SUPPORTING INFORMATION

Solid and Fluid Segments within the Same Molecule of Stratum Corneum Ceramide Lipid

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Supplementary Figures

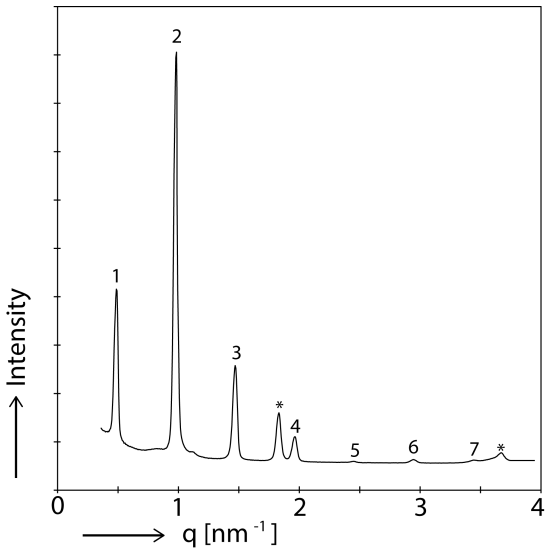

Fig. S1. SAXD pattern of the EOS sample, showing a co-existence of the LPP and crystalline CHOL. The Arabic numerals (1, 2, 3, etc.) in the SAXD profile indicate the different diffraction orders attributed to the LPP with a repeat distance of 12.8 nm. The peaks originating from crystalline CHOL are indicated by an asterisk (*).

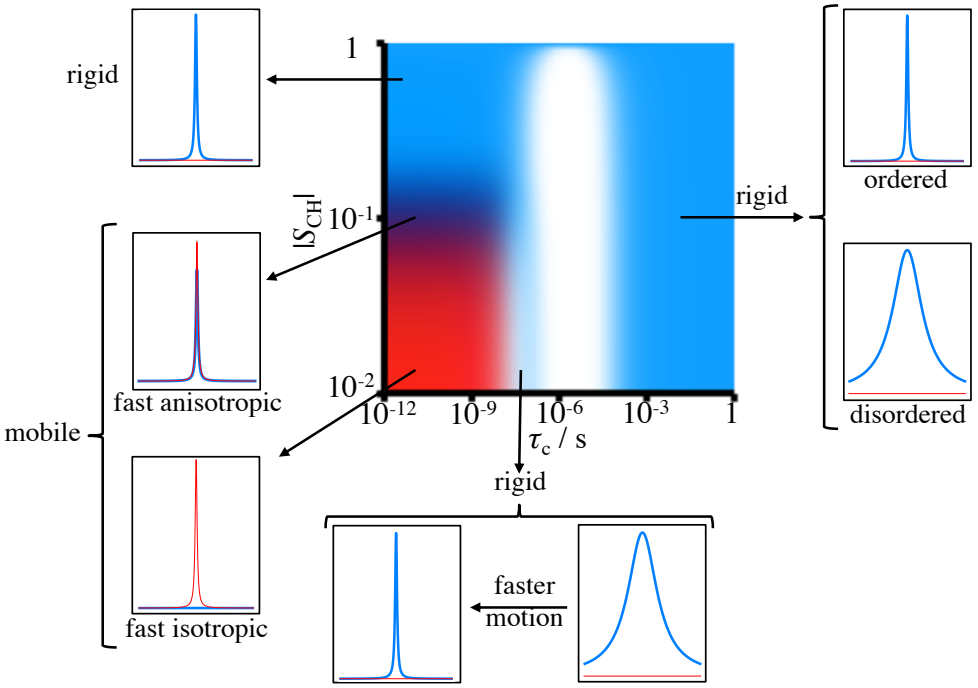

Fig. S2. Theoretical CP (blue) and INEPT (red) signal enhancement in PT ssNMR experiment as a function of τ_c (rotational correlation time) and $|S_{CH}|$ (C-H bond order parameter) for a CH_2 segment at the solid-state NMR experimental conditions that we used in this study, e.g., 11.72 T magnetic field and 5 kHz MAS (adapted from (Nowacka et al., 2013)). White indicates the absence of signal for both CP and INEPT. Corresponding lineshapes and intensities of CP (blue) and INEPT (red) signals in different regimes are also shown.

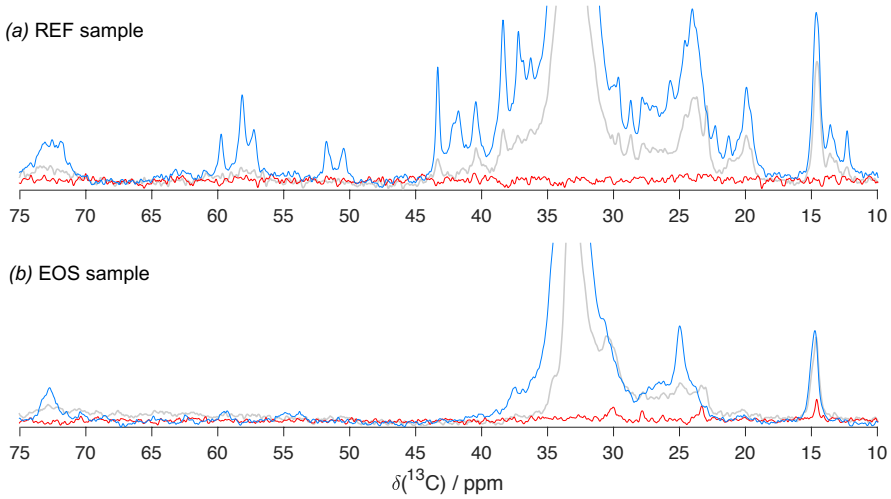

Fig. S3. ^{13}C MAS NMR spectra (DP: grey, CP: blue, INEPT: red) acquired at 125 MHz ^{13}C frequency, 5 kHz MAS, and 68 kHz TPPM ^{1}H decoupling for the REF (a) and the EOS (b) samples equilibrated at 32 °C and 99.5% RH D_2O.

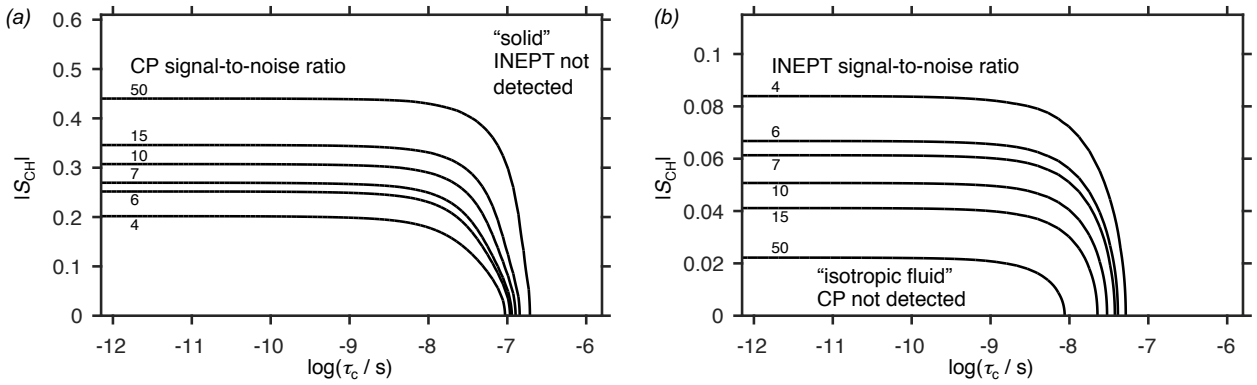

Fig. S4. Quantitative interpretation of the phenomenological terms "solid" and "isotropic fluid" defined from the presence or absence of CP and INEPT signals in the PT ssNMR experiment. (a) Detection limit (lines) of INEPT within the two-dimensional (τ_c - $|S_{CH}|$)-space for CP signal-to-noise ratios as indicated in the figure. A "solid" segment is observed as a CP signal without an accompanying INEPT peak having the same chemical shift and lineshape. (b) As in (a), but for an "isotropic fluid" inferred from an INEPT signal without corresponding CP. The lines are calculated from the theoretical CP and INEPT intensities in Fig. S2 assuming that a peak can be detected if its signal-to-noise ratio is above 2. The INEPT signal-to-noise ratios in (b) correspond to the values for the EOS segments in the INEPT spectrum in Fig. 3b (E1 and ω–2: 4; E3: 6; E2 and E4: 7; ω–1: 10; ω: 15), which through the detection limits in (b) give upper bounds on the values of $|S_{CH}|$ consistent with the data in Fig. 3b (E1 and ω–2: 0.08; E3: 0.07; E2 and E4: 0.06; ω–1: 0.05; ω: 0.04).

References

Nowacka A *et al.* (2013) Signal intensities in 1H-13C CP and INEPT MAS NMR of liquid crystals. *Journal of Magnetic Resonance* **230,** 165–175.