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CONTROL OF DIPOLAR SWITCHES ON GRAPHENE BY A LOCAL ELECTRIC FIELD

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Abstract

The realization of molecular electronic devices relies on the ability to perform elementary operations with functional molecules. Molecular switches are established candidates to realize basic electronic functions and data storage. Macrocyclic molecules such as phthalocyanines and their derivatives provide a family of compounds that can be switched by external stimuli between two stable states. Using scanning tunneling microscopy we investigated tin phthalocyanine on graphene. We show that these molecules can be reversibly switched between two states and that the interaction of their electric dipole with a local electric field drives the switching yield and direction. The control at the single molecule level of the molecular conformation in a bidimensional lattice is then used to achieve high density data storage.

Introduction

Molecular switches can toggle between different stable states under external excitation. They play a key role in biology due to their ability to sense their environment.[1] They have been intensively studied as building blocks to realize basic functions in molecular electronics.[2] Most molecular switches rely on stereoisomerization,[3,4] tautomerization[5–7] or electrocyclization.[8] Macrocyclic compounds from the families of porphyrins and phthalocynanines have been particularly investigated in that context. Shuttlecock shaped lead phthalocyanine (PbPc) and tin phthalocyanine (SnPc) are characterized by a non planar structure with the central metal atom protruding out of the molecular plane leading to two stable states with the metal atom pointing on one side or the other of the molecule. These two conformations are identical in gas phase but are uneven on a substrate where the metal atom can point toward the vacuum region (up state) or the substrate (down state).

The charge distribution in these molecules induces a permanent electric dipole perpendicular to the molecular plane.[9] The switching of these molecules can be activated at the single molecule level with a scanning tunneling microscope (STM).[10–12] For PbPc, the two conformers are spontaneously present on a substrate, but no tip-induced switching could be achieved.[12–14] For SnPc on Ag(111), only an irreversible switching from up to down conformers could be induced.[10] A reversible switching has been achieved using a decoupling layer of SnPc[10] or Perylenetetracarboxylic dianhydride (PTCDA).[12] C. Nacci *et al.* have shown that single SnPc molecules can be reversibly switched when they are adsorbed on a semiconducting substrate of InAs(111).[11] The activation process of molecular switches by STM can involve an inelastic excitation eventually combined with an electric field[6,11,15,16] or resonant tunneling.[2,7,8,10,17–19] The local electric field in a STM junction has been employed in previous works to achieve molecular manipulation.[20–25] In the case of SnPc, the existence of a permanent electric dipole opens the opportunity to use an electric field to control the switching yield and direction, but the proper molecule-substrate combination has to be found to observe and investigate this mechanism. In particular it is expected to

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invert the switching direction by reversing the bias polarity. In previous studies, for second layer SnPc molecules, a reversible switching was observed at positive bias without evidence of dipolar interaction.[10] On PTCDA, an up to down conversion was measured at negative bias, whereas a down to up conversion was eventually observed at positive bias but suffered from a lack of reproducibility.[12] In the case of InAs substrate, an up to down transition was induced at negative bias, while a positive bias led to a down to up transition accompanied by a lateral displacement.[11]

With the recent advent of low dimensional materials, there has been a rise of interest for combining molecules with two dimensional materials.[26–32] Here we show that the combination of SnPc with graphene allows to obtain a system where the molecules in direct contact with the substrate can be reversibly switched and where the yield and direction of the switching is controlled by the interaction of the electric field with the molecular dipole. We also emphasize the specificity of the graphene substrate by comparing to the case of a Au(111) substrate where the switching is irreversible due to a quenching of the molecular dipole. In addition we show that data storage can be achieved with that system. Indeed, SnPc molecular lattice has been proposed as a suitable candidate to store binary information in idealized experimental conditions.[9] However a reliable binary data storage requires a periodic array and a controllable reversible switching with different writing parameters for the two bit values. These conditions have not been reached in the above mentioned molecular systems and are fulfilled on graphene.

Methods

Multilayer ($\approx$5-10) graphene samples were obtained on SiC(000$\bar{1}$) by annealing the substrates in ultrahigh vacuum (UHV) at 1320°C for 12 min under a silicon flux of $\approx$1ML/min. After synthesis, the sample was transferred in air to a UHV chamber and degassed for a few minutes before the measurements. SnPc molecules (TCI Chemical) were sublimated using

a low temperature effusion cell (Dr. Eberl MBE-Komponenten GmbH) under vacuum at 300° C onto the samples at the STM stage maintained at ≈5 K. STM measurements were performed with a low-temperature STM apparatus (Omicron) working at 4.6 K at a pressure lower than 1×10^{-10} mbar. The dI/dV spectra were acquired using a lock-in detector at a frequency of ca. 823 Hz and a modulation amplitude of 35 mV. The measurements were performed with an electrochemically etched tungsten tip. Before measuring on graphene, the tip was calibrated on a Au(111) surface until it shows the Shockley surface state feature in the spectroscopic measurements.

Density Functional Theory (DFT) calculations have been performed in order to characterize accurately the SnPc molecule on graphene in support of the experimental results. Hence, we have used the very efficient localized-orbital basis set DFT code Fireball[33] to optimize the molecular geometries, determine the total energy of the system and the electronic densities. In particular we have modelled the molecular network on graphene, considering a 9×9 square cell of graphene with four SnPc molecules on top, before optimizing it until the forces went lower than 0.1 eV/Å. Also, we have determined the electronic properties of the single SnPc molecule on a 15×15 hexagonal cell of graphene, by optimizing two molecular structures, one with the Sn atom in up position and the other with the Sn atom in down position. We have consequently determined the corresponding electrostatic dipoles from the atomic positions and electronic charges. By varying rigidly the position of the Sn atom between the down and up states, we have determined the energy barrier of molecular switching, as well as the intermediate dipoles along the switching process. Finally, once we have obtained the atomic and electronic structure with Fireball, we use a standard W tip within the non-equilibrium Keldysh Green function formalism to estimate the tunneling current for the STM simulations.[34,35]

Results and Discussion

On a Au(111) substrate, single SnPc molecules exhibit two types of topographical signatures with a node or a maximum in the center (Fig 1a) which are attributed to down and up conformations respectively. The up configuration is more frequent (we observed 86% of molecules in the up state on a sample of 370 molecules). This distribution is supported by our ab initio calculations that give a total energy of the up molecule that is 0.47 eV below the total energy of the down molecule on Au(111). These two configurations are better distinguished in the conductance maps (Fig. 1(b-c)) that reflect the downshift in the electronic spectrum of the molecules measured by dI/dV spectroscopy (Fig. 1d). A conductance map at negative bias also reveal a contrast between up and down configurations (supplementary information Fig. S1). For the up conformation two resonances are measured at 1.1 V and -1 V. When measuring the spectrum from positive to negative bias, an abrupt decrease is observed around -1.5 V. The voltage of the jump was measured between -1.5 V and -1.7 V on different molecules. This jump corresponds to the switch of the SnPc molecule from up to down. In all our attempts it was not possible to switch back the molecule from down to up, using a sample bias voltage ranging between -4 V and +4 V. The spectroscopy of the down state reveals a resonance at +0.8 V, although the features are less pronounced on that conformation, possibly because of a stronger interaction with the substrate, which corresponds to the LUMO of the molecules. The only difference comes from the intensity of the central protusion due to the position of the Sn atom. The irreversibility of the switching is similar on Au(111) to what has been reported on Ag(111).[10]

On graphene, the low molecule-surface interaction prevents single molecule imaging as previously reported for other molecules.[30,32] Therefore, after molecule deposition on graphene at low temperature, the sample was annealed to room temperature to allow for diffusion and subsequently cooled down for measurements. As a result, the molecules arrange in a nearly square lattice with unit cell vectors $a = 1.34 \pm 0.01$ nm , $b = 1.31 \pm 0.02$ nm at an angle of $91 \pm 1°$ (Fig. 2a). This lattice corresponds to the lowest energy structure obtained by
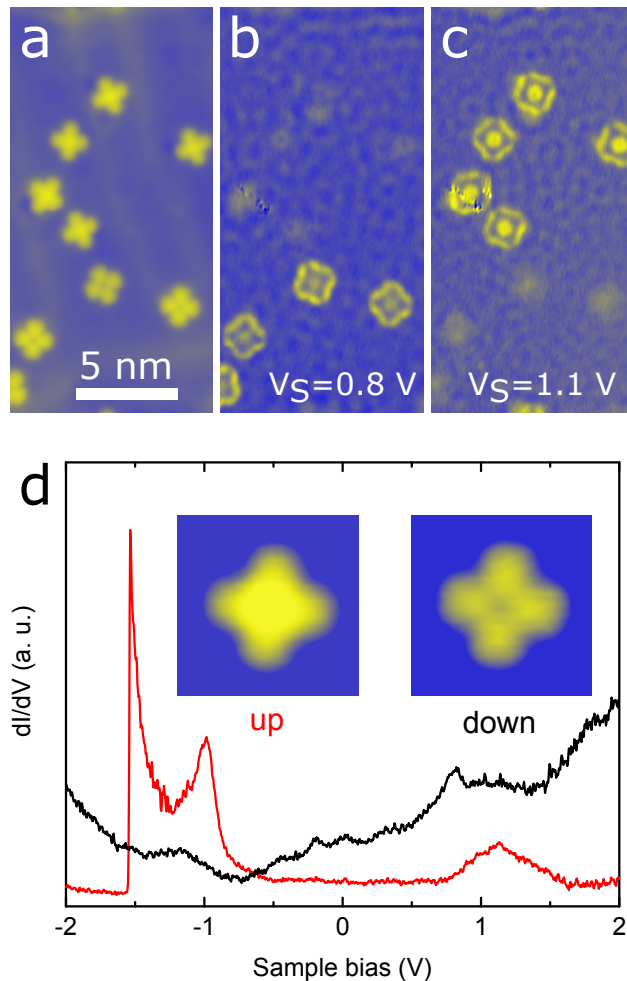
Figure 1: (a) STM image of SnPc on Au(111) (1 V, 200 pA). The five molecules on top are in the up state. The four molecules in the bottom part are in the down state obtained after tip induced switching. (b-c) Conductance maps at 0.8 V (b) and 1.1 V (c) of the same area as in (a). (d) dI/dV spectra of up (red) and down (black) conformations of SnPc molecules. The spectra where measured by ramping the sample bias voltage from positive to negative values. At the end of the dI/dV measurement of the up state the molecule switches to a down state at - 1.53 V. The insets show the STM image of up and down states of SnPc ((1 V, 200 pA, image size 2.5 nm×2.5 nm).

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optimizing the molecular structure on graphene using Density Functional Theory (DFT) calculations (see Methods for details) as shown in Fig. 2b. Experimentally, we find that all molecules are naturally in the up state. This is due to a higher stability of the up state for which the total energy is lower by 0.94 eV as revealed by our *ab initio* calculations performed on the two configurations shown in Fig. 2c. Moreover, the adsorption energy is -3.2 eV for a molecule in the up state and -1.2 eV for the down state (see supplementary information Fi. S2). Our calculations also reveal that the SnPc is acting as an electron acceptor with a fractional negative charge of 0.038 electron for the up state and 0.048 electron for the down state. Inside the molecule, the Sn atom has an extra negative charge of 0.59 electron for the up state and 0.64 electron for the down state. In gas phase, the extra charge of the Sn atom is found to be 0.61 electron, therefore the charge of the Sn atom changes by -0.02 electron for the up state and +0.03 electron for the down state. The increase of the Sn charge for the down state can be due to the stronger molecule-graphene interaction. Due to the non-homogeneous distribution of the charge in the molecule, the SnPc exhibits a dipole of 2.33 D for the up state and 4.27 D for the down state with a contribution in the z direction of 2.14 D for up and -3.75 for down. In the gas phase, the calculated dipole is 2.76 D in the z direction. In contrast to the case of metallic substrates, it is possible to reversibly switch the molecules between the two states with the STM tip on graphene as shown in Fig. 2d. With the STM tip above a molecule, a voltage sweep between 3 V and - 3 V leads to two subsequent switching at negative and positive bias. When ramping the bias voltage from 3 V to -3 V, a jump appears in the I(V) curve at negative bias corresponding to a switch of the molecule from the up to the down state. reversing the ramping a jump appears at positive bias corresponding to a down to up transition. Therefore, the I(V) curve exhibits a hysteresis loop indicating a remarkable dependence of the switching direction with the voltage polarity. Successive images taken before and after voltage ramping show the the two types of switching events (Fig. 2e). To unambiguously identify the up and down conformers in the topographical images, we have calculated STM images from the optimized configurations

obtained in DFT (see Methods). The images show that the up state exhibits a bright spot in the center of the molecule while the down state exhibits a depletion in the center of the molecule, in full agreement with the experimental images (Fig. 2f). We also measured the electronic spectrum of the two states by dI/dV spectroscopy revealing a downshift of the molecular states for the down configuration as compared to the up state (Fig. 2g) similar to what has been measured on Au(111) (Fig. 1d).
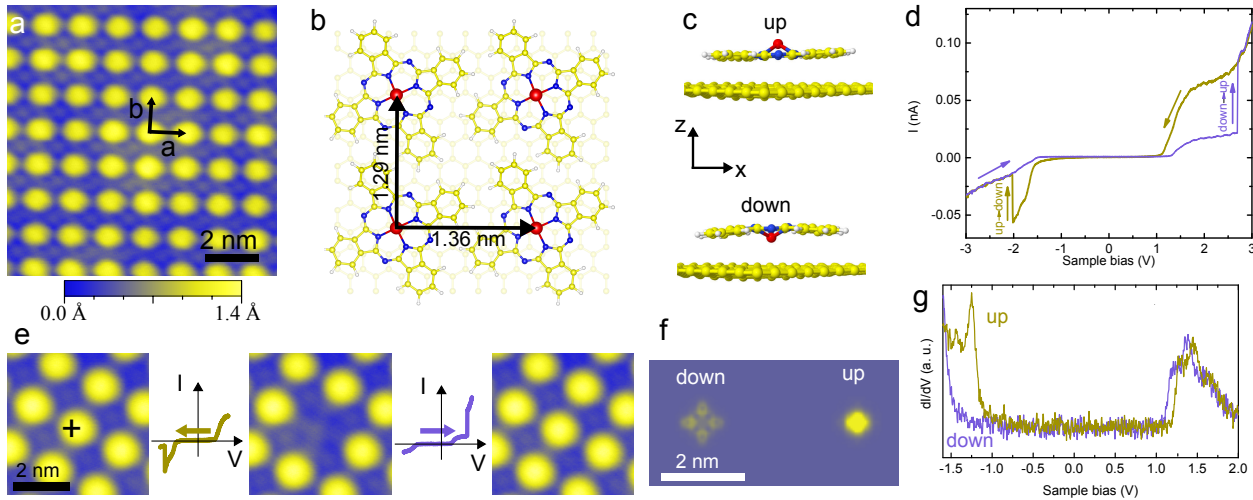

Figure 2: (a) STM image of a SnPc lattice on graphene measured at 1.5 V, 5 pA. All molecules are spontaneously in up state. (b) Calculated structure of the SnPc lattice on graphene in the up state. Color code for atoms: C-yellow, H-white, N-blue, Sn-red. (c) Calculated structure of SnPc in up (top) and down (bottom) states on a monolayer of graphene. (d) I(V) signal measured with the STM tip above the center of a SnPc while ramping the bias voltage from 3 V to -3 V (yellow curve) and then from -3 V to 3 V (blue curve). The arrows indicate the direction of voltage ramping. (e) Successive images (1.5 V, 10 pA) recorded on the same area in its pristine state (left), after switching the central molecule by ramping the bias voltage from +3V to -3 V (center) and switching back by ramping the bias voltage from -3 V to 3 V (right). The I(V) signal recorded during the manipulation is indicated between the corresponding images. The arrows indicate the arrows indicate the direction of the voltage sweep. (f) Calculated STM images of SnPc on graphene in the up state (left) and down state (right) at 1.5 V. (g) dI/dV spectroscopy measured at the center of a SnPc molecule in up state (yellow) and in down state (blue).

The I(V) curves obtained during the voltage sweep show that the switching of the molecules occurs only in one direction at a given voltage polarity. However, when the tunneling conditions are optimized, by approaching the STM tip and measuring on long timescale,

we observed that it is possible to reverse the switching at both polarities as evidenced by the emergence of a telegraph signal in the tunneling current. Figure 3a shows the signal measured for sample bias voltages of 2.4 V and -2.3 V. The lifetime of up and down state are clearly different, a higher lifetime is observed for the up (down) state at positive (negative) bias voltage. The difference of lifetime is partly due to the fact that the tunneling current is different for the two levels. In order to quantify the efficiency of switching excitation independently of the value of the tunnel current, we calculated the yield corresponding to the number of switch per electron. For each plateau in the current signal we calculated the yield $Y = e/I\tau$ where e is the electron charge, I is the mean value of the tunneling current and τ is the time spent in the state. Then we calculate the mean value of the yield $\overline{Y}$ for the up or the down state. The voltage dependence of the yields is reported in Fig. 3b,c. At positive bias, the down to up yield is around two orders of magnitude larger than the up to down transition. At negative bias this trend is inverted. Note that by changing the tip height to modify the tunneling current at a fixed bias voltage, the yield shows small variations (see supplementary information Fig. S3).

The inversion of the relation between the two yields with the bias polarity is an evidence of the interplay between the molecular dipole and the electric field. In Fig. 3d we present a simple dipolar interaction picture describing the expected typical energy profile of the molecule along the switching reaction coordinates under the application of an electric field. In the absence of an electric field, the up state has a lower energy than the down state as mentioned above. In the up state, SnPc has an electric dipole $\vec{P}$ with a positive component along the z axis (from graphene to vacuum). In the down state, the dipole is in the opposite direction. Under the application of an electric field $\vec{E}$, a dipolar potential energy $-\vec{P}.\vec{E}$ adds up to the molecule energy. When the electric field is positive (negative) along the z direction, the dipolar energy is positive (negative) for the down state and negative (positive) for the up state. This energy is larger for the down state due to a larger electrostatic dipole.

In the middle position where the metal atom is in the molecular plane, there is no dipole
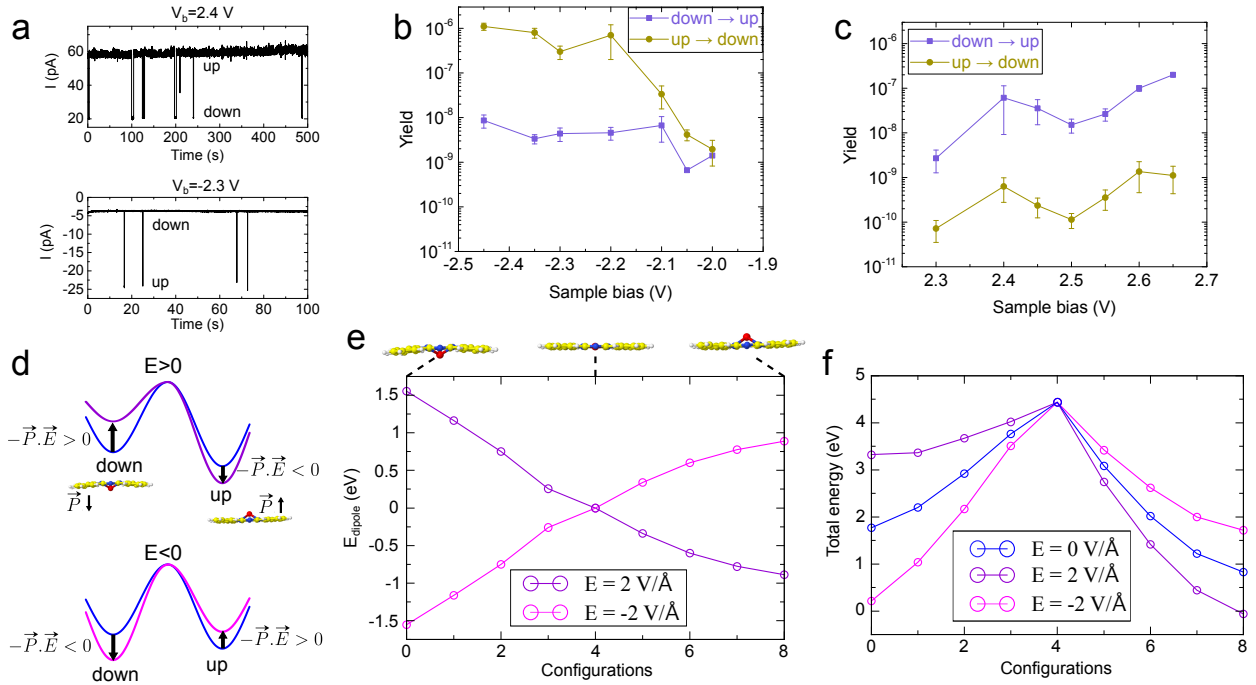
Figure 3: (a) Tunnel current recorded above a SnPc molecule while applying a bias voltage 2.4 V (top) and -2.3 V (bottom). The tip-sample separation was reduced from the starting setpoint of 1.5 V, 5 pA by 0.2 Å for negative bias measurements and 0.8 Å for positive bias. The same conditions were applied for data shown in (b) and (c). (b) Switching yield for down to up (blue) and up to down (yellow) at negative bias voltages. (c) Same as (b) for positive bias voltage. (d) Schematic illustration of the role of the electric field on the switching of SnPc molecules. The blue curve corresponds to the energy profile of a molecule as function of its conformation from down to up state. When a positive electric field is applied (top part) the potential energy corresponding to the interaction of molecular dipole with the electric field is positive for the down state and negative for the up state. The resulting expected energy profile of the molecule under positive electric field is shown with the purple curve. The bottom part shows the effect of a negative electric field. (e) Dipole energy calculated for down (0), up (8) and intermediate configurations with an electric field of 2 V/Å. The schemes show the molecular conformations for states 0, 4 and 8. (f) Calculated total energy of SnPc on graphene for molecular configurations going from down state (0) to up state (8). Energy calculated without electric field, and with positive and negative electric field. The zero energy was set to be at the bottom of the graph and correspond to a calculated total energy of -76510 eV.

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moment in the z direction, therefore the dipolar energy cancels. Therefore, for positive bias, the energy of the down state increases and the energy of the up state decreases, leading to a lower energy barrier for down to up transition than for the up to down transition. This explains well the higher yield for down to up transition measured experimentally (Fig. 3c). At negative bias, the electric field and dipolar energies are reversed and the up to down transition is favored (larger yield in Fig. 3b). It is worth noticing another difference between the positive and negative electric field cases. The application of a negative electric field increases the energy of the up state and decreases the energy of the down state. Without electric field the up state has a lower energy, the application of a negative electric field can invert the situation and can lead to a up state with a higher energy than the down state. Therefore at negative bias, an increase of the electric field amplitude could progressively induce an inversion of the switching yields relation.

At low negative electric field, a higher yield is expected for the down to up transition, while at large electric field it is the up to down transition that is expected to show a higher yield. This could explain that in Fig. 3b the yields are close around -2 V and the down to up yield becomes larger than up to down when the bias amplitude is increased. Another set of data measured on the same molecule with a larger tunnel current confirm an inversion of the yields order at -2 V (supplementary information Fig. S4). In order to test the dipolar model hypothesis, we performed further DFT calculations. Hence, we have considered 9 molecular configurations consisting in relaxed down (0) and up (8) states, and intermediate configurations with the Sn atom displaced between the two final positions (supplementary information Fig. S5). For each configuration we have computed the dipole momentum in the z direction (from the atomic position and their respective electronic charges obtained in DFT) and calculated the corresponding potential energy due to its interaction with an applied electric field of 2 V/Å(Fig. 3e). The dipolar energy was then added to the DFT calculated potential energy in order to obtain the total energy shown in Fig. 3f. For a positive electric field the energy of the down state increases and the energy of the up state

decreases. For a negative electric field, the trend is reversed. The energy variation of the down state is larger than that of the up state which is due to the larger dipole of the down state. The calculations agree well with the model described above based on the interaction of the molecular dipole with the applied electric field that drives the switching yield of the molecules. This interaction explains the crucial difference between the properties of SnPc on Au(111) and on graphene. The calculated spatial distribution of charge density shows that on Au(111) the charge density of the molecule and the substrate merge together while on graphene they are well separated (supplementary information Fig. S6). As a consequence the molecule keeps its dipole on graphene but not on Au(111) and the electric field effect measured on graphene does not occur on the metallic substrate. Finally, the hysteretic behaviour of molecule switching due to the dipolar interaction allows for a perfect control of the state of molecules in a monolayer. This allows to store binary data as demonstrated by writing an artificial pattern as shown in Fig. 4. Since all molecules are initially in the up state, the pattern was realized by switching selected molecules to the down state. The switching was done by placing the tip above selected molecules and applied a voltage pulse of -2.5 V during 100 ms. The resulting pattern is stable and no spontaneous switching was observed in the timescale of the experiment. Considering each molecule as one bit of memory with an area corresponding to the molecular lattice unit cell 1.75 nm^2, the SnPc on graphene allows to store information with a very high density of 57 Tbit/cm^2.
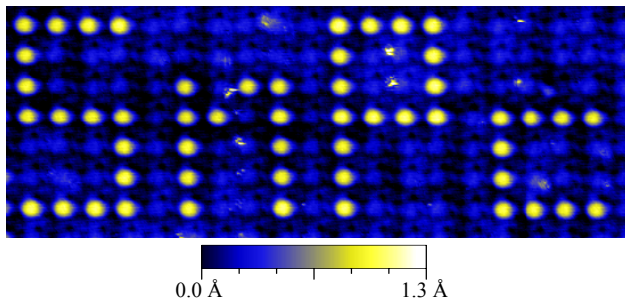

Figure 4: STM image of an artificial pattern written in a SnPc molecular lattice on graphene 27 nm ×10 nm (1.85 V, 3 pA).

Conclusions

In conclusion, SnPc molecules on graphene were shown to form bidimensional array of molecular switch. In contrast to the case of metallic substrates where a switching can be induced by STM irreversibly from up to down state, the switching on graphene is reversible. We have shown that the electric field plays an essential role in the control of the molecular switches. The molecules tend to switch in order to align their electric dipole with the applied electric field. As a result, $I(V)$ curves show a hysteresis evidencing that negative electric field (from tip to sample) favors a switching from the up state to the down state while a positive field favors a switching in the other direction. This mechanism is reproducible and the two states of molecules are stable, allowing for storing binary information as demonstrated by writing an artificial pattern in a molecular lattice.

Supporting Information Available

SnPc on Au(111). Adsorption energy of up and down states on graphene. Switching yield for different tip heights. Switching yield at negative bias voltage. Molecular conformations for calculated energies in a switching event. Spatial distribution of charge density for SnPc on Au(111) and on graphene.

Acknowledgement

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