## **Supplementary Materials**

Sample	<i>T</i> <sub>Cr→Sm</sub> °C	T <sub>Iso→Sm</sub> °C	Water Content mol%
C12C12imBF4	53	71	0
C12C12imBr	50	107	7
$\frac{3 \text{ wt\% } C_{12}C_{12}\text{im}Br-d_3}{\text{in } C_{12}C_{12}\text{im}Br}$	50	107	0.6 (D <sub>2</sub> O) 6 (H <sub>2</sub> O)

**Table S1.** Phase transition temperatures in C<sub>12</sub>C<sub>12</sub>imX samples (X = BF<sub>4</sub>, Br).

**Table S2.** Dipolar couplings  $d_{CH}$ , quadrupolar splittings Q, and their ratios in the alkyl chain of the C<sub>12</sub>C<sub>12</sub>imBr cation in smectic A phase at 102 °C.

Carbon	$d_{\rm CH},{ m Hz}$	/ <i>Q</i> /, Hz	$ Q/d_{\rm CH} $
C1	-1284	14750	11,5
C2	-2132	24280	11,4
C3	-1790	20650	11,5
C4	-1730	20100	11,6
C5	-1576	18440	11,7
C6	-1517	17600	11,6
C7	-1376	15870	11,5
C8	-1231	14290	11,6
C9	-1017	11940	11,7
C10	-818	9677	11,8
C11	-586	6900	11,8

**Table S3.** Calculated dipolar coupling,  $d = b \cdot P_2^{(PM)} \cdot S \cdot (-0.5)$ , for imidazolium ring inclined at the angle  $\phi = 35^{\circ}$  to the molecular axis. Order parameter S = 0.55. Dipolar coupling constants in the principal frame of the interaction,  $b_{SI} = -(\mu_0 / 8\pi^2)(\gamma_S \gamma_I \hbar / r_{SI}^3)$ , were calculated with the inter-atomic distances obtained from DFT-optimized cation geometry.

Pair	b, Hz	$P_2^{(\rm PM)}$	<i>d</i> , Hz calculated	<i>d</i> , Hz experimental
C(2)-H(2)	-22000 <sup>a)</sup>	-0,500	-3025	-3000
C(4)-H(4)	-22000 <sup>a)</sup>	-0,292	-1767	-1600
C(2)-C(4)	-713	-0,453	-88,8	-85
C(4)-C(5)	-3020	-0,007	-5,8	~0
N(1)-H(2)	1225	-0,373	125,7	123
N(1)-H(5)	1208	-0,490	162,8	148

<sup>a)</sup> Accepted values for the dipolar couplings with account for vibration effects.



**Figure S1.** <sup>13</sup>C spectra of the sample C<sub>12</sub>C<sub>12</sub>imBr spinning at different angles. The sample was in the smectic A phase at 60 °C. Spectra were recorded at spinning speed of 10 kHz and without proton decoupling. Spinning angles were 52.1° (**a**), 54.7° (magic angle) (**b**), and 58.0° (**c**). Only signals of imidazolium ring are shown. Doublets due to <sup>13</sup>C-<sup>1</sup>H J-coupling are observed in the spectrum (**b**). In off-MAS spectra (**a**) and (**c**), powder line-shapes are observed due to contributions of the <sup>13</sup>C residual chemical shift anisotropy and <sup>13</sup>C-<sup>1</sup>H dipolar interactions.