Contribution of in-situ GISAXS measurements to the study of semi-fluorinated alkane layers at the air/water interface

P. Fontaine[1], L. Bardin[1,2], M.-C. Fauré[2,3], E. Filipe[4], M. Goldmann[2, 3, 1]

[1] SIRIUS Beamline, Synchrotron SOLEIL, L'Orme des Merisiers, Saint Aubin, BP48, 91192 Gif sur Yvette Cedex, France

[2] Institut des NanoSciences de Paris, Sorbonne Universités, CNRS-UMR 7588, 4 place Jussieu F-75005 Paris, France

[3] Faculté des Sciences Fondamentales et Biomédicales, Université Paris Descartes, 45 rue des Sts-Pères, 75006 Paris, France

[4] Centro de Quimica Estrutural, Instituto Superior Tecnico (IST), Av. Rovisco Pais, 1049-001 Lisboa, Portugal.

Despite the lack of polar head group semifluorinated alkanes ($C_nF_{2n+1}C_mH_{2m+1}$, FnHm for short) form Langmuir monolayers *ie.* mono-molecular thick layer at the air-water interface. The molecular and sub-nanometric structure of such layers remains controversial in the literature until Grazing Incidence Small Angle X-ray Scattering (GISAXS) was applied in-situ on the surface of water.

Using this technique, we demonstrated that these molecules on liquid surface self-assemble in a hexagonal array of nano-domains with a very large parameter (typ. 30 nm) [1] (Fig 1-A). Such structure was not expected since only disordered domains where evidenced by AFM on solid substrates [2]. This network is observed on water for different hydrocarbon chain length [3]. We succeed to reproduce this structure on solid (silicon) substrate using a spin-coating technique and found the same structure with the same lattice spacing by Atomic Force Microscopy (AFM) immediately after deposition [4].

However, the stability even after collapse [5] of such domains remains puzzling. On high-resolution AFM images, the domains shape appears as separated by a hump (Fig. 1-B). Macroscopic measurement combined with GISAXS and wide-angle x-ray scattering (GIXD) suggest that some molecules do not belong to the domains made of upright molecules. Indeed, we make simulations of the Q_{xy}-Q_z GISAXS spectrum using the BornAgain software of truncated cone domains surrounding a corona representing lying molecules (Fig. 1-C) that qualitatively reproduce the out-of-plane behaviour of the experimental GISAXS spectra with only one fit parameter, the angle of the truncated cone.

The presence of such lying molecules could explain the stability of the structure against coalescence of the domains upon compression of the monolayer in relationship with the polar nature of the substrate and the dipole of the SFA molecules [6].

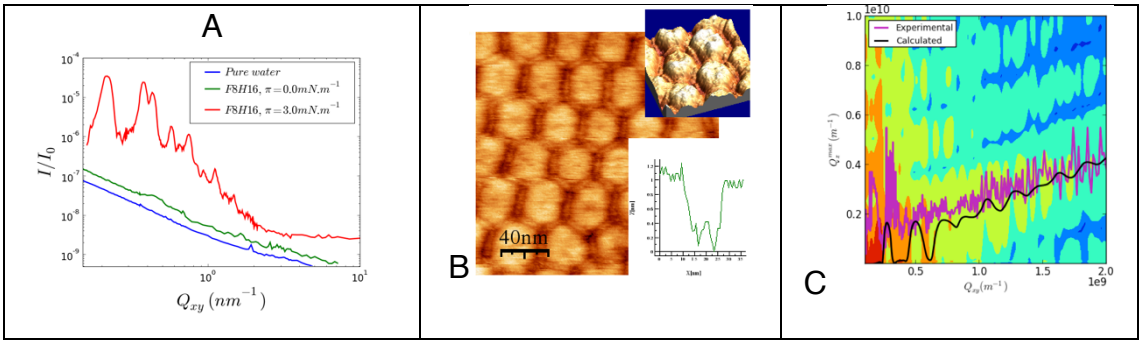

Figure 1: – A: Qz-integrated GISAXS spectrum of a F8H16 monolayer. All diffraction peaks can be indexed on a hexagonal lattice of parameter 33.6nm. B: AFM image of a spin-coated F8H18 layer on silicon substrate. C: Simulated GISAXS spectra of FnHm domains surrounded by a corona of lying molecules, lines are the position of the maximum of intensity along Qz for simulation and experiment.

Finally, we will show that recent in-situ and time resolved GISAXS experiments performed just after the deposition of the molecule through the classical Langmuir monolayer deposition scheme during the solvent evaporation give interesting information about the formation of the final nanostructured lattice at the air-water interface.

References

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