SUPPORTING INFORMATION

Title: Non-intercalating nano-substrates create asymmetry between bilayer leaflets
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Figure S1. Normalized water densities (ρ/ρ_0) in bilayer configurations involving a (a) 10% hydroxylated substrate and (b) 20% hydroxylated substrate. The average positions of the phosphate groups, $\langle PO_4 \rangle$, and their distances $\langle d \rangle$ from the substrate surface are also indicated.

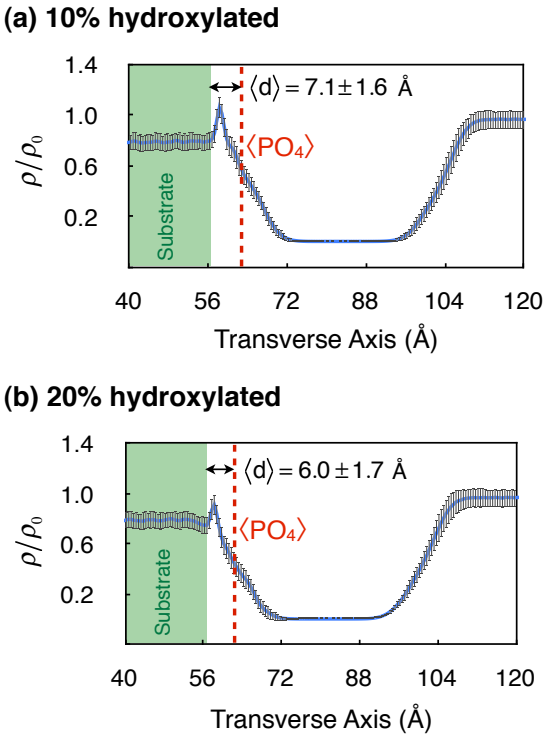

Figure S2. Hydration numbers, n(r), of lipid phosphates, cholines and carbonyls as a function of distance r. The substrates have only a minor effect on the hydration numbers of phosphates, cholines and carbonyl groups.

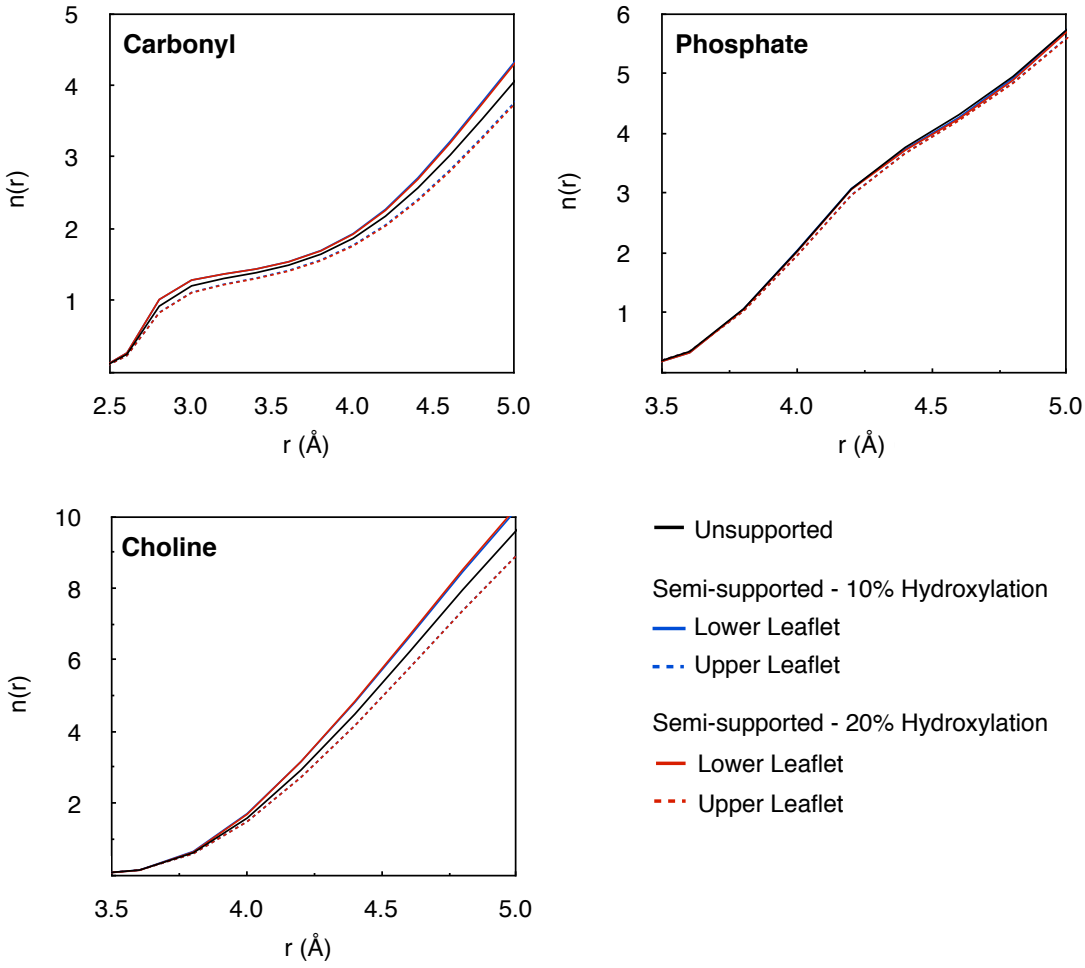

Figure S3. Local environment of substrate hydroxyls. (a) Number, n(r), of water molecules, lipid phosphates and lipid choline groups as a function of distance r from the substrate hydroxyl oxygen. (b) Three dimensional view of a representative local environment of a substrate hydroxyl. The substrate surface is drawn as a mesh, and the hydroxyls groups attached to the substrates are shown explicitly. The atomic coordinates belong to the 20% hydroxylated system. We find that the lipid head groups do not coordinate directly with the hydroxyl groups of the substrates.

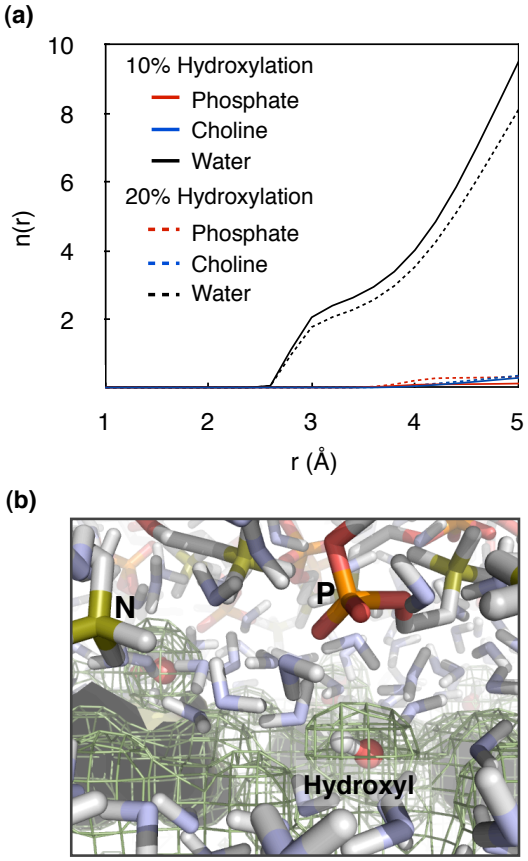

Figure S4. Deuterium order parameters (S_{CD}) of lipid tails. The order parameter tensor, S, is defined as

$$S_{ij} = 1/2\left\langle 3\cos\theta_i \cos\theta_j - \delta_{ij} \right\rangle, \qquad [1]$$

where θ_i is the angle between the i^{th} molecular axis and the bilayer normal, and δ_{ij} is the Kronecker delta. Since these simulations were carried out using united atom force field, the various components of the order parameter tensors were obtained from the relative positions of the neighboring carbons in hydrocarbon chain. The order parameters for the saturated and unsaturated carbons S_{CD} were determined separately using the relationships [Douliez, J. P. *et al*. Biophys. J. 1995, 68, 1727-1739]

$$S_{CD}^{sat} = -2S_{xx}/3 - S_{yy}/3 \text{ and } S_{CD}^{unsat} = -S_{zz}/4 - 3S_{yy}/4 \pm \sqrt{3}S_{yz}/2. \qquad [2]$$

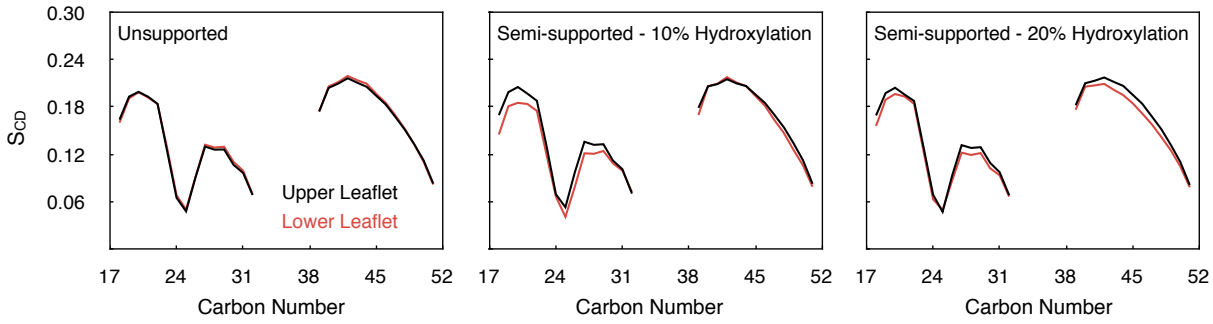

Figure S5. Average charge densities in unsupported POPC bilayer. The charge densities of the water molecules and the POPC lipids are plotted separately as red and blue lines, respectively. The total charge densities, which are the sums of the charge densities of water molecules and lipids, are drawn as solid black lines.

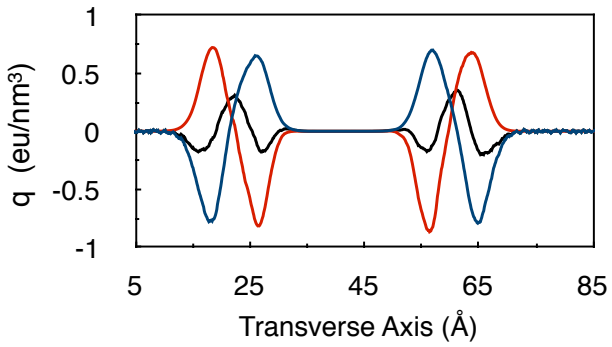

Figure S6. Water orientation with respect to the bilayer normal. θ is the angle between the water dipole and the bilayer normal.

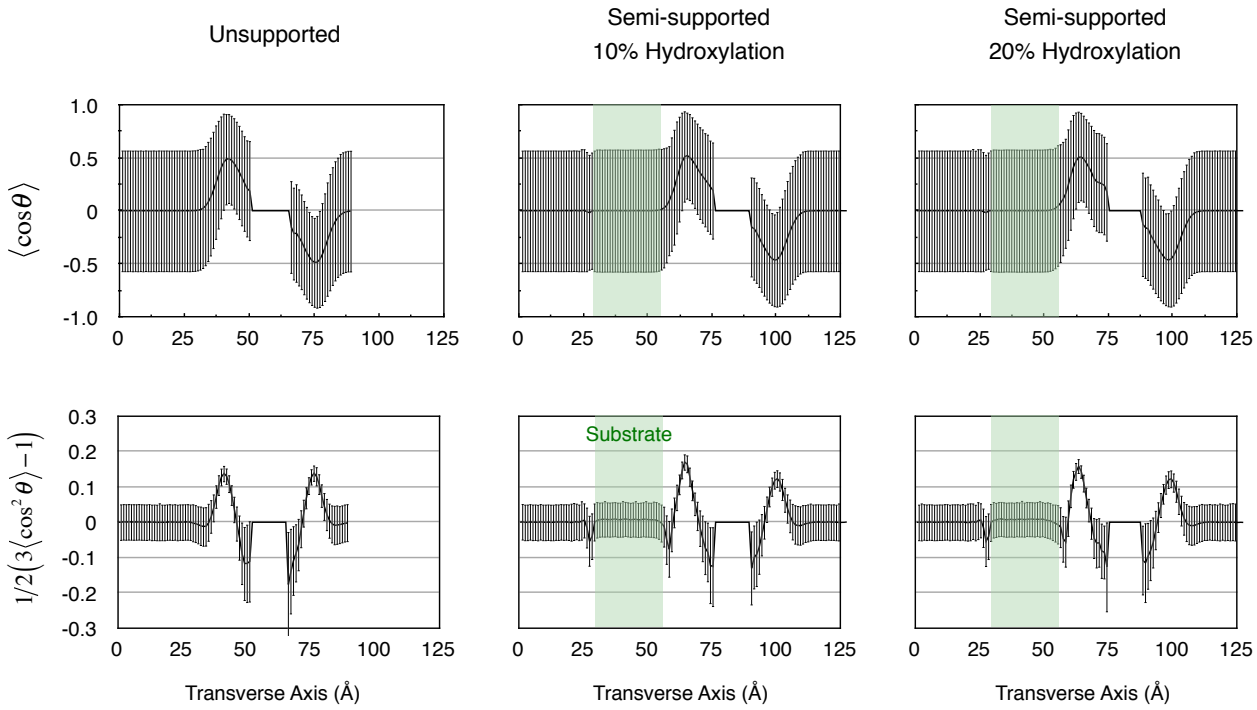

Figure S7. Distribution of terminal hydrocarbons along the transverse axis. The distributions from the three bilayer configurations are aligned with each other such that the midpoints between their respective phosphate density peaks coincide. The interaction with the hydrophilic substrate increases lipid interdigitation.