Cation Conformational Changes of 1-Butyl-3-methylimidazolium HPSTAR Halides at High Pressures 558-2018

Fengjiao Chen,^{†,‡} Guoyong Fang,[§][®] Zhipeng Yan,[‡] Yuexiao Pan,[§][®] Jianbo Liu,^{*,†}[®] and Lin Wang^{*,‡}

[†]Key Laboratory of Advanced Materials (MOE), School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

[‡]Center for High Pressure Science and Technology Advanced Research (HPSTAR), Shanghai 201203, China

[§]College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325035, China

ABSTRACT: The cation structural changes of two 1-butyl-3-methylimidazolium halides, [BMIM]Cl and [BMIM]Br, are investigated by in situ Raman spectroscopy, infrared spectroscopy, and synchrotron X-ray diffraction as a function of hydrostatic pressure. The [BMIM]⁺ cations of [BMIM]Cl take the *TT* conformation under ambient conditions, undergo significant changes at 3.4 GPa, which is related to the potential formations of some new cation conformations, and take another conformation from 6.8 to 35.6 GPa. Correspondingly, crystalline [BMIM]Cl has a structure transition at 3.4 GPa, originating directly from the cation conformational changes. The [BMIM]⁺ cations totally transform into the *GT* conformer, if the diamond anvil cell-loaded sample is treated at 423 K for 12 h in a furnace before being cooled down to room temperature. It is the first time to observe the complete conformational transition from one conformer (*TT*) to another (*GT*) for the [BMIM]⁺ salts in experiments. The cations preserve the *GT* conformation as pressure reaches 44.6 GPa for heat-treated [BMIM]Cl. As a comparison, without and with the heat



treatment, the [BMIM]⁺ cations of [BMIM]Br keep the GT conformation at high pressures up to 29.6 GPa, as it is a relatively stable state. Moreover, a notable photoluminescence emerges at high pressures over 20.0 GPa and is maintained in the decompression process, as a result of the pressure-induced polymerization of a small portion of the [BMIM]⁺ cations.

INTRODUCTION

Room temperature ionic liquids (RTILs) have attracted intense attention in recent years due to their excellent performance as reaction media, catalysts, extractants, and especially electrolytes in high-energy-density batteries.^{1–8} Their ions are generally asymmetric, complex, flexible, controllable, and available in a wide variety.^{9–13} Moreover, the cations of RTILs usually have delocalized electrostatic changes.¹⁴ Therefore, the RTILs usually have relatively low melting points (around room temperature), negligibly small vapor pressures, and high thermal stability.^{15–17} The mechanical and thermodynamic properties of RTILs depend mostly on the nature and sizes of both their cation and anion constituents,^{18–20} so the stacking of RTILs is influenced not only by the long-range electrostatic forces, but also by the geometric structures of cations and anions.

The 1-butyl-3-methylimidazolium cation ($[BMIM]^+$) contains one imidazole-ring and two alkyl-chains, as shown in Figure 1. The $[BMIM]^+$ cation is a prototypical organic cation



Figure 1. Pattern of the $[BMIM]^+$ cation with all atoms numbered (hydrogen atoms are not shown).

that can generate a variety of RTILs, if combined with different anions. Therefore, the determination of the cation structures in both crystal and liquid states is of essential importance in the studies of the [BMIM]⁺ salts. Previous research has confirmed the conformational isomerism and crystal polymorphism of two typical 1-butyl-3-methylimidazolium halides: [BMIM]Cl and [BMIM]Br.²¹⁻²³ It is shown that [BMIM]Cl owns two polymorphs: the orthorhombic system with the melting point of 315 K (crystal I) and the monoclinic system with the melting point of 334 K (crystal II).^{21,22} On the contrary, [BMIM]Br possesses only one crystal structure, namely, the orthorhombic system (crystal I).^{22,23} In the monoclinic polymorph of [BMIM]Cl, the *n*-butyl group of the [BMIM]⁺ cation is the *TT* conformer, where the first *T* stands for the *trans* conformer around the C7-C8 bond and the second T for the trans conformer around the C8-C9 bond, as shown in Figure 1. However, the *n*-butyl group holds the GT conformer in the orthorhombic polymorph of [BMIM]Cl and [BMIM]Br, where G represents the gauche conformer around the C7-C8 bond. Therefore, it is the conformations of cations that determine the crystal structures of 1-butyl-3-methylimidazolium halides.²⁴⁻²⁹ Moreover, it was also verified that crystal I is more thermodynamically stable.²¹ In fact, using the ab initio method,

Received:February 10, 2018Revised:April 19, 2018Published:April 19, 2018

The Journal of Physical Chemistry C

Hunt et al. predicted that the cations of [BMIM]Cl have six conformers due to the orientation of the *n*-butyl groups.³⁰ Saouane et al. confirmed that the solid-state [BMIM][PF₆] has three polymorphs that can be crystallized as a function of low temperature or high pressure.³¹ The flexibility of the *n*-butyl group induces the different crystal structures of the [BMIM]⁺ salts, which is also affected by external environments.

High pressure has been considered an effective and clean way to tune crystal structures as well as the orientations of chemical bonds, especially the branched chain alkyl-group covalent bonds and the hydrogen bonds. Thus, it would be very interesting to study the pressure effects on the intermolecular and intramolecular interactions in the [BMIM]⁺ salts. For instance, there are many reports on the high-pressure properties of one class of RTILs, the imidazolium-based RTILs.^{11,12,16} Several research groups have explored the structure transitions of these RTILs at high pressures, mainly working on the cation structure changes and intermolecular interactions.^{24,28,32-35} Chang et al. concentrated on the rotational isomers of the [BMIM]⁺ cations coexisting in different conditions.²⁴ Turner et al. found two local energy minima for the 1-ethyl-3-methylimidazolium ([EMIM]⁺) cations, corresponding to the more stable nonplanar and less stable planar forms.³² Similarly, Yoshimura et al. reported that the conformational isomerism of the [EMIM]⁺ cations sharply changes when pressure reaches 7.2 GPa.³³ Moreover, Su et al. showed that $[BMIM][BF_4]$ displays non-monotonic pressureinduced frequency shifts and undergoes four successive structure transitions at high pressures, and believed that these transitions might be associated with the conformational changes in the butyl-chain.²

In this paper, we investigated the cation conformations and structure transitions of crystalline [BMIM]Cl and [BMIM]Br at high pressures and high temperatures. First, the [BMIM]+ cations of [BMIM]Cl take the TT conformers under ambient conditions, with the corresponding crystal structure being monoclinic. However, as pressure reaches 3.4 GPa, the conformation of the cations undergoes a significant change, which is metastable with the coexistence of at least three cation conformations. Simultaneously, the crystal structure also undergoes a notable transition at this point. Afterward, the cations take a new conformation from 6.8 to 35.6 GPa (the highest pressure in this experiment). Furthermore, the $[BMIM]^+$ cations of [BMIM]Cl totally transform into the GT conformer from the TT one, if the diamond anvil cell (DAC)loaded sample is treated at 423 K for 12 h in a furnace before being cooled down to room temperature. Then, the cations continuously maintain the GT conformer, as pressure reaches 44.6 GPa (the highest pressure in this experiment). Therefore, the GT conformation is more stable than the TT one. Second, for [BMIM]Br, the [BMIM]⁺ cations possess the GTconformation under ambient conditions and preserve it after the heat treatment, even at high pressures over 30.0 GPa, confirming that the GT conformation is extremely stable. It should be pointed out that there are plenty of hydrogen bonds between the cations and anions in crystalline [BMIM]Cl and [BMIM]Br,³⁶⁻⁴³ which, to a certain extent, determine their crystal stacking. The hydrogen bonds strengthen the interactions between cations and anions, and thus enhance the rigidity of the cations, which plays an important role in the cation conformations and structure transitions. In addition, it is noteworthy that a photoluminescence emerges at high pressures over 20.0 GPa and remains in the decompression

process, which originates from the pressure-induced polymerization of a small proportion of the $[BMIM]^+$ cations.^{29,44}

EXPERIMENTS AND COMPUTATIONS

The samples investigated in this paper are the commercially available products with a purity of 98% (Aladdin). The highpressure experiments were performed with a DAC equipped with a 300 μ m diamond culet at the rate of about 1 GPa/min. The T301 stainless steel gaskets were preindented to 45 μ m with a 120 μ m hole to serve as the sample chamber. A ruby ball was loaded with the sample to perform the in situ high pressure measurements via the R1 ruby fluorescence band shift,⁴⁵ and it would not react with the samples or influence the high-pressure experimental testing. All sample preparations were completed in a glovebox filled with argon. Both [BMIM]Cl and [BMIM] Br were crystalline initially, and were recrystallized when the DAC-loaded samples were treated at 423 K for 12 h in a furnace before being cooled down to room temperature. The heating rate and cooling rate are about 1 K/min in the furnace. The Raman spectra were recorded in a backscattering geometry, with a visible laser excitation of 532 nm (Renishaw inVia) with power less than 50 mW. The infrared absorption measurements were carried out with Hyperion 2000, giving a resolution of 2 cm⁻¹. The high-pressure synchrotron X-ray diffraction (XRD) experiments were performed at the beamline 4W2 of the Beijing Synchrotron Radiation Facility. The XRD patterns were collected in an angle-resolved geometry on a charge-coupled device detector with a focused monochromatic beam at a wavelength of $\lambda = 0.6199$ Å. The diffraction patterns were analyzed and integrated by using the FIT2D program to obtain the 1D intensity distribution as a function of the 2θ scattering angle.⁴

In order to figure out the conformational changes at high temperatures and high pressures, we assigned the Raman bands to the corresponding vibrations. The crystal structures of [BMIM]Cl and [BMIM]Br were obtained from refs 21, 22, and 47. The conformers of the [BMIM]⁺ cations were further optimized at M06-2X/6-311(d,p) level,^{48,49} and their Raman spectra were also simulated and corrected by a scale factor of 0.983.⁵⁰ All the calculations were performed with Gaussian 09 program.⁵¹

RESULTS AND DISCUSSION

Crystal Structures and Cation Conformations of [BMIM]Cl and [BMIM]Br under Ambient Conditions. We obtained the Raman spectra of [BMIM]Cl and [BMIM]Br under ambient conditions, as shown in Figure 2. The cations of [BMIM]Cl and [BMIM]Br take the *TT* and *GT* conformation, respectively, which is consistent with the previous work.²¹ The different Raman signals originate from the different conformations of the n-butyl group. The Raman bands in the spectral region from 500 to 800 cm⁻¹ are the characteristic bands of the different conformers of the [BMIM]⁺ cations.²⁴ In order to determine the differences between the two conformations, we assign these characteristic bands to the corresponding vibration modes in Table 1. As shown in Figure 2, the TT conformer has two characteristic bands at 628 and 736 cm⁻¹, which represent the symmetric and asymmetric deformational vibrations of the imidazolium ring coupled to the C-N stretching of the *n*-butyl (TT) and methyl groups, respectively. However, the corresponding vibrations of the GT conformer exhibit red-shifts to 597 and 700 cm⁻¹. In addition,



Figure 2. (a) Experimental Raman spectra of [BMIM]Cl and [BMIM] Br under ambient conditions, at a 1 cm⁻¹ resolution, with a 532 nm laser used for irradiation; (b) calculated Raman bands of the *TT* and *GT* conformations.

the *GT* conformer has a new characteristic band at 491 cm⁻¹, representing the C7–C8–C9–C10 deformation of the *n*-butyl group. In the Raman experiments, the bands at 626.3 and 730.0 cm⁻¹ are two of the characteristic bands of [BMIM]Cl, and the bands at 501.5, 602.8, and 699.5 cm⁻¹ are three of the characteristic bands of [BMIM]Br. All these calculated values are consistent with the experimental data, indicating that the Raman spectral differences between [BMIM]Cl and [BMIM]Br originate from the structure variations of the *n*-butyl groups of the [BMIM]⁺ cations.

According to the previous work, crystalline [BMIM]Cl with the TT conformation has a monoclinic $(P2_1/c)$ system; as a comparison, crystalline [BMIM]Br with the GT conformation has an orthorhombic $(Pna2_1)$ system.²¹ Therefore, it is the conformations of cations that determine the crystal structures of the [BMIM]⁺ salts. Interestingly, the [BMIM]⁺ cations in all polymorphs appear in pairs with their mirrors, no matter the TT or GT conformer, as shown in Figure 3a-d. These figures show the optimized structures of the TT and GT rotamers and mirrors of the $[BMIM]^+$ cations at M06-2X/6-311(d,p) level. The calculated results indicate that the TT rotamer stretches out of the *n*-butyl group, while the *GT* rotamer compresses the *n*-butyl group, which is in accordance with the experimental data. Although the interactions between cations and anions via electrovalent bonds are the primary forces in ionic crystals, the ionic bonds are very weak in crystalline [BMIM]Cl and [BMIM]Br due to their relatively large, complex, and asymmetric cations. Actually, the cations interact with anions mainly by the hydrogen bonds C-H…Cl in these two samples, so their crystal structures and properties are quite different from those of ordinary ionic crystals.35

Conformational Transitions of [BMIM]⁺ Cations with Pressure and Temperature. In order to investigate the influences of pressure and temperature, both [BMIM]Cl and [BMIM]Br are compressed to about 1 GPa, and then treated at 423 K for 12 h in a furnace before being cooled down to room temperature. As mentioned already, the [BMIM]⁺ cations of [BMIM]Cl take the *TT* conformation in the monoclinic crystal structure under ambient conditions. When pressure reaches 1.0 GPa, all the Raman bands show blue-shifts. This is because the intermolecular and intramolecular distances are shortened by pressure, and the ionic and covalent bonds are thus enhanced, Table 1. Vibration Assignments (cm⁻¹) of the Characteristic Bands of the TT and GT Conformations Optimized at M06-2X/6-311(d,p) Level

| | assignment | C7-C8-C9-C10 deformation of the n-butyl (GT) | symmetric deformational vibrations of the imidazolium ring coupled to the $C-N$ stretching of the <i>n</i> -butyl (<i>GT</i>) and methyl groups | | | asymmetric deformational vibrations of the imidazolium ring coupled to the C–N stretching of the n -butyl (GT) and methyl groups | | | butyl (GT) stretching | | | |
|---|---------------------|----------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------|-----|-----|--------------------------------------------------------------------------------------------------------------------------------------------------|-----|-----|-----------------------|-----|-----|-----------------------|
| | intensity (a.u.) | 1.3 | 6.1 | 0.3 | 0.4 | 2.1 | 0.9 | 0.2 | 6.4 | 0.7 | 1.9 | 1.1 |
| - | corrected*0.983 | 491 | 597 | 634 | 660 | 200 | 746 | 771 | 819 | 854 | 880 | 895 |
| | GT | 499 | 607 | 645 | 671 | 712 | 759 | 785 | 833 | 869 | 895 | 910 |
| | assignment | | symmetric deformational vibrations of the imida zolium ring coupled to the C–N stretching of the n -butyl (TT) and methyl groups | | | asymmetric deformational vibrations of the imidazolium ring coupled to the C–N stretching of the <i>n</i> -butyl (<i>TT</i>) and methyl groups | | | | | | butyl (TT) stretching |
| 0 | intensity (a.u.) | 0.4 | 3.5 | 0.5 | 1.2 | 2.1 | 0.3 | 0.2 | 0.1 | 0.9 | 0.9 | 6.0 |
| | corrected*0.983 | 434 | 628 | 635 | 667 | 736 | 740 | 756 | 796 | 862 | 880 | 914 |
| | TT | 441 | 639 | 646 | 679 | 749 | 753 | 769 | 810 | 877 | 895 | 930 |



Figure 3. Optimized structures (a and b) of the TT and GT conformers, and their mirrors (c and d) of the [BMIM]⁺ cations at M06-2X/6-311(d,p) level.

so the Raman bands move to high frequencies. Then, the compressed sample is heat-treated in the same way. It is found that the characteristic bands of [BMIM]Cl present significant changes, which are completely different from the initial Raman signals, but are the same as the Raman bands of [BMIM]Br under ambient conditions, as shown in Figure 4a. Therefore, it can be concluded that the cations of [BMIM]Cl are converted from the *TT* conformation to the *GT* one after the heat treatment. [BMIM]Br also undergoes the same process, but the cation conformation does not change before and after the heat treatment, as shown in Figure 4b. In other words, the cations of

[BMIM]Br always take the *GT* conformation under ambient conditions, at 1.0 GPa, and at 1.0 GPa after the heat treatment.

The only difference between these two samples is their anions, which determine the environment of the $[BMIM]^+$ cations, with the radius of Cl⁻ and Br⁻ being 1.81 and 1.96 Å, respectively. According to the previous work,²¹ the cations in the monoclinic and orthorhombic crystals have six and seven closest anions, respectively. In the orthorhombic system, the cation coordinations are higher and the radius of Br⁻ is larger, so the *n*-butyl (*GT*) is compressed more significantly by the surrounding anions and the cations take the *GT* conformation. When [BMIM]Cl is heated, the *n*-butyl (*TT*) is compressed and then transformed into the *GT* conformation that is still preserved as temperature drops to room temperature. Therefore, the *GT* conformation is more stable for the [BMIM]⁺ cations, even though the anions may influence the orientation of the *n*-butyl group.

Raman and Infrared Spectra of [BMIM]Cl and [BMIM] Br at High Pressures. The Raman and infrared spectra are very effective methods in analyzing structures of matter. In our experiments, [BMIM]Cl without and with the heat treatment (conditions A and B) are both compressed to more than 30.0 GPa, and we collect the in situ Raman and infrared spectra during these compression processes. As pressure increases, the Raman and infrared spectral bands of crystalline [BMIM]Cl exhibit blue-shifts, and are weakened and broadened, because the energies of ionic bonds, covalent bonds, and hydrogen bonds increase, and the crystal lattices distort.



Figure 4. Raman spectra of (a) [BMIM]Cl and (b) [BMIM]Br under ambient conditions, at 1.0 GPa, and at 1.0 GPa with the heat treatment, with a 532 nm laser used for irradiation.



Figure 5. In situ Raman spectra of [BMIM]Cl in condition A as a function of pressure at a 1 cm⁻¹ resolution, with a 532 nm laser for irradiation, from (a) 100 to 600 cm⁻¹; (b) 600 to 1200 cm⁻¹; (c) 1200 to 1700 cm⁻¹; and (d) 2800 to 3400 cm⁻¹.



Figure 6. In situ infrared spectra of [BMIM]Cl in condition A at different pressures for various bands, at a 2 cm⁻¹ resolution, from (a) 600 to 1100 cm⁻¹; (b) 1100 to 1700 cm⁻¹; and (c) 2700 to 3400 cm⁻¹.

First, we investigate the cation conformational changes and structure transitions for [BMIM]Cl in condition A. In the highpressure Raman experiments, the most significant change occurs at 3.4 GPa, as shown in Figure 5. At least 18 new vibration bands (marked with asterisk in Figure 5a–d) appear in the region from 1100 to 3500 cm⁻¹ at this pressure. When pressure reaches 6.8 GPa, the Raman spectrum is quite different from the previous one: some bands vanish and some new ones emerge (marked with solid circle in Figure 5a–d), indicating the continuous changes of the [BMIM]⁺ cations from 3.4 to 6.8 GPa. For instance, the characteristic band at 626.3 cm⁻¹ splits into three at 3.4 GPa and then merges into one in Figure 5b. In order to confirm the transitions in the high-pressure Raman spectra, the infrared spectra from 600 to 3400 cm⁻¹ are also

Article



Figure 7. In situ Raman spectra of [BMIM]Cl in condition B as a function of pressure, at a 1 cm⁻¹ resolution, with a 532 nm laser for irradiation, from (a) 100 to 600 cm⁻¹; (b) 600 to 1250 cm⁻¹; (c) 1200 to 1800 cm⁻¹; and (d) 2750 to 3300 cm⁻¹.

collected from 0.7 to 31.2 GPa and back to 1.0 GPa in decompression process, as shown in Figure 6. When pressure reaches 3.7 GPa, at least 11 new bands arise (marked with solid diamond in Figure 6a-c), which are consistent with the Raman signals. Similarly, the infrared spectrum at 6.1 GPa is also significantly different from the one at 3.7 GPa (marked with solid circle in Figure 6a-c).

As we know, the different Raman spectra originate from the different [BMIM]⁺ cation conformations, so the spectral changes at 3.4 GPa reflect the conformational variations of the [BMIM]⁺ cations and the structure transitions in crystalline [BMIM]Cl. At 3.4 GPa, the cations are in a metastable state: several cation conformations coexist, since all these conformations have minimal energies. On the contrary, only one conformation is preserved according to the Raman signals at 6.8 GPa, and the characteristic bands remain unchanged with pressure, indicating that this cation conformation is stable. In consideration of the geometry of *n*-butyl group, the $[BMIM]^+$ cations have 16 different conformations, so it is difficult to determine the possible conformations at 3.4 GPa, as there is no effective method to predict the stable one. When pressure exceeds 23.2 GPa, all the Raman bands become much weaker, and some are even undetected. Furthermore, at 35.6 GPa, almost no Raman band can be detected, which is not only because the Raman bands become extremely weak, but also because a photoluminescence emerges at high pressures. As a comparison, the infrared bands are still present at 31.2 GPa, albeit all the bands have become very broad.

In the Raman experiments, the 532 nm laser excites the photoluminescence of [BMIM]Cl, whereas in the infrared experiments, the mid-infrared band energy cannot stimulate the photoluminescence. This is because a small portion of [BMIM] Cl polymerizes at high pressures and thus leads to photoluminescence. ^{52–54} During the decompression process, the photoluminescence is also strong, and the Raman bands are still

undetectable, indicating that the polymerization is irreversible. More details of the photoluminescence will be discussed later.

In the decompression process, when pressure drops to 1.0 GPa, the infrared spectrum is the same as the initial one at 0.7 GPa, as shown in Figure 6a–c, suggesting that most of the cation conformation is reversible in decompression. Simultaneously, the Raman bands in the region from 100 to 300 cm⁻¹ undergo the most complex and remarkable changes with pressure. The bands in this region are assigned to the bends of the long chains and the interactions of cations and anions, which are more susceptible to high pressure, indicating that crystalline [BMIM]Cl with the *TT* conformation in the monoclinic system is not a stable state.

Second, in condition B, [BMIM]Cl is also compressed to 44.6 GPa in the high-pressure Raman experiments, as shown in Figure 7. As mentioned above, the initial TT conformation of the [BMIM]⁺ cations has been completely transformed into the *GT* one by the heat treatment. [BMIM]Cl in condition B keeps the same characteristic bands with pressure, indicating that the cations always possess the GT conformation. The Raman band at 1444.6 cm⁻¹ at 10.3 GPa splits into two at higher pressures, as shown in Figure 7c. More than one vibration mode is assigned to this band, including the ring in-plane asymmetric stretching, the $CH_2(N)CN$ stretching, and the butyl HCH symmetric stretching. These stretchings have different sensitivities to pressure and different rates of movement at high pressures. It is worth pointing out that some Raman bands can still be detected at 44.6 GPa, which is obviously distinct from the case in condition A, because [BMIM]Cl in condition B is better crystallized by the heat treatment. In fact, the Raman signals are often used to characterize the degree of crystallization and stressing. If the crystal lattice is perfect, the spectral peak width is very narrow, and the intensity is very high. Instead, if crystallization is not good enough, the vibration energy will be in a relatively large range, so the peak width is



Figure 8. In situ infrared spectra of [BMIM]Cl in condition B as a function of pressure, at a 2 cm⁻¹ resolution, from (a) 600 to 1120 cm⁻¹; (b) 1100 to 1700 cm⁻¹; and (c) 2800 to 3400 cm⁻¹.



Figure 9. In situ Raman spectra of [BMIM]Br in condition A as a function of pressure, at a 1 cm⁻¹ resolution, with a 532 nm laser for irradiation, from (a) 100 to 600 cm⁻¹; (b) 600 to 1200 cm⁻¹; (c) 1200 to 1700 cm⁻¹; and (d) 2700 to 3300 cm⁻¹.

broad, and the intensity is weak. Actually, the Raman bands of many crystals become broader at high pressures.

Again, a photoluminescence emerges in condition B when pressure is over 20.0 GPa, and its intensity increases with pressure, which has a great impact on the detection of the Raman signals. Therefore, the Raman bands of initial [BMIM] Cl almost cannot be detected at 35.6 GPa, owing to the interference of strong photoluminescence. However, some broad and weak Raman signals can still be detected at 44.6 GPa, since recrystallized [BMIM]Cl has better Raman bands. The emergence of photoluminescence suggests that a small portion of the sample in condition B also polymerizes at over 20.0 GPa, which is the same as condition A. In the high-pressure infrared experiments, although the spectra are sensitive to pressure,



Figure 10. In situ infrared spectra of [BMIM]Br in condition A as a function of pressure, at a 2 cm⁻¹ resolution, from (a) 600 to 1150 cm⁻¹; (b) 1150 to 1700 cm⁻¹; and (c) 2800 to 3350 cm⁻¹.



Figure 11. In situ Raman spectra of [BMIM]Br in condition B as a function of pressure, at a 1 cm⁻¹ resolution, with a 532 nm laser for irradiation, from (a) 100 to 600 cm⁻¹; (b) 580 to 1250 cm⁻¹; (c) 1200 to 1700 cm⁻¹; and (d) 2700 to 3300 cm⁻¹.

[BMIM]Cl after decompression to 1.7 GPa has the same spectra as the one at 2.2 GPa, as shown in Figure 8, indicating that most [BMIM]Cl in condition B is restored in the decompression process.

Now, we move on to [BMIM]Br. In condition A, it is also compressed to 29.6 GPa and then decompressed to 0.5 GPa in

the high-pressure Raman and infrared experiments, as shown in Figures 9 and 10. It is intriguing that the Raman and infrared spectra of [BMIM]Br at different pressures are very similar to the ones of [BMIM]Cl in condition B, as they have the same GT cation conformation. The most distinct differences lie in the low frequency region from 100 to 300 cm⁻¹, where their



Figure 12. Selected angle dispersive synchrotron XRD patterns of (a) [BMIM]Cl obtained in compression up to 4.1 GPa and (b) [BMIM]Br obtained in compression up to 4.4 GPa.

different crystal structures induce the different Raman bands. The Raman spectra of [BMIM]Br in condition B in Figure 11 are also similar to the ones in condition A, because the conformation is not significantly influenced by the heat treatment. When [BMIM]Br in condition B is compressed to 33.5 GPa, the Raman characteristic bands are unchanged, as shown in Figure 11, indicating that the [BMIM]⁺ cations still hold the stable *GT* conformation.

XRD Experiments of [BMIM]Cl and [BMIM]Br at High Pressures. Here, we briefly discuss the XRD results of [BMIM]Cl and [BMIM]Br at high pressures. We performed the in situ XRD experiments on crystalline [BMIM]Cl from 2.4 to 4.1 GPa, as shown in Figure 12a. The XRD patterns undergo an obvious change from 3.2 to 4.1 GPa, indicating a structure transition of crystalline [BMIM]Cl, and thus confirm the structure transition at 3.4 GPa in the high-pressure Raman experiments. By comparing the XRD and Raman spectra, we find that it originates from the pressure-induced cation isomerism; in other words, the pressure-induced conformational changes of cations account for this transition.

Moreover, from the XRD patterns in Figure 12b, we cannot observe any structure change of [BMIM]Br from 2.2 to 4.4 GPa. At the same time, the cation conformation of [BMIM]Br maintains the *GT* one during compression. Altogether, we are allowed to conclude that the cation conformations play an important role in determining the crystal structures of 1-butyl-3-methylimidazolium halides.

Photoluminescence at High Pressures in Compression and Decompression. Last, we focus on the photoluminescence in our experiments. As mentioned earlier, a photoluminescence emerges at around 20 GPa, regardless of the heat treatment or not for both [BMIM]Cl and [BMIM]Br, as shown in Figure 13a-d. It is found that this photoluminescence is preserved in the continuous compression and subsequent decompression processes. According to our previous work on 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl),²⁹ the mechanism for photoluminescence is the pressure-induced polymerization of the [EMIM]+ cations.52 The chains polymerized from the cations have photoluminescent properties, which is common in other organic synthetic materials.⁵³⁻⁵⁷ The infrared spectra of [BMIM]Cl and [BMIM]Br in conditions A and B at about 1 GPa are the same as the ones at about 1 GPa decompressed from about 30 GPa, indicating that the vibration bands are reversible in the decompression process. Therefore, we can conclude that only a small portion of the samples polymerize at high pressures and are maintained during decompression. In fact, although obvious

changes take place at high pressures, most of the samples compressed to about 30 GPa keep the initial structures.

It is interesting to point out that the emission maxima of [BMIM]Cl and [BMIM]Br in conditions A and B continuously increase, once the photoluminescence appears, as shown in Figure 13e,f. The chains of different lengths have different photoluminescence frequencies accordingly: the longer the chain is, the lower the maximal emission energy will be.58,59 Since the cations polymerize into chains in different numbers, the peaks of photoluminescence are very broad. It is noteworthy that the photoluminescence frequencies of the polymers of [BMIM]Cl and [BMIM]Br are obviously lower than those of [EMIM]Cl.²⁹ Besides, it is reasonable that the photoluminescence frequencies increase with pressure, but it is unusual that the frequencies still increase during decompression. As a consequence, we believe that the cations also experience some changes during decompression, i.e., some shorter chains polymerize in this process, which will excite the high photoluminescence energies. This also explains the fact that the photoluminescence intensities increase by almost an order of magnitude during decompression. The differences in the photoluminescence energies are not obvious for [BMIM]Cl and [BMIM]Br in conditions A and B, as shown in Figure 13e,f. This is because [EMIM]Cl is amorphous in condition A and is crystalline in condition B. However, both [BMIM]Cl and [BMIM]Br in conditions A and B are crystalline. The amorphous samples tend to form shorter chains, whereas the crystalline samples tend to form longer ones.

CONCLUSIONS

In this paper, we have investigated the conformational changes of the [BMIM]⁺ cations and the structure transitions in [BMIM]Cl and [BMIM]Br induced by high temperature and high pressure. First, when compressed to 3.4 GPa, [BMIM]Cl is in a metastable state, with the coexistence of several cation conformations. However, only one conformation is maintained with pressure, indicating that the initial TT conformation is unstable and another conformation transformed at 6.8 GPa is stable at high pressures. Besides, the cations of [BMIM]Cl totally transform into the GT conformer from the TT one, if the DAC-loaded sample is treated at 423 K for 12 h in a furnace before being cooled down to room temperature. This is the first time to observe the complete conformational changes in experiments. The heated [BMIM]Cl keep the GT conformation with pressure up to 44.6 GPa, showing that the GT conformation is more stable than TT one. Second, the cations of [BMIM]Br possess the GT conformation, and preserve it at high pressures and high temperatures, indicating that the GT



Figure 13. Room temperature photoluminescence spectra of (a) [BMIM]Cl in condition A; (b) [BMIM]Cl in condition B; (c) [BMIM]Br in condition A; and (d) [BMIM]Br in condition B, with a 532 nm laser used for irradiation. The pressure dependence (e and f) of the maximal peak frequencies of the photoluminescence energies for [BMIM]Cl and [BMIM]Br in conditions A and B.

conformation is extremely stable. Furthermore, the XRD data show that the crystal structures are transformed together with the conformational changes. By comparing these aspects for [BMIM]Cl and [BMIM]Br at high pressures, it can be concluded that the conformational changes play an essential role in the structure transitions during compression. In addition, a small portion of the sample polymerizes, leading to a photoluminescence when pressure is over 20 GPa. The pressure-induced polymerization is a "green" chemical process, as the reactions can be performed in the absence of any solvent or catalyst, and thus reduces the environmental impacts to the most extent.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: jbliu@mail.tsinghua.edu.cn. *E-mail: wanglin@hpstar.ac.cn.

ORCID 💿

Guoyong Fang: 0000-0001-6817-3790 Yuexiao Pan: 0000-0001-5574-8057

9329

The Journal of Physical Chemistry C

Jianbo Liu: 0000-0001-6516-6966

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We are greatly thankful to Nan Li for frequent and fruitful discussions. All our experiments were performed in HPSTAR. This work is supported by the joint fund of the National Natural Science Foundation of China and Chinese Academy of Sciences Fund (No. U1332104). The XRD experiments were carried out at the beamline 4W2 of the Beijing Synchrotron Radiation Facility, supported by the Chinese Academy of Sciences (Nos. KJCX2-SW-N03 and KJCX2-SW-N20). The work at Tsinghua University is supported by the Ministry of Science and Technology of China (No. 2017YFB0702401), the National Natural Science Foundation of China (Nos. 51571129 and 51631005), and the Science Challenge Project (No. TZ2016004).

REFERENCES

(1) Wasserscheid, P.; Keim, W. Ionic Liquids—New "Solutions" for Transition Metal Catalysis. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772–3789.

(2) Wei, G.-T.; Yang, Z.; Chen, C.-J. Room Temperature Ionic Liquid as a Novel Medium for Liquid/Liquid Extraction of Metal Ions. *Anal. Chim. Acta* 2003, 488, 183–192.

(3) Galiński, M.; Lewandowski, A.; Stępniak, I. Ionic Liquids as Electrolytes. *Electrochim. Acta* **2006**, *51*, 5567–5580.

(4) Armand, M.; Endres, F.; MacFarlane, D. R.; Ohno, H.; Scrosati, B. Ionic-Liquid Materials for the Electrochemical Challenges of the Future. *Nat. Mater.* **2009**, *8*, 621–629.

(5) Shaplov, A. S.; Marcilla, R.; Mecerreyes, D. Recent Advances in Innovative Polymer Electrolytes based on Poly(ionic liquid)s. *Electrochim. Acta* **2015**, *175*, 18–34.

(6) Osada, I.; de Vries, H.; Scrosati, B.; Passerini, S. Ionic-Liquid-Based Polymer Electrolytes for Battery Applications. *Angew. Chem., Int. Ed.* **2016**, *55*, 500–513.

(7) Shi, C.; Jing, Y.; Xiao, J.; Wang, X.; Jia, Y. Liquid-Liquid Extraction of Lithium Using Novel Phosphonium Ionic Liquid as an Extractant. *Hydrometallurgy* **201**7, *169*, 314–320.

(8) Quijada-Maldonado, E.; Torres, M. J.; Romero, J. Solvent Extraction of Molybdenum (VI) from Aqueous Solution Using Ionic Liquids as Diluents. *Sep. Purif. Technol.* **2017**, *177*, 200–206.

(9) Welton, T. Room-Temperature Ionic Liquids, Solvents for Synthesis and Catalysis. *Chem. Rev.* **1999**, *99*, 2071–2084.

(10) Buzzeo, M. C.; Evans, R. G.; Compton, R. G. Non-Haloaluminate Room-Temperature Ionic Liquids in Electrochemistry—A Review. *ChemPhysChem* **2004**, *5*, 1106–1120.

(11) Fukumoto, K.; Yoshizawa, M.; Ohno, H. Room Temperature Ionic Liquids from 20 Natural Amino Acids. J. Am. Chem. Soc. 2005, 127, 2398–2399.

(12) Mudring, A.-V. Solidification of Ionic Liquids: Theory and Techniques. *Aust. J. Chem.* **2010**, *63*, 544–564.

(13) Gehrke, S.; von Domaros, M.; Clark, R.; Holloczki, O.; Brehm, M.; Welton, T.; Luzar, A.; Kirchner, B. Structure and Lifetimes in Ionic Liquids and Their Mixtures. *Faraday Discuss.* **2018**, *206*, 219–245.

(14) Padua, A. A. H.; Costa Gomes, M. F.; Canongia Lopes, J. N. Molecular Solutes in Ionic Liquids: A Structural Perspective. *Acc. Chem. Res.* **2007**, *40*, 1087–1096.

(15) Anthony, J. L.; Maginn, E. J.; Brennecke, J. F. Solubilities and Thermodynamic Properties of Gases in the Ionic Liquid 1-*n*-Butyl-3methylimidazolium Hexafluorophosphate. *J. Phys. Chem. B* **2002**, *106*, 7315–7320.

(16) Shah, J. K.; Brennecke, J. F.; Maginn, E. J. Thermodynamic Properties of the Ionic Liquid 1-*n*-Butyl-3-methylimidazolium Hexafluorophosphate from Monte Carlo Simulations. Green Chem. 2002, 4, 112–118.

(17) Earle, M. J.; Esperança, J. M. M. S.; Gilea, M. A.; Canongia Lopes, J. N.; Rebelo, L. P. N.; Magee, J. W.; Seddon, K. R.; Widegren, J. A. The Distillation and Volatility of Ionic Liquids. *Nature* **2006**, *439*, 831–834.

(18) Shah, J. K.; Maginn, E. J. A Monte Carlo Simulation Study of the Ionic Liquid 1-*n*-Butyl-3-methylimidazolium Hexafluorophosphate: Liquid Structure, Volumetric Properties and Infinite Dilution Solution Thermodynamics of CO₂. *Fluid Phase Equilib.* **2004**, *222*, 195–203.

(19) Deetlefs, M.; Hardacre, C.; Nieuwenhuyzen, M.; Sheppard, O.; Soper, A. K. Structure of Ionic Liquid-Benzene Mixtures. *J. Phys. Chem. B* **2005**, *109*, 1593–1598.

(20) Hayes, R.; Warr, G. G.; Atkin, R. Structure and Nanostructure in Ionic Liquids. *Chem. Rev.* **2015**, *115*, 6357–6426.

(21) Holbrey, J. D.; Reichert, W. M.; Nieuwenhuyzen, M.; Johnson, S.; Seddon, K. R.; Rogers, R. D. Crystal Polymorphism in 1-Butyl-3methylimidazolium Halides: Supporting Ionic Liquid Formation by Inhibition of Crystallization. *Chem. Commun.* **2003**, *14*, 1636–1637.

(22) Saha, S.; Hayashi, S.; Kobayashi, A.; Hamaguchi, H.-o. Crystal Structure of 1-Butyl-3-methylimidazolium Chloride. A Clue to the Elucidation of the Ionic Liquid Structure. *Chem. Lett.* **2003**, *32*, 740–741.

(23) Ozawa, R.; Hayashi, S.; Saha, S.; Kobayashi, A.; Hamaguchi, H.o. Rotational Isomerism and Structure of the 1-Butyl-3-methylimidazolium Cation in the Ionic Liquid State. *Chem. Lett.* **2003**, *32*, 948– 949.

(24) Holbrey, J. D.; Reichert, W. M.; Rogers, R. D. Crystal Structures of Imidazolium Bis(trifluoromethanesulfonyl)imide 'Ionic Liquid' Salts: The First Organic Salt with a *cis*-TFSI Anion Conformation. *Dalton T.* **2004**, *15*, 2267–2271.

(25) Chang, H.-C.; Chang, C.-Y.; Su, J.-C.; Chu, W.-C.; Jiang, J.-C.; Lin, S. H. Conformations of 1-Butyl-3-methylimidazolium Chloride Probed by High Pressure Raman Spectroscopy. *Int. J. Mol. Sci.* **2006**, *7*, 417–424.

(26) Chang, H.-C.; Jiang, J.-C.; Su, J.-C.; Chang, C.-Y.; Lin, S. H. Evidence of Rotational Isomerism in 1-Butyl-3-methylimidazolium Halides: A Combined High-Pressure Infrared and Raman Spectroscopic Study. J. Phys. Chem. A 2007, 111, 9201–9206.

(27) Su, L.; Zhu, X.; Wang, Z.; Cheng, X.; Wang, Y.; Yuan, C.; Chen, Z.; Ma, C.; Li, F.; Zhou, Q. In Situ Observation of Multiple Phase Transitions in Low-Melting Ionic Liquid [BMIM][BF₄] under High Pressure up to 30 GPa. *J. Phys. Chem. B* **2012**, *116*, 2216–2222.

(28) Su, L.; Li, L.; Hu, Y.; Yuan, C.; Shao, C.; Hong, S. Phase Transition of $[C_n\text{-mim}][PF_6]$ under High Pressure up to 1.0 GPa. J. Chem. Phys. **2009**, 130, 184503.

(29) Chen, F.; You, T.; Yuan, Y.; Pei, C.; Ren, X.; Huang, Y.; Yu, Z.; Li, X.; Zheng, H.; Pan, Y.; et al. Pressure-Induced Structural Transitions of a Room Temperature Ionic Liquid—1-Ethyl-3methylimidazolium Chloride. *J. Chem. Phys.* **2017**, *146*, 094502.

(30) Hunt, P. A.; Gould, I. R. Structural Characterization of the 1-Butyl-3-methylimidazolium Chloride Ion Pair Using ab Initio Methods. J. Phys. Chem. A **2006**, 110, 2269–2282.

(31) Saouane, S.; Norman, S. E.; Hardacre, C.; Fabbiani, F. P. A. Pinning Down the Solid-State Polymorphism of the Ionic Liquid [bmim][PF₆]. *Chem. Sci.* **2013**, *4*, 1270–1280.

(32) Turner, E. A.; Pye, C. C.; Singer, R. D. Use of ab Initio Calculations toward the Rational Design of Room Temperature Ionic Liquids. *J. Phys. Chem. A* **2003**, *107*, 2277–2288.

(33) Yoshimura, Y.; Abe, H.; Takekiyo, T.; Shigemi, M.; Hamaya, N.; Wada, R.; Kato, M. Superpressing of a Room Temperature Ionic Liquid, 1-Ethyl-3-methylimidazolium Tetrafluoroborate. *J. Phys. Chem. B* **2013**, *117*, 12296–12302.

(34) Carvalho, P. J.; Álvarez, V. H.; Marrucho, I. M.; Aznar, M.; Coutinho, J. A. P. High Pressure Phase Behavior of Carbon Dioxide in 1-Butyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide and 1-Butyl-3-methylimidazolium Dicyanamide Ionic Liquids. *J. Supercrit. Fluids* **2009**, *50*, 105–111.

The Journal of Physical Chemistry C

(35) Yoshimura, Y.; Shigemi, M.; Takaku, M.; Yamamura, M.; Takekiyo, T.; Abe, H.; Hamaya, N.; Wakabayashi, D.; Nishida, K.; Funamori, N.; et al. Stability of the Liquid State of Imidazolium-Based Ionic Liquids under High Pressure at Room Temperature. *J. Phys. Chem. B* **2015**, *119*, 8146–8153.

(36) Suarez, P.; Einloft, S.; Dullius, J.; De Souza, R.; Dupont, J. Synthesis and Physical-Chemical Properties of Ionic Liquids Based on 1-*N*-Butyl-3-methylimidazolium Cation. *J. Chim. Phys. Phys.-Chim. Biol.* **1998**, *95*, 1626–1639.

(37) Huang, J.-F.; Chen, P.-Y.; Sun, I.-W.; Wang, S.-P. NMR Evidence of Hydrogen Bonding in 1-Ethyl-3-methylimidazoliumtetrafluoroborate Room Temperature Ionic Liquid. *Inorg. Chim. Acta* **2001**, *320*, 7–11.

(38) Aggarwal, A.; Lancaster, N. L.; Sethi, A. R.; Welton, T. The Role of Hydrogen Bonding in Controlling the Selectivity of Diels-Alder Reactions in Room-Temperature Ionic Liquids. *Green Chem.* **2002**, *4*, 517–520.

(39) Dupont, J. On the Solid, Liquid and Solution Structural Organization of Imidazolium Ionic Liquids. J. Braz. Chem. Soc. 2004, 15, 341–350.

(40) Dong, K.; Zhang, S.; Wang, D.; Yao, X. Hydrogen Bonds in Imidazolium Ionic Liquids. J. Phys. Chem. A 2006, 110, 9775–9782.

(41) Tsuzuki, S.; Tokuda, H.; Mikami, M. Theoretical Analysis of the Hydrogen Bond of Imidazolium C_2 -H with Anions. *Phys. Chem. Chem. Phys.* **2007**, *9*, 4780–4784.

(42) Lungwitz, R.; Spange, S. A Hydrogen Bond Accepting (HBA) Scale for Anions, Including Room Temperature Ionic Liquids. *New J. Chem.* **2008**, 32, 392–394.

(43) Hunt, P. A.; Ashworth, C. R.; Matthews, R. P. Hydrogen Bonding in Ionic Liquids. *Chem. Soc. Rev.* **2015**, *44*, 1257–1288.

(44) Bai, Y.; Yu, Z.; Liu, R.; Li, N.; Yan, S.; Yang, K.; Liu, B.; Wei, D.; Wang, L. Pressure-Induced Crystallization and Phase Transformation of Para-xylene. *Sci. Rep.* **2017**, *7*, 5321.

(45) Mao, H. K.; Bell, P. M.; Shaner, J. W.; Steinberg, D. J. Specific Volume Measurements of Cu, Mo, Pd, and Ag and Calibration of the Ruby R_1 Fluorescence Pressure Gauge from 0.06 to 1 Mbar. *J. Appl. Phys.* **1978**, *49*, 3276–3283.

(46) Hammersley, A. P.; Svensson, S. O.; Hanfland, M.; Fitch, A. N.; Hausermann, D. Two-Dimensional Detector Software: From Real Detector to Idealised Image or Two-Theta Scan. *High Pressure Res.* **1996**, *14*, 235–248.

(47) Hayashi, S.; Ozawa, R.; Hamaguchi, H.-o. Raman Spectra, Crystal Polymorphism, and Structure of a Prototype Ionic-liquid [bmim]Cl. *Chem. Lett.* **2003**, *32*, 498–499.

(48) Zhao, Y.; Truhlar, D. G. Density Functionals with Broad Applicability in Chemistry. *Acc. Chem. Res.* **2008**, *41*, 157–167.

(49) Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Functionals. *Theor. Chem. Acc.* 2008, 120, 215–241.

(50) Alecu, I.; Zheng, J.; Zhao, Y.; Truhlar, D. G. Computational Thermochemistry: Scale Factor Databases and Scale Factors for Vibrational Frequencies Obtained from Electronic Model Chemistries. *J. Chem. Theory Comput.* **2010**, *6*, 2872–2887.

(51) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. *Gaussian 09*, Revision A.02; Gaussian, Inc.; Wallingford, CT, 2009.

(52) Wang, B.; Qin, L.; Mu, T.; Xue, Z.; Gao, G. Are Ionic Liquids Chemically Stable? *Chem. Rev.* **2017**, *117*, 7113–7131.

(53) Osaheni, J. A.; Jenekhe, S. A. Efficient Blue Luminescence of a Conjugated Polymer Exciplex. *Macromolecules* **1994**, *27*, 739–742.

(54) Jenekhe, S. A.; Osaheni, J. A. Excimers and Exciplexes of Conjugated Polymers. *Science* **1994**, *265*, 765–768.

(55) Williams, E. L.; Haavisto, K.; Li, J.; Jabbour, G. E. Excimer-Based White Phosphorescent Organic Light-Emitting Diodes with Nearly 100% Internal Quantum Efficiency. Adv. Mater. 2007, 19, 197–202.

(56) Hao, J. M.; Yu, B. Y.; Van Hecke, K.; Cui, G. H. A series of d¹⁰ Metal Coordination Polymers Based on a Flexible Bis(2-methylbenzimidazole) Ligand and Different Carboxylates: Synthesis, Structures, Photoluminescence and Catalytic Properties. *CrystEng-Comm* **2015**, *17*, 2279–2293.

(57) Boixel, J.; Zhu, Y.; Le Bozec, H.; Benmensour, M. A.; Boucekkine, A.; Wong, K. M.-C.; Colombo, A.; Roberto, D.; Guerchais, V.; Jacquemin, D. Contrasted Photochromic and Luminescent Properties in Dinuclear Pt(II) Complexes Linked through a Central Dithienylethene Unit. *Chem. Commun.* **2016**, *52*, 9833–9836.

(58) Houlding, V. H.; Miskowski, V. M. The Effect of Linear Chain Structure on the Electronic Structure of Pt(II) Diimine Complexes. *Coord. Chem. Rev.* **1991**, *111*, 145–152.

(59) Nguyen, T.-Q.; Wu, J.; Doan, V.; Schwartz, B. J.; Tolbert, S. H. Control of Energy Transfer in Oriented Conjugated Polymer-Mesoporous Silica Composites. *Science* **2000**, *288*, 652–656.