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两个三维锌(Ⅱ)配位聚合物的晶体结构及荧光性质

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摘要:通过水热合成的方法制备了 2 个 Zn(Ⅱ)配位聚合物{[$Zn_{1.5}$(dbim)$_{1.5}$(btc)]·6H_2O}$_n$ (**1**)和{[Zn(dbim)$_{0.5}$(btec)$_{0.5}$(H_2O)]·H_2O}$_n$ (**2**) (dbim=1-(4-((2,6-dimethyl-2*H*-benzo[*d*]imidazol-3(3*H*)-yl)methyl)benzyl)-2,7-dihydro-2,5-dimethyl-1*H*-benzo[*d*]imidazole,H_3btc=1,3,5-苯三酸,H_4btec=1,2,4,5-苯四甲酸)。结构分析表明配合物 **1** 是一个三节点(3,4,4)-连接的网络,拓扑符号为(5^2·6·7·8^2)(5^2·6) (5^2·6^2·8^2)。配合物 **2** 是一个(3,4)-连接的网络,拓扑符号为(8^3)(8^5·10)。配合物 **1** 和 **2** 的固态荧光与配体 dbim 不同。

关键词:Zn(Ⅱ);晶体结构;拓扑;荧光
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Two 3D Zn(Ⅱ) Coordination Complexes Constructed From a Semi-rigid Bis(dimethylbenzimidazole) Ligand and Different Multi-carboxylic Acids: Structures and Fluorescence Properties

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Abstract: Two Zn(Ⅱ) coordination complexes, formulated as {[$Zn_{1.5}$(dbim)$_{1.5}$(btc)]·6H_2O}$_n$ (**1**) and {[Zn(dbim)$_{0.5}$(btec)$_{0.5}$(H_2O)]·H_2O}$_n$ (**2**) (dbim=1-(4-((2,6-dimethyl-2*H*-benzo[*d*]imidazol-3(3*H*)-yl)methyl)benzyl)-2,7-dihydro-2,5-dimethyl-1*H*-benzo[*d*]imidazole, H_3btc=trimesic acid, H_4btec=1,2,4,5-benzene tetracarboxylic), have been obtained by hydrothermal reactions. Complex **1** is a trinodal (3,4,4)-connected topology net with the point symbol of (5^2·6·7·8^2)(5^2·6) (5^2·6^2·8^2), while complex **2** possesses a (3,4)-connected 3D topology with the point symbol of (8^3)(8^5·10) topology. Additionally, complexes **1** and **2** exhibit different photoluminescence behaviors in solid state compared to ligand dbim. CCDC:1584788, **1**; 1584789, **2**.

Keywords: Zn(Ⅱ); crystal structure; topology; fluorescence

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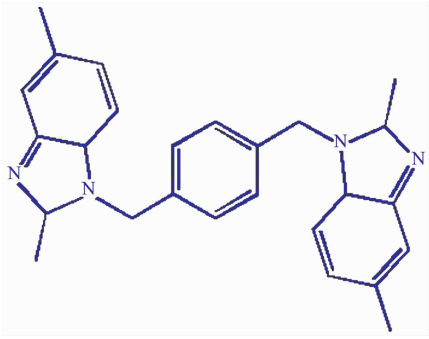
To date, the design and construction of coordination complexes have been quickly developing because of their intriguing structural motifs and potential applications[1-9]. The researches in this field have been concentrated on the structural tuning of the resulting complexes via selecting proper metal centers and different organic ligands[10-12]. As far as we can see, 1-(4-((2,6-dimethyl-2*H*-benzo[*d*]imidazol-3(3*H*)-yl)methyl) benzyl)-2,7-dihydro-2,5-dimethyl-1*H*-benzo[*d*]imidazole (dbim) (Scheme 1) has been rarely mentioned as the semi-rigid N-donor ligand in metal-organic coordination polymer materials. Not only two dimethylbenzimidazole of dbim can freely twist around two -CH_2- groups with disparate angles to produce unlike conformations, but also the existence of the methyl in the imidazole ring and benzene ring can boost the donated electrons ability of dbim, which is conducive to enrich coordination ability of dbim with metal ions.



Scheme 1　Structure of ligand dbim

The polycarboxylate ligands, as a star in the coordination chemistry, are also of especial interest and have been widely used to fabricate various coordination complexes, owing to their strong coordination ability and diverse coordination modes[13-17]. In addition, the two-ligand assembly system is capable of providing more variability to build complicated and fascinating structures. Therefore, multidentate O-donor carboxylate ligands, trimesic acid (H_3btc) and 1,2,4,5-benzene tetracarboxylic (H_4btec) are introduced, and two diverse 3D complexes, $\{[Zn_{1.5}(dbim)_{1.5}(btc)]\cdot 6H_2O\}_n$ (**1**) and $\{[Zn(dbim)_{0.5}(btec)_{0.5}(H_2O)]\cdot H_2O\}_n$ (**2**) were synthesized. The crystal structure analysis of the complexes, and the effect of different multi-carboxylates on the final frameworks, are also discussed. The structural differences demonstrate that the backbones of the multi-carboxylates are key factors in formation of the final coordination complexes. Moreover, the photoluminescence of the complexes **1** and **2** were also reported.

1　Experimental

1.1　Materials and method

All reagents and solvents were commercially available except for dbim, which was synthesized according to the literature[18]. FT-IR spectra were recorded on a FTIR-7600 spectrophotometer with KBr pellets in 400~4 000 cm^{-1} region. Elemental analyses (C, H and N) were carried out on a FLASH EA 1112 elemental analyzer. The luminescence spectra for the powdered solid samples were measured at room temperature on a F7000 fluorescence spectrophotometer. The excitation slit and emission slit were both 2.0 nm.

1.2　Synthesis of $\{[Zn_{1.5}(dbim)_{1.5}(btc)]\cdot 6H_2O\}_n$ (1)

A mixture of $Zn(Ac)_2\cdot 2H_2O$ (0.2 mmol), dbim (0.1 mmol), H_3btc (0.2 mmol) and NaOH (0.2 mmol) in H_2O (10 mL) was kept in a 25 mL Teflon-lined stainless steel vessel at 140 ℃ for four days. After the mixture was cooled to room temperature at a rate of 5 ℃·h^{-1}, colorless crystals suitable for X-ray diffraction were obtained with a yield of 55% (based on Zn). Anal. Calcd. for $C_{96}H_{96}N_{12}O_{18}Zn_3$(%): C, 60.61; H, 5.08; N, 8.83. Found(%): C, 60.57; H, 5.09; N, 8.81. IR (KBr, cm^{-1}): 3 418(w), 2 862(vw), 2 359(w), 1 698(w), 1 615(s), 1 567(s), 1 516(s), 1 493(s), 1 415(w), 1 330(s), 1 286(w), 1 259(w), 1 172(w), 1 100(w), 1 035(w), 994(w), 936(w), 867(w), 803(s), 726(s), 670(w).

1.3　Synthesis of $\{[Zn(dbim)_{0.5}(btec)_{0.5}(H_2O)]\cdot H_2O\}_n$ (2)

A mixture of $Zn(Ac)_2\cdot 2H_2O$ (0.2 mmol), dbim (0.1 mmol), H_4btec (0.1 mmol), NaOH (0.2 mmol) and H_2O (10 mL) was placed in a 25 mL Teflon-lined stainless steel container. The mixture was sealed and heated at 160 ℃ for three days. After the mixture was cooled to ambient temperature at a rate of 5 ℃·h^{-1}, colorless crystals of **2** were obtained with a yield of 49% (based on Zn). Anal. Calcd. for $C_{18}H_{18}N_2O_6Zn$(%):

C, 51.01; H, 4.28; N, 6.61. Found (%): C, 50.98; H, 4.27; N, 6.63. IR (KBr, cm^{-1}): 3 424 (m), 3 378(m), 2 923(w), 1 612(vs), 1 511(w), 1 488(s), 1 405(s), 1 355 (vs), 1 135(s), 1 037(w), 868(m), 815(s), 759(m), 682 (m), 607(m), 508(w).

1.4 Crystal structural determination

The data of **1** and **2** were collected on a Xcalibur Eos Gemini CCD diffractomer (Cu $K\alpha$ for **1**, λ = 0.154 18 nm; Mo $K\alpha$ for **2**, λ =0.071 073 nm) at temperature of (20±1) ℃. Absorption corrections were applied by using multi-scan program. The data were modified for Lorentz and polarization effects. The structure of complex **1** was solved and refined by full-matrix least squares on F^2 using OLEX2[19], while the structure of complex **2** was 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[20]. 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** and **2** are summarized in Table 1. Selected bond lengths and bond angles of **1** and **2** are listed in Table 2.

CCDC:1584788, **1**; 1584789, **2**.

Table 1 Crystal data and structure refinement details for complexes 1 and 2

Complex	1	2
Formula	$C_{96}H_{96}N_{12}O_{18}Zn_3$	$C_{18}H_{18}N_2O_6Zn$
Formula weight	1 902.08	423.71
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	$P2_1/c$
a / nm	3.432 8(4)	1.070 2(2)
b / nm	1.781 82(5)	1.012 0(2)
c / nm	2.237 1(2)	1.668 2(3)
β / (°)	136.44(2)	93.15(3)
V / nm^3	9.430(3)	1.804(6)
Z	4	4
D_c / ($g\cdot cm^{-3}$)	1.264	1.560
Absorption coefficient / mm^{-1}	1.412	1.400
F(000)	3 720	872
θ range / (°)	4.635~70.276	1.91~25.00
GOF	1.023	0.992
R_1[a] [$I>2\sigma(I)$]	0.060 5	0.071 3
wR_2[b] [$I>2\sigma(I)$]	0.169 4	0.188 0

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

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

1					
Zn(1)-N(1)	0.202 4(4)	Zn(2)-N(3)	0.204 2(3)	Zn(1)#2-N(6)	0.201 1(4)
Zn(1)-O(1)	0.200 9(2)	Zn(1)#3-O(4)	0.199 1(2)	Zn(2)-O(5)	0.199 4(2)
Zn(1)-N(6)#4	0.201 1(4)	Zn(1)-O(4)#5	0.199 1(2)	Zn(2)-N(3)#6	0.204 1(3)
Zn(2)-O(5)#6	0.199 4(2)				
N(6)#4-Zn(1)-N(1)	128.30(16)	O(1)-Zn(1)-N(1)	103.66(11)	O(1)-Zn(1)-N(6)#4	106.34(12)
O(4)#5-Zn(1)-N(1)	104.03(12)	O(4)#5-Zn(1)-N(6)#4	106.90(14)	O(4)#5-Zn(1)-O(1)	105.84(10)
N(3)#6-Zn(2)-N(3)	119.53(18)	O(5)-Zn(2)-N(3)#6	105.24(11)	O(5)#6-Zn(2)-N(3)#6	112.04(11)
O(5)-Zn(2)-N(3)	112.04(11)	O(5)#6-Zn(2)-N(3)	105.23(11)	O(5)#6-Zn(2)-O(5)	101.38(14)

Continued Table 2

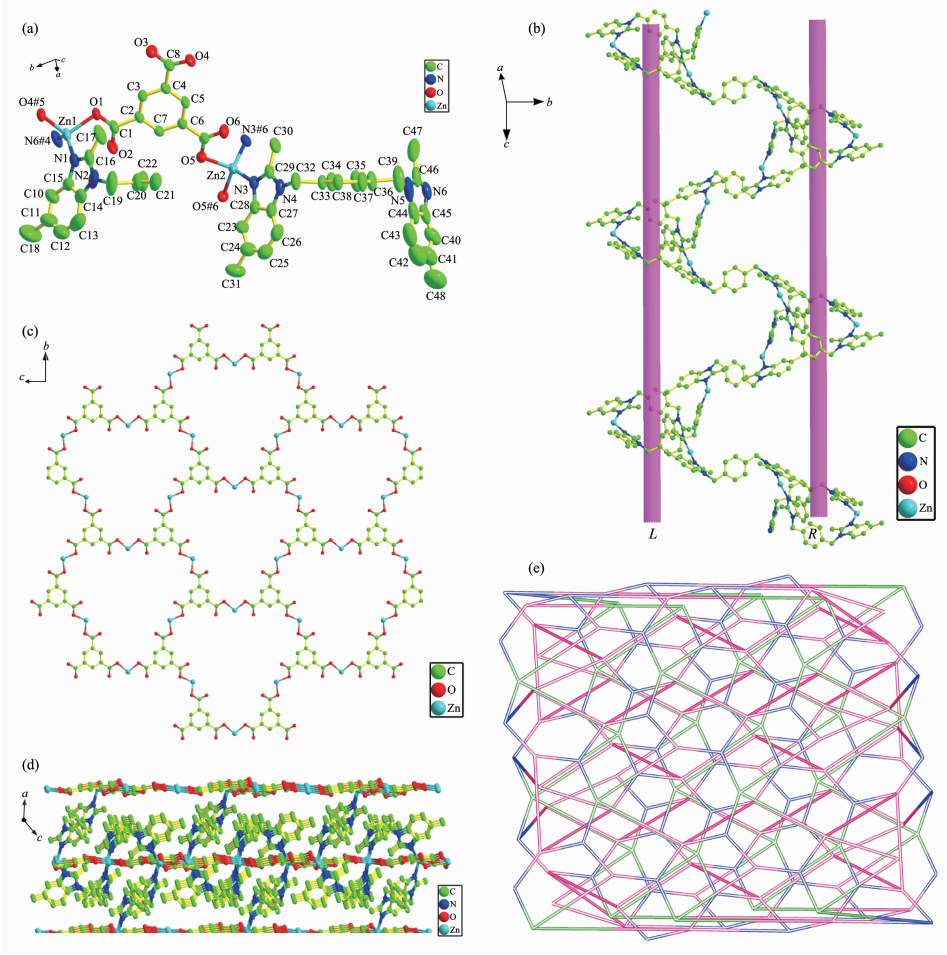
			2		
Zn(1)#1-O(3)	0.195 1(3)	Zn(1)-O(5)	0.193 1(3)	Zn(1)-O(1)	0.195 0(3)
Zn(1)-O(3)#3	0.195 1(3)	Zn(1)-N(1)	0.200 0(4)		
O(5)-Zn(1)-O(1)	109.30(15)	O(5)-Zn(1)-O(3)#3	117.12(14)	O(1)-Zn(1)-O(3)#3	102.28(13)
O(5)-Zn(1)-N(1)	114.13(18)	O(1)-Zn(1)-N(1)	112.04(14)	O(3)#3-Zn(1)-N(1)	101.26(14)

Symmetry codes: #2: 1−*x*, −1+*y*, 3/2−*z*; #3: 1/2−*x*, −1/2+*y*, 1/2−*z*; #4: 1−*x*, 1+*y*, 3/2−*z*; #5: 1/2−*x*, 1/2+*y*, 1/2−*z*; #6: 1−*x*, *y*, 3/2−*z* for **1**; #1: −*x*+2, *y*+1/2, −*z*+1/2; #3: −*x*+2, *y*−1/2, −*z*+1/2 for **2**.

2　Results and discussion

2.1　Crystal structure of {[$Zn_{1.5}$(dbim)$_{1.5}$(btc)]·6H_2O}$_n$ (1)

As illustrated in Fig.1a, the asymmetric unit of complex **1** consists of two crystallographically independent Zn(Ⅱ) ion, one and a half dbim ligands, one btc^{3-} ligand and six lattice water molecules. Zn1(Ⅱ) ion is four-coordinated by two carboxylate oxygen atoms (O1 and O4#5) from two btc^{3-} anions, two nitrogen atoms (N1 and N6#4) from two dbim ligands. The Zn1-O1/O4#5 bond distances are 0.200 9(2)/0.199 1(2)



Symmetry codes in (a): #4: 1−*x*, 1+*y*, 1.5−*z*; #5: 0.5−*x*, 0.5+*y*, 0.5−*z*; #6: 1−*x*, *y*, 1.5−*z*

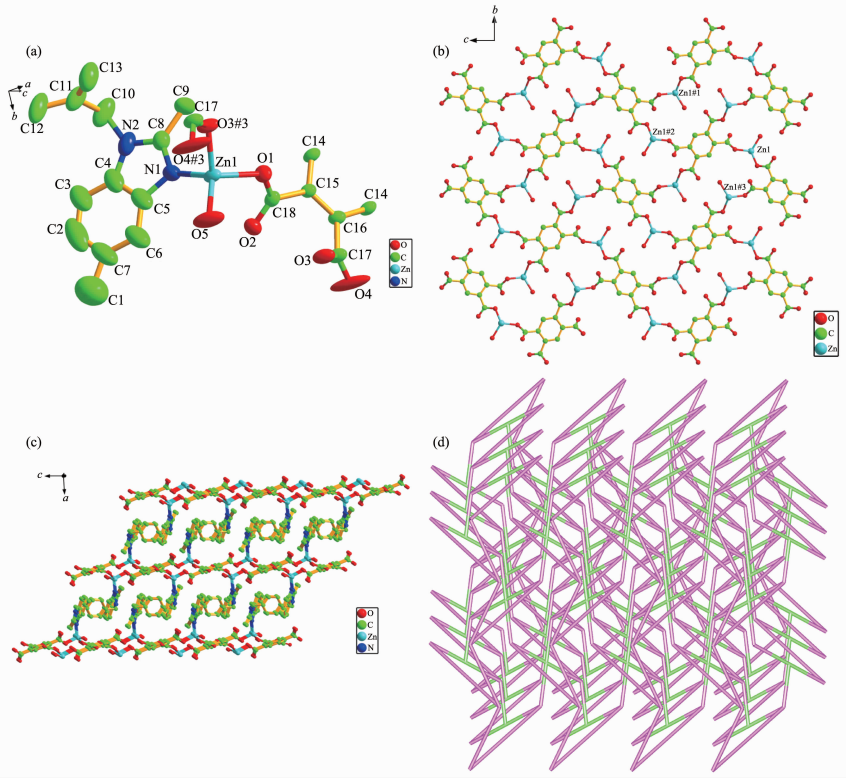
Fig.1　(a) Coordination environment of Zn (Ⅱ) ion in **1** with hydrogen atoms omitted for clarity; (b) 1D *meso*-helix chain built though Zn(Ⅱ) ions and dbim linkers in **1**; (c) 2D layer structure of **1** constructed by Zn(Ⅱ) ions and btc^{3-} linkers; (d) Schematic view of 3D framework built by 1D Zn(Ⅱ)/dbim and 2D Zn(Ⅱ)/btc^{3-} layers in **1**; (e) Schematic description of a (3,4,4)-connected 3D network with ($5^2\cdot6\cdot7\cdot8^2$)($5^2\cdot6$) ($5^2\cdot6^2\cdot8^2$) topology for **1**

nm, while the Zn1-N1/N6#4 bond lengths are 0.202 4(4) /0.201 1(4) nm, respectively. Zn2 atom is also four-coordinated geometry, which is completed by two oxygen atoms (O5 and O5#6) originating from two different btc^{3-} anions and two nitrogen atoms (N3 and N3#6) from two dbim ligands. Both of the distances of Zn2-O5/O5#6 are 0.199 4(2) nm, while the Zn2-N3/N3#6 bond lengths are 0.204 2(3)/0.204 1(3) nm.

There are two independent dbim ligands in complex **1**. dbim-Ⅰ exhibit asymmetrical *cis*-conformation with an $N_{donor}\cdots N-C_{sp^3}\cdots C_{sp^3}$ torsion angles of 108.256° and 114.981°. While dbim-Ⅱ exhibit symmetrical *trans*-conformation with an $N_{donor}\cdots N-C_{sp^3}\cdots C_{sp^3}$ torsion angle of 59.528°. The two types of dbim act as bidentate mode to link two adjacent Zn(Ⅱ) ions alternately to give rise to a *meso*-helix chain, as portrayed in Fig.1b. The Zn⋯Zn distances across the dbim bridges are 1.199 1 nm (dbim-Ⅰ) and 1.322 8 nm (dbim-Ⅱ), separately. The btc^{3-} anion presents a tridentate coordination mode, with three carboxylate groups adopting the monodentate modes. The Zn(Ⅱ) ions are connected by btc^{3-} anions to form a 2D sheet structure (Fig.1c), which is connected by dbim ligand via the Zn-N connection to generate a 3D framework (Fig.1d). As discussed above, each btc^{3-} anion links three Zn(Ⅱ) ions, and accordingly, the btc^{3-} can be regarded as a 3-connected node. As for each Zn1(Ⅱ) ion and Zn2(Ⅱ) ion, they links two btc^{3-} anions and two dbim ligands, respectively. Hence, the Zn1(Ⅱ)ion and Zn2(Ⅱ) ion are treated as a 4-connector, respectively. According to the simplification principle, the resulting structure of complex **1** is a trinodal (3,4,4)-connected topology net with point symbol of $(5^2\cdot6\cdot7\cdot8^2)(5^2\cdot6)(5^2\cdot6^2\cdot8^2)$ (Fig.1e).

2.2 Crystal Structure of $\{[Zn(dbim)_{0.5}(btec)_{0.5}(H_2O)]\cdot H_2O\}_n$ (2)

As illustrated in Fig.2a, the asymmetric unit of complex **2** consists of one Zn(Ⅱ) ion, half a dbim



Symmetry codes: #3: 2–*x*, –0.5+*y*, 0.5–*z* in (a); #1: 2–*x*, 0.5+*y*, 0.5–*z*; #2: 2–*x*, 2–*y*, 1–*z*; #3: 2–*x*, –0.5+*y*, 0.5–*z* in (b)

Fig.2 (a) Coordination environment of Zn(Ⅱ) ion in **2** with hydrogen atoms omitted for clarity; (b) 2D sheet generated by Zn(Ⅱ) ions and $btec^{4-}$ linkers in **2**; (c) Schematic view of 3D framework built by 2D Zn(Ⅱ)/$btec^{4-}$ layers and dbim pillars in **2** with H atoms omitted for clarity; (d) Schematic view of the 3D topology network with the point symbol of $(8^3)(8^5\cdot10)$ for **2**

ligand, half a $btec^{4-}$ ligand, one coordinated water molecule and one lattice water molecule. Each Zn(Ⅱ) ion is four-coordinated by two carboxylate oxygen atoms (O1 and O3#3) from two $btec^{4-}$ anions, one nitrogen atom (N1) from one dbim ligand and one oxygen atom (O5) from one water molecule. The Zn-O bond distances vary from 0.193 1(3) to 0.195 1(3) nm, while the Zn-N1 bond length is 0.200 0(4) nm. Ligand dbim adopts symmetric *trans*-conformation with an $N_{donor}\cdots N-C_{sp^3}\cdots C_{sp^3}$ torsion angle of 74.697°. The $btec^{4-}$ anion presents a quadridentate coordination mode, with four carboxylate groups showing a monodentate mode. The Zn(Ⅱ) ions are connected by $btec^{4-}$ anions to form a 2D sheet structure (Fig.2b), which is connected by dbim ligand in a *tran*-conformation via the Zn-N connection to generate a 3D pillar-layered framework (Fig.2c). To further demonstrate the overall 3D structure of **2**, we can consider each Zn(Ⅱ) as a 3-connecting node, which is linked to three equivalent nodes through one dbim ligand and two $btec^{4-}$ ligands. Moreover, the $btec^{4-}$ ligand can be simplified as a 4-connecting node and dbim is defined as a linker, the 3D framework of **2** can be described as $(8^3)(8^5\cdot10)$ topology (Fig.2d).

2.3 Effect of dbim and carboxylate co-ligands on structures of 1 and 2

As described above, the semi-rigid dbim ligand presents two independent conformation (dbim-Ⅰ and dbim-Ⅱ, respectively) in **1**. dbim-Ⅰ exhibit asymmetrical *cis*-conformation, while dbim-Ⅱ exhibit symmetrical *trans*-conformation. The two types of dbim bridges adjacent Zn(Ⅱ) ions alternately to give rise to a meso-helix chain. However, in **2**, dbim adopts single symmetric *trans*-conformation and serves as bridging pillar linking adjacent 2D Zn(Ⅱ)/$btec^{4-}$ layer, which makes 2 show 3D pillar-layered framework. The semi-rigid dbim can rotate freely when coordinating with central metal ions because of the flexible nature of the $-(CH_2)-$ spacers, which can greatly beautify and enrich the structure of complexes.

The carboxylate anions have important influence on the constructing of resultant 3D structures. In this work, we selected two multi-carboxylic acids (btc^{3-} and $btec^{4-}$) as co-ligands. By introducing ligand btc^{3-}, 3D (3,4,4)-connected $(5^2\cdot6\cdot7\cdot8^2)(5^2\cdot6)(5^2\cdot6^2\cdot8^2)$ topology net **1** are obtained. When $btec^{4-}$ is introduced into the synthetic procedure of **2**, 3D (3,4)-connected $(8^3)(8^5\cdot10)$ topology are built. These results show diverse carboxylate co-ligands exert a pivotal influence on the features and overall structures of the resultant complexes.

2.4 Photoluminescence properties

Fluorescence properties of the coordination complexes with d^{10} metal centers have attracted more interest owning to their potential applications[21-23]. Hence, the solid-state photoluminescent spectra of free dbim ligand and Zn(Ⅱ) complexes **1**~**2** were investigated at ambient temperature, as depicted in Fig.3. The free ligand dbim displayed an emission band at 314 nm (λ_{ex}=252 nm). As reported before[24], the photoluminescent spectra of H_3btc and H_4btec showed different emission peak at 395 nm (λ_{ex}=355 nm) and

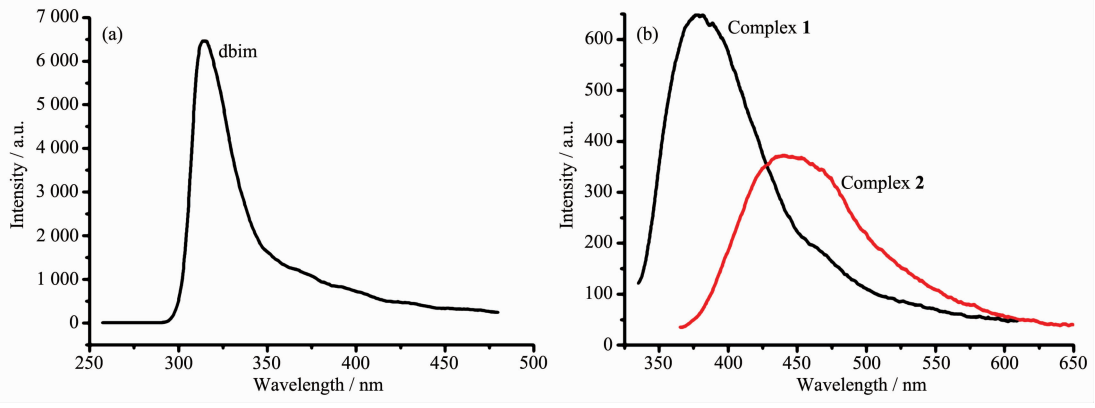


Fig.3　Photoluminescent spectra of ligand dbim (a) and complexes **1**~**2** (b) in solid state at room temperature

340 nm (λ_{ex}=310 nm), respectively. For complex **1**, excited at 317 nm, it gave rise to an emission band at 380 nm (Fig.3). As compared to dbim ligand, a red shift (66 nm) was observed. As compared to H_3btc ligand, a smaller hypsochromic shift (15 nm) was observed. The emission spectrum of complex **2** displayed an emission band centered at 446 nm with excitation maximum at 355 nm and the emission band presented larger red shifts (106 and 132 nm) compared with those of ligand H_4btec and dbim, respectively. According to the reference[24], the emission spectra of **1** and **2** are similar to those of H_3btc and H_4btec ligand, respectively, which also be mainly ascribed to the intraligand emission of H_3btc and H_4btec ligand, respectively[24-28].

3 Conclusions

In conclusion, by the introduction of two different multi-carboxylic acid co-ligands, two varied 3D architectures can be constructed from Zn(Ⅱ) salts and the semi-rigid bis(dimethylbenzimidazole) ligand. The successful fabrication of complexes **1** and **2** may furnish meritorious insights into the construction of wonderful frameworks. Moreover, **1** and **2** exhibit fluorescence properties, and maybe display potential for optical materials.

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