LARGE ORGANIZED SURFACE DOMAINS SELF-ASSEMBLED FROM NON-POLAR AMPHIPHILES

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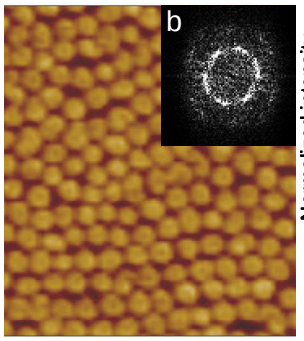
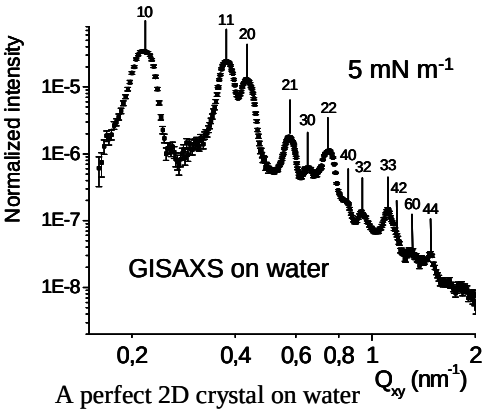
The discovery that Langmuir-Blodgett (LB) monolayers of small $C_nF_{2n+1}C_mH_{2m+1}$ (*FnHm*) diblock molecules (e.g. *F*8*H*16) consist of ordered arrays of unusually large (~30-60 nm), discrete self-assembled surface domains (or hemimicelles, Figure), and *not* the presumed continuous, featureless film, had not been anticipated.[1, 2]

These surface micelles differ in several essential ways from all previously reported or predicted molecular surface aggregates: they self-assemble spontaneously, even at zero surface pressure, depending solely on a critical surface concentration; are very large (~100 times the length of the diblock); involve thousands of molecules (orders of magnitude more than classical micelles); yet are highly monodisperse; self-organize in close-packed hexagonal patterns (2-dimensional crystals); their size is essentially independent from pressure; they do not coalesce, and are unexpectedly sturdy for soft matter (persisting even beyond surface film collapse).



Discrete self-assembled surface micelles



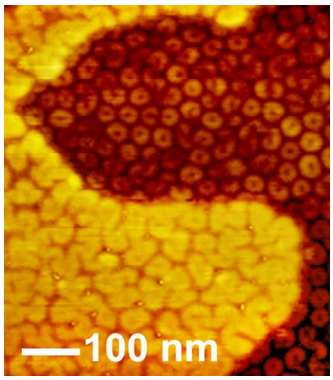
A perfect 2D crystal on water

Large surface micelles were observed by us[3-8] and others[9, 10] for numerous diblocks, using LB transfer, spin-coating, dip-coating techniques, or expulsion from mixed monolayers, and on diverse supports, establishing that hemimicelle formation and ordering are intrinsic properties of (perfluoroalkyl)alkanes. Notably also, they involve "incomplete" surfactants with limited amphiphilic character, further illustrating the outstanding capacity for perfluoroalkyl chains to promote self-assembly and interfacial film structuring.

X ray reflectivity determined a perfluoroalkyl-chain-up orientation.[3] Theoretical investigations assigned self-assembly and hemimicelle stability to electrostatic dipole-dipole interactions at the interface between *Fn*- and *Hm*-sub-layers.[11]

Grazing-incidence small-angle X-ray scattering (GISAXS) data collected directly on the surface of water demonstrated unambiguously the presence of surface micelles in monolayers of diblocks, prior to LB transfer for AFM imaging.[6, 8] An almost perfect 2-dimensional crystal (12 assignable diffraction peaks; Figure), was characterized, definitely establishing that self-assembly, and regular nanopatterning, were not caused by transfer or induced by the solid support, also providing the first direct identification of surface micelles on water, and also of such large-size domains using GISAXS.

Revisiting Langmuir film compression behavior after we realized that it actually was a compression of nanometric *objects*, led to further unanticipated observations: compression could be pursued far beyond the documented film "collapse", resulting, (e.g. for *F*8*H*20) in the building-up of one, and eventually two, superimposed less-organized bilayers of diblocks on top of the initially formed monolayer of hemimicelles.[12] Remarkably, the latter withstood the final irreversible collapse of the composite films.



2-Stories of self-assembled molecular nano-objects

"Gemini" tetrablocks, di(*FnHm*), with two *Fn*-chains and two *Hm*-chains, provided two superposed layers of discrete micelles (Figure, right), apparently the first example of thin films made of *stacked* discrete self-assembled nanoobjects.[13, 14]

Decoration of solid surfaces with domains of predetermined size of these small "non-polar" molecules is straightforward. Initial examples of applications include deposition of metal dots and catalytic oxidation of CO, and use for nanopatterning of SiO_2 films.

[1] M. P. Krafft *Acc. Chem. Res*. **2012**, 45, 514-524.

[2] M. P. Krafft, J. G. Riess *Chem. Rev.* **2009**, 109, 1714-1792.

[3] M. Maaloum, P. Muller, M. P. Krafft *Angew. Chem. Int. Ed.* **2002**, 41, 4331-4334.

[4] G. Zhang, M. Maaloum, P. Muller, N. Benoit, M. P. Krafft *Phys. Chem. Chem. Phys.* **2004**, 6, 1566-1569.

[5] G.-F. Zhang, P. Marie, M. Maaloum, P. Muller, N. Benoit, M. P. Krafft *J. Am. Chem. Soc*. **2005**, 127, 10412-10419.

[6] P. Fontaine, M. Goldmann, P. Muller, M.-C. Fauré, O. Konovalov, M. P. Krafft *J. Am. Chem. Soc.* **2005**, 127, 512-513.

[7] A. Gonzàlez-Pérez, C. Contal, M. P. Krafft *Soft Matter*. **2007**, 3, 191-193.

[8] L. Bardin, M.-C. Fauré, D. Limagne, C. Chevallard, O. Konovalov, E. J. M. Filipe, G. Waton, M. P. Krafft, M. Goldmann, P. Fontaine *Langmuir*. **2011**, 7, 13497–13505.

[9] A. Mourran, B. Tartsch, M. O. Gallyamov, S. Magonov, D. Lambreva, B. I. Ostrovskii, I. P. Dolbnya, W. H. de Jeu, M. Moeller *Langmuir*. **2005**, 21, 2308-2316.

[10] M. O. Gallyamov, A. Mourran, B. Tartsch, R. A. Vinokur, L. N. Nikitin, A. R. Khokhlov, K. Schaumburg, M. Möller *Phys. Chem. Chem. Phys.* **2006**, 8, 2642-2649.

[11] A. N. Semenov, A. Gonzàlez-Pérez, M. P. Krafft, J.-F. Legrand *Langmuir*. **2006**, 22, 8703-8717.

[12] C. de Gracia Lux, J.-L. Gallani, G. Waton, M. P. Krafft *Chem. Eur. J.* **2010**, 16, 7186-7198

[13] C. de Gracia Lux, M. P. Krafft *Chem. Eur. J.* **2010**, 16, 11539-11542.

[14] C. de Gracia Lux, J.-L. Galliani, G. Waton, M. P. Krafft *ChemPhysChem*. **2012**, 13, 1454-1462.