

Effect of Water on the Molecular Structure and Arrangement of Nitrile-Functionalized Ionic Liquids

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Water changes the physical properties of ionic liquids (ILs). In this paper, the effect of water on ILs is investigated at the molecular level. The molecular structure and arrangement of 1-butyronitrile-3-methylimidazolium halide, in the presence and absence of the intruded water molecule, have been elucidated by single-crystal X-ray crystallography and near-infrared Raman spectroscopy. Water molecule is found to change the conformation of the *n*-butyronitrile chain of the cation. The hydrogen bonding interaction between the anion and water molecule, leading to loose molecular packing, is most likely to be responsible for the change. Distinct molecular structures and arrangements of ILs with and without water molecule have been presented here for the first time. As the unique properties of ILs are related to their structures and molecular arrangements, the presence of water, wanted or unwanted, must be carefully examined in any kind of IL research and applications.

Introduction

The past few years have witnessed a steady growth of research in the field of ionic liquids (ILs)¹ because of their unique properties, which opens up the possibility of realizing a vast range of novel applications such as in organic synthesis,² electrochemistry,³ and biocatalysis.⁴ These nonvolatile, nonflammable ILs are also used as better heat-transfer fluids and lubricants.⁵ Recent discovery of magnetic ionic liquids has further broadened the scope of IL applications.^{6,7} ILs represent a fundamental and significant departure from the conventional liquids in their constitution itself. In ILs, molecular ions are building blocks as opposed to the molecules in traditional molecular liquids and therefore the Coulombic interaction is the dominate interaction rather than the dipolar and other higher order interactions. In addition to these interactions, there are relatively weaker interactions such as H-bonding, π -stacking and aliphatic interactions. The nature of the interactions in different ILs may however differ from one to another. Even though there have been lots of studies on their applications, little has been explored with regard to their structures in the solid and liquid phases. The solid-state structures of IL compounds provide the foundation in understanding the structural principles that govern the organization of ions even in the liquid state where direct determination of the structure is rather difficult. Recently, ourselves^{8–10} and Holbrey et al.¹¹ have independently found the crystal polymorphism of a prototype IL, 1-butyl-3-methylimidazolium (bmim), chloride, and bromide. The polymorphism was attributed to the rotational isomerism of the butyl group in the bmim cation. The *trans*–*trans* (TT) form exists in one crystal and the *gauche*–*trans* (GT) form exists in the other. We further extended our study and proved the coexistence of two conformers in the liquid phase of ILs with the help of Raman spectroscopy. The existence of local structure

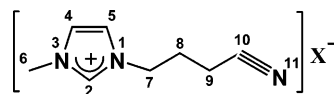
in bmimX in the liquid phase was first suggested by unusually slow equilibration time between the TT and GT forms of bmim⁸ and further demonstrated by wide-angle X-ray scattering.¹²

It has been recognized that many ILs are hygroscopic and can absorb a significant amount of water from the atmosphere.^{13–15} The physical properties of ILs, such as polarity, viscosity, solubility, and conductivity, not only change by the presence of water but also depend on the amount of water absorbed. Very recently, the dependence of the activity of cofactor-dependent enzyme-catalyzed oxidation in a functionalized ionic liquid upon the water content has been examined, and a significant effect of the water was observed.¹⁶ The authors commented that the role of water present as impurity is very important and requires extensive investigation. An adverse effect of unwanted presence of water in ILs has also been reported recently by Rodgers and co-workers,¹⁷ which exactly contradicts the “green” nature of ILs. Hence, information on the structures of ILs and their interactions with water are important not only in the fundamental research but also in practical applications. Various experimental techniques such as near-IR,¹⁵ fluorescence,¹⁴ NMR spectroscopy,¹⁸ and surface-sensitive vibrational spectroscopy, sum frequency generation (SFG)^{19,20} along with the theoretical studies,^{21,22} have been employed to study the interaction between water and ILs. The SFG vibrational spectroscopic study indicates the orientational rearrangement of the cation of a hydrophobic IL on the equilibration with water vapor.²⁰ Even though all of these studies point out that water has profound effect on the structures and properties of ILs, these techniques fail to provide a direct picture on the molecular level structure, arrangement, and interaction between IL and water.

Recently, a relatively new type of ILs, defined as task-specific or functionalized ILs,^{23,24} are attracting a considerable amount of attention. Functionalized ILs can be considered a unique subclass of ILs which possess some unique features due to the presence of functional groups which otherwise are not present in the ordinary ILs. Incorporation of functional groups allows

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CHART 1: 1-Butyronitrile-3-methylimidazolium Halide, nbmimX (Where X = Cl or I)

these ILs to interact with the dissolved substrates in specific ways. These functionalized ILs are finding an increasing number of applications^{23,24} in synthesis, separation, catalysis, and electrochemistry.

We have synthesized and studied the nitrile functional group incorporated methylimidazolium cation based ILs as shown in Chart 1.

Single-atom halogen anions have been chosen to reduce the complexity of the system and also to focus our study on the organic cation moiety. Nitrile-incorporated imidazolium cation based ILs was first reported by Dyson et al. and have been shown to be good solvents and ligands for the catalysis reactions.²⁵

During the course of investigation on structural aspects of these functionalized ILs, we discovered that water affects the molecular structure of the IL, thereby affecting the whole molecular arrangement. Here, we present vivid pictures of molecular structures and arrangements of two functionalized ILs with and without water molecules, as obtained by single-crystal X-ray crystallography. In the case where obtaining a single crystal was not possible, Raman spectroscopy provided us with valuable information leading to the same conclusion. To the best of our knowledge, this is the first molecular level report which clearly depicts the influence of water on the molecular structure and arrangement of ILs.

Experimental Section

Synthesis and Crystal Preparation. Under dry N₂ atmosphere, redistilled *N*-methylimidazole (Aldrich Chemicals), and 1-halobutyronitrile (Wako Chemicals)²⁶ (1:1.3 mole ratio) were stirred either at room temperature (~25 °C for the chloride salt) or at ~0 °C (for the iodide salt) for 36 h. The resultant viscous liquids were washed with dry ethyl acetate for several times and dried under high vacuum to get the required white solid products. The white products were recrystallized under different conditions for different crystals, as follows: (i) The dry (i.e., without water molecule) 1-butyronitrile-3-methylimidazolium chloride, nbmimCl, crystal was obtained by recrystallization from dry acetonitrile at room temperature. (ii) The nbmimCl·H₂O crystal was obtained from diethyl ether and dry acetonitrile mixture at room temperature. We suspect that it was the diethyl ether, which brought the intruder water molecule in to the crystal system. (iii) Small rectangular-shaped 1-butyronitrile-3-methylimidazolium iodide, nbmimI, crystals were obtained from dry acetonitrile at -20 °C. Slow crystallization (at room temperature) gave big crystals. On exposure to air for a few seconds, these big transparent crystals became opaque.

Instrumentation. X-ray diffraction experiments were carried out using a Rigaku/MSC Mercury CCD system with graphite-monochromated Mo K α radiation (λ = 0.710 70 Å), either at low temperature or at room temperature. A single crystal with approximate dimensions of 0.6 × 0.4 × 0.2 mm was mounted in a N₂-filled sealed glass capillary. All the operations were done in a N₂-filled glovebox. Data were collected and processed using CrystalClear (Rigaku)²⁷ software. Structures were solved by direct methods (either SIR97^{28,29} or SHELXS-97³⁰). The non-hydrogen atoms were refined anisotropically while hydrogen atoms were refined isotropically.

TABLE 1: Crystal Data³¹ and Structural Details for nbmimCl, nbmimCl·H₂O, and nbmimI

	nbmimCl	nbmimCl·H ₂ O	nbmimI
chem. formula	C ₈ H ₁₂ N ₃ Cl	C ₈ H ₁₄ N ₃ ClO	C ₈ H ₁₂ N ₃ I
fw	185.66	203.66	277.11
cryst syst	monoclinic	monoclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> ₁ 2 ₁ / <i>n</i> ₁	<i>P</i> 1
<i>a</i> (Å)	8.745(4)	7.216(5)	7.866(2)
<i>b</i> (Å)	10.993(5)	13.874(5)	7.928(2)
<i>c</i> (Å)	10.410(5)	10.896(5)	9.050(2)
α (deg)	90	90	87.380(6)
β (deg)	102.383(2)	99.055(5)	87.004(6)
γ (deg)	90	90	75.926(5)
vol (Å ³)	977.5(8)	1077.3(10)	546.4(2)
<i>Z</i>	4	4	2
<i>D</i> _{calcd} (g cm ⁻³)	1.26	1.26	1.68
temp (±1, K)	148	293	148
measd	5327	6522	3905
unique reflns	1583	1934	2295
data/param	10.02	15.59	18.81
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.034	0.055	0.029
wR2 (all data)	0.082	0.1569	0.087
GOF	1.092	1.070	1.064

A laboratory-made Raman spectrometer employing a Q-switched Nd:YAG laser (wavelength, 1064 nm; repetition rate, 10 kHz; Spectra Physics X30-106QA) as an excitation source was used to acquire Raman spectra at room temperature. Scattered Raman signals were collected at 90° geometry and focused on the entrance slit of a single polychromator (Horiba Jobin-Yvon, TRIAX320) through a notch filter to eliminate Rayleigh scattering. An InP–InGaAsP near-infrared image intensifier was used to intensify the signal, and finally signal was detected by a thermoelectrically cooled (-70 °C) CCD detector (Princeton Spec-10: 256B). The detector was gated (100 ns) synchronously with a laser pulse to eliminate the effect of room light and also to reduce the dark noise. The spectral resolution was ~10 cm⁻¹. The laser power at the sample point was ~150 mW, while the typical exposure time was 2 min. The samples were placed either in a screw cap or in a sealed vial.

Results and Discussion

The crystal data and structural details as determined by single-crystal X-ray diffraction technique are presented in Table 1.

The structure of nbmimCl determined from these data is shown in Figure 1 (left). The asymmetric unit contains only one cation and one anion. The imidazolium ring is found to be planar and approximately regular pentagonal, indicating appreciable charge delocalization in the ring. The conformational flexibility inherent in the *n*-butyronitrile side chain is of particular interest to us. In nbmimCl, the *n*-butyronitrile chain is found to be in an all-trans conformation. The crystal structure and the parameters of nbmimCl crystal match well with those reported by Dyson et al.,²⁵ and all-trans conformation is also evident in their crystal system. This all-trans conformation was also observed in one of the crystal polymorphs of 1-butyl-3-methylimidazolium chloride, bmimCl.⁹

The nbmim-functionalized ILs are found to be highly hygroscopic. During the crystallization of nbmimCl from diethyl ether and acetonitrile mixture at room temperature, we unexpectedly obtained crystals of nbmimCl·H₂O, where a water molecule crept into the system. Fortunately, we could also obtain a single-crystal suitable for the X-ray crystallographic study. The structure obtained from the X-ray study is shown in Figure 1 (right). In addition to the presence of one water molecule with one cation (nbmim) and one anion (Cl⁻) in the asymmetric unit, the striking difference is the change of conformation of the

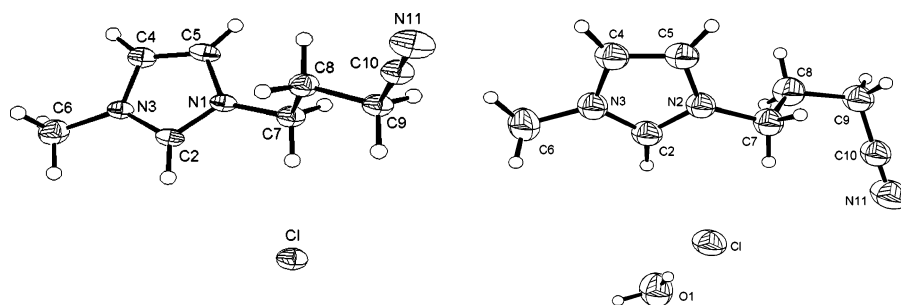


Figure 1. (Left) Crystal structure of 1-butyronitrile-3-methylimidazolium chloride, nbmimCl. The *n*-butyronitrile side chain has all-trans conformation. (Right) Crystal structure of nbmimCl·H₂O. The *n*-butyronitrile chain has trans-gauche (with respect to C7–C8 and C8–C9 bonds, respectively) conformation.

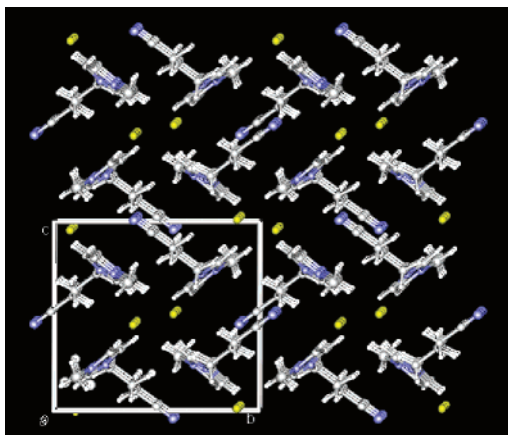


Figure 2. View (down to *a*-axis) of molecular arrangement in the nbmimCl crystal.

n-butyronitrile side chain of the nbmimCl cation. Following the number scheme shown in Figure 1, the conformation around the C8–C9 bond is changed from trans to gauche. The torsion angles involving C7–C8 and C8–C9 bonds are found to be 168.5 and 59.5° for nbmimCl·H₂O, whereas, for nbmimCl, these are 174.7 and 179.0°, respectively. This observation itself suggests that water molecule changes the molecular conformation of the cation. At this point, it is worth mentioning that so far we have not encountered this “trans-gauche” (with respect to C7–C8 and C8–C9 bonds, respectively) conformation in any other ILs where the cation is either nbmim or bmim. Hence, it appears that water molecules somehow stabilize this unusual conformation. However, water is found to have no appreciable influence on the bond lengths and bond angles of the imidazolium ring.

Coming to the conclusion that a water molecule is responsible for the change of conformation of the *n*-butyronitrile chain, we were motivated to search for the reason. To do so, we looked into the molecular arrangement to discover what made this trans-gauche structure stable. We have observed that molecular arrangements in ILs arise out of competitive influence of the Coulombic force, the van der Waals attractive forces (such as

H-bonding), and the aliphatic interaction by hydrocarbon chains.⁹ Figure 2 shows the molecular arrangement of nbmimCl in the crystal, viewed along the *a*-axis. This arrangement is quite similar to what we have seen for bmimCl, the crystal 1 polymorph (i.e., trans-trans conformation of the *n*-butyl chain).^{9,32} A couple of nbmim cations form a pair through an aliphatic interaction of a stretched *n*-butyronitrile group. These pairs stack together and form columns in which all the imidazolium ring planes are parallel to one another. Figure 2 also shows the channels made by cation pillars in which chloride anions are accommodated as a chain. The distance between two chloride anions in the chain is too large to have any specific interaction. Chloride anions are found to be away from the methyl groups and rather close to the hydrophobic region produced by the *n*-butyronitrile chains. Table 2 shows all the possible hydrogen bonding that exists in the nbmimCl crystal between a cation and adjacent chloride anions. All three hydrogens of the imidazolium ring are found to have H-bonding interaction with chloride anions. The H-bondings involving C4–H and C5–H are almost linear (C4–H···Cl, 2.62 Å, 172°; and C5–H···Cl, 2.70 Å, 168°). Other than imidazolium hydrogens, methylene hydrogens at C7 of the *n*-butyronitrile side chain and one of the methyl hydrogens at C6 are found to have close contact with chloride anions that are less than the sum of the van der Waals radii (3.0 Å).

On the other hand, for the nbmimCl·H₂O system, which is distinguished by the presence of H₂O and gauche conformation around the C8–C9 bond, there are *only* three C–H···Cl hydrogen bonds connecting a cation and anions in addition to the two H-bonds between the water oxygen molecule and the chloride anion. Figure 3 shows the molecular arrangement in the crystal for nbmimCl·H₂O. All the hydrogen bonds are tabulated in Table 3. Figure 4 shows the two strong classical hydrogen bonds that keep the water molecules together with chloride anions (2.22, 2.27 Å and 173, 165°, respectively), thus making a rhombohedra-like (H₂O)₂(Cl[−])₂ complex. No direct interaction between water and cation is observed, even though the presence of water is responsible for the change of the structure of the cation. Among the three C–H···Cl hydrogen bondings, the strongest one is found between C2–H and the

TABLE 2: Hydrogen Bonding Parameters for nbmimCl Crystal System

donor (D)–H···acceptor (A)	[ARU] ^a	H···A (Å)	D···A (Å)	D–H···A angle (deg)
C(2)–H···Cl	[4554.02]	2.66	3.5240	147
C(4)–H···Cl	[3666.02]	2.62	3.5402	172
C(5)–H···Cl		2.70	3.5865	168
C(6)–H···Cl	[4554.02]	2.76	3.6898	157
C(7)–H···Cl	[2545.02]	2.67	3.5483	146
C(7)–H···Cl	[3566.02]	2.73	3.6139	149

^a Translation of ARU(asymmetric residue unit) code to equivalent position code: [4554.] = *x*, 1/2 – *y*, –1/2 + *z*; [3666.] = 1 – *x*, 1 – *y*, 1 – *z*; [2545.] = –*x*, –1/2 + *y*, 1/2 – *z*; [3566.] = –*x*, 1 – *y*, 1 – *z*.

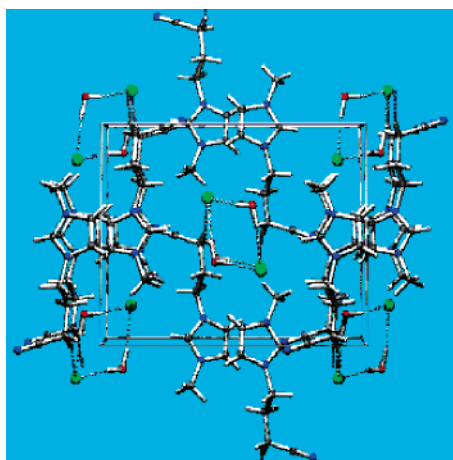


Figure 3. View (down to *a*-axis) of molecular arrangement in nbmimCl·H₂O crystal. H-bondings between O—H and C9—H with Cl[−] anion are shown. (Cl, O, N, C are shown as green, red, blue, and black circles, respectively.)

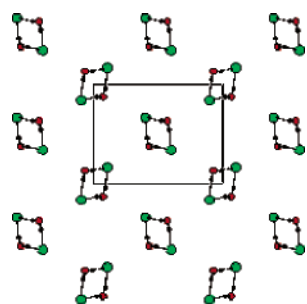


Figure 4. Hydrogen-bonded assembly of water molecules (small circle) and chloride anions (bigger circle) in [nbmim]Cl·H₂O crystal. Cation is not shown for clarity.

chloride anion (2.65 Å, 149°). Two other relatively weaker H-bondings are located between C7—H and C9—H with the chloride anion. Out of these two hydrogen bonds, C9—H···Cl is found to be more linear and stronger. It is worth noting that *this* H-bonding is absent in the nbmimCl system (i.e., without the water molecule). An easy comparison between Tables 2 and 3 reveals that the nbmimCl·H₂O system contains half of the C—H···Cl hydrogen bonds compared to that of nbmimCl connecting the cation and anion. This fact indicates that the cations and anions in nbmimCl·H₂O are loosely packed. Most probably, this loose packing is to accommodate the intruder water. It also appears that the water molecule changes the position of chloride anion and takes it away from the imidazolium ring, and that may be one possible reason hydrogen bonding involving C4—H, C5—H, and the chloride anion are absent in the nbmimCl·H₂O system. On the other hand, the H-bonding, between C9—H and the chloride anion helps to achieve the new conformation (i.e., gauche) around the C8—C9 bond so that it can accommodate the H-bonded chloride and water molecule together. Also, this chloride—water hydrogen-bonded complex makes the effective size of the anion bigger

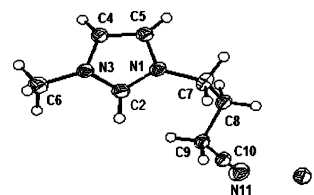


Figure 5. Crystal structure of nbmimI. The *n*-butyronitrile chain has gauche—trans (with respect to C7—C8 and C8—C9 bonds, respectively) conformation.

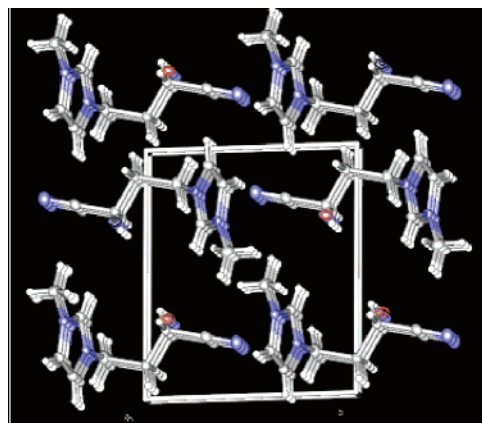


Figure 6. View (down to *a*-axis) of molecular arrangement in transparent nbmimI crystal. Red ellipse indicates the position of iodide anions.

and is located close to C9—H with a favorable angle to have H-bonding interaction.

Unlike the nbmimCl system, where we were able to confirm the existence of the two isomers by single-crystal X-ray diffraction, the effect of water on the iodide derivative of the same cation, nbmimI, was studied by near-IR—Raman spectroscopy in addition to single-crystal X-ray diffraction technique. During the preparation of crystals, it was observed that the transparent crystals of nbmimI become opaque when they are exposed to air momentarily. We have determined the molecular structure of nbmimI (transparent crystal) by single-crystal X-ray diffraction technique (shown in Figure 5).

The *n*-butyronitrile side chain is in a gauche (the torsion angle around the C7—C8 bond is 67.6°)—trans (the torsion angle around C8—C9 is 173.9°) conformation. This is the same conformation that has been found in one of the polymorphs in bmimCl.¹⁰ The distance and angle between C2—H and I[−] are quite favorable to have strong H-bonding interaction (2.90 Å, 173°; the sum of the van der Waals radii is 3.18 Å). No other strong H-bonding is detected in this system. Figure 6 shows the molecular arrangement in the crystal. The packing is similar to that of nbmimCl except the fact that close association of *n*-butyronitrile chains (hydrophobic region) is absent in the nbmimI crystal.

As stated earlier, when these nbmimI crystals were exposed to air momentarily, they became opaque. Hereafter, we will be

TABLE 3: Hydrogen Bonding Parameters for nbmimCl·H₂O Crystal System

donor (D)—H···acceptor (A)	[ARU] ^a	H···A (Å)	D···A (Å)	D—H···A angle (deg)
O(1)—H···Cl	[2655.03]	2.22	3.1699	173
O(1)—H···Cl	[4555.03]	2.27	3.2169	165
C(2)—H···Cl		2.65	3.4809	149
C(7)—H···Cl		2.83	3.6704	146
C(9)—H···Cl	[4555.03]	2.81	3.7574	166

^a Translation of ARU(asymmetric residue unit) code to equivalent position code: [4555.] = $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; [2655.] = $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

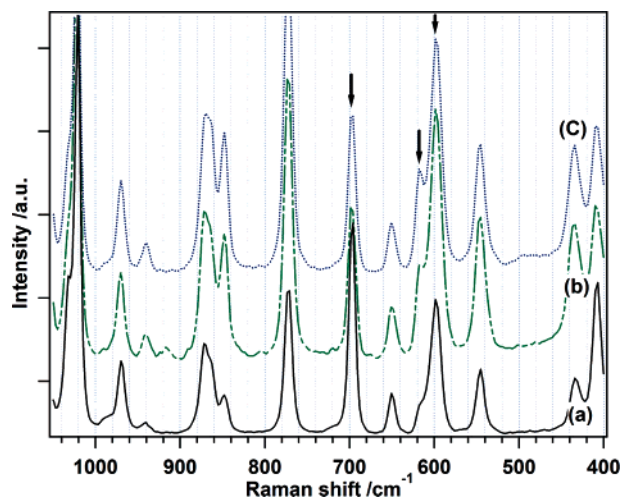


Figure 7. Raman spectra of (a) transparent, (b) opaque, and (c) moisture-included crystals of nbmimI.

using the “transparent” terminology to address nbmimI without moisture, (for which we have the single-crystal X-ray structure) and “opaque” for moisture-included nbmimI.

An attempt to determine the crystal structure of opaque nbmimI crystal was not successful due to the lack of suitable single crystals. It has been shown that Raman spectroscopy can be very useful for elucidating the structure of 1-butyl-3-methylimidazolium (bmim) cation based ILs.^{8,10,32} Raman spectra of the transparent and opaque nbmimI crystals are shown in Figure 7. Several skeletal modes of the imidazolium ring give rise to characteristic Raman bands in this wavenumber region. The bands at 600 and 695 cm⁻¹ (marked by arrows in Figure 7) are the characteristic bands for the gauche conformation around the C7–C8 bond. These bands arise out of deformation vibration of the imidazolium ring that is coupled with the CH₂ rocking vibration of the C8 methylene group. Comparing the Raman spectra of the transparent and opaque nbmimI crystals, we note that the two spectra differ considerably with respect to intensities of some bands. The intensity ratio of the 695 and 771 cm⁻¹ bands differs in the transparent and opaque crystals. Similar observation is also observed for the 848 and 872 cm⁻¹ bands. Notably, the marker band for the trans conformation (around C7–C8)^{8,10} clearly appears at 617 cm⁻¹ in the opaque crystal. The appearance of this marker band indicates the formation of the trans conformation around C7–C8 on absorption of moisture from the air. We deliberately exposed the transparent crystal to the open air for a few seconds and recorded the Raman spectrum (Figure 7, top). This spectrum resembles quite well that of the opaque crystal (with stronger appearance of 617 cm⁻¹ band), indicating that the structural change is due to the moisture. We also observed a weak peak of the O–H stretch band at 3300 cm⁻¹ in the Raman spectrum of the nbmimI opaque crystal (see Supporting Information). This peak was absent for a transparent crystal. The position of the peak (3300 cm⁻¹) suggests that H₂O is present in the system as strongly hydrogen bonded.

In conclusion, we have determined the structures of nitrile-incorporated ILs with and without water molecule by single-crystal X-ray diffraction technique and Raman spectroscopy. It is found that a water molecule changes the conformation of the *n*-butyronitrile side chain in 1-butyronitrile-3-methylimidazolium cation based ILs. Water molecules make a H-bonding network with anions and displace the anion position, thereby disturbing the stable molecular structure and arrangement.

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Supporting Information Available: (1) Crystallographic information files (CIF) for nbmimCl, nbmimCl·H₂O, and nbmimI and (2) Raman spectra of transparent and opaque nbmimI crystals showing the presence of O–H stretch band at 3300 cm⁻¹ for opaque crystal. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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