

Electronic Supplementary Information

Spontaneous self-assembly of partially fluorinated bolaamphiphiles into ordered layered structures

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Table S1 Phases and transition temperatures observed in the investigated compounds

Compound		Phase transitions $T/^{\circ}\text{C}^{[a]}$		
X1	Cr 83	(M ₁	65)	Iso
X2	Cr 70	Col _{sq} / <i>p4mm</i>	94	Iso
X3	Cr < 20	g 50 Col _{hex} / <i>p6mm</i>	67	Iso
X4	Cr 64	Col _{sq} / <i>p4mm</i>	92	Iso
T1	Cr 87	Col _{hex} / <i>p6mm</i>	229	Iso
A1	Cr 113	-	-	Iso
A2	Cr 63	Col _{hex} / <i>p3m1</i>	190	Iso

^[a] Abbreviations: Cr = crystalline solid, Iso = isotropic liquid, Col_{sq}/*p4mm* = square columnar phase with simple *p4mm* lattice, Col_{hex}/*p6mm* = hexagonal columnar phase with *p6mm* lattice, Col_{sq}/*p3m1* = hexagonal columnar phase with trigonal *p3m1* lattice, Col = columnar phase with unknown lattice, M₁ = mesophase of unknown structure, g = glassy state; values in parenthesis refer to monotropic (metastable) phases.

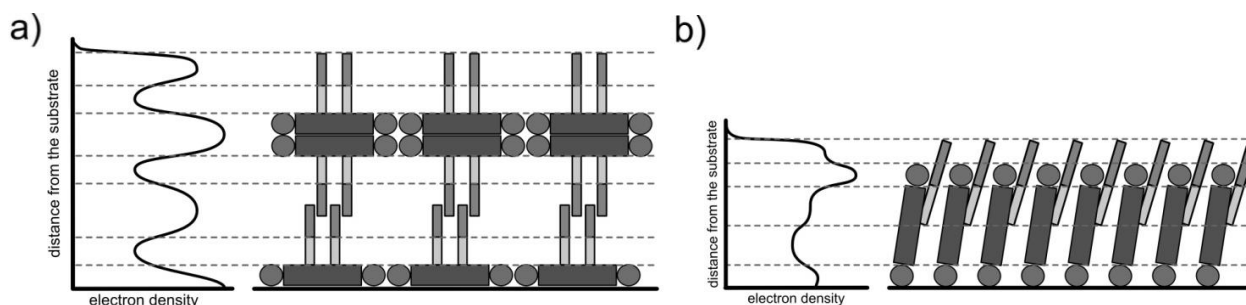


Figure S1 Schematic molecular structures of films: a) trilayer of compound X4 and b) Sm-like monolayer of a T-shaped compound. The dashed lines represent boundaries between the slabs, into which the films were divided for the XRR fitting procedure. To the left of the schematics are presented sketches of predicted changes of electron density with the distance from the substrate. The values of electron density for each slab were based on

the elemental composition of the slab and the value of area per molecule in the film, which was measured in Langmuir experiments. Thus calculated electron densities were treated as starting parameters for the fitting procedure and were allowed to vary only in a limited range during the fitting.

X-shaped bolaamphiphiles

Ellipsometry

To confirm the XRR results, additional experiments were conducted with use of spectroscopic ellipsometry.

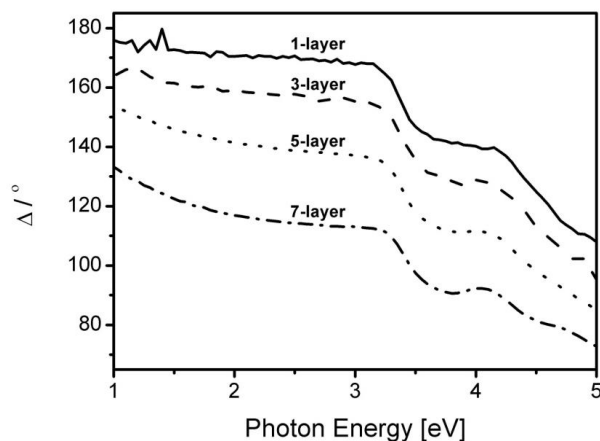


Figure S2 Phase retardation (Δ) as a function of photon energy plotted for a 1-, 3-, 5-, and 7-layer films of **X4** obtained by Langmuir-Blodgett (LB) method.

We followed the method used by Navailles *et al.*¹ For two wavelengths, corresponding to 3 and 4.15 eV, we calculated the $\delta\Delta$ parameter ($\delta\Delta = \Delta_0 - \Delta$, where Δ_0 is the delta value for clean silicon substrate and Δ is the delta value measured for the sample). For ultrathin films this parameter is proportional to the thickness of the film.

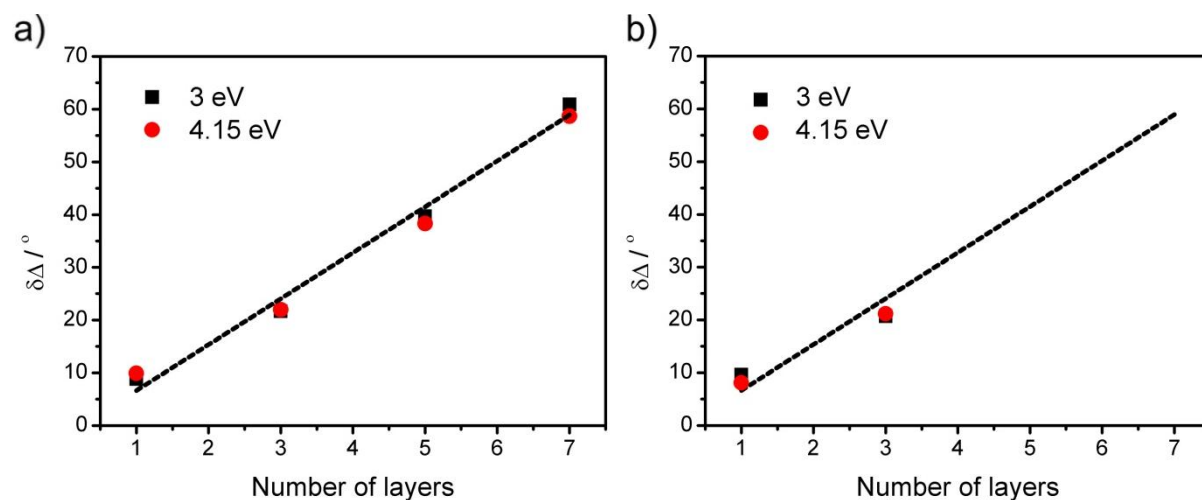


Figure S3 The plots present results obtained for a) Langmuir-Blodgett films of 1-, 3-, 5-, and 7-layers of **X4** and b) drop-casted 1- and 3-layer films of **X4**.

The thickness ratio of multilayers and monolayer matches the XRR results perfectly. The increase of thickness upon layering transitions is proportional to the number of layers. Thickness of the drop-casted (DC) films is practically the same as the Langmuir-Blodgett (LB) films. For drop-casted $L=5$ and $L=7$ films it was not possible to obtain reliable results – ellipsometric measurements were strongly distorted. This confirms that only ordered mono- and trilayer films were formed via drop-casting, while for $L=5$ and $L=7$ DC films irregular aggregates were present on top of the film.

ATR-FTIR and PM-IRRAS measurements

ATR-FTIR spectrum of compound **X4** was recorded. Two peaks (at 2919.6 cm^{-1} and 2851.7 cm^{-1}) corresponding to C-H bonds in alkyl chains were detected. At around 1500 cm^{-1} several peaks from aromatic rings were visible. The most intensive peak came from aromatic ether groups (according to Coates² it should be located in the $1230\text{-}1270\text{ cm}^{-1}$ range and was in fact recorded at 1254 cm^{-1}). The C-F vibrational bands usually appear at around $1000\text{-}1400\text{ cm}^{-1}$. The C-F band from trifluoromethyl group is split into two peaks, one for the symmetric mode and one for the asymmetric.³ The carbon-fluorine bands are so strong that they may obscure any carbon-hydrogen bands that might be present in this range.⁴

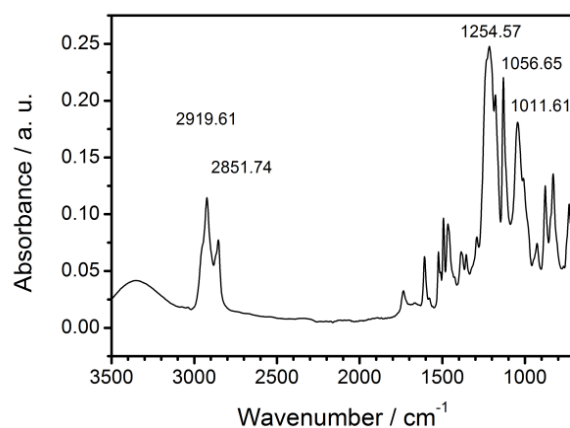


Figure S4 ATR-FTIR spectrum of compound **X4**.

PM-IRRAS spectra of Langmuir-Blodgett films of compound **X4** were also recorded. The samples were transferred onto gold surface. The equipment allowed for acquisition in the range of 700 cm^{-1} to 3500 cm^{-1} . At around $1900\text{-}2400\text{ cm}^{-1}$ the peaks from residual CO_2 and other artificial peaks appeared, therefore this spectral region was unavailable for analysis.

Two films were studied: a monolayer (transferred at 20 mN m^{-1} – before reaching the plateau on the $\pi(A)$ isotherm) and a trilayer (transferred at 35 mN m^{-1} – after the plateau region). Even despite the films were extremely thin, we were able to observe the most important bands. Spectra of both films are presented in **Figure S5** and **S6**.

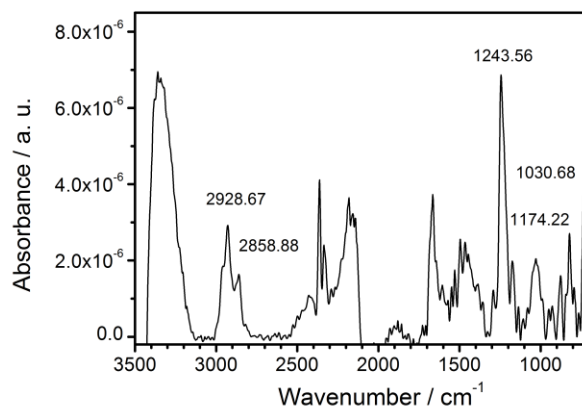


Figure S5 PM-IRRAS spectrum of a monolayer film of **X4** transferred at 20 mN m⁻¹.

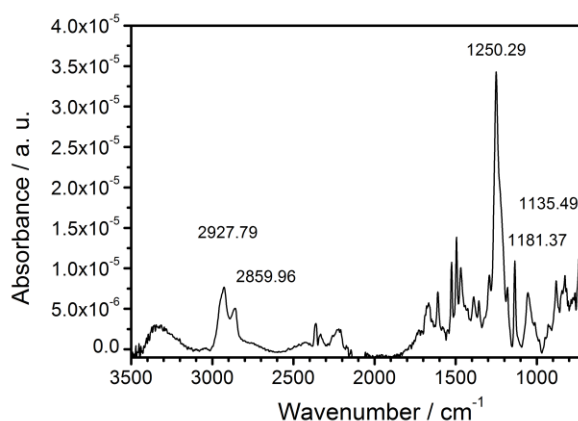


Figure S6 PM-IRRAS spectrum of a trilayer film of **X4** transferred at 35 mN m⁻¹.

In case of both mono- and trilayer films C-C bands at around 2800 - 3000 cm⁻¹ were clearly visible. Since the spectra were recorded with use of PM-IRRAS technique, only the bands corresponding to vibrations in the direction perpendicular to the surface were observed. It means that the side chains were aligned perpendicular to the surface.

The analysis of C-H stretching bands in the 2800 - 3000 cm⁻¹ region is very useful for characterization of thin films containing aliphatic chains.^{5,6} When condensed phase is observed, two peaks are usually present at 2920 cm⁻¹ and 2850 cm⁻¹. In case of a liquid phase monolayer, these values are shifted to 2928 cm⁻¹ and 2858 cm⁻¹, respectively.

Since the spectra were recorded with use of PM-IRRAS technique, only the bands corresponding to vibrations in the direction perpendicular to the surface could be observed. The peaks at 2859 cm⁻¹ and 2928 cm⁻¹ indicate that the side chains are perpendicular to the surface and appear as a liquid sublayer. This is perfectly in line with the model presented in **Figure S1a**. The rigid core of the **X4** molecule is aligned parallel to the surface. One molecule covers around 1.2 nm². The cross section area of

aliphatic chain is around 0.2 nm^2 and perfluorinated chain around 0.28 nm^2 .⁷ Two chains aligned perpendicular and to the core need around 0.6 nm^2 . Therefore, in both cases (mono and trilayer films) the alkyl chains were packed loosely.

The intensities of the peaks at 2928 cm^{-1} and 2858 cm^{-1} of monolayer and trilayer again support the presented reasoning. We normalized the intensities of the spectra by the number of molecular layers (the intensity of the spectrum obtained for trilayer film was divided by 3). After such procedure the spectra of mono and trilayer films overlapped nearly perfectly (**Figure S7**). This implies that the side chains in all the layers of a trilayer film were aligned identically as in a monolayer – perpendicular to the surface (see scheme in **Figure S1a**). Slight difference in the ratios of intensities of signals at 2928 cm^{-1} and 2858 cm^{-1} was noticed. This was probably caused by the fact that trilayer film was transferred at 35 mN m^{-1} , when the film was not fully compressed. This allowed for some tilt of the molecules and slight irregularities.

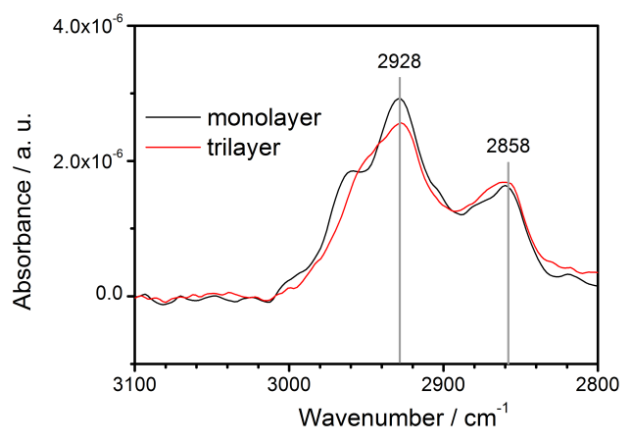


Figure S7 PM-IRRAS spectra of monolayer and trilayer films of **X4** normalized by the number of layers.

UV-Vis

UV-Vis spectrum of solution of **X4** was recorded (0.2 mg/ml in HPLC grade chloroform). The result is shown in **Figure S8a**. Attempting to record the absorption spectra of Langmuir-Blodgett films, mono- and trilayer films were transferred onto quartz plates at 20 mN m^{-1} and 35 mN m^{-1} , respectively. Well-developed spectrum was observed only in case of the trilayer (**Figure S8b**). The reason of the observed phenomenon is formation of multilayer stacks. During compression not only the average area per molecule changes (increasing “concentration” of absorbing molecules), but also, because of the layering transition, the thickness of the film (and the length of the optical path) increases.

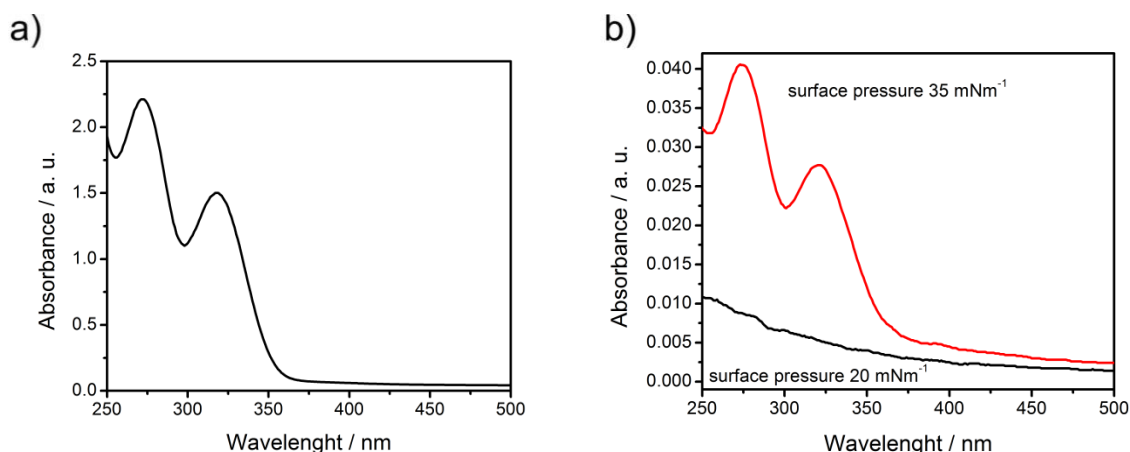


Figure S8 UV-Vis spectra of compound **X4** a) solution and b) Langmuir-Blodgett films transferred at different values of surface pressure.

T-shaped bolaamphiphiles

UV-Vis

The UV-Vis spectrum of compound **T1** is slightly different comparing to compound **X4**. This was probably caused by the small difference in geometry of the aromatic rings of the core of the molecule. The results of the UV-Vis measurements of compound **T1** are shown in **Figure S9**. Films were transferred onto quartz plates at different surface pressures. Up to 25 mN m⁻¹ the measured absorbance of the films was almost zero. However, in case of film transferred at 40 mN m⁻¹ the spectrum was well-developed. Such a difference could not be caused solely by an increase of the number of molecules present in the beam path. The area per molecule at 25 mN m⁻¹ was around 0.45 nm² and at 40 mN m⁻¹ around 0.39 nm², so the expected difference in the film absorbance would be around 10%. The observed dramatic change can be explained in the terms of the molecular arrangement. In the main text of the paper and in the previous section (analysis of $\pi(A)$ isotherms) we proved that the molecules in the film rearrange from Lam-like to Sm-Like at around 30 mN m⁻¹. In case of molecules lying flat at the surface (Lam-like arrangement) the intensity of UV-Vis spectra is almost zero. As the molecules rise to form Sm-like layer, not only the orientation of the molecules respectively to the beam changes, but also the film thickness increases – and, consequently, so does the optical path length. This result supports the proposed structure of a film of T-shaped bolaamphiphiles (**Figure S1b**).

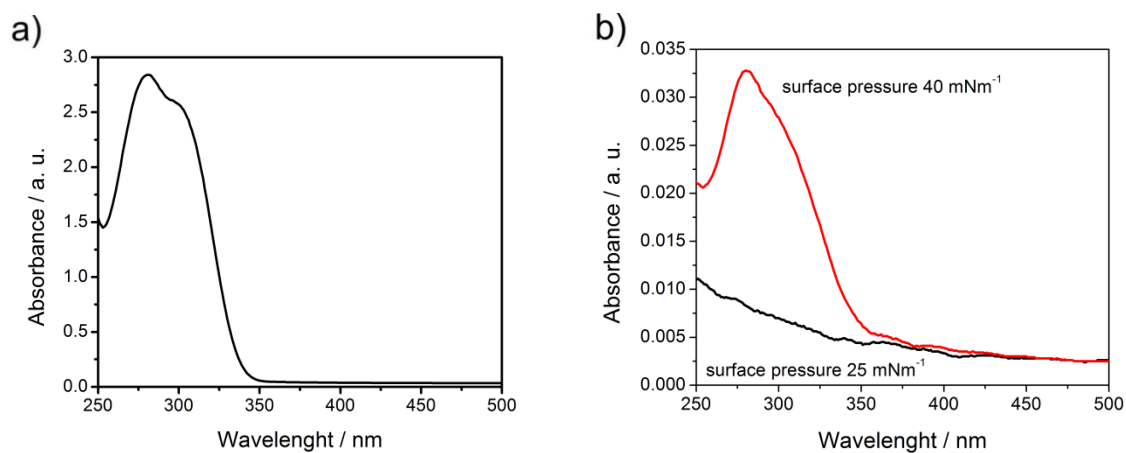


Figure S9 UV-Vis spectra of compound **T1** a) solution and b) Langmuir-Blodgett films transferred at different values of surface pressure.

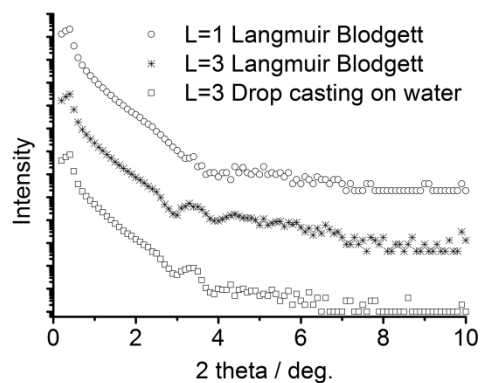


Figure S10 Results of XRR measurements of films of **X5**.

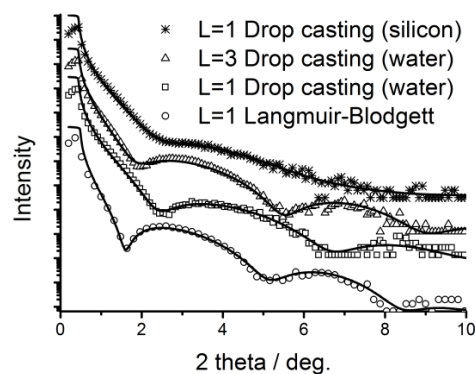


Figure S11 Comparison of XRR patterns of films of **T2**.

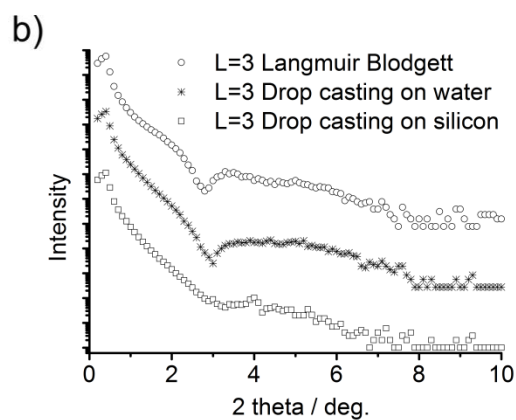
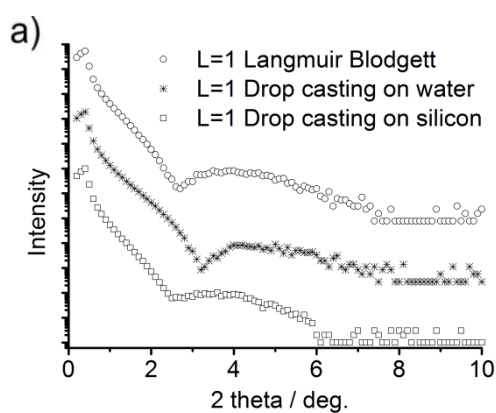


Figure S12 Comparison of XRR patterns of films of **A1**.

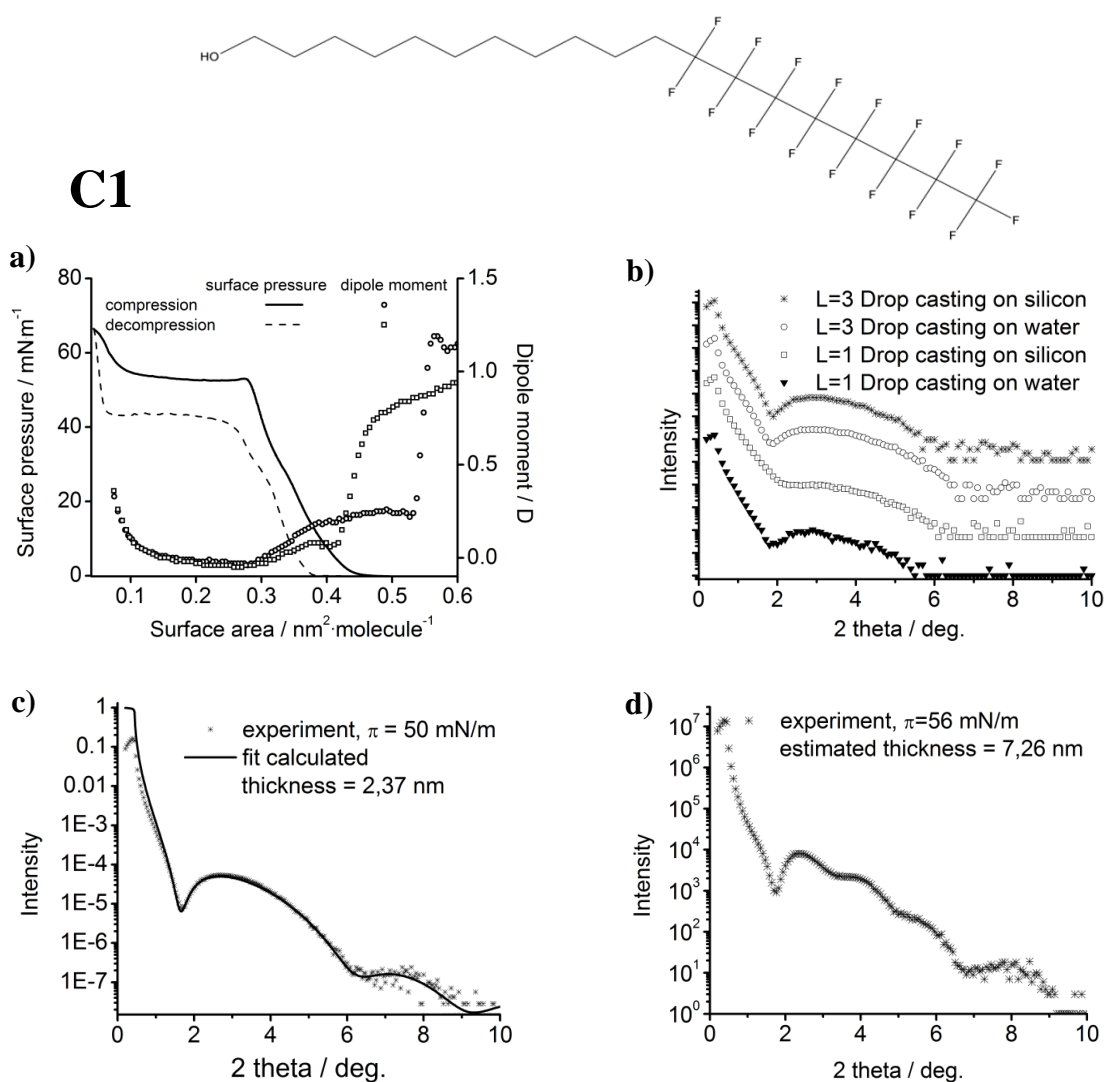


Figure S13 Set of results for compound **C1** (partially fluorinated nonadecanol). Picture **a)** shows $\pi(A)$ isotherms and surface potential recorded during compression-decompression cycle. Characteristic plateau indicate that the layering transition to trilayer film occurs the process (ratio of values of area at the beginning and end of the plateau close to 3). This was confirmed with use of XRR (patterns presented in **c)** for monolayer and **d)** trilayer film). It was impossible to fit the XRR pattern obtained for trilayer film with use of reasonable set of parameters, therefore only estimated thickness is presented. Picture **b)** shows the results of drop-casting experiments – only monolayer films were formed with use of this method.

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⁴ *Infrared Spectroscopy: Fundamentals and Applications*, B.H. Stuart, p.82, John Wiley & Sons (2004)

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