

Atomic scale control of single molecule charging

G. Mikaelian, N. Ogawa, X. W. Tu, and W. Ho^{a)}

Department of Physics and Astronomy and Department of Chemistry, University of California, Irvine, California 92697-4575

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A scanning tunneling microscope was used to study charging of single copper phthalocyanine molecules adsorbed on an ultrathin Al_2O_3 film grown on a NiAl(110) surface. A double-barrier tunnel junction is formed by a vacuum barrier between the tip and the molecule and an oxide barrier between the molecule and the NiAl. In this geometry the molecule can be charged by the tunneling electrons. This charging was found to be strongly dependent on the position of the tip above the molecule and the applied bias voltage. © 2006 American Institute of Physics.

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The amount of charge in a molecule exerts a strong influence on its structure and reactivity. The transfer of an electron can lead to a conformational change and alter the reaction pathway of the molecule through redox energetics.¹⁻³ Furthermore, charge transfer plays an important role in the transport properties of single molecules.⁴⁻¹¹ The scanning tunneling microscope (STM) has been used for the manipulation of atoms and molecules to build artificial nanostructures that exhibit the relationship between the geometric and the electronic properties at the atomic scale.¹²

Here, we demonstrate that at a fixed bias voltage across the tunnel junction, resonant electron transfer only occurs when the tip is positioned over a certain region within the molecule. This region is found to be bias dependent, showing atomic scale control of single molecule charging. The phenomenon is demonstrated for single copper phthalocyanine (CuPc) molecules adsorbed on a thin (0.5 nm) Al_2O_3 film grown on the NiAl(110) surface. A double-barrier tunnel junction is formed, consisting of the molecule in between the oxide barrier and the vacuum gap.^{13,14} In such a junction, the energy of the lowest unoccupied molecular orbital (LUMO) varies for different positions of the tip over the molecule. This variation gives rise to the observed phenomenon.

There have been several efforts to study single-electron processes in two-dimensional electron gas, quantum dots, and single atoms using scanning probe techniques,¹⁵⁻¹⁸ and the spectroscopy of different metal phthalocyanines adsorbed on metal surfaces was extensively studied by STM.¹⁹ In the experiments presented here, STM is used to study spatially dependent charging of single organic molecules with submolecular resolution. The experiments were conducted with a homebuilt ultrahigh-vacuum STM operated at 11 K.²⁰ Thin (~ 0.5 nm) Al_2O_3 film, covering $\sim 50\%$ of the surface, was prepared by exposing the clean NiAl(110) surface to 140 Langmuirs (1 Langmuir = 1 s of exposure at 1×10^{-6} Torr) of O_2 at 750 K, and then annealing to 1300 K. CuPc was thermally sublimed from an alumina crucible onto the oxidized surface at 11 K.

^{a)}To whom correspondence should be addressed. Electronic mail: wilsonho@uci.edu

Electron transport through single CuPc molecules [left inset of Fig. 1(a)] in a double-barrier junction [right inset of Fig. 1(a)] was recently studied with the STM.^{13,14} Several adsorption geometries with distinct spectroscopic features are possible due to the oxide inhomogeneity. For some of the adsorption geometries the differential conductance spectroscopy shows a relatively broad band, consisting of a series of

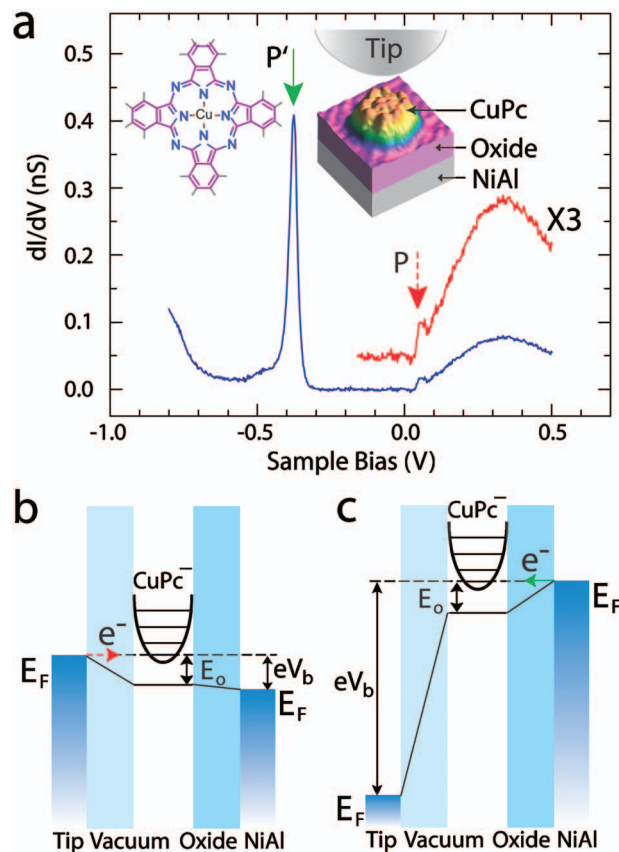


FIG. 1. (Color) Conduction through the affinity (CuPc^-) level of a CuPc molecule. (a) dI/dV spectra of the CuPc molecule. Insets: (left) schematics of the CuPc molecule, and (right) the double barrier junction geometry. The origin of the first peak in the vibronic progression (P) is illustrated in the tunneling diagram (b) ($V_b > 0$). The sharp peak (P'), corresponds to the tunneling diagram in (c) ($V_b < 0$).

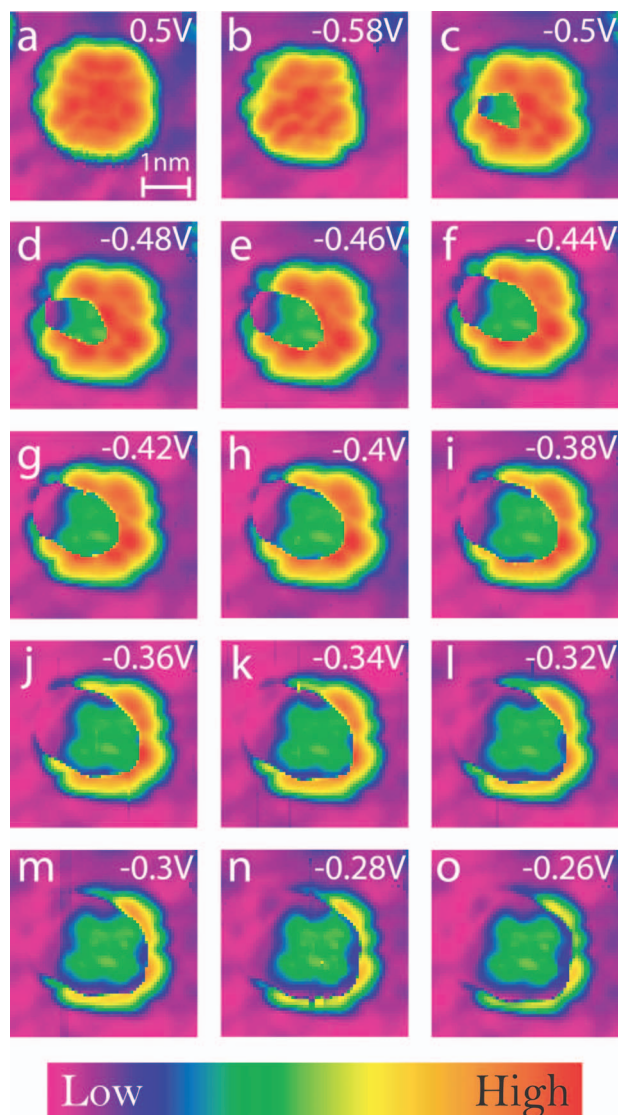


FIG. 2. (Color) Topographic images of CuPc molecules for different sample bias values. (a),(b) Images taken at positive and negative sample bias values. (c)–(o), For less negative bias values a depression with sharp edges appears in the image of the molecule. As the size of the depression increases a crosslike structure positioned in the center of the molecule emerges. The molecule is neutral when the tip is positioned above the hole and negatively charged when the tip is positioned above the molecule outside the hole. The tunneling current for all the images was 17.5 pA.

vibronic states^{13,14} at positive sample bias (LUMO), and a sharp peak on the negative bias side¹⁴ [Fig. 1(a)]. We denote the first peak in the vibronic progression as P and the sharp peak as P' [Fig. 1(a)].

The nature of these peaks is explained in Figs. 1(b) and 1(c). At positive sample bias, electrons tunnel from the tip to the molecule, and then to the NiAl [Fig. 1(b)]. An increase in the conductance (peak P) is observed, when the energy of the first vibronic state is aligned with the Fermi level of the tip (additional vibronic states are resolved at higher bias voltages in d^2I/dV^2 spectra¹³). At negative sample bias, electrons tunnel in the opposite direction, and a sharp peak (P') in the conductance appears, when the first vibronic state of the CuPc is aligned with the Fermi level of the NiAl [Fig. 1(c)]. Thus both P and P' are due to tunneling through the LUMO

of the CuPc molecule. The magnitude difference in the positions of the sharp peak and the first vibronic peak is due to the high dielectric constant of the oxide layer compared to vacuum, which results in a voltage drop across the vacuum gap being about seven times larger than the voltage drop across the oxide. The difference in the intensity of P and P' is explained by considering a two-step tunneling process in the junction, where the tunneling rate through the vacuum gap is much slower than the rate through the oxide. This results in a much greater number of vibronic and tip states that are available for tunneling.¹⁴ For both bias polarities, the lifetime of the negatively charged state of the molecule on oxide is drastically increased compared to tunneling through a molecule adsorbed directly on a metal surface.^{18,21} Density-functional theory calculations show that in the double-barrier tunnel junctions by varying the width of one of the tunnel barriers and the bias of tunneling electrons it is possible to achieve charging of a molecule by a single electron during electron transport.²² Since the tunneling rate between the tip and the molecule is much smaller than the tunneling rate between the molecule and the NiAl substrate, CuPc molecule is charged when the sample bias value is less negative than the position of the sharp peak (P').

Thin insulating films electronically decouple adsorbed molecules from the metallic substrate and the topographic STM images represent the geometry of the orbitals responsible for tunneling.²³ Since tunneling for both bias polarities occurs through the same molecular state, topographic (constant current) images of single CuPc molecules taken at positive and negative sample bias values [Figs. 2(a) and 2(b)] have the same symmetry, which in this case corresponds to that of the two fold degenerate e_g orbital.

Since the charge state of the molecule depends on the applied voltage, topographic images taken with the sample bias around the charging threshold reflect the spatial control of the single molecule charging in the double barrier junction. This effect is usually influenced by the observation that the position of the charging peak depends on the distance between the tip and the molecule.¹⁴ When the tip is moved closer to the molecule position of the sharp peak shifts towards the Fermi level, resulting in a change of the tunneling current. This change is compensated by the feedback loop. The variation in the tip-molecule distance due to the topography of the molecule is large enough to “broaden” the sharp peak so that topographic images do not have a simple interpretation. However, about 10% of the molecules with the sharp peak are adsorbed on sites where the position of the sharp peak does not shift or shifts negligibly with varying tip-molecule distance. For those molecules, topographic images taken at sample bias values close to P' show an unusual depression (“hole”) with very sharp boundary within the molecule [Fig. 2]. For less negative sample bias values, the size of this depression gradually increases, revealing a crosslike structure positioned at the center of the molecule [Figs. 2(e)–2(o)]. The position of the center of the hole usually does not coincide with the center of the CuPc and varies from one molecule to another, but the edges of the hole are always sharp, and the crosslike shape always appears.

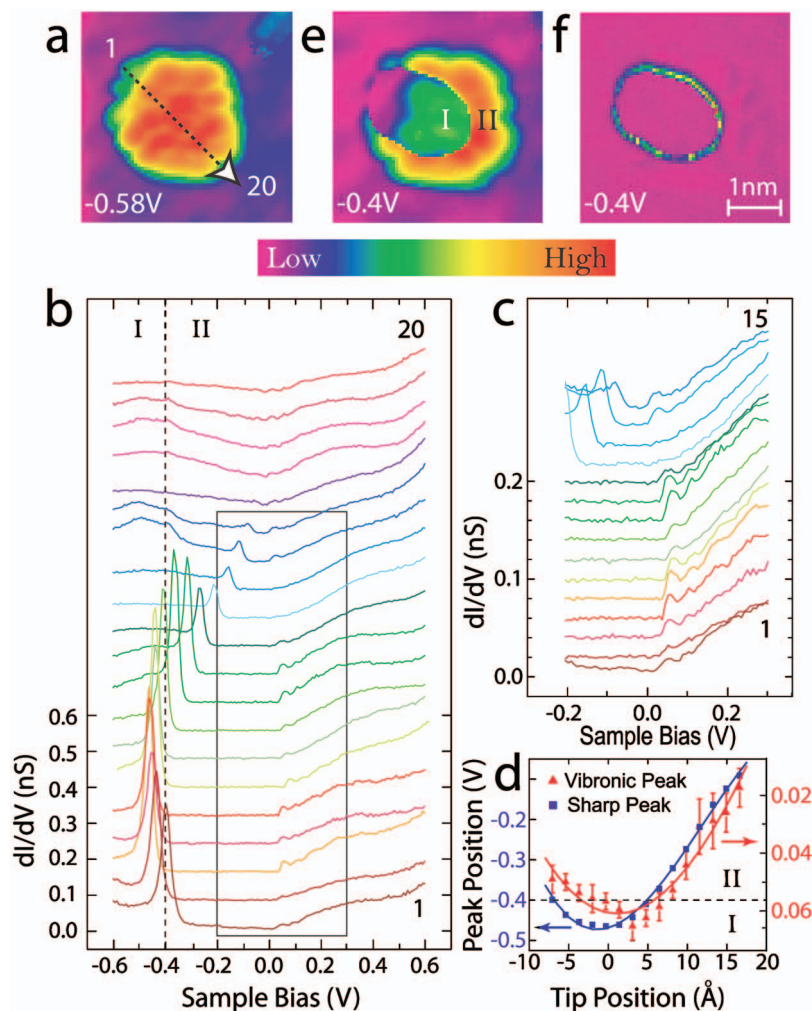


FIG. 3. (Color) Correspondence between topography and dI/dV spectroscopy. (a) Topographic image of a CuPc molecule taken at negative sample bias below the sharp peak. (b) 20-point dI/dV mapping, at equidistant points along the arrow in (a), shows that the sharp peak is closer to the Fermi level for the outer parts of the molecule. (c) At the positive side of the spectra, the onset of the vibronic progression also shows the similar shift. (d) Positions corresponding to the sharp peak (left vertical scale) and the first vibronic peak (right vertical scale). The vibronic peak position is scaled to take into consideration the voltage drop across the oxide to yield E_0 (Refs. 13 and 14). (e) Topographic image taken at -0.4 V. This value is less negative than the position of the sharp peak for the inner part of the molecule (region I), and more negative than that for the periphery of the molecule (region II). (f) dI/dV image of the molecule taken at -0.4 V shows the locus of positions for the sharp peak at -0.4 V, corresponding to the boundary between regions I and II.

In order to understand the nature of the hole, we obtained a spatial mapping of the differential conductance by measuring dI/dV spectra at 20 equidistant points across the molecule [dashed arrow in Fig. 3(a)]. The series of spectra in Fig. 3(b) shows variation in the position of P' for different locations of the tip above the molecule. The position of P' has its most negative value above the center of the hole and shifts to less negative values at the periphery of the hole. The variation in the corresponding positions of P is smaller, but it exhibits the same trend—position of P at the periphery of the hole is closer to the Fermi level of NiAl than at the center of the hole [Fig. 3(c)]. Positions of the sharp peak, P' , and the corresponding vibronic peak, P , are plotted in Fig. 3(d). The ratio P'/P is approximately constant (7.6 ± 1.0) for all spectra, with small variations for different parts of the molecule, attributed to the oxide inhomogeneity.

The topographic image taken at sample bias value -0.4 V is shown in Fig. 3(e). In this image we divide the molecule into two regions. Region I is the part of the molecule inside the hole and region II is the outer part of the molecule. This value of the sample bias is shown in Figs. 3(b) and 3(d) with dashed lines. The dashed line in Fig. 3(b) divides dI/dV spectra into two distinct regions. In region I, the sharp peak voltage is more negative than the chosen bias, and in region II, it is less negative. To verify that regions I and II in the topographic image [Fig. 3(e)] correspond to

regions I and II in Fig. 3(b) and 3(d), we take dI/dV image at -0.4 V. The image shows a “ring” corresponding to the spatial positions of the sharp peak at -0.4 V [Fig. 3(f)], which coincides with the boundary between regions I and II. Thus when the tip is positioned above region II, part of the LUMO is below the NiAl Fermi level, as shown in Fig. 1(c), and the molecule is charged. When the tip is positioned above region I, the LUMO of CuPc is higher than the Fermi level of NiAl, and electrons tunnel directly between the NiAl and the tip. Since tunneling is influenced by the presence of the CuPc molecule in the junction through its effects on the tunneling barrier and the density of states, the topography of an uncharged molecule is obtained.²⁴ In the image taken at -0.58 V [Fig. 2(b)], the molecule is charged for all positions of the tip above it. As the sample bias approaches zero, the size of region I gradually increases [Fig. 2]. For the most part of the image taken at sample bias value -0.26 V [Fig. 2(o)], the molecule is uncharged and the topographic image reveals a crosslike structure.

The phenomenon was also observed for single naphthalocyanine molecules adsorbed on thin aluminum oxide film. For both molecules the symmetry of the hole does not represent the symmetry of the molecule, which implies that the phenomenon is attributed not only to the behavior of the isolated molecule but is a property of the molecule-oxide complex specific to the adsorption site of the molecule. The

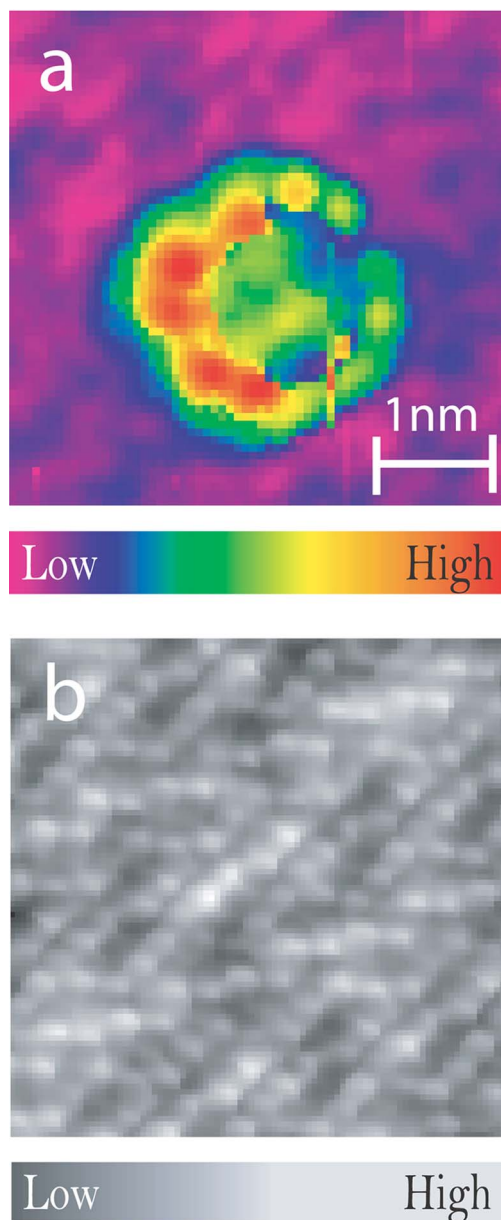


FIG. 4. (a) STM image of the molecule with a hole. (b) STM image of the same area after removing the molecule with the STM tip. The protrusions are Al atoms.

conductance of adsorbed molecules can be influenced by nearby point charges.²⁵ Since the described behavior is exhibited by about ten percent of those molecules with charging peak (P') and the center of the hole can be found at a variety of locations for different molecules, it is possible that the molecules are adsorbed on a defect site. To check this we removed a molecule with the STM tip and imaged the adsorption site with an atomic resolution [Fig. 4]. In the Fig. 4(b) protrusions correspond to the Al atoms,^{26,27} and there are no Al vacancies at the adsorption site of the molecule. However, we cannot exclude a charged defect due to a missing oxygen atom. The shift in the peaks of the LUMO [Figs. 3(c) and 3(d)] is attributed to the tip-dependent potential the molecule-oxide complex experiences in the junction. Theo-

retical calculations of this potential for different tip positions over the molecule and molecular adsorption sites on the oxide are required to obtain a quantitative understanding of the shift.

Unusual topographic features were found in single CuPc molecules adsorbed on thin Al_2O_3 film grown on NiAl(110) surface. These features were attributed to a very strong dependence of the charging of the molecules during the electron transport in the double-barrier tunnel junctions on the position of the STM tip within the molecule. These experiments demonstrate a new strategy for controlling conductance and the charged state of single molecules and can be applicable for future molecular electronics devices.

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