

# Reversible aggregation of X-Shaped bolaamphiphiles with partially fluorinated lateral chains at the air/water interface†

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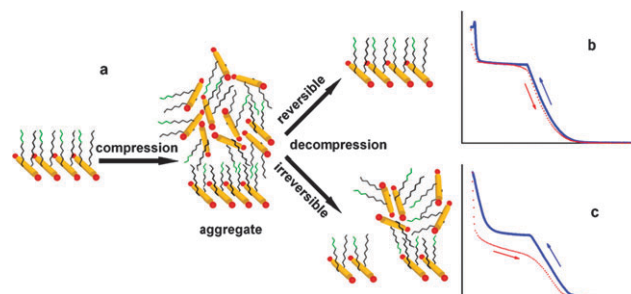
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Langmuir films of four X-shaped bolaamphiphiles were studied using surface pressure and Kelvin potential measurements, Brewster angle microscopy and X-ray reflectivity. The partially fluorinated bolaamphiphiles exhibit an unusual reversibility and reproducibility of Langmuir isotherms, and create very stable and well defined single- or triple layers which can be transferred to solid substrates.

Thin organic films are of importance for numerous nano-technological applications, such as superhydrophobic, anti-bacterial or command surfaces and for molecular electronic devices, to mention only few.<sup>1</sup> Besides the spontaneous self-assembly, the transfer of preformed monomolecular films onto surfaces (*e.g.* Langmuir–Blodgett films) is one of the most commonly used techniques for preparation of such thin films.<sup>2</sup> However, ordered Langmuir films can presently be prepared in a well defined way only for layers of a monomolecular thickness. Upon further compression a disordered aggregation of the molecules takes place. After expansion of the collapsed film a majority of the molecules remains in random, disordered aggregates, *i.e.* the repeated compression/decompression runs are irreversible and irreproducible (Fig. 1(c)).

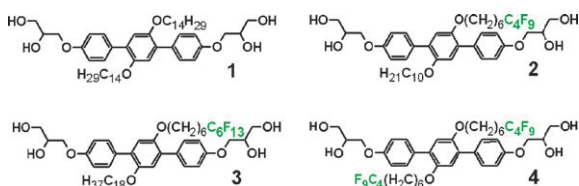
In this communication we present new amphiphiles, with partially fluorinated<sup>3</sup> chains (compounds **2–4**), giving not only monolayers, but also defined trilayer structures of high stability and showing perfect reversibility. Even after complete collapse of the mono- or multilayers the next compression gives exactly the same isotherm as the first one (Fig. 1(b)). This allows the



**Fig. 1** Sketch showing compression of monolayer to aggregates after complete collapse, (a), and two ways of their disintegration during decompression: (b) a monolayer recovered in the perfectly reversible process illustrated by an isotherm of compound **2**, (c) the aggregates coexisting with a monolayer in a typical irreversible process observed for compound **1**.

preparation of defined trilayer Langmuir films and to transfer them directly onto solid substrates in only one dipping run.

We have studied the four compounds **1–4** belonging to the group of X-shaped polyphilic molecules,<sup>4</sup> where a rigid and linear *p*-terphenyl core is terminated with two polar groups (glycerol units), leading to a bolaamphiphilic core unit<sup>5</sup> which is connected at the central part with two lateral lipophilic chains. In previous work these X-shaped polyphiles were investigated with respect to the formation of new liquid-crystalline mesophases with highly complex structures.<sup>4,6</sup> Compounds **1** and **4** were reported previously,<sup>7</sup> and the synthesis of compounds **2** and **3** will be described in a separate manuscript together with their bulk self-assembly behaviour (for analytical data see ESI†). Herein, we focus on the unusual self-assembly behaviour of these materials at the air/water interface. Langmuir isotherms were recorded with simultaneous surface potential measurements and Brewster angle microscopy (BAM) observations. The  $\pi(A)$  isotherms for compound **2** are shown in Fig. 2(a) as the best example. There are two sharp breaks occurring in the slope of the isotherms. After an initial increase a broad plateau is reached at  $\pi = 20 \text{ mN m}^{-1}$ , corresponding to an area  $A = 1.10 \text{ nm}^2$  per molecule. This corresponds roughly to the area required by the bolaamphiphilic core at the surface ( $2.2 \text{ nm} \times 0.45 \text{ nm} +$  some extra space for the oxygen atoms carrying the lateral chains). A second rise starts at  $A = 0.37 \text{ nm}^2$  and its maximum is reached at  $A = 0.30 \text{ nm}^2$ . Hence, the ratio of the areas per molecule at both ends of the plateau is very close to 3. It suggests triple layer formation which sets in at the beginning of the plateau. Similar isotherms were recorded for compounds **2**, **3** and **4** (Fig. S1 in ESI†). It can be assumed that the polar terminal groups of compounds **1–4** interact strongly with the water



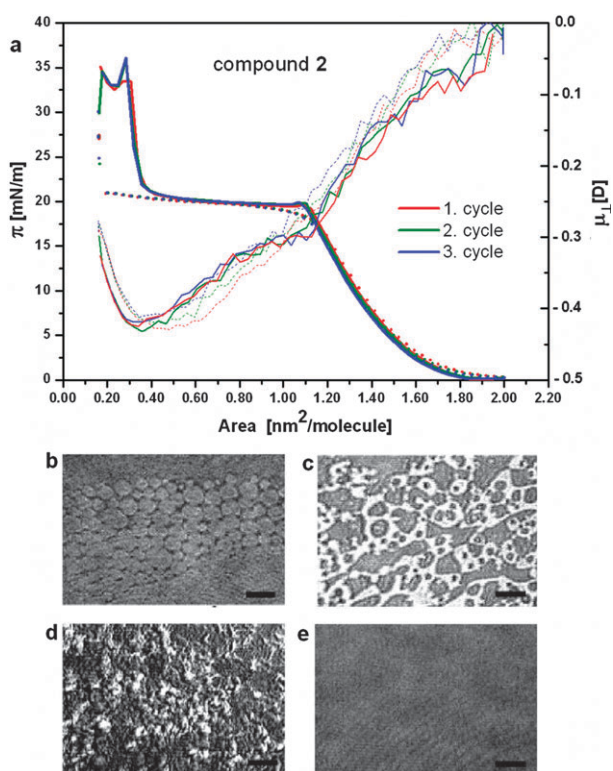
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† Electronic supplementary information (ESI) available: Analytical data, isotherms of four bolaamphiphiles, a comparison of effective dipole moments of fluorinated and non-fluorinated compounds and electron density profiles optimized in XRR fits. See DOI: 10.1039/b922638a



**Fig. 2** Reversible isotherm of compound **2** (three cycles) giving the same surface pressure at the plateau: solid and dotted lines correspond to compression and decompression runs, respectively (a); the BAM images show: (b) coexistence of gas and expanded liquid (2D foam) at  $\pi = 0 \text{ mN m}^{-1}$ , (c) coexistence of monolayer (darker areas) and trilayer (brighter areas) at area  $0.73 \text{ nm}^2 \text{ molecule}^{-1}$  (plateau region), (d) aggregates after complete collapse, (e) uniform film of the monolayer recovered after decompression to  $1.2 \text{ nm}^2 \text{ molecule}^{-1}$ ; the scale bar corresponds to  $250 \mu\text{m}$ .

surface causing these molecules to lie flat on the air/water interface creating very stable Langmuir films. The lateral chains should be packed on top of the layers formed by the aromatic cores. Additionally, the fluorinated parts of the side chains enhance the stability of these layers due to an increase of hydrophobicity.<sup>8</sup>

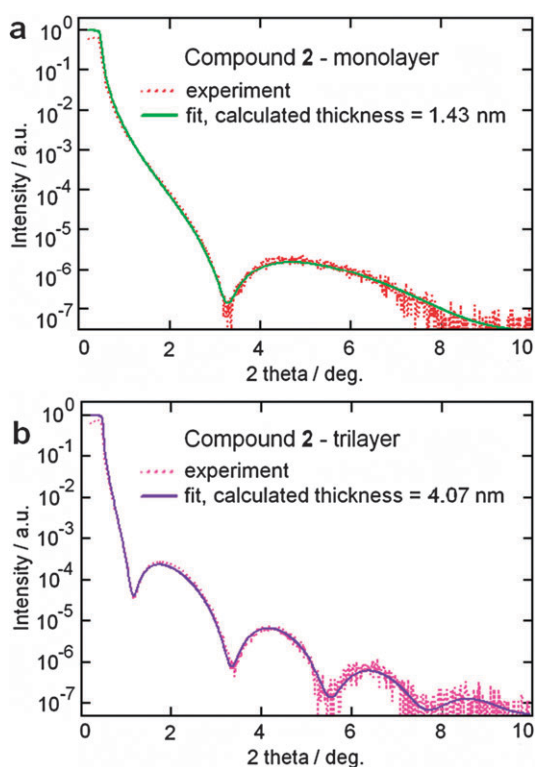
The most important feature of the isotherms of compounds **2–4** with fluorinated segments is their reversibility and reproducibility in spite of the compression to complete collapse of the film and even for the highest possible compression/decompression rate of  $1.50 \text{ nm}^2 \text{ molecule}^{-1} \text{ min}^{-1}$  (usually experiments were carried out at much lower velocities of approximately  $0.05 \text{ nm}^2 \text{ molecule}^{-1} \text{ min}^{-1}$ ). Three cycles for compound **2** are shown in Fig. 2(a). The reversibility manifests as the perfectly overlapping isotherms,  $\pi(A)$ , with the same surface pressure at the plateau observed in both directions. However, only polyphiles with fluorinated lateral chains give these perfectly reversible isotherms, whereas for non-fluorinated compounds such as **1** this process is irreversible (Fig. S2a in ESI†).

Simultaneously with the surface pressure the surface potential was measured using the Kelvin-electrode method. The surface-potential changes during the compression/decompression cycles were converted to a vertical component of a dipole moment of the molecule,  $\mu_{\perp}$ , according to Helmholtz model.<sup>9</sup> In partially fluorinated compounds, the dipole moment

of fluorinated parts (especially the  $-\text{CF}_3$  groups, giving a main contribution to the total dipole moment of the chains), is oriented in opposite direction with respect to the dipole moment of non-fluorinated chains.<sup>10</sup> During compression of compounds with fluorinated chains  $\mu_{\perp}(A)$  decreases, indicating the rising up of the fluorinated parts of the chains. An opposite effect *i.e.* an initial increase of  $\mu_{\perp}(A)$  is observed in the non-fluorinated compound **1** (Fig. S2a in ESI†). This could be interpreted in the following way: at the onset of the plateau the molecules are packed in a 2D film with maximum density. On further compression (in the plateau region) the molecules are removed from the surface by “escape into the third dimension” during formation of the triple layer. The dipole moments of the molecules in the second and third layers compensate because they are oriented in opposite directions. For compound **2** the decrease of  $\mu_{\perp}$  continues after reaching the plateau region, but with reduced slope of  $\mu_{\perp}(A)$ , which means that the dipole moments of the molecules in the second and third layers are not fully compensated. Such compensation of  $\mu_{\perp}$  is observed for compound **4** with two fluorinated chains as can be seen in Fig. S2c in ESI† (the curve of  $\mu_{\perp}(A)$  in a plateau region is almost horizontal). These observations support the idea of well-organized trilayer formation where a double layer is organized on top of the surface layer (Fig. S1 in ESI†), as proposed for rod-like facial amphiphiles.<sup>11</sup>

The BAM images in the plateau region show the coexistence of two liquid phases of very different thickness (Fig. 2(c)). This is in line with the proposed formation of closely packed and well defined trilayers and also indicates the fluidity of these layers. This fluidity seems to be responsible for the reversibility and it might be caused by the lateral attachment of the chains which is highly unfavourable for crystalline packing of both the aromatics as well as the chains. The relatively short  $R_F$  segments seem to further distort the packing of the lipophilic molecular segments and hence increase the flexibility of the layers allowing fast reorganization of the molecules during compression and expansion. The reversibility is slightly reduced for compounds **3** and **4** (see Fig. S1, ESI†) with a higher degree of fluorination, probably due to the onset of chain segregation. Hence, the degree of fluorination is crucial to the special behaviour of the bolaamphiphiles. Detailed studies of the isotherms performed with larger amounts of the studied compounds revealed subsequent singularities on the isotherms related to formation of even thicker multilayers of very well defined thickness, which will be a subject of a subsequent report.

Formation of the trilayer structure was additionally verified by X-ray reflectivity (XRR) measurements of transferred films.<sup>‡</sup> The samples for these studies were prepared by transfer of the film at an appropriate surface pressure onto a silicon substrate. For each compound the monolayer was transferred at the surface pressure below the plateau (at  $\pi = 15 \text{ mN m}^{-1}$ ) and the expected trilayer was transferred well above the plateau, but below the next singularity in the isotherm (at  $\pi = 30 \text{ mN m}^{-1}$ ). Transfer ratios were always close to unity, often slightly bigger than 1, which means that the layer on the silicon wafer (after transfer) is even better organized than on the water surface. The results obtained for compound **2** are shown in Fig. 3 as an example. The obtained reflectivity curves are very similar to those obtained for freely suspended



**Fig. 3** Results of X-ray reflection from the monolayer (a) and the trilayer (b) of compound **2** transferred onto the silicon substrates at surface pressures of 15 and 30 mN m<sup>-1</sup>, respectively.

liquid-crystalline smectic films,<sup>12</sup> indicating a perfectly layered structure. A film thickness was obtained as one of the parameters in the equation used to fit the experimental data.<sup>‡</sup> The layer transferred before the plateau region has a thickness of 1.43 nm (Fig. 3(a)) which is in good agreement with a monolayer structure where the terphenyls lie flat on the surface and the two lateral chains are organized on top of the layer formed by the bolaamphiphilic cores. The film transferred at surface pressure  $\pi = 30$  mN m<sup>-1</sup> has a thickness of 4.07 nm (Fig. 3(b)), which corresponds to approximately three times the thickness of the monolayer film transferred at  $\pi = 15$  mN m<sup>-1</sup>, confirming a well-defined trilayer assembly with a small interdigitation of the lateral chains. A maximum appearing in the reflection spectrum of the monolayer corresponds to a Bragg peak. The spectrum of the trilayer contains the Bragg peak distorted by a form factor<sup>12</sup> and the characteristic subsidiary maxima.

The highly reversible self-assembly of the fluorinated X-shaped molecules is the result of their rod-like and bolaamphiphilic structure and the competing interactions provided by the two laterally attached flexible chains with one or two short fluorinated segments. Self-assembly on the water surface leads to fluid layers where the terphenyl cores are organized parallel to the surface and the flexible chains form liquid-like layers on top of the aromatics. We suppose that the trilayers are created through a rollover mechanism<sup>11</sup> as proposed for rod-like facial amphiphiles and for rod-like liquid crystals with polar terminal groups,<sup>13</sup> especially cyanobiphenyls.<sup>14</sup> The unique feature of compounds **2–4** reported here is that compression and expansion cycles are completely reversible even at very high compression and expansion rates. The order of the film is

completely retained during transfer to a solid substrate. This allows the rapid and simultaneous transfer of the three layers in each dipping run. High reversibility seems to be due to the liquid-crystalline character of the multilayer structures, which resemble the lamellar phases found for some of the X-shaped bolaamphiphiles as liquid-crystalline bulk phases.<sup>4</sup> The fluidity of these structures, which seems to be increased by partial fluorination of the side chains, prevents the monolayers from chaotic aggregation, improves the stability of the films at the air/water interface, and allows the formation of defined triple layers with a perfection comparable with freely suspended films of the smectic liquid crystals.<sup>12</sup> This method might, for example, find application in producing well ordered thin films of  $\pi$ -conjugated oligomers for use in organic electronics applications.

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## Notes and references

<sup>‡</sup> Performed on a Bruker D8 Discover diffractometer: Cu-K $\alpha$  radiation was used and the monochromatic parallel beam was formed by 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 a theoretical model using the software package Leptos 4.02.

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