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Single-Molecule Chemistry of Metal Phthalocyanine on Noble Metal Surfaces

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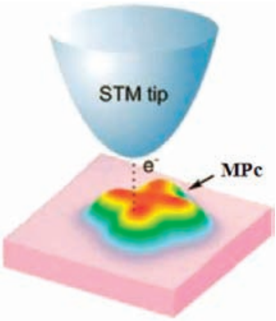

To develop new functional materials and nanoscale electronics, researchers would like to accurately describe and precisely control the quantum state of a single molecule on a surface. Scanning tunneling microscopy (STM), combined with first-principles simulations, provides a powerful technique for acquiring this level of understanding. Traditionally, metal phthalocyanine (MPc) molecules, composed of a metal atom surrounded by a ligand ring, have been used as dyes and pigments. Recently, MPc molecules have shown great promise as components of light-emitting diodes, field-effect transistors, photovoltaic cells, and single-molecule devices. In this Account, we describe recent research on the characterization and control of adsorption and electronic states of a single MPc molecule on noble metal surfaces.

In general, the electronic and magnetic properties of a MPc molecule largely depend on the type of metal ion within the phthalocyanine ligand and the type of surface on which the molecule is adsorbed. However, with the STM technique, we can use on-site molecular “surgery” to manipulate the structure and the properties of the molecule. For example, STM can induce a dehydrogenation reaction of the MPc, which allows us to control the Kondo effect, which describes the spin polarization of the molecule and its interaction with the complex environment. A specially designed STM tip can allow researchers to detect certain molecule−surface hybrid states that are not accessible by other techniques. By matching the local orbital symmetry of the STM tip and the molecule, we can generate the negative differential resistance effect in the formed molecular junction. This orbital symmetry based mechanism is extremely robust and does not critically depend on the geometry of the STM tip.

In summary, this simple model system, a MPc molecule absorbed on a noble metal surface, demonstrates the power of STM for quantum characterization and manipulation of single molecules, highlighting the potential of this technique in a variety of applications.

Introduction

Molecular adsorption on surfaces is an important issue in fundamental physical science, and it is also significant for various applications in new industries, such as heterocatalysis and nanoelectronics. In recent years, rapid progress in nanotechnology has drastically enhanced our capability to explore surface adsorption systems at the single-molecule level. Metal phthalocyanine (MPc) molecules, traditionally used as dyes and pigments, are composed of a metal atom and a surrounding ligand ring (Figure 1). Recently, it was shown that MPc also has great potential in applications such as light-emitting diodes,[1] field-effect transistors,[2] photovoltaic cells,[3] and single-molecule devices.[4,5] Due to their versatility for various applications, MPc molecules have become a model system for surface chemistry and nanotechnology.[6−12]

MPc provides a relatively standard and stable chemical environment for the central metal atom. When it is adsorbed onto the surface, the metal−ligand interaction and molecule−surface interaction are the two most important parameters to determine various physical and chemical properties of this adsorption system. Delicate molecule−surface coupling states have been

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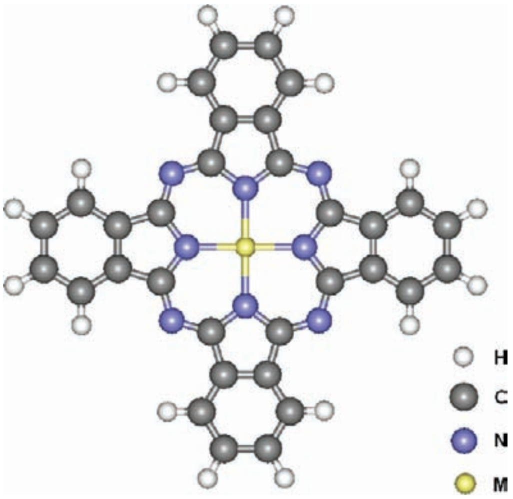

FIGURE 1. Ball-and-stick model of a metal phthalocyanine, with a metal ion M at the center of the molecule.

observed for a CoPc on the Au(111) surface.[13] Combination of different metal atoms in MPc and different surfaces will lead to very different geometrical, electronic, and magnetic properties.[14]

Scanning tunneling microscopy (STM) is a powerful tool for surface science.[15] With an ideally sharp tip, STM can obtain a two-dimensional surface image corresponding to local density of states (LDOS) of the sample surface near the Fermi energy (E_F).[16] On the other hand, if the coordinate of the STM tip on the sample surface is kept and the applied voltage is varied, a current−voltage ($I-V$) curve, also known as scanning tunneling spectrum (STS), can be obtained. Its differential dI/dV spectrum roughly represents the relationship between the density of state (DOS) and the energy. In other words, information for both spatially and energetically resolved DOS can be revealed by a real space STM dI/dV mapping technique.[17] Since STM probes the electronic structure instead of atomic structure of the sample, theoretical simulation based on density functional theory (DFT) becomes a necessary tool to interpret and predict STM experimental observations.[18]

STM has been utilized by many groups to study MPc adsorbed surfaces.[6−9] MPc adsorption systems with different central metal atoms have been well characterized and distinguished by STM .[14] More importantly, it has been shown that single molecule manipulation can be realized by STM, for instance, to restore the quenched magnetic moment in a CoPc adsorbed on a Au(111) surface.[9] A specifically designed STM tip can also be used as an electrode of a molecular junction to realize various functions such as negative differential resistance.[10]

It is very convenient in STM experiments to observe magnetic properties of adsorbed molecules by checking the possible Kondo effect in the STS spectrum. Kondo effect refers to the exchange interaction between localized spins and conduction electrons. Such an interaction could significantly modify the transport properties of the studied systems. Kondo effect was used to explain the resistance minimum in metal at low temperature caused by magnetic impurity scattering. Recently, Kondo effect in quantum dot[19−24] or single-molecule systems[25−28] has attracted increased interest. In such systems, a high-order virtual tunneling process may effectively flip the spin on the quantum dot or molecule. Successive spin flips then screen the local spin and form an intermediate spin-singlet state between electrodes and quantum dot on short time scales. Due to this state, a peak appears in the tunneling density of states (dI/dV spectrum) at the electrode Fermi level. This characteristic Kondo peak changes with temperature, and it typically can be fitted by the Fano model.[29] Kondo temperature is an important parameter in the Fano model to describe the resonance width.

In this Account, we focus on interactions between MPc and the noble metal surface on which it adsorbs. Electronic structure engineering by changing substrate, central metal atom, and STM tip and also by STM manipulation is demonstrated. The related physical/chemical mechanisms and implications to different possible applications are discussed.

CoPc on Different Surfaces

The MPc−surface interaction is found to be strongly dependent on the surface type and its structure. For example, by precise thickness control of thin films, different quantum-well states can form in silicon-supported Pd islands. When MnPc is adsorbed onto such Pd islands, oscillating Kondo temperatures as a function of film thickness will be found.[33]

CoPc adsorbed on Au, Ag, and Cu surfaces has been studied.[30] The STM topographic images for CoPc on Au(111) and Ag(111) surfaces are similar, but a distortion is observed for CoPc on Cu(111). A dI/dV spatial map gives the LDOS at a specific energy, thus providing more information with energy resolution than topographic images. We measure the dI/dV map at energy points where a peak exists in the DOS curve. The dI/dV patterns for CoPc on Au and Ag surfaces are similar, except for an about 0.6 eV energy shift of the peak positions, which should originate from the 0.6 eV work function difference between Au(111) and Ag(111) surfaces. However, the dI/dV maps for CoPc on the Cu(111) surface are strikingly dif-

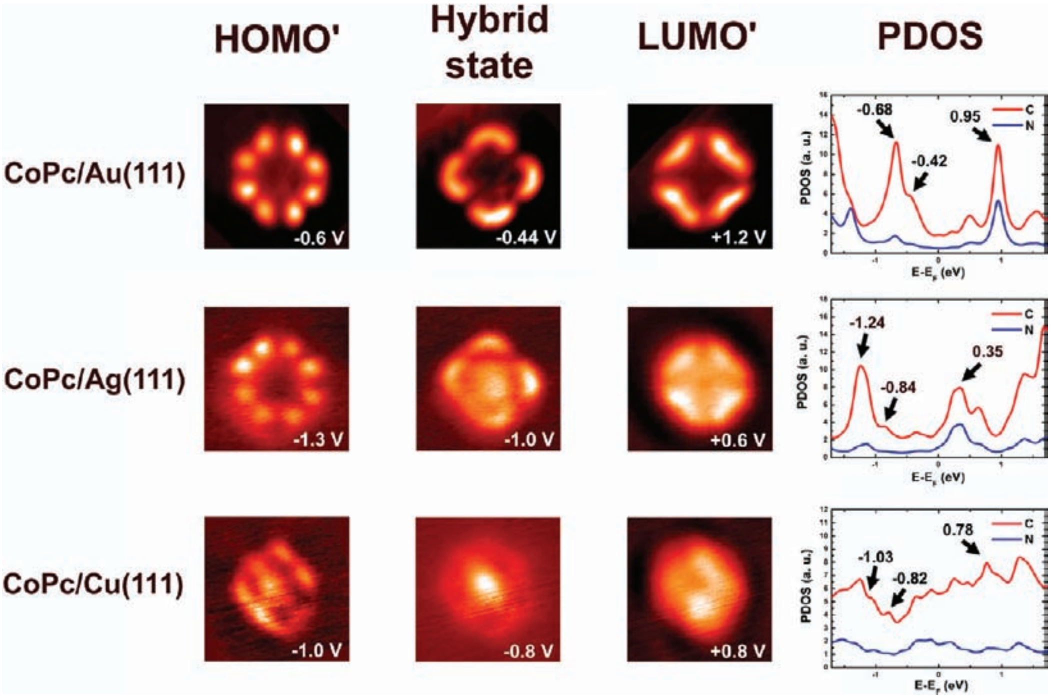

FIGURE 2. d*I*/d*V* spatial maps for CoPc adsorbed on Au (top), Ag (middle), and Cu (bottom) surfaces. The three left columns correspond to the HOMO-derived state (HOMO′), the state with fewer molecular components (hybrid state), and the LUMO-derived state (LUMO′), respectively. The bias values at which we obtain the d*I*/d*V* map are marked at the corner of each map. In the right column, calculated PDOS curves for C and N atoms composing lobes of CoPc are shown with the states corresponding to those experimental maps being pointed out.

ferent (Figure 2), indicating very distinct CoPc−Cu(111) surface interactions from those between CoPc and the Au or Ag surface.

The difference between Cu and Au or Ag surfaces can be understood by DFT calculations. According to the calculation results, the favorable adsorption site of CoPc on Au(111) and Ag(111) surfaces is the hcp site, while the bridge site becomes more favorable for the Cu(111) surface. A clear geometry deformation of the CoPc molecule is observed when it is adsorbed onto the Cu(111) surface. Projected density of states (PDOS) for CoPc on the Cu surface is also quite different from those for CoPc on Au and Ag surfaces (see Figure 2).

Different Metal Atoms in the MPc Molecule

An attractive feature of MPc is that the Pc ligand provides a similar chemical environment, and many different kinds of metal atoms can stably sit in the center of the molecule. Differences between the adsorptions of CoPc and CuPc on the Au(111) surface have been studied more than 10 years ago.[7] From their STM topographic images, one can easily distinguish these two molecules: for CuPc, the central metal atom appears as a hole, but the Co atom in CoPc gives a protrusion in the STM image. This is because the Co(II) d^7 system has significant d-orbital character near the E_F, while the Cu(II) d^9 system does not. Further studies[31] indicate that similar behavior can also be observed for FePc and NiPc.

Aiming to central metal atom based electronic structure engineering, we have systematically studied several 3d transition metal phthalocyanines on the Au(111) surface by DFT calculations.[14] First, we consider the possible adsorption sites of MPc molecules on the Au surface. On the Au(111) surface, we have top, bridge, hcp-hollow, and fcc-hollow sites.[32] The stable adsorption configuration is found to depend on the central metal atom type: MnPc prefers the top site, while other MPc (M = Fe, Co, Ni, or Cu) molecules prefer the hcp-hollow site. The distance between the metal atom M and the Au surface for MnPc and FePc are smaller than those for the other three molecules, which suggests that the interaction between these two molecules and the Au surface may be relatively stronger.

Except for NiPc, all other four MPc molecules have local magnetic moments (Table 1). After the molecules are adsorbed onto the Au(111) surface, different behaviors are observed: the magnetic moment on CoPc totally disappears, spin polarizations for MnPc and FePc are weakened, NiPc remains spin unpolarized, and the magnetic structure of CuPc is hardly affected by the substrate, too.

TABLE 1. Theoretically Calculated Electronic Magnetic Moment (μ_B) of MPc Molecules and Comparisons with STS Experimental Results

	magnetic moment (theoretical results)		whether Kondo effect was observed in STS experiments for MPc on Au(111)
MPc	single	adsorbed on Au(111)	
MnPc	3.17	2.95	no, but observed on Pb island[33]
FePc	2.03	1.05	yes[34]
CoPc	1.09	0.00	no[9]
NiPc	0.00	0.00	not available
CuPc	0.54	0.54	no[14]

Experimentally, the Kondo effect has been observed in the absorption systems with MnPc, FePc, and dehydrogenated CoPc (see Table 1).[9,33,34] We do not expect to observe Kondo effect for NiPc or intact CoPc on the Au(111) surface, since there is no local magnetic moment. Although it has a local magnetic moment, so far there is no report on Kondo effect for CuPc. To explain this paradox, the angle-momentum resolved PDOS (Figure 3) is analyzed. For the adsorbed MnPc and FePc, the d_{xz}, d_{yz}, and d_{xy} orbitals of the central metal atom dominate around E_F, and the d_{z^2} orbital dominates for CoPc. However, for CuPc, the $d_{x^2-y^2}$ dominates around E_F. Since the $d_{x^2-y^2}$ orbital is mainly distributed parallel to the surface, its interaction with the two electrodes should be much weaker than those of the other three MPc molecules. As a result, the Kondo temperature of adsorbed CuPc may be too low to be observed under current experimental conditions.

Orbital Symmetry Match between STM Tip and Molecule

So far, we have demonstrated the possibility of electronic structure engineering by changing the central metal atom of MPc and the surface. When we use STM as a research tool, we have many things to deal with the STM tip. Delicate STM tip modification has been widely used for various purposes.[35−38] The most popular STM tip modification technique is based on molecular adsorption on the tip, which generally leads to a sharper tip. However, the adsorption of molecules onto the STM tip is very difficult to precisely control. Recently, we have developed a simple STM tip modification method to generate a "blunter" tip to achieve higher resolution in the energy scale.[13]

For CoPc on the Au(111) surface, a molecule−surface hybrid state, which is difficult to observe using a conventional W STM tip, can be detected by a modified tip with coated Fe layers on the conventional W tip. Both W and Fe/W tips give very similar single-molecule topographic images (Figure 4), which indicates that both tips provide a good spatial resolution. However, there is a remarkable difference between the STS curves in the negative bias region obtained by positioning tips upon molecular center: the dI/dV curve measured with the Fe/W tip has four peaks, among which the −0.4 V peak (II_{Fe}) has never been reported before and disappears when it is probed with a W tip. On a clean Au surface, there is no large difference between dI/dV curves measured with the two tips, indicating that the new II_{Fe} peak is not introduced by a STM tip resonant state. This peak is not very sensitive to the position of the Fe/W tip on the molecule. However, the dI/dV curve measure by W tip is sensitive to the tip position.

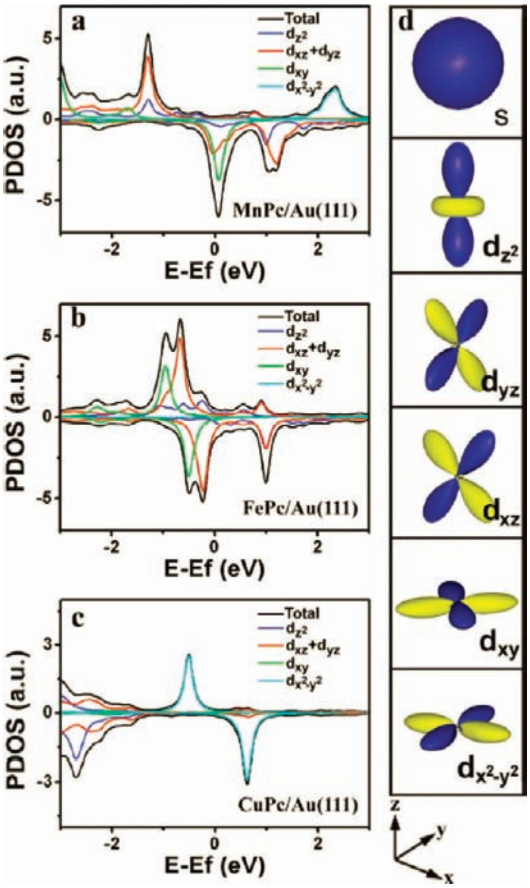

FIGURE 3. (a−c) DOS projected on d orbitals with different symmetries in metal ions of different MPc molecules adsorbed on the Au(111) surface. Black curves represent the total DOS of metal ions, while blue, red, green, and cyan curves represent PDOS of d_{z^2}, d_{xz}, d_{yz}, d_{xy}, and $d_{x^2-y^2}$, respectively. (d) Schematic models of the s-type orbital of one electrode (such as the STM tip) and five d orbitals with different symmetries. Reproduced from ref 14.

STS spectra are simulated using a modified Bardeen approach,[15] where the wave function match between tip and sample is formulated with the Fermi golden rule. Good agreement between simulated and experimental spectra has been achieved. As shown in Figure 5, frontier orbital of W tip is s-like, while it is d_{yz}-like for the Fe/W tip. LDOS of the CoPc adsorbed on Au(111) surface around −0.4 eV is mainly distributed around the ligand instead of the central Co atom. Due to the nonlocal character of this frontier orbital, the "blunter"

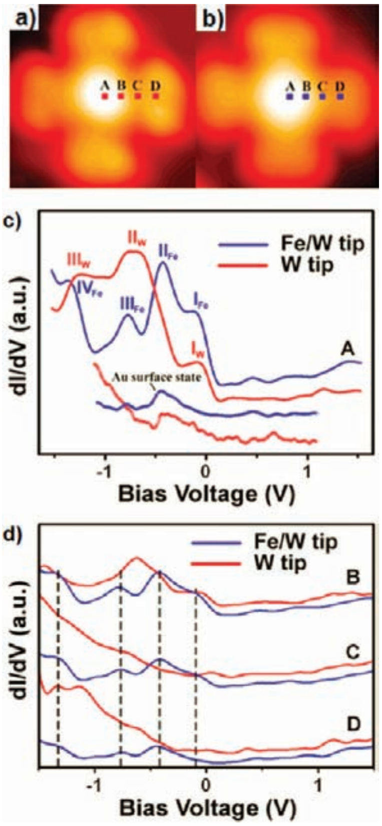

FIGURE 4. (a) STM topographic image obtained at −1.3 V and 0.4 nA with a W tip. The red dots are the positions for STS measurements. (b) STM topographic image obtained at −1.3 V and 0.4 nA with the Fe/W tip. The blue dots are the positions for STS measurements. (c, d) d*I*/d*V* curves measured above the CoPc molecule. Blue curves for the Fe/W tip, and the red curves are for the W tip. The positions where the tip was put are marked above the STS curves. The two d*I*/d*V* curves at the bottom of panel c were measured for a clean Au surface. The d*I*/d*V* curves are shifted vertically for a clearer presentation. Reproduced from ref 13.

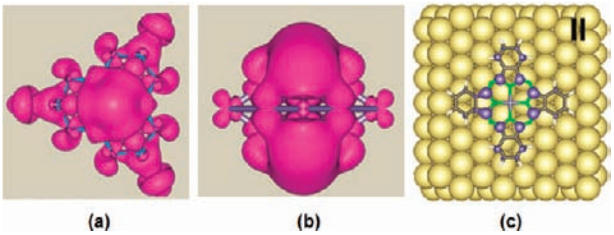

FIGURE 5. (a) Isosurfaces of the electronic charge density with an isovalue of 1.0×10^{-4} e/Å^3 for the lowest unoccupied molecular orbital of the W tip. (b) Isosurfaces of the electronic charge density with an isovalue of 1.0×10^{-4} e/Å^3 for the next lowest unoccupied molecular orbital of the Fe/W tip. (c) Isosurfaces of the electronic charge density with an isovalue of 1.0×10^{-4} e/Å^3 for the orbital at −0.42 eV of CoPc/Au(111) adsorption system. Reproduced from ref 13.

Fe/W tip matches the surface orbital at about −0.4 V well, which contributes a large tunneling matrix element to enhance the II_{Fe} peak in d*I*/d*V* spectrum.

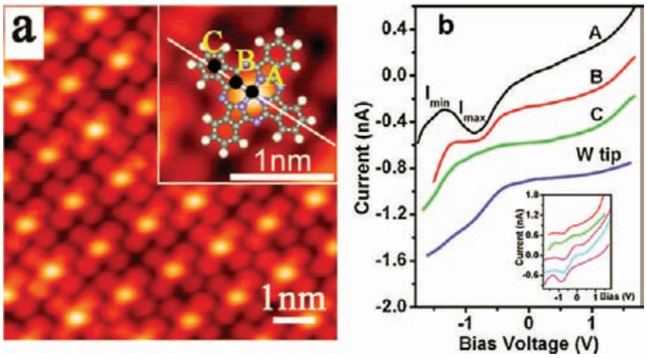

FIGURE 6. (a) CoPc monolayer on a Au(111) surface (7.5 × 7.5 nm^2, 1.2 V, 0.2 nA). The inset in (a) is a magnified molecule image (at −0.7 V and 0.2 nA) with a superimposed CoPc ball-stick sketch. (b) *I*−*V* curves measured with the Ni tip (at 1.2 V and 0.2 nA) over sites A, B, and C (marked in the inset of panel a) and with the W tip (at −1.0 V and 0.4 nA) over site A. The inset in panel b shows the results of five different Ni tips over site A taken at 1.2 V and 0.5 nA. The curves in panel b and its inset are shifted vertically for clarity by separations of 0.3 nA. Reprinted with permission from ref 10, Copyright 2007, American Physical Society.

The previous result has demonstrated that there is plenty of room in STM tip preparation to probe richer chemistry and physics on the surface. In fact, STM can do more than surface characterization. For example, substrate−molecule−tip structure forms an excellent model system for molecular junctions, which is the fundamental unit used in nano- and molecular electronics.[39,40]

In nano- and molecular electronics, negative differential resistance (NDR) is an important phenomenon related to two-terminal logic devices.[39] NDR has been realized based on the interaction between two localized narrow energy states[41] or chemical change in the molecule involving reaction processes.[42,43] In STM, observing NDR typically requires a sharp tip to produce the localized narrow energy state.[40,44] Using the CoPc adsorbed on the Au(111) surface as an example, we have demonstrated that local orbital symmetry matching between tip and molecule may also play an important role in NDR.[10]

When we substitute the conventional W tip with a Ni tip, STS for CoPc on a Au(111) surface clearly shows a NDR effect with a maximum current at −0.87 V and a minimum current at −1.34 V (Figure 6). The NDR effect is sensitive to the offset from the Co atom: a slight increase of the tip offset from the Co atom (position B in Figure 6a) can smear out the NDR effect, and a normal monotonic behavior in the *I*−*V* curve is recovered when the Ni tip is placed upon the benzene ring of CoPc (position C in Figure 6a). However, the NDR ratio (I_{max}/I_{min}) does not change with respect to the applied electric field or vertical tip−sample distance.

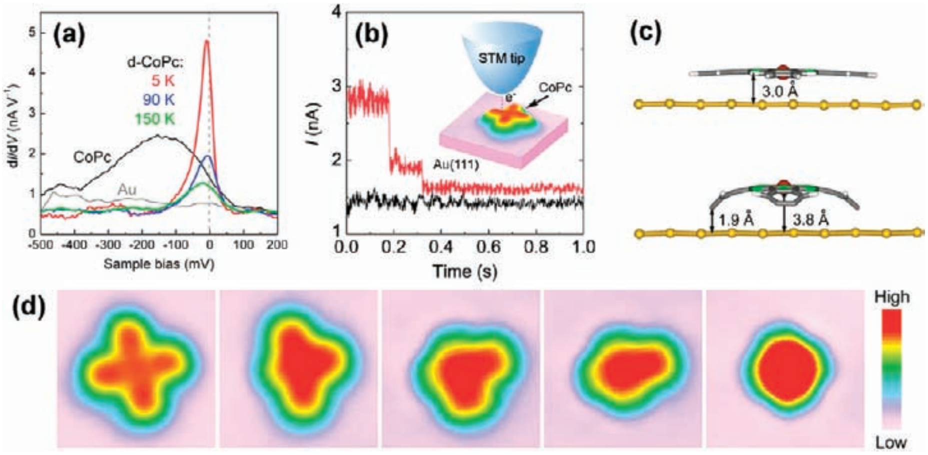

FIGURE 7. (a) Typical d*I*/d*V* spectra measured at the center of a CoPc molecule at 5 K (black line), showing a d_{z^2} orbital-mediated resonance, and a d-CoPc molecule at 5, 90, and 150 K (colored lines), showing strong resonance near the E_F. A spectrum from bare Au(111) (gray line) is shown for comparison. (b) Current versus time during two different voltage pulses on the brink of one lobe of CoPc. Black and red lines correspond to 3.3 and 3.6 V, respectively. The inset is a diagram of the dehydrogenation induced by the STM current. (c) The optimized computational model for the CoPc (upper panel) and d-CoPc (lower panel) adsorbed on Au(111). (d) STM images of a single CoPc molecule during each step of the dehydrogenation process, from an intact CoPc on the left side to d-CoPc on the right side. (Image area: 25 × 25 Å^2). The color scale represents apparent heights, ranging from 0 Å (low) to 2.7 Å (high). Reprinted with permission from ref 9, Copyright 2005, American Association for the Advancement of Science (AAAS).

We note that neither the Ni nor the W electrode is of narrow band, and CoPc is very stable on the Au(111) surface under the present experiment conditions, which also excludes the possibility of chemical change on the absorbed molecule. Therefore, there should be a new mechanism for the NDR effect observed in the CoPc/Au(111) system with the Ni STM tip. DFT calculations have been performed for the Ni tip and for CoPc adsorbed on the Au(111) surface. Since the observed NDR behavior occurs at negative sample bias voltage, we focus on the occupied sample states and unoccupied tip states. PDOS of the Co atom near the E_F is dominated by its 3d orbitals, and there are three peaks corresponding to $d_{x^2-y^2(xy)}$, $d_{xz(yz)}$, and d_{z^2} below the E_F. The energy of the second peak matches the energy point where NDR is observed. On the other hand, DOS for both Ni and W tips have broad bands around the E_F. However, d orbtials of different symmetries are evenly mixed for the W tip, but the $d_{xz(yz)}$ orbitals completely dominate in the DOS of the Ni tip near the E_F, with a sharp spectral profile at 0.23 eV and a full width at half-maximum (fwhm) of 0.4 eV. Such a fwhm fits quite well the energy region where the NDR was found in experiment.

With DOS of both sample and tip, the *I*−*V* curve can be simulated with the modified Bardeen approach. According to spatial-symmetry mismatching, the electron tunneling probability between two orbitals with different magnetic quantum numbers is extremely small. We thus expect that the match between the $d_{xz(yz)}$ orbitals of the Co and Ni tip will cause the experimentally observed NDR, which is confirmed by direct *I*−*V* spectrum simulation.

Single-Molecule Surgery

Single-molecule surgery can be used to tune the magnetic properties of the MPc adsorbed surface systems, which is very desirable in spintronics[45] applications. By controlling the charge and spin state of a molecule using a gate voltage, researchers have found that the Kondo effect can be tuned reversibly.[27] One can also change the chemical environment of a magnetic atom to control the Kondo temperature (T_K), as demonstrated by different $CoCu_n$ clusters on a Cu(111) surface.[46] Single-molecule manipulation is required for on-site chemical environment change. STM can realize single-molecule manipulation by applying a strong bias voltage pulse, so it provides a powerful means to tune the Kondo effect.

For CoPc adsorbed on a Au(111) surface, as already mentioned previously, since the magnetic moment on Co in free CoPc is completely quenched by the molecule−substrate interaction, no Kondo effect is observed. The broad resonance centered around 150 meV below the E_F is the Co d_{z^2} orbital-mediated tunneling peak.

Interestingly, we found that the Kondo effect can be recovered by applying high-voltage pulses on the lobe edges of the CoPc molecule.[9] In a typical current trace simultaneously measured during the application of a 3.6 V pulse on one of the four lobes of a CoPc molecule (Figure 7b), there appear two sudden drops of the current signal, indicating the sequential dissociation of the two H atoms from the benzene ring. The dehydrogenation process is also proven by the topographic images, which show that the bridge lobes in the four-lobe

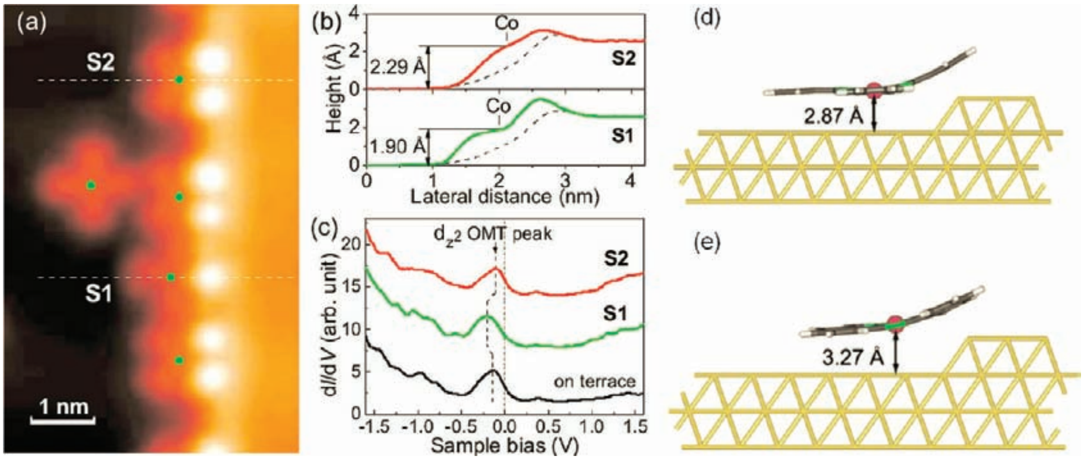

FIGURE 8. (a) High-resolution topographic STM images showing four CoPc adsorbed on a Au step. (b) Line profiles along the dashed lines in panel a. The sites of Co ion are determined by subtracting out the line profile of a bare Au step and indicated with vertical dashes. (c) d*I*/d*V* spectra measured over the Co centers of S1 and S2 CoPc molecules. A d*I*/d*V* spectrum over the Co center of a CoPc adsorbed on the terrace is also presented for comparison. The spectra are shifted vertically for a better visual effect. (d, e) Theoretically calculated adsorption configurations for molecules S1 (d) and S2 (e) on Au(111) monatomic steps. Reprinted with permission from ref 11, Copyright 2008, American Institute of Physics.

structure of the CoPc STM image disappear sequentially. Theoretical STM simulations for CoPc and dehydrogenated CoPc (d-CoPc) molecules agree well with experiment.

An increase of about 0.8 Å in apparent height of the molecular center (the Co ion) is observed after dehydrogenation. In contrast with intact CoPc, the d-CoPc molecule is difficult to move with the STM tip, indicating a stronger interaction between the d-CoPc molecule and substrate. This implication is confirmed by first-principles calculations, where the optimized geometry of d-CoPc adsorbed on a Au surface is no longer planar, with the end C atoms strongly bound to the gold substrate (Figure 7c). The upward shift of the central Co atom recovers the magnetic moment in the d-CoPc adsorption system, which leads to a significant Kondo peak near the E_F in the d*I*/d*V* spectrum of d-CoPc. The fitted Kondo temperature T_K is about 208 K, much higher than the previously reported temperature for magnetic atoms or clusters on surfaces.[47−50] In our control experiment with CuPc, no Kondo peak was found both before and after dehydrogenation.

A realistic surface may contain steps and defects. Effects of surface steps on the interaction between absorbed molecule and surface has been studied.[11] Most CoPc molecules adsorbed on monatomic steps of Au(111) have one or two of their lobes anchored on the higher terrace. We denote these two configurations as S1 and S2, respectively. Due to the featureless LDOS of Co ion at small positive biases, the Co−Au distance can be roughly determined by the apparent height measured from the topographic images obtained at the same set point (with the same current and bias voltage). The apparent height of Co ions in S1 is higher than that in S2, as confirmed by DFT calculations (Figure 8). In d*I*/d*V* spectra, the d_{z^2} orbital-mediated tunneling peak is slightly shifted for CoPc adsorbed on step compared with that adsorbed on terrace.

Similar to those on terrace, S1- and S2-type CoPc can also be dehydrogenated via STM voltage pulse. Although the original molecules can be well-defined in two configurations, the treated molecules have various geometric structures. Applying a voltage pulse on one lower lobe (voltage pulse on upper lobes leads to sliding away of the molecule onto the lower terrace) may lead to a nonlocal change in the whole molecule. For example, a single voltage pulse on a lower lobe can cause the dehydrogenation of the opposite lobe. Interestingly, the Kondo effect can be observed for CoPc on step just after one or two lower lobes are treated.

The experimentally observed Kondo temperature T_K strongly depends on the measured molecule−surface distance, and it can be well fitted by a simple empirical model based on the s−d exchange interaction between the localized spin and the surrounding conduction electrons.[11] T_K exponentially decreases with exchange interaction *J* between the localized spin and conduction electrons, with *J* depending on d_{Co-Au}. When d_{Co-Au} is too small (smaller than 3.3 Å), the Co ion interacts strongly with the Au substrate. Therefore, considerable hybridization and charge transfer between Co 3d orbitals and Au make the magnetic moment completely quenched. In addition, in the presence of asymmetric crystal fields acting on the Co ion, a nondegenerated state may become energetically favorable compared with the degenerate spin 1/2 state, which also prohibits the Kondo spin-flip processes. For a large d_{Co-Au} (larger than 3.7 Å), the exchange interaction J decays exponentially to zero, and T_K will approach a limit beyond the ability of current STM. Only for intermediate d_{Co-Au}, Kondo effect can be observed.

Concluding Remarks

Using the systems of MPc adsorbed on surfaces as examples, we have demonstrated that quantum control can be realized at the single-molecule scale by different means. By substituting the central metal atom M in MPc or by modifying the substrate surface, we can perform electronic structure engineering for the molecule absorbed surface systems, so as to switch on and off the Kondo effect. The STM manipulation technique can also be adopted to change the chemical environment of a metal atom. With a specially designed STM tip, we can probe a new molecule–surface hybrid state or form a molecular junction presenting a NDR effect. The combination of STM/STS and first-principles simulation has proven to be a powerful tool to study the geometrical and electronic structures of single molecules on surfaces.

We note that the ability to control the quantum world is very important for us. For example, it is critical in future electronics applications and new energy technology. Specifically, the ability to observe and control a single molecule on a surface may open many new possibilities. Single molecule manipulation is an important ingredient of the bottom-up approach of electronics. STM itself can be used to construct molecular junctions and to thus study transport properties in molecular electronics. The system of a molecule being adsorbed on a surface is also widely used as a model system for catalysis research. Bonding or charge transfer between molecule and surface are often very important for modulating the performance of catalysis.

Of course, it is never an easy target to fully control the quantum world. Although STM is indeed a powerful tool, what it measures corresponds to LDOS (for an ideal STM tip) instead of individual atoms. Therefore, interpretation of the STM observations is typically not straightforward, and time-consuming first-principles calculations are usually required. Tip preparation is also a big challenge. In most cases, a very sharp STM tip is a prerequisite. However, sometimes a carefully designed STM tip that is not necessarily very sharp in geometry but has specific frontier orbitals is also useful.

Many exciting works are expected in this field. Using a magnetic STM tip or applying an external magnetic field can provide more flexibility to control the quantum world. Combination of STM with other techniques, such as optical spectroscopy, is also an important direction.

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BIOGRAPHICAL INFORMATION

Zhenyu Li received his Ph.D. in chemistry from University of Science and Technology of China (USTC) in 2004 under the supervision of Prof. Jinlong Yang. Since then, he has been working as a postdoctoral researcher in Prof. D. S. Kosov's research group at University of Maryland, College Park, and in Prof. Shaul Mukamel's group at University of California, Irvine. Currently, he is an associate professor at USTC. He is the recipient of the national excellent doctoral thesis award. His research interests include electronic structure theory and computation, electron transport in molecular electronics, and theoretical spectroscopy.

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FOOTNOTES

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