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# Ionic liquid as reaction medium for the synthesis and crystallization of a metal-organic framework: $(BMIM)_2[Cd_3(BDC)_3Br_2]$ (BMIM = 1-butyl-3-methylimidazolium, BDC = 1,4-benzenedicarboxylate)

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## Abstract

An ionic liquid, 1-butyl-3-methylimidazolium bromide, is used as reaction medium for the synthesis and crystallization of a coordination polymer, $(BMIM)_2[Cd_3(BDC)_3Br_2]$ (**1**) (BMIM = 1-butyl-3-methylimidazolium, BDC = 1,4-benzenedicarboxylate), which forms an anionic two-dimensional framework with the imidazolium cations located between the layers. This compound is thermally stable up to ca. 340 °C and exhibits blue emission in solid state at room temperature. Other characterizations by IR and UV–visible spectra are also described.

*Keywords:* Ionic liquid; Imidazolium bromide; Coordination polymer; Blue emission

Many Efforts have been made on the research of metal-organic materials with extended frameworks, which may exhibit potential properties such as ion-exchange, sorption, catalytic and nonlinear optical properties through crystal engineering [1]. Even though exact prediction is unrealistic, structures of these materials are influenced by the subtle interplay of many factors such as the geometric preference of metal ions, the sizes and shapes of the organic building blocks, templates and solvent systems. Recently, there has been an upsurge in the research of near-ambient temperature ionic liquids (ILs), or organic molten salts, owing to their potential synthetic, electrochemical, photoelectrochemical and phase transfer applications [2], which can be attributed to their characteristic physicochemical properties such as tuneable solvation strength, solubility, high thermal stability, ionic conductivity and heating behaviour under microwave radiation [3]. In contrast with conventional solvents, mostly volatile organic compounds (VOC), ionic liquids are non-flammable, nearly non-volatile, and are often thought as environmentally benign reaction media [4], although it should be noted that the toxicity of ionic liquids has been reported [5]. Compared with their success in organic synthesis, examples of using ionic liquids in inorganic solid-state synthesis are relatively rare. Hydrothermal or solvothermal method has long been used to synthesize multidimensional frameworks, in which structure-directing organic templates can be incorporated [6]. Recently, ionothermal system has been investigated as a new synthetic media in an attempt to prepare zeolite-like phosphates [7]. There were also numerous reports that nanoparticles were grown in ionic liquids [8], and that dialkylimidazolium cations were used as templates in aqueous solution for the synthesis of zeolites and MCM-41 [9]. Examples of coordination polymers, $[Cu(1,3\text{-bis(4-pyridyl)propane})](BF_4)$ and $[Cu_3(tpt)_4](BF_4)_3 \cdot (tpt)_{2/3} \cdot 5\,H_2O$ (tpt = 2,4,6-tris(4-pyridyl)-1,3,5-triazine) prepared by ionothermal method in 1-butyl-3-methylimidazolium tetrafluoroborate, form cationic networks with charge-compensating $BF_4^-$ anions incorporated [10]. Polycarboxylates have been extensively used as organic linkers to bind metal

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centers to form a variety of open frameworks [11]. Recently, we have published the ionothermal synthesis of (EMIM)[Cd(BTC)] (EMIM = 1-ethyl-3-methylimidazolium, BTC = 1,3,5-benzenetricarboxylate), with a 3D anionic framework and imidazolium cations as counterions [12]. We have been continuing to explore the ionothermal synthesis of polycarboxylate-based metal-organic frameworks, to investigate the feasibility of using ionic liquids as common reaction media.

Here we report the ionothermal synthesis of a two-dimensional (2D) metal-organic framework: $(BMIM)_2[Cd_3(BDC)_3Br_2]$, which exhibits intense blue luminescence. In this experiment, the ionic liquid, 1-butyl-3-methylimidazolium bromide, was prepared under microwave radiation [13]. The starting reagents, $Cd(NO_3)_2 \cdot 4H_2O$ and 1,4-benzenedicarboxylic acid, in a 3:1 ratio, dissolved completely in the ionic liquids, forming a clear colorless viscous solution at 160 °C. It was kept for 15 days until many colorless crystals formed [14]. The stoichiometric ratio did not give any solid-state product. The products are not stable in water but are stable in alcohol and acetone. Thermogravimetric and differential thermal analyses indicate **1** is stable up to ca. 340 °C, following by an abrupt endothermic weight loss owing to the collapse of the 2D framework. The identity of the bulk product is confirmed by elemental analysis, and by comparing the experimental and simulated X-ray powder diffraction patterns. The crystal structure of **1** has been characterized by single-crystal X-ray diffraction analysis, [15] which reveals that **1** contains an anionic 2D framework built by cross-linking trimeric $Cd_3O_{12}Br_2$ units with BDC ligands (Fig. 1). Each $Cd_3$ trimer is composed of a $CdO_6$ octahedron, sitting at a centre of inversion, sandwiched by two distorted $CdO_5Br$ octahedra ($d(Cd \cdots Cd) = 3.5882(3)$ Å) in an edge-sharing fashion. Each $Cd_3$ trimeric unit is surrounded by six BDC ligands, extending into a 2D network, which contains triangular meshes with three edges of 10.29 Å × 10.29 Å × 10.30 Å (Fig. 2a). These $[Cd_3(BDC)_3Br_2]_n^{2n-}$ layers are perpendicular to the (1 0 0) crystallographic direction. Terminal Cd-Br bonds are found to point toward the interlayered space, with the partially negatively charged Br atoms interacting with the positively charged aromatic rings of imidazolium cations. Interestingly, the 2D $[Cd_3(BDC)_3Br_2]_n^{2n-}$ anionic framework of **1** is closely related to the neutral $[Zn_3(BDC)_3(H_2O)_2]_n$ framework in $[Zn_3(BDC)_3(H_2O)_2] \cdot 4DMF$ [16], in which terminal Zn–$OH_2$ bonds point toward the interlayered space, where DMF solvent molecules are located. It has been reported the aromatic C–H ⋯ $X^-$ (X = Cl, Br, I) hydrogen bonds are important in stabilizing many imidazolium salts [17]. In **1**, the imidazolium C–H ⋯ $Br^-$ hydrogen bonding interactions ($d(C \cdots Br) = 3.927(5)$ Å, and $d(H \cdots Br) = 3.359$ Å) are relatively weak and do not contribute significantly to crystal packing. Therefore the interactions between the imidazolium cations and the 2D anionic framework are mainly electrostatic in nature. It should also be noted that the more hydrophobic imidazolium butyl groups stretch into the vicinity of BDC benzene rings (Fig. 2b). There are two crystallographically distinct BDC ligands, in which the dihedral angles between their aromatic rings and the (1 0 0) planes are 70.1(1)° and 56.95(9)°, respectively. In both of them, the carboxylate groups are nearly coplanar to the aromatic rings, with the dihedral angles to be 17.1(5)f, 10.9(5)° for the first and 9.6(5)° for the second BDC. The IR spectrum of **1** exhibits characteristic bands of carboxylates, with

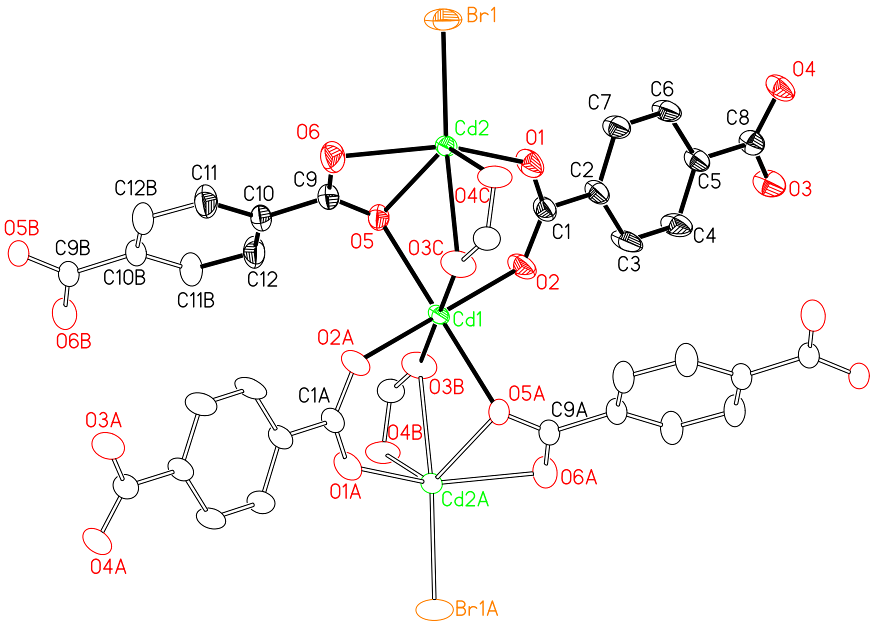

Fig. 1. The ORTEP view and labeling scheme of the trimeric building block. The asymmetric unit is shown with 50% probability displacement ellipsoids. All hydrogen atoms are omitted for clarity.