

# Stacking behavior of 2-D assemblies of octa-alkoxyl-substituted phthalocyanine studied by scanning tunneling microscopy

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## Abstract

In this paper we report the observations of the bilayer structures of octa-alkoxyl-substituted phthalocyanine formed with high stability on graphite surfaces through direct deposition from solutions. The high resolution scanning tunneling microscope (STM) images of the overlayer assembly display discernible shifts. The bilayer structures are simulated by molecular mechanics method and the calculated results agree well with the experimental observations, indicating that the observed overlayer shift could be attributed to the  $\pi$ - $\pi$  interaction associated with phthalocyanine. The results suggest that the multilayer growth of PcOC8 is jointly affected by  $\pi$ - $\pi$  interactions, especially together with Van der Waals interactions.

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## 1. Introduction

Constructing molecular nanostructures by utilizing the intermolecular interactions of various strengths has been extensively pursued in recent studies. In particular, relatively weak and revers-

ible intermolecular forces have been the subjects of focused investigations. While studies on monolayer structures are stringent in understanding the assembling processes, the knowledge of the formation process of multilayer structures is of significant importance. Many electronic and optoelectronic devices rely on the growth of multilayered molecular thin films. The structural, morphological, electronic as well as optical properties of the molecular films are crucial for their applications. One of the prevalent preparation approaches is the growth of heterogeneous structures, where a key aspect of the process is the

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influence of the first molecular layer on the structures of the second and subsequent layers, and the result of the growth will be directly relevant to the properties of the molecular film.

As an extensively studied system, phthalocyanine (Pc) films are used as molecular components in a number of electronic and optoelectronic devices [1]. Efforts of revealing the multilayer structures at molecular resolution could be found in a number of earlier studies [2–9]. For example, the first and second monolayers of InPc-Cl were studied on a SnS<sub>2</sub> surface [2]. InPc-Cl formed three perfect corner-to-corner square lattice domains, and each domain was rotated by 60° with respect to the first layer. The three surface Pc nuclei have each been aligned along a principal axis of the SnS<sub>2</sub> surface, with the assumption that terrace sites, also aligned along these axes, are responsible for the “templating” of a measurable fraction of the Pc deposits. A fourth Pc nucleus with the same symmetry and packing structure is shown depositing over the first layer, allowing this layer to slip in the *x* and *y* directions by about half of a molecular diameter. Subsequent layers adopt this same halide-up/halide-down alternation between layers. The spacing between phthalocyanines (Pcs) in each layer accommodates the halide from a Pc layer directly above, allowing a layer-to-layer spacing from about 0.34–0.38 nm, which is essentially the closest distance in these Van der Waals solids [3]. In 1996, Strohmaier et al. reported PbPc monolayers on MoS<sub>2</sub> characterized using STM, with direct observation of the second layer [4]. Recently, Schlettwein et al. [5] characterized thin film morphology of hexadecafluorophthalocyaninatooxovanadium (F<sub>16</sub>PcVO) which were vapor-deposited under organic molecular beam epitaxy (OMBE) conditions on the (100) surfaces of NaCl, KCl, and KBr and on quartz glass by the tapping mode of atomic force microscopy (AFM). Using the same approach, Bayliss et al. claimed that the structure and morphology of the second layer are influenced strongly by the properties of the first layer, independent of the growth conditions used to deposit the second layer, and this templating effect extends to structures involving more than two layers [6]. In addition, Bishop et al. explained the hydrocarbon multilayer assemblies

on Pt(1 1 1) from the aspects of thermal desorption energetics and desorption kinetics [7,8]. The binary molecular system of C<sub>60</sub> and copper phthalocyanine (CuPc) molecules has also been investigated by STM at room temperature and at 50 K [9].

We reported previously that using a monolayer of alkane as a buffer layer, copper phthalocyanine (CuPc) can be immobilized on the surface of highly oriented pyrolytic graphite (HOPG) [10], and highly resolved STM images of CuPc molecules were obtained. Since the Pcs can be substituted with various functional groups and thus possess a wide range of functionalities, it is of genuine interest to explore the stacking effects of the substituted Pcs which consist both extended  $\pi$  component and saturated alkyl parts. In this work, we demonstrate that multilayer molecular structures of octa-alkoxyl-substituted phthalocyanine can be assembled by the similar approach [10]. The joint effects of  $\pi$ - $\pi$  interaction of Pc cores and the interaction between Pc cores and alkoxyl substituents can be investigated with STM imaging.

## 2. Experiment and calculation

Octa-alkoxyl-substituted phthalocyanine (purity > 95%) denoted as PcOC8 was obtained from Aldrich and used without further purification. The solution of PcOC8 molecules was made in a solvent of toluene (HPLC-grade, Aldrich) with a concentration of less than 1 mM. A droplet of the solution was deposited onto a freshly cleaved surface of HOPG. We would like to note that the sample preparation conditions are approximately the same as reported in earlier work [10]. The only difference we observed was that the bilayer structures could be obtained more readily with slightly higher solution concentration. We would like to add that monolayer structure was observed simultaneously with the bilayers at the same sample surface.

The experiment was performed on a Nanoscope IIIa SPM (Digital Instruments, Santa Barbara, CA) at room temperature in ambient conditions. The STM tips were mechanically formed Pt/Ir wire (90/10). The STM images showing height data were recorded after the solvent was completely

evaporated using constant current mode of operation. The specific tunneling conditions were given in the figure captions. The bias voltage was applied to the sample.

The molecular mechanics method was applied to simulate the multilayer structures using the CHARMM force field in InsightII 2000 [11]. The energy minimizations were carried out with the energy gradient tolerance at  $0.01 \text{ kcal/mol}\text{\AA}^2$ . The non-bond cutoff distance was set to  $15 \text{ \AA}$ . For the structure where the lower and upper layers are exactly overlapped, the center–center offset is  $0 \text{ \AA}$ . The stable structures were obtained via optimization from several initial configurations of different center–center offset values.

### 3. Results and discussions

A characteristic monolayer of PcOC8 arrays is shown in Fig. 1, where the submolecular structure of individual molecule is clearly resolved. It is noticed that the core of the PcOC8 molecule appears as a bright four-lobe “flower”, surrounded by obscure zigzag lines representing the alkyl parts. The diagonal width of the central bright moieties is measured to be about  $1.6 \pm 0.1 \text{ nm}$ , which is consistent with the estimated diameter of  $1.7 \text{ nm}$  for the octahydroxyl-substituted phthalocyanine. The measured lattice constants,  $a$  and  $b$ , are about  $2.7 \pm 0.1 \text{ nm}$  and  $2.9 \pm 0.1 \text{ nm}$ , respectively. All data have already been calibrated with

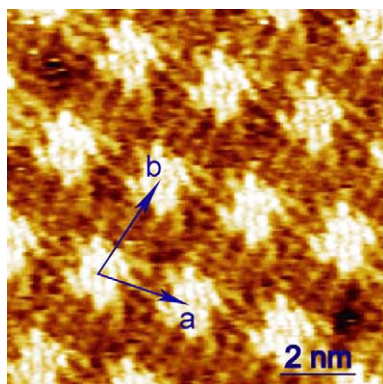


Fig. 1. A typical STM image of monolayer of PcOC8 arrays. (Scan area:  $10 \text{ nm} \times 10 \text{ nm}$ ; tunneling conditions:  $684 \text{ pA}$ ,  $-753 \text{ mV}$ .)

the same difference ratio between the lattice constants of the graphite images and those of the normal graphite ( $0.25 \text{ nm}$ ).

Under the approximate tunneling conditions, we were also able to observe the bilayer structures of well ordered domains of PcOC8 molecules, with an example shown in Fig. 2a. In the upper left corner of Fig. 2a, the featureless area is ascribed to the bare surface of HOPG possibly covered with mobile adsorbates that cannot be resolved. The boundary of the molecular layers displays sharp edges, indicating a rather strong interlayer interaction between the molecules. Two layers of molecules both consist of several domains, as evidenced by the slight discontinuity of the molecular lattices. It has been noticed that, in the two self-assembled layers, the characteristic dimension and symmetry of the domains are comparable. There is no ob-

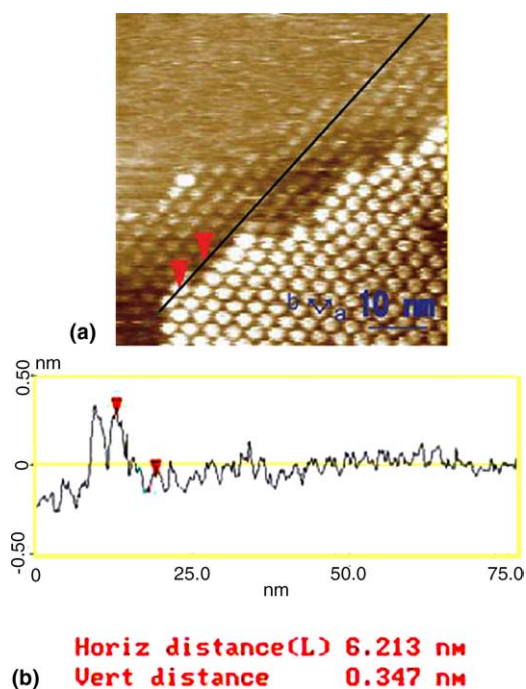


Fig. 2. (a) STM image of a bilayer structure of PcOC8 on HOPG obtained in ambient conditions. The second layer is visible in the image as the exposed monolayer. (Scan area is  $56.8 \text{ nm} \times 56.8 \text{ nm}$ . Tunneling conditions is  $852 \text{ pA}$  and  $-805 \text{ mV}$ .) (b) Cross sectional profile along the marked line in (a). (For interpretation of the reference in colour in the text, the reader is referred to the web version of this article.)

servable rotation of molecular lattices on one layer relative to those on the other. The measured lattice constants in two layers are nearly the same. Unit cell data are summarized in Table 1. The measurements of the unit cell parameters of the monolayer are based on several tens of images and independent measurements. Slight image distortions were observable in some of the scans, and are not contributing significantly to the overall statistical results.

From Fig. 2a, we can observe the obvious height difference between the two layers of molecules. According as the cross sectional profile displayed in Fig. 2b, the upper layer is measured to be about 0.3 nm higher than the lower one, which agrees with the height of the phthalocyanine reported previously [12]. In both lower and upper layers, the diagonal width of the central bright moieties is about  $1.6 \pm 0.1$  nm, which is consistent with the estimated diameter of 1.7 nm for phthalocyanine. The multilayer assembly of PcOC8 was stable enough to endure repeated scanning.

It can be observed that the molecules at the boundary of the second layer do not overlap entirely with those in the first layer. The axes in the direction of the  $\vec{a}$  vector (shown in Fig. 2a) of molecules in the upper layer almost overlaps with that of the molecules in the lower layer except for a slight shift. In contrast, in the  $\vec{b}$  direction, we can determine that the axes of the molecules in the upper layer shift, in parallel with the axes of molecules in the lower layer. Namely, the offset is along the  $\vec{a}$  vector and a nearly negligible shift along the  $\vec{b}$  vector. From Fig. 2b, we can determine the relative shift between the axes of molecules in two layers. In Fig. 2b, the two red arrows correspond to the red arrow markers in Fig. 2a, between which the horizontal distance is measured to be 6.2 nm (equal to  $2a + L$ , “ $a$ ” is the lattice

constant of the lower layer). Therefore, the shift  $L$  in distance of the axes of molecules between two layers is measured to be about 0.4 nm, which is consistent with the results of the molecular mechanics simulation as discussed later in this work. This distance is about one fourth diameter of PcOC8. The shift distance in the other direction is very slight which is about 0.1 nm using the same method. That distance is considered within the range of measurement error of the STM.

To study the interaction among the molecules and the interaction between the molecules and substrate, we focused on the overlayer structure of the self-assembled octa-alkoxyl-substituted phthalocyanine on HOPG. The multilayer formation and the two-dimensional crystal on the graphite surface are governed by weak forces including Van der Waals interactions, electrostatic interactions,  $\pi$ – $\pi$  interactions, etc. These weak forces can be divided into two parts, i.e. the intermolecular interaction of the interlayer and that of the intralayer. In the present system, the alkyl chains interact through close packings within each layer, which is driven mainly by Van der Waals interactions [13]. On the other hand, the cores of the PcOC8s are large  $\pi$  systems, and there are strong  $\pi$ – $\pi$  interactions between them. It is well known that  $\pi$ – $\pi$  interactions are ubiquitous in nature, especially in bio-macromolecules and aggregations of aromatic molecules such as the double helix of DNA and aromatic molecule crystals. The  $\pi$ – $\pi$  interaction prompts the molecules to aggregate coplanar with their center offset. Previous theoretical studies have identified that  $\pi$ – $\pi$  interactions are actually the result of  $\pi$ – $\sigma$  attractions that overcome  $\pi$ – $\pi$  repulsions. In another word, electrostatic effects determine the geometry of interaction and Van der Waals make the main contribution for  $\pi$ – $\pi$  interactions [14].

The molecular mechanics analysis was employed to model the observed assembly structures. The PcOC8 molecule was first constructed from phthalocyanine core according to X-ray diffraction data [15,16]. The optimum structure of PcOC8 molecule, similar to that in our previous report [12], was obtained through optimization using CHARMM force field. Bilayers consisting of a total of 32 PcOC8 molecules were then built, and

Table 1  
Unit cell parameters of the upper layer and lower layer lattices ( $\beta$  is the angle between  $a$  and  $b$ )

	Upper layer	Lower layer
$a$	$2.8 \pm 0.1$ nm	$2.9 \pm 0.1$ nm
$b$	$2.9 \pm 0.1$ nm	$2.9 \pm 0.1$ nm
$\beta$	$75^\circ \pm 5^\circ$	$70^\circ \pm 5^\circ$

were fully optimized without any constraint. Starting from initial structures with different center–center offset values of 0, 1, 2, 3, 4, and 5 Å, the most stable structures were achieved, and the center–center offset distance between the lower and upper layers is 3.9 Å along the transverse alkyl-chain direction (namely along  $\bar{a}$  vector) and about 1.5 Å along the other direction. In the optimized configuration, the alkyl chains of the neighboring molecules within the same layer are interdigitated within the plane. The optimized offset value of 3.9 Å is in good agreement with the experimentally measured value of 4.0 Å. Fig. 3a presents the optimized self-assembled structure involving eight

molecules stacking in two layers. A slightly tilted side view is given in Fig. 3 to facilitate the better viewing of the bilayer structure. Fig. 3b shows the side view of Fig. 3a. Fig. 3b only displays two PcOC8 molecules, respectively in the upper and the lower layer. From the proposed stacking schematics, the distance of the same N–N atoms which are respectively situated on two PcOC8 molecules can be measured as 5.044 Å, and the angle between the N–N line and the lower-layer plane of PcOC8 molecule is 39.358°. We can also obtain the shift distance of the two layers molecules as about 3.9 Å. In the present system, Van der Waals interaction is  $-138.54$  kcal/mol, indi-

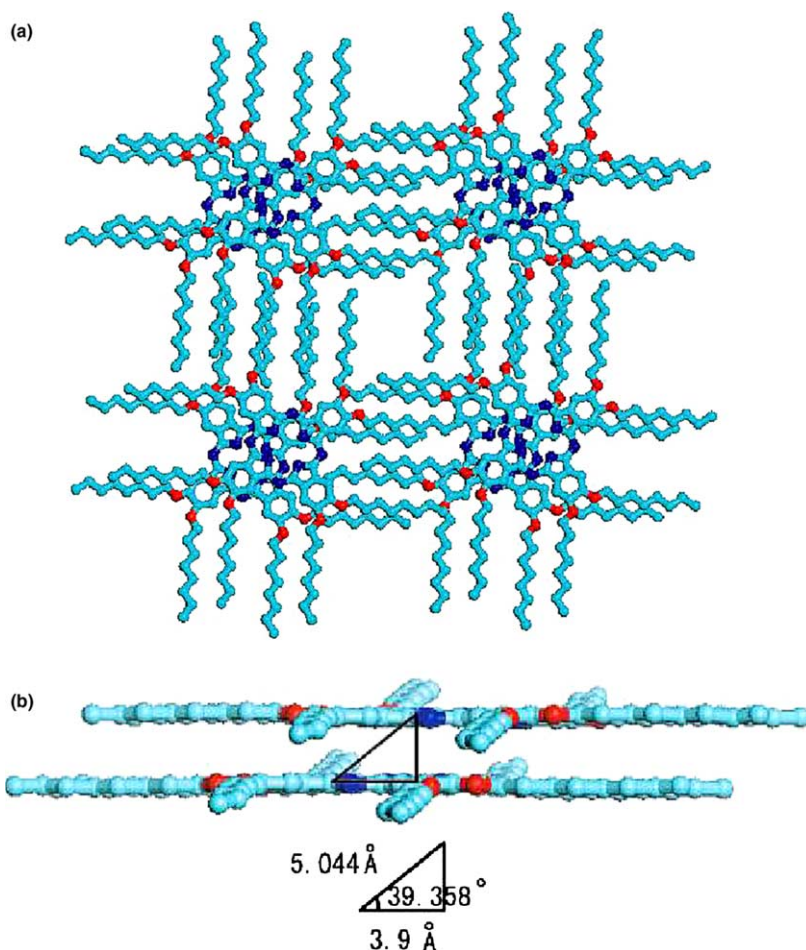
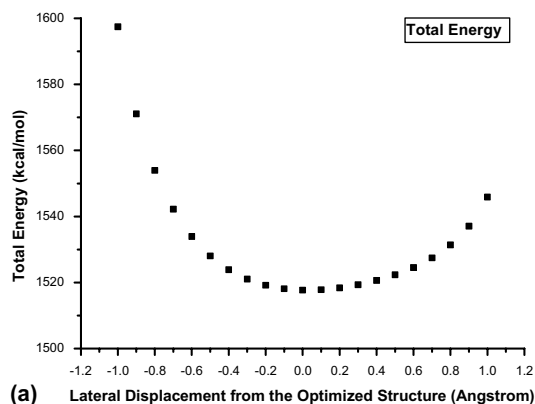
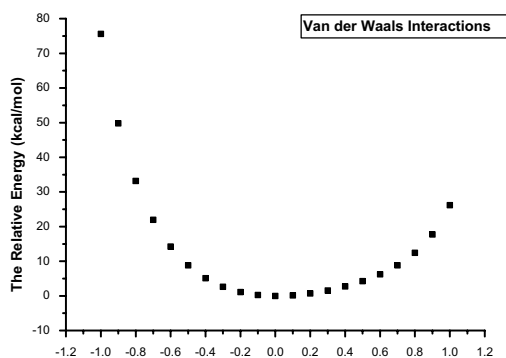


Fig. 3. (a) Proposed stacking schematics of eight PcOC8 molecules. (b) Side view of the proposed stacking schematics of two PcOC8 molecules.

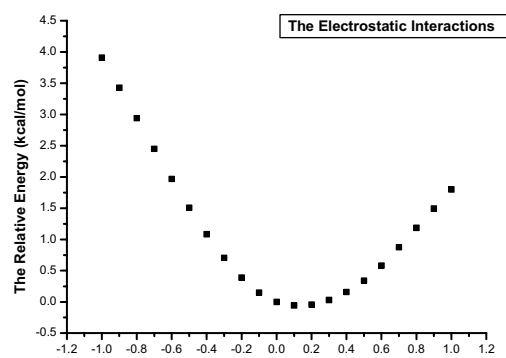
cating a strong attraction force to the offset bilayer structures. While the electrostatic interaction is



(a) Lateral Displacement from the Optimized Structure (Angstrom)



(b) Lateral Displacement from the Optimized Structure (Angstrom)



(c) Lateral Displacement from the Optimized Structure (Angstrom)

Fig. 4. (a) The total energies as the function of the lateral displacement from the optimized structure. (b) Van der Waals interactions as the function of the lateral displacement from the optimized structure. (c) The electrostatic interactions as the function of the lateral displacement from the optimized structure.

–7.13 kcal/mol, which is significantly smaller compared with that of Van der Waals interactions. By using this optimized geometry, we shifted one layer of molecules laterally and calculated the single-point energy, as shown in Fig. 4a. Even as expected we also obtained the lowest total energy in the optimized geometry. Fig. 4b and c, respectively show the Van der Waals interactions and the electrostatic interactions as the function of lateral displacement from the optimized structure, in which the energies are the relative values to that of the optimized structure. Obviously, Van der Waals interactions have much stronger contributions to the energy of the optimized geometry than the electrostatic interactions. We also studied the differential coefficient of Van der Waals interactions and the electrostatic interactions at the different lateral displacement, which are nearly equal to zero around 3.9 Å offset to prove the lowest energy point there. Therefore, we can also deduce that the driving force for this optimized structure should be Van der Waals interactions rather than the electrostatic interactions. Apparently, the multilayer growth of PcOC8 is appreciably affected by  $\pi$ – $\pi$  interactions, while Van der Waals interactions dominate the magnitude of the overall interactions.

#### 4. Conclusions

The observations presented in this work demonstrate that stable bilayer structures of octa-alkoxyl-substituted phthalocyanine can be obtained at ambient conditions. The molecular mechanics simulation results suggest that the  $\pi$ – $\pi$  interactions of Pc cores could be directly reflected in the stacking geometry of PcOC8. The calculations by the molecular mechanics simulation agree well with the experiments and thus provide a supportive insight on the multilayer structures.

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