Supporting Information
for

Headgroup organization and hydration of methylated phosphatidylethanolamines in Langmuir monolayers

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Confidence limits

Table S1: Confidence limits of structural parameters describing the lipid molecules in a Langmuir monolayer on pure water were derived from a mapping of the least-squares differences between the experimental data and the model reflectivity, χ^2. We determined the χ^2 values for models in which one parameter was deliberately detuned in small steps from the global minimum while all remaining parameters were readjusted to the new, higher minima. Hence, one-dimensional sections through the multidimensional χ^2 landscape were created. As a criterion to determine the confidence limit of the mapped parameter, we chose an increase of 10% over the global minimum value.

lipid	π (mN/m)	$\Delta\sigma_{\text{cw}}$ (Å)	$\Delta\sigma_{\text{int}}$ (Å)	Δd_{chain} (Å)	Δz_{P} (Å)	Δz_{N} (Å)	Δz_{dry} (Å)
DPPE	10	$^{+0.05}_{-0.08}$	$^{+0.27}_{-0.08}$	$^{+0.18}_{-0.24}$	$^{+0.31}_{-0.36}$	$^{+0.93}_{-1.24}$	$^{+0.48}_{-1.80}$
	20	$^{+0.02}_{-0.05}$	$^{+0.26}_{-0.12}$	$^{+0.21}_{-0.16}$	$^{+0.27}_{-0.40}$	$^{+0.66}_{-1.40}$	$^{+1.20}_{-1.50}$
	30	± 0.04	$^{+0.21}_{-0.26}$	$^{+0.17}_{-0.16}$	$^{+0.39}_{-0.21}$	$^{+0.48}_{-1.57}$	$^{+2.08}_{-0.66}$
	40	$^{+0.06}_{-0.07}$	$^{+0.25}_{-0.47}$	$^{+0.23}_{-0.19}$	$^{+1.39}_{-0.37}$	$^{+1.69}_{-0.88}$	$^{+0.36}_{-0.98}$
DPPE-N-Me	10	$^{+0.05}_{-0.06}$	$^{+0.58}_{-0.17}$	$^{+0.22}_{-0.17}$	$^{+0.45}_{-0.80}$	$^{+1.11}_{-1.55}$	$^{+1.14}_{-0.95}$
	20	$^{+0.05}_{-0.06}$	$^{+0.55}_{-0.24}$	$^{+0.19}_{-0.16}$	$^{+0.50}_{-0.77}$	$^{+1.33}_{-1.62}$	$^{+1.18}_{-1.27}$
	30	$^{+0.03}_{-0.06}$	$^{+0.61}_{-0.19}$	$^{+0.19}_{-0.14}$	$^{+0.48}_{-0.59}$	$^{+1.87}_{-1.33}$	$^{+0.47}_{-2.75}$
	40	$^{+0.03}_{-0.10}$	$^{+0.28}_{-0.70}$	$^{+0.26}_{-0.25}$	$^{+0.63}_{-0.91}$	$^{+2.23}_{-1.78}$	$^{+0.48}_{-2.97}$
DPPE-N-Me$_2$	10	± 0.07	$^{+0.48}_{-0.22}$	$^{+0.26}_{-0.25}$	$^{+0.69}_{-0.61}$	$^{+1.60}_{-0.98}$	$^{+1.01}_{-0.86}$
	20	$^{+0.02}_{-0.07}$	$^{+0.22}_{-0.34}$	$^{+0.17}_{-0.21}$	$^{+0.18}_{-0.65}$	$^{+0.89}_{-2.81}$	$^{+0.11}_{-2.81}$
	30	$^{+0.03}_{-0.05}$	$^{+0.28}_{-0.15}$	$^{+0.06}_{-0.11}$	$^{+0.46}_{-0.59}$	$^{+1.57}_{-1.29}$	$^{+0.33}_{-2.19}$
	40	± 0.07	$^{+0.18}_{-0.93}$	$^{+0.19}_{-0.21}$	$^{+0.92}_{-0.48}$	$^{+1.69}_{-2.06}$	$^{+0.97}_{-3.41}$
DPPC	10	$^{+0.08}_{-0.07}$	$^{+0.33}_{-0.08}$	$^{+0.25}_{-0.20}$	$^{+0.36}_{-0.40}$	$^{+0.74}_{-0.98}$	$^{+0.49}_{-0.68}$
	20	$^{+0.09}_{-0.07}$	$^{+0.32}_{-0.38}$	$^{+0.21}_{-0.19}$	$^{+1.42}_{-0.25}$	$^{+2.17}_{-2.86}$	$^{+2.21}_{-2.51}$
	30	$^{+0.04}_{-0.11}$	$^{+0.40}_{-0.65}$	$^{+0.22}_{-0.18}$	$^{+1.02}_{-1.03}$	$^{+1.56}_{-3.10}$	$^{+2.18}_{-2.40}$
	40	$^{+0.09}_{-0.04}$	$^{+0.03}_{-0.37}$	$^{+0.16}_{-0.21}$	$^{+1.01}_{-0.80}$	$^{+2.42}_{-1.91}$	$^{+0.34}_{-3.49}$

X-ray reflectivities

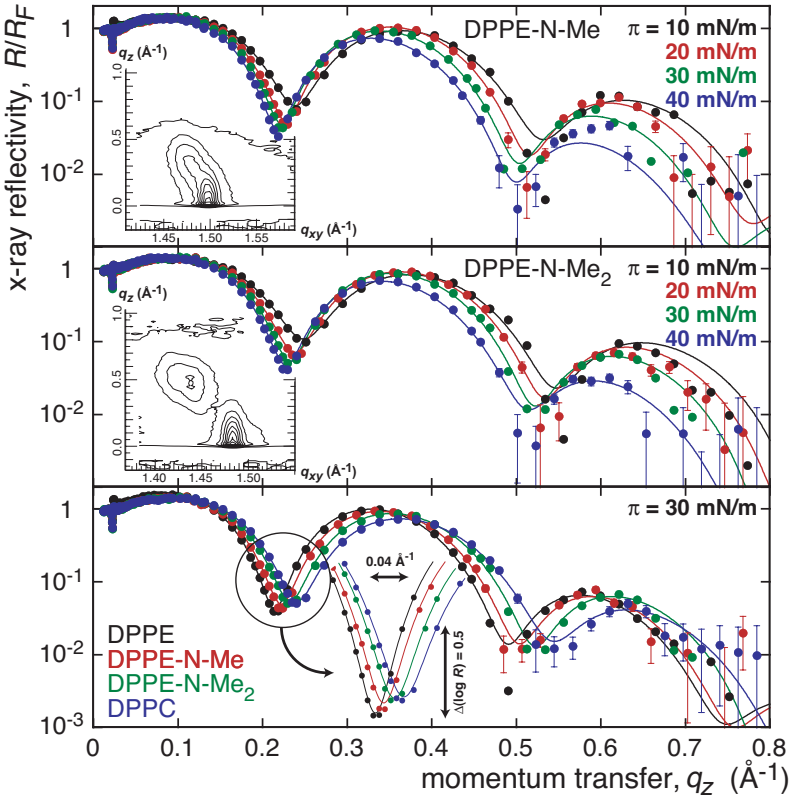

Figure S1: Top panels: Representative XR data of methylated DPPE surface monolayers on water as indicated. The inset shows representative results on grazing-incidence x-ray diffraction at $\pi = 40$ mN/m. Bottom: Homologous series of lipids at the same surface pressure, $\pi = 30$ mN/m. The inset exemplifies the systematic shift of XR curves with increasing headgroup size. Error bars were determined from counting statistics. Continuous lines show best fits derived from VRDF models. Data are the same as those shown in Figure 2.

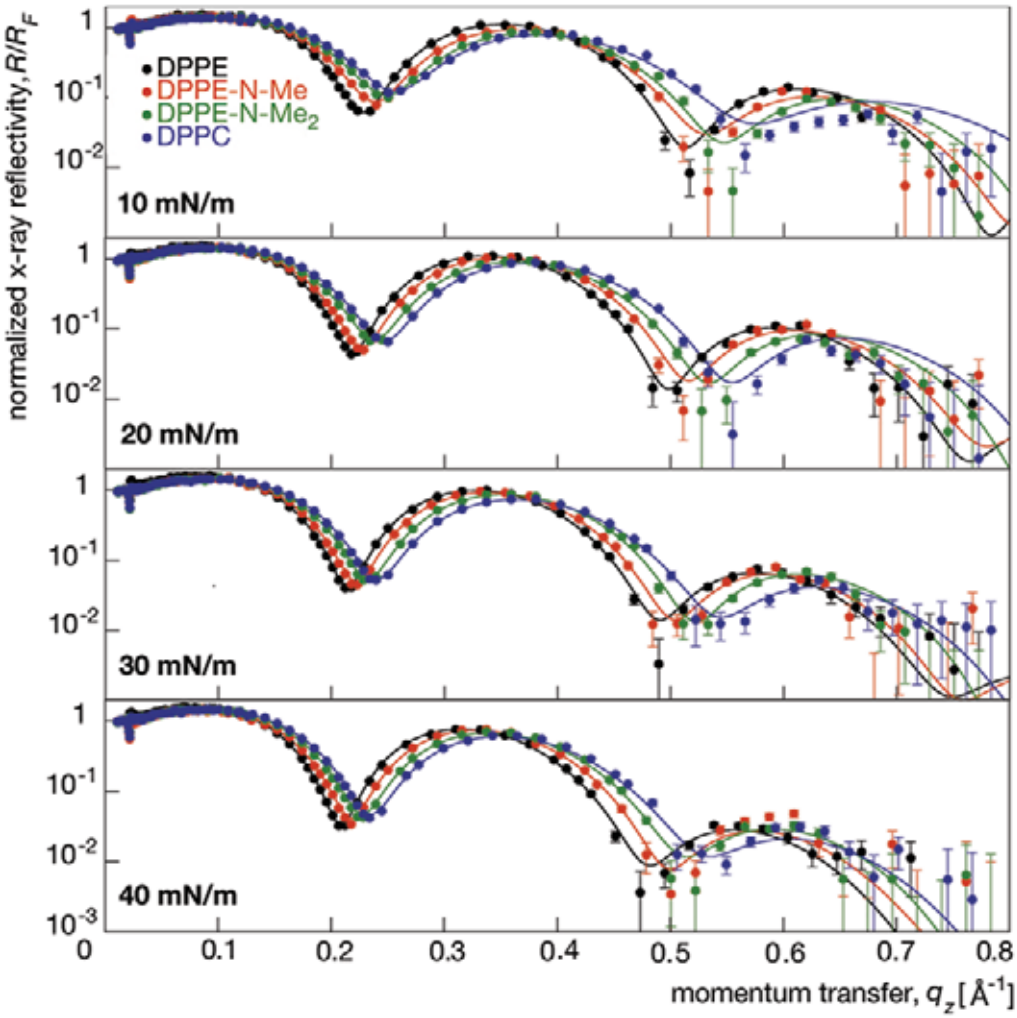

Figure S2: Comparison of the X-ray reflectivities for all four lipids at four different surface pressures.

Electron density profiles

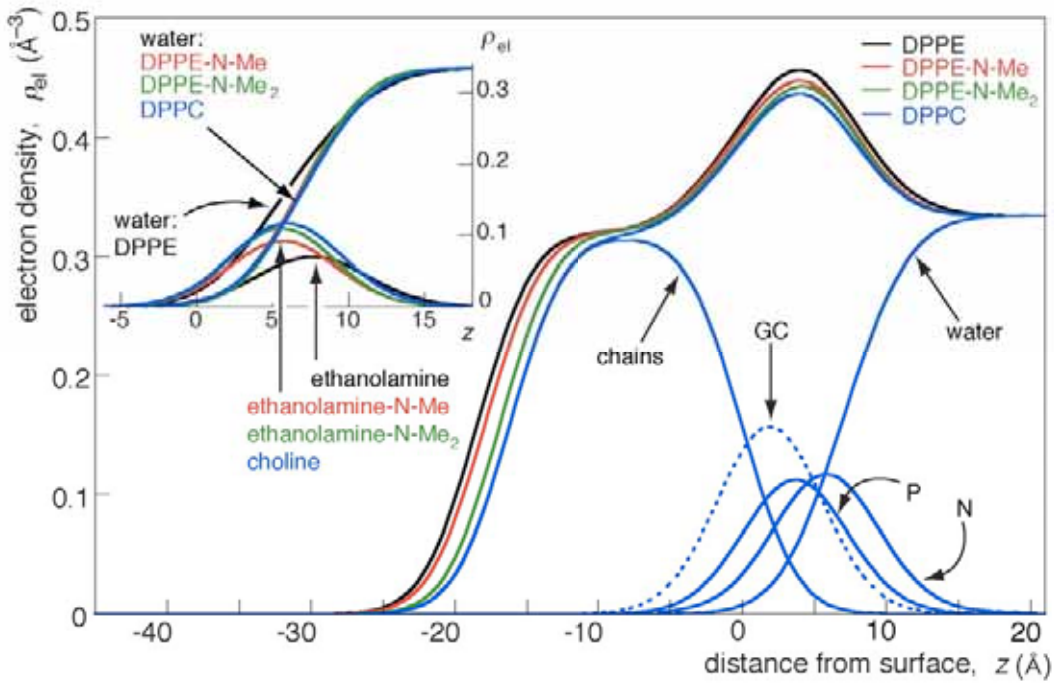

Figure S3: VRDF-derived electron density profile describing the XR of DPPE, DPPE-N-Me, DPPE-N-Me$_2$ and DPPC monolayers at π = 30 mN/m (*c.f.* Fig. S1). The interface between the hydrophobic chains and the GC subfragment defines the origin of the z axis. Inset: Close-up of the thermal distributions of the ethanolamine fragments for all molecular species at this pressure together with the respective water distributions. While the water distributions at the DPPE-N-Me, DPPE-N-Me$_2$ and DPPC headgroups are indistinguishable, it is distinctively different for the DPPE headgroup. Data are the same as those shown in Figure 3.

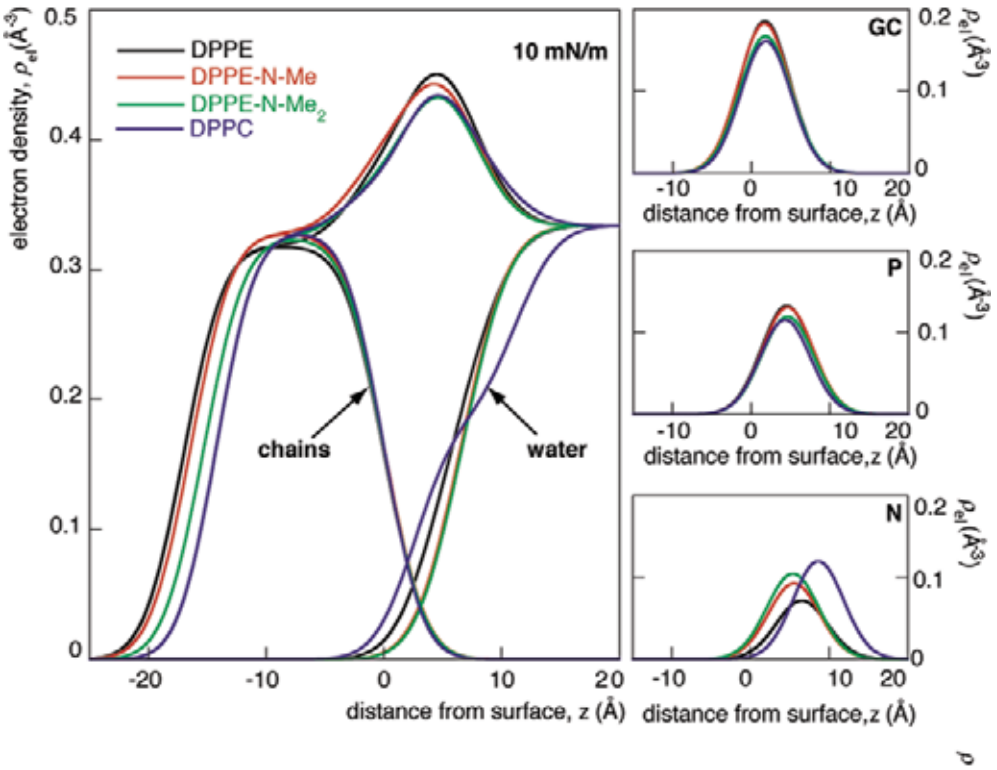

Figure S4a: VRDF-derived electron density profiles describing the XR of all four lipids at π = 10 mN/m.

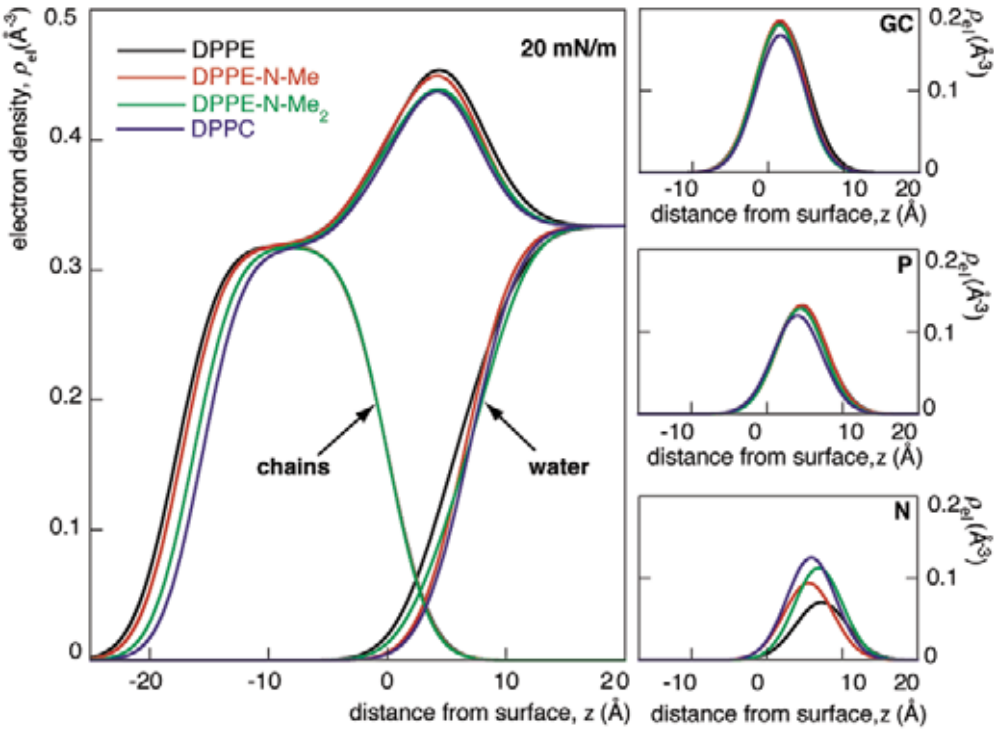

Figure S4b: VRDF-derived electron density profiles describing the XR of all four lipids at π = 20 mN/m.

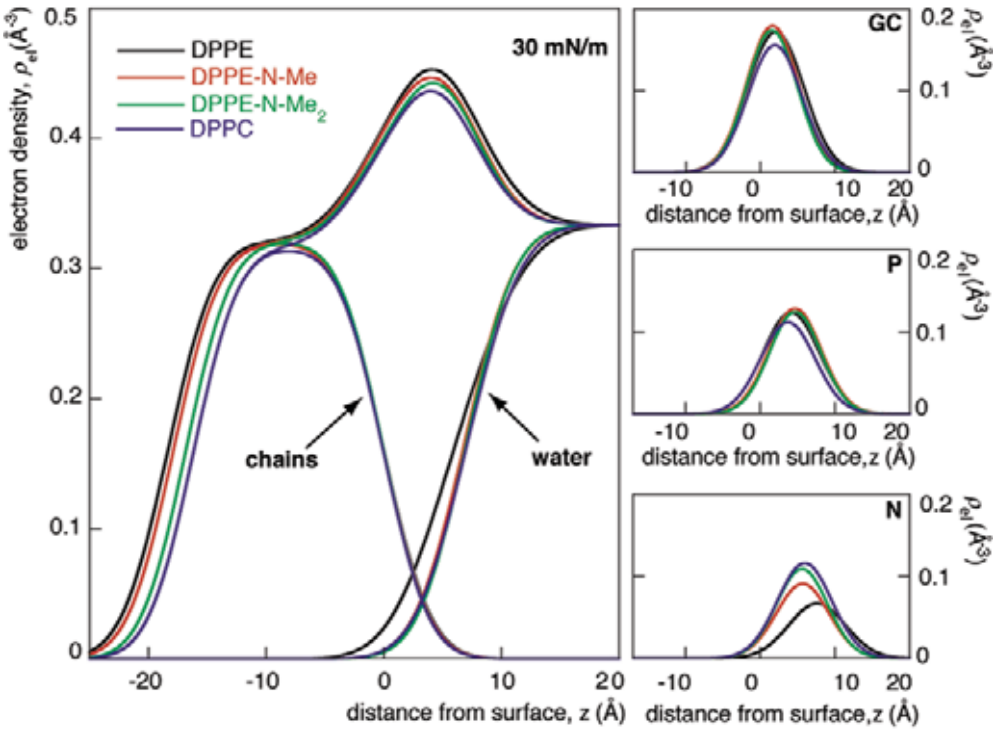

Figure S4c: VRDF-derived electron density profiles describing the XR of all four lipids at π = 30 mN/m.

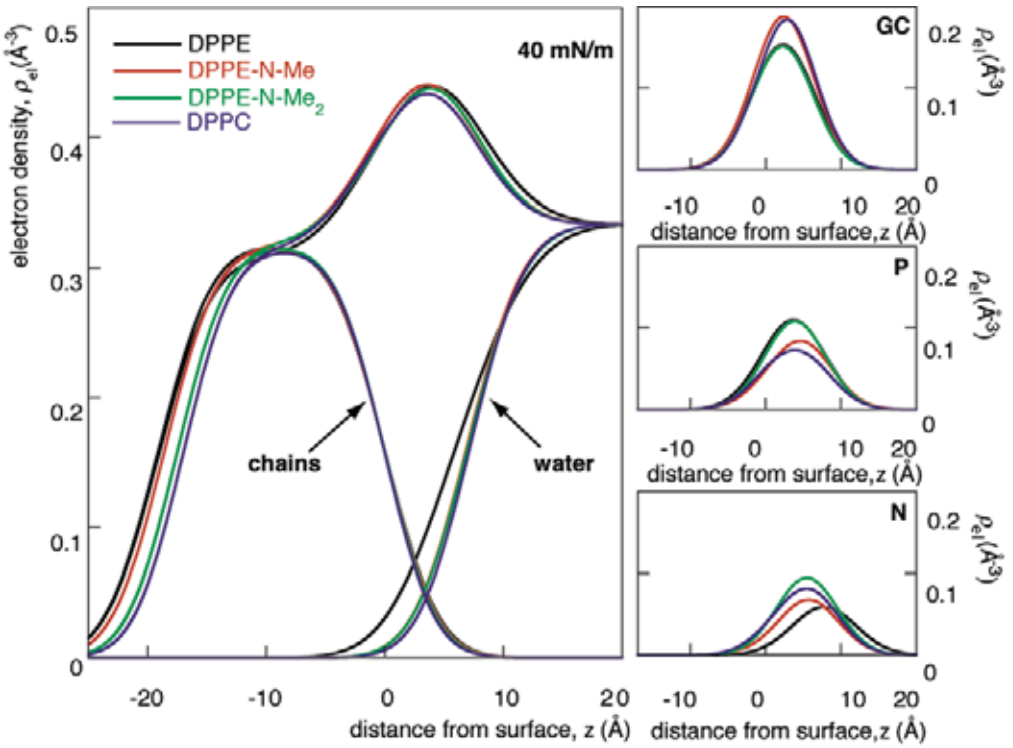

Figure S4d: VRDF-derived electron density profiles describing the XR of all four lipids at π = 40 mN/m.