Electronic Supplementary Information

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

Debashis Majhi, Jing Dai, Andrei V. Komolkin, and Sergey V. Dvinskikh*

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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

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>H$_2$O mole fraction a)</th>
<th>$T_{Cr\rightarrow Sm}$, °C</th>
<th>$T_{Iso\rightarrow Sm}$, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{12}$mimCl</td>
<td>0.004</td>
<td>36</td>
<td>118</td>
</tr>
<tr>
<td>$C_{12}$mimCl·H$_2$O</td>
<td>0.48</td>
<td>30</td>
<td>154</td>
</tr>
<tr>
<td>$C_{12}$mimBr</td>
<td>0.025</td>
<td>40</td>
<td>102</td>
</tr>
<tr>
<td>$C_{12}$mimBr·H$_2$O</td>
<td>0.50</td>
<td>36</td>
<td>129</td>
</tr>
</tbody>
</table>

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 $\delta_{\parallel}$ and $\delta_{\perp}$, corresponding to LC domains with the director oriented parallel and perpendicular to the magnetic field, respectively, and with isotropic chemical shift $\delta^{\text{iso}} = (\delta_{\parallel}^{LC} + 2\delta_{\perp}^{LC})/3$. 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 $k=0.42$. 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.

Figure S2b. Cross-sections along dipolar dimension from 2D PDLF spectrum in $C_{12}$mimBr-H$_2$O smectic A phase at 107 °C are shown for the alkyl chain carbons.
**S3. **$^{13}$C-$^1$H APM-CP experiment in spinning sample

![Diagram of APM-CP pulse sequence]

**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.

![Cross-sections along dipolar dimension from 2D APM-CP spectrum]

**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.

![Comparison of C-H bond order parameters $S_{CH}$]

**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\textsuperscript{7} was modified by (i) using ADRF CP for $^{13}$C signal enhancement\textsuperscript{8} and (ii) setting the excitation delay $\tau$ to generate double quantum (DQ) coherences according to range of dipolar couplings to be measured.\textsuperscript{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 $\tau = 0.83$ 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 $\Delta \nu$, contributed by the C-C dipolar coupling depend on the frequency difference $\Delta \delta$ between involved spins. When $\Delta \delta$ is small compared to the splitting $\Delta \nu$, the dipolar coupling is given by $d_{CC} = \Delta \nu/3$, while for the opposite case $d_{CC} = (\Delta \nu - J)/2$. 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.\textsuperscript{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 °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 $S_{\text{CH}}$ in the imidazolium ring of the C$_{12}$mim cation with different anions.

![Graph showing bond order parameters $S_{\text{CH}}$ for different anions]

**Figure S7.** Bond order parameters $S_{\text{CH}}$ in the imidazolium ring for the anhydrous C$_{12}$mimX salts with different anions $X = \text{BF}_4, \text{I}, \text{Cl}, \text{and Br}$. Data are compared at approximately the same difference temperature $\Delta T$ with respect to clearing temperature $\Delta T=T-T_C \approx 20^\circ\text{C}$.

S8. $^1$H isotropic chemical shifts

![NMR spectrum showing $^1$H 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$\cdot$H$_2$O

Figure S9. Water diffusion coefficients, $D_{iso}$ (○), $D_{\parallel}$ (■), and $D_{\perp}$ (●) in the isotropic and smectic A phases of C$_{12}$mimBr$\cdot$H$_2$O ionic liquid. Lines are guides for the eye.

References