Journal of
Scanning Probe Microscopy
Vol. 2, 19–23, 2007

Study and Manipulation of Single Functionalized Molecules by Low Temperature STM*

L. Grill[1,*], M. Alemani[1,†], K.-H. Rieder[1,‡], F. Moresco[1,¶], G. Rapenne[2], C. Joachim[2], M. V. Peters[3], and S. Hecht[3]

[1] *Institut für Experimentalphysik, Freie Universität Berlin, 14195 Berlin, Germany*
[2] *CEMES-CNRS, 29 rue Jeanne Marvig, 31055 Toulouse, France*
[3] *Institut für Chemie, Humboldt-Universität zu Berlin, 12489 Berlin, Germany*

RESEARCH ARTICLE

Two types of functionalized molecules, wheels and switches, are studied with a low temperature scanning tunneling microscope. Lateral manipulation of wheel-dimer molecules is performed on a Cu(110) surface. If suitable parameters are chosen, not only a hopping, but also a rolling motion of the molecular wheels can be induced if the surface corrugation in the direction of motion is sufficient. The experimental observations clearly reflect the different mechanisms of hopping and rolling. While mostly only one wheel rolls, in some cases the rolling of both wheels is observed. The isomerization of single azobenzene derivatives on Au(111) is induced by applying a bias voltage between tip and sample. The process turns out to be perfectly reversible as the molecules, adsorbed in highly ordered islands, precisely restore their initial appearance after two subsequent switching events from *trans* to *cis* and back to *trans*. A detailed investigation of the driving process, studying the dependence of the threshold voltage on the tip-sample distance, reveals different mechanisms.

Keywords: Scanning Tunnelling Microscopy, Single Molecule Manipulation, Molecular Electronics, Nanoscale Systems, Functionalized Molecules.

1. INTRODUCTION

The investigation of single functionalized molecules has become an important research field in the last years, driven by the prospect for fundamental device miniaturization.[1–3] Understanding and controlling molecular motion and conformational changes of single molecules is very important in this regard. For this purpose, the scanning tunneling microscope (STM) at low temperature constitutes a powerful tool, as it not only allows imaging with submolecular resolution, but also permits the manipulation of atoms and molecules in a highly reliable way.[4] By tuning the distance between the STM tip end apex and the surface, the active forces during manipulation vary in origin and strength,[5] enabling to induce intramolecular changes or lateral displacement.[6] Additional to direct interatomic forces between tip and molecule, various processes can be achieved by exciting molecules with tunneling electrons[7,8] or by the intense electric field present in the STM junction.[9] This article focuses on two types of functionalized molecules, wheels and switches, i.e., molecules that can roll on a surface or can be reversibly switched between stable states.

In the last years, it has been shown with various systems that single molecules can be displaced in a very controlled way on a surface by lateral manipulation with the STM tip.[10–13] The molecules typically undergo a hopping motion from one adsorption site to the next. However, no rolling motion of a molecular wheel has been demonstrated so far, although this is a very common mechanism at the macroscopic scale. On the other hand, the rotation of single wheel molecules on metal surfaces has been induced thermally[14] or by STM manipulation,[15] but in all cases the wheel was adsorbed flat on the surface, i.e., having its rotational axis perpendicular to the surface, and therefore unsuitable for the displacement of a molecular machine. Wheel-shaped triptycene groups were mounted on a wheelbarrow molecule,[16] but it was not possible to displace this molecule on the surface without modifying it. In the following, manipulation experiments with the so-called wheel-dimer molecule are presented, where two triptycene groups are connected by an axle consisting of carbon atoms (Fig. 1(a)). In this way, the molecular

*Author to whom correspondence should be addressed.
†Present address: Department of Physics, University of California, Berkeley, USA.
‡Present address: Swiss Federal Laboratories for Materials Research, Zurich, Switzerland.
¶Present address: Qimonda GmbH, Dresden, Germany.
*This paper was presented at ICMAT 2007 Symposium G.

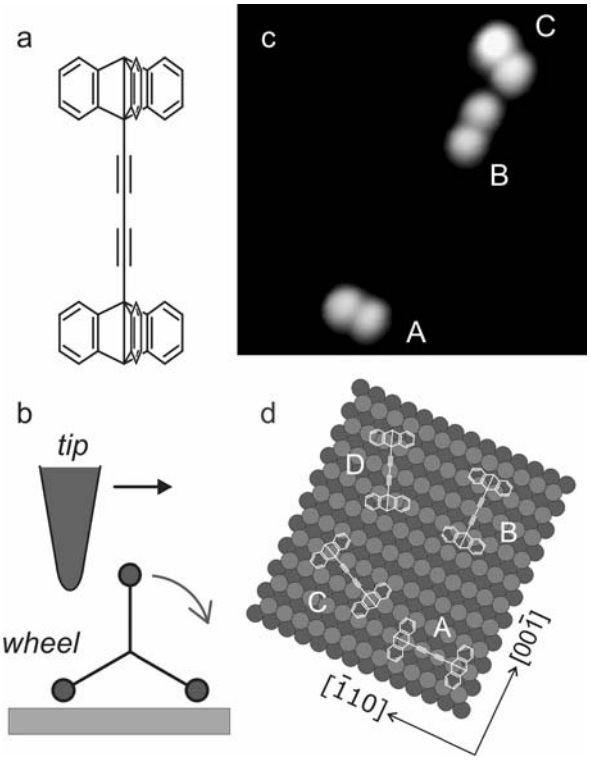

Fig. 1. (a) Chemical structure of the wheel-dimer molecule. (b) Scheme of the manipulation experiment. (c) STM image (13×13 nm^2) of three wheel-dimer molecules adsorbed on Cu(110). The scheme in (d) shows the four observed molecular configurations A–D (same substrate orientation as in the STM image). Reprinted with permission from [20], L. Grill et al., *Nat. Nanotechnol.* 2, 95 **(2007)**. © 2007, Nature Publishing Group.

wheels are standing upright and, as will be shown below, capable to roll on a surface.

2. EXPERIMENTAL DETAILS

Experiments were performed at the Freie Universität Berlin in an ultra-high-vacuum chamber with a base pressure of 10^{-10} mbar. Small amounts of molecules (submonolayer range) were deposited at room temperature onto the Cu(110) and Au(111) surfaces, which have been cleaned before by Ne ion sputtering and subsequent annealing. The temperature of the molecule evaporator, a Knudsen cell, was controlled by a thermocouple. STM images were taken in constant-current mode at temperatures between 5 K and 30 K with a homebuilt low temperature STM.[17] The wheel-dimer molecules have been synthesized at the CEMES-CNRS Toulouse and the azobenzene molecules at the Humboldt University Berlin.

3. RESULTS

In order to understand the motion of a molecule in detail, it is important to study the manipulation signal, i.e., tunneling current at constant tip height or vice versa, during the motion, because the STM images before and after manipulation do not hold information about the type of movement in between. In the common hopping mode of atoms and molecules, saw-tooth-shaped signals with descending (pulling mode) or ascending (pushing mode) edge and are observed, exhibiting a periodicity that corresponds to the surface lattice structure.[18, 19] The shape of a rolling signal instead is unknown, but it is expected to be fundamentally different from these in shape and periodicity.

The basic idea of the experiment is shown in Figure 1(b): The STM tip is moved across the molecular wheels, i.e., perpendicular to the molecular axle, in order to induce a rolling motion of the two wheels. The Cu(110) surface has been chosen as substrate, because it exhibits an anisotropic corrugation due to its close-packed rows of copper atoms in [−110] direction. After deposition at room temperature, the molecules first saturate the step edges and then adsorb isolated on the terraces. As can be seen in the STM image of Figure 1(c), each molecule appears as two lobes, which correspond to the two molecular wheels as was confirmed by calculations.[20] Four different molecular orientations (named A–D in Fig. 1(d)) are found, whereas A (the most common configuration[20]) and B are the most promising ones by means of manipulation, because the molecular axle is parallel or perpendicular to the copper rows of the surface.

Figure 2 shows manipulation experiments of the wheel-dimer in orientation A. The tip is moved across the molecular axle at constant height, while the tunneling current is recorded (in real time). If rather small tip heights, i.e., a vertical feed Δz[21] of at least 4 Å, are used, characteristic sawtooth-shaped signals are recorded during manipulation (Fig. 2(b)). This means that the molecules hop (in a pushing or pulling mode[18]) from one copper row to the next, giving rise to a signal periodicity of 3.6 Å, the distance between the close-packed rows on the surface. However, the signal shape changes dramatically if larger tip heights ($\Delta z \leq 4$ Å) are used during manipulation (Fig. 2(c)). A hat-shaped signal appears, which is assigned to a rolling motion of the molecular wheels, because its (reproducible) shape, completely different from the hopping signal, exhibits a periodicity of about 7 Å. This distance corresponds to the lateral motion of a wheel after a 120° rotation around the molecular axle.[20]

The fact that the rolling signal is mirror-symmetric is not surprising as the motion itself is also expected to be symmetric: Steps (1) and (3) should be similar by means of the tunneling current signal (Fig. 2(d) shows the three steps of the rolling motion). Accordingly, the central intensity maximum in the manipulation curve could be caused by the molecular configuration having the wheel adsorbed "on top" and the two lower maxima reflect the moments in which the tip approaches the wheel from one side or is leaving from the other side.[22] Note that rolling is possible only across the copper rows (in [00–1] direction) and

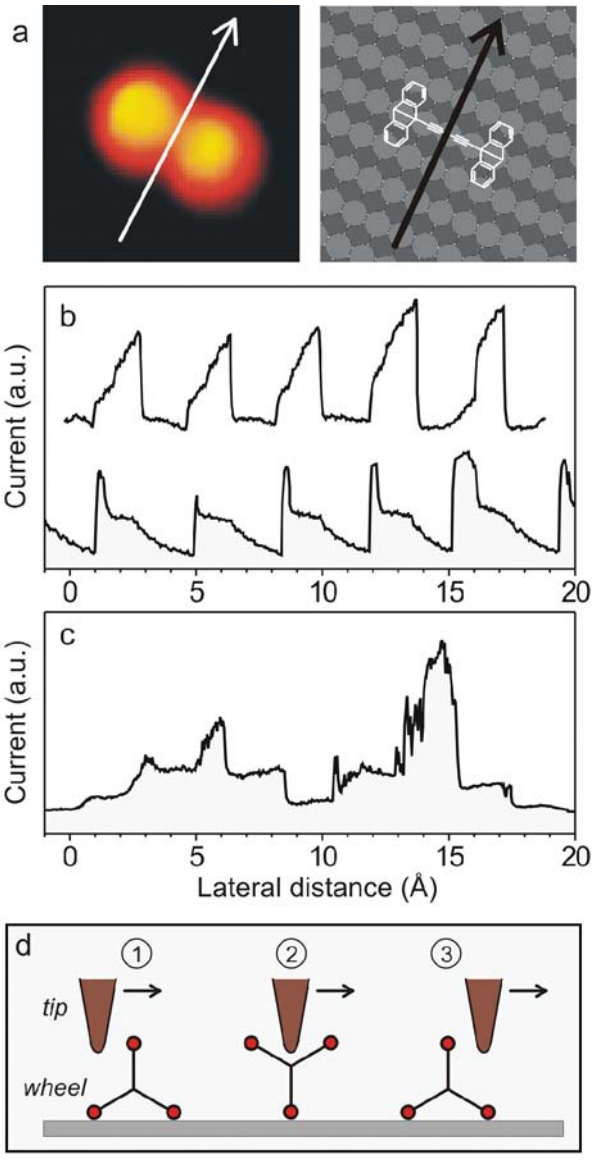

Fig. 2. (a) STM image (3×3 nm^2), left panel, and corresponding scheme, right panel, of the manipulation experiment. The wheel-dimer molecule is oriented parallel to the close-packed copper rows of the substrate (configuration A), the arrows mark the tip pathway. (b–c) Tunneling current signals during manipulation. (d) Scheme of the rolling mechanism in three steps (see text). Reprinted with permission from [20], L. Grill et al., *Nat. Nanotechnol.* 2, 95 **(2007)**. © 2007, Nature Publishing Group.

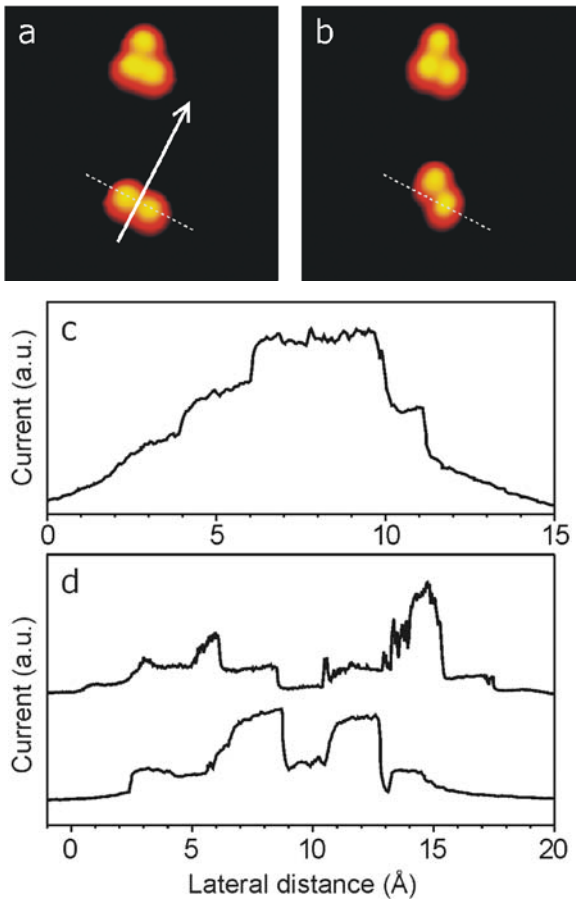

Fig. 3. STM images (9×9 nm^2) before (a) and after (b) lateral manipulation with the STM tip (the arrow indicates the pathway and the dashed line marks the initial position of the molecular axle) with the corresponding tunneling current signal in (c). (d) shows manipulation curves with more than one rolling signal. Reprinted with permission from [20], L. Grill et al., *Nat. Nanotechnol.* 2, 95 **(2007)**. © 2007, Nature Publishing Group.

not along them, revealing that the surface must provide a sufficient corrugation for this kind of motion.

Typically, the wheel-dimer molecules are not moved far on the surface if a rolling signal is recorded, but one wheel is left in its initial position while the other one moves (Figs. 3(a–b)). Accordingly, in all these cases only one hat-shaped rolling signal is observed during manipulation (Fig. 3(c)), meaning that only one of the two wheels is rolling while the other one only changes its orientation on the surface. The presence of two hat-shaped signals (as in Fig. 2(c)) reflects a rare case and can be explained by the rolling of both wheels. This behavior seems to depend on the precise shape of the tip apex, allowing access to both wheels during manipulation. As a result of this, the time lag between the two rolling processes varies and therefore the distance of the two signals (on the x-axis) in the manipulation curve changes, leading to separated or superimposed hat-shaped signals (upper and lower curve in Fig. 3(d), respectively).

Molecular switches represent very interesting systems by means of device miniaturization for future molecular electronics, because such molecules can exhibit various stable states with different physical and chemical properties.[23] Azobenzene molecules are prototypes of a molecular switch as they can adopt two configurations, the *trans* and the *cis* isomer.[24] As shown by calculations, the *trans–cis* isomerization leads to a change in the molecular conductance if the molecule is placed between two electrodes,[25,26] an important property for a possible use in future nano-circuits. In order to decouple the molecules from the substrate, we have chosen to equip the azobenzene molecule with four lateral *tert*-butyl

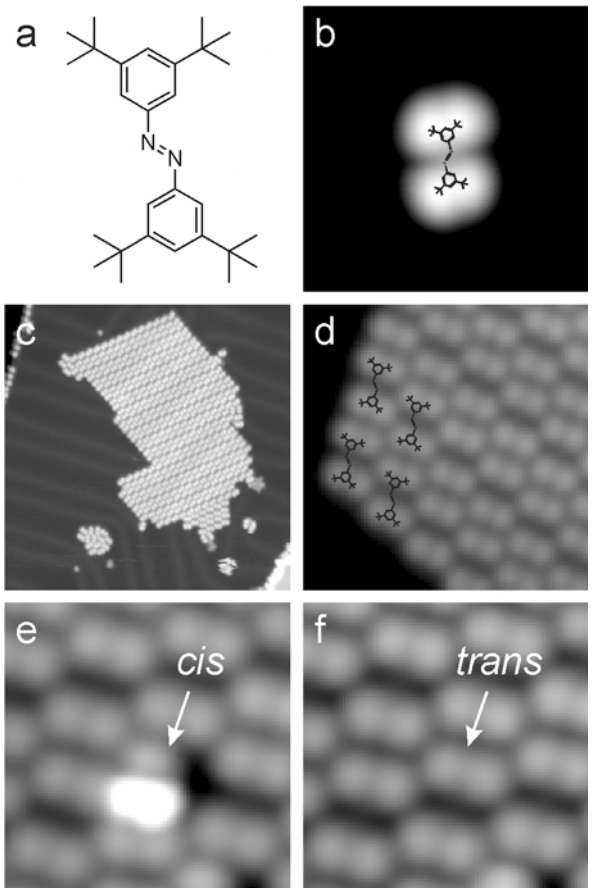

Fig. 4. (a) Chemical structure of the TBA molecule. (b) STM image (4.6×4.6 nm^2) of a single molecule, appearing as four lobes, with the superimposed chemical structure. (c) STM image (40×40 nm^2) of a large molecular island. The exact adsorption configuration is determined in (d) from the corner of an island (the choice of the molecular chirality for the superimposed molecular model is arbitrary). (e–f) STM images (3.5×3.5 nm^2) of a few molecules within an island before and after applying a voltage pulse, causing the switching of the *cis* isomer into the *trans* state (marked by arrows). Reprinted with permission from [27], M. Alemani et al., *J. Am. Chem. Soc.* 128, 14446 **(2006)**. © 2006, American Chemical Society.

groups that should increase the distance to the surface, but does not change significantly the electronics of the molecular core. The resulting molecule, 3,3′,5,5′-tetra-*tert*-butylazobenzene (TBA), is shown in Figure 4(a).

After deposition of these molecules onto Au(111), single molecules appear as four lobes with a rhombic shape and an apparent height of 2.7 ± 0.1 Å (Fig. 4(b)). From the molecular dimensions in the gas phase, the origin of the lobes is determined as the *tert*-butyl groups (the central azobenzene part is hardly visible). Hence, all molecules are found in the planar *trans* state on the surface, i.e., the thermodynamically favoured isomer. As the molecules are mobile on the surface at room temperature, most of them form highly ordered islands consisting of parallel rows (Fig. 4(c)). The exact adsorption configuration is determined from the corner of an island (Fig. 4(d)).

Isomerization of the molecules is induced by positioning the STM tip above a molecular island and applying a voltage pulse between tip and sample of about 1–100 seconds duration. After such a pulse, several molecules within the island appear with a larger height of 4.1 ± 0.3 Å (Fig. 4(e)). This new molecular configuration has a characteristic appearance of a central intense lobe and three weaker lateral lobes in triangular shape. By applying another pulse, the molecule changes back to the initial state (Figs. 4(e–f)). Thus, as the *trans* isomer can be precisely restored (and this process can be reproduced many times), we assign the observed molecular changes to an isomerization process from *trans* to *cis* and back to *trans*. This interpretation is confirmed by a shift of the molecular LUMO.[27] The *cis* isomer is therefore not planar, in agreement with the gas phase configuration and STM results

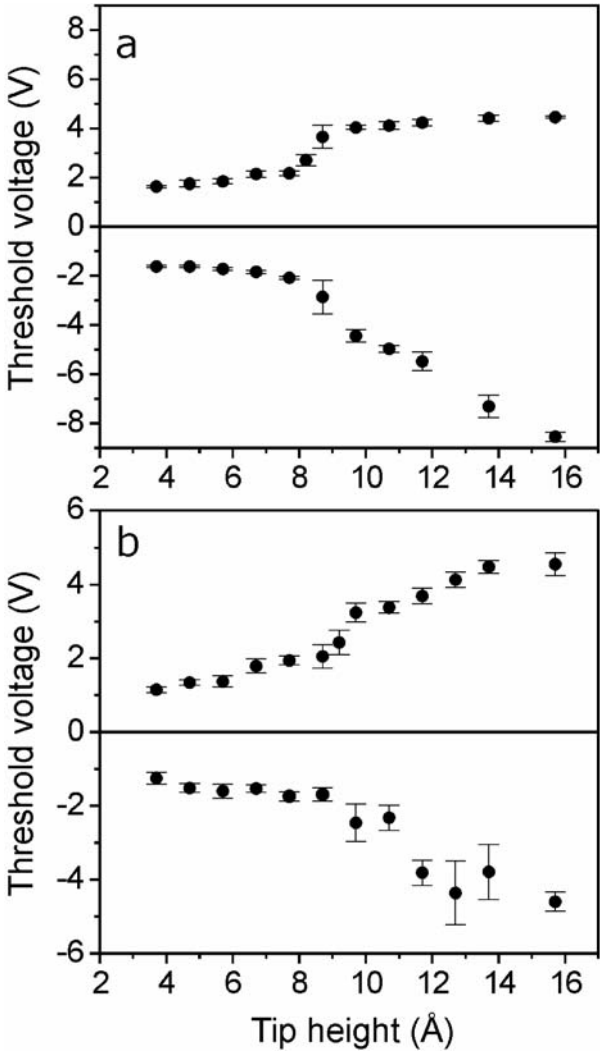

Fig. 5. Threshold voltage, required for the switching event, as a function of the tip height for the *trans* → *cis* (a) and the *cis* → *trans* (b) isomerization. Reprinted with permission from [27], M. Alemani et al., *J. Am. Chem. Soc.* 128, 14446 **(2006)**. © 2006, American Chemical Society.

of the pure azobenzene molecule.[28] The threshold voltage, i.e., the smallest bias voltage where isomerization is observed, turns out to be slightly larger for the *trans* → *cis* than for the opposite direction (at tip heights of about 6 Å). This behavior leads to the effect that, during a pulse suitable for *trans* → *cis* isomerization, the *cis* molecules start to switch back to the *trans* state if a sufficient number of *cis* isomers in the island is achieved.[27]

In order to determine the driving process, we have studied the dependence of the threshold voltage on the tip height (Fig. 5). The results show that it is possible to switch the molecules with positive and negative bias voltage polarities and that the threshold value changes with the tip-surface distance. At rather small tip heights below about 8 Å (thus at values characteristic for STM imaging), the threshold voltage changes only slightly, which means that the isomerization is probably induced by the tunneling electrons in the junction (this mechanism has recently been reported[28, 29]), similar to photo-isomerization causing excitation of the molecule. At larger tip heights (beyond about 9 Å), the threshold voltage turns out to increase approximately linearly, at different slopes for the four cases, with the tip height. This behavior, together with the observation that isomerization can still be induced at large tip heights of 12–16 Å (where almost no tunneling current is flowing) and even above,[27] strongly points to an electric field-induced isomerization. This mechanism has not been observed experimentally so far, but was recently predicted by theory.[30]

The slopes of the data points at large tip heights correspond to electric fields between 0.1 and 0.7 V/Å, which is less than the calculated ones (about 1–2 V/Å).[30] This is likely due to the presence of the surface (calculations were done for the gas phase) that enhances the permanent dipole and the polarizability of the molecule. The different slopes for the four cases in Figure 5 are probably caused by the delicate balance of these two properties along the reaction paths.

4. CONCLUSIONS

In conclusion, we have shown how the STM can be used to image and to trigger functionalized molecules on metal surfaces. While wheel-dimer molecules can be rolled on a Cu(110) surface upon lateral manipulation with the tip, reversible isomerization of azobenzene derivatives is induced by applying voltage pulses in the STM junction. Analysis of the manipulation signal in the first case and of the dependence of the isomerization on the STM parameters in the second case allows the characterization of the processes and the underlying mechanisms.

Acknowledgments: Funding by the Deutsche Forschungsgemeinschaft (through contract no. GR 2697/1-1 and the SFB 658) and by the European Integrated Project PICO INSIDE is gratefully acknowledged.

References and Notes

1. J. K. Gimzewski and C. Joachim, *Science* 283, 1683 (**1999**).
2. C. Joachim, J. K. Gimzewski, and A. Aviram, *Nature* 408, 541 (**2000**).
3. W. R. Browne and B. L. Feringa, *Nat. Nanotechnol.* 1, 25 (**2006**).
4. J. A. Stroscio and D. M. Eigler, *Science* 254, 1319 (**1991**).
5. L. Grill, K.-H. Rieder, F. Moresco, S. Stojkovic, A. Gourdon, and C. Joachim, *Nano Lett.* 6, 2685 (**2006**).
6. L. Grill, F. Moresco, P. Jiang, C. Joachim, A. Gourdon, and K.-H. Rieder, *Phys. Rev. B* 69, 035416 (**2004**).
7. W. Ho, *J. Chem. Phys.* 117, 11033 (**2002**).
8. M. Lastapis, M. Martin, D. Riedel, L. Hellner, G. Comtet, and G. Dujardin, *Science* 308, 1000 (**2005**).
9. M. A. Rezaei, B. C. Stipe, and W. Ho, *J. Chem. Phys.* 110, 4891 (**1999**).
10. A. J. Heinrich, C. P. Lutz, J. A. Gupta, and D. M. Eigler, *Science* 298, 1381 (**2002**).
11. L. Grill, K.-H. Rieder, F. Moresco, S. Stojkovic, A. Gourdon, and C. Joachim, *Nano Lett.* 5, 859 (**2005**).
12. L. Gross, K.-H. Rieder, F. Moresco, S. M. Stojkovic, A. Gourdon, and C. Joachim, *Nat. Mater.* 4, 892 (**2005**).
13. F. Moresco, *Phys. Rep.* 399, 175 (**2004**).
14. J. K. Gimzewski, C. Joachim, R. R. Schlittler, V. Langlais, H. Tang, and I. Johannsen, *Science* 281, 531 (**1998**).
15. F. Chiaravalloti, L. Gross, K.-H. Rieder, S. M. Stojkovic, A. Gourdon, C. Joachim, and F. Moresco, *Nat. Mater.* 6, 30 (**2007**).
16. L. Grill, K.-H. Rieder, F. Moresco, G. Jimenez-Bueno, C. Wang, G. Rapenne, and C. Joachim, *Surf. Sci.* 584, L153 (**2005**).
17. G. Meyer, *Rev. Sci. Instrum.* 67, 2960 (**1996**).
18. L. Bartels, G. Meyer, and K.-H. Rieder, *Phys. Rev. Lett.* 79, 697 (**1997**).
19. D. L. Keeling, M. J. Humphry, P. Moriarty, and P. H. Beton, *Chem. Phys. Lett.* 366, 300 (**2002**).
20. L. Grill, K.-H. Rieder, F. Moresco, G. Rapenne, S. Stojkovic, X. Bouju, and C. Joachim, *Nat. Nanotechnol.* 2, 95 (**2007**).
21. An initial tip height of about 7 Å (determined from I(z) measurements) is the reference point for vertical feeds towards the surface.
22. S.-W. Hla, *Nat. Nanotechnol.* 2, 82 (**2007**).
23. B. L. Feringa, Molecular Switches, Wiley-VCH, Weinheim (**2001**).
24. T. Hugel, N. B. Holland, A. Cattani, L. Moroder, M. Seitz, and H. E. Gaub, *Science* 296, 1103 (**2002**).
25. C. Zhang, M.-H. Du, H.-P. Cheng, X.-G. Zhang, A. E. Roitberg, and J. L. Krause, *Phys. Rev. Lett.* 92, 158301 (**2004**).
26. M. delValle, R. Gutierrez, C. Tejedor, and G. Cuniberti, *Nat. Nanotechnol.* 2, 176 (**2007**).
27. M. Alemani, M. V. Peters, S. Hecht, K.-H. Rieder, F. Moresco, and L. Grill, *J. Am. Chem. Soc.* 128, 14446 (**2006**).
28. B.-Y. Choi, S.-J. Kahng, S. Kim, H. Kim, H. W. Kim, Y. J. Song, J. Ihm, and Y. Kuk, *Phys. Rev. Lett.* 96, 156106 (**2006**).
29. J. Henzl, M. Mehlhorn, H. Gawronski, K.-H. Rieder, and K. Morgenstern, *Angew. Chem. Int. Ed.* 45, 603 (**2006**).
30. G. Füchsel, T. Klamroth, J. Dokic, and P. Saalfrank, *J. Phys. Chem. B* 110, 16337 (**2006**).