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Synthesis, structures and luminescence of two 2-D microporous metal-organic frameworks in the zinc (cadmium)-dicarboxylate-imidazolate system

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Two 2-D microporous metal-organic frameworks, [Zn(BDC)(MbIm)]·2DMF (1) and $[Cd_3(BDC)_3(MbIm)_2(DMF)_2]$ ·2DMF (2), have been synthesized by solvothermal reaction of 1,4benzenecarboxylic acid (H₂BDC) and 2-methylbenzimidazole (MbIm) with zinc/cadmium nitrate. Single crystal X-ray diffraction-analysis indicates that 1 consists of the well-known zinc paddle-wheel motif which is linked by bridging dicarboxylates to form 2-D square grids. The 2-D layers stack offset due to the effect of the spatial structure of MbIm ligand and hydrogenbonding interaction between MbIm and guest molecules. Similarly, 2 is constructed by sixconnected $Cd_3(\mu-O_2CR)_6(MbIm)_2$ units and bridging carboxylates, resulting in a 2-D layer structure with triangular grids. Topology analysis reveals that 1 exhibits a 2-D tetragonal plane network with $\{4^4\cdot6^2\}$ topology symbol, while 2 possesses a 6-connected $\{3^6\cdot4^6\cdot5^3\}$ topological network. Analysis of the luminescence spectra demonstrates that the complexes have good luminescent intensities with greater red-shift (82 nm for 1 and 69 nm for 2) corresponding to free MbIm. Elemental analyses, infrared spectra (IR), powder X-ray diffraction (PXRD), and thermogravimetric analyses (TGA) of 1 and 2 have been investigated.

Keywords: Metal-organic frameworks; Paddle-wheel motif; Solvothermal synthesis; Luminescence; Microporous framework

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1. Introduction

The design and construction of metal-organic frameworks (MOFs) is of interest, due to their intriguing structures and potential application as crystalline functional solid-state materials, in gas adsorption and separation, ion conductivity and transport, luminescence, catalysis, analytical chemistry, etc. [1-7]. The combination of flexibility of linkers (organic ligands) with diverse geometry, size and functionality and richness of connectors (metal ions/clusters) has led to various MOFs with different structures and properties [8, 9]. For example, a series of MOFs based on Zn(BDC)(H₂O)·(DMF) (MOF-2, one of the first materials constructed from a paddlewheel structure) [10] are synthesized by replacing connectors (eg. Cu^{2+} , Fe^{2+}) and linkers (eg. Cl₂-BDCH₂, dichlorobenzene-1,4-dicarboxylic acid) [11-14]. Replacing connectors has been investigated extensively, while the strategy of replacing terminal ligands is rarely reported. Generally, the combination of ditopic organic carboxylates and metal ions/clusters through coordination interactions can lead to 2-D layers with various grids and further linking into a 3-D framework by hydrogen-bond interaction. For instance, Chen and co-workers reported a microporous framework, $Cu(BDC-OH)(H_2O) \cdot 0.5DEF$ (where BDC-OH = 2-hydroxybenzene-1,4-dicarboxylic acid), which exhibits approximately square grids in 2-D microporous layers and diamond pores in 3-D perspective [11]. Consequently, the effect of packing mode of layers on crystal structure and porosity is very important in 2-D networks. The packing mode is commonly influenced by terminal ligands and solvent molecules because terminal ligands have a certain spatial structure and tend to form hydrogen-bond interactions with adjacent layers or solvent molecules (bridging two layers), further influencing the interlayer distance and offset.

Rational selection of terminal ligands, to some extent, is a factor in determining the structures and properties of 2-D frameworks. Benzimidazole has been extensively studied in the preparation of zeolitic imidazolate frameworks (ZIFs) [15-17], but the application of 2-substituent benzimidazole (especially MbIm) in metal-dicarboxylate-imidazolate system is relatively rare. Several reasons contribute to the employment of MbIm in this research: (i) The introduction of MbIm may increase the complexity of pore composition and framework, resulting in multifunctionality of the pores [18-20]; (ii) Benzimidazole derivatives with a greater conjugative effect usually exhibit strong luminescence and can be a suitable candidate for luminescent MOFs [21-23]; (iii) As an interesting N-containing ligand, MbIm possesses two

kinds of coordination modes — monodentate or bidentate, which may lead to diversity of crystal structures [24-26]. Transition metal ions (such as Zn^{2+} and Cd^{2+}) often show strong coordination for imidazolates and carboxylates, which may effectively restrain the tendency for phase separation when multicomponent ligands are used in the synthesis of MOFs [27, 28].

Herein, two new zinc(cadmium)-dicarboxylate-imidazolate frameworks, $[Zn(BDC)(MbIm)]\cdot 2DMF$ (1) and $[Cd_3(BDC)_3(MbIm)_2(DMF)_2]\cdot 2DMF$ (2), have been synthesized under the same conditions, exhibiting 2-D microporous layers arising from metal clusters and bridging dicarboxylates and MbIm as terminal ligand bridging the adjacent layers through hydrogen-bonding interactions (scheme 1). Their synthesis, crystal structures, luminescent properties and other properties are discussed.



Scheme 1. Synthesis of 1 and 2.

2. Experimental

2.1. Materials and measurements

2-Methylbenzimidazole (MbIm) was prepared according to the literature procedure [29, 30]. All other materials were obtained from commercial sources and used without purification. Elemental analyses of C, H and N were performed on a Perkin-Elmer 240C analytical instrument. IR spectra were recorded on an AVATAR360 FT-IR spectrophotometer using discs from 4000-400 cm⁻¹. Thermogravimetric analyses (TGA) were performed on a NETZSCH STA 449F3 analyzer under N₂. Powder X-ray diffraction (PXRD) patterns were measured by a Bruker D8 Advance diffractometer (Cu/K α , λ = 1.5418 Å). The solid state luminescent spectra were recorded at room temperature on a Hitachi-F-7000 instrument.

2.2. Crystallographic studies

X-ray diffraction for **1** and **2** were performed on a Bruker SMART APEX II diffractometer at 293 K with graphite monochromated Mo/K α radiation ($\lambda = 0.71073$ Å). The structure, established with direct methods, was refined by weighted full-matrix least-square refinements on F^2 using SHELXS-97 [31]. All the non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogens of the organic ligands were placed in geometrically idealized positions and refined using a riding model with 1.2 × U_{eq} of the attached atoms. A summary of the parameters for data collection and refinement of **1** and **2** are listed in table 1. Selected bond lengths (Å) and angles (°) for **1** and **2** are given in table S1.

2.3. Preparation of 2-methylbenzimidazole (MbIm)

A mixture of acetic acid (1.44 g, 24 mmol) and o-phenylenediamine (2.16 g, 20 mmol) was refluxed for 12 h in hydrochloric acid (4.5 M, 16 mL). The resulting gray solution was poured into ice water (50 mL) with vigorous stirring and then neutralized by saturated sodium carbonate solution. The white solid product was collected and washed with distilled water (Yield: 65%). IR (KBr, cm⁻¹): 3059(m), 2991(m), 2917(m), 2787(m), 2678(m), 1449(s), 1418(s), 1386(m), 1271(s), 1026(m), 736(s).

2.4. Synthesis of [Zn(MbIm)(BDC)] DMF (1)

A solid mixture of zinc(II) nitrate hexahydrate $Zn(NO_3)_2 \cdot 6H_2O$ (17.6 mg, 0.05 mmol), terephthalic acid (16.6 mg, 0.1 mmol) and 2-methylbenzoimidazole (13.3 mg, 0.1 mmol) was dissolved in DMF (3 mL) in a 20 mL vial to obtain a colorless solution. The vial was tightly capped and heated at 5 °C/min to 100 °C in a programmable oven for 96h, and then cooled to room temperature at a rate of 10 °C h⁻¹ to obtain colorless block-shaped crystals of **1** (Yield: 61% based on Zn). Elemental analysis (%) for $C_{22}H_{26}N_4O_6Zn$ Calcd: C, 51.98; H, 5.12; N, 11.03. Found: C, 51.86; H, 5.21; N, 11.12. IR (KBr, cm⁻¹): 3127(m), 2929(m), 1666(s), 1501(m), 1458(m), 1386(s), 1283(m), 1254(w), 1089(w), 822(m), 746(s).

2.5. Synthesis of [Cd₃(MbIm)₂(BDC)₃(DMF)₂]•2DMF (2)

This complex was prepared in a similar procedure as for **1** by using $Cd(NO_3)_2 \cdot 4H_2O$ (17.1 mg, 0.055 mmol) in place of $Zn(NO_3)_2 \cdot 6H_2O$. The resulting colorless crystalline product of **2** was

obtained in 50% yield (based on Cd). Elemental analysis (%) for C₅₂H₅₆N₈O₁₆Cd₃ Calcd: C, 45.01; H, 4.04; N, 8.08. Found: C, 45.08; H, 4.12; N, 8.01. IR (KBr, cm⁻¹): 3434(m), 3130(m), 2930(m), 1655(s), 1602(s), 1574(s), 1505(m), 1456(m), 1385(vs), 1281(m), 843(m), 750(s), 523(m).

3. Results and discussion

3.1. Crystal structure of 1

Single-crystal structure analysis reveals that the paddle-wheel structure of 1 is structurally similar to the well-known MOF-2 [10]. This complex crystallizes in monoclinic space group C2/c. In the asymmetrical unit of the unit cell, each Zn(1) exhibits a distorted square pyramidal geometry with four oxygens from four independent carboxylate groups and one nitrogen of MbIm in the apical position as shown in figure 1a. Both the Zn-O bond lengths (from 2.0303(18) Å to 2.0532(16) Å) and the Zn-N bond length (2.0053(19) Å) fall in the normal range [32, 33], and Zn(1) lies 0.40 Å above the basal O1-O3a-O2-O4a plane. The Zn…Zn distance of 3.0236(3) Å in 1 is longer than the value in MOF-2 (2.940(3) Å), which may be caused by the coordinated geometry. Similar to MOF-2, two Zn ions and four carboxylates consist of a Zn₂(O₂CR)₄ SBU, where each carboxylate is bonded to two adjacent Zn ions in a di-monodentate mode. The remaining carboxylate groups of BDC ligands extend from the Zn₂(O₂CR)₄ SBU at approximately 90°, resulting in 2-D microporous layers with quadrangular pores (see figure 1b). The first type of diamond pore has maximum diameter of 7.4 Å with consideration of the van der Waals radii, while the methyl groups of MbIm stretch into the pore to form the second type of hourglass-shaped pore (figure 1c). The layers are packed along an axis by intermolecular hydrogen-bonding interactions between O of DMF and methyl C of MbIm ligand, resulting in two types of 1-D pores (figure 2). Complex 1 exhibits total solvent-accessible volume of 52.9% of the unit cell volume, as calculated using PLATON [34]. Topology analysis reveals that if the repeat unit $Zn_2(O_2CR)_4(MbIm)_2$ can be considered as a four-connected node, and the bdc^{2-} can be viewed as linear linkers, then 1 can be simplified into a tetragonal plane framework with the point symbol of $\{4^4 \cdot 6^2\}$ (figure 1d).

Compared with those previously reported for $Zn(BDC)(DMF)(H_2O)$ (MOF-2) and Zn(BDC)(DMF) [35], the crystal structure of **1** reveals a similar 2-D layer with square grids. However, the packing mode of the 2-D layers and the complexity of pores are completely

different, mainly influenced by displacement of the terminal ligands coordinating to the peripheral Zn(II) ions. As shown in table 2, the perpendicular separation between layers of MOF-2 and Zn(BDC)(DMF) is 4.21 Å and 6.10 Å, respectively. In **1**, the offset of adjacent layers is much larger, 9.54 Å. Because **1** needs to stack with a large offset to accommodate the MbIm molecules.

3.2. Crystal structure of 2

This compound was prepared in a similar procedure as 1 using Cd(NO₃)₂·4H₂O instead of $Zn(NO_3)_2 \cdot 6H_2O$. Single-crystal X-ray analysis reveals that 2 crystallized in monoclinic space group P21/c and exhibits two types of coordinated Cd(II) ions in the asymmetrical unit of the unit cell (figure 3a). All the Cd-O bond lengths (from 2.210(6) Å to 2.455(5) Å) and the Cd-N bond length (2.252(5) Å) fall in the normal range [32, 36]. In each Cd₃(µ-O2CR)₆(MbIm)₂ SBU, the two symmetry-related Cd(1) ions with a distorted $[CdO_5N]$ octahedral geometry are six coordinate with one nitrogen from MbIm, one oxygen of DMF and four oxygens from three individual carboxylates. The three carboxyl groups bridge to central Cd(2), resulting in an approximately octahedral coordination environment. Each bridging carboxylate radiates from the $Cd_3(\mu-O_2CR)_6(MbIm)_2$ at approximately 60° angles to form a 2-D layer with triangular grids in the bc plane (figure 3b). The pores of as-synthesized 2 are occupied by DMF molecules, with solvent-accessible void volume of 26.7% by PLATON [34]. The six-connected SBUs and the 2-D networks of 2 are similar to those of linear trinuclear $M_3(COO)_n$ complexes — [NH₂ET₂]₂[Zn₃(µ-BDC)₄]·2.5DEF [37] and [Zn₃(NH₂BDC)₃(H₂O)₂]·5DMF [38]. In both complexes, the 2-D layers are linked into a 3D structure with bridging BDC²⁻ ligands. However, in 2, the MbIm ligand coordinates to peripheral Cd(II) as a terminal ligand, preventing the 2-D extending to a 3-D framework. From a topological viewpoint, two MbIm ligands and three Cd(II) ions constitute one repeat unit $Cd_3(MbIm)_2$, and each unit as a node links six BDC^{2-} ions, therefore 2 can be viewed as a 6-connected plane with $\{3^6 \cdot 4^6 \cdot 5^3\}$ topology (figure 3c).

3.3. Powder X-ray diffraction patterns and thermal analysis

The X-ray powder diffraction (XRD) was conducted to check the phase purity of **1** and **2** (see figure S3). All the peaks in experimental patterns almost match those in the calculated patterns

from the single-crystal X-ray diffraction data, indicating the purity of the as-synthesized complexes.

According to TGA data measured under nitrogen from 30 °C to 800 °C, both **1** and **2** show high thermal stability and decompose about 370 °C, as shown in figure S4. With increase of temperature, **1** exhibits weight loss of 14.67% from 110 °C to 220 °C, corresponding to one guest DMF (Calcd: 14.39%). Then evaporation of another DMF is divided into two stages: a mild reduced phase (220-310 °C) and a sharp reduced phase (310-360 °C). The total weight loss of 28.62% in the temperature range of 110-360 °C is consistent with the loss of two DMF molecules (Calcd: 28.78%). This phenomenon can be caused by differences of intensity of hydrogen-bonding interaction between the guest DMF molecules and crystal framework [39]. **2** loses 11.21% weight at 100-220 °C, corresponding to release of two DMF molecules (Calcd: 10.54%), and begins to collapse at 370 °C.

3.4. Luminescent properties of 1 and 2

To systematically study the luminescent properties of 1 and 2, the solid-state emission spectra of MbIm, H₂BDC, 1 and 2 have been recorded at room temperature. Similar to previously reported zinc (cadmium) coordination polymers [40, 41], figure 4 indicates that 1 and 2 exhibit ligandcentered strong luminescent emission at 441 nm ($\lambda_{ex} = 372$ nm) and 428 nm ($\lambda_{ex} = 330$ nm), respectively. Free MbIm and H₂BDC have also been investigated under the same conditions and exhibit luminescent emission band at 359 nm ($\lambda_{ex} = 305$ nm) and 390 nm ($\lambda_{ex} = 350$ nm), respectively, which may be attributed to the π^{x} - π transitions [42, 43]. MbIm plays a main role in luminescence of 1 and 2. Complex 1 displays red-shifts of 82 nm and 51 nm from the ligand emission bands of free MbIm and H₂BDC, while the red-shift of **2** is 69 nm (relative to MbIm) and 38 nm (relative to H₂BDC), respectively. In order to systematically evaluate the luminescent properties of 1 and 2 with similar materials, a detailed comparison is listed in table 3. The redshifts of 1 and 2 are far larger than the values of other compounds, which makes them potential luminescent materials. The enhanced luminescence and larger red-shifts of 1 and 2 could be caused by charge transfer from the respective ligands to the d¹⁰ metal ions, Zn(II) and Cd(II), ligand-to-metal charge transition (LMCT), which contributes to increase in the rigidity of the ligand and reduces the loss of energy [34-46]. In addition, the red-shift and luminescent emission intensity of 1 is much higher than for 2, which may be primarily assigned to the high molar ratio

(MbIm:H₂BDC = 1:1) of MbIm in 1 (1:3 in 2) and the different structures caused by the heterolinks in this work.

4. Conclusion

We have synthesized two 2-D microporous metal-organic frameworks based on zinc(cadmium)dicarboxylate-imidazolate system under solvothermal conditions. After the terminally coordinated water molecules of MOF-2 are substituted by MbIm ligands, the crystal structure and properties of 1 are quite different. Complex 1 needs greater interlayer distance and offset to accommodate MbIm. Similar to 1, MbIm is a terminal ligand coordinating to the peripheral Cd(II) ions in 2, and further linking 2-D layers by intermolecular hydrogen-bonding interactions. Topology analysis reveals that 1 exhibits a 2-D layer network with a tetragonal plane framework with the point symbol of { $4^{4} \cdot 6^{2}$ }, while 2 possesses a 6-connected plane with { $3^{6} \cdot 4^{6} \cdot 5^{3}$ } topology. In comparison with other zinc and cadmium coordination polymers based on BDC and benzimidazole derivatives [40, 43], both 1 and 2 show strong luminescence along with red-shift (82 nm for 1 and 69 nm for 2), which makes them possess potential application in luminescent materials. On the basis of the current work, our group is committed to prepare a new class of coordination polymers with better luminescent properties through increasing the rigidity of ligands and functionalizing the organic ligands for higher electronic delocalization.

Supplementary material

Details of the refinement procedures for the crystal structures are supplied. The deposition numbers of **1** and **2** are CCDC 1417969 and 1417970, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data-request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033.

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Complex	1	2
Formula	$C_{22}H_{26}N_4O_6Zn$	$C_{52}H_{56}N_8O_{16}Cd_3$
FW	507.86	1386.28
T (K)	293	296
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	P21/c
a (Å)	22.4814(4)	16.9678(5)
b (Å)	10.9583(2)	9.6195(3)
c (Å)	21.6165(4)	18.8606(6)
α (°)	90	90
β (°)	110.667(1)	109.133(1)
γ (°)	90	90
$V(Å^3)$	4982.69(16)	2908.41(16)
Z	8	2
$D_{C} (g \text{ cm}^{-3})$	1.354	1.583
F(000)	2112	1392
μ (mm ⁻¹)	1.028	1.159
Theta Min-Max [°]	1.9, 27.5	2.4, 27.6
Data collected/uniq. (Rint)	21595/5763(0.018)	23545/6744(0.018)
$\mathbf{R}_1, w\mathbf{R}_2 \left[\mathbf{I} > 2 \operatorname{sigma}(I^2) \right]$	0.0503, 0.1727	0.0557, 0.1705
R_1 , wR_2 (all data)	0.0758, 0.2195	0.0646, 0.1952
Goodness-of-fit on F^2	1.08	1.07
Residues (e $Å^{-3}$)	-2.39/1.26	-2.82/1.98

Table 1. Crystal data and structure refinement for 1 and 2.

Table 2. Comparison of the effect of different terminal ligands on the packing modes of the layers.

Compound	Terminal ligand	Interlayer distance (Å)	Interlayer offset (Å)
7n(BDC)(MhIm).(DME)	MbIm	10.51	0.54
$Z_{n}(DDC)(HO)(DME)[10]$		5 20	4.21
$\Sigma \Pi(BDC)(\Pi_2 C) \cdot (DMF) [10]$		5.29	4.21
$2n_2(CB-BDC)_2(H_2O)_2 \cdot (H_2O)_3(DMF)_{1.8}$ [33]	H_2O	6.55	3.21
Zn(BDC)(DMF) [32]	DMF	5.11	6.10

Complexes	Ligand emission bonds (λ _{ex})/nm	Complex emission bonds (λ_{ex})	Red-shift (nm)
Complex 1	359(305)	441(372)	82
Complex 2	359(305)	428(330)	69
$[Zn(bimb)(bdc)] \cdot H_2O$ [28]	428/464(350)	432/465(350)	4/1
${[Zn(imb)(SO_4)] \cdot H_2O}_n [23]$	305(271)	313(271)	6
${[Cd_2(imb)(SO_4)_2H_2O] \cdot CH_3OH}_n [23]$	305(271)	336(271)	31
${[Cd(imb)(bdc)(H_2O)] \cdot CH_3OH}_n [41]$	305(285)	336(300)	31
${[Cd(imb)(Hbtc)(CH_3OH)] \cdot 2H_2O \cdot CH_3OH}_n [41]$	305(285)	323(283)	18
${[Cd(PPDA)(H_2O)] \cdot H_2O}_n [36]$	400(270)	435(328)	35
${Zn(HPPDA)_2(H_2O)_4}_n$ [36]	400(270)	419(300)	19

Table 3. Comparison of luminescent properties with zinc (cadmium) coordination polymers based on (bimb, imb, PPDA).

Figure captions

Figure 1. (a) Paddle-wheel coordination environment of Zn^{2+} in **1**. Color code: Zn, blue; C, gray; N, green; O, red. Hydrogens have been omitted for clarity. (b) One layer viewing along the *a* axis. (c) View of alternating diamond and hourglass-shaped pores. (d) 2-D $4^4 \cdot 6^2$ topological layer in the *bc* plane.

Figure 2. View of two kinds of C-H···O hydrogen bonds linking adjacent layers of **1** [symmetry codes: (a) -1/2+x, -3/2+y, -1+z; (b) -x, -y, -z; (c) -1/2+x, -1/2+y, -1+z; (d) -x, -1-y, -z].

Figure 3. (a) The coordination environment of Cd(II) in **2**; (b) Space-filling representation of 2-D triangular channels in the *bc* plane; (c) 2-D $3^{6} \cdot 4^{6} \cdot 5^{3}$ topological layer, with the six-connected SBUs as the node and BDC as the stick.

Figure 4. Solid-state emission and excitation spectra of MbIm, H_2BDC , 1 and 2 at room temperature.







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Graphical abstract

