# Rolling a single molecular wheel at the atomic scale

## L. GRILL<sup>1</sup>\*, K.-H. RIEDER<sup>1</sup>, F. MORESCO<sup>1</sup>, G. RAPENNE<sup>2</sup>, S. STOJKOVIC<sup>2</sup>, X. BOUJU<sup>2</sup> AND C. JOACHIM<sup>2</sup>

<sup>1</sup>Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany <sup>2</sup>Nanosciences Group, CEMES-CNRS, 29 rue Jeanne Marvig, 31055 Toulouse, France \*e-mail: leonhard.grill@physik.fu-berlin.de

Published online: 21 January 2007; doi:10.1038/nnano.2006.210

The design of a single-molecule machine consisting of functional components requires a detailed understanding of its mechanical motion<sup>1,2</sup>. The scanning tunnelling microscope (STM) is the only available tool for driving and imaging such a nanoscale machine on a surface. Both lateral hopping motions and conformational changes of single molecules can be induced using the STM tip<sup>3,4</sup>. However, no rolling of a wheel has been demonstrated so far at the nanoscale, even though this is a very useful motion at the macroscopic scale. Here we show how the rolling of a single molecule equipped with two wheels (0.8 nm in diameter) can be induced by the STM tip. The characteristics of the rolling are recorded in the STM feedback loop manipulation signal and in real time. We capture unambiguous signatures of the conformational change happening during the rolling. Our approach of controlling the intramolecular mechanics provides a path towards the bottom-up assembly of more complex molecular machines.

By tuning the distance between the STM tip end apex and the surface and then moving the tip laterally, large molecules can be displaced in a controlled way to a new predetermined position on a surface<sup>5</sup>. If the tunnelling current is kept constant during a manipulation sequence, the variation of the feedback loop height signal carries information about the molecular motion on the surface<sup>6</sup>. Using this technique, only a very few studies of a singlewheel molecule have been conducted so far, concerning either the thermally induced random rotation of a molecular wheel within a supramolecular bearing made of the same molecules<sup>7</sup> or its controlled rotation along the edge of a molecular island by STM manipulation<sup>8</sup>. However, in all experiments performed so far, the wheel was adsorbed flat on the surface. Its axis of rotation was therefore oriented perpendicular to the surface and such a wheel cannot be mounted on a board to enable the motion of a molecular machine. In a pushing mode, the STM manipulation signal of a single C60 molecule on Si(100) was reported and presents a fine structure superimposed to the periodic manipulation 'hopping' signal. This was interpreted as a rotation of the fullerene during its hopping from one adsorption site to the next<sup>9</sup>. A nanocar has been synthesized by mounting four  $C_{60}$ molecules as wheels on a non-rigid molecular board<sup>10</sup>, but no manipulation signal was reported to assess the possible rotation of these C<sub>60</sub> wheels<sup>11</sup>. The motion of this nanocar was thermally activated, which does not carry an experimental proof of a rotation of the wheel during its hopping from one adsorption site

to the next. Triptycene groups, acting as wheels, were mounted on a wheelbarrow molecule<sup>12</sup>, but it was not possible to reposition this molecule on a Cu(100) surface<sup>13</sup>.

In a constant-height mode, the distance between the tip apex and a large molecule is not controlled by the STM feedback loop, that is, by the electronic transparency of the molecule. Therefore, larger forces can be applied on the molecule to induce intramolecular conformational changes. For example, for mechanical molecular machines, important conformational changes are the controlled rotation of wheels or gears relative to other fixed parts of an intramolecular machinery. At large and small tip heights, respectively, conformational changes and lateral translation of a molecule can be induced as a result of the different force strengths<sup>14</sup>. In this case, a fine structure, caused by intramolecular motion induced by the tip apex, may superimpose on the periodic manipulation signal<sup>6</sup>. The variation of the feedback loop signal during the manipulation is still the only way to characterize experimentally how one single-molecule machine performs.

Figure 1a presents our wheel-dimer molecule ( $C_{44}H_{24}$ ), where two triptycene wheels (of our previously designed wheelbarrow<sup>12</sup>) are connected by a C=C-C=C axle. When adsorbed on a metal surface, this molecule exhibits two intramolecular degrees of freedom: the independent rotation of each wheel around the central axle. In order to induce a rolling motion (as schematically presented in Fig. 1b) by lateral STM manipulation, we have chosen a Cu(110) surface, which exhibits an anisotropic corrugation due to its close-packed rows of copper atoms in the [110] direction. After deposition at room temperature, the molecules first saturate the step edges and then adsorb as isolated molecules on the Cu(110) terraces (Fig. 1c).

For a rolling motion, the orientation of the molecules with respect to the surface is of great importance. As shown in Fig. 2a, the wheel-dimer molecules adsorb in various orientations, in particular with the molecular axle parallel (orientation A) and perpendicular (B) to the copper rows. For orientations A, B and D, the STM image of a wheel-dimer is symmetric, with apparent wheel heights of  $3.0 \pm 0.2$  Å (some molecules in orientation C appear asymmetric with one wheel having a larger STM apparent height of about 3.5 Å, probably due to a different adsorption of the two wheels on the Cu(110) surface). Calculations of the molecular conformation in orientation A (Fig. 2d) show that the central molecular axle is located above a close-packed copper row





**Figure 1** Molecules with two wheels (0.8 nm in diameter) for rolling. a, Chemical structure of the wheel-dimer molecule ( $C_{44}H_{24}$ ). b, Scheme of a manipulation using the STM tip to induce a rolling motion (arrows indicate the rotation of the wheels). Hydrogen atoms of the molecule are not plotted, but were considered for the indicated distance. c, STM image of the Cu(110) surface after deposition of 0.05 monolayers at room temperature (image size is  $100 \times 100 \text{ nm}^2$ ). The [ $\overline{1}10$ ] direction of the close-packed rows of the substrate is indicated.



**Figure 2** Adsorption of molecular wheel-dimers on a Cu(110) surface. a, STM image of three wheel-dimer molecules adsorbed on Cu(110) ( $13 \times 13 \text{ nm}^2$ ). The inset (with the same scaling) shows the substrate in atomic resolution ( $4 \times 4 \text{ nm}^2$ , tunnelling current = 1 nA, bias voltage = 0.1 V). **b**, Schematic representation showing that four different orientations A–D can be distinguished. **c**, Calculated molecular configuration of the wheel-dimer in orientation A, adsorbed parallel to the close-packed copper rows. **d**, A histogram of the observed molecular orientations shows their statistical distribution (the line is drawn to guide the eye): 44% in orientation A ( $\phi = 0^\circ$ ), 11% in B, 32% in C and 13% in D. Molecules in orientation A are parallel and in B perpendicular to the close-packed copper rows; C is rotated by about 26° and D by about 69° with respect to the [ $\overline{110}$ ] direction. **e**, The corresponding calculated STM image (3.3 × 2.2 nm<sup>2</sup>).

and the lower benzene rings of the wheels are distorted as a result of their chemisorption on the Cu(110) surface. For orientation A, the calculated STM image is in very good accordance with the experimental ones, consisting of two lobes at a distance of  $8.7 \pm 0.3$  Å, which corresponds to the intramolecular distance between the two wheels of a single molecule (Fig. 2e). The same level of agreement can be obtained for the other conformations, but with small differences in the adsorption conformation. These differences have no influence on the molecular mechanics driven by the tip apex discussed in the following.

Lateral motion of the molecules in orientation A on the surface leads to typical periodic manipulation signals as presented in Fig. 3a (curves I and II). These sawtooth-shaped signals can be assigned to a pushing (ascending edge) and a pulling (descending edge) mode of manipulation<sup>15</sup>. The 3.6 Å periodicity of these signals corresponds to the distance between two atomic rows on the Cu(110) surface. Hence, the molecule is hopping from one adsorption site (copper row) to the next during the manipulation.

However, these are not the only observed signals for orientation A. We have also recorded a completely different manipulation signal (curve III in Fig. 3a) that we assign to the rolling of a wheel within our molecule. First, the periodicity of the recorded signal is about 7 Å and therefore corresponds to a lateral motion of a wheel after a 120° rotation (around the molecular axle). Second, a standard hopping motion over two adsorption sites can be excluded because the signal does not show any pulling or pushing signature. Instead, this hat-shaped signal exhibits one intense peak at the centre and smaller maxima on both sides. Even though the intensity distribution slightly changes from one case to another, the overall shape remains the same and was recorded many times. A rolling manipulation is always obtained at larger tip heights (vertical feed  $\Delta z \leq 4$  Å; the initial tip height is about 7 Å) as compared to a hopping signal where the tip apex must be approached further down towards the surface ( $\Delta z \ge 4$  Å).

When the same lateral manipulation is performed on a molecule in orientation B, the manipulation signal shows a clear pushing signature with a 2.5-Å periodicity (Fig. 3b). For comparison, molecules in orientation A undergo only a hopping motion when manipulated in the direction parallel to the central axle (Fig. 3c). In both cases, no rolling signal has been recorded. In order to study the role of the substrate lattice, we have also manipulated the wheel-dimer molecules on a Cu(100) surface. Very regular characteristic pulling and pushing signals were recorded (Fig. 3d) with no evidence of a rolling signal. This is in agreement with the rather small corrugation of the Cu(100) surface, compared to Cu(110). Owing to the chemical structure of the wheel, a rolling motion occurs only if the molecule is manipulated perpendicular to its axle and along a surface direction of sufficient corrugation.

When the molecule found in orientation A is manipulated in a hopping or a rolling mode with equivalent tip apex pathways, the lateral displacement of the molecule turns out to be different (Fig. 4). In the pushing mode, the molecule follows the complete pathway of the tip (4 nm in the case shown). In the rolling mode, on the other hand, the molecule does not follow the tip apex up to the end. Instead, one wheel moves and the other remains in its initial position (Fig. 4c). This difference is characteristic of the two types of motion: in the case of a hopping mechanism, the initial conditions for manipulation are restored after each hopping step, allowing large displacements. For a rolling motion (Fig. 4g), the tip reaches the other side of the molecule after inducing a  $120^{\circ}$  rotation to a wheel. In this case, the starting conditions are not met any more and the displacement of the molecule is limited to a single rolling process.



Figure 3 Rolling and hopping of wheel-dimers by lateral manipulation with the STM tip. The left column shows STM images (all  $3 \times 3$  nm<sup>2</sup>) before the manipulation (the arrows mark the pathway) and the right column the corresponding manipulation signals (periodicities are indicated by dashed lines). **a,b**, Molecule in orientation A (**a**) and in orientation B (**b**), manipulation in both cases across the molecular axle. **c**, Molecule in orientation A and manipulation along the axle (in this case manipulation was done in the constant-current mode). **d**, For comparison, the wheel-dimer molecule is adsorbed on Cu(100), manipulation is done across the molecular axle and along a  $\langle 011 \rangle$  direction of the substrate.

The manipulation signal during the rolling motion (Fig. 4e) corresponds to a  $120^{\circ}$  rotation of the left wheel of the molecule. It is remarkable that in all cases where we observed this signal one wheel is left in its initial position (and no long pathways occurred). The presence of two hat-shaped signals in Fig. 3a is rather an exception and can be explained by the alternate rotation of the two wheels. It turns out that the lateral distance, that is, on the *x*-axis, between the two signals can vary, leading to a superimposition of the two hat shapes in some cases (curve IV in Fig. 3a). This effect is due to the variable starting point of the two wheel rotations, which depends on the precise tip apex shape. Notice that the hat-shaped signal is mirror-symmetric, in contrast

## LETTERS



**Figure 4** Different lateral displacements according to rolling and hopping mechanisms. Comparison of lateral manipulations of a single wheel-dimer molecule at large (left panel) and small heights (right panel) of the STM tip. **a**,**b**, STM images before the manipulation. **c**,**d**, STM images after the manipulation. Arrows mark the pathway of the tip apex during the manipulation and dashed lines indicate the initial position of the wheel-dimer molecules (all images  $9 \times 9 \text{ nm}^2$ ). **e**,**f**, Corresponding plots of current signals during the manipulation were used for the assignment of the molecular motion. **g**, Scheme of the rolling mechanism. Step (1) is the tip approach towards the molecule, step (2) is a 120° rotation of a wheel around its molecular axle and in step (3) the tip reaches the other side of the molecule. It shows that, in principle, only one rotation of a wheel can be induced (the direction of movement is marked by arrows).

to the sawtooth-like signal of a hopping mode. This observation is in accordance with the schematic model of the rolling mechanism in Fig. 4g, because the first and third step are similar and therefore give rise to a comparable tunnelling current, whereas the central step (2) reveals a more intense signal.

A clear signature of the rolling of a single molecular wheel perpendicular to a surface and mounted on a molecular axle was recorded. During the experiment, we maintained a direct link between the molecule and the macroscopic scale, the tunnelling current being the only way to bring up information from the molecule to the controller. This demonstrates how the rolling mechanism can now be mastered at the atomic scale by selecting an adsorption surface adapted to the wheel chemical structure.

## **METHODS**

Experiments were performed under ultrahigh vacuum conditions (base pressure of  $10^{-10}$  mbar) using a homebuilt STM (ref. 16). The wheel-dimer molecules were deposited from a Knudsen cell (at about 490 K) onto the Cu substrates, which were cleaned by Ne ion sputtering and subsequent annealing at 800 K. The sample was kept at room temperature during deposition, which enables thermal diffusion (on Cu(110), the molecules are still mobile at 140 K sample temperature). All STM images were taken at temperatures between 20 and 30 K with a tunnelling current of 0.2 nA and a bias voltage of 0.8 V on the sample (if not specified differently). The corresponding tip height of around 7 Å (determined from *I*(*z*) curves measurements) is the reference point for vertical feeds  $\Delta z$ . Manipulation experiments were carried out in the constant-height mode (if not mentioned differently) at a bias voltage of -30 mV (with a tip speed of a few nanometres per second).

The optimized molecular conformation on the Cu(110) surface has been calculated using the new ASED<sup>+</sup> semi-empirical technique<sup>17</sup> completed by standard molecular mechanics calculations, and the corresponding STM images have been calculated using the ESQC technique<sup>18</sup>.

# Received 13 October 2006; accepted 19 December 2006; published 21 January 2007.

### References

- Joachim, C. & Gimzewski, J. K. Single molecular rotor at the nanoscale. Structure and Bonding 99, 1–10 (2001).
- Zheng, X. *et al.* Dipolar and nonpolar altitudinal molecular rotors mounted on an Au(111) surface. J. Am. Chem. Soc. 126, 4540–4542 (2004).
- 3. Gross, L. *et al.* Trapping and moving metal atoms with a six-leg molecule. *Nature Mater.* **4**, 892–895 (2005).
- Jung, T. A., Schlittler, R. R., Gimzewski, J. K., Tang, H. & Joachim, C. Controlled room-temperature positioning of individual molecules: molecular flexure and motion. *Science* 271, 181–184 (1996).
- Beton, P. H., Dunn, A. W. & Moriarty, P. Manipulation of C<sub>60</sub> molecules on a Si surface. Appl. Phys. Lett. 67, 1075–1077 (1995).
- Moresco, F. et al. Recording intramolecular mechanics during the manipulation of a large molecule. Phys. Rev. Lett. 87, 088302 (2001).
- Gimzewski, J. K. et al. Rotation of a single molecule within a supramolecular bearing. Science 281, 531–533 (1998).
- Chiaravalotti, F. et al. A rack-and-pinion device at the molecular scale. Nature Mater. 6, 30–33 (2007).
   Keeline, D. L. et al. Bond breaking coupled with translation in rolling of covalently bour
- Keeling, D. L. et al. Bond breaking coupled with translation in rolling of covalently bound molecules. *Phys. Rev. Lett.* 94, 146104 (2005).
- Shirai, Y. et al. Surface-rolling molecules. J. Am. Chem. Soc. 128, 4854–4864 (2006).
  Shirai, Y., Osgood, A. J., Zhao, Y., Kelly, K. F. & Tour, J. M. Directional control in thermally driven single-molecule nanocars. Nano Lett. 5, 2330–2334 (2005).
- Jimenez-Bueno, G. & Rapenne, G. Technomimetic molecules: synthesis of a molecular wheelbarrow. *Tetrahedron Lett.* 44, 6261–6263 (2003).
- Grill, L. et al. Imaging of a molecular wheelbarrow by scanning tunneling microscopy. Surf. Sci. Lett. 584, L153–L158 (2005).
- Grill, L. et al. Controlled manipulation of a single molecular wire along a copper atomic nanostructure. Phys. Rev. B 69, 035416 (2004).
- Bartels, L., Meyer, G. & Rieder, K.-H. Basic steps of lateral manipulation of single atoms and diatomic clusters with a scanning tunneling microscope tip. *Phys. Rev. Lett.* **79**, 697–700 (1997).
- Meyer, G. A simple low-temperature ultrahigh-vacuum scanning tunneling microscope capable of atomic manipulation. *Rev. Sci. Instrum.* 67, 2960–2965 (1996).
   Annelie P. & Institute of Anne institute for the construction of the state of the
- Ample, F. & Joachim, C. A semi-empirical study of polyacene molecules adsorbed on a Cu(110) surface. *Surf. Sci.* 600, 3243–3251 (2006).
  Sautet, P. & Joachim, C. Calculation of the benzene on rhodium STM images. *Chem. Phys. Lett.*
- Sautet, P. & Joachim, C. Calculation of the benzene on rhodium STM images. *Chem. Phys. Lett.* 185, 23–30 (1991).

## Acknowledgements

We acknowledge the European Integrated Project PICO INSIDE and the Deutsche Forschungsgemeinschaft (DFG) (contract no. GR 2697/1-1) for financial support.

## Author contributions

L.G., K.-H.R., E.M., G.R. and C.J. conceived and designed the experiments. L.G. performed the experiments and analysed the data. G.R. synthesized the molecules and S.S., X.B. and C.J. were in charge of the theory and the STM image calculation. L.G. and C.J. co-wrote the paper.

### Competing financial interests

The authors declare that they have no competing financial interests.

Reprints and permission information is available online at http://npg.nature.com/reprintsandpermissions/