Supporting Information

Metastable State during Melting and Solid-Solid Phase Transition of $[C_nMim][NO_3]$ (n = 4-12) Ionic Liquids by Molecular Dynamics Simulation

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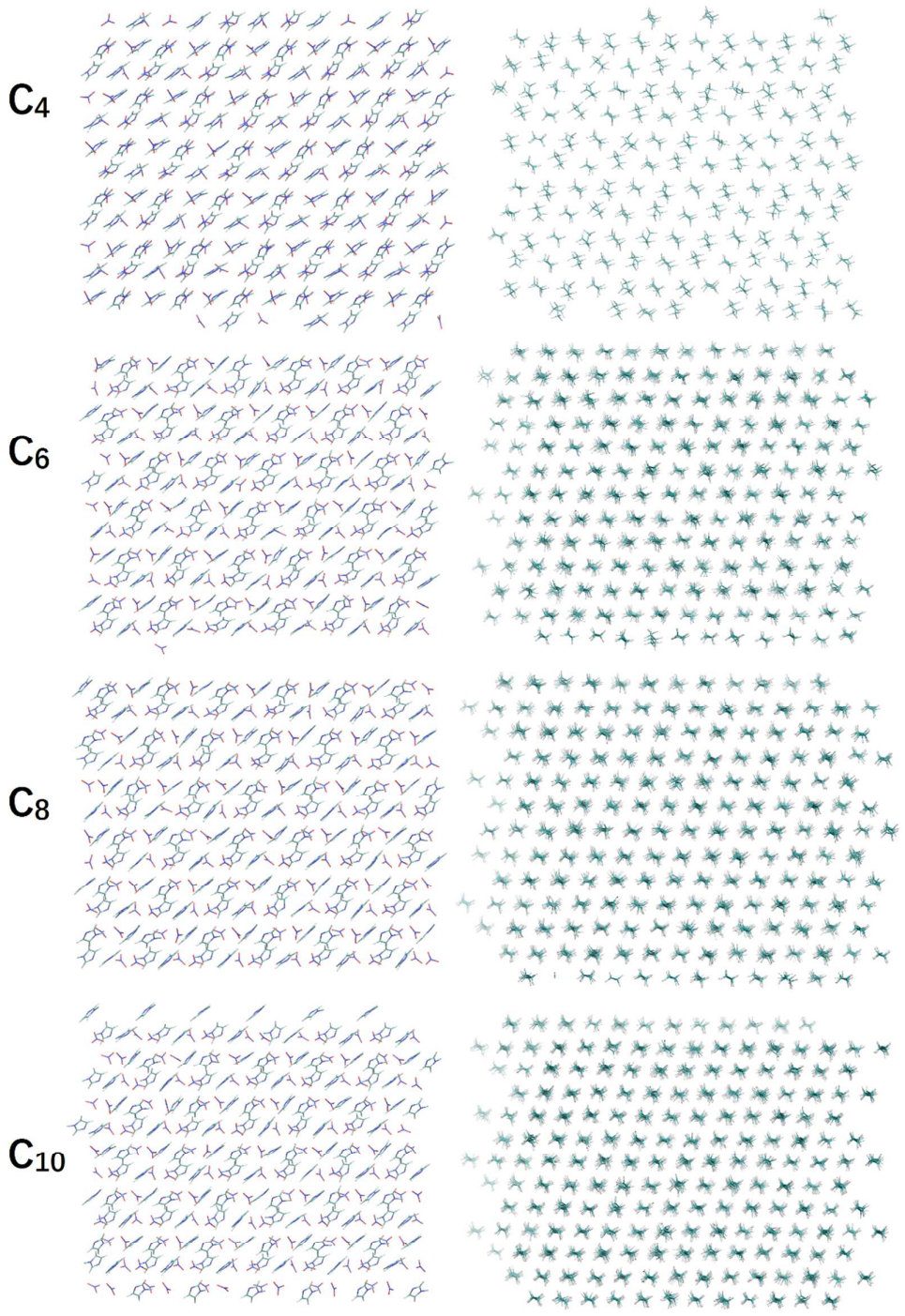

Figure S1. Snapshots of the crystal structures of C_4, C_6, C_8 and C_{10} at $T = 200$ K taken from [001] direction (left column) showing the ordered arrangement of the polar layer and from the direction along the alkyl chains (right column) showing the arrangement of alkyl chains.

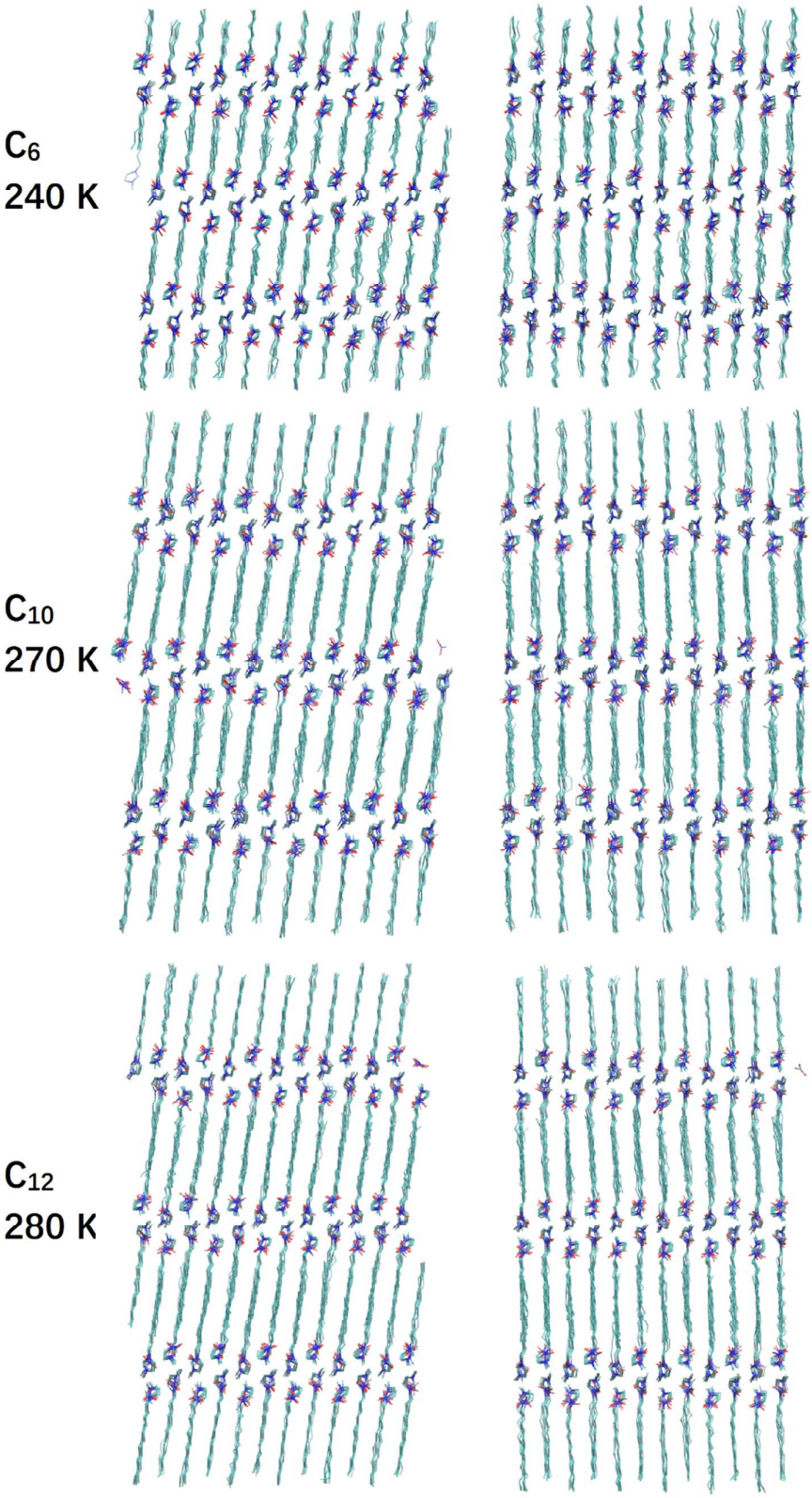

Figure S2. Snapshots of the structures before (left column) and after (right column) the solid-solid phase transitions taken from the [100] direction.

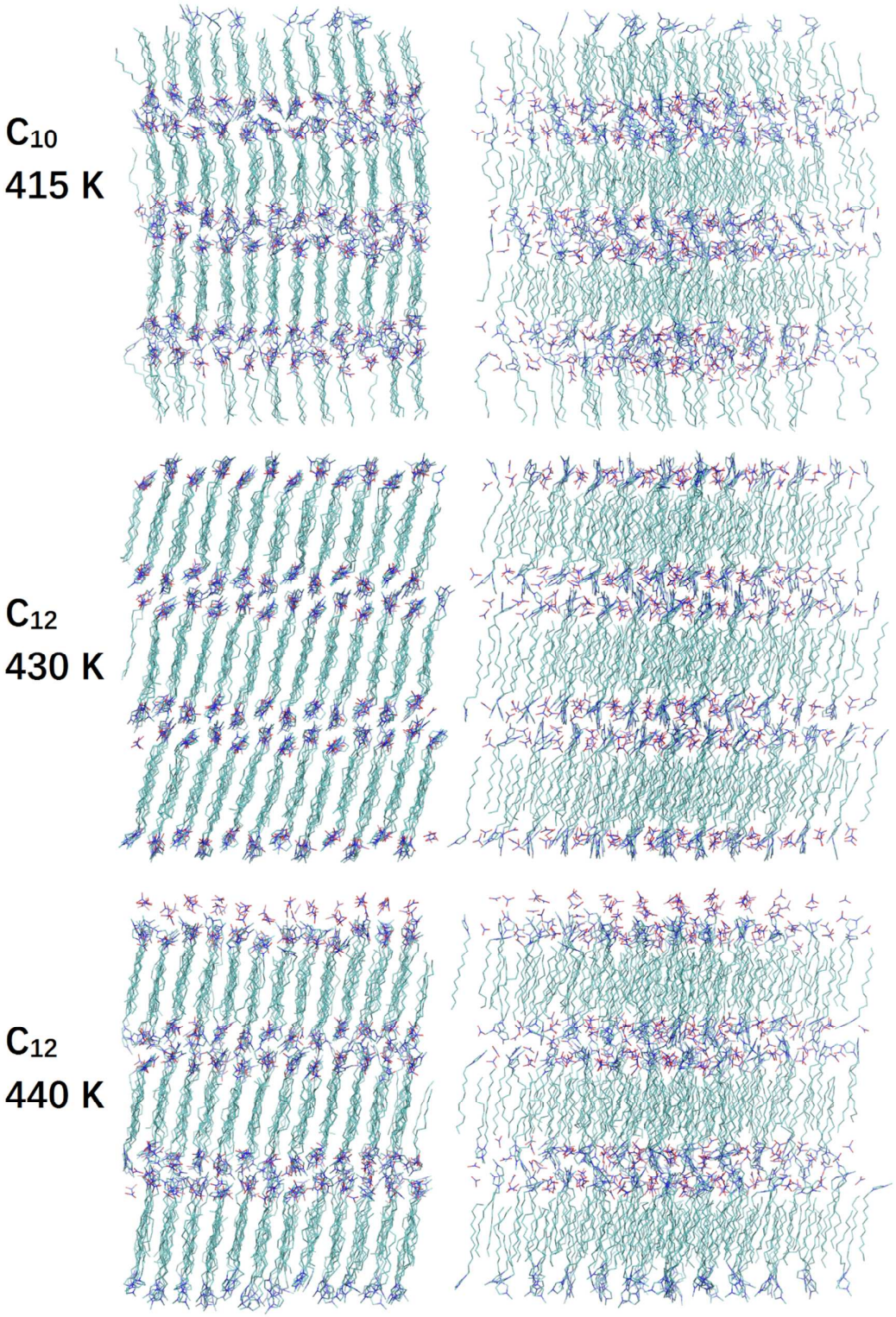

Figure S3. Snapshots of the metastable states taken from the [100] direction (left column) and from the [110] direction (right column).

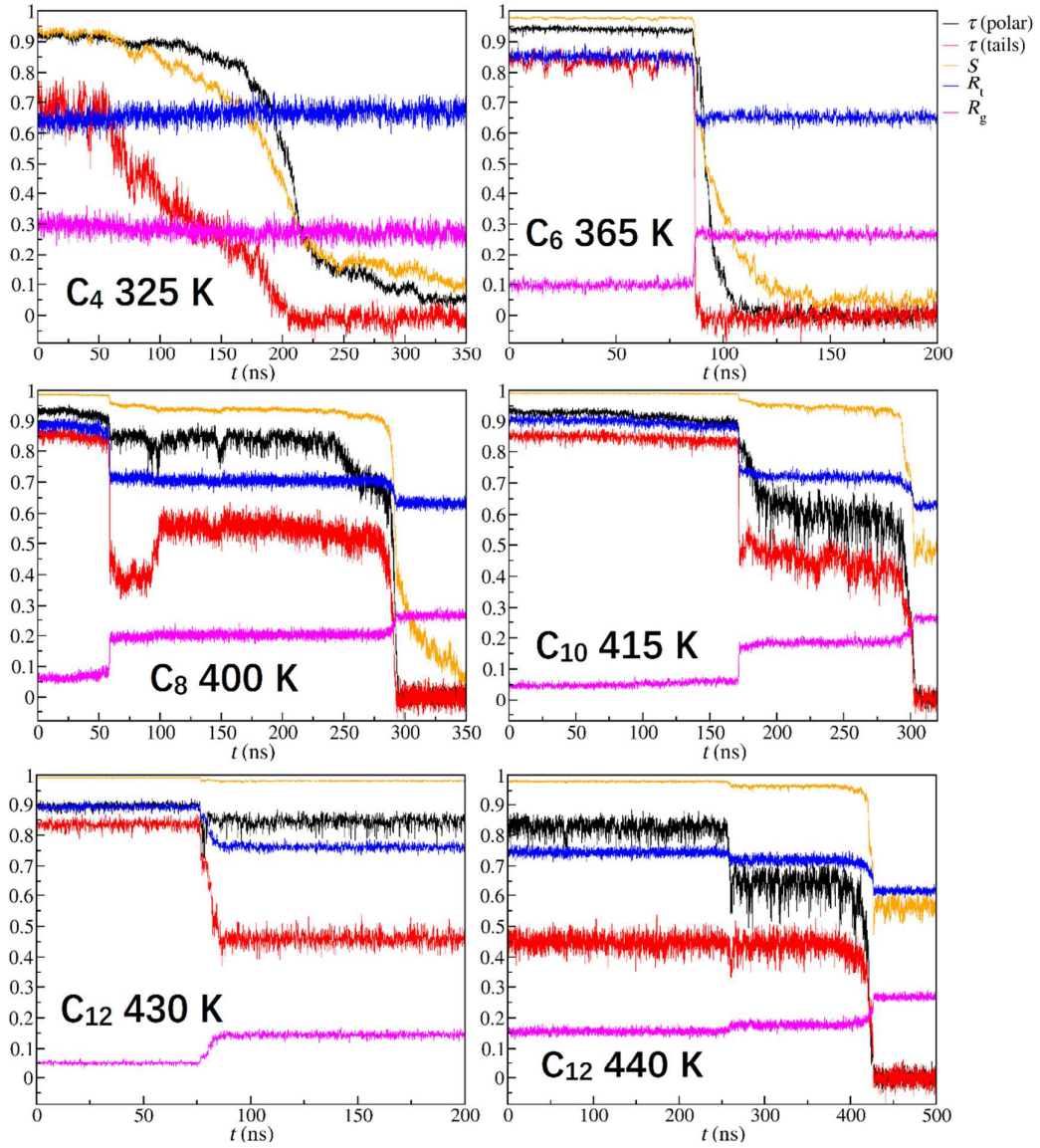

Figure S4. Order parameters versus time during single simulations at the melting points. τ(polar): translational order parameter of polar sites, τ(tail): translational order parameter of tails, S: orientational order parameter, R_t: number ratios of *trans*-conformations, R_g: number ratios of gauche conformations.

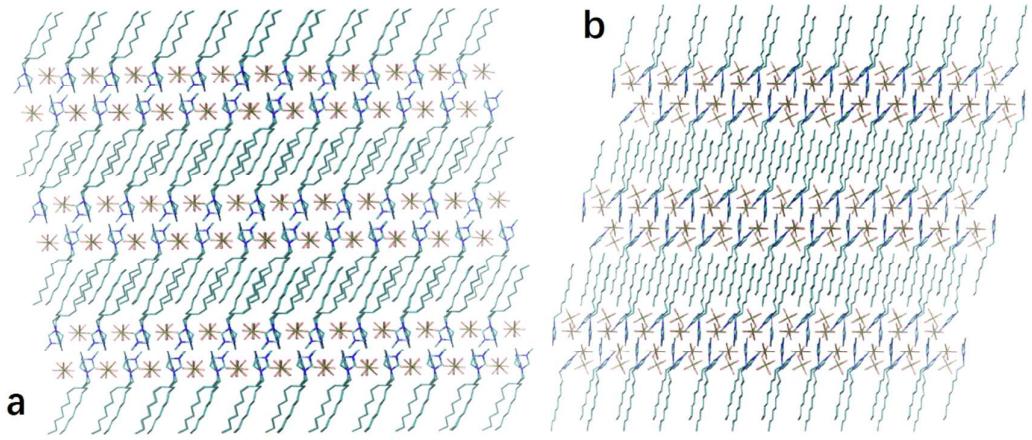

Figure S5. Snapshots of crystal structures of $[C_{10}mim][PF_6]$ at T = 10 K from the [110] direction. (a) Structure constructed according to the lattice constants reported in ref 3. (b) Structure obtained by replacing nitrates by hexafluorophosphates in our manually constructed C_{10} structure.

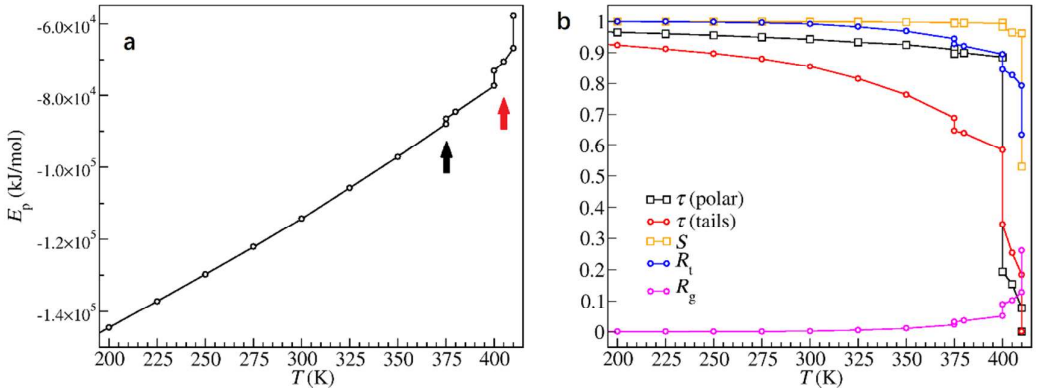

Figure S6. Data of $[C_{12}mim][Cl]\cdot H_2O$ during heating from T = 200 K to 410 K. (a) caloric curve;(b) order parameters, τ(polar): translational order parameter of polar sites, τ(tail): translational order parameter of tails, S: orientational order parameter, R_t: number ratios of *trans*-conformations, R_g: number ratios of gauche conformations.

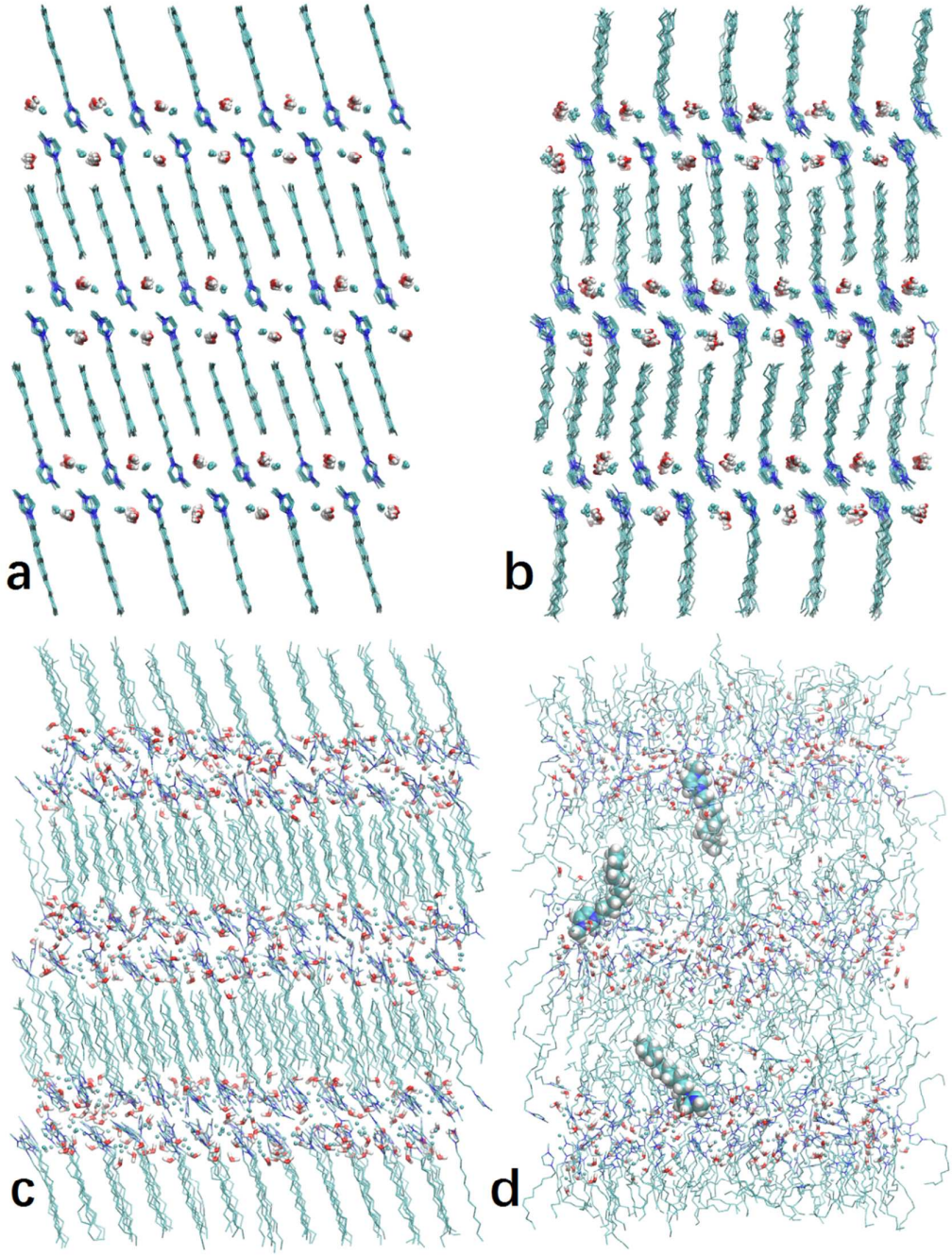

Figure S7. Snapshots of structures of $[C_{12}mim][Cl]\cdot H_2O$. (a) crystal from ref 4 at T = 200 K, from [100] direction; (b) crystal at T = 380 K, [100] direction; (c) metastable state at T = 400 K, [010] direction; (d) liquid crystal at T = 410 K.

Table S1. Potential Energies of Various Structures at T = 10 K in the *NVT* ensemble.

Structure	E_p (kJ/mol)
C_4 (our structure)	-156139 ± 10.8
C_4 (all-*trans*)	-154884 ± 11.3
C_4 (experiment[a])	-160104 ± 11.3
C_{10} (our structure)	-178134 ± 14.8
C_{10} (experiment[b])	-174009 ± 13.7
C_{10} (Figure S5a)	-155027 ± 15.8
C_{10} (Figure S5b)	-155953 ± 14.1
C_{12} (our structure)	-186536 ± 14.7
C_{12} (experiment[c])	-178532 ± 15.3

[a]The structure is obtained by replacing the experimental anions reported in refs 1 and 2 by nitrates.

[b]The same way as (a) for ref 3.

[c]The same way as (a) for ref 4.

Table S2. Lattice Parameters, Layer Spacings and Densities of $[C_{12}mim][Cl]\cdot H_2O$ at T = 200 K and at T = 375 K before (I) and after (II) the Solid-solid Phase Transition.

	200 K	375 K - I	375 K - II
a (Å)	5.196(8)	5.37(2)	5.40(2)
b (Å)	8.12(1)	8.25(2)	8.29(3)
c (Å)	22.41(3)	23.0(1)	23.5(2)
α (°)	84.6(1)	79(1)	73(2)
β (°)	82.1(2)	85.6(3)	85.8(3)
γ (°)	83.5(1)	81.8(2)	81.3(2)
d (Å)	22.13(3)	22.61(5)	22.55(6)
ρ (g cm^{-3})	1.092(1)	1.020(3)	1.015(2)

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