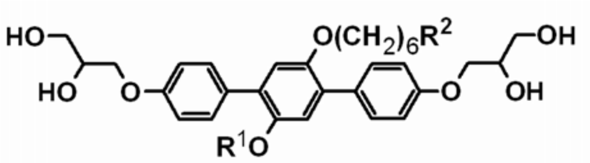
Electronic Supplementary Information

Reversible Aggregation of Bolaamphiphiles with Partially Fluorinated Lateral Chains at the Air/Water Interface

Patrycja Nitoń,[a] Andrzej Żywociński,[a] Robert Hołyst,*[a,b] Robert Kieffer,[c] Carsten Tschierske*[c] Jan Paczesny,[a] Damian Pociecha[d] and Ewa Górecka[d]

[a] *Institute of Physical Chemistry PAS, Kasprzaka 44/52, 01-224 Warsaw, Poland*
[b] *Cardinal Stefan Wyszyński University, WMP-SNŚ, Dewajtis 5, Warsaw , Poland*
[c] *Martin-Luther-University Halle-Wittenberg, Institute of Chemistry, Organic Chemistry, Kurt-Mothes Str. 2, D-06120 Halle, Germany*
[d] *University of Warsaw, Faculty of Chemistry, Pasteura 1, 02-093 Warsaw, Poland.*

General formula of X-shaped bolaamphiphiles:



Analytical data:

Synthesis and full analytical data of compounds **1** (R^1 = $C_{14}H_{29}$, R^2 = C_8H_{17}) and **4** (R^1 = $(CH_2)_6$-C_4F_9, R^2 = C_4F_9) were already reported (R. Kieffer, M. Prehm, B. Glettner, K. Pelz, U. Baumeister, F. Liu, X. B. Zeng, G. Ungar and C. Tschierske, *Chem. Commun.* 2008, **47**, 3861).

Compound 2 (R^1 = $C_{10}H_{21}$, R^2 = C_4F_9)**:** cr 70 Col_{squ}/*p*4*mm* 94 is (°C); ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, ^3J = 8.61 Hz, 4H, Ar-H), 6.94 (d, ^3J = 8.71 Hz, 4H, Ar-H), 6.91 (s, 2H, Ar-H), 4.15-4.11 (m, 2H, CHO), 4.09-4.04 (m, 4H, CH_2OH, CH_2O), 3.88-3.85 (m, 6H, CH_2OH, CH_2O), 2.48 (bs, 4H, OH), 2.06-1.93 (m, 2H, CH_2CF_2), 1.68-1.62 (m, 4H, OCH_2**CH_2**), 1.58-1.51 (m, 2H, **CH_2**CH_2CF_2), 1.41-1.30 (m, 6H, CH_2), 1.29-1.24 (m, 12H, CH_2), 0.87 (t, ^3J = 6.85 Hz, 3H, CH_3); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 157.48, 157.45 (C-4,21), 150.37, 150.09 (C-11,14), 131.53 (C-9,16), 130.57 (C-7,8,17,18), 130.12, 130.04 (C-10,15), 116.40, 116.23 (C-5,6,19,20), 114.07, 114.04 (C-12,13), 70.50 (C-2,23), 69.75 (C-3,22), 69.57, 69.42 (CH_2O), 63.74 (C-1,24), 31.97, 31.09, 30.86, 30.64, 29.65, 29.60, 29.49, 29.38, 29.36, 29.23, 28.82, 26.17, 25.88, 22.74, 20.20 (CH_2), 14.14 (CH_3); ^{19}F-NMR (188 MHz, $CDCl_3$): δ = -81.48 (t, ^3J = 9.91 Hz, 3F, CF_3), -114.85-(-115.01) (m, 2F, CH_2CF_2), -124.87 (s, 2F, CF_2), -126.38-(-126.49) (m, 2F, **CF_2**CF_3). anal. calc. for $C_{44}H_{57}F_9O_8$.: C 59.72 %, H 6.49 %; found: C 59.44 %, H 6.90 %.

Compound 3 (R^1 = $C_{18}H_{27}$, R^2 = C_6F_{13}): g 50 Col_{hex}/*p*6*mm* 67 is (°C); ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, ^3J = 8.61 Hz, 4H, Ar-H), 6.94 (d, ^3J = 8.72 Hz, 4H, Ar-H), 6.91 (s, 2H, Ar-H), 4.14-4.10 (m, 2H, CHO), 4.09-4.06 (m, 4H, CH_2OH), 3.88-3.83 (m, 6H, CH_2O), 3.78-3.73 (m, 2H, CH_2O), 2.34 (bs, 4H, OH), 2.02-1.97 (m, 2H, CH_2CF_2), 1.69-1.62 (m, 4H, OCH_2**CH_2**), 1.56-1.52 (m, 2H, **CH_2**CH_2CF_2), 1.40-1.24 (m, 34H, CH_2), 0.86 (t, ^3J = 6.74 Hz, 3H, CH_3); ^{13}C-NMR (125

MHz, $CDCl_3$): δ = 157.49, 157.45 (C-4,21), 150.32, 150.05 (C-11,14), 131.49, 131.47 (C-9,16), 130.63 (C-7,8,17,18), 129.98, 129.89 (C-10,15), 116.20, 116.01 (C-5,6,19,20), 113.99, 113.96 (C-12,13), 70.41 (C-2,23), 69.53, 69.36 (C-3,22), 69.21, 69.19 (CH_2O), 63.67, 63.63 (C-1,24), 31.89, 30.94, 30.76, 29.68, 29.62, 29.58, 29.32, 29.27, 29.07, 28.70, 26.05, 25.77, 22.65, 20.05 (CH_2), 14.06 (CH_3); ^{19}F-NMR (188 MHz, $CDCl_3$): δ = -81.23 (t, ^3J = 9.22 Hz, 3F, CF_3), -114.64-(-114.81) (m, 2F, CH_2CF_2), -122.33 (s, 2F, CF_2), -123.29 (s, 2F, CF_2), -123.93 (s, 2F, CF_2) -126.52 (s, 2F, $\mathbf{CF_2}CF_3$); anal. calc. for $C_{54}H_{73}F_{13}O_8$: C 59.12 %, H 6.71 %; gef.: C 58.68 %, H 6.67 %.

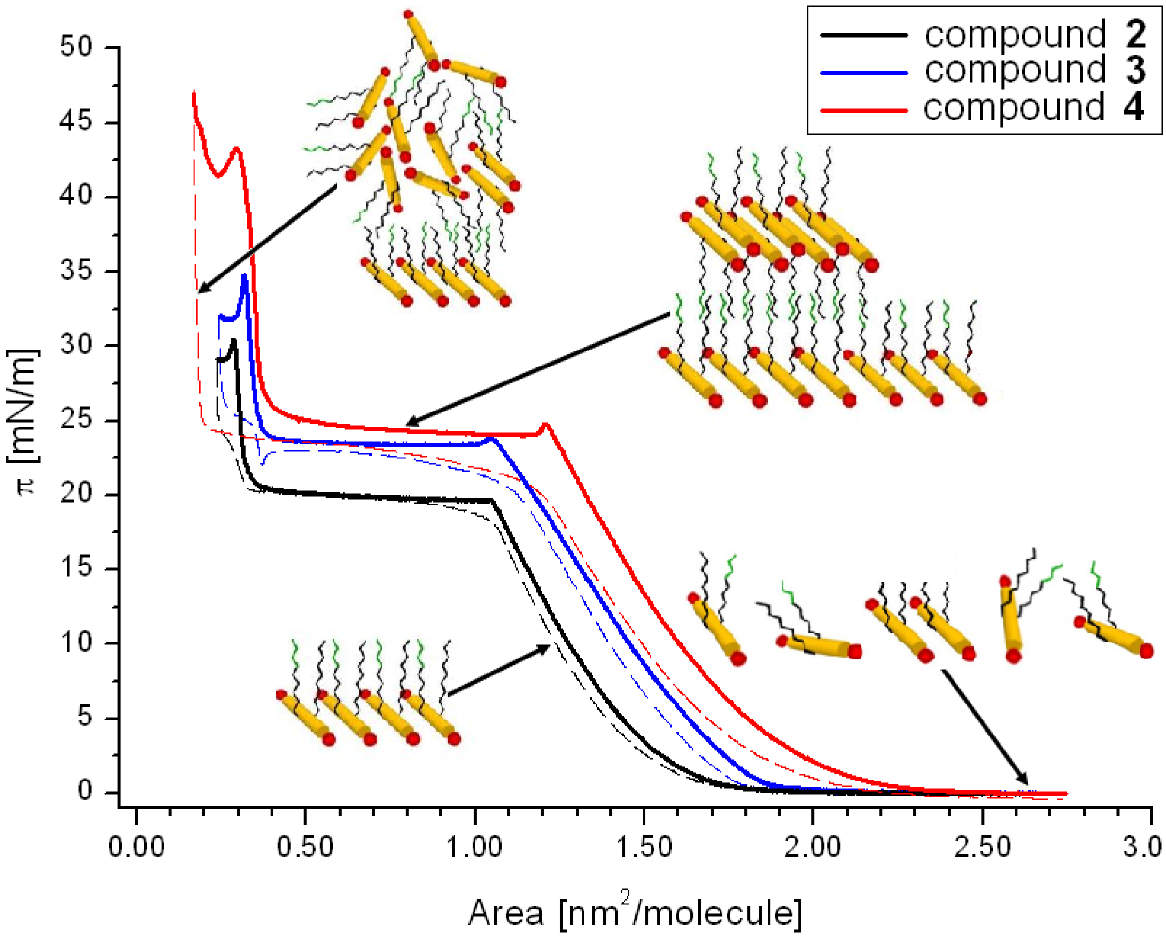


Fig. S1 Reversible isotherms of three partially fluorinated bolaamphiphiles: solid and dashed lines correspond to compression and decompression runs, respectively; compounds **2** and **3** contain one partially fluorinated chain and exhibit perfect reversibility (plateaus appear at the same surface pressure in both directions); compound **4** contains two partially fluorinated chains and shows small hysteresis but exhibits higher stability of the film and excellent reproducibility (the same isotherms in subsequent cycles, not shown in this plot).

Comment: for decompression run of compound **3** a small peak of metastable state, even bigger than during compression run, is visible at the onset of the plateau. It is a direct proof of high stability of the organized trilayer structure.

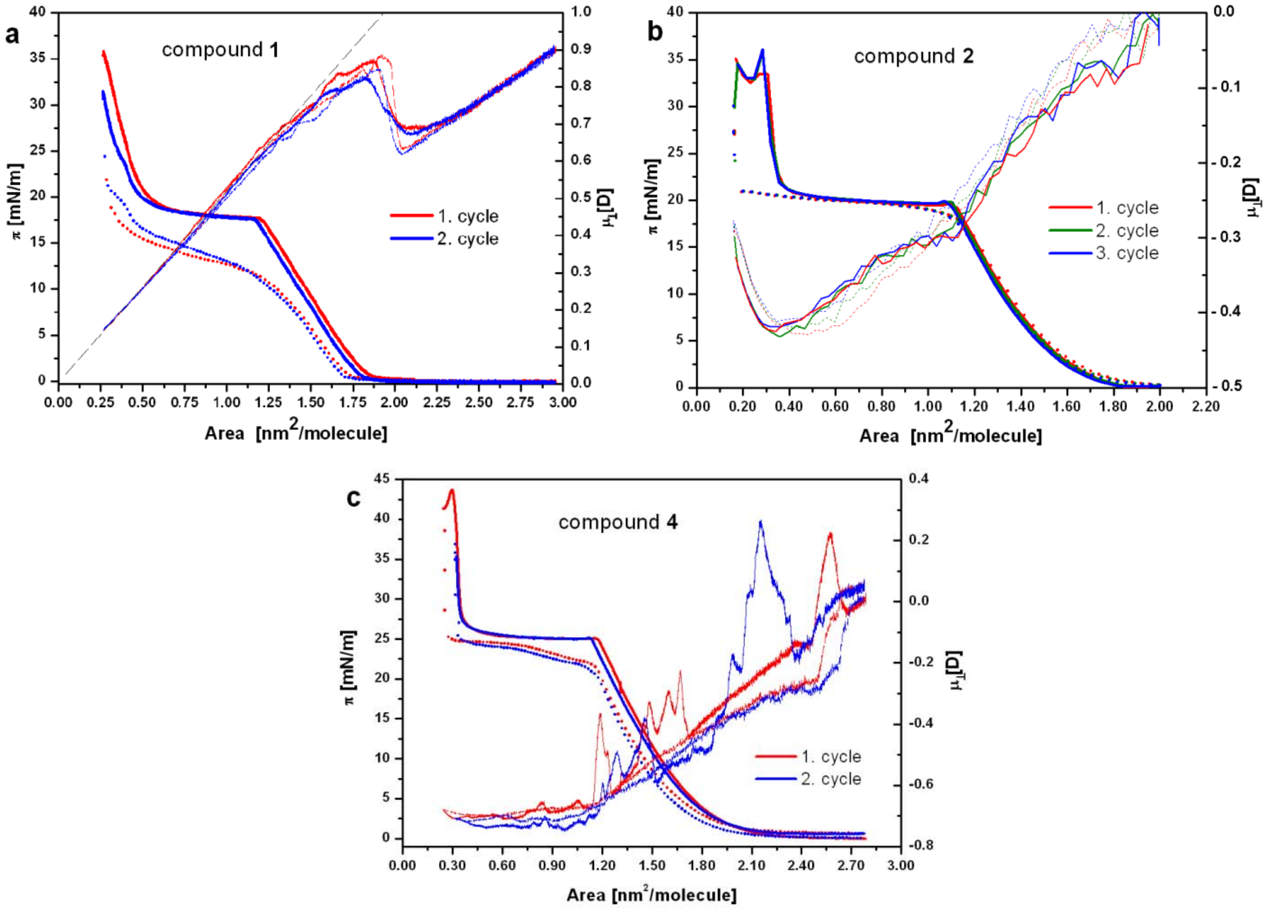


Fig. S2 Comparison of $\pi(A)$ and $\mu_{\perp}(A)$ isotherms for three X-shaped bolaamphiphiles of similar structures: (**a**) non-fluorinated compound **1**; two cycles of compression/decompression runs are shown. (**b**) compound **2** with one partially fluorinated lateral chain; the same three cycles as in the main text are shown for comparison. (**c**) two cycles of isotherm of compound **4,** partially fluorinated in both lateral chains.

Comment: Compound **1** is a molecule which gives an irreversible and irreproducible isotherm with significant hysteresis. Compounds **2** and **4** represent examples of perfect reversibility and reproducibility, although compound **4** shows a small hysteresis. The curve of the vertical component of the dipole moment, $\mu_{\perp}$, for compound **1** with non-fluorinated chains differs significantly from those with fluorinated chains (compounds **2** and **3**). Compound **1** shows a positive jump of dipole moment when the monolayer becomes compact, then $\mu_{\perp}$ starts to decrease and in the range of building up of the trilayer it decreases even faster. For partially fluorinated chains the dipole moment continuously decreases and slower decrease begins at the onset of the trilayer proving a partial compensation of oppositely oriented chains in the second and third layers.

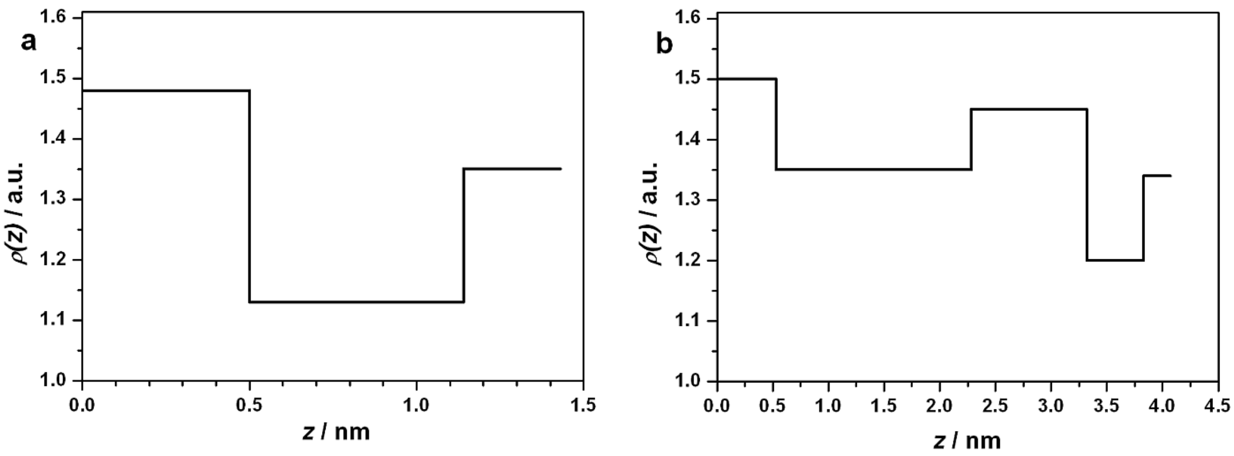


Fig. S3 Electron density profiles for monolayer (**a)** and trilayer (**b**) optimized in fitting procedure of experimental x-ray reflectivity data; *z* is a distance from the silicon substrate.