Self-assembly and growth of manganese phthalocyanine on an Au(111) surface*

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Self-assembly and growth of manganese phthalocyanine (MnPc) molecules on an Au(111) surface is investigated by means of low-temperature scanning tunneling microscopy. At the initial stage, MnPc molecules preferentially occupy the step edges and elbow sites on the Au(111) surface, then they are separately adsorbed on the face-centered cubic and hexagonal closely packed regions due to a long-range repulsive molecule–molecule interaction. After the formation of a closely packed monolayer, molecular islands with second and third layers are observed.

Keywords: self-assembly, manganese phthalocyanine, scanning tunneling microscopy

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1. Introduction

Organic semiconductor thin films have attracted considerable attention in recent decades due to their potential applications in optoelectronic and spintronic devices,[1−5] whose performance is essentially governed by both their molecular building blocks and the morphology of their organic thin films.[6−8] Since the initial nucleation and structure of the first few layers of molecules play a crucial role in morphology evolution during film growth, a fundamental understanding of the growth and structure of the molecular monolayer on clean ordered surfaces is a major requirement for tailoring the physical properties of organic electronic and optical devices.[9−12]

Metal phthalocyanines (MPcs) are a family of molecules each consisting of a central metal ion and a macrocycle of alternating carbon and nitrogen atoms (Fig. 1(a)). Depending on the central metal ion, the bandgaps and the spin configurations of MPc molecules can be tuned, which is highly desirable for potential applications in both organic electronic and spintronic devices.[13−16] In recent years, the self-assembly of various MPcs, including FePc, NiPc, CoPc, CuPc and SnPc on graphite,[12,17,18] NaCl,[19] Au(111),[6,20,21] Ag(111) and Cu(111)[19,22−25] surfaces were studied at the molecular level by means of scanning tunneling microscopy (STM), and densely packed two-dimensional islands and overlayers were commonly observed. In 2009, the formation of novel Kagome lattices of MPc molecules on graphene and metal surfaces were reported.[26,27] However, few reports address on the detailed growth scenario of MPcs on solid surfaces from initial nucleation to the completion of a monolayer and the formation of multilayers.

In this paper, we present a low temperature (LT) STM investigation of the self-assembly of manganese phthalocyanine (MnPc) on an Au(111) surface. We find that at the initial stage, the MnPc molecules preferentially occupy the step edges and the elbow sites of the herringbone reconstruction of Au(111). With increasing coverage, the MnPc molecules are dispersively adsorbed on the face-centered cubic and the hexagonal closely packed regions due to a long-range repulsive molecule–molecule interaction mediated by the substrate. An ordered closely packed monolayer is formed at the monolayer coverage.

After a complete wetting of the Au(111) surface, molecular islands with second and the third layers are observed, showing that the growth of MnPc on Au(111) follows the Stranski–Krastanov (SK) mode. Unlike the flat configuration that the MnPc molecules adopt in the first layer, the ones in the second and the third layers are tilted, suggesting that the coupling between the molecule in the second layer and

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the Au(111) substrate has been significantly weakened and the molecules tend to crystallize in a way that is similar to that in bulk.

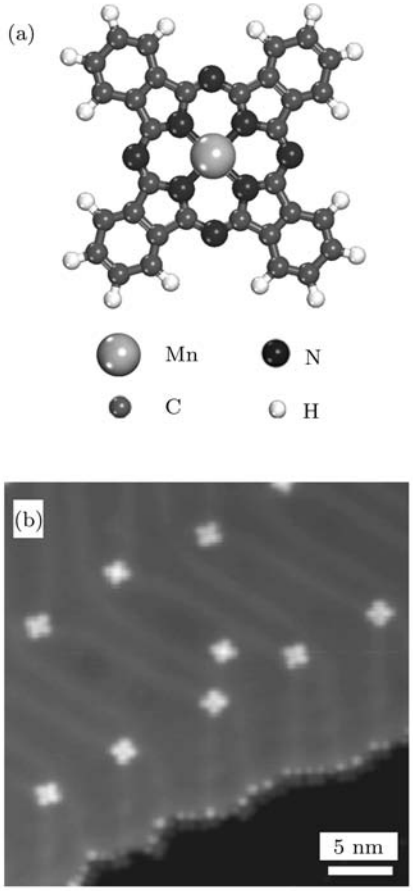


Fig. 1. (a) Chemical structure of MnPc molecules; (b) STM image of MnPc molecules adsorbed on Au(111) step edges and elbow sites with the coverage of ∼0.02 ML (sample bias: $V = -140$ mV, tunneling current: $I = 0.01$ nA).

2. Experiment

Our experiments were carried out in an ultrahigh vacuum (the base pressure is 1×10^{-10} mbar, 1 mbar = 100 Pa) LT-STM system (Unisoku, Japan), equipped with standard surface preparation facilities.[28] The Au(111) (Mateck, Germany) surface was prepared by repeated cycles of Ar^+ sputtering and annealing at 500 °C. The surface structure and cleanliness of Au(111) were checked by STM prior to the deposition of MnPc molecules. Commercial MnPc molecules (Sigma-Aldrich, 97% purity) were purified via vacuum sublimation before deposition. The MnPc molecules were deposited from a Knudsen-type evaporator, while the Au(111) substrate was held at room temperature (RT). One monolayer (ML) refers to the completion of a closely packed MnPc layer on Au(111) surfaces, as estimated by STM. STM images were acquired in constant-current mode and all given voltages refer to the sample. All measurements were performed with an electrochemically etched tungsten tip at 4.2 K.

3. Results and discussion

Clean Au(111) surface exhibits a well-known $22\times\sqrt{3}$ herringbone reconstruction, consisting of alternating face-centered cubic (fcc) and hexagonal close-packed (hcp) regions. After vapour deposition of ∼0.02 ML MnPc molecules (Fig. 1(a)) onto clean Au(111) at RT, we observe a preferential decoration of the step edges and the elbow sites of Au(111) surface, as seen in Fig. 1(b). Similar behaviour has been reported for a variety of molecules on Au(111) because of the higher electronic potential energies of these sites than that of the fcc and hcp regions.[9,29,30] Each MnPc molecule located at the elbow sites of the flat terrace of Au(111) is imaged as a "cross" with a bright protrusion at the molecular center, consistent with the molecular 4-fold symmetry. Previous experiments and calculations suggest that the bright protrusion at the molecule's centre originates from the metal ion's orbitals, while the faint cross corresponds to the planar aromatic skeleton of the MPc molecule.[20,21] The MnPc molecules adopt flat configurations after adsorption on Au(111) terraces due to the molecule–substrate interaction, which is mainly through the hybridization of the dz^2 orbital of MnPc with the Au substrate. However, for molecules at the step edges, the characteristic features are two protrusions centred above the uppermost benzene rings and an alignment of the molecular axis parallel with the [−211] direction of the substrate, showing that the MnPc molecules adsorb across the step edges of the Au(111) surface, similar to CoPc, FePc and HBC molecules' adsorption on Au(111).[10,11,31]

At an increasing coverage of ∼0.1 ML, MnPc separately adsorbs on the fcc regions of Au(111), leaving the hcp regions entirely empty (Fig. 2(a)), much like FePc on Au(111).[6] The average distance between molecules along the fcc regions is 5.52 nm, much larger than what we can expect from a simple van der Waals interaction between MnPc molecules, suggesting a net long-range repulsive molecule–molecule interaction. The preferential anchor of MnPc molecules on the fcc regions indicates that the adsorption of MnPc molecules on the fcc regions is more stable than

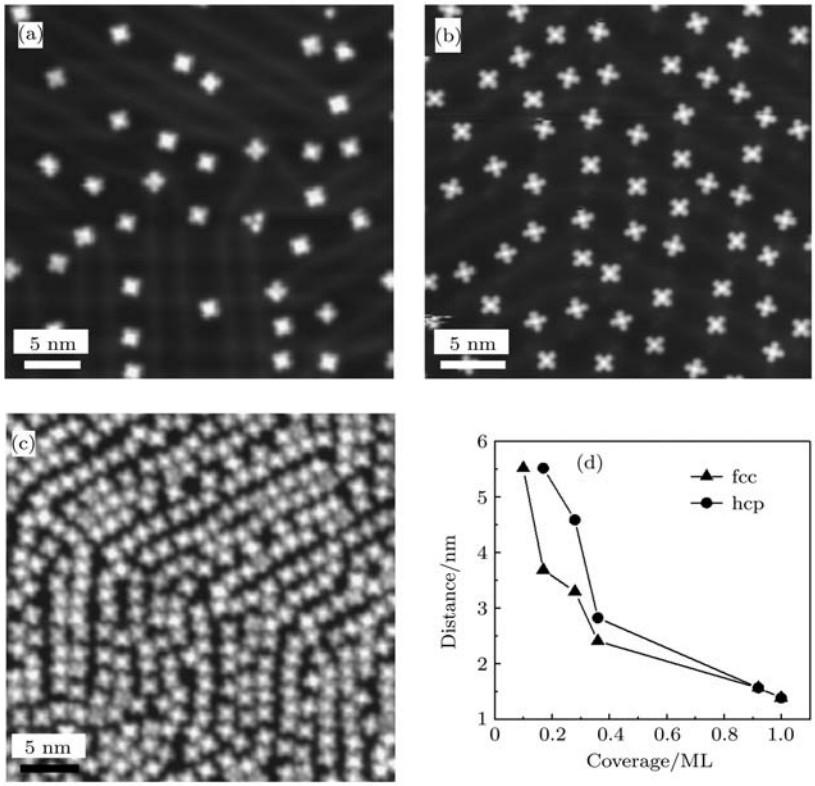


Fig. 2. Topographic images of a MnPc molecular submonolayer on an Au(111) surface. (a) MnPc molecules preferentially adsorbed on elbow and fcc sites at ∼0.1 ML ($V = -0.96$ V, $I = 0.01$ nA); (b) both fcc and hcp sites are occupied by ∼0.2 ML of MnPc ($V = -268$ mV, $I = 0.01$ nA); (c) no closely packed islands are observed even at the coverage of ∼0.9 ML ($V = -197$ mV, $I = 0.02$ nA); (d) mean nearest-neighbour separations of MnPc molecules on Au(111) at different sites versus the molecular coverage.

that on the hcp regions. This is in line with a higher reactivity of the fcc regions because the electronic potential energy of the fcc regions is higher than that of the hcp ones. At the coverage of ∼0.2 ML, the accommodation of MnPc molecules on the hcp regions is observed (Fig. 2(b)), despite of the continued availability on the fcc regions. No closly packed islands are observed, even at the coverage of ∼0.9 ML, as seen in Fig. 2(c). Statistical analysis (Fig. 2(d)) reveals that the mean nearest-neighbour separation between MnPc molecules decreases monotonously with increasing coverage. There are three different principal physical mechanisms of the long-range repulsive interaction between molecules, namely, interference between the surface state of the substrate due to scattering by the molecules,[32,33] repulsive interaction between intrinsic molecular dipoles[24] or repulsive interaction between extrinsic molecular dipoles due to the charge transfer from the surface.[34,35] Previous density functional theory (DFT) calculations show that MPc molecules are not intrinsically dipolar molecules, but significant charge transfers from the MnPc molecules to the Au(111) surface.[35] Therefore, we propose that the dipolar repulsive interaction between the MnPc molecules due to the charge transfer between the molecules and the surface gives rise to the dispersive distribution of MnPc molecules on the Au(111) surface.

A highly ordered closely packed thin film of MnPc is formed at the coverage of 1 ML. The whole Au(111) surface is completely covered by MnPc molecules and a zigzag pattern is clearly visible, as shown in Fig. 3(a). This zigzag pattern stems from the herringbone reconstruction of the Au(111) surface, indicating that the reconstruction is not destroyed or lifted upon deposition of the MnPc molecules under this deposition condition. The MnPc molecules still adopt a flat configuration similar to that observed in submonolayer coverage. The arrows superimposed on Fig. 3(b) show the basis vectors of the square unit cell of the MnPc monolayer, which is further evidenced by the corresponding fast Fourier transform (FFT) pattern shown in the inset of Fig. 3(a). The square lattice of the MnPc monolayer reflects the impact of the 4-fold symmetry of the MnPc molecules on the formation of two-dimensional crystals, akin to the crystallization of other flat MPc molecules on noble metal surfaces. However, considering the mismatch between the 3-fold symmetry of the Au(111) surfaces and the 4-fold symmetry of the MnPc molecules, it is not surprising to

observe the formation of domain walls in the zoomed-in STM images such as the one shown in Fig. 3(b).

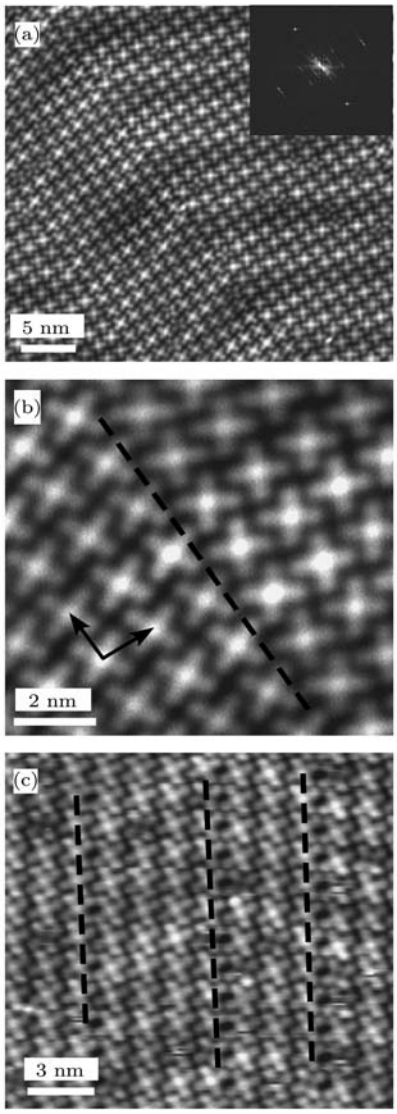


Fig. 3. STM images of the MPc molecular monolayer on an Au(111) surface. (a) The first monolayer of MnPc molecules on the Au(111) surface ($V = -245$ mV, $I = 0.01$ nA), with the insert showing the corresponding FFT pattern. (b) A close-up STM image, with the dashed line indicating the domain wall ($V = -245$ mV, $I = 0.01$ nA). The arrows represent the basis vectors of the square unit cell of the MnPc monolayer. (c) Domain walls of another kind observed in the MnPc molecular monolayer and indicated by dashed lines ($V = -195$ mV, $I = 0.01$ nA).

One can see that the domain wall (indicated by the dashed line in Fig. 3(b)) arises from the MnPc molecules in the adjacent domains at an angle of 60° with respect to each other, similar to the case of FePc molecules on Au(111).[13] By inserting one lobe of a MnPc molecule in one domain into another MnPc molecule that belongs to the other domain, a nearly seamless connection between the two domains is achieved, which is expected to significantly reduce the total energy of the whole system. Domain walls arising from a lateral lattice shift between neighbouring domains are also commonly observed. As illustrated in Fig. 3(c), the molecular orientations of MnPc in neighbouring domains are identical. However, the lattices of the neighbouring domains show a lateral shift along one of the lattice vectors, forming arrays of pits along the domain walls (indicated by dashed lines in Fig. 3(c)).

Further increasing coverage leads to the formation of the second-layer or multilayer MnPc islands on the top of the wetting layer, as demonstrated by Fig. 4(a).

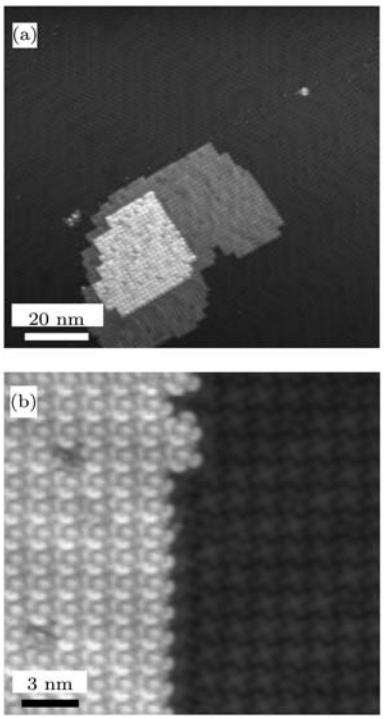


Fig. 4. (a) Large-scale STM images of the MnPc multilayer on Au(111) (∼1.2 ML, $V = -197$ mV, $I = 0.02$ nA); (b) high-resolution STM images of the second layer of MnPc molecules ($V = -353$ mV, $I = 0.01$ nA).

The zigzag pattern from the Au(111) surface reconstruction is still observable as a modulation of the second layer island, indicating that the Au(111) surface reconstruction is not destroyed. The formation of the third-layer islands prior to the completion of the second layer suggests that the growth of MnPc on Au(111) follows an SK mode.[36] The difference between the growth behaviour of the second layer and that of the first layer indicates a remarkably weaker effect of the Au(111) surface reconstruction on the growth of the second layer. The interaction between the molecules of the second layer and the substrate is distinctly weak because of the screening effect of the first layer. Zoomed-in STM images (Fig. 4(b)) reveal that the MnPc molecules in the second layer

exhibit asymmetric structures, indicating a nonplanar adsorption configuration. In the second layer, structures formed by the MnPc molecules have finer details than those in the first layer, suggesting that the molecular orbitals are efficiently decoupled from the Au substrate by the wetting layer so that molecules in the second layer tend to have a configuration similar to that in bulk.[37,38]

4. Conclusions

We have investigated the self-assembly and growth of MnPc molecules on an Au(111) surface. The MnPc molecules first preferentially occupy the step edges and the elbow sites of the herringbone reconstruction of Au(111). With increasing coverage, a dispersive growth mode influenced by a long-range interaction is observed. After a closely packed MnPc monolayer is formed, we found molecular islands in the multilayer, due to the weaker molecule–substrate interaction above the wetting layer. This work is helpful for better understanding of surface-mediated molecular film growth mechanisms.

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