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Pushing and Pulling a Sn Ion through an Adsorbed Phthalocyanine Molecule

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Abstract: Molecule-based functional devices on surfaces may take advantage of bistable molecular switches. The conformational dynamics and efficiency of switches are radically different on surfaces compared to the liquid phase. We present a design of molecular layers which enables bistable switching on a surface and, for the first time, demonstrate control of a single switch in a dense and ordered array at the spatial limit. Up and down motion of a central Sn ion through the frame of a phthalocyanine molecule is achieved via resonant electron or hole injection into molecular orbitals.

1. Introduction

Molecular switches on surfaces are intensely investigated because they provide insight into conformational dynamics of molecules and are potential components in molecule-based functional devices.[1−3] A prerequisite for applications such as data storage on a single molecule level will be the ability to switch a single molecule reversibly in densely packed arrays. External stimuli like light,[4,5] temperature,[6] and electric fields[7,8] have been used in the past to induce conformational changes. However, these stimuli do not provide single molecule selectivity. By contrast, the current injected from a scanning tunneling microscope tip is spatially localized to submolecular dimensions.[9−20] An additional problem arises due to lateral electron transport at metal surfaces, which may lead to nonlocal effects of current injection. This has prevented addressing a single molecule in a layer.[21] To counteract the nonlocal effect appropriate buffer layers can be used. The spacer moreover increases the lifetime of electronic excitations.[22]

Here, we demonstrate that single molecule switching can be attained in self-assembled layers utilizing the vertical motion of the central ion of tin−phthalocyanine (SnPc). The switching is constrained to the molecular frame and thus eliminates the need for lateral free space within the layer. Moreover, the switching event is confined to the specifically addressed molecule; i.e., adjacent molecules are not affected and retain their switch state. Owing to the SnPc adsorption structure in the second molecule layers and in higher layers, we can perform switching in a densely packed and ordered molecule array. We show that an irreversible switch of the vertical Sn position from up to down is feasible for molecules directly adsorbed on the metal substrate. A reversible interconversion of the two molecule conformations is achieved for molecules residing on a SnPc molecular buffer layer. The bistable states of this switch can be clearly discriminated in scanning tunneling microscopy images due to their high on/off conductance ratio. A comprehensive analysis including density functional calculations shows that switching is achieved via electron or hole injection. In particular, the efficiency of the switching process can be

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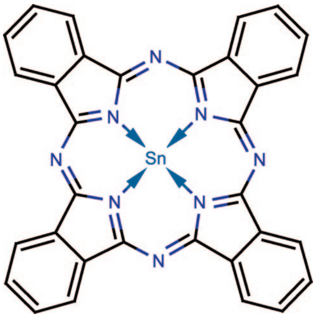

Figure 1. Molecular structure of SnPc.

understood in terms of resonant electron or hole tunneling to single molecular orbitals.

2. Experimental Section

The measurements were performed in a home-built ultrahigh vacuum scanning tunneling microscope operated at 7 K and in ultrahigh vacuum with a base pressure of 10^{-9} Pa. Ag(111) surfaces and W tips were cleaned by argon ion sputtering and annealing. A tantalum crucible was used to sublime highly purified SnPc molecules on the sample surface at room temperature. SnPc molecules adsorb on Ag(111) and remain intact. All STM images presented in this article were acquired in the constant-current mode with the voltage applied to the sample. Tunneling spectroscopy of the differential conductance was performed with a standard lock-in technique.

3. Results and Discussion

The structure of tin−phthalocyanine (SnPc) molecules is shown in Figure 1. According to previous X-ray diffraction experiments[23] and ab initio calculations,[24] which were performed for gas phase SnPc molecules, the central Sn atom does not belong to the molecular plane. Consequently, the molecule exhibits a shuttlecock geometry. Upon adsorption of SnPc on Ag(111), X-ray standing wave spectroscopy revealed the coexistence of two molecule conformations.[25] These conformations are characterized by two vertical positions of the Sn atom. In one conformation the Sn atom points toward the vacuum and is separated from the molecular plane by ∼0.09 nm, while in the other conformation the Sn atom points toward the surface and exhibits a distance of ∼0.05 nm from the molecular plane. In the following we refer to these conformations as Sn-up and Sn-down. Our calculations of the optimized structure of SnPc on Ag(111) using state-of-the-art all-electron density functional methods are in agreement with the previous observations (Figure 2A, B). In constant-current scanning tunneling microscopy (STM) images acquired at 7 K, Sn-up molecules appear with a central protrusion (Figure 2C and 2E), while Sn-down molecules exhibit a depression at the center (Figure 2D and 2F). A similar behavior was observed for SnPc adsorption on Ag(111),[26] on InSb(100),[27] and on highly oriented pyrolytic graphite,[28] and for PbPc adsorption on MoS_2[29] where molecules likewise appeared with bright and dark centers in STM images. Other phthalocyanine molecules appear uniformly with dark centers, e.g., CuPc,[30−36] H_2Pc,[36] and NiPc,[37] while others appear with bright centers, e.g., CoPc[35,37] and FePc.[39] We further find that the C_4 symmetry of the free molecule is reduced to C_2 upon adsorption on Ag(111), whose lattice exhibits a C_6 symmetry. This reduction of symmetry has also been reported for FePc on Cu(111)[40] and for CoPc on Cu(111).[41]

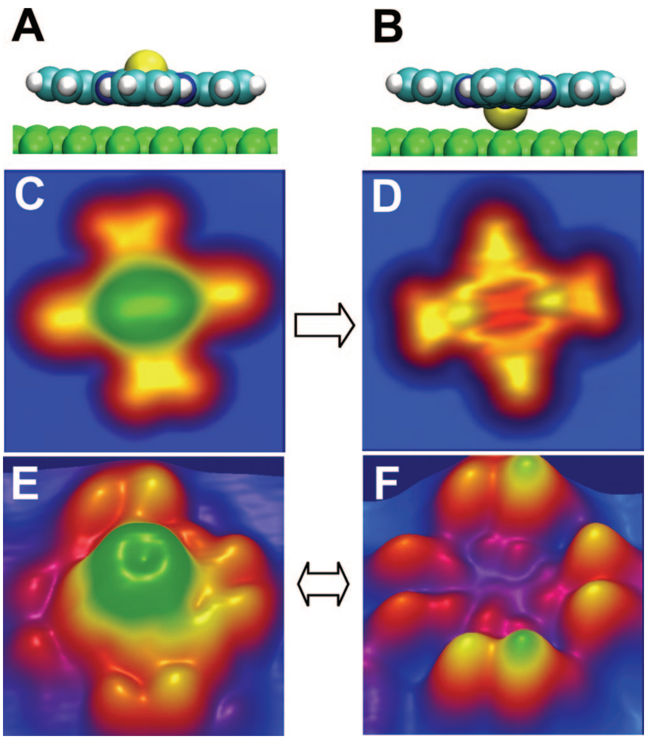

Figure 2. Adsorption conformations of SnPc on Ag(111) and on a SnPc layer. Side views of Sn-up (A) and Sn-down (B) molecules with fully relaxed adsorption geometry. (C and D) Pseudo-three-dimensional presentation of constant-current STM images of Sn-up (2.0 × 2.0 nm^2, −0.2 V, 0.05 nA) and Sn-down (2.0 × 2.0 nm^2, −0.05 V, 0.05 nA) molecules adsorbed on Ag(111). (E and F) STM images of Sn-up (2.0 × 2.0 nm^2, 0.9 V, 0.2 nA) and Sn-down (2.0 × 2.0 nm^2, −1.8 V, 0.2 nA) molecules adsorbed on a single SnPc layer. The single arrow between (C) and (D) illustrates the irreversible switching from Sn-up to Sn-down conformations, while the double arrow between (E) and (F) illustrates the reversible switching.

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Next, we tried to interconvert the Sn-up and Sn-down conformations. The switching properties of single molecules are summarized in Figure 2C−F. Molecules, which are directly adsorbed on the metal surface, may be transformed irreversibly from the Sn-up to the Sn-down conformation (Figure 2C and 2D, single arrow), while molecules residing on a SnPc buffer layer may be switched reversibly between the two conformations (Figure 2E and 2F, double arrow). We note that molecules which adsorb in the second layer or higher layers appear asymmetric in STM images. This observation may be traced to a tilt of the molecular plane. A similar tilt has been observed for FePc on Cu(111),[40] for CoPc on Au(111),[42] and for FePc on Au(111)[43] already in the second molecule layer and agrees well with bulk molecular properties.[44] The STM images presented in Figure 2C−F show unambiguously that the switching of SnPc molecules leads to bistable states which can be clearly discriminated. These states can be attributed to different molecular conformations rather than to purely electronic states. Indeed, the presence of Sn-up and Sn-down conformations of SnPc molecules on Ag(111) has been shown by X-ray standing wave spectroscopy experiments.[25] The different positions of the central Sn relative to the molecular frame correspond to different distances from the tip of the microscope. This ~0.14 nm distance change is consistent with an observed current variation by a factor of ~25 (Figure 3A). Our interpretation is in agreement with findings for PbPc adsorption on MoS_2.[29] The geometry of PbPc with Pb lying outside the molecular plane is similar to SnPc. Upon adsorption on MoS_2, STM images show two molecule conformations, which have been related to two vertical positions of the Pb atom. Most importantly, the reversible conformation change observed for SnPc exclusively affects the addressed molecule. The vertical translation of the central ion leaves the molecular frame unaffected. The SnPc molecule thus meets the key requirements for a molecular storage device: the size in the range of nanometers and the independence of the states of individual molecules or data bits. In the following we describe the switching process in more detail and suggest mechanisms which may drive this process.

Detailed measurements were performed to characterize the switching of SnPc adsorbed directly on Ag(111). Figure 3A shows a representative time series of the tunneling current passed through a Sn-up molecule with the tip centered above the Sn atom. Prior to opening the feedback loop the sample voltage V_S was set to $-$ 2.1 V and the current to 1.4 nA. After ~160 ms the current suddenly dropped by ≈ 95% to ≈ 0.06nA signaling the transformation from Sn-up to Sn-down. This irreversible change was confirmed by subsequent imaging (Figures 2C and 2D). Inducing the switching requires a sample voltage of $V_S \leq -1.9$ V. Figure 3B shows a strong increase of the yield, i.e., the number of switching events per tunneling electron, at this voltage. Spectra of the differential conductance (d*I*/d*V*) acquired at the center of a Sn-up molecule (upper data set in Figure 3C) exhibit a characteristic peak at ~ -2 V. Our calculations show that this peak is the spectroscopic signature of the second-to-highest occupied molecular orbital (HOMO−1), while the somewhat broader feature at ~ -1.4 V is related to the HOMO. Maps of d*I*/d*V* recorded at -1.9 V simultaneously with STM topographs reveal the spatial distribution of the HOMO−1 (Figure 3D and 3E) and show that it is localized at the central tin atom of Sn-up molecules, while Sn-down molecules are almost invisible at this voltage. In fact, d*I*/d*V* spectra taken on Sn-down molecules are featureless around -2 V (lower curve in Figure 3C). The localization of the HOMO−1 at the Sn site is also consistent with our calculations (see Supporting Information).

The localization of the HOMO−1 and its apparent importance for driving the conformation change from Sn-up to Sn-down offers the unique opportunity to induce highly localized switching (Figure 3G−I). Sn-up molecules denoted as P in Figure 3G and as Q in Figure 3H were addressed individually as described above and turned subsequently to Sn-down molecules denoted as p in Figure 3H and as q in Figure 3I. To suppress occasional lateral translations of molecules during the switching process (Q to q, Figure 3H and 3I) we fabricated a densely packed monolayer of SnPc on Ag(111). In this molecular layer the same conformational transformations from Sn-up to Sn-down were induced with the same parameters found for the single molecules (Supporting Information). In particular, these experiments make scenarios unlikely in which conformation changes are caused by modified adsorption sites, rotations of the molecule, or “flipover” processes.[13] Molecules with Sn-up conformation and adsorbed in the second or a higher layer likewise permit an irreversible and local switching to the Sn-down conformation at sample voltages corresponding to the energy of the HOMO−1 (Figure 3J−L).

By combining the experimental observations and calculated results, we arrive at the following hole attachment mechanism which drives the irreversible transition from Sn-up to Sn-down. Owing to resonant tunneling out of the HOMO−1 of Sn^{2+} to the tip, a positively charged molecule $(SnPc)^+$ is created, similar to a transient oxidation of the molecule by hole attachment. The transiently oxidized Sn^{3+} is smaller than Sn^{2+} which favors a new position of Sn^{3+} within the molecular plane. The calculated barrier height for transforming a nonplanar $(SnPc)^+$ to a transient $(SnPc)^+$, where Sn^{3+} is closer to the molecular plane, is 1.5 eV (Figure 3F and Supporting Information). In the experiment, we apply a voltage of ~ -2 V which provides ample energy for the tunneling electrons to induce the conformational change and to move the Sn^{3+} further to the substrate surface. As soon as Sn^{3+} binds to Ag(111), charge transfer from the substrate will turn the molecule to its neutral state. For this stable Sn-down conformation no clear HOMO−1-related spectroscopic feature was detected in d*I*/d*V* spectra (Figure 3C, lower curve) which we attribute to a stronger coupling of the Sn-down molecule to the metal surface.

The irreversible switching from Sn-up to Sn-down, discussed so far, is achieved through hole attachment to the molecule. Here, we arrive at an irreversible switching from Sn-up to Sn-down. Below we present a reversible switch realized via electron attachment. To this end the molecule has been effectively decoupled from the metal surface by a SnPc buffer layer. Indeed, we found that SnPc molecules residing on the decoupling layer enable reversible switching between the Sn-up and Sn-down conformations. The switching parameters are different from those obtained for molecules directly adsorbed on Ag(111). In particular, unoccupied states of the molecules appear to play an important role in this particular process. Figure 4A shows the d*I*/d*V* spectrum of a Sn-up molecule adsorbed on top of a SnPc buffer layer. The prominent peak at ~2.6 V is attributed to the second-to-lowest unoccupied molecular orbital (LUMO+1). For Sn-down molecules

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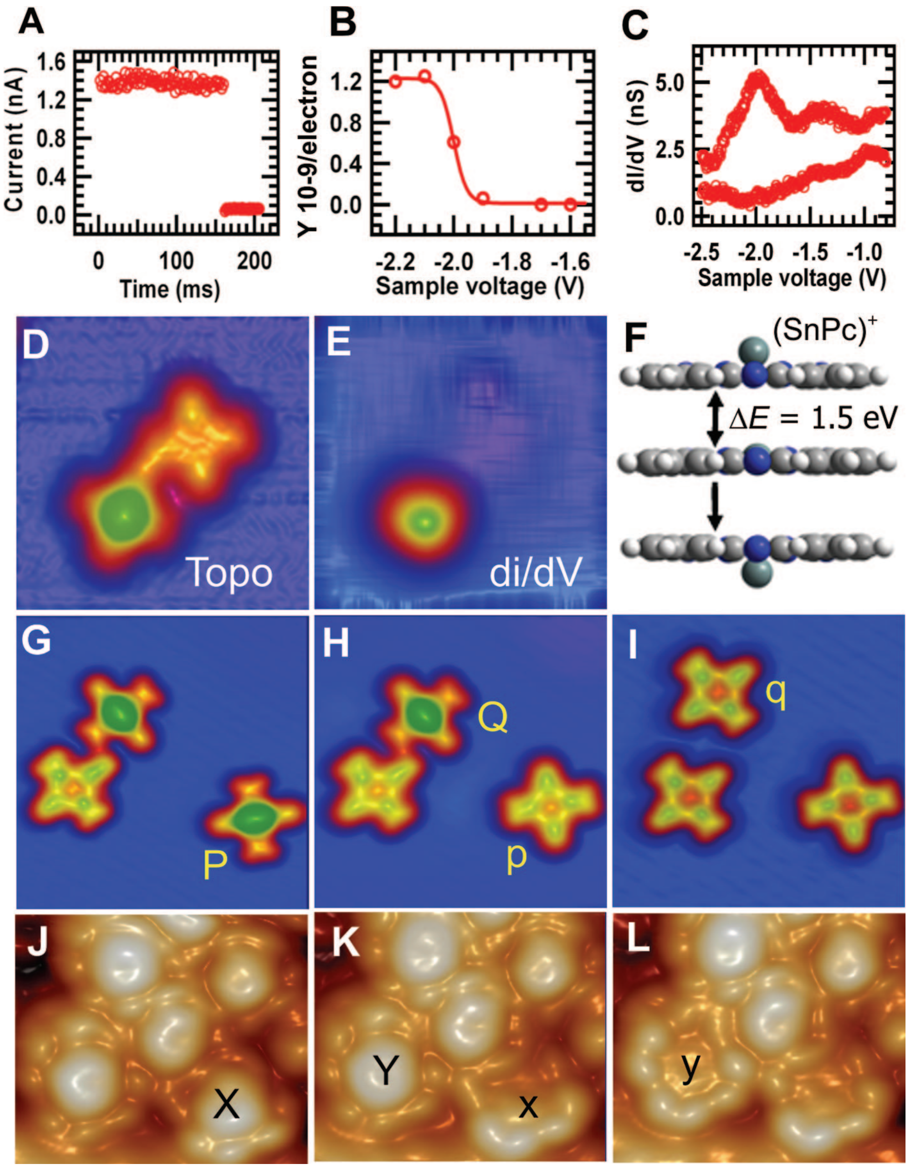

Figure 3. Irreversible switching of SnPc molecules residing on Ag(111) and on a SnPc buffer layer induced by hole attachment. (A) Time series of tunneling current acquired on the center of a Sn-up molecule with constant sample voltage of − 2.1 V and with a time resolution of 0.1 ms. (B) Number of switching events per tunneling electron (yield *Y*) as a function of sample voltage. (C) Spectra of the differential conductance (d*I*/d*V*) taken on Sn-up (upward pointing arrow) and on Sn-down (downward pointing arrow) molecule (tunneling gap parameters: −0.5 V, 0.2 nA). (D and E) Simultaneously recorded STM image and map of d*I*/d*V* of Sn-up (lower left) and Sn-down (upper right) molecule (4.4 × 4.4 nm^2, −1.9 V, 0.2 nA). (F) Schematic illustrating the switching from Sn-up via a planar molecule geometry to Sn-down. Transforming the nonplanar, positively charged Sn-up to a planar molecule requires an energy of 1.5 eV and is a reversible process (double arrow). The irreversible switching to Sn-down (single arrow) occurs when the Sn atom contacts the Ag(111) surface. (G−I) Sequence of STM images illustrating individual switching of Sn-up molecules [P in (G) and Q in (H)] to Sn-down molecules [p in (H) and q in (I)] on Ag(111) at a sample voltage of − 2 V (5.3 × 5.3 nm^2, −0.1 V, 0.05 nA). (J−L) Sequence of STM images illustrating individual switching of Sn-up molecules [X in (J) and Y in (K)] to Sn-down molecules [x in (K) and y in (L)] residing on a SnPc layer at a sample voltage of −2 V (5.0 × 4.6 nm^2, 1.4 V, 0.09 nA).

d*I*/d*V* spectra look similar and are not shown here. We found that the threshold voltage for a reversible switch is 2.8 V consistent with the injection of electrons into the LUMO+1. The reversibility of the switch is illustrated by a time series of the tunneling current acquired on a Sn-up molecule (Figure 4B). Prior to opening the feedback loop, the tunneling gap was defined at 4 V and 0.15 nA. A voltage of 4 V was chosen to obtain a sufficiently high switching rate. We then observed a two-level system characterized by tunneling currents of 0.15 nA and ~0.02 nA which correspond to Sn-up and Sn-down molecules, respectively. With increasing current the number of fluctuations between the two levels in a given time interval increased. With these parameters individually addressed, SnPc molecules were switched to the desired conformation as clearly shown by the sequence of STM images in Figure 4D−J. For this purpose the tip was positioned above the center of a Sn-down molecule and a time series of the current was acquired. After reaching one of the two current levels the voltage was reduced below the threshold voltage and the molecule was imaged. Starting from a column of Sn-down molecules (Figure 4D) single molecules were transformed to Sn-up molecules one by one until the same column consisted of Sn-up molecules only (Figure 4H). These molecules were then individually switched back to their initial Sn-down conformation (Figure 4J). In essence, the columns of four single SnPc molecules can be addressed, i.e., read and overwritten, like a four-bit memory cache. Given that the position of individual molecules in a close packed layer will remain stable, the cache

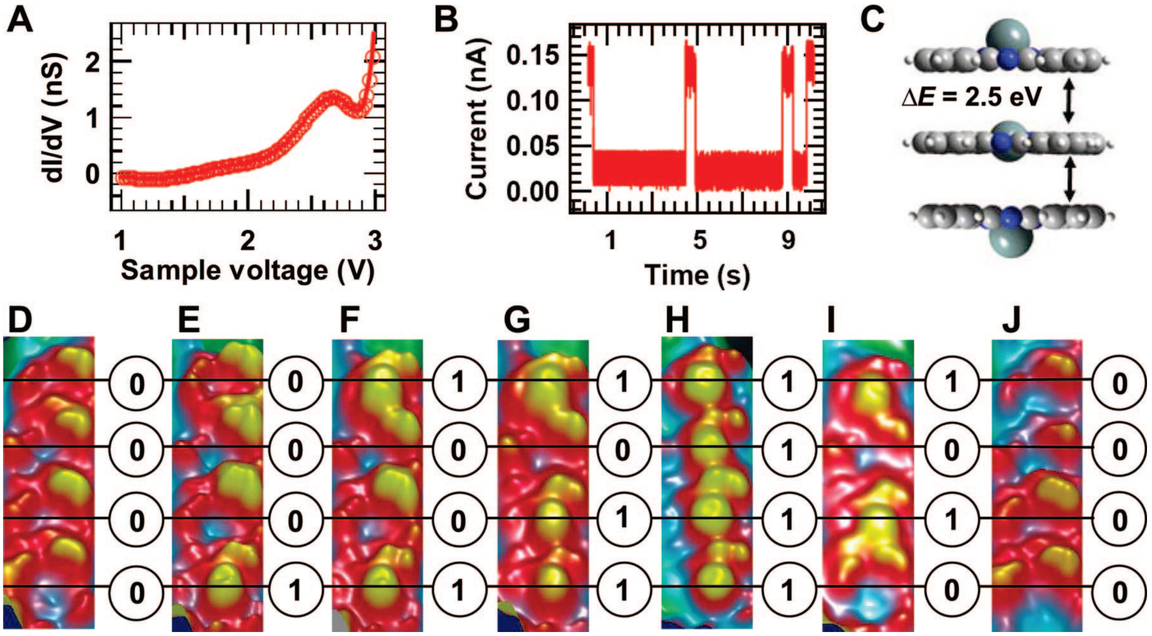

Figure 4. Reversible switching of SnPc molecules residing on a SnPc decoupling layer by electron attachment. (A) Spectrum of d*I*/d*V* of unoccupied states acquired on a single Sn-up molecule residing on a SnPc buffer layer adsorbed on Ag(111). The peak at 2.6 V is the spectroscopic signature of the LUMO+1. (B) Time series of tunneling current measured on a Sn-up molecule with open feedback loop (tunneling gap parameters: 4 V, 0.15 nA) and a time resolution of 2 μs. (C) Schematic illustrating the reversible transformation of a neutral or negatively charged Sn-up molecule via a planar molecule geometry to a Sn-down molecule. The calculated energy barrier is 2.5 eV. (D−J) Sequence of STM images of the same column of SnPc molecules which were switched from the Sn-down conformation (D) one by one to the Sn-up conformation (H) and back to the Sn-down conformation (J) by applying 4 V at the center of the individually addressed molecules (2.5 × 7.5 nm^2, 3.0 V, 0.03 nA). The numbers added to the STM images illustrate binary digits where 1 corresponds to Sn-up and 0 corresponds to Sn-down.

will remain operational even after multiple read/write operations. Interconversion of two molecule conformations have also been reported for single Zn(II)EtioporphyrinI,[10] single TbrPP-Co,[11] and single chlorophyll-a[12] molecules. For SnPc, as reported here, the molecular frame does not change; i.e., the switching process is essentially limited to the interior of the molecule, which enables single molecule switching in dense arrays.

The most likely mechanism leading to the reversible switching is the excitation of intramolecular vibrations.[45] The resonant transfer of tunneling electrons to the LUMO+1 gives rise to a negatively charged and thus transiently reduced molecule. Upon leaving the molecule the electron may deposit energy to vibrational degrees of freedom of the molecule and thus excite the switching process. The barrier height for inducing the switching was estimated by our calculations (Figure 4C and Supporting Information). Turning a negatively charged or neutral SnPc from the nonplanar to the almost planar geometry requires an energy of 2.5 eV which is in good agreement with the threshold voltage found in the experiments. The SnPc buffer layer plays an important role in the proposed mechanism of vibrationally excited states. A weak electronic coupling of the molecule to the metal substrate[46,47] leads to an increased lifetime of an additional electron attached to the molecule which in turn gives rise to an efficient energy transfer to intramolecular vibrations. The absence of a reversible switching of molecules directly adsorbed on Ag(111) and at positive voltages is in agreement with this picture. Stronger coupling of the molecule to the metal surface enables rapid transfer of the attached electron to the substrate. The buffer layer likewise inhibits the lateral propagation of the injected hot electrons and thus suppresses the nonlocal switching of molecules.

4. Conclusions

Starting from single SnPc molecules adsorbed on Ag(111), which allow a localized but irreversible conformational switching, we demonstrated that a densely packed SnPc layer effectively decouples second layer molecules from the metal surface and enables local and reversible switching. The bistable conformational states of the molecules can be clearly discriminated from each other and are spatially confined to the addressed molecule.

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Supporting Information Available: We show calculated charge density contours of SnPc in vacuum, which particularly show the localization of the HOMO−1 at the Sn site for Sn-up molecules. We further show calculations of the energy required to push the Sn atom through the molecular plane for differently charged molecules. An experimentally acquired STM image of SnPc molecules in a closed layer on Ag(111) demonstrates that switching is not related to a change of the adsorption site. This information is available free of charge via the Internet at http://pubs.acs.org.

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