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Electron transport through single phthalocyanine molecules studied using scanning tunneling microscopy

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Using low-temperature scanning tunneling microscopy, electron transport across single H_2- or Co-phthalocyanine molecules was studied. The molecules were adsorbed onto clean Cu(111) surface and Co nanostructures on Cu(111) and were contacted through a controlled approach of the tip. Soft phonons from the molecular side groups promote a discrete jump to contact followed by bond formation. Molecular conductances strongly depend on the substrate but not on the central atom of the molecules. This is explained by charge transfer and hybridization of the molecular orbitals with the substrate states as seen by scanning tunneling spectroscopy.

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In the last few decades, remarkable progress has been made in the semiconductor industry towards the miniaturization of electronic devices following Moore's law. The physical limits of this top-down approach will be reached in the foreseeable future as devices of the size of single atoms or molecules will be required. A new approach in miniaturization of electronic devices is the study of molecular electronics, i.e., the fabrication of circuits at the molecular scale. Electron transport through single molecules is at the heart of this approach and has as such become a question of general interest in view of its possible applications.[1,2]

The most important characteristics of a molecular junction are the electron transfer rates between the metal electrodes contacting the molecule and the molecule itself, as well as the transmission of electrons through the molecular orbitals. Yet, surprisingly, very few quantitative studies directly address these parameters.[3] This discrepancy reflects an insufficient control of the molecular adsorption geometry, compounded by the lack of control of the electrode geometry in the common break junction experiments.[4] An alternate, more precise method to contact single molecules is the use of scanning tunneling microscopy (STM).[3,5–8] Indeed, STM enables the imaging of the substrate, which plays the role of one of the electrodes, and of the molecules on this substrate before contacting a single molecule at a well defined position. The family of phthalocyanine (Pc) molecules has received much attention due to their thermal stability, as well as the ability to tune their structural, chemical, and transport properties by substituting the metal cation (Me) within the Pc molecular cage or by grafting atoms or radicals onto the side groups [see Fig. 1(a)]. For Pc molecules adsorbed on a metal substrate, recent reports on controlling the Kondo effect[9] or studying their vibrational states during single molecule electron transport[10] have been published.

Determining the precise experimental geometry of a molecular junction is of considerable importance towards a convergence with *ab initio* theoretical calculations. In the context of molecular spintronics, it is also essential to understand the nature of hybridization between a molecule and a magnetic surface. The behavior of Pc molecules on magnetic (Co) and nonmagnetic (Cu) surfaces is the aim of our work. In this Brief Report, we present an experimental study of the contact and electrical transport between CoPc or H_2Pc molecules and a Cu(111) or Co/Cu(111) surface using STM. At first, distance curves were recorded, in which the tunneling current I was measured as a function of the distance between tip and sample until a molecular junction was formed. We used inelastic scanning tunneling spectroscopy (ISTS) to show how soft phonon modes within the molecular side groups promote the observed abrupt formation of the molecular junctions. Finally, scanning tunneling spectroscopy (STS) was performed on the molecules to explain the difference in conductance of the molecules when placed on the Co or Cu surface.

The experiments were carried out with a home-built ultra-

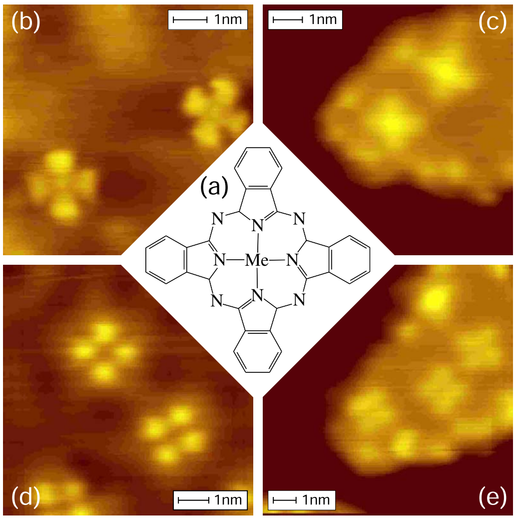

FIG. 1. (Color online) (a) Chemical structure of a Me-phthalocyanine molecule consisting of four benzene pyrole groups connected over four nitrogen bonds. The nitrogen sites of the pyrole can form a complex compound with a metal cation (Me). Here Me=H_2,Co. (b)–(d) Topographic scans at $T=4.2$ K of CoPc (b) on Cu(111) and (c) on Co/Cu(111), and H_2Pc (d) on Cu(111) and (e) on Co/Cu(111).

high vacuum STM at 4.2 K. The tungsten STM tips were cleaned *in situ* by Ar^+ sputtering and annealing. An atomically clean and flat Cu(111) single crystal was used as a substrate. Auger-electron spectroscopy showed no contamination on the Cu surface and low energy electron diffraction revealed sharp spots and low background, indicating a high crystal quality. STM scans revealed atomically clean terraces of widths exceeding 50 nm. A submonolayer amount of Co was deposited onto Cu(111) by electron-beam evaporation, resulting in the formation of pseudomorphic double-layer islands of Co.[11] Finally, a small amount of purified H_2Pc or CoPc was deposited from a Knudsen cell, followed by STM experiments at 4.2 K. During the deposition of the molecules, a sample temperature of around 270 K was maintained to avoid molecular diffusion on the bare Cu toward the step edges of the Co islands. Topographic measurements reveal that both molecules were adsorbed on the Co islands as well as on the bare Cu. Figures 1(b)–1(e) show a small area scan for the two different molecules on bare Cu(111) and Co/Cu(111). Note that, in these scans, the CoPc molecules display a bright spot in the center of the molecule—corresponding to the Co site—while H_2Pc displays a depression.

After choosing a single molecule from topographical scans, current versus distance curves were obtained in the following way: the STM tip was positioned above a molecule at a low bias voltage of typically 10 mV. Then the feedback loop of the STM was opened, and by ramping the voltage of the z piezo, the tip was moved toward the sample surface in a controlled manner. During the tip approach, the tunneling current I was recorded. Afterward, the tip was retracted back to its initial position. The approach was repeated 25 times over the same molecule.

We present in Fig. 2(a) experiments on the formation of a CoPc molecular junction using a STM tip. The initial tip approach on bare Cu(111) reveals an exponential increase of the current that reflects the reduction of the tunneling barrier width as expected. The extracted work function of 4.3 eV on Cu agree well with previous work functions measured in the STM geometry.[12] The tip approach toward a CoPc molecule that is adsorbed onto Cu initially shows the same behavior, yet deviates from the expected exponential dependence below a certain distance. The current rises superexponentially, which can be explained by a partial lifting of the molecule due to the close proximity of the tip. Ultimately, the molecule jumps into contact with the tip, thereby bridging the tunnel junction formed by the STM tip and the Cu(111) surface. All subsequent approach curves reveal an almost constant conductance of the molecular junction, i.e., the bond that is initially formed remains intact after returning to the initial tip-sample distance. In this bridged position of the molecule, a relatively high conductance of 0.1 G_0 was observed, which most likely reflects the conductance via the delocalized π orbitals of the molecule.

After measuring several distance curves in the bridged position, but before proceeding with the topographical scan, the feedback loop is closed again. In order to reach the original set-point current, the tip is retracted until the current drops, i.e., until the molecular bridge is broken. When the topographic scan was continued after taking the distance curves, the molecule disappeared from the image [see Fig. 2(c)]. This indicates that, in the process of breaking the bridge, the CoPc molecule was transferred to the tip.[13] Obviously, the Pc forms a more stable bond to the W tip than to the Cu surface, as is expected from the low chemical reactivity of Cu compared to W. Measurements of H_2Pc on Cu(111) show similar results [see Figs. 2(b) and 2(d)]. The same behavior of the tunneling current, including the jump to contact, was observed and similar values for the conductance, ~0.1 G_0, were found. Apparently, neither the contact behavior nor the conductance is influenced by the central metal cation. This further proves that the conductance is not related to the central Pc metal atom but to the delocalized π electron system of the organic ligands.

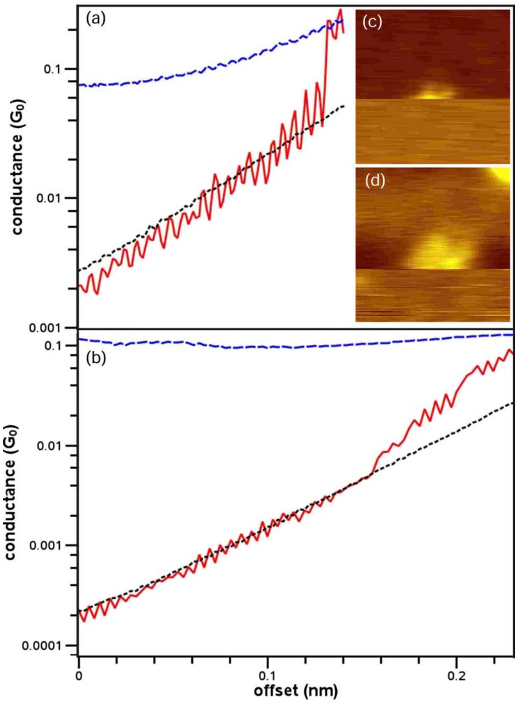

FIG. 2. (Color online) Tip approach experiments on (a) CoPc and (b) H_2Pc on Cu(111) show how distance curves measured atop the molecule (solid red/gray line) deviate over a 0.2 nm distance range from those measured on bare Cu (dotted black line) and upon a subsequent approach (dashed blue/dark gray line) remain essentially constant, reflecting the molecular contact. Here, the offset stands for the displacement of the tip toward the surface. (c) CoPc ($5\times5 nm^2$) and (d) H_2Pc ($7\times7 nm^2$) topographical scans showing the abrupt transfer of the molecules to the tip after recording distance curves.

Measurements of H_2Pc and CoPc on the Co/Cu(111) islands (Fig. 3) show a similar "jump-to-contact" behavior as on bare Cu(111). However, in contrast to the experiments on Cu(111), the subsequent distance curves measured on Co start essentially at the original current set point. This means that the molecule-tip bond that occurs during the jump to contact is broken again when the tip is retracted. In agreement with this finding, the molecule can also be seen in a topographic scan taken after the tip retraction (see the insets of Fig. 3). Thus the Pc molecules form a stronger bond to Co than to Cu. Furthermore, we observe a conductance of

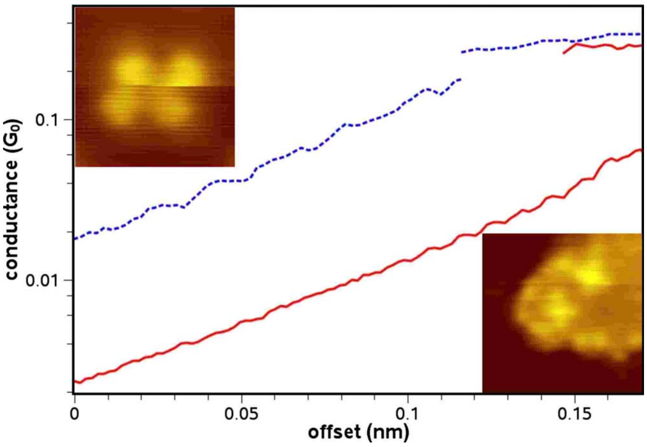

FIG. 3. (Color online) Averaged distance curves measured atop CoPc (solid red/gray line) and H_2Pc (dotted blue/dark gray line) molecules adsorbed onto Co/Cu(111) reveal a reversible jump-to-contact behavior. For CoPc above approximately 0.13 nm there are two curves: the upper one is the average after a jump, the other without a jump. The offset between the two data sets reflects the different current set points for these measurements. Insets: topographical scans of H_2Pc [upper left; $(3\times3\ \mathrm{nm}^2)$] and CoPc [lower right; $(8\times8\ \mathrm{nm}^2)$] during taking distance curves.

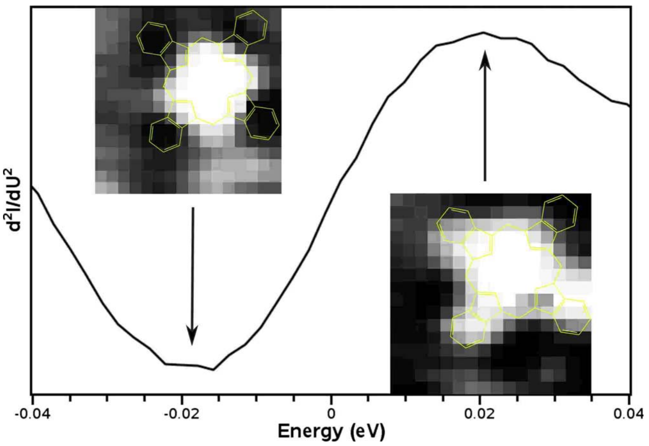

FIG. 4. (Color online) Energy dependence of ISTS for CoPc on Co/Cu(111). Insets: $d^2I/dU^2(\pm20\ \mathrm{meV})$ spatial maps, with high inelastic excitation probability on the molecular side groups. The molecular overlay serves as a guide to the eyes.

$\sim0.3\ G_0$ across both CoPc or H_2Pc molecular junctions on a Co surface, which is approximately a factor of 3–4 higher than on a Cu surface. These findings suggest that the resistance of the molecular junction is not only given by the molecule itself, but also by the details of the contact between the molecule and the electrodes.

Our extensive studies on assembling CoPc and H_2Pc molecular junctions indicate that the molecular jump is more likely to occur if the tip approaches the benzene side groups rather than the center of the molecule. In the sudden jump to contact, the molecule geometry is changed in a conformational transition between two local minima of the total energy: the flat lying and the bridging configuration. As this transition is due to a mechanical soft mode, it should be related to low energy phonons of the flat molecule. ISTS measurements were carried out by measuring the second derivative of the tunneling current, which can reveal vibronic excitations.[14] Indeed, when the energy of the tunneling electrons is sufficient to create an inelastic excitation in the form of a phonon, a peak in d^2I/dU^2 appears.[15] Spatial resolution was achieved by recording inelastic spectra at different positions of the Pc molecule. Figure 4 shows the d^2I/dU^2 spectrum of a CoPc molecule on Co/Cu(111). An inelastic excitation at around ±20 meV appears in the spectrum as an antisymmetric combination of a peak and a dip. This excitation falls within the same energy range as the excitation energy of benzene-substrate phonons.[16] To locate the vibronic excitation within the molecule, we plotted the value of the inelastic spectrum at ±20 meV as a function of tip position atop the molecule (see insets of Fig. 4). A high inelastic excitation probability is indicated by a combined dark feature at negative and a bright feature at positive bias. We thus see that the excitations are located on the side groups of CoPc and can therefore be associated with a vibrational mode of the molecular side group. These low energy vibrations represent the molecular degrees of freedom of the molecular jump to contact when the tip is close enough to the molecule (see Figs. 2 and 3).

To gain more insight into the transport properties of the molecular junctions, spatial STS measurements were performed by opening the feedback loop for each tip position. The spatially resolved differential conductance dI/dU was in turn measured using lock-in techniques. Since the differential conductance is proportional to the local density of states (LDOS) at the tip position,[17] this allows both to measure the LDOS of the molecule as function of energy and to laterally map the LDOS at a specific energy, i.e., to image the molecular orbitals. The experimental results for CoPc are shown in Fig. 5. The energy-dependent LDOS, which was averaged over all individual spectra recorded above different positions of the molecule, exhibits peaks reflecting the molecular-orbital energy levels.[18] The spectra for CoPc on Co and on Cu have a similar overall shape, but the spectrum of CoPc on Co appears to be shifted by approximately +500 meV relative to that of CoPc on Cu. This shift is confirmed by the similar shape of the molecular orbitals when acquired on the relevant molecular-orbital energy levels [see within Fig. 5 the scan pairs (c)-(f) and (d)-(g) and their corresponding energy positions on panel (a)]. A similar behavior was found regarding H_2Pc molecules, where a shift of 400 mV is observed. We note that the molecular orbitals, which are strongly hybridized with the metal states of the substrate, differ from the orbitals in vacuum.[19] This energy shift indicates an electron transfer from the molecule to the less noble Co surface, suggesting a stronger bond as evidenced above. As a consequence, one molecular orbital is shifted to the Fermi energy, leading to a high LDOS at the Fermi edge. This in turn accounts for the higher molecular junction conductance when the molecules are placed on Co, since in this case electrons can be transferred efficiently from the electrodes to the molecule. Given the similar work functions $\phi=4.94$ eV for Cu(111) (Ref. 20) and $\phi=5.03$ eV for Co(111),[21] this 0.5 eV energy shift cannot be explained within the interface dipole model (see, e.g., Ref. 22), but

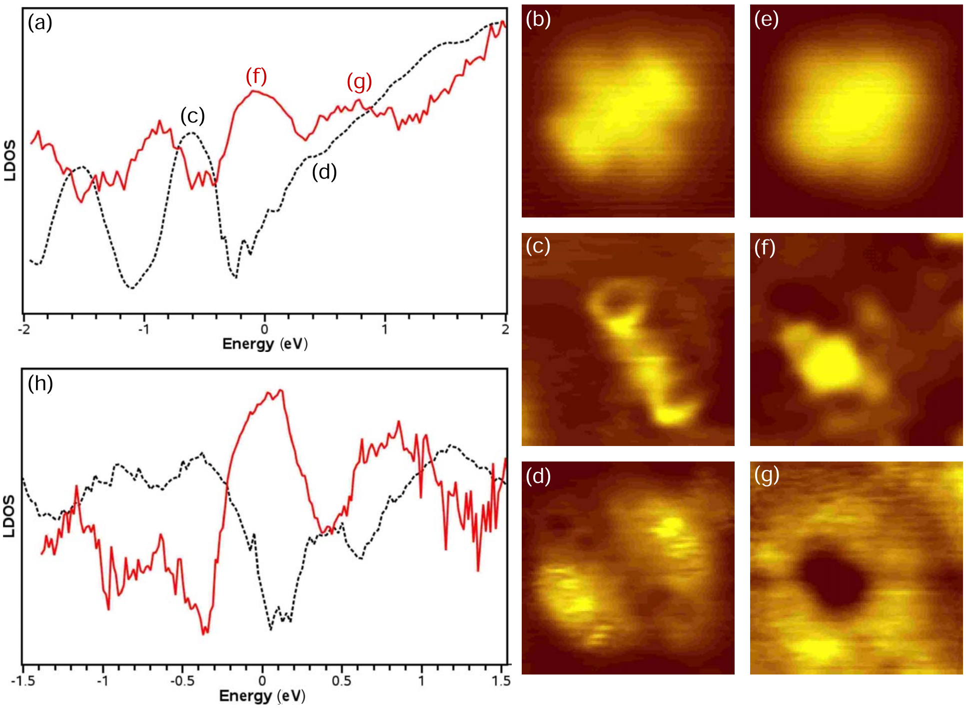

FIG. 5. (Color online) (a) Energy dependence of the LDOS for CoPc on Cu(111) (dotted black line) and Co/Cu(111) (solid red/gray line). Topographical scans of CoPc on (b) Cu and (e) Co. Spatial maps of the molecular orbitals at (c) 600 meV on Cu and (f) 100 meV on Co and at (d) 400 meV on Cu and (g) 800 meV on Co. The scans all span 2.5×2.5 nm^2. (h) Energy dependence of the LDOS for H_2Pc on Cu(111) (dotted black line) and Co/Cu(111) (solid red/gray line).

likely reflects fundamentally different adsorption mechanisms (physisorption vs chemisorption).[4]

In conclusion, we have presented systematic studies on assembling Pc molecular junctions with a STM tip. We have clarified the "jump-to-contact" mechanism that relates junction formation to a bending of the Pc molecular side groups due to soft phonons. We find that neither the contact behavior nor the conductance is influenced by the Pc's central metal cation. The measured conductance across our molecular junctions depends strongly on the metallic surface through the parameters of hybridization and charge transfer. On the Co substrate, the Pc molecule exhibits metallic behavior, while on Cu it is semiconducting with a gap at the Fermi energy. Our results, which nicely illustrate the interplay between the mechanical or adhesive properties of, and the charge transfer or electrical conduction across, a molecular junction, can help account for the large scatter of the conductance in molecular break junction experiments reported thus far.[4]

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