Combined scanning tunneling microscopy and kinetic Monte Carlo study on kinetics of Cu-coordinated pyridyl-porphyrin supramolecular self-assembly on a Au(111) surface

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We have studied the kinetics of Cu-coordinated pyridyl-porphyrin supramolecular self-assembly on Au(111) using scanning tunneling microscopy (STM) through evaluating the island density variation as a function of substrate temperature and molecular deposition rate. We analyzed the experimental data using the classical nucleation theory and derived a molecular diffusion barrier of 0.68 ± 0.06 eV, a pyridyl-Cu bonding energy of 0.20 ± 0.09 eV, and a critical nucleus size of three. These results are confirmed by kinetic Monte Carlo (KMC) simulations. We also studied the postnucleation phenomena and revealed that below 373 K unstable islands (with sizes equal or smaller than the critical nucleus size) were formed upon the deposition and dissolved subsequently.

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I. INTRODUCTION

Supramolecular self-assembly invoking noncovalent binding has provided us an efficient and versatile tool for fabricating well-ordered nanostructures.^{1–3} Recently self-assembly of supramolecular metal-organic coordination networks (MOCN) on surfaces has become an active field as this approach is able to generate two-dimensional (2D) nanostructures with novel functions providing potential applications.^{4–6} The 2D supramolecular metal-organic coordination assembly process occurs spontaneously at appropriate temperatures following the deposition of the building blocks, i.e., organic linkers and metal atoms, on a planar substrate. A wide range of 2D MOCN systems that exhibit intricate structural features has been formed.^{7–15} However, these 2D systems frequently contain inhomogeneities, such as structural defects, polymorphic phases, and small domains, which would generally limit performance in practical device applications. The difficulty of fabricating high-quality 2D supramolecular MOCN systems can be attributed to limited knowledge of the self-assembly kinetics. In order to overcome this challenge, the formation kinetics of the 2D supramolecular coordination self-assembly must be understood. This includes quantification of the intermolecular bonding strength and the kinetic barriers that define mass transport, such as the adsorbate diffusion barrier. Through this understanding, strategies can then be developed for suppressing the defective features that prevent long-range ordering of 2D supramolecular MOCN layers.

In general 2D supramolecular coordination self-assembly is governed by the same principles that dictate conventional three-dimensional (3D) supramolecular chemistry. Nonetheless, new features arise in the planar geometry due to 2D confinement, such as asymmetric adsorption of the adsorbates on the surface, which reduces the degrees of freedom of motion. In addition 2D supramolecular self-assembly implies a special set of intermolecular interactions. At the same time, the interaction of the adsorbates with the surface, which constrains their translational and rotational motions, plays a role of comparable importance with that of intermolecular bonds in the self-assembly process. The interplay of all these features is expected to determine the self-assembled structures.

The diffusion of molecular adsorbates on surfaces has been addressed both theoretically and experimentally.^{16–21}

Scanning tunneling microscopy (STM) has been used to study the motion of organic molecular systems on various surfaces. For example, the thermal migration of the molecule PVBA (4-trans-2-(pyrid-4-yl-vinyl) benzoic acid) on Pd(110) was found to be strictly confined along one-dimensional Pd-surface atom rows. It obeys an Arrhenius law with a diffusion barrier of 830 ± 30 meV and a prefactor of $7.6 \times 10^{-6 \pm 0.4} \text{ cm}^2 \text{ s}^{-1}$.²² Another interesting example comes from a comparative STM study on the motion of two related molecules, hexa-*tert*-butyl decacyclene (HtBDC) and decacyclene (DC), on a Cu(110) surface,²³ revealing the geometrical difference of the two molecules is accompanied by marked differences in their migration barriers, prefactors, and mean jump lengths. Recently Eichberger *et al.* reported an unexpected phenomenon in which Cu-coordinated porphyrin dimers diffuse more rapidly than the molecular monomers on a Cu(111) surface.¹⁹ However, only a few studies have addressed the coordination bonding strength.^{24–26} Lin *et al.* characterized the Cu-carboxylate coordination bonds on the Cu(100) surface with variable-temperature STM and obtained a bonding energy of 0.31 eV.²⁶ Clair *et al.* calculated metal-carboxylate coordination bonds on a Au(111) surface using density-functional theory.²⁴ Alternatively, kinetic Monte Carlo (KMC) simulations have been used to study the supramolecular assembly.^{27–29} For example, self-organized Frechet dendron's pattern observed by STM was reproduced by Monte Carlo simulations.²⁸ Molecular-bonding energies could be derived by comparing the KMC simulated pattern and images from STM experiments.²⁷ However, due to the complexity of supramolecular systems, practical methods to measure both the molecular-diffusion barrier and the binding energies are rare.

Classical nucleation theory developed in the investigation of inorganic thin-film growth and epitaxy is well-established.³⁰ From the kinetic-rate equations that describe atom nucleation and growth behavior, a relationship between bonding energy, diffusion barrier, and island density can be established. This method has been used to describe C₆₀ diffusion on insulating substrate³¹ and pentacene film aggregation.³² It is conceivable that this method can also be applied to study supramolecular systems, which may enable us to obtain the information of the energies that control the supramolecular self-assembly.

In this paper the self-assembly kinetics of tetra-pyridyl-porphyrin (TPyP) molecules coordinated by copper atoms on

a Au(111) substrate is investigated by STM and KMC simulations. We attempt to apply classical nucleation theory to this supramolecular self-assembly system. In Sec. II experimental procedures and simulation details are introduced. In Sec. III A island densities as a function of substrate temperature and molecular deposition rate are analyzed, and a value containing diffusion barrier and binding energy is obtained. Section III B shows the results of KMC simulations that derive the energies of diffusion barrier and bonding energy by reproducing the experimentally observed island shape. Sec. III C focuses on the postnucleation behavior observed in both temperature and rate dependence of saturation island density. We find that this behavior can be attributed to the initial formation of unstable small islands. Section VI provides further discussion and concludes our findings.

II. EXPERIMENTAL SETUP AND SIMULATION

Experiments were performed in an ultrahigh-vacuum system (Omicron Nanotechnology) with base pressure below 5×10^{-10} mbar. A single-crystalline Au(111) substrate was prepared by Argon-ion sputtering and annealing to ~ 900 K, resulting in terraces of ~ 100 -nm wide. Copper atoms were first deposited by an electron-beam evaporator on the substrate, which was held at room temperature (300 K). Copper islands could always be found along the steps of the Au(111) under all experimental conditions, indicating that copper atoms were always sufficient for the coordination binding. We therefore may neglect the influence of the shortage of copper atom during supramolecular self-assembly. We afterwards heated the substrate and held it at a temperature in the range between 300 K and 450 K and deposited TPyP molecules on the substrate using an organic molecular-beam deposition source (Dodecon). During the deposition the molecular deposition rate was fixed at a constant value between 5×10^{-5} and 1.6×10^{-3} monolayer per second (ML/s; 1 ML is defined as the self-assembled structure that occupies the entire surface), which was calibrated from dividing the overall coverage of the self-assembled networks by deposition-time duration. We prepared different samples with different deposition rates and at different substrate temperatures. Once the molecule deposition was completed, the substrate was cooled down to 300 K for STM measurements. To minimize the influence of structural defects, such as steps, we selected areas with large terraces and fewer structural defects in data acquisition and analysis. The STM measurements were performed at 300 K in constant-current mode at 1.0–1.4 V positive or negative bias and 0.2–0.4 nA tunneling current.

We performed the KMC simulations following the protocol of 2D atomic epitaxy^{33,34} but with several modifications to assess the supramolecular self-assembly. In contrast to the KMC simulations developed for atomic epitaxy, here a square-shaped molecule occupies an area covering seven substrate-lattice sites along its diagonal [cf. inset in Fig. 5(a)] according to the size of a TPyP molecule and the Au(111) surface-lattice constant. The rules that govern the KMC evolution of the self-assembled structures are as following. (i) Molecules are deposited onto the substrate randomly both in space and time, with deposition rate R (ML/s). All impinging molecules

are assumed to stick and no desorption is allowed. (ii) The monomers diffuse randomly on an open terrace. Hopping to the nearest-neighboring site occurs at a rate given by $h_d = \nu_0 \exp(-E_d/kT)$, where ν_0 is the attempt frequency and E_d is the diffusion barrier. We adopt typical values of $\nu_0 = 1 \times 10^{12}$ Hz,^{18,35} $k = 8.62 \times 10^{-5}$ eV/K. (iii) If two molecules encounter in a corner-to-corner configuration, a coordination bond is formed [cf. inset in Fig. 5(a)] with bond energy E_b . The rate of releasing a bonded molecule from a molecular island is given by $h_d = \nu_0 \exp[-(E_d + nE_b)/kT]$, where n is the number of bonds that connect this molecule to its neighboring molecules. (iv) The molecular islands with size larger than one will not diffuse. Hopping over an island is also not allowed.

Simulations were performed on a square of 1400×1400 lattice sites, corresponding to one monolayer of molecular island containing 200×200 molecules. We did not use the hexagonal lattice of Au(111) for simplicity. The different symmetry of the substrate mostly influences the orientation of the network but not the island density, thus the analysis is valid. We first deposited molecules on the surface with a constant deposition rate within a certain time interval while the system was kept at a certain temperature. Once the deposition was completed, the temperature of the system dropped exponentially to 300 K (dropped to half of the initial temperature in ~ 15 min). And we extended the simulation time to three hours after deposition to simulate the actual experiments. All parameters used in the simulations were in accordance with experiments.

III. RESULTS AND DISCUSSION

A. Experimental results

Figure 1(a) is a typical STM topograph showing rectangular-shaped islands of ordered-molecular networks. The networks are in three orientations due to the three-fold symmetry of the Au(111) substrate. Within each island TPyP molecules form rhombic networks with the coordinative pyridyl-Cu-pyridyl bonds as linkage.³⁶ A model of the network is shown in Fig. 1(b), with a molecule dimension of 1.5 nm and a network periodicity of 1.9 ± 0.1 nm. Detailed discussion of the network structure can be found in Ref. 36. Influence of the electric fields induced by STM tip on diffusion, and nucleation process can be excluded, as the two successive yet identical area STM images did not show any effects caused by the scanning.

Figure 2 shows STM images of the sample that the molecular deposition was accomplished on a substrate temperature of 300, 363, 393, and 428 K, respectively, with a constant deposition rate and a constant molecular coverage. Clearly at higher substrate temperatures the island density is relatively lower and vice versa. It is also obvious that the islands tend to grow into a rectangular compact shape at 300 K and 363 K [e.g., Fig. 2(a), 2(b)], but the edges become kinked and irregular at 428 K. The smallest stable island in the STM data is a square consisting of four molecules. One may also find some short linear molecular chains. Since their quantity is very few, we neglect them in the analysis. We did not consider the situation above 430 K due to the following two reasons:

FIG. 1. (Color online) (a) STM topograph showing Cu-coordinated TPyP rhombus networks. Image size: 90 nm $\times$ 55 nm. (b) Model of the TPyP-Cu network which is marked by the rectangle in (a). A copper atom (orange) connects two nitrogen atoms (blue) of the pyridyl ligand (carbon atom in gray, hydrogen atom in white).

first, the network islands grow too large, i.e., comparable to the size of Au(111) terrace, above 430 K; second, the network is not the only structure above 430 K and other structures, for example, close-packing phase, may appear. Both effects would introduce complexity in analyzing the island density.

We have quantitatively analyzed the island density (averaging at least 10 large-scale STM images of 200 nm $\times$ 200 nm for each sample) as a function of substrate temperature at the deposition as well as molecular deposition rate. Figure 3(a) shows the dependence of island density on the substrate temperature at coverage of ~ 0.14 ML and at a molecular deposition rate of 1.17×10^{-3} ML/s. In the temperature range between 373 and 433 K the island density drops exponentially over one order of magnitude with respecting the inverse temperature. Below 373 K, the island density is independent of the temperature. We attribute this behavior to postnucleation effects³⁷ and will discuss it in detail later. The atomic nucleation theory of island growth asserts the island density is determined by the mobility of atoms as well as interatomic binding. Therefore the relevant energetic values can be extracted from systematical study of the variation of island density. The classical nucleation theory based on a rate-equation approach predicts an exponential relationship between density of stable islands n_x and substrate temperature T for 2D-island growth at complete condensation^{30,35}

$$n_x \sim \eta(\theta, i) \left(\frac{R}{v_0} \right)^p \exp \left(-\frac{E}{kT} \right), \quad (1)$$

FIG. 2. (Color online) STM images of TPyP-Cu networks grown at different substrate temperature of (a) 300 K, (b) 363 K, (c) 393 K, and (d) 428 K. Image size: 200 nm $\times$ 200 nm. The deposition rate is 1.17×10^{-3} ML/s and the coverage is about 0.14 ML. The circle in (a) marks the smallest stable island, a square tetramer, observed in the experiments.

where

$$p = \frac{i}{i+2}, \quad E = \frac{E_i + iE_d}{i+2}, \quad (2)$$

in which E_d is the surface-diffusion barrier of adsorbates; E_i is the total binding energy of an island with the critical nucleus size i , which is the number of nearest-neighbor bond within a critical nucleus times the bonding energy E_b , e.g., for square island $E_i = 2E_b$ as $i = 3$, $E_i = 4E_b$ as $i = 4$; v_0 is the attempting frequency; and R is the molecular deposition rate. Since the TPyP molecules self-assemble 2D single-layer networks on Au(111) surface and desorption of TPyP molecules from the surface can be neglected in the experimental temperature range of 300–433 K, this supramolecular system satisfies the condition of using the rate Eqs. (1) and (2). Hence we apply the nucleation theory to the supramolecular coordination self-assembly system, where E_b refers to the Cu-pyridyl coordination bond energy and E_d refers to the TPyP molecular diffusion barrier on Au(111).

From the slope of the island density n_x versus the inverse temperature $1/T$ shown in Fig. 3(a), the value of E can be extracted using Eq. (1). The slope of the linear fit above 373 K in Fig. 3(a) results in $E = 0.49 \pm 0.02$ eV. This value is a combination of E_b and E_d , which contains the undetermined critical nucleus size i . The most straightforward way to obtain the critical nucleus size is to measure the rate dependence of the island density $n_x(R)$ according to Eqs. (1) and (2). Figure 3(b) shows a double-logarithmic plot of n_x versus R at two substrate temperatures of 300 and 395 K. The reason we choose two different temperatures is to find out whether i depends on temperature within the experimental temperature

FIG. 3. (a) The measured island density of TPYP-Cu networks as a function of substrate temperature during the molecular deposition with a flux 1.17×10^{-3} ML/s and coverage of 0.14 ML. (b) Double-logarithmic plot of island density as a function of deposition flux at two substrate temperature, 310 K and 395 K. The coverage is around 0.14 ML at both temperatures.

range. At 395 K, $i = 3$ fit the data best, implying that trimer is the critical nucleus and tetramer is the smallest stable island. At 300 K, the island density is found to be constant for the high deposition rate, which will be discussed later as ascribed to postnucleation; in the low-rate regime, $i = 3$ yield the best fitting too. Hence, at both temperatures, the smallest stable islands are of four molecules. This result is consistent with the experimental observation that the smallest islands are square-shape islands consisting of four molecules. With $i = 3$ we obtain the following result: $2E_b + 3E_d = 2.45 \pm 0.08$ eV.

B. KMC Simulation

To determine the binding energy E_b and the diffusion barrier E_d , we turn to the analysis of island density and shape with KMC simulations. We adopt the parameter with different E_b (0.10, 0.20, and 0.30 eV) and E_d (0.75, 0.68, and 0.62 eV) given their combination satisfies $2E_b + 3E_d = 2.45 \pm 0.08$ eV. To corroborate the experimental measurements, islands with size smaller than four molecules are not

FIG. 4. (Color online) (a) Comparison of KMC simulated and experimentally obtained island density versus temperature. The simulations are of three different sets of energy values. (b) Comparison of KMC simulated ($E_b = 0.20$ eV, $E_d = 0.68$ eV) and experimentally obtained island density versus deposition flux.

accounted when calculating island density. The comparisons between measured and simulated island densities as a function of $1/T$ are shown in Fig. 4(a). Apparently, the simulation using $E_b = 0.10$ eV fits the experimental data agreeable at the low-temperature regime but deviates remarkably at high-temperature regime; the simulation using $E_b = 0.30$ eV fits well at high temperature but fails to show any feature of postnucleation at lower temperatures. The simulation using $E_b = 0.20$ eV reproduces the experimental results in whole temperature range, displaying a similar slope at high temperatures and the features of postnucleation at low temperatures. Nevertheless, at $E_b = 0.20$ eV the simulated island density is higher than experimental results in the low temperature regime. This difference may be given by the diffusion of dimeric clusters,¹⁸ an effect ignored in our simulations. There are more dimers in low temperature than in high temperature and thus the influence of dimer diffusion is more obvious in this regime. Figure 4(b) shows the simulated island density as a function of deposition rate. Overall the simulations reproduce the experimental results moderately showing good agreement

FIG. 5. (Color online) KMC simulations of TPyP-Cu island assembled at 360 K with different energetic values: (a) $E_b = 0.10$ eV, $E_d = 0.75$ eV (inset shows a square tetrameric island on the substrate lattice); (b) $E_b = 0.20$ eV, $E_d = 0.68$ eV; and (c) $E_b = 0.30$ eV, $E_d = 0.62$ eV. The deposition flux and coverage are 1.17×10^{-3} ML/s and 0.14 ML, respectively. Images are an area of 700×700 lattice sites from the simulated 1400×1400 lattice sites, which corresponds to about $200 \text{ nm} \times 200 \text{ nm}$. Each light dot (diamond in shape) stands for a TPyP molecule.

in slope. The difference of absolute value may also come from the dimer diffusion.

We also analyzed the island shape by simulations. Note that the islands of the supramolecular networks are rather compact under all experimental temperatures. The compact and regular island is commonly observed in atomic nucleation and growth on metal surface, which was attributed to edge diffusions. However, the edge diffusion mechanism could hardly be applied to the supramolecular networks since a TPyP molecule that is attached to a molecular network edge has to first break the existing bond and hop seven steps along the network edge to reach the next coordination site in order to form a new bond. During the seven hopping the molecule is more likely to hop away randomly rather than move straight along the edge. Based on these considerations we exclude the edge-diffusion effect as the main reason for the compact islands.

In compact islands nearly all the molecules at the edge are stabilized by three bonds. Only minimal portion of molecules that are located at corners or kinks are with two bonds. Thus the compact-shape arrangement gives the lowest total energy since more coordination bonds form and less pyridyl ligands remain uncoordinated. We attribute the compact islands to a balance between the intermolecular and molecule-to-substrate interactions. Figure 5(a) shows the simulated islands with a binding of $E_b = 0.10$ eV ($E_d = 0.75$ eV) at 360 K. We can find substantial amount of molecular monomers, indicating bond breaking due to thermal activation becomes significant with such weak binding. Actually, as we compare this frame with the one several minutes later, we may find the existing islands are unstable and their boundaries are under continuous changes. This instability is ascribed to the dynamic equilibrium between molecular monomer attached to and desorbed from the islands due to the weak bonding. However, the experimental data reveal the islands are rather stable, i.e., their boundaries are almost unchanged in subsequently scanned STM images. Therefore $E_b = 0.10$ eV underestimates the bond strength. Figure 5(c) shows the simulated islands with a strong binding ($E_b = 0.30$ eV and $E_d = 0.62$ eV). Here the boundary of molecular islands becomes quite irregular. The roughness

comes from the increasing percentage of edge molecules absorbed to the islands with only one or two bonds, and these molecules are stabilized due to the high-binding energy. Other types of defects, for example, empty sites inside islands, are also common under this parameter. These structures are not observed in experimental data. If even higher bonding energy is applied, we expect that fractal islands will appear. The extreme case is the diffusion-limited aggregation. So, $E_b = 0.30$ eV overestimates the bond strength. Figure 5(b) shows the simulated islands with a moderate binding of $E_b = 0.20$ eV and $E_d = 0.68$ eV. Overall the simulated islands resemble the experimental STM observations of the 363 K sample both in island shape and density. Based on the comparison of the experimental data and simulated results, we can narrow the values of the Cu-pyridyl binding energy as $E_b = 0.20 \pm 0.09$ eV and the molecular diffusion barrier as $E_d = 0.68 \pm 0.06$ eV.

C. Postnucleation effects

To better understand the dynamic process that happened in the postnucleation stage, we tracked the time-evolution of island density after deposition in the simulations. Figure 6(a) displays both the stable island density n_x and the total island density $n_x + n_{1\sim3}$ (including the islands smaller than the critical nucleus size) at 0 s, 240 s, and 3.3 hours after deposition at 300 K, respectively. The total island density, $n_x + n_{1\sim3}$, shows a nearly constant drop over all temperatures from 0 to 240 s (see that the whole curve keeps its shape but shifts downwardly). From 240 s to 3.3 hours the total island density at high temperatures only decreases slightly. At low temperature regime ($T < 380$ K) the total island density descends in a way that after 3.3 hours a plateau appears, i.e., being almost independent of temperature. In contrast the stable island density n_x remains the same at all time (0 s, 240 s, and 3.3 hours) after the deposition at all temperatures except at 300 K n_x increases from 0 to 240 s. The increase in number of stable islands around 300 K indicates additional islands formed after deposition, which represents a character of postnucleation.³⁷

FIG. 6. (Color online) KMC simulated ($E_b = 0.20$ eV, $E_d = 0.68$ eV) time evolutions of island densities after deposition. (a) Stable island density n_x (black) and total island density $n_x + n_{1-3}$ (gray) versus temperature at 0 s, 240 s, and 3.3 h after deposition. (b) Island density of different size (monomer n_1 , dimer n_2 , trimer n_3 , tetramer n_4 , and total stable island n_x) after deposition as a function of time at 310 K.

Furthermore we monitor the time-evolution of the population density of islands of a specific size of monomer (n_1), dimer (n_2), trimer (n_3), and tetramer (n_4) as well as n_x . The results are plotted in Fig. 6(b). It can be seen that the island density of monomer, dimer, and trimer all drop sharply in the first few hundred seconds right after deposition (the deposition is completed at $t = 0$). After three hours the islands that are smaller than four ultimately disappear, while the island density of tetramer reaches a static value. This result again confirms the

conclusion that the critical nucleus size $i = 3$. For the islands larger than the critical nucleus size, the island density n_x shows a noticeable enhancement around 240 s after the deposition, which corresponds to the additional stable nucleuses formed as a result of the disappearance of the smaller islands. After that enhancement the density of stable islands gradually approaches a constant level. These postnucleation effects can be attributed to the fact that the molecular monomer diffusion is not sufficient when the substrate temperature is low during molecular deposition. So right after the deposition the surface has an appreciable amount of islands whose size is smaller than the critical nucleus size. These unstable islands dissolve at the postnucleation stage and as a result, the total island density drops. For the samples that the molecules were deposited at high temperature substrate, however, the molecules diffuse efficiently on the substrate and therefore stable larger islands will form upon deposition, so the island density remains the same and postnucleation effects are not obvious.

IV. CONCLUSIONS

We have investigated the growth kinetics of Cu-coordinated TPyP molecules self-assembled on a Au(111) surface by means of STM and KMC simulations. Keeping the copper atoms sufficient in the self-assembly processes, we can apply the classical nucleation theory developed for the atomic island growth to this supramolecular system and derive important parameters, e.g., molecular diffusion barrier and bonding energy. The obtained diffusion barrier of TPyP on Au(111), 0.68 eV, is smaller than TPyP on Cu(111), 0.96 eV,¹⁸ which might be attributed to the fact that gold substrate is more inert than copper.^{38,39} The coordination bonding energy, 0.20 eV, is smaller than the dissociation energy of the Cu-carboxylate bonding as trimesic acid molecules are connected by a copper atom, 0.31 eV.²⁶ This difference is consistent with the chemistry that carboxylate ligand is stronger than pyridyl ligand.

At last, we note that TPyP molecules in this study has four-fold symmetry which allows us to simplify them to square dots diffusing on surface and nucleating to square networks without considering the molecular rotational degree of freedom. For other systems that comprise molecules of orientational anisotropy, rotational degree of freedom must be taken into consideration when applying this method.

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