

# Selective Adsorption of Copper Phthalocyanine Atop Functionalized Organic Monolayers

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Received: December 31, 2002; In Final Form: July 29, 2003

We report the observation of site-selective adsorption of copper phthalocyanine (CuPc) atop organic surfaces. The organic surfaces consist of monolayers of various alkane derivatives (stearic acid, 1-octadecanol, and 1-iodooctadecane) adsorbed on the surface of highly oriented pyrolytic graphite (HOPG). Our scanning tunneling microscopy (STM) studies show that the alkane derivatives form templates, which can provide different adsorption sites for the CuPc. The observed selective adsorption behavior is attributed to a dominating preference of the CuPc for adsorption on the hydrocarbon-chain portions of the supporting layers. We also discuss the results of molecular mechanics simulations, which support the STM observations.

## Introduction

The adsorption and assembling of organic molecules at surfaces and interfaces has been the subject of extensive study for many years. Surface adsorption of organic species of all ranges have been characterized by STM and other techniques.<sup>1–5</sup> These investigations have advanced the understanding of the microscopic behavior of surface reactions, adsorption processes, and adsorbate structures, such as the binding site of individual molecules with respect to the substrate lattices, conformational states of individual molecules, and the surface molecular structures, as well as defects and domains that are present in ordered structures.

Over the past two decades marked advances in STM capabilities have enabled increasingly detailed studies of an ever-expanding variety of single molecules adsorbed on surfaces. Such single-molecule studies have predominantly involved inorganic or metallic substrates, mostly under UHV conditions.<sup>2</sup> However, little work has been done on the adsorption of single organic molecules on organic supports, a process that may be of general interest for the construction of molecular electronics or mechanical devices.

It is well-known that alkanes and alkane derivatives physisorb on HOPG as well-ordered 2-dimensional monolayers, as identified by different techniques such as STM and electron scattering.<sup>1,5–7</sup> Typically, alkane derivatives adsorb with their functional groups paired together on the surface of HOPG due to hydrogen bonding or dipolar interaction between functional groups. Given the wide range of functionalities with which alkanes can be derivatized, such monolayers can transform the surface of HOPG into an ideal template for investigating the possible site-dependent adsorption behavior of organic molecules. Compared with nanofabricated surface,<sup>8</sup> such alkane-derivative-modified surfaces are organic in nature rather than metallic or semiconducting, and could have expanded compositional flexibility. The relative polarity and the polar/unpolar area ratio could be modified readily by changing the functional group and the chain length of the alkane derivatives. In this work, using monolayers of stearic acid, 1-octadecanol, and 1-iodooctadecane as model systems, we investigated the adsorption

behavior of copper phthalocyanine on these monolayer-modified surfaces and site-selective adsorption was directly observed by STM. This provides direct evidence of a selective adsorption of organic molecules on an organic substrate.

## Experimental Section

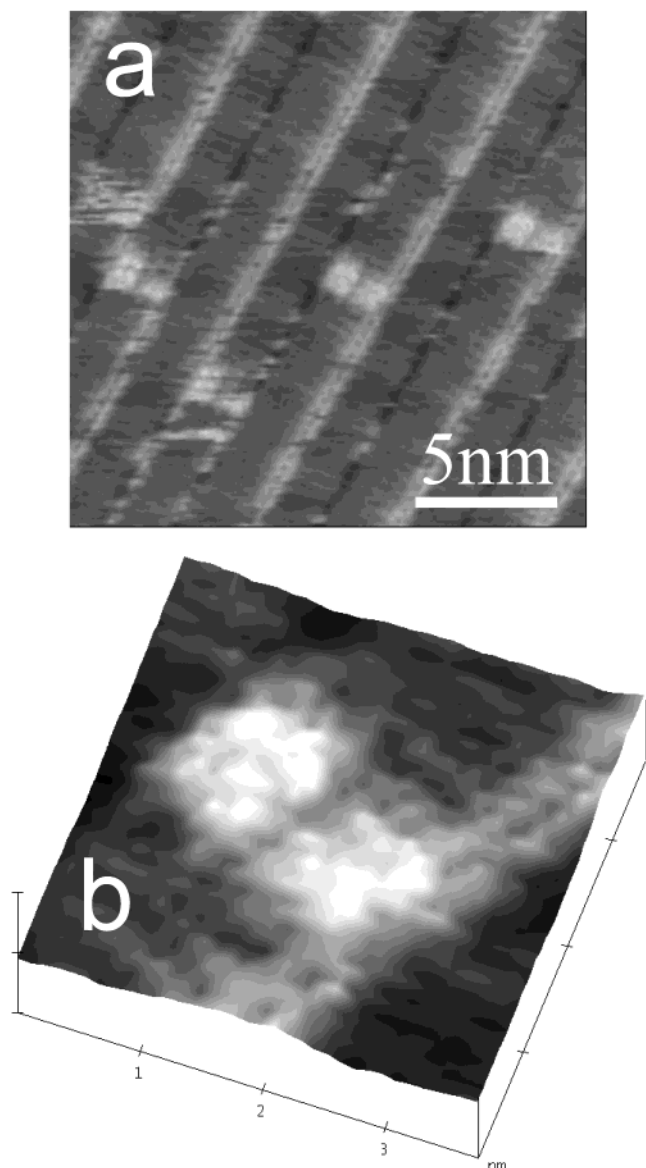
The organic molecules, copper phthalocyanine (CuPc), stearic acid, 1-octadecanol, and 1-iodooctadecane (C18I), were all purchased from Acros Co. and used as received. The samples were prepared by dissolving CuPc together with one of the alkane derivatives in toluene. Subsequently a droplet of the solution was deposited onto the surface of freshly cleaved HOPG. The difference of experimental conditions in this study from our previous report<sup>9,11,12</sup> is that the molar ratio of CuPc to the alkane derivatives is less than 1:100 in this work to prevent crystallization of CuPc, and the concentration of alkane derivatives is less than 1 mM. The STM experiments were carried out under ambient conditions on a Nanoscope IIIA SPM system (Digital Instruments, Santa Barbara, CA). The tip was mechanically formed Pt/Ir wires (90/10).

ESFF force field was used in the present work to simulate the adsorption of CuPc on alkane derivatives. The van der Waals interaction and electrostatic interaction are involved in the calculations. All potential parameters were adopted from the default values of ESFF provided by the Insight II program. Energy minimization and docking methods were used to obtain the molecular orientations and intermolecular interactions. The energy minimizations were carried out by using the Conjugate Gradient method with total energy gradient tolerance (RMS value) at 0.1 kcal/(mol·Å). The stable structures were obtained via optimization from several initial configurations. During energy minimizations the graphite surface was fixed and all adsorbed molecules were free to translate and rotate. The cutoff distances for van der Waals interaction and electrostatic interaction are 30 and 50 Å, respectively, which are far enough so that the interaction can be neglected. The models were built and minimized with use of Builder, Discover3, and Docking codes at the Insight II interface on a SGI workstation.

## Results and Discussion

When adsorbed onto the surface of HOPG from nonpolar organic solution, stearic acid and 1-octadecanol form lamellae

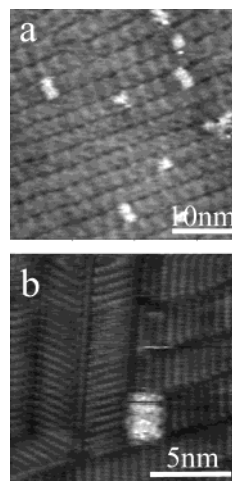
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**Figure 1.** (a) Isolated CuPc molecules adsorbed exclusively on the hydrocarbon-chain portion of 1-iodooctadecane lamellae; (b) high-resolution image of a pair of CuPc molecules.

structures based on hydrogen bonding.<sup>7</sup> As demonstrated in previous reports, stearic acid forms an interdigitated structure on the HOPG surface, in which carboxyl groups are located in the regions between the alkane lamellae.<sup>10</sup> In the case of 1-octadecanol, a herringbone structure can be observed when adsorbed onto the graphite surface, and the hydroxyl groups are located alternatively,<sup>7</sup> while for 1-iodooctadecane (C18I) molecules densely packed structures prevail in which the headgroups pair together with the carbon chains oriented parallel to the substrate surface and perpendicular to the lamellae boundaries. This head-to-head structure of C18I is considered to be associated with the dipolar interaction.

When a binary mixture of CuPc and C18I with a large excess of C18I is coadsorbed on the surface of HOPG under the above-mentioned sample preparation condition, the surface is covered with large regions of C18I, and a uniform assembly of CuPc and C18I has also been observed as demonstrated previously.<sup>11,12</sup> As this assembling structure is destroyed by STM scanning at low bias, the lamella of C18I merged together and there are isolated CuPc molecules observable on top of the C18I lamellae (Figure 1a,b). During the STM experiments, several  $100 \times 100$



**Figure 2.** (a) CuPc selectively adsorbed on the monolayer of stearic acid; (b) CuPc adsorb on the monolayer of 1-octadecanol.

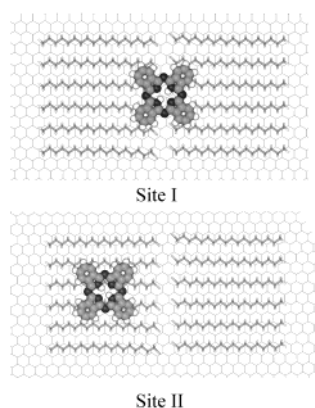
$\text{nm}^2$  areas were scanned, and about a hundred isolated CuPc molecules were observed. In the STM images, iodine atoms appear as bright spots. These isolated CuPc molecules and CuPc dimers are observed to be located exclusively on top of the hydrocarbon-chain portions of the supporting layers. In most cases the axis of the CuPc dimers is nearly parallel to the carbon chain of the C18I molecules. From the cross-sectional profile, the width of the CuPc molecule is measured to be 1.65 nm, and the height is 0.23 nm, in agreement with a planar adsorption configuration, with the molecular plane of CuPc parallel to the surface of HOPG.

Here the scanning of the STM tip at low bias is considered to simply supply the disturbing effect to break the CuPc molecules from assembly on the surface, and since low bias scanning was not necessary for the stearic acid/CuPc and 1-octadecanol/CuPc systems which will be discussed below, it is not considered to provide any activation energy to push the molecules into their adsorption sites, and the selective adsorption observed here is believed to be spontaneous.

When CuPc coadsorbs with stearic acid, both isolated and CuPc molecular dimers were detected on top of the stearic acid monolayer (Figure 2a). As observed in the experiments, these CuPc molecules all are located on top of the alkane part of stearic acid lamellae, again on top of hydrocarbon-chain portions of the supporting layers. As in the case of C18I, the CuPc dimers are oriented with the axis nearly parallel to the alkane chain of stearic acid. Figure 2b shows a CuPc pair located on top of the monolayer of 1-octadecanol. It could be seen that this CuPc pair orients parallel to the carbon chain of 1-octadecanol, and locates on the alkane part of the monolayer, rather than on top of the functional groups. Submolecular resolution images can be obtained on CuPc molecules in all of the above studies, and the observed 4-fold symmetry of CuPc is in accordance with the characteristic molecular structure of CuPc. Since the molar ratio of CuPc to alkane derivatives is kept less than 1:100, any crystallization effect of CuPc is substantially suppressed.

The above observation of the adsorption behavior of CuPc indicated that the alkane parts are more favorable locations for CuPc to adsorb than the functional groups. Because the polarity of the functional group is greater than that of the alkane parts, these results indicate that CuPc adsorbs selectively on the nonpolar part of the surface.

It was noticed that in most of the images the CuPc pairs seem to prefer to be adjacent to the headgroups. This could be the result of two possible causes. The first is that there may be some



**Figure 3.** Stable adsorption configurations represent local free energy minima obtained by molecular mechanics simulation. Site I in which CuPc adsorbed on the top of the trough linked by head-to-head functional groups, and site II in which CuPc adsorbed on the alkyl moiety. The alkane derivative presented here is C18I.

attractive interaction due to dipolar functional groups. Second, since the length of a CuPc molecular pair is 2.6 to 2.7 nm, which approximately equals the 2.6-nm width of hydrocarbon-chain portions of the lamellae, therefore the location of the CuPc dimers adjacent to the headgroups may be caused simply by geometrical commensuration. At present we attribute the stabilization mechanism to the second possibility though the first possibility could not be ruled out.

For physisorption systems, molecular mechanics is useful and practical to explore the intermolecular and substrate–adsorbate interactions.<sup>13</sup> For the present coadsorption systems, the experimental results illustrate that the alkyl derivative monolayer adsorbed on graphite preferentially and CuPc molecules adsorb with noticeable selectivity. The alkyl derivative monolayer is an inert substrate compared with graphite surface. Herein free energy minimization was carried out by using the ESFF force field to achieve the favored adsorption states. There are mainly two possible adsorption sites considered, i.e., site I in which CuPc adsorbs on the top of the trough linked by head-to-head functional groups, and site II in which CuPc adsorbs on the alkyl moiety. In the initial structures the CuPc molecule is located on functional groups and different parts of alkyl chains, respectively, and is free to translate during the energy minimization. Local minima atop both I and II were achieved. Figure 3 illustrates the minimized adsorption states of CuPc on the adlayer of C18I as an example.

The calculated results suggest that the system potentials at site I are higher than those at site II by about 21 kJ/mol for the three alkane derivatives used in this study. This comparison indicates that site II is a free-energy-favored adsorption state, which is consistent with the STM observation. It should be acknowledged that, in general, there exist two complementary factors for  $\pi$ – $\pi$  interaction. One is attractive van der Waals interaction while the other is repulsive electrostatic interaction.<sup>14</sup> In the present work, the main reason for the emergence of selective adsorption can also be associated with the following two factors. The trough linked by head-to-head functional groups is about 3 Å in width and the number of atoms per area in the trough is less than at other sites of the organic monolayer. Therefore, van der Waals interaction between adsorbed CuPc and underlying organic substrate could be reduced when CuPc adsorbs on the top of the trough. In addition, the trough is linked by groups with high electron density and large polarity, and the electrostatic repulsion between the electron concentrated  $\pi$  ring of CuPc and functional groups will be stronger than that

between CuPc and alkyl. These two factors could induce the site-selective adsorption behavior of CuPc on the alkyl moiety to achieve the free-energy-favored adsorption state.

According to the simulation results, for single molecule adsorption, the optimum structure is that with CuPc molecule in the center of the alkyl chain. As discussed before, based on STM observation CuPc molecules seem to prefer to be adjacent to the headgroups and we attribute this simply to geometrical commensuration. In fact, in the STM experiments it is clear that most CuPc molecules are observed to exist as dimers and scan lines always can be found near an isolated molecule, which indicates one of the molecules in the dimer has been disrupted by the tip. Therefore, the adsorption configuration of isolated single CuPc molecule adjacent headgroups may not present an energy minimum, as in the optimized conformation in Figure 3. One thing that should also be noticed is that the transition barrier along an alkyl chain is very small, and the disturbance of tip scan may cause lateral movement of a molecule until it meets a barrier such as the headgroups, which has a higher energy barrier to hinder its migration. In this work the molecular mechanics simulation is carried out to qualitatively illustrate the selective adsorption, but only one CuPc molecule is considered in the simulation. The simulation of side-by-side packing of two CuPc molecules along the alkyl chain has not been carried out, which may involve intermolecular interactions between CuPc molecules.

In our previous work, we have reported the different assembling behavior of phthalocyanine with alkane derivatives introduced by different substitution and functional groups.<sup>11,12</sup> The variation of assembling behavior is attributed to the alteration of intermolecular interactions of both species. As the strength of the intermolecular interaction increases, the assembling behavior of these two-component systems changes from uniform single-molecular-array-like assembly to phase separation. The results presented in this work dealt with a different regime where no assembling of CuPc molecules is present. The individually adsorbed CuPc molecules adsorb exclusively on the hydrocarbon-chain portion of lamellae of alkane derivatives. In addition, the comparison between the single molecule adsorption results of this study and the array-like assemblies in the previous work<sup>11,12</sup> for the binary mixture of the same CuPc and alkane derivatives could be indicative of the crystallization effect of CuPc in obtaining the array-like assemblies.

In summary, selective adsorption behavior of CuPc on different parts of a monolayer of alkane derivatives, C18I, stearic acid, and 1-octadecanol was observed by STM. Molecular mechanics simulations on these systems provide results consistent with the experiments. On the basis of this result it could be conceived that other organic molecules could display similar site-selectivity in the adsorption process on the alkane derivative modified HOPG surface.

**Acknowledgment.** The authors are grateful for the financial support from the National Natural Science Foundation (Grant Nos. G20073053, 20303023), the National Key Project on Basic Research (Grant No. G2000077501), and the Outstanding Innovation Group Foundation (Grant No. 20121301). The authors are also indebted to the reviewer of the manuscript for many constructive comments and generous effort for improving the manuscript.

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