

Studies of Self-Organization of Semi-Fluorinated Alkanes on Different Substrates with DriveAFM

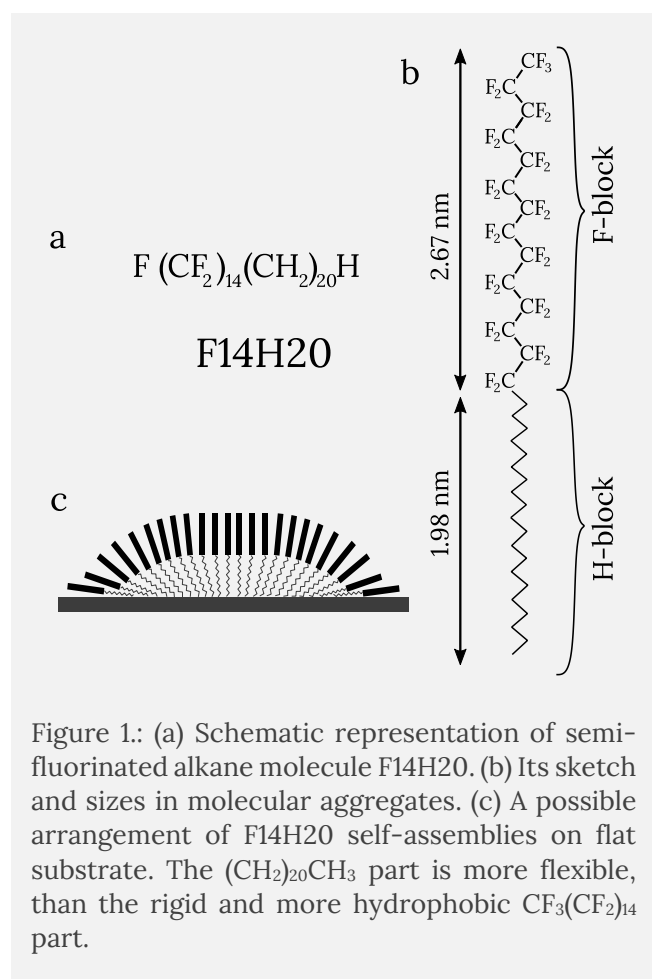


Figure 1.: (a) Schematic representation of semi-fluorinated alkane molecule F14H20. (b) Its sketch and sizes in molecular aggregates. (c) A possible arrangement of F14H20 self-assemblies on flat substrate. The $(\text{CH}_2)_{20}\text{CH}_3$ part is more flexible, than the rigid and more hydrophobic $\text{CF}_3(\text{CF}_2)_{14}$ part.

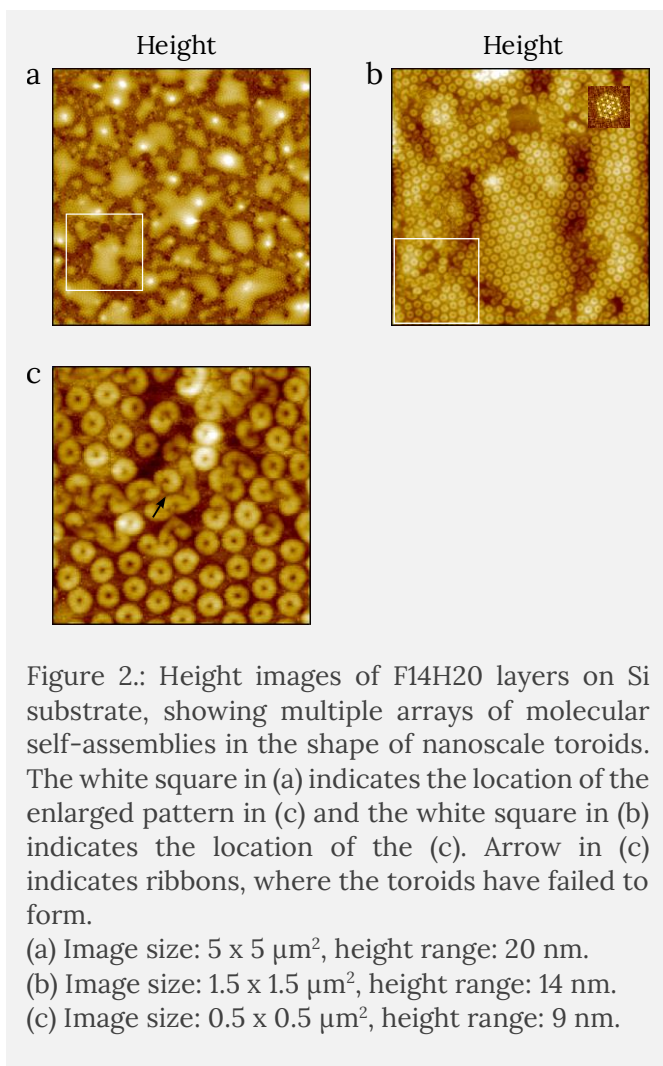
Semifluorinated alkanes: $\text{F}(\text{CF}_2)_n(\text{CH}_2)_m\text{H}$

This application note concerns AFM studies of self-assembled semi-fluorinated alkanes on Silicon, HOPG and MoS_2 substrates. These molecules are formed of covalently linked sequences of $-\text{CF}_2-$ and $-\text{CH}_2-$ groups with $-\text{CF}_3$ and $-\text{CH}_3$ terminals, respectively. Their molecular composition $\text{F}(\text{CF}_2)_n(\text{CH}_2)_m\text{H}$ can be connoted as FnHm (Figure 1a). The compounds consist of two incompatible subunits that segregate into distinct domains like block copolymers, but without polydispersity in molecular weight. Structural ordering of such compounds is controlled by the strong incompatibility of the constituting segments, and also by the

fact that the van der Waals cross-section of the flexible hydrocarbon segment is 25–30% smaller than that of the rigid helical perfluorinated segment, (Figure 1b). X-ray reflectivity studies of F14H20 films suggested that the fluorinated chains are oriented normal to the surface layer and where the alkyl segments are tilted with an angle between the two segments. This justifies the tentative model of F14H20 self-assembly, Figure 1c.

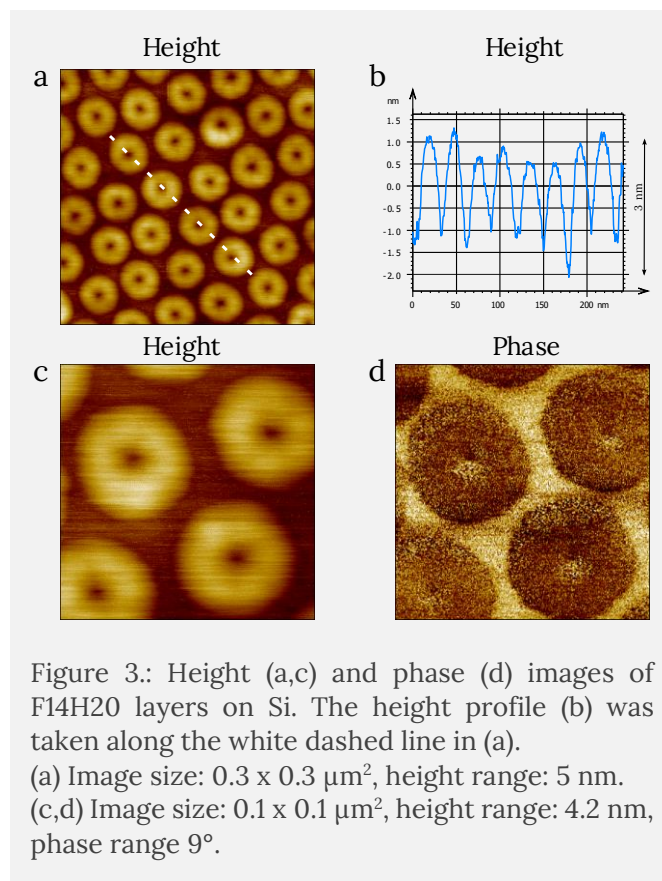
Experimental details

The competition between ordering of the hydrocarbon blocks and fluorocarbon blocks results in a distinct, yet not fully understood, polymorphism of their self-assemblies depending on solvent, substrate, deposition, and temperature. In addition to F14H20 alkanes, we also used F12H12 and F12H20 compounds. The samples were prepared by spin-casting of their solutions in perfluorodecaline on Si, HOPG and MoS_2 . The antagonistic nature of the two building units and the mismatch in cross section between the perfluoro and the perhydro-alkyl tail result in distinct superstructure formation in their adsorbates on flat substrates. AFM is the essential technique allowing visualization of self-assemblies of the semifluorinated alkanes as shown by the images shown below. All AFM measurements were performed at room temperature and we have used the DriveAFM microscope in dynamic mode using photo-thermal excitation of the probe (CleanDrive). Commercially available soft dynamic mode cantilevers with spring constants in the 1–10 N/m range were applied in these experiments.



F14H20

The height images of F14H20 on Si in Figure 2a-c show multiple arrays of molecular self-assemblies in the shape of nanoscale toroids. In the elevated areas, the toroids are arranged in hexagonal order as documented by Fourier transform pattern of the image, which is shown in the top right insert in Figure 2b. In the valleys one can notice short, curved ribbons – likely precursors of the toroids that are formed during drying of solvent. One of such locations is shown in Figure 2c. The F14H20 toroids are displayed at higher magnification in Figure 3a-c. The height profile across four toroids shows that these structures are ca. 40 nm in diameter and 2.5 nm in height. The height is smaller than the length of the molecules, which is



4.6 nm. This difference can be explained by the tilt of the molecules and sample depression by AFM probe. The profile also reveals that the central cavities are ca. 10 nm in diameter, and in the cavities, the probe almost reaches the substrate. The toroids look smooth, without any fine structures.

The F14H20 molecules on HOPG are assembled in different morphologies dependent on the adsorbate thickness. Figure 4a shows some ultrathin layers with a thickness comparable to the molecular length. Geometrical constraints imposed by the interfaces in combination with competing ordering of the building blocks resulted in arrays of straight ribbons, which are arranged in three-fold symmetry. The array of ribbons extends over two HOPG terraces. The ribbon width varies from 50 to 70 nm and have a height of about 2.5 nm. In case of higher F₁₄H₂₀ adsorbate density, whose surface is displayed in Figure 4b, the flat ribbons coexist with arrays of toroids and patches of disordered material. Few

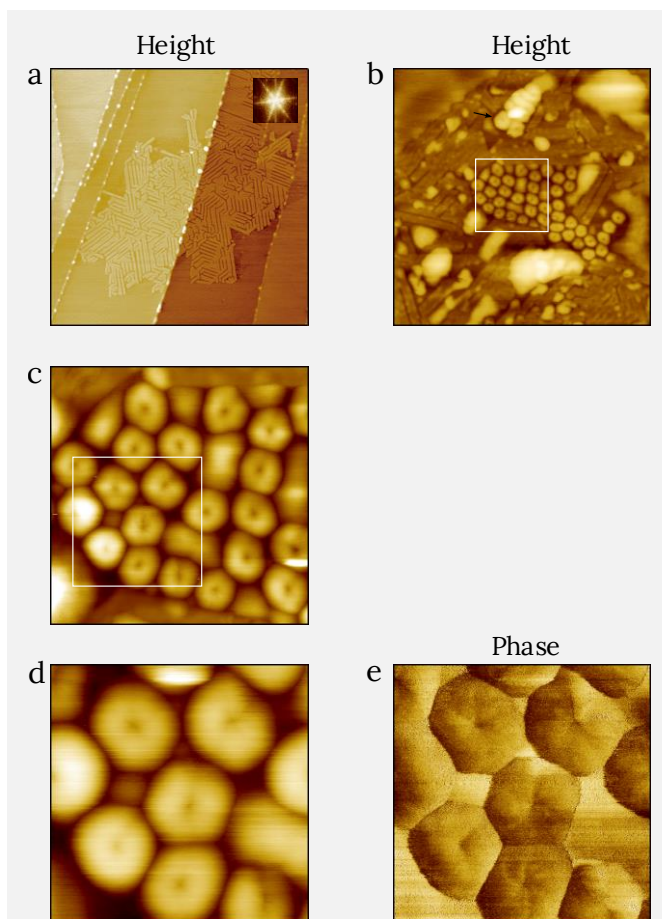


Figure 4.: Height (a,b,c,d) and phase (e) images of F14H20 layers on HOPG showing their self-assemblies in ultrathin layer (a) and in thicker adsorbate in (b-e). White square in (b) indicates the location of zoomed-in area in (c), and white square in (c) indicates the zoomed-in area in (d,e). The black arrow in (b) indicates larger toroids.

(a) Image size: $4 \times 4 \mu\text{m}^2$, height range: 6 nm.
 (b) Image size: $1 \times 1 \mu\text{m}^2$, height range: 25 nm.
 (c) Image size: $0.3 \times 0.3 \mu\text{m}^2$, height range: 8 nm.
 (d,e) Image size: $0.15 \times 0.15 \mu\text{m}^2$, height range: 10 nm, phase range 8° .

large toroids with diameter of terraces in the center of this figure have 60 nm are seen in the top center of the image. The ensemble of toroids in the center of the image is confined between sets of differently oriented ribbons, Figure 4b-c. These toroids are close in dimensions to those observed on Si substrate. Yet they exhibit various deformations being squeezed by their surrounding (Figure 4d). The phase image in Figure 4e also shows an appearance of sectors in the individual species.

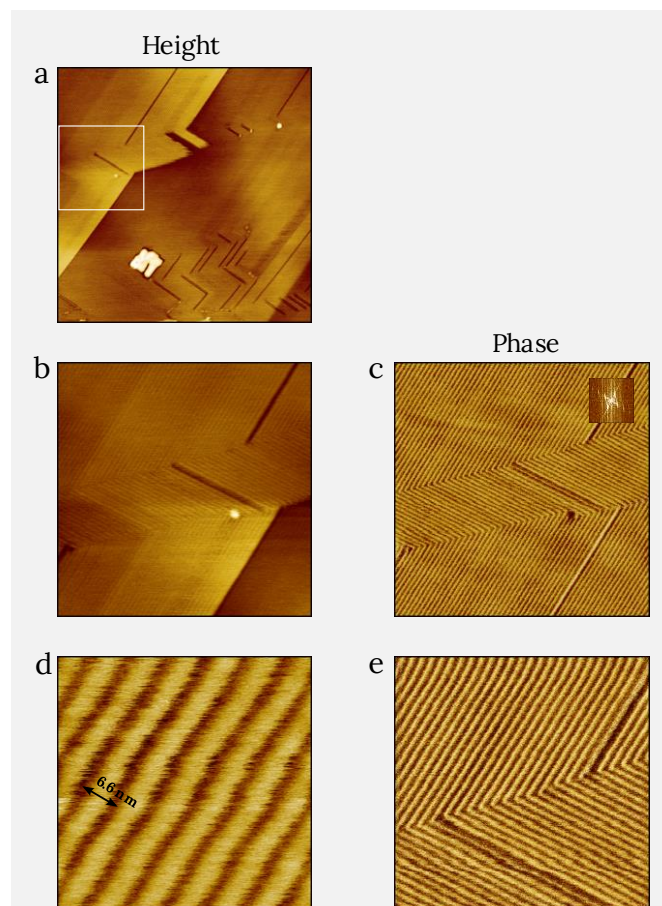


Figure 5.: Height and phase images of F12H12 layer on HOPG. The angles between sets of differently oriented lamellae are close to 90 degrees as evidenced by Fourier transform pattern in the insert in top right corner of (c). The white rectangle in (a) shows the location of the zoomed-in area in (b,c).

(a) Image size: $1 \times 1 \mu\text{m}^2$, height range: 2 nm.
 (b,c) Image size: $0.4 \times 0.4 \mu\text{m}^2$, height range: 1.5 nm, phase range 2° .
 (d) Image size: $50 \times 50 \text{ nm}^2$, height range: 0.25 nm.

F12H12

AFM imaging of F12H12 self-assembly was performed on HOPG substrate. Figure 5a shows terraces with lamellar layers having a small number of defects. The latter are seen as dark strips with orthogonal orientations and an inclusion in a shape of the raised rectangular domain. The linear features of the lamellar layers became resolved with different orientations in height and phase images of 400 nm on side, (Figures 5b-c). In the height image the darker strips are 0.4 nm in depth and 1.3 nm

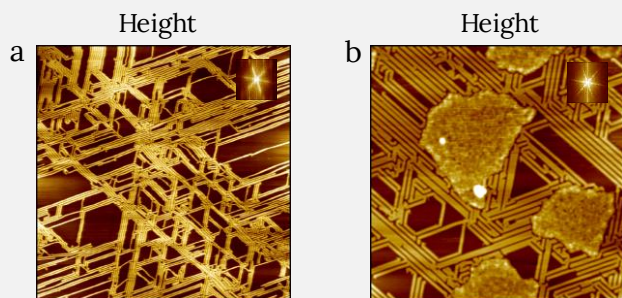


Figure 6.: Height images of F12H20 self-assemblies on MoS₂. Fourier transform patterns, which are shown in the inserts in (a) and (b) point out the trigonal symmetry of the self-assemblies' arrangements.

(a) Image size: 5 x 5 μm^2 , height range: 2.6 nm.

(b) Image size: 2 x 2 μm^2 , height range: 3.5 nm, phase range 2°.

in width, indicating vacancies of the lamellar layer. According to the depth the missing sheets are single molecular blocks. The Fourier transform pattern, which is inserted in the top right corner of Figure 5c confirms the orthogonal orientation of neighboring lamellar domains. Therefore, the intermolecular interactions of F12H12 molecules have guided this orientation and the substrate effect was reduced.

A small detail of part of one sheet and the boundary between differently oriented lamellar sheets are shown in height and phase images in Figures 5d-e, respectively. The measurements of the spacings in the lamellar layers show that the width of individual lamellae is 6.6 nm. This suggests that bimolecular arrangement of the alkane chains in the lamellae as the length of F12H12 molecule is only around 3.5 nm. The ribbons continue across the boundary albeit rotated by 90°.

F12H20

F12H20 adsorbate on MoS₂ is characterized by multiple straight ribbons. However, these ribbons are not orthogonal as the F12H12 on HOPG, but arranged in trigonal

order, as shown in Figures 6a-b. This is evidenced by Fourier transform

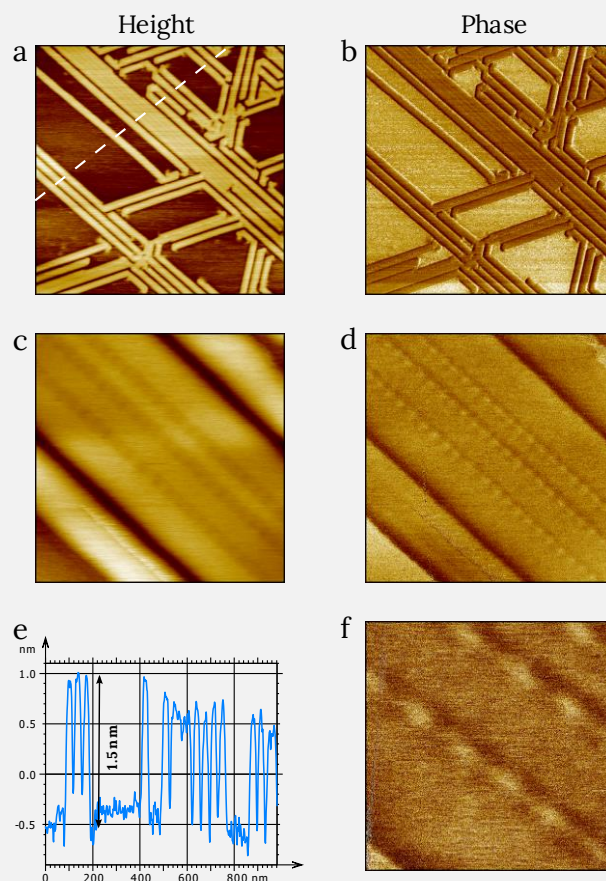


Figure 7.: Height and phase images of F12H20 self-assemblies on MoS₂. The height profile along the direction shown with white dashed line in (a) is presented between images (c) and (d)

(a,b) Image size: 1 x 1 μm^2 , height range: 2.5 nm, phase range 20°.

(b,c) Image size: 0.15 x 0.15 μm^2 , height range: 2 nm, phase range 6°.

(f) Image size: 50 x 50 nm², phase range 5°.

patterns inserted in the images at the top right. Four adsorbate patches seen in Figure 6b indicate that not all adsorbate converted into the ribbons. Even though lattices of surface carbon atoms in HOPG and sulfur atoms in MoS₂ are different, on these substrates semi-fluorinated alkanes adopt the same symmetry. Therefore, a match between periodicities of -CH₂-groups in normal alkanes and HOPG lattice is the main reason for lamellar orientational order on this substrate.

The dimensions of the ribbons were measured in the images with higher magnification (Figures 7a-e). The height profile images in Figures 7e shows that the ribbons are 1.5 nm in height and their width generally varies in the 30-40 nm range. At some locations thinner ribbons are noticed. One of such regions, where four ribbons interconnect with each other, is displayed in Figure 7c-d. Short bridges of 6 nm in length are linking the neighboring ribbons with periodicity of ca. 9 nm. They are the only fine features seen at sub-40 nm scale, Figure 7f.

Conclusion

The capabilities of visualization of semi-fluorinated alkanes with dynamic mode AFM are demonstrated in this document. Diverse nanoscale structures were observed in adsorbates of semi-fluorinated alkanes. In these materials the dissimilarities of nature of the two building units and their geometry result in formation of toroids, ribbons, and their intermediates. Further efforts in visualization of molecular arrangement in these structures are needed with imaging at sub-100 nm scale and help of off resonance tapping (WaveMode). In addition, scanning tunneling microscopy, which also can be applied for molecular-scale visualization of ultrathin layer of these examined compounds on atomically flat conducting substrates, might be useful in this respect.

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