Surface Structures of a Ferroelectric Liquid Crystal on Graphite observed by Scanning Tunnelling Microscopy

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Scanning tunnelling microscopic observation of a smectic liquid crystal of $(S)\text{-C}_{10}\text{H}_{21}\text{O–C}_6\text{H}_4\text{–C}\equiv\text{C–C}_6\text{H}_3\text{F–CO}_2(\text{CH}_2)_3\text{CH(Me)Et}$ on graphite strongly indicates two possible surface structures of the material; a surface stabilized flat monolayer with a fixed molecular orientation and a helicoidal structure in which the molecules are tilted in different directions from layer to layer.

Scanning tunnelling microscopy (STM) has been successfully applied to the studies of several liquid crystals.[1—4] In this work STM has been used in studying the surface structures of a ferroelectric liquid crystal phase of (*S*)-4-methylhexyl 4-[4-(decyloxy)phenylethynyl]-2-fluorobenzoate (MDOPEFB)[5] which forms the smectic C* phase at room temperature.

The structures and properties of ferroelectric liquid crystals are studied mainly in relation to their application as display materials.[6,7] In the bulk of an Sc* liquid crystal, the molecules are aligned in one direction within a layer at a fixed tilt angle from the layer normal, but the tilt direction rotates on moving from layer to layer (a helicoidal structure).[6—8] However, as Clark and Lagerwall suggested,[9] molecular orientation can be fixed in thin cells and controlled with an electric field. On solid surfaces, too, the molecules may align themselves all in one direction if the effect of surface stabilization is large enough. Therefore, two different surface structures are possible for a liquid crystalline material.

The molecular structure and the size of MDOPEFB are shown in Figure 1. The phase sequence was obtained by microscopic observation and differential scanning calorimetric measurement.

$$\text{Crystal}\xrightarrow{292.0\,\text{K}}\text{Sc}^{*}\xleftrightarrow[311.3\,\text{K}]{312.3\,\text{K}}\text{S}_{\text{A}}\xleftrightarrow[320.0\,\text{K}]{321.1\,\text{K}}\text{Isotropic}$$

The material was first melted by heating with a hair drier to form a thin layer on the surface of freshly cleaved highly oriented pyrolytic graphite. The STM measurement was performed at room temperature so that the material stayed in the Sc* phase in the bulk. For the STM observation, a Nanoscope II (Digital Instruments) was used in the constant height scanning mode. An electrolytically etched tungsten tip was used as the probe. The tip penetrated the liquid crystal and only the part closest to the graphite surface was imaged.

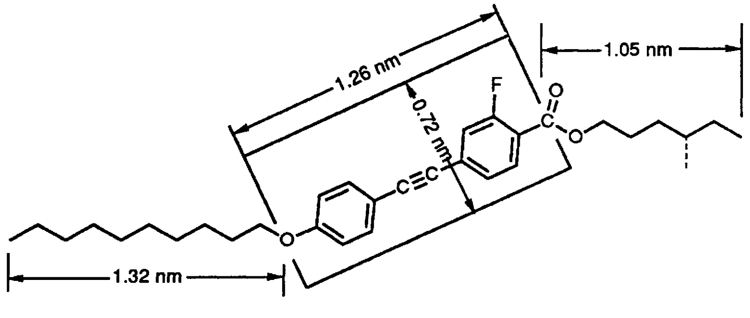

Figure 1. The molecular structure and size of MDOPEFB.

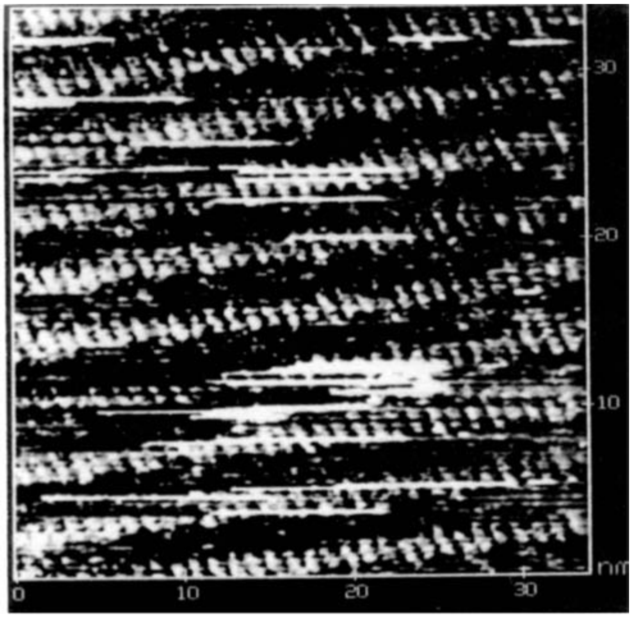

Figure 2. STM image of MDOPEFB on graphite: a 33.8 nm × 33.8 nm top view of a surface stabilized non-helicoidal smectic C* structure. Diphenylacetylenic cores appear as long, bright spots, and the lamellar structure is clearly visible. The bias voltage was +679.3 mV and the setpoint current was 0.30 nA.

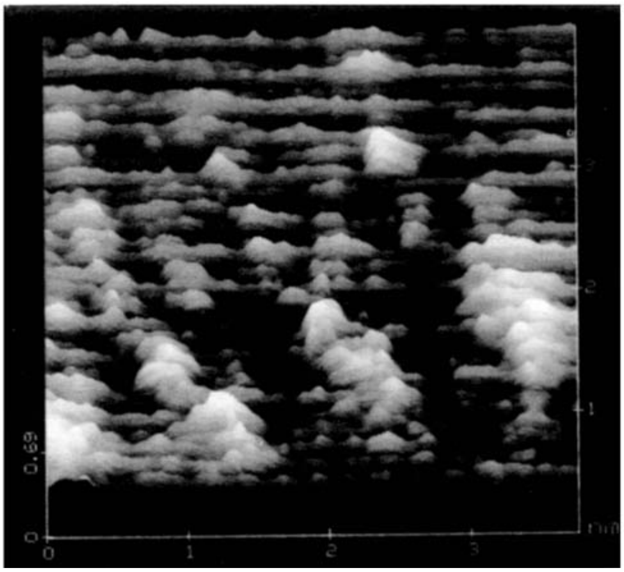

Figure 3. STM image of MDOPEFB on graphite: a 3.75 nm × 3.75 nm oblique view of the interlayer region of the same structure as shown in Figure 2. In the middle of the figure, alkyl chains of molecules in two neighbouring layers are observed with interdigitation (see text). Voltage and current settings as for Figure 2.

The sample potential *vs.* the probe and the setpoint current are indicated in the figure captions.

Figure 2 shows the STM image of a smectic structure obtained for MDOPEFB.† The rigid diphenylacetylenic cores appear as long, bright spots. The lamellar structure is clearly visible. The core images are tilted at an angle of about 22° from the layer normal. No regularity is assumed for the molecular spacing within a layer of Sc* phase in the bulk. However, as observed, the molecules are aligned on the graphite surface with a regular spacing of 1.12 nm, which is much larger than the core width of the molecule shown in Figure 1.

The lamellar spacing observed in Figure 2 is 3.78 nm, about the same as the molecular length calculated for the structure shown in Figure 1. The molecules probably lie flat on the surface in a fully extended form, the phenyl rings having a strong interaction with the graphite surface.

Figure 3 is an oblique view of a further magnified STM image of the interlayer region. The cores of a smectic layer appear at the bottom of the figure. In the middle, alkyl chains of molecules in two layers are observed with some interdigitation, which may be the cause of the large molecular spacing compared to the width of the molecule. However, since the lamellar spacing is nearly equal to the calculated molecular length, interdigitation should not occur on a large scale unless molecular movement is assumed along the molecular axis. A detailed analysis will be necessary to discuss the point further.

Figure 4 shows a more commonly observed STM image of the same molecule on graphite.† In this case the core images look parallel within a layer but the tilt angle is different from layer to layer. This strongly suggests the presence of another surface structure reflecting the helicoidal smectic C* structure of the bulk. In this case the molecular spacing within a layer is smaller than that of the surface stabilized flat structure.

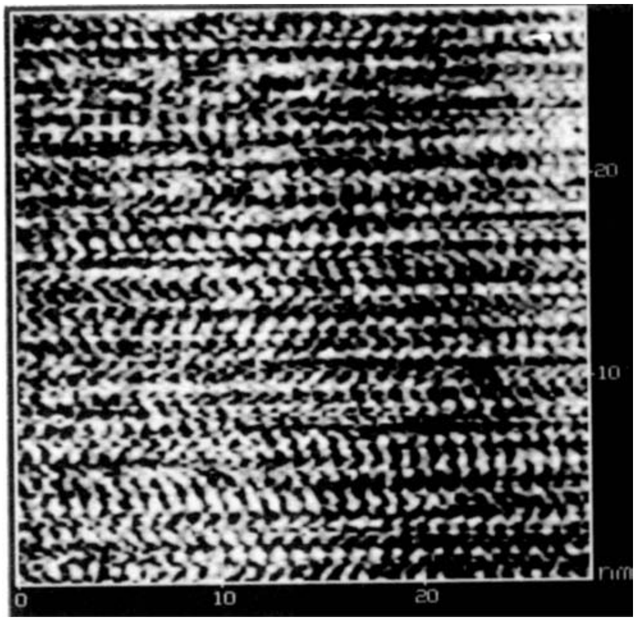

Figure 4. STM image of MDOPEFB on graphite: a 28.1 nm × 28.1 nm top view of a structure reflecting the helicoidal smectic C* structure of the bulk. The bias voltage was +550.2 mV and the setpoint current was 0.23 nA.

It is not yet clear how we can control the degree of surface stabilization and choose between the two different structures. Control of the sample temperature and the bias voltage are expected to be very important. The electric field applied during the STM observation may aid the alignment of the polar molecules. Measurement at a negative potential also

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† The images of Figures 2 and 4 were obtained in separate experiments, although the two structures can be observed for different parts of the same thin layer sample.

gave a vague image of a smectic structure. However, racemic MDOPEFB gave no regular STM patterns.

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