

Studies of CuPc Adsorption on Graphite Surface and Alkane Adlayer

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Molecular mechanics simulation was employed to study the adsorption of copper phthalocyanine (CuPc) on HOPG and alkane adlayer. It is shown that CuPc and C₃₄H₇₀ have similar adsorption energies on graphite surface. Attributed to the strong molecule–molecule interaction and the large lateral diffusion barrier, the two-dimensional monolayer of C₃₄H₇₀ is preferentially formed, which is consistent with STM observations. Due to the lateral corrugation barrier of CuPc on alkane and the roughness of alkane monolayer, the diffusion mobility of CuPc on alkane layer was decreased and the stability of two-dimensional monolayers of CuPc was improved.

Introduction

Great efforts are being made to construct microstructures and molecular devices at the atomic level using techniques such as molecular self-assembly, molecular beam epitaxy, supermolecular science, etc.^{1,2} To realize the aims, it is important to understand the behavior of adsorbates at interface and the mechanisms leading to well-ordered overlayers. Scanning tunneling microscopy (STM) has been a powerful tool to explore molecule adsorption at very localized scales with atomic resolution. In past years the imaging of organic molecules on solid surfaces with STM has been characterized by remarkable progress, which has advanced the knowledge on the microscopic behavior of molecular adsorption processes and adsorbate structures.^{3–5}

For their potential use in electronics and optoelectronic application, planar π -stacking organic molecules on various substrates such as highly oriented pyrolytic graphite (HOPG), MoS₂, Si(111), Au(100), Cu(111), etc., have been extensively studied by STM and other surface analysis techniques. Copper phthalocyanine is one archetypal molecule belonging to this group. In earlier works, the highly resolved images of CuPc on Cu(100) was obtained using UHV STM.⁶ On Si(100), the shape of CuPc molecule and three adsorption configurations were observed by UHV STM.⁷ STM studies of CuPc monolayer prepared by molecular beam epitaxy have shown that on HOPG and MoS₂,⁸ the close-packed two-dimensional array formed with quadratic unit cell. All these experiments were done in ultrahigh vacuum conditions, in which the molecular motion induced thermally or by STM tip was overcome; whereas under ambient conditions, CuPc adsorbed directly on graphite cannot be imaged by STM. Studies⁹ of alkylated CuPc have shown that the molecules can be satisfactorily immobilized on graphite surface. In recent experiments,¹⁰ a stable nanoscaled domain of CuPc was observed by STM in ambient through mixing CuPc with the long chain alkane C₃₄H₇₀. It was illustrated that the CuPc domain adsorbed directly on the top of the C₃₄H₇₀ molecular layer. It is worth understanding the factors that affect the stability and construction of molecular microstructures.

Monolayer stability of self-assembled organic species on solid surfaces is an interplay of molecule–molecule and molecule–substrate interactions. In the case of organic molecular layer

adsorbed on graphite, the interactions are typically van der Waals force and electrostatic force. Within the basal plane of substrate, the stability of the adsorbed molecules is also affected by the thermal motion of molecules and the disturbances of STM tip in the scanning process. The molecule–substrate interactions can be adjusted by various approaches, such as substrate properties¹¹ and experimental conditions. A significant amount of efforts have been put into improving substrate and preparation conditions to achieve optimal film stability. Overall, the interactions are adjusted in order to prevent the motion and diffusion.

So far, few theoretical work has been reported to analyze detailedly the adsorption mechanism of CuPc on different substrates and the effects on the stability of two-dimensional monolayer. In this work, molecular mechanics simulation of CuPc adsorbed on HOPG and alkane layer was performed with MSI InsightII program. The adsorption barrier on different substrates and different sites was obtained. Comparing STM observation, the effect of the lateral corrugation barriers on the stability of two-dimensional monolayer was discussed.

Method

For sufficiently large systems and physisorption processes, molecular mechanics method (MM) is efficient and practical. Herein the adsorption of CuPc and C₃₄H₇₀ was studied by MM. The ESFF force field developed for organic and organometallic compounds was used to simulate the CuPc adsorption configuration, whereas the graphite surface was included as stationary internal potential. As expressed by eq 1, the potential energy for the adsorbate–substrate system is given by

$$E = \sum_b D_b [1 - e^{(-\alpha(r_b - r_b^0))}] + \sum_a \frac{2K_a}{n^2} (1 - \cos(n\theta_a)) + 2K_a^{(-\beta(r_{13} - \rho_a))} + \sum_\tau D_\tau \left(\frac{\sin^2 \theta_1 \sin^2 \theta_2}{\sin^2 \theta_1^0 \sin^2 \theta_2^0} + \text{sign} \frac{\sin^n \theta_1 \sin^2 \theta_2}{\sin^n \theta_1^0 \sin^n \theta_2^0} \cos[n\tau] \right) + \sum_o D_o \phi^2 + \sum_{nb} \left(\frac{A_i B_j + A_j B_i}{r_{nb}^9} - 3 \frac{B_i B_j}{r_{nb}^9} \right) + \sum_{nb} \frac{q_i q_j}{r_{nb}} \quad (1)$$

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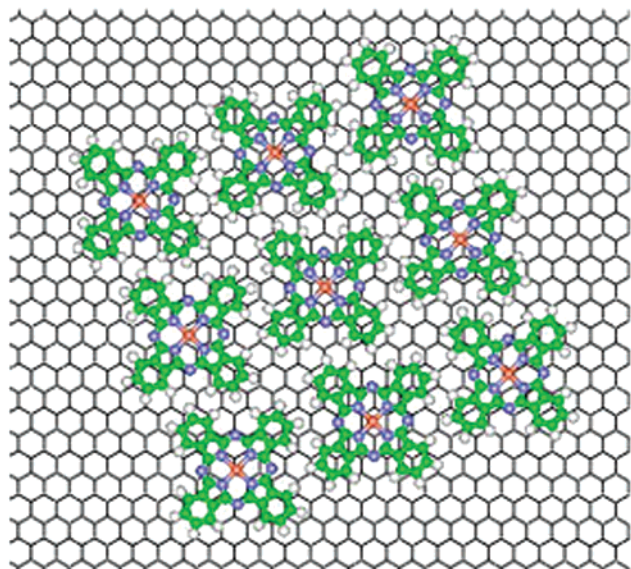


Figure 1. The minimized structure of CuPc assembled on graphite surface by ESFF calculations.

The first three terms describe the bonding valent interactions for a square planar ligand–metal complex, and the last terms are nonbond interactions, i.e., van der Waals interactions (Lennard–Jones potential) and Coulombic interactions. The potential parameters of ESFF force field were adopted from the default given by InsightII program.

The models of CuPc on graphite and on alkane layer were built for energy minimization. The adsorption orientations of CuPc on different sites were considered. The monolayer of $C_{34}H_{70}$ including 10 molecules in a lamellae was modeled for analysis of the alkane adsorption, and the $C_{18}H_{38}$ monolayer composed of 20 molecules in two lamellae was used as alkane substrate on which CuPc molecules adsorbed. The energy minimizations were carried out by a combination of the steepest descent, conjugated gradient, and Broyden–Fletcher–Goldfarb–Shanno methods until the root-mean-square derivative was less than $0.01 \text{ kcal mol}^{-1} \text{ \AA}^{-1}$. The graphite was fixed during energy minimizations. All structures were built and optimized with Builder and Discover3 program on SGI workstation at InsightII interface.¹²

Results and Discussions

1. CuPc on HOPG. The stable adsorption configurations of single CuPc molecule on graphite on different sites and with

different orientations were obtained by energy minimization. It was found that the adsorption energies (i.e., molecule–substrate interactions, E_{ad}) for CuPc molecule in these configurations are the same, about -61.40 kcal/mol , and the vdW force is the key force between the molecule and the substrate, much stronger than the electrostatic attractions. The calculated results mean that CuPc molecules on these sites show similar adsorption barriers (defined as $-E_{ad}$) and has no preferential adsorption configuration on graphite surface. It implies that the lateral corrugation barrier of CuPc on graphite surface is smaller.

Figure 1 presents the minimized structure of the assembly of nine CuPc molecules on HOPG, which is similar to the monolayer structure of CuPc on HOPG by MBE method.⁸ It is shown that CuPc molecules are closely packed with quadratic unit cell and lie on graphite with the molecular plane parallel to the substrate. To minimize the intralayer vdW potential, CuPc rotates about an axis normal to the substrate such that the phenyl groups of one molecule fit into the hollow site of an adjacent molecule. The distance of neighboring CuPc molecules is 1.40 nm , in agreement with STM results (1.37 nm)^{8,10} and CuPc bulk parameter (1.46 nm).¹³

To investigate the CuPc–CuPc intermolecular force, two CuPc molecules were modeled and minimized. Two packing patterns (parallel pattern and stacking pattern, presented in Figure 2) were considered. The former is concerned with growth of thin film and the later occurs in bulk structure. The interaction of the parallel packing is -2.03 kcal/mol (vdW -2.73 , ele 0.7), and -24.64 kcal/mol (vdW -32.54 , ele 7.75) for stacking pattern. It is obvious that the interaction between stacking CuPc molecules is much weaker than the graphite attraction. Thus the monolayer of CuPc on HOPG is preferential to multilayer growth.

2. $C_{34}H_{70}$ on HOPG. Similar to our previous studies on long chain alkane adsorbed on graphite surface, the single molecule and close packing of $C_{34}H_{70}$ were constructed and optimized using ESFF force field. Herein, only the configuration of the carbon skeleton parallel to graphite surface was studied on the basis of the STM observations¹⁴ and the theoretical studies.^{15,16} The minimized structure of the assembly including 10 $C_{34}H_{70}$ molecules is given in Figure 3. The distance between $C_{34}H_{70}$ is 0.45 nm with the methylene hydrogens located above the hole of the graphite hexagon. The interaction energy between neighboring $C_{34}H_{70}$ molecules is -19.05 kcal/mol . The adsorption energy for $C_{34}H_{70}$ molecule is -61.43 kcal/mol . The adsorption energy and the unit cell parameter for $C_{34}H_{70}$ and CuPc are summarized in Table 1. It is seen that $C_{34}H_{70}$ and

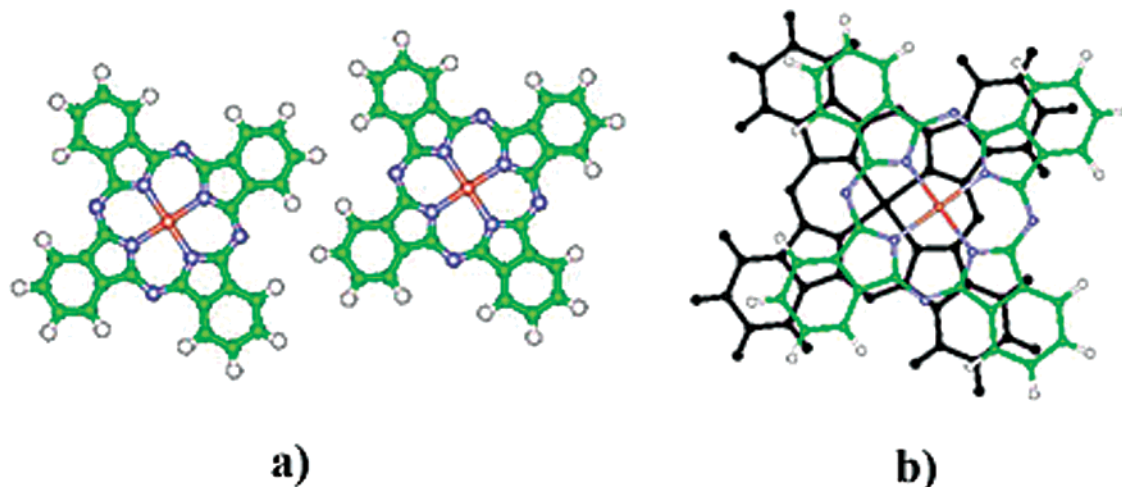


Figure 2. Optimized packing structures of two CuPc molecules. (a) parallel pattern; (b) stacking pattern.

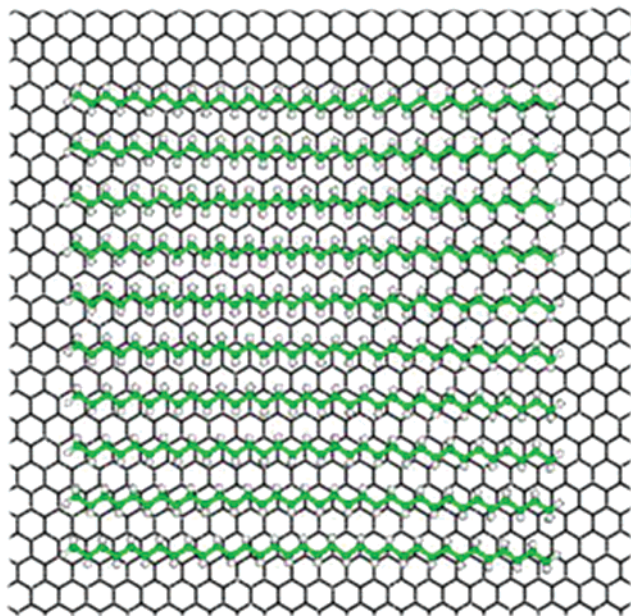


Figure 3. Assembly structure of long chain alkane $C_{34}H_{70}$ obtained by ESFF calculations.

TABLE 1: The Adsorption Energy (E_{ad}) and Two-Dimensional Crystallization Energy (E_{2D}) for CuPc and $C_{34}H_{70}$ on HOPG (unit: kcal/mol)

item	CuPc on HOPG	$C_{34}H_{70}$ on HOPG
E_{ad}	-61.40	-61.43
E_{ad-vdW}	-61.42	-61.25
$E_{ad-coulombic}$	-0.03	-0.02
S^a	1.96	1.97
$E_{ad/s}^b$	-31.33	-31.18
E_{2D}	-8.12	-38.10

^a S , the area of unit cell of CuPc and $C_{34}H_{70}$ (unit: nm^2). ^b $E_{ad/s}$ is the energy density, $E_{ad/s} = E_{ad}/S$.

CuPc have similar adsorption barriers and the adsorption energy densities are nearly identical because of the similar size of the unit cell areas.

3. CuPc on Alkane Adlayer. STM experiments indicated that the adsorption of the mixture of $C_{34}H_{70}$ and CuPc was not coadsorption, $C_{34}H_{70}$ monolayer on graphite surface was formed preferentially and CuPc domains adsorbed directly on alkane layer. Our previous simulation of CuPc adsorbed on $C_{34}H_{70}$ adlayer using ESFF force field method¹⁰ has shown that CuPc adsorption configurations have similar adsorption barrier about 45 kcal/mol, except for 5 kcal/mol smaller for CuPc located at the trough between two adjacent alkane lamellae. The lateral corrugation barrier means that CuPc adsorbed on alkane buffer would have no preferential adsorption orientations. The simulation results are consistent with the STM observations, which show that the uniform domain structures has no modulation effect associated with the underlying alkane layer and the adsorbed CuPc molecules display little evidence for preferential adsorption orientations relative to the underlying alkanes. Meantime, it is also noted that some of CuPc domain boundaries coincide with alkane lamellae trough, which is supportive to the simulation results that the adsorption barrier at trough sites is relatively lower and the adsorption interaction is somewhat weaker than other sites. On the other hand, although the alkane adlayer functions as a weak-binding substrate and produces little effect on two-dimensional assembling structure of CuPc, the lateral corrugation barrier is higher than thermal motion and enough to overcome the thermal diffusion.

4. Stability of Two-Dimensional Monolayer. The adsorption process and the stability of the monolayer are affected by thermodynamic and kinetic factors. The molecule–substrate interaction (the adsorption energy), the lateral molecule–molecule interaction, as well as the lateral diffusion play important roles in the formation and stability of the two-dimensional monolayer. On the basis of the above calculations on adsorption energies, it is difficult to determine the adsorption preference of any species of the mixture.

In the adsorption process of CuPc and $C_{34}H_{70}$ mixture, the formation of a two-dimensional monolayer is related to the nucleation procedure, which is controlled by not only molecule–substrate interactions but also molecule–molecule interactions (i.e., two-dimensional crystallization energy, E_{2D}). Though these two species display similar adsorption barrier on HOPG indicated in the above calculated results, the lateral molecule–molecule interactions of CuPc and $C_{34}H_{70}$ are very different. The lateral molecule–molecule interaction is mainly van der Waals interaction and increases with an increase in their contact surface area. In the ordered two-dimensional structures, the linear hydrocarbons $C_{34}H_{70}$ on HOPG have a lot larger contact surface area between them than do the CuPc's on HOPG. For the monolayer of CuPc on HOPG, the calculated two-dimensional crystallization energy is -8.12 kcal/mol (Table 1), much weaker than that of $C_{34}H_{70}$ on HOPG which is -38.10 kcal/mol. The stronger molecule–molecule interactions of $C_{34}H_{70}$ prompt the nucleation and improve the stability of a two-dimensional crystal. While for CuPc, due to the weak molecule–molecule interaction, the molecules escape easily from two-dimensional crystal in the nucleation procedure and the two-dimensional crystal is dynamically difficult to form, especially under the perturbation of the tip and thermal motion.

Furthermore, the lateral diffusion is very different for these two species. As shown in above sections, CuPc has a similar adsorption barrier at different sites. The molecular mechanics studies have shown that the stable adsorption configuration of $C_{34}H_{70}$ on HOPG is that alkane molecules are in good commensuration with underlying graphite lattice. It requests that long chain alkanes adsorb on HOPG with the methylene hydrogens located above the hollow site of the graphite hexagon, otherwise the adsorption stability is decreased on other sites and orientations. It implies that CuPc has a small diffusion barrier and $C_{34}H_{70}$ has a high diffusion barrier on graphite surface. Thus the lateral diffusion of CuPc on HOPG occurs easier than $C_{34}H_{70}$. As the result, combined the weak molecule–molecule interaction and the small diffusion barrier, the formation of the two-dimensional structure of CuPc is more difficult than that of $C_{34}H_{70}$, whereas the formation of the two-dimensional structure of $C_{34}H_{70}$ is preferential and is more stable to be observed by STM.

The stabilities of the two-dimensional structure of CuPc on different substrates, i.e., on HOPG and on $C_{34}H_{70}$ layer, are related with the same factors. It is known that graphite is a kind of inert substrate and interacts with the organic adsorbates through physisorption, which is made up of vdW and Coulombic interactions. It is seen from CuPc adsorption on alkane layer that, as a kind of organic substrate, the alkane layer is a weaker binding substrate comparing with graphite and strongly binding metal substrates. The adsorption barrier for CuPc on alkane adlayer is 45 kcal/mol or and 40 kcal/mol,¹⁰ much smaller than that on graphite surface (61.40 kcal/mol). The lateral molecule–molecule interaction between CuPc on alkane layer is dominant and the CuPc two-dimensional structure is similar to the bulk structure due to the weaker binding to the alkane substrate.

It is noted that the lateral diffusion of CuPc on alkane is different from that on graphite surface. For CuPc on alkane layer, the adsorption barrier at trough sites is relatively lower by about 5 kcal/mol than at other sites as mentioned in the previous section. On the other hand, the lateral corrugation barrier of CuPc on graphite is much smaller, which is less than 0.2 kcal/mol. Like organic layers growing on top of alkanethiol layer,¹⁷ the corrugation of the substrate surface affects the formation of CuPc monolayer. Comparing with the basal plane of graphite, the substrate surface of alkane layer is more corrugated, which decreases the molecular motion induced by tip or thermal diffusion. As a result, the immobility of CuPc molecules on alkane layer is improved due to the lateral diffusion barrier and the roughness of the substrate, and the two-dimensional structures of CuPc are stabilized and can be easily observed by STM.

Summary

The adsorption of CuPc on graphite surface and on long chain alkane layer was investigated using molecular mechanics simulations. The calculations by ESFF force field show that for CuPc adsorbed on graphite, the weaker molecule–molecule interaction and the small diffusion barrier decrease the stability of CuPc two-dimensional structure, thus the adsorption of C₃₄H₇₀ is preferential. Due to the roughness of alkane monolayer and lateral diffusion barrier of CuPc on alkane layer, the diffusion mobility of CuPc was decreased and the stability of CuPc two-dimensional monolayer was improved. The calculations are consistent with STM observations.

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