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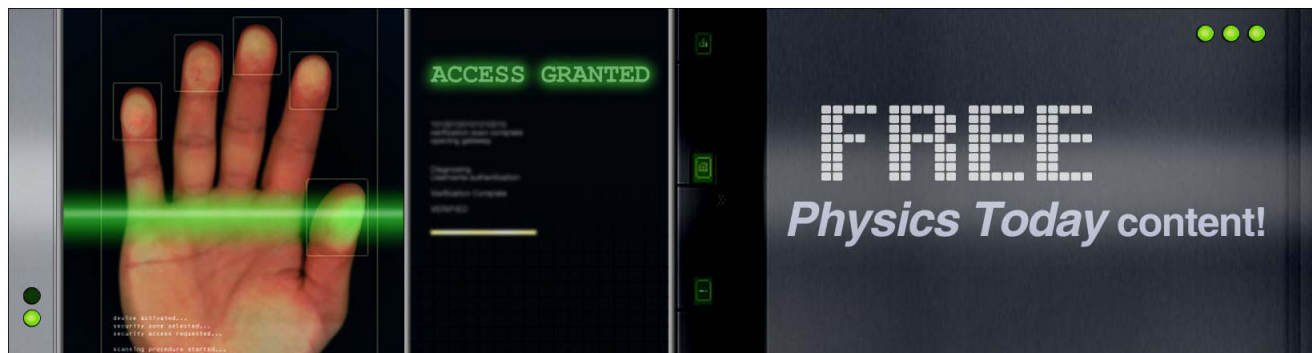
Selective adsorption of metal-phthalocyanine on Au(111) surface with hydrogen atoms

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Metal phthalocyanine (MPc, M = Mn, Fe) molecules grown on reconstructed Au(111) with and without hydrogen atoms at submonolayer coverage are investigated by low temperature scanning tunneling microscopy. It is found out that the attachment of H atoms to the central metal of the MnPc molecules leads to the change of the molecules' selective adsorption from fcc to hcp regions at low coverage. The two configurations of MnPc molecules on Au(111) are replaced by only one configuration of H-MnPc/Au(111). FePc molecules adsorb on fcc regions of Au(111) with two configurations, which are similar to that of MnPc. However, unlike H-MnPc, H-FePc molecules have two configurations on Au(111). Density function theory calculations show that the different configuration change by attachment of H atoms for MnPc and FePc molecules is due to the electronic structure change at the central metal atoms of the molecules. © 2013 AIP Publishing LLC.
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The control and manipulation of functional molecules on solid surfaces is a fundamental issue for the development of electronics and optoelectronics.[1–4] Metal phthalocyanines (MPcs), metal porphyrins (MPs), and their derivatives are a family of functional molecules exhibiting desirable electronic structures and spin properties.[5–10] In recent years, it has been shown that the binding of small gas molecules (such as NO, CO, NH_3, and so on) to these molecules results in a change of molecular conformations and a reorganization of molecule arrays, exerting a dramatic effect upon the electronic structures and spin states.[11–17] However, most of the previous studies focus on the decoration of a MPcs or MPs adlayer rather than separate individual molecules on surfaces. In addition, despite the great importance of hydrogen in the chemical and energy industries, the decoration of MPcs with hydrogen has seldom been addressed. Recently, by H atom adsorption and desorption, information storage using reversible single spin state switching (ON/OFF of the Kondo effect) has been demonstrated on single MnPc molecules on Au(111).[18] However, control and manipulation of the selective adsorption still have not been well investigated.

In this letter, we report on an observation of the selective adsorption of MPc (M = Mn and Fe) molecules on fcc regions of a reconstructed Au(111) substrate at very low coverage using a low temperature scanning tunneling microscope (LT-STM). Interestingly, attachment of a hydrogen atom changes the site selectivity of MnPc, while it does not change that of FePc. Moreover, the two configurations of MnPc/Au(111) change to only one configuration after H decoration, due to a great change in the d_{z^2} orbital of the Mn ion caused by H attachment. However, FePc molecules still have two configurations after H decoration because of the nearly unchanged electronic structures of the central Fe ion.

Experiments were carried out in an ultrahigh vacuum (base pressure of 1×10^{-10} mbar) LT-STM system (Unisoku),

equipped with standard surface preparation facilities. An atomically flat Au(111) surface was prepared by repeated cycles of sputtering with argon ions and annealing at 800 K. Commercial MnPc and FePc molecules (Sigma-Aldrich, 97% purity) were sublimated from a Knudsen-type evaporator after thermal purification, while the Au(111) substrate was held at room temperature (RT). One monolayer refers to a close-packed layer of MPcs covering the whole Au(111) surface, as examined by STM. STM images were acquired in the constant-current mode with bias voltage applied to the sample. All images were obtained with electrochemically etched tungsten tips at 4.2 K. Hydrogen atoms are acquired by dosing and decomposing H_2 molecules on Au(111) at room temperature.[18]

In addition to the experiments, density function theory (DFT) calculations were performed using the Vienna *ab-initio* simulation package (VASP). A Perdew Burke Ernzerhof (PBE) generalized gradient approximation for the exchange-correlation energy, projector augmented wave (PAW)[19] pseudopotentials and a plane wave basis set were used. The cutoff energy for the plane waves was 400 eV. All parameters were well tested to ensure a total energy convergence of about 1 meV per atom. In structural relaxations, all atoms were fully relaxed until the net force on every atom was smaller than 0.02 eV/Å.

The clean Au (111) surface exhibits a well-known $22 \times \sqrt{3}$ herringbone reconstruction, due to the strain-induced surface contraction in the $[1\bar{1}0]$ direction.[20–22] The surface presents alternating fcc and hcp regions separated by domain walls (DWs), which appear as slightly elevated ridges. To release surface stress, the uniaxial domains are periodically bent 120°,[21] giving rise to ordered arrays of elbows.[23–25] After deposition of ~0.02 ML MnPc on Au(111), we observe that all MnPc molecules are preferentially accomodated at the pointed elbow sites of the reconstructed Au(111), as seen in Fig. 1(a). Similar behavior has been reported for a variety of molecules on Au(111) because the electronic potential energies of these sites are higher than those of the fcc and

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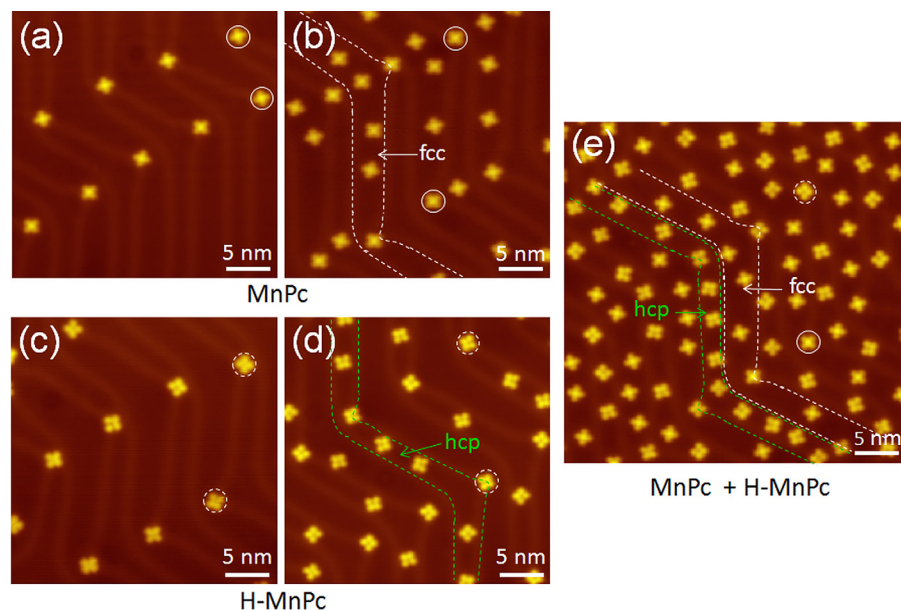
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FIG. 1. Different preferential adsorption sites for MnPc and H-MnPc molecules on Au(111). (a) MnPc and (c) H-MnPc at coverage of 0.02 ML, occupying the pointed elbow sites (indicated by white circles). (b) MnPc and (d) H-MnPc at coverage of 0.08 ML, with additional MnPc and H-MnPc molecules mainly occupying the fcc and hcp regions, respectively. (e) MnPc and H-MnPc coadsorbed at coverage of 0.16 ML. While these two molecules compete to occupy the pointed elbow sites, most MnPc and H-MnPc molecules occupy the fcc and hcp regions, respectively. Scanning parameters: sample bias: $U = -0.2$ V, tunneling current: $I = 10$ pA.

hcp regions.[23–25] Each MnPc molecule is imaged as a "cross" with a bright protrusion at the molecular center, consistent with the molecular configuration. The central protrusion of MnPc originates from the $3d$ orbital of Mn^{2+} ions, while the cross corresponds to the planar aromatic skeleton, which is parallel to the Au(111) surface due to the molecule-substrate interaction. After the pointed elbow sites are completely occupied, additional MnPc molecules prefer to separately adsorb on the fcc regions of the Au(111) surface, as shown in Fig. 1(b), with a ~0.08 ML MnPc coverage. The average separation between MnPc molecules along the fcc regions is ~5.5 nm, indicating a net long-range repulsive molecule-molecule interaction.[26] The preferential anchoring of MnPc molecules on the fcc region shows that the adsorption of MnPc molecules is more stable on the fcc regions than on the hcp regions. Therefore, the molecule-substrate interaction for MnPc molecules on different regions of Au(111) decrease in the sequence of elbow sites > fcc regions > hcp regions. At a coverage of ~0.15 ML, the accommodation of separated MnPc molecules on the hcp regions is observed, despite the availability of the fcc regions.

The topography and adsorption behaviors of the MnPc molecules are significantly different after exposure to H_2 at RT. Figs. 1(c) and 1(d) show typical STM images after the MnPc/Au(111) samples depicted in Figs. 1(a) and 1(b) were dosed with 1 Langmuir (L) of H_2 at RT, respectively. It is seen that each molecular center shows a depression instead of a bright protrusion, suggesting a remarkable modification of the molecular electronic structure. We have confirmed that the molecules with depressed centers are McPc with an H atom chemically bonded to the Mn ion, namely, H-MnPc, which exhibits different spin state from that of MnPc.[18] Nevertheless, the H-MnPc molecules are also preferentially anchored at the pointed elbow sites of the Au(111) surface at a coverage of ~0.02 ML, similar to the original MnPc molecules. However, after complete occupation of the pointed elbow sites, the additional H-MnPc molecules prefer to separately adsorb on the hcp regions instead of the fcc ones (as shown in Fig. 1(d) with a coverage ~0.08 ML), in contrast to that of the original MnPc molecules. This behavior

indicates that it is more stable for the H-MnPc molecules to adsorb on the hcp regions than on the fcc regions. Thus, we conclude that the molecule-substrate interactions for H-MnPc molecules on different regions of Au(111) decrease in the sequence of elbow sites > hcp regions > fcc regions. At a coverage of ~0.16 ML, we observe the adsorption of individual H-MnPc molecules on the fcc regions, despite of the availability of the hcp regions.

For organic molecules, the fcc and hcp regions of Au(111) exhibit different affinities to the molecules and the fcc regions are usually found to capture molecules more effectively.[24,25,27–29] Thus, adsorption behavior of H-MnPc molecules with hcp regions as their preferential sites after the full decoration of pointed elbows is very interesting, especially for the skeleton of MnPc and H-MnPc is the same. Our calculation shows that the density of states (DOS) of adsorbates around the Fermi level is different: there are d_{z^2} states in MnPc, while they are nearly absent in H-MnPc.[18] This difference in molecular orbitals could give rise to different interaction with the substrate and result in the different selective adsorption behaviors. Besides, a stacking effect ("ABC" stacking for fcc regions, and "ABA" stacking for hcp regions) and local strain of the reconstructed Au(111) surface may be the origin for the selective deposition of H-MnPc in the hcp region at initial coverage.

As MnPc and H-MnPc molecules have different preferential adsorption sites on Au(111), we thought it would be interesting to coadsorb these two molecules. In the first step, we prepared ~0.08 ML H-MnPc molecules on Au(111). Then, MnPc molecules of ~0.08 ML were deposited on the as-prepared H-MnPc molecules sample [Fig. 1(e)]. As expected, at non-elbow sites, MnPc and H-MnPc molecules mainly adsorb at their own preferential adsorption sites— namely, fcc and hcp regions, respectively. The two kinds of molecules compete to occupy the pointed elbows (as indicated by the white circles), which are the most favorable adsorption sites for both MnPc and H-MnPc molecules when depositing them separately, suggesting that the adsorption energies of MnPc and H-MnPc are comparable at these regions.

For comparison, we also coadsorbed MnPc and H-MnPc in 1 ML coverage. First, we prepared 1 ML of MnPc [Fig. 2(a)]. With a little amount of H_2 dosing at RT, some MnPc molecules are converted to H-MnPc [Fig. 2(b)]. To get knowledge of the adsorption sites of H-MnPc, we processed the image by filtering the small features and made the herringbone structure more clear [Fig. 2(c)]. Then by overlaying the positions of H-MnPc [derived from Fig. 2(b)] onto the filtered image, we can see easily where the H-MnPc molecules are with respect to the reconstructed Au(111). Unlike the situation of low coverage in Fig. 1(e), the H-MnPc molecules occupy random sites rather than the previously preferential adsorption sites of elbow and hcp region. This is because at low coverage, both MnPc and H-MnPc can diffuse freely at RT, when the sample is prepared. Thus, when we cool down the sample gradually, both of them can diffuse and, finally, occupy their preferential adsorption sites. However, at 1 ML coverage, the molecules are close-packed and the diffusion of H-MnPc is hindered even at RT. H-MnPc molecules will not find the preferential adsorption sites, and just locate randomly on the sample surface. Besides, H atoms hopping among several molecules during sample preparation is not expected because the bonding of an H atom to the top of the Mn ion is very stable at and below RT (the temperature required to desorb H atoms is 500 K, Ref. 18). Thus, as the diffusion of both H-MnPc molecules and H atoms are quenched, once an H_2 molecule is decomposed at the Au(111) surface, the atomic H will reach the top of a Mn ion randomly and form an H-MnPc without site selectivity.

At 1 ML, although we tried to convert all the MnPc molecules into H-MnPc by dosing H_2 ($\sim$240 L) to the sample, 10% of the MnPc molecules were still unchanged [Fig. 2(d)]. Therefore, the efficiency is 0.0036 ML/Langmuir. At $\sim$0.1 ML, all MnPc can be converted to H-MnPc by H_2 of

10 L, thus, the efficiency to convert is at least 0.01 ML/Langmuir. We noticed a much lower H_2 decomposition efficiency at 1 ML. The lower efficiency is reasonable because the Au(111) surface as the catalyst is completely covered by molecules. Although H_2 can still contact the Au(111) surface through the small space between the MnPc molecules, the possibility is reduced.

In addition to the change of preferential adsorption site from fcc regions for MnPc to hcp regions for H-MnPc, the binding of H atoms also changes the adsorption configuration of MnPc. Two configurations of MnPc/Au(111) (labeled as I and II in Fig. 3(a), respectively) can be identified. For configuration I, the molecular axes are directed along the $[1\bar{1}0]$ and $[11\bar{2}]$ directions of the gold substrate, whereas for configuration II the molecular axes rotate with respect to the molecular center by $\sim$15° compared to configuration I. It should be noted that there are three equivalent orientations for both configuration I and II, due to the three-fold symmetry of the Au(111) surface. Further statistical analysis reveals that the number of molecules with configuration II is larger than that of configuration I, suggesting that configuration II is energetically more favorable than configuration I. However, with H atom attachment, all original MnPc molecules with configuration I or II turn to H-MnPc molecules with configuration I′ (which has the same orientation as configuration I of MnPc) [Fig. 3(b)].
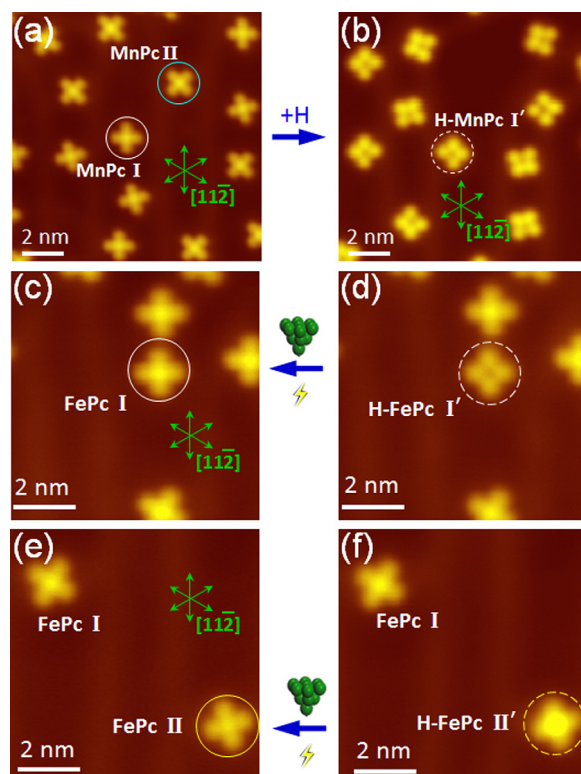
FIG. 3. STM images of MPcs and their counterparts with H attached on Au(111). (a) MnPc/Au(111), showing two configurations: I and II. (b) All MnPc molecules are converted to H-MnPc with configuration I′ under H_2 gas dosing. (c) and (d) An H-FePc molecule with configuration I′ (d) was converted to an FePc molecule with configuration I (c) by a STM pulse. (e) and (f) an H-FePc molecule with configuration II′ (f) was converted to FePc molecule with configuration II (e) by a STM pulse. An unchanged FePc molecule with configuration I is given nearby as a reference in (e) and (f). Scanning parameters: U = −0.2 V, I = 10 pA.
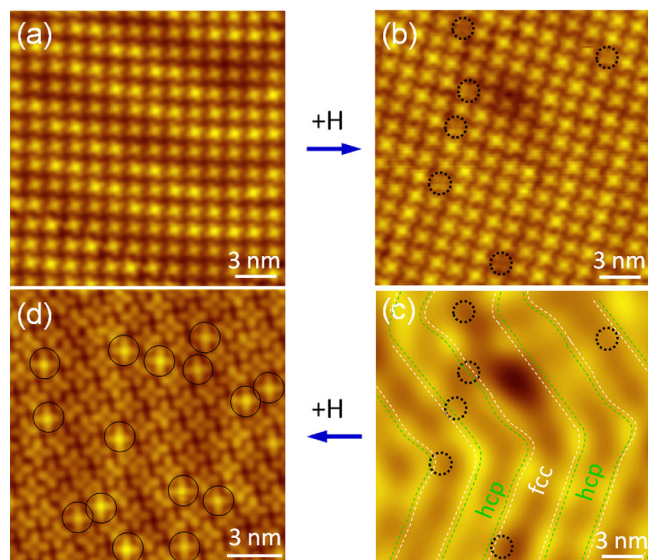

FIG. 2. STM images of coadsorption of MnPc and H-MnPc at 1 ML coverage. (a) 1 ML of MnPc as the starting point. (b) Image taken after dosing a little H_2 to 1 ML of MnPc. (c) Fourier filter image of (b), showing random adsorption sites for H-MnPc molecules at 1ML coverage. (d) Image taken after dosing a large amount of H_2, $\sim$240 L; about 10% of the molecules are still MnPc. Scanning parameters: sample bias: U = −0.2 V, tunneling current: I = 10 pA.

For comparison, we also studied the attachment of hydrogen atoms to FePc molecules on Au(111) surface. Similar to MnPc, after all pointed elbow sites of the reconstructed Au(111) are occupied by FePc molecules, additional FePc molecules prefer to separately adsorb on the fcc regions of the Au(111) surface [Fig. S1(a)][27,30] with two adsorption configurations.[10] After dosing a small mount of H_2 to the sample at RT, some of the FePc molecules are converted to H-FePc molecules. Contrary to H-MnPc, H-FePc molecules still adsorb on fcc site selectively [Fig. S1(b)].[30] Each of the two configurations of FePc molecules has its corresponding H-FePc configuration counterpart, and show remarkably different apparent heights. This differs from MnPc molecules in that the two configurations of MnPc molecules are replaced by only one configuration of H-MnPc. We designated the two configurations of H-FePc as I′ and II′, which have the same orientation with configuration I and II of FePc, respectively.

The brightness of FePc with configuration I and configuration II are slightly different: the molecular center of configuration I is a little brighter than that of configuration II [Fig. 3(e)]. But H-FePc of configuration I′ and II′ are plainly different. As seen from Fig. 3(d), H-FePc with configuration I′ has a depressed center similar to that of H-MnPc; while H-FePc with configuration II′ has an even brighter center than normal FePc molecules [Fig. 3(f)]. After a STM pulse of 1.75 V for 1 s, the H-FePc molecules with either configuration I or II (feedback off at gap: 0.2 V/0.1 nA) turn into to pristine FePc molecules [Figs. 3(c) and 3(e)]. To quantitively analyse their apparent heights, we plotted the line profiles of FePc molecules with the four configurations. The heights of FePc with configuration I and II are 185 and 175 pm, respectively, which shows little difference, while the heights of H-FePc with configuration I′ and II′ are 125 and 230 pm, respectively—a remarkable difference. This difference reflects that although FePc in either configuration is decorated with an H atom, the local DOS (LDOS) is different, leading to the very different apparent heights.

To understand the different configurational changes of MnPc and FePc with H attachment, we calculated the electronic structures of free-standing MnPc, FePc, and their counterparts with H attachment by using DFT calculations. We found that the H decoration induces changes of electronic structures of the central metal atoms. After attachment of an H atom to the Fe ion, the d_{z^2} orbital of H-FePc changes little, suggesting that the adsorption of H-FePc/Au(111) is similar to that of FePc/Au(111), which also has two favorable adsorption configurations. However, after attachment of an H atom to the Mn ion, the d_{z^2} orbital of H-MnPc changes much: the highest occupied state of d_{z^2} moves to lower energy, while the lowest unoccupied state of d_{z^2} shifts to a higher energy [see the red arrows in Fig. 4]; furthermore, the original highly spin polarized state changes to a weakly spin polarized one. This large change in electronic states could give rise to the change from the two configurations of MnPc/Au(111) to only one configuration after H decoration.

In summary, we find that at submonolayer coverage, both MnPc and FePc molecules adsorb at fcc regions of Au(111) selectively after all pointed elbows are occupied. The attachment of an H atom to the central metal atom of the
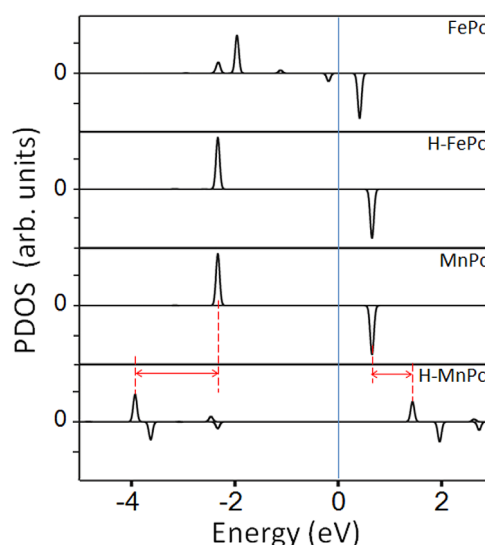

FIG. 4. Projected DOS (PDOS) of free-standing MPcs and their counterparts with H attached, showing that the d_{z^2} orbital of H-FePc changes little from FePc while that of H-MnPc changes a lot from MnPc (indicated by the red arrows).

MnPc changes the selective adsorption sites from fcc regions to hcp regions. In addition, the two configurations of MnPc molecules are replaced by only one configuration of H-MnPc. By contrast, H-FePc molecules on Au(111) still stay on fcc regions with two configurations and show remarkably different apparent heights. Our results are helpful for controlling molecular configurations on Au(111) and for potential application in spin manipulation and its application in quantum data processing and recording.

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[30] See supplementary material at http://dx.doi.org/10.1063/1.4813545 for "The same selective adsorption sites for FePc molecules with/without an H atom attachment."