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# Hydrothermal syntheses, crystal structures and properties of three coordination frameworks based on a new semirigid ligand and benzenedicarboxylate

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Three novel polymers, $\{[Cd(m\text{-bdc})(\mathbf{L})]\cdot H_2O\}_n$ (**1**), $[Co(m\text{-bdc})(\mathbf{L})_{0.5}(H_2O)]_n$ (**2**) and $[Zn_5(\mathbf{L})_2(p\text{-bdc})_5(H_2O)]_n$ (**3**) based on 1,1′-bis(pyridin-3-ylmethyl)-2,2′-biimidazole (**L**) ligand and benzenedicarboxylate isomers, have been prepared and structurally characterized. Compound **1** exhibits a 2D architecture with $(4^2\cdot6)(4^2\cdot6^7\cdot8)$ topology, which is synthesized by **L** and 1,3-benzenedicarboxylate (*m*-bdc) ligands. Compound **2** is constructed from 1D chains that are linked by **L** ligands extending a 2D (4,4) grid. Compound **3** is a 3D framework with $(4^3)(4^6\cdot6^{18}\cdot8^4)$ topology, which is composed of trinuclear clusters and five-coordinated metal centers joined through 1,4-benzenedicarboxylate (*p*-bdc) and **L** ligands. Moreover, the fluorescent properties of **L** ligand, compounds **1** and **3** are also determined.

## 1. Introduction

Metal organic frameworks (MOFs) have received much attention in the field of supramolecular chemistry and crystal engineering because of their diverse structures and promising applications in catalysis, nonlinear optics, luminescent materials, porous materials and microelectronics [1–5]. It is well-known that the structural and functional information of such target materials significantly relies on the metal and ligand precursors. In this case, the design of new types of ligands for constructing unusual MOFs is obviously not trivial at this stage and a variety of organic ligands containing nitrogen donor or oxygen donor have been intensely investigated due to their excellent coordination abilities [6,7]. Nowadays, increasing attention has been focused on flexible or semirigid ligands because they can change their conformations according to the requirements of different metal atoms and may induce structures with novel topologies or properties [8]. Some novel structures such as helical, interpenetrating frameworks constructed from flexible ligands have been obtained [9–12]. Meanwhile, the use of ligand with multiple flexible arms containing coordination sites has also aroused people's interests recently [13], and variation in the category and relative arrangement of the arms in this ligand might be expected to generate assemblies of varying dimensionalities with novel structural and functional properties.

2,2′-Biimidazole ($H_2$biim) has received much attention because of its potential applications in supramolecular chemistry, biochemistry, cluster science and antitumor drugs [14]. However, designing and constructing novel MOFs from the derivatives of $H_2$biim remain largely unexplored [15–17]. With the aim of preparing new materials with beautiful architectures and as a continuing study of $H_2$biim [18], we have synthesized a new two-armed ligand based on $H_2$biim, that is 1,1′-bis(pyridin-3-ylmethyl)-2,2′-biimidazole (**L**) (Scheme 1). **L** ligand possesses interesting features that are helpful to the formation of versatile coordination structures: (I) **L** is a modified version of $H_2$biim and more flexible than $H_2$biim because of the presence of the $-CH_2-$ spacer between $H_2$biim and pyridyl units and can change its conformational geometry according to the demands of metal centers. (II) **L** ligand can provide two kinds of nitrogen atoms to coordinate with metal atoms, namely, nitrogen atom from the imidazole ring ($N_{im}$) and nitrogen atom from the pyridyl ring ($N_{py}$). Recently, Kim, Hupp and Chen reported a series of porous MOFs constructed from mixed organic linkers, exhibiting interesting properties [19–21]. Enlightened by them and to facilitate the generation and crystallization of metal complexes with the **L**

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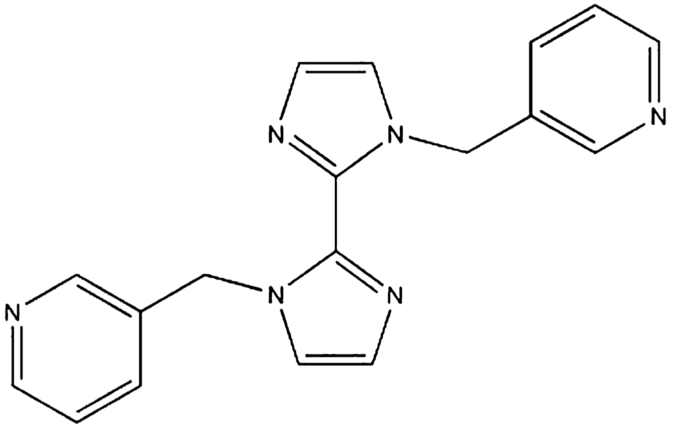

**Scheme 1.** 1,1′-Bis(pyridin-3-ylmethyl)-2,2′-biimidazole (**L**).

ligand, we introduce benzenedicarboxylate (bdc) isomers (*m*-bdc and *p*-bdc) as co-ligands to prepare new inorganic–organic hybrid materials. First, bdc isomers exhibit versatile coordination behavior and some examples constructed from bdc isomers have been reported [22,23]. Second, bdc isomers contain two carboxyl groups at distinct positions, which may engender significant special effect and may induce novel structures. Finally, the deprotonated carboxyl groups can act as anionic organic ligands to coordinate with the metal center as well as to compensate the charge [24]. The possibility of **L** and bdc ligands to coordinate with metal ions potentially allows access to frameworks of novel topologies. Additionally, MOFs constructed from mixed ligands might be expected to exhibit useful properties or beautiful topologies.

In this paper, three unprecedented MOFs have been obtained and characterized by single-crystal X-ray diffraction, which are assembled by transition metal ions combined with **L** ligand and bdc isomers in different molar ratios. Compared with complexes constructed from $H_2$biim and bdc ligands, there are many differences in the three compounds, which may be due to the steric effect and different coordination modes of **L** and bdc ligands. Herein, we report the syntheses and single-crystal X-ray structural characterizations of the three compounds. The XRPD for compounds **1** and **3** and the infrared spectra for compounds **1**–**3** have also been examined. Compound **1** is a 2D binodal (3,5)-connected structure with $(4^2 \cdot 6)(4^2 \cdot 6^7 \cdot 8)$ topology, which is constructed from cadmium salt, **L** and *m*-bdc ligands. Compound **2** is constructed from 1D chains formed by dinuclear subunits and the 1D chains are linked by the **L** ligand exhibiting a 2D (4,4) grid. Compound **3** is a 3D binodal (3,8)-connected network and its Schläfli symbol is $(4^3 \cdot 6^3)(4^6 \cdot 6^{18} \cdot 8^4)$ topology. Moreover, fluorescent properties of the **L** ligand, compounds **1** and **3** are also examined in the solid state, indicating that they may be suitable as candidates of fluorescent materials.

## 2. Experimental section

The reagents and solvents were commercially available and used as received without further purification. $H_2$biim was prepared according to the reported procedure [25]. Elemental analyses (C, N and H) were performed on a Perkin-Elemer 2400 CHN elemental analyzer. FT-IR spectra were recorded in the range 400–4000 $cm^{-1}$ on an Alpha Centaurt FT/IR Spectrophotometer as KBr pellets. All measurements were performed at room temperature. The X-ray powder diffraction (XRPD) patterns were recorded on a Siemens D5005 diffractometer with Cu KR ($\lambda = 1.5418$ Å) radiation. The emission/excitation spectra were recorded on a Varian Cary Eclipse spectrometer.

### 2.1. Synthesis of the **L** ligand

The **L** ligand was synthesized according to the reported literature [26]. To a solution of $H_2$biim (1 mmol) in 15 mL DMSO was added 2 mmol 3-picolyl chloride hydrochloride and 4 mmol NaOH. After the reaction mixture was stirred for 10 h at 50–60 °C, the solvent was removed under vacuum. The rest were dissolved in 50 mL water and then extracted by dichloromethane. The organic layer was dried by anhydrous $MgSO_4$ and then filtered. After evaporating the solvent of dichloromethane, the products would be obtained yielded by 70%.

### 2.2. Syntheses of complexes

$\{[Cd(m\text{-bdc})(\mathbf{L})] \cdot H_2O\}_n$ (**1**): A mixture of $Cd(OAc)_2 \cdot 2H_2O$ (0.2 mmol), **L** (0.2 mmol), *m*-bdc (0.2 mmol), NaOH (0.4 mmol), and $H_2O$ (9 mL) was placed in a 14 ml Teflon-lined stainless steel vessel, and then the vessel was sealed and heated at 150 °C for 3 days. After the reaction mixture was slowly cooled down to room temperature at the rate of 5 °C/h, colorless block crystals of compound **1** were obtained. Yield: 70%. Anal. Calcd. for $C_{104}H_{80}N_{24}O_{20}Cd_4$: C, 51.29; H, 3.31; N, 13.80. Found C, 51.13; H, 3.35; N, 13.86. IR ($cm^{-1}$): 3422 (w), 3106 (w), 1194 (w), 1131 (w), 61 (w), 1480 (m), 1432 (m), 1278 (m), 717 (m), 1603 (s), 1551 (s), 1386 (s), 750 (s).

$[Co(m\text{-bdc})(\mathbf{L})_{0.5}(H_2O)]_n$ (**2**): A mixture of $Co(OAc)_2 \cdot 2H_2O$ (0.2 mmol), **L** (0.1 mmol), *m*-bdc (0.2 mmol), NaOH (0.4 mmol), and $H_2O$ (9 mL) was placed in a 14 mL Teflon-lined stainless steel vessel, and then the vessel was sealed and heated at 150 °C for 3 days. After the reaction mixture was slowly cooled down to room temperature at the rate of 5 °C/h, purple block crystals of compound **2** were obtained. Yield: 50%. Anal. Calcd. for $C_{34}H_{28}N_6O_{10}Co_2$: C, 51.14; H, 3.53; N, 10.52. Found C, 51.04; H, 3.37, N, 10.46. IR ($cm^{-1}$): 3439 (w), 1574 (w), 1483 (w), 1274 (w), 1538 (m), 1443 (m), 1608 (s), 1396 (s), 735 (s).

$[Zn_5(\mathbf{L})_2(p\text{-bdc})_5(H_2O)]_n$ (**3**): A mixture of $Zn(OAc)_2 \cdot 2H_2O$ (0.5 mmol), **L** (0.2 mmol), *p*-bdc (0.5 mmol), NaOH (1.0 mmol), and $H_2O$ (9 mL) was placed in a 14 mL Teflon-lined stainless steel vessel, and then the vessel was sealed and heated at 150 °C for 3 days. After the reaction mixture was slowly cooled down to room temperature at the rate of 5 °C/h, colorless block crystals of compound **3** were obtained. Yield: 65%. Anal. Calcd. for $C_{76}H_{56}N_{12}O_{22}Zn_5$: C, 50.26; H, 3.11; N, 9.25. Found C, 50.02; H,

**Table 1**
Crystal data and structure refinement for compounds **1**–**3**

| Complex | **1** | **2** | **3** |
|---|---|---|---|
| Empirical formula | $C_{26}H_{20}N_6O_5Cd$ | $C_{17}H_{14}N_3O_5Co$ | |
| $C_{76}H_{56}N_{12}O_{22}Zn_5$ 1816.28 | Formula weight | 608.88 | 399.24 |
| Crystal system | Monoclinic | Triclinic | Triclinic |
| Space group | *P*21/*c* | *P*−1 | *P*−1 |
| *a* (Å) | 14.0452(10) | 8.830(5) | 9.953(3) |
| *b* (Å) | 8.9061(7) | 10.010(5) | 13.276(4) |
| *c* (Å) | 20.0847(15) | 10.839(5) | 16.945(5) |
| $\beta$ (deg) | 97.3740(10) | 67.916(5) | 76.527(5) |
| *V* (Å3) | 2491.6(3) | 772.2(7) | 1954.3(9) |
| *Z* | 4 | 2 | 1 |
| $\mu$ ($mm^{-1}$) | 0.93 | 1.15 | 1.594 |
| *T* (K) | 293(2) | 293(2) | 293(2) |
| Final $R_1$, w$R_2$ $[I > 2\sigma(I)]$[a] | 0.0419, 0.1103 | 0.0290, 0.0697 | 0.0322, 0.0726 |
| Final $R_1$, w$R_2$ (all data)[b] | 0.0715, 0.1272 | 0.0333, 0.0725<br>0.0448, | 0.0785 |

[a] $R_1 = \Sigma \| F_0| - |F_c \| / \Sigma || F_0|$.
[b] $wR_2 = \Sigma[w(F_0^2 - F_c^2)2] / \Sigma[w(F_0^2)^2]^{1/2}$.