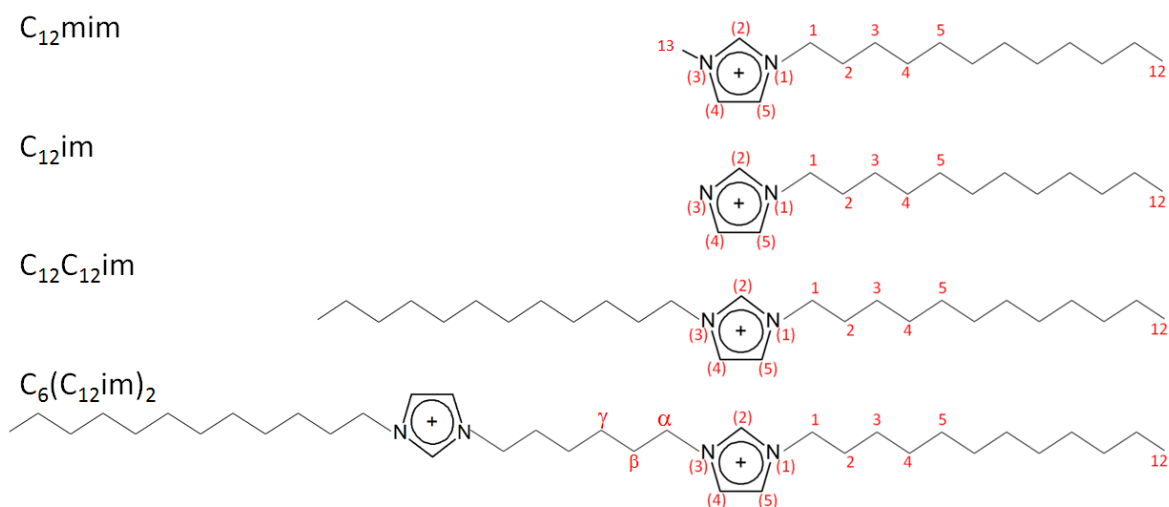


Electronic Supplementary Information

Insights into cation-anion hydrogen bonding in mesogenic ionic liquids: an NMR study

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S1. Materials



Scheme S1. Cation structures and atom labelling.

Table S1. Phase transition temperatures and water contents in the samples used for NMR measurements.

	H ₂ O content, ^{a)} mol%	$T_{Cr} \rightarrow T_{Sm}$, °C	$T_{Iso} \rightarrow T_{Sm}$, °C
C ₁₂ mimCl	0.4	36	118
C ₁₂ mimBr	3	40	102
C ₁₂ mimI	3	37	67
C ₁₂ mimBF ₄	2	30	48
C ₁₂ imCl	0	21	75
C ₁₂ imBF ₄ ^{b)}	0	n/a	86
C ₁₂ imC ₁₂ Br	5	50	107
C ₁₂ imC ₁₂ BF ₄	1	53	71
C ₆ (C ₁₂ im) ₂ Br ₂	5	63	132
C ₆ (C ₁₂ im) ₂ (BF ₄) ₂	0	n/a	71

^{a)} estimated from ¹H NMR spectra

^{b)} monotropic smectic phase

S2. Synthesis

S2a. Synthesis of $C_{12}imC_{12}BF_4$ and $C_{12}imC_{12}Br$ was carried out following the reported procedures.¹⁻³ To synthesize $C_{12}imC_{12}Br$, 1.2 mmol of 1-bromododecane (Fluorochem Ltd, UK) was added dropwise to 1 mmol of 1-dodecylimidazole (Fluorochem Ltd, UK) acetonitrile solution under stirring conditions in an N_2 atmosphere. The mixture was refluxed for 72 h at 70°C under the same conditions. The solution was subsequently condensed by evaporation, and the oily product was washed with diethyl ether. The white precipitate was purified by recrystallization in an ethanol/diethyl ether mixture. The final product was dried under a vacuum. To synthesize $C_{12}imC_{12}BF_4$, ion exchange was performed by adding sodium tetrafluoroborate (1.2 mmol) to the acetonitrile solution of $C_{12}imC_{12}Br$ (1 mmol). The mixture was stirred at room temperature for 24 h. After filtering to remove NaBr salt, the product was condensed by evaporation and washed with diethyl ether to obtain a white solid. The product was recrystallized from an ethanol/diethyl ether mixture and dried under a vacuum.

S2b. Synthesis of $C_6(C_{12}im)_2(Br)_2$ and $C_6(C_{12}im)_2(BF_4)_2$ was carried out following the literature procedures.³⁻⁶ One mmol of 1,6 di-bromohexane was added dropwise to a 1-dodecylimidazole 2.2 mmol acetonitrile solution. The reaction mixture was stirred under a nitrogen atmosphere in a reflux condenser for 3 days. The solution was subsequently condensed by evaporation and the product was washed with diethyl ether. The obtained white precipitate was purified by recrystallization in an ethanol/diethyl ether mixture. The purified material was vacuum-dried. To synthesize $C_6(C_{12}im)_2(BF_4)_2$, ion exchange was performed by adding sodium tetrafluoroborate (1.2 mmol) to the acetonitrile solution of $C_6(C_{12}im)_2Br_2$ (1 mmol). The mixture was stirred at room temperature for 24 h. After filtering to remove NaBr salt, the product was condensed by evaporation and washed with diethyl ether to obtain a white solid. The product was recrystallized from an ethanol/diethyl ether mixture and dried under a vacuum.

S2c. Synthesis of $C_{12}imBF_4$ and $C_{12}imCl$ was carried out following the literature procedures.⁶ Slight excess amount of concentrated acid (HBF_4 or HCl) was dropwise added in 1-dodecylimidazole solution in diethyl ether at 0°C. The salt precipitated as a white solid after cooling at -20°C overnight. After filtering, the product was dried in a desiccator for 48 h.

S2a. Template synthesis of ILC-MCM41 composite was carried out following the reported procedures.^{7,8} Ionic liquid $C_{12}mimX$ ($X=Br$ or BF_4) (2.46 mmol) was dissolved in sodium hydroxide solution (15 ml, 0.24 mol/L). Water was added for a total volume of 150 ml. The solution was heated under stirring. When the temperature reached 80°C, tetraethyl orthosilicate (TEOS, 11.3 mmol) was added dropwise. After stirring for 2 h at 80°C, the solution was aged at 80°C for 24 h. The product was filtered with water and ethanol and dried.

S2b. Impregnation of ILC in MCM41. Ordered porous silica MCM41 impregnated with ionic liquid $C_{12}mimCl$ was prepared according to reported procedures.⁹ MCM41 was heated at a temperature of 150°C for 2 h, followed by vacuum drying (12 h). The ILC/ethanol solution was added dropwise to the MCM-41 powder under stirring. The solution was stirred for 5 h at room temperature. Ethanol was evaporated by heating the sample at 80°C followed by exposing the sample to a vacuum for 24 h.

S2c. Synthesis of KIT6 materials. Porous silica KIT6 was synthesised following the reported procedure.¹⁰ 4.0 g of poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (Pluronic P123) was dissolved in 144 ml of distilled water and 7.9 g of 37 wt % HCl (4.3 ml) solution under stirring at 35°C. After complete dissolution, 4.0 g (4.93ml) of n-butanol was added. After 1 h stirring, 8.6 g of tetraethyl orthosilicate (TEOS) was added to obtain a homogeneous clear solution. This mixture was left under vigorous stirring at 35°C for 24 h. The synthesis was carried out in a closed polypropylene bottle. Subsequently, the mixture was aged at 100°C for 24 h. The white precipitated product was filtered and dried at 100°C for 24 h. Mesoporous material was obtained after calcination at 550°C.

S2d. Impregnation of ILC in KIT6. The $C_{12}mimBF_4$ /KIT6 material was prepared by following the reported procedures.^{11,12} KIT6 was dried in an oven at 150 °C. IL (1 mmol) was dissolved in 2ml ethanol. The solution was added to the KIT6 material (144 mg) dropwise and stirred for 1 h at 25°C. Ethanol was evaporated at 80°C followed by exposing the sample to a vacuum at 100°C for 24 h.

S3. Hydration effect on proton chemical shift

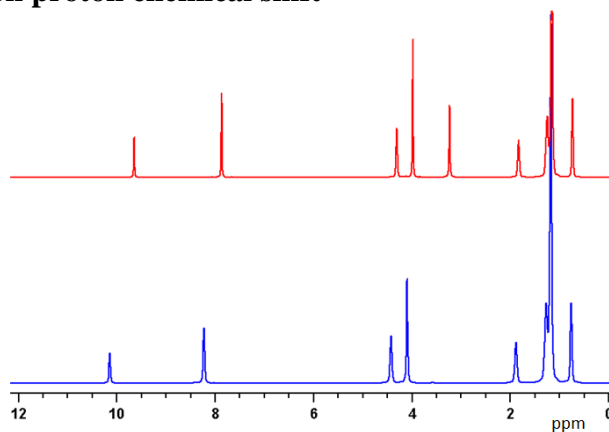


Fig. S1. Proton NMR spectra in the isotropic phase of ionic liquid crystal $C_{12}mimBr$ in dry (bottom) and 100 mol% hydrated materials (top).

S4. Effect of protic substitution

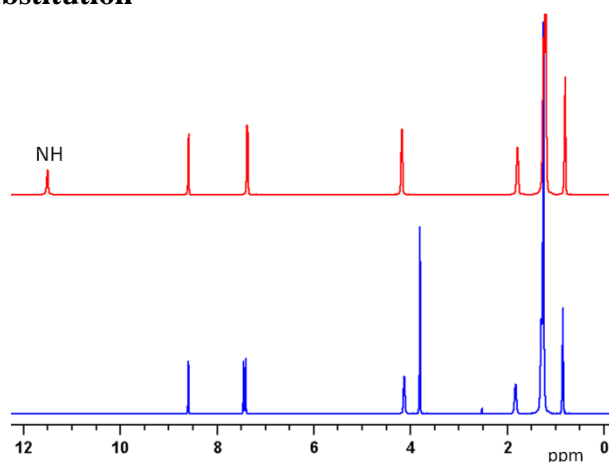


Fig. S2. Proton NMR spectra in the isotropic phase of $C_{12}mimBF_4$ (bottom) and protic $C_{12}imBF_4$ (top).

S5. Effect of MAS on proton spectra of ILC in smectic phase

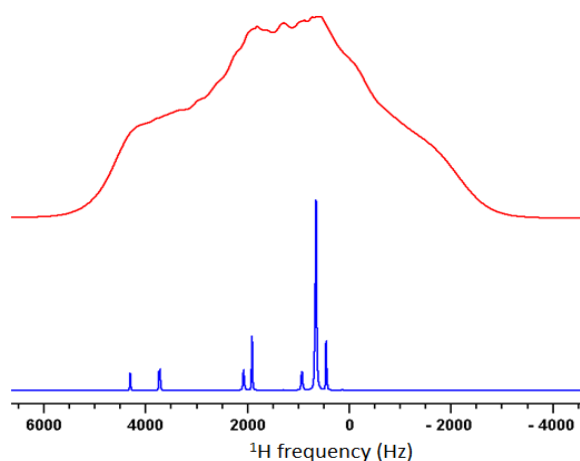


Fig. S3. Static (top) and MAS (bottom) spectra of $C_{12}mimBF_4$ in the smectic phase. Proton spectrum of the static sample is strongly broadened by homonuclear dipolar interactions.

S5. HETCOR NMR in solid phase and in nanoconfined state.

Two-dimensional ^1H - ^{13}C heteronuclear correlation (HETCOR) spectra were recorded at the resonance frequencies of 500 and 125 MHz for ^1H and ^{13}C , respectively, and at the sample spinning speed of 8 kHz. Cross-polarization contact time was set to 100 μs . For proton homonuclear and heteronuclear decoupling, FSLG¹⁴ and TPPM¹⁵ sequences were applied with nutation frequencies of 71 and 75 kHz, respectively. The frequency scaling factor of the FSLG sequence was calibrated to 0.54 by measuring spectra at different proton frequency offsets. The evolution time in the indirect time domain was incremented with 92 μs in 128 steps, at each with 8 collected transients.

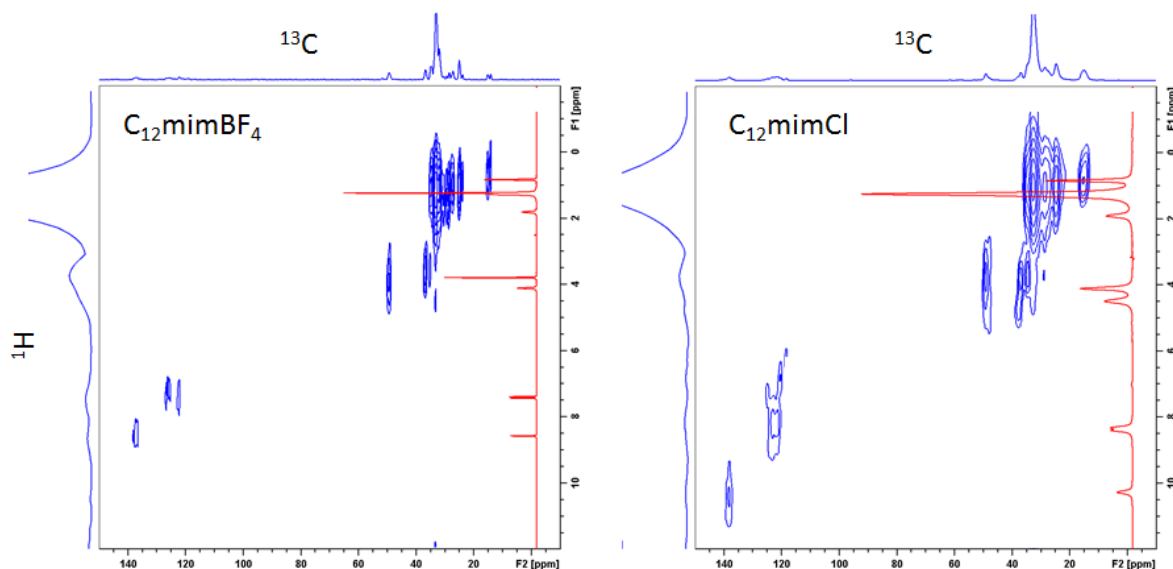


Fig. S4. ^1H - ^{13}C HETCOR spectra in $\text{C}_{12}\text{mimBF}_4$ and $\text{C}_{12}\text{mimCl}$ in the solid phase. Spectra were measured at 8 kHz spinning speed and 10°C. Red lines are 1D proton spectra in isotropic ($\text{C}_{12}\text{mimBF}_4$) and smectic ($\text{C}_{12}\text{mimCl}$) phases.

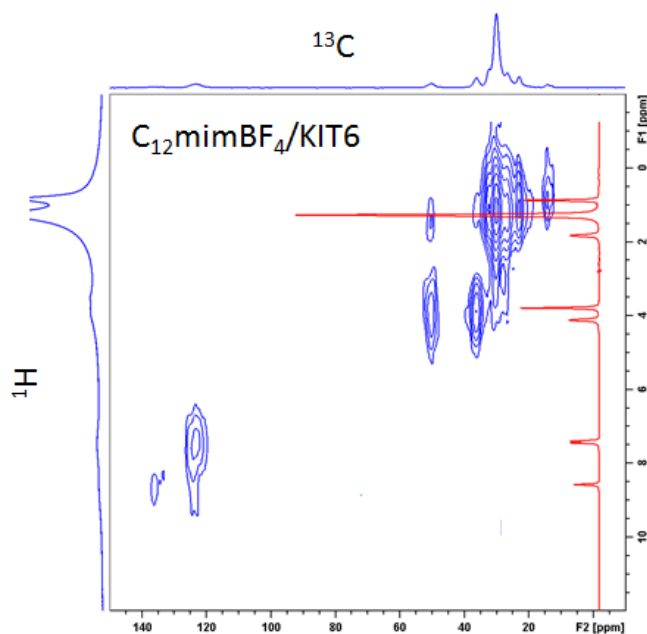


Fig. S5: ^1H - ^{13}C HETCOR spectrum in $\text{C}_{12}\text{mimBF}_4/\text{KIT6}$ porous composite. Spectrum was measured at 8 kHz spinning speed and 25°C. The red line is 1D proton spectrum in the smectic phase.

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