

基于柔性双(甲基苯并咪唑)和羧酸配体的 Cd(II)/Co(II)/Zn(II)配合物的合成和表征

张兆沛^{1,2} Vlasenko Volodymyr Anatoliyovych² 刘润强³ 杨 里⁴ 刘 露^{*4} 张裕平⁴

(¹河南科技学院生命科技学院,河南科技学院现代生物育种河南省协同创新中心,新乡 453003)

(²Agrotechnologies and Environmental Use Department,
Sumy National Agrarian University, Sumy, 40021, Ukraine)

(³河南科技学院资源与环境学院,新乡 453003)

(⁴河南科技学院化学化工学院,新乡 453003)

摘要: 通过水热或溶剂热合成的方法制备了 3 个 Cd(II)/Co(II)/Zn(II) 配位聚合物 $[\text{Cd}(\text{hbmb})_{0.5}(\text{pta})]_n$ (**1**), $[\text{Co}(\text{hbmb})(1,4\text{-bdc})]_n$ (**2**) 和 $[\text{Zn}_2(\text{hbmb})_{1.5}(\text{bptc})(\text{H}_2\text{O})] \cdot 0.5\text{hbmb} \cdot 3\text{H}_2\text{O}$ (**3**) (hbmb=1,1'-(1,6-己烷)双-(2-甲基苯并咪唑), H_2pta =邻羧基苯乙酸, 1,4- H_2bdc =1,4-苯二乙酸, H_4bptc =3,3',4,4'-二苯甲酮四羧酸)。单晶结构解析表明配合物 **1** 是一个 4-连接的二维平面网络, 拓扑符号为 $(4^4 \cdot 6^2)$ 。配合物 **2** 是一个 4-连接的二维褶皱网络, 拓扑符号为 $(4^2 \cdot 6)(4^2 \cdot 6^3 \cdot 8)$ 。配合物 **3** 是一个(3,4,4)-连接的三重穿插网络, 拓扑符号为 $(4^2 \cdot 6^2 \cdot 8^3)(4 \cdot 6^2)(4 \cdot 6^4 \cdot 8)$ 。其中配合物 **1** 属于单斜晶系, 空间群为 $P2_1/c$, $a=0.758\ 32(15)\ \text{nm}$, $b=1.452\ 8(3)\ \text{nm}$, $c=1.911\ 3(5)\ \text{nm}$, $\beta=112.26(3)^\circ$, $Z=4$; 配合物 **2** 属于单斜晶系, 空间群为 $P2_1/n$, $a=1.090\ 8(2)\ \text{nm}$, $b=1.873\ 1(4)\ \text{nm}$, $c=1.301\ 9(3)\ \text{nm}$, $\beta=91.09(3)^\circ$, $Z=4$; 配合物 **3** 属于三斜晶系, 空间群为 $P\bar{1}$, $a=1.119\ 6(2)\ \text{nm}$, $b=1.481\ 2(3)\ \text{nm}$, $c=1.926\ 6(4)\ \text{nm}$, $\alpha=89.72(3)^\circ$, $\beta=87.65(3)^\circ$, $\gamma=68.28(3)^\circ$, $Z=2$ 。

关键词: 配合物; 晶体结构; 拓扑

中图分类号: O614.24²; O614.81²; O614.24¹ 文献标识码: A 文章编号: 1001-4861(2019)09-1642-09

DOI: 10.11862/CJIC.2019.194

Syntheses, Characterization and Crystal Structures of Cd(II)/Co(II)/Zn(II) Complexes Based on Flexible Bis(methylbenzimidazole) and Carboxylate Ligands

ZHANG Zhao-Pei^{1,2} Vlasenko Volodymyr Anatoliyovych² Liu Run-Qiang³

YANG Li⁴ LIU Lu^{*4} ZHANG Yu-Ping⁴

(¹School of Life Science and Technology, Henan Institute of Science and Technology, Collaborative Innovation Center of Modern Biological Breeding of Henan Province, Henan Institute of Science and Technology, Xinxiang, Henan 453003, China)

(²Agrotechnologies and Environmental Use Department, Sumy National Agrarian University, Sumy, 40021, Ukraine)

(³School of Resource and Environmental Sciences, Henan Institute of Science and Technology, Xinxiang, Henan 453003, China)

(⁴School of Chemistry and Chemical Engineering, Henan Institute of Science and Technology Xinxiang, Henan 453003, China)

Abstract: Three Cd(II)/Co(II)/Zn(II) coordination complexes, formulated as $[\text{Cd}(\text{hbmb})_{0.5}(\text{pta})]_n$ (**1**), $[\text{Co}(\text{hbmb})(1,4\text{-bdc})]_n$ (**2**), $[\text{Zn}_2(\text{hbmb})_{1.5}(\text{bptc})(\text{H}_2\text{O})] \cdot 0.5\text{hbmb} \cdot 3\text{H}_2\text{O}$ (**3**) (hbmb=1,1'-(1,6-hexane)bis-(2-methylbenzimidazole), H_2pta =homophthalic acid, 1,4- H_2bdc =1,4-benzenedicarboxylic acid, H_4bptc =3,3',4,4'-benzophenone tetracarboxylic acid), have been obtained by hydrothermal/solvothermal reactions. Complex **1** is a flat 4-connected 2D topology net with point symbol of $(4^4 \cdot 6^2)$, complex **2** features a undulated 2D network with point symbol of $(4^2 \cdot 6)$

收稿日期: 2018-12-17。收修改稿日期: 2019-06-23。

河南科技学院高层次人才科研启动项目, 河南省博士后科研项目, 河南省高等学校重点科研项目(No.16A150007), 河南省教育厅科学技术研究重点项目(No.13A880301)和河南科技学院标志性创新工程项目(No.2015BZ02)资助。

*通信联系人。E-mail: liululu2012@126.com

($4^2 \cdot 6^3 \cdot 8$), while complex **3** (3,4,4)-connected 3-fold interpenetrating network with a vertex symbol of ($4^2 \cdot 6^2 \cdot 8^3$)($4 \cdot 6^2$)($4 \cdot 6^4 \cdot 8$) topology. Crystal data are monoclinic, space group, $P2_1/c$, $a=0.758\ 32\ (15)\ \text{nm}$, $b=1.452\ 8\ (3)\ \text{nm}$, $c=1.911\ 3(5)\ \text{nm}$, $\beta=112.26(3)^\circ$, $Z=4$ for **1**; and monoclinic, space group, $P2_1/n$, $a=1.090\ 8(2)\ \text{nm}$, $b=1.873\ 1(4)\ \text{nm}$, $c=1.301\ 9(3)\ \text{nm}$, $\beta=91.09(3)^\circ$, $Z=4$ for **2**; and triclinic, space group, $P\bar{1}$, $a=1.119\ 6(2)\ \text{nm}$, $b=1.481\ 2(3)\ \text{nm}$, $c=1.926\ 6(4)\ \text{nm}$, $\alpha=89.72(3)^\circ$, $\beta=87.65(3)^\circ$, $\gamma=68.28(3)^\circ$, $Z=2$ for **3**. CCDC: 1885275, **1**; 1885276, **2**; 1885277, **3**.

Keywords: coordination complex; crystal structure; topology

The thriving regions of crystal engineering have offered a sane junction between aesthetics of crystalline architectures and their potential applications, of which the eventual destination is to triumphantly acquire target materials that own tailored structures and physicochemical properties^[1-10]. So far, although lots of 0D/1D/2D/3D frameworks have been reported, the construction of novel-innovative architectures and a systematic study still require a long-term challenge^[11-13]. Flexible N-donors ligands are highly attractive, because their free conformation allows for greater structural diversity. Carboxylates serving as co-ligands have also been extensively adopted to build new complexes^[14-17]. Furthermore, the two-ligand assembly system could provide more variability to fabricate complicated structures. Taking this idea into consideration, in this paper, we choose 1,1'-(1,6-hexane)bis-(2-methylbenzimidazole) (hbmb) as the flexible N-donor ligand and three disparate O-donor carboxylates, homophthalic acid (H_2pta), 1,4-benzenedicarboxylic acid (1,4- H_2bdc) and 3, 3',4, 4'-benzophenone tetracarboxylic acid (H_4bptc), as auxiliary ligands in the synthesis of metal-organic coordination polymer materials. At last, three new complexes, $[\text{Cd}(\text{hbmb})_{0.5}(\text{pta})]_n$ (**1**), $[\text{Co}(\text{hbmb})(1,4\text{-bdc})]_n$ (**2**) and $\{[\text{Zn}_2(\text{hbmb})_{1.5}(\text{bptc})(\text{H}_2\text{O})] \cdot 0.5\text{hbmb} \cdot 3\text{H}_2\text{O}\}_n$ (**3**) were prepared successfully. The structures of **1~3** have been determined by single-crystal X-ray diffraction analyses and further characterized by infrared spectra, elemental analyses. Besides, the effect of flexible ligand hbmb and three carboxylate co-ligands on the frameworks of **1~3** are debated in detail.

1 Experimental

1.1 Materials and methods

All reagents and solvents were commercially

available except for hbmb, which was synthesized according to the literature^[18]. FT-IR spectra were recorded on a FTIR-7600 spectrophotometer with KBr pellets in $400\sim 4\ 000\ \text{cm}^{-1}$ region. Elemental analyses (C, H and N) were carried out on a FLASH EA 1112 elemental analyzer.

1.2 Synthesis of $[\text{Cd}(\text{hbmb})_{0.5}(\text{pta})]_n$ (**1**)

A mixture of $\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ (0.1 mmol), hbmb (0.1 mmol), H_2pta (0.05 mmol), EtOH (5 mL) and H_2O (5 mL) was placed in a 25 mL Teflon-lined stainless steel container. The mixture was sealed and heated at $160\ ^\circ\text{C}$ for three days. After the mixture was cooled to ambient temperature at a rate of $5\ ^\circ\text{C} \cdot \text{h}^{-1}$, colorless irregular-shaped crystals of **1** were obtained with a yield of 10% (based on Cd). Anal. Calcd. for $\text{C}_{21}\text{H}_{21}\text{CdN}_2\text{O}_4$ (%): C, 52.78; H, 4.42; N, 5.86. Found(%): C, 52.75; H, 4.40; N, 5.90. IR (KBr, cm^{-1}): 3 056(w), 3 027(w), 2 931(m), 2 863(w), 1 562(s), 1 508(m), 1 459(m), 1 388(w), 1 292(m), 1 238(m), 1 153(m), 1 014(m), 941(s), 833(w), 746(s), 673(s).

1.3 Synthesis of $[\text{Co}(\text{hbmb})(1,4\text{-bdc})]_n$ (**2**)

A mixture of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.1 mmol), hbmb (0.1 mmol), 1,4- H_2bdc (0.2 mmol), H_2O (8 mL) was placed in a 25 mL Teflon-lined stainless steel container at $120\ ^\circ\text{C}$ for three days. After the mixture was cooled to room temperature at a rate of $5\ ^\circ\text{C} \cdot \text{h}^{-1}$, purple irregular-shaped crystals suitable for X-ray diffraction were obtained with a yield of 15% (based on Co). Anal. Calcd. for $\text{C}_{30}\text{H}_{30}\text{CoN}_4\text{O}_4$ (%): C, 63.26; H, 5.30; N, 9.83. Found(%): C, 63.31; H, 5.31; N, 9.80. IR(KBr, cm^{-1}): 2 937(m), 2 865(m), 1 814(vs), 1 461(s), 1 334(vs), 1 292(w), 1 137(m), 1 081(m), 1 016(s), 927(m), 887(m), 811(vs), 744(vs), 595(s).

1.4 Synthesis of $\{[\text{Zn}_2(\text{hbmb})_{1.5}(\text{bptc})(\text{H}_2\text{O})] \cdot 0.5\text{hbmb} \cdot 3\text{H}_2\text{O}\}_n$ (**3**)

A mixture of ZnCO_3 (0.1 mmol), hbmb (0.1 mmol),

H₄bptc (0.05 mmol), H₂O (7 mL) was placed in a 25 mL Teflon-lined stainless steel container. The mixture was sealed and heated at 160 °C for three days. After the mixture was cooled to ambient temperature at a rate of 5 °C · h⁻¹, yellow block-shaped crystals of **3** were obtained with a yield of 5% (based on Zn). Anal. Calcd. for C₆₁H₆₆Zn₂N₈O₁₃(%): C, 58.61; H, 5.32; N, 8.96. Found (%): C, 58.65; H, 5.29; N, 8.99. IR (KBr, cm⁻¹): 3 427 (s), 2 036(w), 1 634(m), 1 493(vw), 1 395(vw), 1 319 (vw), 1 254(vw), 1 188(m), 1 112(m), 797(s), 623(w).

1.5 Crystal structural determination

The data of the **1**~**3** were collected on a Rigaku Saturn 724 CCD diffractometer (Mo K α , λ =0.071 073

nm) at temperature of (20±1) °C. Absorption corrections were applied by using multi-scan program. The data were modified for Lorentz and polarization effects. The structures were solved by direct methods and then refined by means of F^2 with a full-matrix least-squares technique that adopted the SHELX-97 crystallographic software package^[19]. The hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. Crystallographic crystal data and structure processing parameters for **1**~**3** are summarized in Table 1. Selected bond lengths and bond angles of **1**~**3** are listed in Table 2.

CCDC: 1885275, **1**; 1885276, **2**; 1885277, **3**.

Table 1 Crystal data and structure refinement details for complexes **1**~**3**

Complex	1	2	3
Formula	C ₂₁ H ₂₁ CdN ₂ O ₄	C ₃₀ H ₃₀ CoN ₄ O ₄	C ₆₁ H ₆₆ Zn ₂ N ₈ O ₁₃
Formula weight	477.80	569.51	1 249.96
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a / nm	0.758 32(15)	1.090 8(2)	1.119 6(2)
b / nm	1.452 8(3)	1.873 1(4)	1.481 2(3)
c / nm	1.911 3(5)	1.301 9(3)	1.926 6(4)
α / (°)			89.72(3)
β / (°)	112.26(3)	91.09(3)	87.65(3)
γ / (°)			68.28(3)
V / nm ³	1.948 7(8)	3.378 1(12)	2.965 3(10)
Z	4	4	2
D_c / (g · cm ⁻³)	1.629	1.422	1.400
μ / mm ⁻¹	1.150	0.689	0.880
$F(000)$	964	1 188	1 304
θ range / (°)	2.70~25.50	2.65~23.50	1.96~25.50
GOF	1.044	1.069	1.015
R_1 [$I > 2\sigma(I)$] ^a	0.071 1	0.090 1	0.055 8
wR_2 [$I > 2\sigma(I)$] ^b	0.227 2	0.145 8	0.129 1

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

Table 2 Selected bond lengths (nm) and bond angles (°) for **1**~**3**

1					
Cd(1)-N(1)	0.222 1(6)	Cd(1)-O(4)#1	0.227 5(11)	Cd(1)-O(3)#2	0.228 2(7)
Cd(1)-O(1)	0.230 4(9)	Cd(1)-O(2)	0.238 9(7)		
N(1)-Cd(1)-O(4)#1	104.8(4)	N(1)-Cd(1)-O(3)#2	99.6(3)	O(4)#1-Cd(1)-O(3)#2	114.2(3)
N(1)-Cd(1)-O(1)	140.6(3)	O(4)#1-Cd(1)-O(1)	106.5(4)	O(3)#2-Cd(1)-O(1)	89.0(3)
N(1)-Cd(1)-O(2)	104.9(2)	O(4)#1-Cd(1)-O(2)	84.7(3)	O(3)#2-Cd(1)-O(2)	144.0(3)
O(1)-Cd(1)-O(2)	55.5(3)				

Continued Table 2

2					
Co(1)-O(3)	0.193 5(3)	Co(1)-O(2)	0.195 0(3)	Co(1)-N(1)	0.202 7(3)
Co(1)-N(3)	0.203 9(3)				
O(3)-Co(1)-O(2)	119.35(11)	O(3)-Co(1)-N(1)	110.46(11)	O(2)-Co(1)-N(1)	103.28(12)
O(3)-Co(1)-N(3)	102.13(12)	O(2)-Co(1)-N(3)	116.00(12)	N(1)-Co(1)-N(3)	104.89(12)
3					
Zn(1)-O(3)	0.194 9(3)	Zn(1)-O(9)#2	0.196 3(2)	Zn(1)-N(1)	0.200 8(3)
Zn(1)-O(5)	0.202 0(3)	Zn(2)-O(1)	0.192 2(3)	Zn(2)-O(7)#2	0.196 6(2)
Zn(2)-N(5)	0.199 4(3)	Zn(2)-N(3)	0.201 5(3)		
O(3)-Zn(1)-O(9)#2	120.67(12)	O(3)-Zn(1)-N(1)	118.10(12)	O(9)#2-Zn(1)-N(1)	109.34(12)
O(3)-Zn(1)-O(5)	101.31(12)	O(9)#2-Zn(1)-O(5)	98.23(11)	N(1)-Zn(1)-O(5)	105.36(12)
O(1)-Zn(2)-O(7)#2	110.46(11)	O(1)-Zn(2)-N(5)	120.79(13)	O(7)#2-Zn(2)-N(5)	106.12(12)
O(1)-Zn(2)-N(3)	108.54(13)	O(7)#2-Zn(2)-N(3)	96.02(12)	N(5)-Zn(2)-N(3)	112.06(14)

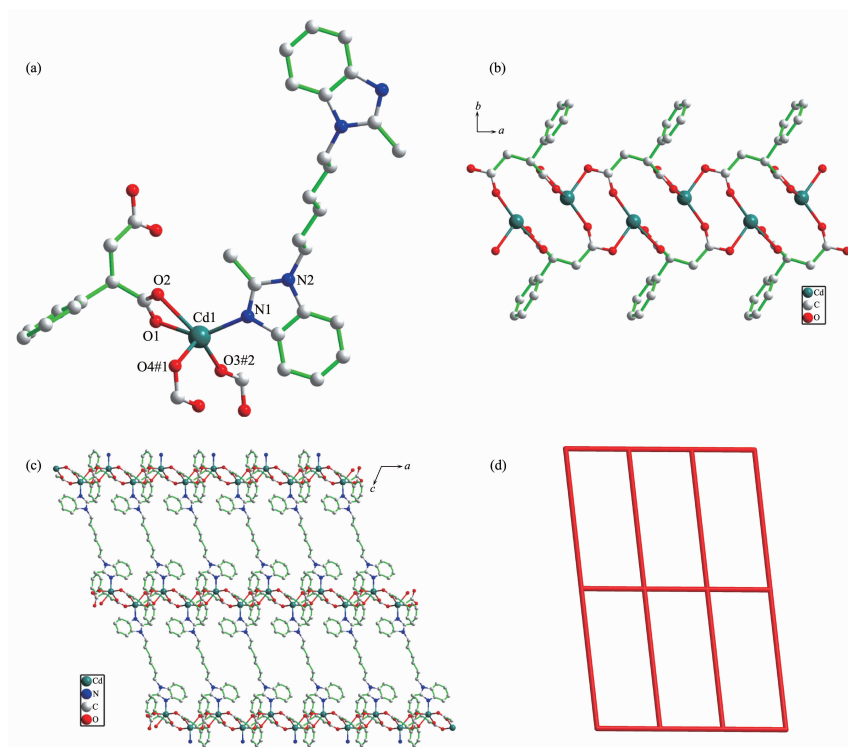
Symmetry codes: #1: $x+1, y, z$; #2: $-x+1, -y+1, -z+2$ for **1**; #2: $x, y-1, z$ for **3**.

2 Results and discussion

2.1 Crystal structure of $[\text{Cd}(\text{hbmb})_{0.5}(\text{pta})]_n$ (**1**)

Structural analysis indicates that complex **1** is a 2D structure with point symbol of $(4^4 \cdot 6^2)$ and crystall-

izes in the monoclinic $P2_1/c$ space group. The asymmetric unit of **1** is composed of one crystallographically independent Cd(II) ion, half a hbmb ligand, and one pta^{2-} ligand. As shown in Fig.1a, the Cd(II) ion exhibits



Symmetry codes: #1: $1+x, y, z$; #2: $1-x, 1-y, 2-z$

Fig.1 (a) Coordination environment of Cd(II) ion in **1** with hydrogen atoms omitted for clarity; (b) One-dimensional (1D) chain generated by Cd(II) ions and pta^{2-} linkers in **1**; (c) Schematic view of the 2D net built by 1D Cd(II)/ pta^{2-} chain and hbmb in **1**; (d) Schematic representation of $4^4 \cdot 6^2$ topology of complex **1**

a five-coordinated environment, which is provided by one nitrogen atom (N1) from one separate hbmb and four oxygen atoms (O1, O2, O3#2, O4#1) from three independent pta²⁻ anions. The structural index parameter (τ)^[20] is close to 0.00, indicating that the geometry around Cd(II) can be described as an ideal square-pyramidal geometry. The Cd-O distances are in a range of 0.227 5(11)~0.238 9(7) nm, while the Cd1-N1 bond length is 0.222 1(6) nm. hbmb shows the symmetric *trans*-conformation with the $N_{\text{donor}} \cdots N-C_{sp^3} \cdots C_{sp^3}$ torsion angle of 72.219°. The two carboxylic groups of pta²⁻ ligand take an inconsistent coordination mode. One carboxylate group of pta²⁻ ligand adopts a chelating bidentate mode, and the other is in a bridging mono-bidentate mode. Each pta²⁻ anion bridges three Cd(II) ions in this way to give rise to a 1D infinite chain (Cd(II)/pta²⁻ chain) along the *c*-axis, containing a binuclear unit [Cd₂(CO₂)₂] with the Cd···Cd separation of 0.424 00 nm (Fig.1b). The Cd(II) ions of two neighboring 1D Cd(II)/pta²⁻ chains were connected by the *trans*-conformational hbmb ligands generating the 2D sheet of **1** (Fig.1c). The bridged Cd···Cd distance along μ -hbmb is 1.643 36 nm. Topological analysis was performed on **1**. As depicted in Fig.1d, if the binuclear unit [Cd₂(CO₂)₂] is taken as a 2-connector and hbmb is defined as linkers, the 2D framework of **1** can be described as (4⁴·6²) topology.

2.2 Crystal structure of [Co(hbmb)(1,4-bdc)]_n (**2**)

Complex **2** crystallizes in the monoclinic space group *P*2₁/*n* and features a 2D network motif. The asymmetric unit consists of one crystallographically unique Co(II) ions, one deprotonated 1,4-bdc²⁻ anions, and one hbmb ligand. As illustrated in Fig.2a, the Co(II) ion displays distorted tetrahedral geometry, defined by two carboxyl oxygen atoms (O2, O3) from two 1,4-bdc²⁻ anions and two nitrogen atoms (N1, N3) from two hbmb ligands. The τ_4 parameters introduced by Houser^[21] of Co1 are 0.88. The Co1-O2 and Co1-O3 bond distances are 0.195 0(3) and 0.193 5(3) nm, respectively, while the Co1-N1 and Co1-N3 bond lengths are 0.202 7(3) and 0.203 9(3) nm, respectively. The hbmb ligand adopts asymmetric *trans*-conformation with two different $N_{\text{donor}} \cdots N-C_{sp^3} \cdots C_{sp^3}$ torsion angles of

73.233° and 88.281°. This kind of hbmb connect the adjacent Co(II) ions giving rise to a 1D Co(II)/hbmb chain along the *b*-axis with a Co···Co separation of 1.090 80 nm (Fig.2b). Interestingly, two carboxylate groups of 1,4-bdc²⁻ both adopt bi-monodentate coor-

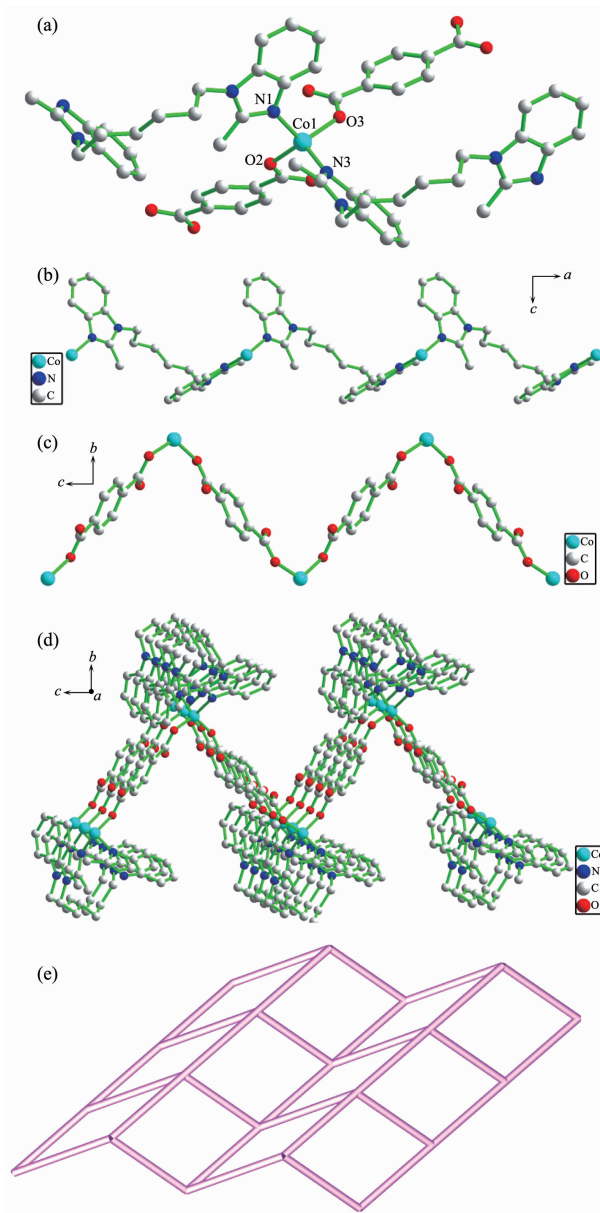


Fig.2 (a) Coordination environment of Co(II) ion in **2** with hydrogen atoms omitted for clarity; (b) 1D chain along *b*-axis alternately generated by ligand hbmb bridging two adjacent Co(II) ions; (c) 1D chain resulting from 1,4-bdc²⁻ anions connecting two adjacent Co(II) ions along *a*-axis; (d) Undulated 2D network bridged by hbmb and 1,4-bdc²⁻ in **2**; (e) Schematic description of a 4-connected 2D network with (4³·6²·8) topology for **2**

dination mode. The nearby Co(II) ions are bridged by 1,4-bdc²⁻ anions to product a 1D Co(II)/1,4-bdc²⁻ chain along the *a*-axis with a Co···Co separation of 1.105 50 nm (Fig.2c). The interlaced connection of the 1D Co(II)/hbmb chain and 1D Co(II)/1,4-bdc²⁻ chain constructs the corrugated 2D network by sharing Co(II) ions (Fig. 2d). Topological analysis was performed on **2**. As depicted in Fig.2e, each Co(II) ion is encircled by four organic ligands (two hbmb ligands and two 1,4-bdc²⁻ ligands). If the Co(II) ion is taken as a 4-connector, the 1,4-bdc²⁻ and hbmb can be defined as linkers, the

2D framework of **2** can be described as (4²·6)(4²·6³·8) topology.

2.3 Crystal structure of {[Zn₂(hbmb)_{1.5}(bptc)(H₂O)]·0.5hbmb·3H₂O}_n (**3**)

Complex **3** exhibits a beautiful 3-fold interpenetrating 3D network, which crystallizes in the triclinic system, space group *P* $\bar{1}$. Each asymmetric unit of **3** consists of two crystallographically independent Zn(II) ions, one and a half hbmb ligands, one bptc⁴⁻, one coordinated water molecule, half a dissociative hbmb and three guest water molecules. Fig.3a illustrates the

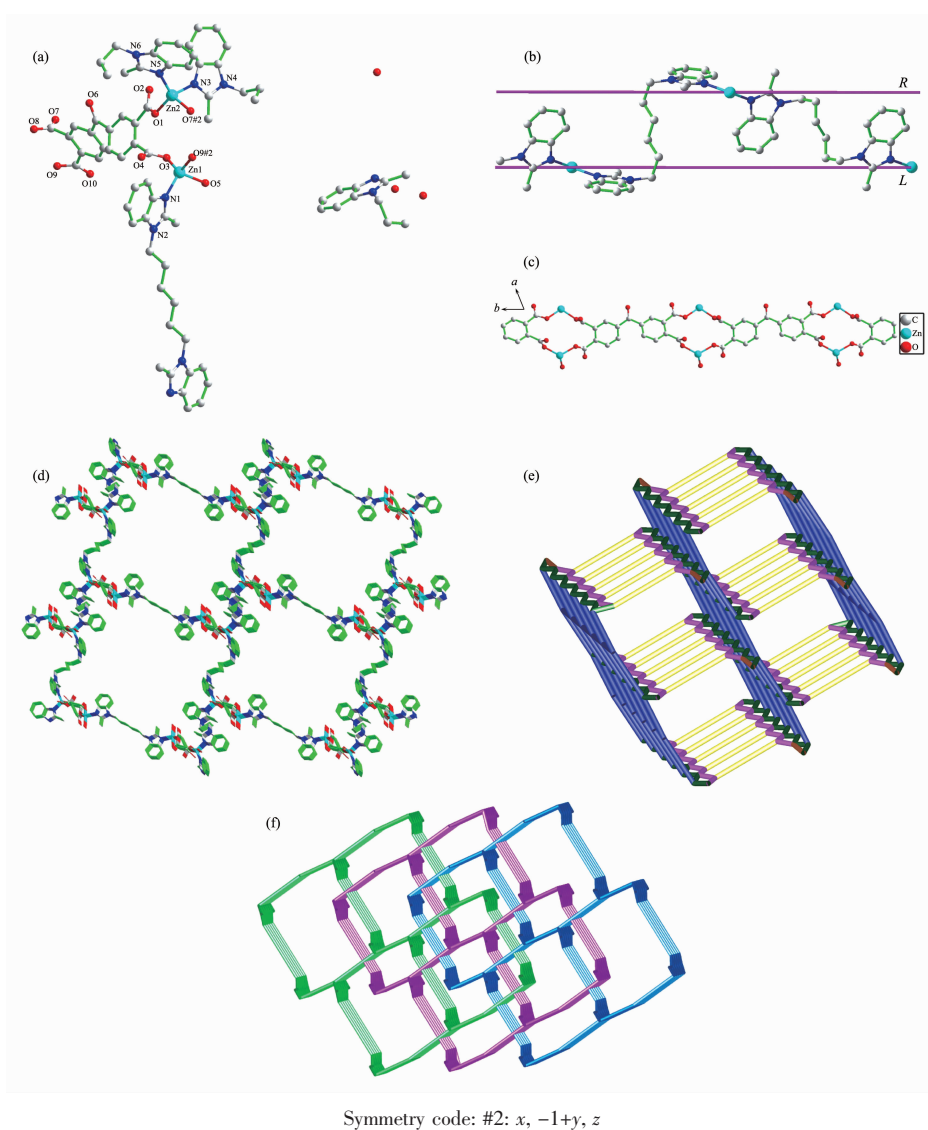


Fig.3 (a) Coordination environment of Zn(II) ion in **3** with hydrogen atoms omitted for clarity; (b) Pseudo meso-helix alternately generated by hbmb-I and hbmb-II bridging two adjacent Zn(II) ions; (c) 1D chains built through Zn(II) ions and bptc⁴⁻ linkers in **3**; (d) Perspective view of 3D coordination framework fabricated by 1D Zn(II)/bptc⁴⁻ chains and 1D Zn(II)/hbmb chains; (e) Single 3D topology network; (f) Schematic representation of 3-fold interpenetrated topology nets for **3**

coordination environment of the Zn (II) ions. The distorted tetrahedral coordination geometry of the central Zn1 ion is completed by one N atom (N1) of one hbmb ligand, two O atoms (O3 and O9#2) of two bptc⁴⁻ anions and one O atom (O5) of one coordinated water molecule. Zn2 ion also shows a distorted tetrahedral coordination geometry, which is defined by two oxygen atoms (O1 and O7#2) from two bptc⁴⁻ anions, and two nitrogen atoms (N3 and N5) from two hbmb ligands. The distortion of tetrahedron can be indicated by the calculated value of the τ_4 parameter introduced by Houser ($\tau_4 \approx 0.85$ for Zn1 and $\tau_4 \approx 0.90$ for Zn2)^[21-22]. The distances of Zn-O/N bond are in a range of 0.192 2(3)~0.202 0(3) nm, which are in the normal range^[23-24]. There are four independent hbmb ligands in complex **3**, all of which exhibit symmetrical *trans*-conformation. $N_{\text{donor}} \cdots N-C_{sp^3} \cdots C_{sp^3}$ torsion angle of hbmb-I is 73.968°. $N_{\text{donor}} \cdots N-C_{sp^3} \cdots C_{sp^3}$ torsion angle of hbmb-II is 62.966°. $N_{\text{donor}} \cdots N-C_{sp^3} \cdots C_{sp^3}$ torsion angle of hbmb-III is 92.459°. $N_{\text{donor}} \cdots N-C_{sp^3} \cdots C_{sp^3}$ torsion angle of hbmb-IV that is dissociative is 75.848°. The two types of hbmb (hbmb-I and hbmb-II) act as bidentate mode to link two adjacent Zn2 ions alternately to generate a pseudo *meso*-helix (Fig. 3b). The Zn2···Zn2 distances across the hbmb bridges are 1.181 11 (hbmb-I) and 1.333 29 (hbmb-II) nm, separately. hbmb-III only connect two Zn1 ions and the Zn1···Zn1 distance across the hbmb-III bridges is 1.630 76 nm. In **3**, the bptc⁴⁻ anions connects four Zn(II) cations, and four carboxylate group all takes bridging monodentate coordination mode. The nearby Zn1 and Zn2 ions are linked together by the carboxylate O atoms of the bptc⁴⁻ to form a 1D Zn(II)/bptc⁴⁻ chain along the *c*-axis containing the 14-membered rings (Fig.3c). In this ring, the Zn1···Zn1 distance is 0.504 89 nm. The combination of 1D chains of Zn(II)/bptc⁴⁻ and Zn(II)/hbmb produces the 3D structure of **3** (Fig.3d). From a topological perspective, each Zn1 ion is surrounded by four organic ligands (two hbmb ligands and two bptc⁴⁻ ligands), each Zn2 ion is surrounded by three organic ligands (one hbmb ligand and two bptc⁴⁻ ligands), and each bptc⁴⁻ ligand is connected to

four Zn ions. Hence, the Zn1 ions can be regarded as 4-connected nodes, the Zn2 ions can be regarded as 3-connected nodes, the bptc⁴⁻ anions are defined as 4-connected nodes and hbmb ligands are considered as linkers, respectively. The 3D framework of **3** can be represented as a (3,4,4)-connected 3-fold interpenetrating network with a vertex symbol of $(4^2 \cdot 6^2 \cdot 8^2)(4 \cdot 6^2)(4 \cdot 6^4 \cdot 8)$ (Fig.3e and 3f).

2.4 Effect of hbmb and carboxylate co-ligands on the structures of 1~3

According to the above description, we find that the flexible hbmb ligand presents symmetric *trans*-conformation in **1** and **3**, asymmetric *trans*-conformation in **2**. All of the $N_{\text{donor}} \cdots N-C_{sp^3} \cdots C_{sp^3}$ torsion angles are different in **1~3**. The free conformations of -(CH₂)-spacer greatly enrich structures of complexes **1~3**. In **1**, hbmb connects two neighboring 1D Cd(II)/pta²⁻ chains by sharing the Cd(II) ions to build a 2D sheet. In **2**, hbmb links the adjacent Co(II) ions, resulting in a 1D Co(II)/hbmb chain. In **3**, hbmb-I and hbmb-II join two adjacent Zn2 ions alternately to produce a pseudo Zn(II)/hbmb meso-helix, while hbmb-III only connect two Zn1 ions. Owing to the flexible nature of the -(CH₂)-spacers, two bis(methylbenzimidazole) groups of hbmb can rotate freely when coordinating with metal centers, which can greatly beautify the structure of complexes **1~3**. On the other side, the carboxylate anions also have significant influence on the constructing of resultant structures of **1~3**. In synthesis process of **1~3**, we have selected three carboxylates as auxiliary ligands. In **1**, each pta²⁻ anion bridges three Cd(II) ions to generate a 1D infinite Cd(II)/pta²⁻ chain containing a binuclear unit [Cd₂(CO₂)₂]. Under the connection of hbmb, **1** shows a flat 2D framework with the point symbol of $(4^4 \cdot 6^2)$. In **2**, we select 1,4-H₂bdc with a rigid spacer and an angle of 180° between the two carboxylic groups as a co-ligand. 1,4-bdc²⁻ anions bridge the nearby Co(II) ions, forming a 1D Co(II)/1,4-bdc²⁻ chain. By sharing Co(II) ions, the interlaced connection of the 1D Co(II)/hbmb chain and 1D Co(II)/1,4-bdc²⁻ chain induce the corrugated 2D framework with the point symbol of $(4^2 \cdot 6)(4^2 \cdot 6^3 \cdot 8)$ of **2**. By introducing tetracarboxylic

acid ligand H_4bptc , 3D 3-fold interpenetrating $(3,4,4)$ -connected $(4^2 \cdot 6^2 \cdot 8^2)(4 \cdot 6^2)(4 \cdot 6^4 \cdot 8)$ networks **3** are obtained. The $bptc^{4-}$ link the nearby Zn1 and Zn2 ions to form a 1D $Zn(II)/bptc^{4-}$ chain containing a 14-membered rings. The above discussions indicate the configuration of hbmb and diverse carboxylate co-ligands play a critical role in the construction resultant complexes. The three different structures also show that more complex carboxylic acid co-ligands will lead to the production of higher dimensional complexes.

2.5 Photoluminescence properties

Currently, the researchers have great interest in fluorescence complexes by reason of their potential applications. Hence, the photoluminescent spectra of complexes **1** and **3**, the free hbmb ligand and two carboxylic acids were investigated at ambient temperature. As depicted in Fig.4, the photoluminescent spectra of the free ligand hbmb, H_2pta and H_4bptc showed different emission peak at 302 nm ($\lambda_{ex}=286$ nm), 330 nm ($\lambda_{ex}=260$ nm) and 425 nm ($\lambda_{ex}=330$ nm), severally. Complexes **1** and **3** exhibited the emission

maxima at 297 nm ($\lambda_{ex}=245$ nm) for **1**, 299 nm ($\lambda_{ex}=245$ nm) for **3**, severally. For **1**, the emission band was blue-shifted (5 and 33 nm) compared with that of the ligand hbmb and H_2pta . The emission spectrum for **3** also presented blue shifts (3 and 126 nm) with respect to the ligand hbmb and H_4bptc . The hypsochromic shifts of the emission peaks of **1** and **3** indicate that the coordination of the ligand to Cd(II)/Zn(II) ions increases the rigidity, leading to less vibrations of the skeleton and reducing the loss of energy by radiationless decay of the intraligand emission excited state^[25].

3 Conclusions

In summary, by introducing different carboxylate co-ligands into Cd(II)/Co(II)/Zn(II)-hbmb system, three varied architectures have been constructed and characterized by single-crystal X-ray diffraction analyses, infrared spectra and elemental analyses. Complexes **1**~**3** exhibit enthralling 2D/3D architectures with versatile topologies. The results of the above work manifest that distinct metal ions and various carboxylate co-ligands can greatly affect the final structures of complexes. In addition, **1** and **3** maybe potential optical materials.

References:

- [1] Lu Z Z, Zhang R, Li Y Z, et al. *J. Am. Chem. Soc.*, **2011**, **133**:4172-4174
- [2] Evans O, Lin W B. *Acc. Chem. Res.*, **2002**, **35**:511-522
- [3] Montney M R, Krishnan S M, Supkowski R M, et al. *Inorg. Chem.*, **2007**, **46**:7362-7370
- [4] Luo H Y, Eberly N, Rogers R D, et al. *Inorg. Chem.*, **2001**, **40**: 493-498
- [5] Qiu W, Perman J A, Wojtas Ł, et al. *Chem. Commun.*, **2010**, **46**:8734-8736
- [6] Carlucci L, Ciani G, Proserpio D M. *Coord. Chem. Rev.*, **2003**, **246**:247-289
- [7] Xiong R G, You X Z, Abrahams B F, et al. *Angew. Chem. Int. Ed.*, **2001**, **40**:4422-4425
- [8] Hou L, Shi W J, Wang Y Y, et al. *Chem. Commun.*, **2011**, **47**:5464-5466
- [9] Wei W, Wang G, Zhang Y, et al. *Chem. Eur. J.*, **2011**, **17**: 2189-2198
- [10] Eddaoudi M, Moler D B, Li H L, et al. *Acc. Chem. Res.*,

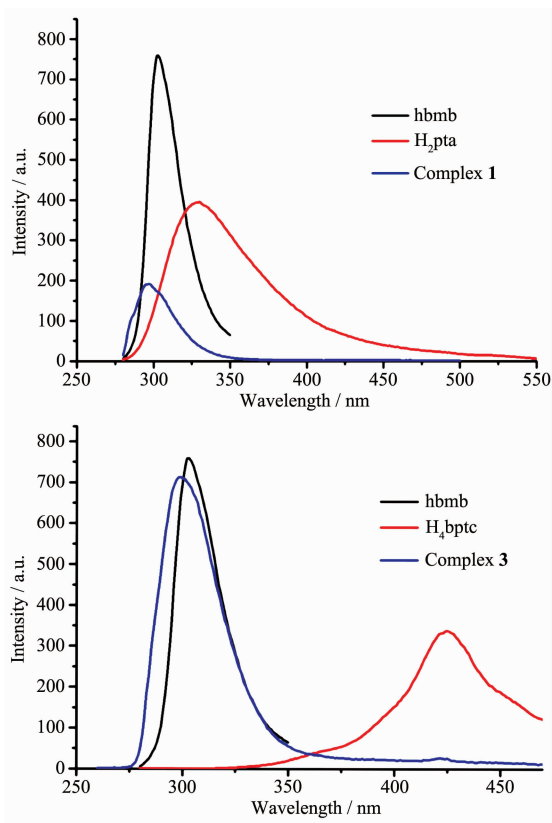


Fig.4 Photoluminescent spectra of free hbmb ligand, free carboxylate ligands and complexes **1** and **3**

- 2001,34**:319-330
- [11]Yuan D Q, Zhao D, Sun D F, et al. *Angew. Chem. Int. Ed.*, **2010,49**:5357-5361
- [12]Su S, Guo Z, Li G, et al. *Dalton Trans.*, **2010,39**:9123-9130
- [13]Lee J Y, Farha O K, Roberts J, et al. *Chem. Soc. Rev.*, **2009,38**:1450-1459
- [14]Henninger S K, Habib H A, Janiak C. *J. Am. Chem. Soc.*, **2009,131**:2776-2777
- [15]Bai H Y, Ma J F, Yang J, et al. *Cryst. Growth Des.*, **2010,10**:1946-1959
- [16]LIANG Li-Li(梁丽丽), LIU Cong-Sen(刘从森), ZONG Zhi-Hui(宗智慧), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2018,34**(7):1365-1372
- [17]XIAO Bo-An(肖伯安), CHEN Shui-Sheng(陈水生). *Chinese J. Inorg. Chem.*(无机化学学报), **2017,33**(2):347-353
- [18]Bronisz R. *Inorg. Chem.*, **2005,44**:4463-4465
- [19]Sheldrick G M. *Acta Crystallogr. Sect. A: Found. Crystallogr.*, **2008,A64**:112-122
- [20]Addison A W, Rao T N, Reedijk J, et al. *J. Chem. Soc. Dalton Trans.*, **1984**:1349-1356
- [21]Yang L, Powell D R, Houser R P. *Dalton Trans.*, **2007**:955-964
- [22]Song X Z, Song S Y, Qin C, et al. *Cryst. Growth Des.*, **2012,12**:253-263
- [23]Li X J, Cao R, Sun D F, et al. *Cryst. Growth Des.*, **2004,4**:775-780
- [24]Martin D P, Braverman M A, LaDuca R L. *Cryst. Growth Des.*, **2007,7**:2609-2619
- [25]Zhang L P, Ma J F, Yang J, et al. *Cryst. Growth Des.*, **2009,9**:4660-4673