

Adlayer Structure of Octa-Alkoxy-Substituted Copper(II) Phthalocyanine on Au(111) by Electrochemical Scanning Tunneling Microscopy

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ABSTRACT Electrochemical scanning tunneling microscopy (ECSTM) has been used to examine the adlayer of octa-alkoxy-substituted copper(II) phthalocyanines (CuPc(OC₈H₁₇)₈) on Au(111) in 0.1 M HClO₄, where the molecular adlayer was prepared by spontaneous adsorption from a benzene solution containing this molecule. Topography STM scans revealed long-range ordered, interweaved arrays of CuPc(OC₈H₁₇)₈ with coexistent rectangular and hexagonal symmetries. High-quality STM molecular resolution yielded the internal molecular structure and the orientation of CuPc(OC₈H₁₇)₈ ad molecules. These STM results could shed insight into the method of generating ordered molecular assemblies of phthalocyanine molecules with long-chained substitutes on metal surface. *Microsc. Res. Tech.* 71:20–25, 2008. © 2007 Wiley-Liss, Inc.

INTRODUCTION

Molecular self-assembly referring to spontaneous organization of molecules into stable and structurally well-defined aggregates has been extensively examined to elucidate the formation of organic networked templates, heterogeneous catalysis, crystal engineering, biosensors, molecular electronics devices, and supramolecular structures (De Feyter and De Schryver, 2005; Gleiche et al., 2000; Hoepfner et al., 2003; Love et al., 2005; Whitesides et al., 1991). These tantalizing applications of organic species are based on the construction of well-defined molecular adlayers, which is the main concern of this study (Uosaki and Yamada, 1999).

Porphyrin and/or phthalocyanine are two of the most prominent examples of this sort, as they have been used in the research of photosynthesis (Balzani, 2001), electrocatalysis (Collman et al., 1994), and molecular devices (Jortner and Ratner, 1997). For example, copper(II) phthalocyanine (CuPc) is used to fabricate field effect transistors (Guillaud et al., 1998; Jortner and Ratner, 1997) and light emitting diodes (LED) (Guillaud et al., 1998). The molecular assembling mechanism of phthalocyanine has been studied using scanning tunneling microscopy (STM) in ultrahigh vacuum (UHV) (Barlow and Hipps, 2000; Hipps et al., 1996; Lackinger and Hietschold, 2002; Lippel et al., 1989; Lu and Hipps, 1997; Lu et al., 1996) and in air (Ogunrinde et al., 2006; Xu et al., 2000). Lippel et al. reported the first STM images of CuPc adlayer on Cu(100) surface (Lippel et al., 1989). Hipps's group systematically studied a series of MPcs including CoPc (Hipps et al., 1996; Lu et al., 1996), CuPc (Hipps et al., 1996; Lu et al., 1996), FePc (Lu and Hipps, 1997), NiPc (Lu and Hipps, 1997), and VOPc (Barlow and Hipps, 2000) on Au(111)

surface in UHV. The adsorption of nonplanar SnPc (Lackinger and Hietschold, 2002) on Ag (111) was also studied in UHV recently. CuPc layers were also studied on *n*-alkane modified highly ordered pyrolytic graphite (HOPG) surface in ambient atmosphere (Xu et al., 2000). Nickel(II) octaethylporphyrin has been studied on graphite in air after solution phase deposition (Ogunrinde et al., 2006).

STM has also been used to study the structure of MPcs adlayers on Au(111) in solution. For example, it is shown that water-soluble 5,10,15,20-tetrakis (*N*-methylpyridinium-4-yl)-21*H*,23*H*-porphine (H₂-TMPyP) molecules are adsorbed in highly ordered arrays on iodine-modified Au(111) (Kunitake et al., 1995), Ag(111) (Ogaki et al., 1996), Pt(100) (Sashikata et al., 1998), and sulfur-modified Au(111) (Wan et al., 2000) surfaces in solution. Tao et al. reported the adlayers of iron(III) protoporphyrin(IX), zinc(II) protoporphyrin(IX), and protoporphyrin(IX) on HOPG in aqueous solutions with both STM (Tao, 1996; Tao et al., 1995) and atomic force microscopy (Tao et al., 1995). Recently, it is shown that water-insoluble MPcs including tetraphenyl-21*H*,23*H*-porphine cobalt(II) (CoTPP) and copper(II) (CuTPP) (Yoshimoto et al., 2003a) dissolved in benzene are adsorbed in highly ordered adlattices on Au(111). It is possible to achieve STM resolution with the quality comparable to those observed in

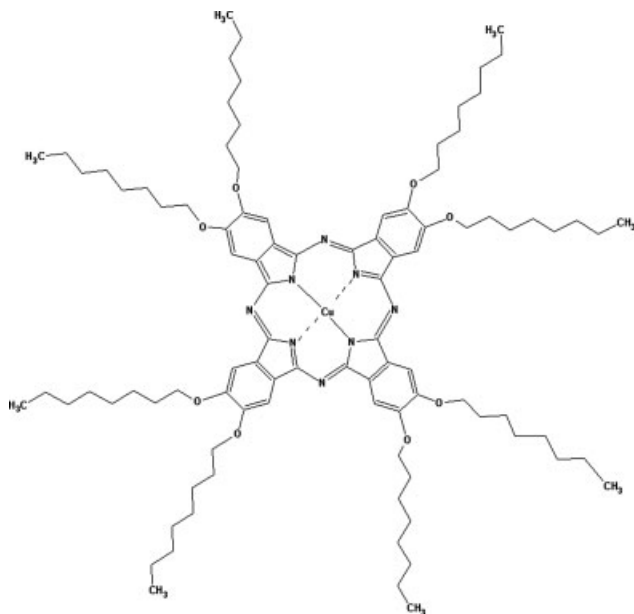
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Chart 1. Chemical formula of $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$.

UHV (Scudiero et al., 2000, 2001). This method was further applied to produce highly organized adlayers of CoPc and CuPc on $\text{Au}(111)$ (Yoshimoto et al., 2003b).

The effect of alkyl substituents on MPcs on the electrical and optical characteristics of phthalocyanines has been examined (Sauer and Wegner, 1988). Bai's group investigated the adsorption of alkyl substituted CuPc and ZnPc on graphite in ambient (Qiu et al., 2000a), alkyl-substituted CuPc layers on stearic acid-modified HOPG (Lei et al., 2001), and alkyl-substituted phthalocyanines and porphyrins on HOPG (Qiu et al., 2000b). Although alkylated water-insoluble molecules were imaged with electrochemical scanning tunneling microscopy (ECSTM) on $\text{Au}(111)$ (He et al., 2002; Klymchenko et al., 2007), there has been no report of alkyl-substituted phthalocyanines/porphyrins on metal surfaces. Here we report an ECSTM investigation of copper(II) 2,3,9,10,16,17,23,24-octakis(octyloxy)-29H, 31H-phthalocyanine ($\text{CuPc}(\text{OC}_8\text{H}_{17})_8$) self-assembled monolayers on $\text{Au}(111)$, aiming at elucidating how molecular adsorption is influenced by the intermolecular and substrate-molecule interactions. On comparing this molecule to those reported previously, the main difference is the presence of long-chained substituents in the ad molecules. High-resolution STM imaging makes it possible to address the intermolecular interactions within the molecular adlayer.

MATERIALS AND METHODS

Materials

Copper(II) 2,3,9,10,16,17,23,24-octakis(octyloxy)-29H, 31H-phthalocyanine ($\text{CuPc}(\text{OC}_8\text{H}_{17})_8$) was obtained from Sigma-Aldrich, and its chemical formula is shown in Chart 1. Benzene (spectroscopy grade) was purchased from Kanto Chemical Co. The aqueous electrolyte solution was prepared with HClO_4

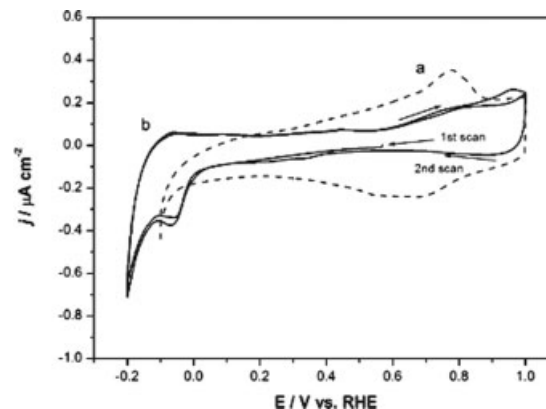


Fig. 1. Typical CV of (a) bare and (b) $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ (first and second scan) adsorbed $\text{Au}(111)$ electrodes in 0.1 M HClO_4 under N_2 atmosphere. The potential scan rate was 50 mV s^{-1} .

(Cica-Merck) and ultrapure water (Milli-Q SP-TOC; $\geq 18.2 \text{ M } \Omega \text{ cm}$).

Sample Preparation

The $\text{Au}(111)$ single-crystal electrode was prepared by the Clavilier method (Clavilier et al., 1980). It was annealed in hydrogen flame and quenched into ultrapure water saturated with hydrogen (Honbo et al., 1990). $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ adlayers were formed by immersing the $\text{Au}(111)$ electrode into a $10\text{-}\mu\text{M}$ $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ benzene solution for about 5 min. The $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ -adsorbed $\text{Au}(111)$ electrode was then rinsed with ultrapure water to prevent contamination, and it was transferred into an electrochemical cell for voltammetric and STM measurements. The observation by STM was performed in HClO_4 solution under potential control. The potentials used were positioned at the double-layer region.

Methods

Cyclic voltammetry was carried out at 20°C using a CHI 600 potentiostat with the hanging meniscus method in a three-compartment electrochemical cell in N_2 atmosphere. Electrochemical STM measurements were performed on a Nanoscope E (Digital Instruments, Santa Barbara, CA) with tungsten tips etched in 1 M KOH. The tips were previously coated with nail polish to minimize the residual faradic current. STM images were taken in the constant-current mode and used with only flatten processing. All potentials are referred to the reversible hydrogen electrode (RHE) in 0.1 M HClO_4 .

RESULTS AND DISCUSSION

Figure 1 shows typical cyclic voltammograms (CVs) of bare and $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ adsorbed $\text{Au}(111)$ electrodes in 0.1 M HClO_4 at a scan rate of 50 mV s^{-1} . The $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ adsorbed $\text{Au}(111)$ sample was obtained by immersion in $10 \text{ }\mu\text{M}$ benzene solution with $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ molecules for 5 min. The open circuit potential (OCP) of a well-defined $\text{Au}(111)$ electrode in 0.1 M HClO_4 was in the range of 0.7–0.75 V (Honbo et al.,

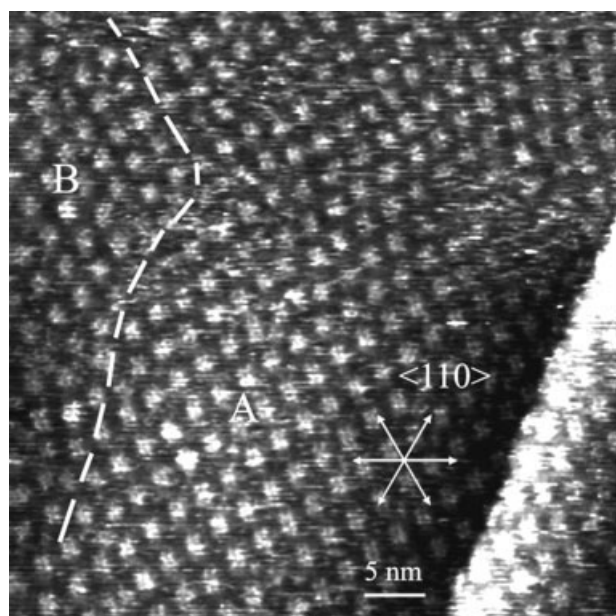


Fig. 2. Large scale ($50 \times 50 \text{ nm}^2$) STM image of a $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ adlayer formed on Au(111) acquired in 0.1 M HClO_4 at 0.3 V versus RHE. The set of three arrows indicates the close-packed directions of the Au(111) substrate. The tunneling current was 1.0 nA with a bias of 0.2 V.

1990). The voltammogram for the bare Au(111) in Figure 1 in the double-layer potential region was identical to that reported previously (Honbo et al., 1990), which showed that a well-defined Au(111) surface was exposed to the HClO_4 solution. The CV profile of an Au(111) electrode immersed in pure benzene for 5 min and rinsed with ultrapure water was essentially the same as that observed on a clean, fresh Au(111) electrode. This result indicates that benzene does not adsorb on the Au(111) surface in the present conditions.

After the preparation of a $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ adlayer on Au(111), the OCP of the $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ adsorbed Au(111) electrode was in the range of 0.5–0.6 V. The potential scan was then started in the negative direction from the OCP in the double-layer region. The decrease in the double-layer charging current in Figure 1 clearly showed that the Au(111) surface was covered with $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ hydrophobic molecules. The repetitive potential cycling between 0.1 and 0.6 V caused no change in the CV profile, suggesting that the $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ adlayer formed on Au(111) was stable in the double-layer potential range. As can be seen in Figure 1, a reductive peak appeared at 0.05 V during the cathodic scan was due to the reduction of the $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ adlayer. The increase in cathodic current commencing at -0.1 V was due to the H_2 evolution reaction. The following ECSTM study was performed at the double-layer region.

Figure 2 shows a typical topography STM scan of a $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ monolayer on a terrace of Au(111). It could be seen that $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ molecules are arranged in a well-ordered two-dimensional array with each molecule appearing as a group of four bright

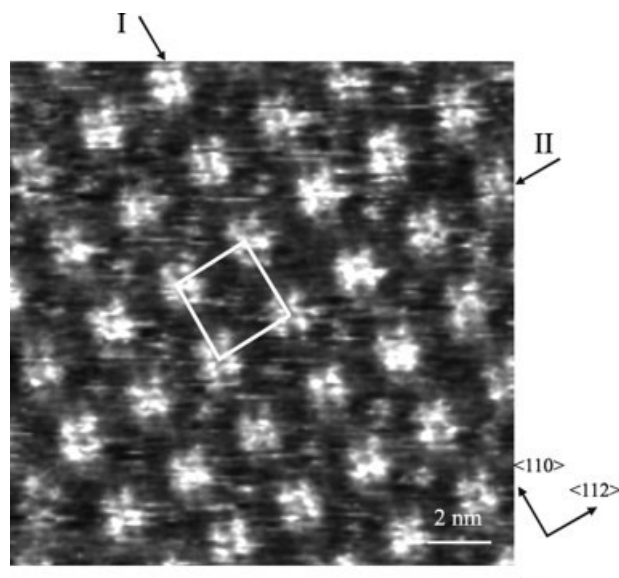


Fig. 3. High-resolution STM images (about $16 \times 16 \text{ nm}^2$) of rectangular symmetrical $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ adlayer on the Au(111) surface in 0.1 M HClO_4 at 0.3 V versus RHE. The tunneling current was 1.0 nA with a bias of 0.2 V.

spots. Typically, two kinds of packing arrangements with square and hexagonal symmetries (marked A and B, respectively) were observed in the adlayer. Irrespective of their symmetry, the molecular adlayer was highly ordered with a few vacancy defects and domain boundaries.

The long-range ordering of the $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ adlayer allowed us to obtain high-quality molecular resolution STM images, as shown in Figure 3. The scan area was about $16 \times 16 \text{ nm}^2$. Each molecule in domain A was imaged as a square-like protrusion of 0.15–0.25 nm above the gold surface. We attribute the fourfold symmetrical bright lobe to the conjugated core of a phthalocyanine molecule, and the average corrugation height 0.2 nm agrees with others (Lippel et al., 1989). The diagonal width of the square-like protrusion is about $1.6 \pm 0.1 \text{ nm}$, which is approximately equal to the previously estimated size of the phthalocyanine ring (Schouten et al., 1995). The surrounding long alkyl substituents were not imaged clearly here; they were supposed to be distributed around the phthalocyanine core (Qiu et al., 2000b).

The central metal cation of Cu^{2+} in the admolecule resulted in a depression in the STM image. According to Hipps and coworkers, corrugation height of a metal center in the STM images depends on its electronic structure, particularly, the electronic configurations in the d orbital. It is proposed that the half-filled d_{z^2} orbital of Co at the center of CoPc could mediate electron tunneling between the tip and the Au(111) substrate, which renders its protrusion appearance in the STM image. In contrast, the Cu center in CuPc produces a completely filled d orbital, yielding a depression in the STM image. This contention is supported by the STM results of CuTPP and CuPc, where square-like protrusions were observed for both molecules on Au(111) (Yoshimoto et al., 2003a,b).

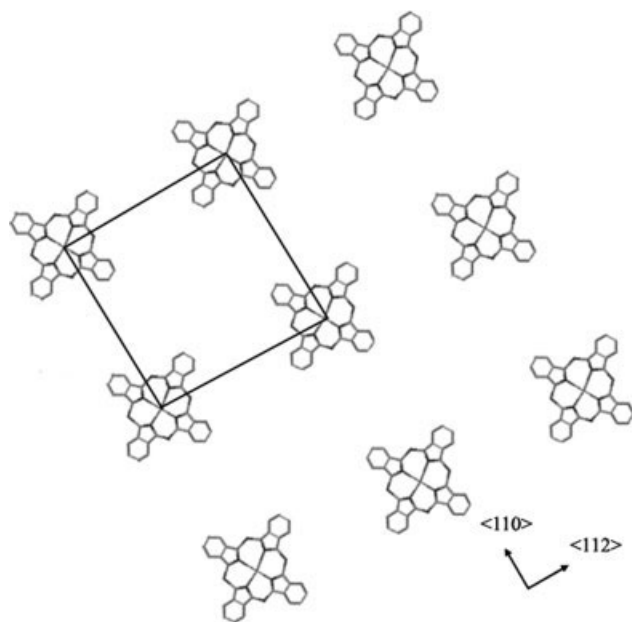


Fig. 4. Proposed model of Pc cores of $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ adlayer on the $\text{Au}(111)$ surface superimposed with $c(9 \times 5\sqrt{3})\text{rect}$ unit cell.

Molecular rows indicated by arrow I and II intersect perpendicularly with an angle of $90^\circ \pm 3^\circ$. They are aligned roughly in the $\langle 110 \rangle$ and $\langle 112 \rangle$ directions (also called $\sqrt{3}$ direction) of the $\text{Au}(111)$ lattice, respectively. The intermolecular spacing measured from the centers of two neighboring molecules was found to be 2.6 ± 0.1 nm and 2.5 ± 0.1 nm in I and II, respectively. The former corresponds to nine times the Au lattice parameter (9×0.289 nm), while the latter is $5\sqrt{3}$ times the Au lattice parameter ($5\sqrt{3} \times 0.289$ nm). All $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ molecules in the adlayer were oriented similarly. The unit cell superimposed in Figure 3 outlines the $c(9 \times 5\sqrt{3})\text{rect}$ structure with one molecule per unit cell, leading to a surface concentration of 2.55×10^{-11} mol cm^{-2} . Figure 4 is a structure model of the square array of $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ molecules on $\text{Au}(111)$. A similar quadratic packing arrangement was also observed on the HOPG substrate (Qiu et al., 2000b). Unfortunately, the present STM results do not allow a precise assignment of the alkyl chains.

Figure 5 shows a typical high-resolution STM image (11×11 nm²) of the hexagonal $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ adlayer on $\text{Au}(111)$. The STM appearance of each $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ molecule as a square-like protrusion suggests that the conjugated phthalocyanine core of each $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ molecule contributed predominantly to the tunneling event. Each protrusion appears 0.15–0.25 nm higher than the $\text{Au}(111)$ substrate, as observed in Figure 3. The $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ molecules were adsorbed with their molecular plane parallel to the $\text{Au}(111)$ substrate. The central Cu cation was not involved in the tunneling process, which leads to a depressive appearance in the STM image. The surrounding long alkyl substituents were not imaged clearly by the STM here, possibly because the alkyl chains were distorted and rotated to optimize inter-

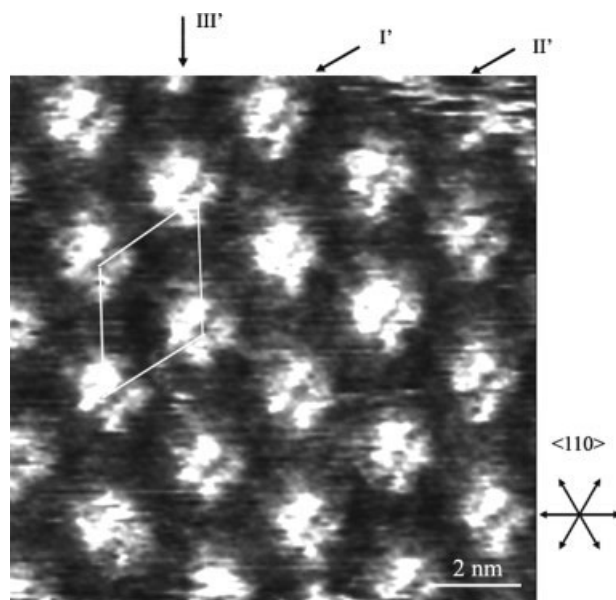


Fig. 5. High-resolution STM images (about 11×11 nm²) of hexagonal symmetrical $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ adlayer on the $\text{Au}(111)$ surface in 0.1 M HClO_4 at 0.3 V versus RHE. The tunneling current was 1.1 nA with a bias of 0.2 V.

molecular interaction (Qiu et al., 2000b). Close examination of the STM image in Figure 5 reveals that all molecular rows are aligned along the $\sqrt{3}$ directions of the $\text{Au}(111)$. The close-packed molecular rows indicated by arrows I' and II' were shifted alternately by one-half of the intermolecular distance. The intermolecular spacing (peak-to-peak distance) along I', II', and III' were measured to be 2.5 ± 0.1 nm, corresponding to $5\sqrt{3} \times 0.289$ nm. This result indicates that this structure is $(5\sqrt{3} \times 5\sqrt{3})\text{R}30^\circ$ with one molecule per unit cell or an equivalent surface concentration of 3.06×10^{-11} mol cm^{-2} . Figure 6 shows a tentative structural model of the hexagonal array. A similar hexagonal structure of $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ was also observed on the HOPG substrate (Qiu et al., 2000b).

Although $c(9 \times 5\sqrt{3})\text{rect}$ and $(5\sqrt{3} \times 5\sqrt{3})\text{R}30^\circ$ structures of $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ molecules seen in Figures 3 and 5 were stable toward prolonged STM imaging, they varied with the alternation of potential. In particular, they prevailed between 0.2 and 0.6 V, but switching the potential to more positive or negative values caused marked changes of the structure of the adlayer. For example, when the potential was held at a potential lower than 0.2 V, the well-ordered arrays of $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ molecules became smaller and smaller until all admolecules desorbed from the Au surface. When the electrode potential was set more positive than 0.6 V, the highly ordered arrays became unclear, and this might be due to the oxidation or a structural change of $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ admolecules at very positive potentials.

The interplay between intermolecular interactions and molecule–substrate interactions determines the thermodynamics and kinetics of the assembling of organic molecules on surfaces (Forrest, 1997). Minimization of surface-free energy is most influential to the

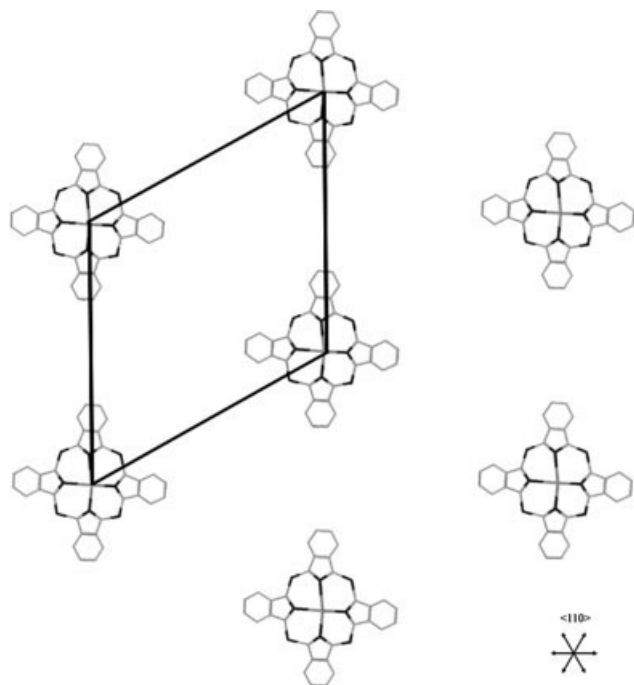


Fig. 6. Proposed model of Pc cores of $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ adlayer on the Au(111) surface superimposed with $(5\sqrt{3} \times 5\sqrt{3})\text{R}30^\circ$ unit cell.

structure of the molecular adlayer. For example, if the molecule–substrate interaction is relatively weak, optimization of intermolecular interaction then dominates the final molecular arrangement. This situation is proven to be beneficial to the monolayer growth of a molecular film. In contrast, a relatively strong molecule–substrate interaction tends to guide the adsorption of molecules in registry with the substrate lattice. In this situation, the structure of an admolecule could subject to distortion to a state different from that of a free molecule. In the case of $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ on Au(111), the molecule–substrate interaction was mainly the van der Waals interaction between the conjugated Pc core and the gold surface, with a marginal enhancing effect from the surrounding alkyl chains. The formation of a square-like molecular array of $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ on Au(111) is indicative of the relatively weak molecule–substrate interaction of this system, as in the case for copper phthalocyanines on graphite and MoS_2 , wherein the molecule structure in the adlayers had less distortions of symmetry from its bulk structures (Collins et al., 1992; Ludwig et al., 1994). Meanwhile, the hexagonal arrangement of $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ might result from compromised interactions to achieve the best fit with the underlying threefold symmetric lattice, where the flexible alkyl chains would have translated and rotated. This was similar to the case of epitaxial growth of copper phthalocyanines on the semiconductor surface (Cox et al., 1999).

CONCLUSIONS

Immersion of an Au(111) substrate into a benzene solution containing $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ yields well-ordered adlayers of $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ on the Au(111) surface.

Packing arrangements and even the internal structure of each $\text{CuPc}(\text{OC}_8\text{H}_{17})_8$ admolecule are determined by in situ STM in aqueous HClO_4 . Molecular adlayers with square and hexagonal symmetry, identified as $c(9 \times 5\sqrt{3})\text{rect}$ and $(5\sqrt{3} \times 5\sqrt{3})\text{R}30^\circ$ are produced simultaneously.

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