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Controlling the charge state of a single redox molecular switch

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Abstract

Scanning tunneling microscopy (STM) and dynamic force microscopy in the non contact mode are used in combination to investigate the reversible switching between two stable states of a copper complex adsorbed on a NaCl bilayer grown on Cu(111). The molecular conformation in these two states is deduced from STM imaging while their charge is characterized by the direct measurement of the tip-molecule electrostatic force. These measurements demonstrate that the molecular bistability is achieved through a charge-induced rearrangement of the coordination sphere of the metal complex, qualifying this system as a new electromechanical single-molecular switch

A molecular switch is a molecule that can be reversibly shifted between two states by an external stimulus [1]. Potential applications of these molecules in the field of nanotechnology are numerous, from memory units [2] to electronic switches [3] and driving elements for molecular motors [4]. Recently, a wide variety of molecular switches have been characterized by different techniques, in particular by scanning tunneling microscopy (STM) [5] to [14]. Most of these studies were performed on metal surfaces. Here, we introduce a new molecular switch, a redox molecule adsorbed on an ultrathin insulating film deposited on a metal. By a combination of STM and non contact atomic force microscopy (nc-AFM) measurements, we unambiguously demonstrate that the as-deposited neutral and square-planar molecule becomes negatively charged and tetrahedral after switching. Our findings on this interplay between conformational change and charge state, although well documented in the chemistry of transition metal complexes, enable to study fundamental phenomena at the single molecule level such as electron transfer between two redox centers or to develop new charge manipulation schemes, such as triggering mechanical motion in a molecule by electron injection.

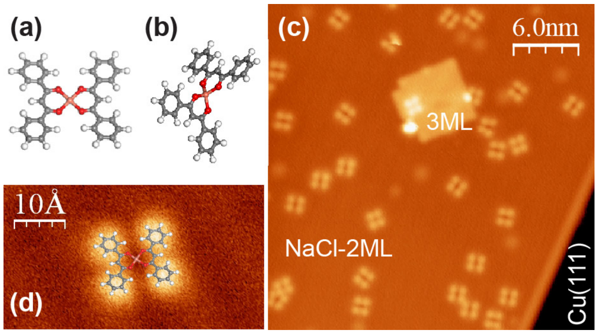

Figure 1: Bis-dibenzoylmethanato-copper $C_{30}H_{22}O_4Cu$ (a) square-planar complex $[Cu(II)(dbm)_2]^0$, (b) tetrahedral complex $[Cu(I)(dbm)_2]^{-1}$. STM images of $Cu(dbm)_2$ on a bilayer of NaCl on Cu(111) (c) Tunneling current It = 1pA, bias voltage Vt = 1V. (d) It = 0.7 pA, Vt = 1.2 V.

A commercial low temperature (5K) microscope (Omicron Nanotechnology-Taunusstein, Germany) equipped with a tuning fork of the qPlus sensor type [15] and a control system from SPECS (Zurich, Switzerland) was used for this study. All the data shown were obtained at 5K. The Cu(111) substrate was cleaned by cycles of Ar^+ sputtering (600 eV) followed by annealing at 750 K. NaCl was deposited by thermal evaporation on this substrate at 300 K in order to get a partial coverage of NaCl bilayer islands. The coordination complex bis-dibenzoylmethanato-copper ($Cu(dbm)_2$: Fig. 1a) was prepared as previously described [16] and characterized by electrochemistry and X-ray diffraction. These molecules were deposited from a heated crucible on the sample maintained at low temperature in the microscope. The resonance frequency of the tuning forks used for this study was of the order of 25 kHz and their quality factor in the range 10,000-20,000. They were equipped with a glued electrochemically etched tungsten tip.

The STM image of one $Cu(dbm)_2$ molecule adsorbed on a NaCl bilayer on Cu(111) presents four bright lobes arranged in an almost square configuration (Fig. 1c and d). A closer examination shows that one of the grooves separating these lobes is more pronounced than the other, suggesting that the ligands are positioned along the connected lobes (Fig. 1d). The apparent molecular height is approximately 100 pm.

Figure 2 shows the reversible switching of two molecules controlled by suitable bias voltage. Applying +2 V (referring to the sample) above the center of a square molecule changed the geometry from flat planar to 3D (Fig. 2a $\Rightarrow$ b and Fig. 2b $\Rightarrow$ c) with an increased height of more than 200 pm (Fig. 2f). Applying -2 V above this molecule restored the initial square conformation (Fig. 2c $\Rightarrow$ d and Fig. 2d $\Rightarrow$ e), demonstrating the complete reversibility of the process. The switching events were detected during the application of the voltage by monitoring the occurrence of sharp transitions in the tunneling current. In the experimental conditions corresponding to Fig. 2, the waiting time before switching was a few hundred milliseconds. The process is highly reliable, with a rate of success approaching 100%. Spontaneous switching was not detected in a time range of several hours demonstrating the stability of the two species. In addition, it was not possible to induce similar transitions on molecules directly adsorbed on Cu(111). This observation shows that NaCl plays an important role in the switching mechanism, either by its specific adsorption properties, or by its electronic decoupling effect for the adsorbed molecules relative to the metallic substrate.

These conformational changes are not unexpected: it is well established that the redox state of the metallic ion in a complex is coupled to its coordination geometry [17]. In its neutral form, $Cu(dbm)_2$ is square-planar (Fig. 1a), as shown by X-ray diffraction [16]. This geometry is typical of Cu(II) coordinated with two singly-charged anionic ligands. Cyclic voltammetry experiments on similar compounds show partial irreversibility due to the rearrangement from this planar to a tetrahedral coordination (Fig. 1b) during the

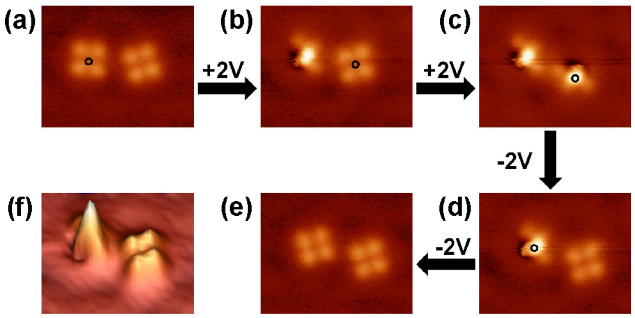

Figure 2: (a)-(e) Sequence of STM images showing the reversible switching of two molecules. The position of the tip above the molecule during the application of the bias voltage is marked by a black circle. (f) 3D representation of image b. Image size: 6.9 nm x 5.5 nm. It = 0.4 pA, Vt = 100 mV.

reduction process [18, 19]. These observations can be rationalized using crystal field theory [20]: in the Cu(II) complex, the electronic configuration of the metal is d^9, and the structure is stabilized by the Jahn-Teller effect. In the negatively charged Cu(I) complex, the metal is d^{10} and therefore, there is no crystal-field stabilization energy preference for any coordination symmetry. The structure is then governed by steric and electrostatic effects and a tetrahedral geometry is adopted [ref. [20] p.212]. Note that similar coordination geometry changes in Cu complexes have been used to control molecular motors in solution [4]. In light of these observations, we interpret the switching behavior as transitions between a square-planar (SP) (Fig. 1a) and a 3D tetrahedral (Td) geometry (Fig. 1b).

Tunneling spectroscopy experiments were performed in order to obtain insight into the electronic structure of the adsorbed molecule in its two states (Fig. 3). The dI/dV spectrum of a SP molecule presents a sharp increase that starts at $V \simeq 1.8$ V and is interrupted, in this particular case, by the switching to the Td state at $V \simeq 2$ V. Imaging the SP molecule in this voltage range was difficult because it tends to switch to the Td state. Nevertheless, it was possible to obtain a complete image at $V = 1.85$ V (image n° 2 in Fig. 3), which is markedly different from the square one: it exhibits 6 lobes, its lateral dimensions are larger, and its height increases to more than 300 pm. In a similar way, the dI/dV spectrum of a Td species exhibits a conductance peak at $V \backsimeq -1.7$ V, and the image becomes much higher as well ($\simeq$ 500 pm) beyond this voltage. Following recent works [21, 22], we attribute these features to molecular ion resonances, which dominate the spectrum at these bias voltages because

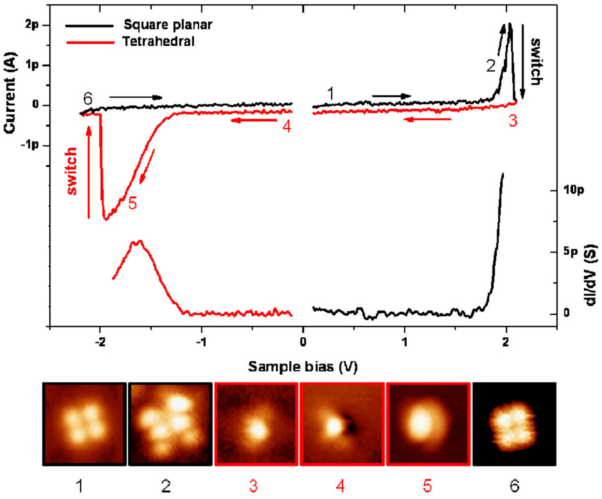

Figure 3: I(V) and dI/dV spectroscopy curves obtained on the SP (black lines) and the Td (red line) species. The numbers that appear on the I-V curves refer to the numbering of the STM images shown below the graph (size: 3.5 nm x 3.5 nm). They are located at the corresponding imaging bias voltage. 1, 2 and 6 (3, 4 and 5) correspond to the SP (Td) species.

the NaCl bilayer partially decouples the molecule electronically from the metallic substrate. Considering the open shell d^9 electronic configuration of Cu(II) in the SP complex, the resonance observed at positive bias is expected to derive from its singly occupied molecular orbital (SOMO), while the resonance associated with the Td complex corresponds to its first occupied level (HOMO). The position of these conductance peaks is in good correspondence with the bias voltages applied to induce the transitions between the two conformations of the molecule. Therefore, the transformation from SP to Td is triggered by the injection of an electron in the SOMO of SP and the reverse one by the retrieval of an electron from the HOMO of Td. This observation suggests that the SP adsorbate is neutral, while the Td one is negatively charged. The sequence shown in Fig. 2b-d and in Fig. 3 could then be considered as an oxido-reduction cycle performed on a single redox center.

This conclusion is strengthened by the observation reported in figure 4, where the difference between the images after (Fig. 4b) and before (Fig. 4a) switching has been calculated (Fig. 4c), following a recently proposed method [14]. The rings that appear surrounding the SP molecule can be attributed to the scattering by the long range electrostatic potential of the localized charge of the two-dimensional electron gas that is confined at the Cu-NaCl interface [9, 14]. But the effect is very weak, and in addition, it does not allow the

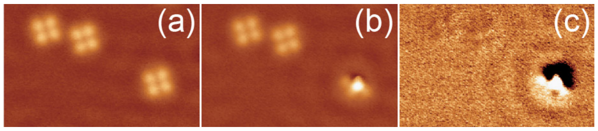

Figure 4: STM images before (a) and after (b) the switching of a molecule. (c) Difference between (b) and (a).

determination of the sign of the charge.

A more direct method consists in characterizing the electrostatic force exerted by the molecule on the tip by nc-AFM, following the method developed in [12, 23, 24]. Electrostatic forces can be distinguished from the other forces involved in AFM by their quadratic dependence on the bias voltage. In nc-AFM [25], the constant-height measurement of the resonance frequency shift Δf as a function of the bias voltage gives a parabola with its maximum at V = V*. This bias voltage minimizes the electrostatic force [26] and is used to build maps of the local contact potential difference (LCPD = (electron charge) x V*) in Kelvin probe force microscopy [27].

Here we use the Δf(V) spectra to characterize the charge state of the adsorbed species, as shown in Fig. 5a. The measurements were performed in the following way: the tip was positioned in the constant current mode (with the tuning fork oscillating) above the object of interest. The distance-controlled loop was then disabled, the distance changed by Δz, and the bias voltage ramped over the predetermined range. The z scale has been corrected by the height of the molecules measured on the constant-current STM image in order to plot the curves on a common scale relative to the substrate.

The curves can be fitted very precisely with parabolas (red lines), the maxima (V*, Δf*) of which were determined for a complete set of measurements at different tip heights, Δz. The resulting V*(Δz) curves, displayed in Fig. 5b, reveal a different behavior for the two molecular states. V^*_{SP} does not deviate significantly from the approximately constant value $V^*_{NaCl} \approx$ -0.4 V over the complete Δz range. In contrast, V^*_{Td} increases for △z lower than 150 pm reaching +0.8 V at Δz = 50 pm. As shown recently [12, 23, 24, 28], the presence of a charge q changes the value of V^* with respect to its value on the substrate. This effect is due to the interaction of q with the potential created by the tip-substrate potential difference V-V^*_{NaCl}. The interaction term is proportional to q(V-V^*_{NaCl}), and consequently, depends on the sign of the charge. The shift of V^*_{Td} toward positive values observed in Fig. 5 indicates

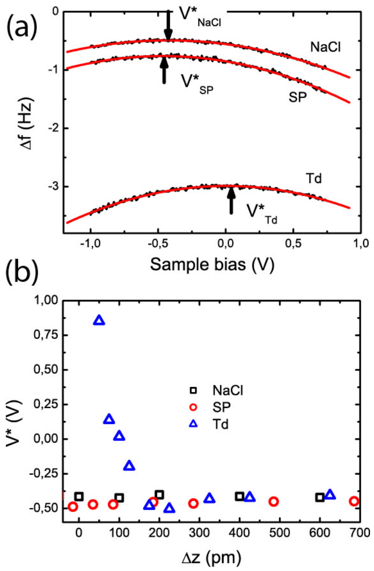

Figure 5: (a) Frequency shift Δf as a function of V above NaCl, a SP and a Td molecule. Δz = 100 pm. Imaging conditions: oscillation amplitude A = 240 pm, It = 0.7 pA, Vt = 400 mV. Each measurement is fitted with a parabola (red lines). (b) V^*(Δz) above NaCl, the SP and the Td molecule.

that the Td molecule is negatively charged, confirming our previous observations. Therefore, we conclude that the SP species can be described as a neutral molecule $[Cu(II)dbm_2]^0$ and the Td one as a negative ion $[Cu(I)dbm_2]^{-1}$. Note that the amplitude of the voltage shift we observe cannot be related in a simple way to the value of the charge as it depends on the tip structure. Moreover, the large value (nearly +1.4 V) we observe in figure 5b cannot be explained with simple models [12, 23, 24, 28] and more realistic calculations are needed to reach a better understanding of these measurements [29].

The frequency shift as a function of Δz at V = V^*_{NaCl} on NaCl, on the SP and on the Td species resulting from the fitting curves displayed in Fig. 5 is shown in Fig. 6a. The corresponding forces, obtained using the method proposed in ref. [30] are shown in Fig. 6b [31].

The experimental points plotted in Fig. 6a where obtained at a tip-NaCl distance of about 700 pm, fixed by the imaging conditions (It = 700 fA and Vt = 400 mV). In this distance regime and at V = V^*_{NaCl}, only the van der Waals interaction contributes to the force on NaCl. When the tip is above a molecule, at the same distance, this term still contributes. The molecular contribution to the force can be isolated by subtracting this

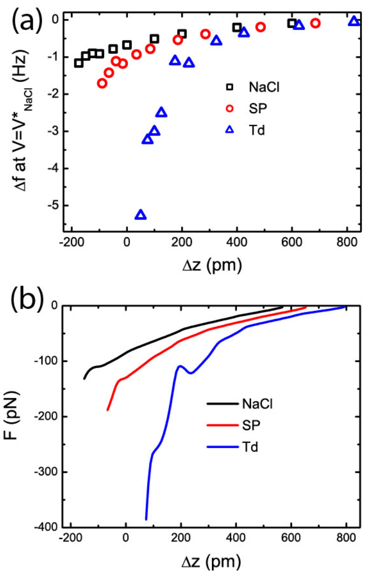

Figure 6: (a) Frequency shift at V = V^*_{NaCl} = -0.4 V and (b) forces above NaCl, a SP and a Td molecule as a function of Δz.

NaCl contribution to the molecular force curves. If the molecular van der Waals and the short-range chemical contributions can be neglected the resulting force curves correspond to the interaction of the charge with its tip and substrate images. For the experiments presented here the maximum force at V = V^*_{NaCl} remains below 400 pN.

These findings open new perspectives. This molecular switch is highly reliable and does not require delicate preparation procedures such as atomic and/or molecular manipulations on NaCl to be operative. The wide possibilities offered by synthetic chemistry render it possible to incorporate such a redox center as a building block in new molecular architectures for charge engineering, in which charges could be used to store, transmit, or even process information. The conformational change associated with charging could be used to reveal easily and unambiguously the presence of a charge, without relying on delicate AFM measurements. Another application would be to utilize this molecular switch as an electromechanical transducer, where the molecular rearrangement associated with the oxido-reduction cycle could be used as a driving mechanism in a synthetic molecular motor [32].

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