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Mechanochemistry induced with a robust functionalized tip

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Abstract: Atomic-scale mechanochemistry is realized from force exerted by a C60-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 Cu(111) and Ag(100), mechanical force has been used as an stimulus to initiate or accelerate chemical reactions through ultrasound and milling.[1–6] Force activated chemistry has been investigated by mass spectrometry, electron spin resonance spectroscopy, vibrational spectroscopy, and X-ray diffraction.[1,2,4,6] 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,[7–15] mechanochemical reactions are less well understood at a single-molecule level.[16–19]

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 ≈ 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 C60-functionalized STM tip from the up state to the down state [Fig. 1(b)]. During this process, the strong bonds within C60 molecule ensure the stability of the tip. We did not accomplish the same reaction with Cu tips. During the reaction, Sn loses ≈ 0.8 electron and the adsorption energy increases by ≈ 1.0 eV. In contrast to earlier work on Ag(111)[20], 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[21,22]. The positions of Sn lead to a protrusion and a depression, respectively, at the center of the molecule. While SnPc is C4 symmetric, the adsorption to Cu(111) reduces the symmetry to C2v 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[23]. 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[20]. 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[22].

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 Sn atom. 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-
Figure 2 (a) Constant-current topograph of SnPc on Cu(111). Image size: (12 nm)², sample voltage V = 0.1 V, current I = 40 pA. (b) Magnified to-pograph of a SnPc-up molecule. (2 nm)², 0.1 V, 40 pA. (c) STM image of the molecule in (b) recorded after applying a voltage pulse at −2.5 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 V. Negative displacements indicate a reduced tip-sample distance.

Figure 3 (a) Topograph of dispersed SnPc molecules and a compact C₆₀ island on Cu(111). (b) Detailed topograph of the C₆₀ island. After recording this image, the C₆₀ molecule indicated by a circle was transferred to the tip. (c) Same area as in (b), imaged after C₆₀ transferred to the tip. (d) The differential conductance spectra dI/dV. The upper curve was obtained at a C₆₀ island on the substrate using a metallic tip. The main features are attributed to the HOMO (−1.8 eV), LUMO (0.3 eV), and LUMO+1 (1.8 eV). The lower curve was recorded on a clean substrate area with a C₆₀ tip. It reveals similar features, albeit at a reversed voltage axis. (e) Current measured while bringing the C₆₀ tip closer to the center of a Sn-up molecule V = 30 mV. Negative displacements correspond to reduced tip-sample distances. (f) Topograph recorded with a C₆₀ tip showing one Sn-down (left most 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 moved closer to the molecule by ≈ 2 Å, 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.
We confirmed by a separate calculation without C until the Sn atom is eventually pushed through the Pc plane. The interaction of SnPc with Cu(111) by electrical means impossible. This reduction is due to the presence of the substrate, rather than the presence of the substrate, the barrier reduces to \(\approx 1\) eV [Fig. 4 (b)]. 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 con version 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 contact 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.

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
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$_{60}$ 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. We use the DFT-D3 method of Grimme 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 used the SIESTA code. The GGA-PBE approximation is used for the exchange-correlation functional.

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

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**Method**

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$_{60}$-functionalized STM tip can be used to realize single molecular mechanocatalysis. 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 cannot 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.

**Figure 5** Full calculation of the pushing process. The calculated system includes the SnPc and C$_{60}$ 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$_{60}$-SnPc distances was generated. For each structure, the C$_{60}$ 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$_{60}$ 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$_{60}$ (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.
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