Supporting Information

Ceramide – Lipid Interactions studied by MD Simulations and Solid-State NMR

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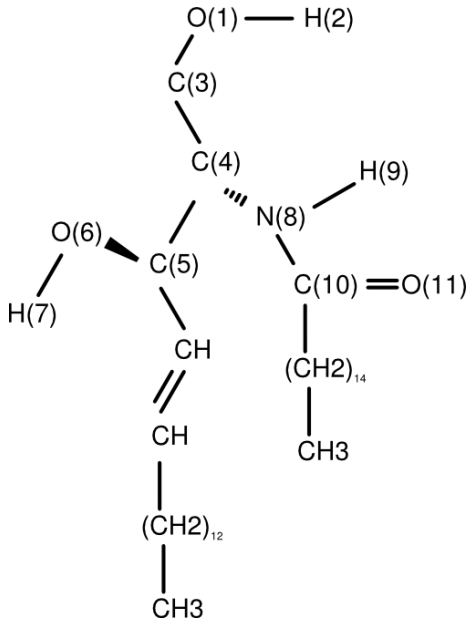

Fig. S1: Chemical structure of C16-Ceramide and force-field parameters used in the MD simulations. The GROMOS87 atom types and partial charges assigned to each of the head group atoms (numbered in the figure from 1 to 11) are: 1 (HO, 0.398e), 2 (OA, -0.548e), 3 (CH2, 0.150e), 4 (CH1, 0.0e), 5 (CH1, 0.150e), 6 (OA, -0.548e), 7 (HO, 0.398e), 8 (N, -0.280e), 9 (H, 0.280e), 10 (C, 0.380e), 11 (O, -0.380e). For the acyl chains, we used the same bonded and non-bonded interaction parameters as those in DMPC.

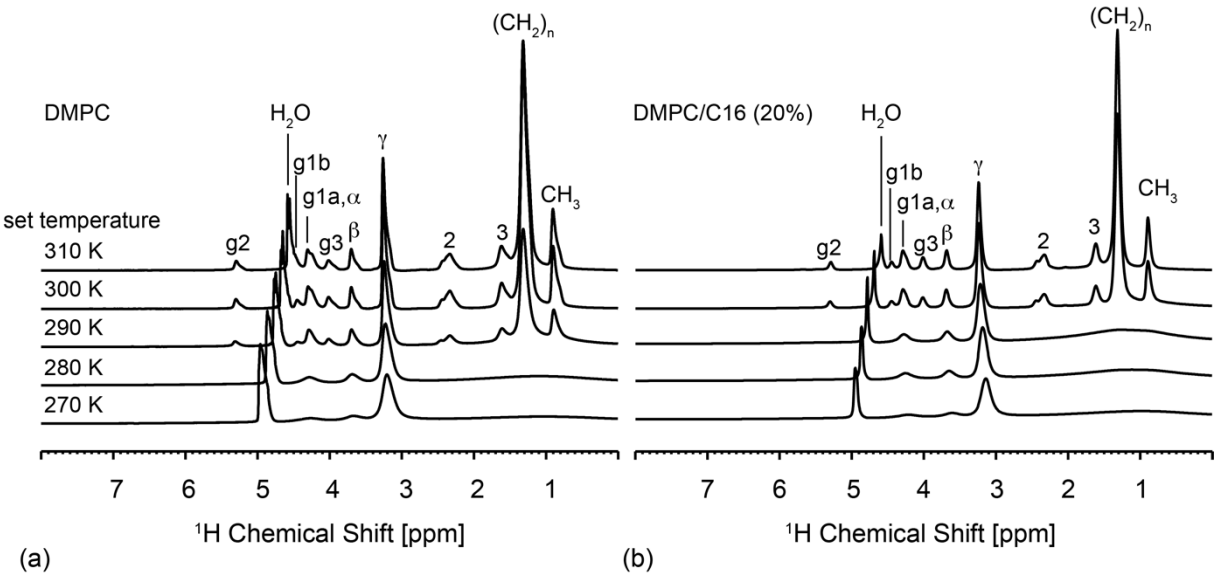

Fig. S2: Temperature-dependent ^{1}H-MAS NMR spectra of DMPC (a) and DMPC/C16 (20%) (b). The lipid main phase transition can be estimated from the CH_2 resonance. It is found around 290 K for DMPC and is slightly elevated to 300 K in the mixture. It should be noted that the reported temperatures correspond to the values set at the instrument. The actual sample temperature is slightly higher due to heating effects caused by RF pulses and friction due to sample rotation. The DMPC main phase transition temperature is known to be 298 K. We can therefore estimate that experimental heating causes a 10 K temperature difference between set and sample temperature.

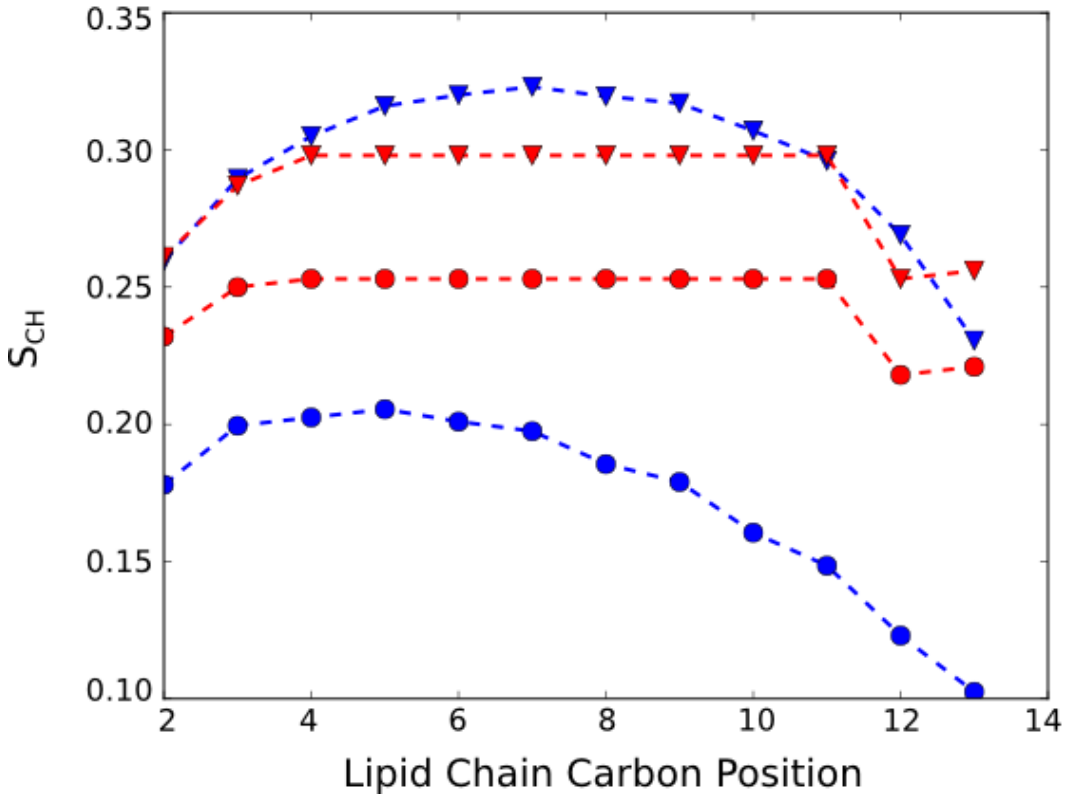

Fig. S3: Simulation (blue) vs experimental (red) order parameters for the DMPC alkyl chains in a pure DMPC bilayer (circles) and a DMPC-C16 mixture (triangles) (same values plotted in Fig. 3a and 5d). Note the simulations were carried at a temperature of 310 K, while the temperature in the NMR experiments was 325 K. The simulated order parameters were determined by calculating an average order parameter for each position of SN1 and SN2 chains.

	DMPC (pure)	DMPC (in mixture)	C16 (in mixture)	
Position	S_{CH}	S_{CH}	Position	S_{CH}
α	0.055	0.061	a	0.292
β	0.035	0.051	b	0.283
γ	not determined	not determined	c	0.280
g_3	0.227	0.222	d	0.225
g_2	0.211	0.204		
g_1	0.101	0.108		
2	0.232	0.261		
3	0.250	0.287		
4-11	0.253	0.298		
12	0.218	0.253		
13	0.221	0.256		
14	not determined	not determined		

Table S1: Numerical values of dipolar C-H order parameters measured with ssNMR, also plotted in Fig. 5. For DMPC, dipolar order parameters were assigned for each carbon atom, as indicated in the first column. For C16, order parameters only for the chain could be detected. Position b is the main CH2 resonance. Other resonances could not be assigned and order parameters are given with decreasing order from a to d.