

## Structures of Self-Assembled Monolayer of Squaraine Molecules Adsorbed on Highly Oriented Pyrolytic Graphite and Au(111) Substrates

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Molecular arrangements of squaraine (SQ) molecules formed on highly oriented pyrolytic graphite (HOPG) and Au(111) substrates in phenyloctane solution were studied by scanning tunneling microscopy (STM). On HOPG, SQ molecules without hydroxyl groups formed row arrangements, in contrast to the herringbone structures previously observed for the SQ molecules with hydroxyl groups, indicating that the chemically added hydroxyl groups play an important role in the formation of the herringbone arrangement. On the other hand, the observed molecular structures on the Au(111) substrate were completely different from those on the HOPG substrate, which was attributed to the specific interactions between the two anilino moieties in a SQ molecule and Au(111) lattices. The obtained results indicate the possibility of structural control of SQ molecules, namely, the photo-absorption property, by changing the kinds of functional groups and substrates.

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### 1. Introduction

Development of the organic optical devices is one of the main goals of current researchers. Among the many organic materials, which have been studied to realize this purpose, squaraine (SQ) molecules (Fig. 1) are interesting because of their highly potential optical characteristics.<sup>1)</sup> Since SQ molecules are photoconductive and show a narrow-band photoabsorption property with high efficiency, i.e., molar extinction coefficient of  $3 \times 10^5 \text{ cm}^{-1} \text{ M}^{-1}$ , they are of great importance in industrial applications such as optical recording media.

The two amine groups on the both sides and the central four-membered ring ( $\text{C}_4\text{O}_4$ ) of a SQ molecule work as electron donors and an electron acceptor, respectively. The donor-acceptor-donor (D-A-D) structure in a SQ molecule induces an intramolecular charge transfer (CT). According to the theoretical studies, intramolecular CT occurs in the photoexcited state as well as in the ground state.<sup>2)</sup> Moreover, since excited electrons are transferred from oxygen atoms to the central  $\text{C}_4\text{O}_2$  unit, SQ molecules in the excited state show a higher localized electronic state compared to the ground state. This localization of the electronic transition plays an important role in the optical characteristics of this material.

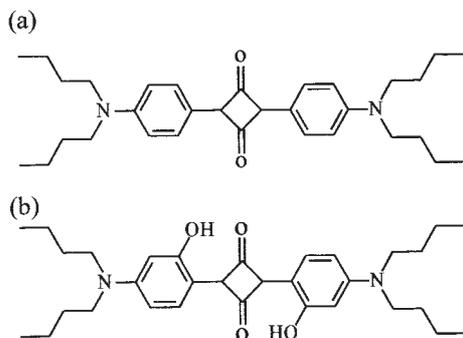


Fig. 1. Schematic molecular structures of bis(4-dibutylamino-2-phenyl)squaraine (SQ) molecule with (a) and without (b) hydroxyl groups.

Recently, fabrication of SQ molecules by the Langmuir-Blodgett (LB) technique has been studied extensively.<sup>3,4)</sup> During photoillumination, an apparent photocurrent was observed, and the high potential of the SQ molecule as a thin organic solar cell was clearly shown. These results accelerated the study of novel SQ interface systems to achieve the development of molecular devices such as photoconductive wires and photodiodes, which has become one of the most attractive trends in the molecular electronics researches. However, a remarkable point is that the observed photo-absorption property crucially depends on the molecular arrangement of the SQ molecules. Therefore, detailed understanding and control of the molecular arrangement of the interface is urgently needed to realize the development and optimal control of those novel SQ interfacial systems.

According to the scanning tunneling microscopy (STM) study of the molecular arrangement of SQ derivatives with short alkyl tails adsorbed on highly oriented pyrolytic graphite (HOPG),<sup>5)</sup> the molecules formed a herringbone arrangement, and no ordered structure was formed in relation to the symmetry of the HOPG lattice. Therefore, it was concluded that the SQ-HOPG interaction was weak compared to the SQ-SQ interaction induced by the intermolecular donor-acceptor CT in a molecule. However, since the SQ molecule used in the experiment was chemically modified with hydroxyl groups added onto the benzene rings as shown in Fig. 1(b), not only Coulomb force but also hydrogen bonding between hydroxyl groups must have played an important role in the formation of the herringbone structure. Therefore, first of all, study on the SQ molecules without hydroxyl groups is necessary.

In addition, it is also important to understand the SQ-substrate interactions as well as the SQ-SQ interaction to control the SQ molecular arrangement for the future development of optical devices. For example, SQ molecules on a Au substrate may form an arrangement different from that on a HOPG substrate, through the interactions between the amine groups in the SQ molecule and the lattice of the Au substrate.

In order to establish the potential of the SQ molecular interface system, we studied SQ-substrate and SQ-SQ interactions by changing the substrate and SQ derivative.

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First, an SQ molecule without hydroxyl groups was used in order to clarify the effect of the hydrogen bonding interaction between SQ molecules. Secondly, a Au(111) substrate was used to examine the influence of the substrate upon the molecular arrangement of the self-assembled monolayer SQ molecules.

## 2. Experimental and Results

Figure 1(a) shows the molecular structures of the bis(4-dibutylamino-2-phenyl) squaraine (SQ) molecule used in this study. The SQ molecules used in the previous study were chemically modified with a hydroxyl group added onto each benzene ring as shown in Fig. 1(b). On the other hand, there is no hydroxyl group in the case of our SQ molecules (Fig. 1(a)). HOPG and atomically flat Au(111) surfaces were used as substrates. Au(111) substrates were prepared by vapor deposition of approximately 75-nm-thick Au films onto freshly cleaved mica sheets. During the Au deposition, the temperature of the mica substrates was kept at 400°C. The deposition rate was 0.8–1.0 Å/s and the vacuum pressure was maintained below  $8.0 \times 10^{-4}$  Pa. Following the deposition, the mica substrate were annealed at 400°C for 1 h. Brief flame-annealing was performed before each experiment. After confirmation of the substrate surface structure in a fluid cell, 1 mM phenyloctane solution containing SQ molecules was introduced into the cell. Mechanically cut Pt/Ir wire was used as a STM tip. All images could be acquired in the solution as in air, indicating the possibility of the future investigation of structural control by such as electrochemical techniques and solvent effect.

Figure 2 shows typical STM images of the SQ molecular

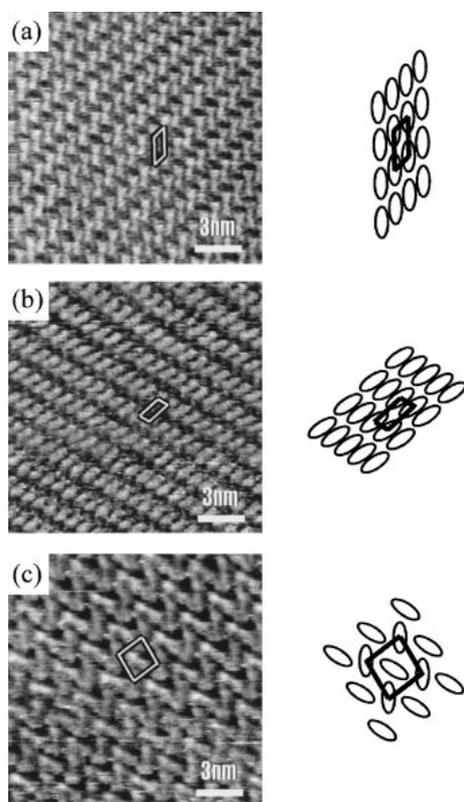


Fig. 2. STM images of typically observed SQ molecular arrangements on HOPG substrate ( $V_s = +1.0$  V,  $I_t = 0.2$  nA) and their schematic models.

Table I. Unit cell data experimentally obtained in this study.

Substrate	Packing structure	Unit cell		
		$a$ (Å)	$b$ (Å)	$\alpha$ (deg)
HOPG	row	$19 \pm 2$	$10 \pm 2$	$46 \pm 2$
	row	$17 \pm 2$	$9 \pm 2$	$73 \pm 2$
	Herringbone	$22 \pm 2$	$20 \pm 2$	$82 \pm 3$
Au(111)	row	$32 \pm 2$	$8 \pm 2$	$90 \pm 2$

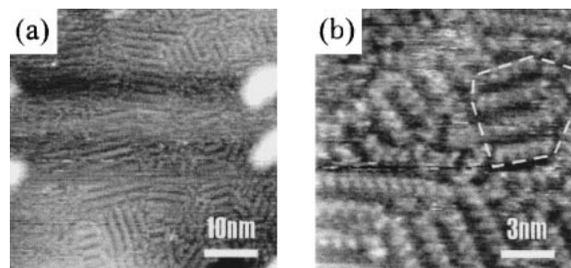


Fig. 3. STM images of typically observed SQ monolayer adsorbed on Au(111) substrate (a) and its magnification ( $V_s = +1.0$  V,  $I_t = 0.1$  nA).

structures on HOPG substrate and their schematic models. In contrast to the previous results,<sup>5)</sup> SQ molecules adsorbed on HOPG substrate formed three different types as shown in Figs. 2(a) to 2(c), namely, two row-type structures ((a) and (b)) and one herringbone-type structure ((c)). The observed unit cells, the data of which are listed in Table I, are schematically shown in the figure.

The row-type molecular arrangements were dominant, and the herringbone-type ones could hardly be observed. These molecular structures were stably observed under the condition of tunnel resistance above 50 GΩ, however, when the STM tip was moved closer to the sample, the molecules became unstable, and the HOPG substrate became visible. From the analysis of the observation, the observed molecular structures were confirmed not as multilayer but as a monolayer.

Figure 3(a) shows a STM image of SQ molecules adsorbed on a Au(111) substrate. The SQ molecules seemed uniformly adsorbed, with their axes parallel to the Au(111) substrate. However, contrary to the ordered homogeneous molecular arrangements on the HOPG substrate, many domains existed, and the molecular arrangements were apparently different from those observed on the HOPG substrate, suggesting that SQ-substrate interaction plays an important role in the case of the Au substrate. Observed lattice constants are also listed in Table I.

## 3. Discussion

### 3.1 SQ molecules on HOPG substrate

As was mentioned, the previous STM result using SQ molecules with hydroxyl groups has shown that there is no lattice matching between the SQ molecules and HOPG substrate, and that SQ-HOPG interaction is not a dominant factor in determining the molecular arrangements.<sup>5)</sup>

According to the previous STM study, SQ molecules with hydroxyl groups form a herringbone structure. The driving force is attributed to the Coulomb force induced by the intermolecular CT between the donor amine groups and

acceptor  $C_4O_2$  ring in a molecule. In contrast to that result, SQ molecules without hydroxyl groups formed rows as shown in Fig. 2, and the herringbone structure could hardly be observed.

To confirm the origin of the interaction resulting in the observed structures, lattice matching between SQ molecules and HOPG lattices was analyzed in detail, in consideration of the  $\pi$  stacking between the two aromatic rings in a SQ molecule and the graphite rings. As a result, the lattice matching could not be found between SQ molecules and the substrate. Thus, SQ-SQ interaction must be dominant compared to the SQ-HOPG interaction in the case of SQ molecules without hydroxyl groups as well as in the case of the previous results obtained for the SQ molecules with hydroxyl groups. Therefore, it is strongly suggested that the existence of hydroxyl groups plays an important role in the formation of the herringbone structure. However, in consideration of the row structures, hydrogen bonding between adjacent molecules is possible even in the row arrangements. Then, the observed difference may arise from the change in the electronic structure induced by the modification of hydroxyl groups instead of the effect of simple hydrogen bonding. In the case of inclusion complexes, effect of the included molecular dipole on the modification of the hydrogen bonding interaction has been reported.<sup>6,7)</sup>

Further experimental and theoretical studies are necessary to understand this effect. However, in any case, we have revealed that the existence of hydroxyl groups, namely, the modification of the molecule, crucially influences the SQ molecular arrangement.

### 3.2 SQ molecules on Au(111) surface

As shown in Fig. 3, the domain structures of the SQ molecules on the Au(111) surface were observed, and the molecular arrangements were completely different from those on HOPG. The molecular rows in the domains were almost in good agreement with the three fold symmetry of the underlying Au(111) substrate. Figures 4(a) and 4(b) show a magnified STM image of the typically observed row structure and its schematic model. Molecules in the alternatively arranged rows are tilted from the row axes as  $79 \pm 2$

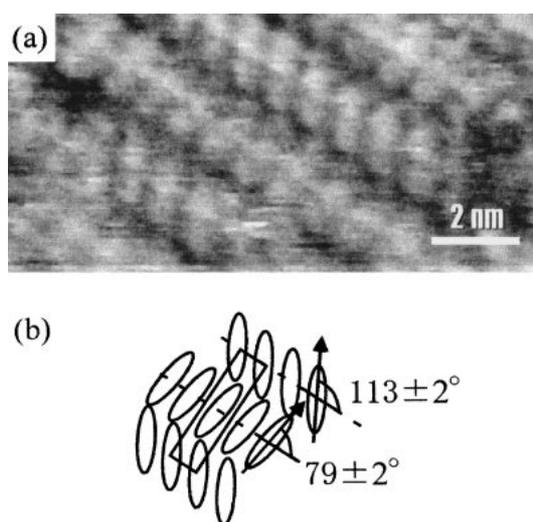


Fig. 4. (a) High-resolution STM image of SQ molecules adsorbed on Au(111) substrate. (b) Schematic model for the structure in (a).

and  $113 \pm 2^\circ$ , respectively, as shown in the schematic model. To clarify the commensuration of the structure with the substrate, we analyzed the lattice matching between the SQ molecules and Au(111) substrate.

Since nitrogen atoms are expected to interact with the Au(111) substrate,<sup>8-10)</sup> the specific interaction between the amine group in a molecule and the lattice structure of the Au substrate was considered. The top, bridge and hollow sites shown in Fig. 5 were considered as the three candidates for the adsorption sites. As shown in the upper part of Fig. 5, the two amine groups in a SQ molecule have a good lattice matching with the Au(111) substrate lattice for all the three adsorption models. Also, as indicated by the arrows in the lower part, there exist many similar matching relationships between the SQ molecules and each lattice structure. However, among the three models, only the hollow site model reproduces the lattice constant and tilt angles of the molecules observed in the STM images.

The molecular packing structure of the hollow site model is shown in Fig. 6. As shown in Fig. 6, the tilt angles of

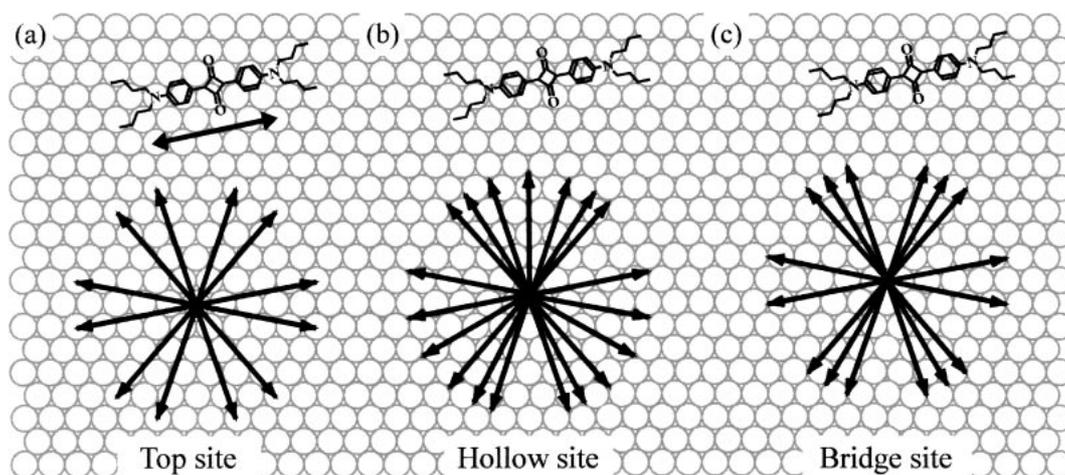


Fig. 5. Positional relationships between SQ molecule and Au(111) substrate for three different adsorption sites of (a) top, (b) hollow and (c) bridge sites. Figures in the upper side show the lattice matching between the two amine groups in the SQ molecule and Au lattices for each model. The arrows in the lower side show the possible lattice matchings.

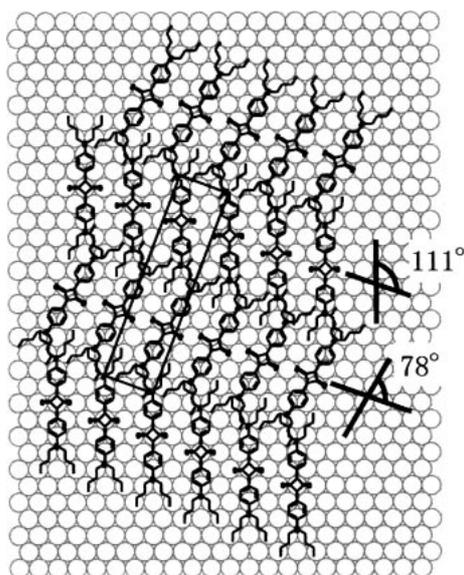


Fig. 6. Proposed molecular packing structures adsorbed on the hollow site.

molecules related to the molecular rows,  $78^\circ$  and  $111^\circ$ , and the lattice constants of  $a = 32.2 \text{ \AA}$ ,  $b = 7.7 \text{ \AA}$ , and  $\alpha = 90^\circ$  are in good agreement with the experimentally obtained values.

Domains with SQ molecules arranged in rows seem different from the three fold symmetry axes as shown by the white dotted area in Fig. 3(b). However, since there are many possible molecular directions to induce the lattice matching as shown in Fig. 5, these structures can also be reproduced well by the hollow site model.

As is well known, molecular arrangement depends on the balance between molecule-molecule and molecule-substrate interactions. In this case, no etch pit structures were observed, suggesting a weak coupling of electronic structures between SQ molecules and Au substrate. However, existence of the lattice matching indicates the clear effect of the molecule-substrate interaction. As the modulation of the interactions by modifying the surface electronic structure by adsorption of other atoms<sup>11,12</sup> or applying electrochemical potential has been reported,<sup>8,9</sup> Au surface is more controllable for the practical arrangement of the adsorbed molecules. Since the optical properties of SQ molecules crucially depend on the molecular arrangement, future development of this material as an organic optical device is expected. Further experiment is now in progress.

#### 4. Conclusion

Molecular arrangements of SQ molecules formed on HOPG and Au(111) substrates in phenyloctane solution were studied by STM. On HOPG substrate, SQ molecules without hydroxyl groups formed row arrangements, in contrast to the herringbone structures previously observed for the SQ molecules with hydroxyl groups, indicating that the chemically added hydroxyl groups play an important role in the formation of the herringbone structure. On the other hand, the observed molecular structures on the Au(111) substrate were completely different from those on the HOPG substrate, which was attributed to the specific interactions between the two amine groups in a SQ molecule and Au(111) lattices. With consideration of the lattice matching between the two amine groups with the three sites, top, bridge and hollow sites, the hollow site model showed the best agreement with the experimental results.

The obtained results indicate the possibility of structural control of SQ molecules, namely, the photoabsorption property, by changing the kinds of functional groups and substrates.

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