Energy Materials

Supplementary Material

The ion-ion correlations in organic ionic plastic crystal

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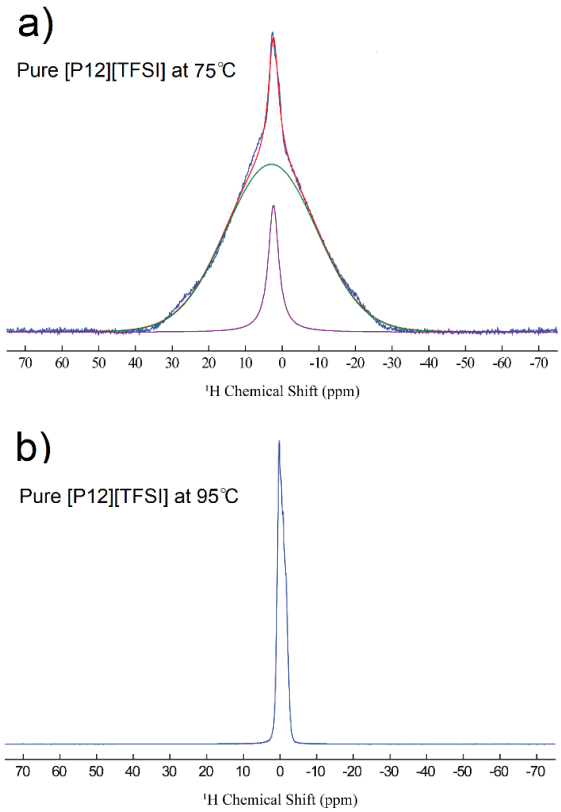
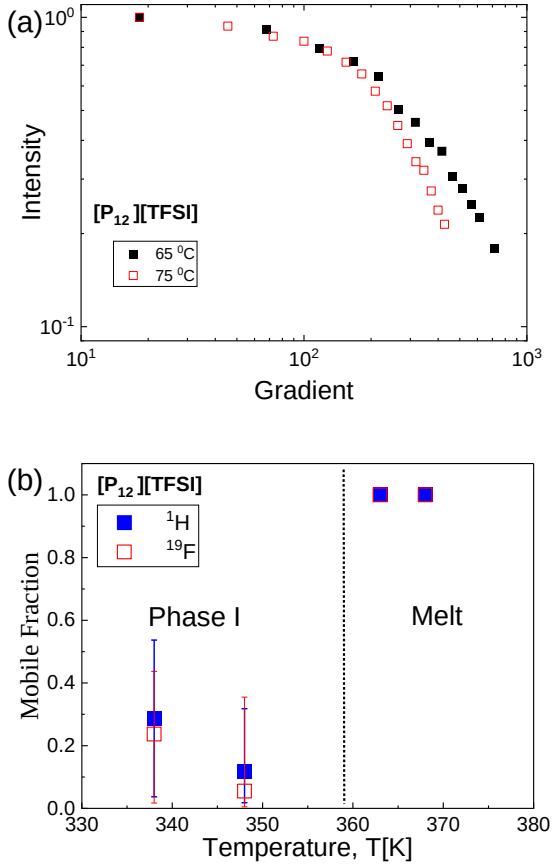
Ion diffusion and ion mobile fraction. For all nuclei at all temperatures, a single mobile species were found to be diffusing. Two methods for mobile portion estimation were used. Below melting points, only a portion of the nuclei contribute to diffusion, as evidenced by a superimposed broad and narrow peak in 1D NMR spectra (Figure S1a). As temperature increases, the proportion of the narrow peak to the broad peak increases (Figure S1b), until only the narrow peak remains after melting, indicating that all ions are mobile. The cation mobile fractions in solid Phase I were estimated by deconvolution of 1D NMR spectrum for 1H (Figure S1). Deconvolution method provides cation mobility fraction equal to ≈12% at 750C. Deconvolution for 19F was not possible due to overlapping probe background signals. Therefore, the fitting of

diffusion decay curves was used to estimate the cation and anion mobility fractions in solid states (Figure S2a). This method provides similarly low value ≈21% for 1H mobile fraction at 750C as from deconvolution method. Thus, the mobile fraction is correlated with translational diffusion rather than rotation. The mobility fraction for 19F and 1H estimated from diffusion curve is presented in Figure S2b. Because of fluorine background problem and fitting procedure, the diffusion curve method leads to big uncertainties, which results in uncertainties in estimation of the inverse Haven ratio.



Supplementary Figure S1. 1D NMR spectrum for ^{1}H in $[P_{12}][TFSI]$ in **(a)** Phase I at $75^{0}C$ and in **(b)** melted state at $95^{0}C$. In melted state only single narrow line is observed, while in Phase I broad and narrow peak are superimposed. The example of deconvolution is shown for $75^{0}C$.



Supplementary Figure S2. a) ^{1}H Diffusion decay curve versus gradient, showing single exponent decay. **b)** Mobile fractions of ^{1}H and ^{19}F in pure $[P_{12}][TFSI]$ as estimated by comparison of diffusing and non-diffusing portions of self-diffusion plots.

Supplementary Table S1. Diffusion coefficients for ^{1}H and ^{19}F in pure $[P_{12}][TFSI]$ at studied temperatures

T (°C)	^{1}H [m^2/sec]	^{19}F [m^2/sec]
65	4.51E-11	3.07E-11
75	5.75E-11	3.91E-11
90	1.48E-10	1.13E-10
95	1.64E-10	1.25E-10