

## Combination Effects of Cation and Anion of Ionic Liquids on the Cadmium Metal–Organic Frameworks in Ionothermal Systems

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The effects of cation and/or anion of two groups of ionic liquids ([EMI]X and [PMI]X, where EMI = 1-ethyl-3-methylimidazolium; PMI = 1-propyl-3-methylimidazolium; X = Cl, Br, and I) on the ionothermal reactions between  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and 1,3,5-benzenetricarboxylic acid ( $\text{H}_3\text{BTC}$ ) were studied. Three different Cd–BTC metal–organic frameworks, [EMI][ $\text{Cd}_2(\text{BTC})\text{Cl}_2$ ](**1**), [EMI][ $\text{Cd}(\text{BTC})$ ](**2**), and [PMI][ $\text{Cd}(\text{BTC})$ ](**3**), were formed into crystalline phases. **1** was obtained from reactions in [EMI]Cl, while the same reactions with Cl replaced by Br or I produced a known compound **2**. The replacement of  $\text{EMI}^+$  by  $\text{PMI}^+$  produced **3**, irrespective of the nature of X.

The ionothermal reaction technique for the syntheses of metal–organic frameworks (MOFs) is a rapidly growing research field in recent years.<sup>1</sup> Ionic liquids (ILs), the solvents for ionothermal reactions, possess interesting and useful physicochemical properties such as high thermal stability and negligible vapor pressures,<sup>2</sup> whose features may be advantageous over the conventional solvents for MOF syntheses with improved safety and reduced environmental problems.

Probably, the more exciting aspect of ILs is the possibility of designing the structures of MOFs. ILs are composed of

organic cations and inorganic or organic anions. The variation of the cation and/or anion can provide a means to tune the solvent properties, which could be a means to design the structures of MOFs.<sup>1,3</sup> For example, Morris' group showed that the hydrophilicity/hydrophobicity of the anion part gives rise to significant changes in the MOF structures.<sup>1h</sup> Furthermore, the ionic species of ILs can participate into MOFs, making the nature of the cation/anion an important variable for the design of MOFs. Many of the MOFs from ionothermal syntheses show that the cations of ILs can function as structure-directing agents. Our recent paper also showed that the tuning of the MOF structures by the variation of the cation of ILs could be extensive.<sup>3b</sup>

However, such efforts toward understanding the influence of the cation and anion were limited until now. Here, we present our results that show more subtle variation by the chemical identity of the halide anion, coupled with the influence of the cation part. Halide anions of ILs are classified as strongly hydrophilic, implying that their behaviors are similar to one another. However, our results demonstrate that there is finer subtlety with the variation of halide ions.

We employed two groups of ILs as solvents for ionothermal reactions between  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and 1,3,5-benzenetricarboxylic acid ( $\text{H}_3\text{BTC}$ ). The ILs we used are [EMI]X (EMI = 1-ethyl-3-methylimidazolium) and [PMI]X (PMI = 1-propyl-3-methylimidazolium) with X = Cl, Br, and I for each group. The ILs were synthesized according to the literature methods.<sup>3a,4</sup>

The nature of X of the [EMI]X solvent system turned out to be a crucial factor in determining the forms of MOFs. When X = Cl, we obtained a new MOF, [EMI][ $\text{Cd}_2(\text{BTC})\text{Cl}_2$ ] (**1**), with Cl taking a part of the MOF structure, while the X = Br and I reactions produced [EMI][ $\text{Cd}(\text{BTC})$ ] (**2**) without any X in the structure. **2** was previously reported by another group.<sup>1b</sup> Quite contrarily,

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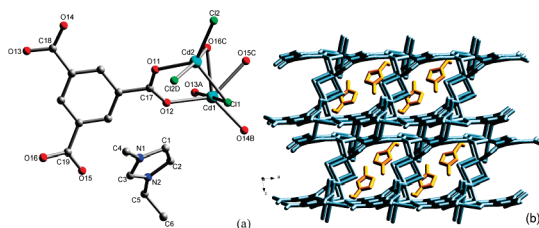
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**Figure 1.** Structure of **1**: (a) asymmetric unit; (b) 3D view along the *b* direction with EMI<sup>+</sup> (orange) located in the channels.

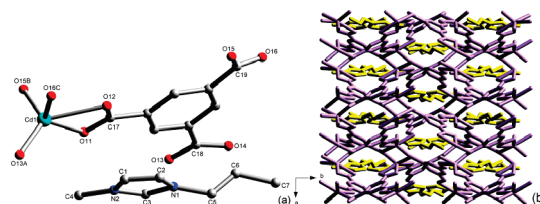
reactions using [PMI]X as solvents turned out to be insensitive to the nature of X, all producing a new MOF, [PMI][Cd(BTC)] (**3**). Interestingly, the frameworks of **2** and **3** show the same topology, although their structures are different in some details.

The crystal structures of **1** and **3** were characterized by single-crystal X-ray diffraction analyses,<sup>5</sup> and the phase identity of **2** was confirmed by comparing the powder X-ray diffraction (PXRD) pattern with the calculated one from the crystal data in the literature.<sup>1b</sup>

There already exist 28 different Cd-BTC MOFs in the literature. These MOFs can be classified into 17 different types depending on the coordination mode of the BTC ligand. The 17 modes span most of the possible combinations of the bonding modes around BTC ligands. These are summarized in the Supporting Information (Scheme S1 and Table S1) along with their references. Compound **1** shows the highest coordination number of 6 for BTC<sup>3−</sup>; compounds **2** and **3** also show a relatively high coordination number of 4. These and our previous analysis on more extensively investigated Zn-BTC MOFs<sup>3b</sup> suggest that MOFs from ionothermal reactions tend to have higher degrees of condensation between the metal and ligand, probably because of the higher polarity of ILs than other types of solvents.

The asymmetric unit of **1** has two Cd atoms, one BTC<sup>3−</sup> ligand, one EMI<sup>+</sup>, and two Cl<sup>−</sup> ligands (Figure 1a). The BTC<sup>3−</sup> ligand is bonded to six Cd atoms in a chelating/bridging bidentate and bis-bidentate fashion (mode Q in Scheme S1). The Cd1 atom is in a distorted six-coordinated CdO<sub>5</sub>Cl octahedron, and Cd2 is in a distorted five-coordinated CdO<sub>2</sub>Cl<sub>3</sub> trigonal bipyramid with  $\tau = 0.652$ .<sup>6</sup> Cd1 is coordinated equatorially by four carboxylic O atoms from three separate BTC<sup>3−</sup> ligands and axially by one carboxylic O atom (O13) and one Cl<sup>−</sup>. Cd2 is surrounded by one carboxylic O atom (O11) and two Cl<sup>−</sup> in the equatorial plane, one carboxylic O atom (O16), and one Cl<sup>−</sup> in the axial position. The Cd–O average distance is 2.30 Å. There are two kinds of  $\mu_2$ -bridging Cl<sup>−</sup> atoms: Cl1 asymmetrically bridges Cd1 and Cd2, with Cd–Cl distances being 2.759(6) and 2.479(5) Å, respectively, and Cl2 links two symmetry-related Cd2 atoms.

The description of the structure of **1** starts from a –Cd–BTC– chain along the *a* direction in which neighboring Cd1



**Figure 2.** Structure of **3**: (a) asymmetric unit; (b) 3D view with the PMI (yellow) lying in the channels.

atoms are linked by O12, O15, and  $\mu_2$ -O16 atoms of BTC<sup>3−</sup> ligands. These neighboring antiparallel chains are paired to form double chains by Cd2–O11 bonds connecting the [Cd<sub>2</sub>Cl<sub>4</sub>] units (Supporting Information, Figure S4a). Connected by the Cd1–O13 bridges, the double chains are fused into a battlement-like 2D layer along the *ac* plane, stacking in an –ABAB– fashion (Supporting Information, Figure S4b). A 3D framework is generated by the 2D layers linked by Cd1–O14 bonds, in which the channels are formed along the *b* direction with 349.6 Å<sup>3</sup> (37.8% of the total volume) extraframework volume calculated by PLATON.<sup>7</sup> The EMI<sup>+</sup> cations anchor in the channels (Figure 1b) and are stabilized by weak d– $\pi$  interactions with the framework in addition to the electrostatic interaction.

Liao et al. reported that the same reaction as for **1** in [EMI]Br, instead of [EMI]Cl, produced **2** without Br in the framework.<sup>1b</sup> We confirmed their result and found that [EMI]I also produced **2** (Supporting Information, Figure S3). It seems that the sizes of X and the Cd–X bond strengths are the factors that determine the structures. To the contrary, such a differentiation by X does not appear in the [PMI]X solvent system.

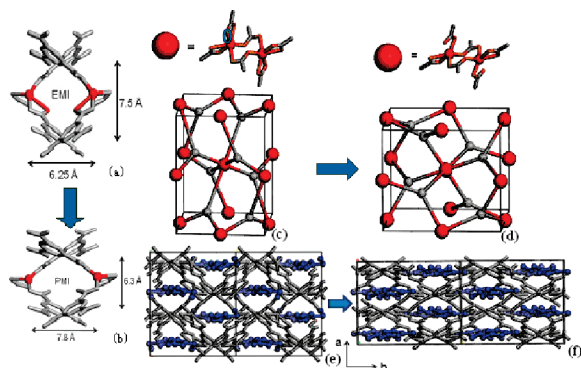
The asymmetric unit of **3** consists of one Cd atom, one BTC<sup>3−</sup> ligand, and one PMI<sup>+</sup>. The asymmetric Cd1 atom is in a slightly distorted five-coordinated square pyramid CdO<sub>5</sub> geometry with  $\tau = 0.015$ ,<sup>6</sup> whose equatorial plane is composed of four O atoms from three BTC<sup>3−</sup> ligands with distances of Cd–O from 2.038(2) to 2.600(1) Å and whose axial position is occupied by a carboxylic O atom (O15; Figure 2a). Four Cd1 atoms are connected by three separate BTC<sup>3−</sup> ligands with chelating and monodentate mode to form a 29-membered ring [Cd<sub>4</sub>(BTC)<sub>3</sub>]. The growth of the 29-membered rings results in a stairlike chain along the *b* direction, and the neighboring antiparallel stairs further extend to form a 2D layer in the *bc* plane (Supporting Information, Figure S5). The neighboring parallel layers are further connected via Cd1–O15 bonds to generate a 3D framework. The channels are formed with 1599.0 Å<sup>3</sup> (48.5%) extraframework volume,<sup>7</sup> which is fully occupied by the PMI<sup>+</sup> cations (Figure 2b). There are  $\pi$ – $\pi$  stacking and electrostatic interactions between the guest and the framework.

Thermogravimetric analysis (TGA) data of **1** and **3** show that they have high thermal stability and start to decompose in single steps at 379 °C for **1** and 383 °C for **3** (Supporting Information, Figure S1). **2** is also reported to have high decomposition temperature.<sup>1b</sup> It seems that the strong

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**Figure 3.** (a and b) Environments of channels occupied with  $\text{EMI}^+$  and  $\text{PMI}^+$  in **2** and **3**, respectively. Note that one  $\text{Cd}-\text{O}$  bond (red) is broken on moving from **2** to **3**. (c and d) Topologies of the  $[\text{Cd}(\text{BTC})]^-$  networks in **2** and **3**, in which red and gray circles represent  $\text{Cd}_2$  dimers and  $\text{BTC}^{3-}$  ligands, respectively. (e and f) Views along  $[001]$  directions in compounds **2** and **3**.

interaction between the guest cations and the frameworks increases the thermal stability of this class of compounds.

It is noteworthy that compounds **2** and **3** have some common features. Both have the same general chemical formula  $[\text{cation}][\text{Cd}(\text{BTC})]$ , and their structures have the same topology with channels in the  $[001]$  directions with  $\text{EMI}^+$  or  $\text{PMI}^+$  cations in the channels. It is interesting that the additional methylene group of the cation on moving from **2** to **3** makes several slight changes in the structure while maintaining the same topology (see Figure 3): (a) the  $[001]$  channel of compound **3** becomes broadened compared to that of compound **2** ( $6.3 \times 7.5 \text{ \AA}^2$  for **2** and  $7.8 \times 6.3 \text{ \AA}^2$  for **3**); (b) the extraframework volume of **3** is also slightly larger with  $1599.0 \text{ \AA}^3$  than that of **2** with  $1563.1 \text{ \AA}^3$ ; (c) the coordination mode of one carboxylic group in the  $\text{BTC}^{3-}$  ligand is changed from chelating for **2** (mode L in Scheme S1 in the Supporting Information) to a monodentate mode for **3** (mode I in Scheme S1 in the Supporting Information) to accommodate the larger  $\text{PMI}^+$  cation. These observations suggest that the topology and the general chemical formula  $[\text{cation}][\text{Cd}(\text{BTC})]$  of **2** and **3** are some of the most favorable

features of the MOFs to be formed in the present systems. In this regard, **1** is a deviation from the general behavior, which may be attributed to the smaller size of Cl than Br or I and the stronger  $\text{Cd}-\text{Cl}$  bond than  $\text{Cd}-\text{Br}$  or  $\text{Cd}-\text{I}$ . The absence of such a deviation in the products from the  $[\text{PMI}]\text{X}$  reactions suggests that the host-guest compatibility of the structure of **1** with  $\text{EMI}^+$  may not be possible with the larger  $\text{PMI}^+$  guests.

In summary, we have explored the ionothermal reaction systems between  $\text{Cd}(\text{NO}_3)_2$  and  $\text{H}_3\text{BTC}$  in two groups of IL media, in which the ILs are  $[\text{EMI}]\text{X}$  and  $[\text{PMI}]\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{and I}$ ). The nature of the halide ion of the  $[\text{EMI}]\text{X}$  solvent system turned out to be a crucial factor in determining the forms of MOFs: a new MOF,  $[\text{EMI}][\text{Cd}_2(\text{BTC})\text{Cl}_2]$ , is obtained from  $[\text{EMI}]\text{Cl}$  solvent, while  $[\text{EMI}]\text{X}$  ( $\text{X} = \text{Br}$  and  $\text{I}$ ) produced  $[\text{EMI}][\text{Cd}(\text{BTC})]$  without any X in the structure. However, reactions using  $[\text{PMI}]\text{X}$  turned out to be insensitive to the nature of halide, all producing a new MOF,  $[\text{PMI}][\text{Cd}(\text{BTC})]$ . The resulting compounds feature 3D structures with IL cations anchoring in the channels, in which the ILs act as structure-directing templates and charge-compensating groups, endowing the MOFs with high thermal stability. Our results show that there is finer subtlety with the variation of halide ions, coupled with the influence of the cation part in the IL.

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**Supporting Information Available:** Experiment section, physical measurements, TGA graphs, IR data, XRPD patterns, X-ray crystallographic files for compounds **1** and **3** (CCDC: 659182 and 659183), and Cd-BTC compounds and coordination modes in the literature. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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