

Scanning tunneling microscopy experiments on single molecular landers

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Molecular landers are molecules comprising of a central rigid molecular wire maintained above a metallic surface by organic spacers, which allows specific ultrahigh vacuum-scanning tunneling microscopy experiments to be performed at the single-molecule level. The understanding of the molecule–surface interactions, intramolecular mechanics, and the possibility to perform extremely precise tip-induced manipulation permit these molecules to be brought in contact with a nanoelectrode and the resulting electronic interaction to be analyzed in well controlled conditions.

contact | molecular wire | nanoelectrodes | single-molecule manipulation

A prerequisite to the use of single molecules as active devices in future molecular-scale electronics (1) is the description and understanding of the important parameters controlling the device properties such as: molecular conformation, substrate structure, molecule–substrate interactions, molecule–electrode electronic coupling, dynamics of the system, etc. For instance, the molecular conformation controls to a large extent the conductance properties. However, the geometry of a surface-adsorbed molecule is often significantly different from the calculated geometry in a vacuum. It is therefore essential to get an accurate description of the conformation of a molecule on the substrate and the intermolecular interactions to be able to design efficient molecular wires or switches. Similarly, it is now recognized that the molecule–electrode contact conductance is a key point in the electron transport process of an electrode–molecule–electrode junction. Consequently, it is vital to describe and understand in detail the molecule–electrode interactions at the atomic level, to learn how an electrode modifies the geometric and electronic properties of a molecule, but also how anchoring a molecule induces electrode modifications.

Most experiments that have been carried out so far in the field of molecular electronics rely on “blind experiments” on molecular electronic junctions (2) by using nanopores, break junctions, or vertical scanning tunneling microscopy (STM) techniques. These experiments do not provide the detailed information necessary for structure/property analysis nor can they rigorously prove transport mechanism for molecular electronic species (3).

Consider a few of the problems posed by the investigations on molecu-

lar electronic junctions in air and at room temperature.

First, working at the nanoscale invokes a severe requirement of ultraclean conditions. It should be remembered that only several nanograms of any organic material, solvent, or water is sufficient to cover a millimeter-scale substrate surface. This quantity is, by several orders of magnitude, smaller than numerous chemical impurities present in any “pure” organic chemical or solvent, or in any laboratory environment. Additionally, clean metal surfaces are excellent reactants prone to chemisorption. For instance, gold surfaces are covered by 10-nm-thick layers of water even in dry air, and analogous films are even present on hydrophobic surfaces like alkane self-assembled monolayers (SAMs) (4). Unfortunately, the presence of water layers in the junction is not passive, creating (water dissociates at low voltage) and transporting ionic currents, which are added, in any junction experiment, to the tunneling ones (5) in a nonlinear way. Reorientation of water molecules next to the positive electrode or electrochemical processes can also dominate junction properties. One popular solution to (partially) get rid of this contaminating layer is to perform a chemical substitution by another chemical, such as alkanethiol on gold surfaces. The active molecules are then grafted by substitution. The major drawback is then that the most reactive sites prone to substitution (pinholes, step edges) are the less controlled ones.

Other factors, which have not often been taken into account, arise from the dynamics of materials. At room temperature, metal surfaces, step edges, and tips are “fluid” at the nanoscale. For instance, the diffusion of empty sites is very rapid with a jump frequency of 10⁸

Hz (6) on a copper metallic surface so that the vacancies move too fast to be imaged by an inherently slow instrument such as the scanning tunneling microscope. Similarly, step edges fluctuate rapidly at room temperature by mass exchange with terraces and neighboring steps, reducing effective resolution of STM images (7). Things are probably even worse for tips and break junctions by using soft and ductile metals such as gold because of the small coordination number of the apex atoms. The migration of metal atoms in the junctions can have crucial influence on the I(V) data. For instance, it has been recently shown that the switching behavior in some metal/molecule/metal junctions could be attributed to the formation and dissolution of individual metallic filaments through the junction (8) and not to a molecular switching process (9). The growth mechanism of these whiskers, driven by increasing current density and/or electric field, could also involve electrochemical processes, thermal migrations, or electromigrations, and the influence of the organic layers on these metallic nanowires still largely have to be explored. Finally, the molecule can show conformational changes under electric field (5).

The dynamics of soft matter at room temperature is an even worse problem that has been rarely addressed. The first difficulty comes from molecule surface diffusion. The positive side of the mobility of organic molecules on surfaces at room temperature is that it allows the

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Abbreviations: LT, low temperature; SAM, self-assembled monolayer; STM, scanning tunneling microscopy.

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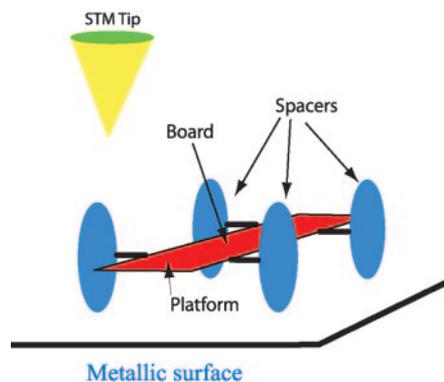


Fig. 1. Concept of molecular lander.

formation of well ordered SAMs, which are then stabilized by intermolecular Van der Waals interactions. The negative side is that this mobility is not completely blocked at room temperature, and that the application of a bias voltage to SAM/gold junctions can lead to potential-induced structure transitions (10). Furthermore, this mobility proceeds through a bond breaking-bond formation mechanism that is still active within the SAM. For instance, it has been recently proposed (11) that this mechanism could explain the random conductance switching observed in STM experiments on oligo(phenylene ethynylene) in alkanethiol SAMs, a result previously attributed (12) to changes in molecular conformation, molecular tilting, or electron delocalization.

All these considerations led us to focus on low-temperature experiments in ultraclean conditions. The only tech-

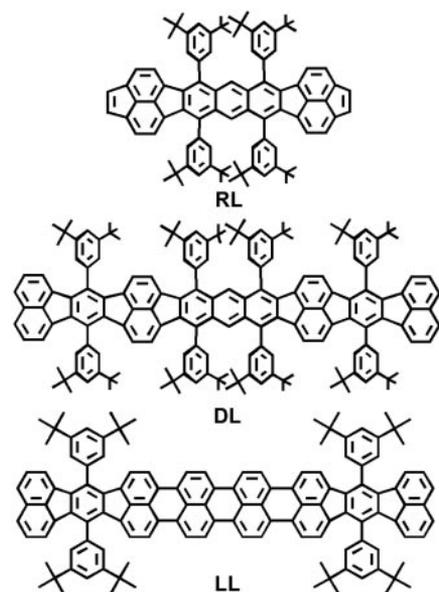


Fig. 2. Some examples of synthesized molecular landers. Shown here are a reactive lander (RL), a double lander (DL), and a long lander (LL).

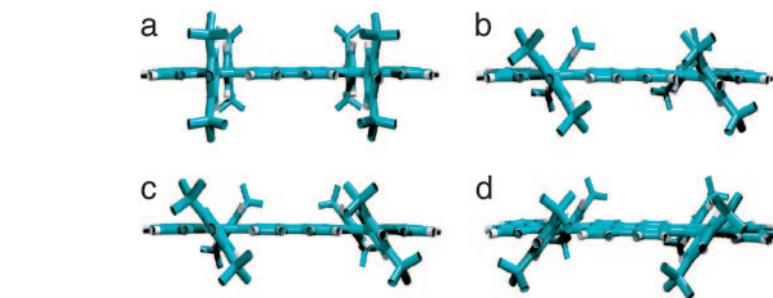


Fig. 3. Some conformations of a molecular lander. (a) Calculated in vacuum. (b–d) Observed on a copper surface.

nique currently allowing highly precise submolecular imaging of a single molecule with the possibility of manipulation and measurement of the electronic properties in perfectly clean and controlled conditions is ultra-high vacuum low temperature (LT) STM in planar geometry. The drawback of this technique is the necessity of using conducting substrates. Bare metallic surfaces act as Lewis acids and are prone to strong coupling with molecules, which would modify the device properties, reduce mobility at LT and, therefore, can prevent manipulation experiments.

Design

To overcome the described constraints, it is necessary to devise molecules (or molecular systems) specifically designed for each type of experiments. The minimum requirements are as follows: (i) a planar design, i.e., the active part of the molecular device must be parallel to the substrate to allow STM imaging; (ii) some rigidity to maintain the chemical architecture and reduce the number of possible conformations; (iii) electronic delocalization to maximize the conductance of the device; (iv) contacting groups at the end of the wire to allow conductance or contact measurements; and (v) an electronic decoupling of the “active part” of the device with respect to the metallic surface.

Our solution is to add molecular spacers maintaining the active part high enough from the surface atoms. This electronic decoupling gives some mobility, which allows STM manipulation even at LT. Moreover, the presence of bulky spacers isolates the molecules one from each other and avoids important intermolecular interactions (cross-talk in conductance experiments). Finally, it provides the solubility required for chemical synthesis and purification by reducing the intermolecular stacking forces in these rigid systems.

These considerations led us (13) to propose the concept of “molecular

lander” by analogy with “planetary lander” spacecrafts as shown on Fig. 1.

Molecules

Some of these landers, used for conductance (14) and contact measurements (see below), are shown in Fig. 2. They comprise either a central anthracene (RL and DL) core or a central oligo-*peri*-naphthalene (LL). Their total lengths range from 18 to 35 Å. The four or eight spacers here are di-*tert*-butylphenyl groups. These groups are at the same time bulky, lift the “board”-shaped polyaromatic conducting core, and are only weakly coupled to the surface, allowing single-molecule manipulations even at LT. These two factors reduce electronic leakage between the board and the metallic substrate in electron transport experiments through the molecular board. Finally, these groups are well known to increase the solubility of the molecule, allowing chemical processing and purifications.

Molecule–Substrate Interactions

The strong interaction between a large polyaromatic molecule and a surface has several critical consequences, so that the functionalities and conformations of the molecules in vacuum or in solution cannot be *a priori* assumed for a surface-adsorbed molecule (15). First, the interaction compresses the molecule on the surface, so that certain conformations not observed in a vacuum or a solution are stabilized. As an example, Fig. 3 shows some of the different stable conformers of a lander observed on different copper surfaces compared with the minimum energy conformer in vacuum (Fig. 3a).

More critically, the strong interaction between the aromatic board and the metal induces significant distortions, such as a bending of the board-spacer bonds (16) (Fig. 4) or a rippling of the polyaromatic board when the molecule is sitting astride a step edge (Fig. 5; ref. 17), deeply modifying the molecule conductance.

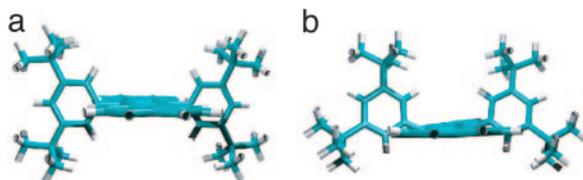


Fig. 4. View along the main axis. (a) View in a vacuum. (b) View on a metallic surface.

However, this molecule–surface interaction is not a “unidirectional” process. It has been recently shown that the substrates cannot be considered as static templates and that molecules can induce important surface restructuring like interfacial roughening, vacancy trapping, and molding.

The stabilization mechanism is as follows: to relax any significant distortions of the molecule and reduce the bond to metal distances, the molecule can block diffusing vacancies, create a well (Fig. 6a), or conversely trap diffusing atoms (Fig. 6b).

The first evidence of the anchoring of a molecule has been reported for hexa-*tert*-Butyl-decacyclene (HtBDC), associated with a trough in an underlying Cu(110) surface (18, 19). This HtBDC molecule has the lander attributes, i.e., a large rigid polyaromatic platform lifted by six *tert*-Butyl spacers. Vacancy trapping by molecular landers appears to be a general phenomenon (20), which is probably common to most molecular devices comprising unsaturated parts.

On the other hand, landers can also behave as molecular molds to stabilize metallic patterns on a substrate (21, 22) (Fig. 6b). Of course, the shape of the structures formed by this “molecular molding” is closely related to the shape of the mold, i.e., the aromatic part of the lander. It allows the fabrication at the atomic level of rails that can be used as perfectly defined electrodes for stud-

ies of the molecule–metal contacts (*vide infra*).

Specific information about the interaction between the board of a lander-type molecule and the metallic substrate has been obtained on Cu(111) by studying the standing wave patterns produced by the surface-state electrons when scattered by the molecules (23). The experiment demonstrates that the central molecular wire, although decoupled from the surface by spacer groups and not visible in STM topographic images, is mainly responsible for the scattering of surface-state electrons. By comparing three different, suitably modified lander-type molecules, the dominant role of the aromatic π -system in molecule–substrate interaction is revealed. The analysis of electronic standing wave patterns produced by molecules on metallic surfaces forms a promising method to characterize, with submolecular resolution, the electronic interaction of a complex molecule with a metallic surface.

In summary, the molecule–substrate (or electrode) interaction is a dual process that not only significantly perturbs the molecule, and therefore its electronic properties, but also may have an important impact on the substrate and, for instance, severely modify the molecule–electrode junctions. It is therefore vital that the design of future molecular systems takes into account these points to obtain the most efficient devices.

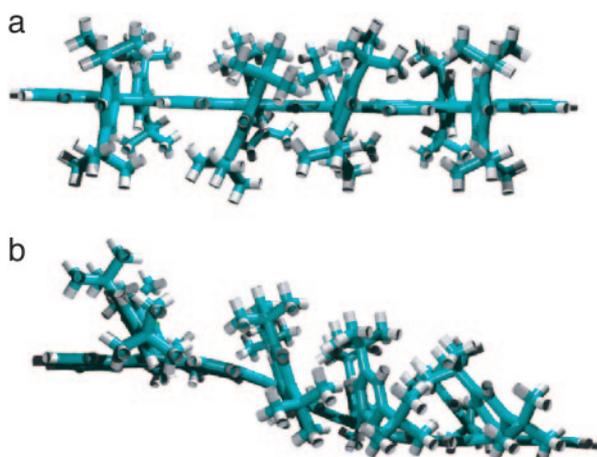


Fig. 5. Side view of a double lander. (a) View in a vacuum. (b) View astride a step edge (2 ml Co/Cu).

STM-Induced Manipulation

At LT, the tip of an STM can be used to move atoms and molecules on a surface and to position them with atomic precision (24). These methods were first applied by the group of Eigler and colleagues (25, 26), and then by the group at the Freie Universität Berlin (27, 28). Two basic techniques can be used to manipulate single atoms and small molecules: the lateral manipulation method, where single particles are moved on a surface without losing contact with it, and the vertical manipulation method, which involves picking up a particle and depositing it at the desired location. Lateral manipulation allows the positioning of adsorbates with great precision and is often used to build nanostructures starting from single adsorbed particles (29). Moreover, by lateral manipulation, it is possible to record in real time the tunneling signal during the manipulation process. Analysis of such manipulation signals allows better understanding of the details of particle movement and adsorbate–tip interactions. In case of manipulation of single atoms or small molecules, it is possible to distinguish between three manipulation types and understand if a particle is pushed, pulled, or slid by the tip along the surface (30).

Recently, lateral manipulation of single atoms or small molecules was applied to the investigation of more complex problems. Nilius *et al.* (31) have used lateral manipulation to study the development of the one-dimensional band structure in gold chains on a NiAl(110) surface. Heinrich *et al.* (32) have shown how CO molecules can be arranged by lateral manipulation to form “molecular cascades,” where the motion of one molecule causes the consequent motion of the another. Moreover, the combined application of different manipulation techniques has shown the possibility of selectively inducing the steps of a complex chemical reaction with the STM tip. For example, the synthesis of single biphenyl molecule from two iodobenzene (Ullmann reaction) has been induced on a Cu(111) substrate by using the STM tip (33).

Intramolecular Mechanics of a Molecule.

Presently, the interest of research is focusing on the manipulation and the controlled position of large organic molecules with the aim of studying deformations or conformational changes. The ability of LT STM to perform controlled manipulation has been extended to complex molecules and the mechanisms of manipulation investigated in detail. In the case of a large molecule,

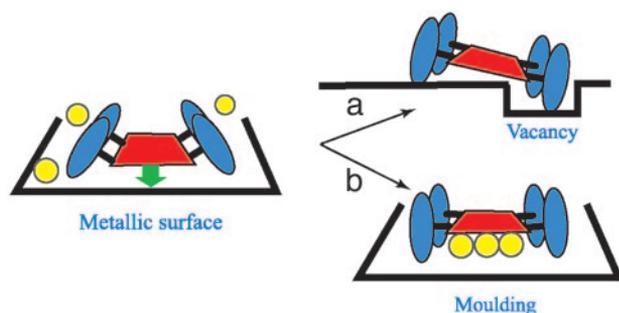


Fig. 6. Relaxation mechanism of a molecular lander. The constraint can be reduced by creation of a vacancy (a) or a metallic nanowire (b).

the analysis of the tunneling signal recorded during a manipulation permits real-time analysis of the molecular deformations induced by the tip apex and the surface atomic corrugation.

Cu-tetra-3,5-di-*tert*-butylphenylporphyrin was the first example of a single intact molecule to be precisely positioned by means of manipulation with the STM tip at room temperature (34). Such controlled positioning was possible because of the specific molecular design, where the lateral groups permit a sufficiently strong surface molecular interaction to prevent thermally activated diffusion and, on the other hand, to decouple the core of the molecule from the substrate, allowing its controlled translation.

By working at LT, we have applied the technique of lateral manipulation at

constant height (35) to investigate the internal mechanics of a Cu-tetra-3,5-di-*tert*-butylphenylporphyrin molecule moving on a Cu(100) surface, inducing motion and deformation of the molecule with the STM tip and monitoring it in real time (36). An example of a manipulation curve recorded during this manipulation experiment is presented in Fig. 7a.

The sequence reflects, first of all, the Cu(100) lattice periodicity. However, details in each period do not simply show a regular sawtooth signal but contains an intraperiodic signature, specific to this type of manipulation. Details of the intramolecular mechanics occurring during the manipulation sequence can be extracted by electron scattering quantum chemistry and molecular mechanics calculations. We found that the main contribution to the signal comes from the movement of the molecular group directly interacting with the tip apex. However, a contribution from lateral groups not directly in contact with the tip can be extracted. The recorded movements are however very small, showing, on one side, the high resolution reached by such experiments and, on the other side, opening the quest for new molecules where larger internal movements and deformations are possible.

Similar to TBPP, the lander presents internal degrees of freedom and shows different conformations. It is therefore possible to investigate its internal movements starting from the manipulation curves. An example of a manipulation curve recorded for a lander moving on the stepped Cu(211) surface is shown in Fig. 7b. The curve has a quite regular sawtooth form. However, it can be shown that it contains information on the mechanical movements of parts of the molecule that are not directly in interaction with the tip apex during the manipulation sequence (37). This finding is due to the fact that the intramolecular deformation induced by the tip can open other tunneling paths, which are not directly located on the part of

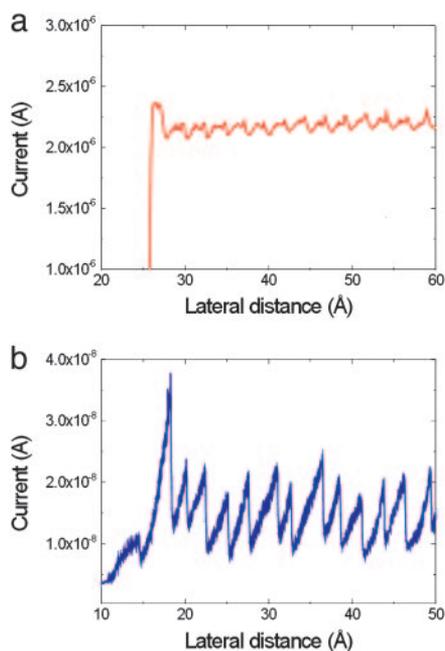


Fig. 7. Manipulation curves at constant height giving the tunnel current in function of the lateral distance. Experiment for tetra-3,5-di-*tert*-butylphenylporphyrin (a) and a lander (b).

the molecule in close contact with the tip apex. Specifically, the manipulation signal is sensitive to the movements of the central board of the molecule, even if the tip pushes the legs. The mechanical deformations of the central board, which cannot be imaged by STM in standard conditions, dominate the manipulation signal.

Conformational changes can also be induced in a complex molecule by manipulation without moving the molecule on the surface. An example is the principle of a conformational molecular switch realized by manipulating a tetra-3,5-di-*tert*-butylphenylporphyrin molecule on a Cu(211) surface (38). To demonstrate the principle of such a switch, we have quantitatively investigated the interaction between the tip apex and a lateral group of the molecule during a vertical manipulation sequence. In particular, we have measured the current passing through this rotating group in real time during its conformational change, demonstrating that the tunneling current strongly depends on the extent of the rotation.

The switching energy required to operate such a molecular switch has been measured by using a noncontact atomic force microscope (39), showing that such rotation of the leg requires an energy of $<100 \times 10^{-21}$ J, which is four orders of magnitude lower than state-of-the-art field effect transistors.

Contacting a Molecular Wire to a Metallic Nanoelectrode. The characterization of the electronic contact between a molecular unit and a metallic electrode is one of the central problems for the development of molecular electronics. An electronic contact is unambiguously defined when the edges of the electrodes are atomically ordered and clean and when the geometry and conformation of the contacted molecule is under control at the atomic scale.

To investigate the contact between a molecular wire and a metallic electrode, we have contacted the wire part of a lander to a step edge of Cu(111) (39). A stable and extremely clean mono-atomic step (0.21 nm in height) was obtained by a controlled crash of the tip into the surface. To bring the molecular wire in contact with the step, a lander lying on a terrace was laterally manipulated by the STM tip in constant height mode.

The lander was manipulated to contact its board to the step edge, as schematically shown in Fig. 8a. After the contacting, an increased tunneling signal corresponding to the contact position can be observed. The STM-electron scattering quantum chemistry extraction of the molecular conformation from the

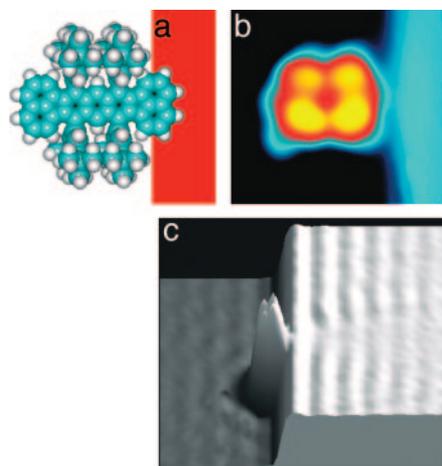


Fig. 8. Contacting a lander to a step edge. (a) Schematic view of the experiment. The naphthalene end contacting the nanoelectrodes is in red. (b) Experimental STM image. (c) Standing wave patterns.

experimental image confirms that the terminal naphthalene group of the wire is on top of the step edge and electronically coupled to the upper terrace. As a consequence, this naphthalene end group is now visible in the STM image of the step edge (Fig. 8*b*).

The apparent height of the contact position in the STM images is related to the electronic interaction between the naphthalene end group of the molecule and the copper atoms of the upper terrace and also depends on the geometry of the system. It varies as a function of both lateral distance between the naphthalene end group and the step edge and vertical distance between this end and the upper terrace. At the experimental contact position, a calculated value of the contact bump of 13 pm (in agreement with an experimental value of ≈ 15 pm) is obtained.

Another way to characterize the contact of the molecular wire end with the Cu(111) step edge is to investigate its effect on the standing wave patterns formed by the surface-state electrons when scattered by adsorbates and steps. When a Lander is contacted with its board perpendicular to the step edge, a striking modification of the parallel standing-wave patterns due to the step is observed on the upper terrace (Fig. 8*c*). Compared with the clean step edge case, the amplitude of the wave is reduced at the naphthalene contact location. This effect extends a few tens of nanometers away from the contact in a characteristic triangular shape. To reproduce the pattern caused by the contacted lander, we used the scattering formalism of Heller *et al.* (40). A simple arrangement of scatterers was used to

model the contact and confirms that the observed perturbation of the standing wave patterns on the upper terrace is caused by the naphthalene end group of the molecular wire. The good agreement between the STM experimental and numerical simulation shows that the molecular π -orbitals of the wire interact with the upper terrace surface state by coupling through the naphthalene end.

The possibility of contacting the molecular wire part of a lander to a metallic nanowire, fitting exactly the dimensions of the molecule, comes from the ability of the lander to behave like molecular molds stabilizing metallic patterns on the substrate described in ref. 21. This ability can be used to investigate the electronic contact between the molecular wire part and the metallic nanowire (41), as schematically shown in Fig. 9*a*.

On Cu(110), the molecule restructures the substrate forming a two-atom-wide nanowire under the molecular wire board. In this case, the central board is in a good position to interact with the metallic copper wire underneath. To observe the small contribution to the tunneling signal due to the contacting board, one should choose a conformation of the molecule where the legs contribute as little as possible to the STM tunneling current. This requirement means that the legs have to be oriented to the opposite end of the central wire to enable the tip access to this molecular wire end.

This conformation has been obtained by moving a lander step by step to the end of its molded copper rail by manip-

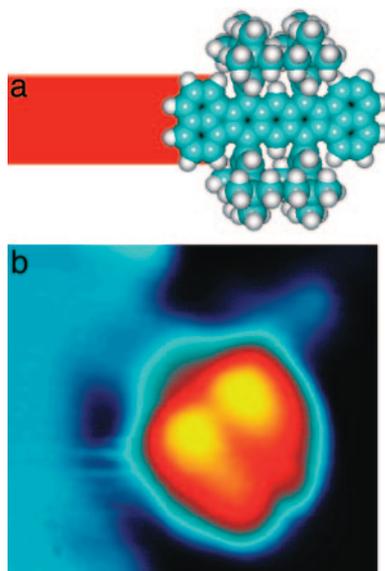


Fig. 9. Contacting a lander to a self-fabricated nanoelectrode. (a) Schematic view of the experiment with the naphthalene end contacting the nanoelectrode in red. (b) Experimental STM image.

ulating the whole molecule to the end of the metallic nanowire with the STM tip. STM images of the lander have been taken at each manipulation step. When the molecule reaches the end of the wire (Fig. 9*b*), the contact position becomes visible in the STM image. In this case, the legs have a favorable conformation, so that the tip has access to the end naphthalene group of the central wire. The contacted end group of the molecular wire is clearly visible and has an apparent relative height of ≈ 20 pm. Moreover, weaker shoulders are visible in the STM images for intermediate positions. Electron scattering quantum chemistry calculations confirm that an electronic interaction between the board and the metallic Cu atomic wire underneath takes place, making the central molecular wire of the lander visible in the STM images.

The reported contact experiments demonstrate that LT STM is a fundamental experimental technique to bring a molecule in contact with a metallic nanoelectrode and to characterize the electronic contact by means of the increased tunneling signal at the contact position. Moreover, on surfaces like Cu(111), the analysis of the standing wave patterns of the surface-state electrons allow further information about the geometry of the contact itself to be deduced.

Perspectives

Although these recent results have given a better understanding of the behavior of molecular devices and their electronic and mechanical properties, the next step toward making molecular devices really usable for molecular electronics will require passing from molecules on metals to molecules on insulators or insulating layers. Although the atomic force resolution imaging and site-specific quantitative force measurement on a single-walled carbon nanotube have been reported (42), submolecular imaging and manipulation of softer molecular devices will probably still remain a challenge for several years (43).

Fortunately, the recent improvements of LT STM allow imaging and manipulation with very small tunnel currents, i.e., at large metallic substrate/tip distances. It opens the way to experiments on molecules on thin films of insulators, such as a few monolayers of alumina on NiAl (44) or sodium chloride on Cu (45). In this geometry, the insulating films maintain the molecule several angstroms from the metal (acting as spacers) so that the molecule/metal electronic coupling is rather small. These substrates permit fuller exploitation of the STM capabili-

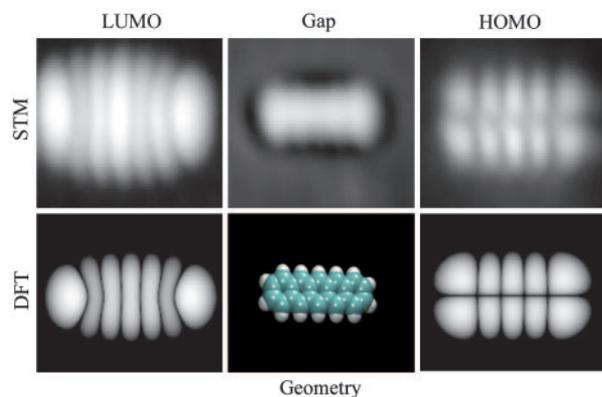


Fig. 10. Calculated and experimental images of pentacene/2 ml NaCl/Cu(111). (Upper) Experimental images. (Lower) Orbital contours of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO).

ties: imaging, manipulation, and spectroscopy. This experimental setup has been recently used to investigate the photochemical properties of a single

porphyrin (44) or the redox states of a single gold atom (45). For example, in the case of pentacene on ultrathin NaCl films, direct images of the unper-

turbed molecular orbitals can be observed (46) as shown in Fig. 10.

Potential future studies along these lines are numerous, such as experiments on molecular switches in on/off states, single-molecule chemistry, contact conductance, or intramolecular energy transport.

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