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Synthesis, structure and properties of three isostructure polymer networks based on mixed ligands

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ABSTRACT

Three isostructure coordination polymers with a general formula: $[ML(bbi)(H_2O)_2]_n$ (M = Co, **1**; Zn, **2**; Cd, **3**) {L = fumaric acid dianion, bbi = 1,4-bis(1H-imidazol-1-yl)butane} have been successfully prepared by adopting liquid diffusion method. Their structures have been determined by single-crystal X-ray diffractions, and further characterized by elemental analysis, FT-IR spectra, Powder X-ray diffractions and thermogravimetric (TGA) studies. The results show that they all possess a three-dimensional (3D) framework constructed by the double helical chains and L dianions and reveal a 3-fold interpenetrating net with a uninodal 4-connected Diamond-related topology. In addition, the photoluminescent properties of **2** and **3** have also been investigated at room temperature.

1. Introduction

Coordination polymers (CPs), as a new kind of molecular material which have infinite metal–ligand backbones connected by coordination bonds are of great current interest not only due to their fascinating architectures and topologies [1], but also their potential applications in magnetism [2], optical properties [3], gas storage/separation [4], catalysis [5]. The great challenge in this field over the past decades is always how to rationally design and construct the desired coordination polymers with anticipating structures and properties [6]. The key to success is the design of the molecular building blocks which direct the formation of the desired architectural, chemical, and physical properties of the resulting solid-state materials. Past researches have confirmed that combination of mixed ligands may result in greater tenability of structural frameworks than that present with single ligands [7]. Since many factors could affect the construction, the most important are the connectors and linkers' number and orientation of their binding sites (coordination numbers and coordination geometries), and various combinations of the connector(s) and linker(s) could affords various specific structural motifs [8].

It is well known that modulation of size and shape of the pores as well as properties of the final materials is possible. Among the various structures, interpenetrating and intervening phenomena are frequently observed especially in polyrotaxane and polycatenane networks [9]. Topologically related coordination polymers where tetrahedral metal cations or octahedral metal cations are linked with linear bridging ligands in tetrahedral fashion (take no account of the coordinated water molecules) are tendentious to form diamondoid networks with various levels of interpenetration from 2- to 12-fold degeneracy [10]. Because the symmetries of the building blocks and network topology fit well with each other. The particular interest in diamondoid structures is attributable to the general robustness of three dimensionally interconnected nets. After an elaborative survey of the reported research findings, we found that the flexible linear ligands, possessing *cis*- and *trans*-conformations, can link metal ions to form metallocycle or meso-helical chain SBUs. As far as we know, 1,4-bis(1H-imidazol-1-yl)butane (bbi) was a good polyimidazolate ligand since its flexible nature of the alkyl ($-CH_2-$) spacers make itself bend and rotate freely, which can prepare the targeted product easy [11]. On the other hand, the multidentate carboxylic ligands such as di-, tri-, and tetra-carboxylates, as well as their derivatives, are widely used for building coordination polymers and can straightly dominate the stretch of the structures [12]. Here, we selected the dicarboxylic ligand H_2L (fumaric acid) based on below considerations: (1) simple formation affords a visualized image to the final structure; (2) the isolated double bond (C=C) generate a electrophilic behaviour which could make H_2L easier to deprotonate and able to coordinate to metal centers in mild conditions; (3) the *trans*-configuration is favorable for the final 3D net.

Herein, three isostructure coordination polymers, namely $[ML(bbi)(H_2O)_2]_n$ (M = Co, **1**; Zn, **2**; Cd, **3**) were synthesized by employing H_2L and bbi ligands under facile liquid diffusion

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conditions. Single-crystal X-ray diffractions indicated the three polymers are isomorphous and reveal a 3-fold interpenetrating net with a uninodal 4-connected Diamond-related topology (according to a topological analysis carried out by using TOPOS 3.0 software). As we usually know, the pore spaces tend to become smaller by the framework interpenetration, catenation, and/or interweaving, because “nature abhors a vacuum”, thus giving a 3-fold interpenetrating framework [13]. And Owing to the 3-fold interpenetration, the channels present in the coordination polymers are all closed.

2. Experimental

2.1. General procedures

Commercially available reagents are used as received without further purification. The ligand bbi was synthesized according to the literature procedures [14].

2.2. Analysis and physical measurements

Elemental analyses for carbon, hydrogen and nitrogen atoms were conducted on a Vario ELIII elemental analyzer at the Analysis center of Anhui University. Fourier transformed Infrared (FT-IR) spectra (4000–500 cm^{-1}) were recorded by using KBr pellets on an NEXUS-870 IR spectrometer. TGA was performed in a N_2 atmosphere (a flow rate of 100 mL/min) on a Q2000 thermal analyzer from 30 to 700 °C, with a heating rate of 10 °C/min. Scanning Electron Microscopy (SEM) images were performed on a Hitachi S4800 microscopy operating at 5.0 kV. The Powder X-ray Diffraction (PXRD) data were collected on a Bruker D8 Phaser automated diffractometer at room temperature, with a step size of $2\theta = 0.02°$. The Solid-state emission/excitation spectra were recorded on a Varian Cary Eclipse spectrometer at room temperature.

2.3. Syntheses of polymers in the form of single crystal

2.3.1. Synthesis of $[CoL(bbi)(H_2O)_2]_n$ (*1*)

$Co(NO_3)_2{\cdot}6H_2O$ (0.0058 g, 0.02 mmol) in 5 mL H_2O was placed at the bottom of a small test tube, then H_2L (0.0023 g, 0.02 mmol) and bbi (0.0038 g, 0.02 mmol) in 5 mL CH_3CN was slowly and carefully layered onto a mixed solution of 2 mL H_2O/CH_3CN (1:1). The resulting solution was placed under a dark circumstance and without any shake. Rodlike pink crystals of **1** began to appear after two weeks (Fig. S1) and the crystals were collected after a month, washed and dried in air (yield 30%, based on Co). *Anal.* Calc. for $C_{14}H_{16}CoO_6N_4$: C, 42.53; H, 4.05; N, 14.18. Found: C, 42.92; H, 4.09; N, 14.48%. IR: (KBr pellet, cm^{-1}): 3127w, 2928m, 2860w, 1552s, 1380s, 1103vs, 985w, 867w, 764w, 682m.

2.3.2. Synthesis of $[ZnL(bbi)(H_2O)_2]_n$ (*2*)

Rodlike colorless crystals of **2** were obtained by following the same procedure as **1** with the replacement of $Co(NO_3)_2{\cdot}6H_2O$ with $Zn(NO_3)_2{\cdot}6H_2O$. *Anal.* Calc. for $C_{14}H_{16}ZnO_6N_4$: C, 41.90; H, 4.00; N, 13.97. Found: C, 41.73; H, 4.12; N, 14.06%. IR: (KBr pellet, cm^{-1}): 3139s, 2935w, 2867w, 1608s, 1372s, 1114m, 958m, 850m, 742m, 695m.

2.3.3. Synthesis of $[CdL(bbi)(H_2O)_2]_n$ (*3*)

Rodlike colorless crystals of **3** were obtained by following the same procedure as **1** with the replacement of $Co(NO_3)_2{\cdot}6H_2O$ with $Cd(NO_3){\cdot}4H_2O$. *Anal.* Calc. for $C_{14}H_{20}CdO_6N_4$: C, 37.50; H, 3.57; N, 12.50. Found: C, 37.78; H, 3.60; N, 12.45%. IR (KBr pellet, cm^{-1}): 3457s, 3314s, 3220w, 1575s, 1392s, 1209s, 972m, 810m, 688m.

2.4. Syntheses of polymers in the form of crystalline powder

0.1 mmol (0.0291 g) $Co(NO_3)_2{\cdot}6H_2O$, 0.1 mmol (0.0301 g) $Zn(NO_3)_2{\cdot}6H_2O$, 0.1 mmol (0.0308 g) $Cd(NO_3)_2{\cdot}4H_2O$ for **1**, **2**, **3** respectively, and 0.1 mmol (0.0116 g) H_2L were dissolved in 10 mL H_2O with magnetic stirring for 0.5 h at room temperature, then 0.1 mmol (0.019 g) bbi was added and keep stirring for 2 h, samples for testing were obtained after wash the products with CH_3OH and H_2O three times each and dry in 60 °C for 6 h. We also

Table 1
Crystal data and structure refinements for polymers **1**–**3**.

	1	**2**	**3**
CCDC numbers	912603	913584	939637
Empirical formula	$C_{14}H_{16}CoN_4O_6$	$C_{14}H_{16}ZnN_4O_6$	$C_{14}H_{20}CdN_4O_6$
Formula weight	395.24	401.68	452.74
T (K)	298(2)	298(2)	298(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$C2/c$	$C2/c$	$C2/c$
a (Å)	14.066(5)	14.048(5)	14.0226(14)
b (Å)	11.787(5)	11.828(5)	12.0988(12)
c (Å)	10.883(5)	10.853(5)	11.0172(11)
β (°)	111.949(5)	111.875(5)	111.7570(10)
V (Å^3)	1673.6(12)	1673.5(12)	1736.0(3)
Z	4	4	4
D_{calc} (g cm^{-3})	1.569	1.594	1.732
$F(000)$	812	824	912
Reflections collected	5797	5768	6285
θ range (°)	2.33–24.99	2.32–25.00	2.30–25.49
R_{int}	0.0238	0.0185	0.0172
Goodness-of-fit (GOF) on F^2	1.048	0.814	1.104
R_1[a] $[I > 2\sigma(I)]$	0.0390	0.0361	0.0361
wR_2[b]	0.1062	0.1027	0.1030
Largest residuals (e Å^{-3})	0.713/-0.660	0.799/−0.749	1.106/−0.576

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

Table 2
Selected bond lengths (Å) and angles (°) for **1**–**3**.

1			
Co(1)–N(1)$^{\#1}$	2.122(2)	Co(1)–O(2)$^{\#1}$	2.126(2)
Co(1)–O(1)$^{\#1}$	2.154(2)		
N(1)–Co(1)–N(1)$^{\#1}$	85.12(13)	N(1)–Co(1)–O(2)	175.81(8)
N(1)$^{\#1}$–Co(1)–O(2)	91.09(10)	O(2)–Co(1)–O(2)$^{\#1}$	92.75(12)
N(1)–Co(1)–O(1)	92.41(9)	O(2)–Co(1)–O(1)	89.48(8)
O(2)$^{\#1}$–Co(1)–O(1)	86.71(8)	N(1)–Co(1)–O(1)$^{\#1}$	91.65(9)
O(1)–Co(1)–O(1)$^{\#1}$	174.48(11)	C(5)–O(2)–Co(1)	128.97(18)
C(1)–N(1)–Co(1)	128.3(2)	C(4)–N(1)–Co(1)	123.5(2)
2			
Zn(1)–N(1)$^{\#1}$	2.120(2)	Zn(1)–O(3)$^{\#1}$	2.148(2)
Zn(1)–O(1)$^{\#1}$	2.1529(19)		
N(1)–Zn(1)–N(1)$^{\#1}$	85.97(12)	N(1)–Zn(1)–O(3)	93.20(8)
N(1)$^{\#1}$–Zn(1)–O(3)	92.16(8)	O(3)–Zn(1)–O(3)$^{\#1}$	172.66(10)
N(1)–Zn(1)–O(1)	176.71(7)	N(1)$^{\#1}$–Zn(1)–O(1)	91.15(9)
O(3)–Zn(1)–O(1)	88.50(8)	O(3)–Zn(1)–O(1)$^{\#1}$	86.40(8)
O(1)–Zn(1)–O(1)$^{\#1}$	91.77(12)	C(6)–O(1)–Zn(1)	129.13(17)
C(2)–N(1)–Zn(1)	128.28(19)	C(1)–N(1)–Zn(1)	123.16(18)
3			
Cd(1)–N(1)$^{\#1}$	2.238(3)	Cd(1)–O(2)	2.249(3)
Cd(1)–O(3)$^{\#1}$	2.271(3)		
N(1)–Cd(1)–N(1)$^{\#1}$	84.36(17)	N(1)–Cd(1)–O(2)$^{\#1}$	174.88(12)
N(1)$^{\#1}$–Cd(1)–O(2)$^{\#1}$	90.80(12)	O(2)$^{\#1}$–Cd(1)–O(2)	94.09(17)
N(1)–Cd(1)–O(3)$^{\#1}$	94.40(12)	O(2)$^{\#1}$–Cd(1)–O(3)$^{\#1}$	87.41(11)
O(2)–Cd(1)–O(3)$^{\#1}$	86.46(11)	N(1)–Cd(1)–O(3)	92.27(12)
O(3)$^{\#1}$–Cd(1)–O(3)	171.00(15)	C(11)–O(2)–Cd(1)	127.6(3)
C(3)–N(1)–Cd(1)	128.8(3)	C(1)–N(1)–Cd(1)	122.9(3)

Symmetry codes for **1**: $^{\#1}$ $-x+1, y, -z+3/2$, $^{\#2}$ $-x+1/2, -y-1/2, -z+1$, $^{\#3}$ $-x+1, -y+1, -z+2$. Symmetry codes for **2**: $^{\#1}$ $-x+2, y, -z+1/2$, $^{\#2}$ $-x+5/2, -y+3/2, -z+1$, $^{\#3}$ $-x+2, -y, -z$. Symmetry codes for **3**: $^{\#1}$ $-x+2, y, -z+3/2$, $^{\#2}$ $-x+2, -y, -z+1$, $^{\#3}$ $-x+3/2, -y+3/2, -z+1$.