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Imaging of a molecular wheelbarrow by scanning tunneling microscopy

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Abstract

We have studied the deposition and imaging of nanoscale molecular wheelbarrows. These molecules integrate—in analogy to macroscopic barrows—two wheels, legs and handles along a polyaromatic platform and were imaged on a clean Cu(100) surface with a scanning tunneling microscope at 7 K. The obtained images are in accordance with calculations and are dominated by the wheels. Several stable conformations of the wheelbarrow were found and identified by comparison with calculated images.

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In a top–down approach, nanoscale machines are the ultra-miniaturized versions of machines of our everyday life. In a bottom–up approach, they result from an monumentalisation procedure, designing the molecule up to a size (or a number of atoms), which provides sufficient resources for the

molecule to be a machine. The design, synthesis and operation of a single molecular machine concern for example computing power and logic gates integrated within a single molecule [1–4] or mechanical machineries embarked in a single molecule [5,6]. Here, atomic scale imaging and manipulation abilities are provided by the scanning tunnelling microscope (STM) since lateral movements [7–9] and intramolecular changes [2,10] can be induced to a single molecule on a metal surface.

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The molecular wheel, a decacyclene-based molecule, was the first example of a molecular system, self-assembled within its supramolecular bearing of neighboring molecules, acting as a simple mechanical rotating unit with a minimum number of atoms. Its continuous but random rotation was observed on a single molecule basis and with sub-molecular resolution by STM [11]. However, an important progress in the development of nanomachines would be the integration of the molecular wheels and bearing parts in the same but more complex molecule, enabling the lateral motion of the entire molecule by the rotation of its wheels. Recently, we have reported the design of a first prototype of such a mechanical nanomachine: a molecular wheelbarrow [12] integrating all the required functionalities from the rotationable wheels to the rear handles (Fig. 1) within one and the same molecule. The multistep chemical synthesis of this molecule has been described elsewhere [13].

In this letter, we present the first STM images of such molecular wheelbarrows adsorbed on a clean Cu(100) surface. To extract the different conformations of the wheelbarrow, the experimental images were compared with calculated ones refining the different stable conformations of the wheelbarrow on a Cu(100) surface.

Experiments were performed in an ultrahigh vacuum chamber with a base pressure of 10^{-10} mbar. The Cu(100) substrate was cleaned by Ne ion sputtering and subsequent annealing at 770 K. The molecules were deposited by “rapid heating” [14] from a tungsten filament (0.25 mm), which is heated by a current pulse of 6 A for a short timeframe of 600 ms. We have already used this method with success for the deposition of large molecular wires [15]. For the measurements with a homebuilt LT-STM [16] the sample was cooled to about 7 K. STM images were taken in constant-current mode and all bias voltages in this work are given with respect to the tip. The extraction of the conformation of the molecules from their STM images was achieved by comparing scan by scan the experimental and calculated STM images. An electron scattering quantum chemistry (ESQC) method [17] was used to calculate the corresponding STM images.

Our wheelbarrow (Fig. 1) consists of a polyaromatic central platform with two wheels, which are connected by a wheel axle (shown in green, red and yellow, respectively). Two 3,5-di-*tert*-butyl phenyl groups, considered as two legs [12], are also connected to the board. Furthermore, two 4-*tert*-butyl phenyl groups are added to the end of the central platform to act as handles of the barrow (in blue). The most important feature of the molecule are the wheels which are able to rotate around the σ -bond (i.e. their wheel axis) so that they should enable a lateral motion of the entire molecule on the surface by rotation, in analogy with a real macroscopic wheelbarrow. In Fig. 1(c), a three-dimensional view of the barrow in the gas phase is presented, obtained by molecular mechanics optimization with a commercial software (HyperChem). It shows the function of the *tert*-butyl phenyl groups: they should maintain the polyaromatic board away from the surface by staying perpendicular to the polyaromatic platform.

Such a molecular-scale machine inevitably displays a high level of complexity due to the integration of several functionalities on the same molecule. This complexity is reflected in its relatively large molecular weight ($C_{140}H_{120}$ has a molecular weight of $1802.45 \text{ g mol}^{-1}$), which is a general problem for the deposition of large molecules due to the possibility of thermal fragmentation. In the present case, the required linear wheel axle includes two thermally sensitive triple bonds. Accordingly, we found that conventional deposition from a Knudsen cell results in dissociation of the molecules and the presence of molecular fragments on the surface as observed by STM. In order to overcome this problem we followed the “rapid heating” procedure [14] (see above).

We have successfully imaged intact molecular wheelbarrows on a Cu(100) surface as shown in Fig. 2(a). At room temperature (the sample temperature during deposition), the molecules are not mobile and therefore found randomly distributed on the Cu(100) terraces. All wheelbarrows studied in this work were found on terraces, indicating a strong interaction with the substrate (hit-and-stick adsorption). Contamination is often visible in the vicinity of the wheelbarrows, since these molecules are also favorable sites for the

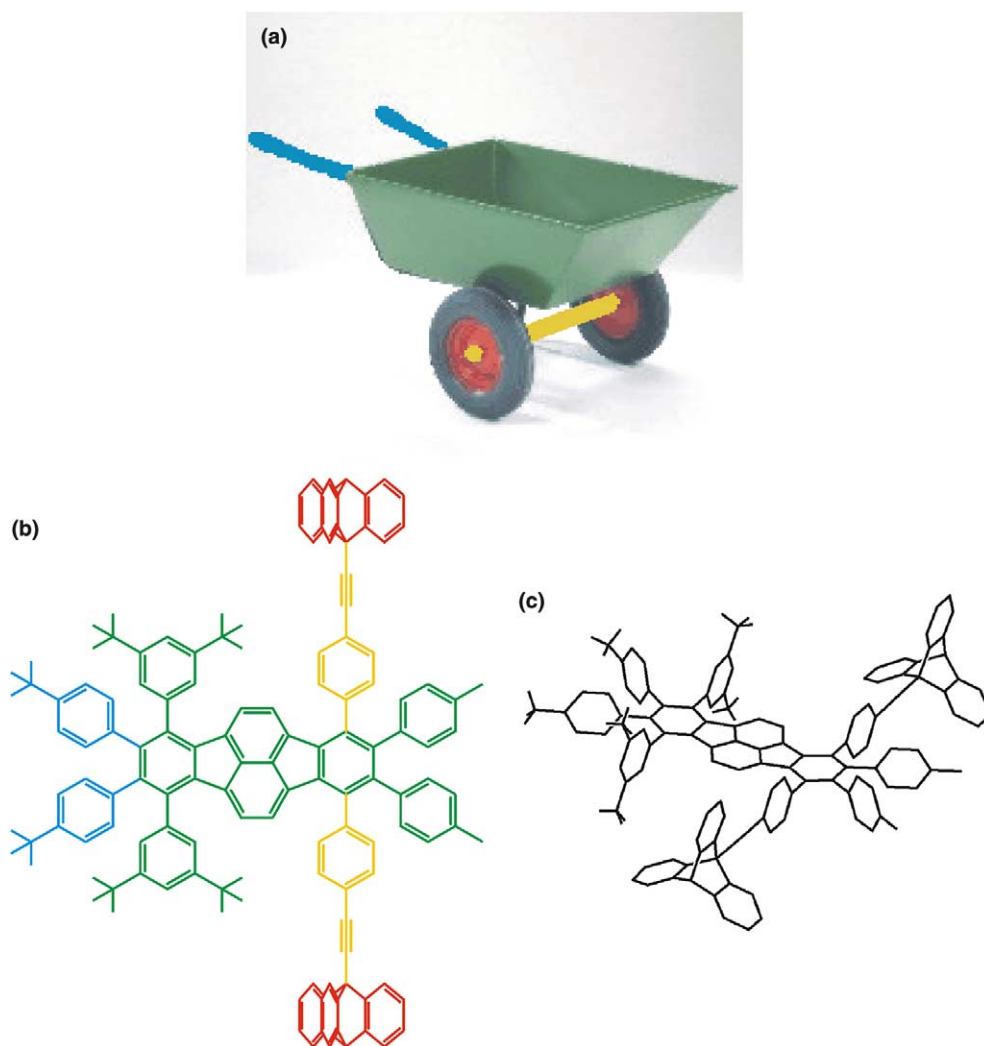


Fig. 1. (a) A macroscopic wheelbarrow (coloured corresponding to the chemical structure in (b)); (b) Chemical structure of a molecular wheelbarrow (the synthesis has been described previously [13]). The triptycene end groups (shown in red) are acting as wheels, the axle is shown in yellow, the central polyaromatic board and the two legs are shown in green and the handles in blue; (c) Three-dimensional model of the molecular wheelbarrow in the gas phase.

adsorption of contaminants. As expected for such a complex chemical structure, it leads to a rather complicated STM image, dominated by three intense maxima separated by various weaker structures. Because of the characteristic dimensions and the equivalency of different molecules in the STM images, it is very likely that intact molecular wheelbarrows have been imaged. However, their exact identification needs a comparison with calculated STM images of the molecule in a theoret-

cally determined stable adsorption configuration on Cu(100). A calculated image, obtained by MM-ESQC calculations, is shown in Fig. 2(b). The similarity with the experimental result is clear as both images exhibit the same distribution of characteristic features: two bumps assigned to the triptycene wheels and another bump from one of the 3,5-di-*tert*-butyl phenyl groups. The relatively large size of these groups (see Fig. 1(c)) is the reason why they dominate the STM images.

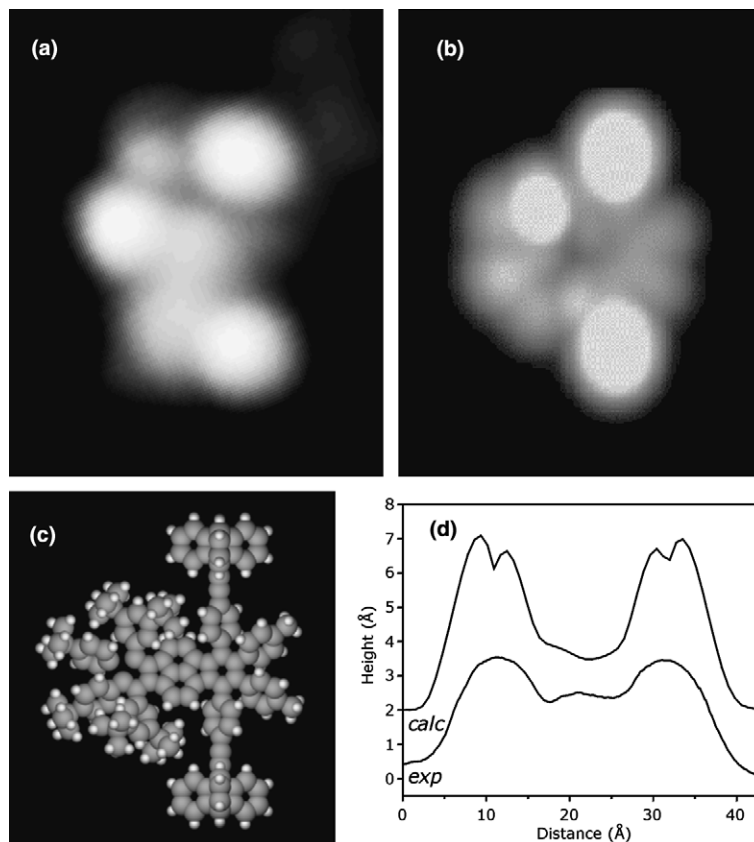


Fig. 2. Comparison of an experimental (a) and a calculated (b) STM image of a molecular wheelbarrow on Cu(100) (both images are $4 \times 5 \text{ nm}^2$ in size). In (a) ($I = 0.3 \text{ nA}$, $U = 0.5 \text{ V}$) contamination is weakly visible in the upper right corner of the image. The calculated image is based on the molecular conformation shown schematically in (c). The experimentally determined (exp) and calculated (calc) height profiles of the wheelbarrow along the wheel axis are compared in (d). The wheelbarrows are equally oriented in the images and the scheme, having a vertically oriented wheel axle in the figure.

From this comparison, the conformation of the wheelbarrow upon adsorption on the Cu(100) surface can be determined, shown in Fig. 2(c): the triptycene wheels are oriented in order to keep two of the three phenyl rings, as a result of their interaction with the substrate, almost parallel to the surface. The asymmetric appearance of the central board derives from the 3,5-di-*tert*-butyl phenyl groups, having the upper one (in Fig. 2) almost perpendicular to the board and the lower one rather parallel. In Fig. 2(d), experimental and calculated line scans across the molecular wheel axis are presented in order to compare the molecular dimensions. The apparent height of the molecule is about 3.5 \AA in the experiment and 5 \AA in the cal-

ulation. While the calculations can resolve the intramolecular structure of the wheels (visible as a double peak), this cannot be achieved in the experiment due to the broader apex of the STM tip in the experiment compared to the ideal atomic tip apex structure used in the calculation. The lateral dimensions are the same within the error, which confirms the assignment of these molecules to the wheelbarrows.

Fig. 2(a) shows an STM image of the most frequent appearance of the wheelbarrow, which is therefore the most common conformation on the surface. However, due to the complexity of the molecule, this is not the only stable conformation of the wheelbarrows. Two additional ones were

identified, which are presented in Fig. 3(a)–(c) and (d)–(f) respectively. The general appearance is almost the same for all conformations, since it is dominated by the molecular wheels (at the upper and lower edge of the images). However, there are several differences resulting from a variation

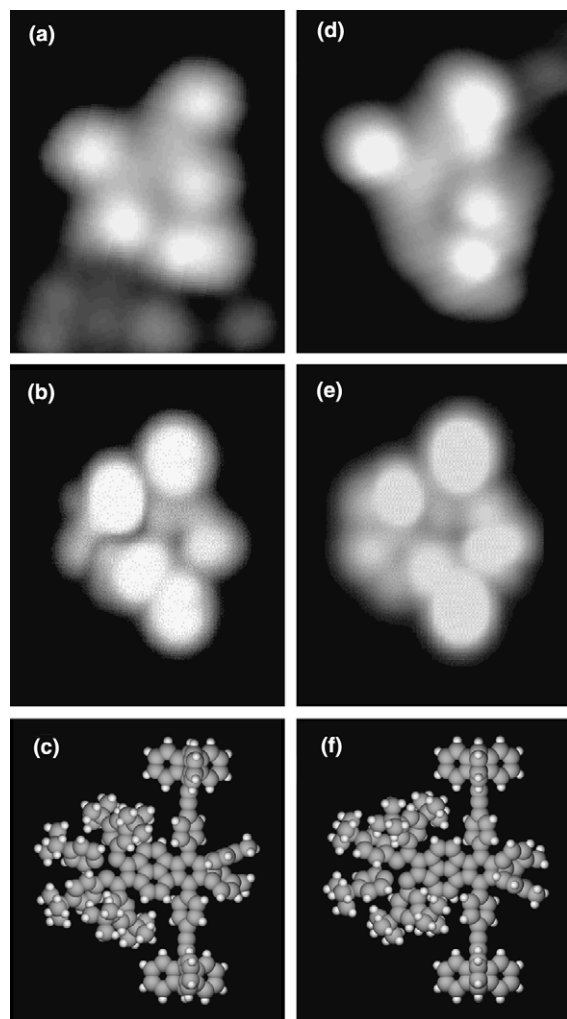


Fig. 3. (a) and (d): STM images of the molecular wheelbarrows in different conformations ($I = 0.2$ nA, $U = 0.5$ V and 1 V respectively) and the corresponding calculated STM images in (b) and (e). All images are 4×5 nm² in size. (c) and (f) show schemes of the two molecular conformations corresponding to (a, b) and (d, e) respectively. Note that in the lower left corner of (a) and the upper right corner of (d) contamination of the surface is visible, which is not part of the molecules.

of the adsorption geometry of the central board. This concerns on the one hand the 3,5-di-*tert*-butyl phenyl groups on the left side of the board (in the figures). They can be arranged in different ways, leading to a change in their STM images. On the other hand, the right end of the central board, close to the wheel axis, differs between the most common conformation shown in Fig. 2 and the others in Fig. 3. Note the distinct intensity maxima in Fig. 3(a) and (d), where only weak contribution to the image was found in Fig. 2(a). This is the result of the changed orientation of the two phenyl rings associated to the central board. While in Fig. 2(a) they are equivalently rotated with respect to their position in the gas phase (perpendicular to the central board), they are less distorted in the conformations of Fig. 3 (see schemes in (c) and (f)). This leads to a more upright position and therefore a larger height in the images. The experimental and calculated STM images ((a), (b) and (d), (e) respectively) are in good accordance, which confirms the assignment to the conformations discussed above.

After the identification of intact wheelbarrows, moving the molecules on the metal surface was attempted by lateral manipulation. The STM tip was used as a tool to move the molecules on the surface [9], taking advantage of attractive or repulsive forces between the tip apex and the molecule. According to the design (Fig. 1), the most favorable direction of manipulation is that along the central board (horizontally in the STM images and schemes) and starting from the rear part of the molecule, i.e. to push at the handles (in blue in Fig. 1). These handles were added to the molecule (compared to the original design [12]) to inhibit the tip apex to pass directly over the central platform. But even with these rear handles, it turned out that a manipulation of these molecules on Cu(100) from the rear part (but also from the front part) is not possible. While at large tip-sample distances the interaction is too weak, the applied forces lead to fragmentation of the wheelbarrows instead of lateral motion upon an approach of the tip. As a result, fragments of the molecules were found in the STM image at the location where the intact wheelbarrow was imaged before. One interpretation is the rather strong

interaction of the aromatic central board with the Cu(100) metal surface, which is also responsible for the hit-and-stick adsorption behaviour of these molecules at room temperature. The interaction of the wheels with the metal surface is very strong, as indicated by their resulting large STM contrast. As a consequence, the central platform is constrained to be very close to the metal surface contrary to what was expected from the design. This large wheel interaction also constrains the two 3,5-di-*tert*-butyl phenyl rear legs to rotate quite strongly relative to the platform with a rotation angle much larger than the 30° (from the perpendicular position in the gas phase) for the case of a Lander molecule on a Cu(100) surface [18]. The resulting conformation is therefore not very suitable for manipulation. The only successful manipulation we have achieved is a change of the internal STM contrast of the central and rear part of the molecule, while keeping the position of the wheels remained fixed. This corresponds to a change in the orientation of the rear legs and handles with no front wheel rotation.

In conclusion, we have shown how a rather complex molecule such as a molecular wheelbarrow can be deposited intact onto a metal surface. After deposition, the molecules are imaged by STM on clean Cu(100) terraces and identified by comparison with calculated images. Three conformations were determined and assigned to different adsorption geometries of the molecules. While the molecular wheels have a characteristic appearance for all conformations, the changes of the adsorption geometry of the central platform are clearly visible in the STM images. Lateral motion of the wheelbarrows is not possible, because of the strong interaction of the two front wheels with the metal surface. This result suggests the exploration of such manipulation on the surface of an ultrathin insulating layer deposited on the metal sur-

face where the interaction is presumably weaker [19].

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