### Aggregation and Layering Transitions in Thin Films of X-, T-, and Anchor-Shaped Bolaamphiphiles at the Air–Water Interface

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Abstract: Aggregation in Langmuir films is usually understood as being a disorderly grouping of molecules turning into chaotic three-dimensional aggregates and is considered an unwanted phenomenon causing irreversible changes. In this work we present the studies of 11 compounds from the group of specific surfactants, known as bolaamphiphiles, that exhibit reversible aggregation and, in many cases, transition to well-defined multilayers, which can be considered as a layering transition. These bolaamphiphiles incorporate rigid  $\pi$ -conjugated aromatics as hydrophobic cores, glycerol-based polar groups and hydrophobic lateral chains. Molecules of different shapes (X-, T-, and anchor) were studied and compared. The key property of these compounds is the partial fluorination of the lateral chains linked to the rigid cores of the molecules. The most inter-

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esting feature of the compounds is that, depending on their shape and degree of fluorination, they are able to resist aggregation and preserve a monolayer structure up to relatively high surface pressures (T-shaped and some X-shaped molecules), or create well-defined trilayers (X- and anchorshaped molecules). Experimental studies were performed using Langmuir balance, surface potential and X-ray reflectivity measurements.

#### Introduction

Development of new technologies, especially nanotechnology, would not be possible without understanding the self-assembly of molecules into materials with well-defined structures in a bottom-up approach.<sup>[1]</sup> For example, organic transistors based on a self-assembled monolayer were recently reported.<sup>[2]</sup> Another example from the field of organic electronics is provided by molecular junctions with  $\pi$ -conjugated

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molecules.<sup>[3]</sup> Hence, it appears that directed self-assembly at surfaces is presently one of the major strategies to achieve functional nanoscale structures. Besides self-assembly on solid surfaces,<sup>[4]</sup> self-assembly of amphiphilic molecules on liquid surfaces (Langmuir films) and transfer of these preformed layers onto solid substrates represents another one of the major strategies.<sup>[1,5]</sup> However, well-defined monomolecular layers could be achieved with the Langmuir technique by compressing thin films of amphiphiles. In attempts to produce multilayers by further compression, a random, disordered aggregation usually takes place instead of self-organization into well-defined multilayers.<sup>[1,5,6]</sup> This unwanted process is frequently observed in Langmuir films because the molecules tend to detach from the interface (escape to the third dimension) and disorderly group into random (semi)crystalline 3D aggregates. Hence, avoiding aggregation of the monolayer, and achieving reversibility of film formation became an important challenge.<sup>[7-11]</sup> To the best of our knowledge, perfect reversibility of compression/decompression isotherms<sup>[12]</sup> was first reported by Tournilhac et al.<sup>[10]</sup> in 1994 and recently, in our previous communication paper.<sup>[11]</sup> The common feature of the amphiphilic compounds used in both reports is the combination of a rodlike mesogenic unit, favouring liquid crystalline self-assembly, with partly fluorinated alkyl chains. Besides their distinct effects on self-assembly, the rodlike  $\pi$ -conjugated moieties introduce functionality, as fluorescent and semiconducting properties, which are of interest with respect to potential applications of the formed thin films.<sup>[13,14]</sup>

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The observation that partially fluorinated alkanes are able to create stable monolayers<sup>[15]</sup> on water surfaces and behave as "primitive surfactants" initiated intense studies of fluorinated alkanes<sup>[16–20]</sup> as well as fluorinated polar amphiphiles.<sup>[21,22]</sup> Systematic studies of some fluorinated alkanes in Langmuir films have shown reversibility of isotherms<sup>[21]</sup> when decompressed before collapse. Hence, it seems that an important way to increase stability of the monolayer and to prevent an irreversible 3D aggregation is a fluorination of particular parts of the amphiphilic molecules.<sup>[8,17,21]</sup>

Bolaamphiphiles<sup>[23]</sup> represent a special type of amphiphiles possessing two hydrophilic groups attached to both ends of an elongated hydrophobic segment. These special amphiphiles, which could likewise be regarded as dimeric end-to-end connected amphiphiles, are known to significantly stabilize membranes (e.g., monolayer lipid membranes of archae bacteria<sup>[24]</sup>) and to form other interesting self-assembled structures, such as liquid crystalline phases in the bulk state,<sup>[25]</sup> and gels<sup>[23]</sup> or helical fibres<sup>[26]</sup> in aqueous systems. Formation of nanowells and pores in lipid membranes represents an additional example of their unique self-assembly capability.<sup>[23]</sup> In their self-assembled structures flexible bolaamphiphiles can adopt different conformations: a linear one, and if the hydrophobic moiety is sufficiently long and flexible, also a reversed U-shape.<sup>[27,28]</sup> Introduction of a rodlike rigid segment as a hydrophobic moiety between the polar groups inhibits deformation to a U-shaped conformation, and hence, should modify the self-assembly behaviour significantly.

One of the most promising classes of rodlike bolaamphiphiles capable of self-assembly into distinct superstructures are those composed of a rigid  $\pi$ -conjugated aromatic core terminated at both ends with hydrophilic hydrogen-bonding glycerol moieties.<sup>[29-31]</sup> This basic structure can be modified through the shape of the core (linear<sup>[29,30]</sup> or bent<sup>[31]</sup>) or by additional lateral chains attached at different positions giving  $T^{-[29]}(\mathbf{T})$ ,  $X^{-[30]}(\mathbf{X})$ , or anchor-shaped<sup>[31]</sup> (A) molecules, as shown schematically in Figure 1. The shape of the molecule, combined with the segregation of the lateral chains into distinct compartments, determines the bulk properties of the compound. This concept of polyphilic bolaamphiphiles led to a wide variety of different highly complex liquid crystalline (LC) soft-matter structures as described by Tschierske et al.<sup>[29-33]</sup> In a previous communication<sup>[11]</sup> we reported three examples of partially fluorinated X-shaped bolaamphiphiles that showed perfect reversibility



Figure 1. Schematic sketches of the bolaamphiphilic molecules under discussion and their abbreviations; molecules assigned as T-shaped are in fact more similar to a  $\lambda$ -shape as the lateral chain is attached at an angle of 60° to the rodlike core.

of Langmuir isotherms even for very high compression/decompression rates and ratios. Herein we report the effects of the number and position of the lateral chain(s) (X- versus Tshaped molecules), the core length (terphenyls versus phenylene ethynylene-type cores), the shape of the rigid core (linear versus bent) and the degree of fluorination on the self-assembly of rigid bolaamphiphiles in Langmuir monoand multilayers. Brewster angle microscopy, surface potential measurements and X-ray reflectivity measurements of transferred films were used as the major tools to investigate the thin films. During film formation, reversibility of the isotherms was observed in all classes of compounds with semiperfluorinated alkyl chains. Generally, the monolayers of gaseous and expanded liquid phases with the aromatic cores lying flat on the water surface were found for all compounds at relatively low surface pressure (see Figure 2c). Upon further increase of the surface pressure, depending on the molecular structure, either triple-layer formation with retention of the orientation of the aromatic cores parallel to the surface (Figure 2a) was observed as a first-order layering transition, or the monolayer structure was retained while the molecules changed their orientation to a tilted or vertical orientation (Figure 2b) in a second-order transition to a condensed-liquid film.

Transformations shown schematically in Figure 2 provide a tool for obtaining well-defined Langmuir films with distinct film thickness (mono- versus trilayers) and distinct directions of the  $\pi$ -conjugated aromatic cores in a reversible



Figure 2. Different types of self-assembled layers at the air–water interface as formed by X-, T- and anchor-shaped bolaamphiphiles and their reorganization by changing the surface pressure; dark grey=rigid aromatic cores (simplified; bent structure of the A compounds is not considered); white circles=polar glycerol groups; light grey=regions of semiperfluorinated chains and alkyl chains (segregation of  $R_F$  and  $R_H$  segments is not considered). a) Lam-like<sup>[33]</sup> trilayer with the aromatic cores organized parallel to the air–water interface, b) smectic-like monolayer with an organization of the aromatic cores, on average, tilted or perpendicular to the air–water interface, c) Lam-like monolayer with a single layer of aromatic cores covering the water surface. A, B and C describe different types of transformations leading from the Lam-like monolayers to trilayers (A=lifting, B=reversible rollover collapse) and to smecticlike monolayers (C=tilting).

surface-pressure-dependent self-assembly process. Moreover, these preformed layers can be transferred onto solid substrates without loss of ordering as revealed by X-ray reflectivity measurements. The combination of 1) anisometric rigid units, favouring liquid-crystalline self-assembly thereby stabilizing the ordering, 2) the general film-stabilizing effect of perfluorinated chains, due to their increased amphiphilicity, and 3) the fluidity of semi-perfluorinated chains (inhibiting crystallization)<sup>[34]</sup> were established as the key features for successful molecular design.

#### **Results and Discussion**

All numerical results obtained in the studies of the 11 bolaamphiphilic compounds are collected in Table 1 for the Xand anchor-shaped compounds  $\mathbf{X}$  and  $\mathbf{A}$ , and for the Tshaped molecules  $\mathbf{T}$  in Table 2. A detailed description of investigations is presented in the following sections according to the shape of the molecules.

**X-shaped bolaamphiphiles**: Six compounds (**X1–X6**) belonging to the group of X-shaped molecules with two types of

Table 1. Data of the Langmuir films and transferred films of compounds  ${\bf X}$  and  ${\bf A}.^{[a]}$ 

Com-	$A_1$	$\pi_1$	$d_1$	$A_2$	$\pi_2$	$d_2$
pound	[nm <sup>2</sup> molecule <sup>-1</sup> ]	$[mN m^{-1}]$	[nm]	[nm <sup>2</sup> molecule <sup>-1</sup> ]	$[mN m^{-1}]$	[nm]
X1	1.20	17.7		0.51	19.2	
X2	1.05	19.7	1.43	0.34	20.6	4.07
X3	1.06	23.4	1.65	0.36	23.8	4.76
X4	1.23	24.1		0.37	25.0	
X5	1.48	9.2		0.71	10.0	
X6	1.57 <sup>[b]</sup>	9.4 <sup>[b]</sup>	$1.57^{[b]}$	0.53 <sup>[c]</sup>	43.0 <sup>[c]</sup>	3.51 <sup>[c]</sup>
A1	1.28	12.2		0.27	13.3	
A2	1.16	20.0	1.43	0.43	21.6	3.71
A3	0.89	26.1		0.30	26.1	

[a]  $A_1$ ,  $\pi_1$ =area and surface pressure at the beginning of the plateau;  $A_2$ ,  $\pi_2$ = area and surface pressure at the end of the plateau;  $d_1$ =thickness of the monolayer transferred below the plateau region;  $d_2$ ,=thickness of the trilayer (for compounds **X2**, **X3** and **A2**, only) transferred above the plateau region. [b] The apparent plateau corresponds to the beginning of the transition to tilted phase ( $A_1$ ,  $\pi_1$ ) and  $d_1$ =thickness of the monolayer of the molecules with horizontally oriented cores. [c] Coordinates ( $A_2$ ,  $\pi_2$ ) correspond to the collapse of the monolayer of tilted molecules and  $d_2$ =thickness of this monolayer (see Figure 5a and discussion in the text).



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rigid cores differing in length were investigated. The lateral chains attached to each core differ in the degree of fluorination. Compounds X1 to X4 with terphenyl cores terminated with two glycerol moieties were recently investigated and detailed analysis of the reversibility of their isotherms was shown for the case of compound X2.<sup>[11]</sup> The isotherms of compounds X1 to X4 are collated in Figure 3a. The most interesting feature of the isotherms of all these X-shaped molecules are the broad plateaus, as often observed for transitions from monolayers to multilayers. In all cases the plateaus are reached at  $\pi = 20-25 \text{ mNm}^{-1}$ , which corresponds to an area (A) of 1.1 to  $1.3 \text{ nm}^2$  molecule<sup>-1</sup>. This area corresponds to the area required by the bolaamphiphilic moiety (aromatic core and polar head groups) lying on the water surface and seems to be additionally affected by the number of fluorinated segments (compare the isotherms of compounds X3 and X4). It can be assumed that before the plateau is reached the polar terminal groups of compounds X1-X4 interact strongly with the water surface causing these molecules to lie flat at the air-water interface. As the plateau is reached the bolaamphiphilic cores become densely packed with the lateral chains arranged on top and covering these layers. Therefore, the molecular area at this kink is mainly determined by the size of the bolaamphiphilic cores (aromatics, glycerols and ether oxygen atoms carrying the lateral chains) and the effect of the flexible lateral chains is smaller. Only in the case of two fluorinated chains (compound X4) does the relatively large diameter of these chains seem to influence the required surface area. Enlargement of the fluorinated parts of the side chains enhances the stability of these layers due to an increase of hydrophobicity (compare compounds X2 and X4). A second rise of the isotherms starts at A = 0.3-0.4 nm<sup>2</sup>molecule<sup>-1</sup>. The ratio of the area per molecule at both ends of the plateau is very close to 3, which suggests that trilayer formation is developing at the beginning of the plateau. This was already proven<sup>[11]</sup> in the case of compound **X2** by comparing the molecular areas at both ends of the plateau as well as by Xray reflectivity measurements (XRR).<sup>[11]</sup> The same conclusion can be drawn for compounds X3 and X4. For example, the film of **X3** was transferred onto silicon wafers at  $\pi = 17$ and 27 mNm<sup>-1</sup> using the Langmuir-Blodgett technique. XRR measurements were performed on these samples to

estimate the thickness of the films and the results are shown in Figure 5a. Values of the layer thickness obtained for compound **X3** from XRR data fitted to the theoretical equation based on the electron density modulation derived initially from modelling (see Figure S2 and Table S1 in the Supporting Information) are equal to  $d_1$ = 1.65 nm for the monolayer and  $d_2$ =4.76 nm for the film transferred at the end of the plateau

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Figure 3. Isotherms and BAM images for X-shaped compounds: a) the hysteresis loop (compression and decompression) for the dialkyl-substituted compound X1 (dashed lines) and the compression runs (only) for semi-perfluorinated compounds X2 ( $\odot$ ), X3 ( $\blacktriangle$ ) and X4 ( $\diamond$ ); b)–d) the BAM images recorded at conditions marked with the same letters on the isotherm of compound X2: b) first domains of the trilayer appearing at the beginning of the plateau, c) and d) the increasing area covered by the trilayer during compression; e) (not marked on the isotherm) the remains of the trilayer in coexistence with the monolayer observed during decompression of compound X2 (not shown) at the right end of the plateau. The white scale bar in image (b) represents a length of 400 µm.

region. This ratio confirms that a trilayer is formed in the plateau region  $(d_2/d_1 \approx 3)$ .

Additional information about the self-assembly of compounds X1-X4 comes from the curve of the vertical component of the dipole moment,  $\mu_{\perp}(A)$ , shown for compound **X3** in Figure 4a. An important contribution to the molecular dipole moment comes usually from the terminal bond of the alkyl chain. In the case of X-shaped molecules, for which the rigid cores with the polar groups are lying flat on the water surface, the terminal C-H or C-F bonds of the lateral chains induce changes in the vertical component of the dipole moment. If during compression of the close-packed monolayer the lateral chains reorganize and the contribution of the chains adopting a vertical orientation increases, the contribution of terminal bonds becomes clearly visible in the  $\mu_{\perp}(A)$  curves, because the dipole moment of the C-H bond is positive and that of the C-F bond is negative. A broad peak in the  $\mu_{\perp}(A)$  curve is observed for compound



Figure 4. Direct comparison of two pairs of compounds a) with different rigid cores and b) with a different degree of fluorination in one lateral chain. a) The isotherms of the compression/decompression runs and the curves of the vertical component of molecular dipole moment for **X3** with a *p*-terphenyl core and for **X6** with a phenylene ethynylene type core are compared; b) two cycles of compression (black lines) and decompression (grey lines) of two compounds with a phenylene ethynylene based rigid core and different side chains (hydrocarbon chains in **X5** and one partially fluorinated chain in **X6**) are shown for comparison; letters c and d mark the conditions at which the BAM images (also marked as c and d) were recorded. c) The aggregates of **X6** after compression beyond collapse and d) the coexistence of liquid and gas phases (2D foam) recovered after decompression. The white scale bar in image (d) represents a length of 400  $\mu$ m.

**X3** upon compression of the monolayer. This shows that during the rise of the isotherm the longer hydrogenated chains are rising up first, causing the increase of the dipole moment. Upon further compression the contribution of vertically aligned fluorinated chains increases and causes the decrease of the curve. In the plateau region no further change of the dipole moment was observed, which supports the proposed model of molecular organization whereby in the plateau region a bilayer of antiparallel-organized mole-



Figure 5. Results of X-ray reflectivity measurements and curves fitted to a theoretical equation for compounds a) X6 and b) X3. The film thicknesses for mono- and trilayers was estimated from the fitted parameters; for more details, see the Supporting Information.

cules (compensated dipole moments) is formed on top of the monolayer, leading to trilayer formation. For trilayer formation a reversible "rollover" mechanism (Figure 2, process **B**) was proposed firstly for rodlike amphiphilic liquid crystals (aromatics perpendicular to or tilted relative to the surface)<sup>[35-39]</sup> and then for T-shaped facial amphiphiles<sup>[40]</sup> that have an arrangement of rodlike aromatics parallel to the surface as also found for the bolaamphiphiles X1-X4. More recently, trilayer formation was also reported for semi-perfluorinated hydrocarbons,<sup>[17]</sup> amphiphiles with bulky aromatic end groups<sup>[41]</sup> and for mixed monolayers formed by co-assembly of cationic lipids with anionic porphyrins.<sup>[42]</sup> For these co-assembled monolayers it was suggested that trilayer formation takes place in a kind of "lifting" process (Figure 2, process A) and the reversibility of the isotherms was explained by line tension of the trilayer domains coexisting with residues of monolayer.<sup>[43]</sup> Though these two modes (rollover or lifting) of reorganization at the monolayer to trilayer transition are difficult to distinguish, a direct transition from trilayer to 9-layer, as observed at high compression ratio for compound A2 (see below), can only be explained by assuming a rollover process.<sup>[44]</sup>

Among the four compounds **X1–X4** only those with fluorinated chains (**X2–X4**) show perfectly reversible  $\pi(A)$  isotherms, although compound **X4** with the highest degree of

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fluorination (two fluorinated segments) exhibits a small hysteresis loop. The isotherms are perfectly reproducible in repeated cycles for **X2** and **X3** with all runs overlapping and are shown in Figure S1 in the Supporting Information.

Compounds X5 and X6 consist of linear rigid cores that are significantly longer than those in compounds X1 to X4, due to the two additional ethynyl groups introduced between the benzene rings. A comparison of the shorter compound X3 with the longer compound X6 is shown in Figure 4a. The isotherm cycle of compound X6 exhibits strong hysteresis (in spite of the presence of a partially fluorinated chain), which makes it distinct from compound X3 that shows completely reversible isotherms. In addition to a reduced reversibility, also the shape of the isotherms of compounds X5 and X6 (compared in Figure 4b) is different from those of compounds X1-X4. Compound X6 contains one partially fluorinated chain that is much longer than the hydrocarbon chain, whereas compound X5 has two relatively short hydrocarbon chains of the same length. The isotherms of compounds X5 and X6 showing two compression/ expansion cycles for each compound are presented in Figure 4b and the Brewster angle microscopy (BAM) images acquired for X6 at the most interesting parts of compression and decompression cycles are shown in Figure 4d and e. The isotherms of both compounds are rather similar, but the film of the fluorinated compound X6 is more stable as it can be compressed to a much higher surface pressure than the nonfluorinated compound X5. Though both compounds exhibit strong hysteresis (no reversibility) the reproducibility is still very good as the second compression curve nearly exactly follows the first one.

Analysis of the areas per molecule  $(A_1 \text{ and } A_2)$  at both ends of the plateau for **X6** resulted in a relation  $A_1 \approx 2A_2$  at  $\pi \approx 10 \text{ mNm}^{-1}$  and this excludes trilayer formation in this case; the ratio  $A_1/A_2 \approx 2$  suggests a bilayer, but this doubtful conclusion will be discussed below. The film of X6 was transferred onto silicon wafers at  $\pi = 8.5$  and  $15.0 \text{ mN m}^{-1}$ using the Langmuir-Blodgett technique. XRR measurements were performed on these samples to estimate the thickness of the films and the results are shown in Figure 5a. The XRR curve measured for the film of compound X6 transferred at the ends of the plateau turned out to be very different from those obtained for the related compound X3 under the same conditions (see Figure 5b). The curve of compound X6 has less peaks, which indicates that the multilayer in this case consists of fewer layers than the structure formed by compound X3, or alternatively, has a different vertical distribution of the electron density. Values of the layer thickness obtained for compound X6 from XRR data fitted to theoretical equations are equal to  $d_1 = 1.57$  nm for the monolayer and  $d_2 = 3.51$  nm for the layers transferred in the plateau region. The single layer thickness  $d_1$  is very similar to that measured for compound **X3**  $(d_1 = 1.65 \text{ nm})$ , whereas  $d_2$  is much smaller than the related value of **X3**  $(d_2 = 4.76 \text{ nm})$ . The very different ratios  $d_2/d_1$  measured for X3 and X6 confirm that whereas compound X3 with a shorter terphenyl-based aromatic core creates a trilayer the X-

shaped compound **X6** with a longer  $\pi$ -conjugated core forms a different structure in the plateau region. Another difference between compounds **X2–X4** and **X5**, **X6** was found for the surface pressure at the first break in the  $\pi(A)$ isotherms, which is much lower for compound **X6** than observed for compounds **X1–X4**, although **X6** has the longest fluorinated tail. Apparently, the surface pressure required for the trilayer formation is not reached for the Langmuir films of **X6** and a different process, requiring less energy, takes place. This is also manifested by the different shape of the  $\mu_{\perp}(A)$  isotherm (Figure 4a) in the plateau region and this will be discussed below in more detail.

Differences can also be observed for the isotherms obtained for the non-fluorinated compounds X1 and X5, and those of the fluorinated compounds X2-X4 and X6. In general, the reversibility is reduced for all non-fluorinated compounds. For example, the alkyl-substituted terphenyl-derived compound X1 shows a strong hysteresis with consecutive cycles systematically shifted towards smaller values of area per molecule being the result of irreversible aggregation. Though this is not observed for compound **X5**, the plateaus in the  $\pi(A)$  isotherms of compounds **X1** and **X5** are strongly rounded-off at the ends, so the molecular areas at these points are hard to estimate and their ratios cannot be calculated. Also, the XRR measurements for these two compounds did not give curves that could be used for fitting and estimation of the thickness of the films. These observations allow us to conclude that non-fluorinated X-shaped bolaamphiphiles collapse at higher surface pressure without creating well-defined multilayers and aggregate instead.

**T-shaped bolaamphiphiles**: The  $\pi(A)$  isotherms of the T-shaped bolaamphiphiles **T1** and **T2** are completely different from those recorded for the X-shaped molecules. These



compounds, which have only one semi-perfluorinated lateral chain, give isotherms without plateaus and only one kink close to the end of the isotherms close to  $A = 0.4 \text{ nm}^2 \text{molecule}^{-1}$  (Table 2). Moreover, their isotherms show strong hysteresis during compression/decompression cycles, whereas the compression runs show perfect reproducibility because in second and subsequent cycles identical compression curves were obtained (for clarity only two cycles for each compound are shown in Figure 6). Examples of BAM images, recorded during compression/decompression runs of compound **T2** confirm reversible aggregation of

Table 2. Data of the Langmuir films and transferred films of compounds  $\mathbf{T}^{[a]}_{\cdot}$ 

$A_1$	$A_2$	$\pi_2$	d
[nm <sup>2</sup> molecule <sup>-1</sup> ]	[nm <sup>2</sup> molecule <sup>-1</sup> ]	[mN m <sup>-1</sup> ]	[nm]
1.16	0.38	43.4	2.70
1.27	0.39	39.5	2.76
	$A_1$ [nm <sup>2</sup> molecule <sup>-1</sup> ] 1.16 1.27	$\begin{array}{ccc} A_1 & & & & \\ [nm^2molecule^{-1}] & & [nm^2molecule^{-1}] \\ \hline 1.16 & & 0.38 \\ 1.27 & & 0.39 \end{array}$	$\begin{array}{ccc} A_1 & & A_2 & & \pi_2 \\ [nm^2molecule^{-1}] & [nm^2molecule^{-1}] & [mNm^{-1}] \\ \hline 1.16 & & 0.38 & & 43.4 \\ 1.27 & & 0.39 & & 39.5 \end{array}$

[a]  $A_1$  = area at the lift-off of the isotherm;  $A_2$ ,  $\pi_2$  = area and surface pressure at the collapse; d = thickness of the monolayer.



Figure 6. The  $\pi(A)$  isotherms of compounds **T1** and **T2**: a) two cycles of compression (black lines) and decompression (grey lines) as well as the dipole-moment changes for compound **T1**. The BAM images for compound **T2** are given as examples: letters b–e mark the conditions at which the BAM images, also marked as b)–e), were recorded: b) the uniform monolayer during compression, c) the aggregates formed after compression beyond collapse, d) aggregates disappearing during decompression, e) coexistence of liquid and gas phases (2D foam) recovered after decompression to  $\pi=0$ . The white scale bar in image (e) represents a length of 400 µm.

the molecules. It should be noted that reversible aggregation does not refer to reversibility of the isotherm in terms of the meaning presented in the discussion of compounds **X1–X4**. Here, 3D aggregates appear only after the kink (Figure 6c) and disintegrate during decompression (Figure 6d) to disappear completely after decompression to  $\pi = 0 \text{ mN m}^{-1}$ . Disintegration occurs during decompression at surface pressures of approximately 15 and 25 mN m<sup>-1</sup> for **T1** and **T2**, respec-

tively, but this very slow process is visible as inflection points on the curves of decompression. Reversible aggregation manifests itself as reproducibility of the isotherms (repeatable subsequent cycles). The reappearing liquid phase forms a two-dimensional foam at  $\pi = 0$  mN m<sup>-1</sup>, as shown in Figure 6e.

Interesting results come from a comparison of the isotherms of compounds **T1** and **T2** that differ exclusively in the length of the rigid aromatic cores. Compound **T1** has a *p*-terphenyl core (L=2.48 nm as measured between the ends of the primary OH groups in a most extended conformation<sup>[45]</sup>), the same as the X-shaped compounds **X1–X4**, whereas **T2** has a longer core (L=2.95 nm) with two additional ethynyl groups, the same as incorporated in compounds **X5** and **X6**. Surprisingly, the areas occupied by these two molecules at higher surface pressures, as estimated from the  $\pi(A)$  isotherms, are nearly identical for both compounds (A=0.39 nm<sup>2</sup>molecule<sup>-1</sup>), though they have a very different length.

XRR measurements performed on films transferred onto silicon wafers at  $\pi = 33 \text{ mNm}^{-1}$  (see XRR curves of compound **T2** in Figure 7 as an example) gave layer thicknesses



Figure 7. X-ray reflectivity data and curve fitted to a theoretical equation obtained for a monolayer of compound **T2** transferred onto a silicon substrate at a surface pressure of  $33.0 \text{ mN m}^{-1}$ . The film was transferred using the Langmuir–Blodgett technique.

equal to d=2.70 and 2.76 nm for the transferred films of compounds **T1** and **T2**, respectively. These values are significantly smaller than that expected for trilayers (e.g., d=4.76 nm for the trilayer of **X3**), but very close to the length of the rigid bolaamphiphilic moiety (**T1**: L=2.48 nm; **T2**: L=2.95 nm; as estimated from CPK models<sup>[45]</sup>).

Surface potential ( $\Delta V$ ) measurements, presented as dipole moment changes,  $\mu_{\perp}(A)$ , shown in Figure 6a for compound **T1** as an example, indicate a sudden decrease of the dipole moment when the surface pressure exceeds  $\pi = 10 \text{ mN m}^{-1}$ . The decrease of  $\mu_{\perp}(A)$  is most probably caused by the fluorinated lateral chains rising up, which provides a negative dipole moment, that is, upon compression above  $\pi =$  $10 \text{ mN m}^{-1}$  the fluorinated chains should adopt an orientation more or less perpendicular to the surface. This is not in line with a trilayer formation in which the symmetric bilayer on top of the monolayer should not significantly contribute to the dipole moment (compare Figure 2a and b). The compressibility modulus,  $C_s^{-1} = -A (d\pi/dA)$ , corresponding to the very small slope of  $\pi(A)$  at the beginning of compression, is equal to 19 mN m<sup>-1</sup> at  $\pi = 3$  mN m<sup>-1</sup> and is typical for expanded liquids.<sup>[46]</sup> During compression the modulus continuously increases to approximately 50 mN m<sup>-1</sup>, which is a typical value for condensed 2D liquid phases.<sup>[46]</sup>

Based on this experimental data the following model of the organization of the T-shaped compounds T1 and T2 in thin films is proposed. At the beginning of compression the molecules are organized with rodlike cores and lateral chains parallel to the air-water interface (see Figure 2c). Upon further compression the molecules remain in a liquidlike state and reorganization takes place by detachment of one of the polar groups from the water surface and continuous rising of the molecules by adopting a randomly tilted, on average, vertical configuration of the rodlike cores. One of the glycerol groups retains contact with the water surface, whereas the other one at the opposite end of the bolaamphiphilic molecule is detached from the surface and is raised to a tilted orientation (see Figure 2, process C). The cross-section of one molecule estimated from the isotherm in Figure 6a is equal to approximately 0.39 nm<sup>2</sup>, which seems to be consistent with the proposed organization of the molecules, on average, perpendicular to the air-water interface (see Figure 2b). The cross-section of the fluorinated part of the chain<sup>[47]</sup> is 0.285 nm<sup>2</sup> and the cross-section of the terphenyl moiety is less than 0.20 nm<sup>2</sup>, hence, there is enough space for an, on average, vertical or slightly tilted arrangement of the rigid cores with the partially fluorinated lateral chains organized in the space between the rodlike cores.

It appears that the topology of the connection of the lateral chain to the rigid aromatic core is responsible for this special kind of behaviour. In fact, in the "T-shaped" molecules the lateral chain is actually attached at an angle of 60° to the aromatic core, which provides a  $\lambda$ -like shape rather than a true T-shape for these molecules (Figure 1b). As a consequence, the lateral chain is closer to one of the polar glycerol groups and restricts the interaction of this polar group with the water surface. The other glycerol unit at the opposite end is less distorted, which makes both polar groups non-equivalent. This non-equivalence seems to allow an easy detachment of the more distorted polar group from the water surface. As a result, upon further compression, a monolayer structure is retained and in this monolayer the aromatic cores adopt a tilted or even vertical orientation with respect to the water surface (see Figure 2b).

The isotherms of both T-shaped molecules **T1** and **T2** are very similar with respect to the molecular area adopted at the transition around  $\pi = 40 \text{ mNm}^{-1}$  as the cross-section of the aromatic cores and lateral chains is nearly identical for both compounds. The effect of the distinct molecular length on the layer thickness is relatively small because the longer aromatic cores provide more space to accommodate the lateral chains and a different degree of average tilt is possible. This model of organization also provides clues for under-

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standing the isotherms observed for the X-shaped compounds **X5** and **X6** as explained in the following section.

X-shaped bolaamphiphiles X5 and X6 with extended rodlike cores: Though the  $\pi(A)$  isotherms of the X-shaped molecules X5 and X6 are similar to those of compounds X1-X4 forming a broad plateau, the areas per molecule  $(A_1 \text{ and } A_2)$ at both ends of the plateau give a relation  $A_1 \approx 2A_2$  at  $\pi$  $\approx\!10\,mN\,m^{-1}$  for compound X6, which is not compatible with trilayer formation and would suggest formation of a bilayer. However, in light of the results obtained for the Tshaped compounds T1 and T2, indicating that reorganization of the molecules within the monolayer is an alternative option for reducing the area per molecule at the air-water interface, there is a second possible explanation as follows. At low surface pressure, compound X6 behaves like the Xshaped amphiphiles X1-X4, adopting an arrangement parallel to the surface with both glycerol units attached to the water surface (Figure 2c). However, for compound X6 this arrangement seems to be less stable at increased surface pressure, so that no trilayer is formed. Instead, a reorganization of the molecules by tilting, as observed for the Tshaped molecules, takes place (Figure 2, process C). The surface area at the collapse of the monolayer is  $A_2 =$ 0.53 nm<sup>2</sup>mol<sup>-1</sup>, which is only a bit larger than that observed for compounds T1/T2. The small difference in required area could be explained by the presence of an additional lateral chain in compound X6.

To distinguish these two possibilities of molecular reorganization the experimentally measured XRR curves of the films transferred at the highest possible surface pressure were compared with the simulated XRR curves for both distinct cases: 1) a bilayer with aromatic cores arranged parallel to the air-water interface created by a lifting mechanism (see Figure 2, process A); and 2) a tilted organization of the aromatics. In the latter case the aliphatic segments are arranged between the aromatics (see Figure 2, process C) and the fluorinated chains form a distinct sublayer on top of the monolayer (see Figure S2 in the Supporting Information). This model provides a distinct electron-density profile that can be compared to the case of bilayer formation in which the highest concentration of fluorinated chains is expected between the sublayers of the aromatic cores situated at the bottom and on top of the hypothetic bilayer. Although the fitting of the measured XRR curves to the vertical (Figure S2, image a) and horizontal (Figure S2, image b) models was almost equally good (the vertical was slightly better), for vertical orientation the fitted parameters describing the electron-density distribution are only slightly different from those estimated from the model, whereas in the case of horizontal alignment the fitted parameters are significantly different from the ones estimated from the model, which shows that this model is less likely (for details, see Table S1 in the Supporting Information).

Additional information was gained from the comparison of the shapes of dipole-moment curves recorded for compounds **X3** and **X6** (Figure 4a), and **T2** (Figure 6a). If a monolayer-to-bilayer transition takes place in the plateau region the dipole moments of the molecules in the lower and upper layers should perfectly compensate and the  $\mu_{\perp}$ (A) curve in this part should be a straight line extrapolated to the coordinate  $\mu_{\perp}(A=0)=0$ . In contrast, for compound X6 with a longer rodlike core, the dipole-moment curve continuously decreases after the first kink in the  $\pi(A)$  isotherm and a decrease continues until the second kink is reached (see Figure 4a). Since  $\mu_{\perp}(A)$  becomes negative at the first kink it indicates that there is a significant contribution of fluorinated chains organized, on average, perpendicularly to the surface. This behaviour of the dipole moment upon compression is the same as that observed for the Tshaped molecules (e.g., T2, see Figure 3a). It supports the idea that for compounds X5 and X6 (compared in Figure 4b) the reorganization of the molecules is similar to that observed for the T-shaped compounds, that is, no triple or double layer is formed in the plateau region. We conclude that the monolayers are retained and a reorganization of the molecules to a randomly tilted or vertical orientation of the aromatic cores takes place (see process C in Figure 2).

The distinct behaviour of compounds X1-X4 on the one hand and X5/X6 on the other hand can be explained by the effect of the longer aromatic cores on the self-assembly behaviour. As the distance between lateral chains and polar groups is larger in compounds X5 and X6 with longer aromatic cores the distorting effect of the lateral chains on the interaction of the polar groups with the water surface is reduced. Chain folding can additionally reduce the effective length of these chains and this further decreases the distortion of the polar groups. Moreover, in compound X6 the disturbing influence of the shorter non-fluorinated alkyl chains is smaller and the glycerol group adjacent to this chain is less distorted than the glycerol group adjacent to the longer fluorinated chain. Therefore, upon film compression the shorter alkyl chains can be easily removed from the water surface and one of the polar groups (the one besides the shorter chain) becomes less distorted than the other one. Hence, the amphiphilic character of the molecules changes: at low surface pressure they behave as symmetric bolaamphiphiles (like compounds X1-X4) retaining an orientation parallel to the surface, which is stable up to  $\pi = 10 \text{ mN m}^{-1}$ (Figure 2, arrangement c). However, at higher surface pressure after the first kink in the isotherm, they behave as nonsymmetric bolaamphiphiles, that is, like compounds T1/T2. Starting from this point a rearrangement takes place in the monolayers to an orientation tilted or perpendicular to the air-water interface (see Figure 2, process C). Therefore, the isotherm of X6 can be considered as a combination of the isotherms of compounds X1-X4 at low surface pressure (until plateau) and the isotherms of T-shaped compounds T1/T2 at high surface pressure. The long semi-perfluorinated chain in compound X6 allows the formation of a separate sublayer of segregated perfluoralkyl chains, which significantly stabilizes these monolayers. However, the presence of a long fluorinated chain seems not to be required, because the symmetric alkyl-substituted compound X5 shows a very

similar isotherm and it is very likely that the same kind of molecular reorganization as proposed for **X6** takes place for **X5**, too.

Anchor-shaped bolaamphiphiles: Compounds A1–A3 from this group resemble the shape of an anchor because a single aliphatic chain is attached to a bent rigid core at the central phenyl ring inside an angle created by the arms of the core (bay position).



All compounds A1, A2 and A3 exhibit isotherms with broad plateaus similar to compounds X1-X6. The isotherms of compound A1 and A2 are shown in Figure 8. Both compounds have the same rigid cores and the same length of aliphatic chains, the only difference between them is that the chain in compound A1 is fully hydrogenated whereas compound A2 contains a fluorinated  $C_6F_{13}$  segment at the end of the chain. The surface pressure at which the monolayers lose their stability is higher for the fluorinated compound A2, which shows that partial fluorination makes the interaction with the water surface stronger. The area of 1.16 nm<sup>2</sup>molecule<sup>-1</sup> at the beginning of the plateau is smaller than the area required by the X-shaped amphiphile X6 comprising a similar, but linear core. The difference between the areas of A2 and X6, measured at the same surface pressure  $\pi = 9.4 \text{ mNm}^{-1}$ , is about  $0.2 \text{ nm}^2 \text{molecule}^{-1}$ , which agrees well with the additional space required by the second  $OCH_2$  group of compound X6. Hence, it can be concluded that the bent aromatic cores lay flat on the water surface with the bend parallel to the surface and fixed on the surface by the two glycerol groups and the ether oxygen atom carrying the lateral chain. The second increase of the surface pressure at the end of the plateau of compound A2 starts at an area of  $0.43 \text{ nm}^2 \text{molecule}^{-1}$  and ends at A =0.4 nm<sup>2</sup>molecule<sup>-1</sup>. Hence, a comparison of the areas per molecule at both ends of the plateau leads to a ratio that is equal to 2.7. In experiments similar to those described for X- and T-shaped molecules the films of compound A2 were transferred onto silicon wafers at  $\pi = 20 \text{ mN m}^{-1}$  (before



Figure 8. Isotherms and BAM images for compounds A1 and A2: two cycles of compression (solid symbols) and decompression (open symbols) are shown in (a); letters b–e mark the conditions at which the BAM images (also marked as b–e) were recorded. b) The uniform monolayer during compression of the homogeneous liquid phase; c) the aggregates formed after compression beyond collapse; d) aggregates disappearing during decompression; e) coexistence of liquid and gas phases (2D foam) recovered after decompression to  $\pi$ =0. The white scale bar in image (e) represents a length of 400 µm.

reaching the plateau) and at  $\pi = 30 \text{ mNm}^{-1}$  (before the second transition). The X-ray reflectivity measurements performed on these samples gave the results shown in Figure 9. Values of the layer thickness obtained from the XRR data fitted to theoretical equations are equal to  $d_1 = 1.43$  nm and  $d_2 = 3.71$  nm, respectively. This value of  $d_1$  is only a little bit smaller than the values found for the monolayers of compounds X3 and X6, and it is also in good agreement with the thickness of a model monolayer formed by the aromatic cores lying flat on water with the disordered fluid semi-perfluorinated chains covering these aromatics. The ratio  $d_2/$  $d_1 = 2.6$  could be either due to a reorganization of the molecules in the monolayers by adopting, on average, a perpendicular organization similar to compounds X5 and X6 or to trilayer formation. Though the compressibility at the end of the plateau region is similar to that observed for the same region of X6, indicating a liquid condensed film, the thickness  $d_2 = 3.71$  nm is much larger than can be explained by a reorganization of the molecules inside the monolayer, even

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Figure 9. X-ray reflectivity data and curves fitted to a theoretical equation obtained for a monolayer and a trilayer of compound **A2** transferred onto the silicon substrates at surface pressures of 20 and 30 mNm<sup>-1</sup>, respectively; the films were transferred using the Langmuir–Blodgett technique.

if the molecules would adopt a perfectly vertical alignment (which only would give d=2.7 nm). Therefore, we assume a trilayer formation in the plateau region of the isotherm of compound **A2**. The fact that the ratio  $d_2/d_1$  is a bit smaller than exactly three could be explained by some intercalation of the lateral chains in the formed trilayer structure. The proposed trilayer formation is also in line with the surface potential measurements (see Figure S4 in the Supporting Information), which indicates an increase of dipole moment in the plateau region. In the case of a transition to a monolayer with molecules organized, on average, perpendicularly to the surface a decrease of the dipole moment, as observed for compounds **T1/T2** and **X5/X6** would be expected due to the negative contribution of the terminal C–F bond of vertically aligned  $R_F$  segments.

The BAM image in Figure 8c shows a rough surface of the film after breakdown of the trilayer at the second kink in the isotherm curve. During decompression the trilayer cannot be recovered, so in the image in Figure 8d the coexistence of the trilayer with aggregates and the monolayer can be observed. The shape of the domains and the fact that their size diminishes during expansion allows us to conclude that the trilayer is still in the liquid state. It is one of the reasons why the isotherm, although irreversible (because of a small hysteresis), is perfectly reproducible in the subsequent compression.

For compound A1 with a non-fluorinated *n*-alkyl chain the second increase of surface pressure occurs at an area per molecule much smaller than that for A2 (Figure 8a) and smaller than the value estimated from the CPK model. The surface pressure increase at a non-realistic value of molecular area is typically observed for completely disordered films, which suggests that disorganized aggregates are created also in this case. In this region the curve of the dipole moment is a nearly straight line going through zero, which means that all of the dipole moments cancel out because of the completely random aggregation (Figure S3 in the Supporting Information). Hysteresis between compression and decompression runs is much stronger here than in the case of **A2**, but the second compression perfectly overlaps with the first one showing perfect reproducibility, too. It means that the aggregation is reversible after decompression of the film to "zero" pressure and the aggregates need time for disintegration. Comparison of the isotherms of compounds **A1** and **A2** (Figure 8a) shows that the partial fluorination of the lateral chain in the case of anchor-shaped molecules increases the stability of the film and its tendency for self organization into trilayers, but does not affect the reproducibility in this case.

Compound A3 has the same fluorinated lateral chain as compound A2, but its rigid core consists of a *m*-terphenyl moiety, so this part of the molecule is smaller than the cores of compounds A1 and A2. This compound has a compression isotherm very similar to the one of compound A2, but with reduced molecular areas at the transition (Figure S5 in the Supporting Information). It shows that this compound also creates a trilayer during compression.

The fact that anchor-shaped compounds form Langmuir films similar to the X-shaped molecules, but distinct from those of T-shaped molecules, could partly be due to the equal distance of the lateral chain from both polar groups in the anchor-shaped bolaamphiphiles. In addition, the combination of the bent shape and substitution inside the bay area between the rodlike wings distorts a parallel alignment of these cores and hence the formation of smectic layers (cores perpendicular to the layers) becomes more difficult. For these reasons a Lam-type organization<sup>[33]</sup> with the cores parallel to the water surface becomes more favourable in this case. Hence, bending the aromatic core of the T-shaped bolaamphiphiles **T**, leading to compounds **A**, has a similar effect as grafting a second lateral chain to the opposite side of the rodlike core leading to compounds **X**.

#### Conclusion

Molecular design leads to new types of bolaamphiphiles capable of self-assembly in distinct modes at the air-water interface. For all compounds here, the densely packed monolayers were formed with the aromatic cores laying flat at the air-water interface. Further compression either leads to a first-order transition with formation of well-defined trilayers (layering transition) by retaining the orientation of the anisometric cores, or to a second-order transition retaining the monolayers by reorganization of the cores into, on average, vertical orientation. It seems that the degree of distortion of the polar groups attached to the ends of the rigid  $\pi$ -conjugated cores by the laterally attached hydrophobic chains is the key factor deciding which type of reorganization is observed in the monolayer. For X-shaped bolaamphiphiles with two relatively long lateral chains of approximately equal length, both exceeding the polar groups at the ends, triple-layer formation is dominating. If one chain is removed (T-shaped bolaamphiphiles) the two polar groups at the opposite ends become distinct and these bolaamphiphiles preferably organize with their anisometric cores perpendicular to the surface with the less-hindered polar group acting as an anchor group. Even slight modification of the molecular structure of the two fundamental types of bolaamphiphiles (T-shaped and X-shaped) can change the self-assembly behaviour dramatically. For example, an elongation of the rigid core of X-shaped compounds reduces the degree of distortion of the polar groups by the lateral chains and it gives rise to reorganization of the monolayers by changing the molecular orientation (compounds **X5** and **X6**). On the other hand, bending the rodlike core of T-shaped molecules (leading to the anchor-shaped compounds) makes the two polar groups equivalent, which favours formation of a trilayer without changing the orientation of the molecules.

Besides the formation of well-defined mono- and trilayers, which can be transferred onto solid supports, a second unique feature observed for these Langmuir films is reproducibility and reversibility of the compression/decompression cycles. Reproducibility of the isotherms, that is, overlapping of subsequent compression runs with (or without) hysteresis loops during decompression, was observed for all compounds. Reversibility of the compression/decompression isotherms, that is, perfect overlapping of compression and decompression runs, was only achieved with short fluorinated segments incorporated into the lateral chain(s). Non-fluorinated compounds do not exhibit reversibility and reversibility is also reduced by elongation of the fluorinated segments. The main reason for reproducibility/reversibility of the Langmuir films seems to be their fluidity provided by the partly fluorinated chains, combined with the preorganization of the amphiphiles due to short-range order induced by alignment of the rigid anisometric units.<sup>[48]</sup>

The thin films resemble the molecular organizations similar to lamellar liquid-crystalline bulk phases of the smectic type if the molecules are organized vertically (e.g., T-shaped molecules), whereas mono- or multilayers with molecules organized parallel to the layer planes are related to Lamtype LC phases<sup>[32a,49]</sup> in which rodlike units are arranged parallel to the smectic layers.<sup>[33]</sup> Remarkably, distinct types of Lam phases were also observed for numerous T- and Xshaped amphiphiles as bulk LC phases.<sup>[29,30a,32a]</sup> Though the investigated bolaamphiphiles as bulk phases are in the crystalline state (see Table S2 in the Supporting Information), at the temperature of investigation of their self-assembly in Langmuir films (23°C) the interaction of the amphiphiles with the water molecules at the interface leads to a phenomenon called "surface melting",<sup>[50]</sup> which gives the possibility to form the fluid thin films. Moreover, hydration increases the effective size of the polar glycerol groups, which is likely to modify the mode of self-assembly. Therefore, the tendency of these molecules to self-assemble in these lamellar structures is considered as a driving force for formation of stable mono- and trilayers, though at the same temperature in the bulk state the pure (non-hydrated) compounds are in the crystalline state or form other non-lamellar LC phases (see Table S2 in the Supporting Information). As there is presently no clear evidence of long-range orientational or

positional order in the Langmuir films it is assumed that any orientational/positional order occurring in the Lam-like structures is of short range, only.

The function of the semi-perfluorinated chains is twofold: 1) they increase the film stability by increasing the amphiphilicity and 2) the fluorinated chains of medium size increase film fluidity due to the mismatch of chain diameter ( $R_{\rm H}$  versus  $R_{\rm F}$ ), and probably, due to the dipole moment introduced at the  $R_{\rm H}$ - $R_{\rm F}$  junctions.<sup>[17,20]</sup> Hence, beside the presence of an anisometric rigid unit, also the partial fluorination of the lateral chains turned out to be a key factor for reversible formation of stable and well-defined mono- and trilayers.

The knowledge gained in these studies might be useful for the design of self-organizing  $\pi$ -conjugated molecules and macromolecules, which are of importance for their applications as organic electronic materials. On the other hand, these molecules being bolaamphiphiles have the potential to interact with lipid membranes either by formation of internal structures, thus modifying membrane flexibility and permeability, or by formation of external structures at the membrane surfaces.<sup>[51,52]</sup> There is also the possibility of stabilization of membrane fragments and membrane proteins,<sup>[53]</sup> which would be useful for applications in biochemistry and biophysics.

#### **Experimental Section**

**Materials**: Compounds **X1**, **X4**, **T1**, **A2** and **A3** have been reported previously. The synthesis of the new compounds and their analytical data are given in the Supporting Information. Chloroform (Sigma–Aldrich, HPLC grade) was used to prepare the solutions. Ethanol 95% (Merck) used for cleaning the trough and the barriers, as well as the other solvents were of analytical grade. Ultra-pure water characterized by a surface tension of 72.75 mN m<sup>-1</sup> at 20 °C and resistivity 18.3 M $\Omega$  m<sup>-1</sup>, used as a subphase in the Langmuir trough was obtained from the Milli-Q water purification system. All solutions for the monolayer spreading were prepared by dissolving the compounds in CHCl<sub>3</sub> to obtain concentrations of approximately 1 mg mL<sup>-1</sup>.

Compression isotherms: Experiments were carried out using the equipment from Nima Technology: a Teflon trough of size 50 mm×750 mm× 10 mm equipped with the two hydrophilic barriers for symmetric compression and a film balance of resolution 0.01 mNm<sup>-1</sup> for surface pressure  $(\pi)$  measurements. A rectangular piece of analytical filtering paper  $(20 \text{ mm} \times 10 \text{ mm} \times 0.1 \text{ mm})$  was used as a surface pressure sensor. The whole system was placed on an active anti-vibration table and closed in a Plexiglas box to prevent the films from dust and air currents. The time delay after spreading of the film and before its compression, necessary for solvent evaporation and film equilibration, was about 20 min. Usually, the films were compressed/decompressed at a rate of 5 cm<sup>2</sup>min<sup>-1</sup>, which corresponds to approximately 0.05-0.15 nm<sup>2</sup> molecule<sup>-1</sup> min<sup>-1</sup> and depends on the amount of substance spread on the film. However, when the reversibility of the isotherms was checked, a compression rate as high as 1.5 nm<sup>2</sup>molecule<sup>-1</sup>min<sup>-1</sup> was applied. For all the compounds studied the isotherms of compression and decompression (hysteresis loops) were recorded at 23 °C controlled with accuracy ±0.2 °C using a cooling/heating circulating bath (Thermo Scientific, USA). Temperature was measured with two  $Pt100\Omega$  resistance thermometers immersed at both ends of the trough and connected to a Keithley multimeter.

Brewster angle microscopy (BAM): The trough was equipped with a Brewster angle microscope (MiniBAM) of a resolution of  $8.3 \,\mu m$  per

pixel from Nanofilm Technology. This technique allows for direct observations of the monolayer during compression and detection of film thickness to distinguish areas of the water surface covered with a monolayer or multilayers. It is also possible to distinguish liquid and solid phases from the shape of the domains and the patterns observed on the interface. A magnification of MiniBAM is not high, so the field of observation is relatively big, that is,  $4.8 \text{ mm} \times 6.4 \text{ mm}$ .

Surface potential (SP): The measuring head with a vibrating electrode from Treck Inc. was mounted on the Langmuir trough and a counterelectrode made of stainless steel was placed on the bottom. The measured surface potential,  $\Delta V$ , was converted to the vertical component of the molecular dipole moment using the Helmholtz equation [Eq. (1)]:

$$\mu_{\perp} = \Delta V A \varepsilon \varepsilon_0 \tag{1}$$

in which  $\mu_{\perp} = \mu \cos \theta$  ( $\theta$  is the angle between the surface normal and the dipole axis) is the average component of the molecular dipole moment normal to the plane of the monolayer, A is the area per molecule,  $\varepsilon$  and  $\varepsilon_0$  are dielectric permittivity constants of the monolayer (which is assumed to be 1) and vacuum, respectively. The surface potential signal is extremely sensitive to a distance between the vibrating electrode and water surface, therefore its stability was checked before each experiment and after cleaning the surface.

**X-ray reflectivity measurements (XRR)**: The measurements were performed using the X-ray diffractometer Bruker D8 Discover.  $Cu_{Ka}$  radiation was used and the monochromatic parallel beam was formed by using a parabolic Goebel mirror. The system was equipped with a Eulerian cradle and reflectometry sample stage, which ensured precise sample positioning. A scintillation counter together with automatic absorber on the primary beam allowed for a linear dynamic range better than 10<sup>8</sup> cps; data were analysed by fitting to the theoretical model using software package Leptos 4.02. The samples of monolayers and multilayers for XRR measurements were prepared on silicon wafers by direct transfer from the water surface to solid substrate using the Langmuir–Blodgett technique.

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- A. Ulman, An Introduction to Ultrathin Organic Films: From Langmuir-Blodgett to Self-Assembly, Academic Press, Boston, 1991.
- [2] T. Sekitani, T. Yokota, U. Zschieschang, H. Klauk, S. Bauer, K. Takeuchi, M. Takamiya, T. Sakurai, T. Someya, *Science* 2009, *326*, 1516–1519.
- [3] F. Anariba, R. L. McCreery, J. Phys. Chem. B 2002, 106, 10355– 10362.
- [4] J. A. A. W. Elemans, S. Lei, S. De Feyter, Angew. Chem. 2009, 121, 7434-7469; Angew. Chem. Int. Ed. 2009, 48, 7298-7332; D. Kühne, F. Klappenberger, R. Decker, U. Schlickum, H. Brune, S. Klyatskaya, M. Ruben, J. V. Barth, J. Am. Chem. Soc. 2009, 131, 3881-3883.

- [5] G. L. Gaines Jr., Insoluble Monolayers at Liquid-Gas Interfaces, Wiley Interscience, New York, 1966.
- [6] Only under certain circumstances the ordered crystals were obtained by folding Langmuir layers: D. Vaknin, W. Bu, S. K. Satija, A. Travesset, *Langmuir* 2007, 23, 1888–1897.
- [7] P. Lo Nostro, Curr. Opin. Colloid Interface Sci. 2003, 8, 223-226.
- [8] M. P. Krafft, F. Giulieri, P. Fontaine, M. Goldmann, *Langmuir* 2001, 17, 6577–6584.
- [9] J. J. Haycraft, C. A. DeVries, H. Garcia Flores, A. Lech, J. P. Hagen, C. J. Eckhardt, *Thin Solid Films* **2007**, 515, 2990–2997.
- [10] F. G. Tournilhac, L. Bosio, J. P. Bourgoin, M. Vandevyver, J. Phys. Chem. 1994, 98, 4870–4877.
- [11] P. Nitoń, A. Żywociński, R. Hołyst, R. Kieffer, C. Tschierske, J. Paczesny, D. Pociecha, E. Górecka, *Chem. Commun.* 2010, 46, 1896– 1898.
- [12] In most of the reported cases the reversibility was not well documented (reversibility was just mentioned in the text, but not shown in the graphs; see refs. [7,8]).
- [13] U. H. F. Bunz, Macromol. Rapid Commun. 2009, 30, 772-805.
- [14] A. Jatsch, E.-K. Schillinger, S. Schmid, P. Bäuerle, J. Mater. Chem. 2010, 20, 3563–3578.
- [15] M. P. Turberg, J. E. Brady, J. Am. Chem. Soc. 1988, 110, 7797-7801.
- [16] G. L. Gaines Jr., Langmuir 1991, 7, 3054-3056.
- [17] C. de Gracia Lux, J.-L. Gallani, G. Waton, M. P. Krafft, *Chem. Eur. J.* 2010, 16, 7186–7198.
- [18] M. Li, A. A. Acero, Z. Huang, S. Rice, Nature 1994, 367, 151-153.
- [19] a) M. Broniatowski, P. Dynarowicz-Łątka, J. Colloid Interface Sci.
   2006, 299, 916–923; b) M. Broniatowski, P. Dynarowicz-Łątka, Langmuir 2006, 22, 6622–6628.
- [20] M. P. Krafft, J. G. Riess, Chem. Rev. 2009, 109, 1714-1792.
- [21] J. G. Riess, Curr. Opin. Colloid Interface Sci. 2009, 14, 294-300.
- [22] M. P. Krafft, M. Goldmann, Curr. Opin. Colloid Interface Sci. 2003, 8, 243–250.
- [23] J. H. Fuhrhop, T. Wang, Chem. Rev. 2004, 104, 2901-2937.
- [24] M. De Rosa, A. Gambacorta, A. Gliozzi, *Microbiol. Rev.* 1986, 70– 80; T. Benvegnu, M. Brard, D. Plusquellec, *Curr. Opin. Colloid Interface Sci.* 2004, 8, 469–479.
- [25] F. Hentrich, C. Tschierske, H. Zaschke, Angew. Chem. 1991, 103, 429–431; Angew. Chem. Int. Ed. Engl. 1991, 30, 440–441.
- [26] K. Köhler, G. Förster, A. Hauser, B. Dobner, U. F. Heiser, F. Ziethe, W. Richter, F. Steiniger, M. Drechsler, H. Stettin, A. Blume, J. Am. Chem. Soc. 2004, 126, 16804–16813.
- [27] A. Meister, M. J. Weygand, G. Brezesinski, A. Kerth, S. Drescher, B. Dobner, A. Blume, *Langmuir* 2007, 23, 6063–6069.
- [28] A reversed U-shape conformation was also observed for bolaamphiphiles with a rigid biphenyl unit and flexible siloxane units decoupling the rigid core from the head groups. In the monolayers the biphenyl cores are arranged parallel to the water surface, similar to *p*terphenyl-based facial amphiphiles reported previously<sup>[40]</sup> and to the X-shaped bolaamphiphiles reported herein. See: N. Mizoshita, T. Seki, *Langmuir* 2005, *21*, 10324–10327.
- [29] M. Kölbel, T. Beyersdorff, X. H. Cheng, C. Tschierske, J. Kain, S. Diele, J. Am. Chem. Soc. 2001, 123, 6809-6818; X. Cheng, M. Prehm, M. K. Das, J. Kain, U. Baumeister, S. Diele, D. Leine, A. Blume, C. Tschierske, J. Am. Chem. Soc. 2003, 125, 10977-10996; M. Prehm, F. Liu, U. Baumeister, X. Zeng, G. Ungar, C. Tschierske, Angew. Chem. 2007, 119, 8118-8121; Angew. Chem. Int. Ed. 2007, 46, 7972-7975; M. Prehm, G. Götz, P. Bäuerle, F. Liu, X. Zeng, G. Ungar, C. Tschierske, Angew. Chem. 2007, 119, 8002-8005; Angew. Chem. Int. Ed. 2007, 46, 7856-7859; M. Prehm, C. Enders, Maryam Y. Anzahaee, B. Glettner, U. Baumeister, C. Tschierske, Chem. Eur. J. 2008, 14, 6352-6368; R. Kieffer, M. Prehm, K. Pelz, U. Baumeister, F. Liu, H. Hahn, H. Lang, G. Ungar, C. Tschierske, Soft Matter 2009, 5, 1214-1227.
- [30] a) R. Kieffer, M. Prehm, B. Glettner, K. Pelz, U. Baumeister, F. Liu, X. B. Zeng, G. Ungar, C. Tschierske, *Chem. Commun.* 2008, 3861–3863; b) B. Glettner, F. Liu, X. Zeng, M. Prehm, U. Baumeister, M. Walker, Martin A. Bates, P. Boesecke, G. Ungar, C. Tschierske, *Angew. Chem.* 2008, 120, 9203–9206; *Angew. Chem. Int. Ed.* 2008,

47, 9063–9066; c) X. Cheng, X. Dong, G. Wei, M. Prehm, C. Tschierske, *Angew. Chem.* 2009, 121, 8158–8161; *Angew. Chem. Int. Ed.* 2009, 48, 8014–8017.

- [31] B. Glettner, F. Liu, X. B. Zeng, M. Prehm, U. Baumeister, G. Ungar, C. Tschierske, Angew. Chem. 2008, 120, 6169–6172; Angew. Chem. Int. Ed. 2008, 47, 6080–6083.
- [32] a) C. Tschierske, *Chem. Soc. Rev.* 2007, *36*, 1930–1970; b) G. Ungar,
   C. Tschierske, V. Abetz, R. Hołyst, M. A. Bates, F. Liu, M. Prehm,
   R. Kieffer, X B. Zeng, M. Walker, B. Glettner, A. Żywociński, *Adv. Funct. Mater.* 2011, *21*, 1296–1323.
- [33] Laminated phases (Lam phases) represent a special type of smectic LC phases whereby the aromatic cores are arranged parallel to the smectic layers.  $Lam_{Iso}$ ,  $Lam_{N}$  and  $Lam_{Sm}$  phases can be distinguished as having no order (isotropic), only orientational order (nematic), or orientational and positional in-plane order (smectic), respectively. These mesophases can be regarded as laminated analogues (2d-analogues) of the corresponding isotropic, nematic and smectic bulk phases; see refs. [32a, 49].
- [34] Though long fluorinated chains are more rigid than hydrocarbon chains the interconnection of the incompatible alkyl chain and RF chains with very different cross-sections provides a packing frustration that disfavours packing in a crystal lattice and hence inhibits chain crystallization.
- [35] M. N. G. de Mul, J. A. Mann, Jr., Langmuir 1994, 10, 2311-2316.
- [36] a) M. Ibn-Elhaj, H. Möhwald, M. Z. Cherkaoui, R. Zniber, *Lang-muir* 1998, 14, 504; b) M. Ibn-Elhaj, H. Riegler, H. Möhwald, M. Schwendler, C. A. Helm, *Phys. Rev. E* 1997, 56, 1844–1852.
- [37] B. Rapp, H. Gruler, Phys. Rev. A 1990, 42, 2215-2218.
- [38] M. C. Friedenberg, G. G. Fuller, C. W. Frank, C. R. Robertson, *Langmuir* 1994, 10, 1251.
- [39] M. Badis, M. H. Guermouche, J.-P. Bayle, M. Rogalski, E. Rogalska, Langmuir 2004, 20, 7991.
- [40] a) J. A. Schröter, R. Plehnert, C. Tschierske, S. Katholy, D. Janietz, F. Penacorada, L. Brehmer, *Langmuir* 1997, 13, 796–800; b) R. Plehnert, J. A. Schröter, C. Tschierske, *Langmuir* 1999, 15, 3773– 3781.
- [41] J. J. Haycraft, C. A. DeVries, H. Garcia Flores, A. Lech, J. P. Hagen, C. J. Eckhardt, *Thin Solid Films* 2007, 515, 2990–2997.

- [42] M. Perez-Morales, J. M. Pedrosa, M. T. Martin-Romero, D. Möbius, L. Camacho, J. Phys. Chem. B 2004, 108, 4457–4465.
- [43] A. M. Gonzalez-Delgado, M. Perez-Morales, J. J. Giner-Casares, E. Munoz, M. T. Martun-Romero, L. Camacho, J. Phys. Chem. B 2009, 113, 13249–13256.
- [44] J. Paczesny, P. Nitoń, A. Żywociński, K. Sozanski, R. Hołyst, M. Fiałkowski, R. Kieffer, C. Tschierske, D. Pociecha, E. Górecka, manuscript in preparation.
- [45] The CPK model (from the names of Robert Corey, Linus Pauling and Walter Koltun) is applied in the Amber package used here for modelling of molecular structures.
- [46] M. Broniatowski, N. Vila-Romeu, P. Dynarowicz-Łątka, J. Fluorine Chem. 2006, 127, 909–915; J. T. Davies, E. K. Rideal, Interfacial Phenomena, 2nd edition, Academic Press, New York, 1963, pp. 265.
   [47] C. W. Purer, E. P. Hawalle, Network 1964, 174, 540, 551.
- [47] C. W. Bunn, E. R. Howells, *Nature* **1954**, *174*, 549–551.
- [48] Shape-persistent T-shaped molecules predominately form solid monolayers. See: L. Liu, K.-S. Moon, R. Gunawidjaja, E. Lee, V. V. Tsukruk, M. Lee, *Langmuir* 2008, 24, 3930–3936.
- [49] a) X. H. Cheng, M. K. Das, S. Diele, C. Tschierske, Angew. Chem.
  2002, 114, 4203-4207; Angew. Chem. Int. Ed. 2002, 41, 4031-4035;
  b) M. Prehm, X. H. Cheng, S. Diele, M. K. Das, C. Tschierske, J. Am. Chem. Soc. 2002, 124, 12072-12073; c) M. Prehm, S. Diele, M. K. Das, C. Tschierske, J. Am. Chem. Soc. 2003, 125, 614-615;
  d) N. M. Patel, M. R. Dodge, M. H. Zhu, R. G. Petschek, C. Rosenblatt, Phys. Rev. Lett. 2004, 92, 015501-015504; e) N. M. Patel, I. M. Syed, C. Rosenblatt, M. Prehm, C. Tschierske, Liq. Cryst. 2005, 32, 55-61.
- [50] J. W. Frenken, J. F. van der Veen, Phys. Rev. Lett. 1985, 54, 134-137.
- [51] M. Brunelle, A. Polidori, S. Denoyelle, A.-S. Fabiano, P. Y. Vuillaume, S. Laurent-Lewandowski, B. Pucci, C. R. Chim. 2009, 12, 188–208.
- [52] M. P. Krafft, J. G. Riess, Biochimie 1998, 80, 489-514.
- [53] E. Chabaud, P. Barthélémy, N. Mora, J. L. Popot, B. Pucci, *Bio-chimie* 1998, 80, 515–530.

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