



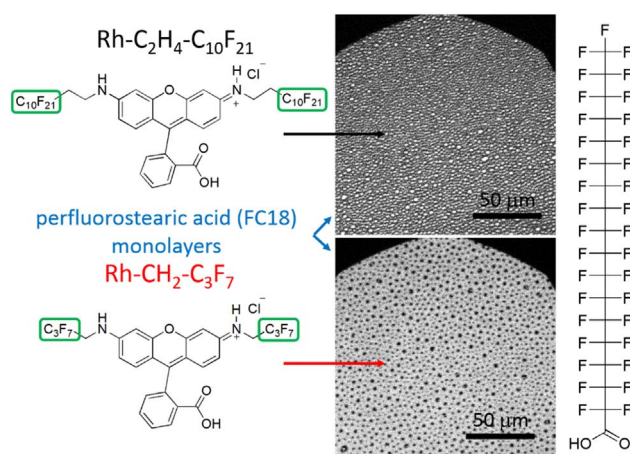
# Mixed Langmuir monolayers of perfluorostearic acid and stearic acid studied by epifluorescence microscopy using fluorinated rhodamines and infrared reflection absorption spectroscopy (IRRAS)



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## GRAPHICAL ABSTRACT



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## ABSTRACT

The fluorophilicity of fluorinated rhodamine-based fluorescence dyes (F-rhodamines) functionalized with  $\text{CH}_2\text{-C}_3\text{F}_7$  ( $\text{Rh-CH}_2\text{-C}_3\text{F}_7$ ) or  $\text{C}_2\text{H}_4\text{-C}_{10}\text{F}_{21}$  ( $\text{Rh-C}_2\text{H}_4\text{-C}_{10}\text{F}_{21}$ ) at both amine groups was tested in mixed monolayers of stearic acid (SA) and perfluorostearic acid (FC18) on a Langmuir trough coupled with epifluorescence microscopy. The composition of the Langmuir monolayers was systematically changed from 100% FC18 to 100% SA in order to investigate the fluorophilicity and lipophilicity of the two F-rhodamines by observing their partitioning behavior within the different monolayers. The F-rhodamine bearing the longer perfluoroalkyl group and alkyl spacer ( $\text{Rh-C}_2\text{H}_4\text{-C}_{10}\text{F}_{21}$ ) showed a substantially higher affinity to the FC18 rich phases in contrast to the F-rhodamine having the shorter perfluoroalkyl chain and alkyl spacer ( $\text{Rh-CH}_2\text{-C}_3\text{F}_7$ ) which was excluded from FC18 as well as from SA domains. The FC18, SA, and FC18/SA 50:50 (mol%) monolayers were further investigated by infrared reflection absorption spectroscopy (IRRAS) in order to investigate the phase behavior of FC18 and SA. It was observed that the orientations of FC18 and SA molecules in the pure and mixed monolayers do not change upon compression. Furthermore, a decrease in the order of the FC18 molecules in the mixed

**Abbreviations:** FC18, perfluorostearic acid; SA, stearic acid;  $\pi$ , surface pressure (mN/m);  $mmA$ , mean molecular area ( $\text{\AA}^2/\text{molecule}$ ); IRRAS, infrared reflection absorption spectroscopy; PFMC, perfluoromethylcyclohexane;  $\text{Rh-C}_2\text{H}_4\text{-C}_{10}\text{F}_{21}$ , rhodamine dye functionalized with two ( $-\text{C}_2\text{H}_4\text{-C}_{10}\text{F}_{21}$ ) moieties;  $\text{Rh-CH}_2\text{-C}_3\text{F}_7$ , rhodamine dye functionalized with two ( $-\text{CH}_2\text{-C}_3\text{F}_7$ ) moieties; GUV, giant unilamellar vesicle; DPPC, 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine; DOPC, 1,2-dioleoyl-*sn*-glycero-3-phosphocholine; F6H2OH, 1H,1H,2H,2H-perfluoro-1-octanol

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monolayer is observed upon the addition of SA. The opposite is not valid in a sense that no loss in order of the SA molecules was observed upon the addition of FC18. This shows that SA partitions more into FC18 phases than FC18 into SA domains. This is due to the weaker van der Waals forces present between the perfluoroalkyl chains in comparison with stronger ones existing between the alkyl chains.

## 1. Introduction

The different van der Waals radii (147 vs. 120 pm) and electro-negativities (3.98 vs. 2.2) of fluorine and hydrogen lead to major changes in the physical properties between fluorinated and non-fluorinated compounds [1]. The C–F bonds are highly polarized and exhibit a very low polarizability which leads to weak intermolecular interactions [2,3]. Therefore, highly fluorinated compounds have low dielectric constants and refractive indices, high vapor pressures, and are simultaneously lipophobic and bear a polar hydrophobicity [3,4]. Liquid-liquid biphasic systems of perfluorinated and aliphatic alkanes at ambient temperatures and pressures tend to phase separate and are miscible above certain upper critical solution temperatures (UCST) due to the reduction of repulsive enthalpic interactions between alkyl and perfluoroalkyl chains with increasing temperature [5–7].

Pure and mixed monolayers composed of perfluorinated or partially fluorinated amphiphiles are readily investigated by surface pressure ( $\pi$ ) – mean molecular area ( $mmA$ ) isotherms coupled mainly with epifluorescence microscopy on the air/water interface [8–10]. Stearic acid (SA) and perfluorostearic acid (FC18) form phase separated monolayers on the air/water interface [11,12]. The two acids are amphiphilic but in a different way, i.e. SA has a hydrophilic head group and a lipophilic  $n$ -alkyl chain, whereas FC18 has a similar hydrophilic head group and a fluorophilic perfluoro- $n$ -alkyl chain. Both chains are hydrophobic but additionally the perfluoro- $n$ -alkyl chains are also lipophobic.

Horváth and Rábai established the term “fluorous” for compounds partitioning favorably in the perfluoromethylcyclohexane (PFMC) phase of a PFMC/organic biphasic system [13]. Shortly after, the PFMC/toluene partition coefficient ( $\ln P_{PFMC/toluene}$ ) became a common parameter used for the quantification of the fluorous character of a certain fluorinated substance [14–16] which is sometimes also referred to as fluorophilicity [17]. However, even highly fluorinated molecules can be poorly fluorous, i.e. they have a negative  $\ln P_{PFMC/toluene}$ , if they contain polar and/or aromatic functional groups in their chemical structures [14,18]. Fluorinated rhodamine-based fluorescence dyes (F-rhodamines) have already been synthesized and used for confocal laser scanning microscopy to detect fluorophilic phase separated domains in 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC)/perfluoropalmitic acid mixed giant unilamellar vesicles (GUVs) [19]. Furthermore, the phase behavior of the system 1,2-dioleoyl-*sn*-glycero-3-phosphocholine (DOPC)/1*H*,1*H*,2*H*,2*H*-perfluoro-1-octanol (F6H2OH) has been correlated with the partition coefficients of the F-rhodamines in several biphasic systems [20]. Keeping in mind that they bear an aromatic core and polar functional groups, it is obvious that their fluorophilicity cannot be judged exclusively on the  $\ln P_{PFMC/toluene}$  value. Here, we focus on the use of F-rhodamines in Langmuir monolayers made from the two immiscible amphiphiles FC18 and SA. The F-rhodamines are then employed to detect the fluorophilic and lipophilic domains on a Langmuir trough coupled with epifluorescence microscopy. The partitioning of the F-rhodamines within the different phases of the

monolayer is expected to shed light on the fluorophilic character of the F-rhodamines under investigation. Thus, monolayers ranging from FC18 to SA were used to test the fluorophilic character of two F-rhodamines, Rh-CH<sub>2</sub>-C<sub>3</sub>F<sub>7</sub> and Rh-C<sub>2</sub>H<sub>4</sub>-C<sub>10</sub>F<sub>21</sub> (Scheme 1) bearing one CH<sub>2</sub>-C<sub>3</sub>F<sub>7</sub> and C<sub>2</sub>H<sub>4</sub>-C<sub>10</sub>F<sub>21</sub> group on each of their amine moieties.

The phase separated monolayers of FC18 and SA provide a two-dimensional (2D) fluorophilic/lipophilic phase separated system that can be used to study and compare the fluorophilic character of fluorescent dyes. Coupling the surface pressure ( $\pi$ ) – mean molecular area ( $mmA$ ) isotherms obtained from the Langmuir monolayer measurements with epifluorescence microscopy on the air/water interface provides important information about the partitioning behavior of the F-rhodamines [21,22].

Infrared reflection absorption spectroscopy (IRRAS) is a well-established experimental method useful for the investigation of molecular conformation and orientation mainly within Langmuir monolayers of single chain amphiphiles, phospholipids, and/or proteins [23,24]. IRRAS is also extensively used to study molecular organization and arrangement of surface active amphiphilic block copolymers and other exotic shaped amphiphiles [25–29]. Moreover, IRRAS is an important experimental technique able to provide insight in structural rearrangements of membrane proteins when bound or partially inserted into the phospholipid membrane [30].

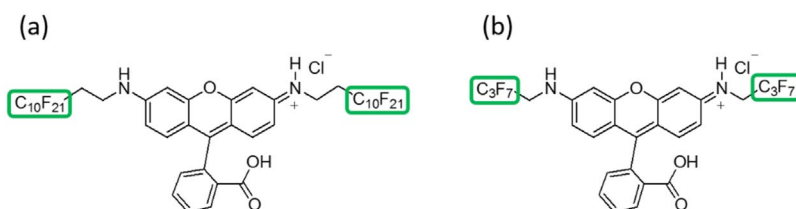
Monolayers of single chain amphiphiles such as SA have been studied in detail with IRRAS at the air/water interface at different pH and temperatures mainly by investigating their symmetric/antisymmetric methylene and carbonyl stretching vibrations [31]. Perfluoro- $n$ -alkanes C<sub>n</sub>F<sub>2n+2</sub> having 14, 16, 20, and 24 carbon atoms are infrared (IR) active mainly in the 1100–1300 cm<sup>-1</sup> region [32] and the molecular orientation of some partially fluorinated alcohols in Langmuir monolayers was already studied with IRRAS [33]. The structure of phase separated Langmuir-Blodgett films of arachidic acid and perfluorotetradecanoic acid (FC14) was investigated with transmission and reflection IR spectroscopy after transfer to solid substrates [34]. The orientation of FC18 Langmuir-Blodgett multilayers was investigated via grazing incidence reflection absorption and transmission IR spectroscopy [35].

Here we use IRRAS to investigate conformation, orientation, and mixing behavior of SA, its perfluorinated analogue FC18, and FC18/SA mixed Langmuir monolayers directly at the air/water interface.

## 2. Materials and methods

### 2.1. Materials

Perfluorostearic acid (FC18) was purchased from Alfa Aesar. Stearic acid (SA) and nonafluorobutyl methyl ether (HFE-7100) were purchased from Sigma-Aldrich. Chloroform, methanol, THF, and diethyl ether were purchased from Carl Roth. The syntheses and characterization of the F-rhodamines depicted in Scheme 1 have been previously reported by Jbeily et al. [19]. The FC18 standard solutions were



Scheme 1. Chemical structures of (a) Rh-C<sub>2</sub>H<sub>4</sub>-C<sub>10</sub>F<sub>21</sub> and (b) Rh-CH<sub>2</sub>-C<sub>3</sub>F<sub>7</sub>.

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