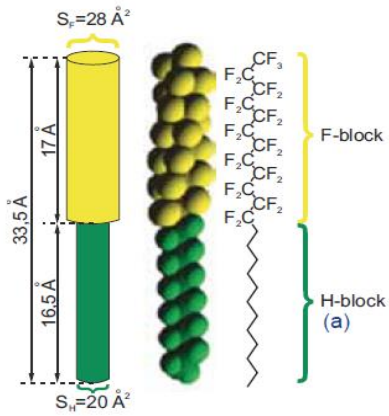
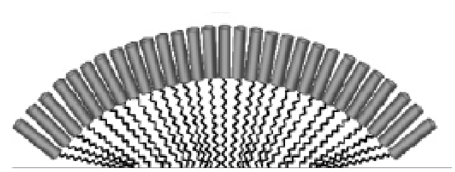
Atomic Force Microscopy View on Structural Organization of Semifluorinated Alkanes, F14H20

Semifluorinated alkanes such as $F(CF_2)_{14}(CH_2)_{20}H$ – F14H20, consist of incompatible fluorinated and hydrogenated parts. These blocks adopt, respectively, helical and all-trans conformations that leads to cross-sections of different size. These dissimilarities govern structural ordering of F14H20 in a variety of nanostructures (ribbons, spirals, toroids/donuts and their intermediates) and morphologies. Visualization of F14H20 nanostructures on different substrates can be performed with AFM, and only general structural models are considered without a complete understanding of the molecular architecture.

Cartoon of semi-fluorinated molecule



Possible structural organization of F14H20 on flat surface



A. Mourran et al “Self-assembly of perfluoroalkyl-alkane F14H20 in ultrathin films” *Langmuir* **2005**, *21*, 2308.

AFM images of the samples with F14H20 on Si are shown in **Figure 1a-b** and **Figure 2a-c**. The F14H20 domains of different size are scattered on the surfaces. The self-assemblies of various type can be resolved at the small scales. The donuts with ~ 4 nm in height dominate among them. The structures are much softer than Si and they are well distinguished in phase images (not shown here).

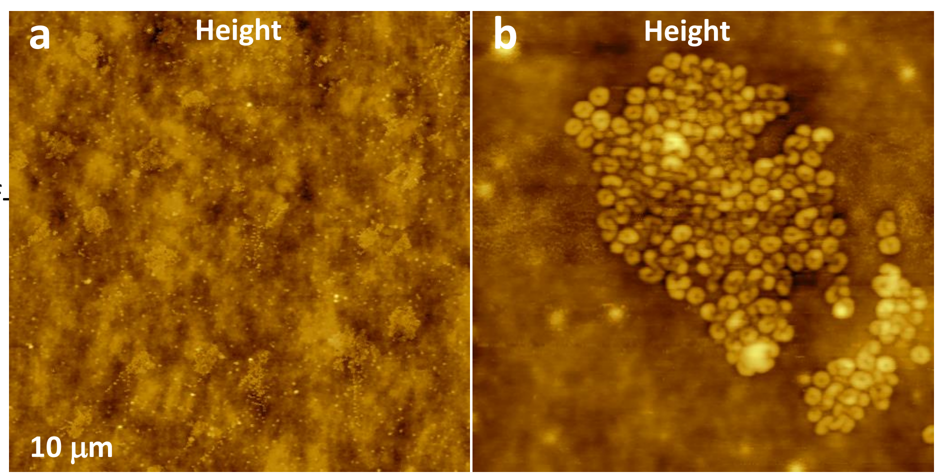


Figure 1a-b. Height images of F14H20 adsorbate on Si.

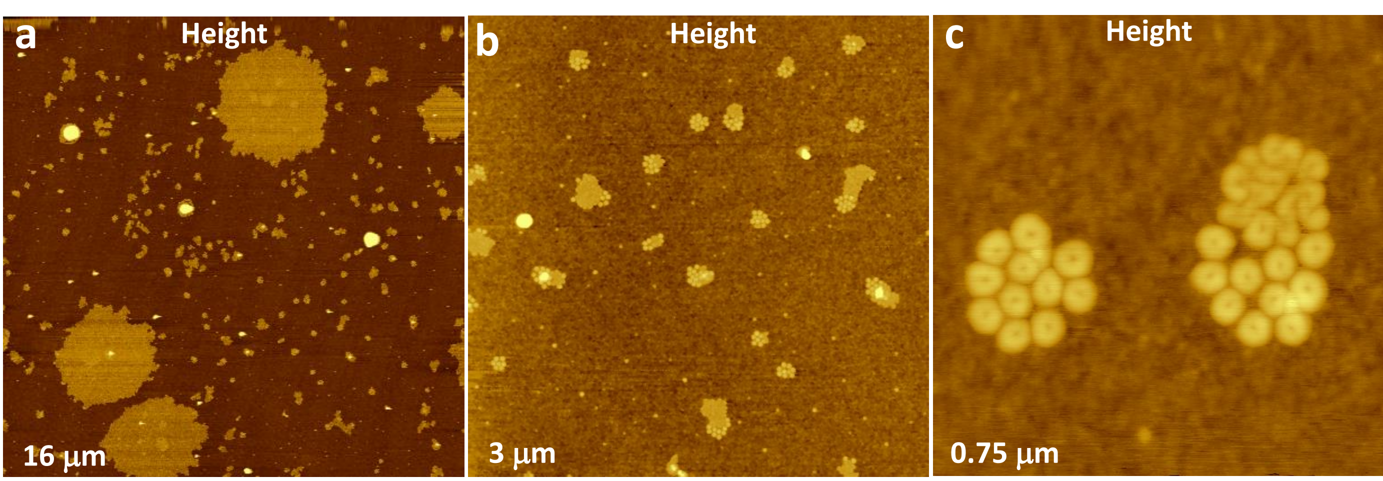


Figure 2a-c. Height images of F14H20 adsorbate on Si.

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The samples of F14H20 on Si can be used for training purposes in AM-PI mode due to small size of the self-assemblies and their softness. It might be a tough sample for D-CNT (aka PeakForce) mode. A special value of this samples is its examination AFM-based electric modes. The F14H20 molecules have a dipole of 3.1 D oriented along the chain at $–CF_2–CH_2$-junction. A surface potential of −0.8 V was detected in macroscopic Kelvin probe study of their L-B layers (*Phys. Rev. E* **2002,** *5,* 051603). It was assigned to vertically oriented molecular chains with fluorinated parts facing air. Electric activity of F14H20 can be noticed in AM-PI mode when a conducting probe is biased with respect to the sample. The electric field changes the probe resonant frequency, and this influences height contrast, **Figure 3a-b**. This effect is not observed in KFM at small voltages, **Figure 4**.

F14H20/Si sample was used to verify the benefit of phase vs amplitude detection in single-pass KFM. The result is obvious from the data shown in **Figure 4b-c,e-f**. The single-pass study also allows recording of dC/dZ (dielectric response) map simultaneously with surface potential and height images, **Figure 4d**. (*Beilstein J. Nanotechnol.* **2011,** *2,* 15)

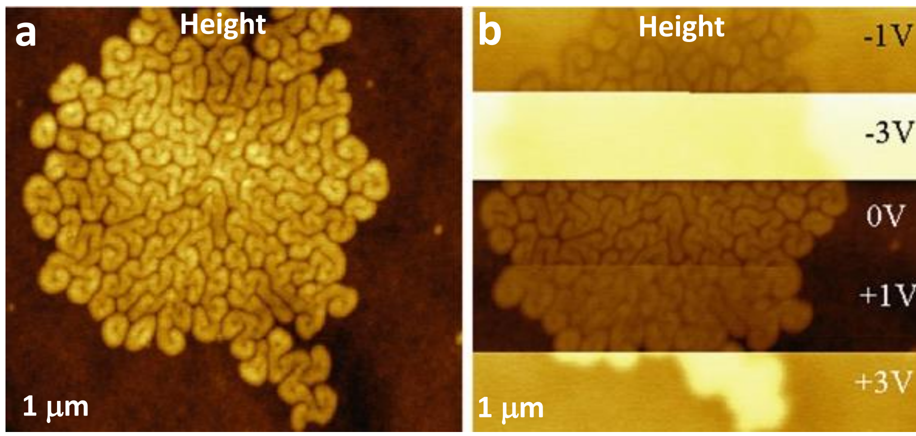
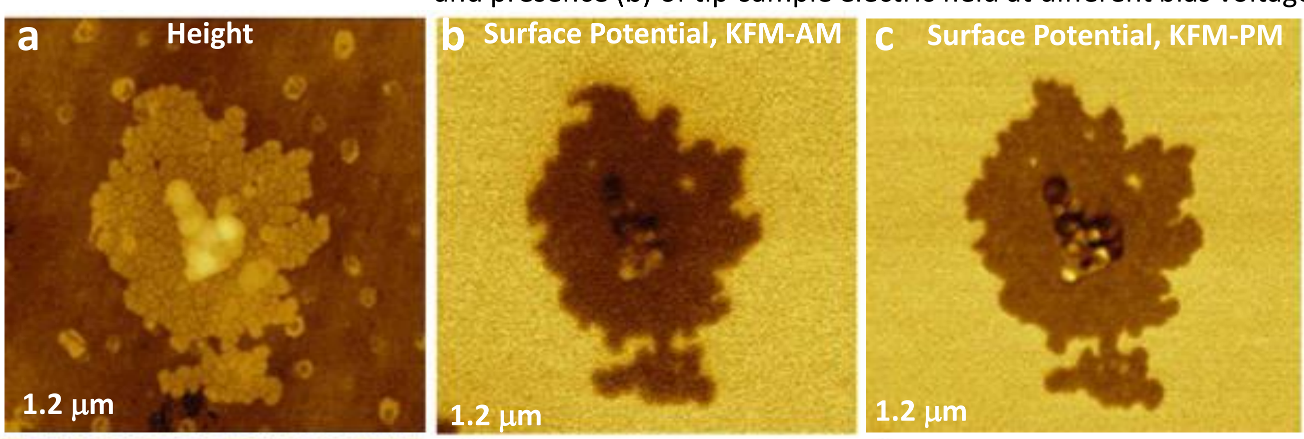
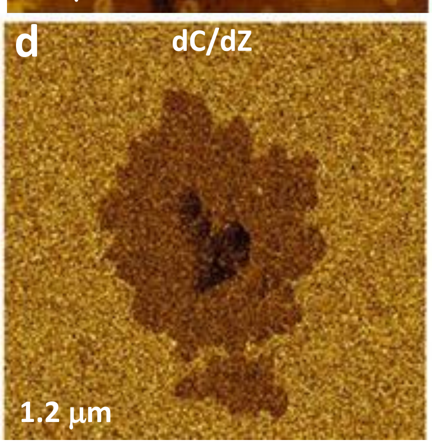


Figure 3a-b. Height images of F14H20 adsorbate on Si in absence (**a**) and presence (**b**) of tip-sample electric field at different bias voltages.





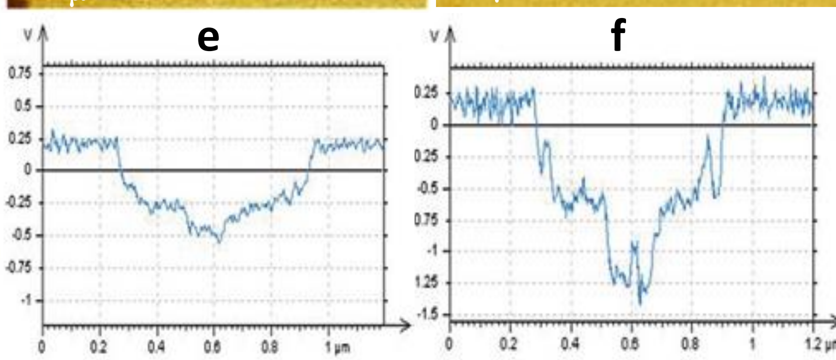


Figure 4a-f. Height (**a**), surface potential (**b**, **c**) and dC/dZ (**d**) images of F14H20/Si. (**e-f**) The potential profiles taken in (**b**) and (**c**).

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In AFM-based electric modes the use of AM-PI operation at high voltages substantially changes the height contrast. This effect was shown **in Figure 1a-b** and the similar observation was made in KFM-PM mode applied to F14H20/Si sample, **Figure 5a**. Here the changes of the height contrast at voltage above 2V also influence the value of surface potential, **Figure 5b**. This unwelcome effect can be avoided with use of amplitude modulation with frequency imaging (AM-FI). AM-FI operation is realized in AFM microscope with phase-locked loop, which holds the probe phase at 90 degrees level, i.e. at the effective resonance frequency. In this case the frequency shift, which disturbs the correct height feedback in AM-PI mode, is not involved in the amplitude-related servo operation. Therefore, height image in **Figure 5c** correctly reproduces surface topography at any applied voltages. The same is true for surface potential image in **Figure 5**d. This example shows that F14H20/Si samples are also useful for verification of different electric modes.

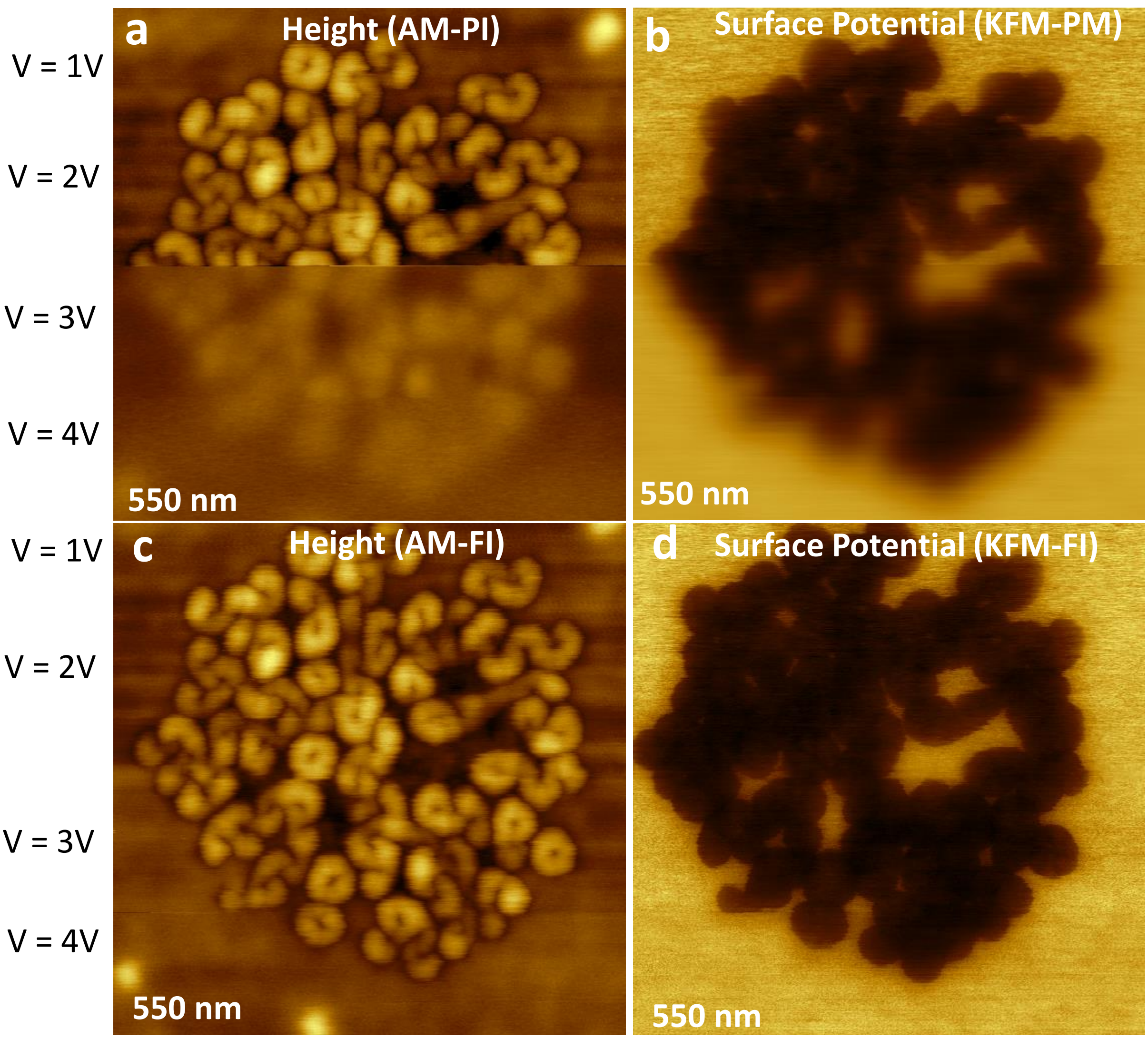

Figure 5a-d. Height and surface potential images, which were recorded at different bias voltages in AM-PI (a), KFM-PI (b) and AM-FI (c) and KFM-FI (d) modes.