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Molecular Structure and Dynamics within Self-Assembled Hexakisalkoxy-triphenylene Monolayers and Alkane Wetting Films

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Adsorption / Interfaces / Liquid Crystals / Scanning Tunneling Microscopy / Wetting

Scanning tunneling microscopy (STM) has been employed to investigate two classes of ultrathin molecular layers on the basal plane of highly oriented pyrolytic graphite (HOPG). First, molecules with three-fold symmetry were studied at solid-fluid interfaces. Structure and dynamics within the first monolayer of hexa-substituted triphenylenes with two different substitutions, $-\text{OC}_7\text{H}_{15}$ and $-\text{OC}_{16}\text{H}_{33}$, could be readily observed, since the molecules exhibit a strong contrast between the triphenylene cores and the alkyl side chains. While the dynamic disorder prohibited atomic-scale resolution imaging, sub-molecular resolution images were suitable to determine packing patterns together with a number of characteristic packing defects. No ordered monolayers could be observed from unsymmetrically substituted triphenylenes like triphenylene dimers, which in bulk materials do only exhibit glassy but no crystalline phases. Secondly, long chain alkanes have been observed, for the first time, in the vicinity of the edge of a solidified alkane-melt drop. The data indicate frozen disordered lamellae at the drop-edge, where the alkane phase is still many monolayers thick, while a columnar phase is found in a thin precursor layer some millimeter away from the drop-edge.

Introduction

Scanning tunneling microscopy (STM) [1] has become an important tool to determine molecular structure, dynamics, and electronic properties at interfaces with molecular materials [2–4]. In particular, monolayers of long chain alkanes and a large series of alkylated molecular moieties with rod-like shapes have been investigated at the interface between their melts or solutions and the basal plane of highly oriented pyrolytic graphite (HOPG) and other atomically flat solid substrates [5–18].

In the present paper, we report on two subjects. First, we present two-dimensional molecular patterns, in which flat molecules with three-fold symmetry may self-assemble at solid-fluid interfaces. While this is an interesting issue from a topological point of view, another interest arises from the fact that as bulk materials the investigated hexakisalkoxy-triphenylenes exhibit discotic liquid crystalline phases [19]. STM may allow to shed some new light on the packing principles and the associated molecular dynamics by observing individual molecules rather than averaging over a microscopic area. Second, we report on molecular structure and dynamics in the vicinity of an alkane-melt drop on HOPG, which was allowed to spread for some time and then quenched to solidify. While the spreading of small liquid drops has been investigated before by, e.g., scanning ellipsometry [20], X-ray reflectometry [21] or surface plasmon spectroscopy [22], the direct observation on the molecular scale is expected to lead to deeper insight.

Experimental

The result reported below have been obtained with a home-built instrument, which together with some experimental procedures has been described elsewhere [9, 10, 13, 23]. A schematic of the experimental set-up is displayed in Fig. 1. The instrument allows STM imaging in-situ at solid-fluid interfaces. It was designed with an emphasis on low currents (as low as 200 fA) and high scanning speeds (up to 100 kHz pixel recording rate). Moreover, a temperature controlled sample stage allows imaging with atomic scale resolution between room temperature and 120°C, which has been used before to observe dynamic order-disorder transitions in monolayers of rod-like molecules [13]. The images were recorded on video tape in real time and digitized later for static image display. In the following, raw data without digital image processing are displayed. All images have been recorded under ambient conditions using Pt/Ir tips, which were either electrochemically etched or mechanically formed. The images have been recorded in the "constant height mode" (displayed is a current profile) at an average current on the order of 1 nA. The tip bias was between +0.7 V and +1.5 V.

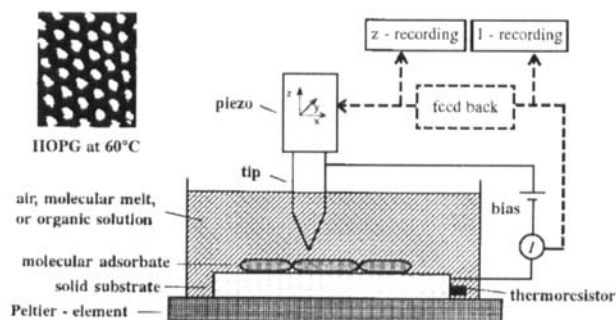


Fig. 1
Schematic of the experimental STM set-up [13]. Inset: Atomically resolved STM image of HOPG in air, recorded at 60°C. Image width: 1.4 nm

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Hexakis-heptyloxytriphenylene (T_7) and hexakis-hexadecyloxytriphenylene (T_{16}) have been synthesized according to a procedure described elsewhere [24,25]. Monomolecular layers were prepared by adsorption at the interface between the basal plane of highly oriented pyrolytic graphite (HOPG, Union Carbide, quality ZYB) and a concentrated but not saturated solution in phenyloctane (Aldrich), as described before [10]. The alkane $C_{30}H_{62}$ (Aldrich, 99%) has been used as received. A molten drop was applied to HOPG and kept horizontally for a few hours. After quenching to room temperatures, STM images were obtained some millimeter away from the drop edge.

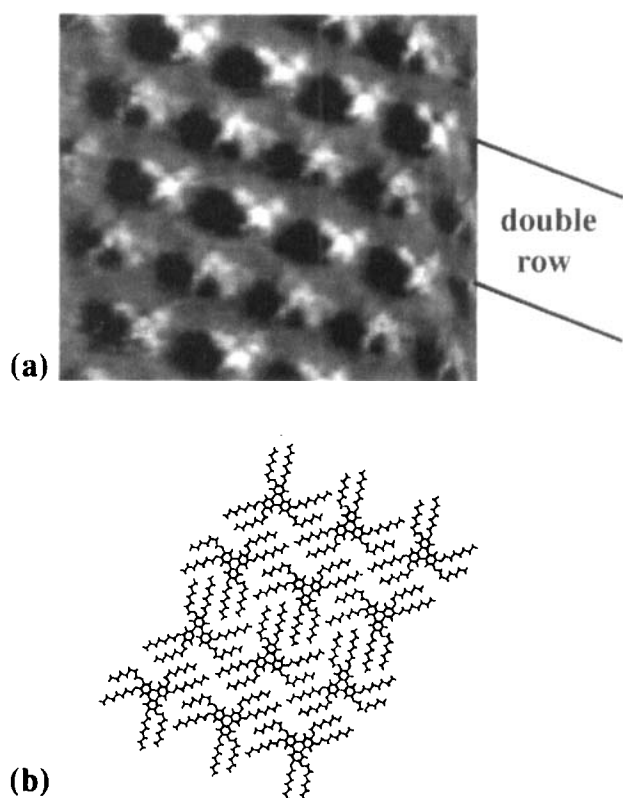


Fig. 2
Hexakisheptyloxy-triphenylene (T_7) monolayer at the interface with a solution and HOPG at room Temperature. (a) STM image. The dark shadow left of the bright triphenylenes is a recording artefact. (b) Corresponding simplified packing model

Results and Discussion

In a first set of experiments the question was addressed, in which way molecules with three-fold symmetry can order in two dimensions. A few preliminary results have been reported recently [16,17]. Fig. 2a displays the STM image of a monolayer of T_7 , adsorbed at room temperature at the interface between an organic solution and HOPG. Clearly visible are the positions of the triphenylene cores, since under the employed conditions the current through aromatic moieties is generally larger than through aliphatic parts [6, 9, 16, 17]. In addition, a substructure is resolved, which shows that the monolayer exhibits a crystalline double row structure within the monolayer plane, in which the orientation of the triphenylenes alternates from row to row. The alkyl side chains could not be resolved, indicating some dy-

namic conformational disorder. Fig. 2b displays a simplified model of the molecular packing pattern, which is compatible with the STM images. The conformation of the alkyls was assumed to be predominantly trans with a few gauche-bonds, in order to allow close packing in two dimensions. Any other well defined conformations would be difficult to justify, since no direct information on conformation and orientation of the alkyl chains is available from the STM images. However, it must be kept in mind that the alkyls will exhibit more conformational disorder than shown in the model.

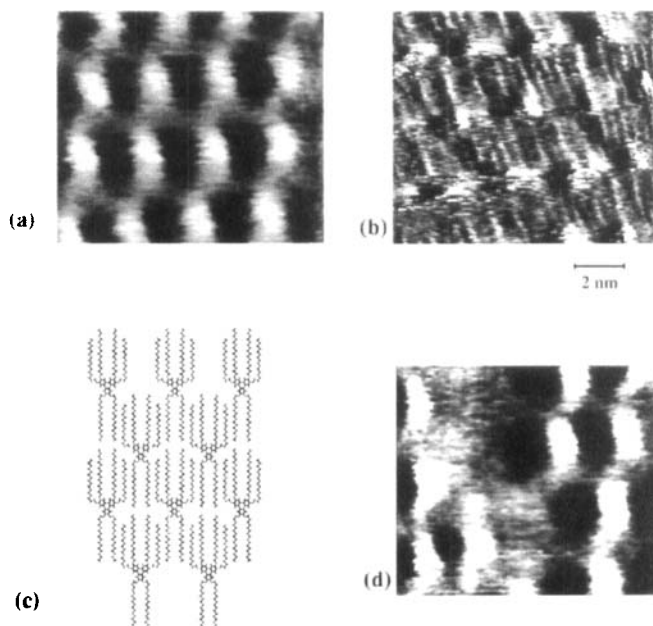


Fig. 3
Hexakis-hexadecyloxy-triphenylene (T_{16}) monolayers at the interface with a solution and HOPG at room temperature. (a) STM image, recorded at high scan speeds and low lateral resolution. (b) STM image, recorded at lower scan speed and higher lateral resolution. (c) Corresponding simplified packing model. (d) Boundary between two domains, which are oriented along two different graphite lattice axes, and cannot exhibit close packing at the domain boundary

Fig. 3a displays a STM image of a well ordered area within a monolayer of T_{16} , prepared in the same way as the T_7 layer. It has been recorded at high scanning speeds, allowing the registration of about 10 frames per second. As a consequence, the resolution is rather low. Nevertheless, the position of the triphenylene cores can be easily determined. Moreover, higher resolution images at lower scan speeds resolve the preferential orientation of the alkyl side chains. Fig. 3b indicates that within a single crystalline domain all alkyl chains are oriented preferentially parallel to each other. Their director coincides with a graphite lattice axis, as determined from images of the underlying graphite lattice at lower tunneling bias (like, e.g., in Fig. 4a). No truly atomically resolved STM-images of the molecules could be obtained, indicating that a considerable degree of dynamic disorder exists. A simplified model of the molecular packing pattern is shown in Fig. 3c.

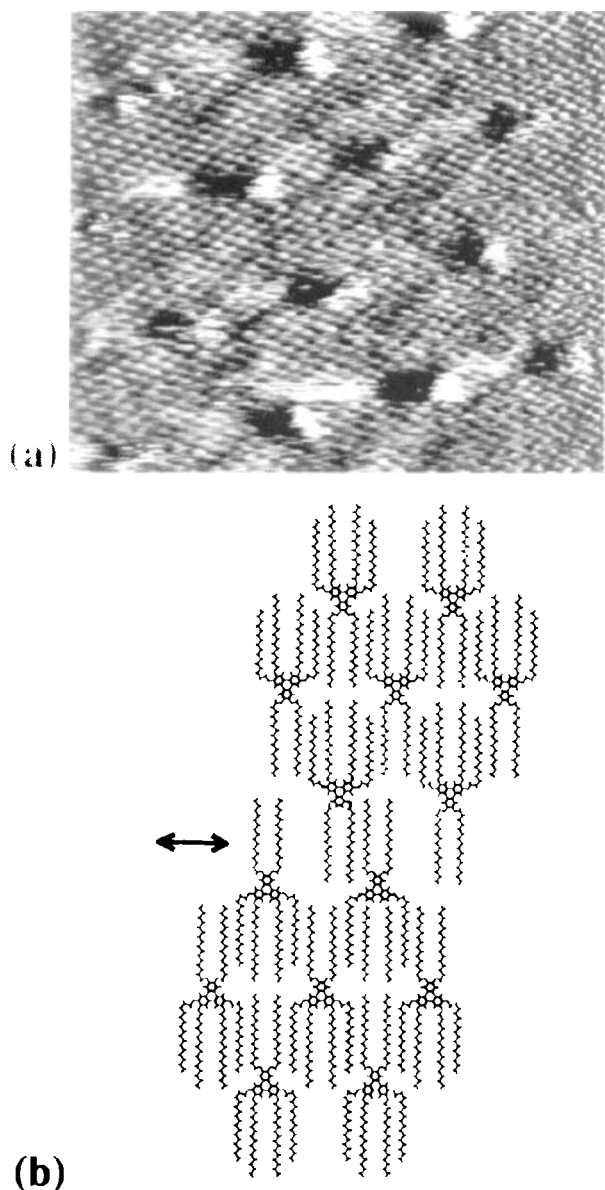


Fig. 4
Hexakis(hexadecyloxy)-triphenylene (T_{16}) monolayer at the interface with a solution and HOPG at room temperature, exhibiting a domain boundary. (a) STM image, recorded at a relatively low bias, at which both the underlying graphite lattice and the position of the triphenylenes are resolved. (b) Corresponding simplified packing model

While the size of the single crystalline domains may grow with annealing time (as it was observed for an dialkylated benzene [9,18]), freshly prepared monolayers exhibit very small domains, which rarely are larger than the one shown in Fig. 3a. Like in the case of dialkylated benzene, characteristic domain boundaries result from the fact that there is a three-fold symmetry in the substrate, and a polar axis of the molecular single crystallites. Fig. 3d shows a STM-image at the boundary between two ordered domains. The area without triphenylene cores results from the fact that if two lamellar monolayers meet at an angle of 120°C (as given by the substrate symmetry), no close molecular pack-

ing is possible. The same has been observed before for alkane monolayers [11].

Other domain boundaries reflect the polarity of the molecular crystallites. Fig. 4a displays a STM image of T_{16} at a low bias, at which both the underlying graphite lattice and the position of the triphenylene cores can be determined. The fact that the monolayer image is not particularly clear, indicates again some dynamic disorder. For instance, it appears that some molecules may occupy two different positions. Nevertheless, the symmetry and the distances between the most likely positions of the triphenylene cores can be measured very accurately. From this it can be concluded that there is a domain boundary running across the image, which separates two crystallites of opposite polarity. From the corresponding model it becomes clear that associated with the domain boundary there is some free volume (probably filled with solvent), which allows the two crystallites to move relatively to each other.

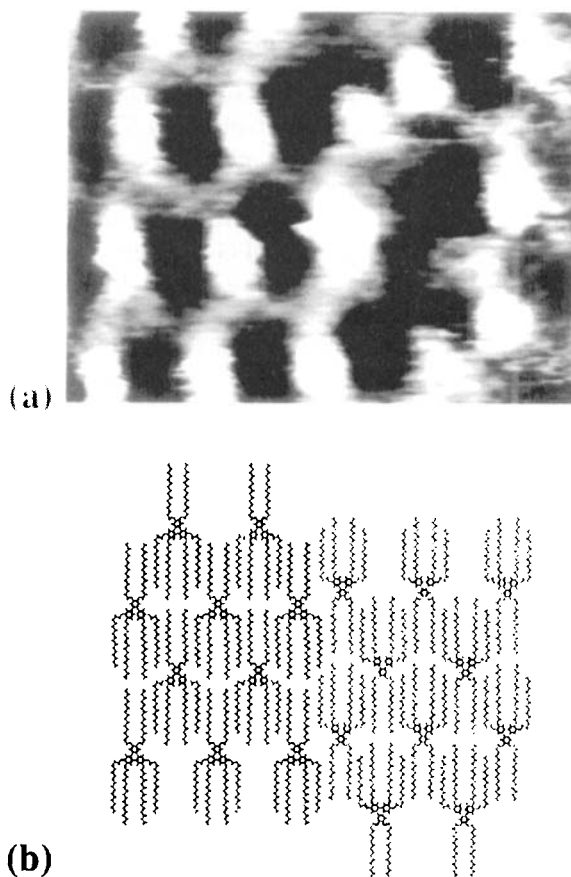


Fig. 5
Hexakis(hexadecyloxy)-triphenylene (T_{16}) monolayer at the interface with a solution and HOPG at room temperature, exhibiting a domain boundary. (a) STM image recorded under the same conditions as Fig. 3a. (b) Corresponding simplified packing model

Similarly, boundaries parallel to the polar axes of the two domains can be observed. Fig. 5a displays a STM image, showing a small section of a rather long domain boundary, and Fig. 5b displays the corresponding model. Employing the fast scanning mode at about 10 frames per second, one

may observe the domain boundary to jump, similar to some domain boundaries in dialkylated benzene [9]. However, while in the dialkylated benzene layers the necessary free volume at the end of the jumping lamella was occurring relatively rarely, it was quite abundant in the T_{16} layers. For this reason the jumps in the T_{16} layers occurred as frequent as on the scale of a few seconds, which is just slow enough to be observed in the fast scanning mode.

Immobilized monolayers were also observed at the interface with a T_{16} melt a few degrees above its bulk melting temperature. The alkyl chains could not be imaged at any bias, indicating considerable dynamic disorder. The triphenylene cores were found to form a slightly distorted hexagonal lattice similar to the one observed at room temperature. However, none of the defects described in Figs. 4 and 5 have been found, indicating that they are associated with the alkyl side chain crystallization. No monolayers were observed at the interface with T_7 -dimer-solutions, indicating that they do not order on a sufficiently long time scale to be observable. Incidentally, the dimers do neither crystallize as bulk materials [25].

In a second set of experiments, the question was addressed, whether the precursor layer surrounding a drop of a wetting molecular fluid can be observed by STM. It was then asked, how molecular structure and dynamics of the quenched system vary as one moves radially away from the drop edge. For this purpose, a drop of an alkane melt, $C_{30}H_{62}$ at 71°C , was applied to HOPG and kept sitting on the horizontal basal plane for a few hours. It was then quenched to room temperature and STM images were obtained near the optically visible edge of the solidified drop, as well as some millimeter outward.

The results indicate, first of all, that STM may be used to determine structure and dynamics in ultrathin wetting layers. Figs. 6a,b display images, which have been obtained near the drop edge, where the layer was probably thicker than a monolayer. Nevertheless, molecularly resolved images of the first monolayer next to the substrate may be recorded. The reason is that both tip and substrate are considerably more rigid than the outer alkane film, which, therefore, can be pushed aside by the scanning tip. Fig. 6a reveals somewhat disordered lamellae of mostly extended alkane molecules, which are oriented perpendicular to the lamella boundaries, and whose molecular long axes are oriented along a graphite lattice axis. Fig. 6b displays a 120° domain boundary between two equivalent domains. These results can be understood on the basis of what has been observed at solid-fluid interfaces before. Long chain alkanes at the interface between HOPG and a melt, which is kept a few degrees above its bulk melting point, have been found to order in domains composed of two-dimensional smectic lamellae [13]. Figs. 6a,b may be attributed to the quenched smectic layers.

Fig. 6c has been recorded some millimeter away from the optically visible drop edge. It shows both the presence as well as the structure of the precursor wetting layer, which may be described as columnar, i.e. the molecules are basically extended and oriented along a graphite axis, but no

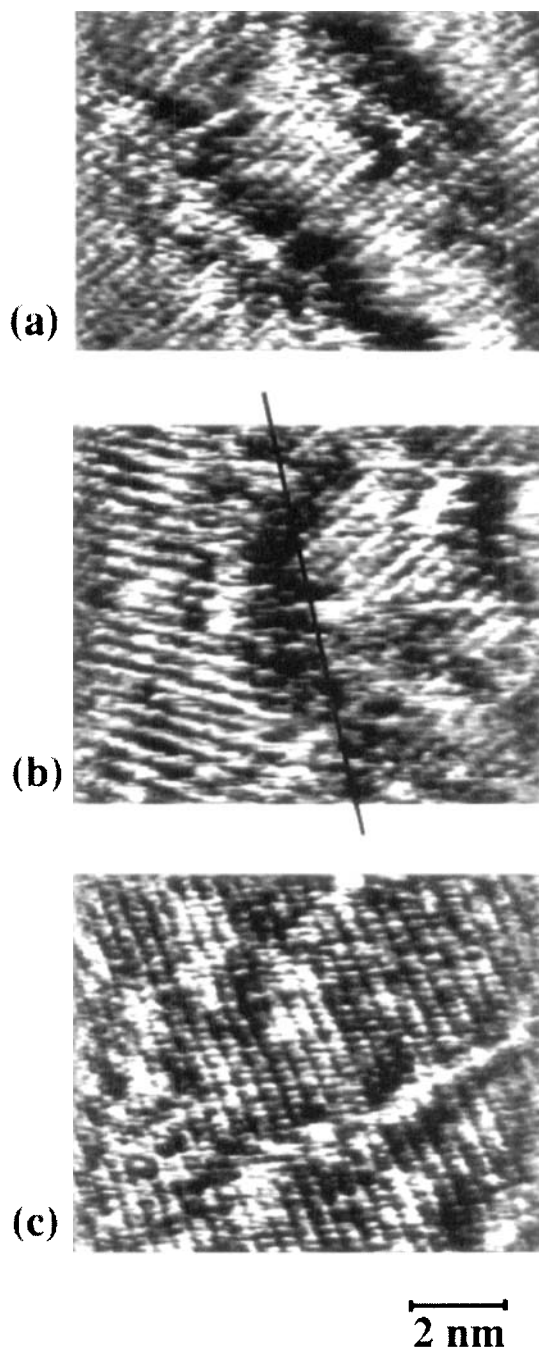


Fig. 6
STM images of a $C_{30}H_{62}$ monolayer on HOPG at different positions near the edge of a quenched drop of the alkane melt. Images (a) and (b) were recorded near the optically visible edge. The line in (b) indicates the boundary between two domains, in which the alkanes are oriented along two different graphite lattice axes. Image (c) was recorded some millimeter away on the originally uncovered side

clean phase separation of the chain ends has been observed. Moreover, the contrast along the molecules varies from scan to scan, indicating some molecular mobility along the molecular long axes. This result can also be interpreted on the basis of previous experimental and theoretical work on alkane monolayers. Molecular dynamics simulations indi-

cated that the stability of crystalline lamellae, reflected in the molecular registry at the lamella boundaries, depends sensitively on the two-dimensional molecular packing density [14]. In the case of $C_{24}H_{50}$, a density, which is 4% smaller than experimentally observed, causes already a loss of registry between adjacent lamellae. Experimentally, a columnar packing has so far only been observed in a monolayer of a much longer alkane, as well as in a binary mixture of two different alkanes, adsorbed to HOPG from solution [15]. The fact that it has been observed in the quenched molecular wetting film indicates that the molecular density within this layer is smaller than at the interface with concentrated solutions of the same material.

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