

# Single-Molecule Chemistry of Metal Phthalocyanine on Noble Metal Surfaces

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**Abstract**—It is very desirable to precisely control the quantum state of a single molecule on surface in applications of electronics and functional materials. Here we combine scanning tunneling microscopy (STM) with first-principles simulation to explore possible ways of control adsorption and electronic states of single metal phthalocyanine (MPc) molecule on noble metal surfaces. Depending on different combinations of metal atom type in MPc and the surface type, molecule-surface interaction may affect the magnetic property of the molecule. Specially designed STM tips are used for MPc on noble metal surface to realize some specific functions, such as detecting molecule-surface hybrid states which are not detectable with conventional tip, and inducing negative differential resistance. More importantly, STM can be used to realize on-site molecular surgery. Kondo effect can thus be controlled by STM induced dehydrogenation reaction of MPc. In summary, MPc absorbed on noble metal surface is a model system, on which we can apply quantum characterization and manipulation using STM and develop various applications.

## BACKGROUND

Molecular adsorption on surfaces is an important issue in fundamental sciences with potentials for various applications in newly arisen industries. As a model system, metal phthalocyanine (MPc) molecules (Fig.1) on metal surfaces have been widely studied [1-4] and many reports revealed their potential in nanotechnology applications [3-5]. This adsorption system presents a subtle chemical environment for the central metal atom. The metal-ligand and molecule-surface interactions determine various properties for the whole system, and their diversities and tunabilities will improve applicability of this system in the future industries. STM is a powerful tool of researching surface and nanostructures at both spatial and energetical scales [6]. Theoretical simulation based on density functional theory (DFT) is often employed to interpret and predict STM experimental observations. In this study, we focus on interactions between MPc and the noble metal surface. Electronic structure engineering by changing substrate, central metal atom, and STM tip and also by STM manipulation is demonstrated. The related mechanisms and implications to possible applications are discussed.

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## CURRENT RESULTS

CoPc adsorbed on Au, Ag, and Cu surfaces are studied to explore MPc-surface interaction. The STM images for CoPc on Au(111) and Ag (111) surfaces are similar, but a distortion is observed for CoPc on Cu (111). The dI/dV patterns for CoPc on Au and Ag surfaces are also similar except for an about 0.6 eV energy shift of the peaks, which originates from work function difference between two surfaces. But the dI/dV maps for CoPc on Cu (111) surface are strikingly different, indicating very distinct CoPc-surface interactions. DFT calculations verify these results.

We have also systematically studied several 3d transition MPc on Au(111) surface by DFT calculations [7]. The stable adsorption configuration depends on the central metal atom type. Smaller M-Au surface distances for MnPc and FePc suggest stronger molecule-surface interactions. Only NiPc has zero local magnetic moment (MM) (Table. 1). After the molecular adsorption, different magnetic behaviors appear. Magnetic property of the adsorbed molecule is related to Kondo effect. Most of calculated magnetic properties are consistent with experimentally observed Kondo effect. But for CuPc with a local MM, there is no report on Kondo effect, which maybe is due to weak interaction between the dominated d orbital of adsorbed CuPc and electrodes.

Delicate STM tip modification has been widely used for various purposes [9]. For CoPc on Au(111) surface, the STS curve by the Fe/W tip upon molecular center has four peaks, among which the -0.4 V peak ( $\Pi_{Fe}$ ) disappears when probing by a W tip. This peak is not very sensitive to the tip position upon the molecule. Simulated STS spectra show good agreement with experimental data. The frontier orbital of W tip is s-like, while it is  $d_{yz}$ -like for the Fe/W tip. LDOS of the adsorbed CoPc around -0.4 eV is mainly distributed around the ligand, and the related states can be assigned as molecule-surface hybrid states. The "blunter" Fe/W tip matches these hybrid orbitals, which enhances the  $\Pi_{Fe}$  peak in STS, and then makes these states visible [10].

Negative differential resistance (NDR) is important in nano-electronics. Here we have demonstrated that local orbital symmetry matching between tip and molecule may also result in NDR [3]. With a Ni tip, STS for CoPc on Au (111) surface clearly show a NDR effect (Fig.2). This NDR is sensitive to the offset from the Co atom, but the NDR ratio does not change with respect to the bias voltage or vertical tip-sample distance. The DFT calculation showed that the second peak ( $d_{xz(yz)}$ ) in PDOS of Co in CoPc below the  $E_F$  just matches the observed NDR, and the  $d_{xz(yz)}$  orbitals dominate in the DOS of

Ni tip near the  $E_F$ . So we can expect that the match between them will cause the NDR, which is confirmed by simulation.

It is always desirable in spintronics applications to tune Kondo effect. A possible way is to change the chemical environment of magnetic atom on site [11] by using STM. For CoPc adsorbed on Au(111) surface, since the MM of Co is completely quenched by the molecule-substrate interaction, no Kondo effect is observed, but it can be recovered by applying high-voltage pulses on the lobe edges of CoPc [2]. The two sudden drops in current trace simultaneously measured during a 3.6 V pulse on one lobe of a CoPc molecule (Fig.3(b)) indicates the sequential dissociation of two H atoms from the benzene ring. In contrast with intact CoPc, the dehydrogenated CoPc (d-CoPc) is difficult to move with STM tip, suggesting a stronger molecule-substrate interaction. DFT calculation shows the d-CoPc on Au surface is no longer planar with the end C atoms bound to the substrate (Fig.3(c)), and the upward shift of the Co atom recovers the magnetic moment of itself, leading to a Kondo peak in the STS. The fitted Kondo temperature is much higher than previous reports for magnetic atoms or clusters on surfaces.

Effects of surface steps on the molecule-substrate interaction have been also studied [4]. Most of CoPc molecules adsorbed on monoatomic steps of Au(111) have one or two of their lobes anchoring on the higher terrace. We denote these two configurations as S1 and S2, respectively. The apparent height of Co ions in S1 is larger than that in S2, as confirmed by DFT calculations. S1- and S2-type CoPc can also be dehydrogenated via STM voltage pulse. The Kondo effect can be observed for CoPc on step just after one or two lower lobes are treated. Only for intermediate dCo-Au, Kondo effect can be observed.

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MPc	Magnetic moment (theoretical results)	
	single	adsorbed on Au(111)
MnPc	3.17	2.95
FePc	2.03	1.05
CoPc	1.09	0.00
NiPc	0.00	0.00
CuPc	0.54	0.54

Table 1. Theoretically calculated electronic magnetic moment ( $\mu_B$ ) of MPc molecules.

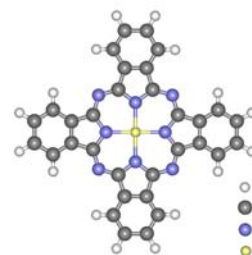


Fig. 1. Model of metal phthalocyanine with metal ion M.

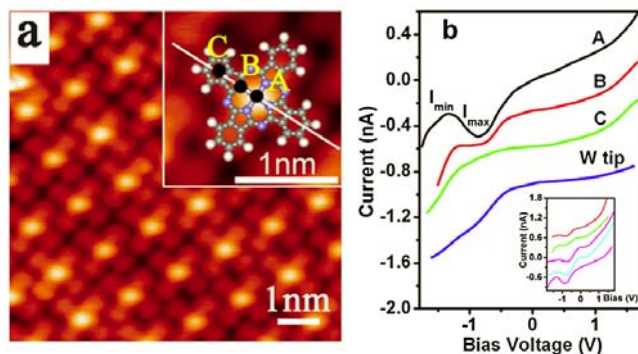


Fig. 2. (a) CoPc monolayer on a Au(111) surface ( $7.5 \times 7.5 \text{ nm}^2$ , 1.2 V, 0.2 nA). The inset is a magnified molecule image (at -0.7 V and 0.2 nA) with a superimposed CoPc sketch. (b) I-V curves measured with the Ni tip (at 1.2 V and 0.2 nA) over sites A, B and C, and with the W tip (at -1.0 V and 0.4 nA) over site A. The inset shows results of five different Ni tips over site A taken at 1.2 V and 0.5 nA. The curves are shifted vertically for clarity.

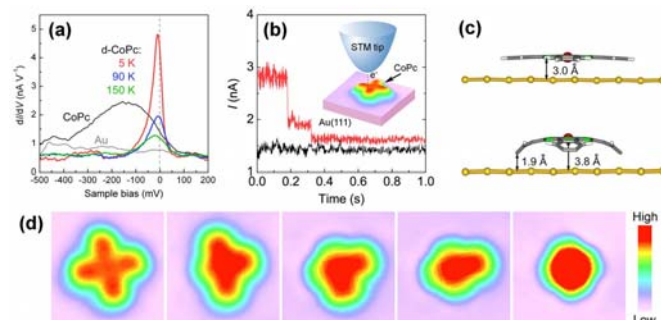


Fig. 3. (a) Typical  $dI/dV$  spectra measured at the center of a CoPc at 5 K (black line), showing a  $d_z^2$  orbital-mediated resonance, and a d-CoPc molecule at different temperatures, showing strong resonance near the  $E_F$ . (b) Current versus time during two different voltage pulses on the brink of one lobe of CoPc. Black and red lines correspond to 3.3 V and 3.6 V, respectively. (c) The optimized models for the CoPc (up) and d-CoPc (down) adsorbed on Au(111). (d) STM images of a CoPc molecule during each step of the dehydrogenation process from left to right. (Image area:  $25 \times 25 \text{ \AA}^2$ ). The color scale represents apparent heights.