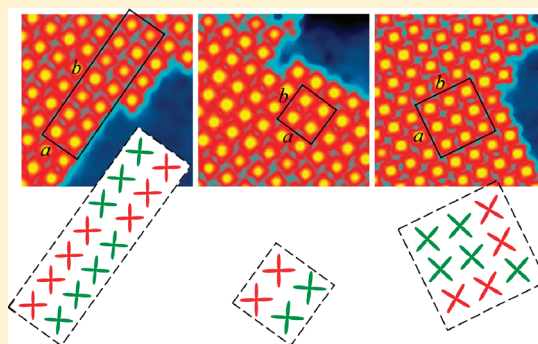


Self-Assembly of Metal Phthalocyanines on Pb(111) and Au(111) Surfaces at Submonolayer Coverage

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ABSTRACT: Self-assembly of manganese phthalocyanine (MnPc) and iron phthalocyanine (FePc) molecules on Pb(111) and Au(111) surfaces is investigated by means of low-temperature scanning tunneling microscopy and density functional theory calculations. Both metal phthalocyanine (MPc) molecules form ordered close-packed islands on Pb(111) with different detail superstructures. In contrast, dispersive single molecules are observed for both MPc molecules on Au(111). The different self-assembling behaviors of MPc molecules on Pb(111) and Au(111) originate from a subtle balance between molecule–molecule and molecule–substrate interactions tuned by the substrate based on our theoretical calculation results.



INTRODUCTION

The performance of molecular nanoelectronic devices essentially depends both on the properties of the building blocks (molecular structure) and on the morphology of the organic monolayer formed by the building blocks.^{1–4} A fundamental understanding of the molecular structure on solid surfaces is a major requirement toward tailoring the physical properties of organic electronic and optical devices.^{5–9}

Metal phthalocyanine molecules (MPcs), each consisting of a central magnetic metal ion and a macrocycle of alternating carbon and nitrogen atoms (Figure 1a), have been attracting considerable interest because of their potential applications in organic electronic and spintronic devices.^{10–12} The formation of densely packed monolayer on graphite,^{13–15} NaCl,^{16,17} Au(111),^{6,18} Ag(111),^{19,20} and Cu(111)^{17,21} surfaces and the Kagome lattice on graphene²² and metal surfaces^{23,24} was revealed by various scanning tunneling microscopy (STM) studies. To date, the substrates used in most STM studies are chemically inert. Thus, investigating an effect of a chemically active substrate on the molecular structure formation and physical properties is strongly needed in the field of molecular interfaces and molecular devices.

Pb(111) is chemically very active compared to graphite, NaCl, and noble metals. The electronic structure of ultrathin Pb film and two-dimensional (2D) islands can be modulated by their thickness, known as quantum size effect.²⁵ Densely ordered monolayers of cobalt phthalocyanine (CoPc)²⁶ and manganese phthalocyanine (MnPc)²⁷ with a square lattice pattern forming a 4×4 superstructure on Pb(111) 2D islands were reported. However, a comparative investigation on molecules adsorbed on the bulk Pb(111) surface is still missing, which might be very helpful for understanding the self-assembling behavior of the molecules and the modification of their physical properties by the substrate. For investigation of the substrate tunability on the

molecular adsorption behavior, we choose Au(111) surfaces for figuring out the assembly mechanism of different kinds of substrates.

In this paper, we present the self-assembly of MnPc and iron phthalocyanine (FePc) on Pb(111) by means of low-temperature (LT) STM. Ordered close-packed islands are observed for growth of both MPc molecules on Pb(111), except that the detailed superstructures are different, while on Au(111) dispersive single molecules are observed, which is attributed to the long-range repulsive interaction between molecules mediated by the Au(111) surface.

EXPERIMENTAL SECTION AND THEORETICAL BASIS

Our 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. The Pb(111) and Au(111) (Mateck, Germany) surfaces were prepared by repeated cycles of Ar⁺ sputtering and annealing at 120 and 600 °C, respectively. The surface structure and cleanliness of Pb(111) and Au(111) were checked by STM prior to the deposition of MPc molecules. Commercial FePc and MnPc molecules (Sigma-Aldrich, 97% purity) were purified via vacuum sublimation before deposition. The MPc molecules were deposited via vacuum sublimation from a Knudsen-type evaporator, while the Pb(111) or Au(111) substrates were held at room temperature (RT). One monolayer (ML) refers to the completion of a close-packed MPc layer on Pb(111) or Au(111) surfaces, as estimated with STM. STM images were acquired in constant-current mode, and all given voltages refer to the sample.

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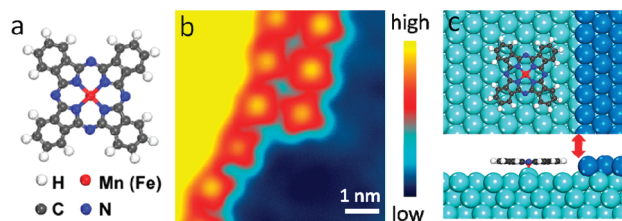


Figure 1. (a) Chemical structure of MPc molecules. (b) STM image of MnPc molecules adsorbed at the lower terrace of a Pb(111) step edge with the coverage of 0.04 ML (sample bias, $V = -22$ mV; tunneling current, $I = 0.06$ nA). (c) Top view (upper) and side view (lower) of the optimized adsorption configuration of a single MnPc molecule adsorbed on the step edge of Pb(111) resulting from DFT calculations (red arrow indicates the Pb step edge).

All experiments were performed with electrochemically etched tungsten tips at 4.2 K.

Density functional theory (DFT) calculations were performed using the Vienna ab initio simulation package (VASP).^{28,29} The generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE)³⁰ was used for the exchange–correlation energy functional. The electron–core interactions were represented by the projector augmented wave (PAW) approximation, and the energy cutoff for plane-wave basis set was 400 eV. Periodic slabs containing four and a half layers of lead substrate were used to model the step edge of Pb(111). To ensure that the interaction between the periodic slabs through vacuum is negligible, the slabs were separated by a vacuum gap of 15 Å. In geometry optimizations, the bottom two layers were fixed, while the adsorbate and the other metal layers are allowed to relax until the forces acting on relaxed atoms were less than 0.02 eV/Å. A single Γ point was used in sampling the Brillouin zone due to the numerical limitations.

RESULTS AND DISCUSSION

Two kinds of MPc molecules, i.e., MnPc and FePc, were separately deposited on the Pb(111) surface at RT. Figure 1b shows a typical STM image after deposition of 0.04 ML MnPc molecules on the Pb(111) surface. It is seen that the lower terraces of the step edges are decorated with MnPc molecules. The preferential adsorption of MnPc molecules at step edges of the Pb(111) surface indicates a high mobility of the molecules on the surface at RT. Each MnPc molecule is imaged as a “cross” with a bright protrusion at the molecular center, consistent with the molecular D_{4h} symmetry, which reveals that the molecular π -conjugated ring is parallel to the surface. We calculated the binding energies for MnPc molecules at three different sites of the Pb(111) surface, namely, lower terrace of the step edges, higher terrace of the step edges, and flat terrace. We found that the adsorption energy for MnPc on the lower terrace of the step edges is ~ 0.3 eV lower than that on the other two sites. As the lower and higher terraces of the step edges of a metal surface usually show an electron-rich and electron-deficient feature, respectively (also known as the Smulochowski effect),³¹ the selective anchoring of MnPc molecules on the lower terrace of the step edges of the Pb(111) surface suggests a charge transfer from the Pb(111) substrate to the MnPc molecules. Figure 1c illustrates the theoretical model of the most favorite configuration for MnPc molecules adsorbed on the Pb(111) surface at very

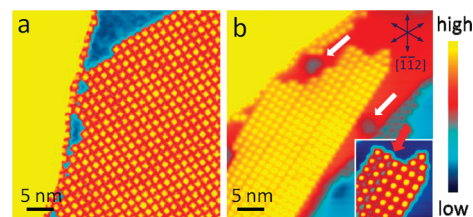


Figure 2. Large-scale STM images of MPc molecules on the Pb(111) surface. (a) Close-packed island of MnPc molecules on the flat Pb(111) terrace ($V = -10$ mV, $I = 0.1$ nA). (b) Similar rectangular structures of the FePc molecule at submonolayer coverage ($V = -2.0$ V, $I = 0.1$ nA). The hexagonal Ar aggregations under the terrace are indicated by white arrows. The inset shows a close-up STM image of the FePc molecular island with the red arrow indicating a unique dislocation line (10 nm \times 10 nm, $V = -2.0$ V, $I = 0.3$ nA). The crystallographic direction of the Pb(111) substrate is determined by the hexagonal edges of Ar aggregations.

low coverage, which is in line with the experimental data. Similar behaviors were also observed for FePc molecules.

After a full occupation of the step edges, 2D islands of MnPc molecules form on the Pb(111) flat terraces, as shown in Figure 2a. The formation of close-packed molecular islands, which is in line with previous reports of MnPc molecules on Pb thin films,²⁷ suggests a net attractive interaction between MnPc molecules on the Pb(111) surface. Similar growth behavior is also observed for FePc molecules on the Pb(111) surface (Figure 2b). The hexagonal depressions indicated by the white arrows (Figure 2b) are assigned to subsurface Ar gas bubbles.³² The hexagon edges are along the close-packed direction of the Pb(111) surfaces, as seen in Figure 2b. Interestingly, we observed one-dimensional dislocation lines every four rows of FePc molecules in a molecular island, as indicated by the red arrow in the inset of Figure 2b. Careful analysis of the line profile reveals that the lattice parameter of the FePc molecular island is 1.32 ± 0.02 nm, much less than four times of the lattice constant of the Pb(111) surface (1.40 nm). The significant lattice mismatch between the FePc molecular island and the Pb substrate results in the formation of stronger strain in the FePc molecular island than that of MnPc islands. We tentatively propose that the strain relief gives rise to the formation of the dislocation lines observed in the FePc molecular islands. As the molecule–molecule interaction is mainly governed by the MPc molecular ligands rather than the central metal ions, a similar molecule–molecule interaction is expected for MnPc and FePc molecules. However, DFT calculations unveil a binding energy of -1.52 eV for FePc on Pb(111), significantly lower than that of MnPc (-1.45 eV) on Pb(111). Therefore, we suggest that the strong molecule–substrate interaction for FePc on Pb(111) induces considerable lattice mismatch between the FePc islands and the substrate, which finally results in the formation of the unique dislocation lines in FePc islands.

The intermolecular distances between the nearest neighbors along different directions of the MnPc molecular island on Pb(111) have an almost identical value of 1.39 ± 0.02 nm, which is nearly four times that of the lattice constant of the Pb(111) surface. Because of this perfect match between the intermolecular distances in the molecular island and lattice constant of the Pb(111) substrate, one might expect the formation of well-ordered large molecular islands, where each unit cell includes a single MnPc molecule.²⁷ Surprisingly, high-resolution STM

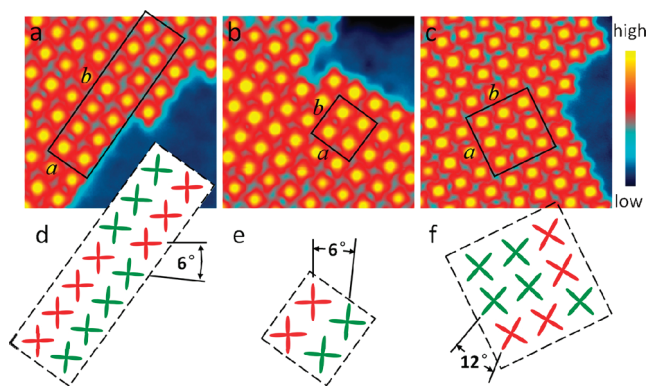


Figure 3. Three kinds of superstructures observed in the MnPc molecular island on the Pb(111) surface, denoted as phase A, B, and C, respectively. (a–c) STM images of phase A, B, and C with the black lines indicating the unit cells ($12 \text{ nm} \times 12 \text{ nm}$; a: $V = -16 \text{ mV}$, $I = 0.16 \text{ nA}$; b: $V = -15 \text{ mV}$, $I = 0.15 \text{ nA}$; c: $V = -20 \text{ mV}$, $I = 0.15 \text{ nA}$). (d–f) Structural models of the unit cells in phase A, B, and C. The crosses with different colors represent MnPc molecules with nonequivalent orientations.

Table 1. Lattice Parameters of Three Superstructures of MnPc Molecules on the Pb(111) Surface

phase	lattice parameters	number of molecules in each unit cell	angle between two nonequivalent molecular orientations
A	$a = 2.75 \text{ nm}$ $b = 9.87 \text{ nm}$ $\gamma = 90 \pm 1^\circ$	14	6°
B	$a = 2.74 \text{ nm}$ $b = 2.78 \text{ nm}$ $\gamma = 90 \pm 1^\circ$	4	6°
C	$a = 4.20 \text{ nm}$ $b = 4.19 \text{ nm}$ $\gamma = 90 \pm 1^\circ$	9	12°

images illustrate the coexistence of three superstructures (Figure 3a–c), which are denoted as phases A, B, and C, respectively. Detailed analysis reveals that the unit cells of all three phases (indicated with black lines in Figure 3a–c) consist of two kinds of molecules with nonequivalent orientations. The structural models of the unit cells of phases A, B, and C are shown in Figure 3d–f, respectively, where the two kinds of molecules with nonequivalent orientations are indicated by the red or green crosses. The lattice parameters of phases A, B, and C are given in Table 1. The absence of dislocation line MnPc islands might be due to the almost perfect lattice match between the lattice of the MnPc islands and the Pb(111) substrate, compared to the situation of FePc islands on Pb(111).

The formation of ordered close-packed 2D islands with various superstructures and large unit cells has been seldom reported for planar MPc molecule self-assembly on solid surfaces up to date (during preparation of this manuscript, we have become aware of the recent observation of a similar superstructure of MnPc on Pb(111)³³). To understand the physical origin of the coexistence of various superstructures of MnPc on Pb(111), DFT calculations were performed. As the unit cells of the three observed superstructures are too large and exceed our

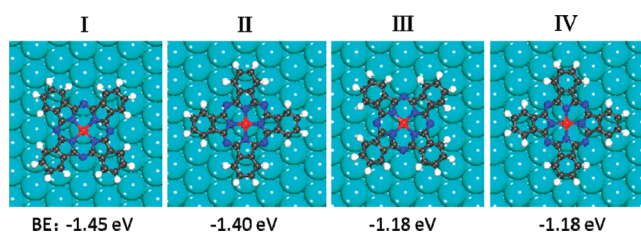


Figure 4. Four optimized adsorption configurations (named configuration I, II, III, and IV, respectively) of a single MnPc molecule on the Pb(111) surface with their corresponding binding energy (BE) underneath. One molecule is put on a 7×8 Pb(111) substrate for calculations.

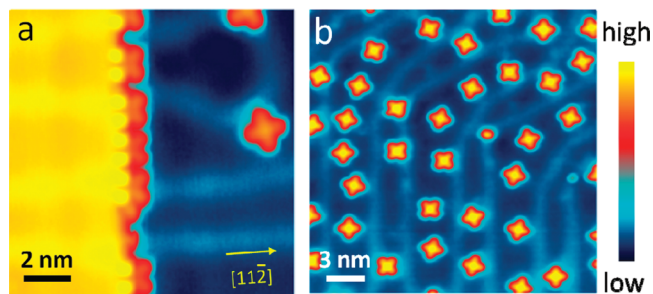


Figure 5. STM images of MPc molecules dispersed on the Au(111) surface at the coverage of 0.02 ML. (a) Several MnPc molecules across a Au(111) step edge with a tilted configuration ($V = -195 \text{ mV}$, $I = 6.75 \text{ pA}$). The arrow indicates the direction of the Au(111) substrate. (b) Isolated MnPc molecule adsorbed on fcc and hcp regions of the Au(111) surface ($V = -220 \text{ mV}$, $I = 3.19 \text{ pA}$).

computational capability, we calculated various adsorption configurations of single MnPc molecule on Pb(111) surfaces. Our DFT calculations unveil four metastable configurations for MnPc on the Pb(111) flat terrace (Figure 4). Among these four configurations, configuration I with the MnPc molecule on the top site of the Pb(111) surface is energetically most favorable with a binding energy of -1.45 eV . Configuration II with the MnPc molecule on the other top site and rotated with respect to the molecular center by $\sim 15^\circ$ compared to the previous one has a binding energy of -1.40 eV . The other two configurations (configuration III and configuration IV), where the MnPc molecules are located on the bridge sites, have an identical binding energy of -1.18 eV , significantly higher than that of configuration I and configuration II. The nearly degenerated binding energies of the adsorption configurations with MnPc molecules on the top sites afford the possibility of the coexistence of three superstructures in 2D MnPc islands.

To further understand the influence of substrates upon the self-assembling behavior of MPc molecules, we separately deposit MnPc and FePc molecules on the Au(111) surface. The 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. Figure 5a illustrates a representative STM image after deposition of 0.02 ML MnPc molecules on Au(111). It is seen that the step edges of the Au(111) surface are also preferentially decorated by MnPc molecules. The characteristic features of this adsorption geometry are two protrusions centered above the uppermost benzene rings and a parallel alignment of the molecular axis with respect to the $[-211]$ direction of the substrate, showing that the MnPc molecules adsorb across the step edges of the Au(111) surface,

similar to CoPc and HBC molecule adsorption on Au(111).^{34,35} Experimental results and DFT calculations indicate that this is also the energetic favorable configuration for FePc on the Au(111) surface.³⁶ This tilted configuration is rather different from a flat configuration for MPc molecules adsorbed at the lower step edges of Pb(111).

At an increasing coverage of ~ 0.3 ML, MnPc molecules dispersively adsorb on the fcc and hcp regions of Au(111) (Figure 5b), suggesting a net long-range repulsive molecule–molecule interaction. Similar behaviors were also observed for FePc molecules on Au(111), consistent with a previous report.⁶ This repulsive interaction may arise from the surface state of the substrate,^{37,38} molecular intrinsic dipole,³⁹ or molecular extrinsic dipole due to the charge transfer from the surface.^{40,41} Statistical analysis (not shown) reveals the absence of the characteristic oscillation of the pair distance between MnPc molecules associated with Friedel oscillations of surface-state electrons. Thus, an interaction mediated by surface electrons can be discarded. In addition, the average pair distance between MnPc molecules decreases monotonously with increasing coverage, and the MPc molecules are not intrinsic dipolar molecules. Therefore, we propose that the dipolar repulsive interaction between the MPc molecules due to the charge transfer from the molecules to the surface determines the dispersive distribution on the Au(111) surface.⁴¹

CONCLUSIONS

We investigated the self-assembly of MnPc and FePc on Pb(111) and Au(111) surfaces by means of LT-STM. Both MnPc and FePc molecules form close-packed islands on Pb(111), whereas the detailed superstructures are different, which are rationalized by the binding energies of various adsorption configurations based on DFT calculations. However, on Au(111), dispersive single molecules are observed for the adsorption of both MnPc and FePc molecules, which is mainly due to repulsive interactions between the molecular dipoles mediated by the Au(111) surface. In addition, MPc molecules adopt a flat configuration on the lower terrace of the step edges of Pb(111), whereas across the step edges of Au(111) they have a tilted configuration at very low coverage. This work about self-assembling behaviors of MPc molecules modulated by the substrate is helpful for a comprehensive understanding and control of the structural and physical properties of the MPc molecules on solid surfaces at a single molecular level.

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