

# Research Report

## Different tips for high-resolution AFM and STM imaging of single molecules

Fabian Mohn, Bruno Schuler, Leo Gross, and Gerhard Meyer

IBM Research – Zurich  
8803 Rüschlikon  
Switzerland

Copyright 2013 by the American Institute of Physics. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics.

The final version of this paper appeared in *Appl. Phys. Lett.* **102**, 073109 (2013) and may be found at <http://dx.doi.org/10.1063/1.4793200>

### LIMITED DISTRIBUTION NOTICE

This report has been submitted for publication outside of IBM and will probably be copyrighted if accepted for publication. It has been issued as a Research Report for early dissemination of its contents. In view of the transfer of copyright to the outside publisher, its distribution outside of IBM prior to publication should be limited to peer communications and specific requests. After outside publication, requests should be filled only by reprints or legally obtained copies (e.g., payment of royalties). Some reports are available at <http://domino.watson.ibm.com/library/Cyberdig.nsf/home>.



Research

Almaden • Austin • Brazil • Cambridge • China • Haifa • India • Tokyo • Watson • Zurich

## **Different tips for high-resolution AFM and STM imaging of single molecules**

Fabian Mohn, Bruno Schuler, Leo Gross,<sup>a)</sup> and Gerhard Meyer

*IBM Research – Zurich, CH-8803 Rüschlikon, Switzerland*

(Dated: 20 January 2013)

We explore new tip functionalizations for atomic force microscopy (AFM), scanning tunneling microscopy (STM), and Kelvin probe force microscopy (KPFM) of organic molecules on thin insulating films. We describe in detail how tips terminated with single Br and Xe atoms can be created. The performance of these tips in AFM, STM, and KPFM imaging of single molecules is compared to other tip terminations and the advantages and disadvantages of the different tips are discussed. The Br tip was found to be particularly useful for AFM and lateral manipulation, whereas the Xe tip excelled in STM and KPFM.

---

<sup>a)</sup>Electronic mail: lgr@zurich.ibm.com

In scanning probe microscopy, it is a commonly known fact that the exact atomic composition of the microscope tip apex has a critical influence on the image contrast. To prepare a good tip in scanning tunneling microscopy (STM) experiments, the tip state can be changed by applying voltage pulses, scanning at reduced set point heights, or even deliberately crashing the tip into the sample. These treatments are usually repeated until a stable tip with proper imaging contrast is obtained. However, these tip preparation procedures are mainly based on chance, and the resulting atomic structure of the tip is usually not known exactly. Since the first demonstration of controlled vertical atomic manipulation with STM<sup>1</sup> it is also possible to produce more defined functionalized tips by terminating the tip apex with individual atoms or molecules picked up from the sample surface. It was recognized early on that picking up single Xe atoms<sup>1-3</sup> or single CO molecules<sup>4,5</sup> from a metal substrate can enhance the resolution in STM imaging of surfaces and adsorbates. More recently, it was found that ultrahigh resolution of the geometrical structure of admolecules can be achieved with STM by bringing molecular hydrogen into the tunneling junction<sup>6</sup>, and the method was also then extended towards other tip terminations<sup>7</sup> (Xe, CO, and CH<sub>4</sub>).

In atomic force microscopy (AFM), the preparation and characterization of the tip is even more difficult than in STM, and consequently, the structure and chemical composition of the tip can often only be inferred indirectly by comparison with density functional theory (DFT) simulations<sup>8,9</sup> or from symmetry arguments<sup>10,11</sup>. Low-temperature scanning probe systems that offer the possibility of simultaneous STM and AFM operation enable the use of the established STM tip preparation techniques in AFM experiments on conducting substrates. Using this approach, it was recently shown that individual organic admolecules can be imaged with atomic resolution with AFM if the microscope tip is functionalized by picking up a single CO molecule or a single Cl atom<sup>12</sup>. The mechanism responsible for this high resolution was identified as Pauli repulsion between the tip atom/molecule and the imaged molecule. Soon thereafter, the possibility of using other tip terminations for high-resolution AFM imaging of molecules was explored in a theoretical DFT study, which predicted a strong influence of the two frontmost atoms of the tip molecule on the image contrast<sup>13</sup>. In this Letter, we describe how tips terminated with single Br, Xe, or Kr atoms or with a single NO molecule can be created in experiments on thin insulating films, and we explore the usefulness of these tips for STM and AFM imaging of single molecules.

Our experiments were performed with a homebuilt combined STM/AFM system using a

qPlus tuning fork force sensor<sup>14</sup> operated in ultrahigh vacuum (UHV,  $p \approx 5 \times 10^{-11}$  mbar) and at low temperature ( $T \approx 5$  K). For our AFM measurements, we operated the force sensor (resonance frequency  $f_0 \approx 28$  kHz, spring constant  $k \approx 1\,800$  N/m, quality factor  $Q \approx 50\,000$ ) in the frequency modulation mode, using oscillation amplitudes between  $0.3 \text{ \AA}$  and  $0.5 \text{ \AA}$ . To prepare the sample surface, NaCl was evaporated at a sample temperature of about 270 K onto a clean Cu(111) single-crystal surface, leading to the formation of (100)-oriented islands of mostly two atomic layers in thickness, which we denote as NaCl(2ML)/Cu(111). Low coverages ( $\sim 0.01 \text{ nm}^{-2}$ ) of Xe, Kr, NO, and CO for tip preparation were deposited on the surface at  $T \approx 10$  K by admitting these gases into the UHV chamber ( $p \approx 5 \times 10^{-8}$  mbar) and opening a shutter to the microscope stage for a few seconds. The organic molecules to be investigated were evaporated onto the cold sample from a piece of Si wafer flash-heated by resistive heating. As the microscope tip, we used a  $25 \mu\text{m}$  PtIr wire sharpened with a focused ion beam. Before creating the different functionalized tips by picking up single adsorbates as described in the following, we first prepared a clean and sharp metallic tip by repeated indentations into the Cu substrate.

In Fig. 1, the creation of a Br-terminated tip is shown. Because of its low sublimation temperature and its highly corrosive properties, Br cannot be easily deposited onto the sample surface. Therefore, we evaporated suitable brominated molecules such as dibromoanthracene (DBA) onto the NaCl(2ML)/Cu(111) surface. By STM manipulation it was possible to dissociate single Br atoms from these molecules, which could then be picked up with the STM/AFM tip to create a Br-terminated tip. This process is shown in Fig. 1(a,b). The left half of Fig. 1(a) shows two DBA molecules, from one of which a Br atom has already been dissociated. The tip was positioned above the intact molecule, and a sample bias voltage of  $V = 1.65$  V was applied. This led to a dissociation of one of the Br atoms from the molecule: The subsequent STM image in the right half of Fig. 1(a) shows a small circularly shaped unit at the former location of the intact DBA molecule. The remainder of the molecule as well as the other nearby molecule both changed their position during the dissociation, as indicated by the red dashed arrows. High-resolution AFM imaging (e.g. with a CO-terminated tip) of dissociated molecules confirmed that the small circular protrusion is a single Br atom dissociated from the molecule at the side that is imaged as a dark depression in the STM topography. No other dissociation products were observed. The dissociated Br atom could easily be picked up from the surface by approaching the tip by

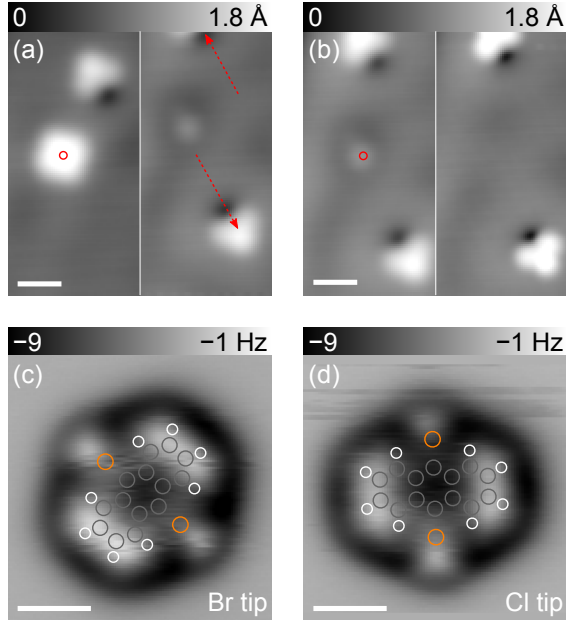


FIG. 1. (Color online) Br-terminated tip. (a) STM constant-current topographies (tunneling current  $I = 2$  pA, sample bias voltage  $V = 0.2$  V) of dibromoanthracene (DBA) on NaCl(2ML)/Cu(111) before (left half) and after (right half) applying a voltage pulse of 1.65 V with the tip at the position indicated by the red circle. (b) STM constant-current topographies ( $I = 2$  pA,  $V = 0.2$  V) before (left half) and after (right half) pickup of a single Br atom by approaching the tip by  $4 \text{ \AA}$  at the position indicated by the red circle. (c,d) Constant-height AFM images (vertical distance  $z = -0.5 \text{ \AA}$  from the STM set point  $I = 2$  pA,  $V = 0.2$  V above the substrate) of a DBA molecule on NaCl(2ML)/Cu(111). The images were recorded with (c) a Br tip and (d) a Cl tip, respectively. The calculated atomic positions are overlaid. Carbon, hydrogen, and bromine atoms are colored in gray, white, and orange, respectively. Scale bars:  $10 \text{ \AA}$  in (a,b),  $5 \text{ \AA}$  in (c,d).

$4 \text{ \AA}$  from the STM set point height, as shown in Fig. 1(b). As can be seen in the right half of this panel, the transfer of the Br atom to the tip apex is immediately recognized by an enhancement of the STM contrast. The Br-terminated tip was found to be very stable, and in Fig. 1(c), a constant-height AFM image of a DBA molecule recorded with a Br tip is shown. It shows an almost identical contrast as the AFM image recorded with a Cl tip shown for comparison in Fig. 1(d). Remarkably, the larger covalent radius of Br compared to Cl did not result in a lower resolution of the AFM image recorded with the Br tip.

Compared to the CO tip, the monatomic Br and Cl tips yield a lower resolution in

AFM imaging, but the images of polyaromatic hydrocarbons are also less distorted<sup>12</sup>. These differences are most likely both due to the fact that the CO molecule can tilt sideways more easily at the tip apex<sup>15</sup>, which leads to the very sharp features in the CO-tip images, as well as a distorted appearance of the imaged molecule<sup>16</sup>. Although the Br-terminated tip yields an identical contrast in AFM imaging as the previously used Cl tip, it has the great advantage that it is much easier to prepare, because the Br atom lying atop the NaCl surface does not need to be extracted from the crystalline NaCl. As an interesting side note, the Br tip was also found to be well suited for lateral manipulation of single DBA molecules on NaCl(2ML)/Cu(111) in the pulling mode, which is usually difficult to achieve on this substrate<sup>17</sup>. Similar tunneling-induced dissociations of single hydrogen and halogen atoms from aromatic hydrocarbons have been reported before in STM studies on metal surfaces<sup>18,19</sup>. The general procedure demonstrated here on the insulating NaCl film (that is, dissociating a target atom from a suitable molecule deposited on the surface), might also prove useful in other cases, where the atomic species of interest is difficult to prepare directly on the surface or difficult to distinguish from other adsorbates.

We now turn to the discussion of the Xe-terminated tip, which has previously been demonstrated to enhance the resolution in STM imaging<sup>1-3,7</sup>. In these studies, the Xe atoms were picked up from a metal substrate, and we show here that this can also be achieved on a thin NaCl film. After admitting Xe gas into the STM chamber, additional protrusions in STM imaging were found at the Cu step edges, as well as on the NaCl islands, where they were mainly localized next to other adsorbates, at defect sites, and at steps between two-monolayer (2ML) NaCl and three-monolayer (3ML) NaCl. The pickup of a Xe atom from such a NaCl step is shown in Fig. 2(a,b). In Fig. 2(a), several protrusions at the edge of a 3ML NaCl island can be distinguished (black dashed circles), which we attribute to individual Xe atoms. After picking up one of them by approaching the tip by 3 Å at the position indicated by the red circle, the STM imaging contrast is greatly enhanced [Fig. 2(b)], similarly to when a Xe atom is picked up from a Cu step edge. It should be noted that between panels (a) and (b) of Fig. 2, the tip height corresponding to the STM set point above the substrate changed by about 1.3 Å: that is, the tip appeared to be longer by that length after pickup of the Xe atom, which is reflected in the different topography scales of the two images. To assess the performance of the Xe tip in the imaging of single molecules, we recorded AFM, STM, and KPFM images of organic molecules on NaCl(2ML)/Cu(111). In Fig. 2(c,d), constant-

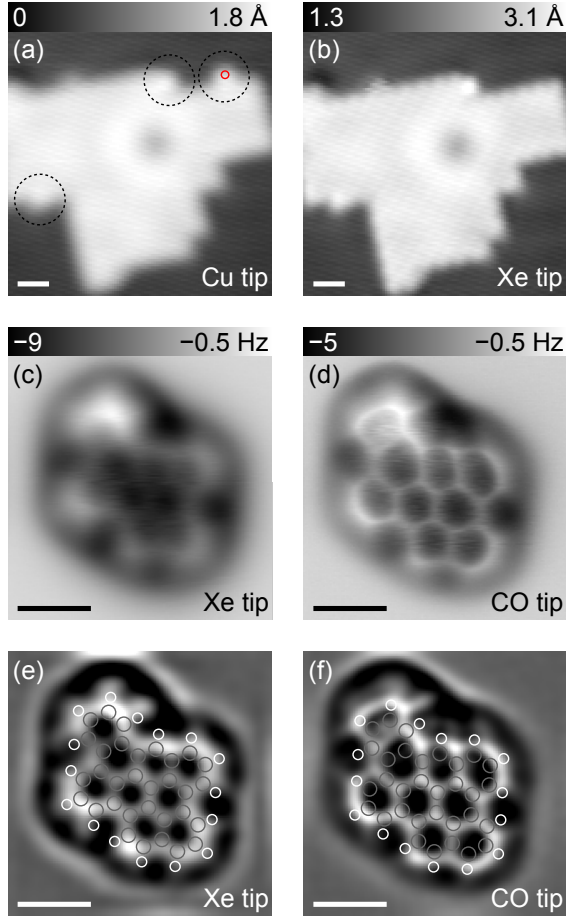


FIG. 2. (Color online) Xe-terminated tip: Creation and AFM imaging. (a) STM constant-current topography ( $I = 2 \text{ pA}$ ,  $V = 0.2 \text{ V}$ ) of a small patch of  $\text{NaCl}(3\text{ML})/\text{Cu}(111)$  on  $\text{NaCl}(2\text{ML})/\text{Cu}(111)$ . Individual Xe atoms can be recognized at the edge of the island, as indicated by the black dashed circles. (b) STM constant-current topography ( $I = 2 \text{ pA}$ ,  $V = 0.2 \text{ V}$ ) after pickup of a Xe atom by approaching the tip by  $3 \text{ \AA}$  at the position indicated by the red circle in (a). (c,d) Constant-height AFM images of a DBNP molecule on  $\text{NaCl}(2\text{ML})/\text{Cu}(111)$ . The images were recorded with (c) a Xe tip and (d) a CO tip, respectively. (e,f) Laplace and low-pass filtered versions of (c) and (d), with atomic positions overlaid. Carbon and hydrogen atoms are colored in gray and white, respectively. Scale bars:  $10 \text{ \AA}$  in (a,b),  $5 \text{ \AA}$  in (c-f).

height AFM images of a dibenzo(cd,n)naphtho(3,2,1,8-pqra)perylene<sup>20</sup> (DBNP) molecule are shown, recorded with a Xe (c) and a CO (d) tip, respectively. The Xe-tip image exhibits a faint atomic resolution, but the chemical structure of the molecule is more obvious in the CO-tip image. On the other hand, the Xe-tip image is much less distorted, as can be

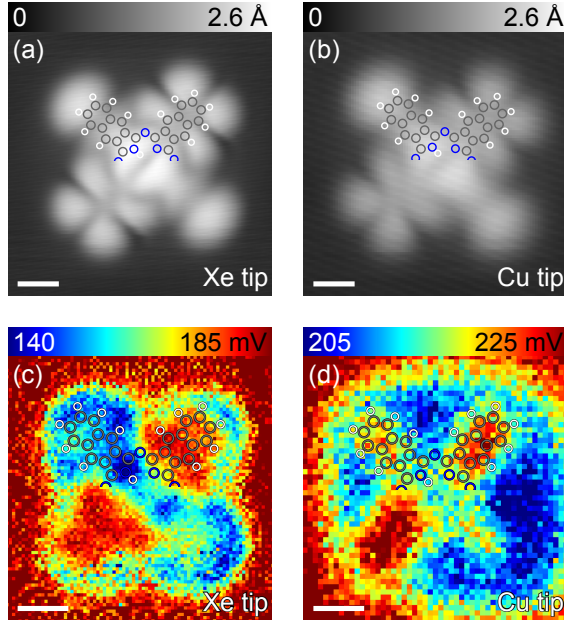


FIG. 3. (Color online) Xe-terminated tip: STM and KPFM imaging. (a,b) STM constant-current topographies ( $I = 2$  pA,  $V = 0.6$  V) of the LUMO resonance of a naphthalocyanine molecule on NaCl(2ML)/Cu(111), recorded with (a) a Xe tip and (b) a Cu tip, respectively. (c,d) LCPD images of a naphthalocyanine molecule on NaCl(2ML)/Cu(111), recorded with (c) a Xe tip and (d) a Cu tip, respectively. The images were both recorded at  $z = 0.8$  Å from the STM set point ( $I = 2$  pA,  $V = 0.2$  V) over the substrate. The atomic positions are overlaid in the upper halves of all panels. Carbon, hydrogen, and nitrogen atoms are colored in gray, white, and blue, respectively. Scale bars: 5 Å.

seen in the Laplace and low-pass filtered images shown in Fig. 2(e,f). Again, we believe that these differences are due to the fact that the CO can bend more easily at the tip apex. The Xe tip was also found to be very useful for STM orbital imaging<sup>21</sup>, where images recorded with CO tips are more difficult to interpret<sup>22</sup>. In Fig. 3(a), an image recorded at the voltage corresponding to the lowest unoccupied molecular orbital (LUMO) resonance of a naphthalocyanine molecule<sup>23</sup> is shown. With the Xe tip, the orbital structure is resolved much clearer than with a Cu-terminated tip [Fig. 3(b)], with the nodal planes appearing more pronounced for the same tunneling parameters. In contrast to STM orbital images recorded with CO-terminated tips, no signs of any  $p$ -wave contributions to the orbital images were observed for the Xe tip, that is, the image directly reflects the real-space structure of the molecular orbital. These findings were also confirmed in measurements of other molecular



orbitals. Finally, we also used the Xe tip to record an image of the local contact potential difference (LCPD) above naphthalocyanine, as recently reported for Cu- and CO-terminated tips<sup>24</sup>. This method corresponds to a traditional KPFM measurement<sup>25</sup> and was shown to be sensitive to the intramolecular charge distribution. The Xe-tip LCPD image shown in Fig. 3(c) shows qualitatively the same contrast as the Cu-tip LCPD image in Fig. 3(d) (that is, a higher LCPD above the molecular lobes perpendicular to the two central hydrogen atoms). However, it exhibits a more pronounced intramolecular contrast, with features comparable to the LCPD images recorded with CO tips at moderate heights (see supplement of Ref. 24). In conclusion, the Xe tip was very easy to prepare on NaCl(2ML)/Cu(111) (it was possible to pick up not only the Xe atoms at NaCl steps, as shown above, but also the ones that were captured by other adsorbates like organic molecules that had been prepared on the surface prior to Xe deposition). It was found to be very stable, even up to the elevated voltages needed to record orbital images, and it is an easy way to enhance the resolution in STM, AFM, and KPFM imaging of single molecules.

Finally, we also created Kr- and NO-terminated tips, but in our experiments they showed less favourable imaging characteristics than the other tips. The Kr tip could be prepared in a similar fashion as the Xe tip, and STM orbital images recorded with Kr tips also showed an enhanced resolution, but in general, it was difficult to create tips that were stable enough to enable reliable imaging. The NO tip was prepared by picking up a single NO molecule from NaCl(2ML)/Cu(111). Interestingly, it behaved quite differently from the CO tip (for example, atomically resolved AFM images of pentacene appeared less distorted). This confirms the influence of the second-frontmost tip atom on the imaging contrast predicted in Ref. 13. However, it was more difficult to prepare a good NO tip than a good CO tip, and in general, the NO tip showed less stable imaging behavior.

In conclusion, we have found that a number of different tip terminations can be prepared by picking up single adsorbates from a thin insulating NaCl film on Cu(111). We have assessed the performance of these tips in STM, AFM, and KPFM imaging of single molecules. We found the Br tip to be particularly useful for lateral manipulation and AFM imaging of single molecules, and the Xe tip for STM orbital imaging and KPFM imaging of single molecules. The combined information from images recorded with different tips – possibly in conjunction with three-dimensional imaging techniques for nonplanar adsorbates<sup>26</sup> – could in the future facilitate the extraction of information about the chemical composition of the

imaged molecules.

We thank Alejandro Criado, Diego Peña, and Enrique Guitián of the Center for Research in Biological Chemistry and Molecular Materials (CIQUS), University of Santiago de Compostela, for providing the DBNP molecules and Rolf Allenspach of IBM Research – Zurich for helpful comments. We would like to acknowledge financial support from the EU projects Herodot and ARTIST, and the ERC Advanced Grant CEMAS.

## REFERENCES

- <sup>1</sup>D. M. Eigler, C. P. Lutz, and W. E. Rudge, *Nature* **352**, 600 (1991).
- <sup>2</sup>B. Neu, G. Meyer, and K.-H. Rieder, *Mod. Phys. Lett.* **9**, 963 (1995).
- <sup>3</sup>A. Yazdani, D. M. Eigler, and N. D. Lang, *Science* **272**, 1921 (1996).
- <sup>4</sup>L. Bartels, G. Meyer, and K.-H. Rieder, *Appl. Phys. Lett.* **71**, 213 (1997).
- <sup>5</sup>H. J. Lee and W. Ho, *Science* **286**, 1719 (1999).
- <sup>6</sup>R. Temirov, S. Soubatch, O. Neucheva, A. C. Lassise, and F. S. Tautz, *New J. Phys.* **10**, 053012 (2008).
- <sup>7</sup>G. Kichin, C. Weiss, C. Wagner, F. S. Tautz, and R. Temirov, *J. Am. Chem. Soc.* **133**, 16847 (2011).
- <sup>8</sup>N. Oyabu, P. Pou, Y. Sugimoto, P. Jelinek, M. Abe, S. Morita, R. Pérez, and O. Custance, *Phys. Rev. Lett.* **96**, 106101 (2006).
- <sup>9</sup>Y. Sugimoto, P. Pou, M. Abe, P. Jelinek, R. Pérez, S. Morita, and O. Custance, *Nature* **446**, 64 (2007).
- <sup>10</sup>G. H. Enevoldsen, T. Glatzel, M. C. Christensen, J. V. Lauritsen, and F. Besenbacher, *Phys. Rev. Lett.* **100**, 236104 (2008).
- <sup>11</sup>J. Welker and F. J. Giessibl, *Science* **336**, 444 (2012).
- <sup>12</sup>L. Gross, F. Mohn, N. Moll, P. Liljeroth, and G. Meyer, *Science* **325**, 1110 (2009).
- <sup>13</sup>C.-S. Guo, M. A. Van Hove, R.-Q. Zhang, and C. Minot, *Langmuir* **26**, 16271 (2010).
- <sup>14</sup>F. J. Giessibl, *Appl. Phys. Lett.* **73**, 3956 (1998).
- <sup>15</sup>Z. Sun, M. P. Boneschanscher, I. Swart, D. Vanmaekelbergh, and P. Liljeroth, *Phys. Rev. Lett.* **106**, 046104 (2011).
- <sup>16</sup>L. Gross, F. Mohn, N. Moll, B. Schuler, A. Criado, E. Guitián, D. Penã, A. Gourdon, and G. Meyer, *Science* **337**, 1326 (2012).

- <sup>17</sup>I. Swart, T. Sonnleitner, J. Niedenführ, and J. Repp, *Nano Lett.* **12**, 1070 (2012).
- <sup>18</sup>S.-W. Hla, L. Bartels, G. Meyer, and K.-H. Rieder, *Phys. Rev. Lett.* **85**, 2777 (2000).
- <sup>19</sup>A. Zhao, Q. Li, L. Chen, H. Xiang, W. Wang, S. Pan, B. Wang, X. Xiao, J. Yang, J. G. Hou, and Q. Zhu, *Science* **309**, 1542 (2005).
- <sup>20</sup>A. Criado, D. Peña, A. Cobas, and E. Guitián, *Chem. Eur. J.* **16**, 9736 (2010).
- <sup>21</sup>J. Repp, G. Meyer, S. M. Stojković, A. Gourdon, and C. Joachim, *Phys. Rev. Lett.* **94**, 026803 (2005).
- <sup>22</sup>L. Gross, N. Moll, F. Mohn, A. Curioni, G. Meyer, F. Hanke, and M. Persson, *Phys. Rev. Lett.* **107**, 086101 (2011).
- <sup>23</sup>P. Liljeroth, J. Repp, and G. Meyer, *Science* **317**, 1203 (2007).
- <sup>24</sup>F. Mohn, L. Gross, N. Moll, and G. Meyer, *Nature Nanotech.* **7**, 227 (2012).
- <sup>25</sup>M. Nonnenmacher, M. P. O'Boyle, and H. K. Wickramasinghe, *Appl. Phys. Lett.* **58**, 2921 (1991).
- <sup>26</sup>F. Mohn, L. Gross, and G. Meyer, *Appl. Phys. Lett.* **99**, 053106 (2011).