Electronic Supplementary Information (ESI)

Understanding Dissolution Process of Chitin Crystal in Ionic Liquids: Theoretical Study

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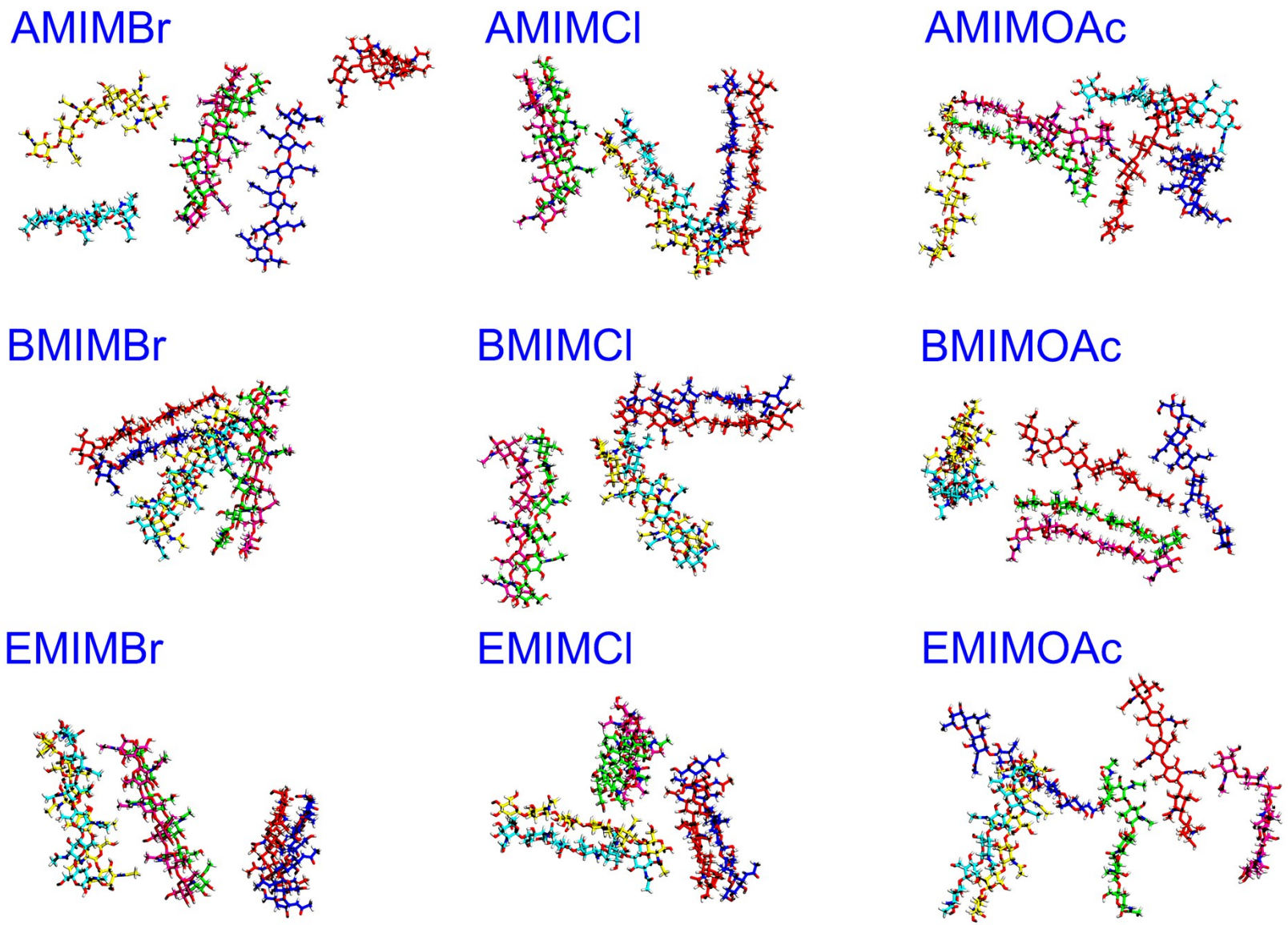
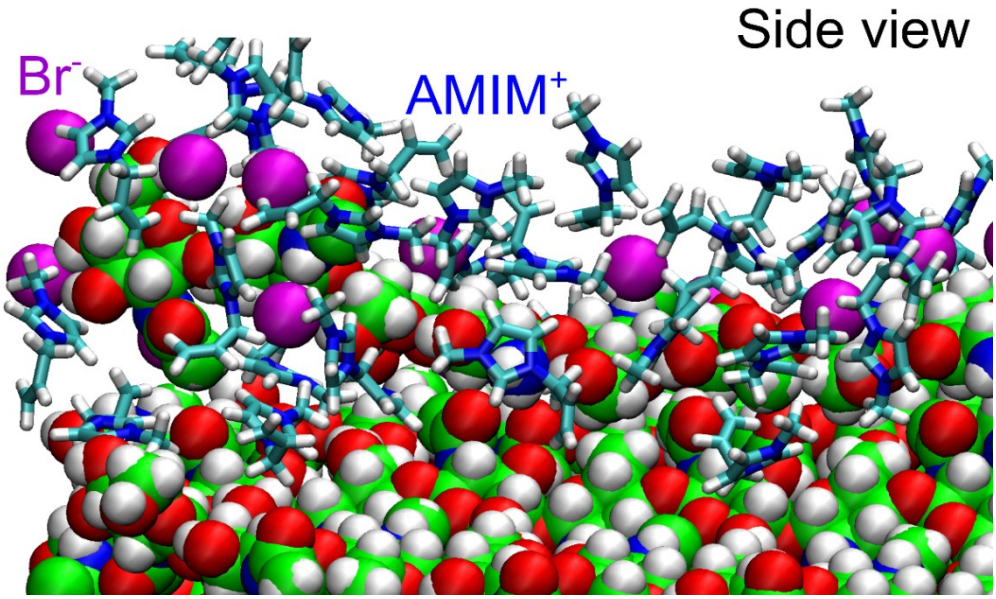


Fig. S1 MD structures of chitin crystals (6-chain × 6-mer model) in various ILs at 450K after 100 ns, with each chain color-coded.



Movie S1 Early stage of chitin dissolution in AMIMBr at 500K for 24-27ns showing chitin crystal (9-chain × 10-mer model; green, red and white spheres), Br^- (magenta spheres) and $AMIM^+$ (blue sticks).

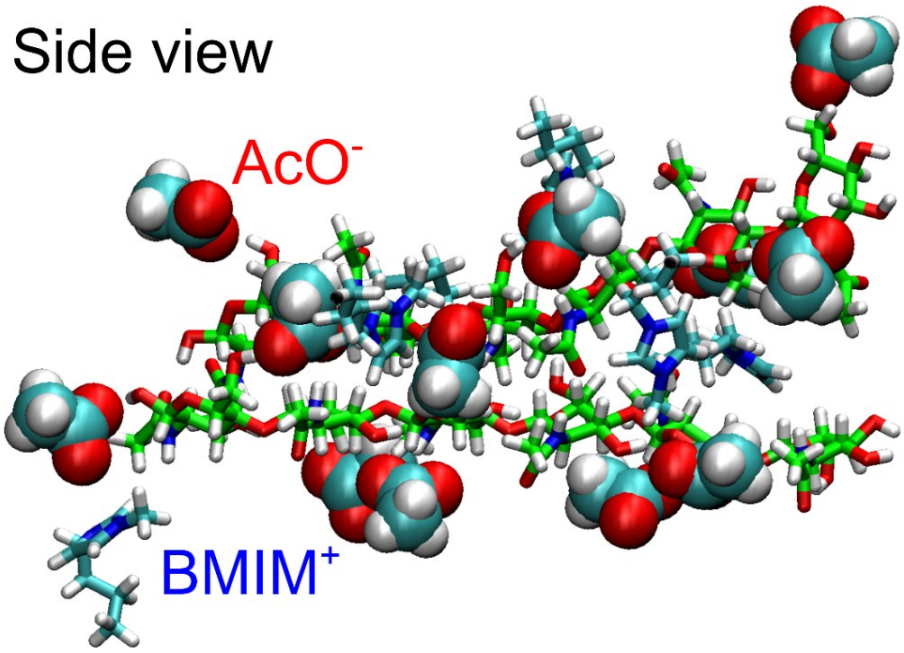


Fig. S2 Dissolution behavior of chitin crystal (6-chain × 6-mer model) in BMIMOAc at 450K after 30 ns showing AcO^- (spheres) and $BMIM^+$ (blue sticks) near the chitin chains.

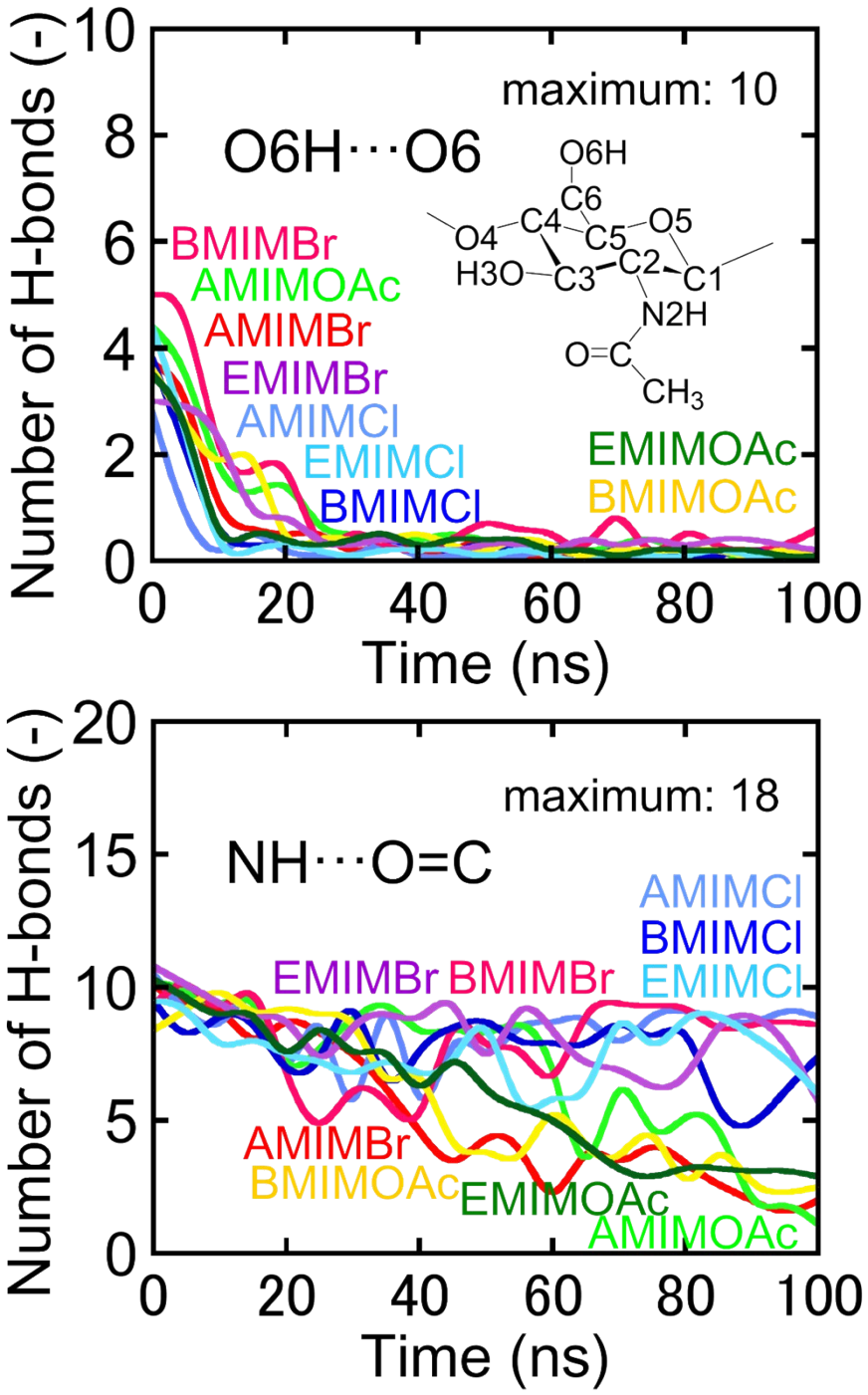
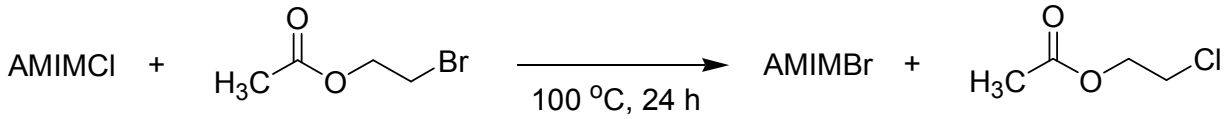


Fig. S3 Number of intermolecular hydrogen bonds in chitin crystals (6-chain × 6-mer model) in various ILs at 450K.

Table S1 Number of the intermolecular hydrogen bonds in chitin crystals (6-chain × 6-mer model at 450K for 51-100 ns)

Hydrogen bonds	AMIMBr	BMIMBr	EMIMBr	AMIMCl	BMIMCl	EMIMCl	AMIMOAc	BMIMOAc	EMIMOAc
NH···O=C	5.8	17.1	15.1	17.5	14.6	14.7	8.9	7.0	7.3
NH···O3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1
NH···O6	0.0	0.0	0.0	0.0	0.1	0.0	0.1	0.4	0.0
O3H···O=C	0.1	0.0	0.2	0.0	0.0	0.0	0.2	0.3	0.0
O3H···O3	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
O3H···O6	0.2	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.1
O6H···O=C	0.7	0.7	0.8	0.4	0.6	0.4	0.8	1.6	0.5
O6H···O3	0.5	0.2	0.2	0.2	0.1	0.3	0.2	0.5	0.1
O6H···O6	0.2	0.9	0.7	0.3	0.3	0.2	0.5	0.4	0.4
Total	8.0	19.9	17.7	19.1	16.3	16.3	11.3	11.2	8.7
Chitin solubility (*wt*%)	10.0	1.0	N/D	0.5	1.0	3.3	5.0	6.0	9.0



Scheme S1 Equimolar reaction of AMIMCl with 2-bromoethyl acetate.

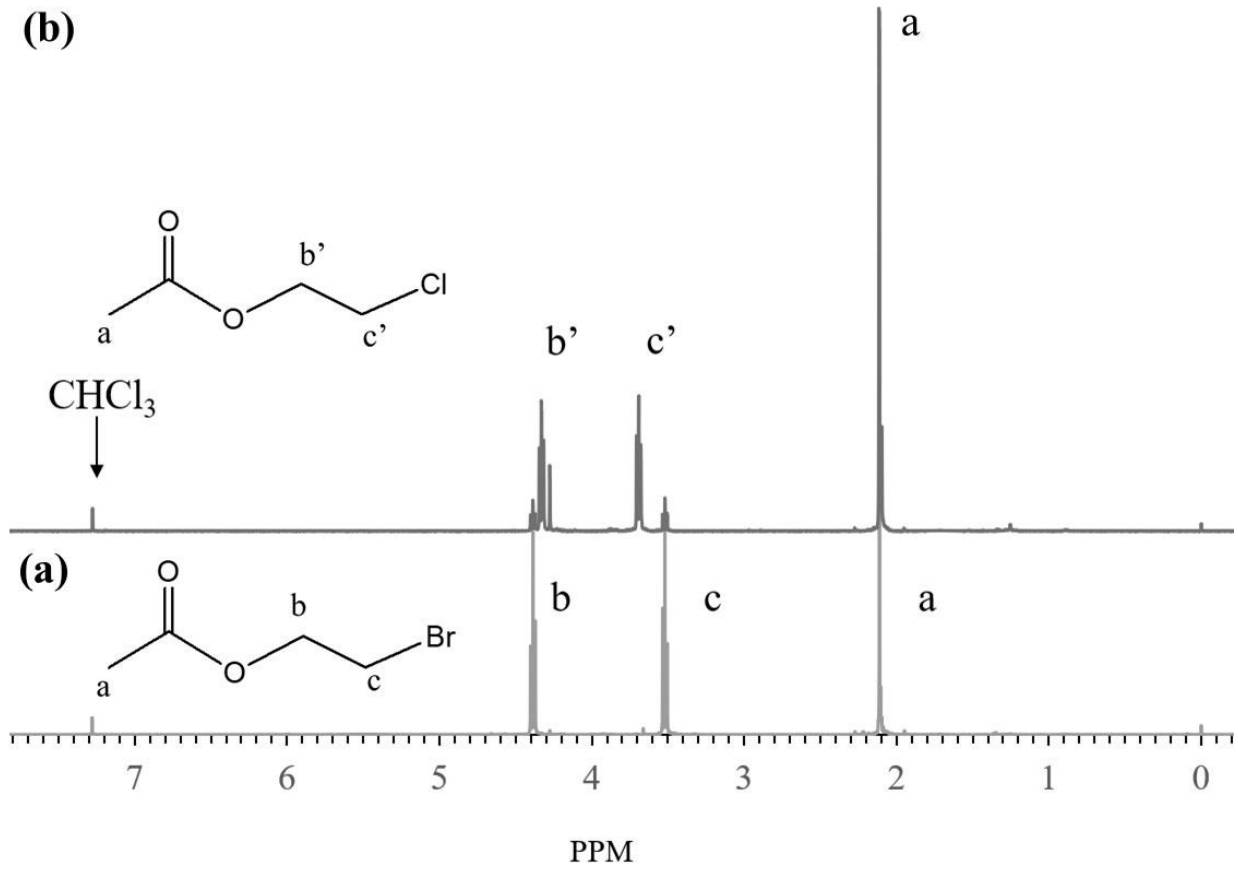


Fig. S4 ^{1}H NMR spectra of (a) 2-bromoethyl acetate and (b) extract with diethyl ether from equimolar reaction mixture of AMIMCl with 2-bromoethyl acetate ($CDCl_3$).

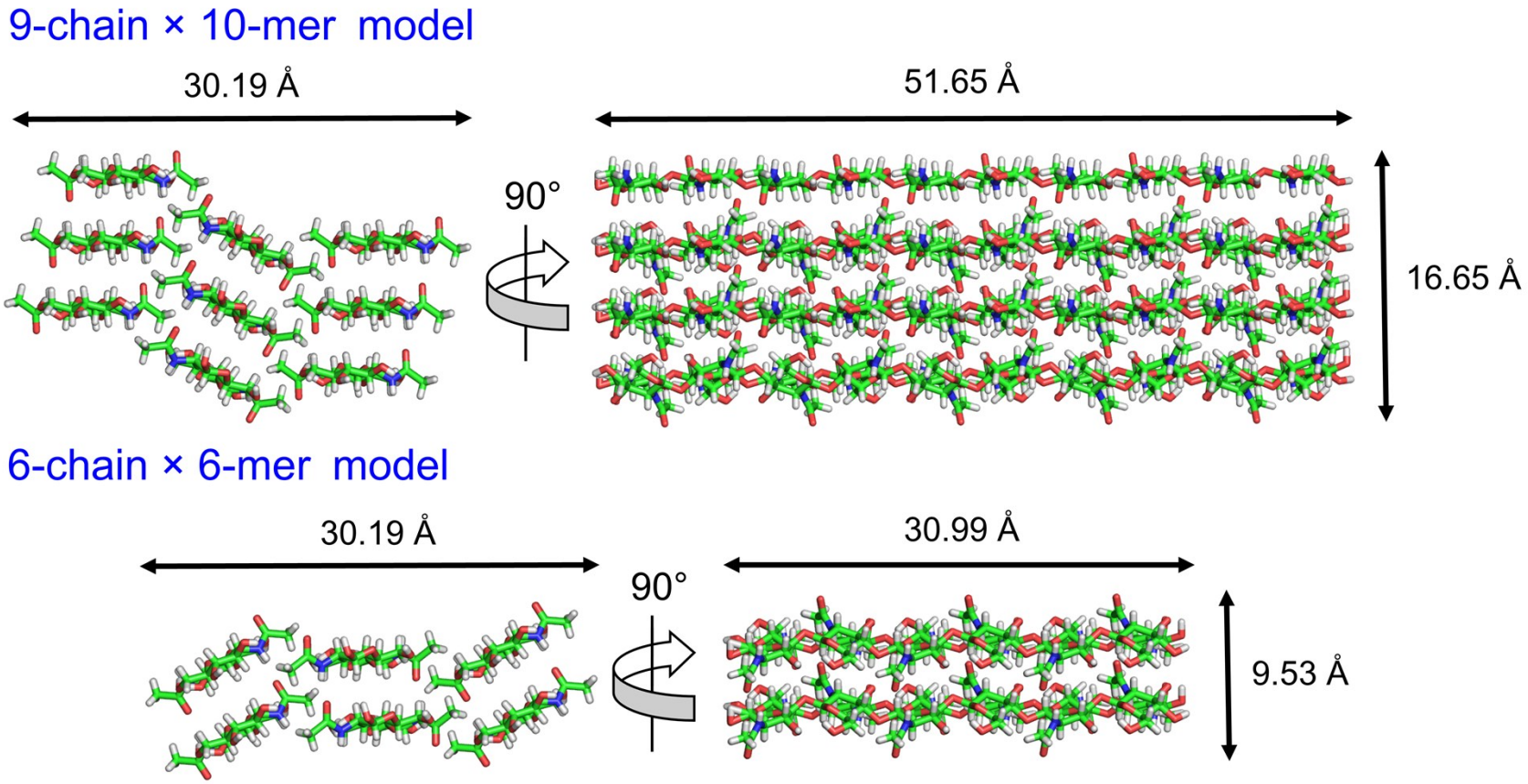
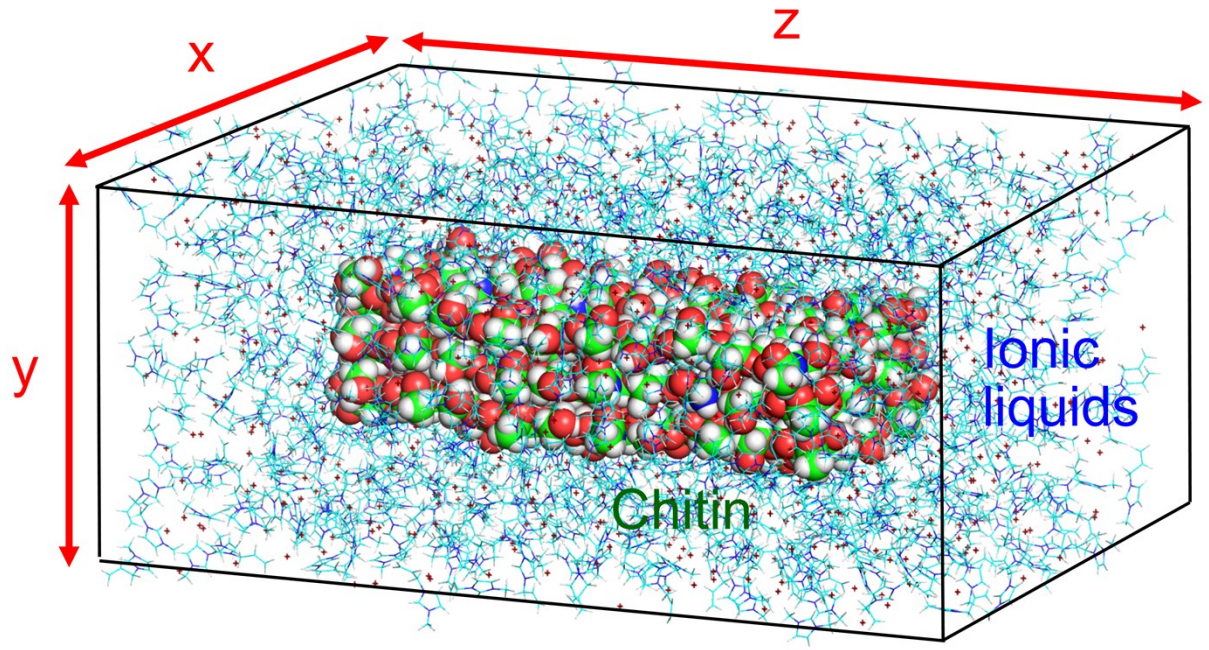


Fig. S5 Slice and side views of the chitin crystal models (9-chain × 10-mer and 6-chain × 6-mer). Color scheme: red (oxygen), green (carbon), blue (nitrogen) and white (hydrogen).

Table S2 Initial box dimensions of chitin/ILs systems for MD simulation

ILs system	Initial box dimensions, x (Å) × y (Å) × z (Å)	
	9-chain × 10-mer model	6-chain × 6-mer model
AMIMBr	42.9 × 60.0 × 85.6	46.5 × 54.2 ×54.3
BMIMBr	45.0 × 63.0 × 89..9	48.9 × 57.0 × 57.0
EMIMBr	42.0 × 58.6 × 83.6	44.5 × 53.7 × 53.7
AMIMCl	42.6 × 59.7 × 85.2	45.2 × 54.5 × 54.5
BMIMCl	44.9 × 62.8 × 89.6	47.5 × 57.3 × 57.3
EMIMCl	41.7 × 58.3 × 83.3	44.1 × 53.2 × 53.2
AMIMOAc	51.3 × 59.8 × 85.4	48.3 × 58.2 × 58.2
BMIMOAc	53.5 × 62.3 × 89.0	53.2 × 59.1 × 59.2
EMIMOAc	50.3 × 58.7 × 83.7	48.4 × 56.4 × 56.4



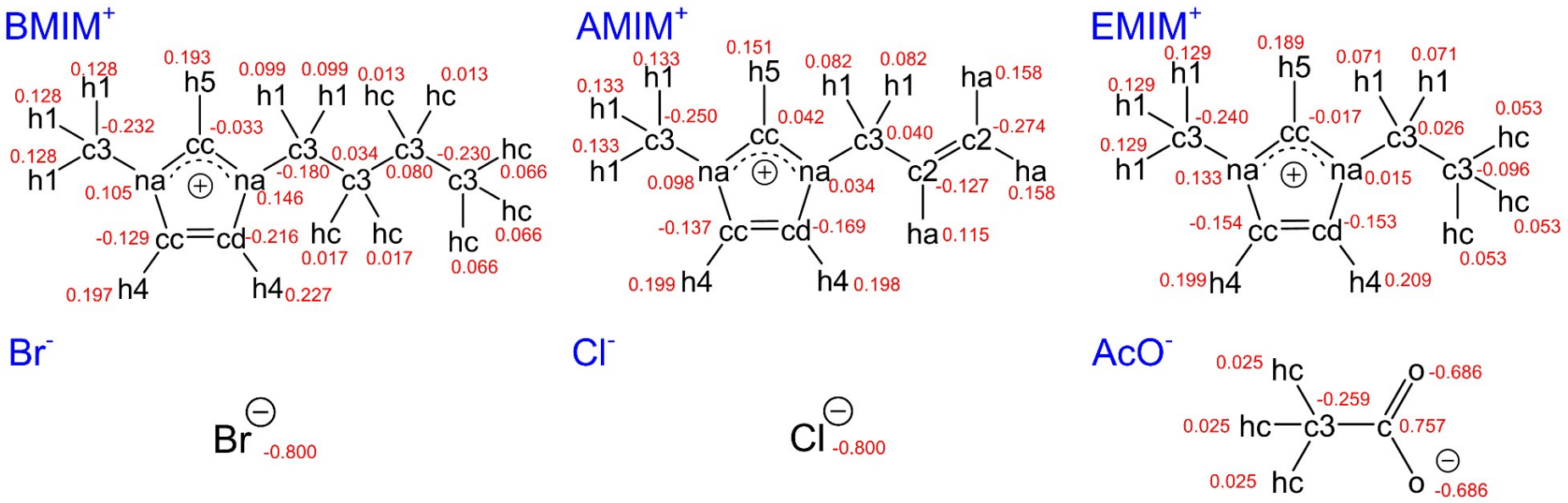


Fig. S6 The force field parameters for imidazolium-based ILs. (Partial charge and atom types for GAFF)