STM Observation of Chiral 1,2-Dihydroxyoctadecane Monolayer Self-assembled on the Graphite Surface

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Chiral 1,2 dihydroxyoctadecane ($C_{16}H_{33}CH(OH)CH_2OH$) self-assembled on graphite surface was observed by STM and the molecular patterns obtained were interpreted by homochiral association of constituent molecules at hydroxyl groups.

Two dimensional (2-D) morphologies of self-assembled molecules are controlled by the intermolecular cohesive forces such as hydrogen bond, electrostatic and van der Waals interactions.[1,2] Monolayers of self-organized molecules have been directly observed at atomic resolution with scanning tunneling microscope (STM) for a wide range of compounds and the resulting morphologies have been discussed with respect to the intermolecular hydrogen bonds.[2,3] Direct observation of chiral assembly of optically active molecules is extremely attractive object from the view point of molecular stereochemistry. Right and left helix hands of epitaxially crystallized syndiotactic polypropylene were observed by atomic force microscopy (AFM).[4] Recently, Walba and his group have obtained the STM images of several chiral mesogens aligned on graphite surface.[5-10] Interestingly, they observed that the pure enantiomer of biphenylbenzoate type mesogen forms a single domain depending on the chirality of constituent molecule, while heterochiral domains are separated from the racemate forming 2-D conglomerate.[7-9] Their observations provided a challenging approach to the goal of "direct detection of molecular chirality".

Since the formation of hydrogen bond network plays an essential role in the process of molecular self-assembly,[2,3] the examination of chiral association can provide useful informations to interpret the chiral morphology. In the present study we communicate the STM observation of chiral 1,2-dihydroxyoctadecane ($C_{16}H_{33}CH(OH)CH_2OH$) monolayer self-assembled at solution-solid interfaces. We discuss here the molecular association responsible for the observed alignment of chiral molecule. Thus, the chiral morphology in macro length scale will be defined by the intermolecular hydrogen bond network either through homochiral or heterochiral association at diol moiety.

Reagent grade of (*R*)- and (*S*)-1,2-dihydroxyoctadecane was purchased from Kankyo Kagaku Center Co. Ltd., and recrystallized from ethanol. The $[\alpha]_D$ values of the recrystallized (*R*) and (*S*)-isomers in ethanol are +9.3° and -9.2° (c 1.0), respectively. The sample crystals were dissolved in phenyloctane to near saturation and a drop of solution was applied on the surface of freshly cleaved highly oriented pyrolytic graphite (HOPG). The STM images were obtained in both constant current mode and constant height mode using Nano-Scope IIIa STM (Digital Instruments). The tunneling tip was a Pt-Ir purchased from Digital Instruments or a tungsten wire which was sharpened by electrochemical etching prior to use.

Edges of multilayers were not observed in any STM images indicating that the observed images are those of monolayers.[11] Figure 1a and 1b show the STM images of monolayer of (*R*) and (*S*)-diol over a scan area of 8 × 8 nm. Like many other hydrocarbon derivatives, the present diol molecules orient parallel to each other forming lamella bands. The distance of the lamella

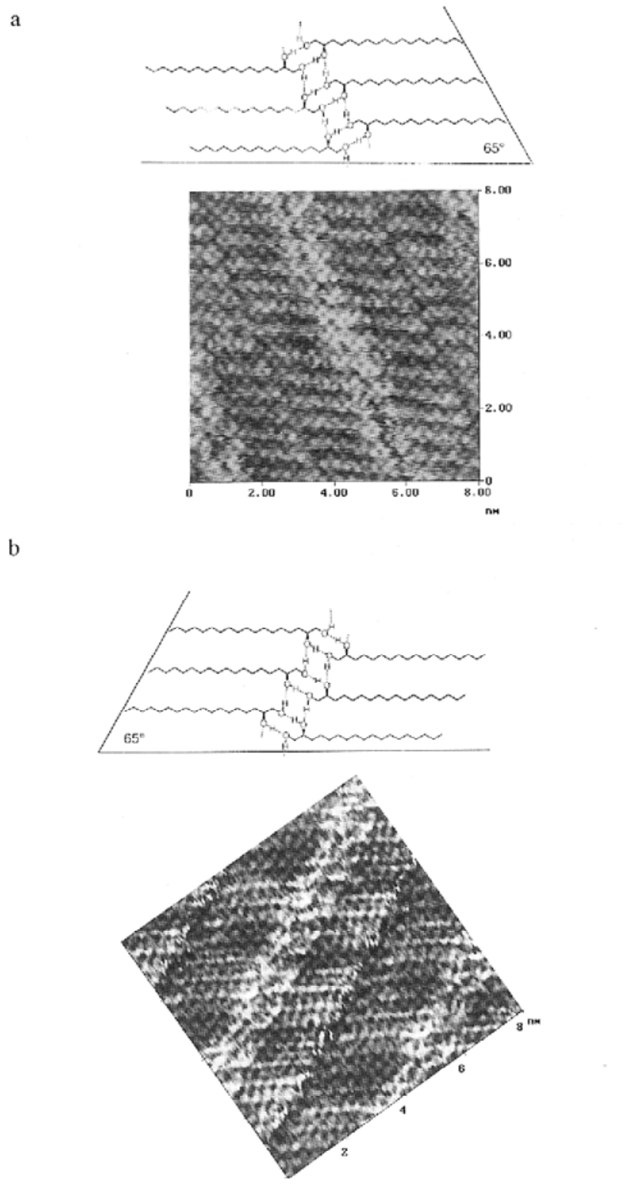

Figure 1. High resolution STM images of (a): (*R*)-1,2-dihydroxyoctadecane monolayer self-assembled on the HOPG surface (Bias: 1246 mV tip positive, set point: 170 pA, Z-range: 0.3 nm, in constant current mode), (b) (*S*)-1,2-dihydroxyoctadecane monolayer self-assembled on the HOPG surface (Bias: 1156 mV tip positive, set point: 298 pA, Z-range: 0.3 nm, in constant current mode) .

band along the molecular axis is around 4.9-5.1 nm, which corresponds roughly double of the molecular length of diol under alkyl chain fully expanded. This indicates that chiral diol molecules in adjacent rows are associated head to head at hydroxyl groups. Therefore the bright part can be attributed to the hydroxyl head group and the dark moiety corresponds to lamella boundary. The molecular axes of the (*R*)-diol are inclined with an angle of 65° with respect to the lamella boundary (Figure 1a). The direction of the lamella bands composed of (*R*)-diol is oriented from left to right toward downward. Although the general appearance of (*S*)-diol molecules is similar to those obtained from (*R*)-diol, the lamella bands are oriented mutually in opposite directions (Figure 1b). Thus pure isomers apparently form enantiomeric molecular patterns to each other. Two distinct morphologies were reproducibly obtained depending on the chirality of constituent molecule in several separated sessions. This means homochiral association of pure enantiomer formed mirror imaged molecular patterns to each other. Then the question arises whether the racemate mixture of enantiomer form 2-D crystal by heterochiral association with (*R*) and (*S*) pair or by homochiral association of diols with pure enantiomer i.e., (*R*,*R*) or (*S*,*S*). Figure 2 shows the STM image of racemate mixture over a scan area of 100 × 100 nm. In this case, the lamella band did not appear straightly but has curvatures in some places. Although the domain boundary is not very clear, racemate mixture appears to segregate into two domains in which the molecular axes are tilt by +65° or -65° against the lamella band. Thus two different domains of pure enantiomers are grown on the graphite surface from racemic solution presumably due to the homochiral association of diol molecules. More than ten times repeated experiments and exchange of the tunneling tips (Pt-Ir or tungsten) always reproduced their own topological features of the domain. Such spontaneous separation has been observed with AFM in LB monolayers[12,13] and with STM for a racemate mesogen.[8]

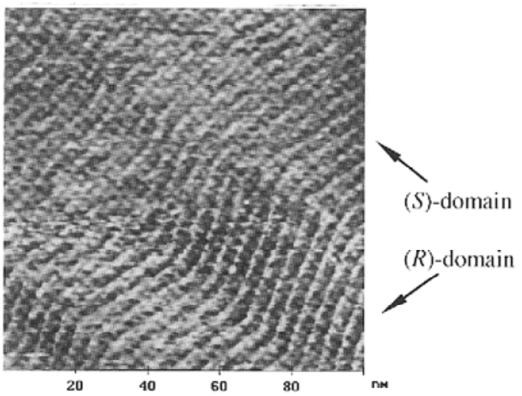

Figure 2. The STM image of racemate mixture of 1,2-dihydroxyoctadecane monolayer self-assembled on the HOPG surface (scan area of 100 × 100 nm, bias: 1780 mV tip positive, set point: 217 pA, Z-range: 0.3 nm, in constant current mode).

It has been suggested that hydrogen bond network between the diol units is responsible for the occurrence of liquid crystalline phases in n-alkane-diol and the related compounds.[14-16] Thereby the hydroxyl groups are organized in polymeric hydrogen bond networks forming parallel sheets.[17] In order to interpret the observed STM images, we have examined the possible models by assuming of intermolecular hydrogen bond network which can link wide range of molecules. Optimized geometry was obtained using molecular mechanics (MM2) implemented on the Tektronix CAChe Worksystem^{TM} loaded on a Power Macintosh 8500/120. Figure 3 shows the top view and side view of a lamella column of (*R*)-diol generated by computer. Although the present molecular mechanics treatment is too simple because the interaction between graphite substrate has not been taken into consideration, the proposed model can reproduce the infinite molecular network and the observed inclination of lamella band. Side view indicates that most of the carbon atoms can stretch nearly horizontally so that they can align flat on the graphite surface. Unlike the homochiral pair (*R*, *R* and *S*, *S*), the model of infinite network by heterochiral association results in mismatching for flat-lying of alkyl chains on graphite surface due to significant deviation from parallel orientation.

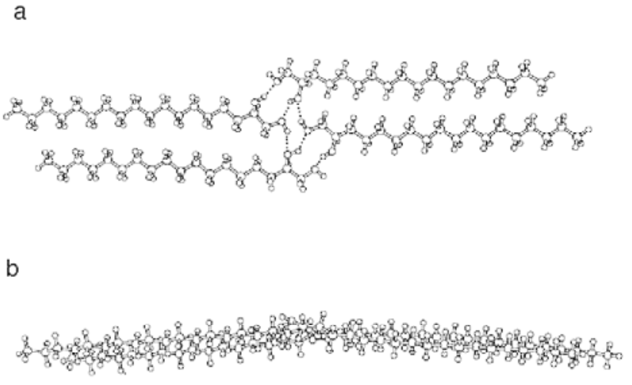

Figure 3. (a) The top view and (b) the side view of a lamella column of (*R*)-1,2-dihydroxyoctadecane generated by computer. Dotted lines show the possible hydrogen bonds between hydroxyl groups.

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