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Hydrogen Bonds in the Crystal Structure of Hydrophobic and Hydrophilic COOH-functionalized Imidazolium Ionic Liquids

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ABSTRACT:

Crystal structures of six COOH-functionalized imidazolium ionic liquids (ILs) were determined, and the different hydrogen bonds were found in the hydrophobic and hydrophilic ionic liquids. For hydrophilic COOH-functionalized ILs based on halide anions, the classic O-H···Cl$^-$ or O-H···Br$^-$ hydrogen bond was observed by single crystal X-ray diffraction, whereas the carboxyl group dimer was present for hydrophobic COOH-functionalized ILs based on $(CF_3SO_2)_2N^-$ (TFSI) and PF_6^- anions. Parallel vibrational spectroscopic studies and DFT calculations have also demonstrated such difference in hydrogen bond structures. The relationship between solubility of ionic liquids in water and their structures was discussed.

Keywords: Hydrogen bond, ionic liquids, carboxyl group, crystal structure, solubility.

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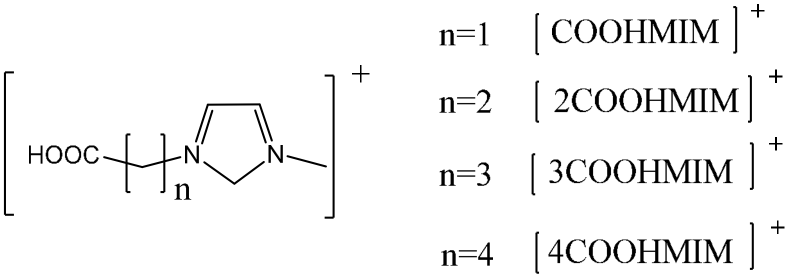
Introduction

In recent years, the synthesis and applications of functionalized ionic liquids (ILs) have received growing attention since their distinctive properties strongly depend on the species of anion and cation, and on the substituent group in the heterocyclic rings. A variety of substituent functionalized ILs such as amino acid[1, 2], carboxylic acid[3-9], nitrile[10-12] and other groups[13] have been developed in order to modify the original physical and chemical properties for a specific purpose. For example, ether or primary alcohol functionality has been shown to influence the miscibility of hydrophobic ILs with water[13].

Many multidentate carboxylic acid ligands have still been used to prepare the metal-organic-framework compounds for catalysis, separation, magnetism, fluorescence, gas adsorption, and molecular recognition[14]. The combination of the carboxylic acid and ionic liquid can give novel COOH-functionalized ILs with unique characters. The initial research in this field was carried out by Fei and coworkers[8]. They synthesized some imidazolium salts with one or two carboxylic acid substituents using the corresponding zwitterions, and determined the pK_a values of these ILs, which were used to coordinate with the different metal ions[4-7]. Afterwards, Li X. *et al.* [15-17] synthesized a series of multicarboxylic-appended imidazolium ILs with chloride or bromide anions as the catalysts and investigated the selective catalytic oxidation of styrene to acetophenone. Li H. and co-workers[18,19] directly dissolved lanthanide oxides and organic ligand into COOH-functionalized ILs and prepared the distinctive luminescent soft materials. Moreover, carboxyl group functionalized betainium, pyridinium, pyrrolidinium, piperidinium, morpholinium, and quaternary ammonium ILs based on TFSI anion were successfully prepared and used to selectively dissolve metal oxides and hydroxides[20-23]. So far, the COOH-functionalized ILs have been explored in catalysis[24-28], electrochemistry[29-30], liquid crystals[9] and liquid–liquid extraction[31]. On the other hand, the crystal structures of hydrophilic COOH-functionalized ILs were scattered in the literatures. For example, Fei *et al.* [8] have determined crystal structures of the

1-carboxypropyl-3-methylimidazolium chloride and 1,3-bis(carboxymethyl)imidazolium chloride, and found that extensive C–H…Br and/or C–H…O hydrogen bonds are present between the chloride and imidazolium. This is the same as the COOH-functionalized ILs with long alkyl chains[9]. The special dimeric structure of 1,3-bis(carboxymethyl)imidazolium bromide was reported [32]. We also devoted ourselves to determining the crystal structure of 1-carboxymethyl-3-methylimidazolium chloride and its properties by a combination of experiments and DFT calculations[33,34]. As for hydrophobic COOH-functionalized ILs, there is little research except for the 1-carboxymethyl-3-methylimidazolium TFSI[21]. Obviously, systematic studies are necessary to design them and control their physical properties because the dependence of the property on the structure is still unclearly. This often makes the synthesis of new ILs with desired properties be planned arbitrarily. Amongst the inherent interactions in ILs, hydrogen bonds influence cation–anion interactions and thus govern not only the properties of the salts but also the chemical reactions that take places in them[35,36]. Therefore, the understanding of hydrogen bond structure is quite important for the design of new ILs.



Scheme 1. Structure of cations of the prepared ionic liquid and their abbreviations

In this work, we synthesized a series of 3-methyl-imidazolium-based compounds having one carboxyl group (COOH-ILs) moiety (Scheme 1) based on Cl^-, Br^-, PF_6^- and TFSI anions, and measured their phychemical properties. Herein, single-crystal structures of six COOH-ILs (Fig. S1), and the selected Infrared and Raman spectra of COOH-ILs with different anions were presented. The role of hydrogen bonds related to the carboxyl groups in these compounds was discussed with respect to their solubility in water. Density functional theory (DFT) calculations were also used to explain the reason for the difference in structure of hydrophobic and hydrophilic ILs.

Results and Discussion

1-Carboxymethyl-3-methylimidazolium chloride ([COOHMIM]Cl) (**1**), 1-carboxypropyl-3-methylimidazolium bromide ([3COOHMIM]Br) (**2**), and 1-carboxypropyl-imidazolium bromide ([3COOHIM]Br) (**3**) were synthesized as previously reported[8, 33]. 1-Carboxyethyl-3-methylimidazolium hexafluorophosphate ([2COOHMIM]PF_6) (**4**), 1-carboxyethyl-3-methylimidazolium bistrifluoromethanesulfonimide ([2COOHMIM]TFSI) (**5**), and 1-carboxypropyl-3-methylimidazolium hexafluorophosphate ([3COOHMIM] PF_6) (**6**) were prepared by anion exchange with the equimolar corresponding salt described in the literature[28]. Crystals **1-6** were obtained by solvent evaporation method and analyzed by single-crystal X-ray diffraction.

Thermogravimetric results show that the prepared compounds **1-6** exhibit excellent thermal stability. The decomposed temperatures are in the range from 250 ºC to 430 ºC, depending on the anion species and length of the alkyl chain. The high thermal stability indicates that these compounds satisfy the special requirements such as ionothermal synthesis. Furthermore, the melting points of compounds **2-6** are below 100 ºC, and consequently they can be regarded as the classic ‘‘ionic liquids’’ defined by a melting point < 100 ºC. The melt point of compound **1** is about 199 °C [33], but it can be used as a precursor to prepare other ionic liquid with the relatively low melting point through the anion exchange.

The most important property of these compounds is their solubility in water. Compounds **1-3** were found to be highly soluble in water and insoluble in some organic solvents with low dielectric constant such as diethyl ether. For example, compound **2** is highly hydrophilic and easily converts into the aqueous as exposed to air. However, ILs **4-6** are almost insoluble in water at room temperature, as we expected, since the ionic liquids based on PF_6^- and TFSI anion are often hydrophobic.

The solubility of ILs **4-6** in water increases with increasing of temperature. The determination of solid-liquid equilibrium phase diagram for compound **6** indicates the upper critical temperature, forming a single phase with water, is about 77.1ºC. This feature has been used in metal ion separation[31] since the cooling of the one-phase mixture results again in phase separation at room temperature.

The solubility of these compounds in water should depend on the solid structure and the solvation with water. Different hydrogen bond structures were found as shown clearly in Fig. 1, and the atom numbering was given in Fig. S1 (ESI †). In the crystal packing of **1**, the neighboring molecules are mainly connected through conventional O—H···Cl and weak C—H···Cl hydrogen-bonds between chloride ion and three cations. Similar interactions were found in crystals **2** and **3**, in which one bromide ion simultaneously interacts with four imidazolium cations through O–H···Br and C—H···Br hydrogen-bonds. Additional N—H···Br hydrogen bond exits in crystal **2** due to the absence of a methyl group in the imidazolium-ring N-3 site. In these cases, the O···X (X=Cl^-, Br^-) distances of the O—H···X hydrogen bonds are 2.979 Å in crystal **1**, 3.183 Å in **2**, and 3.222 Å in **3**, respectively. The detailed parameters are given in Table 1. Besides the classic hydroxyl hydrogen bonds, our expected C—H···X hydrogen bonds involving an imidazolium-ring C-2 site hydrogen atom were observed for these three compounds. It has been confirmed that this type hydrogen bond is not negligible in controlling the structures and physical properties of ionic liquids[36,37]. For hydrophobic ILs **4-6**, except for the complicated C—H···F and C—H···O hydrogen bonds (not shown in Fig. 1) formed between anions and cations, a cyclic dimeric O–H···O structure between two cations was found. The dimeric structures in both **4** and **5** are central symmetric, and two carboxyl groups lie in one plane. The lengths of O–H···O hydrogen bonds are 2.681 for **4** and 2.668 Å for **5**, respectively. These values are consistent with the experimental O–H···O hydrogen bond lengths (2.70 Å)[38]. However, two O–H···O hydrogen bonds in dimer of **6** are not equivalent (2.621 and 2.597 Å) and this dimer twists about 2.3 º. In addition, C–H···O or C–H…F weak interactions assist the dimer hydrogen bond network and most of hydrogen atoms on the cationic moieties are weakly bonded.

Based on the above experimental results, it can be clearly seen that the ionic liquids studied in this work can be divided into two groups according to the hydrogen bond structure of the carboxyl group. The first group includes the hydrophilic ionic liquids based on Br^-, Cl^- anion, in which classic O–H···X hydrogen bonds are present. This kind of interaction was also found in other hydrophilic COOH-ILs such as 1-carboxymethyl-3-decylimidazolium bromide[3], 1-carboxymethyl-3-octylimidazolium bromide[39], and [3COOHMIM]Cl[8]. By contrast, the second group includes the hydrophobic ionic liquid based on $TFSI^-$ and PF_6^- anion, and two carboxyl groups form homodimer joined by two O–H···O hydrogen bonds as seen in organic carboxylic acids. Nockemann[21] *et al.* also found that the two cations of [COOHMIM]TFSI form pairs connected by strong hydrogen bonds with an O···O distance of 2.62–2.65 Å.

The difference in the hydrogen bond structure of these two groups of ionic liquids can also be identified by infrared and Raman spectroscopy since the hydrogen bonds have a strong effect on the vibrational spectra. The C=O stretching band in an infrared spectrum is distinguished, and often observed in the 1780 cm^{-1} region for isolated carboxylic acids.[40] Once hydrogen-bond formation, this band shifts to the 1720 cm^{-1} [40]. In our work, strong IR bands with broad bandwidth were observed in the region from 1722 to 1708 cm^{-1} for a series of COOH-ILs. This indicates the presence of the strong hydrogen bonds. Another important fact is about the continuous bands in the 2900-2300 cm^{-1} region (Fig. S2, ESI†), which has been assigned to C–H···X and O–H···X vibrations [41,42]. The strong and broad bands were observed for the hydrophilic COOH-ILs, whereas the weak and narrow bands for the hydrophobic COOH–ILs were present. This is well explained that the O(C)–H···X hydrogen bond in hydrophilic ILs is often stronger than the corresponding O–H···O and C–H···F hydrogen bonds in the hydrophobic ILs. For organic acid dimer, the infrared band of OH group is generally located at 2800–3000 cm^{-1} [43], unfortunately it is difficult to be identified since the partly overlapped by the νC–H vibrations.

Alternatively, the carboxylic acid dimer is best characterized by the Raman band in the region of 1680-1640 cm^{-1}, where no band in this region in an infrared spectrum is found[44, 45]. Generally, the local inversion center of dimer gives rise to two νC=O modes; the Raman-active in-phase band is located at lower position (~30-50 cm^{-1}) than the infrared-active out-of-phase band. The carbonyl Raman bands of seven selected COOH-ILs are given in Fig. 2. For three hydrophilic ILs all the positions are higher than 1700 cm^{-1}. But for the hydrophobic ILs, the C=O out-of-phase stretching bands were clearly observed in the approximately 1640-1670 cm^{-1} region with weak intensity as suggested by literature[46], indicating that hydrogen bond can occur between two carboxyl groups to produce a dimer. In this region of infrared spectra no band are present (not shown). The presence of C=O out-of-phase stretching Raman bands here would be fairly good evidence for the formation of dimer for the hydrophobic ILs.

Recent studies[35,47] confirmed that the interaction between water and halide anion is stronger than that of two COOH groups. Wang *et al.*[48] theoretically demonstrated that the water molecule is strongly hydrogen bonded with halide anions. From the above lower vibrational positions and the X-ray data of hydrogen bonds (Table 1), it can be preferred that the interactions in COOH-functionalized ILs aqueous are in the order: X···O-H(water) > X···O-H(carboxyl group) > O-H···O (two carboxyl groups). On the other hand, the interaction between PF_6^-/TFSI anion and COOH group is weaker. This can be directly demonstrated by DFT calculations[48] and vibrational spectroscopy[49]. In order to probe the interaction between anion and cation in this case of COOH-ILs, we chose, respectively, the **1** and **6** as the model compounds of hydrophilic and hydrophobic COOH-functionalized ILs, and optimized their dimeric structures using B3LYP [50-52] and wb97xd[53] methods at 6-311++G(d,p) basis set in the Gaussian09 program [54]. The final optimized structures are given in Fig. 3 and Table S1. In the beginning of the optimization, the initial geometries were constructed according to dimer through two O-H···O hydrogen bonds (Fig. 3***a***), and the experimental crystal structure (Fig. 3***b***) for **1**. The calculated results show that the structure ***b*** with one O-H···Cl^- hydrogen bond is more stable than structure ***a*** by 77.46 kJ/mol (B3LYP method) and 96.39 kJ/mol (wb97xd method), respectively. This is supported by X-ray crystal structure, in which the structure ***a*** does not exist. Fig. 3***c*** and 3***d*** give the optimized structures for compound **6**. On the contrary to Fig. 3***a***, both of them were derived from the crystal structure. Using the geometry similar to structure ***a*** as the initial structure, the optimization for **6** always converged to the structure ***c***, in which the alkyl chains on the cations twist together and form a hollow ring with the two associated carboxyl groups. Two PF_6^- anions are above and below this ring, respectively. If we fully destroy these two O-H···O hydrogen bonds between two carboxyl groups, the optimization always leads to the structure ***d***, in which no interaction between two carbonyl group occurs, and the anion-cation strongest hydrogen interaction is C(methylene)-H···F interaction. The calculated energies indicate that the structure ***c*** is more stable than ***d*** only by 15.49 kJ/mol (B3LYP method) and 0.25 kJ/mol (wb97xd method), respectively. Since the wb97xd method is more reliable for the calculation of weak interaction and hydrogen bond[55], both structures ***c*** and ***d*** are approximately stable. In fact, the crystal structure of hydrophobic COOH-functionalized ILs studied in this work is the combination of structure ***c*** and ***d*** according to the stacking structure. Apparently, the O-H···O hydrogen bonds are not dominating factor in this case. The electrostatic potential diagrams (Fig. S3, ESI†) of structures ***c*** and ***d*** show that the alkyl chains and imidazole rings create a hydrophobic region, keeping water away. The only interacting site is F atoms of PF_6^- anion. Moreover, two cations containing COOH group self-associate together and lose the chance to interact with water. Therefore, the low solubility in water for these ILa is desired according to weak solvation of PF_6^- anion. In addition, it can also be supposed that if one wants to dissolve the hydrophobic COOH-functionalized ILs, the dimer should be destroyed at the beginning. For example, when we dissolved these hydrophobic ionic liquid based on TFSI and PF_6^- anion into DMSO-d6 solvent, the Raman bands characterizing the dimer of COOH group disappeared, and new bands at about 1718 cm^{-1} were found as shown in Fig. 4. These indicate that the dimer is almost completely dissociated in the mixture with DMSO-D6.

The difference in feature of hydrogen bonds in these ILs can be clearly shown by the Atoms in Molecules (AIM) analysis[56]. The electronic charge densities (ρ), and its Laplacian values ($\nabla^2\rho$), kinetic energy density (G(r)), potential energy density (V(r)) energy density (H(r)) at bond critical points calculated at wb97xd/6-311++G(d,p) level are shown in Table S2. Generally, normal hydrogen bonds are characterized as electrostatic interaction with a ρ value in the 0.002~0.04 a.u. and positive values for $\nabla^2\rho$ and H(r)[57]. The O-H···O hydrogen bonds in the structure **c** are classified as this type. The other hydrogen bonds list in Table S2 belong to the partially covalent and partially electrostatic charge-assisted hydrogen bond[57] due to the positive $\nabla^2\rho$ *and negative* H(r) values. The larger positive value for ρ and more negative value for H(r) distinguish the O-H···Cl$^-$ hydrogen bond as the stronger hydrogen bond, partly resulting in that the structure ***b*** is more stable than ***a***.

Compared with the 1,3-dialkylimidazolium based ILs, the tendency of formation hydrogen bond with the water molecules increases due to the introduction COOH groups. However, the anions play a major role in the solubility in water[58], the ILs based halide ions with smaller size are almost miscible with water, depending on the strong interaction between water and anion. The halide ions also strongly interact with OH group of the COOH-functionalized imidazolium cation, resulting in the O-H···X hydrogen bond instead of the dimer of carboxyl groups. Only when the interaction between anion and cation is broken, the hydrogen bond between two cations will occur. For example, in the case of [COOHMIM]Cl crystalline hydrate[35], all of Cl$^-$ anions preferentially interact with water molecules, and two cations associate through one O-H···O hydrogen bond since the Cl$^-$···O-H(water) interaction is much stronger than Cl$^-$···O-H(carboxyl group). It is explained by the weaker strength of H-bonding between the COOH groups with PF_6^-/ TFSI$^-$ anion [37, 41] that the cation-cation cyclic dimeric structures are preferred for the hydrophobic COOH-ILs. The direct association of two cations further will further decrease the solubility in water.

Conclusions

A series of carboxyl-based imidazolium ILs have been synthesized, and six of them have been analyzed by X-ray diffraction analysis. The crystal structures and vibrational spectroscopic studies showed that two carboxyl groups of the hydrophobic ionic liquids form a cyclic dimeric structure. Strong O-H···X (X=Cl^-, Br^-) hydrogen bonds between chloride or bromide and COOH groups were observed for the hydrophilic ILs. This is a competitive result of various interactions with different strength. This result can be used as a certain rule to guide to design the new task-specific ILs.

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Notes

Electronic supplementary information (ESI) available: Experimental and theoretical calculation sections, ORTEP drawings (Fig. S1), Infrared spectra (Fig. S2), Atom Coordinates (Table S1), the calculated energies (Table S2), and AIM analysis (Table S3). CCDC 865453, 924047, 924048, 924049, 974649, and 974650.

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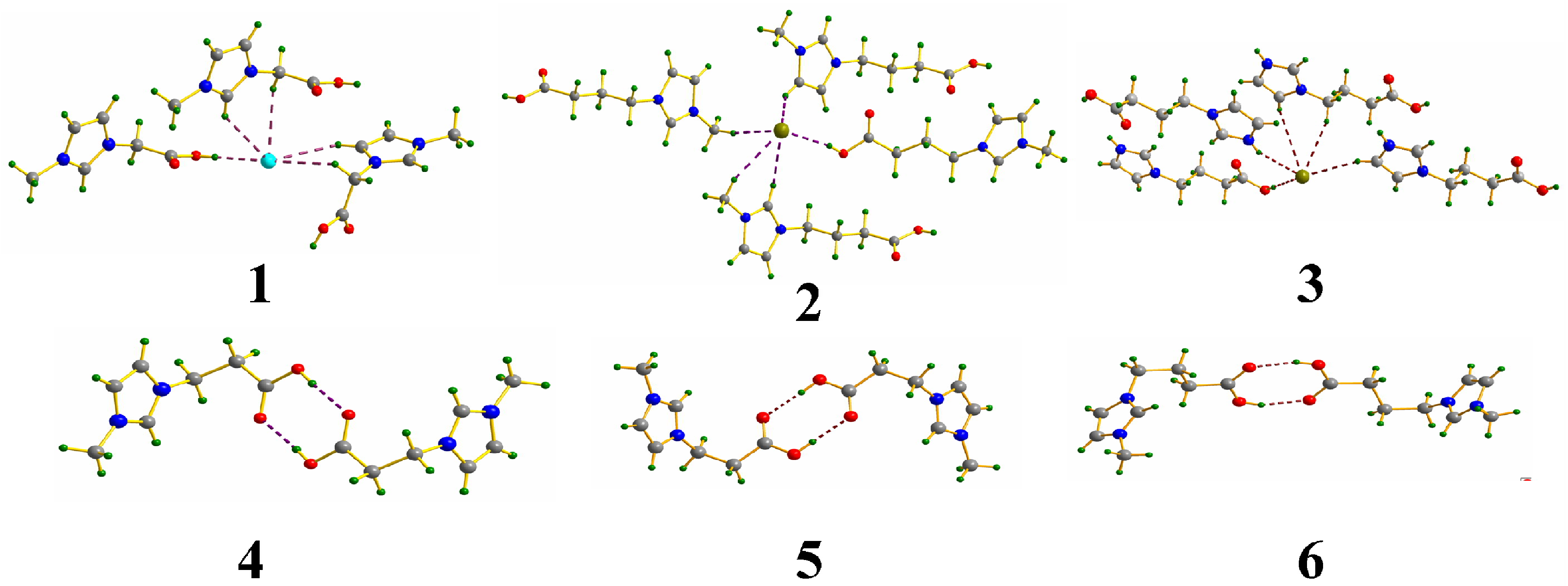
Captions of the figures

Fig. 1 Hydrogen bonds in the crystals 1-6.

Fig. 2 Raman spectra of [2COOHMIM]TFSI (a), [3COOHMIM]PF_6 (b), [4COOHMIM]PF_6 (c), [2COOHMIM]PF_6 (d), [3COOHMIM]Br (e), [2COOHMIM]Cl (f), and [COOHMIM]Cl (g).

Fig. 3 The different optimized geometries of [COOHMIM]Cl (a,b) and [3COOHMIM]PF_6 (c,d).

Fig. 4 Raman spectra of [2COOHMIM]TFSI (a), and [3COOHMIM]TFSI (b) in DMSO-d6 solutions



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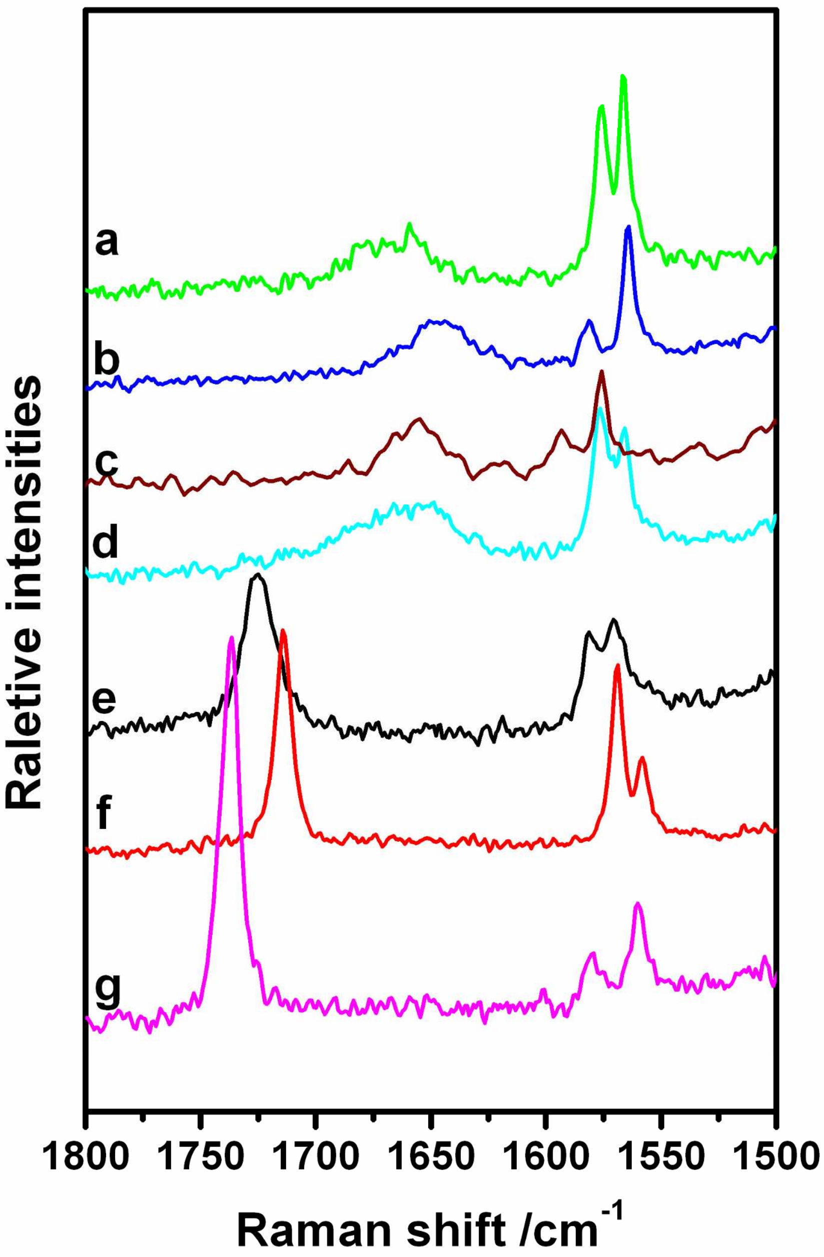

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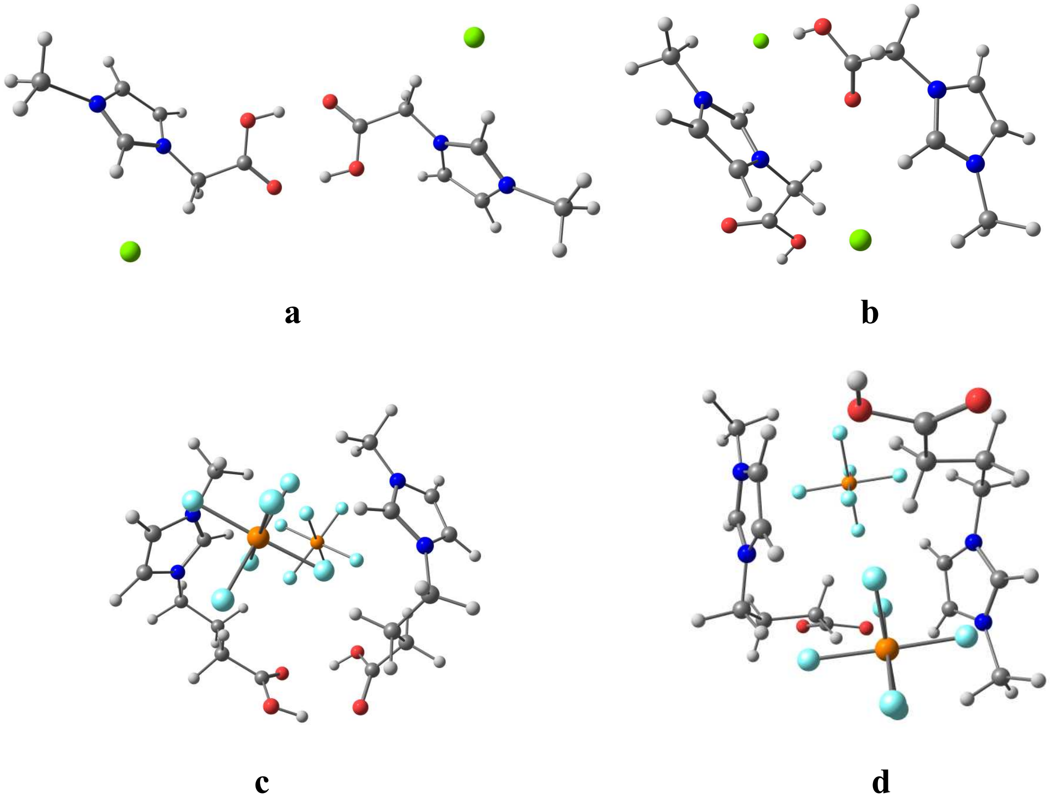

a **b**

c **d**

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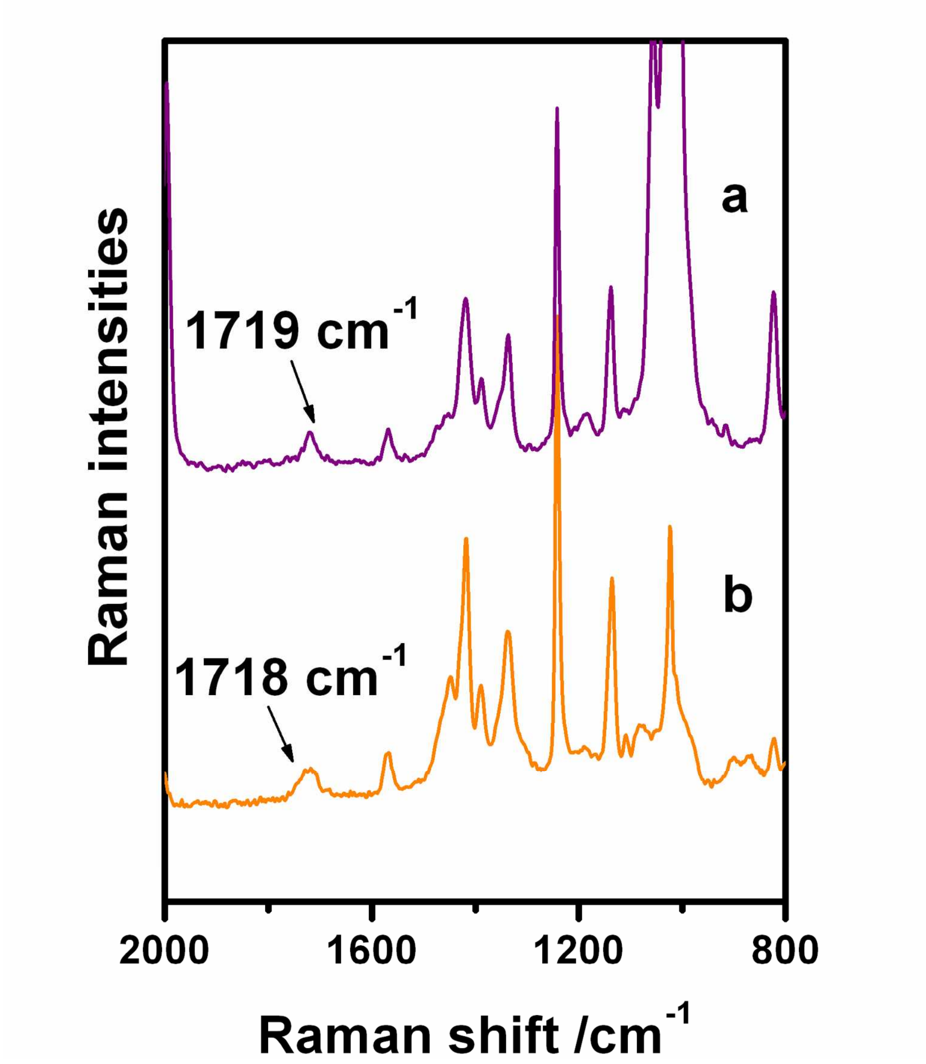

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Table 1 Selected hydrogen bond parameters of compounds **1-6**

Compound	D−H···A	*d*(H···A)/Å	*d*(D···A)/Å	θ(D−H···A)/°	Symmetry code
1	$O-H\cdots Cl^{i}$	2.167	2.979	170.8	i: *x*, 1+*y*, *z*
2	$O-H\cdots Br^{i}$	2.380	3.183	166.2	i: 1−*x*,0.5+*y*, 1.5−*z*
3	$O-H\cdots Br^{i}$	2.400	3.222	175.8	i: x+1, y, z+1
4	$O-H\cdots O^{i}$	1.805	2.681	178.7	i: 2-x, 2-y, 2-z
	$O^{i}-H^{i}\cdots O$	1.805	2.681	178.7	
5	$O1-H1\cdots O2^{i}$	1.848	2.668	175.5	i: -1−*x*, -*y*, 1−*z*
	$O1^{i}-H1^{i}\cdots O2$	1.848	2.668	175.5	
6	$O1—H1\ldots O3^{i}$	1.806	2.621	170.8	i: *x*, −*y*+1.5, *z*+0.5
	$O4—H4\ldots O2^{ii}$	1.788	2.597	169.1	ii: *x*, −*y*+1.5, *z*−0.5

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Hydrogen Bonds in the Crystal Structure of Hydrophobic and Hydrophilic COOH-functionalized Imidazolium Ionic Liquids

Xiao-Peng Xuan, Liang-Liang Chang, Heng Zhang, Na Wang and Yang Zhao*

Classic O-H••• X (halide ion) hydrogen bond and carboxyl group dimer were observed, respectively, for hydrophilic and hydrophobic COOH-functionalized ionic liquids.