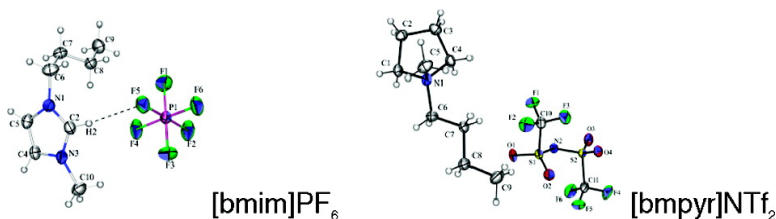## Communication

In situ Crystallization of Low-Melting Ionic Liquids

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[bmim]PF$_6$ [bmpyr]NTf$_2$

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In situ Crystallization of Low-Melting Ionic Liquids

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Studies of low-melting organic salts ("ionic liquids") are driven by intrinsic interest as well as by possible technical applications. The latter give rise to a series of practical challenges, particularly relating to purity, purification, recovery, and recycle. Zone melting,[1] the basis of the current study, is a possibly generic approach to ionic liquid purification and focuses attention on their phase behavior and crystallizability. While subambient zone melting of molecular organics has been described,[1a] there are, as far as we are aware, no published reports of organic salts being subjected to zone melting. Up to now, detailed consideration of the molecular structures of very low-melting ionic liquids in the solid state has depended on simulations and theoretical approaches[2] and on studies of analogues that are crystalline at ambient temperatures.[3] In fact, the lowest-melting ionic liquid for which a single-crystal X-ray structure is available is 1,3-dimethylimidazolium bis(trifluoromethanesulfonyl)amide[4] with a melting point of 22 °C. We report below the crystal and molecular structures of five ionic liquids, [emim]BF$_4$ (emim = 1-ethyl-3-methylimidazolium), **1**, [bmim]PF$_6$ (bmim = 1-butyl-3-methylimidazolium), **2**, [bmim]OTf (OTf = trifluoromethanesulfonate), **3**, [hexpy]NTf$_2$ (hexpy = *N*-hexylpyridinium and NTf$_2$ = bis(trifluoromethanesulfonyl)amide), **4**, and [bmpyr]NTf$_2$ (bmpyr = 1-butyl-1-methylpyrrolidinium), **5**, with a melting point of −1.3, +1.9, +6.7, −3.6, and −10.8 °C, respectively. **1**−**3**, prototypes of the so-called "neutral" ionic liquids, have been intensively investigated since first reported[5−7] in the early to mid 1990s. While the liquid structure and related simulations and theoretical studies of **1**[8] and **2**[9] have been described, surprisingly, their crystal and molecular structures are not known. **4** is of interest as there are no reports of crystal and molecular structure determinations for very low-melting *N*-alkylpyridinium salts.[10,11] The structure of an analogue of **5** (mp 40−55 °C) has been reported.[12]

Solidification of ionic liquids often results in glass formation,[13] a phenomenon of wider significance and interest.[14] However, by combining[15] Differential Scanning Calorimetry (DSC) and cryo-crystallography, we have established conditions under which single crystals of ionic liquids, **1**−**5**, can be grown. We have applied a modification of an in situ cryo-crystallization method, developed for gases and liquids by Boese et al.,[18] to avoid ionic liquid glass formation on cooling. We have grown single crystals of as-supplied commercially available (Merck KGaA) low-melting ionic liquids, **1**−**5**, from their melts. The molten material was first introduced into a Lindemann glass capillary (3 cm × 0.3 mm diameter), sealed by flame, and mounted vertically on a Bruker APEX CCD diffractometer in a stream of cold N$_2$ (Oxford Cryosystem) and cooled to −150 °C at ca. 6 °C/min. A 1 mm long section of the lower portion of the capillary was heated with an IR laser (using an optical heating and crystallization device[18] (Bruker AXS)) to create a molten zone that was slowly moved along the length of the capillary. The bulk temperature was increased in 10 °C steps, and the initiation of seed crystal formation was observed using a

video camera. The sample was then held at this temperature while the intensity of the scanning laser beam was slowly reduced to zero, promoting crystallization. Once the capillary was found to contain a polycrystalline column, the zone-melting technique described by Boese et al.[18,19] was applied to melt and regrow the crystals. Several melting and crystallization scans were made before a reasonable quality single crystal could be grown. Single-crystal diffraction data on **1** (collected at −100 °C), **2** (−80 °C), **3** (−73 °C), **4** (−148 °C), and **5** (−143 °C) were obtained using ω scans, and the crystal structures were solved and refined using standard methodology.[20]

Features of the crystal and molecular structures of compounds **1**−**5** that are noteworthy include the nature of hydrogen bonding between cation and anion,[5] anion disorder,[3] and crystal packing.

For **1**,[20] [emim]BF$_4$, DSC shows that crystallization does not occur on cooling to −173 °C, whereas, on heating, it occurs at ca. −65 °C, with a phase transition observed at ca. −20 °C, before melting is seen at −1.3 °C. The first data collected at −54 °C (immediately after crystallization) showed disorder at the anion (Figure 1a). A completely ordered structure was obtained from data[20] collected at −100 °C (Figure 1b). The imidazolium cations and BF$_4$ anions are linked via weak C−H···F interactions (H···F ≤ 2.6 Å). The cations are oriented such that they display intermolecular C−H···π interactions[21] and π···π stacking with a horizontal displacement that possibly contributes to the stability of the crystal packing (Figure 1c).

2,[20] [bmim]PF$_6$, also fails to crystallize on cooling, but on heating, does so at ca. −40 °C, followed by a phase transition at ca. −10 °C, before melting at +1.9 °C. The single crystal was grown at −30 °C, but to avoid possible disorder, data were collected at −80 °C. The ions in the crystal lattice are connected via C−H···F interactions (Figure 1d). Each PF$_6^-$ ion is involved in six different C−H···F interactions connecting four different imidazolium cations in the lattice. **3**,[20] [bmim]OTf, in contrast, crystallizes on cooling at ca. −20 °C, and on heating, a phase transition occurs at ca. −22 °C, before melting is seen at +6.7 °C. The [bmim]OTf was crystallized by cooling to −20 °C, and data were collected at −73 °C. The ions are packed in the lattice via ionic interaction between F$_3$CSO$_3^-$ and the imidazolium cation (Figure 2a). Further, several C−H···O hydrogen bonds (H···O ≤ 2.6 Å) connect adjacent cations to anions to build the lattice (Figure 2b).

4,[20] [hexpy]NTf$_2$, crystallizes at ca. −40 °C in the heating cycle and melts at −3.6 °C. A single crystal of **4** was grown at −10 °C. The anion was disordered at −30 °C, whereas the data collected at −148 °C yielded an ordered structure. **4** is only the second organic salt[4] in which the anion adopts a *cisoid* conformation (C−S···C−S dihedral angle = 34.5(2) and 24.7(3)°; Figure 2c). The cation and the anion are connected via interionic C−H···X (X = N, O) hydrogen bonds (H···X ≤ 2.6 Å) and weak C−H···F interactions (Figure 2d). **5**,[20] [bmpyr]NTf$_2$, does not crystallize on cooling, but at ca. −60 °C on heating. It melts at −10.8 °C. In this case, the
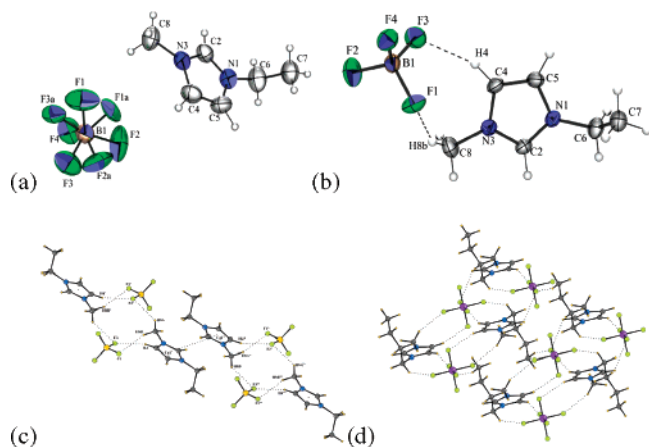
Figure 1. (a) Disordered [emim]BF$_4$ at −54 °C. (b) Ordered [emim]BF$_4$ at −100 °C. (c) Interionic interactions in [emim]BF$_4$. (d) Interionic interactions in [bmim]PF$_6$. (See ref 20.)
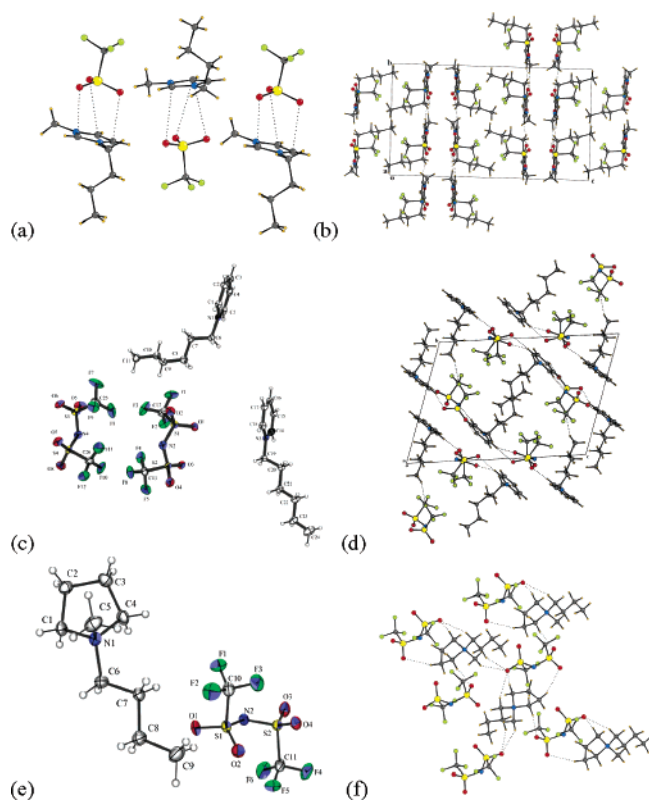

Figure 2. (a) Interionic interaction in [bmim]OTf. (b) Packing of ions in [bmim]OTf. (c) Asymmetric unit of [hexpy]NTf$_2$ with *cisoid* anion conformation. (d) Packing of [hexpy]NTf$_2$. (e) Asymmetric unit of [bmpyr]-NTf$_2$ with *transoid* anion conformation. (f) Interionic interactions in [bmpyr]-NTf$_2$. (See ref 20.)

NTf$_2$ anion adopts a *transoid* conformation (C−S···C−S dihedral angle = 161.7(2)°; Figure 2e). The ions pack in the lattice via a number of weak C−H···O hydrogen bonds (Figure 2f).

Some materials, such as [bmim]BF$_4$ and [bmim]N(CN)$_2$, have, so far, resisted crystallization by the methods described above. Modified methods are under investigation to bring this about.

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