

The electronic supplementary information file

For

**Fine probing the effect of replacing  $[\text{PF}_6]^-$  with  $[\text{PF}_3(\text{C}_2\text{F}_5)_3]^-$   
on the local structure and nanoscale organization of  $[\text{bmim}]^+$ -  
based ionic liquids using MD simulation**

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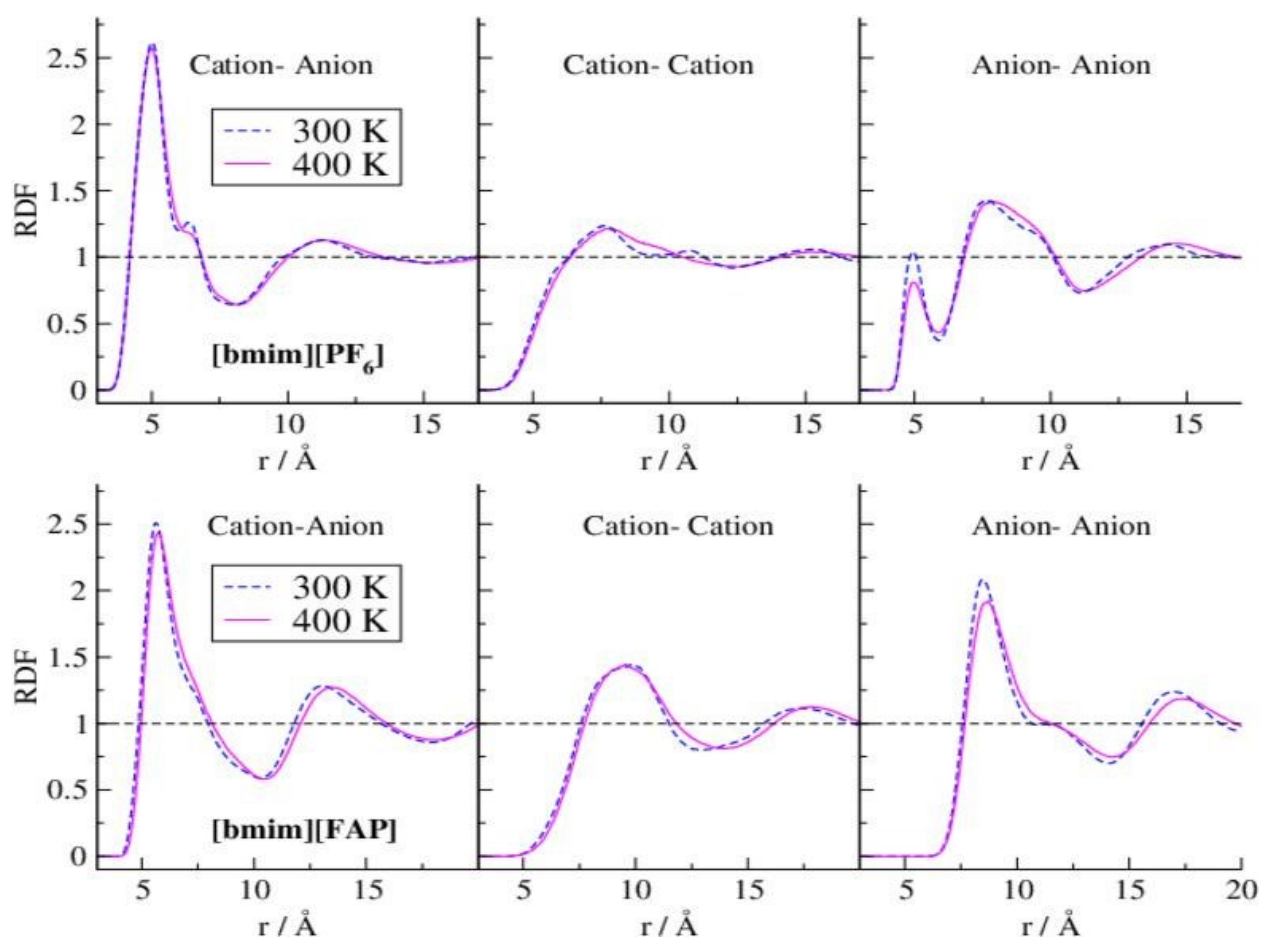
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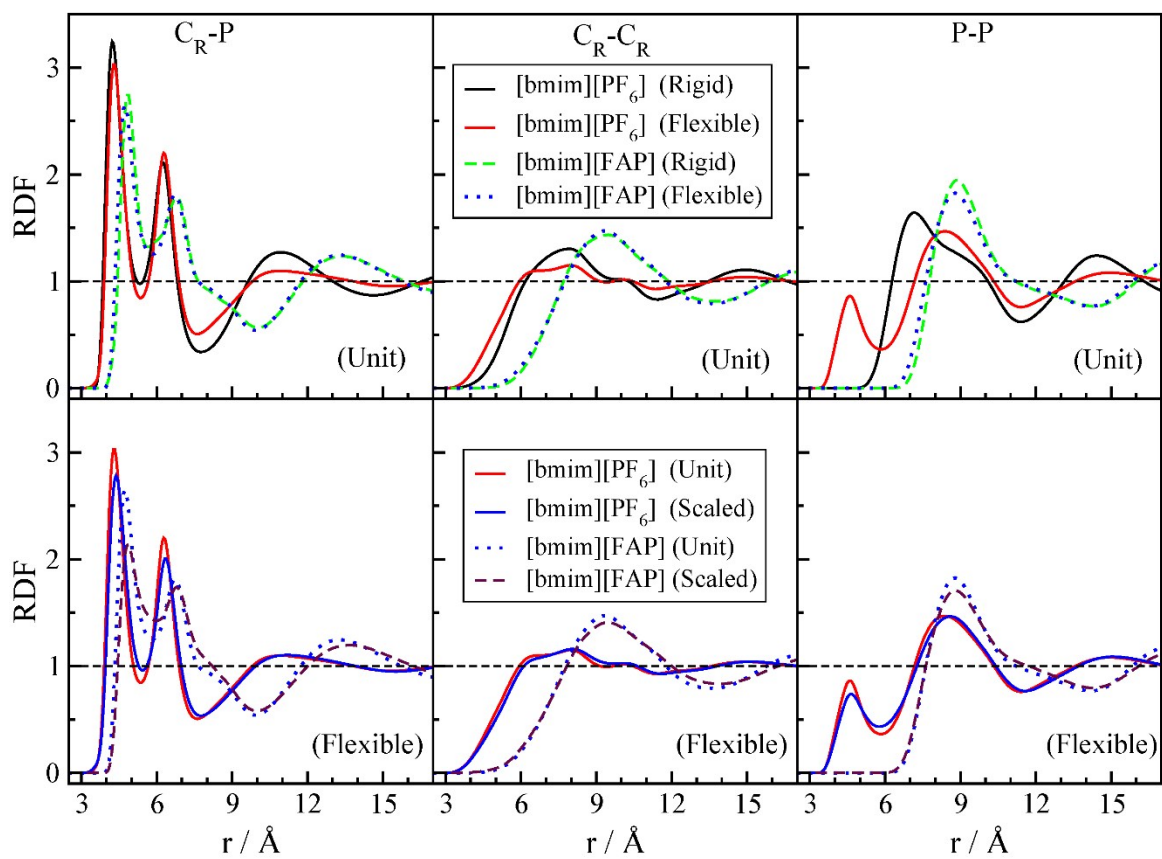
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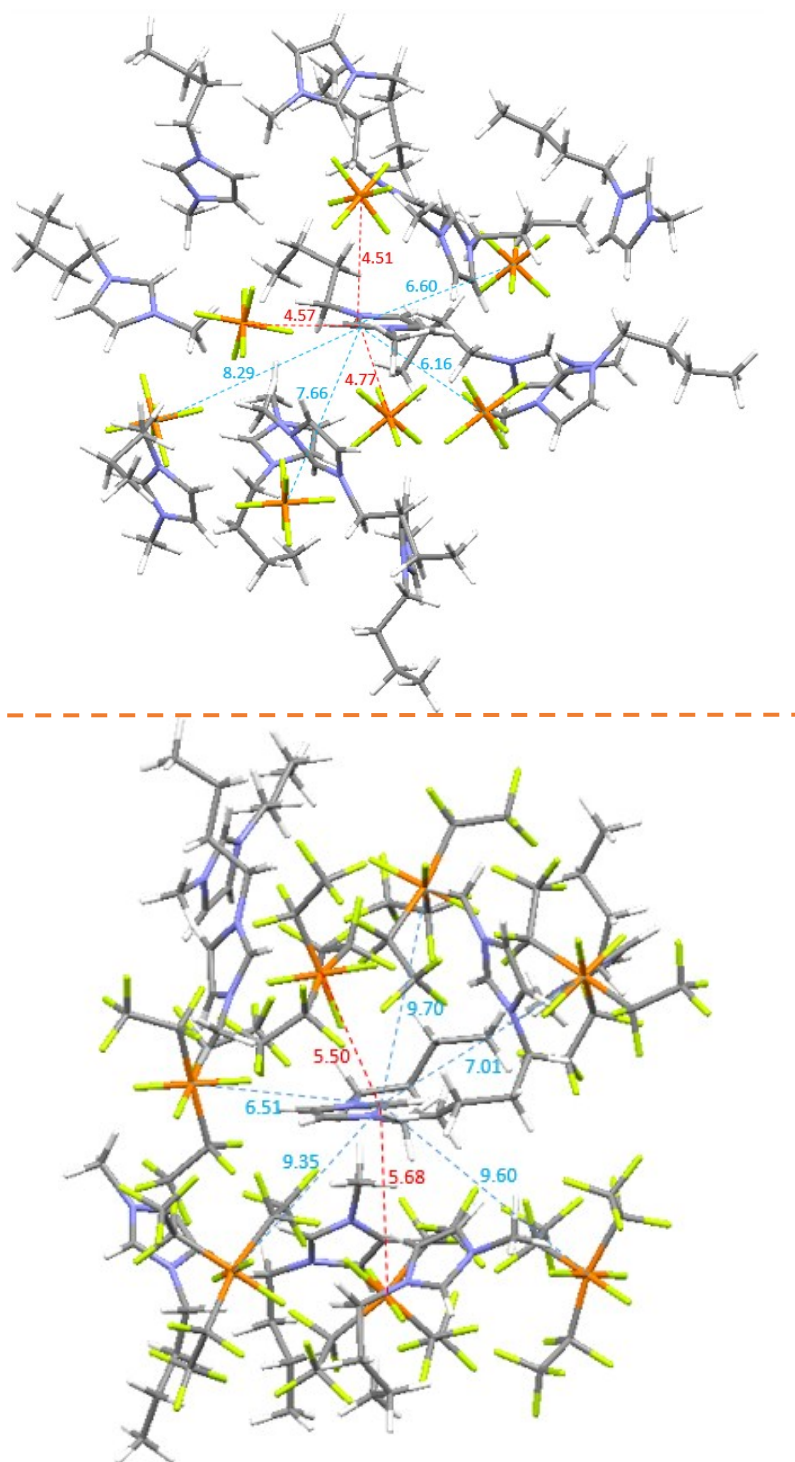
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**Fig. S1.** Effect of temperature on the COM RDFs between the cation-anion (left), cation-cation (middle), and anion-anion (right) extracted from the simulations of the ILs using fully flexible ions and the unit charge model.

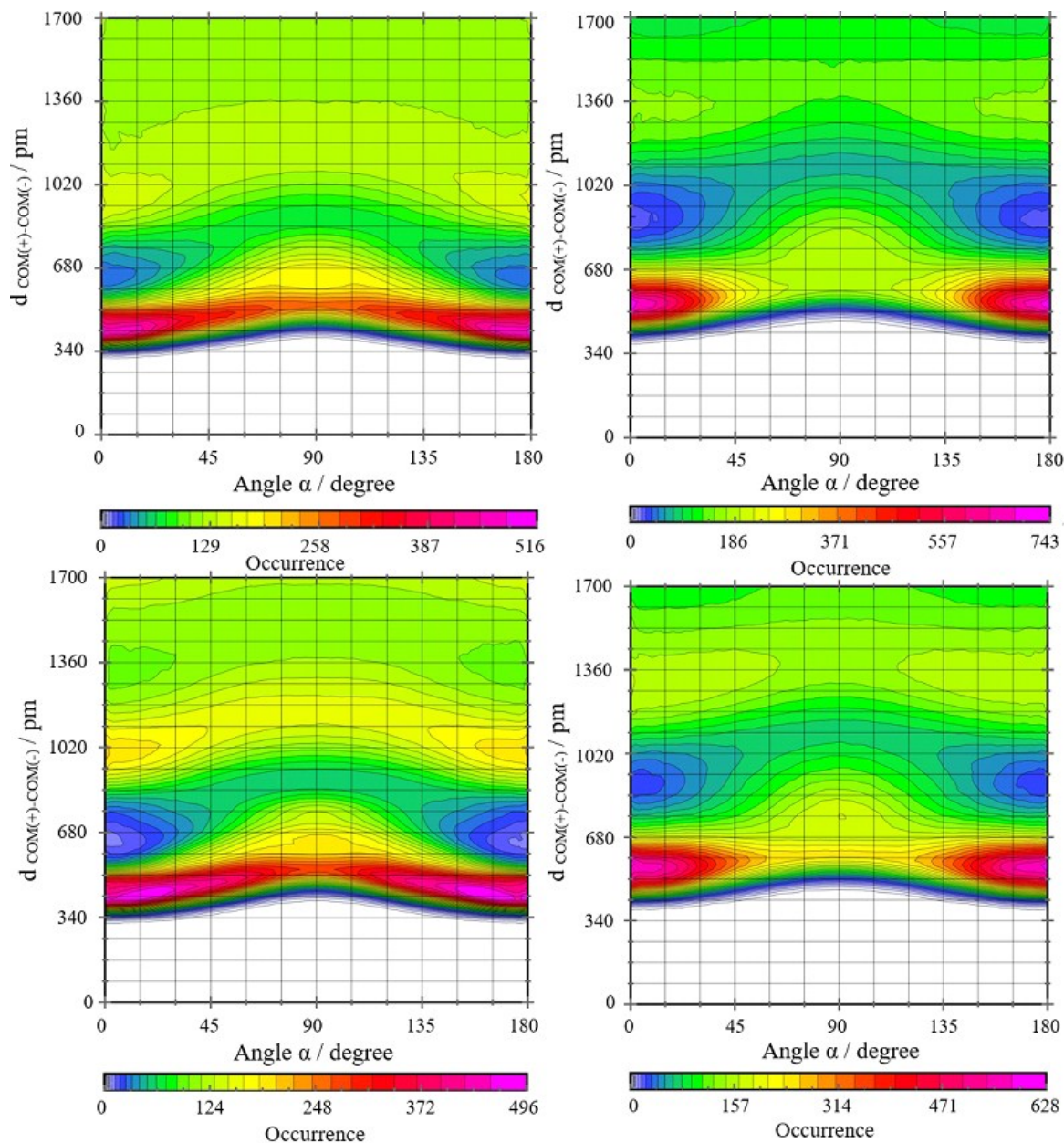


**Fig. S2.** Effect of a rigid or flexible structure of the anion (above panels) and a unit or scaled charge model (below panels) on the key atomic site-site RDFs of the [bmim][PF<sub>6</sub>] and [bmim][FAP] ILs at 400 K.

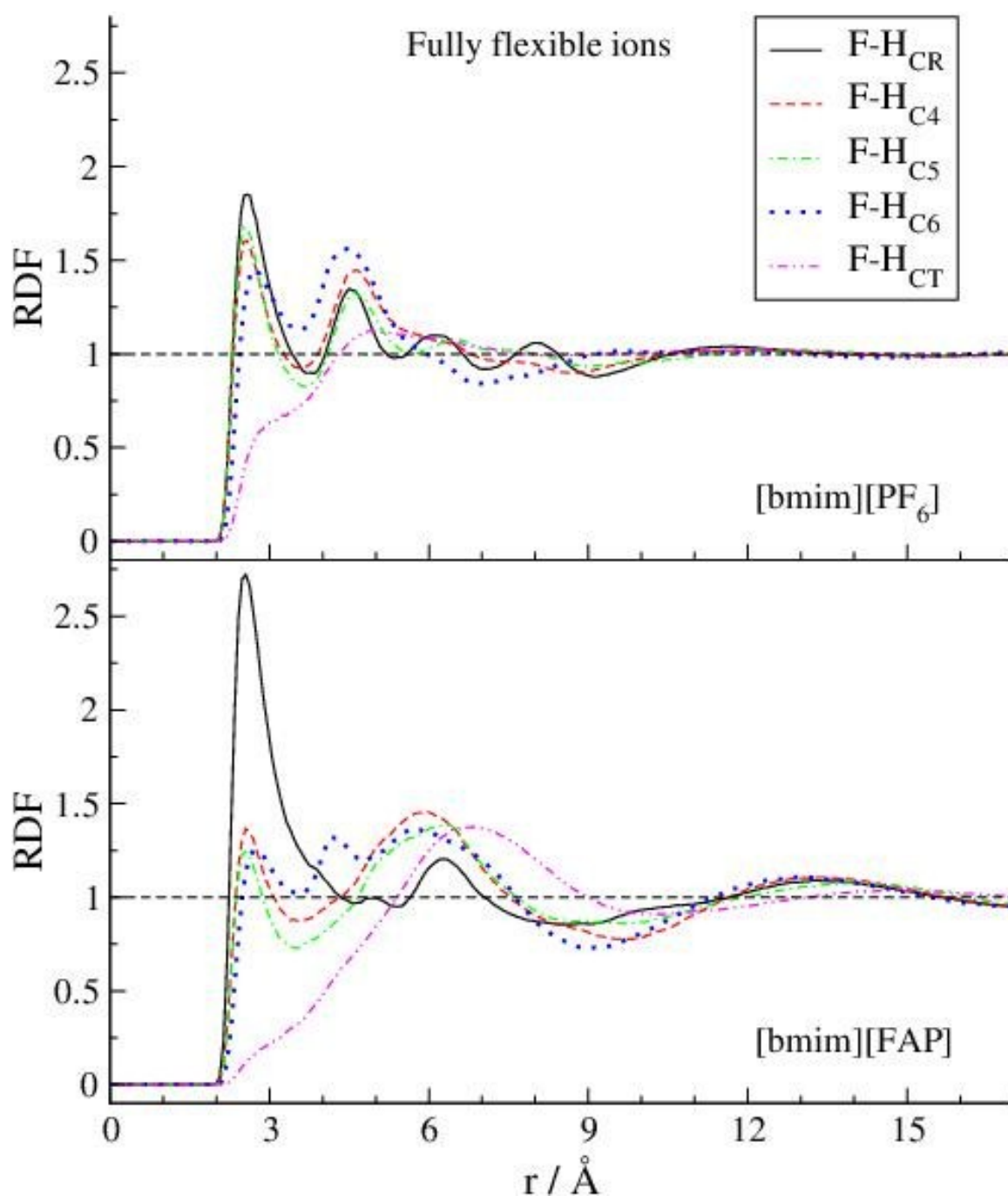


**Fig. S3.** Selected snapshots of the several ionic nearest-neighbors from the simulation boxes of [bmim][PF<sub>6</sub>] (top), and [bmim][FAP] (down) at 400 K along with the (C<sub>R</sub>...P) intermolecular distances (in Å) for near and far distances in red and blue, respectively.

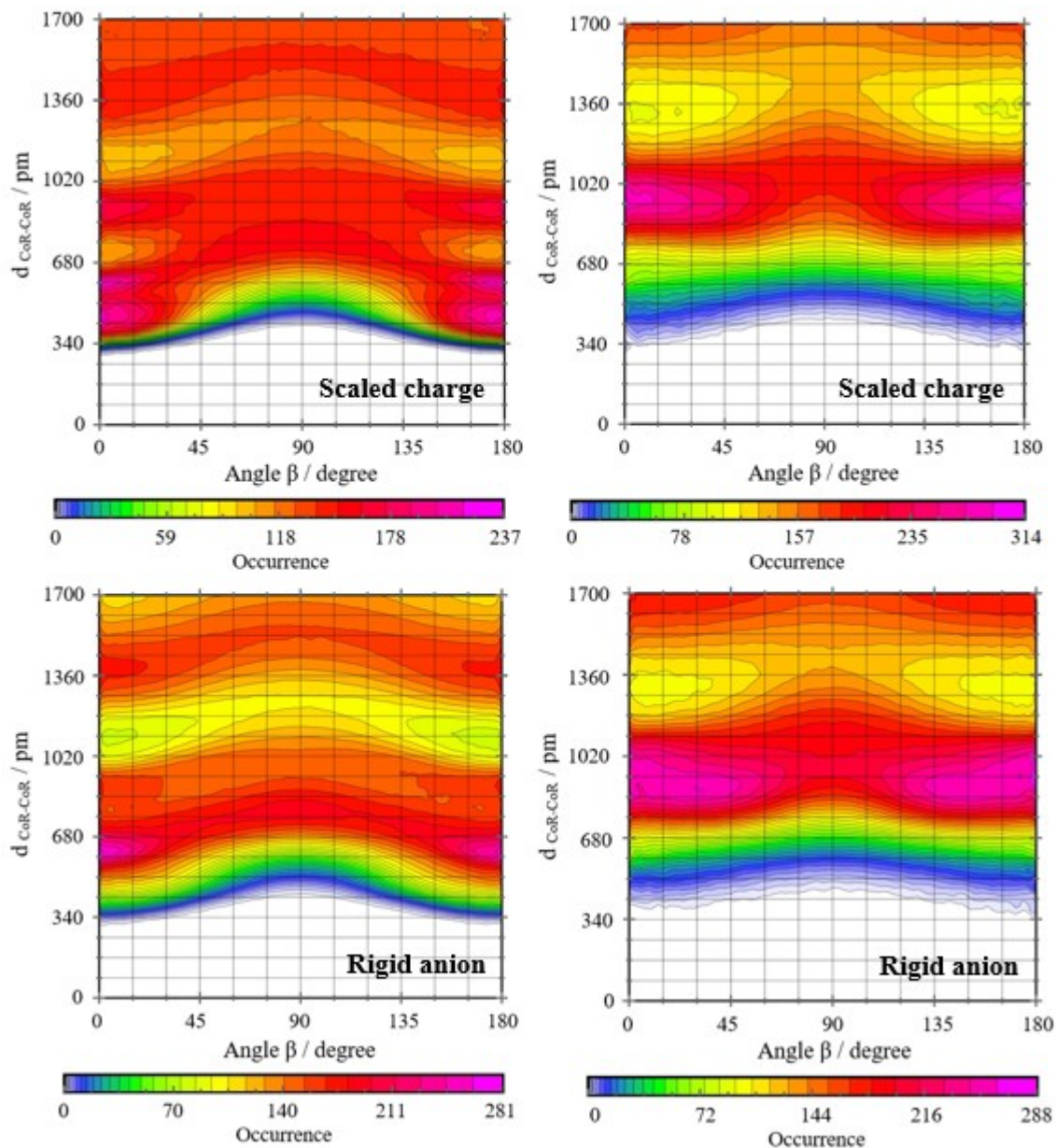
To gain more understanding of the relative orientations of the neighboring anions around each cation, we chose two snapshots from the inside of the simulation boxes of the target ILs. The relative orientations of neighboring ions in Fig. S3 help to interpret the sharp (C<sub>R</sub>-P) RDF peaks in Fig.S2. Comparing Figs. S2 and S3 it is found that the origin of the first two peaks in (C<sub>R</sub>-P) RDF is the different positions of the anions around the reference [bmim]<sup>+</sup>, so that the first (C<sub>R</sub>-P) RDF peak is mainly due to placing the anion above or below the ring plane of the imidazolium cation, and the second RDF peak is mainly due to approximately situating the anion in the plane of the imidazolium ring.



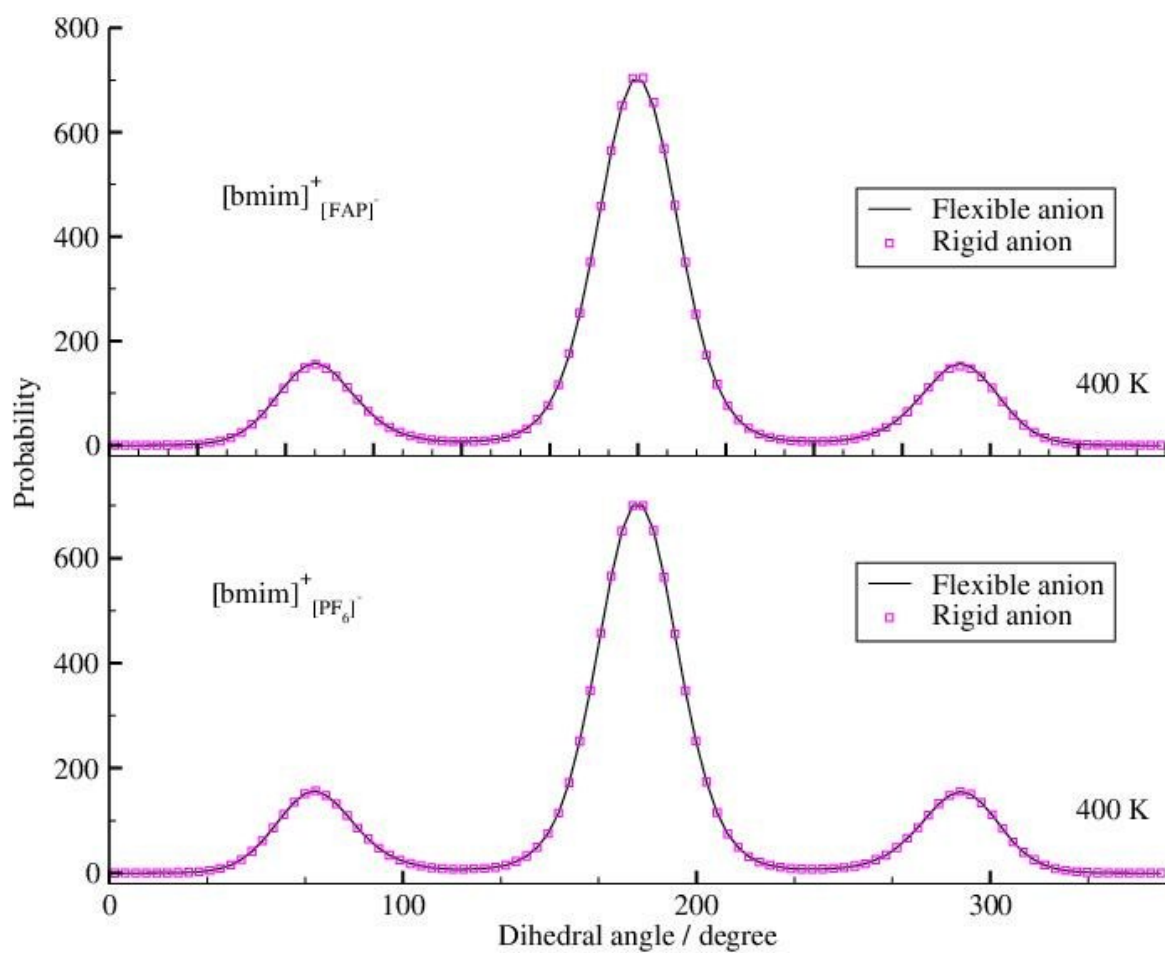
**Fig. S4.** CDFs of the distance between the COM of the cation and the anion,  $d_{\text{COM}(+)\text{-COM}(-)}$ , and the angle  $\alpha$  showing the relative orientation of the anions toward the ring plane of the  $[\text{bmim}]^+$  cations in the same as Fig. 6 of the main text. The left and right panels are related to the  $[\text{bmim}][\text{PF}_6]$  and  $[\text{bmim}][\text{FAP}]$  ILs, respectively. The above panels are related to the simulations using fully flexible ions and the scaled charge model. The below panels are related to the systems with the rigid anion and the unit charge model.



**Fig. S5.** RDFs describing the distribution of the different H atoms of the imidazolium cation around the fluorine atoms that were directly connected to the P atom of the anions in the [bmim][PF<sub>6</sub>] (upper panel) and [bmim][FAP] (bottom panel) ILs at 400 K. These RDFs calculated from the simulation using fully flexible ions and the unit charge model.

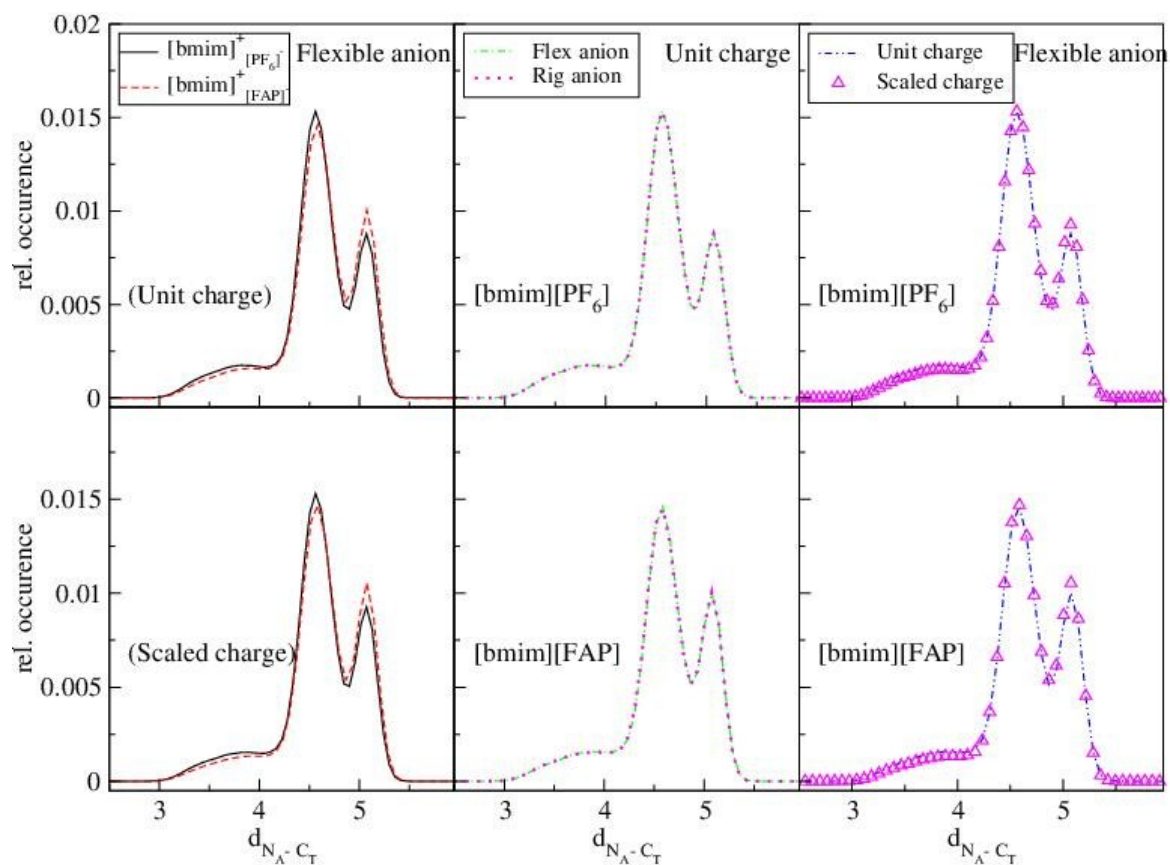


**Fig. S6.** CDFs between the nearest-neighbor cations in [bmim][PF<sub>6</sub>] (left) and [bmim][FAP] (right) from the simulations using fully flexible ions and the scaled charge model in the upper panels, and from the simulations using the rigid anions and the unit charge model in the bottom panels. These CDFs (in the same as Fig. 9 of the main text) include the distance between *the center of ring (CoR)* of the two [bmim]<sup>+</sup> cations,  $d_{CoR-CoR}$ , and the angle  $\beta$  between the ring orthogonal vector and the vector connecting the *CoR* of the neighboring cations.



**Fig. S7.** Effect of considering the rigid or flexible structure for the anion counterion on the dihedral angle distribution of the butyl side chain of [bmim]<sup>+</sup>.





**Fig. S8.** Effect of anion type (left panels), a rigid or flexible model of the anion (middle panels), and a unit or scaled charge model (right panels) on the histogram of the intramolecular ( $N_A-C_T$ ) distance of the cation as a good indicator of the different butyl side chain conformations in the [bmim][PF<sub>6</sub>] and [bmim][FAP] ILs at 400 K.