Exploring Nanoscale Organization of Normal Alkanes on HOPG Substrate with DriveAFM

Normal alkanes: $C_{60}H_{122}$; $C_{122}H_{246}$, $C_{242}H_{486}$ and $C_{390}H_{782}$

Normal alkanes C_nH_{2n+2} are linear chain molecules, which are typically extended, and they form ordered lamellar structures and crystals. When the size of the chains increases to $n > 120$, such ultra-long alkanes manifest chain folding – the main driver behind polymer crystallization. The longest alkane addressed in this application note, $C_{390}H_{782}$, is a perfect model of linear polyethylene, and crystallization of these species have many common features. The lamellar 2D organization has been detected in thin and ultra-thin layers of alkanes on highly oriented pyrolytic graphite (HOPG) and other layered crystals such as MoS_2. On these substrates the molecular orientation exhibits three-fold symmetry that guides the related orientation of the alkane lamellae. As the lamellae are formed of fully elongated chains, their width equals to the alkane length when the molecules are aligned perpendicular to the lamellar edges. The length of different alkanes from $C_{18}H_{38}$ to the ultra-long one - $C_{390}H_{782}$ changes as listed in Figure 1a. The lamellar width can be smaller when molecules are tilted at some angle to the lamellar edges. Figure 1b shows a sketch of the alkane lamellae that should have thickness of individual alkane molecule (0.5 nm). The lamellar order of all these alkanes on HOPG can be revealed in AFM images at room temperature as melting temperature of $C_{18}H_{38}$ crystals is around 28-30°C and longer alkanes melt at higher temperatures. It is known that lamellar ordering of alkanes, which is facilitated by intermolecular interactions on atomically flat surfaces like HOPG, is preserved at temperatures higher than melting temperature of alkane crystals. This was confirmed by detection of $C_{390}H_{782}$ lamellar layers on HOPG at temperatures 50 degrees above melting temperature of these alkanes (130°C)[1].

The lamellar edges are formed of $-CH_3$ end groups, which are bulkier than $-CH_2-$ groups of the chains. The related height variations should be reflected in topography of lamellar sheets formed on atomically flat substrates. In this application note we demonstrate how the

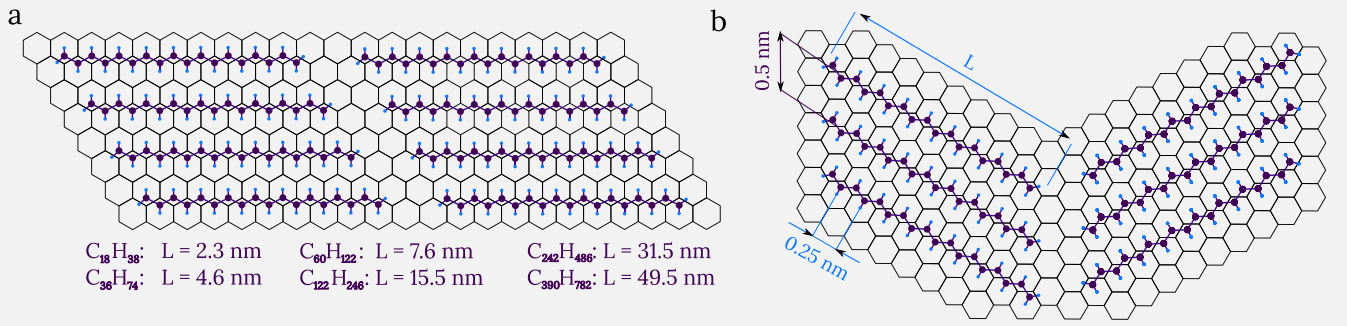

Figure 1.: Self-organization of normal alkane molekules (C_nH_{2n+2}) on HOPG surface. The HOPG surface is depicted as a honeycomb lattice, the carbon atoms are dark purple circles and the hydrogen atoms are light blue circles. (a) Horizontal packing with molecular chains in different lamellae parallel to each other. (b) V-shaped packing, with the molecules in different lamellae positioned at angle to each other. Text below the sketch (a) indicates lengths L of alkane molecules of different molecular weights.

lamellar structures of normal alkanes with different chain length on HOPG can be visualized with AFM and what peculiar nanoscale features can be detected.

Experimental details

The samples of different alkanes were prepared by spin-casting of their solutions in toluene (concentration is around 10 mg/ml) on a freshly cleaved surface of HOPG. All AFM measurements were performed at room temperature and in most cases, we have used DriveAFM in dynamic mode using photo-thermal excitation of the cantilever (CleanDrive) instead of piezo-electric drive. Few studies were also made in WaveMode, in which the cantilever was photothermally oscillated off-resonance at a frequency of 3 kHz. Commercially available soft dynamic mode cantilevers with spring constants in the 1-10 N/m range were applied in these experiments.

Imaging of $C_{60}H_{122}$

Visualization of lamellar order of normal alkane $C_{60}H_{122}$ with molecular length of 7.5 nm is displayed in Figures 2a-d. A 1 µm wide area, which is shown in Figure 2a, consists of several terraces covered by barely seen fine linear features. Several nanoscale size droplets most likely represent alkane material, which was not spread on the substrate. The height image recorded at a smaller location in the center of this area reveals a periodical pattern with the spacing of 7.5 nm. Height and phase images in Figure 2c-d present a location with two HOPG crystalline terraces, which displays the periodical arrays of linear features with different orientations. The width of these features corresponds to $C_{60}H_{122}$ length that allows their assignment to the alkane lamellae. The height depressions, which are noticed

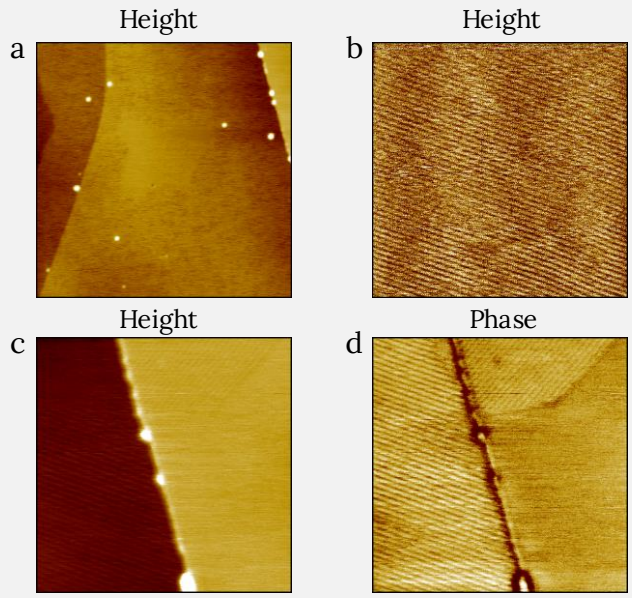

Figure 2.: Height (a,b,c) and phase (d) images of $C_{60}H_{122}$ layer on HOPG. (a) Terraces of HOPG with fine line features representing the alkane assemblies, small droplets are likey the alkane matertial, not spread on the surface. (b) Zoom in the center of the image (a) showing a periodic pattern of alkane assemblies with the period of 7.5 nm. (c,d) Height and phase images showing two HOPG crystalline terraces with the arrays of linear features with different orientations.
(a) Image size: 1 x 1 µm^2, height range: 2.4 nm. (b) Image size: 0.4 x 0.4 µm^2, height range: 0.1 nm. (c,d) Image size: 0.4 x 0.4 µm^2, height range: 1.8 nm, phase range 48°.

perpendicular to the lamellar edges on the lower terrace, are ~0.2 nm in height. These features can be assigned to -CH_3 terminals that are slightly higher than -CH_2- groups of the lamellar sheet. However, the end -CH_3 groups are more mobile than -CH_2- groups of the chain, and they can be stronger depressed by the probe tip. These local stiffness variations are most likely responsible for the phase contrast in Figure 2d.

Imaging of $C_{122}H_{246}$

Multiple lamellar sheets of $C_{122}H_{246}$ alkanes cover the surfaces of two substrate terraces, which are separated by a diagonal border in the area displayed in the height

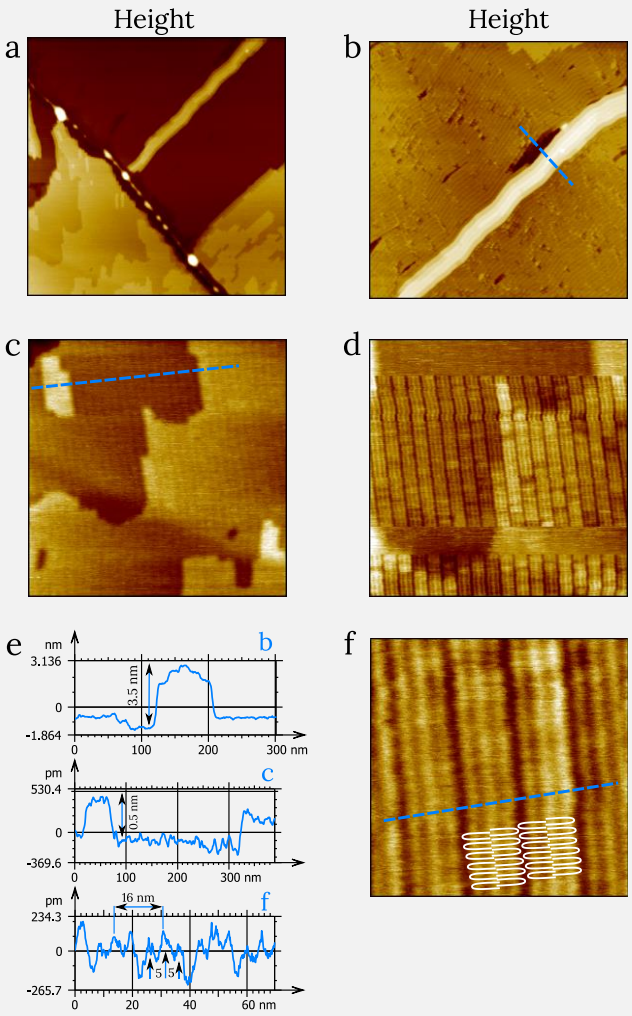

Figure 3.: Height images of $C_{122}H_{246}$ layer on HOPG. The low tip-force interactions were used for images in (a)-(c). The image in (d) was recorded at low and high tip-forces: the scanning started at the top of the image at low force, later the force was increased, and the visibility of lamellar structures has improved. (e) The cross-sections along the blue dashed lines in images (b,c,f). (f) A tentative pattern of lateral chain folding was overlayered on the height image.
(a) Image size: 1.5 x 1.5 µm², height range: 7 nm.
(b) Image size: 1 x 1 µm², height range: 5 nm.
(c) Image size: 0.5 x 0.5 µm², height range: 3 nm.
(d) Image size: 0.3 x 0.3 µm², height range: 1.2 nm.
(f) Image size: 76 x 76 nm², height range: 0.5 nm.

image of Figure 3a. At the top part of the image, wavy structures of 15-16 nm in width are distinguished at 1 µm scan size, as shown in Figure 3b. This width is close to $C_{122}H_{246}$ molecular length, indicating that they represent $C_{122}H_{246}$ lamellae. The strips with similar width have formed the raised ribbon with height of 3.5 nm (Figure 3e). Several overlaying strips have composed the ribbon, and they oriented like the wavy structures occupied most of the area. Several dark blocks ~15-16 nm in width represent the missing parts of the lamellae. The terraces of multiple overlaying alkane lamellae, which are noticed on the left from the border in Figure 3a, are displayed in the height image in Figure 3c. The steps between top layers are ~0.5 nm consistent with the diameter of individual alkane molecules (Figure 3e). The faint ribbon-like contrast variations in this image hint on a regular surface order with the periodical spacing close to the alkane width. To improve structure visualization, the tip-sample force interaction was increased by lowering the set-point amplitude. The related effect is obvious in height image in Figure 3d, which was recorded in the scanning from the top. At the top, scanning was performed at small tip force. Then the tip-force was raised the height contrast was drastically increased. The linear features became resolved not only with the spacing of 15-16 nm but also at smaller periodicities. This observation was verified towards the bottom of the image where the set-point was raised for some scan lines and lowered again. The related image changes have supported the effect.

The image pattern revealed at high-force imaging can be explained by double folding of alkane molecules that leads to appearance additional spacing of 5 nm. This situation is sketched in Figure 3f.

Imaging of $C_{242}H_{486}$

Adsorbate of $C_{242}H_{486}$ on HOPG is characterized by smooth areas covering the substrate terraces and by few raised droplets of the alkane that were not spread on the substrate, Figure 4a. A weak stripped pattern is noticed on smooth areas, and it is

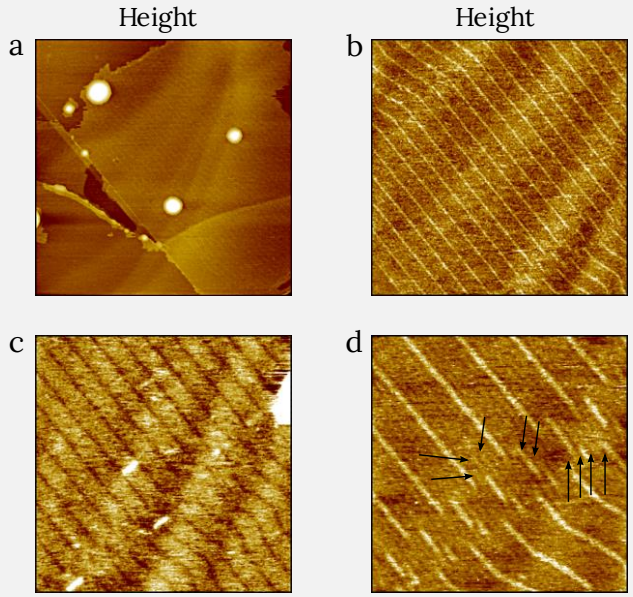

Figure 4.: Height images of $C_{242}H_{486}$ layer on HOPG. The images in (a), (b) and (d) were obtained at low force, and the image in (c) - at higher tip-force. Arrows in (d) point out the fine sub-lamellar features most likely caused by lateral chain folding.
(a) Image size: 1.5 x 1.5 μm², height range: 11 nm.
(b) Image size: 0.5 x 0.5 μm², height range: 0.25 nm.
(c) Image size: 0.4 x 0.4 μm², height range: 0.3 nm.
(d) Image size: 0.2 x 0.2 μm², height range: 0.25 nm.

more pronounced in the height image of a smaller location, Figure 4b. The white lines of around 5 nm in width and ~0.2 nm in height most likely represent the lamellar edges formed by terminal $-CH_3$ groups. The lines' separation of ~30 nm matches the length of $C_{242}H_{486}$ chains, and this supports of the assignment. This image was recorded at low tip-sample forces. At higher forces, the stripped pattern with depressed lines was observed, Figure 4c. This contrast change can be explained by tip-induced depressed of the lamellar boundaries formed by $-CH_3$ terminal groups. In addition, a few of short bright rods are observed on the lamellar surface. They can be assigned to individual alkane chains, which were not incorporated into the lamellar layer. Fine lamellar features were detected at the location, where the lamellar order was perturbed, Figure 4d. In addition to the shift of white lines of the lamellar borders, at some locations inside individual lamellae, there are weak features with smaller spacings. These features are indicated with black arrows, and their separations are ~6 nm. Therefore, a lateral folding of $C_{242}H_{486}$ chains looks possible.

Imaging of $C_{390}H_{782}$

Folding of macromolecules is common for single crystals of ultra-long alkanes and folding of $C_{390}H_{782}$ chain in 5 segments leads to 10 nm thick lozenge-type crystals of this alkane. A chain folding of flat-lying $C_{390}H_{782}$ chains, which takes place in few surface locations, was reported only once.

Surface morphology of $C_{390}H_{782}$ layer on HOPG is shown in Figure 5a. Many dark and bright blocks with dimensions of their sides close to 49.5 nm - length of $C_{390}H_{782}$ alkane are detected on this surface. This hints on lamellar order of the top layers. The height image of smaller area (Figures 5b) shows bright features, which can be assigned to the boundaries of lamellae of various size and orientation. The top layer is not complete, and multiple dark vacancies with lamellar dimensions are spread on the surface.

In the attempts to visualize fine details of the lamellar order we have performed imaging at raised tip-forces. The height and phase images, which were recorded at these conditions, revealed depressed lamellar borders as seen in Figures 5c-d. The distance between the bright and dark lamellar edges are close to 49 nm that suggests only small chain tilt with respect to the boundaries.

Fine details in the curved lamellar ribbons were detected in the height image in Figure 5e, which was recorded in WaveMode. This off-resonance mode is characterized by a stronger tip-force interaction compared to Dynamic Mode. Therefore, more structural features can be

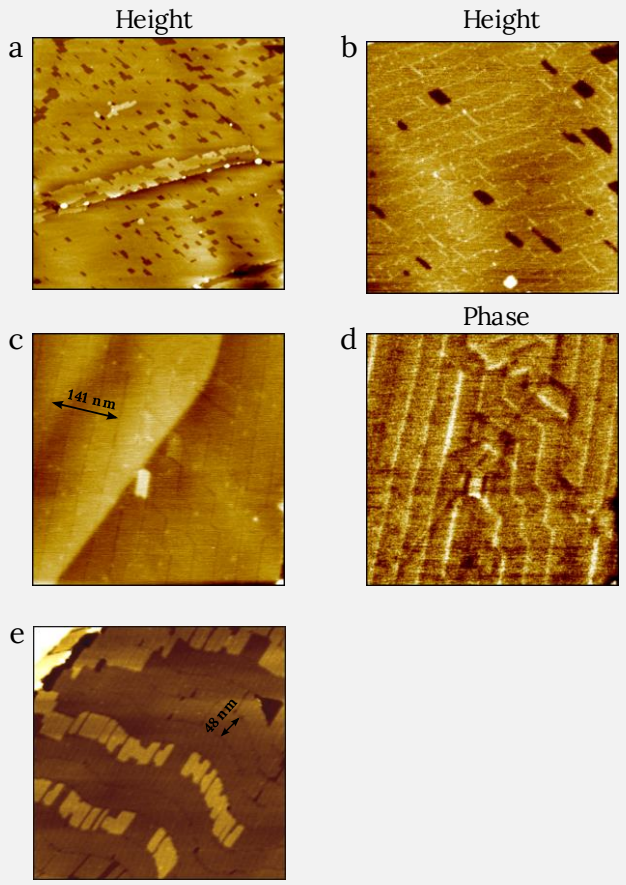

Figure 5.: Height (a,b,c,e) and phase (d) images of $C_{390}H_{782}$ adsorbate on HOPG. The images in (a)-(d) were recorded in dynamic mode in low-force (a-b) and high-force (c-d) operations. The image in (e) was obtained in WaveMode. The inserts in (c) and (e) indicate the width of three and one lamellae, respectively.
(a) Image size: 2 x 2 μm^2, height range: 2 nm.
(b) Image size: 0.6 x 0.6 μm^2, height range: 0.7 nm.
(c,d) Image size: 0.5 x 0.5 μm^2, height range: 0.7 nm, phase range: phase range 5°.
(e) Image size: 0.5 x 0.5 μm^2, height range: 4.5 nm.

visualized. The boundaries of the curved lamellar ribbons are seen with a darker contrast, and individual ribbons exhibit multiple lines with spacings down to 10 nm, which are perpendicular to the boundaries. The parts of the top ribbons epitaxially grown on the underlying lamellae show that they can be split into individual blocks of extended chains. A few dark vacancies with similar dimensions are noticed in the surface as well.

Conclusion

In summary, AFM studies of normal and ultra-long alkanes reveal a set of fine structural features related to the lateral chain folding and lamellar architecture in their layers on HOPG. The formation of these nanoscale structures on atomically flat surfaces can be used for better understanding of alkane and polymer crystallization.

References

1. Zhang, R. *et al.*, Nature Comm. **12** (2021) 1710

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