Adsorption behavior of iron phthalocyanine on a Ag(110) surface*

Wu Ke(吴 珂), Huang Qi-Huan(黄齐晅), Zhang Han-Jie(张寒洁), Liao Qing(廖 清), and He Pi-Mo(何丕模)†

Physics Department, Zhejiang University, Hangzhou 310027, *China*

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An investigation on the growth behavior of FePc on a Ag (110) surface is carried out by using scanning tunneling microscopy (STM). At an FePc coverage of 3.5 ML, an ordered superstructure (densely packed) with a lateral shift is observed. The densely packed superstructure can be attributed to the substrate commensuration and the intermolecular van der Waals attractive interaction. The in-plane lateral shift in the superphase is specifically along the direction of $[1\bar{1}0]$ azimuth. The results provide a new perspective to understanding the intermolecular and the molecule–substrate interactions.

Keywords: organic semiconductor, scanning tunneling microscopy, lateral shift, intermolecular interaction

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1. Introduction

Recently, metal phthalocyanines (MPcs) and their derivatives have attracted much attention due to their potential applications in thin film transistors,[1−6] solar cells,[7−8] and organic electronic devices.[9] The applications mentioned above raise the requirement for highly ordered molecular films, and therefore understanding the growth behavior and the electronic properties of the MPc thin film is required.

In addition to low energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS) studies,[10] a lot of scanning tunneling microscopy (STM) investigations were intensively carried out to determine the adsorption geometries and the electronic structures of the MPc thin films during the last decade. Hipps *et al.* reported that for the ordered monolayers of CuPc, NiPc, CoPc, and FePc on Au(111), the significant d orbital character of Fe(II) d^6 near the Fermi energy is responsible for the specific contrast in the molecular center.[11] Cheng *et al.*'s experiments of FePc adsorption on Au(111) indicated that the adsorption behavior is governed by a coverage-dependent competition between the molecule–substrate and the intermolecular interactions.[12] The FePc adsorption on Cu(111) shows short-range ordered domains, and in comparison with FePc/Au(111), the interaction between FePc and Cu(111) is stronger.[13] The ordered FePc square lattice on the highly oriented pyrolitic graphite (HOPG) is the result of the interplay between the intermolecular van der Waals molecule–molecule and the molecule–substrate interactions, and the commensurate hexagonal lattice is not the dominant phase.[14] For the FePc adsorption on Ag(111), several structures have been observed,[15] among which a commensurate lattice appears to be the most stable phase, the oblique FePc lattice is commensurate to Ag(111) by annealing the substrate at 475 K.[16] By combining the results of STM with the density functional theory (DFT) calculations, Casarin *et al.* reported the self-assembly properties of FePc on Ag(110).[17] In this work, we report our recent investigation on the growth of FePc on Ag(110) by using the scanning tunneling microscopy (STM). The growth behavior and the adsorption structure of FePc on Ag(110) are addressed.

2. Experiments

The experiments were performed in a multifunctional ultrahigh-vacuum (UHV) VT-SPM system (Omicron Instruments for Surface Science) with a base

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†Corresponding author. E-mail: phypmhe@zju.edu.cn

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pressure lower than 2×10^{-8} Pa. The system detail has been described elsewhere.[18,19] In brief, it consisted of a fast-entry lock, a preparation chamber, an analysis chamber, and an STM chamber.[20] The system was equipped with a resistive-heating Ta-boat FePc evaporator, a low-energy electron diffraction (LEED) optics, an X-ray photoemission spectrometer (XPS), etc.

The clean Ag(110) surface was obtained by several circles of argon-ion sputtering and annealing. The sample cleanliness was checked by XPS and STM measurements. The FePc (Sigma, 99%) was purified by pre-heating overnight just below the deposition temperature, and then thermally evaporated at 540 K onto the Ag(110) surface held at room temperature (RT) with a deposition rate of about 0.1 ML/min. All the STM images were recorded with constant current mode at room temperature, and all the given bias voltages were referred to the sample.

3. Results and discussion

At a low coverage, no high resolution STM image of the FePc film can be obtained due to the high mobility of the molecule on the Ag(110) surface, which indicates a weak molecule–substrate interaction between the FePc molecule and the Ag(110) surface.

When the coverage reaches about 3.5 ML, a multilayer ordered superstructure of densely packed FePc emerges. A large scale image of the multilayer FePc on Ag(110) is shown in Fig. 1. The image shows the dominate structure with a rectangular unit cell containing one molecule. Careful studies of the higher resolution image (Fig. 2(a)) show that the FePc molecules are assembled into an ordered phase with unit vectors ($\boldsymbol{a}$, $\boldsymbol{b}$) and the molecular wires run at an angle $\alpha = 35.26°$ relative to the $[1\bar{1}0]$ direction of the Ag(110) surface. Here $\boldsymbol{a} = -3\boldsymbol{p} + 3\boldsymbol{q}$, and $\boldsymbol{b} = 4\boldsymbol{p} + 2\boldsymbol{q}$, where $\boldsymbol{p}$ is the unit vector along $[1\bar{1}0]$ of Ag(110), and $\boldsymbol{q}$ is the unit vector along [001] of Ag(110). If the in-plane shift (which will be discussed in detail in the following) is taken into account, the packing density is 0.453 nm^{-2}. This commensurate multilayer structure suggests that the interaction between the FePc molecule and the Ag(110) surface cannot be neglected. However, compared to the weak molecule–substrate interaction, it is the intermolecular interaction that dominates the conformation of this quasi-quadratic superstructure. It is proposed that the dispersion force[21] plays the most important role in the intermolecular interaction of several benzene–benzene configurations,[22,23] therefore, the intermolecular van der Waals attractive interaction takes responsibility for this densely packed phase.[14]



Fig. 1. Large scale STM image for 3.5 ML FePc on Ag(110) (85 nm × 85 nm, $V = -0.987$ V, $I = 0.075$ nA).

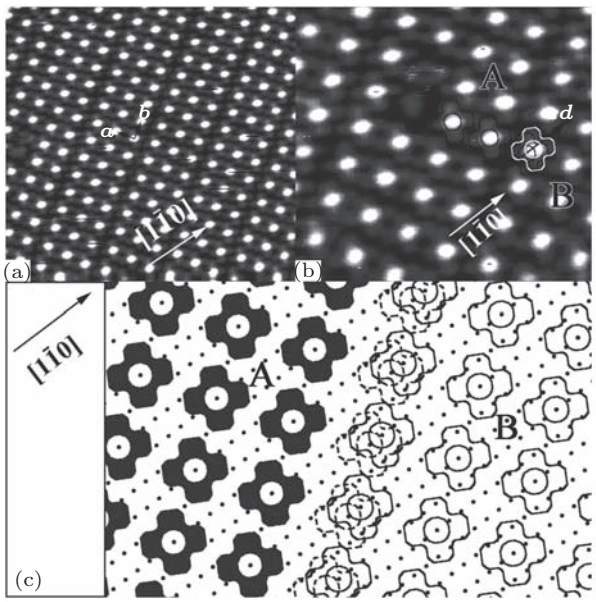


Fig. 2. (a) STM image of densely packed FePc (22.36 nm × 21.21 nm, $V = -1.779$ V, $I = 0.052$ nA), $\boldsymbol{a}$ and $\boldsymbol{b}$ are the unit vectors. (b) High resolution STM image (10.91 nm × 10.14 nm, $V = -1.853$ V, $I = 0.032$ nA), which shows the lateral shift labeled by $\boldsymbol{d}$. (c) Schematic adsorption structure of FePc on Ag(110), where clovers represent FePc molecules, and small dots represent Ag atoms.

Figure 3 shows the ordered lattice in a 50 nm^2 scale. The FePc molecules form a flat-lying adsorption configuration. The molecules are arranged in the structure of benzene ring with one molecule pointing towards the aza-bridge N of the neighboring

molecules, which is similar to the structure obtained by Åhlund *et al.*[14]

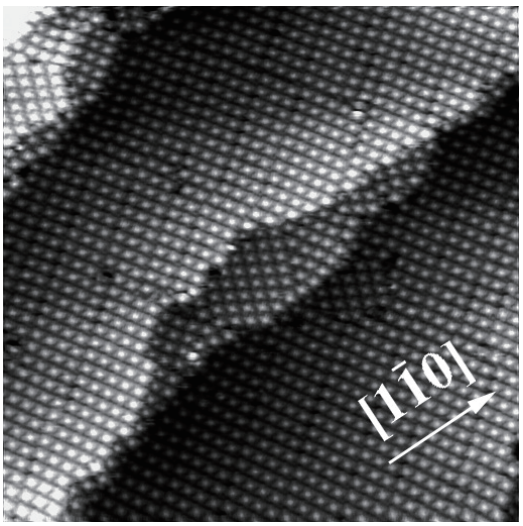


Fig. 3. Magnified STM image showing the flat-lying adsorption configuration of FePc (50 nm × 50 nm, $V = -1.071$ V, $I = 0.037$ nA).

The molecules stacking in two successive layers are not exactly superimposed. Accordingly, the setting angle, defined as the angle between the stacking direction and the molecular plane, is smaller than 90°. The lateral shift between the molecules belonging to the topmost and the underlying layers is about (3.0±0.15) Å. The stacking mode is the so-called (+)-stacking.[24,25] The stacking in the column whose main alignment direction is not perpendicular to the molecular plane reduces the superposition of neighborly stacked molecules.[17]

Two domains are shown in Fig. 2(c). The structures drawn with solid lines and surrounding shadows represent domain A, and the structures drawn with solid lines without surrounding shadow represent domain B. The molecules drawn with dashed lines are used to show the assumed adsorption sites extended from domain A's molecular rows. The shifts along unit vectors $\boldsymbol{a}$ and $\boldsymbol{b}$ are found to be $1/3\boldsymbol{p} - 1/3\boldsymbol{q}$ and $2/3\boldsymbol{p} + 1/3\boldsymbol{q}$, respectively. Evidently, the shift labeled by $\boldsymbol{d}$ in Fig. 2(b) is just the substrate unit vector in [1$\bar{1}$0] of Ag(110), running in parallel to the azimuth direction along the terrace edge. This specifically favored direction of the lateral shift could be taken as a fingerprint of the molecule–substrate interaction. Furthermore, it should be noticed that due to the existence of this shift, the periodicity along unit vector $\boldsymbol{a}$ suffers a reduction, while the other one along unit vector $\boldsymbol{b}$ does not suffer such a reduction.

This variation can be attributed to the competition between intermolecular repulsive and attractive interactions. The repulsive interaction arises from the molecular magnetic moment. For the FePc molecules, the central ion is in an $S = l$ state, and the spin–orbit interaction removes the degeneracy of the triplet state.[26,27] When FePc is adsorbed on a metal substrate, the molecular magnetic moment suffers a reduction due to the interaction between the central Fe atom and the underlying substrate.[28] Though Tsukahara *et al.* confirmed that the coupling of the adsorbed FePc molecule with the Cu(110) substrate is strong enough to convert the state from $S = 1$ to $S = 0$, they also anticipated that when the coverage reaches more than 1ML, the first layer electronically decouples FePc in the second layer from the Cu substrate, and hence the triplet state will survive.[27] In the present case, no stable STM image can be obtained for the FePc films at low coverages, which suggests that the molecule–substrate interaction is weak. For the multilayer FePc film, FePc can be considered as a molecule at the $S = 1$ state with unweakened molecular moment. Therefore, the intermolecular repulsive interaction can be attributed to the parallelly aligned moments from adjacent FePc molecules if the FePc film is described as an Ising system[29] in which the molecular moment is perpendicular to the molecule plane. As discussed above, the attractive interaction mainly arises from the dispersion force. Therefore, as consequences of the closely arranged benzene like rings, the attractive interaction among the FePc molecules experiences value penalty when the benzene–benzene distance increases from the initial value to one larger than that of the equilibrium position.[23] Along vector $\boldsymbol{a}$, this interaction weakens more extraordinarily due to the larger unit parameter compared to that in the direction of vector $\boldsymbol{b}$. Accordingly, in the direction of vector $\boldsymbol{a}$, the repulsive interaction is superior, and the periodicity in this direction is more inclined to compromise in the form of a lateral shift along [1$\bar{1}$0] azimuth.

4. Conclusion

We carried out scanning tunneling microscopy measurements for FePc self-assembly grown on Ag(110). At the FePc coverage of about 3.5 ML, an ordered densely packed multilayer phase with quasi-quadratic unit cell was observed. This phase (superstructure) also showed an in-plane lateral shift specif-

ically along the direction of $[1\bar{1}0]$ azimuth, and the shift along unit vectors of $\boldsymbol{a}$ and $\boldsymbol{b}$ could be defined as $1/3\boldsymbol{p} - 1/3\boldsymbol{q}$ and $2/3\boldsymbol{p} + 1/3\boldsymbol{q}$, respectively, where $\boldsymbol{p}$ and $\boldsymbol{q}$ are unit vectors of the Ag(110) surface. The growth behavior of FePc on Ag(110) can be understood based on the laterally intermolecular interaction and the molecule–substrate interaction.

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