

Mechanisms of Reversible Conformational Transitions in a Single Molecule

X. H. Qiu, G. V. Nazin, and W. Ho*

Department of Physics and Astronomy and Department of Chemistry, University of California, Irvine, CA 92697-4575, USA
(Received 26 April 2003; revised manuscript received 1 July 2004; published 5 November 2004)

The reversible interconversion between two nonplanar conformations of single Zn(II) Etioporphyrin I molecules adsorbed on a NiAl(110) surface at 13 K was induced by a scanning tunneling microscope (STM). The threshold voltage for the conformational change at negative sample bias depends linearly on the tip-sample distance, suggesting an electrostatic force mechanism. The reverse conversion involves inelastic electron tunneling via a molecular electronic resonance at 1.25 eV. In contrast with the photon-induced conformational changes, an electrically induced mechanism is realized with the STM.

DOI: 10.1103/PhysRevLett.93.196806

PACS numbers: 85.65.+h, 68.37.Ef, 68.43.Fg, 82.37.Gk

The conformational structure of molecules adsorbed on surfaces is dictated by the subtle balance between the molecule-substrate interactions and the internal mechanics of the molecules. Understanding this complex interplay and being able to control the conformational structures of adsorbed molecules would provide a deeper understanding of chemical dynamics on surfaces [1,2] and enable molecule-based applications in functional devices [3,4]. The scanning tunneling microscope (STM) provides a unique approach to directly investigate the molecule-substrate interactions [5] and molecule's internal motions under external perturbations [6,7]. The ability to alter the conformation of a single molecule on the surface is also expected to clarify the structure-specific properties, such as molecular conductivity and electroluminescence of [8,9].

Here, we report the use of the STM to image, induce, and determine the mechanisms of the conformational changes of Zn(II) Etioporphyrin I (ZnEtioI) molecules adsorbed on NiAl(110) at 13 K. The deformation of the ZnEtioI upon adsorption was directly revealed by the identification of the two nonplanar conformers of the molecule. The structural flexibility of the porphyrin macrocycle allows the molecule to undergo reversible transitions between the two conformational states. From the characteristics of threshold voltages for the transitions, mechanisms involving the electrostatic force and temporary formation of a molecular anion are implicated.

Experiments were conducted with a homemade variable-temperature STM in ultrahigh vacuum. The single-crystal NiAl(110) was prepared by repeated cycles of Ne⁺ sputtering and annealing. The Al atoms are displaced 0.22 Å above the Ni atoms to form alternating rows and troughs along the [001] direction on the NiAl(110) surface [10]. 1,3,5,6-tetramethyl-2,4,6,8-tetraethylporphyrin Zinc(II) (ZnEtioI) was thermally evaporated onto NiAl(110) at 13 K.

The molecular structure of ZnEtioI is shown in Fig. 1. In solutions, noncoordinated ZnEtioI exhibits a planar geometry with C_{4h} symmetry [11]. In contrast, STM images of ZnEtioI molecules adsorbed on NiAl(110) re-

veal two nonplanar conformations, as shown in Fig. 1. In both conformations (type I and type II), two opposite lobes of a molecule appear more pronounced than the other two lobes, and the molecule possesses a C_2 symmetry with a saddle shape. The alternating arrangement of the ethyl and methyl groups at the periphery of ZnEtioI yields the two adsorption-induced chiralities [12], as distinguished by the asymmetric lobes in the STM images for type I and type II conformations. The populations for the two chiralities are statistically equal.

Density functional theory (DFT) calculations using the generalized gradient approximation (GGA) for exchange correlation and the VASP codes were carried out to determine the structure and energetics of the two conformations [13]. Two structures resembling the experimental conformations were found and are shown in Fig. 1: clover shape with nearly C_4 symmetry (type II) and saddle shape with C_2 symmetry (type I). The adsorption height from the molecular structure was calculated to be in the range 3.25–3.55 Å. In comparison, the apparent height of the molecules from STM images varies around 3 Å, depending on the bias voltage. But contrary to experiment, the calculated barrier between the two conformations is negligible (<10 meV) [13].

Porphyrin molecules in solutions and solid phases can adopt nonplanar structures [14]. Porphyrin molecules adsorbed on surfaces mostly adopt the planar configuration, as evidenced by the uniform four-lobe structure in STM images [15]. In some cases, the bulky peripheral substituents of the molecule change their orientations with respect to the porphyrin ring because of interactions with the substrate or the STM tip [5,7]. However, the deformation of the porphyrin plane remains difficult to identify. The saddle geometry of ZnEtioI on NiAl(110) is indicative of a distortion of the macrocyclic skeleton of the molecule [16].

Figure 2(a) shows an I - V measurement acquired over the center of a ZnEtioI molecule initially in a type I structure. Two steplike changes in current, occurred at 1.35 V and -1.38 V, respectively, were recorded as the sample bias was ramped from -1.8 V to 1.8 V (red curve)

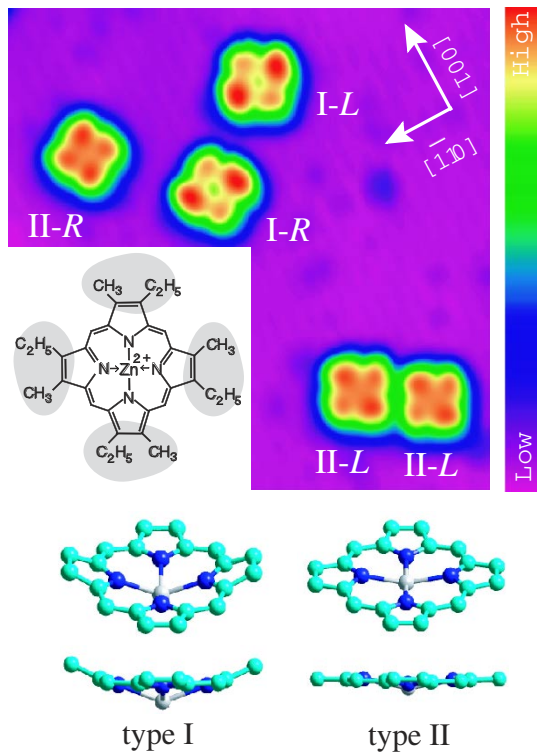


FIG. 1 (color online). STM image of ZnEtioI molecules adsorbed on the NiAl(110) surface at 13 K. The image, 104 Å by 104 Å, was acquired at a sample bias of 0.7 V and tunneling current of 0.1 nA. The color palette represents a variation in apparent height of 3.3 Å. The adsorption conformations of the molecules are denoted as type I and type II. The two molecules in type I conformation exhibit adsorption-induced chiralities that can be distinguished by the “propeller” shape of their STM images. For the three molecules in type II conformation, the molecule in the top left corner has different chirality from the two molecules in the bottom-right corner. The two chiralities are labeled *R* and *L* in the image, denoting the ethyl group to be on the right (left) of the methyl group. Molecular structure of ZnEtioI is superimposed over a schematic representation of the four-lobe STM image expected for ZnEtioI with a planar configuration. Bottom: DFT calculations yield two structures resembling the two types of conformations [13]; the perspective 3D and side views illustrate the nonplanar porphyrin macrocycle in the two conformations. The measured height differences between the molecular lobes in type I and type II molecules are 0.4 Å and 0.1 Å, respectively.

and from 1.8 V to -1.8 V (blue curve). The abrupt increase in current at 1.35 V indicates the conductance through the molecule suddenly switched to a higher conducting state [17]. At -1.38 V, the jump in current corresponds to a sudden decrease of conductance through the molecular junction. Repeating the voltage cycle, the I - V curves were found to be reversible, except that the abrupt changes in current occurred at different voltages, as shown in Fig. 2(b) for a series of 21 I - V curves recorded consecutively over the same molecule. Apparently, a wider voltage variation is measured for the steplike

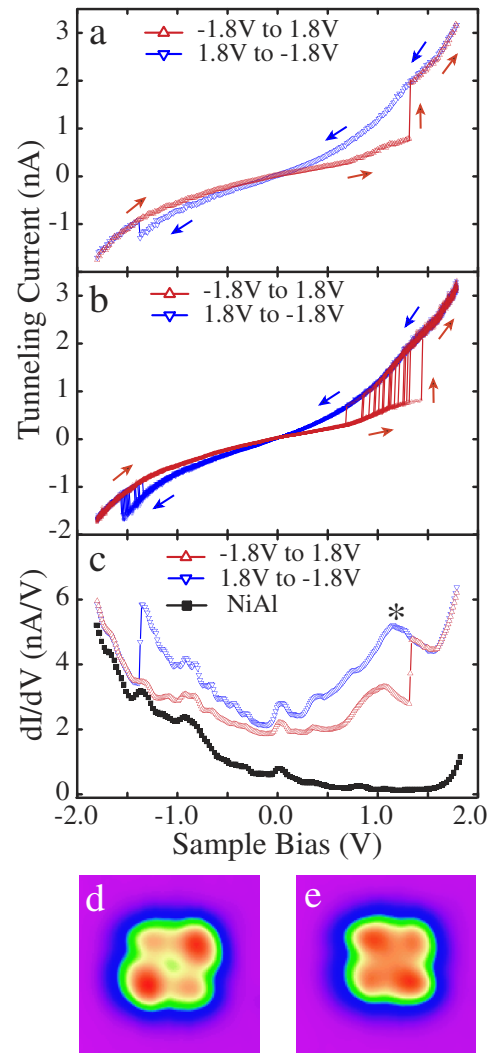


FIG. 2 (color online). (a) I - V characteristics of a ZnEtioI molecule. The STM tip was positioned over the center of a molecule in type I conformation. After turning off the feedback, the sample bias was decreased from the imaging condition (0.7 V) to the beginning of the voltage cycle, -1.8 V. The pair of I - V curves corresponds to variation of the tunneling current as the sample bias was ramped up from -1.8 V to 1.8 V, and then ramped down from 1.8 V to -1.8 V. The voltage step size is 12 mV. (b) A set of 21 pairs of I - V curves recorded consecutively over the molecule, showing variations in the threshold voltages for reversible current jumps. (c) dI/dV spectra recorded simultaneously with the two I - V curves shown in (a), compared to a background spectrum acquired over clean NiAl(110) surface. The dI/dV curves were recorded by a lock-in amplifier, with an ac modulation of 10 mV rms amplitude added to the sample bias. An electronic state at ~ 1.25 V (*) is evident in spectra taken over the molecule. (d) Image of a molecule in type I- L conformation. (e) Image of a type II- L conformation. Each image size is 33 Å by 33 Å.

change in current at positive bias compared to that at negative bias.

The differential conductance (dI/dV) is related to the local density of states in the tunnel junction. In Fig. 2(c),

most of the features in the dI/dV curves recorded over the molecule are consistent with those over the bare NiAl(110) surface, except for the two abrupt current jumps and a pronounced electronic state at around 1.25 V. The voltage range for the abrupt current variations at positive bias in Fig. 2(b) coincides with this broad electronic state. Similar to an electronic resonance at ~ 1.7 eV in STM dI/dV spectra reported for metal tetraphenylporphyrins adsorbed on Au(111) [18], the dI/dV peak at 1.25 V in Fig. 2(c) is attributed to a molecule-derived state involving the π^* lowest unoccupied molecular orbital (LUMO) of ZnEtioI molecule.

The origin of the current jumps in the I - V curves can be understood by imaging the molecule after sensing an abrupt current change. The molecule was in type I state [Fig. 2(d)] at the start of the sample bias scan from -1.8 V to 1.8 V. After detecting a jump in current at about 1.25 V, the sample bias was decreased to 0.7 V for imaging. The molecule was found to change to a different configuration, as shown in Fig. 2(e). Based on the apparent height and size of the molecular lobes, we identify this new configuration as the type II conformation. The tip was repositioned over this type II conformation and the sample bias was raised from 0.7 V to 1.8 V. No jump in current was observed. As the voltage was ramped down to -1.8 V, a sudden decrease in current was detected at around -1.38 V, similar to that of the blue curve in Fig. 2(a). The sample bias was restored to the image condition of 0.7 V. STM image shows that the molecule has changed back to type I conformation, identical to Fig. 2(d).

The images in Figs. 2(d) and 2(d) show that the chirality of the molecule remains the same during the conformational changes, ruling out the possibility that the molecule underwent a “flipover” process [19]. Additionally, we found that the molecules trapped inside self-assembled islands showed spectroscopic features and conformational changes consistent with those observed for an isolated molecule, making it unlikely that the observed variations in molecular images are caused by different adsorption sites or rotation of the molecule. We further demonstrate in Fig. 3 a sequence of controlled transitions between type I and type II conformations of individual ZnEtioI molecules, illustrating the reversible interconversion between the bistable states of the molecule.

A series of I - V curves, similar to Fig. 2(b), was obtained at a different tunneling gap. The voltages corresponding to the two current jumps at positive and negative sample bias exhibit different behaviors as a function of tip-substrate displacement (Fig. 4). The threshold voltage for a ZnEtioI molecule to switch from type II to type I conformation increases linearly in magnitude as the tip moves away from the substrate surface. The slope of this linear dependence yields a constant electric field of 0.26 V/Å [20]. In contrast, the threshold

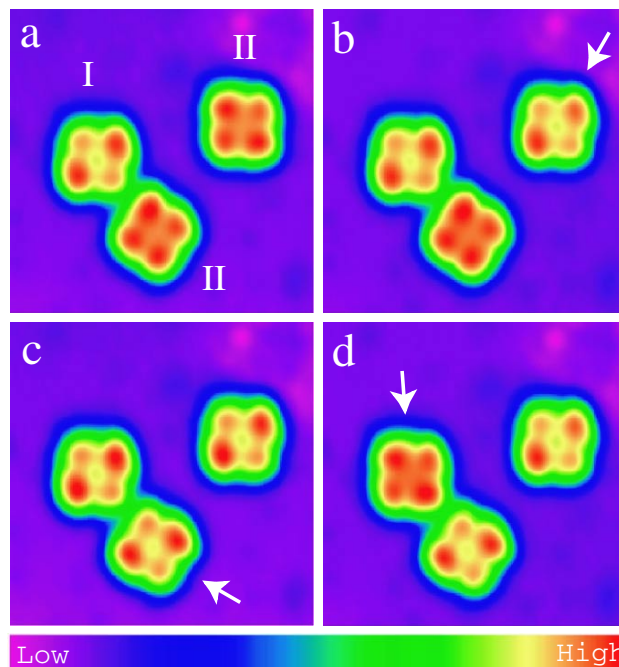


FIG. 3 (color online). A sequence (a)–(d) of STM images showing the controlled, reversible conformational changes of individual ZnEtioI molecules on NiAl(110) at 13 K. In each image, the molecule pointed by arrow underwent a transformation from its previous conformational state. A molecule with type I conformation was transformed into type II conformation when the STM tip was positioned over the molecule and the sample bias was raised to 1.8 V for 100 ms. A reverse transformation from type II to type I conformation was accomplished by lowering the sample bias to -1.8 V for 100 ms. The size of each image is 73 Å by 73 Å. The images were taken with a sample bias of 0.7 V and tunneling current of 0.1 nA. The color palette represents a variation in apparent height of 3.3 Å.

for the transition from type I to type II spans a much broader voltage range and exhibits a weak dependence on the tunneling gap. Most significant is the overlap of the voltage range with the molecular electronic state revealed in the dI/dV curves in Fig. 2(c).

The anisotropy of the NiAl(110) surface influences the orientation of the adsorbed ZnEtioI. STM images that resolve the surface atoms reveal that the center of the molecule, the central metal ion (Zn^{2+}), is over the bridge site along the Ni trough. A pair of opposite pyrrole rings of the molecule could be located over the neighboring Al rows and the other two rings over the Ni trough. Because of the different electronic properties of Ni and Al atoms and the surface corrugation, the four pyrrole rings would experience nonuniform interactions with the substrate, leading to nonplanar molecular geometries. Similar distortion is found for ligand-coordinated Zn porphyrin molecules [14]. This structural distortion generates a molecular dipole moment normal to the surface, associated with the Zn^{2+} and the porphyrin ring. The linear dependence of the bias voltage for conformational change

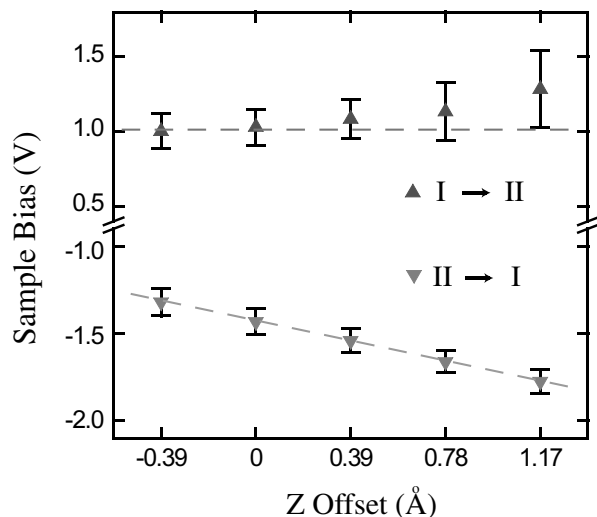


FIG. 4. Variations of threshold voltages for a ZnEtIol molecule to undergo the reversible conformational transitions from type I to type II and from type II to type I as a function of the change in tip-substrate separation. (Zero corresponds to the tunneling gap set by sample bias of 0.7 V and tunneling current of 0.1 nA). Positive (negative) value corresponds to tip displacement away from (toward) the surface. The statistics for each point in the plot is obtained from 21 to 30 I - V curves. The dashed lines in the plot serve to guide the eyes. The large range of sample bias for type I to type II transition reflects the mechanism involving broad electronic resonance.

(from type II to type I at negative bias voltage) on the tip-sample separation is evidence for a mechanism involving the electric field acting on the dipole and overcoming the energy barrier for conformational change. The transition from type I to type II at positive bias voltage is dominated by a mechanism involving inelastic electron tunneling. An electron from the STM tip temporarily occupies the molecular resonance at 1.25 eV before inelastic tunneling into a lower electronic state of the substrate. The energy released in this inelastic tunneling process provides the energy for the molecule to overcome the barrier for type I to type II transition [21].

The structural flexibility of the metalloporphyrin macrocycle is a prerequisite for the realization of interconversion of molecular conformations. The ability to reversibly switch between conformational states of an individual molecule and determine the underlying mechanisms provides a description of molecular mechanics that is important in our understanding of chemical and biological processes.

We are greatly indebted to S. Gao and R. Q. Wu for insightful discussions. Support of this work by the Chemical Science, Geo- and Bioscience Division, Office

of Science, U.S. Department of Energy under Grant No. DE-FG03-01ER15157 is gratefully acknowledged.

*Corresponding author; electronic address: wilsonho@uci.edu

- [1] J.K. Gimzewski and C. Joachim, *Science* **283**, 1683 (1999).
- [2] W. Ho, *J. Chem. Phys.* **117**, 11033 (2002).
- [3] Z. J. Donhauser *et al.*, *Science* **292**, 2303 (2001).
- [4] J. Lahann *et al.*, *Science* **299**, 371 (2003).
- [5] T. A. Jung *et al.*, *Science* **271**, 181 (1996).
- [6] J. Gaudioso, L. J. Lauhon, and W. Ho, *Phys. Rev. Lett.* **85**, 1918 (2000).
- [7] F. Moresco *et al.*, *Phys. Rev. Lett.* **86**, 672 (2001); **87**, 088302 (2001).
- [8] A. Troisi and M. A. Ratner, *J. Am. Chem. Soc.* **124**, 14528 (2002).
- [9] X. H. Qiu, G. V. Nazin, and W. Ho, *Science* **299**, 542 (2003).
- [10] S. -C. Lui *et al.*, *Phys. Rev. B* **39**, 13149 (1989).
- [11] K. K. Anderson *et al.*, *J. Am. Chem. Soc.* **115**, 12346 (1993).
- [12] X. H. Qiu, G. V. Nazin, A. Hotzel, and W. Ho, *J. Am. Chem. Soc.* **124**, 14804 (2002).
- [13] S. Gao (to be published). The weak interactions between the closed-shell molecule and the surface are notoriously difficult to calculate within the DFT. The present state of DFT-GGA scheme does not allow reliable treatment of weakly interacting systems involving van der Waals or dipole-dipole forces.
- [14] J. A. Shelnutt *et al.*, *Chemical Society Reviews* **27**, 31 (1998).
- [15] X. Lu, K. W. Hipps, X. D. Wang, and U. Mazur, *J. Am. Chem. Soc.* **118**, 7197 (1996).
- [16] T. Yokoyama, S. Yokoyama, T. Kamikado, and S. Mashiko, *J. Chem. Phys.* **115**, 3814 (2001).
- [17] The current change is transient, faster than the sampling speed of approximately 200 μ s for our instrument.
- [18] L. Scudiero, D. E. Barlow, U. Mazur, and K. W. Hipps, *J. Am. Chem. Soc.* **123**, 4073 (2001).
- [19] H. Yanagi, K. Ikuta, H. Mukai, and T. Shibusani, *Nano Lett.* **2**, 951 (2002).
- [20] By bringing the tip into contact with the bare metal surface, we determined the tunneling gap to be ~ 5.5 Å. The substrate and the tip apex were approximated by a pair of parallel electrodes.
- [21] As the tip is displaced away from the substrate surface, the tunneling current at a given bias decreases exponentially. Since the transition from type I to type II at positive bias is induced by hot electron excitation, it is likely that the apparent increase of the average transition voltage observed for increasing tip-surface distance is due to the lower flux of tunneling electrons. For sufficiently fast ramp rate and reduced tunneling current, an apparent increase in the transition voltage can occur.