Ionothermal synthesis, structures, properties of cobalt-1,4-benzenedicarboxylate metal–organic frameworks

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ARTICLE INFO

ABSTRACT

Eight kinds of 1-methyl-3-alkylimidazolium halide [RMI]X (R=ethyl (E), propyl (P), butyl (B) and amyl (A); MI = imidazolium; X= Cl$^-$, I$^-$) ionic liquids (ILs) were used as reaction media and obtained a series of 2D [RMI]$_2$[Co$_3$(BDC)$_3$X$_2$] frameworks through the ionothermal reactions of 1,4-benzenedicarboxylic acid (H$_2$BDC) with Co(NO$_3$)$_2$·6H$_2$O. The 2D [RMI]$_2$[Co$_3$(BDC)$_3$X$_2$] frameworks exhibit a same (3,6) topology network with [RMI]$^+$ cations locating in the interlayer space. [RMI]$^+$ cations play a template role in the structure constructions, whose influence combining with the effect of X$^-$ anions pass to the TG behaviors. The decomposition temperatures of the [RMI]$_2$[Co$_3$(BDC)$_3$X$_2$] frameworks decrease with the alkyl chains in [RMI]$^+$ cations, and the compounds containing Cl$^-$ show higher thermal stabilities than those with I$^-$. However, compounds **1–8** exhibit two similar broad emissions at ca. 380 and 390 nm, assigned to ILCT. The RMI$^+$ templates and the X$^-$ anions do not exert their influence on the fluorescence.

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1. Introduction

Metal-organic frameworks (MOFs) materials with structural diversities have gained considerable attention due to the applications in many fields, such as catalysis, [1,2] ion-exchange, [3] drug-delivery, [4] gas sorption and separation, [5,6] and so forth [7,8]. Ionothermal synthesis is a new emerging environmental friendly synthesis method, [9–11] in which ionic liquids (ILs) behave as reaction media, structural templates or charge-compensating groups [12,13]. ILs possess many distinguished features compared to the traditional solvents: high ionic conductivity, non-flammability and negligible vapor pressure [14–16]. Therefore, ionothermal synthesis is reasonably expected to offer significantly different reaction environments to produce new-type MOF materials. A great of effort has been devoted to ionothermal synthesis applied in MOF materials [17–19]. Based on our previous work on M-BTC (M=Zn, Cd, Ni; H$_3$BTC=benzene-1,3,5-tricarboxylic acid) [20] and M-BDC (M=Zn, Co; H$_2$BDC=1,4-benzenedicarboxylic acid) [21], a combination effect of ionic liquid cationic and anionic parts was demonstrated, in which RMI$^+$ cation exhibits structural template and the halide anion controls the structural fashion and the property regulation through their hydrophilicity/

hydrophobicity or nucleophilicity/basicity behaviors [19c,20c]. The present work is an ongoing part of our work. Herein, we explored the effect of ILs on the structural formation and properties of Co-BDC system, especially the roles of the IL anionic parts plays. We selected Co(NO$_3$)$_2$ reacting with simple H$_2$BDC ligand under two kinds of 1-methyl-3-alkylimidazolium halide [RMI]X (R=ethyl to amyl; MI = imidazolium; X=Cl$^-$, I$^-$) ILs to eliminate the effect of metal center and ligands on the structure. Eight 2D compounds, [RMI]$_2$[Co$_3$(BDC)$_3$X$_2$], were obtained from the above synthetic processes, which show the same negative 2D [Co$_3$(BDC)$_3$X$_2$]$^{2-}$ skeletons. With the observation on single crystal structure, powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), fluorescence and FT-IR, our work clearly indicates a combinational effect of RMI$^+$ cations and X$^-$ anions on the MOF structures and the TG behaviors.

2. Experimental

2.1. Materials and physical measurements

The reagents and solvents were used directly as supplied commercially without further purification except two kinds of 1-methyl-3-alkylimidazolium halide ILs synthesized from the reactions of 1-alkyl halide with 1-methylimidazole according to the literature processes. [22] Degassed alkyl halide (alkyl = ethyl to

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amyl; X=Cl⁻, I⁻) were refluxed with the distilled 1-methylimidazole to give the two kinds of eight ILs. The ILs were washed with ethyl acetate, and then dried under a vacuum at least for 10 h ([EMI]Cl: white solid, [PMI]Cl: colorless oil, [BMI]Cl: white solid, [AMI]Cl: colorless oil, [EMI]I: yellow solid, [PMI]I: yellow oil, [BMI]I: yellow oil, [PMI]I: yellow oil). Elemental analysis of C, H and N was carried out on a Vario EL III elemental analyzer. FT-IR spectra were collected from KBr pellets (Aldrich, > 99%, FT-IR grade) with a Bruker Tensor 27 FT-IR spectrometer in the range of 4000–400 cm⁻¹. TGA were carried out in N_2 atmosphere on a SDT Q600 V⁸.3 Build 101 instrument with a heating rate of 10 °C·min⁻¹ and a N_2 flow rate of 20 cm³·min⁻¹. PXRD data for the materials were collected at ambient temperature with a Rigaku D/Max–3c (Japan) diffractometer (Cu-Kα₁,₂ X-radiation, $\lambda_1 = 1.540598$ Å and $\lambda_2 = 1.544426$ Å), equipped with an X'Celerator detector and a flatplate sample holder in a Bragg–Brentano para-focusing optics configuration (40 kV, 50 mA). Intensity data were collected by the step counting method (step being 0.02°) in continuous mode in the range of $5 \leq 2\theta \leq 60°$. Fluorescence spectra were acquired on a Hitachi F-4600 fluorescence spectrophotometer with the excitation and emission slits setted to 5 nm.

2.2. Synthesis of the compounds

Synthesis of [EMI]₂[Co₃(BDC)₃Cl₂] (**1**). 2.0 mmol, 0.5825 g Co(NO₃)₂·6H₂O and 0.50 mmol, 0.0831 gH₂BDC were placed in a crystallisation vial placed in a 25 mL teflon-lined stainless-steel autoclave mixed with 1.005 g [EMI]Cl. The mixture was kept inside the furnace at 160 °C for 5 days, and then naturally cooled to ambient temperature. The blue crystals of **1** suitable for single crystal X-ray diffraction were collected after soak clearing with acetone. IR data (in KBr, cm⁻¹) for **1**: 3703(w), 3325(w), 3145(m), 3097(s), 2989(m), 1583(s), 1383(s), 1306(m), 1167(s), 1018(w), 825(m), 740(s), 624(w), 557(m). Elemental analysis (%), Found (calcd): C, 45.05(44.93); H, 3.31(3.56); N, 5.75(5.82).

Synthesis of compounds 2–8. Compounds **2–8** were synthesized from the similar preparation process as described in compound **1**.

[PMI]₂[Co₃(BDC)₃Cl₂] (2): 2.5 mmol, 0.7275 g Co(NO₃)₂·6H₂O and 0.50 mmol, 0.0833 g H₂BDC mixed with 0.8 mL (ca. 0.93 g) [PMI]Cl. IR data (in KBr, cm⁻¹) for **2**: 3660(w), 3138(w), 3082(w), 2966(w), 1601(s), 1389(s), 1308(s), 1166(m), 1014(w), 825(m), 744(s), 557(m). Elemental analysis (%), Found (calcd): C, 46.05(46.08); H, 3.91(3.87); N, 5.69(5.66).

[BMI]₂[Co₃(BDC)₃Cl₂] (3): 1.5 mmol, 0.4365 g Co(NO₃)₂·6H₂O and 0.50 mmol, 0.0834 g H₂BDC mixed with 1.0026 g [BMI]Cl. IR data (in KBr, cm⁻¹) for **3**: 3666 (w), 3298(w), 3142(m), 3088(m), 2963(m), 1963(w), 1841(w), 1593(s), 1385(s), 1307(s), 1160(m), 1010(w), 825(s), 742(s), 625(w), 543(s). Elemental analysis (%), Found (calcd): C, 47.02(47.17); H, 3.97(4.16); N, 5.61(5.50).

[AMI]₂[Co₃(BDC)₃Cl₂] (4). 1.5 mmol, 0.4359 g Co(NO₃)₂·6H₂O and 0.50 mmol, 0.0832 g H₂BDC mixed with 0.9 mL (ca. 0.99 g) [AMI]Cl. IR data (in KBr, cm⁻¹) for **4**: 3718(w), 3282(w), 3133(m), 3087(m), 2961(m), 1944(w), 1682(m), 1597(s), 1392(s), 1296(s), 1164(m), 1010(w), 740(s), 625(w), 555(s). Elemental analysis (%), Found (calcd): C, 48.15(48.20); H, 4.40(4.43); N, 5.42(5.35).

[EMI]₂[Co₃(BDC)₃I₂] (5). 1.0 mmol, 0.2914 g Co(NO₃)₂·6H₂O and 0.50 mmol, 0.0833 g H₂BDC mixed with 1.0031 g [EMI]I. IR data (in KBr, cm⁻¹) for **5**: 3722(w), 3408(w), 3151(m), 3103(m), 2974(w), 1591(s), 1156(m), 1385(s), 1302(m), 1164(m), 1018(w), 825(s), 746(s), 555(s). Elemental analysis (%), Found (calcd): C, 38.15(37.75); H, 3.11(2.99); N, 4.78(4.89).

[PMI]₂[Co₃(BDC)₃I₂] (6). 1.0 mmol, 0.2915 g Co(NO₃)₂·6H₂O and 0.50 mmol, 0.0830 g H₂BDC mixed with 1.0 mL (ca. 1.51 g) [PMI]I. IR data (in KBr, cm⁻¹) for **6**: 3830(w), 3737(w), 3415(w), 3133(m), 3101(m), 2962(m), 1631(s), 1592(s), 1383(s), 1302(s), 1160(m), 1018(m), 902(w), 825(s), 746(s), 555(s). Elemental analysis (%), Found

(calcd): C, 38.95(38.90); H, 3.41(3.26); N, 4.85(4.77).

[BMI]₂[Co₃(BDC)₃I₂] (7). 1.0 mmol, 0.2911 g Co(NO₃)₂·6H₂O and 0.50 mmol, 0.0836 g H₂BDC mixed with 1.0 mL (ca. 1.52 g) [BMI]I. IR data (in KBr, cm⁻¹) for **7**: 3581(w), 3384(w), 3141(m), 3102(m), 1592(s), 1492(m), 1387(s), 1302(s), 1167(m), 1014(m), 890(w), 819(s), 740(s), 554(s). Elemental analysis (%), Found (calcd): C, 39.93(40.06); H, 3.40(3.36); N, 4.74(4.67).

[AMI]₂[Co₃(BDC)₃I₂] (8). 1.0 mmol, 0.2915 g Co(NO₃)₂·6H₂O and 0.50 mmol, 0.0834 g H₂BDC mixed with 1.2 mL (ca. 1.83 g) [AMI]I. IR data (in KBr, cm⁻¹) for **8**: 3591(w), 3149(m), 3102(m), 2952(m), 1600(s), 1500(m), 1388(s), 1301(s), 1166(m), 1007(m), 871(w), 831(s), 740(s), 628(w), 540(s). Elemental analysis (%), Found (calcd): C, 41.28(41.03); H, 3.87(3.77); N, 4.63(4.56).

2.3. Single crystal X-ray diffraction

Single crystals of compounds **1–8** were manually harvested from crystallisation vials and mounted on Hampton Research CryoLoops using FOMBLIN Y perfluoropolyether vacuum oil (LVAC 25/6, purchased from Aldrich) [23] with the help of a Stemi 2000 stereomicroscope equipped with Carl Zeiss lenses. Data were collected on a Rigaku Mercury CCD diffractometer equipped with a graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 (2) Kolpotocheirodon the intensity data were collected by the ω scan technique and were reduced using CrystalClear program. [24] The crystal structures of compounds **1–8** were solved by direct method using SHELXTL™ package of crystallographic software [25] and refined by fullmatrix least-squares technique on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at geometrically calculated positions to their carrier atoms and refined with isotropic thermal parameters included in the final stage of the refinement. The summaries of the structural determination and refinement for **1**-**8** are listed in Supporting Information (Tables 1 and 2). The selected bond distance and angles are listed in Supporting Information (Table S1).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center (the deposition CCDC numbers 1452374-1452381 for compounds **1–8** respectively). These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_re quest/cif.

3. Results and discussion

3.1. Crystal structures of compounds 1–8

With the corresponding RMI⁺ cations anchoring in the inter-layer spaces and X⁻ anions as the terminal ligand, similar 2D layered compounds **1–8**, [RMI]₂[Co(BDC)₃X₂] (X=Cl, RMI = EMI (**1**), PMI (**2**), BMI (**3**), AMI (**4**); X=I, RMI = EMI (**5**), PMI (**6**), BMI (**7**), AMI (**8**)), were obtained. These structures possess the same [Co₃(BDC)₃X₂]²⁻ skeleton framework (Fig. 1), including the same coordination spheres of the Co(II) centers (Fig. 2 and Fig. S1) and the coordination fashions of the BDC²⁻ ligands. Therefore, only the structure of compound **1** will be discussed in detail. The asymmetric unit of compound **1** comprises of one and a half Co(II) centers, one and a half BDC²⁻ ligands, one Cl⁻ and one EMI⁺ (Fig. 2). The total four positive charges on one and a half Co(II) centers and EMI⁺ cation are neutralized by one and half BDC²⁻ ligands and one Cl⁻ to keep charge balance. BDC²⁻ ligands in compound **1** exhibit two kinds of μ_4 coordination fashions: bis-bidentate and bis-bridging monodentate coordination fashions (Scheme 1). Two independent Co1 and Co2 centers show different coordination geometries: a distorted tetrahedron coordination