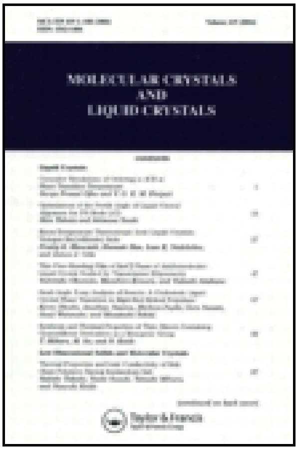

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The Molecular Arrangement of Polar Organic Molecules by Scanning Tunneling Microscope

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THE MOLECULAR ARRANGEMENT OF POLAR ORGANIC MOLECULES BY SCANNING TUNNELING MICROSCOPE

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Abstract The scanning tunneling microscope (STM) was utilized to observe the molecular images of a newly synthesized liquid crystal, 6-(dodecyloxy-phenyl)-3-chloropyridazine (DOPCP), which contains two kinds of electric dipoles directed parallel as well as perpendicular to the molecular axis. The sample adsorbed on the graphite substrate showed the interdigitated double rows structures with a singular repeating unit composed of five molecules. Also, the appearance of several different STM images suggests that the electric interaction induced from the electric dipoles and van der Waals force influences greatly on the structure formation in this polar molecule.

INTRODUCTION

Recently, the STM has been applied to observe directly the molecular aggregate structures of several organic materials.[1-3] Especially, the liquid crystals of n-alkyl cyanobihenyl (*m* CBs; where *m* is the number of carbons in the alkyl group) have been extensively investigated and revealed to show various STM images depending on the kinds of substrates and the length of the alkyl chains.[4-10] So far, two different molecular structures of single-row and double-rows structures have been reported for the *m* CB molecules. In a previous study,[11] we examined a newly synthesized polar molecule, DOPCP, which contains the electric dipole along the molecular axis, and got slightly different STM images, named "interdigitated double rows structure", with the molecular packing much denser than the *m* CBs. Moreover, a computer simulation image revealed the molecular arrangement, which agreed well with the observed STM image.

In this study, the STM observation was conducted on an another newly synthesized (DOPCP) molecule, which contains the electric dipole moments perpendicular as well as parallel to the molecular axis, in order to study in detail the role of an electric interaction upon the formation of the molecular structures.

EXPERIMENTAL

Sample

An examined sample of DOPCP is the organic molecule of newly synthesized liquid crystal with the molecular formula of $C_{12}H_{25}O$-C_6H_4-$C_4N_2H_2$-Cl, which was kindly supplied by Prof. Taniguchi's research group of Kyushu university. As shown in Fig.1, this molecule consists of pyridazine and benzene rings, alkyl chain and Cl atom at its end. The molecule has the electric dipole moment directed perpendicularly to the molecular axis, existed in the pyridazine ring, in addition to that along the

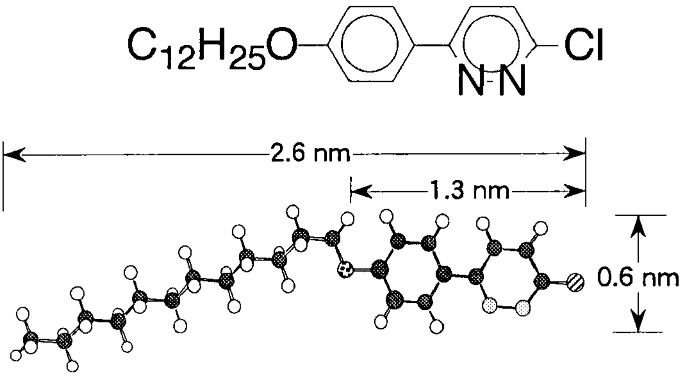

FIGURE 1 Crystal structure of DOPCP molecule.

molecular axis. This molecule has a molecular length of 2.6nm, exhibits a liquid crystalline phase in the temperature range between 122 and 147 ℃, and crystallizes into a whisker form.

Sample Preparation

The sample preparation is a very important part to get fine STM images. Therefore, we have tried various method including a solution casting, a spin coating, and a vacuum evaporation methods. Empirically, we learned that the following vacuum adsorption method is the most suitable one to get the best sample as thin as a monolayer. The sample was prepared using the sample cell shown in Fig. 2, which was installed in a vacuum oven. At the lower part of the cell a powder sample was set, while at the upper part a highly oriented pyrolytic graphite (HOPG) as a substrate was set immediately after its cleavage. First, the interior of oven was filled with a nitrogen gas after evacuation, and the sample cell was heated to the evaporation temperature of about 140 ℃ and kept for 30 minutes. Then, a brass block of 8 cm in diameter and 2.2 cm in thickness was set upon the brass substrate, to which the HOPG was stuck, as a thermal sink. At this moment, the evacuation of the vacuum oven was restarted and the heater was switched off in order to cool the substrate for the sample adsorption. Several trials were made by changing the sample preparation conditions such as the evaporation temperature, keeping time period, and the distance between the sample and the HOPG substrate.

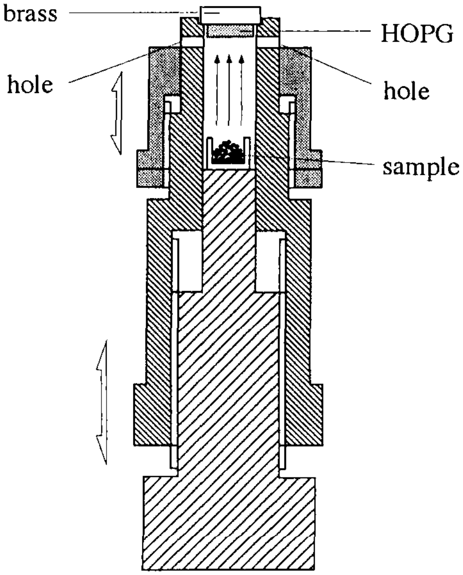

FIGURE 2 Preparation cell for STM sample.

STM Measurements

The STM system used here was the one constructed in our laboratory.[12] A sample chamber was specially designed so as to reduce mechanical, electric and acoustic noises as low as possible, and filled with dry N_2 gas in order to avoid the influence of moisture. The STM images were taken with a constant tunneling current of 100~150 pA and a tip bias of 1.0 V. The time period for getting one flame was 26 seconds. As the image processing with a computer, only a tilting compensation was conducted, but other processing such as fast Fourier transformation were not utilized in order to avoid any distortion of the original images.

The STM measurements were performed for the samples prepared as stated above, which were set in the STM sample chamber. Since the tentative STM examination for the samples revealed that most part are composed of the overlapped layers but a monolayer exists only in limited regions, and so the STM observations were carried out quite many times at various places to get fine STM images from such the monolayer region. Also, it was found that the monolayer region extends two-dimensionally over several tens of nanometers.

RESULTS AND DISCUSSIONS

The STM images obtained here for the DOPCP molecule revealed various features probably due to the slight differences in the formation processes of the molecular aggregates and in the degrees of the interaction between the molecules and the graphite substrates, although the samples were prepared under almost same conditions. In all the STM images, however, the molecules always faced their head groups of pyridazine and benzine rings each other, forming the repeating unit consisted of five molecules.

Figure 3 (a) shows one of the STM images obtained, showing alternating bright and dark rows. These rows have the separation period of about 25-27 nm, which is almost comparable to the molecular length of this DOPCP, about 2.6 nm. The brighter parts in the image are judged to correspond to the positions of pyridazine and benzene rings of a head group, while the alkyl chains are seen as comparatively dark rows. From this image, it is supposed that five molecules form a repeating unit, as

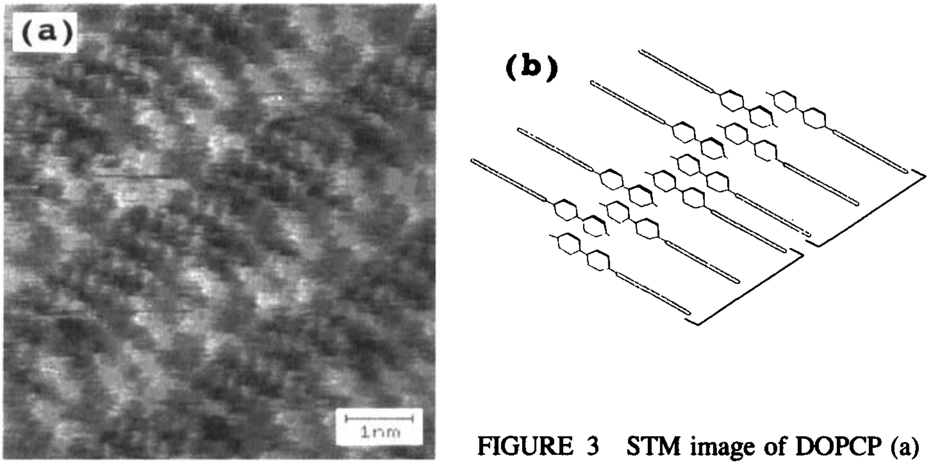

FIGURE 3 STM image of DOPCP (a) and its repeating unit (b). See Color Plate V.

illustrated schematically in Fig. 3 (b).

In the repeating unit, the two and three sets of molecules interdigitate each other, neighbouring their pyridazine rings. The molecules arrange parallel but at slightly slid positions, and form the row with an intersecting angle of about 75° to the molecular axis. The interdigitated double-row structure observed here for DOPCP molecules is the same as the case of DOPPC molecules as reported previously,[11] but the formation of the repeating unit with an odd number, namely 5, molecules seems to be the first case among the STM observations so far reported for organic molecules.

The repeating unit of the five molecules is 2.1 nm, and the separation space of the neibouring molecules is 2.1 nm/5=0.42 nm. This value agrees well with the one observed for the STM image for n-alkane molecules (n-$C_{33}H_{68}$) on HOPG,[13] and is almost comparable with the separation distance (0.426 nm) of the carbon atoms with the same quantum state in HOPG crystal. These facts suggest that the interaction between the alkyl chains in DOPCP molecules and the carbon atoms of the HOPG substrate affects the molecular aggregation of this molecule, and serves as a stabilizing factor of the alkyl chains.

Figure 4 (a) shows an another STM image, which reveals similarly the

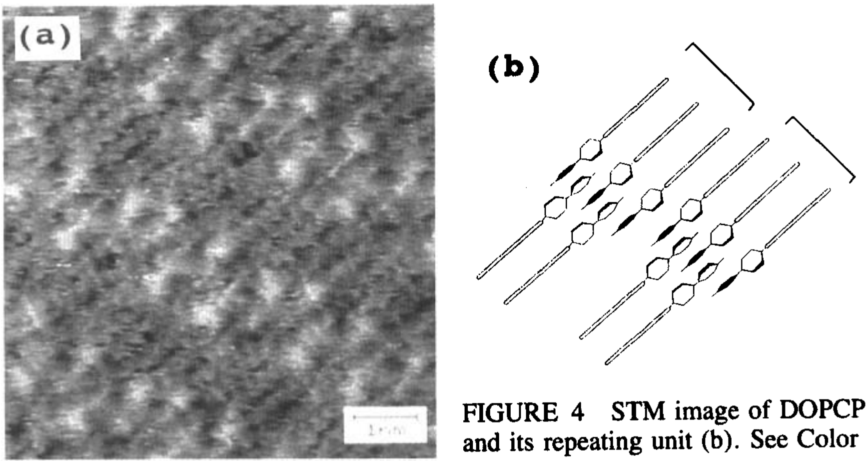

FIGURE 4 STM image of DOPCP (a) and its repeating unit (b). See Color Plate VI.

repeating unit composed of five molecules. In this case, however, the details in the molecular arrangement are slightly different from those in Fig. 3 (a). First, the images corresponding to the pyridazine rings seem rod-like rather than a flat ring, suggesting the rotation of the pyridazine rings around their molecular axis. Second, the sequential arrangement of these repeating units composed of five molecules are not smooth, but rather in step-wise. Similar step-wise arrangements of a group of molecules have been reported for 8CB adsorbed on HOPG by D.P.E. Smith et al.[5,7] and M. Shigeno et al.[9] In this case, the number of the molecules forming the group is an even number of 8, and the molecules form a double-row structure and biphenyl rings always look as a pair of flat rings, revealing the faces of these rings are parallel to the graphite substrate. At present, the reason is not yet clarified why such the step-wise arrangement of a five molecules unit takes place. Although several factors can be simply speculated such that the arrangement may be induced to relax the stresses caused upon the formation of the repeating unit, to compromise the electrostatic interaction between the dipole moments located at the pyridazine rings , and to minimize the total energy of the molecular aggregates upon the graphite substrate, further detailed analysis including a computer simulation is certainly necessary for getting reasonable answers.

So far, two different features for DOPCP molecules were revealed in the

STM images of Figs. 3 (a) and 4 (a). Which feature is more stable in these two molecular arrangements ? If we consider the clearness in the STM images, Fig. 3 (a) seems to reveal more clear images of alkyl chains than Fig. 4 (a). In addition, if we examine in detail the STM image, there exist some pyridazine rings with not only a rod-like shape but also the parallel arrangement. These points may imply that the molecular arrangement shown in Fig 3 (a) is energetically more stable that that in Fig. 4 (a).

Next, the molecular arrangement of DOPCP is discussed form the viewpoint of the electric interaction. As shown in Fig. 5 (a), this molecule contains the electric dipoles along the molecular chain direction from Cl to O atoms and perpendicularly in the pyridazine ring. In order to minimize the interaction energy of the electric dipoles along the chain direction, it is reasonable for the molecules to arrange anti-parallel. While, the dipoles

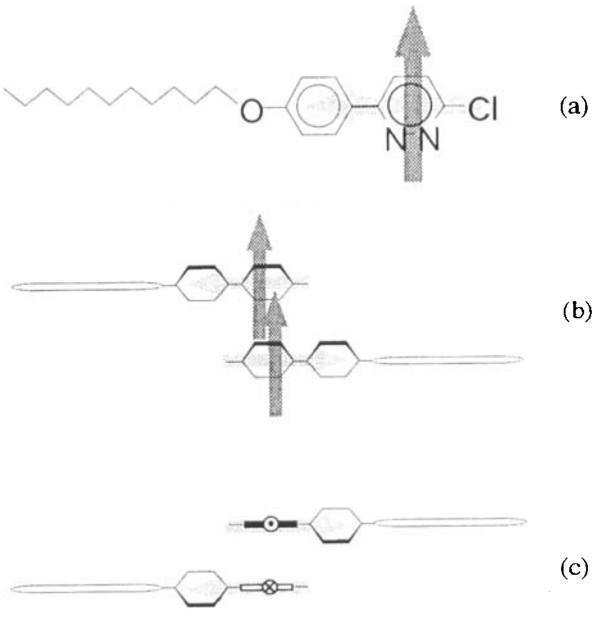

FIGURE 5 Two electric dipole moments in DOPCP molecule (a) and the dipole interaction between neighbouring molecules with different arrangements (b) and (c). and denote that the direction of the dipole moment in a pyridazine ring directs upward and downward, respectively.

belonging to the pyridazine ring will be enhanced by arranging the ring parallel to the substrate and directing the dipole moment into one direction, as schematically drawn in Fig. 5 (b), or will be compensated by rotating the plane of the pyridazine ring respective to that of the benzene ring and arranging the dipole moments anti-parallel, as shown in Fig. 5 (c). Although other arrangements of molecules are supposed to exist, these two arrangements are judged to be probably the most energetically stable ones. Actually, the STM images shown in Figs. 3 (a) and 4 (a) are considered to correspond to the molecular arrangements based on the Fig. 5 (b) and (c), respectively. The computer simulation, as done in a previous paper,[11] will provide further details on this matter, too.

SUMMARY

We observed the STM images of a newly synthesized liquid crystal DOPCP by utilizing the high resolution STM constructed in our laboratory. The observed image showed the molecular arrangement composed of the repeating unit of five molecules. The dipole moments directed perpendicular to the molecular axis existed in the pyridazine ring as well as along the molecular chain was revealed to influence greatly on the molecular arrangements. Two different STM images observed here were understood qualitatively by considering these electric interaction between the dipole moments. Also, it was suggested that van der Waals interaction between the alkyl chains in DOPCP molecules and the carbon atoms of the HOPG substrate serves as a stabilizing factor of the chains.

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