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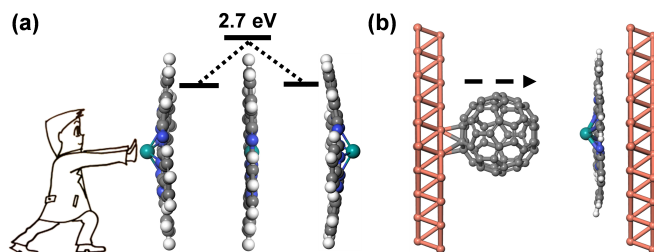
# Mechanochemistry induced with a robust functionalized tip

Yajie Zhang, Yongfeng Wang\*, Jing-Tao Lü\*, Mads Brandbyge, Richard Berndt

**Abstract:** Atomic-scale mechanochemistry is realized from force exerted by a C<sub>60</sub>-functionalized scanning tunneling microscope tip. Two conformers of tin phthalocyanine can be prepared on coinage metal surfaces. A transition between these conformers is induced on Cu(111) and Ag(100). Density functional theory calculations reveal details of this reaction. Because of the large energy barrier of the reaction and the strong interaction of SnPc with Cu(111), the process can not be achieved by electrical means..

Mechanical force has been used as a stimulus to initiate or accelerate chemical reactions through ultrasound and milling<sup>[1–6]</sup>. Force activated chemistry has been investigated by mass spectrometry, electron spin resonance spectroscopy, vibrational spectroscopy, and X-ray diffraction<sup>[1,2,4,6]</sup>. These methods average spectroscopic signals from a large number of molecules. Although many stimulating results on atomic and molecular manipulation with STM or AFM have been reported,<sup>[7–15]</sup> mechanochemical reactions are less well understood at a single-molecule level.<sup>[16–19]</sup>

In previous work, metal tips have been used to exert force on a target molecule and to induce a reaction. Unfortunately, metal tips tend to be flexible and, consequently, functionalized tips may be useful to trigger reactions with high activation barriers. Here, tin phthalocyanine (SnPc) is investigated as a model system for mechanochemistry [Fig. 1(a)]. The SnPc molecule has a shuttlecock structure, where Sn atom is located outside the Pc plane. When SnPc is adsorbed on Cu(111), the Sn ion either points towards the substrate (Sn-down) or vacuum (Sn-up). A reaction barrier of  $\approx 2.7$  eV prevents transitions between these conformers. We use mechanical manipulation to overcome this barrier. The Sn ion in SnPc adsorbed to a Cu(111) substrate is pushed with a C<sub>60</sub>-functionalized STM tip from the up state to the down state [Fig. 1(b)]. During this process, the strong bonds within C<sub>60</sub> molecule ensure the stability of the tip. We did not accomplish the same reaction with Cu tips. During the reaction, Sn loses  $\approx 0.8$



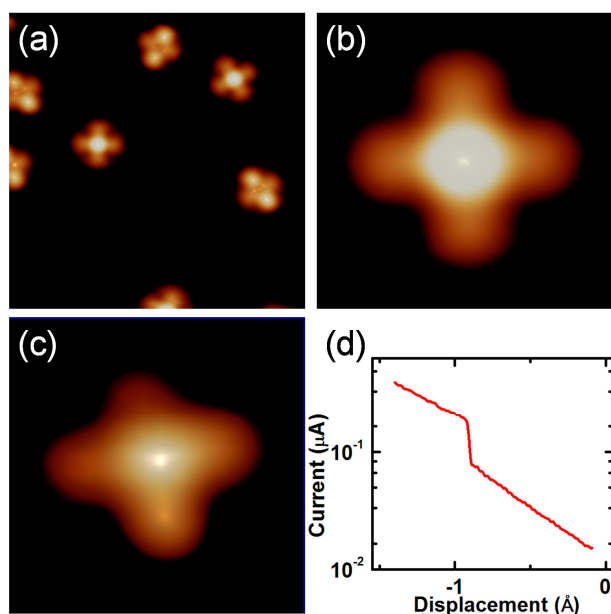
**Figure 1** (a) The height of the energy barrier preventing the motion of the Sn ion of Sn phthalocyanine (gas phase) through the ring structure is calculated to be  $\approx 2.7$  eV. (b) Model structure of a C<sub>60</sub> tip pushing SnPc on Cu(111).

electron and the adsorption energy increases by  $\approx 1.0$  eV. In contrast to earlier work on Ag(111)<sup>[20]</sup>, this reaction could not be induced by electrical current or field. These observations highlight the unique opportunities of single molecule mechanochemistry for studying reactions on surfaces.

The Sn-up and Sn-down configurations of SnPc are conveniently discernible in STM images<sup>[21,22]</sup>. The positions of Sn lead to a protrusion and a depression, respectively, at the center of the molecule. While SnPc is C<sub>4</sub> symmetric, the adsorption to Cu(111) reduces the symmetry to C<sub>2</sub> as shown in Fig. 2(a). This reduction is more obvious for Sn-down molecules due to a stronger molecule-surface interaction which is 1.0 eV larger than that of Sn-up molecule on Cu(111) from DFT calculations. The molecules are isolated from each other possibly because the repulsion induced by quantum interference of the surface state electrons exceeds the intermolecular attraction from C-H...N hydrogen bonds<sup>[23]</sup>. On the Ag(111) surface, a configuration change from the Sn-up to Sn-down state has been induced via hole injection into an occupied molecular states. This was achieved by applying negative voltage pulses to the sample<sup>[20]</sup>. Similar attempts to switch SnPc molecules on Cu(111) failed. Voltage pulses in the range from  $-4$  to  $4$  V applied to Sn-up molecules at various tip surface distances either left the molecule unchanged or caused its decomposition. Figs. 2 (b) and 2 (c) show an example. One lobe of the molecule appears lower after a current/voltage pulse presumably due to the breaking of C-H bonds<sup>[22]</sup>.

Given the failure of electrical manipulation, we tried to push the central Sn atom through the Pc ring with mechanical force. To this end, the STM tip was centered above a SnPc molecule, the current-feedback of the microscope was disabled and the tip was brought closer to the central Sn ion. To characterize the approaching process, the current was simultaneously recorded [Fig. 2 (d)]. Afterwards, the tip was retracted again and the surface was imaged. Typically, the contacted molecule had dis-

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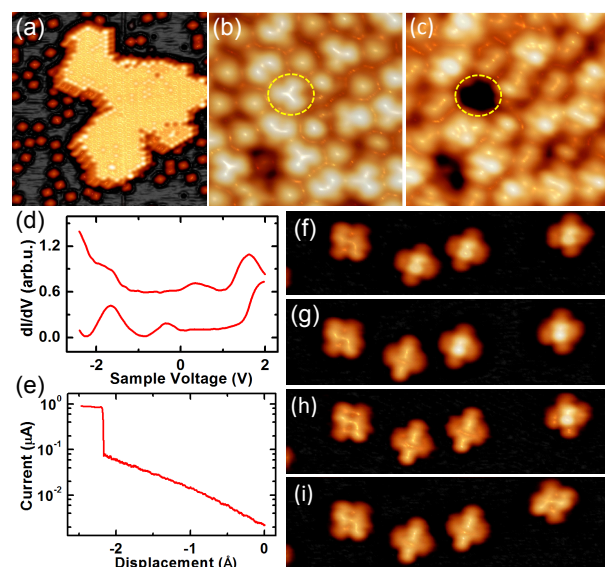
**Figure 2** (a) Constant-current topograph of SnPc on Cu(111). Image size:  $(12 \text{ nm})^2$ , sample voltage  $V = 0.1 \text{ V}$ , current  $I = 40 \text{ pA}$ . (b) Magnified topograph of a SnPc-up molecule.  $(2 \text{ nm})^2$ ,  $0.1 \text{ V}$ ,  $40 \text{ pA}$ . (c) STM image of the molecule in (b) recorded after applying a voltage pulse at  $-2.5 \text{ V}$  for a period of 10 seconds to the molecular center with current feedback disabled. Instead of being switched from Sn-up to Sn-down, the upper lobe appears lower in the STM image. (d) Current as a function of tip displacement towards the SnPc molecule with  $V = 0.1 \text{ V}$ . Zero displacement is defined by feedback parameters of  $0.1 \text{ V}$  and  $0.7 \text{ nA}$ . Negative displacements indicate a reduced tip-sample distance.

appeared from the image and the image itself appeared blurred. These observations suggest that the abrupt jump in the current originates from a transfer of the molecule to the tip apex. Not surprisingly, the metallic tip is reactive towards the SnPc molecules. Related experiments were performed with decomposed SnPc molecules [Fig. 2 (c)]. Apparently these molecules are more firmly attached to the Cu(111) substrate and do not transfer to the tip. Rather, we observed changed image contrasts as expected from atomic rearrangements at the tip apex.

A less reactive and robust STM tip appeared to be necessary to push the Sn atom through the Pc ring. We therefore prepared  $C_{60}$ -functionalized tips, which have been shown to be stable at the harsh conditions that occur during the formation of a highly conductive molecular contact<sup>[24,25]</sup>.  $C_{60}$  molecules were deposited on Cu(111) surfaces that had previously been partially covered with SnPc. Fig. 3 (a) shows that  $C_{60}$  forms close-packed islands among isolated SnPc molecules. In high-resolution STM images [Fig. 3 (b)] the three main orientations of  $C_{60}$  on the Cu(111) surface are resolved<sup>[26]</sup>. To pick up a  $C_{60}$  molecule, the STM tip was firstly centered above a molecule [circle in Fig. 3 (b)] and then brought closer to the surface until the current, which was simultaneously recorded, showed an abrupt increase. After this procedure, the area was imaged again [Fig. 3 (c)] to verify that the contacted  $C_{60}$  molecule had been removed from the surface. Following Ref.<sup>[27]</sup>, we also verified the transfer of the  $C_{60}$

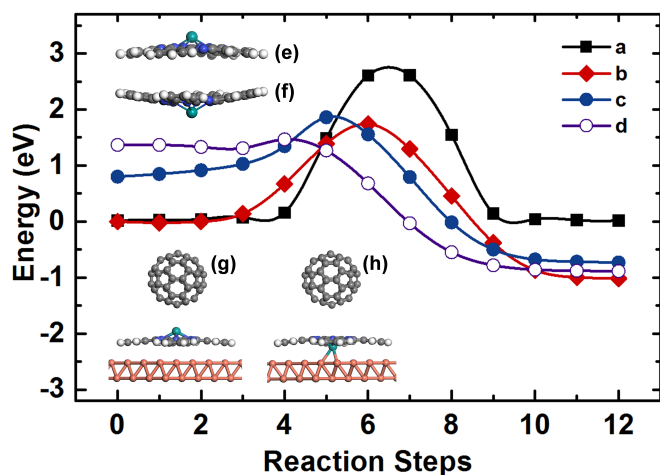
molecule to the tip by scanning tunneling spectroscopy. Spectra recorded with a  $C_{60}$ -tip on clean Cu(111) [lower curve in Fig. 3 (d)] are closely related to those observed from  $C_{60}$  on the substrate (upper curve). The voltage scale appears to be inverted between the two spectra because the molecular levels are pinned to either the tip or the sample.

When scanning Sn-up molecules with the  $C_{60}$ -modified tip, the central Sn ion is the highest protrusion and thus serves to image the  $C_{60}$  molecule at the tip. Fig. 3 (f) shows that the  $C_{60}$  molecule at the tip makes the Sn ion appear twice with similar heights. By comparison with images of  $C_{60}$  on Cu(111) measured with metallic tips<sup>[26]</sup> we infer that the molecule at the tip points to the sample with a hexagon-hexagon bond.



**Figure 3** (a) Topograph of dispersed SnPc molecules and a compact  $C_{60}$  island on Cu(111). (b) Detailed topograph of the  $C_{60}$  island. After recording this image, the  $C_{60}$  molecule indicated by a circle was transferred to the tip. (c) Same area as in (b), imaged after  $C_{60}$  transferred to the tip. (d) The differential conductance spectra  $dI/dV$ . The upper curve was obtained at a  $C_{60}$  on the substrate using a metallic tip. The main features are attributed to the HOMO ( $-1.8 \text{ eV}$ ), LUMO ( $0.3 \text{ eV}$ ), and LUMO+1 ( $1.8 \text{ eV}$ ). The lower curve was recorded on a clean substrate area with a  $C_{60}$  tip. It reveals similar features, albeit at a reversed voltage axis. (e) Current measured while bringing the  $C_{60}$  tip closer to the center of a Sn-up molecule  $V = 30 \text{ mV}$ . Negative displacements correspond to reduced tip-sample distances. (f) Topograph recorded with a  $C_{60}$  tip showing one Sn-down (leftmost molecule) and three Sn-up molecules. (g-i) Topographs displaying the stepwise conversion of the Sn-up molecules to the Sn-down states.

The thus prepared tip was used to contact Sn-up molecules at the center. First, the leftmost Sn-up molecule in Fig. 3 (f) was used. Fig. 3 (e) displays the evolution of the current. Once the tip was moved closer to the molecule by  $\approx 2 \text{ \AA}$ , the current drastically increased. Subsequent imaging with the same tip [Fig. 3 (g)] revealed that the SnPc molecule had been converted to Sn-down. The same process was repeated with the other Sn-up molecules of Fig. 3. Again, they changed from Sn-up to Sn-down. To be noted, the process can only be achieved at the molecular center.



**Figure 4** Results of DFT calculations of the reaction barrier to the motion of the Sn ion through the phthalocyanine frame at several typical tip-sample distances. The  $x$  axis represents steps along minimum energy path. (a) Barrier calculated without substrate and tip. The barrier height is  $\approx 2.7$  eV. (b–d) Barriers obtained taking substrate and tip into account. The tip was modeled by a  $C_{60}$  molecule, the Cu substrate was represented by two Cu layers. For calculating the barrier, the motion of the Sn ion was constrained to the line connecting the  $C_{60}$  and SnPc molecules. The distances between the lowest C-dimer and the Cu substrate were 7.92, 6.92, 6.42 Å in (b), (c) and (d), respectively. The barrier height is reduced drastically from (b) to (d). This reduction is due to the downward motion of the Sn atom pushed by the  $C_{60}$  tip. (e, f) Initial and final structures of the SnPc molecule corresponding to reaction path (a). (g, h) Initial and final structures of reaction path (b).

To gain further insight into the experimental results, we performed DFT calculations of the atomic motion and the reaction barriers during the pushing process. Fig. 4 shows results of nudged elastic band (NEB) calculations<sup>[28]</sup> of the flipping barrier at several tip-molecule distances. The purpose of this calculation is to show that the  $C_{60}$  tip may be used to push the Sn atom downward in position and upward in energy, eventually leading to flipping to the other side of the phthalocyanine frame. To keep the calculations tractable the  $C_{60}$  tip was modeled by a  $C_{60}$  molecule and the Cu substrate was represented by two Cu layers. Details of the calculation performed with the Vienna ab-initio simulation package (VASP)<sup>[29]</sup> can be found in the Method section. For a single SnPc molecule (without tip and substrate), the calculated barrier for Sn motion through the molecular plane is  $\approx 2.7$  eV [Fig. 4 (a)], similar to the previously reported result.<sup>[30]</sup> In the presence of the substrate, the barrier reduces to  $\approx 1.8$  eV [Fig. 4 (b)]. We confirmed by a separate calculation without  $C_{60}$  tip that, this reduction is due to the presence of the substrate, rather than the pushing by the  $C_{60}$  tip. The large energy barrier and the strong interaction of SnPc with Cu(111) make the switching of SnPc on Cu(111) by electrical means impossible.

Moving the  $C_{60}$  tip closer to the SnPc molecule lowers the position of Sn atom and reduces barrier to  $\approx 1$  eV [Fig. 4 (c)]. Continuing the movement further reduces the barrier [Fig. 4 (d)], and until the Sn atom is eventually pushed through the Pc plane. The reduction of the barrier in is due to the motion of Sn atom pushed

by the  $C_{60}$  tip, the initial system energy goes up in [Figs. 4 (c) and (d)]. In these calculations, neither the electric field in the junction nor the current play a role. This shows that the force exerted on the Sn ion by the  $C_{60}$  tip enables the transition from Sn-up to Sn-down.

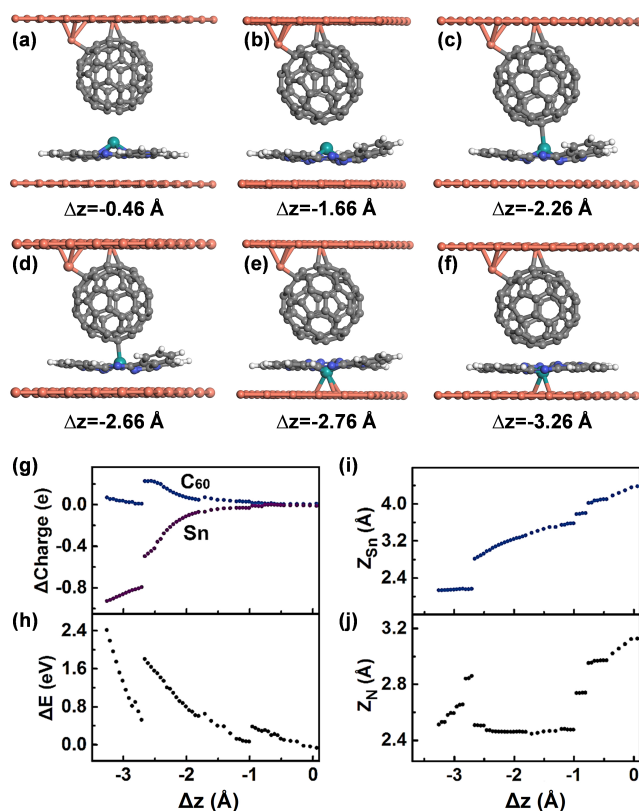
With the above general picture in mind, we treated a more realistic structure that includes the Cu(111) substrate and the tip, as schematically shown in Fig. 1 (b). The STM tip was modeled by a  $C_{60}$  molecule adsorbed on two (111) layers of Cu, the substrate was comprised of the SnPc molecule and three Cu layers. The choice of Cu as the tip material is motivated by the procedure used to prepare tips in the experiments. Typically, the tip, which was originally made from etched W wire, was brought into contact with the Cu substrate to obtain a sharp apex. For a set of 65 tip-sample separations, we relaxed the atomic positions of the  $C_{60}$  and SnPc molecules. To be able to treat these large numbers of atoms and configurations we used the SIESTA code (see Method section for details).

The calculations reproduce the main experimental result: A threshold distance, the Sn ion is pushed through the phthalocyanine plane. Typical structures before, during, and after the transition from Sn-up to Sn-down are shown in Figs. 5 (a–f). Before this transition takes place, a gradual electron transfer occurs from the Sn atom to the  $C_{60}$  molecule. Fig. 5 (g) displays the change of Mulliken charges at the Sn atom and  $C_{60}$  molecule. During the up-to-down transition, a sudden decrease of electron on Sn is found. Sn loses  $\approx 0.8$  electron. It reflects the formation of a chemical bond between the Sn ion and the Cu atoms of the substrate. The potential energy accumulated in the system before the up-to-down transition is  $\approx 1.8$  eV [Fig. 5 (h)]. The calculated maximum force is  $\approx 1.1$  nN. The transition is also evident from the evolution of the heights of the Sn ion and averaged position of four central N atoms above the substrate [Figs. 5 (i) and (j)]. In summary, the DFT calculations are consistent with the experimental results, and confirm that the mechanical interaction with a  $C_{60}$  tip forces the molecular conformation change and the formation of a chemical bond to the substrate.

The role of the substrate in the above experiments is twofold, it enables the application of a force and it participates in the chemical reaction. We therefore investigated a number of other surfaces using the same approach. Similar to the case of Cu(111), a conversion of SnPc molecules from the up to the down state was accomplished on Ag(100) using  $C_{60}$  tips. On Au(111) and Au(110) surfaces, however, no reaction could be induced. Either the contacted SnPc molecule laterally moved from its initial position or the  $C_{60}$  tip was destroyed during the processes. Presumably, the lower reactivity of Au has two detrimental effects. First, the barrier for lateral hopping of SnPc on Au substrates is expected to be lower than on Cu. Second, the  $C_{60}$  molecule is less firmly attached to the Au-covered tip<sup>[27]</sup>.

In man-made chemical reactions the energy required to overcome reaction barriers is usually provided in a stochastic manner by heating or illumination. On the contrary, mechanochemistry as demonstrated here is a more deterministic process. Through the force exerted with a STM tip, the system is driven along the





**Figure 5** Full calculation of the pushing process. The calculated system includes the SnPc and C<sub>60</sub> molecules as well as 3 (2) layers of Cu representing the substrate (tip). There are 6 × 7 Cu atoms in each layer. A series of 65 structures with different C<sub>60</sub>-SnPc distances was generated. For each structure, the C<sub>60</sub> and SnPc molecule were relaxed. (a–f) Typical relaxed structures obtained at characteristic tip-sample distances. Here, Δz = 0 corresponds to a distance of 7.92 Å between the lowest C-C dimer and the Cu surface. As the C<sub>60</sub> molecule is pushed downward, the Sn ion first moves downward, then passes the ring structure, and finally binds to the Cu surface. (g) Mulliken charges on C<sub>60</sub> (blue) and Sn (purple) molecules during the pushing process. (h) Relative change of the total energy during the pushing. (i, j) Heights of the Sn ion and averaged position of four central N atoms above the Cu substrate. The total energy of the Δz = 0 structure is chosen as the reference. In (g–j), the discontinuity at ≈ -2.7 Å corresponds to an abrupt motion of the Sn ion from the up to the down positions. Smaller jumps in (h) and (i) at ≈ -1 Å indicate lateral hops of the SnPc molecule on the substrate.

reaction path [Fig. 4]. In this respect, mechanical force offers a unique opportunity of realizing reactions in a deterministic way.

We have shown that mechanical force from a C<sub>60</sub>-functionalized STM tip can be used to realize single molecular mechanochemistry. DFT calculations reveal details of the process from Sn-up to Sn-down state of SnPc on Cu(111). Due to the large energy barrier and the strong interaction of SnPc with Cu(111), the reaction can not be achieved by electrical means. Our results highlight the unique role of mechanics in triggering chemical reactions at single molecular level. As a further step, it would be interesting to measure the force required to trigger this reaction using AFM.

## Method

The experiments were performed with a homebuilt ultrahigh vacuum STM operated at 5.0 K. Cu(111), Ag(100), Au(111), and Au(100) surfaces were cleaned by repeated cycles of argon ion bombardment and annealing. C<sub>60</sub> and SnPc molecules were thermally sublimated from tantalum crucibles at room temperature. All STM images were acquired in the constant-current mode and the voltage applied to the sample.

For the reaction barrier calculation, we used the VASP implementation of the DFT, where the electron-ion core interaction is treated using the Projected Augmented Wave (PAW) method<sup>[31]</sup>. We use the DFT-D3 method of Grimme<sup>[29]</sup> to account for the van der Waals (VDW) interaction between the molecules. For the full calculation, due to the large number of atoms involved, we use the SIESTA code. The GGA-PBE approximation is used for the exchange-correlation functional<sup>[32]</sup>.

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**Keywords:** Mechanochemistry · Force chemistry · Surface chemistry · Scanning tunneling microscope · Phthalocyanine

- [1] J. Sohma, *Prog. Polym. Sci.* **1989**, *14*, 451.
- [2] T. Q. Nguyen, H. H. Kausch, *Macromolecules* **1990**, *23*, 5137.
- [3] P. G. Gillespie, R. G. Walker, *Nature* **2001**, *413*, 194.
- [4] K. Lien Nguyen, T. Friščić, G. M. Day, L. F. Gladden, W. Jones, *Nat Mater.* **2007**, *6*, 206.
- [5] C. R. Hickenboth, J. S. Moore, S. R. White, N. R. Sottos, J. Baudry, S. R. Wilson, *Nature* **2007**, *446*, 423.
- [6] I. Halasz, A. Puškarić, S. A. J. Kimber, P. J. Beldon, A. M. Belenguer, F. Adams, V. Honkimäđki, R. E. Dinnebier, B. Patel, W. Jones, V. Štrukil, T. Friščić, *Angew. Chem. Int. Ed.* **2013**, *52*, 11538.
- [7] J. A. Stroschio, D. M. Eigler, *Science* **1991**, *254*, 1319.
- [8] W. Ho, *J. Chem. Phys.* **2002**, *117*, 11033.
- [9] S.-W. Hla, K.-H. Rieder, *Ann. Rev. Phys. Chem.* **2003**, *54*, 307.
- [10] F. Moresco, *Phys. Rep.* **2004**, *399*, 175.
- [11] N. Lorente, R. Rurali, H. Tang, *J. Phys.: Condens. Matter* **2005**, *17*, S1049.
- [12] A. J. Mayne, G. Dujardin, G. Comtet, D. Riedel, *Chem. Rev.* **2006**, *106*, 4355.
- [13] O. Custance, R. Perez, S. Morita, *Nat. Nanotech.* **2009**, *4*, 803.
- [14] L. Grill, *J. Phys.: Condens. Matter* **2010**, *22*, 084023.
- [15] K. Morgenstern, N. Lorente, K.-H. Rieder, *Phys. Status Solidi B* **2013**, *250*, 1671.
- [16] F. Moresco, G. Meyer, K.-H. Rieder, H. Tang, A. Gourdon, C. Joachim, *Phys. Rev. Lett.* **2001**, *86*, 672.
- [17] L. Grill, K.-H. Rieder, F. Moresco, S. Stojkovic, A. Gourdon, C. Joachim, *Nano Lett.* **2006**, *6*, 2685.

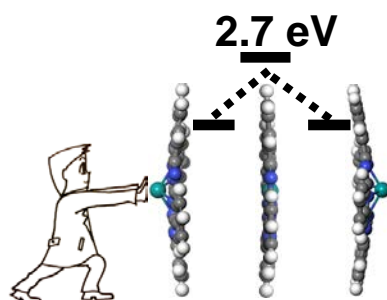
- [18] S. P. Jarvis, S. Taylor, J. D. Baran, N. R. Champness, J. A. Larsson, P. Moriarty, *Nat. Commun.* **2015**, *6*, 8338.
- [19] J. N. Ladenthin, T. Frederiksen, M. Persson, J. C. Sharp, S. Gawinkowski, J. Waluk, T. Kumagai, *Nat. Chem.* **2016**, *8*, 935.
- [20] Y. F. Wang, J. Kröger, R. Berndt, W. A. Hofer, *J. Am. Chem. Soc.* **2009**, *131*, 3639.
- [21] Y. F. Wang, J. Kröger, R. Berndt, W. A. Hofer, *Angew. Chem.* **2009**, *121*, 1287.
- [22] Y. F. Wang, J. Kröger, R. Berndt, H. Vázquez, M. Brandbyge, M. Paulsson, *Phys. Rev. Lett.* **2010**, *104*, 176802.
- [23] Y. F. Wang, X. Ge, C. Manzano, J. Kröger, R. Berndt, W. A. Hofer, H. Tang, J. Cerda, *J. Am. Chem. Soc.* **2009**, *131*, 10400.
- [24] G. Schull, T. Frederiksen, A. Arnau, D. Sánchez-Portal, R. Berndt, *Nat. Nanotechnol.* **2011**, *6*, 23.
- [25] T. Frederiksen, G. Foti, F. Scheurer, V. Speisser, G. Schull, *Nat. Commun.* **2014**, *5*, 3659.
- [26] N. Néel, J. Kröger, L. Limot, T. Frederiksen, M. Brandbyge, R. Berndt, *Phys. Rev. Lett.* **2007**, *98*, 065502.
- [27] G. Schull, T. Frederiksen, M. Brandbyge, R. Berndt, *Phys. Rev. Lett.* **2009**, *103*, 206803.
- [28] G. Henkelman, B. P. Uberuaga, H. Jónsson, *J. Chem. Phys.* **2000**, *113*, 9901.
- [29] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.
- [30] J. D. Baran, J. A. Larsson, *Phys. Chem. Chem. Phys.* **2010**, *12*, 6179.
- [31] G. Kresse, D. Joubert, *Phys. Rev. B* **1999**, *59*, 1758.
- [32] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865.

Entry for the Table of Contents (Please choose one layout)

Layout 1:

## COMMUNICATION

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