Characteristic Molecular Patterns Formed by *N*-Octadecylbenzamide and *N*-8-Quinolyloctadecanamide Self-assembled on a Graphite Surface

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Self-assembled monolayers of *N*-octadecylbenzamide (ODB) and *N*-8-quinolyloctadecanamide (ODQ) have been observed on the solution-solid interface by scanning tunneling microscope (STM). ODB molecules form stripe shaped lamella structure whereas ODQ gave a mosaic pattern in which four molecular sets are interlocked alternately like jigsaw pieces.

Monolayers of numerous compounds having long alkyl chain(s) including alkanes, amines, alcohols and fatty acids have been directly observed by STM at solution and solid interfaces.[1-4] They form characteristic molecular patterns, which have been interpreted in terms of intermolecular and molecule-substrate interactions.[2,4,5] For example, formation of hydrogen bond networks in amphiphile molecules often plays an important role to define the macro scale morphologies of two dimensional (2D) crystals.[2,6] For the discussion and interpretation of molecular patterns, identification of functional group from the obtained images is essentially important. Conjugated π-systems such as aromatic rings provide a useful "marker" in a molecular image since area of higher electronic conductance appears as brighter spots.[7,8] Furthermore, aromatic ring moiety often controls the molecular alignment mode due to the steric effect of bulky ring as well as the strong interaction with the substrate such as highly oriented pyrolytic graphite (HOPG). In the present study we communicate the STM observation of ODB and ODQ self-assembled at solution-solid interface and discuss the molecular association mode responsible for the observed molecular patterns.

ODB was prepared by the reaction of benzoyl chloride with octadecyl amine. Pure compound was obtained by recrystallization from hexane. Reaction of 8-aminoquinoline and stearoyl chloride gave ODQ. This compound was purified by silica gel chromatography with chloroform as an eluent. ODB or ODQ was dissolved in phenyloctane to near saturation and a drop of the solution was applied on the surface of freshly cleaved HOPG. The STM images were obtained at room temperature (25 °C) either by constant current mode or constant height mode using NanoScope 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.[6]

The STM image of self-assembled monolayer of ODB over a scan area of 100 × 100 nm is given in Figure 1. Well-ordered ODB monolayer forms 2D crystals consist of stripe shaped lamella bands. The bright region can be attributed to the phenyl head group and dark moiety to the alkyl chains. On the basis of lamella band distance, ODB molecules are considered to align head to tail manner in most of 2D crystals, but one can see tail to tail boundaries where the band width appears much larger. Figure 2 shows the high resolution image of ODB molecules over scan area 8 × 8 nm along with the

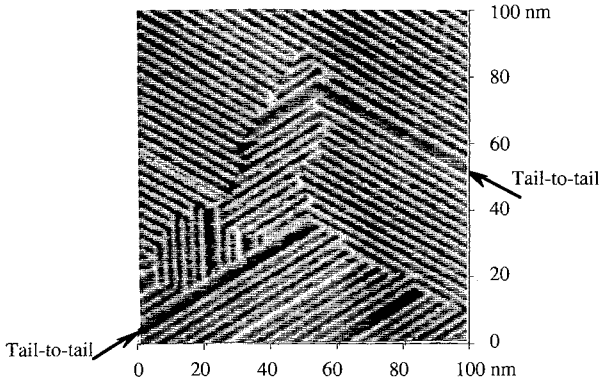

Figure 1. The STM image of ODB monolayer self-assembled on the HOPG surface (Bias: 1.49 V tip positive, set point: 201 pA, Z-range: 0.5 nm in constant current mode).

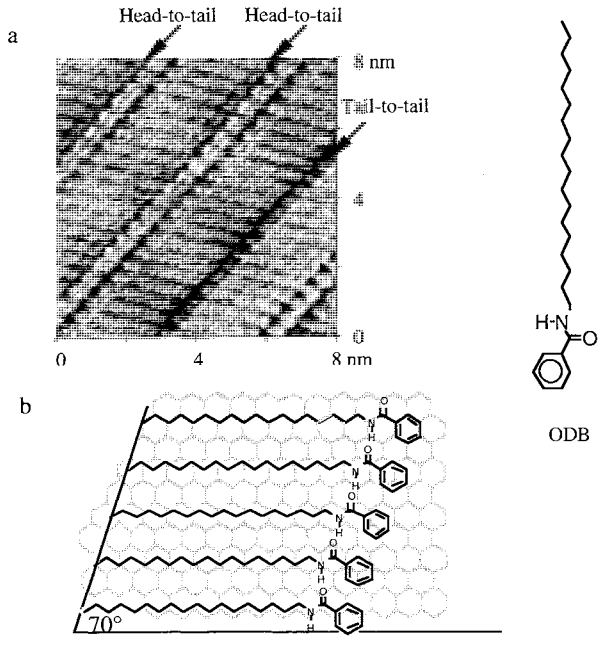

Figure 2. (a) High resolution STM image of ODB monolayer self-assembled on the HOPG surface (Bias: 1.28 V tip positive, set point: 302 pA, Z-range: 0.3 nm in constant current mode). (b) The schematic drawing of proposed molecular arrangement.

schematic drawing of proposed molecular arrangement. We can clearly distinguish the phenyl rings as the head group and alkyl chains as the tail group. Head to tail as well as tail to tail alignments can be observed. The distance between head to tail is ca. 2.7 nm, which is consistent with the molecular length of ODB with alkyl chain fully expanded. The molecular axis of ODB appears to be inclined with the angle of ca. 70° vs. the

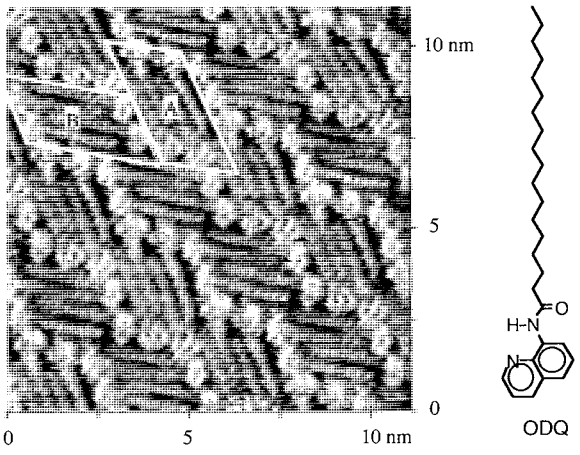

Figure 3. High resolution STM image of ODQ monolayer self-assembled on the HOPG surface (Bias: 1.47 V tip positive, set point: 196 pA, Z-range: 0.5 nm in constant current mode).

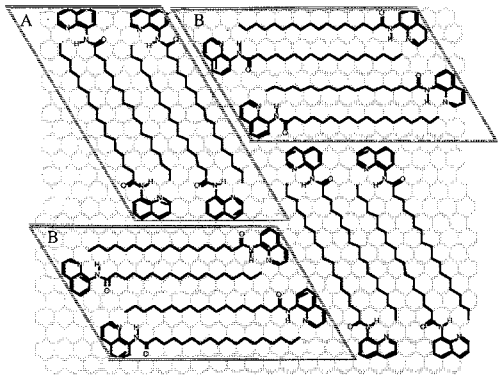

Figure 4. The possible geometry of molecular alignment of ODQ monolayer on the HOPG surface.

orientation of the lamella boundary. This inclination can be interpreted by the formation of hydrogen bond network interconnected at amide groups as illustrated in Figure 2b. The observed image reveals Moiré pattern which can be attributed to mismatch between ODB molecules and the substrate lattice. An enhanced contrast in the image appears with a period of roughly five molecules of ODB.[3,7] The molecular model depicted in Figure 2b can rationalize the periodicity of the observed Moiré pattern.

Figure 3 shows the STM image of ODQ over a scan area of 11 × 11 nm. Remarkably bright quinoline ring and alkyl chain moieties are clearly distinguished by the image. Different from many other hydrocarbon derivatives, ODQ molecules form unusual mosaic pattern in which molecular blocks consist of four sets of ODQ molecules are alternately packed. Thus each molecular block is interlocked like jigsaw pieces with the intersect angle of ca. 60°. This result suggests that ODQ molecules align by the influence of graphite surface where the C-C-C atomic angle is 120°. The possible geometry of molecular alignment is schematically represented in Figure 4, where the graphite substrate acts as template. Four ODQ molecules in each block appear to take an interdigitated geometry, where quinoline head groups alternately point in opposite direction. Unlike the ODB monolayer, bulky quinoline moiety might prevent the formation of hydrogen bond network. The length of ODQ along the molecular axes is roughly 2.9 nm and the separation of alkyl chains is ca. 0.47 nm. These values are consistent with those estimated from the molecular model. It is of note, that the alkyl chains of ODQ in A block and B block (Figure 3) incline different orientation with respect to the long axes of quinoline ring. That is, including graphite sheet, these two molecular units cannot be superposed. Thus, two types of molecular units are mutually mirror image and therefore they are not congruent. Spontaneous segregation of enantiomorphorous domains has been observed in self-assemble of achiral molecules.[7-10] As far as we know, chiral symmetry breaking of the present type where enantiomeric molecular blocks alternately packed is very rare example.

References and Notes

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