Supporting Information

Influence of linkage type (ether or ester) on the monolayer characteristics of single-chain glycerols at the air-water interface

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Experimental details

Alkylation reaction

1-O-Hexadecyl-2,3-O-isopropylidene-*sn*-glycerol (**1a**) and
3-O-hexadecyl-1,2-O-isopropylidene-*sn*-glycerol (**1b**)

0.05 mol of 30% potassium hydride suspension (6,06 ml) are placed in an oven-dried flask under argon. To remove the mineral oil, 5 ml of dried toluene are added and the mixture is stirred. It is allowed to settle and the oil / toluene mixture is decanted off. This process is repeated again. 15 ml of dry toluene are then added to the purified potassium hydride. Then the mixture is cooled to 0 ° C. 0.05 mol (6.6 g) of the 2,3-O- resp. 1,2-O-isopropylidene-sn glycerol in 15 ml dry toluene were dropped into the stirred slurry. The mixture was stirred 18 h at room temperature. Then 0.033 mol (10.17 g) hexadecyl bromide in 30 ml dry toluene were added and the mixture was heated 10 h under reflux. After cooling down 10 °C 30 ml water was added and mixture was stirred vigorously. The organic layer was separated and the water phase was extracted with 20 ml ether. The organic layers were combined washed with saturated ammonium chloride followed by water. The solution was dried, evaporated and purified by column chromatography using heptane/chloroform and gradient technique. Yield: 75-78% for the enantiomeric glycerol derivatives.

Hydrolysis:

The chromatographed enantiomeric alkylisopropylidene glycerols are refluxed in a mixture of 100 ml of dried methanol and 0.5 g of pyridinium tosylate for 10 h. After the mixture has cooled, the solvent is removed in vacuo and the residue is taken up in chloroform, washed with water, dried over sodium sulfate and the chloroform is removed. The crystallized hexadecylglycerols are recrystallized from heptane.

1-O-hexadecyl-*sn*-glycerol [(S)-3-Hexadecyloxy-1,2-propanediol] (**2a**):

Yield: 6,9g (67%, two steps), Fp.: 63.5-64 °C. (not corrected), ESI-MS.: 339.48 (M+Na) $[\alpha]_{25}^{D}$ = -3.03 (c = 1, chloroform) . EA.: requires C,72.10, H,12.74

found C,72.19, H,12.67

3-O-hexadecyl-*sn*-glycerol [(R)-3-Hexadecyloxy-1,2-propanediol] (**2b**)
Yield: 7,3g (70 %, two steps) Fp.: 63.5-64.1 °C (not corrected), ESI-MS.: 339.21 (M+Na)
$[\alpha]_{25}^{D}$= +3.04 (c= 1, chloroform) . EA.: requires C,72.10, H,12.74
found C,72.03 H,12.78
^{1}H-NMR: (400MHz, $CDCl_3$) δ=0.88 (t, J=7.1 Hz, 3H, -CH_3), 1.19-1.34 (m, chain C_3-C_{15}, 26H), 1.57 (quint. J=7.5 Hz, C_2 chain, 2H), 2.39 (br., s, OH, 2H), 3.42-3.56 (m, 4H, ROC*H*$_2$-CH_2, -C*H*2OCH_2CH2), 3.64 (dd, J=5,1Hz, 1H, -C*H*H-OH), 3.72 (dd, J=3,9 Hz, 1H, -CH*H*-OH), 3.81-3.91 (m, 1H, =C*H*-OH)ppm.

^{13}C-NMR (100MHz,$CHCl_3$) δ=14.31, 22.92, 26.3, 29.45-29.90, 32.10, 64.50, 70.61, 72.71, 71.90ppm.

GIXD data at different surface pressures and different temperatures

Table S1. Bragg peak (Q_{xy}) and Bragg rod (Q_z) positions and the corresponding full-widths at half-maximum of hexadecyl-*rac*-glycerol monolayers at 10 °C and different surface pressures π.

π, mN/m	Q_{xy}, Å^{-1}	Q_z, Å^{-1}	Q_{xy}, Å^{-1}	Q_z, Å^{-1}	Q_{xy}, Å^{-1}	Q_z, Å^{-1}
1	1.248 0.057	0.905 0.28	1.455 0.012	0 0.28		
10	1.310 0.054	0.818 0.27	1.456 0.012	0 0.27		
14	1.342 0.056	0.762 0.26	1.458 0.012	0 0.27		
16	1.316 0.054	0.830 0.28	1.427 0.031	0.415 0.28		
30	1.404 0.045	0.682 0.25	1.455 0.020	0.341 0.25		
50	1.498 0.045	0.300 0.25	1.502 0.012	0.150 0.25		

Table S2. Lattice parameters of hexadecyl-*rac*-glycerol monolayers at 10 °C and different surface pressures π. a, b and α, β are lattice parameters of the unit cell, d is the lattice distortion, t is the polar tilt angle, A_{xy} is the molecular area and A_0 is the cross-sectional area of an alkyl chain.

π, mN/m	a/b, Å	α/β, °	d	t, °	A_{xy}, Å^2	A_0, Å^2
1	6.196 5.315	108.7 125.7	0.21388	41.7	26.8	20.0
10	5.769 5.191	112.5 123.8	0.14547	36.9	24.9	19.9
14	5.576 5.133	114.2 122.9	0.11341	34.1	24.0	19.9
16	4.962 5.381	125.1 117.5	0.10491	32.2	23.7	20.0
30	4.930 5.109	122.3 118.8	0.04699	25.9	22.1	19.8
50	4.826	120.2	0.00355	11.3	20.2	19.8

	4.839	119.9				

Table S3. Bragg peak (Q_{xy}) and Bragg rod (Q_z) positions and the corresponding full-widths at half-maximum of 1-hexadecyl-*sn*-glycerol monolayers at 5 °C and different surface pressures π.

π, mN/m	Q_{xy}, Å^{-1}	Q_z, Å^{-1}	Q_{xy}, Å^{-1}	Q_z, Å^{-1}	Q_{xy}, Å^{-1}	Q_z, Å^{-1}
1	1.447 0.013	0.122 0.26	1.292 0.059	0.864 0.26	1.230 0.062	0.986 0.26
25	1.449 0.013	0.321 0.26	1.429 0.027	0.452 0.26	1.381 0.053	0.773 0.26
30	1.454 0.013	0.309 0.25	1.442 0.025	0.425 0.25	1.405 0.045	0.734 0.25
40	1.462 0.019	0.320 0.26	1.439 0.076	0.640 0.26		

Table S4. Lattice parameters of 1-hexadecyl-*sn*-glycerol monolayers at 5 °C and different surface pressures π. a, b and α, β are lattice parameters of the unit cell, d is the lattice distortion, t is the polar tilt angle, A_{xy} is the molecular area and A_0 is the cross-sectional area of an alkyl chain.

π, mN/m	a/b/c, Å	α/β/γ, °	d	t, °	A_{xy}, Å^2	A_0, Å^2
1	5.176 5.437 6.089	127.0 123.0 110.0	0.19736	42.1	26.4	19.6
25	4.977 5.150 5.222	122.7 119.4 117.9	0.05657	29.4	22.6	19.7
30	4.962 5.093 5.136	121.9 119.4 118.6	0.04097	27.7	22.2	19.6
40	4.937 5.016 5.016	121.0 119.5 119.5	0.02103	24.0	21.6	19.7

Table S5. Bragg peak (Q_{xy}) and Bragg rod (Q_z) positions and the corresponding full-widths at half-maximum of 1-hexadecyl-*sn*-glycerol monolayers at 10 °C and different surface pressures π.

π, mN/m	Q_{xy}, Å^{-1}	Q_z, Å^{-1}	Q_{xy}, Å^{-1}	Q_z, Å^{-1}	Q_{xy}, Å^{-1}	Q_z, Å^{-1}
1	1.451 0.014	0110 0.26	1.280 0.061	0871 0.26	1.225 0.059	0.981 0.26
5	1.452 0.014	0.132 0.26	1.313 0.049	0.778 .26	1.257 0.053	0.910 0.26
10	1.449 0.014	0.176 0.26	1.348 0.042	0.706 0.26	1.284 0.051	0.882 0.26
20	1.451 0.016	0.269 0.26	1.413 0.033	0.516 0.26	1.346 0.047	0.785 0.26
30	1.461 0.014	0.317 0.25	1.451 0.032	0.352 0.25	1.402 0.046	0.669 0.25
40	1.476 0.028	0.2676 0.26	1.449 0.054	0.5352 0.26		
	or					

40	1.481 0.026	0.237 0.25	1.473 0.016	0.309 0.25	1.456 0.065	0.546 0.25

Table S6. Lattice parameters of 1-hexadecyl-*sn*-glycerol monolayers at 10 °C and different surface pressures π. a, b and α, β are lattice parameters of the unit cell, d is the lattice distortion, t is the polar tilt angle, A_{xy} is the molecular area and A_0 is the cross-sectional area of an alkyl chain.

π, mN/m	a/b/c, Å	α/β/γ, °	d	t, °	A_{xy}, Å^2	A_0, Å^2
1	5.199 5.433 6.158	127.1 123.6 109.2	0.20937	42.4	26.7	19.7
5	5.134 5.363 5.930	126.2 122.6 111.2	0.17479	38.9	25.7	20.0
10	5.073 5.326 5.725	125.5 121.3 113.2	0.14183	36.5	24.8	19.9
20	4.973 5.220 5.361	123.9 119.5 116.6	0.08697	30.7	23.2	19.9
30	4.924 5.096 5.131	122.4 119.1 118.4	0.05041	25.5	22.1	19.9
40	4.886 4.977 4.977	121.2 119.4 119.4	0.02446	20.3	21.2	19.9
	or					
40	4.889 4.946 4.973	120.9 119.8 119.3	0.02003	20.6	21.1	19.7

Table S7. Bragg peak (Q_{xy}) and Bragg rod (Q_z) positions and the corresponding full-widths at half-maximum of 1-hexadecyl-*sn*-glycerol monolayers at 20 °C and different surface pressures π.

π, mN/m	Q_{xy}, Å^{-1}	Q_z, Å^{-1}	Q_{xy}, Å^{-1}	Q_z, Å^{-1}	Q_{xy}, Å^{-1}	Q_z, Å^{-1}
1	1.447 0.012	0.099 0.26	1.283 0.047	0892 0.28	1.233 0.052	0.991 0.28
10	1.449 0.013	0.124 0.27	1.340 0.036	0.790 0.27	1.292 0.040	0.914 0.27
20	1.451 0.013	0.195 0.25	1.400 0.032	0.597 0.26	1.345 .039	0.792 0.26
30	1.458 0.012	0.339 0.26	1.445 0.032	0.361 0.26	1.394 0.041	0.700 0.26
35	1.461 0.024	0.32 0.24	1.422 0.040	0.64 0.24		

Table S8. Lattice parameters of 1-hexadecyl-*sn*-glycerol monolayers at 20 °C and different surface pressures π. a, b and α, β are lattice parameters of the unit cell, d is the lattice distortion, t

is the polar tilt angle, A_{xy} is the molecular area and A_0 is the cross-sectional area of an alkyl chain.

π, mN/m	a/b/c, Å	α/β/γ, °	d	t, °	A_{xy}, Å^2	A_0, Å^2
1	5.206 5.417 6.109	126.7 123.5 109.8	0.19852	42.6	26.5	19.5
10	5.102 5.292 5.722	125.0 121.8 113.2	0.13770	38.1	24.8	19.5
20	5.003 5.207 5.397	123.7 120.0 116.2	0.08739	31.7	23.4	19.9
30	4.935 5.116 5.162	122.6 119.2 118.2	0.05421	26.7	22.2	19.9
35	4.923 5.058 5.058	121.7 119.1 119.1	0.03574	24.2	21.7	19.8

Table S9. Bragg peak (Q_{xy}) and Bragg rod (Q_z) positions and the corresponding full-widths at half-maximum of octadecyl-*rac*-glycerol monolayers at 5 °C and different surface pressures π.

π, mN/m	Q_{xy}, Å^{-1}	Q_z, Å^{-1}	Q_{xy}, Å^{-1}	Q_z, Å^{-1}	Q_{xy}, Å^{-1}	Q_z, Å^{-1}
1	1.277 0.046	0.929 0.25	1.439 0.010	0 0.25		
10	1.334 0.043	0.849 0.25	1.441 0.010	0 0.25		
13	1.354 0.048	0.817 0.24	1.442 0.010	0 0.24		
14	1.398 0.039 1.359 0.051	0.768 0.24 0.872 0.24	1.442 0.010 1.429 0.021	0 0.24 0.436 0.24		
15	1.360 0.076	0.868 0.24	1.429 0.021	0.434 0.24		
20	1.398 0.060	0.820 0.23	1.439 0.017	0.410 0.23		
30	1.416 0.049	0.744 0.22	1.449 0.028	0.372 0.22		
40	1.478 0.097	0.638 0.21	1.460 0.013	0.319 0.21		

Table S10. Lattice parameters of octadecyl-*rac*-glycerol monolayers at 5 °C and different surface pressures π. a, b and α, β are lattice parameters of the unit cell, d is the lattice distortion, t is the polar tilt angle, A_{xy} is the molecular area and A_0 is the cross-sectional area of an alkyl chain.

π, mN/m	a/b, Å	α/β, °	d	t, °	A_{xy}, Å^2	A_0, Å^2
1	5.956 5.285	111.4 124.3	0.16503	41.4	26.0	19.5

10	5.596 5.181	114.6 122.7	0.10537	37.1	24.4	19.5
13	5.453 5.192	116.6 121.7	0.06637	35.3	24.1	19.6
14	5.246 5.086 4.998 5.256	117.9 121.0 123.2 118.4	0.04174 0.06581	32.7 32.7	22.9 23.1	19.4 19.4
15	4.999 5.253	123.2 118.4	0.06486	32.2	23.1	19.5
20	4.995 5.142	121.9 119.1	0.03816	30.4	22.4	19.4
30	4.970 5.086	121.5 119.2	0.03048	27.7	22.1	19.5
40	4.990 4.929	119.2 120.4	0.01640	23.3	21.2	19.5

Table S11. Bragg peak (Q_{xy}) and Bragg rod (Q_z) positions and the corresponding full-widths at half-maximum of octadecyl-*rac*-glycerol monolayers at 10 °C and different surface pressures π.

π, mN/m	Q_{xy}, Å^{-1}	Q_z, Å^{-1}	Q_{xy}, Å^{-1}	Q_z, Å^{-1}	Q_{xy}, Å^{-1}	Q_z, Å^{-1}
1	1.443 0.011	0 0.25	1.272 0.052	0.918 0.25		
10	1.445 0.010	0 0.25	1.330 0.044	0837 0.25		
15	1.448 0.011	0 0.24	1.359 0.044	0.783 0.24		
17	1.441 0.025	0.392 0.24	1.380 0.089	0.784 0.24		
20	1.449 0.027	0.377 0.24	1.396 0.135	0.754 0.24		
30	1.451 0.030	0.348 0.24	1.415 0.028	0.696 0.24		
40	1.463 0.014	0.301 0.22	1.466 0.082	0.602 0.22		

Table S12. Lattice parameters of octadecyl-*rac*-glycerol monolayers at 10 °C and different surface pressures π. a, b and α, β are lattice parameters of the unit cell, d is the lattice distortion, t is the polar tilt angle, A_{xy} is the molecular area and A_0 is the cross-sectional area of an alkyl chain.

π, mN/m	a/b, Å	α/β, °	d	t, °	A_{xy}, Å^2	A_0, Å^2
1	5.998 5.287	110.9 124.6	0.17459	41.2	26.1	19.6
10	5.627 5.179	114.2 122.9	0.11345	36.8	24.5	19.6
15	5.463 5.127	115.6 122.2	0.08629	34.2	23.7	19.6

17	4.967 5.186	122.8 118.6	0.05682	29.6	22.6	19.7
20	4.948 5.136	122.4 118.8	0.04905	28.4	22.3	19.6
30	4.960 5.086	121.6 119.2	0.03321	26.2	22.0	19.8
40	4.963 4.952	119.9 120.1	0.02733	22.3	21.3	19.7

Table S13. Bragg peak (Q_{xy}) and Bragg rod (Q_z) positions and the corresponding full-widths at half-maximum of octadecyl-*rac*-glycerol monolayers at 15 °C and different surface pressures π.

π, mN/m	Q_{xy}, Å^{-1}	Q_z, Å^{-1}	Q_{xy}, Å^{-1}	Q_z, Å^{-1}	Q_{xy}, Å^{-1}	Q_z, Å^{-1}
1	1.267 0.049	0.912 0.25	1.447 0.011	0 0.25		
5	1.295 0.050	0.870 0.25	1.449 0.011	0 0.25		
10	1.324 0.047	0.827 0.25	1.451 0.011	0 0.25		
20	1.372 0.042	0.749 0.24	1.451 0.019	0 0.25		
25	1.385 0.058	0774 0.24	1.444 0.020	0.387 0.24		
30	1.419 0.063	0.708 0.24	1.455 0.017	0.354 0.24		
40	1.453 0.053	0.630 0.24	1.466 0.017	0.315 0.24		

Table S14. Lattice parameters of octadecyl-*rac*-glycerol monolayers at 15 °C and different surface pressures π. a, b and α, β are lattice parameters of the unit cell, d is the lattice distortion, t is the polar tilt angle, A_{xy} is the molecular area and A_0 is the cross-sectional area of an alkyl chain.

π, mN/m	a/b, Å	α/β, °	d	t, °	A_{xy}, Å^2	A_0, Å^2
1	6.041 5.289	110.4 124.8	0.18419	41.2	26.2	19.7
5	5.854 5.232	112.0 124.0	0.15497	39.0	25.4	19.7
10	5.673 5.177	113.5 123.2	0.12561	36.7	24.6	19.7
20	5.396 5.102	116.1 121.9	0.07598	32.7	23.4	19.7
25	4.959 5.170	122.7 118.7	0.05483	29.2	22.5	19.6
30	4.946 5.072	121.6 119.2	0.03312	26.5	21.9	19.6
40	4.934 4.979	120.6 119.7	0.01184	23.4	21.3	19.6

Table S15. Bragg peak (Q_{xy}) and Bragg rod (Q_z) positions and the corresponding full-widths at half-maximum of octadecyl-*rac*-glycerol monolayers at 20 °C and different surface pressures π.

π, mN/m	Q_{xy}, Å^{-1}	Q_z, Å^{-1}	Q_{xy}, Å^{-1}	Q_z, Å^{-1}	Q_{xy}, Å^{-1}	Q_z, Å^{-1}
5	1.284 0.038	0.882 0.25	1.450 0.010	0 0.25		
10	1.314 0.032	0.829 0.25	1.452 0.008	0 0.25		
15	1.346 0.033	0.782 0.25	1.456 0.008	0 0.25		
20	1.460 0.021	0.330 0.25	1.400 0.018	0.660 0.25		
40	1.468 0.017	0.300 0.24	1.443 0.019	0.600 0.25		

Table S16. Lattice parameters of octadecyl-*rac*-glycerol monolayers at 20 °C and different surface pressures π. a, b and α, β are lattice parameters of the unit cell, d is the lattice distortion, t is the polar tilt angle, A_{xy} is the molecular area and A_0 is the cross-sectional area of an alkyl chain.

π, mN/m	a/b, Å	α/β, °	d	t, °	A_{xy}, Å^2	A_0, Å^2
5	5.929 5.250	111.2 124.4	0.16810	39.8	25.7	19.7
10	5.737 5.192	112.9 123.5	0.13727	37.1	24.8	19.8
15	5.550 5.131	114.5 122.7	0.10733	34.6	23.9	19.7
20	4.904 5.114	122.7 118.6	0.05515	25.2	22.0	19.9
40	4.915 5.000	121.1 119.4	0.02277	22.6	21.4	19.8

Table S17. Bragg peak (Q_{xy}) and Bragg rod (Q_z) positions and the corresponding full-widths at half-maximum of 1-octadecyl-*sn*-glycerol monolayers at 5 °C and different surface pressures π.

π, mN/m	Q_{xy}, Å^{-1}	Q_z, Å^{-1}	Q_{xy}, Å^{-1}	Q_z, Å^{-1}	Q_{xy}, Å^{-1}	Q_z, Å^{-1}
1	1.245 0.044	1.029 0.24	1.309 0.039	0.877 0.24	1.433 0.011	0.152 0.24
10	1.307 0.037	0.931 0.23	1.363 0.048	0.750 0.23	1.437 0.012	0.181 0.23
20	1.396 0.038	0.764 0.23	1.424 0.037	0.426 0.23	1.445 0.022	0.338 0.23
25	1.399 0.025	0.721 0.23	1.451 0.046	0.329 0.23	1.462 0.012	0.392 0.23
30	1.447 0.035	0.704 0.23	1.472 0.042	0.295 0.23	1.526 0.025	0.409 0.23

Table S18. Lattice parameters of 1-octadecyl-*sn*-glycerol monolayers at 5 °C and different surface pressures π. a, b and α, β are lattice parameters of the unit cell, d is the lattice distortion, t is the polar tilt angle, A_{xy} is the molecular area and A_0 is the cross-sectional area of an alkyl chain.

π, mN/m	a/b/c, Å	α/β/γ, °	d	t, °	A_{xy}, Å^2	A_0, Å^2
1	5.169 5.435 5.950	126.2 122.0 111.8	0.16733	42.4	26.1	19.3
10	5.083 5.301 5.588	124.4 120.7 114.9	0.11020	37.4	24.4	19.4
20	5.014 5.115 5.190	121.8 119.9 118.4	0.03988	28.8	22.6	19.8
25	4.918 5.101 5.140	122.6 119.1 118.3	0.05372	27.3	22.1	19.6
30	4.789 4.872 5.051	122.3 120.7 117.0	0.06319	26.0	20.8	18.7

Table S19. Bragg peak (Q_{xy}) and Bragg rod (Q_z) positions and the corresponding full-widths at half-maximum of 1-octadecyl-*sn*-glycerol monolayers at 10 °C and different surface pressures π.

π, mN/m	Q_{xy}, Å^{-1}	Q_z, Å^{-1}	Q_{xy}, Å^{-1}	Q_z, Å^{-1}	Q_{xy}, Å^{-1}	Q_z, Å^{-1}
1	1.268 0.045	0.951 0.24	1.310 0.049	0.850 0.24	1.438 0.011	0.101 0.24
10	1.348 0.060	0.876 0.23	1.383 0.039	0.739 0.23	1.446 0.013	0.137 0.23
20	1.415 0.052	0.710 0.23	1.447 0.021	0.427 0.23	1.455 0.014	0.283 0.23
30	1.423 0.052	0.679 0.24	1.464 0.40	0.287 0.24	1.502 0.051	0.392 0.24

Table S20. Lattice parameters of 1-octadecyl-*sn*-glycerol monolayers at 10 °C and different surface pressures π. a, b and α, β are lattice parameters of the unit cell, d is the lattice distortion, t is the polar tilt angle, A_{xy} is the molecular area and A_0 is the cross-sectional area of an alkyl chain.

π, mN/m	a/b/c, Å	α/β/γ, °	d	t, °	A_{xy}, Å^2	A_0, Å^2
1	5.181 5.352 5.876	125.3 122.5 112.2	0.15452	40.3	25.7	19.6
10	5.058 5.189 5.426	123.1 120.8 116.1	0.08271	35.2	23.6	19.3
20	4.969 5.052 5.080	121.3 119.6 119.1	0.02661	26.7	21.9	19.6
30	4.831 4.970 5.099	122.7 120.0 117.3	0.06231	26.1	21.3	19.2

Table S21. Bragg peak (Q_{xy}) and Bragg rod (Q_z) positions and the corresponding full-widths at half-maximum of 1-octadecyl-*sn*-glycerol monolayers at 15 °C and different surface pressures π.

π, mN/m	Q_{xy}, Å^{-1}	Q_z, Å^{-1}	Q_{xy}, Å^{-1}	Q_z, Å^{-1}	Q_{xy}, Å^{-1}	Q_z, Å^{-1}
1	1.235 0.054	0.966 0.23	1.290 0.042	0.850 0.23	1.442 0.012	0.116 0.24
10	1.293 0.038	0.880 0.23	1.345 0.039	0.743 0.23	1.445 0.012	0.137 0.22
20	1.353 0.046	0.806 0.23	1.405 0.031	0.598 0.23	1.449 0.013	0.208 0.22
30	1.400 0.042	0.718 0.24	1.438 0.032	0.414 0.24	1.455 0.020	0.304 0.24
40	1.438 0.032	0.633 0.22	1.458 0.043	0.349 0.22	1.462 0.020	0.284 0.22

Table S22. Lattice parameters of 1-octadecyl-*sn*-glycerol monolayers at 15 °C and different surface pressures π. a, b and α, β are lattice parameters of the unit cell, d is the lattice distortion, t is the polar tilt angle, A_{xy} is the molecular area and A_0 is the cross-sectional area of an alkyl chain.

π, mN/m	a/b/c, Å	α/β/γ, °	d	t, °	A_{xy}, Å^2	A_0, Å^2
1	5.196 5.428 6.067	126.6 123.0 110.4	0.18957	41.5	26.4	19.8
10	5.098 5.303 5.697	124.9 121.5 113.6	0.13192	36.7	24.8	19.8
20	5.003 5.196 5.358	123.4 119.9 116.6	0.07897	31.9	23.2	19.7
30	4.964 5.099 5.159	122.1 119.5 118.3	0.04528	27.3	22.3	19.8
40	4.945 5.014 5.027	121.0 119.6 119.4	0.02039	23.9	21.6	19.8

Table S23. Bragg peak (Q_{xy}) and Bragg rod (Q_z) positions and the corresponding full-widths at half-maximum of 1-octadecyl-*sn*-glycerol monolayers at 20 °C and different surface pressures π.

π, mN/m	Q_{xy}, Å^{-1}	Q_z, Å^{-1}	Q_{xy}, Å^{-1}	Q_z, Å^{-1}	Q_{xy}, Å^{-1}	Q_z, Å^{-1}
5	1.268 0.042	0.924 0.24	1.315 0.031	0.817 0.24	1.446 0.010	0.107 0.24
10	1.293 0.024	0.891 0.24	1.337 0.023	0.768 0.24	1.449 0.009	0.123 0.24
20	1.351 0.039	0.785 0.24	1.406 0.033	0.589 0.24	1.455 0.013	0.196 0.23
30	1.407 0.047	0.637 0.25	1.447 0.042	0.349 0.25	1.470 0.028	0.288 0.25
40	1.438 0.034	0.592 0.24	1.468 0.023	0.298 0.24	1.496 0.056	0.294 0.24

Table S24. Lattice parameters of 1-octadecyl-*sn*-glycerol monolayers at 20 °C and different surface pressures π. a, b and α, β are lattice parameters of the unit cell, d is the lattice distortion, t is the polar tilt angle, A_{xy} is the molecular area and A_0 is the cross-sectional area of an alkyl chain.

π, mN/m	a/b/c, Å	α/β/γ, °	d	t, °	A_{xy}, Å^2	A_0, Å^2
5	5.151 5.342 5.874	125.6 122.5 111.9	0.16038	39.4	25.5	19.7
10	5.111 5.285 5.728	124.9 122.0 113.1	0.13788	37.4	24.8	19.7
20	4.986 5.189 5.370	123.7 120.0 116.3	0.08542	31.3	23.2	19.8
30	4.918 5.058 5.139	122.3 119.6 118.0	0.05092	24.4	22.0	20.0
40	4.849 4.951 5.045	122.0 120.0 118.0	0.04562	22.4	21.2	19.6

Bragg peaks, Bragg rods and surface plots

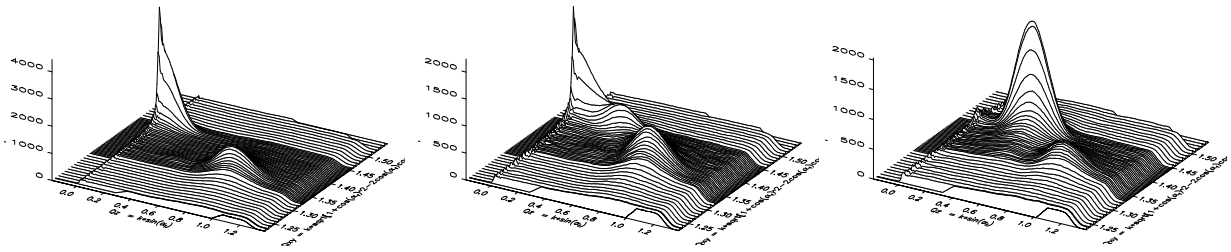

Figure S25. 3D plots of the corrected X-ray intensities versus the in-plane and out-of-plane scattering vector components Q_{xy} and Q_z for mono-octadecyl-*rac*-glycerol monolayers on water at 5 °C, measured at 13 mN/m (left), 14 mN/m (middle) and 15 mN/m (right).

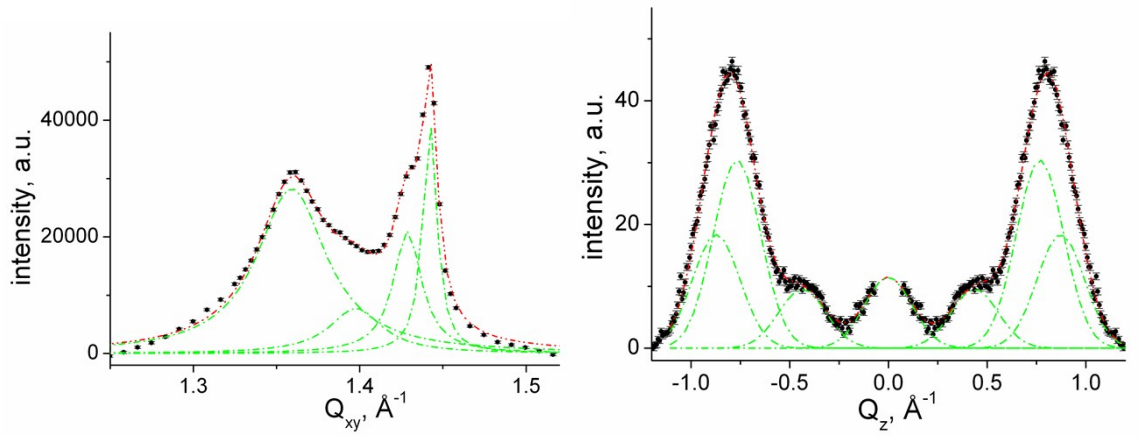

Figure S26. GIXD data of mono-octadecyl-*rac*-glycerol monolayers on water at 5 °C and 14 mN/m. The Bragg peaks (left) and the Bragg rods (right) with the corresponding fits (green and red lines) show the co-existence of both NN- and NNN-tilted phases.

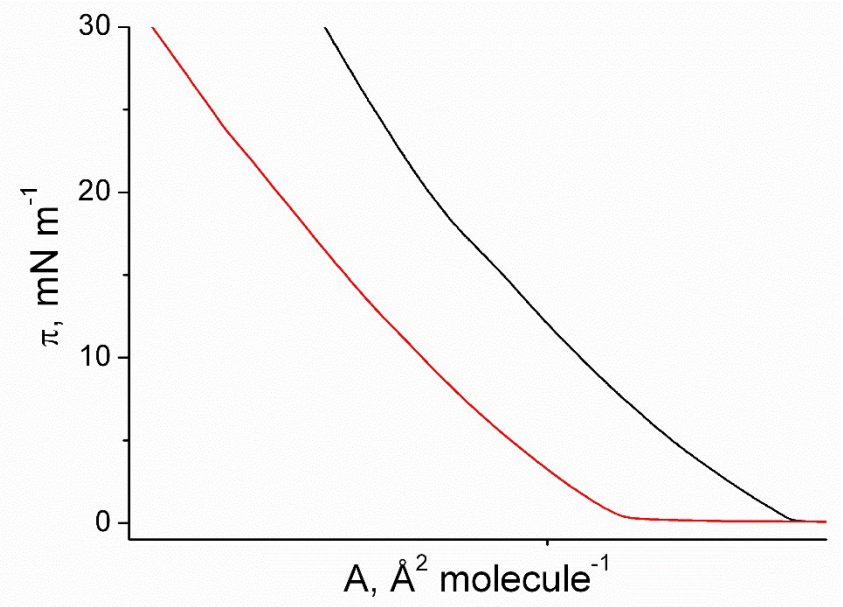

Figure S27. π-A isotherms of mono-octadecyl-rac-glycerol at 5 °C (black) and at 20 °C (red). The curves have been shifted for clarity.