Supplementary Information for

"Unique Phase Behavior of a Room-Temperature Ionic Liquid, Trimethylpropylammonium Bis(fluorosulfonyl)amide: Surface Melting and its Crystallization"

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Prior to the precise experiments using our ultra-sensitive DSC, a pre-experiment was performed using a commercially available DSC with normal resolution and normal scanning speed. The purpose of the pre-experiment was to get an overall picture of the phase behavior of the sample, $[N_{1113}][FSA]$. The scanning speed was 5 K/min (83.3 mK/s) and the sensitivity of the heat flux was thought to be about 2-3 mW. As shown in Fig. SI-1, the DSC pattern was very simple, namely an exothermic peak and an endothermic one.

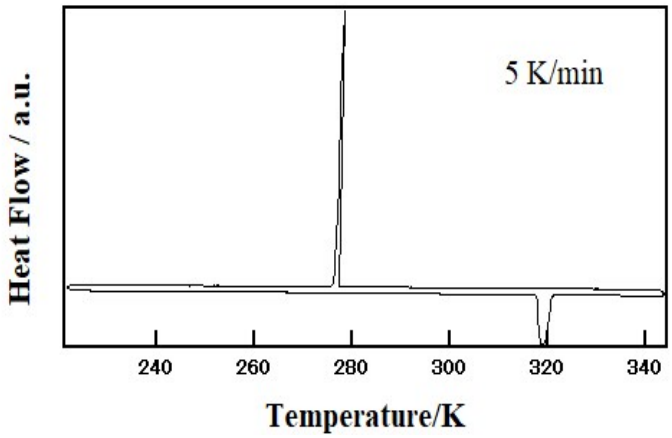

Fig. SI-1 Overall DSC trace of $[N_{1113}][FSA]$ using a commercially available DSC with the scanning speed of 5K/min.

The overall DSC trace for the same sample obtained using the ultra-sensitive DSC with the sensitivity of 2 nW is shown in Fig. SI-2. The scanning speed was 1 mK/s. The DSC trace was very complex, having several exothermic peaks. Fig. SI-3 is an enlarged view of the region where crystallization occurs over three cycles. As seen from the figure, the intensities of the exothermic

peaks were reproducible, although the order of their appearance was different.

Fig. SI-4 shows a DSC trace of another sample in the crystallization region.

From these experiments, we concluded as follows;

(1) There are some domains or chunks with thermally different environment in the sample.

(2) Structural relaxation of crystallization is thought to occur independently in each domain or chunk with different thermal environment. The ultra-sensitive DSC can detect each relaxation separately ((Fig. SI-2~4)).

(3) The wider exothermic peak in the pre-experiment (Fig. SI-1) is thought to be the pattern overlapped by several peaks caused by domains or chunks.

(4) Generation of such domains or chunk would strongly depend on the sampling.

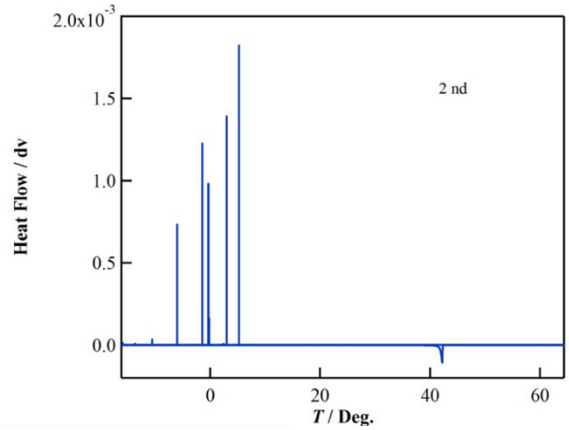

Fig. SI-2 Overall DSC trace of $[N_{1113}][FSA]$ using our ultra-sensitive DSC with the scanning speed of 1mK/s.

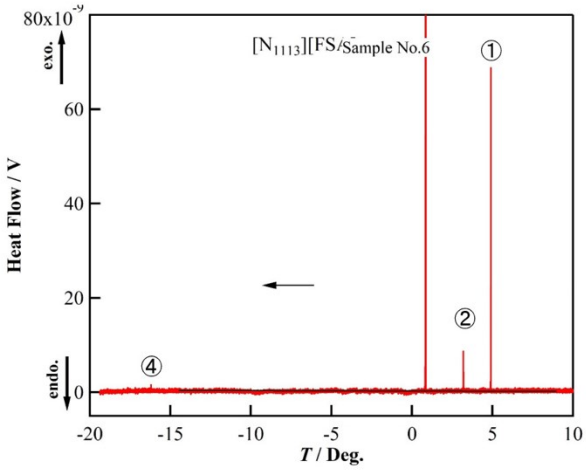

Fig. SI-3 The enlarged view of the region where crystallization occurs over three cycles. Each cycle is distinguished by different color, red, blue and green.

We thought that it was necessary to obtain the sample without such thermally different domains or chunks. After many trials changing the experimental conditions, we finally obtained the sample whose DSC trace is shown in Fig. 2 in the text. Namely, the adequate sampling is preheating the sample in liquid state at 400 K for 6 hours, about 80 K above the melting point, and then slow cooling to room temperature. The final pattern always has a strong exothermic peak (**peak a**), extremely weak exothermic peak (**peak b**) and a broad endothermic peak (**peak c**) (see Fig. 2 in the text), which we regard the DSC trace intrinsic to the sample itself.

The photograph of the sample which was prepared above and gave the DSC pattern of Fig. 2 in the text is shown in Fig. SI-5.

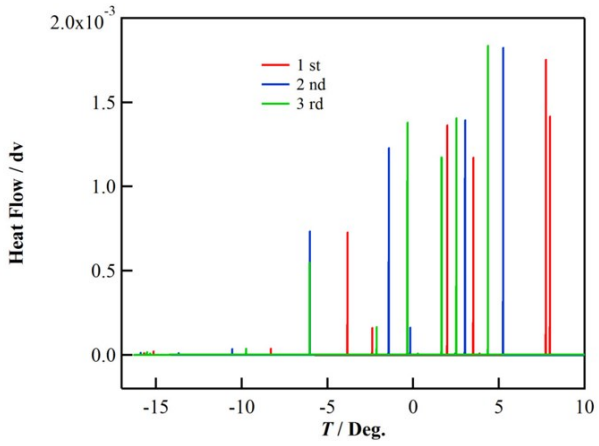

Fig. SI-4 The enlarged view of the region where crystallization occurs for another sample.

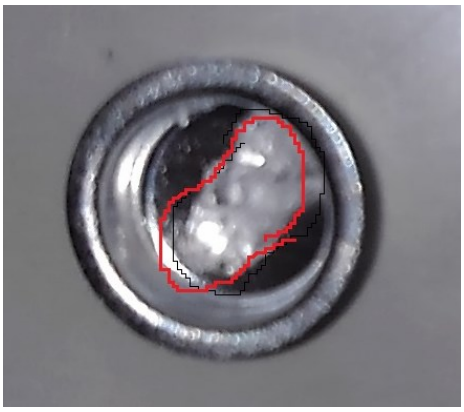

Fig. SI-5 The photograph of the sample which was prepared with the mentioned method and gave the DSC pattern of Fig. 2 in the text.