

Conductance Hysteresis and Switching in a Single-Molecule Junction

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Voltage-controlled conductance hysteresis and stepwise switching in a reversible manner were observed in a single-molecule double-barrier junction defined by a scanning tunneling microscope (STM) at ~ 10 K. In situ visualization and characterization of the junction using the STM revealed that the charge bistability of a single molecule on a polar alumina film is responsible for the conductance hysteresis and switching. It was also found that the relative stability between different charge states depends on the multiple adsorption configurations of molecules on the surface.

The realization of controllable hysteresis and reversible switching in the current–voltage (I - V) characteristic of a molecular junction, instead of random or stochastic switching, has been a subject of intense research efforts in molecular electronics.^{1–6} Similar to the role of magnetic hysteresis in magnetic storage devices, voltage-controlled conductance hysteresis and switching underlie the principle behind a molecular memory device operating at the nanometer scale.⁷ Such hysteresis and switching in I - V curves and differential conductance (dI/dV) plots have been observed in different experimental configurations, such as crossed-wire tunneling junction,^{2–4} magnetic bead junction,² single nanowire field-effect transistor,⁵ and STM junction.^{2,6,8}

Different mechanisms, leading to such switching behaviors, have been proposed. One mechanism involves the switching between different charge states of a single molecule. The stabilization of multiple charge states for a molecule could be assisted by the ionic relaxation of the insulating substrate in contact with the molecule.^{1,9–12} In contrast, external perturbations such as the electrical field could also induce a change in the stereochemical geometry of the molecule without charge transfer (conformational change),^{6,13} resulting in a modification of the molecular electronic structure and consequently the I - V characteristic. Discrimination between different mechanisms is hindered in part by the unknown nature of the molecular junctions, such as the adsorption geometry of the molecules and their nanoenvironment, as well as the nature of the data.

In this letter, we report the use of a scanning tunneling microscope (STM) to form a single-molecule double-barrier junction by positioning the STM tip over an individual molecule adsorbed on a thin insulating alumina film grown on the NiAl(110) surface (Figure 1A). For specific adsorption geometries, we observed reversible hysteretic switching in the I - V and differential conductance (dI/dV) spectra that could be controlled with the applied bias voltage. The imaging capability of the STM enabled visualization of the molecular electronic states

before and after switching events. The experimental data revealed the mechanism of conductance hysteresis and switching.

The experiments were conducted with a home-built ultrahigh-vacuum STM operated at ~ 10 K. The alumina film was prepared by exposing a clean NiAl(110) surface to 110 Langmuirs (1×10^{-6} Torr for 110 s) of O_2 at 770 K and then annealing to 1300 K. Nearly 50% of the NiAl(110) surface was covered by a thin (~ 0.5 nm) alumina film.¹⁴ Magnesium porphine (MgP, Figure 1C) molecules were thermally sublimed onto the oxidized surface at ~ 10 K. Bias voltage (V_b) refers to the sample voltage with respect to the tip.

The alumina film grown on the NiAl(110) has a large unit cell (1.79 nm \times 1.06 nm) and is inhomogeneous.¹⁴ Because of the complex structure of the oxide layer and possible out-of-plane distortions in the porphyrin molecules,¹⁵ a number of different MgP adsorption geometries on the oxide surface are present in the STM images (Figure 1B). One specific type of MgP molecules, denoted by M1 and M2 in Figure 1B, appears as two-lobe structure when imaged with sample bias (V_b) larger than 1.2 V. The direction of the lobes is always perpendicular to the [001] direction of the underlying NiAl(110). The I - V curves and dI/dV spectra measured over the molecules exhibit hysteresis and stepwise switching between two different states, as shown for one cycle in Figure 1D. In the forward scan (ramping V_b up), a sudden drop occurs at positive bias (~ 0.85 V) in both the tunneling current and dI/dV signals; in the backward scan, another sudden drop occurs at negative bias (~ -1.2 V) and the molecule is switched back to its original state. This behavior could be cycled repeatedly and the switching voltages are almost the same for a given bias sweeping speed.¹⁶ In contrast, tunneling spectroscopy on the bare oxide surface adjacent to the molecules does not show any switching. This result suggests that the hysteresis and switching originate from the single-molecule junction. Individual switching events could also be imaged by the STM during the course of a topographic scan, as shown in Figure 1E,F.

In our experiment, both the vacuum gap between the tip and the molecule and the oxide film between the molecule and the NiAl substrate present barriers for electron tunneling (Figure

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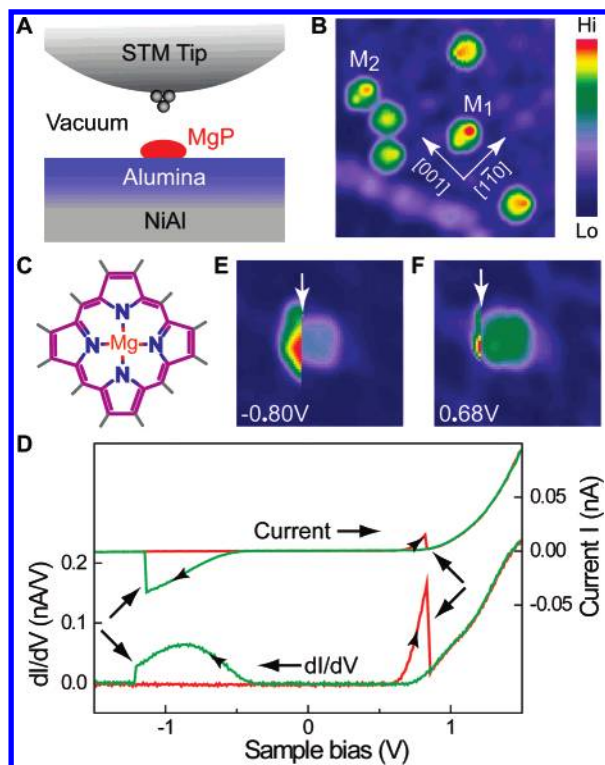


Figure 1. (A) Schematic of a single-molecule double-barrier junction. (B) STM image of individual magnesium porphine (MgP) molecules adsorbed on an oxidized NiAl(110) surface. The scan size is 12 nm by 12 nm, $V_b = 2.0$ V. All the STM topographic images in this paper were taken at $|I| = 30$ pA. (C) Molecular structure of MgP. (D) I - V (top) and dI/dV - V (bottom) spectra measured over a molecule such as M1 and M2 in (B), showing forward (red) and backward (green) scans. The dI/dV signal was recorded with the lock-in technique. The tunnel gap was set at $V_b = 1.5$ V and $I = 93$ pA. The bias modulation was 10 mV (rms) at 400 Hz. The I - V curve was recorded without bias modulation in a different bias sweep. Therefore, the switching bias voltages, as marked by black arrows, vary slightly. (E, F) Images in which the molecule switched while scanning at negative and positive bias, respectively. The slow scan direction is from the left to the right.

1A). Direct tunneling from the STM tip to NiAl (or vice versa) is less probable than two-step tunneling via the intermediate molecular states. The dI/dV spectra are a direct measure of the electronic states from the sandwiched molecule.¹⁷ In one of the bistable conditions (before switching in the forward scan), no occupied states are observed near the Fermi level and the threshold for the lowest unoccupied molecular orbital (LUMO) is around 0.55 V. Whereas, after the molecule switches at ~ 0.85 V to the other bistable condition, the onset of the unoccupied states is shifted up by 0.15 V. In addition, a new occupied molecular state is observed at negative bias (threshold is ~ -0.45 V).

A series of STM images taken at various V_b in the range for the different bistable conditions is shown in Figure 2. STM images taken in the absence of the new occupied state are shown in Figure 2A,B. In the zero-conductance region below the onset of unoccupied states, the STM images are very similar to Figure 2A and are relatively featureless. The image taken at the onset of the unoccupied states shows an electronic contour (Figure 2B), which matches with one of the calculated LUMOs, named LUMO- α (Figure 2C).^{18–21} The height of this image is larger than that taken at V_b in the zero-conductance region, because the tunneling process is mediated by the presence of molecular electronic states rather than direct tunneling from the STM tip to NiAl (or vice versa). After the molecule switches to the other bistable condition, the images taken at the onset of the new

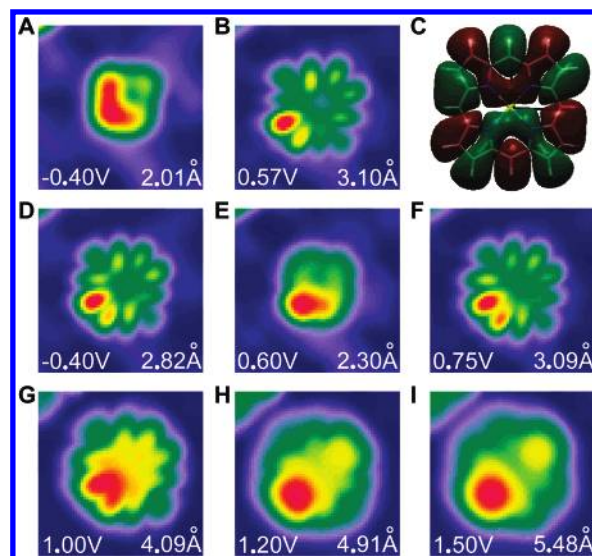


Figure 2. (A,B) Images of a neutral molecule before charging. (C) The DFT calculation of the LUMO electron density for a free, planar MgP.²¹ After switching at the positive bias, the molecule is charged with one extra electron. (D–I) The images for the anion. The scan size is 2.47 nm by 2.47 nm. The imaging bias V_b (V) and apparent height (\AA) are marked in each image.

occupied state and at the onset of the slightly up-shifted unoccupied state show similar pattern to LUMO- α (Figure 2D,F). As V_b increases, LUMO- β , the orbital orthogonal to LUMO- α , emerges and smears out the electronic pattern, as shown in Figure 2G–I.

The combination of STM images and spectra strongly suggests that the conductance hysteresis is due to charging and discharging of the MgP molecule. In the absence of the new occupied state, the molecule is neutral. At positive bias, an electron resonantly tunnels from the STM tip into the LUMO- α (Figure 3A) and becomes trapped in the molecule, forming an anion (Figure 3B). The newly formed half-filled occupied state becomes the singly occupied molecular orbital (SOMO); the other spin-degenerate state remains as singly unoccupied molecular orbital (SUMO).²² They are separated by a Coulomb energy U , as indicated in Figure 3B. A lower bound for U is given by the SOMO onset to the SUMO onset of ~ 1.15 eV. The molecular anion could be switched back to its neutral state by allowing the extra electron to tunnel out of the molecule and into the STM tip at negative bias (Figure 3C).

The identification of the neutral and anionic states and their bistability are consistent with theoretical calculations done on different charge states of the magnesium porphine (MgP) molecule in free space.^{20,21} The total energy calculation, which combines the electronic energy at its equilibrium molecular geometry for different charge state and zero-point energy of the molecular vibrational degrees of freedom, suggests that the neutral and the anion are much more stable than the cationic and the doubly anionic charge state by more than 2 eV. The total energy between the anion and the neutral differs only by 0.17 eV, favoring the charge bistability of the molecule on a surface. Comparison between the electronic structures of the neutral molecule and that of the anion at their respective equilibrium geometries confirms the occupation of LUMO- α with one extra electron when the molecule is charged from the neutral to the anion. It should be noted that the equilibrium geometries for the neutral state and for the anionic state are very close, implying negligible structural change of the molecule followed by charging.

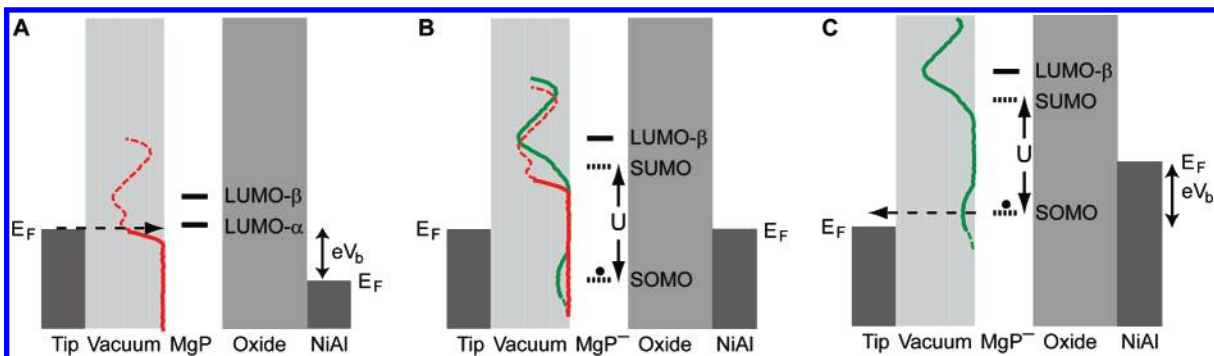


Figure 3. (A) Energy diagram showing an electron injecting into the LUMO- α of a neutral molecule at positive bias. (B) The half-occupied LUMO- α becomes the SOMO for the negatively charged molecule. Coulomb energy U prohibits transferring of another electron into the molecule. The previously spin-degenerate state becomes the SUMO. (C) Energy diagram showing release of the electron in the SOMO at negative bias and the molecule returns to be neutral. The dashed lines in the spectra are the extrapolated local density of states for the neutral (red curve) or charged (green curve) molecule.⁸

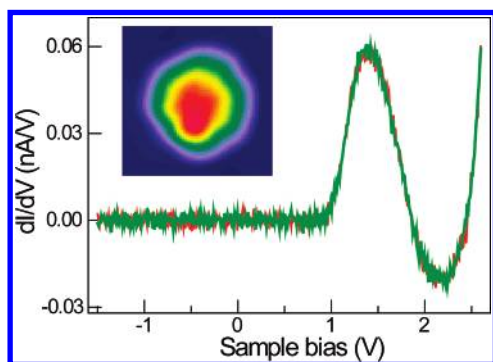


Figure 4. dI/dV spectra measured over a molecule with different adsorption geometry. The forward (red curve) and backward (green curve) scans overlap and do not show hysteresis and switching. The inset shows the image taken at 2.0 V. The scan size is 3.4 nm by 3.4 nm.

The adsorption of the molecule on the oxidized surface could affect the relative stability of different charge states. One key effect is the adsorption geometry of the molecule. In the experiments, only a specific type of MgP molecules such as M1 and M2 in Figure 1B presented the conductance hysteresis and switching, the manifestation of charge bistability. Such phenomena were not observed on other molecules with different adsorption geometries on the surface. For example, the molecule on the oxidized surface shown in Figure 4 does not exhibit conductance hysteresis and switching. Another effect of the molecular adsorption on the oxidized surface is the response of the alumina film to the different charge states of the molecule. For each charge state of the molecule, the ions in the alumina film relax to minimize the potential energy and stabilize the molecule. The energy stabilization for different charge states leads to the formation of a double-well potential energy profile due to the ionic relaxation in the alumina film and the polarization of the molecular electronic states. The neutral and the anionic molecules occupy the two potential minima and there is an activation barrier separating them. This effect is similar to the mechanism of multiple charge stability observed for single atoms adsorbed on a thin NaCl or MgO film.^{10–12} Therefore, the inclusion of the oxide surface in the theoretical calculations is important. However, the structure of the alumina film grown on NiAl(110) surface is complex, consisting of a large unit cell (1.79 nm \times 1.06 nm) and multiple molecular adsorption sites.¹⁴ The exact adsorption geometry in our experiments could not be precisely retrieved from the STM images. The high tunneling

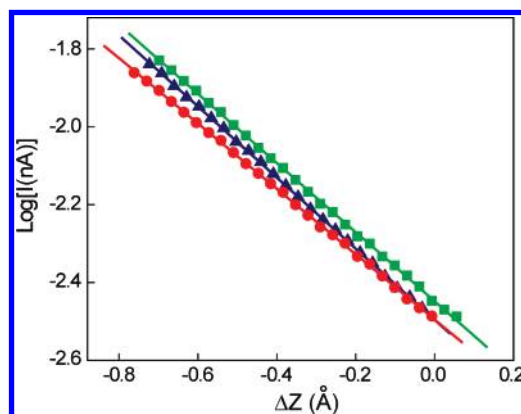


Figure 5. The I - Z curves measured over a molecule before (red circles), after charging (green squares), and over the bare alumina surface (blue triangles). The extracted effective barrier heights correspond to 3.54 ± 0.03 eV for the neutral molecule and 3.96 ± 0.03 eV for the negatively charged molecule. In comparison, the effective barrier height measured over the bare alumina gives 4.17 ± 0.03 eV.

current and low bias voltage used to image the structure of alumina film would perturb or chemically modify the molecule.¹⁴

The relative stability of the neutral and anionic states of the molecule on the surface could be inferred from measurement of the effective tunnel barrier height, which reflects the modification of the local surface potential due to molecular adsorption. The effective barrier heights were extracted from the I - Z curves measured over a molecule before and after charging, as shown in Figure 5.²³ The effective barrier heights are 3.54 ± 0.03 eV for the neutral molecule and 3.96 ± 0.03 eV for the negatively charged molecule. In comparison, the effective barrier height measured over the bare alumina gives 4.17 ± 0.03 eV. The change in the effective barrier height could be attributed to the ionic relaxation in the alumina film, screening effects in the metal substrate (NiAl) and the STM tip, and polarization of the molecular electronic states.⁹

In conclusion, we have demonstrated a powerful approach to study interfacial charge transfer and transport with the STM to define, image, and characterize a single-molecule double-barrier tunnel junction. This approach enabled us to unambiguously determine that charge bistability is responsible for the conductance hysteresis and switching observed on a single molecule with a specific adsorption geometry. Furthermore, we found that the relative stability between different charge states of a molecule depends on its adsorption configuration on the

surface. Experiments on single molecules by the STM are able to correlate chemical structure and functionality in a heterogeneous environment. These properties should be considered in the design of molecular electronics devices based on conductance hysteresis and switching, as well as in the development of theoretical models and calculations.

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- (22) Strictly speaking, STM measures the affinity and ionization levels of the molecule by transiently filling one electron into the molecule ($V_b > 0$) or transiently withdrawing one electron out of the molecule ($V_b < 0$).
- (23) To measure the effective barrier height contributions from the vacuum and alumina film, the sample bias V_b is restricted to avoid tunneling through the trapped molecular states.