Electronic supplementary information

Surface free energy tuning of supported mixed lipid layers

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COMPRESSIBILITY OF PURE AND MIXED POPC/TO MONOLAYERS

The compressibility moduli C_s^{-1} of pure and mixed POPC/TO layers assembled on water and electrolyte subphases are depicted in Figure S1 and Figure S2, respectively. At the water subphase the pure TO monolayer collapse (abrupt decrease of C_s^{-1} toward zero value) is observed at 12.5 mN/m and the corresponding value of the compressibility modulus is 71.6 mN/m indicating that the monolayer is in the liquid phase. For a pure POPC monolayer collapse occurs at about 45 mN/m and the peak value of the compressibility modulus is about 128 mN/m, corresponding to a liquid-condensed (LC) phase.
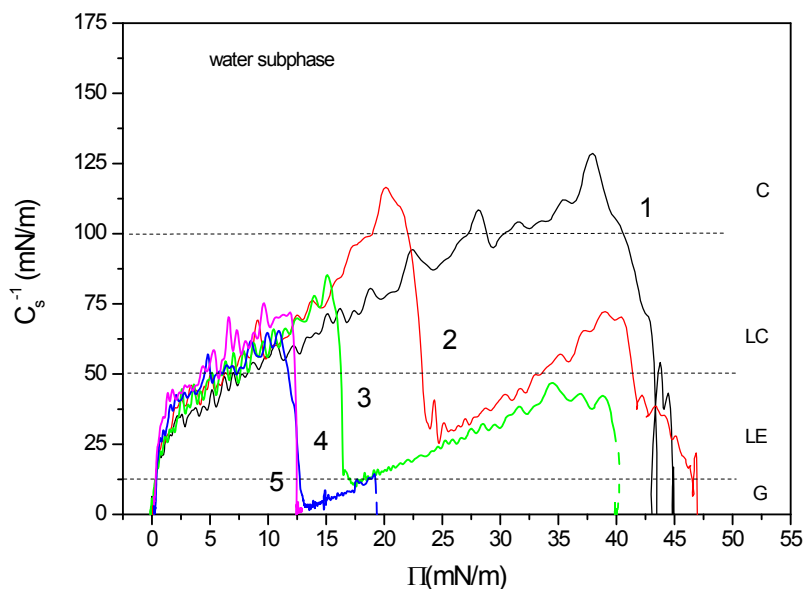

Figure S1. Compressibility modulus (C_s^{-1}) of pure and mixed layers assembled on water subphase *vs*. surface pressure. POPC:TO mixing ratios: 1:0, 3:1, 1:1, 1:3 and 0:1 (curves 1-5, respectively). Dash-lines represent approximate boarders between the phases of a layer (G = gaseous, LE = liquid expanded, L = liquid, LC = liquid condensed, C = condensed).[1]

For monolayers assembled on the electrolyte subphase the collapse is observed at slightly higher pressures than at the water subphase, namely at 12.7 mN/m and at 49 mN/m for TO and POPC, respectively. The corresponding peak values of the compressibility moduli are significantly higher amounting 100 mN/m and 160 mN/m for TO and POPC, respectively, and correspond to a LC phase. For a mixed system there are two pressures at which the monolayer collapses. First one corresponds to

ejection of the component with the lower collapse pressure from the mixed monolayer (here TO). For the mixed POPC/TO layers the first collapse pressure increases with decrease of TO amount in the layer. The second collapse pressure of the mixed layer for high TO molar fractions (>0.5) is lower than that of a pure POPC layer but also increases with decrease of the TO molar fraction.
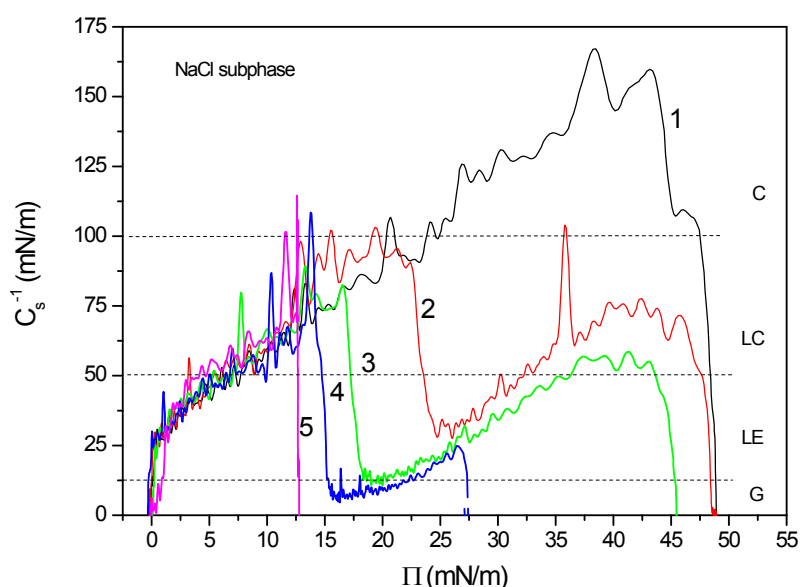

Figure S2. Compressibility modulus (C_s^{-1}) of pure and mixed layers assembled on 0.55 M NaCl subphase *vs*. surface pressure. POPC:TO mixing ratios: 1:0, 3:1, 1:1, 1:3 and 0:1 (curves 1-5, respectively). Dash-lines represent approximate boarders between the phases of a layer (G= gaseous, LE = liquid expanded, LC= liquid condensed, C = condensed)[1].

Here, it is worth noting that on both subphases, irrespective of the mixed layer stoichiometry, after the ejection of TO the layer is left in a state corresponding to a LE phase. The subsequent compression leading to second collapse does not reach a condensed phase as is the case with a pure POPC layer. The collapse, even for low TO molar fraction, occurs in a state corresponding to the L/ LC phase, thus indicating that expulsion of TO domains from the mixed layer left the layer in the state preventing dense and homogeneous packing of molecules as is the case with pure POPC layer. We assume that the reason for this is that prior to the ejection of TO the structure of the mixed layer is that of intermixed domains of POPC and TO corresponding to the LE/LC phase, and that after the expulsion of TO the remained

domains of POPC with increase in pressure cannot arrange to form such a homogenous compact layer as is the case with gradual organization in the pure POPC layer. Thus the layer remains in the state corresponding to the LE/LC phase.

AFM IMAGES OF SUPPORTED LIPID LAYERS.

To provide an insight into supported layers' topographies AFM imaging was used. The representative results of AFM measurements of supported mixed and pure layers assembled on water and on the 0.55 M NaCl subphases are shown in Figure (S3)

All images show uniform substrate coverage with relatively homogenous and compact organized monolayer. However, roughness analysis of corresponding section profiles show increase of roughness with increase of TO molar fraction within the monolayer. This is especially noticeable in layers assembled on NaCl subphase for which the corresponding values of R_a (the average roughness parameter) are 0.084± 0.002 and 0.123±0.005 for POPC and TO layer, respectively, while for those assembled on water are 0.078± 0.005 to 0.107± 0.001 for POPC and TO layer, respectively.

An interesting feature of pure TO layer assembled on NaCl subphase is the appearance of the subordering spatial periodicity (16 ± 2 nm) and superordering spatial periodicity (94 ± 5 nm) in cross section profile in Figure S3d, related to the molecular ordering in the layer. Such ordering of the lipid molecules within the monolayer transferred from the NaCl subphase is compliant with recent findings[2] revealing the influence of electrostatic interactions of sodium and chloride ions positioned around lipid polar heads on the compactness of the layer and resulting in a more rigid lipid ordering in comparison to that of a layer assembled on pure water.
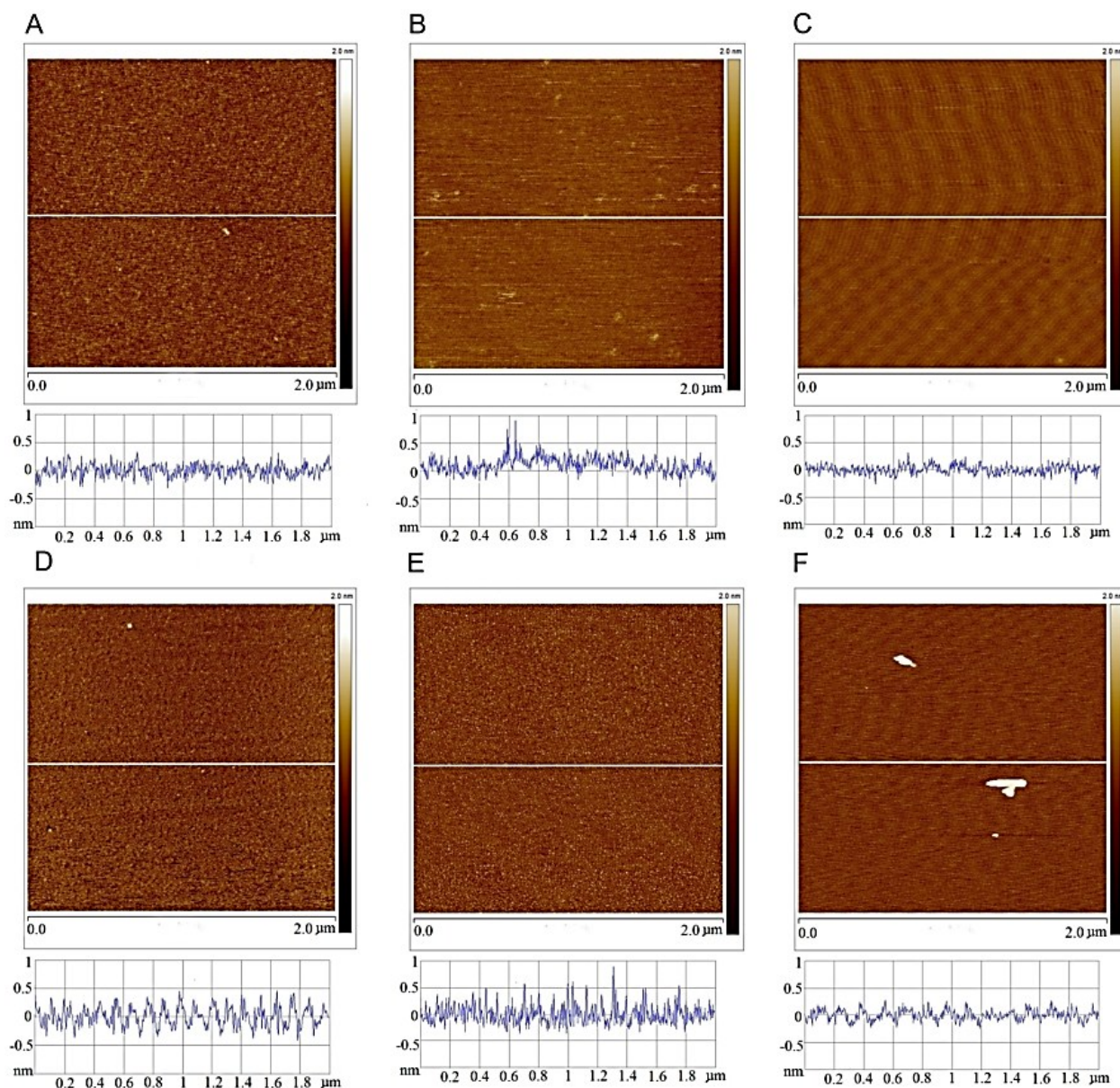
Figure S3: AFM images (scan size 2μm×2μm, vertical scale 3 nm) and corresponding cross-section profiles of pure and mixed layers on mica. The images and height profiles in the upper row of the figure (a-c) correspond to the layers assembled on the water subphase and these in the lower row (d-f) to the layers assembled on 0.55 M NaCl subphase. Plates a) and d) correspond to pure TO layer, b) and e) to a mixed layer with TO molar fraction 0.5, and plates c) and f) to a pure POPC layer.

References

1 M. Broniatowski and P. Dynarowicz-Latka, *J. Fluorine Chemistry*, 2004, **125**, 1501-1511.

2 S. Šegota, D. Vojta, G. Pletikapić and G. Baranović, *Chem. Phys. Lipids,* 2015, **86**, 17-29.

DIELECTRIC CONSTANT OF FRACTAL STRUCTURES

If the space between the charges is filled with a dielectric the dielectric reduces the electrostatic force as compared to free space by a factor κ (dielectric constant or relative permittivity).

The dielectric constant κ of a fractal structure is given by (Risović *et al. J. Phys. Chem. B,* 2002**, 106***,* 9810-9814):

$$\kappa - 1 \propto R^{D-d}$$

where, R is the size of the structure, D its fractal dimension, d the corresponding embedding (Euclidean) dimension and the proportionality constant includes also the term α/ε_0 (α = polarizability).

This relation clearly shows that the relative permittivity is not only a characteristic of the material but for fractal structures also depends on extent and D of the considered structure. Consequently, for a fractal structure, all physical quantities related to the relative permittivity, such as polarization and specific capacity, shall exhibit similar scaling.

For a given R increase in fractal dimension results in decrease of dielectric constant. Hence, increase in electrostatic force.