

Site Selective Adsorption and Templated Assembling: Effects of Organic–Organic Heterogeneous Interface Studied by Scanning Tunneling Microscopy

Shengbin Lei, Chen Wang,* Lijun Wan, and Chunli Bai*

Key Laboratory of Molecular Nanostructure and Nanotechnology, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P. R. China

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Observations of significant template effects of the organic molecular support of tridodecylamine (TDA) lamellae structure with scanning tunneling microscopy (STM) is presented. The site selective adsorption and directional diffusion of single molecules and molecular clusters of copper phthalocyanine (CuPc) are identified. In addition, bimolecular CuPc band structure is achieved as the result of the selective adsorption and diffusion. These results could be beneficial to the construction of molecular nanostructures using organically functionalized substrates as templates.

Self-assembling of nanometer-sized building blocks into designed molecular architectures at surfaces represents one of the major goals of supramolecular chemistry and material science, given the perspective of the potential applications of these systems in nanotechnology, such as for molecular information storage devices or organically functionalized surfaces.¹ Covalent and noncovalent interactions such as metal–ligand binding, hydrogen bonding, and electrostatic interactions were successfully used for the design of supramolecular architectures. To control the ordering of molecules in the 2D monolayer structure, directional noncovalent modes of interaction, such as hydrogen bonding, are of great help and importance.^{2–7} Recently, novel heterogeneous two-dimensional patterns of phthalocyanine were reported to be formed via coadsorption of two or more molecular species.^{7–9} The formation of such heterogeneous assemblies is directly associated with the intermolecular interactions, and more interestingly, the assembly of these ordered structures is based on electrostatic or van der Waals interaction, which lacks directional selectivity. It is further plausible to expect that the 2D molecular assemblies may serve as templates for constructing 2D molecular structures.

In this work, we demonstrate clearly the template effects of the lamella of tridodecylamine (later noted as TDA) molecules on the adsorption, diffusion, and assembling structures of copper phthalocyanine. By coadsorption of TDA with copper phthalocyanine (CuPc), isolated CuPc molecules and clusters could be stabilized at the alkane part of the lamellae. The lateral diffusion of single CuPc molecules as well as clusters of adsorbed CuPc molecules is exclusively along the direction of the TDA lamellae. Furthermore, with higher CuPc coverage, well-ordered bimolecular CuPc bands were developed as a result of molecular templating of TDA lamellae. Such effects have never been observed on lamella of simple alkanes,¹⁰ possibly due to the lack of functional groups that could establish sufficient diffusion barriers for the overlayer adsorbates. This concept could be generalized to the construction of molecular templates for novel molecular nanostructures.

The surface assembly of TDA was prepared by depositing a drop of TDA directly onto the surface of freshly cleaved

graphite. Coadsorption of CuPc on the TDA template was prepared by depositing a drop of TDA containing CuPc on the surface, the concentration of CuPc ranged from less than 0.1 mM to saturation. The as-prepared samples were scanned by an STM either immediately or after annealing at 50 °C in air for 3 h and cooled to room temperature under ambient conditions. The STM experiments were carried out on the liquid/graphite interface, by immersing the tip in the liquid, under room temperature on a Nanoscope IIIA SPM system (Digital Instruments, Santa Barbara, CA). The tip was mechanically formed Pt/Ir wires (90/10). The typical tunneling conditions are bias 500–800 mV and setpoint 500 pA to 1.0 nA.

When deposited on the surface of graphite, well-ordered lamellar structures of TDA could be identified. A high-resolution STM image (Figure 1a) reveals that TDA molecules adsorb with their carbon chains parallel to the basal plane of graphite and with a 90° angle to the lamellar axis. To obtain a close-packing structure on the surface, the symmetry of TDA molecules is observed to be reduced from 3-fold to a linear conformation. The amino groups located in the center of the lamellae appear with a higher contrast with respect to the alkyl part under positive bias (Figure 1a).

When coadsorbed with TDA at a low Pc:TDA ratio, CuPc dimers are most commonly observed, with a smaller population of quadrimers. From large scale view one can observe the two CuPc molecules located on both sides of the amino group of the TDA lamellae. The high-resolution image (Figure 1a) reveals that the two CuPc molecules lie side by side in the dimer, which is apparently different from the joggle conformation in the 2D crystal domain.¹⁰ In addition, the two CuPc molecules in the dimer are distinctly separated from each other. The width of the dark trough between the two molecules is measured to be 0.6–1.0 nm depending on the different parts of the molecule. The intermolecular distance measured from the molecular center of these two molecules is 1.94 ± 0.02 nm, larger than the 1.45 nm distance in the 2D crystal structure.¹⁰ Compared with the TDA lamellae structure, the trough between the CuPc molecules is precisely the location of amino groups in the underneath TDA lamellae. In the high-resolution images, such as in Figure 1a, features of amino groups can even be identified in the trough. This implies a CuPc-atop-TDA conformation.

* To whom correspondence should be addressed. E-mail: clbai@iccas.ac.cn, wangch@iccas.ac.cn.

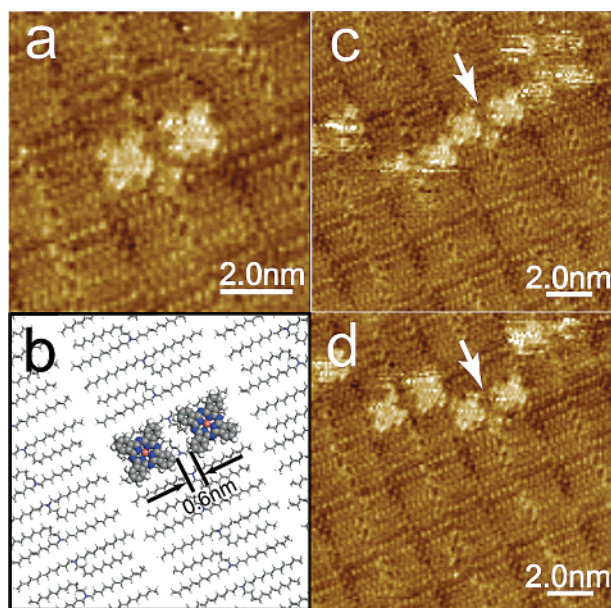


Figure 1. (a) High-resolution image obtained on one CuPc dimer. (b) Corresponding model of the dimer structure. (c), (d) Dimer movement recorded by STM. The CuPc dimer marked in (c) migrated for a distance of one and a half CuPc molecular width along TDA lamella during the STM scan. The images were recorded in sequence and a scan rate of 12.11 Hz.

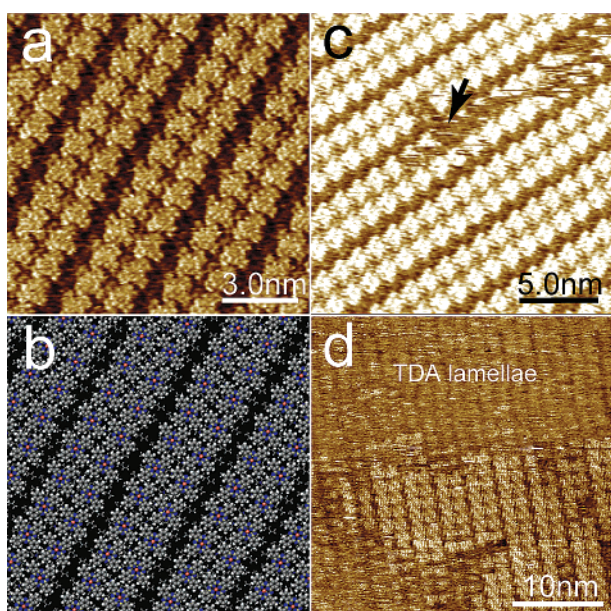


Figure 2. (a) High-resolution image of CuPc bimolecular bands. (b) Molecular model corresponding to the structure shown in (a). In the area marked by a dark arrow in (c), some CuPc molecules are removed by the STM tip and underlying alkyl chains of TDA lamellae can be clearly revealed. The brightness of this image is adjusted to give the best contrast of the underlying alkyl chains. (d) One to one correspondence of CuPc double row bands to underneath TDA lamellae. Both observations can serve as direct evidence for the CuPc-atop-TDA configuration.

More direct evidence of the CuPc-atop-TDA conformation is the observation of dimer movement. Figure 1c,d shows two consecutive images recorded in sequence. In regard to the positions of the neighboring dimers, the CuPc dimer marked by an arrow in Figure 1c migrated downward for a distance of about one and a half CuPc molecule widths along the TDA lamella. The blurry and dissociated dimers observed in the image

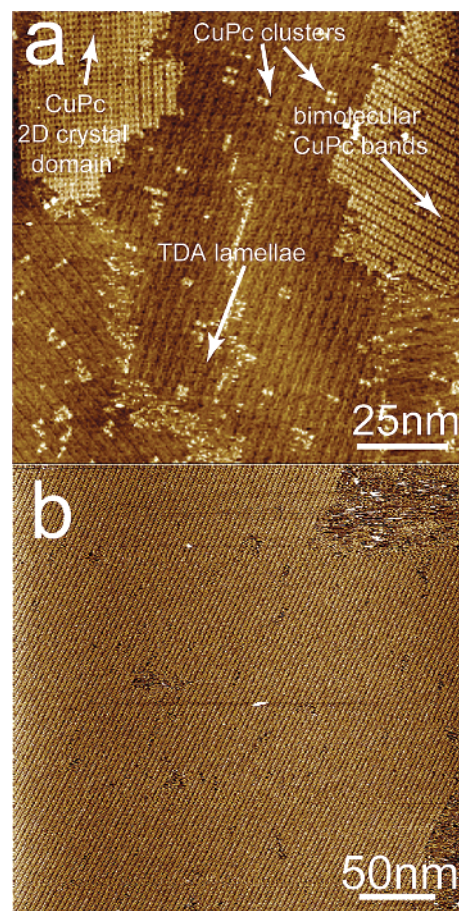


Figure 3. Comparison of assembling structure before (a) and after (b) thermal annealing. In (a), which is typical for a room temperature prepared sample, uncovered TDA lamellae, a CuPc 2D crystal domain, and bimolecular CuPc bands could be seen to coexist on the surface. For the sample after annealing, large areas of uniform bimolecular CuPc bands are commonly observed (b).

are considered to be caused also by the migration of CuPcs on the TDA monolayer during tip scanning.

As the CuPc:TDA ratio increases, bimolecular CuPc bands could be readily observed. As measured from the STM image, the repeating period of this assembling structure is consistent with the 3.37 ± 0.05 nm width of the TDA lamellae, which suggests the ordering of CuPc molecules is induced by the TDA lamellae. High-resolution STM observation (Figure 2a) reveals that the arrangement of CuPc in these bimolecular bands is the same as that in the 2D crystals: joggled together with each other, showing an intermolecular distance of 1.45 nm. There is an apparent dark trough between these bimolecular bands; the width of this trough is about 0.7 nm, larger than the 0.3–0.4 nm trough that separates the TDA lamellae.

A structural model of this bimolecular band structure has been proposed, as shown in Figure 2b. The bimolecular bands have never been observed in the adsorption of pure CuPc or CuPc with other alkane derivatives, such as alkyl halide and alcohol,⁶ and apparently should be attributed to the template effect of TDA. It was observed that when some of the CuPc molecules were removed by tip scanning, alkyl chains of TDA molecules could be clearly observed (Figure 2c). This could be direct evidence of the existence of TDA lamellae underneath CuPc bands.

To further prove the TDA lamellae template-induced CuPc band structure, two additional tests were also applied. One is applying a large voltage pulse to the tip to destroy the band

structure, and the other is decreasing the applied bias to 20 mV to move the CuPc molecules away from the tip. Both means can work with satisfactory reproducibility. The STM image in Figure 2d shows the TDA lamellae simultaneously with the CuPc bands, which can distinctly reveal the one-to-one relationship of the TDA lamellae to CuPc bands and strongly suggests a template-induced ordering of CuPc molecules.

The thermal stability of the observed CuPc bimolecular band structure was also tested by annealing. The size and uniformity of the domains containing bimolecular bands were apparently improved, and the existence of 2D crystallization of CuPc observed on room temperature prepared samples is almost completely eliminated. A comparison of the typical assembly structure before and after thermal annealing (Figure 3) clearly shows this tendency. This indicates that the template-induced bimolecular band structure is a thermodynamically stable state, even more stable than the 2D crystallization domains of CuPc.

From the STM observation it can be identified that the dark trough between CuPc bimolecular bands correspond to the alkyl ends in the TDA lamellae underneath. The orientation of CuPc molecules in the bands is also different (rotate about $26 \pm 2^\circ$ with respect to the lamella axis) from that in the dimer (parallel to the lamellar axis), which could suggest the CuPc molecule feels stronger intermolecular interactions in the CuPc bands than that in the dimers. In the TDA template-induced assembling of CuPc bands, the repulsion between the CuPc molecule and amino group appears to be compensated by attractive interaction between the CuPc molecules, whereas in the dimer structure the situation is different and CuPc molecules are in a relatively isolated state. This difference is currently attributed to the different strength of van der Waals attraction each CuPc molecule endures in the bimolecular band from that in the individual dimers, which is caused by different numbers of adjacent CuPc molecules in these structures. The mechanism

of this interaction is interesting and worthy to be explored. The immobilized individual CuPc monomers and dimers could provide potential candidates for the single molecule measurements and local molecular environment detection.¹¹

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Supporting Information Available: Large scale and high-resolution views of the assembling structures of TDA. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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