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两个基于柔性双苯并咪唑配体的锌配位聚合物的合成、晶体结构和荧光性质

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摘要:以 1,4-双(2-甲基苯并咪唑-1-亚甲基)苯(bmb)和 2 个芳香多羧酸 1,2,4,5-均苯四酸(H_4btec)、4-(3,4-二羧基苯甲酰)邻苯二甲酸(H_4dcbp)为配体,在水热条件下合成了 2 个锌配位聚合物$\{[Zn(bmb)_{0.5}(btec)_{0.5}(H_2O)]\cdot H_2O\}_n$ (**1**)和$\{[Zn_2(bmb)_2(dcbp)]\cdot 5H_2O\}_n$ (**2**),并用 X 射线单晶衍射、红外光谱、元素分析和粉末衍射对其结构进行了表征。晶体结构测试表明 2 个聚合物均为复杂的三维框架结构,配体 bmb 在 2 个配合物中均为μ_2-η^1:η^1 的配位模式。此外还研究了 2 个配合物的荧光性质和热稳定性。

关键词:配位聚合物;锌;晶体结构;荧光
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Syntheses, Crystal Structures and Luminescence Properties of Two Zn(Ⅱ) Coordination Polymers Based on Flexible Bisbenzimidazole Ligand

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Abstract: Two new coordination polymers, $\{[Zn(bmb)_{0.5}(btec)_{0.5}(H_2O)]\cdot H_2O\}_n$ (**1**) and $\{[Zn_2(bmb)_2(dcbp)]\cdot 5H_2O\}_n$ (**2**) were synthesized under hydrothermal conditions and characterized by single-crystal X-ray diffractions, IR spectra, elemental analyses and powder X-ray diffractions (bmb=1,4-bis(2-methylbenzimidazol-1-ylmethyl) benzene, H_4btec= 1,2,4,5-benzenetetracarboxylic acid, H_4dcbp =4-(3,4-dicarboxybenzoyl)phthalic acid). Structural analyses reveal that both polymers **1** and **2** exhibit complicated 3D frameworks in which bmb acts as linker with μ_2-η^1:η^1 coordination mode. Thermal stabilities and solid-state luminescence at room temperature of **1** and **2** also were investigated. CCDC: 1907377, **1**; 1907378, **2**.

Keywords: coordination polymers; zinc; crystal structure; luminescence

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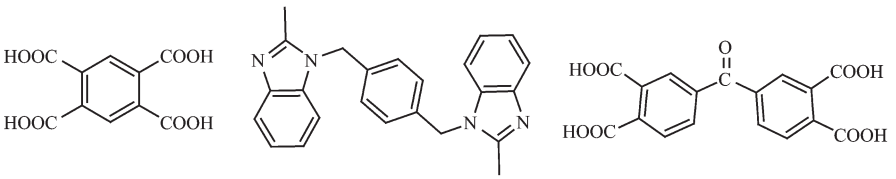
0 Introduction

Coordination polymers (CPs) have been extensively investigated in the past few decades. Because of their vast applications such as gas storage[1-2], catalysis[3-4], molecular magnetism[5-6] and luminescence[7-9], CPs play a significant role in the development of functional materials. The properties of CPs mainly depend on the organic ligands and the center metal ions because they are involved in the formation of the final CPs[10-11]. This provides us with the opportunity to rationally select the precursors, which enables synthesis of CPs for specific structures and properties.

Aimed at the production of sensors and diodes, luminescent CPs materials have emerged as a rapidly growing field of research. The luminescence of CPs is commonly caused by the conjugated organic ligands and metal ions with closed shell electron configuration[12-14]. CPs based on d^{10} metal ions often display excellent luminescence behavior[15-18]. Among these, Zn (Ⅱ) CPs with organic linkers are one kind of the most interested luminescent CPs[19-21].

It is well known that polycarboxylate ligands and N-containing heterocyclic ligands are excellent candidates for the construction of CPs for their strong coordination abilities and diverse coordination modes[22-25]. As a member of N-containing heterocyclic ligands, 1,4-bis(benzimidazol-1-yl)-benzene (bbix) has been studied in the synthesis of CPs[26-27]. It is noteworthy that bbix based CPs exhibits interesting structures and luminescent properties. Our research has focused on its derivatives, 1,4-bis(2-methylbenzimidazol-1-ylmethyl)benzene (bmb). The extra methyl of bmb will inevitably cause larger steric resistance. Does this affect its coordination abilities and consequently affect the structures and properties of the final CPs? Considering above mentioned points, we have synthesized some CPs based on bmb [28]. As a continuation of our work, herein, two CPs, $\{[Zn(bmb)_{0.5}(btec)_{0.5}(H_2O)]\cdot H_2O\}_n$ (**1**) and $\{[Zn_2(bmb)_2(dcbp)]\cdot 5H_2O\}_n$ (**2**), were synthesized based on bmb and polycarboxylate ligands (H_4btec =1,2,4,5-benzenetetracarboxylic acid, H_4dcbp =4-(3,4-dicarboxybenzoyl)phthalic acid) (Scheme 1). The structures, thermal stabilities and luminescent properties of complexes **1** and **2** were studied in detail.



H_4btec　　bmb　　H_4dcbp

Scheme 1　Structures of the ligands

1 Experimental

1.1 Materials and measurement

All chemicals and reagents were commercially available and used without further purification. Ligands H_4btec and H_4dcbp were purchased from Alfa Aesar and bmb was synthesized according to the literature method[29]. Elemental analyses (C, H and N) were performed on a Elementar Vario EL Ⅲ elemental analyzer. IR spectra were recorded on a Bruker EQUINOX55 spectrophotometer in the 4 000~400 cm^{-1} region using KBr pellets. Thermogravimetric analyses (TGA) data were collected on a Perkin-Elmer TAG-7 instrument with a heating rate of 10 ℃·min^{-1}. Powder X-ray diffraction (PXRD) measurements were carried out on a Bruker D8 Advance diffractometer with Cu $K\alpha$ radiation (λ=0.154 18 nm) from 5° to 50° (2θ) at room temperature, using an operating voltage of 45 kV and an operating current of 40 mA. The luminescent spectra in solid states were performed on a Hitachi F-4500 fluorescence spectrophotometer at room temperature.

1.2 Synthesis of $\{[Zn(bmb)_{0.5}(btec)_{0.5}(H_2O)]\cdot H_2O\}_n$ (1)

A mixture of $Zn(CH_3COO)_2\cdot 2H_2O$ (44 mg, 0.2 mmol), bmb (73.2 mg, 0.2 mmol), H_4btec (0.2 mmol,

50.8 mg), and water (10 mL) was sealed in a Teflon-lined stainless steel vessel (25 mL) and heated at 150 ℃ for 5 days, and then cooled to room temperature naturally. The colorless block crystals of **1** were obtained with the yield of 41% based on Zn. Anal. Calcd. for $C_{17}H_{16}N_2O_6Zn$(%): C, 49.83; H, 3.94; N, 6.84. Found (%): C, 50.13; H, 3.98; N, 6.72. IR (KBr, cm^{-1}): 3 422(s), 3 089(w), 1 623(m), 1 461(m), 1 384 (s), 1 277(m), 1 155(w), 837(m), 751(s), 668(m), 550 (m), 479(m).

1.3 Synthesis of $\{[Zn_2(bmb)_2(dcbp)]\cdot 5H_2O\}_n$ (2)

Complex **2** was prepared by $Zn(CH_3COO)_2\cdot 2H_2O$ (44 mg, 0.2 mmol), bmb (73.2 mg, 0.2 mmol), and H_4dcbp (0.2 mmol, 71.6 mg) using the same procedure for complex **1**. Colorless block crystals of **2** were obtained with the yield of 33% based on Zn. Anal. Calcd. for $C_{65}H_{60}N_8O_{14}Zn_2$(%): C, 59.69; H, 4.62; N, 8.57. Found (%): C, 59.54; H, 4.71; N, 8.43. IR (KBr, cm^{-1}): 3 422(s), 1 712(w), 1 648(m), 1 596(m), 1 510(s), 1 476(m), 1 412(s), 1 363(m), 1 291(w), 1 138(m), 1 013 (w), 868(m), 762(s), 672(m), 613(m), 509(m), 475(m).

1.4 Structural determination

Single crystal X-ray diffraction data of the two complexes were collected on a Rigaku Saturn 724 CCD diffractomer (Mo $K\alpha$, λ=0.071 073 nm) at room temperature. Absorption corrections were applied by using multi-scan program. The structures were solved by direct methods and refined with a full-matrix least-squares technique based on F^2 with the SHELXTL software[30]. All non-hydrogen atoms were refined anisotropically, the hydrogen atoms of water molecules were located from difference Fourier maps and the other hydrogen atoms were generated geometrically. Crystal data and structural refinement parameters for **1** and **2** are summarized in Table 1. The selected bond lengths and angles for **1** and **2** are listed in Table 2.

CCDC: 1907377, **1**; 1907378, **2**.

Table 1 Crystal data and structure refinement for 1 and 2

Complex	**1**	**2**
Formula	$C_{17}H_{16}N_2O_6Zn$	$C_{65}H_{60}N_8O_{14}Zn_2$
Formula weight	409.73	1 307.95
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a / nm	1.058 8(2)	1.247 5(3)
b / nm	0.998 9(2)	1.247 5(3)
c / nm	1.656 0(3)	2.072 7(4)
α / (°)		98.61(3)
β / (°)	97.03(3)	106.64(3)
γ / (°)		103.74(3)
V / nm^3	1.738 3(6)	2.918 8(13)
Z	4	2
D_c / ($g\cdot cm^{-3}$)	1.554	1.488
μ / mm^{-1}	1.449	0.899
F(000)	828	1 356
Reflection collected	20 799	29 953
Unique reflection	4 691	10 257
Goodness-of-fit on F^2	1.168	1.114
R_{int}	0.040 9	0.053 0
R_1, wR_2 [$I>2\sigma(I)$]	0.042 9	0.060 8
R_1, wR_2 (all data)	0.050 3	0.085 5
Largest diff. peak and hole / ($e\cdot nm^{-3}$)	460 and −460	420 and −430

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

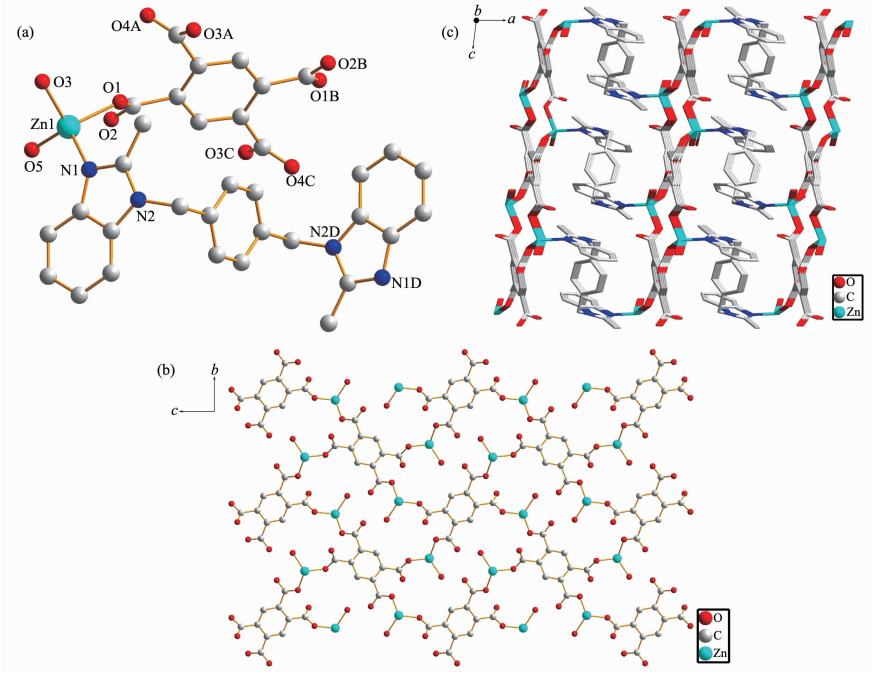
1					
Zn-O1	0.195 2(2)	Zn1-O5	0.193 1(2)	Zn1-O3	0.196 2(2)
Zn1-N1	0.200 5(2)				
O1-Zn1-N1	101.25(9)	O1-Zn1-O3	102.18(8)	O5-Zn1-O1	118.12(8)
O5-Zn1-N1	112.43(10)	O5-Zn1-O3	111.85(9)	O3-Zn1-N1	110.08(9)
2					
Zn1-O1	0.194 5(3)	Zn1-O4A	0.194 8(3)	Zn1-N1	0.202 0(3)
Zn1-N5	0.204 8(3)	Zn2-O6B	0.191 9(3)	Zn2-O8	0.193 2(3)
Zn2-N4C	0.201 5(3)	Zn2-N8D	0.202 8(3)		
O1-Zn1-O4A	102.47(13)	O1-Zn1-N1	128.08(13)	O1-Zn1-N5	98.67(13)
O4A-Zn1-N1	119.42(12)	O4A-Zn1-N5	101.84(12)	O1-Zn1-N5	101.02(13)
O6B-Zn2-O8	106.91(13)	O6B-Zn2-N4C	101.13(14)	O6B-Zn2-N8D	106.51(14)
O8-Zn2-N4C	123.27(13)	O8-Zn2-N8D	115.07(12)	N4C-Zn2-N8D	102.16(13)

Symmetry codes: A: $-x+1, -y+2, -z+1$; B: $-x+1, -y+3, -z$; C: $-x+1, -y+3, -z+1$; D: $x+1, y+2, z$ for **2**.

2　Results and discussion

2.1　Crystal structure of {[Zn(bmb)$_{0.5}$(1, 2, 4, 5-btec)$_{0.5}$(H$_2$O)]·H$_2$O}$_n$ (1)

Single-crystal X-ray diffraction analysis reveals that polymer **1** crystallizes in monoclinic system with $P2_1/c$ space group. The asymmetric unit of **1** consists of one Zn(Ⅱ) ion, a half bmb, a half 1,2,4,5-btec^{4-}, one coordinated water molecule and one lattice water molecule. As shown in Fig.1a, Zn1 is surrounded by one nitrogen atom (N1) from one bmb ligand, two oxygen atoms (O1, O3) from two different 1,2,4,5-btec^{4-} anions, and one oxygen atom (O5) from coordinated water molecule. The Zn-O bond lengths are in a range



Symmetry codes: A: $2-x, -0.5+y, 0.5-z$; B: $2-x, -y, -z$; C: $x, 0.5-y, -0.5+z$; D: $1-x, -y, -z$

Fig.1　(a) Coordination environment of Zn(Ⅱ) ion in **1** with hydrogen atoms omitted for clarity; (b) 2D sheet structure of **1**; (c) 3D framework of **1**

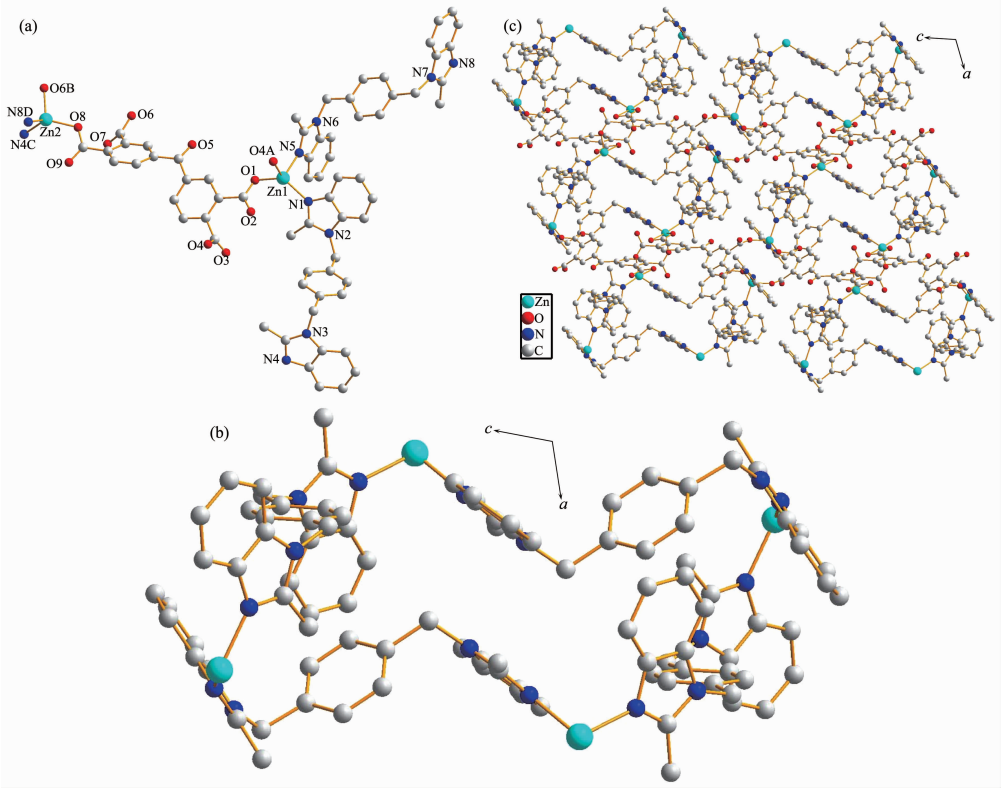
of 0.193 14(19)~0.196 22(17) nm, while the Zn-N ones is 0.200 5(2) nm. The coordination geometry of Zn1 can be described as a distorted tetrahedral geometry.

In **1**, the deprotonated 1,2,4,5-btec^{4-} adopts a μ_4-η^1:η^1:η^1:η^1 coordination mode. Four carboxylate groups coordinate with four Zn(Ⅱ) ions monodentately to generate a 2D sheet (Fig.1b). The adjacent sheets are further connected by the bmb ligand in μ_2-η^1:η^1 mode to give a 3D framework (Fig.1c). The bridging bmb is extremely symmetric and displays *trans*-conformation. Two benzimidazole rings are coplanar and the dihedral angle between each benzimidazole and phenyl ring is 84.94°. The 3D framework is consolidated by intermolecular O–H···O hydrogen bonds (O5···O6 0.263 5(3) nm, O5···O2 0.263 2(3) nm, O6···O4 0.277 6(3) nm, O6···O3 0.276 4(3) nm).

2.2 Crystal structure of {[Zn_2(bmb)$_2$(dcbp)]·5H_2O}$_n$ (2)

Using a longer polycarboxylic acid ligand H_4dcbp instead of 1,2,4,5-H_4btec under the same reaction conditions affords complex **2**, which belongs to the triclinic space group $P\bar{1}$. There are two crystallographically independent Zn(Ⅱ) ions, two bmb ligands, one dcbp anion, and five lattice water molecules (Fig.2a) in the asymmetric unit of **2**. The Zn1/Zn2 are surrounded by two nitrogen atoms (N1, N5/N4, N8) from two different bmb ligands, two carboxyl oxygen atoms (O1, O4/O6, O8) from two dcbp ligands to give a distorted tetrahedron geometry, respectively.

In **2**, two bmb ligands both show μ_2-η^1:η^1 mode to coordinate with two Zn(Ⅱ) ions. In this manner, four bmb connect four adjacent Zn(Ⅱ) ions to form a Zn_4(bmb)$_4$ secondary building units (SBUs) (Fig.2b). One bmb displays trans-conformation, and the dihedral angle between benzimidazole ring and benzene are 85.96(2)° and 77.16(2)°, and the dihedral angle between two benzimidazole rings is 19.55(1)°. The other bmb displays *cis*-conformation. The dihedral angle between benzimidazole ring and benzene are 84.38(2)° and 82.46(3)°, and the dihedral angle between two benzimidazole rings is 3.64(2)°. Then



Symmetry codes: A: 1–*x*, 2–*y*, 1–*z*; B: 1–*x*, 3–*y*, –*z*; C: 1–*x*, 3–*y*, 1–*z*; D: 1+*x*, 2+*y*, *z*

Fig.2 (a) Coordination environment of Zn(Ⅱ) ion in **2** with hydrogen atoms omitted for clarity; (b) Zn_4(bmb)$_4$ SBUs in **2**; (c) 3D framework of **2**

these SBUs are jointed by dcbp ligands in the μ_4-η^1:η^1:η^1:η^1 mode to give a 3D framework (Fig.2c). The framework is also stabilized by intermolecular O–H···O hydrogen bonds (O11···O3 0.277 4(4) nm, O11···O9 0.277 7(4) nm, O12···O3 0.279 8(4) nm, O12···O14 0.285 1(5) nm, O14···O11 0.280 2(5) nm).

2.3 PXRD patterns and thermal analyses

Powder X-ray diffraction (PXRD) patterns of **1** and **2** were determined at room temperature to characterize their purity. As shown in Fig.3, the peak position of the measured patterns matched well with the simulated ones, indicating the purity of the samples. The thermal stability of **1** and **2** were investigated under nitrogen atmosphere by thermogravimetric analyses (TGA). As shown in Fig.4, polymer **1** lost its lattice water molecules at 123 ℃ (Obsd. 4.25%, Calcd. 4.43%). The release of coordinated water molecules (Obsd. 4.48%, Calcd. 4.43%) occurred in a temperature range of 213~318 ℃. Then the further weight losses are attributed to the decomposition of **1**. Polymer **2** lost lattice water molecules from room temperature to 157 ℃ (Obsd. 6.73%, Calcd. 6.88%). The framework is stable up to 312 ℃, then the weight decreased quickly and continuously until 600 ℃. The main residue should be ZnO (Obsd. 15.48%, Calcd. 15.67%).

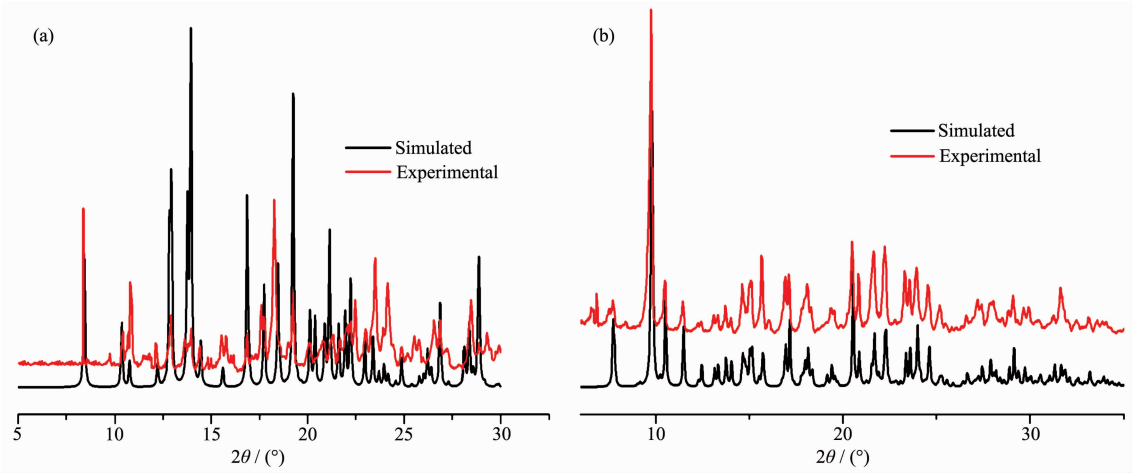


Fig.3 PXRD patterns of **1** (a) and **2** (b)

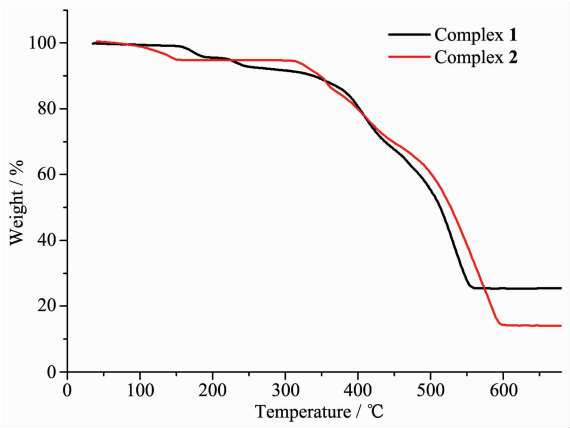


Fig.4 TGA curves of complexes **1** and **2**

2.4 Photoluminescence properties

The solid state luminescence properties of complex **1** and **2** together with bmb, H_4btec and H_4dcbp were measured at room temperature (Fig.5). The free ligand bmb shows intense emission band at 309 nm upon excitation at 293 nm, which can be attributed to the $\pi\rightarrow\pi^*$ transitions. The emission of 1,2,4,5-H_4btec and H_4dcbp is very weak compared to bmb and have no contribution to the luminescence of complexes **1** and

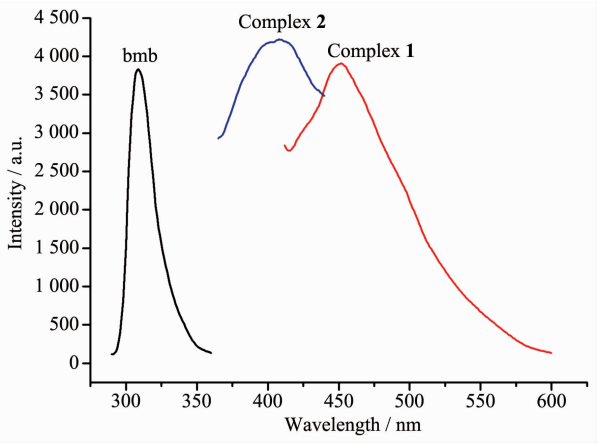


Fig.5 Solid-state photoluminescent spectra of bmb and complexes **1~2**

2. The maximum emission peaks of **1** and **2** are located at 451 nm (λ_{ex}=391 nm) and 409 nm (λ_{ex}=327 nm), respectively. The emissions of complexes **1** and **2** can probably be assigned to intraligand charge transitions of bmb[28].

3 Conclusions

In summary, two Zn(Ⅱ) coordination polymers with bmb and different carboxylic acid co-ligands have been synthesized and characterized. Complexes **1** and **2** all feature different 3D frameworks structures. The solid-state luminescent properties of **1** and **2** were investigated, and the emissions were assigned to intraligand charge transitions of bmb. The investigation should motivate further research of bmb as building block in the construction of coordination polymers.

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