

Self-Assembly and Immobilization of Metallophthalocyanines by Alkyl Substituents Observed with Scanning Tunneling Microscopy

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Received: September 30, 1999; In Final Form: January 20, 2000

Using CuPcOC₈ and ZnPcOC₈ as examples, we have demonstrated that metal phthalocyanines with covalently attached long alkyl chains can be immobilized at the interface of the organic solution and the basal plane of HOPG. Highly resolved images of the molecules can be obtained in a range of bias voltages. The high stability and close-packed assembly are attributed to the van der Waals interaction between the alkyl chains and the graphite substrate, which substantially increased the desorption barrier of the combined molecule. In addition, it is illustrated that the desorption barrier is further enhanced by the 2-D crystallization of alkane chains. It is hoped that this method could provide a complementary approach to prepare an ordered two-dimensional array of molecular films, and facilitate the STM studies of fine molecular structures.

I. Introduction

Scanning tunneling microscopy (STM) has emerged as a powerful tool to investigate organic molecules adsorbed on conductive solid substrates with atomic scale resolution.^{1–3} One particularly appealing substrate is the basal plane of highly oriented pyrolytic graphite (HOPG) because it is chemically inert and easy to obtain large-scale atomically flat terraces. In addition, in contrast to the strong interaction between the adsorbates and metal substrate, physisorbed molecular monolayers on graphite provide an opportunity to image the molecules with a minimum of substrate perturbation.^{1,4} This provides a direct approach to study the molecular orbital properties and its polarizability, which is a prerequisite for the understanding of the origin of STM contrast.

A major obstacle in the STM studies of organic molecules on graphite is the thermally activated diffusional motion of the molecules on inert substrate at room temperature. This thermal effect could sometimes tremendously deteriorate STM resolutions. Different approaches have been successfully demonstrated for a wide range of specimens, such as reduced temperature and ultrahigh vacuum conditions,^{3,5} electrochemical control,⁶ and matrix molecule coadsorption method.^{7,8} Immobilization involving chemical processes, such as establishing chemical bonding between adsorbate and substrate (such as thiols on noble metals), are also very attractive in this field. These practices form an important front of surface functionalization. One may notice that the main goal of these endeavors would be to develop methods of molecular immobilization for generalized sample systems (i.e., increase the desorption barrier of the molecules of interest) as well as experimental conditions while keeping the properties of molecular species intact. It is shown that chemically attaching the molecules with specific functional groups could directly control their interaction with the substrate and could be a feasible way to immobilize small adsorbates on substrate.⁹ For the basal plane of graphite, it has long been proposed that long alkyl substituents could favor the adsorption

stability of organic molecules at the solution–graphite interface.^{10,11} For example, the nCB's monolayer on graphite surface exhibited greater immobility with the increasing of the alkyl chain length.^{2,11} Another important feature of the aliphatic chain is that it is readily differentiated from other parts of the molecules, such as aromatic rings, hybrid, and halogen-atom-containing groups,³ in the STM images. Therefore, alkylating the object molecules with suitable alkyl substituents could be envisioned as useful to facilitate the immobilization of the molecules on inert surfaces such as graphite, and has little disruption to the electronic properties of the object molecules.

In this report, we present the observation that metal phthalocyanines could be stabilized and dispersed on the basal plane of graphite by using linear alkyl substituents as molecule anchors. It is shown that a large area of uniformly distributed molecular layer can be reproducibly obtained, with two distinct symmetries, 4-fold and close packing, indicating that alkane connectors have certain rigidity as well as flexibility. Highly resolved images of octa-substituted phthalocyanines can be obtained in a range of bias voltages, as the molecules are fixed by the anchors of alkyl chains. The physical mechanism of the immobilization is discussed by considering the desorption barrier for the combined molecular system, as well as the effects of 2D crystallization of the surrounding alkyl chains. This method is deemed as applicable to other molecular systems, especially planar molecules such as porphyrins, PTCDA, etc.

II. Experiment

Copper(II) and Zinc(II) 2,3,9,10,16,17,23,24-octakis(octyloxy)-29H,31H- phthalocyanine (purity ~95%), denoted CuPcOC₈ and ZnPcOC₈, were obtained from Aldrich and used without further purification. The samples were dissolved in phenyloctane (HPLC grade, Aldrich) or toluene (HPLC grade, Aldrich) with a concentration of less than one percent. A droplet of the solution was deposited onto a freshly cleaved surface of HOPG (quality ZYB, Digital Instruments). The substrate was heated to 60 °C for about 5 min and cooled slowly to room temperature.

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The experiment was performed on Nanoscope IIIa SPM (Digital Instruments, Santa Barbara, CA) at room temperature in ambient conditions. STM tips were mechanically formed PtIr wire (90/10).

All the STM images were recorded using the constant current mode of operation. The specific tunneling conditions were given in the figure captions.

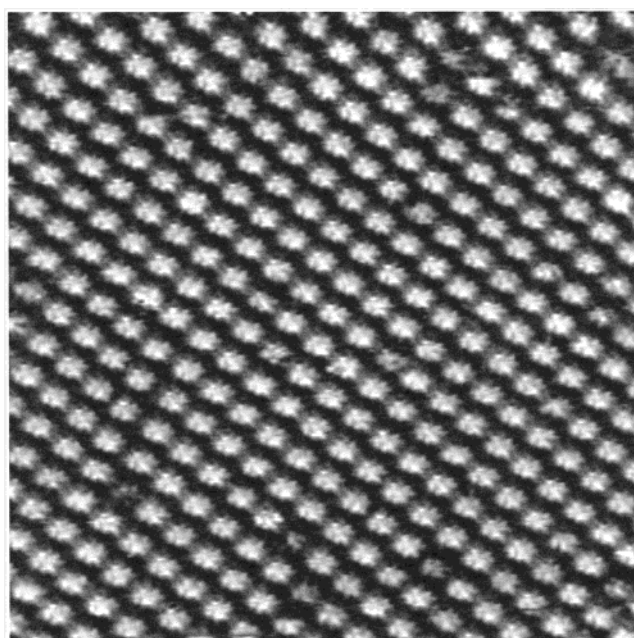
The preliminary calculation of the electronic densities of molecular orbitals (MO) was calculated with ZINDO/1 method by Hyperchem program. The desorption energy of the alkane molecules in single and assembled state was obtained with Insight II software on a SGI workstation.

III. Result and Discussion

The molecular structure of MPcOC_8 ($M = \text{Cu(II)}, \text{Zn(II)}$) is characterized by a flat aromatic core surrounded by eight flexible hydrocarbon chains. Presented in Figure 1 is a large scale STM image of CuPcOC_8 molecules adsorbed on HOPG surface. It is seen that the CuPcOC_8 molecules, appearing as bright spots with 4-fold symmetry, form a well-ordered two-dimensional array. Two kinds of packing arrangement with nearly quadratic and hexagonal symmetries were observed coexisting in the monolayer. The distances between the centers of the neighboring bright spots in the two arrangements are nearly equal. Unit cell data are summarized in Table 1. Although molecular defects were sometimes observed in the monolayer, the formed two-dimensional network could be reproducibly observed in large areas, indicating a high stability of this self-assembly configuration.

Figure 2, parts a and b, are high-resolution images of CuPcOC_8 and ZnPcOC_8 , respectively, where the submolecular structure of individual molecules is clearly resolved. It is noticed that the core of CuPcOC_8 molecule appears as a bright four-lobed "flower", with a noticeable central depression inside and surrounded by obscure zigzag lines. The diagonal width of the central bright moieties is about $1.6 \text{ nm} \pm 0.1 \text{ nm}$, which is consistent with the diameter of 1.7 nm estimated for the octahydroxyl-substituted phthalocyanine.¹² Figure 3, parts a and b give the calculated electron density contour of HOMO and LUMO at 1 \AA above the molecular plane for CuPcOC_8 . Comparing the shape and diameter between the observed images and the theoretical calculations, we attribute the 4-fold symmetrical bright moieties as the conjugated phthalocyanine rings, while the surrounding zigzag lines interconnecting the bright spots correspond to the long alkyl substituents.


Both electronic and topographic structures should be considered in analyzing the observed contrast for organic molecules by STM. There are a number of theoretical approaches dedicated to the contrast mechanisms. The electron-scattering-quantum-chemistry (ESQC) methodology provides a venue to obtain electronic characteristics of the surface-bound species,¹³ which is an improvement of simple molecular orbital simulations. It is also worth pointing out that the simulated contrast of adsorbate may be related not only to the wave function of the tip (tip state), but also to the electron affinity of the tip atom (which could be related to the local polarization).^{13,14} Therefore, different contrast may appear as the result of the uncertainty of tip atoms. Furthermore, as being extensively studied, the topographic effects,¹⁵ the polarizability of the functional group,¹⁶ as well as the overlapping between the electronic states of tip and sample¹³ also need to be considered for a full understanding of the tunneling process for organic molecules adsorbed on surface. In the current study, the contrast for the alkane regions is predominantly due to the topographic structure of the



$M = \text{Cu (II)}, \text{Zn (II)}$

Figure 1. STM image of self-assembled monolayer of CuPcOC_8 on graphite surface. Scanning area is $40.6 \text{ nm} \times 40.6 \text{ nm}$. The STM imaging condition is 262 pA , -723 mV . (inset) Molecular structure of MPcOC_8 ($M = \text{Cu}, \text{Zn}$).

TABLE 1: Unit Cell Data of the Quadratic and Hexagonal Arrangement of MPcOC_8 ($M = \text{Cu}, \text{Zn}$)

	quadratic	hexagonal
a	$2.6 \text{ nm} \pm 0.1 \text{ nm}$	$2.6 \text{ nm} \pm 0.1 \text{ nm}$
b	$2.6 \text{ nm} \pm 0.1 \text{ nm}$	$2.7 \text{ nm} \pm 0.1 \text{ nm}$
β	$90^\circ \pm 5^\circ$	$65^\circ \pm 5^\circ$

molecule,¹⁵ i.e., the protruded positions of hydrogen atoms, which are positioned higher than the Pc conjugate ring as revealed in Figure 3d. On the other hand, the observed higher contrast of the central region is attributed to the electronic structures of phthalocyanines. Given the complexity of the interaction between tip and adsorbate, adsorbate and substrate,

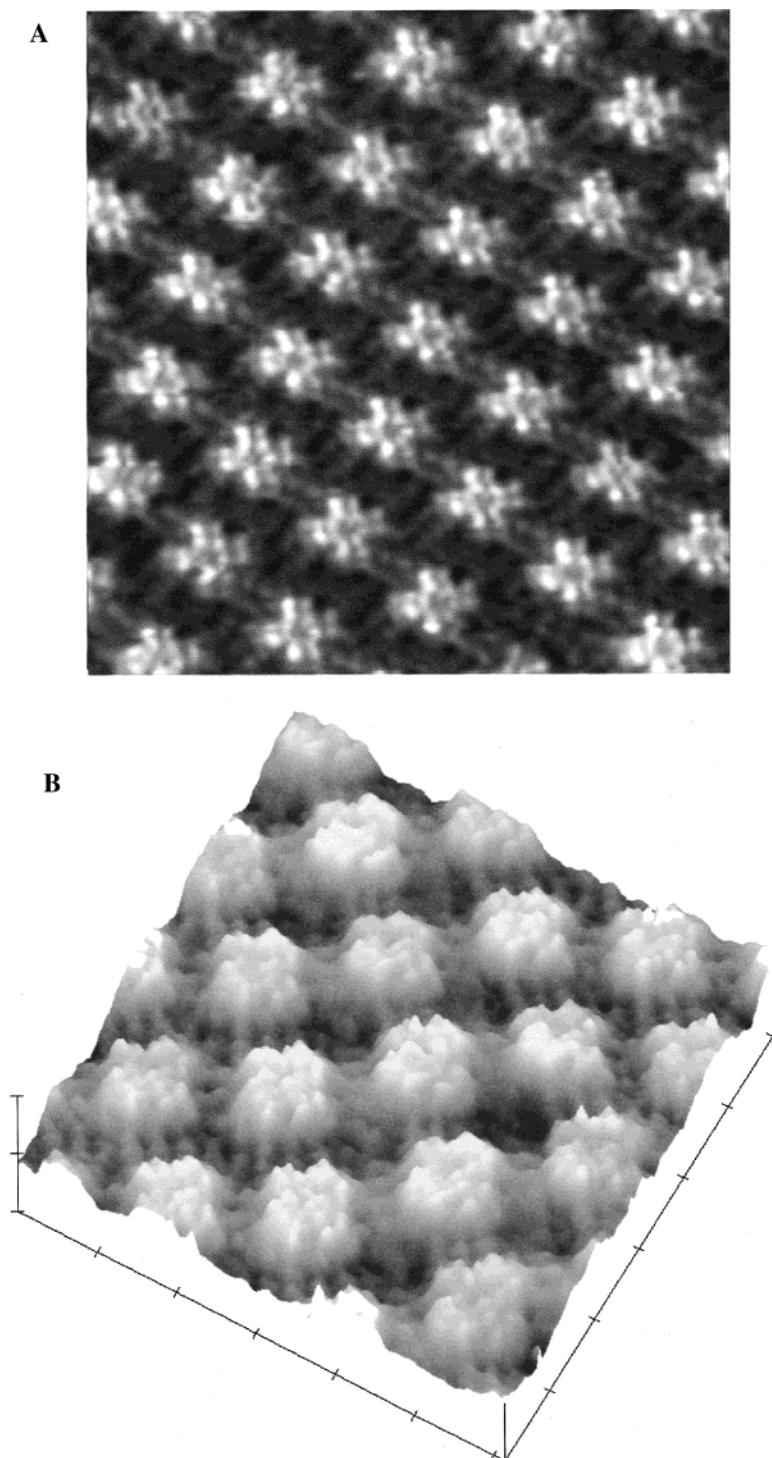


Figure 2. (a) A higher resolution STM image of CuPcOC₈ showing the 4-fold symmetry of each molecule. Scanning area is 14.6 nm × 14.6 nm. The imaging condition is 398 pA, -648 mV. (b) STM image of ZnPcOC₈ showing the interdigitating alkyl chains between aromatic rings. Scanning area is 13.2 nm × 13.2 nm. The imaging condition is 405 pA, -797 mV.

accumulation of experimental evidence is essential to the development of theoretical models.

Detailed examination of Figure 2 reveals that the alkyl chains of the adjacent molecules interdigitate. This is in contrast to the disordered configuration of the alkyl chains in the discotic mesophase of MPcOC₈, and also explains the reason the intermolecular spacing in this two-dimensional crystallization is significantly shorter than the intercolumnar spacing in discotic mesophase.¹² The highly ordered arrangement of the long alkyl substituents in this self-assembly suggests that the MPcOC₈

assembling process might be affected by the graphite substrate, which could confine the translation and rotation of the alkyl chains.

Highly resolved images of CuPcOC₈ and ZnPcOC₈ molecules could be obtained in a wide range of bias voltage. While the higher bias voltage produced stronger image contrast between the aromatic ring and the alkyl substituents, lowering the voltage led the alkyl chains to become more pronounced. Further lowering the bias voltage, the underlying graphite substrate became visible. By measuring the relative height at the single

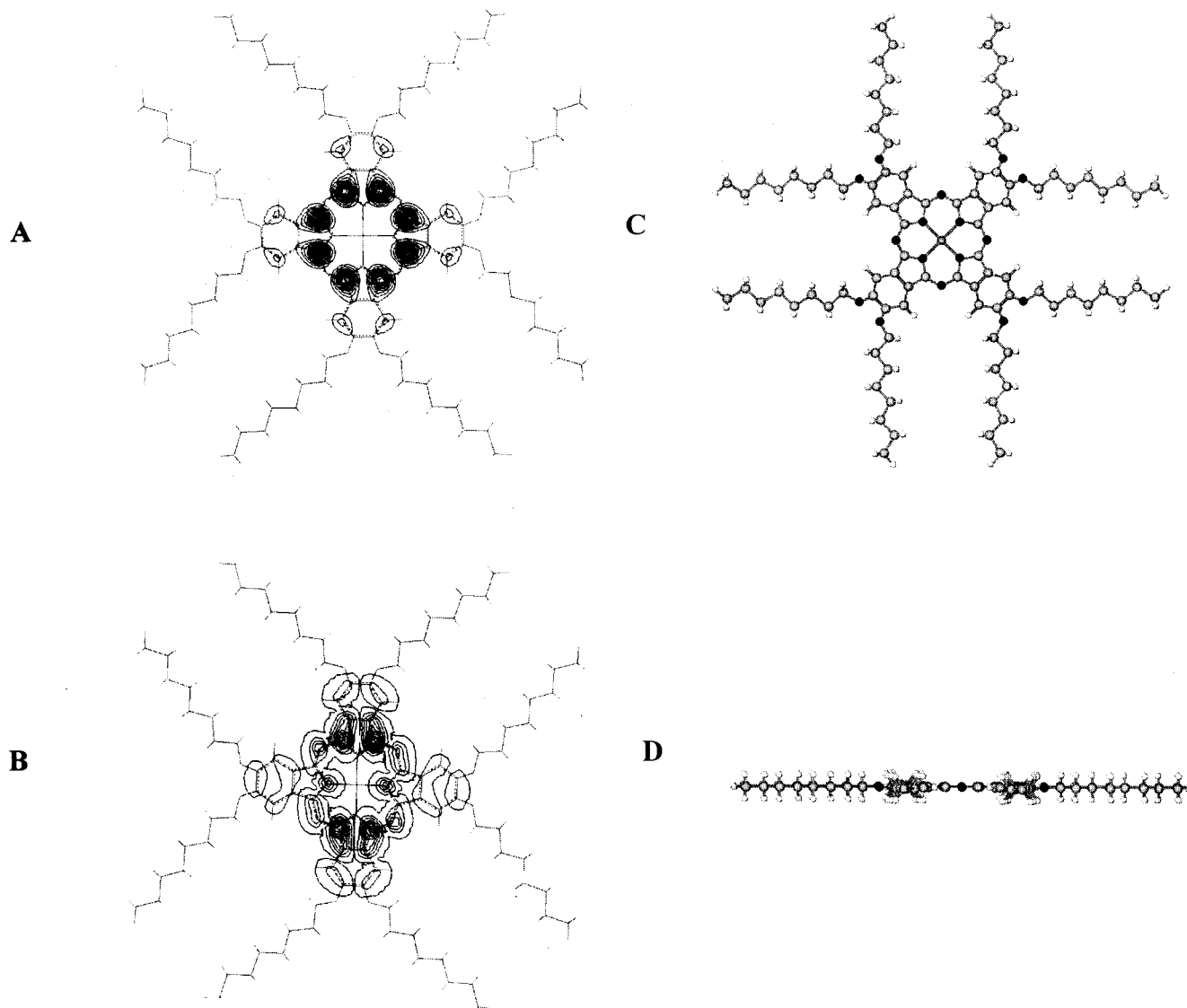


Figure 3. Molecular orbitals of octa-alkoxy-substituted phthalocyanine: (a) HOMO, (b) LUMO; molecular structure of MPcOC_8 ($M = \text{Cu, Zn}$) molecules from (c) top view and (d) side view.

molecular defect, it is estimated that the height of the phthalocyanine rings is about 0.2 nm–0.4 nm and dependent on the applied bias voltage. This indicates that CuPcOC_8 molecules are adsorbed with their molecular plane parallel to the graphite substrate.^{3,8,12}

Figure 4 illustrates the proposed molecular arrangement in the case that the MPcOC_8 molecules self-assembled in quadratic symmetry. The quadratic arrangement for CuPcOC_8 and ZnPcOC_8 is also reported for Pc molecules formed on graphite surface with MBE method, which is proposed to result from the commensurability of the aromatic rings with the underlying graphite substrate. On the other hand, it is energetically favorable to align the long alkyl substituents along the carbon chain direction of the graphite plane due to the registry between alkane and graphite lattice. Therefore, the flexible alkyl chains attached to the Pc ring could have relative translation and rotation to achieve the largest fitness with the underlying 3-fold symmetric graphite lattice. This process thus led to a more complex packing pattern, such as the hexagonal arrangement. Quantitative understanding of 2-D crystallization will require further experimental and theoretical studies of the adsorbate–adsorbate and adsorbate–substrate interactions.

The greater stability of the alkylated MPc on graphite in the present experiment can be qualitatively interpreted by consider-

ing the adsorption energy of the combined molecular system. It is well-known that for molecules physisorbed on substrate surface at temperature T , the desorption rate ν is determined by the desorption law,

$$\nu \propto \exp(-E_{\text{de}}/kT)$$

where E_{de} is the desorption energy, and k is Plank constant.

If one defines the desorption energies associated with the aromatic ring of MPc and octyl groups as E_{MPc} and E_{alkyl} , respectively, and assuming each segment of the combined molecule still retains its independent nature, the desorption rate of the combined molecule MPcOC_8 is the multiple of the desorption probability of each segment:

$$\nu = \nu_{\text{alkyl}}^8 \nu_{\text{MPc}} \propto \{\exp(-E_{\text{alkyl}}/kT)\}^8 \exp(-E_{\text{MPc}}/kT) = \exp\{-(8E_{\text{alkyl}} + E_{\text{MPc}})/kT\}$$

The driving force for alkane adsorption is a very interesting topic. It has been realized that the desorption energy for the alkane part could be divided into two parts. One is due to the direct interaction between the alkane and the substrate (HOPG), denoted as $E_{\text{C8-HOPG}}$. The other part is contributed by the 2D crystallization of alkanes, $E_{2\text{D}}$. Since the observed alkane parts

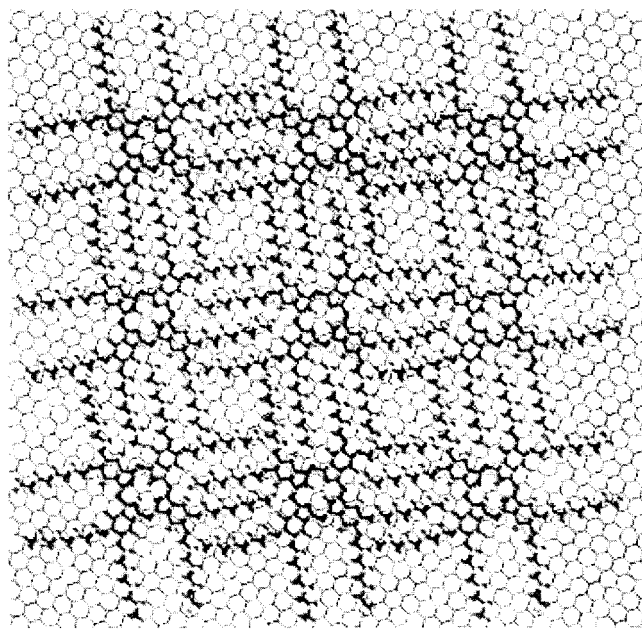


Figure 4. Schematic representation of the quadratic arrangement of MPcOC₈ (M = Cu, Zn) as deduced from STM images.

in the STM images are arranged in parallel, the approximation of 2D crystallization should be appropriate. The total desorption energy is therefore:

$$E_{\text{alkyl}} = E_{\text{C8-HOPG}} + E_{2\text{D}}$$

According to Hentschke et al.'s calculation, each $-\text{CH}_2$ of long-chain alkane adsorbed on graphite will provide an adsorption potential of about 70 meV,¹⁷ when the alkyl chain lies parallel to the *a* axis (or *b* axis) of graphite. In our case, the desorption energy associated with the eight octyl groups (a total of 64 $-\text{CH}_2$) is thus nearly 4 eV.

The 2D crystallization of alkane chains (via van der Waals interaction) introduces additional adsorption strength of the surface-bound alkanes. We have performed molecular mechanics simulation, using CVFF force field, on the adsorption of alkane on graphite surface. The calculation indicates that an additional desorption energy from 2D crystallization will be required to remove a single alkane molecule from an alkane self-assembly on graphite substrate. A densely packed system including 10 octane molecules with two possible orientations of carbon skeleton^{17,18} were modeled in our calculation. In the flat orientation, the additional desorption energy of 4.0 and 8.7 kcal/mol are needed for the side and inner molecule in this alkane array, respectively. In the case of vertical orientation, the values would be 5.4 kcal/mol for a side molecule and 10.8 kcal/mol for the inner molecules. The details of the calculations will be presented in another work. If we assume that half of the eight octyl groups in MPcOC₈ are side chains and the other half are inner chains in the alkyl regions, one could thus estimate the additional desorption energy associated with the octyl groups as 64.9 kcal/mol (or 2.8 eV per MPcOC₈) with all the alkyls in vertical conformation, and 50.9 kcal/mol (or 2.2 eV per MPcOC₈) with the alkyls in the flat conformation. It is therefore worthwhile to point out that 2D crystallization of alkyls could have appreciable effect in stabilizing the molecular assemblies.

Comparison experiments were carried out using unsubstituted phthalocyanines, and we were unable to observe any uniform molecular layers under similar conditions. This could be attributed to the reduced affinity of unsubstituted phthalocyanines to the solid substrate. For a combined molecule of MPcOC₈, the desorption barrier of ($8E_{\text{alkyl}} + E_{\text{MPC}}$) is significantly higher than a single phthalocyanine molecule. A quantitative comparison would require the similar calculations of nonsubstituted phthalocyanine systems and will be presented in another work.

IV. Conclusion

Using CuPcOC₈ and ZnPcOC₈ as examples, we have demonstrated that phthalocyanines with covalently bonded long alkyl chains could be immobilized at the interface of the organic solution and the basal plane of HOPG. Highly resolved images could be reproducibly obtained in a range of voltages. The high stability and close packed assembly are attributed to the van der Waals interaction between the alkyl chains and the graphite substrate, which substantially increased the desorption barrier of the combined molecule. The similarity between the image of alkylated CuPcOC₈ and the previous results of CuPc indicates that the alkyl substituents have little influence on the image contrast of the internal structure of phthalocyanine. It is hoped that this method could provide a complementary method to prepare an ordered two-dimensional array of molecular films, and facilitate the STM studies of fine structures of molecules.

Acknowledgment. The authors thank the financial support from National Natural Science Foundation, and the Foundation of the Chinese Academy of Sciences.

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