Supplementary Materials (ESI) for Soft Matter

Electronic Supplementary Information

Assembly of Phospholipids Modified with Poly(Ethylene Glycol) at Aqueous-Liquid Crystal Interfaces: Phase Segregation of Phospholipid Mixtures Driven by Nematic Ordering

Michael I. Kinsinger,[a] David M. Lynn*[a,b] and Nicholas L. Abbott*[a]

[a]*Department of Chemical and Biological Engineering and* [b]*Department of Chemistry, University of Wisconsin – Madison, 1415 Engineering Drive, Madison, Wisconsin 53706*

Selection of DSPE-PEG2000-F as a Fluorescent Probe

Experiments described in the main text that were designed to provide insights into i) the possible desorption of PEG-lipids from the aqueous-air interface into the aqueous subphase and ii) the lateral distributions of PEG-lipids at aqueous-LC interfaces used mixed monolayers of DPPC and 10 mol% of the fluorescently labeled lipid DSPE-PEG2000-F. We note that DSPE-PEG2000-F has two 18-carbon tails in contrast to the two 16-carbon tails of DPPE-PEG2000 (a fluorescently labeled analog of DPPE-PEG2000 was not commercially available). However, isotherms collected using 10 mol% DSPE-PEG2000-F were nearly identical to isotherms collected using 10 mol% DPPE-PEG2000 (Figure S1), which suggests that, in the context of these experiments, DSPE-PEG2000-F can be used as an appropriate substitute for DPPE-PEG2000.

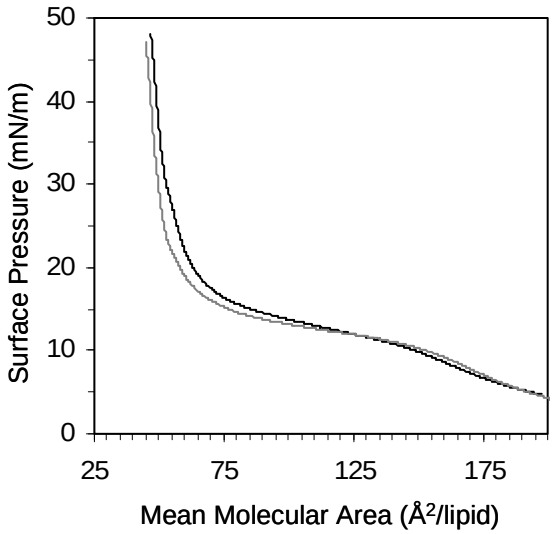

Figure S1: Surface pressure – area isotherms of mixed lipid films of DPPC/10 mol% DPPE-PEG2000 (black line) and DPPC/10 mol% DSPE-PEG2000-F (gray line) at the air-PBS interface.

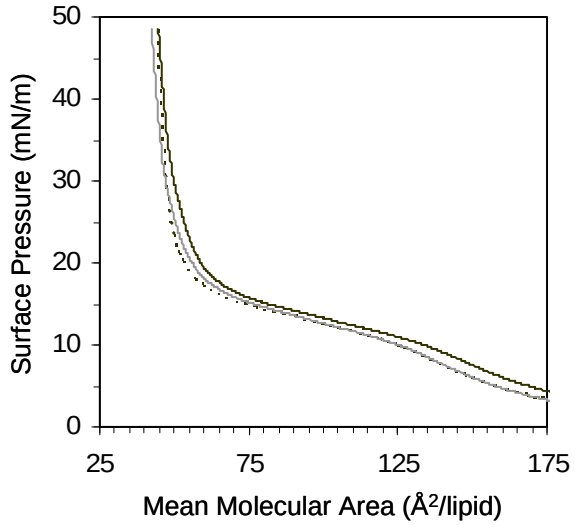

Figure S2: Surface pressure – area isotherms recorded during the repeated compression of a 10 mol% DPPE-PEG2000/90 mol% DPPC monolayer. The solid black line indicates the initial compression of the film, the dashed line indicates the subsequent expansion of the film, and the solid gray line indicates the second compression of the film.

Estimation of Lipid Mean Molecular Area on the Basis of Fluorescence Images

To gain insights into the possibility of differences in the lateral densities of lipids at aqueous-LC interfaces, we calculated the mean molecular area of DPPC and PEG-lipids within the domains of planar and homeotropic alignment at the aqueous-LC interface using the fluorescence images shown in Figures 4 B and 4D of the main text. For these calculations the following assumptions were made: i) the excitation and emission of the fluorescent labels (lissamine rhodamine B and carboxyfluorescein) were not dependent on the ordering of the LC, ii) the intensity of the collected fluorescence emission was directly proportional to the interfacial density of the labeled phospholipids, and iii) the lateral distribution of DPPE-R was representative of the distribution of DPPC at the aqueous-LC interface. The following set of equations was then used to calculate the approximate interfacial density of lipids within the planar and homeotropic domains.

$$\frac{[PEG\text{-}F]_H}{[PEG\text{-}F]_P} = \frac{I_{PEG\text{-}F,H}}{I_{PEG\text{-}F,P}}$$

$$\frac{[DPPE\text{-}R]_H}{[DPPE\text{-}R]_P} = \frac{I_{DPPE\text{-}R,H}}{I_{DPPE\text{-}R,P}}$$

$$[PEG\text{-}F]_P = \frac{[PEG\text{-}F]_O}{\frac{I_{PEG\text{-}F,H}}{I_{PEG\text{-}F,P}} A_H + A_P}$$

$$[DPPE\text{-}R]_P = \frac{[DPPE\text{-}R]_O}{\frac{I_{DPPE\text{-}R,H}}{I_{DPPE\text{-}R,P}} A_H + A_P}$$

$$[Lipid]_H = [DPPE\text{-}R]_H + [PEG\text{-}F]_H$$

$$[Lipid]_P = [DPPE\text{-}R]_P + [PEG\text{-}F]_P$$

Where $[PEG\text{-}F]_H$, $[DPPE\text{-}R]_H$, and $[Lipid]_H$ correspond to the molecules per unit area of DSPE-PEG2000-F, DPPE-R, and total lipid within the homeotropic domains, respectively; $[PEG\text{-}F]_P$, $[DPPE\text{-}R]_P$, and $[Lipid]_P$ correspond to the molecules per unit area of DSPE-PEG2000-F, DPPE-R, and total lipid within the planar domains, respectively; $I_{PEG\text{-}F,H}$ and $I_{DPPE\text{-}R,H}$ correspond to the fluorescence intensity of DSPE-PEG2000-F and DPPE-R, respectively calculated by Image J within the homeotropic regions; $I_{PEG\text{-}F,P}$ and $I_{DPPE\text{-}R,P}$ correspond to the fluorescence intensity of DSPE-PEG2000-F and DPPE-R, respectively calculated by Image J within the planar regions; $[PEG\text{-}F]_O$ and $[DPPE\text{-}R]_O$ correspond to the overall molecules per unit area of DSPE-PEG2000-F and DPPE-R, respectively across the entire interfacial area; A_H and A_P correspond to the fraction of the interfacial area displaying homeotropic and planar alignment, respectively. For the above calculations the background florescence intensity of a PBS/5CB interface in the absence of lipid was subtracted from values of the florescence intensity of the PBS/5CB interfaces decorated with labeled lipids.

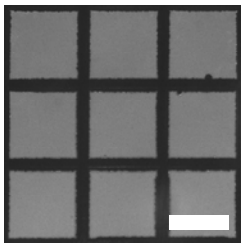

Figure S3: Fluorescence micrographs of a lipid monolayer composed of 10 mol% DPPE-PEG2000/ 1 mol% DPPE-R/89 mol% DPPC transferred to the interface between a PBS solution and microscope immersion oil at an areal density of 46 $Å^2$/lipid. Scale bar = 200 μm.