

## Supplementary materials

# NMR Spectroscopic Study of Orientational Order in Imidazolium-Based Ionic Liquid Crystals

Jing Dai, Debashis Majhi, Boris B. Kharkov, Sergey V. Dvinskikh

### 1. Ionic liquid crystals samples $C_{12}mimX$ data

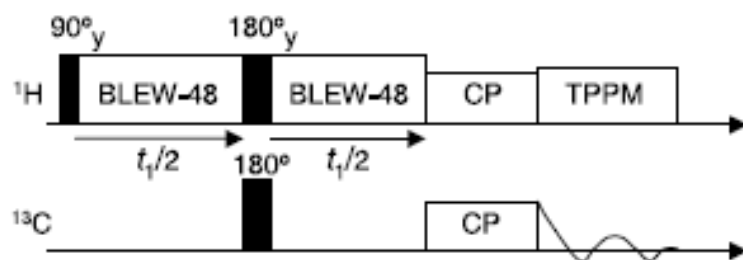
**Table S1.** Structural and thermodynamic data.

$C_{12}mimX$ CAS	X anion	X ionic volume [1], $nm^3$	H <sub>2</sub> O content		$T_{Cr} \rightarrow T_{Sm}$ $^{\circ}C$	$T_{Iso} \rightarrow T_{Sm}$ $^{\circ}C$
			wt%	Mol%		
114569-84-5	Cl	0.047	0.025	0.4	36	118
61546-00-7	Br	0.056	0.16	3	40	102
81995-09-7	I	0.072	0.14	3	37	67
244193-59-7	BF <sub>4</sub>	0.079	0.027	0.5	30	48

### 2. Experimental details and pulse sequence for PDLF experiment

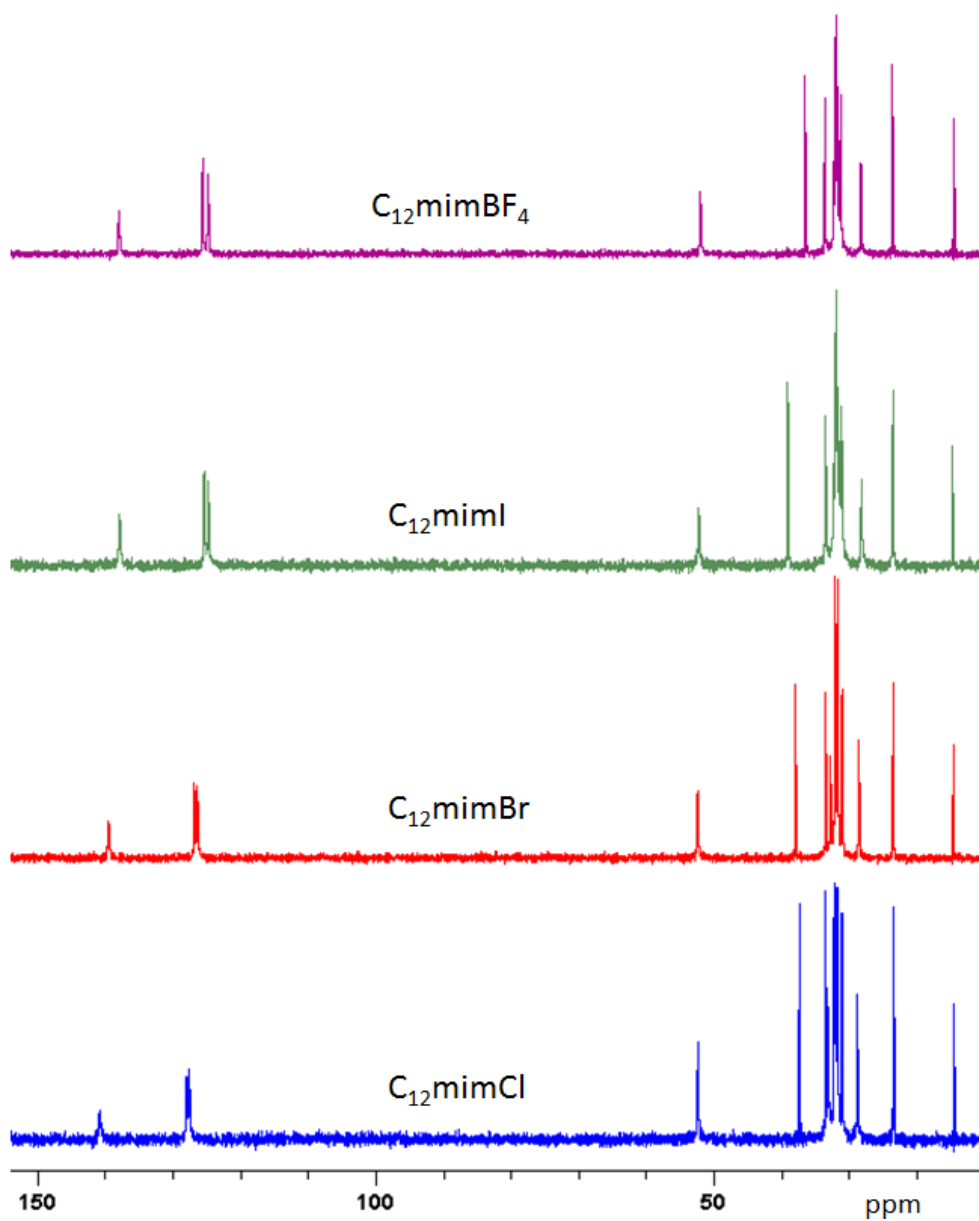
Experiments were performed using Bruker 500 Avance III spectrometer at Larmor frequencies of 500.1 and 125.7 for  $^1H$  and  $^{13}C$ , respectively. The  $^1H$  and  $^{13}C$  90° pulse lengths were 8 and 9  $\mu s$ , respectively. For heteronuclear proton decoupling in the mesophase, Spinal64 sequence [2] with the  $^1H$  nutation frequency of 23 kHz was used during acquisition time of 120 ms. To enhance the intensity of the  $^{13}C$  signal, proton-to-carbon cross polarization (CP) with adiabatic demagnetization in the rotating frame (ADRF) [3] was applied with maximum nutation frequency of 16 kHz and contact time in the range 10-20 ms.

Dipolar  $^1H$ - $^{13}C$  spectra were recorded using proton detected/encoded local field (PDLF) NMR spectroscopy [4]. In the indirect time period  $t_1$  of the PDLF experiment,  $^1H$  magnetization evolves in the presence of the local dipolar fields of rare  $^{13}C$  (Figure S2). Application of the proton homonuclear decoupling sequence BLEW-48 scales the heteronuclear couplings  $d_{CH}$  with a factor of  $k \approx 0.42$  [5]. A pair of 180° pulses is applied at  $t_1/2$  to refocus  $^1H$  chemical shifts while retaining the  $^1H$ - $^{13}C$  couplings. The proton magnetization is transferred to  $^{13}C$  spins via CP and the carbon signal is detected under  $^1H$  heteronuclear decoupling. The evolution time in indirect time domain was incremented with 384  $\mu s$  in 256 steps, at each with two collected transients. Proton homonuclear decoupling during the evolution time was achieved by the BLEW-48 sequence with nutation frequency of 31.2 kHz. The temperature was regulated with an accuracy of 0.1  $^{\circ}C$ . The temperature shift and temperature gradient within the sample, caused by the decoupling irradiation, were calibrated by observing the change in the  $^{13}C$  spectral line widths and positions. Decoupling power, irradiation time, and repetition delay were adjusted to limit heating effects to  $<0.5$   $^{\circ}C$ .



**Figure S1.** PDLF pulse sequence to record dipolar  $^{13}\text{C}$ - $^1\text{H}$  spectra.

### 3. One-dimensional $^{13}\text{C}$ NMR spectra



**Figure S2.** 1D  $^{13}\text{C}$  CP NMR spectra in smectic phase of  $\text{C}_{12}\text{mimCl}$  at  $107^\circ\text{C}$ ,  $\text{C}_{12}\text{mimBr}$  at  $91^\circ\text{C}$ ,  $\text{C}_{12}\text{mimI}$  at  $55^\circ\text{C}$ , and  $\text{C}_{12}\text{mimBF}_4$  at  $38^\circ\text{C}$ .

## References

1. Marcus, Y. Ionic and molar volumes of room temperature ionic liquids. *J. Mol. Liq.* **2015**, *209*, 289-293.
2. Fung, B.M.; Khitritin, A.K.; Ermolaev, K. An improved broadband decoupling sequence for liquid crystals and solids. *J. Magn. Reson.* **2000**, *142*, 97-101.
3. Lee, J.S.; Khitritin, A.K. Thermodynamics of adiabatic cross polarization. *J. Chem. Phys.* **2008**, *128*, 114504.
4. Dvinskikh, S.V.; Zimmermann, H.; Maliniak, A.; Sandström, D. Separated local field spectroscopy of columnar and nematic liquid crystals. *J. Magn. Reson.* **2003**, *163*, 46-55.
5. Burum, D.P.; Linder, M.; Ernst, R.R. Low-power multipulse line narrowing in solid-state NMR. *J. Magn. Reson.* **1981**, *44*, 173-188.