

Supporting Information

Comparative Structural Study in Monolayers of GPI Fragments and Their Binary Mixtures

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Contents

Experimental Section	S2
<i>Materials and Monolayer Experiments</i>	<i>S2</i>
<i>Surface Pressure – Area Isotherms</i>	<i>S2</i>
<i>Grazing Incidence X-ray Diffraction (GIXD)</i>	<i>S2</i>
<i>GIXD experimental and analyzed data</i>	<i>S3</i>
<i>Monolayers of compound 1</i>	<i>S3</i>
<i>Monolayers of compound 2</i>	<i>S4</i>
<i>Monolayers of compound 3</i>	<i>S6</i>
<i>Two-component monolayers of compounds 1 and 3</i>	<i>S6</i>
<i>Two-component monolayers of compounds 2 and 3</i>	<i>S8</i>
References	S10

Experimental Section

Materials and Monolayer Experiments

Compound **1** (1,2-distearoyl-sn-glycerol) is commercially available (Sigma). Compounds **2** (1,2-distearoyl-sn-glycero-3-phospho-*myo*-inositol) and **3** (GlcN α 1 \rightarrow 6*myo*Ino-1-phosphodistearylglycerol) were prepared according to the reported procedures.¹⁻³ For the monolayer experiments, 1 mM solutions of **2** and **3** (Figure 1 of the manuscript) were prepared in a mixture of chloroform (Merck, Germany; purity >99.8%), methanol (Merck, Germany; purity >99.9%) and ultrapure water (Millipore, resistivity of 18M Ω cm) in a 6:2:0.2 volume ratio. The spreading solutions of compound **1** were prepared only in chloroform.

Surface Pressure – Area Isotherms

The pressure/area (π/A) isotherms were recorded during compression of the monolayer on a computer-interfaced Langmuir trough (R&K, Potsdam, Germany) including a surface pressure microbalance with filter paper Wilhelmy plate. The results were plotted as surface pressure (π) versus the area per molecule. The bare surface was checked for purity by compression before each measurement. The temperature of the different aqueous solutions used as subphase was maintained by an external thermostat.

The Langmuir layers were prepared by spreading the solutions of the compounds at the air/subphase interface. Before compression, the monolayers were left to equilibrate for 15 minutes in order to allow the evaporation of the spreading solvents. Each measurement was repeated at least two times to prove the reproducibility of results. In order to avoid dust contamination of the interface and to ensure a constant humidity, the Langmuir trough was placed in a sealed box.

Grazing Incidence X-ray Diffraction (GIXD)

The grazing incidence X-ray diffraction measurements were carried out at the undulator beamline BW1 using the liquid surface diffractometer at HASYLAB, DESY (Hamburg, Germany). The experimental setup and evaluation procedures have been described in detail elsewhere.⁴⁻⁷

The setup is equipped with a temperature controlled Langmuir trough (R&K, Potsdam, Germany), which is enclosed in a sealed, helium-filled container. The synchrotron X-ray beam is monochromated to a wavelength of 1.304 Å and is adjusted to strike the helium/water interface at a grazing incidence angle $\alpha_i = 0.85\alpha_c$ ($\alpha_c = 0.13^\circ$ is the critical angle for total reflection) illuminating approximately 2×50 mm² of the monolayer surface. A MYTHEN detector system (PSI, Villigen, Switzerland) measures the diffracted signal and is rotated to scan the in-plane Q_{xy} component values of the scattering vector. A Soller collimator in front of the MYTHEN restricted the in-plane divergence of the diffracted beam to 0.09° . The vertical strips of the MYTHEN measure the out-of-plane Q_z component of the scattering vector between 0.0 and 0.75 Å⁻¹.

The diffraction data consist of Bragg peaks at diagnostic Q_{xy} values obtained by summing the diffracted intensity over a defined vertical angle or Q_z -window. The in-plane lattice repeat distances d

of the ordered structures in the monolayer are calculated from the Bragg peak positions: $d = 2\pi/Q_{xy}$. To estimate the extent of the crystalline order in the monolayer, the in-plane coherence length L_{xy} , is approximated from the full-width at half-maximum (fwhm) of the Bragg peaks using $L_{xy} \sim 0.9(2\pi)/\text{fwhm}(Q_{xy})$ using the measured $\text{fwhm}(Q_{xy})$ corrected for the instrumental resolution. Integrating the diffracted intensity normal to the interface over the Q_{xy} window of the diffraction peak yields the corresponding Bragg rod. The thickness of the scattering unit is estimated from the fwhm of the Bragg rod using $0.9(2\pi)/\text{fwhm}(Q_z)$.

GIXD experimental and analyzed data

Monolayers of compound 1 prepared on the water surface at 20°C

π [mN/m]	Q_{xy1} [\AA^{-1}]	Q_{z1} [\AA^{-1}]	Q_{xy2} [\AA^{-1}]	Q_{z2} [\AA^{-1}]	Q_{xy3} [\AA^{-1}]	Q_{z3} [\AA^{-1}]
3.3	1.494 0.016	0.099 0.255	1.482 0.058	0.282 0.255	1.469 0.016	0.381 0.255
5	1.500 0.018	0.09 0.255	1.479 0.038	0.353 0.255		
10.5	1.510 0.017	0.0 0.255	1.498 0.092	0.194 0.255		
15	1.518 0.019	0 0.255				
25	1.520 0.021	0 0.254				
35	1.522 0.021	0 0.255				

Table 1. GIXD results of monolayers of **1** prepared on the surface of water at 20°C: Peak and rod positions and the corresponding full-widths at half-maximum (fwhm) in the region of chain lattices

π [mN/m]	a/b/c [\AA]	$\alpha/\beta/\gamma$ [$^\circ$]	distortion d	tilt t [$^\circ$]	Tilt direction	A_{xy} [\AA^2]	A_0 [\AA^2]
3.3	4.839 4.898 4.925	120.9 119.8 119.2	0.020680	16.3	obl	20.7	19.8
5	4.929 4.860	119.1 120.5	0.018886	15.5	NN	20.6	19.9
10.5	4.856 4.817	119.5 120.2	0.010666	8.5	NN	20.2	19.9
15	a=b=c= 4.779	$\alpha=\beta=\gamma$ = 120	0	0			19.8
25	a=b=c= 4.773	$\alpha=\beta=\gamma$ = 120	0	0			19.7
35	a=b=c= 4.767	$\alpha=\beta=\gamma$ = 120	0	0			19.7

Table 2. GIXD results of monolayers of **1** prepared on the surface of water at 20°C: Lattice parameters a, b, c and α , β , γ , of the unit cell, lattice distortion (d), chain tilt (t) from the surface normal, in plane area per alkyl chain (A_{xy}) and chain cross-sectional area (A_0).

Monolayers of compound 2 prepared on the water surface at 20°C

π [mN/m]	Q_{xy1} [\AA^{-1}]	Q_{z1} [\AA^{-1}]	Q_{xy2} [\AA^{-1}]	Q_{z2} [\AA^{-1}]	Q_{xy3} [\AA^{-1}]	Q_{z3} [\AA^{-1}]
2	1.489 0.016	0 0.26	1.452 0.045	0.484 0.26		
8	1.495 0.031	0 0.26	1.474 0.062	0.390 0.26		
15	1.505 0.019	0 0.26	1.495 0.031	0.305 0.26		
20	1.514 0.018	0 0.26	1.503 0.068	0.196 0.26		
30	1.522 0.014	0 0.26				

Table 3. GIXD results of monolayers of **2** prepared on the surface of water at 20°C: Peak and rod positions and the corresponding full-widths at half-maximum (fwhm) in the region of chain lattices

π [mN/m]	a/b/c [\AA]	$\alpha/\beta/\gamma$ [$^\circ$]	distortion d	tilt t [$^\circ$]	Tilt direction	A_{xy} [\AA^2]	A_0 [\AA^2]
2	5.040 4.915	118.30 120.85	0.03383	21.2	NN	21.3	19.8
8	4.945 4.876	119.05 120.47	0.01895	17.0	NN	20.8	19.8
15	4.864 4.831	119.56 120.22	0.00891	13.3	NN	20.3	19.7
20	4.839 4.804	119.51 120.24	0.00975	8.6	NN	20.1	19.8
30	a=b=c= 4.767	$\alpha=\beta=\gamma$ = 120	0	0			19.7

Table 4. GIXD results of monolayers of **2** prepared on the surface of water at 20°C: Lattice parameters a, b, c and α , β , γ , of the unit cell, lattice distortion (d), chain tilt (t) from the surface normal, in plane area per alkyl chain (A_{xy}) and chain cross-sectional area (A_0).*Monolayers of compound 2 prepared on the surface of a 2 mM CaCl₂ solution at 20°C*

π [mN/m]	Q_{xy1} [\AA^{-1}]	Q_{z1} [\AA^{-1}]	Q_{xy2} [\AA^{-1}]	Q_{z2} [\AA^{-1}]	Q_{xy3} [\AA^{-1}]	Q_{z3} [\AA^{-1}]
2	1.491 0.017	0.081 0.26	1.475 0.038	0.452 0.26	1.449 0.032	0.533 0.26
6	1.496 0.025	0 0.254	1.474 0.059	0.415 0.26		
10	1.503 0.018	0 0.26	1.486 0.046	0.332 0.26		
15	1.509 0.024	0 0.26	1.498 0.069	0.247 0.26		
20	1.520 0.013	0 0.26	1.516 0.055	0.125 0.26		
30	1.524 0.016	0 0.26				

Table 5. GIXD results of monolayers of **2** prepared on the surface of a 2 mM CaCl₂ solution at 20°C: Peak and rod positions and the corresponding full-widths at half-maximum (fwhm) in the region of chain lattices

π [mN/m]	a/b/c [Å]	$\alpha/\beta/\gamma$ [°]	distortion d	tilt t [°]	Tilt direction	A_{xy} [Å ²]	A_0 [Å ²]
2	4.856 4.943 4.996	121.5 119.8 118.7	0.03320	21.6	201.9 140.6 262.1	21.0	19.6
6	4.946 4.874	119.0 120.5	0.01985	18.1	NN	20.8	19.7
10	4.901 4.845	119.24 120.38	0.01522	14.5	NN	20.5	19.8
15	4.855 4.819	119.51 120.24	0.00978	10.8	NN	20.2	19.8
20	4.789 4.777	119.8 120.1	0.00351	5.4	NN	19.8	19.7
30	a=b=c= 4.760	$\alpha=\beta=\gamma=$ 120	0	0			19.6

Table 6. GIXD results of monolayers of **2** prepared on the surface of a 2 mM CaCl₂ solution at 20°C: Lattice parameters a, b, c and α , β , γ , of the unit cell, lattice distortion (d), chain tilt (t) from the surface normal, in plane area per alkyl chain (A_{xy}) and chain cross-sectional area (A_0).

Monolayers of compound 2 prepared on the surface of 10m M PBS at 20°C

π [mN/m]	Q_{xv1} [Å ⁻¹]	Q_{z1} [Å ⁻¹]	Q_{xv2} [Å ⁻¹]	Q_{z2} [Å ⁻¹]	Q_{xv3} [Å ⁻¹]	Q_{z3} [Å ⁻¹]
2	1.475 0.0119	0.082 0.26	1.441 0.027	0.589 0.26	1.408 0.033	0.671 0.26
4	1.477 0.013	0.073 0.26	1.447 0.037	0.562 0.26	1.417 0.030	0.635 0.26
7	1.482 0.016	0.047 0.26	1.459 0.030	0.540 0.26	1.432 0.028	0.587 0.26
10	1.486 0.015	0.028 0.26	1.453 0.029	0.497 0.26	1.440 0.030	0.525 0.26
30	1.518 0.0125	0 0.254				

Table 7. GIXD results of monolayers of **2** prepared on the surface of a 10mM PBS solution at 20°C: Peak and rod positions and the corresponding full-widths at half-maximum (fwhm) in the region of chain lattices

π [mN/m]	a/b/c [Å]	$\alpha/\beta/\gamma$ [°]	distortion d	tilt t [°]	Tilt direction	A_{xy} [Å ²]	A_0 [Å ²]
2	4.922 5.038 5.157	122.2 120.1 117.7	0.0536	27.5	204.5 142.1 264.4	21.9	19.5
4	4.914 5.018 5.122	122.0 120.1 117.9	0.0478	26.2	205.2 143.0 265.1	21.8	19.5
7	4.892 4.984 5.063	121.7 119.9 118.3	0.03961	24.5	205.9 143.3 266.0	21.5	19.5
10	4.906 4.950 5.063	121.3 120.5 118.2	0.03763	22.4	207.8 146.0 267.4	21.4	19.8
30	a=b=c= 4.779	$\alpha=\beta=\gamma=$ 120	0	0			19.8

Table 8. GIXD results of monolayers of **2** prepared on the surface of surface of a 10mM PBS solution at 20°C: Lattice parameters a, b, c and α , β , γ , of the unit cell, lattice distortion (d), chain tilt (t) from the surface normal, in plane area per alkyl chain (A_{xy}) and chain cross-sectional area (A_0).

Monolayers of compound 3 prepared on the surface of 10m M PBS at 20°C

π [mN/m]	Q_{xv1} [\AA^{-1}]	Q_{z1} [\AA^{-1}]	Q_{xv2} [\AA^{-1}]	Q_{z2} [\AA^{-1}]	Q_{xv3} [\AA^{-1}]	Q_{z3} [\AA^{-1}]
2	1.429	0.200	1.404	0.850	1.087	1.05
	0.054	0.26	0.048	0.26	0.23	0.26
30	1.451	0.217	1.453	0.787	1.089	1.004
	0.023	0.26	0.046	0.26	0.05	0.26

Table 9. GIXD results of monolayers of **3** prepared on the surface of a 10mM PBS solution at 20°C: Peak and rod positions and the corresponding full-widths at half-maximum (fwhm) in the region of chain lattices

π [mN/m]	a/b/c [\AA]	$\alpha/\beta/\gamma$ [$^\circ$]	distortion	tilt t [$^\circ$]	A_{xy} [\AA^2]	A_0 [\AA^2]
2	4.804	134.9	0.3185	45.1	27.7	19.6
	6.205	113.7				
	6.316	111.3				
30	4.668	135.9	0.3415	43.4	26.9	19.5
	6.219	112.1				
	6.228	111.9				

Table 10. GIXD results of monolayers of **3** prepared on the surface of surface of a 10mM PBS solution at 20°C: Lattice parameters a, b, c and α , β , γ , of the unit cell, lattice distortion (d), chain tilt (t) from the surface normal, in plane area per alkyl chain (A_{xy}) and chain cross-sectional area (A_0).*Two-component monolayers of compounds 1 and 3 prepared on the surface of water at 20°C*

π [mN/m]	Q_{xv1} [\AA^{-1}]	Q_{z1} [\AA^{-1}]	Q_{xv2} [\AA^{-1}]	Q_{z2} [\AA^{-1}]	Q_{xv3} [\AA^{-1}]	Q_{z3} [\AA^{-1}]
2	1.480	0.0	1.441	0.486		
	0.032	0.27	0.036	0.27		
5	1.485	0.0	1.453	0.449		
	0.046	0.27	0.035	0.27		
10	1.498	0.0	1.472	0.334		
	0.018	0.27	0.05	0.27		
20	1.516	0.0				
	0.028	0.27				
30	1.520	0.0				
	0.025	0.27				

Table 11. GIXD results of mixed monolayers of **1** and **3** (1:1 molar ration) prepared on the surface of water at 20°C: Peak and rod positions and the corresponding full-widths at half-maximum (fwhm) in the region of chain lattices

π [mN/m]	a/b/c [\AA]	$\alpha/\beta/\gamma$ [$^\circ$]	distortion d	tilt t [$^\circ$]	Tilt direction	A_{xy} [\AA^2]	A_0 [\AA^2]
2	5.081	118.2	0.03592	21.4	NN	21.6	20.1
	4.947	120.9					
5	5.030	118.5	0.02925	19.8	NN	21.3	20.0
	4.922	120.7					
10	4.958	118.8	0.02348	14.8	NN	20.8	20.1
	4.872	120.6					
20	4.785	120.0	0.0	0	NN	19.8	19.8
30	4.773	120.0	0.0	0	NN	19.7	19.7

Table 12. GIXD results of monolayers of **1** and **3** (1:1 molar ration) prepared on the surface of water at 20°C: Lattice parameters a, b, c and α , β , γ , of the unit cell, lattice distortion (d), chain tilt (t) from the surface normal, in plane area per alkyl chain (A_{xy}) and chain cross-sectional area (A_0).

Two-component monolayers of compounds **1** and **3** prepared on the surface of PBS at 20°C

π [mN/m]	Q_{xy1} [\AA^{-1}]	Q_{z1} [\AA^{-1}]	Q_{xy2} [\AA^{-1}]	Q_{z2} [\AA^{-1}]	Q_{xy3} [\AA^{-1}]	Q_{z3} [\AA^{-1}]
2	1.486 0.025	0.0 0.27	1.456 0.076	0.531 0.27		
4	1.482 0.036	0.0 0.27	1.448 0.082	0.500 0.27		
10	1.499 0.032	0.0 0.27	1.476 0.064	0.353 0.27		
20	1.524 0.018	0.0 0.27	1.499 0.072	0.104 0.27		
30	1.525 0.018	0.0 0.27				

Table 13. GIXD results of mixed monolayers of **1** and **3** (1:1 molar ratio) prepared on the surface of PBS at 20°C: Peak and rod positions and the corresponding full-widths at half-maximum (fwhm) in the region of chain lattices

π [mN/m]	a/b/c [\AA]	$\alpha/\beta/\gamma$ [$^\circ$]	distortion d	tilt t [$^\circ$]	Tilt direction	A_{xy} [\AA^2]	A_0 [\AA^2]
2	5.018 4.916	118.6 120.7	0.02737	23.0	NN	21.2	19.5
4	5.050 4.935	118.4 120.7	0.03118	21.9	NN	21.4	19.8
10	4.941 4.865	118.9 120.5	0.02072	15.5	NN	20.7	19.9
20	4.867 4.787	118.9 120.5	0.02217	4.6	NN	20.1	20.0
30	4.757	120	0	0	-	19.6	19.6

Table 14. GIXD results of monolayers of **1** and **3** (1:1 molar ratio) prepared on the surface of PBS at 20°C: Lattice parameters a, b, c and α , β , γ , of the unit cell, lattice distortion (d), chain tilt (t) from the surface normal, in plane area per alkyl chain (A_{xy}) and chain cross-sectional area (A_0).

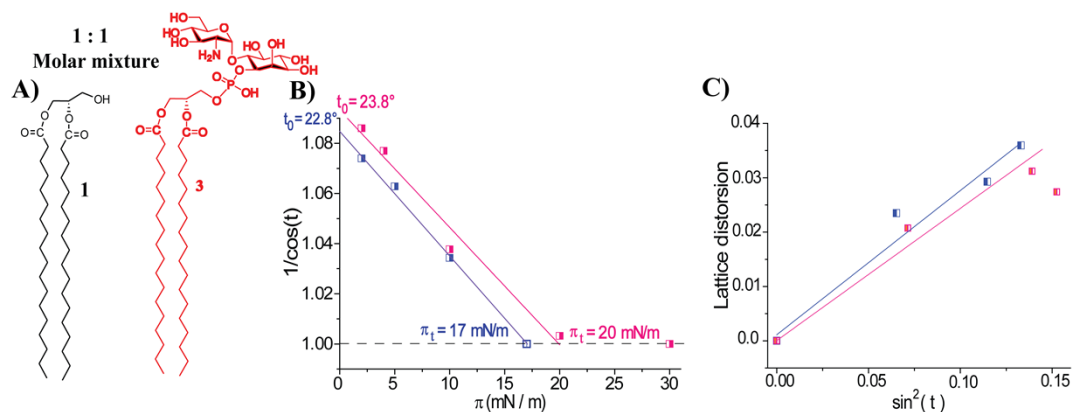


Figure 1S. A) Chemical structures of compounds **1** and **3** studied as a 1:1 molar ratio binary mixture in monolayers; B) Variation of the tilt angle of the alkyl chains (t) represented as $1/\cos(t)$ with the lateral surface pressure (π). Extrapolation of $1/\cos(t)$ to 1 gives the transition surface pressure (π_t) at which the tilt angle becomes zero, while the extrapolation to $\pi = 0$ yields the maximum tilt angle (t_0) of the chains (blue squares – water subphase, 20 °C, pink squares – PBS, 20°C); C) Lattice distortion versus $\sin^2(t)$ (from GIXD data) on different subphases: blue squares –water subphase, 20 °C, pink squares – PBS, 20°C.

Two-component monolayers of compounds 2 and 3 prepared on the surface of water at 20°C

π [mN/m]	Q_{xy1} [\AA^{-1}]	Q_{z1} [\AA^{-1}]	Q_{xy2} [\AA^{-1}]	Q_{z2} [\AA^{-1}]	Q_{xy3} [\AA^{-1}]	Q_{z3} [\AA^{-1}]
2	1.466 0.017	0.078 0.28	1.392 0.065	0.679 0.28	1.357 0.056	0.757 0.28
6	1.475 0.018	0.071 0.28	1.405 0.050	0.644 0.28	1.372 0.045	0.715 0.28
10	1.480 0.022	0.049 0.28	1.442 0.043	0.556 0.28	1.407 0.053	0.605 0.28
15	1.473 0.019	0.055 0.28	1.429 0.068	0.582 0.28	1.398 0.039	0.637 0.28
20	1.476 0.024	0.034 0.28	1.440 0.077	0.575 0.28	1.405 0.056	0.609 0.28
30	1.487 0.026	0.0 0.28	1.458 0.079	0.466 0.28		
40	1.500 0.029	0 0.28	1.482 0.045	0.425 0.28		

Table 15. GIXD results of mixed monolayers of **2** and **3** (1:1 molar ration) prepared on the surface of water at 20°C: Peak and rod positions and the corresponding full-widths at half-maximum (fwhm) in the region of chain lattices

π [mN/m]	a/b/c [\AA]	$\alpha/\beta/\gamma$ [$^\circ$]	distortion d	tilt t [$^\circ$]	Tilt direction	A_{xy} [\AA^2]	A_0 [\AA^2]
2	5.003 5.132 5.405	123.3 121.1 115.6	0.09198	31.8	206.1 141.7 265.1	23.1	19.6
6	4.969 5.088 5.342	123.2 121.0 115.8	0.08615	30.1	206.2 142.0 265.2	22.7	19.6
10	4.908 5.030 5.163	122.4 120.1 117.4	0.05844	25.6	206.2 143.6 266.0	21.9	19.7
15	4.943 5.053 5.209	122.4 120.4 117.2	0.06083	26.9	206.1 143.3 265.8	22.2	19.8
20	4.919 5.042 5.168	122.4 120.1 117.5	0.05691	26.0	207.4 144.9 267.3	22.0	19.8
30	5.009 4.912	118.7 120.7	0.02643	20.4	NN	21.1	19.8
40	4.915 4.856	119.2 120.4	0.01616	18.4	NN	20.6	19.5

Table 16. GIXD results of monolayers of **2** and **3** (1:1 molar ration) prepared on the surface of water at 20°C: Lattice parameters a, b, c and α , β , γ , of the unit cell, lattice distortion (d), chain tilt (t) from the surface normal, in plane area per alkyl chain (A_{xy}) and chain cross-sectional area (A_0).

Two-component monolayers of compounds 2 and 3 prepared on the surface of PBS at 20°C

π [mN/m]	Q_{xy1} [\AA^{-1}]	Q_{z1} [\AA^{-1}]	Q_{xy2} [\AA^{-1}]	Q_{z2} [\AA^{-1}]	Q_{xy3} [\AA^{-1}]	Q_{z3} [\AA^{-1}]
2	1.467	0.077	1.392	0.678	1.359	0.755
	0.015	0.28	0.060	0.28	0.046	0.28
6	1.474	0.078	1.417	0.620	1.386	0.698
	0.015	0.28	0.051	0.28	0.035	0.28
10	1.473	0.066	1.416	0.613	1.385	0.679
	0.015	0.28	0.063	0.28	0.027	0.28
20	1.478	0.040	1.446	0.559	1.415	0.599
	0.020	0.28	0.058	0.28	0.062	0.28
30	1.489	0.034	1.465	0.492	1.439	0.526
	0.020	0.28	0.026	0.28	0.052	0.28
40	1.499	0	1.473	0.409		
	0.023	0.28	0.057	0.28		
45	1.505	0	1.490	0.288		
	0.036	0.28	0.058	0.28		

Table 17. GIXD results of mixed monolayers of **2** and **3** (1:1 molar ration) prepared on the surface of PBS at 20°C: Peak and rod positions and the corresponding full-widths at half-maximum (fwhm) in the region of chain lattices

π [mN/m]	a/b/c [\AA]	$\alpha/\beta/\gamma$ [$^\circ$]	distortion d	tilt t [$^\circ$]	Tilt direction	A_{xy} [\AA^2]	A_0 [\AA^2]
2	5.003	123.3	0.09145	31.8	206.3	23.1	19.6
	5.125	121.1			141.8		
	5.401	115.5			265.1		
6	4.957	122.7	0.07257	29.1	205.2	22.5	19.6
	5.068	120.7			141.8		
	5.272	116.5			264.5		
10	4.960	122.7	0.07263	28.6	205.9	22.5	19.7
	5.071	120.7			142.5		
	5.276	116.5			265.3		
20	4.912	122.1	0.05029	25.4	206.8	21.8	19.7
	5.019	119.0			144.6		
	5.130	117.8			266.7		
30	4.872	122.7	0.03942	22.3	206.8	21.3	19.7
	5.959	119.9			145.1		
	5.041	118.3			266.8		
40	4.954	118.8	0.02346	17.8	NN	20.7	19.7
	4.869	120.6					
45	4.886	119.3	0.01340	12.6	NN	20.4	19.9
	4.837	120.3					

Table 18. GIXD results of monolayers of **2** and **3** (1:1 molar ration) prepared on the surface of PBS at 20°C: Lattice parameters a, b, c and α , β , γ , of the unit cell, lattice distortion (d), chain tilt (t) from the surface normal, in plane area per alkyl chain (A_{xy}) and chain cross-sectional area (A_0).

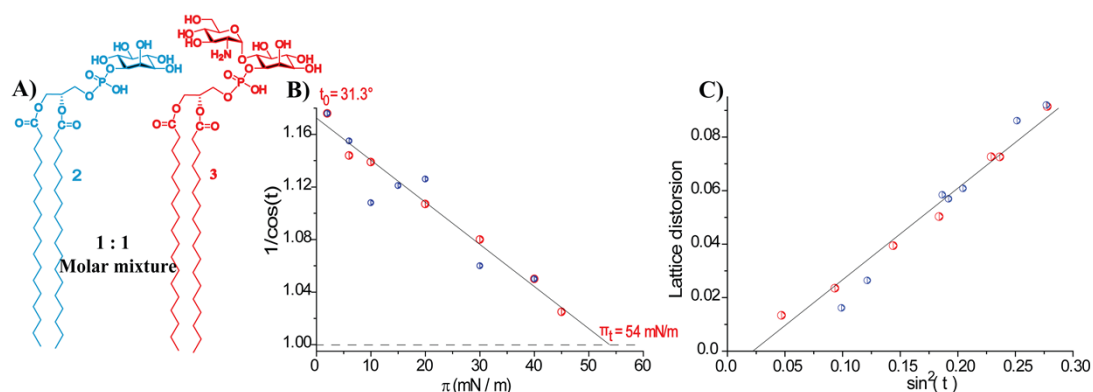


Figure 2S. A) Chemical structures of compounds 2 and 3 studied as a 1:1 molar ratio binary mixture in monolayers; B) Variation of the tilt angle of the alkyl chains (t) represented as $1/\cos(t)$ with the lateral surface pressure (π). Extrapolation of $1/\cos(t)$ to 1 gives the transition surface pressure (π_t) at which the tilt angle becomes zero, while the extrapolation to $\pi = 0$ yields the maximum tilt angle (t_0) of the chains (blue circles – water subphase, 20 °C, red circles – PBS, 20 °C); C) Lattice distortion versus $\sin^2(t)$ (from GIXD data) on different subphases: blue circles – water subphase, 20 °C, red circles – PBS, 20 °C.

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