# Structural chemistry and stimuli-responsive phase transition of *N*,*N'*-dialkylimidazolium nonafluorobutanesulfonate ionic liquids

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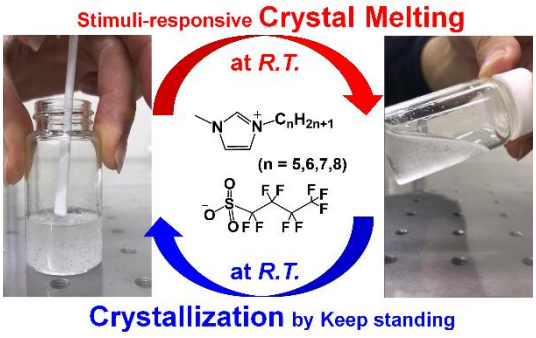
Ionic liquids (ILs) are composed of organic cations and anions, and exhibit low melting points (mp, below 100ºC). Although a melting point seems to strongly correlate with the molecular structure of IL, its precise structure and arrangement are usually quite difficult to be determined because of its liquefaction tendency.[1] If the structure of IL in a crystalline phase is revealed, we can discuss more about melting behavior of ILs from the structural aspects.

Here, we synthesized a series of *N*,*N'*-dialkylimidazolium room temperature ionic liquids (RTILs) with nonafluorobutanesulfonate ([$C_n$mim][NFBS] $n$ = 5–8), and characterized them by elemental analysis, NMR, SCXRD and DSC. Although any [$C_n$mim][NFBS] studied here were viscous "ILs" right after the preparation, they have crystallized after standing at room temperature for several hours or days. Mechanical stimuli like agitation with a spatula onto the crystalline [$C_n$mim][NFBS] ($n$ = 5–7) resulted in unexpected melting of these salts, while such a behavior was not observed for [$C_8$mim][NFBS]. The DSC analyses clarified that [$C_n$mim][NFBS] ($n$ = 5–7) exhibit multiple phase transitions from 268 K to 303 K including several pre-melting stages probably due to molecular motions of the alkyl or perfluoroalkyl chains. Furthermore, any of [$C_n$mim][NFBS] studied here exhibit negative d$P$/d$T$ slopes in a pressure dependency of the melting point. Such a characteristic thermal behavior would be ascribed to the C–H···O and C–H···F hydrogen bond networks to form hydrophilic and hydrophobic domains in the crystal lattices and also to give loosely packed crystal structures.[2]

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