

Perfluoroalkyl chains as tools for film surface nano-patterning and soft microbubble engineering and decoration



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ABSTRACT

Molecular perfluoroalkylated components provide powerful tools for the elaboration, stabilization and control of organized nano- and micrometre scale soft matter constructs. The examples discussed here include patterning of thin interfacial films with self-assembled organized domains of fluorocarbon/hydrocarbon diblocks, formation and stabilization of size-controlled, resilient soft-shell microbubbles for ultrasound diagnostic imaging, and microbubbles self-assembled from a perfluoroalkylated amphiphile and decorated with iron oxide nanoparticles on their outer surface that are both highly echogenic and magnetic. The latter devices have potential as contrast agents for both ultrasound and magnetic resonance imaging, and as targeted drug delivery agents and devices.

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1. Introduction and scope

This paper is in part based on a lecture given at the 4th Asian Symposium on Advanced Materials in Taipei, Taiwan in October 2013. It is about some of the most fragile and ephemeral constructs found in the realm of soft matter: patterned interfacial thin films self-assembled from small molecules, discrete microbubbles with shells made from small amphiphilic molecules, and multi-scale functional microbubbles also self-assembled from small molecules and decorated with metal oxide nanoparticles. It summarizes and discusses the efforts devoted to preparing and investigating such soft matter constructs. The aims of these efforts is to understand the fundamentals that determine their formation, stability and properties, and to implement them with potential uses in mind, in particular in theranostics, as contrast agents for diagnosis and as drug delivery systems. Such uses can require functionalization of the bubble's shell.

This proceeding emphasizes the role that highly fluorinated components can play in the engineering of functional soft matter constructs. Introduction of fluorinated moieties, usually linear perfluoroalkylated chains, renders molecules highly amphiphilic and prone to spontaneous supramolecular assembly. The strong tendency for fluorinated moieties to separate from non-fluorinated

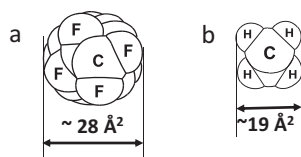
moieties, and for the fluorinated rods to align, induces ordering and specific phase behaviour in interfacial films. A brief reminder of some basic characteristics and properties of perfluoroalkylated chains and molecules relevant to molecular self-assembly is therefore provided. The potential of fluorocarbons and fluorinated surfactants as components of self-assembled interfaces and colloids will be outlined and illustrated using some selected results from the author's and other research groups.

2. Reminders about perfluoroalkylated chains and molecules relevant to their aptitude for driving self-assembly

Compared to hydrogen, fluorine is much more electronegative, has a higher ionization potential, and is bulkier and less polarizable. The C–F bond is more stable and, in most circumstances, much less reactive and biologically much more inert than the C–H bond. Perfluoroalkyl chains, C_nF_{2n+1} , are bulkier than hydrocarbon chains, helical and more rigid (Scheme 1). They are covered with a very dense electron sheath, which translates into low polarisability and low intermolecular cohesiveness. They are simultaneously extremely hydrophobic and strongly lipophobic, leading to segregation, compartmentation and ordered self-assembly. Fluorocarbons, C_nF_{2n+2} , as compared to hydrocarbons, are more stable, more inert, have lower surface tensions, higher spreading coefficients, are more volatile, more compressible, have much lower water solubilities and Ostwald coefficients, and much higher gas-dissolving capacities. Several reviews have

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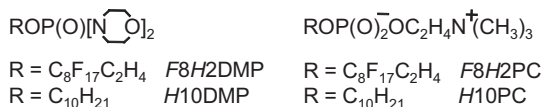
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Scheme 1. Comparison of the cross-sections of (a) a helical, bulky fluorinated chain with (b) a trans-planar hydrocarbon chain.

been dedicated to the structural and functional properties of perfluoroalkylated materials [1–3].

Grafting a perfluoroalkylated chain on an organic molecule generates or strongly enhances its amphiphilic character, leading to strongly increased surface activity and providing much lower surface tensions than their hydrogenated counterpart [1,4,5]. Fluorinated surfactants are both more effective and more efficient than their hydrogenated analogues, as shown in Fig. 1 for perfluoroalkylated derivatives of phosphocholine (PC) and dimorpholinophosphate (DMP) and their hydrogenated analogues [6].



The simple association of a perfluorinated chain with a perhydrogenated chain, as in a C_nF_{2n+1}C_mH_{2m+1} diblocks (*FnHm*), already engenders considerable amphiphilic character and properties typical of surfactants, without need for any polar function. *FnHm* diblocks are amphiphilic, amphisteric and amphidynamic [2].

An unexpected finding was that even simple short perfluorocarbons (e.g. perfluorohexane), when they are located at an interface, can acquire an amphiphilic character that is revealed by surface activity and promotion of ordering, although the isolated C₆F₁₄ molecule is perfectly symmetrical and apolar. For example, the co-surfactant activity of perfluorohexane vis-à-vis the phospholipid dimyristoylphosphatidylcholine resulted in a highly significant lowering of surface tension, by 10 mN m⁻¹ at 20 °C [7,8], and eventually to a significant contribution to stabilization of phospholipid-coated microbubbles [7,9]. The formation of stable Langmuir films from fluorocarbon C₂₀F₄₂ is also remarkable, as it demonstrates that strong hydrophobic interactions can suffice to organize molecules at interfaces despite the absence of interactions with water [10]. An example of promotion of ordering driven

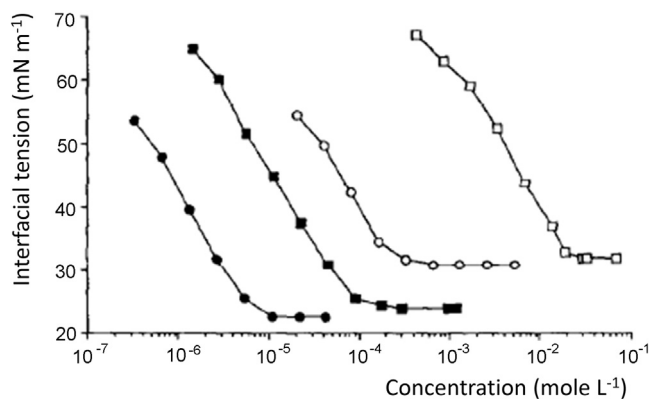


Fig. 1. Variation of the surface tension versus concentration of aqueous solutions of perfluoroalkylated single-chain amphiphiles derived from phosphocholine and dimorpholinophosphate, and of their hydrogenated analogues at 25 °C: solid circles: F8H2DMP; empty circles: H10DMP; solid squares: F8H2PC; and empty squares: H10PC.

Adapted from [6].

by perfluoroalkylated chains include insertion of *FnHm* diblocks in phospholipid bilayer membranes, leading to vesicles with a higher stability [11–13].

3. Ordered surface film nano-patterning

Fluorinated amphiphiles can display behaviour markedly different from that of their hydrogenated analogues at interfaces. Thus, *FnHm* diblocks (typically $n = 8–12$; $m = 14–20$), when spread at the air/water interface or on solid supports such as silicon, mica, graphite, a phospholipid film, or a liquid crystal, do not produce the uniform homogenous monolayer usually observed with standard surfactants, but thin patterned films that consist of colloidal monolayers made of monodisperse, nanometer-size molecular surface domains (or hemimicelles) (Fig. 2) [3,14–17]. The film structure, chain orientation, solid phase structure, crystal parameter, layer arrangements, stability and behaviour of these films have been determined using a wide panoply of physical methods [18,19]. Here are a few noteworthy features of these films and domains: the domains form spontaneously at the surface of water, even at zero surface pressure; they involve thousands of molecules, yet are quite monodisperse; the domains self-organize into close-packed hexagonal arrays, producing two-dimensional crystals; they were never seen to merge upon compression; they persist even after Langmuir film collapse; analysis of the compressibility

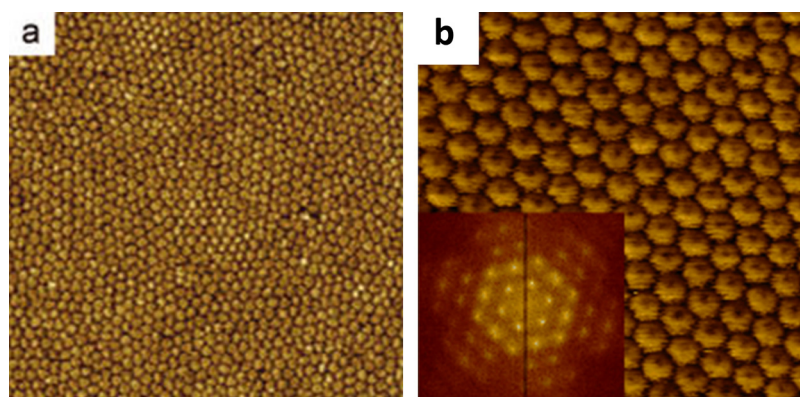


Fig. 2. Nanopatterned interfacial film showing arrays of organized self-assembled domains of small fluorocarbon-hydrocarbon diblocks C_nF_{2n+1}C_mH_{2m+1} (*FnHm*). (a) A F8H16 Langmuir monolayer transferred on a silicon wafer at 7 mN m⁻¹ (the area of the image is 1 μm × 1 μm). Adapted from [2]. (b) A F12H18 Gibbs film adsorbed at the surface of a 0.2 μL droplet of the liquid-crystal forming compound 4-dodecyl-4'-cyanobiphenyl (12CB). The inset shows a FFT plot of the height image showing a well-defined hexagonal lattice (lattice parameters: $a = 39.9$ nm, $b = 38.7$ nm, $\gamma = 58.2^\circ$). Adapted from [17].

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