIG. 4. Calculated potential energy of the Lander molecule on the Cu nanostructure plotted as a function of the lateral position along the $[1\overline{1}0]$ direction from a chosen point on the upper terrace (the Lander molecule is on the upper terrace for small and on the lower terrace for large distance values). The insets show schematically the fixed molecular conformations of (a) (all legs are rotated towards the upper terrace) and (b) (legs are rotated towards the lower terrace). *A*, *B*, and *C* indicate minima of interest in the curves (see the text).

well presented in Fig. 4 corresponds to the stabilization of the molecule-Cu atomic wire system on the Cu(110) surface. The width of this well depends on the tooth length. Its average depth is around 20 kcal/mol independent of the wire length. Notice that the Lander molecule can fabricate short and long atomic wires even though different lengths did not lead to observable effects on the manipulation process.

In Fig. 4, an energy potential modulation is visible inside the well corresponding to the copper surface lattice constant of 2.5 Å. Additionally, there are three more pronounced minima *A*, *B*, and *C* and a significant potential barrier. From the top terrace towards the atomic wire, this barrier is due to a different torsion angle of the legs of the molecule located on the Cu wire compared to the flat terrace. As demonstrated recently,[18] the legs are more vertical on the Cu wire compared to adsorption on a flat terrace. As a consequence, it costs at least 10 kcal/mol for the molecule to pass from this distorted conformation to the one on the copper atomic wire. Among the three minima, *A* corresponds to the stable conformation of the molecule on the Cu wire when docked at the step edge. The lowest energy is reached with the molecular legs rotated towards the upper terrace [Fig. 4(a)], which explains why this is the most frequently found conformation [see Fig. 1(b)]. At the end of the Cu wire, another stable conformation *B* corresponds to two legs almost away from the Cu wire and the other two still maintaining the central board on the Cu wire. Notice that there is no minimum *B* present in Fig. 4(a), indicating that in the stable position at the end of the nanostructure the legs of the molecule are rotated towards the lower terrace. Minimum *C* reflects a conformation where two legs are on the upper and two on the lower terrace.

To confirm the calculated potential energy curve experimentally, STM images of the Lander molecule were taken at each manipulation step. Three different positions, shown in Figs. 5(d)–5(f), are observed before the molecule is pushed away from the tooth. The first position in Fig. 5(d) is the initial one, already discussed in Fig. 1. Contrary to the ‘‘typical’’ configuration in which the vast majority of molecules adsorb in a parallel conformation, the imaged Lander molecule is here in an anti-parallel conformation. This is reflected by the rhombic shape, i.e., the legs on opposite sides of the central board are crossed. Only about 10% of the Lander molecules adsorb directly in this conformation, which can also be achieved artificially by lateral manipulation (see Sec. IV). To point out the different molecular positions, a rectangle of the two atoms wide copper wire underneath, reproducing the average dimensions (8.0±0.2 Å wide and 17.7±0.4 Å long), is drawn in the STM images of Figs. 5(d)–5(f). Note that the height of this copper wire is that of the upper terrace. In a few cases (about 3%), the copper wire is even longer than the molecule as already mentioned above. In Fig. 5(f) the molecule has reached the end of the wire, which corresponds to position *B* in Fig. 4(b). This conformation is shown enlarged in Fig. 5(g), in good agreement with the calculated image in Fig. 5(h): The two lobes near to the Cu wire appear much brighter in the STM image than the other ones, showing that the molecule is tilted with respect to the flat conformations on the nanostructure or on the terrace. Any further tip-induced shift results in a complete removal from the nanostructure leaving the molecule on the lower terrace. The intermediate stable position in this series corre-

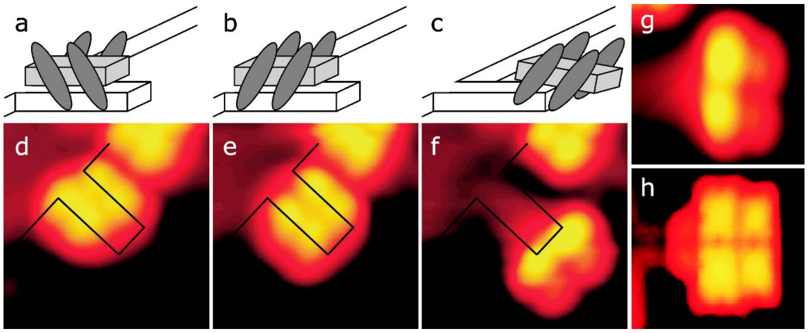

FIG. 5. (Color online) (a)–(c) Schematic models and (d)–(f) corresponding STM images (45×45 Å^2) during the lateral manipulation along a tooth. The black lines mark the step edge and the position of the Cu nanostructure underneath the Lander molecule as determined from a STM image after the removal of the molecule. (g) STM image of the final position with a tilted molecular board and (h) corresponding calculated image (both 25×23 Å^2).

sponds to the conformation in Fig. 2(b) where the legs are rotated towards the lower terrace and a lateral shift has occurred.

In order to determine the exact position of the Lander molecule along its Cu wire, experiment and calculations are compared by means of linescans across the molecule. The resulting curves are plotted in Fig. 7 for the three stable positions, showing a very good agreement. The differences between calculated and experimental line scans are mainly due to the very pointed tip in the calculations, permitting a better access to the molecule. According to the calculations, the central polyaromatic board is tilted when manipulated at the end of the Cu wire. As one can see from the comparison of the linescans across the legs, the difference in height between the two legs is larger for the tilted molecule than for those exhibiting a flat central wire, as already supposed in Fig. 5(g). This tilt, induced by the attractive van der Waals interaction between the polyaromatic board and the substrate, causes a slight lifting of the upper end of the board [see Fig. 5(c)].

VI. ELECTRONIC INTERACTION BETWEEN THE LANDER WIRE AND THE ATOMIC Cu WIRE

When adsorbed on a Cu(100) or Cu(110) terrace, the central wire of the Lander molecule series does not seem to contribute to the STM image. The central board is far away from the surface and its electronic coupling with the metal surface is too weak to be detected even by a sub-pA sensitive STM preamplifier. When adsorbed on a Cu atomic wire, the central board is in a good position to interact more strongly with the electronic surface state of the Cu wire underneath. To investigate this effect, constant-current scans were calculated along the central board using the STM-ESQC technique. At first, considering the complete molecule and the different leg orientations, then taking into account only the central wire without the legs. Notice that when the legs are suppressed for the calculation, they are simply substituted by four hydrogen atoms to saturate the corresponding σ bond. However, the altitude and conformation of the central board is kept unchanged.

By comparing curves *A* and *B* in Figs. 6(c) and 6(d), 2.2 Å of the contrast is accounting for the legs and 0.8 Å for the central wire which interacts with the copper wire underneath. Furthermore, the large contribution of the legs to the tunneling current overshadows the central board contrast, which appears in the line scan only as a very small shoulder at the end of the Lander molecule. To observe this small contribution at a given end of the molecular wire, one should choose a conformation of the molecule where the legs contribute as less as possible to the STM tunneling current. This means that the legs have to be oriented to the opposite end of the central wire in order to enable the tip access to this molecular wire end.

The dependence of the relative height of this shoulder on the legs conformation is presented in the scans across the Lander legs (*C*) in Figs. 6(c) and 6(d). These scans were calculated with the molecule in the most stable position (*A* in Fig.4) along the Cu wire. In both cases, the shoulder fits nicely to the contribution of the molecular wire alone. However, the shoulder becomes more intense in the height profiles along the whole wire if the Lander molecule is in a position *B* at the end of the copper wire [*B* in Fig. 4(b)]. In this case the board is not in a planar, but in a tilted conformation with respect to the wire underneath [see Figs. 7(f) and 7(i) below].

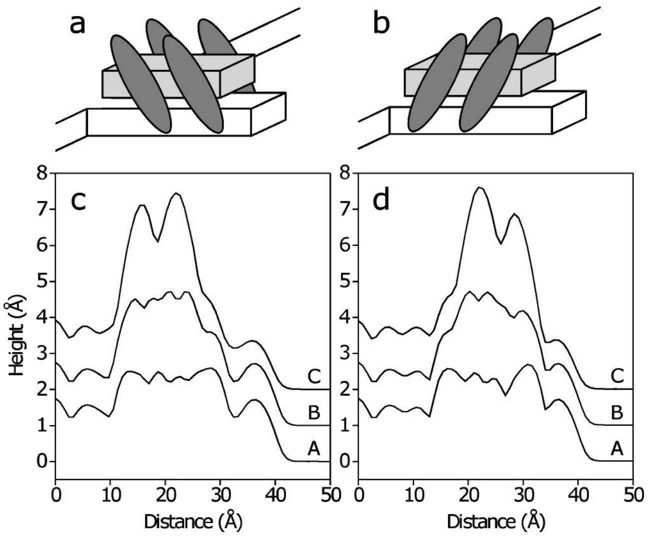

FIG. 6. Comparison of two conformations with the legs rotated towards the upper [(a) and (c)] and lower [(b) and (d)] terraces. Schematic models are presented in (a) and (b) while (c) and (d) show the corresponding calculated linescans across the Lander molecule in the $[1\bar{1}0]$ direction. Line scans across the central board are plotted in *A* (using only the polyaromatic board without butylphenyl groups in the calculations) and *B* (using the entire Lander molecule) while *C* reflects the height profile across the legs. *B* and *C* are shifted upwards by 1 and 2 Å, respectively, for a better visibility.

Figure 7 shows a comparison of calculated and experimental height profiles across the Lander molecule. At the edge of the front legs, no net shoulder is observed in the STM experimental images when the Lander molecule is adsorbed in its initial position (see Fig. 1), with the legs oriented towards the step edge as presented in the left panel of Fig. 7. At the right end of the molecule, the slope of the scan in Fig. 7(g) is less abrupt than what can be expected from an equivalent scan taken on a Lander molecule deposited on a flat terrace. The absence of any shoulder can be attributed to a tip effect, obviously less perfect at the apex end than in the calculation. In this case, the tip apex has to face an abrupt change in corrugation at the end of the wire, so that the tip end facets become relevant in the apparent STM scan slope. After manipulating the legs in the opposite direction with the board at the same position (median panel), a very weak shoulder can be observed in the experimental STM linescans across the Lander molecule as predicted by the calculation.

The interaction shoulder becomes more evident if the molecule is manipulated towards the end of the copper wire [position *B* in Fig. 4(b)]. This is the case in the right panel of Fig. 7 with the legs oriented towards the lower terrace. Both linescans, across the central wire and across the legs, match

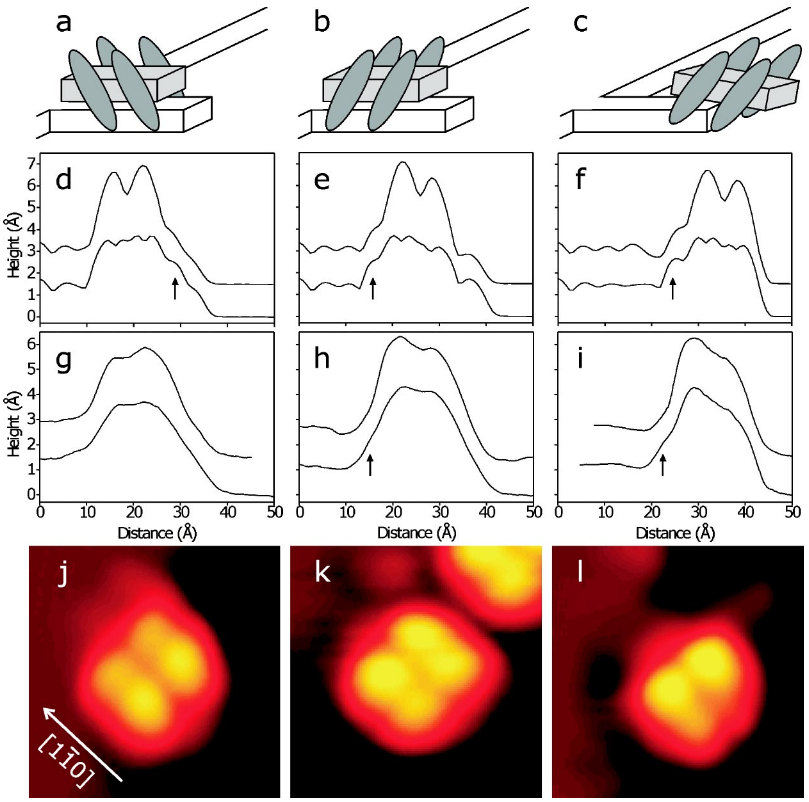

FIG. 7. (Color online) Comparison of calculated [(d)–(f)] and experimentally determined [(g)–(i)] linescans across the center (lower curves) and across a pair of legs (shifted upwards by 1.5 Å for clarity) of the Lander molecule in the initial (left panel), intermediate (median panel) and final position (right panel). The arrows indicate shoulders attributed to the central wire. Models of the molecular conformations are shown in (a)–(c) and the corresponding experimental STM images in (j)–(l) (40×40 Å^2).

the calculations very well. Such a good agreement confirms that an electronic interaction between the board and the metallic Cu atomic wire underneath takes place. A good choice of the leg orientation renders the central molecular wire of the Lander molecule visible in the STM images at the end of the molecule. This effect is not observed if the Lander molecule is adsorbed on a flat Cu terrace.

This latter conformation of the Lander molecule at the end of the copper wire is very similar to the one reached by STM manipulation at a monoatomic step edge on Cu(111).[12] In that case, one naphthalene end of the molecular wire was positioned to interact with the upper terrace of the Cu(111) step edge. A very small contact bump, characteristic for this interaction, was observed with an apparent relative height of about 20 pm. In the present case, a larger part of the central molecular wire interacts with the Cu atomic wire. The corresponding shoulder characterizes the electronic interaction of the naphthalene end group with the Cu atomic wire with an apparent relative height of about 80 pm, indicating a better electronic interaction with the atomic wire underneath than in the Cu(111) case. This interaction may be further improved by changing the chemical composition of the wire end while maintaining this peculiar cofacial interaction between the molecular π orbital of the central board and the metallic atomic wire.

VII. CONCLUSION

Controlled conformational changes have been induced with the STM tip to single Lander molecules adsorbed on a Cu atomic wire. By means of a gentle lateral manipulation process, just one pair of molecular legs can be rotated reversibly, keeping the central board fixed. Lateral displacements of the Lander molecule along the nanostructure have been separated into monoatomic steps and three different positions can be distinguished. Theoretical calculations confirm that the central wire is in contact with the metallic Cu atomic wire and that this electronic interaction can be observed in the STM image. It appears as a shoulder in the STM contrast when the legs are manipulated in a favorable conformation, so that the tip has access to the end naphthalene group of the central wire. The contact shoulder is clearly visible for the case of a Lander molecule positioned at the end of the Cu atomic wire. Moreover, weaker shoulders are visible in the STM images for intermediate positions.

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