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Voltage-Induced Bistability of Single Spin-Crossover Molecules in a Two-Dimensional Monolayer

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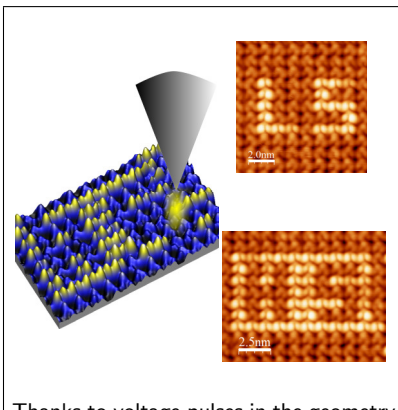
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Abstract

Bistable spin-crossover molecules are particularly interesting for the development of innovative electronic and spintronic devices as they present two spin states that can be controlled by external stimuli. In this paper, we report the voltage-induced switching of the high spin/low spin electronic states of spin crossover molecules self-assembled in dense 2D networks on Au(111) and Cu(111) by scanning tunneling microscopy at low temperature. On Au(111), voltage pulses lead to the non-local switching of the molecules from any - high or low - spin state to the other followed by a spontaneous relaxation towards their initial state within minutes. On the contrary, on Cu(111), single molecules can be addressed at will. They retain their new electronic configuration after a voltage pulse. The memory effect demonstrated on Cu(111) is due to an interplay between long range intermolecular interaction and molecule/substrate coupling as confirmed by mechanoelastic simulations.

TOC Graphic



Thanks to voltage pulses in the geometry of a scanning tunneling microscope it is possible to address single spin-crossover molecules in a 2D molecular network on Cu(111). Thus "LS" was written with molecules in low spin state and "HS" with molecules in high spin state.

Molecular electronics and spintronics aim at using molecules as elementary components.¹⁻³ In particular, switchable single molecules⁴⁻⁹ are attracting lot of interest for applications such as memory devices. Spin-crossover (SCO) molecules are prototypes of switchable and bistable components that are presently considered in this area.¹⁰⁻¹⁶ Their two electronic spin states reversibly switch with various stimuli (including temperature, light, electric field) via a transition process involving structural changes (volume and metal-ligand distances).^{17,18} Accordingly, they present a diagram of potential energy vs internal coordinate with two minima separated by an energy barrier similarly to bistable molecules. However, the occurrence of bistability (hysteretic transition) in spin crossover materials mainly results from cooperative elastic interactions taking place in the assembly of molecules.¹⁹ The size decrease, mandatory to incorporate the molecule-based systems in electronic devices, completely modifies the cooperativity as demonstrated for nanoparticles²⁰⁻²² and thin films.²³⁻²⁶ The bistability derived from cooperative interactions was still evidenced for patterned SCO dots,^{27,28} or for single nanoparticles using electrical²⁹ or optical read-out. In the context of electronic or spintronic devices, a first fundamental issue is to preserve their switchable properties when molecules are connected to a conducting surface for electrical addressing.³⁰⁻³² The bistability of a very few examples of single SCO molecules was evidenced by scanning tunneling microscopy. A low-temperature memristive behavior governed by the local energy barrier occurs for isolated molecules when decoupled from the metallic substrate.^{33,34} And very recently, a similar effect was reported on a tetramer of SCO molecules deposited directly on Ag(111).³⁵ Another issue that is especially relevant for high-density storage, is to avoid interference (or interplay) between molecules in self-assembled monolayers. In the case of conformational or volume-dependent process like SCO, the control over this requirement represents an open question and a true bottleneck. As a whole, the switching of single SCO molecules belonging to a well-organized 2D array and importantly, in direct contact with a conducting substrate without affecting neighboring molecules is still a challenge.

Here, we demonstrate by scanning tunneling microscopy (STM) measurements the bista-

bility of single SCO molecules self-assembled in a two-dimensional monolayer on Cu(111). This bistability stems from the delicate balance between intermolecular interactions within the monolayer and the interaction between the molecules and the substrate as evidenced by complementary STM measurements and mechano-elastic simulations. We show that the degree of intermolecular cooperativity within a monolayer of SCO molecules is larger when they are adsorbed on Au(111) than on Cu(111). This information is corroborated by the voltage-induced bistability of single molecules evidenced on Cu(111) and absent on Au(111).

The two dimensional molecular layers grown on metallic substrates are composed of $[\text{Fe}^{\text{II}}((3, 5\text{-}(\text{CH}_3)_2\text{Pz})_3\text{BH})_2]$ (Pz = pyrazolyl) spin-crossover molecules, called FeMPz in the following, which exhibit a hysteretic thermal transition between a diamagnetic low spin (LS) state and a paramagnetic high spin (HS) state at a temperature around 190 K in bulk.³⁶ On both Au(111)^{37,38} and Cu(111)^{39,40} substrates, the molecules FeMPz self-assembled in a molecular 2D network (see Figure S1 in SI). At low temperature, as evidenced by XAS experiments, the molecules coexist in both high spin and low spin states that are imaged by STM at 0.3 V as dark and bright molecules, respectively.³⁹ Unfortunately, no direct signature, such as Kondo peak, can be resolved in tunnelling spectroscopy measurements for a direct assignment of the paramagnetic HS state.^{16,37} Therefore, the assignment of the high/low spin state to the dark/bright molecules is realized by comparing STM and XAS measurements both at low temperature (see SI and Figure S2).

Voltage pulses can be used to trigger the transition of a single molecule from one spin state to the other.^{33,34,41} The manipulation with voltage pulses has thus been tested on both metallic substrates. Figure 1.a and 1.b presents two examples of voltage pulses applied on molecules adsorbed on Au(111). For the first example, a series of four consecutive pulses of 0.6 V (for 10 ms) is applied on four nearby molecules - two bright and two dark molecules - as schematized by the black points in Figure 1.a. Interestingly, as can be seen in the STM topographic image recorded after the voltage pulse application, the molecules on which the pulses have been applied are still in their initial state while a defect of bright molecules has

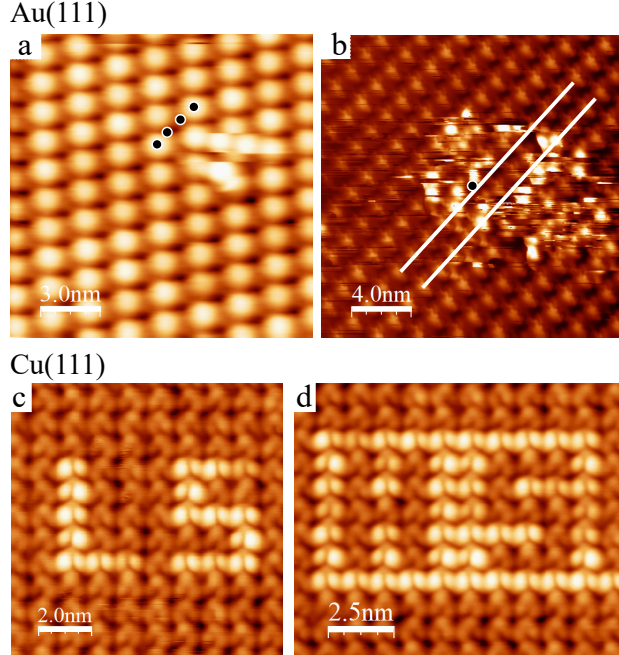


Figure 1: Induced switching by voltage pulses. a) $15 \times 15 \text{ nm}^2$ STM topographic image acquired after the application of four voltage pulses at 0.6 V on the different application points marked by the black dots ($V = 0.3 \text{ V}$, $I = 20 \text{ pA}$, z varies from 0 to 1.7 \AA). b) $20 \times 20 \text{ nm}^2$ STM current image after a voltage pulse at 2.2 V (10 ms) applied at the location of the black dot ($V = 0.3 \text{ V}$, $\langle I \rangle = 10 \text{ pA}$, I varies from 0 to 250 pA). The white lines are aligned along the dense direction of the outer superstructure to highlight the phase shift in the inner domain. c) $10 \times 10 \text{ nm}^2$ and d) $10 \times 12.5 \text{ nm}^2$ topographic images where “LS” and “HS” have been written by voltage pulses ($V = 0.3 \text{ V}$, $I = 3 \text{ pA}$, z varies from 0 to 2.63 \AA).

appeared nearby, evidencing a non-local switching process.⁴¹ The 4-bright-molecule defect is stabilized for a few minutes (typically two minutes) before the network recovers its initial superstructure (see Figure S3 in SI). Applying larger voltage pulse can lead to the formation of larger defective area as presented in Figure S3 (see SI), where lines of four or seven bright molecules are observed. Most probably, these 4-bright-molecule and 7-bright-molecule lines can be stabilized because of their commensurability with the thermal state superstructure.³⁷ Applying a voltage pulse of 2.2 V in the middle of the image locally induces a phase-shifted domain (Figure 1.b). Within less than fifteen minutes (few scans), the inner domain is healed (Figure S4). Therefore, applying voltage pulses enables the conversion of some molecules from the HS state to the LS one (dark to bright) but single molecule bistability is not

achieved within the 2D network on Au(111) as the original electronic state is spontaneously recovered.

On the contrary, on Cu(111), we demonstrated the bistability of single molecules in the 2D network. Figures 1.c and 1.d present STM images where first all the molecules were switched to the HS (dark) state, then one by one single molecules were switched back by voltage pulse to the LS (bright) state to write ‘HS’ and ‘LS’ letters (the switching procedure is discussed below). These features have been scanned for thirteen hours at a bias voltage of 0.3 V and they remain intact with only few visible defects (Figure S5).

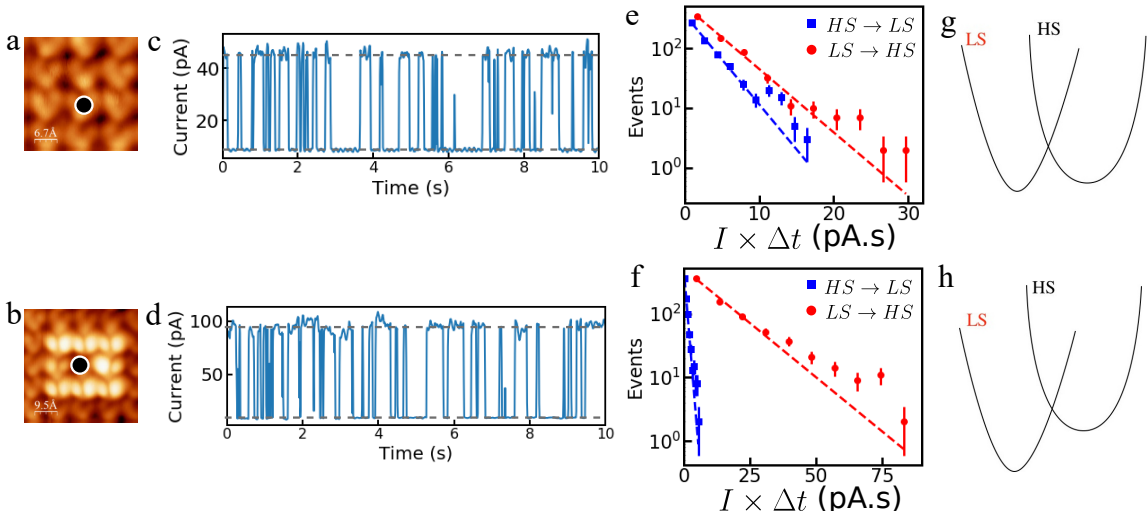


Figure 2: Voltage pulses on Cu(111). a) $3.5 \times 3.5 \text{ nm}^2$ STM topographic image of the initial state with dark (HS) neighbors ($V = 0.3 \text{ V}$, $I = 5 \text{ pA}$) and b) $4.8 \times 4.8 \text{ nm}^2$ STM topographic image of the initial state with bright (LS) neighbors ($V = 0.3 \text{ V}$, $I = 5 \text{ pA}$). The black dots indicate the position of the voltage pulses in both environments. c), d) Typical $I(t)$ -traces recorded during voltage pulses of 0.5 V for dark (HS) and bright (LS) neighbors, respectively. e), f) Distribution of current times duration ($I \times \Delta t$) of each plateau of the $I(t)$ -traces for dark (HS) and bright (LS) neighbors, respectively. The red circles (blue squares) correspond to the experimental distribution of events from bright (LS) to dark (HS) (dark (HS) to bright (LS)) molecules. The dotted lines correspond to mono-exponential fits of each distribution. g), h) Schematics of the relative potential energies of the LS and HS states at 0.5 V depending in both environments.

We then investigated in more details the tunneling conditions to switch the molecules from one spin state to the other on Cu(111). The first observation was realized by scanning at 0.7 V an area with a high proportion of LS molecules. We observed by zooming out

that in the area scanned at 0.7 V all the molecules are now appearing black at 0.3 V with clear-cut edges (see Figure S6 in SI). Thus, for this voltage bias the molecular switching from the LS state to the HS state is favored. The reverse switching can also be induced by using lower bias values. To investigate in more details the possibility to locally induce the switching of the molecules at positive voltage along with the influence of their first neighbors, we considered two initial situations: either a molecule surrounded by dark (HS) molecules (Figure 2.a) or a molecule surrounded by bright (LS) molecules (Figure 2.b). For both cases, there is a threshold voltage of 0.45 V below which no switching is observed within the temporal window of a few minutes. Above this threshold, the switching can be induced. During voltage pulses of 0.5 V, the tunneling current has been recorded as a function of time and typical $I(t)$ -traces are presented in Figures 2.c and 2.d for HS (dark) or LS (bright) neighbors, respectively. From the analysis of the $I(t)$ -traces, it is possible to extract a yield for the switching from the HS state (dark) to the LS state (bright) ($Y_{HS \rightarrow LS}$) and from the LS state (bright) to the HS state (dark) ($Y_{LS \rightarrow HS}$) for both environments. The yield is defined as $Y = \frac{e}{I\tau}$, with e the electron charge, I and τ the characteristic current and time for each switching extracted from the distribution of the current times duration (see Figures 2.e and 2.f and SI). When surrounded by molecules in the HS state, both switching events (from HS to LS and LS to HS) are equally probable with equivalent yield values of $Y_{HS \rightarrow LS} = 5.5 \cdot 10^{-8}$ and $Y_{LS \rightarrow HS} = 3.9 \cdot 10^{-8}$. In this environment, for a bias voltage of 0.5 V, the potential energies of both spin states are thus equivalent as schematized in Figure 2.g. On the contrary, when surrounded by molecules in the LS state, the switching yield from HS-to-LS ($Y_{HS \rightarrow LS} = 18.6 \cdot 10^{-8}$) is one order of magnitude larger than the switching yield from LS-to-HS ($Y_{LS \rightarrow HS} = 1.3 \cdot 10^{-8}$). At the same bias voltage of 0.5 V, the HS state is therefore destabilized compared to the LS one (Figure 2.h) probably due to the internal pressure in the molecular monolayer.²² Often, the final state imaged after the voltage pulse reveals that some of the bright neighbors are switched to the dark state. This clearly underlines that if the molecules can be addressed individually, the neighborhood is still influencing the

switching properties. For higher bias voltage values, the current traces are more noisy and the HS state is favored as evidenced by the possibility to create ‘dark’ area.

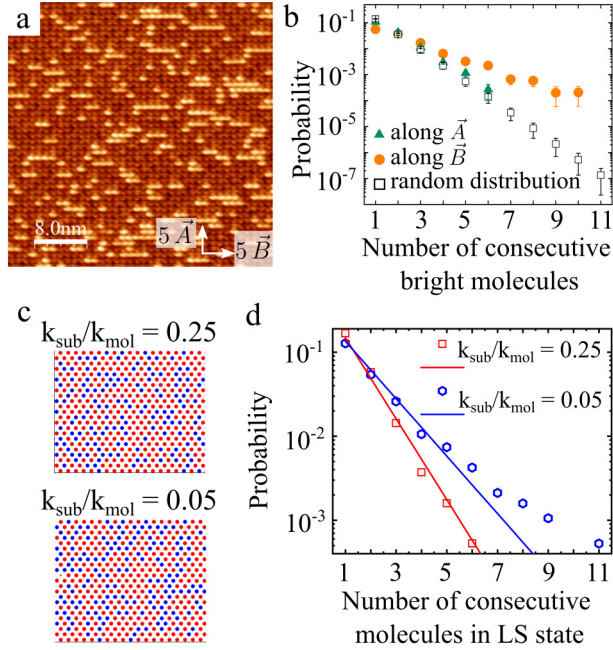


Figure 3: Cooperativity in the molecular network on Cu(111) for the thermal. a) $40 \times 40 \text{ nm}^2$ STM topographic image of the thermal state at $V = 0.3 \text{ V}$ and $I = 5 \text{ pA}$. The white arrows indicate the directions of the molecular lattice vectors. Their norms correspond to $5 \|\vec{A}\|$ and $5 \|\vec{B}\|$. b) Probability to have n consecutive bright molecules in the thermal state measured along \vec{A} (green triangles) and \vec{B} (orange dots) and compared to a random distribution (empty squares). Experimentally, the error bars correspond to the standard deviation. On the random distribution, it comes from the error done on p_b value. c) Snapshots of the thermal state for $k_{mol} = 4 \text{ N.m}^{-1}$ and $k_{sub} = 1 \text{ N.m}^{-1}$ (top) and $k_{sub} = 0.2 \text{ N.m}^{-1}$ (bottom). The molecules in LS (HS) state are coded in blue (red). d) Probabilities to have n consecutive molecules in LS state in red for $k_{sub} = 1 \text{ N.m}^{-1}$ and in blue for $k_{sub} = 0.2 \text{ N.m}^{-1}$. The probabilities obtained from the mechanoelastic model (symbols) are compared to a random distribution (lines).

Thus, on Cu(111), molecules can be individually addressed and their spin state stabilized while on Au(111) only large defects are obtained which quickly disappeared. A key factor is the balance between the cooperativity in the molecular layer and the molecule-substrate interaction. Figure 3.a presents a typical STM topographic image on Cu(111) of the thermal state which corresponds to the low temperature state well below the thermal transition. This state is measured at 4.6 K and at a bias voltage of 0.3 V just after cooling down the sample

from room temperature (tip approach and scanning at 0.3 V and 50 pA to avoid any switching of the molecules). The main difference, with the Au substrate, is the organization of the LS molecules observed at 0.3 V. Indeed, on Au(111) an order lattice of LS and HS molecules is developed over a large area (up to $100 \times 100 \text{ nm}^2$)³⁷ indicating strong interactions between the molecular spin states. On Cu(111), the distribution of the bright (LS) molecules seems more random (compare Figure 3.a and Figure S2). To have a better understanding of the bright molecule distribution, we measured the probability of observing n consecutive bright molecules along \vec{A} (green triangles) and along \vec{B} (orange dots) as reported in Figure 3.b. The measured probabilities are compared to the probability to have n consecutive bright molecules for a random distribution of bright molecules which is given by $p_b^n(1 - p_b)^2$ with p_n being the measured proportion of bright molecules ($p_b = 0.25 \pm 0.03$). The measured probabilities are larger than what is expected for a random distribution especially along the direction \vec{B} . This indicates that, when adsorbed on Cu(111), correlations exist between the molecules even though they are weaker than on Au(111).

In order to rationalize the experimental results and get insight into the influence of the substrate nature on the single molecule bistability behavior, we performed mechanoelastic simulations.⁴²⁻⁴⁴ We investigated the influence of the molecule-substrate interaction on the local correlations. For this purpose, we fixed a value for the intermolecular interaction (k_{mol}) to 4 N.m^{-1} and calculated the thermal state for two different molecule-substrate interactions ($k_{sub} = 0.2$ and 1 N.m^{-1}), which are represented in Figure 3.c. The first effect of varying k_{sub} is the change in the proportion of the HS/LS molecules within the thermal state as previously reported.^{26,38} We obtained proportions of molecules in low spin state (p_{LS}) of 0.46 and 0.34 for k_{sub} values of 0.2 and 1 N.m^{-1} , respectively. As presented in Figure 3.d, we then determined in the thermal state the probability to have n consecutive LS molecules along the three equivalent directions of the triangular lattice. For a k_{sub} value of 1 N.m^{-1} the probability to have n consecutive LS molecules follows a random distribution (lines in Figure 3.d). On the contrary, for a reduced value of k_{sub} (0.2 N.m^{-1}), the measured probability is away from the

random distribution. Correlation between the molecules can also be quantified through the Moran index which decreases while the interaction to the substrate increases (see Figure S8 in SI). Thus, increasing the interaction between the molecules and the substrate leads to the decrease of the correlations inside the molecular layer. This also suggests that the molecules interact more with the Cu(111) substrate than with the Au(111).

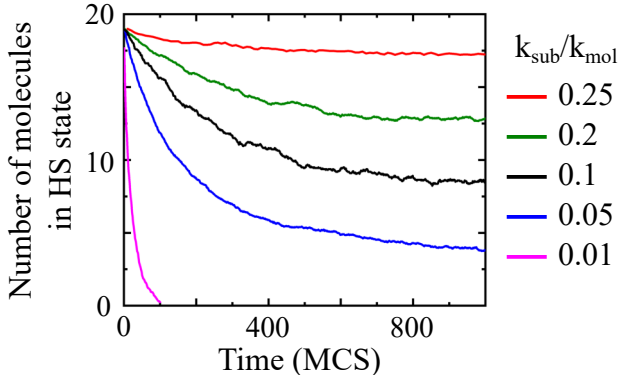


Figure 4: Relaxation of a cluster of molecules in HS state in an environment of molecules in LS state as a function of time (in Monte Carlo steps) for different ratio of k_{sub}/k_{mol} with $k_{mol} = 4 \text{ N.m}^{-1}$.

To explain the role of the substrate on the stability of the switched molecules, we performed a second mechanoelastic simulation. The initial state consists in a cluster of nineteen molecules in the HS state surrounded by molecules in the LS state. The relaxation of the HS molecules in the cluster is simulated for different k_{sub}/k_{mol} ratios for a given k_{mol} of 4 N.m^{-1} . The relaxation curves in Figure 4 are obtained by averaging 100 relaxation curves (see Figure S9 in SI). The typical relaxation time for the cluster increases as the value of k_{sub} increases. This indicates that the spin state of the molecules can be stabilized by the substrate interaction. This is consistent with our observation that a switched state is more stable on Cu(111) than on Au(111).

The different experiments and simulations described here highlight the role of the substrate nature on the local correlation in the molecular layers and the possibility to stabilize at will a molecule in a given spin state. The molecular layer on Au(111) presents a

strong cooperativity as evidenced by the long range correlation in the superstructure and the impossibility to control or stabilize any specific feature. On Cu(111), the long range correlation is weaker leading to a relatively larger molecule-substrate interaction responsible of the bistability of the single molecules within the 2D monolayer. This work opens the way for ultrahigh-density memory devices that can be electrically addressed and read-out using spin crossover molecules.

Methods

Experimental methods

Prior to the molecular deposition, the metallic Cu(111) and Au(111) single crystals are cleaned under ultra high vacuum (UHV, base pressure of 10^{-10} mbar) by sputtering (Ar^+ ions at 600 eV or 900 eV for Cu(111) or Au(111) respectively) and annealing (450° C for both substrates) cycles. Molecules FeMPz are then sublimated under UHV at a temperature of 85°C from a home-made Knudsen-cell-like evaporator on the metallic substrate. During the molecular sublimation the single crystals are kept at low temperature (around 5 K). The samples are then annealed at room temperature to enable the formation of the molecular islands. All the measurements have been carried out on a low temperature scanning tunneling microscope (STM, Omicron) operating at 4.6 K. The STM images have been processed using Wsxm software.⁴⁵

Mechanoelastic simulations

For the mechanoelastic simulations, spin-crossover molecules are represented as balls arranged in a triangular configuration and linked to their first neighbors situated in the same layer by springs with an elastic constant k_{mol} . The ball radii code for the molecular spin states by taking a value of 0.22 nm and 0.2 nm for the HS and the LS states, respectively. The distance between two LS molecule centres is 1 nm. The interaction to the substrate is taken into account by linking each spin-crossover molecule to three surface molecules in

a face centred cubic configuration by springs with an elastic constant k_{sub} . The intrinsic parameters of the system are $\Delta H = 1500 \times 10^{-23}$ J and $\Delta S = 9.7 \times 10^{-23}$ J.K⁻¹, thus giving a thermal transition temperature around 155 K.

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