Metal-free phthalocyanine (H$_2$Pc) molecule adsorbed on the Au(111) surface: formation of a wide domain along a single lattice direction

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Abstract

Using low-temperature scanning tunneling microscopy (STM), we observed the bonding configuration of the metal-free phthalocyanine (H$_2$Pc) molecule adsorbed on the Au(111) surface. A local lattice formation started from a quasi-square lattice aligned to the close-packed directions of the Au(111) surface. Although we expected the lattice alignment to be equally distributed along the three crystallographically equivalent directions, the domain aligned normal to the ridge of the herringbone structure was missing in the STM images. We attribute this effect to the uniaxial contraction of the reconstructed Au(111) surface that can account for the formation of a large lattice domain along a single crystallographical direction.

Keywords: nanomaterials, STM, molecule lattice

1. Introduction

The phthalocyanine (Pc) molecule has long been studied for a variety of applications in catalysis and sensors [1], and recently in electronic materials with an envision of single-molecule devices. The Pc molecule can contain various metal atoms at its center, and such metal–Pc (MPc) complexes are expected to play an important role in controlling the molecular device via their spins. Research in this direction has been accelerated by a recent success in the synthesis of lanthanide phthalocyanine molecules with single-molecule magnet properties [2–5]. Different from normal MPc, these molecules have a metal atom sandwiched by two Pc ligands. Scanning tunneling microscopy (STM) has played an important role in the characterization of Pc films [6]. However, STM can only reveal the topmost surface, and the direct information of the interface cannot be obtained with this technique [7–10]. In studying the adsorption of the double-layer molecules, it might be necessary to compare the results with those obtained on metal-free Pc, as the bottom Pc layer does not contain a metal atom. Contrary to numerous reports of MPc on the Au(111) surface [2, 11–17], the studies of metal-free Pc film growth in the low-coverage regime are scarce.

Au(111) is an intriguing surface. The fcc (111) surface should have three equivalent close-packed directions: [101], [011] and [110]. However, owing to the surface reconstruction which appears as a herringbone structure, they are not equivalent on the reconstructed Au(111) surface. The ridge of the herringbone structure is perpendicular to one of these quasi-close-packed directions. For an MPc film, quasi-square lattices were commonly formed when the coverage was close to a monolayer, as clearly demonstrated for the molecules of CoPc [2, 13–15] and FePc [11, 12].

The molecular lattice should be aligned to one of the three quasi-close-packed directions of the Au(111) surface.
An Au(111) single crystal was prepared with standard Ar sputtering and annealing techniques and used as the substrate. The metal-free phthalocyanine molecules (H₂Pc, Wako Japan) were evaporated from a tantalum boat, which was resistively heated to about 550 K. Phthalocyanine was carefully degassed before deposition, and the pressure during the deposition was better than 1 × 10⁻⁸ Torr. The Au(111) substrate was kept at room temperature during the deposition, and we kept the deposition rate at ∼ 1 ML min⁻¹ (ML stands for monolayer). No annealing was performed after the deposition. The substrate cleaning, deposition and low-temperature STM observation were carried out in the interconnected UHV chambers, without exposing the sample to the atmosphere. The STM head was placed in a tube-like stainless steel chamber, which was inserted to a helium dewar. The dewar was attached to an air-suspended table and located below the floor level. The assembly of the tube scanner, STM tip, sample holder and inertia slider for the coarse motion of the tip were suspended by springs for vibration isolation. The sample temperature was kept at ∼4.5 K during the STM experiments.

However, no areas with three coexisting domains were found for CoPc and FePc, and Cheng et al noted that only one lattice direction was observed even on a large terrace [12]. This is an unusual case of the lattice formation on the Au(111) surface—for example, six different domains could be observed on the Au(111) surface (three equivalent crystal directions and two chiral degrees of freedom in the molecule) as an ordered lattice of terephthalic acid molecules was forming through the head–tail hydrogen bonding between adjacent molecules [18]. To the best of our knowledge, the formation mechanism of large domains in MPc film has not been revealed.

In this article, we characterize the bonding configuration of the metal-free phthalocyanine (H₂Pc) molecules adsorbed on the Au(111) surface, as observed at ∼4.5 K. Molecular hopping on the surface is frozen at this temperature, making possible to visualize individual molecules and monitor the film growth. In a low-coverage region, we observed isolated H₂Pc molecules both on the fcc and hcp domains with an almost equal probability. The histogram of azimuthal rotational angle of the molecules suggests that the molecular symmetry axes are aligned to the three quasi-close-packed directions of the substrate, however, the distribution is unequal between the three directions.

With the increasing molecular coverage, we observed formation of a local quasi-squared lattice aligned to the three quasi-close-packed directions of the Au(111) surface. Among the three directions, however, we could not observe a domain that was aligned normal to the local ridge of the herringbone structure. This result can be attributed to the uniaxial contraction of the reconstructed Au(111) surface. It can account for the formation of a large molecular lattice domain along a single direction, if it is combined with the presence of a chevron-shaped long-range ordering of the Au(111) surface reconstruction.

### 2. Experimental details

All experiments were performed in ultra-high vacuum (UHV). An Au(111) single crystal was prepared with standard Ar⁺ sputtering and annealing techniques and used as the substrate. The metal-free phthalocyanine molecules (H₂Pc, Wako Japan) were evaporated from a tantalum boat, which was resistively heated to about 550 K. Phthalocyanine was carefully degassed before deposition, and the pressure during the deposition was better than 1 × 10⁻⁸ Torr. The Au(111) substrate was kept at room temperature during the deposition, and we kept the deposition rate at ∼ 0.1 ML min⁻¹ (ML stands for monolayer). No annealing was performed after the deposition. The substrate cleaning, deposition and low-temperature STM observation were carried out in the interconnected UHV chambers, without exposing the sample to the atmosphere. The STM head was placed in a tube-like stainless steel chamber, which was inserted to a helium dewar. The dewar was attached to an air-suspended table and located below the floor level. The assembly of the tube scanner, STM tip, sample holder and inertia slider for the coarse motion of the tip were suspended by springs for vibration isolation. The sample temperature was kept at ∼4.5 K during the STM experiments.
et al performed density functional theory simulation of this reconstruction and compared the areas of the fcc, hcp and ridge domains with previous experimental results [19, 20, 22]. They found that fcc and hcp domains occupy 31% (34%) and 19% (22%) of the total area, respectively, in theoretical (experimental) STM images. The calculated (experimental) values can be converted to \( \sim 1.96 \) (2.16) nm and \( \sim 1.21 \) (1.38) nm in terms of the lengths of the domains perpendicular to the fcc and hcp ridges, respectively. This is illustrated in figure 1(a), showing the theoretical widths of the 1st ridge, fcc, 2nd ridge and hcp domains.

The STM image of figure 1(b) corresponds to the low coverage of \( \text{H}_2\text{Pc} \) molecules, and the cross-like bright features are well-separated individual \( \text{H}_2\text{Pc} \) molecules. The molecules are adsorbed on the fcc and hcp domains, but not at the ridge, that makes them arranged in lines.

Chen et al reported the adsorption of FePc on the Au(111) surface in a low-coverage regime (< 0.1 ML), in which FePc molecules were found only in the fcc region [12, 23]. They concluded that the adsorption of FePc is more stable on fcc than that on the hcp domain. We could not confirm this observation, however.

To measure the azimuthal rotation of each molecule, we have examined the lines connecting the centers of the two diagonal phenyl rings (we call them center lines hereafter). The angle \( \theta \) is measured from the vertical direction to the clock-wise direction as indicated in figure 1(c). In the range \( 0^\circ \leq \theta < 90^\circ \) we should see three center lines separated by an increment of 30°, reflecting the threefold symmetry of the substrate. An example is presented in figure 1(c). One of the two center lines of a molecule is aligned to one of the close-packed directions of the substrate (A1, A2 or C). Such bonding configuration (configuration I) has been proposed for the MPc adsorption on the Au(111) surface. Chen et al reported that for FePc adsorption on Au(111), 85% of the isolated FePc molecules have this configuration [12, 23]; the rest assume configuration II, where the molecule is azimuthally rotated \( \sim 15^\circ \) from configuration I. Hereafter we denote the alignment to the angles \( \theta = 0, 30 \) and \( 60^\circ \) as Config_I(C), Config_I(A1) and Config_I(A2).

The measured azimuthal angle distribution is shown in figure 1(b) as histograms of the number of molecules versus angle \( \theta \). The distribution has maxima near A1, A2 and C both for hcp and fcc regions, however the molecules are not equally distributed among the three angles—the C group is smaller than A1 and A2, and this difference is beyond the statistical error.

We may consider that the overall bonding configuration of an isolated \( \text{H}_2\text{Pc} \) molecule is close to Config_I. However, the distribution is rather broad, especially for Config_I(C). This might suggest some other stable configuration like Config_HII proposed in the FePc case, even though we could not clearly resolve other bonding configurations. We speculate that \( \text{H}_2\text{Pc} \) has also a metastable configuration near the close-packed alignment that results in the observed broad distribution.

There is no difference in the number of molecules adsorbed on the fcc and hcp domains in figure 1. This fact is not trivial, as the fcc domain should be at least 1.5 times larger than the hcp domain; we explain it using figure 1(a), where the width of the fcc domains is \( \sim 1.9 \) nm. The diameter of the molecule can be estimated as the nearest-neighbor distance (nnd) of the close-packed molecules. The nnd of \( \text{H}_2\text{Pc} \) on the graphite surface was reported as \( \sim 1.3 \) nm [24, 25]. The fcc domain is wide enough to accommodate one molecule, but not two molecules. Thus, even though the fcc domain has 1.3 times larger area than the hcp site, the area available for adsorption is not proportional to this ratio.

Let us discuss the small occupation of group C, starting with the effect of the two ridges which are sandwiching the hcp region. The Pc molecule can fit the hcp domain with Config_I(A1), but it would extend to the ridge area in Config_I(C). Although the reported height difference between the hcp and ridge areas is small (\( \sim 0.1 \) Å), the molecule seems to avoid straddling the two regions. This is probably because the molecule loses the adsorption energy in the tilted adsorption configuration.

This mechanism does not fully explain the low concentration of Config_I(C) in the fcc domain, since it is wide enough to accommodate a single \( \text{H}_2\text{Pc} \) molecule in any configuration. We might have to consider the existence of uniaxial contraction of the Au atoms in the C direction, which amounts to 5%, but is smaller in the A1 and A2 directions. We speculate that for the bonding between the \( \text{H}_2\text{Pc} \) molecule and the Au(111) substrate, the relative positions of the phenyl rings and the substrate atoms are critical. The shrinkage of the substrate lattice should cause a shift of such relative positions and render the Config_I(C) unfavorable.

With the increasing molecular coverage, the intermolecular spacing decreases and eventually small domains form. Here we examine both the azimuthal orientation of each molecule and the lattice directions in the early stage of the film formation.

It was reported that \( \text{H}_2\text{Pc} \) molecules form a quasi-square lattice on highly oriented pyrolytic graphite surface [25], and similar ordering was observed for FePc [11, 12], CoPc [2, 13–15], NiPc [11], CuPc [2, 15, 16] and SnPc [17].

The STM images of figures 2(a) and (b) were obtained on different sites of the same sample, in which the average coverage was estimated as 0.2 ML, and the histogram of the azimuthal angle of the molecules is plotted in figures 2(c) and (d), respectively. In the hcp region, the fraction of the molecules assuming Config_I(C) is further reduced compared to figure 1(b). This is because of the higher local coverage. If we compare the molecular chains composed of Config_I(C) and Config_I(A1), the steric repulsion between the phenyl rings of neighboring molecules starts to appear with longer intermolecular distance in the former case. The chain of Config_I(C) does not favor accommodation of many molecules and therefore is underrepresented in the histograms.

In the fcc region, even though the images of figures 2(a) and (b) were obtained on the same surface, the formation degree of the ordered lattice is different, and there are more square-shaped ordered clusters in figure 2(b). The reduction in the number of the Config_I(C) molecules is not obvious in the
Figure 2. STM images (a, b) and the respective azimuthal rotational angle distributions (c, d) for the molecular coverage at the onset of the lattice formation.

The fcc region of figure 2(a), since the population ratio $(A1+A2)/C$ is almost same as in figure 1. However, when the squares of four molecules are formed in figure 2(b), the group C molecules almost disappear, and most molecules belong to the group A1. This suggests that the alignment of the azimuthal rotation of the molecule is significantly enhanced with the lattice formation. In this particular area, it is dominated by the Config_I(A1) molecules.

The formation of the square-shaped clusters can be illustrated with the STM image of figure 3, which is obtained from a surface having the same average molecular coverage as in figure 2. It reveals two molecular lattice types: Lattice(A1) and Lattice(A2) which are schematically presented in figures 4(a) and (c), respectively.

The lattice can be described with two unit vectors $a$ and $b$ expressed by the matrix $(a_b) = \begin{pmatrix} s & t \\ s & t \end{pmatrix}$. We name it Lattice(A1) because here $a$ is parallel to the A1 direction. Similarly, we consider two other equivalent lattices shown in figures 4(c) and (d) and label them as Lattice(A2) and Lattice(C), respectively.

In addition to the lattice direction, there should be another freedom of the molecule’s azimuthal rotation angle that results in chirality of the adsorbed molecules. This is illustrated in figure 4(b) with a structure which is chiral to that of figure 4(a); we label it Lattice$(A1)'$. The molecular axes are aligned to the A2 and C directions for Lattice(A1) and Lattice$(A1)'$, respectively.

Figure 3 reveals that Lattice(A1) and Lattice(A2) appear with almost equal probabilities. However, as shown in figure 2(b), there is no lattice aligned to the C direction, that is, Lattice(C).

One mechanism of these observed phenomena could be that molecular lattice expands beyond the width of the fcc domain and reaches the ridge part. However, it cannot explain the absence of Lattice(C) because the extension to the ridge domain is the smallest for the Lattice(C) configuration. We speculate that the small occupation of the Lattice(C) configuration is due to the contraction of the gold substrate by 5% in the C direction. If the molecules occupy the same bonding configuration, the steric repulsion between the phenyl rings of the neighboring molecules is expected to increase, making Lattice(C) energetically less favorable. The effect of the substrate contraction is smaller for Lattice(A1) and Lattice(A2).

As discussed above, only two of the three quasi-equivalent lattices appear in the fcc region in the STM images. This makes an interesting ordering near the kink of the herringbone structure. The corresponding STM images are shown in figures 5(a) and (b) and modeled in figure 5(c). Two domains are represented by ridge1 and ridge2 in the figure, and, as discussed above, the Lattice(C) does not form. Other two lattices are illustrated in figure 5(c), where 1_A1 and
Figure 5. (a, b) STM image of H$_2$Pc at higher coverage. Panel (a) presents ridges 1 and 2. (c) Schematic of the lattice configuration for the domains of ridge 1 and ridge 2.

Figure 6. (a, b) STM image of H$_2$Pc at 1 ML coverage. 1_A2 belong to the ridge1 (1_C is missing). Note that 1_A1 and 2_A2, but not 1_A2 and 2_A1 fragments, have ‘common’ configurations; in other words, the former pair can coexist at the kink region. The occupation of the kink region by the lattice of the common configuration can be seen all over the surface, and an example is shown in figure 5(b).

The area where the Au reconstruction structure is covered by the ridge1 and ridge2 can only be occupied by the lattice of ‘common’ configuration. This is actually observed with increasing molecular coverage, as illustrated in figure 6. Figure 6(a) shows the ridge1 and ridge2, as well as a schematic drawing of the common lattice configuration. Here the lattice follows the expected direction. The magnified image of figure 6(b) clearly resolves the azimuthal angle of the molecules expected from our model.

The chiral domains presented in figures 4(a) and (b) for Lattice(A1) and Lattice(A1)′ were observed in the monolayer film. The corresponding STM image is shown in figure 7(a) and modeled in figure 7(b). There are two domains separated by the domain boundary, and the molecules point to different directions in the two domains, although their lattice directions are equivalent. These two domains correspond to Lattice(A1) and Lattice(A1)′ with the respective molecular axes aligned to the A2 and C directions.

As the film coverage is close to a monolayer, it could be argued that the domain boundary in figure 7 is two islands, which are grown in two different ridges and are colliding with each other. In this case, the above argument assuming coexistence of Lattice(A1) and Lattice(A1)′ in a single domain is no more adequate. However, the observed area was dominated by the ridges aligned to a single direction. Thus even though the colliding two domains might have grown from different ridges, these ridges can be assumed to
be parallel and the Lattice(A1)–(A1)′ argument should remain valid.

4. Summary

Low-temperature scanning tunneling microscopy was applied to study the bonding configuration of the metal-free phthalocyanine (H₂Pc) molecule adsorbed on the Au(111) surface. We observed formation of a quasi-square lattice aligned to one of the three close-packed directions of the Au(111) surface. Owing to the reconstruction of the Au(111) surface, the resulting molecular lattice is not equally distributed along the three close-packed directions. The ridge of the local herring bone of the reconstructed Au(111) surface is perpendicular to one of these three directions, which we label as C direction, and the probability for the molecular lattice to align to this direction is very small compared to the other directions. We attribute this effect to the uniaxial contraction of the reconstructed Au(111) surface, which can account for the formation of a large lattice domain along a single direction.

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