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Observation of Liquid Crystal Molecule on Graphite by Scanning Tunneling Microscopy

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Molecules of liquid crystals(LCs) adsorbed on highly-oriented pyrolytic graphite(HOPG) were imaged by scanning tunneling microscopy(STM). Planar layer structures induced by the HOPG surface were obtained. Molecular packing models for the STM images are introduced with the aid of a molecular orbital calculation. Also we discuss the rearrangement of the LC alignment during the continuous STM measurement.

Keywords: graphite, STM, molecular arrangement, molecular orbital calculation

INTRODUCTION

The substrate alignment of liquid crystals(LCs) is a widely-used technique to produce director configurations in LC display cells. It is supposed that the alignment of LC is induced by the physisorption of LC molecules onto the substrate. It was shown that properties of the adsorbed LC molecules are significantly different from those of the bulk LC.[1–3] They sometimes have a relatively-high order parameter and a relatively-high phase transition temperature, and seem to behave as a crystalline. In order to study the substrate-LC interface, it is effective to observe the adsorbed LC molecules directly. Recently periodic molecular images of LCs on the graphite were observed by scanning tunneling microscopy (STM).[4–6] Structures of the adsorbed LC were obtained with molecular-scale resolution. In this paper, we report various molecular-scale behaviors of LCs adsorbed on the highly-oriented pyrolytic graphite(HOPG). Also the translation of STM images into molecular arrangements is performed with the aid of a molecular orbital calculation.

EXPERIMENTAL

Samples were prepared by applying a drop of LC onto a freshly cleaved and homogeneous surface of the HOPG in air. LCs used for experiment are listed in

TABLE I

Liquid crystals for STM observation

Sample name	Chemical structure	Clearing temp. (℃)
6CB	$CH_3-(CH_2)_5-\langle\bigcirc\rangle-\langle\bigcirc\rangle-CN$	29
7CB	$CH_3-(CH_2)_6-\langle\bigcirc\rangle-\langle\bigcirc\rangle-CN$	42.8
8CB	$CH_3-(CH_2)_7-\langle\bigcirc\rangle-\langle\bigcirc\rangle-CN$	40.5
98P	$CH_3-CH_2-CH(CH_3)-(CH_2)_5-O-\langle\bigcirc\rangle-\langle\bigcirc\rangle-(CH_2)_7-CH_3$	56.3

Table I. The LC was heated above an isotropic temperature and was gradually cooled down to room temperature, about 24°C. The schematic of the apparatus for the STM measurement fabricated by Seiko Instruments Inc. is shown in Figure 1. The STM observation was carried out in air with the probing tip submerged in the LC. The tip was made of mechanically-ground platinum. The variable-current images were converted into videosignals for monitoring and recording successively.[7] The variable-current image provides the tunneling current density passing through the LC molecule which seems to be strongly concerned with the electron density of the LC molecule. The molecular orbital calculation for LC molecule is an effective method for interpretation of the STM image.

The MNDO calculation of the LC molecular orbital was performed using the program MOPAC.[8] The highest-occupied molecular orbital(HOMO) for a free molecule was obtained.

RESULTS AND DISCUSSIONS

Figures 2(a) and 2(b) show the results of the molecular orbital calculation for free 8CB and 7CB molecules, respectively. The HOMO shown in these figures is the curved surface of 0.05 a.u.$^{-2/3}$.

Electrons are concentrated along biphenyl rings and are absent from alkyl chain in the HOMO. Accordingly, it is expected that a higher tunneling current flows through biphenyl rings as compared with the alkyl chain. Figure 3(a) shows the STM image of 8CB. The bright part corresponds to the higher current region and the dark part corresponds to the lower current region, respectively. The long axis of the LC molecule is slightly tilted out of a line perpendicular to the row. The result of the molecular orbital calculation is superimposed on the STM image as shown in Figure 3(b). The bright circle fits perfectly into the high electron density region, *i.e.*, biphenyl rings. Figure 3(c) shows the LC molecular arrangement for 8CB separated from Figure 3(b). The planar layer structure consisting of a 4×2

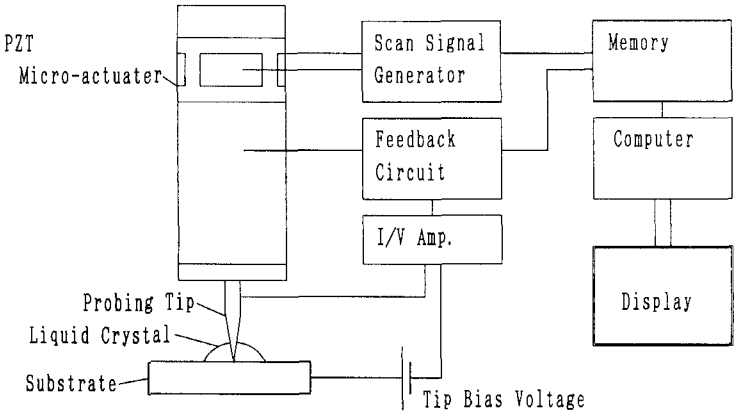

FIGURE 1 Schematic of the apparatus for STM measurement.

unit cell can be seen. Figure 4(a) shows the STM image of 7CB. The molecular pattern differs slightly from that of 8CB. Figure 4(b) shows the LC molecular arrangement for 7CB superimposed on the STM image. The LC molecular arrangement itself is shown in Figure 4(c). In the case of 7CB, the director is almost vertical to the row but molecules are interposed between rows. LC phases of the samples at room temperature are a smectic A phase for 8CB and a nematic phase for 7CB. However, both STM images show highly-ordered structures independent of their bulk phases. The physisorbed LC molecules are condensed on the HOPG surface by interaction between the LC and the HOPG. The difference in the carbon number of alkyl chain causes the change in the interaction or the packing condition. As a result, the different patterns for 8CB and 7CB were observed. The molecular arrangement of 7CB and 8CB was almost unchanged with the tip bias polarity during the STM measurement. It is interesting to note that a reproducible shift in the molecular arrangement of 6CB was observed during the continuous STM measurement. Figure 5(a) and (b) show STM images of 6CB which were taken one minute and four minutes after the tip bias voltage changed from -1.8 to 1.8 V, respectively, during the continuous measurement at the same point. The pattern of the STM image shifts as the time goes. Each corresponding molecular arrangement superimposed on the STM image is presented in Figure 6(a) and (b). The layer structure shown in Figure 6(a) seems similar to 8CB and is composed of a 2×2 unit cell. However, this configuration of molecular packing changes as shown in Figure 6(b). In order to explain the rearrangement of 6CB, we consider the following assumptions. When the tip bias voltage is negative, the tunneling current is disturbed by the external force *ex.* ionic current, *etc.*, and the molecular arrangement can not make any STM images. When the bias voltage is reversed, the external distortion is removed and LC molecules are rearranged on the HOPG to form a stable packing shown in Figure 6(b) via a transient metastable alignment shown in Figure 6(a). 6CB also shows a nematic phase at room temperature but the relatively-low clearing temperature predicts the weak intermolecular force which originates a probability of many metastable molecular arrangements and the unstability at the negative bias voltage. However, 7CB and 8CB have the higher clearing

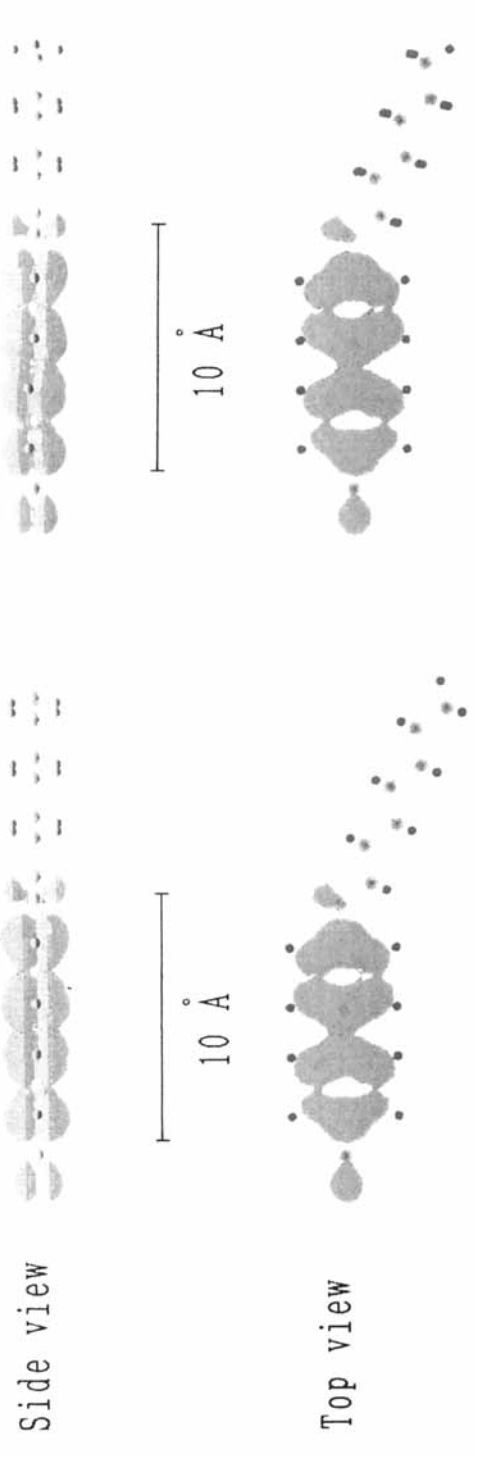

FIGURE 2 Molecular orbital calculations for free molecules; (a), HOMO for 8CB; (b), HOMO for 7CB. See Color Plate VI.

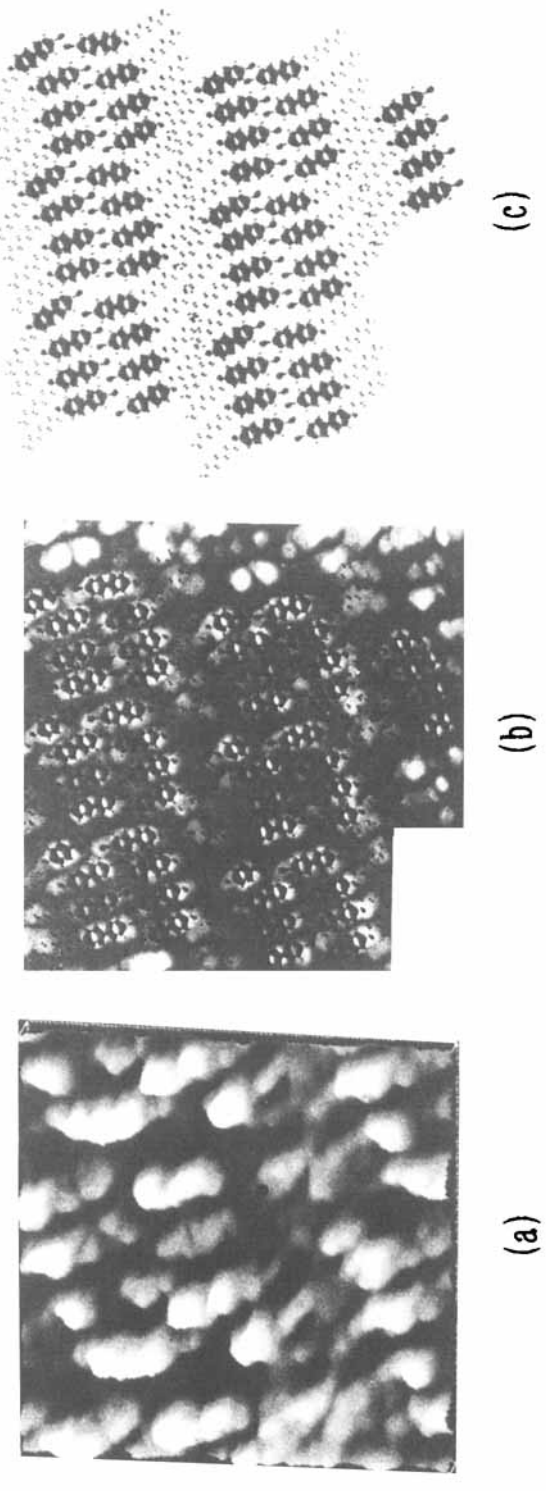

FIGURE 3 (a), STM image of 8CB (area:5×5 nm² tip bias:0.8V tunneling current:100pA); (b), molecular arrangement for 8CB superimposed on the STM image; (c), molecular arrangement for 8CB. See Color Plate VII.

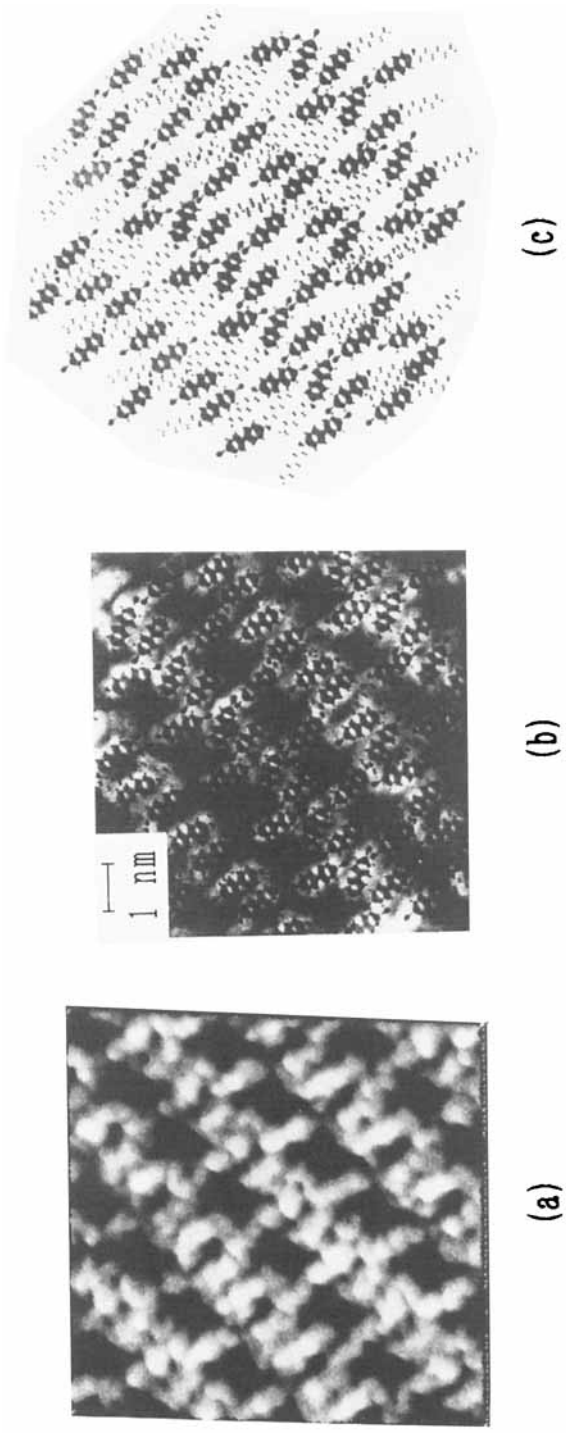

FIGURE 4 (a), STM image of 7CB (area:8×8 nm^2 tip bias:1.9V tunneling current:100pA); (b), molecular arrangement for 7CB superimposed on the STM image; (c), molecular arrangement for 7CB. See Color Plate VIII.

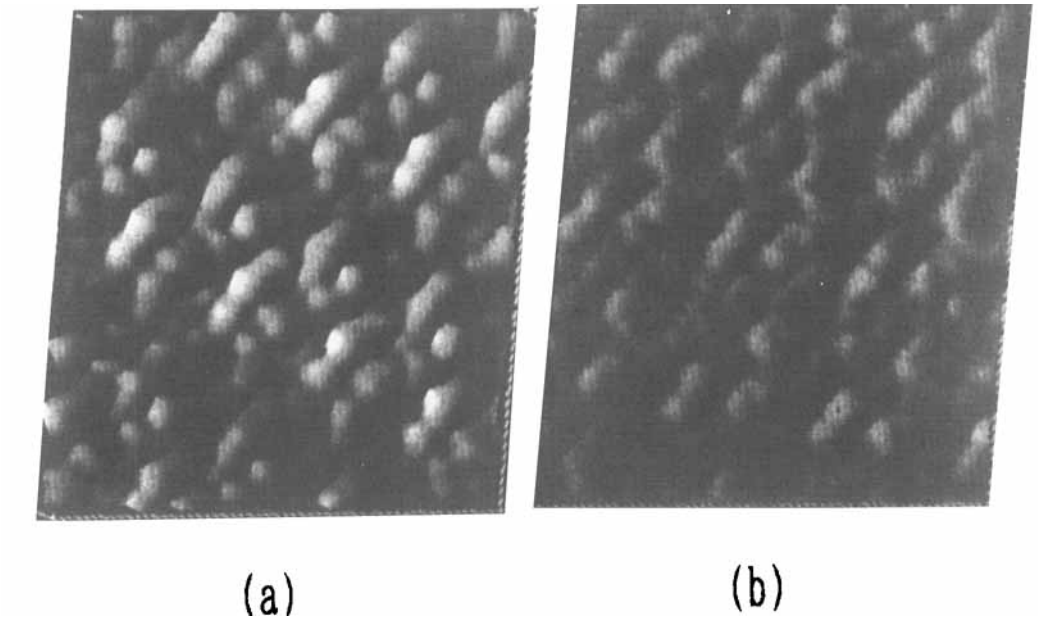

FIGURE 5 Continuous STM images of 6CB (area:7.5×7.5 nm² tunneling current:100pA); (a), observed 1 minute after tip bias changed from −1.8V to 1.8V; (b), observed 4 minutes after tip bias changed from −1.8V to 1.8V. See Color Plate IX.

temperature and the molecules strongly interact at room temperature. The strong intermolecular force makes the rigid structure on the HOPG which is not altered by the affection of the external distortion *ex.* changing the tip bias polarity.

Another example of the molecular rearrangement is shown in Figure 7(a) and (b). When the bias voltage is set at 1.05V, the domain boundary of 98P is obtained as shown in Figure 7(a). The layer structures with a distance of 2.7 nm is bent at the boundary. The gradation of the domain boundary was observed during the continuous STM measurement. After the 200-seconds operation, the boundary shifts to the left as shown in Figure 7(b). 98P has a smectic C* phase at room temperature. It is well known that the smectic C* LC has a bistability on one plane in a thin cell.[9] The molecular orientation is rapidly switched by applying an external electric field with its spontaneous polarization opposite to the electric field. Since the spontaneous polarization is perpendicular to the molecular long axis, the LC can maintain the parallel alignment in both bistable states on the surface. It is possible that the application of bias voltage, the electric field about 10^7V/cm, induces the rearrangement of the molecular orientation. However, the movement is remarkably slow as compared with a well-known smectic C* LC cell and was not observed in other uniform and homogeneous domains. The strong LC-HOPG interaction possibly prevents from the response to the external stimulation. The deformation occurs and proceeds gradually in the domain boundary where the anchoring of LC molecule weakens. In the case of *m*CB, the external electric field introduces a homeotropic alignment which is unstable on the HOPG. If the LC-

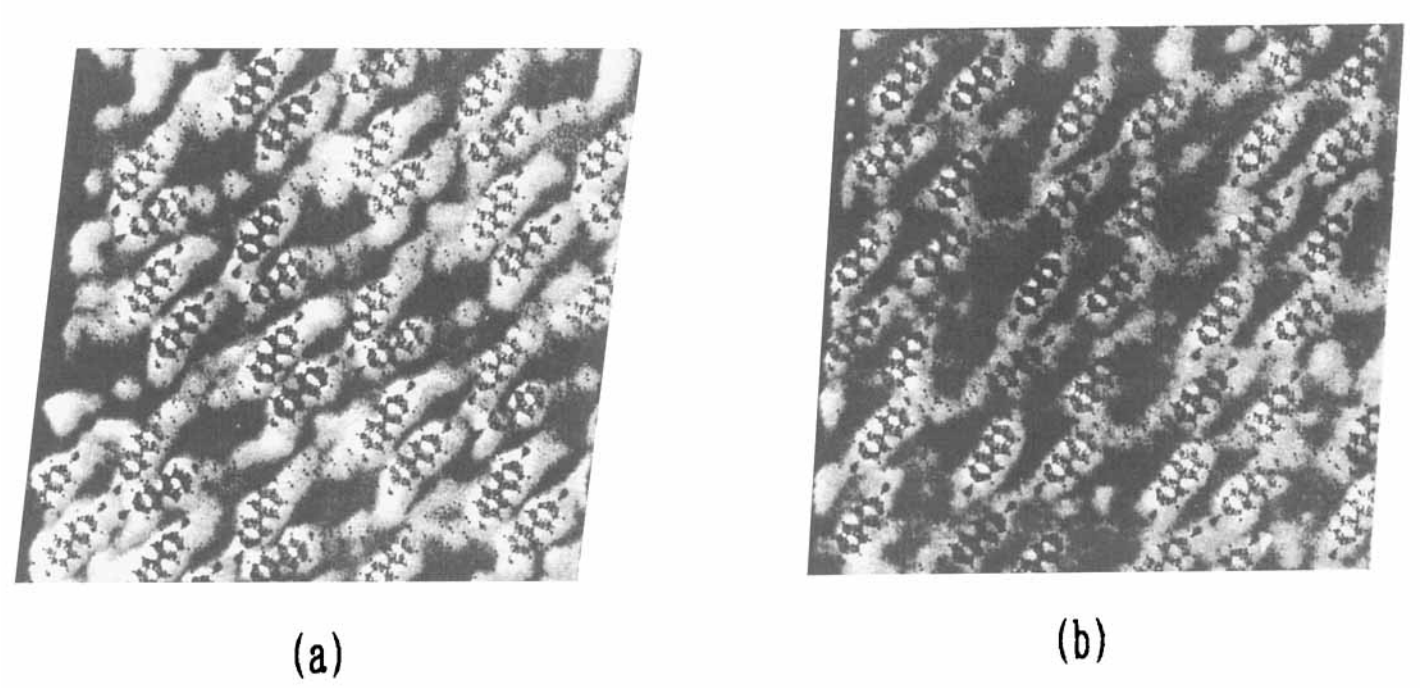

FIGURE 6 Molecular arrangements for 6CB superimposed on Figure 5(a) and (b); (a), corresponding to Figure 5(a); (b), corresponding to Figure 5(b). See Color Plate X.

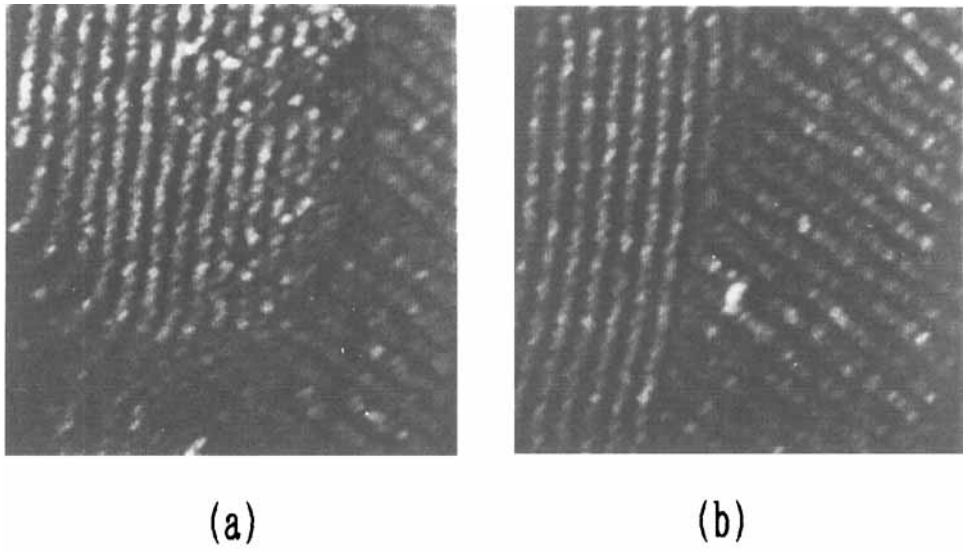

FIGURE 7 Continuous STM images of 98P, (area:50×50 nm² tip bias:1.05V tunneling current: 100pA); (a), originally observed; (b), observed after 200 seconds. See Color Plate XI.

HOPG interaction is stronger than the external forces, the homogeneous arrangement will be kept on the surface as previously presented.

CONCLUSION

The molecular arrangements of *m*CB and 98P LCs were observed by STM on the HOPG. The adsorbed *m*CB LC molecules are arranged on the HOPG to be a condensed phase as a crystalline under the influence of the carbon number of alkyl chain. The calculation of the molecular orbital proves a homogeneous alignment with the biphenyl rings approximately parallel to the HOPG surface in *m*CB LC. In the case of 6CB, the transient metastable arrangement was also observed. The study of the continuous STM image in 98P indicates that the rearrangement of molecular orientation is induced by the electric field of bias voltage.

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