Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Understanding ionic mesophase stabilization by hydration: A solid-state NMR study

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S1. Materials and Methods

Ionic mesogenic materials C_{12}mimCl and C_{12}mimBr (1-dodecyl-3-methylimidazolium chloride and bromide, respectively) were purchased from ABCR GmbH, Karlsruhe. Monohydrated samples were prepared by equilibrating for about 12 h in a desiccator with RH≈85%, stabilized by a saturated KCl solution. Representative NMR spectra of samples in mesophase are shown in Fig. S1a,b.

Table S1. Water contents and phase transition temperatures

Ionic liquid	H_2O mole fraction [a)]	$T_{Cr\rightarrow Sm}$, °C	$T_{Iso\rightarrow Sm}$, °C
C_{12}mimCl	0.004	36	118
C_{12}mimCl·H_2O	0.48	30	154
C_{12}mimBr	0.025	40	102
C_{12}mimBr·H_2O	0.50	36	129

[a)] Water content was estimated from ^{1}H NMR spectra in isotropic phase

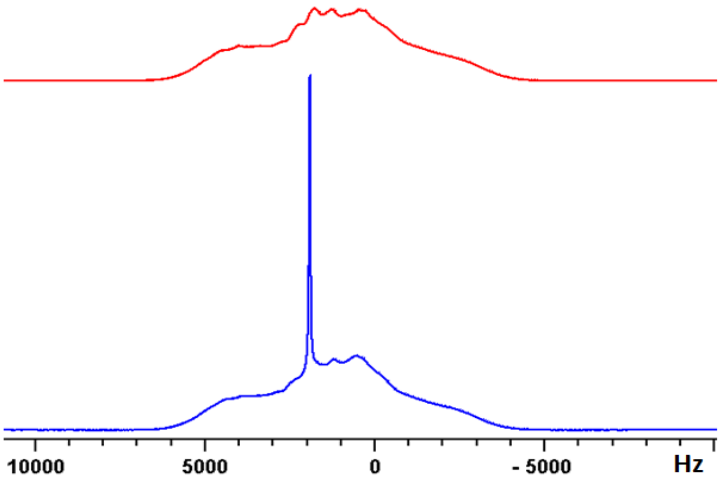

Figure S1a. Proton NMR spectra in smectic A phase of anhydrous (top, 95°C) and monohydrated (bottom, 120°C) C_{12}mimCl salt.

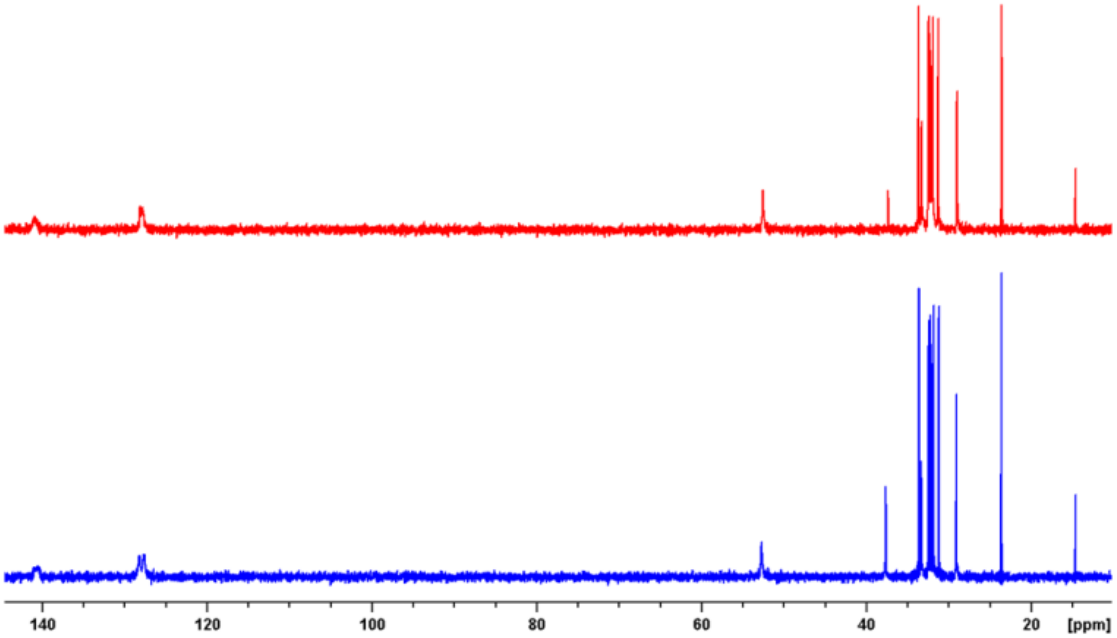

Figure S1b. Carbon-13 cross-polarization (CP) proton-decoupled NMR spectra in the smectic A phase of anhydrous (top, 95°C) and monohydrated (bottom, 120°C) C_{12}mimCl salt.

In uniaxial mesophases, the rigid-lattice CSA tensor is averaged into an axially symmetric tensor with principal components $\delta_{\|}$ and $\delta_{\perp}$, corresponding to LC domains with the director oriented parallel and perpendicular to the magnetic field, respectively, and with isotropic chemical shift $\delta^{\text{iso}} = (\delta_{\|}^{LC} + 2\delta_{\perp}^{LC})/3$. In our samples, which exhibit a negative anisotropy of the diamagnetic susceptibility, the director aligns in the plane perpendicular to the magnetic field of the spectrometer. Hence, the observed chemical shifts are determined by the $\delta_{\perp}^{LC}$ values.[1]

S2. ^{13}C-^{1}H PDLF experiment in static sample

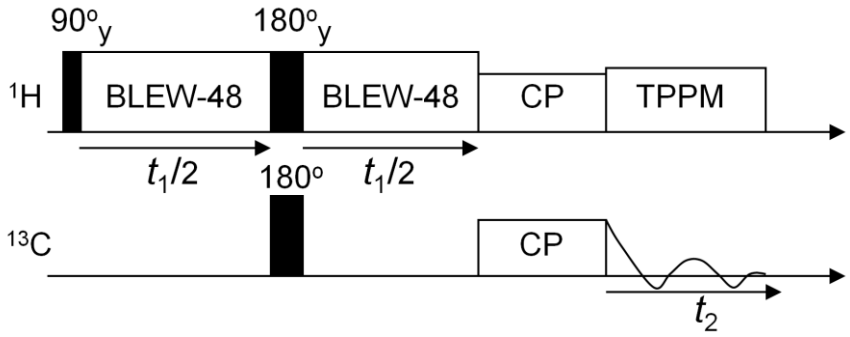

Figure S2a. PDLF pulse sequence to record dipolar ^{13}C-^{1}H spectra in static samples. In the indirect time period t_1 of the PDLF experiment,[2] proton (^{1}H) magnetization evolves in the presence of the local dipolar fields of rare ^{13}C spins. Application of the proton homonuclear decoupling sequence BLEW-48 scales the heteronuclear couplings d_{CH} with a factor of $k\approx0.42$.[3] A pair of 180° pulses is applied at $t_1/2$ to refocus ^{1}H chemical shifts while retaining the ^{1}H–^{13}C couplings. The proton magnetization is transferred to ^{13}C spins via CP and the carbon signal is detected under TPPM ^{1}H heteronuclear decoupling.[4]

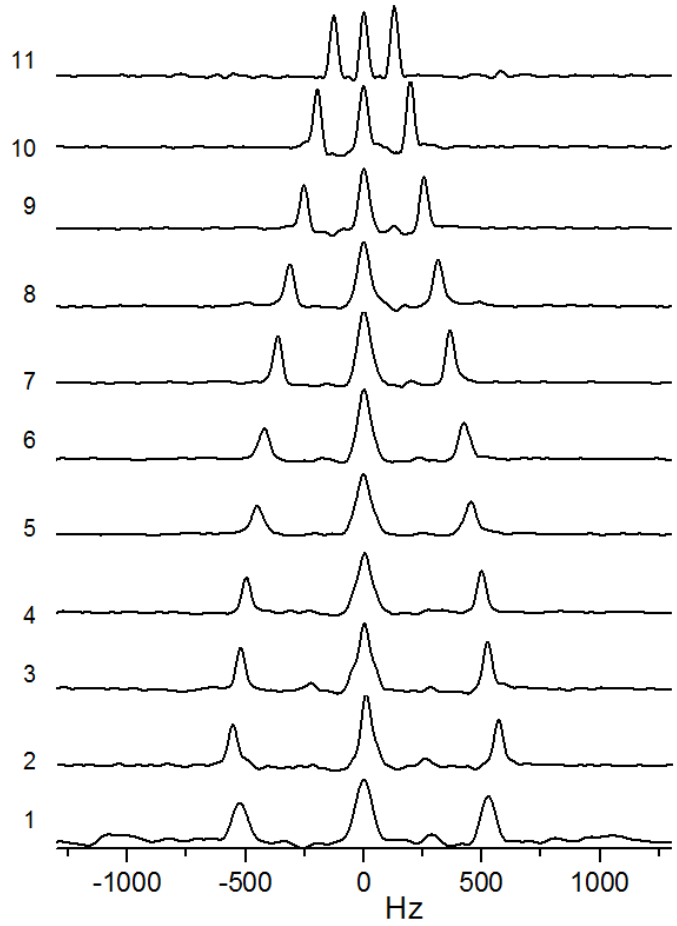

Figure S2b. Cross-sections along dipolar dimension from 2D PDLF spectrum in C_{12}mimBr·H_2O smectic A phase at 107 °C are shown for the alkyl chain carbons.

S3. ^{13}C-^{1}H APM-CP experiment in spinning sample

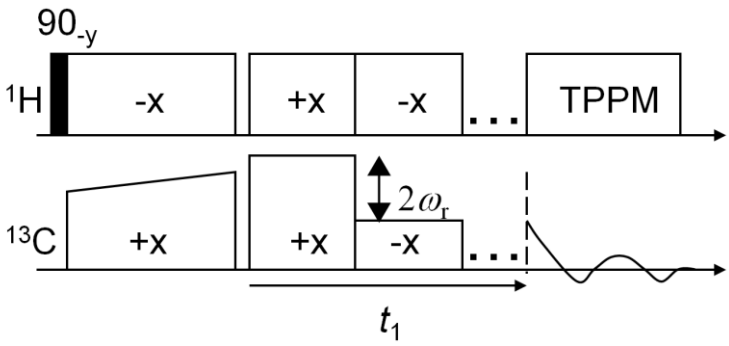

Figure S3a. APM-CP pulse sequence to record dipolar ^{13}C-^{1}H spectra in spinning samples.[5,6] After the CP signal enhancement, the dipolar evolution period is initiated by inverting the phase of the ^{1}H spin-lock field. The rf fields during t_1 period are phase- and amplitude-modulated to achieve the ^{1}H-^{13}C heteronuclear dipolar recoupling. Finally, the ^{13}C signal is detected in the presence of the heteronuclear ^{1}H decoupling.

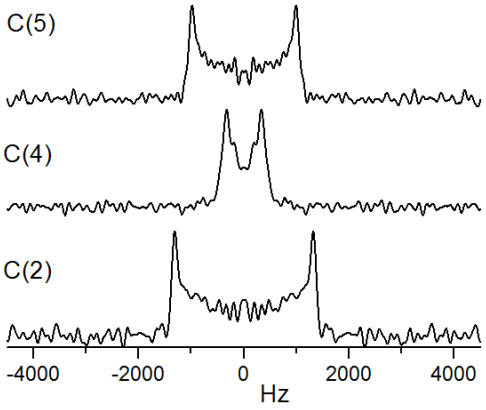

Figure S3b. Cross-sections along dipolar dimension from 2D APM-CP spectrum in C_{12}mimCl smectic A phase at 73 °C are shown for the imidazolium carbons. Spectra were measured at 5 kHz sample spinning speed and with average recoupling radio-frequency field of $\gamma B_1/2\pi$ = 28 kHz.

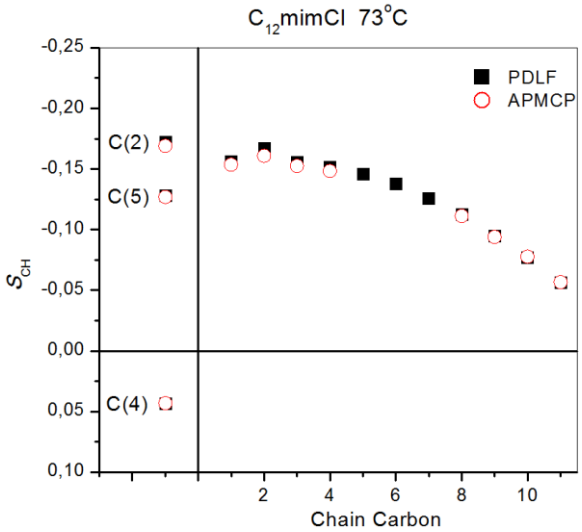

Figure S3c. Comparison of the C-H bond order parameters S_{CH} obtained from PDLF and APM-CP experiments in C_{12}mimCl smectic A phase at 73 °C. Carbon sites 5–7 of the alkyl chain were not resolved in APM-CP spectrum.

S4. ^{13}C-^{13}C dipolar CP-INADEQUATE experiment at natural isotopic abundance.

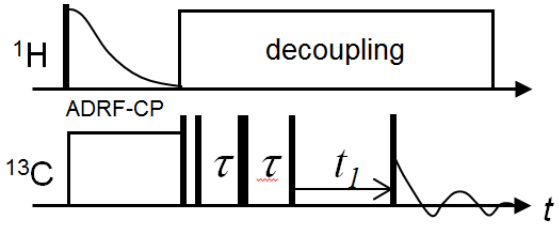

Figure S4a. INADEQUATE pulse sequence[7] was modified by (i) using ADRF CP for ^{13}C signal enhancement[8] and (ii) setting the excitation delay τ to generate double quantum (DQ) coherences according to range of dipolar couplings to be measured.[9]

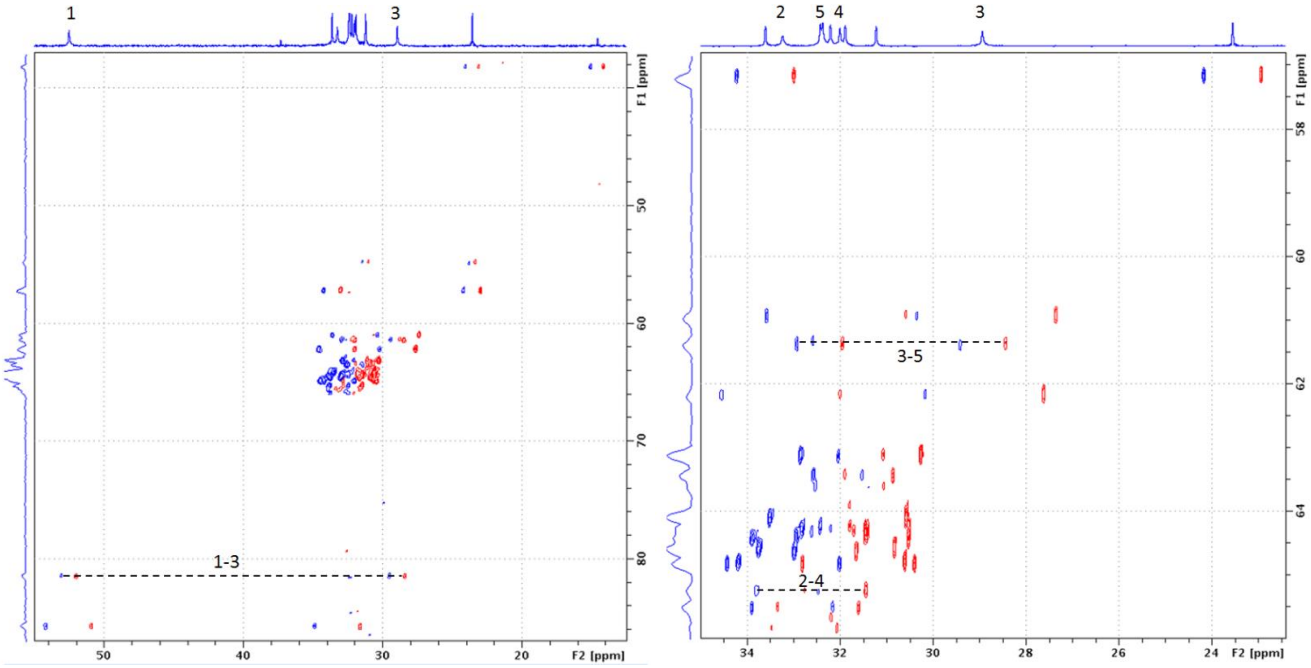

Figure S4b. ^{13}C-^{13}C INADEQUATE spectra in the smectic A phase of C_{12}mimCl at 95 °C. The excitation delay in DQ-filter is set to τ = 0.83 ms. Correlation peaks between chain carbons 1-3, 2-4, and 3-5 separated by two bonds are indicated by dashed lines. The observed splittings Δν, contributed by the C-C dipolar coupling depend on the frequency difference Δδ between involved spins. When Δδ is small compared to the splitting Δν, the dipolar coupling is given by d_{CC}=Δν/3, while for the opposite case d_{CC} = (Δν–J)/2. For intermediate cases, numerical analysis was performed to determine d_{CC}. For carbons separated by two bonds, literature values of the J-coupling are small, within 0-2 Hz range, and were neglected in the analysis.[10]

S5. ^{13}C-^{15}N dipolar spectroscopy at natural isotopic abundance.

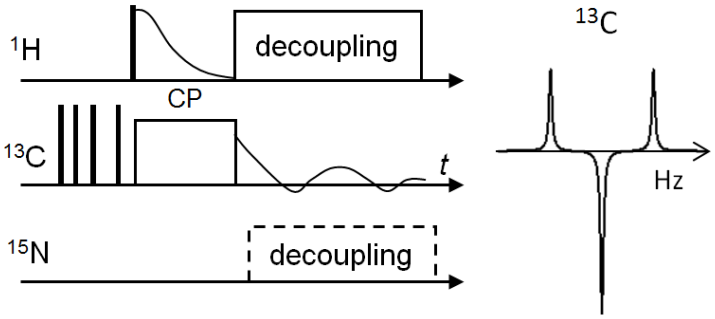

Figure S5a. ^{13}C CP spectra acquired without and with ^{15}N decoupling in alternate scans are subtracted from each other.[11,12] In the resulting difference spectrum, the central peak of uncoupled spins is suppressed while the signal of ^{13}C–^{15}N coupled pairs is preserved. A dipolar interaction with abundant ^{1}H spins is removed by proton decoupling applied to both spectra. In the scans acquired without nitrogen decoupling, the ^{13}C–^{15}N coupled pairs lead to dipolar doublets in the ^{13}C spectrum, whereas they contribute to a residual central peak in the scans with ^{15}N decoupling. The difference spectrum thus represents a superposition of the ^{13}C–^{15}N doublet and the central peak of the opposite sign.

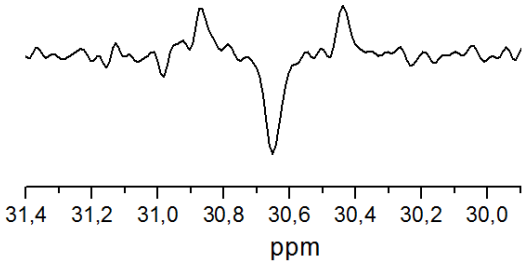

Figure S5b. ^{13}C-^{15}N dipolar spectrum acquired by recording ^{13}C difference spectra with nitrogen-15 decoupling in alternating scans. 8k scans were accumulated with a relaxation delay of 4 s (12 h measurement time).

S6. Natural abundance deuterium (NAD) NMR

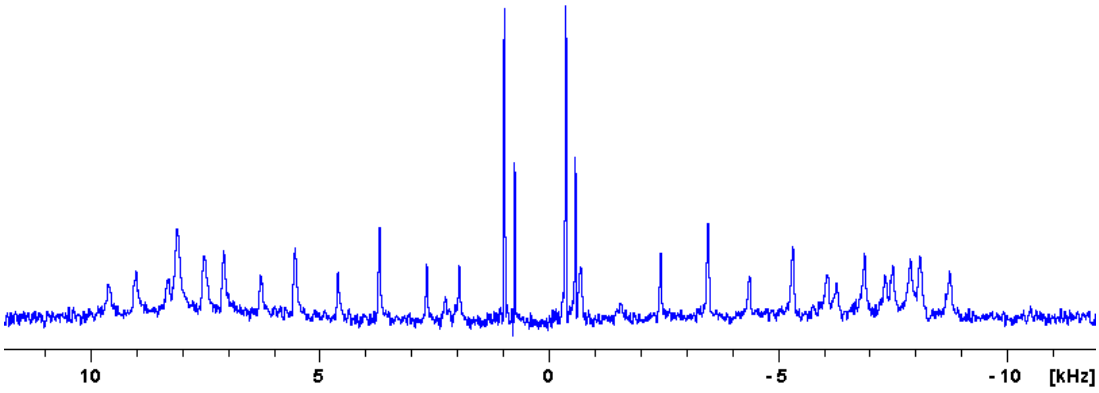

Figure S6. ^{2}H NMR spectrum of C_{12}mimCl in smectic A phase at 110 ^{0}C. Spectrum is measured at the natural isotopic abundance of ^{2}H (0.015%) and in the presence of ^{1}H decoupling. 128k scans were accumulated with relaxation delay 0.5s (18 h experimental time).

S7. Bond order parameters S_{CH} in the imidazolium ring of the C_{12}mim cation with different anions.

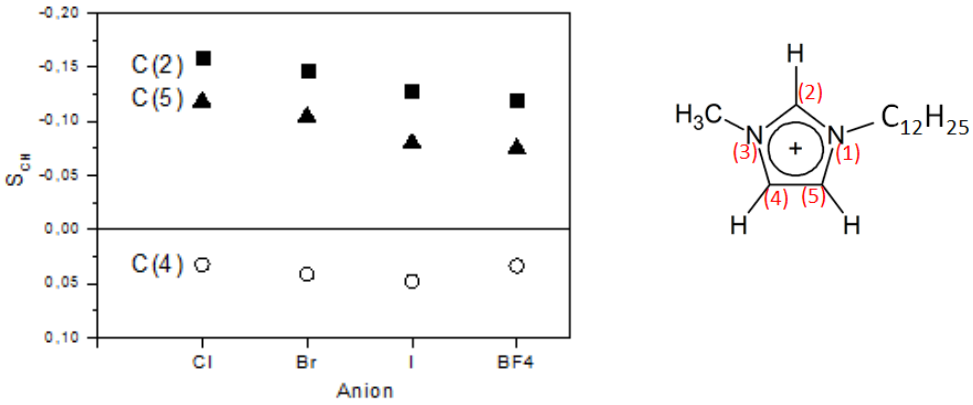

Figure S7. Bond order parameters S_{CH} in the imidazolium ring for the anhydrous C_{12}mimX salts with different anions X = BF_4, I, Cl, and Br. Data are compared at approximately the same difference temperature ΔT with respect to clearing temperature $\Delta T = T - T_C \approx 20^oC$.

S8. ^{1}H isotropic chemical shifts

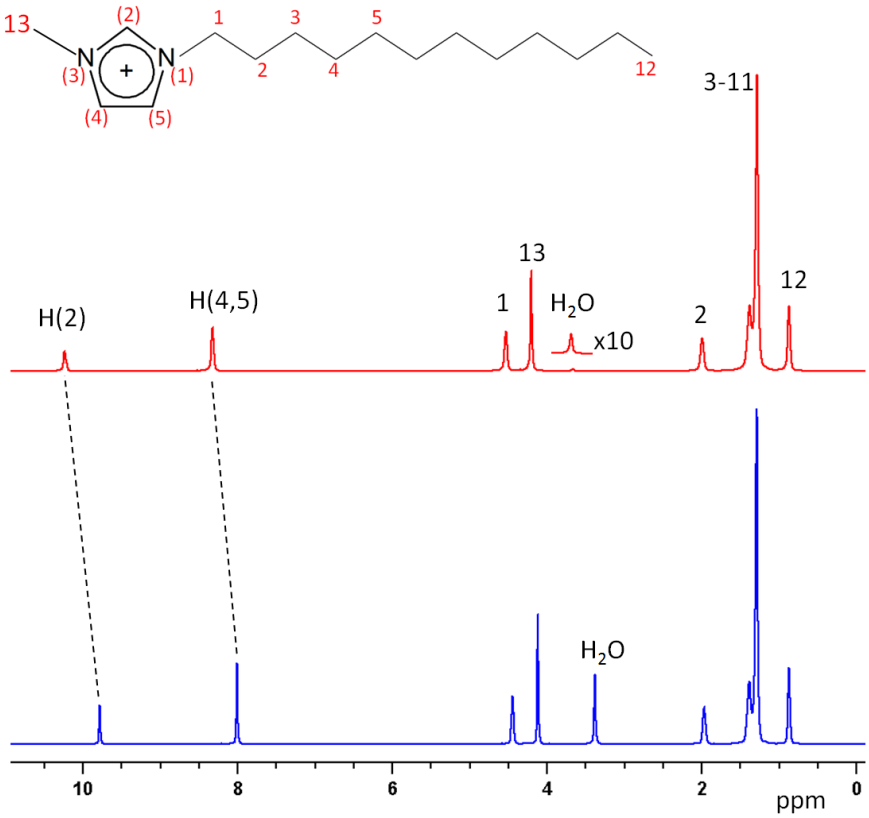

Figure S8. ^{1}H chemical shift spectra of anhydrous (top) and monohydrated C_{12}mimBr (bottom) samples in the isotropic phase.

S9. Water translational diffusion in C_{12}mimBr·H_2O

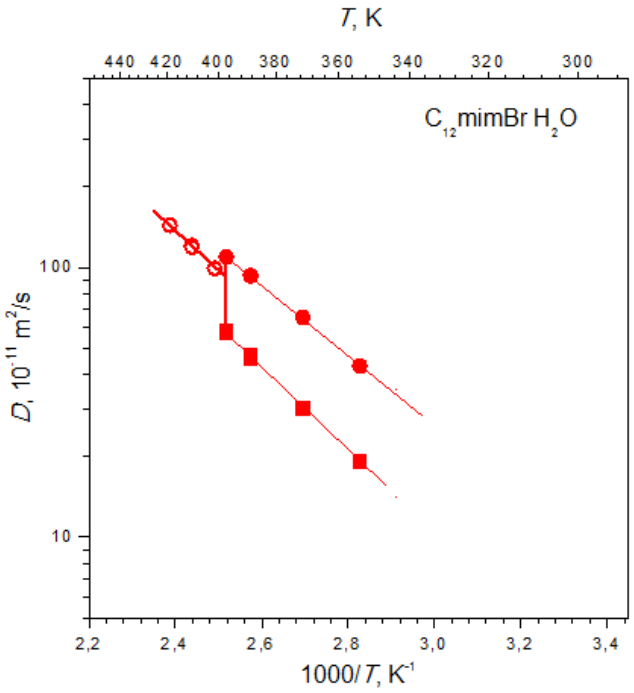

Figure S9. Water diffusion coefficients, D_{iso} (o), $D_{\|}$ (■), and $D_{\perp}$ (●) in the isotropic and smectic A phases of C_{12}mimBr·H_2O ionic liquid. Lines are guides for the eye.

References

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