Supplemental Information

Graphical Comparison of Experimental and Simulation Crystal Structures

A graphical comparison of the two crystalline supercells, as viewed along the *b* axis which exhibits the smallest amount of dimensional shift. Figure S1a represents the experimental data, while figure S1b is the result after 2.5ns of simulation time. The crystalline orientations and relative ion positions are well preserved over the lifetime of the simulation.

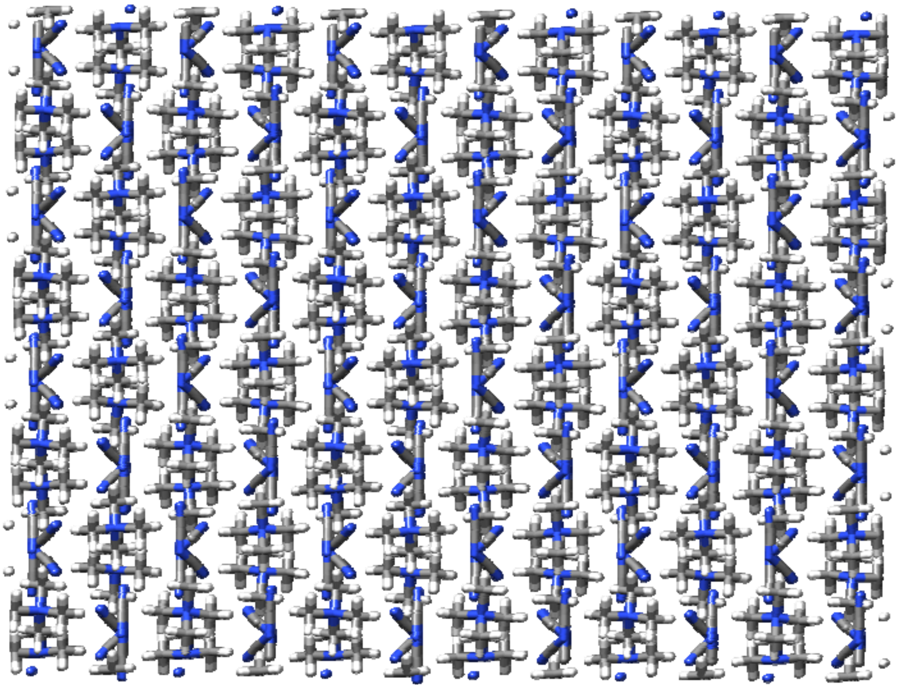

Figure S1a

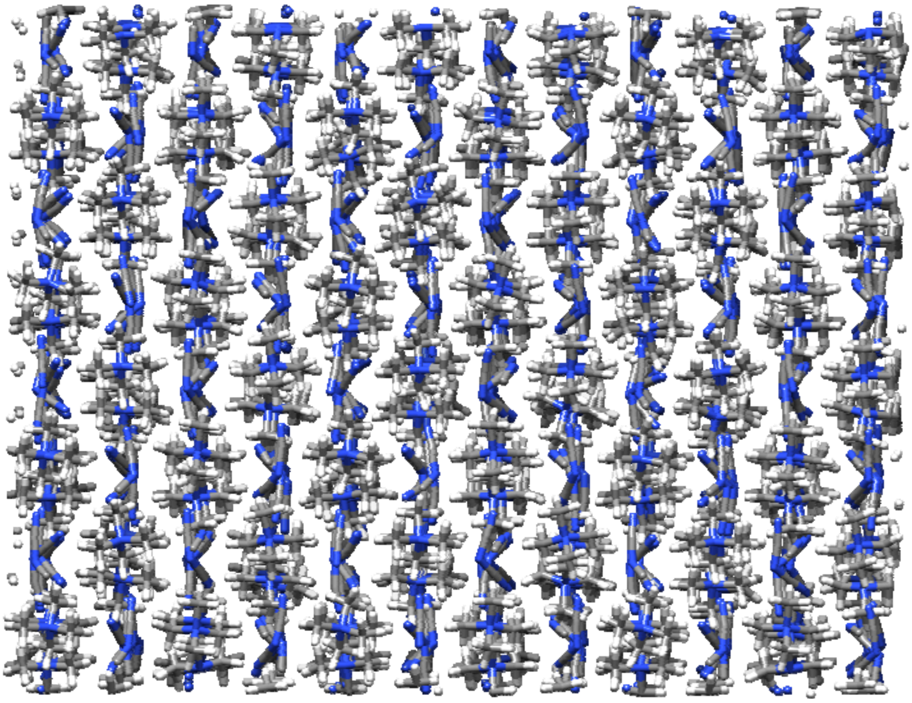

Figure S1b

N,N,N,N-Tetramethylammonium dicyanamide crystal as seen looking along the <*b*> lattice vector for (a) the structure as derived from x-ray crystallography and (b) the as-simulated structure. Both are at 123K.

Comparison of N,N,N,N Tetramethyl Ammonium Autocorrelation Functions Across Different Basis Vectors

Unlike the DCA autocorrelation functions, the TMA ACFs exhibit a singular decay profile regardless of the basis vector investigated in both the crystalline and liquid system. Figure S2 presents the autocorrelation function for a system well into the crystalline region at T=250K as well as one above the melting point at T=475K. While the characteristic decay constants are necessarily different due to the temperature difference, the overall decay curves for all three vectors at a single temperature are well fit by a single KWW function.

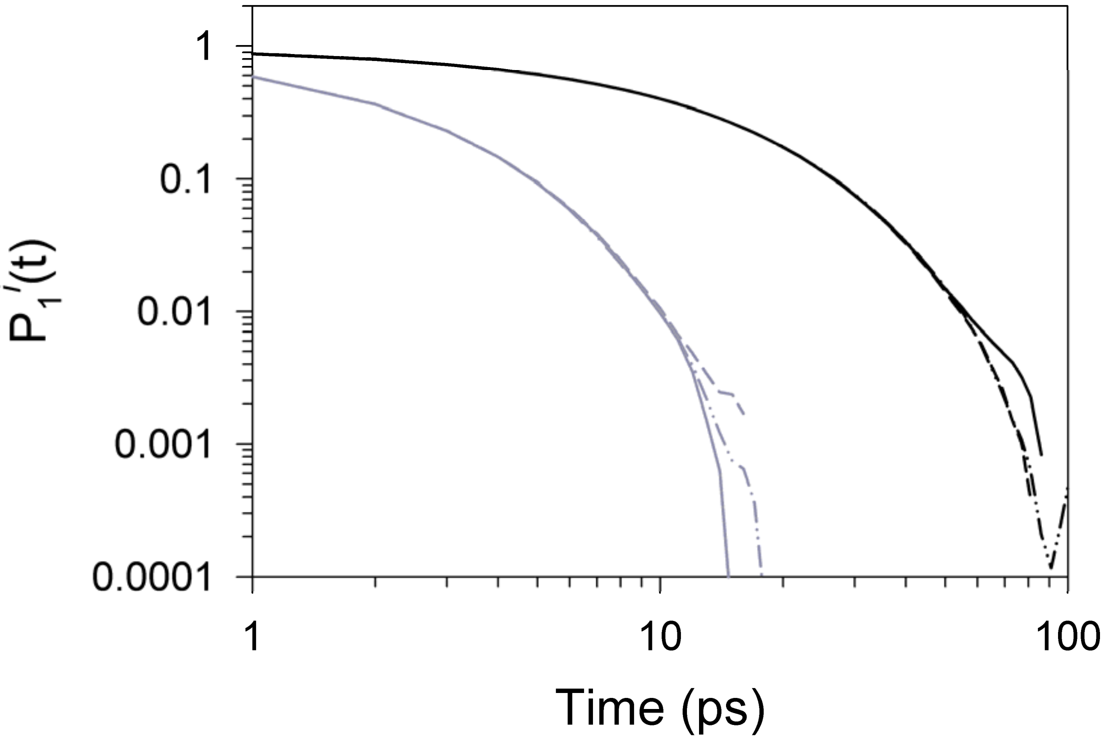

Figure S2

ACFs for N,N,N,N-TetramethylAmmonium in the crystalline system at T=250K (black) and in the liquid system at T=475K (grey) for the *x* (solid), *y* (dashed), and *z* (dash-dot-dot) basis vectors.

$P_2^i(t)$ ACF for dicyanamide

For temperatures below the melting point, the dicyanamide ion exhibits slow relaxation of the $P_2^i(t)$ ACFs, with $P_2^y(t)$ and $P_2^z(t)$ decaying somewhat faster than $P_2^x(t)$, as shown in Fig. S3. The lack of decay over all but the highest crystalline temperatures implies that rotations occur in an almost strictly planar fashion, with one plane containing the *y/z* axes, and the other embedding the *x* axis.

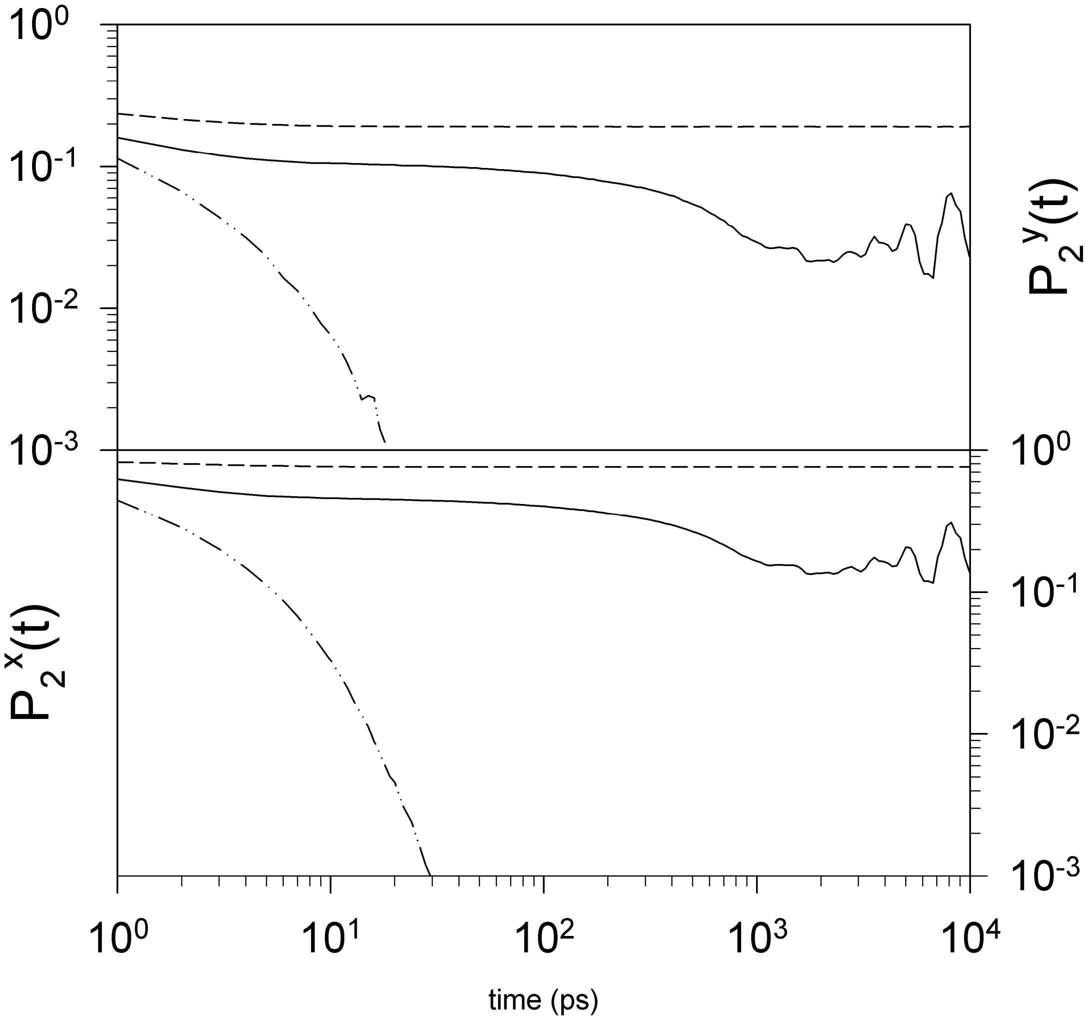

Figure S3

$P_2^i(t)$ ACFs for the dicyanamide ion at 300K (short dash), 425K (solid line) and 550K (dash-dot-dot).

Crystalline Diffusion

In order to determine the amount of diffusion within the crystalline systems, we investigated the average mean square displacement for the ionic species over time. For all three systems we investigate (pristine crystal, crystal with 0.3% vacancy, thin film), there is net displacement of the ions over time. However, for the pristine crystal the long term value of the displacement becomes constant, representing “rattling” of ions within the local crystalline cage. For the defective crystal the displacement grows slowly, with noticeable artifacts in the displacement trace which may represent effective shifting of the vacancies, formation of slip planes (which would be limited due to finite size effects within the crystal and hard to actually resolve), or other similar activated effects. For the thin film, the MSD is reminiscent of a slower liquid due to the melting of the film over time. Figure S4 includes representative traces from the simulated systems for the TMA ion, with the film system being represented by an outer layer as well as the centermost layer. MSD behavior of the DCA ion is qualitatively similar in all cases.

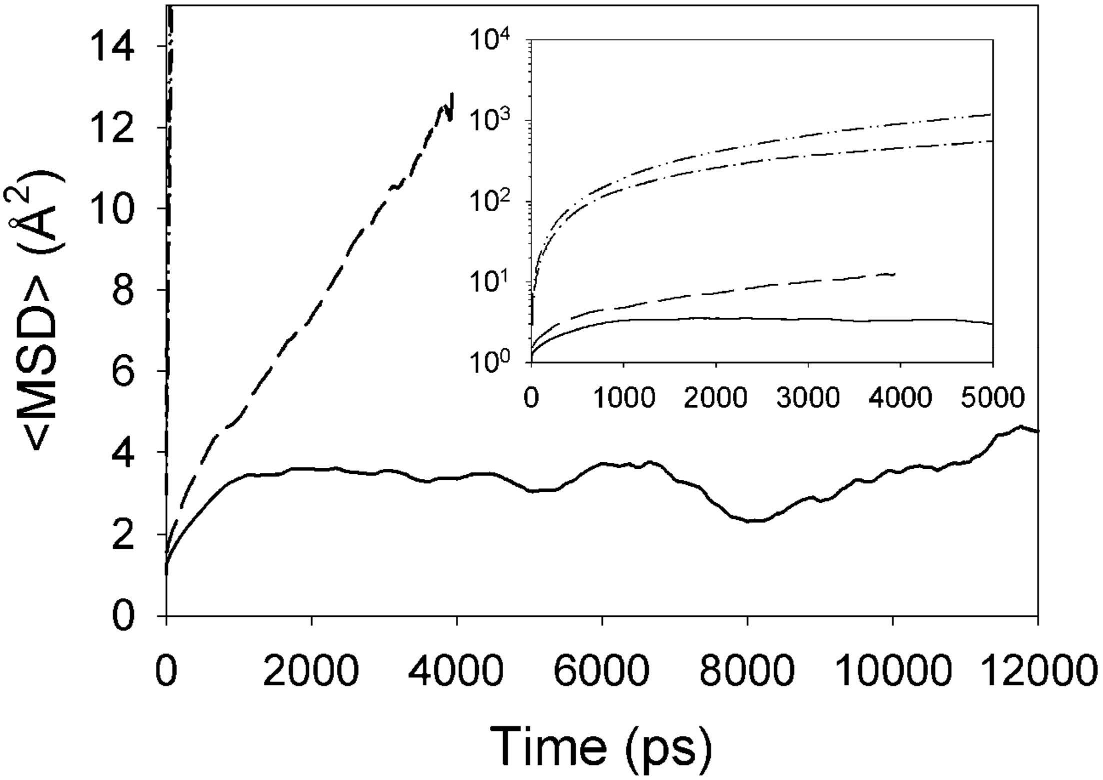

Figure S4.

Average mean squared displacement for the TMA ion in the perfect crystal (solid), 0.3% ion vacancy crystal (dashed), thin film inner layer (dash-dot) and thin film outer layer (dash-dot-dot). The main graph shows the comparison between the states on a linear-linear plot, highlighting differences between the perfect and defective crystal, while the inset shows the data on a log-linear plot to highlight the tremendous difference between the thin film and infinite crystal states.

Example Plot for Calculation of α_D

As described in the text, the dynamic degree of ion correlation (α_D) is extracted from the collective conductivity expression derived via the Einstein equations. This extraction is accomplished by graphically locating the plateau region of constant α_D value which occurs within time intervals which represent 2-4% of the overall simulation time. For intervals larger than this, statistics lead to poor convergence of α_D, while for intervals shorter than this sub-diffusive phenomena can skew the ion-ion correlation values. An example for the simulations performed in this paper is presented in Figure S5, where simulation lengths are 10ns or longer. Useful data can be seen for all species in the 100-200ps range plateaus.

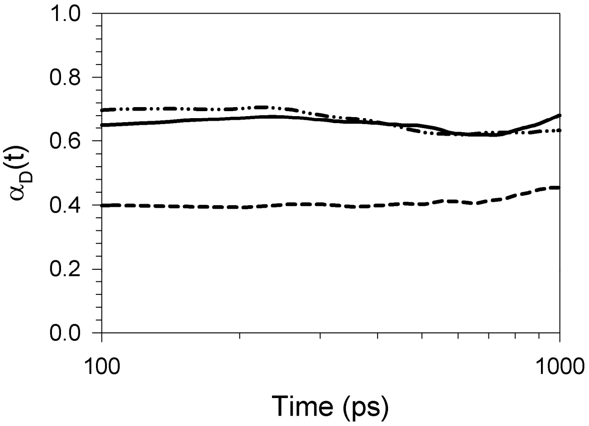

Figure S5

Calculation of the apparent degree of ion correlation for the TMADCA system in the defect-laden crystal at 425K (short dashes), and the liquids at 450K (solid) and 550K (dash-dot-dot).