Supplementary Information

Toward Understanding the Structural Heterogeneity and Ion Pair Stability in Dicationic Ionic Liquids

Song Li,[a] José Leobardo Bañuelos,*[b,c] Pengfei Zhang,[c] Guang Feng,*[d] Sheng Dai,[c,e] Gernot Rother[c] and Peter T. Cummings[a]

[a] *Department of Chemical and Biomolecular Engineering, Vanderbilt University, Nashville, TN 37235, USA.*
[b] *ISIS Facility, STFC Rutherford Appleton Laboratory, Harwell Oxford,Didcot,OX11 0QX. Email:jose.banuelos@stfc.ac.uk*
[c] *Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA.*
[d] *State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan 430074, China. Email: gfeng@hust.edu.cn*
[e] *Department of Chemistry, University of Tennessee, Knoxville, TN 37996, USA*

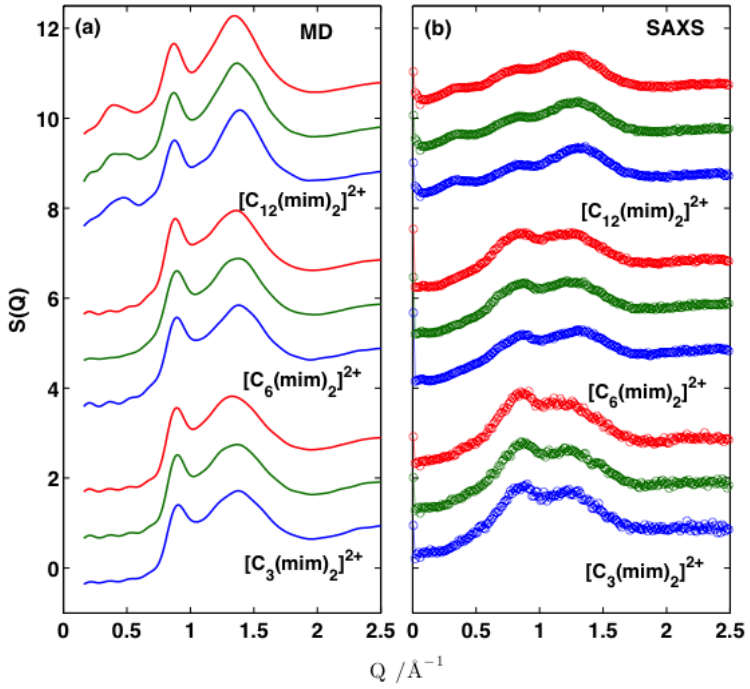

Figure S1. Total static structure function of $[C_n(mim)_2](Tf_2N)_2$ from MD simulation (a) and SAXS (b). The blue, green and red lines denote the data obtained at 280, 320 and 360 K, respectively.

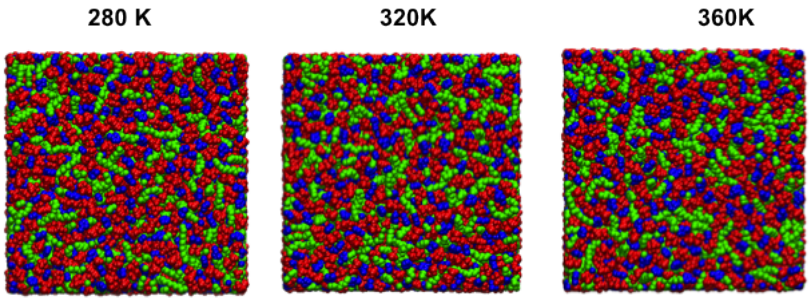

Figure S2. Snapshots of $[C_{12}(mim)_2](Tf_2N)_2$ from MD simulation at 280, 320 and 360 K: red, anion; blue, cation head; green, alkyl chain.

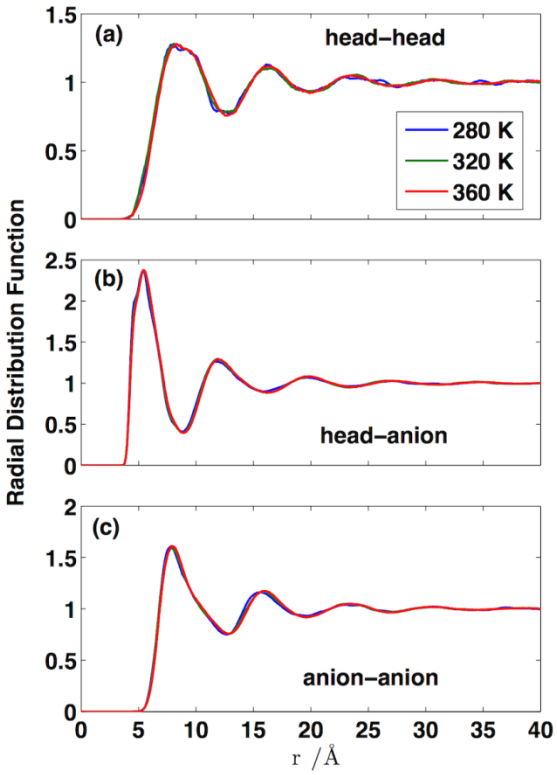

Figure S3. Radial distribution functions of cation head-head (a), head-anion (b) and anion-anion (c) of $[C_{12}(mim)_2](Tf_2N)_2$ calculated from MD simulation at 280, 320 and 360 K.

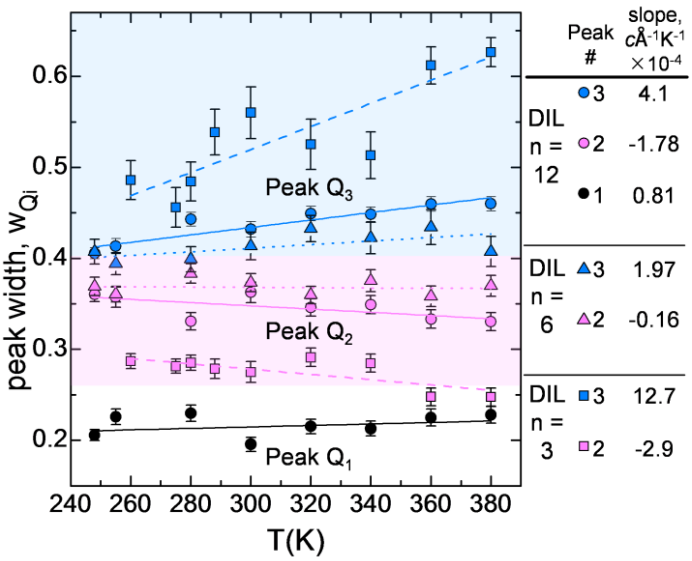

Figure S4. Peak width parameter for peaks Q_1, Q_2, and Q_3 plotted as a function of temperature. The slopes of each linear fit to the temperature-dependent data are shown to the right.

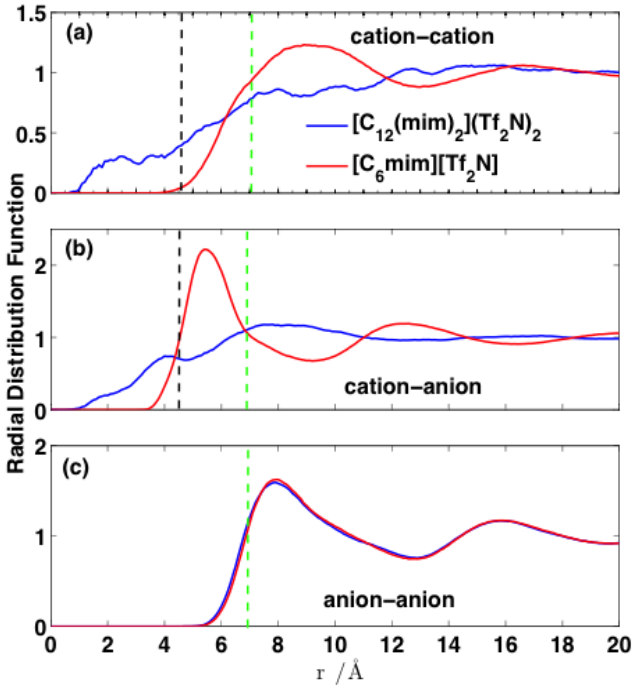

Figure S5. Radial distribution functions of cation-cation (a), cation-anion (b) and anion-anion (c) of $[C_{12}(mim)_2](Tf_2N)_2$ and $[C_6mim][Tf_2N]$ calculated from MD simulation at 320 K. The black and green dashed lines denote the positions at 4.5 Å and 7 Å, respectively.

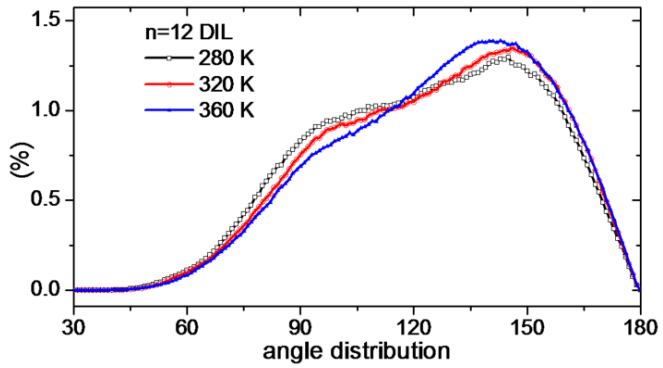

Figure S6. Dication linking chain angle distribution at 280K, 320K, and 360K for n = 12 DIL from MD simulation.