Semifluorinated thiols in Langmuir monolayers – A study by nonlinear and linear vibrational spectroscopies

Diogo Volpati [a,*], Anna Chachaj-Brekiesz [b], Adriano L. Souza [a], Caio Vaz Rimoli [a], Paulo B. Miranda [a], Osvaldo N. Oliveira Jr. [a], Patrycja Dynarowicz-Łątka [b]

[a] São Carlos Institute of Physics, University of São Paulo – USP, PO Box 369, 13566-590 São Carlos, SP, Brazil
[b] Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Kraków, Poland

HIGHLIGHTS

- Semifluorinated alkanethiol monolayer becomes more rigid upon increasing the hydrophobic part.
- Peak at 2874 cm^{-1} in the SFG spectra should be attributed to the CH$_2$ group next to the polar group.
- The gauche defects is increased by increasing either the fluorinated or hydrogenated chain.
- The tilt angle of the terminal CF$_3$ group lies between 35° and 45° according to SFG measurements.
- Increasing the monolayer surface pressure, the fluorinated segment gets slightly more upright.

GRAPHICAL ABSTRACT
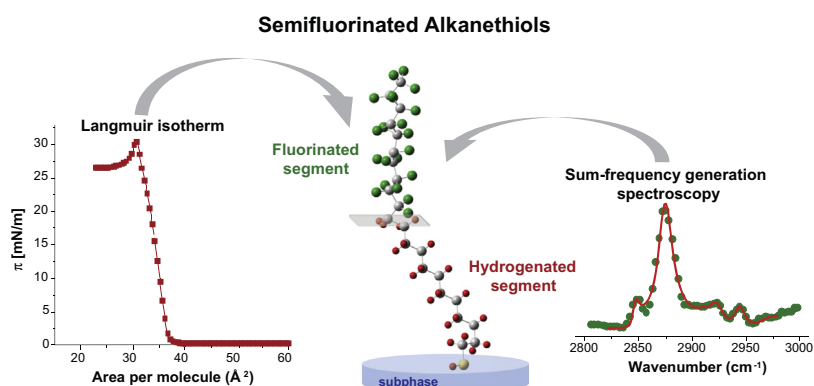
ABSTRACT

A series of semifluorinated thiols of the general formula C$_m$F$_{2m+1}$C$_n$H$_{2n}$SH (abbr. F$_m$H$_n$SH) have been synthesized and characterized in Langmuir monolayers with surface pressure-area isotherms, complemented with polarization-modulated reflection absorption spectroscopy (PM-IRRAS) and sum-frequency generation (SFG) techniques. A comparative analysis was performed for compounds having the same length of fluorinated segment (F$_{10}$) and variable length of the hydrogenated part (H$_6$, H$_{10}$, H$_{12}$), and having identical hydrogenated segment (H$_{12}$) connected to a fluorinated moiety of different lengths (F$_6$, F$_8$, F$_{10}$). For the sake of comparison, an alkanethiol (H$_{18}$SH) was also examined, and F$_{10}$H$_{10}$COOH and F$_{10}$H$_{10}$OH molecules were used for helping the assignment of SFG spectra of CH stretches. SFG was applied to investigate the hydrocarbon chain and the terminal CF$_3$ group, while PM-IRRAS was used to probe CF$_2$ groups. The number of gauche defects in the hydrocarbon chain increased with the increasing length of the molecule, either by elongation of the hydrogenated or perfluorinated part. SFG measurements recorded at three polarization combinations (ppp, ssp, sps) enabled us to estimate the tilt angle of the terminal CF$_3$ group in semifluorinated thiol molecules as ranging from 35° to 45°, which is consistent with nearly vertical fluorinated segments. Upon increasing the surface pressure, the fluorinated segment gets slightly more upright, but the hydrocarbon chain tilt increases while keeping the same average number of gauche defects. The extent of disorder in the hydrogenated segment may be controlled by varying the size of the fluorinated segment, and this could be exploited for designing functionalized surfaces with insertion of other molecules in the defect region.

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* Corresponding author.
E-mail address: diogovolpati@gmail.com (D. Volpati).

1. Introduction

Perfluorinated and hydrogenated chains are mutually phobic to each other, which reflects in their limited solubility with tendency to phase separation as originally observed by Scott in 1948 [1]. The high incompatibility between fluorinated and hydrogenated segments arises from their different structure and properties [2], governed by distinct atomic properties of fluorine and hydrogen. Significant differences between C–F *vs* C–H bonds then appear, as summarized in Scheme 1. Firstly, fluorine atoms are larger than hydrogen (van der Waals (VdW) radius of 0.147 nm *vs* 0.12 nm), the C–F bond being longer than the C–H bond, and therefore the cross-sectional area of perfluorinated segment is 25–30% larger than for the hydrogenated chain. Due to steric reasons, reflected in different tetrahedral angles [3], the conformational freedom is reduced for perfluorinated tails, forming rigid chains arranged preferably in helical conformation as compared to flexible *zig-zag* hydrogenated moieties [4]. The helical structure of 13/6 (units per turn) of perfluorinated polymers was proven with X-ray diffraction [5], but 15/6 and 15/7 helix conformations (depending on temperature) have also been reported [6]. Wang and Ober [7] suggested that in the helical perfluorinated moiety the planar *zig-zag* conformation is possible as well. Also striking are differences in electronegativity (Pauling's scale) of carbon (2.5) and fluorine (4.0) *versus* hydrogen (2.1) [8]. Fluorinated tails are surrounded by a dense electron cloud of low polarizability [9], which results in: (a) low intermolecular interactions; (b) low tendency to form *gauche* defects, as the energy barrier between *trans* and *gauche* conformations and between different *gauche* conformations in perfluorinated molecules is 3–5 times the value for linear hydrocarbons, and (c) an effective shield protecting the carbon atoms from chemical attack, being responsible for their inertness and higher stability as compared to hydrocarbons. The cohesive energy between perfluorinated chains is lower than between hydrogenated ones (see Scheme 1). A comparison with the cohesive energy between water molecules (72 mN/m) explains the higher incompatibility of fluorinated *versus* hydrogenated chains with water. Perfluorinated amphiphiles are more hydrophobic [10,11] and surface active than their hydrogenated analogues – the CMC (critical micelle concentration) of a fluorinated surfactant is equal to the corresponding hydrogenated one with *ca.* 1.5 times longer chain [12]. Last but not least, the C–F bond is the strongest, most stable covalent bond ever found in organic chemistry [13]. Its dipole moment is much larger than that of C–H [14].

The antagonistic nature of fluorinated and hydrogenated blocks is brought together in semifluorinated molecules, making them unique for studying the close interplay between these incompatible segments within one molecule. The simplest and the earliest studied molecules of this kind have been semifluorinated alkanes (SFAs) of the general formula $F(CF_2)_m(CH_2)_nH$ [15]. The presence of two opposing segments makes semifluorinated alkanes an interesting class of compounds, which show a peculiar behavior both in bulk and at interfaces [16,17]. Their highly asymmetric structure results in surface activity (so-called *primitive surfactants* [18]) when dissolved in organic solvents, and allows for Langmuir monolayer formation at the free water surface, despite the absence of a polar group [19]. The introduction of a polar group into the semifluorinated chain results in the so-called *semifluorinated amphiphiles*, whose stability at the air/water interface is enhanced, enabling their transfer onto solid supports. Over the years, various kinds of semifluorinated amphiphiles have been synthesized and characterized in Langmuir monolayers, e.g. alcohols [20,21], carboxylic acids [22–28], thiols [29], thioethers [30] and lipids [31].

This paper is aimed at elucidating the influence of a fluorinated segment on the structure and orientation of the hydrogenated

PERFLUORINATED –(CF₂)ₘ–	*vs*	HYDROGENATED –(CH₂)ₙ–
bond length		
C-F 1.33-1.38 Å		C-H 1.2 Å
bond dipole moment		
1.4 D		0.4 D
chain cross-section		
0.27-0.35 nm²		0.18-0.22 nm²
dihedral angle		
F-C-C-F 46-49°		H-C-C-H 60°
chain conformation		
rigid helix		flexible zig-zag (all trans)
electron density around hydrocarbon backbone		
High		small
cohesive energy		
very low (10-15 mN/m)		low (25-30 mN/m)
hydrophobicity/liophobicity		
very hydrophobic/lipophobic		hydrophobic/lipophilic

Scheme 1. Comparison of the properties of perfluorinated and hydrogenated chains.

segment in semifluorinated molecules spread in Langmuir monolayers. We were inspired by the finding that a small increment in the fluorinated chain length can modify significantly film organization and properties, as observed for fluorinated double-chain monomorpholinophosphates [32]. In the latter paper, disorder was found to be hindered by increasing the fluorinated segment and facilitated by increasing the hydrogenated fragment. This conclusion, however, has been drawn by examining molecules differing to a small extent as regards to the length of fluorinated and hydrogenated chains, e.g. the hydrogenated segment contained only 1 or 2 carbon atoms. Our research hypothesis was to confirm this finding, applying a broader selection of semifluorinated molecules. For our investigations we have chosen semifluorinated thiols, which are of special importance due to their ability of forming chemisorbed layers that have many applications, especially in the emerging area of functionalized metal or oxide interfaces [33,34]. The sulfhydryl group has also advantages when studying hydrophobic parts of amphiphilic molecules alone, for it is small and does not interfere with water molecules as it does not ionize nor forms hydrogen bonds.

Although studies about the impact of fluorination on the structure and properties have been performed for chemisorbed layers (for a review see [33]), the literature lacks systematic investigations for films at the free water surface. Therefore, the aim of this paper was to fulfill this gap. For this purpose, a series of semifluorinated thiols of the general formula $C_mF_{2m+1}C_nH_{2n}SH$ (*abbr.* F$_m$H$_n$-SH) were synthesized. We have compared compounds with identical fluorinated length (perfluorodecane moiety) but differing in the methylene chain length (F$_{10}$H$_6$SH, F$_{10}$H$_{10}$SH, F$_{10}$H$_{12}$SH), as well as with the same hydrogenated part (dodecane segment) attached to perfluorinated moieties of different lengths (F$_6$H$_{12}$SH, F$_8$H$_{12}$SH, F$_{10}$H$_{12}$SH). This enabled us to study the influence of varying the length of the fluorinated chain while keeping the length of the hydrocarbon tail constant, and *vice versa*. By comparing the results for semifluorinated derivatives of eicosanethiol (F$_{10}$H$_{10}$SH and F$_8$H$_{12}$SH), it was possible to infer structural properties of compounds with the same length of hydrophobic part (20 carbon atoms altogether), but with different degrees of fluorination. For the sake of comparison, hydrogenated thiol (octadecanethiol, $C_{18}H_{37}$SH, *abbr.* H$_{18}$SH) was also used. For our investigations we have employed the Langmuir monolayer technique complemented with polarization modulated-infrared reflection absorption (PM-IRRAS) and sum-frequency generation (SFG) vibrational spectroscopies, which are particularly useful for probing molecules at interfaces. Successful examples of applying PM-IRRAS include: