

基于 1-丁基苯并咪唑和对苯二甲酸混合配体的锌(II)和铜(II) 一维配位聚合物:晶体结构和弱相互作用

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摘要: 用 1-丁基苯并咪唑和对苯二甲酸与 $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 或 $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ 反应合成了两个锌(II)和铜(II)的一维配位聚合物 $[\text{Zn}(\text{L})_2(\text{TP})]_n$ (**1**)和 $[\text{Cu}(\text{L})_2(\text{TP})]_n$ (**2**)(L =1-丁基苯并咪唑, TP =对苯二甲酸根)。配位聚合物 **1** 和 **2** 通过 $\text{C}-\text{H} \cdots \text{O}$ 或 $\text{O}-\text{H} \cdots \text{O}$ 氢键形成了二维超分子层。测定了 **1** 和 **2** 的荧光发射光谱。

关键词: 1-丁基苯并咪唑; 对苯二甲酸; 锌(II); 铜(II); 配位聚合物

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Two Zinc(II) and Copper(II) 1D Coordination Polymers Based on 1-Butylbenzimidazole and Terephthalate Mixed-ligands: Crystal Structures and Weak Interactions

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Abstract: The two 1D coordination polymers $[\text{Zn}(\text{L})_2(\text{TP})]_n$ (**1**) and $[\text{Cu}(\text{L})_2(\text{TP})]_n$ (**2**) (L =1-butylbenzimidazole, TP =terephthalate ion) have been prepared via the reaction of 1-butylbenzimidazole, terephthalic acid and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, respectively. The structures of these complexes were characterized by X-ray diffraction analysis. In the crystal packings of coordination polymers **1** and **2**, 2D supramolecular layers are formed through $\text{C}-\text{H} \cdots \text{O}$ or $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds, respectively. The fluorescence emission spectra of **1** and **2** are described. CCDC: 899947, **1**; 899948, **2**.

Key words: 1-butylbenzimidazole; terephthalic acid; zinc(II); copper(II); coordination polymer

0 Introduction

The research on metal-organic polymers has become an interesting field in both supramolecular and material science owing to their intriguing structural diversity and physical properties^[1-2]. In crystal engineering, the most important driving forces

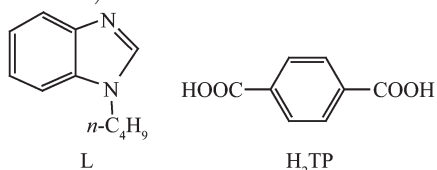
are coordination^[3], however, some weak interactions, such as hydrogen bonding^[4] and $\pi-\pi$ stacking interactions^[5], often affect the structures of complexes, and they can further link discrete subunits or low-dimensional entities into high-dimensional supramolecular networks^[6-7]. For chemists, crystal engineering is still a big challenge because the coordination mode of metal

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ions and ligand self-assembly into supramolecular is not easily controlled. Ligands containing imidazole ring play important roles in coordination chemistry, and they can coordinate with a variety of transition metals to form one-, two- and three-dimensional coordination polymers through the use of nitrogen atom of imidazolyl^[8-9]. As a building block to construct some porous coordination polymers, terephthalate ligand may form coordination architectures of diverse sizes and shapes. In the metal complexes, the zinc(II) and copper(II) as connecting nodes have a wide range of coordination numbers, furthermore, their polynuclear complexes have good fluorescence properties^[10-12]. We are interested in constructing functional coordination polymers using terephthalates as bridging ligands, 1-substituentbenzimidazole as monodentate ligands and transition metal as connecting nodes. In the paper, we report the preparations, crystal structures, weak interactions and fluorescence properties of two zinc(II) and copper(II) coordination polymers, $[\text{Zn}(\text{L})_2(\text{TP})]_n$ (**1**) and $[\text{Cu}(\text{L})_2(\text{TP})]_n$ (**2**) (L = 1-butylbenzimidazole, TP = terephthalate ion).



1 Experimental

1.1 General procedures

Melting points were determined with a Boetius Block apparatus. ^1H NMR spectra were recorded on a Varian Mercury Vx 400 spectrometer at 400 MHz. Chemical shifts, δ , are reported in ppm relative to the internal standard TMS for ^1H NMR. Elemental analyses were measured using a Perkin-Elmer 2400C Elemental Analyzer. IR spectra (KBr) were taken on an Bruker Equinox 55 spectrometer. The luminescent spectra were conducted on Cary eclipse fluorescence spectrophotometer.

1.2 Preparation of 1-butylbenzimidazole (**L**)

A THF solution (20 mL) of benzimidazole (1.000 g, 8.4 mmol) was added to a suspension of oil-free sodium hydride (0.240 g, 10.2 mmol) in THF (20 mL)

and stirred for 1 h at 60 °C. Then THF (20 mL) solution of n-butane bromide (1.280 g, 9.3 mmol) was dropwise added to above solution. The mixture was continued to stir for 48 h at 60 °C and a yellow solution was obtained. The solvent was removed with a rotary evaporator and H_2O (50 mL) was added to the residue. Then the solution was extracted with CH_2Cl_2 (3×20 mL), and the extracting solution was dried over anhydrous MgSO_4 . After removing CH_2Cl_2 , a pale yellow liquid 1-butylbenzimidazole was obtained. Yield: 1.360 g (92%). ^1H NMR (400 MHz, CDCl_3): δ 0.95 (t, J =7.3, 3H, CH_3), 1.38 (m, 2H, CH_2), 1.88 (m, 2H, CH_2), 4.37 (t, J =7.0, 2H, CH_2), 7.84 (m, 2H, PhH), 8.11 (m, 2H, PhH), 9.13 (s, 1H, 2-bimiH) (bimi: benzimidazole).

1.3 Preparation of coordination polymer (**1**)

A *N,N*-dimethylformamide solution (8 mL) containing terephthalic acid (H_2TP) (50 mg, 0.3 mmol) was added to an aqueous solution (5 mL) of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (89.2 mg, 0.3 mmol). After ca. 5 min of vigorous mixing, a methanol solution (8 mL) of 1-butylbenzimidazole (0.100 g, 0.6 mmol) was added and the pH value of the solution was adjusted to ca. 7 by triethylamine. The reaction mixture was stirred for 30 min at 40 °C. The filtrate of the above mixture was allowed to evaporate slowly under ambient conditions, and colorless single crystals suitable for X-ray analysis were obtained within two weeks. Yield: 94.2 mg (54%) (based on H_2TP); mp: 292~294 °C. Anal. Calcd. for $\text{C}_{30}\text{H}_{32}\text{ZnN}_4\text{O}_4$ (%): C, 62.33; H, 5.58; N, 9.69. Found (%): C, 62.56; H, 5.34; N, 9.88. IR (KBr, cm^{-1}): 3 095 v, 2 959s, 2 925m, 2 867m, 1 623vs, 1 607vs, 1 515m, 1 461 m, 1 383s, 1 354vs, 1 341s, 1 296m, 1 254m, 1 208 m, 819s, 774vs, 636m.

1.4 Preparation of coordination polymer (**2**)

A *N,N*-dimethylformamide solution (8 mL) containing terephthalates (50 mg, 0.3 mmol) was added to an aqueous solution (5 mL) $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (72.5 mg, 0.3 mmol). After ca. 5 min of vigorous mixing, a methanol solution (8 mL) of 1-butylbenzimidazole (0.100 g, 0.6 mmol) was added and the pH value of the solution was adjusted to ca. 7 by triethylamine. The reaction mixture was stirred for 30 min at 40 °C. The filtrate of the above mixture was allowed to

evaporate slowly under ambient conditions. Blue crystals suitable for X-ray analysis were obtained within seven days. Yield: 107.5 mg (53%) (based on H_2TP); mp: 168~170 °C. Anal. Calcd. for $\text{C}_{34}\text{H}_{37}\text{CuN}_4\text{O}_7$ (%): C, 60.30; H, 5.51; N, 8.27. Found (%): C, 60.56; H, 5.76; N, 8.56. IR (KBr, cm^{-1}): 3 568s, 3 174m, 2 954s, 2 872s, 1 706m, 1 565m, 1 511m, 1 399m, 1 354s, 1 300m, 1 196 m, 1 009m, 926m, 740s, 557m, 520m.

1.5 X-ray data collection and structure determinations

Single-crystal X-ray diffraction measurements of **1** (0.25 mm×0.24 mm×0.23 mm) and **2** (0.24 mm×0.20 mm×0.18 mm) were collected on a Bruker SMART APEX II CCD diffractometer at 296(2) K with Mo $K\alpha$ radiation (0.071 073 nm) by ω scan mode. There was no evidence of crystal decay during data collection in

all cases. Semiempirical absorption corrections were applied by using SADABS and the program SAINT was used for integration of the diffraction profiles^[13]. All structures were solved by direct methods by using the SHELXS program of the SHELXTL package and refined with SHELXL^[14] by the full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms on F^2 . All hydrogen atoms were generated geometrically (C-H bond lengths fixed at 0.093~0.097 nm), assigned appropriated isotropic thermal parameters and included in structure factor calculations. Selected bond lengths (nm) and angles (°) and crystal data and structure refinement for **1** are presented in Table 1 and Table 2. Figures were generated by using Crystal-Maker^[15].

CCDC: 899947, **1**; 899948, **2**.

Table 1 Crystallographic data for coordination polymer **1** and **2**

	1	2
Empirical formula	$\text{C}_{30}\text{H}_{32}\text{ZnN}_4\text{O}_4$	$\text{C}_{30}\text{H}_{34}\text{CuN}_4\text{O}_5 \cdot 0.5\text{C}_8\text{H}_6\text{O}_4$
Formula weight	577.97	677.22
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a / nm	0.110(7)	0.096(2)
b / nm	0.209(1)	0.214(5)
c / nm	0.142(7)	0.155(4)
β / (°)	120.803(3)	95.351(4)
V / nm^3	0.284(3)	0.321(1)
Z	4	4
D_c / ($\text{g} \cdot \text{cm}^{-3}$)	1.351	1.401
Abs coeff / mm^{-1}	0.906	0.735
$F(000)$	1208	1416
Cryst size / mm	0.25×0.24×0.23	0.24×0.20×0.18
T / K	296(2)	296(2)
θ_{\min} , θ_{\max} / (°)	1.93, 25.01	2.31, 25.03
No. of data collected	14 340	17 264
No. of unique data	5 008	5 667
No. of refined params	354	418
Goodness-of-fit on F^2	1.009	1.065
Final R indices ($I > 2\sigma(I)$)		
R_1	0.031 9	0.044 5
wR_2	0.071 1	0.125 6
R indices (all data)		
R_1	0.051 2	0.065 9
wR_2	0.079 1	0.138 2

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

1					
Zn1-O1	0.195(2)	Zn1-O3	0.196(2)	Zn1-N1	0.200(2)
Zn1-N1	0.201(2)				
O1-Zn1-O3	96.3(7)	O1-Zn1-N1	108.8(8)	O3-Zn1-N1	108.8(8)
O1-Zn1-N3	111.7(8)	O3-Zn1-N3	112.8(8)	N1-Zn1-N3	116.3(8)
2					
Cu1-N1	0.197(3)	Cu1-N3	0.198(3)	Cu1-O1	0.198(2)
Cu2-O4	0.197(2)	Cu1-O5	0.234(2)		
N1-Cu1-O4	87.7(1)	N1-Cu1-O1	93.2(1)	O4-Cu1-O1	170.5(9)
N1-Cu1-N3	171.2(1)	O4-Cu1-N3	90.8(1)	O1-Cu1-N3	86.9(1)
N1-Cu1-O5	94.8(1)	O4-Cu1-O5	100.0(9)	O1-Cu1-O5	89.3(9)
N3-Cu1-O5	94.0(1)				

2 Results and discussion

2.1 Synthesis and characterization of ligand L and coordination polymers **1** and **2**

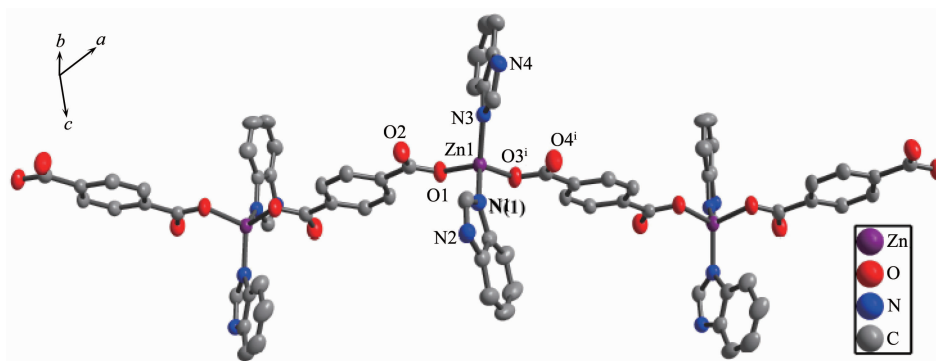
1-Butylbenzimidazole (L) was prepared from benzimidazole by alkylation with *n*-butane bromide, and obtained as a pale yellow liquid. The ligand L is very soluble in common organic solvents (such as CH₂Cl₂, CH₃OH, CH₃CN and DMF etc.), therefore, crystallization of its complexes with inorganic metal salts occurs readily.

Coordination polymers **1** and **2** were prepared by the reaction of ligand L, terephthalic acid and Zn(NO₃)₂·6H₂O or Cu(NO₃)₂·3H₂O in the presence of Et₃N in *N,N*-dimethylformamide and methanol solution. The crystals of **1** and **2** suitable for X-ray diffraction were grown by evaporating slowly its DMF/

CH₃OH solution at room temperature. Complexes **1** and **2** are stable and can retain their structural integrity at room temperature for a considerable length of time. Molecular structures of **1** and **2** were demonstrated by X-ray analysis.

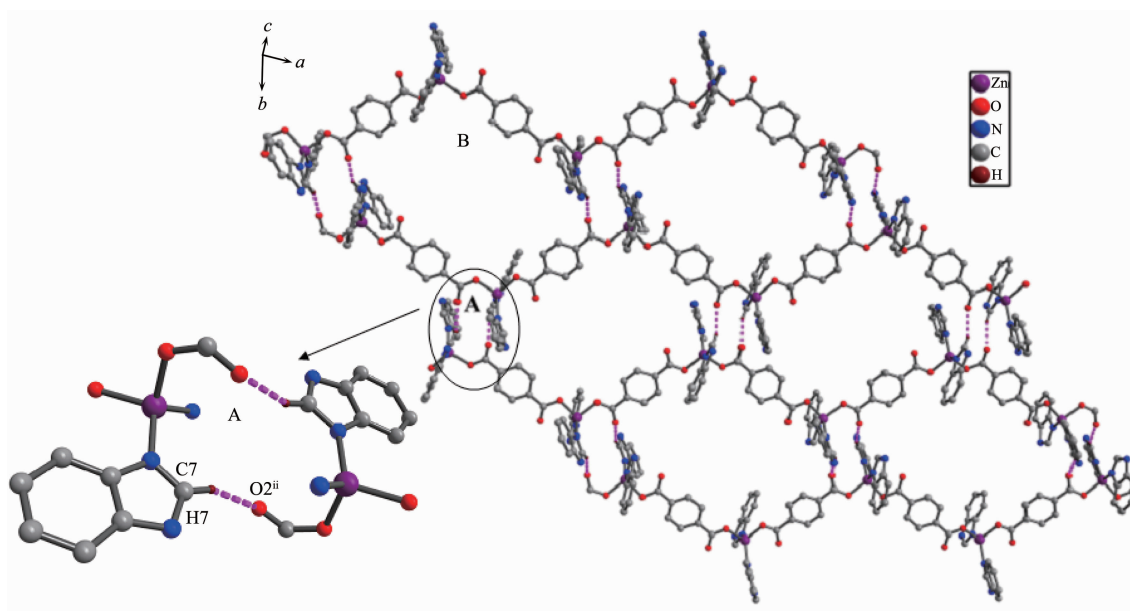
2.2 Structure of coordination polymer [Zn(L)₂(TP)]_n (**1**)

Analysis of crystal structure of **1** showed that 1D coordination polymer is formed through Zn(II) ions and bridging terephthalates as shown in Fig.1a, where each tetracoordinated Zn(II) center adopts a distorted tetrahedral geometry formed by two carboxylate oxygen donors from two different terephthalate bridges (Zn-O being 0.195(2) nm and 0.196(2) nm, respectively) and two nitrogen donors from two benzimidazolyls (Zn-N being 0.200(2) nm and 0.201(2) nm, respectively). The bond angles around Zn(II) center are from 96.3(7)°



All hydrogen atoms and butyl groups are omitted for clarity; Symmetry code: ⁱ 1+x, 3/2-y, 1/2+z

Fig.1a 1D coordination polymeric chain of **1**



Butyl groups and all hydrogen atoms except those participating in the C-H \cdots O hydrogen bonds were omitted for clarity; Symmetry code: ⁱⁱ $-3+x, 3/2-y, -3/2+z$

Fig.1b 2D supramolecular layer by hydrogen bonds in **1**

Table 3 H-Bonding geometry for **1** and **2**

	D-H \cdots A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle \text{D-H}\cdots\text{A} / (^\circ)$
1	C(7)-H(7) \cdots O(2) ⁱ	0.093(2)	0.227(1)	0.314(3)	156.4(2)
2	O(6)-H(6) \cdots O(2) ⁱⁱ	0.081(2)	0.167(2)	0.249(3)	172.0(1)
	O(5)-H(5B) \cdots O(7) ⁱⁱⁱ	0.081(2)	0.224(2)	0.307(3)	163.7(1)

Symmetry code: ⁱ $-3+x, 1.5-y, -1.5+z$; ⁱⁱ $-x, 2-y, 1-z$; ⁱⁱⁱ $0.5-x, 1.5+y, 0.5-z$.

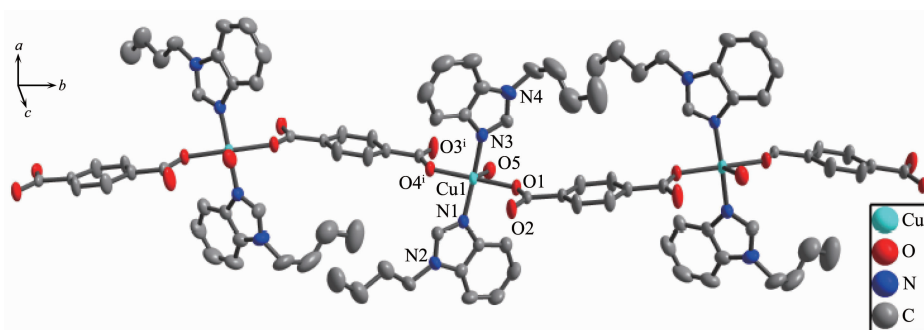
to 116.3(8) $^\circ$, all of which fall in normal range^[11]. Each terephthalate ligand in a μ -2 way connects two Zn(II) centers leading to a zigzag chain, where the Zn-Zn-Zn angles defined by the orientation of the two terephthalate ligands is 121.4(2) $^\circ$ and adjacent Zn-Zn distance is 0.110(4) nm. The two adjacent benzene rings from two different terephthalates are nearly parallel with the dihedral angle of 6.7(3) $^\circ$, and the dihedral angle of two benzimidazole rings linked on same Zn(II) ion is 40.0(1) $^\circ$.

In the crystal packing of **1** (Fig.1b), 2D supramolecular layers are formed by inter-chain C-H \cdots O hydrogen bonds^[4] (the data of hydrogen bonds being given in Table 3), in which oxygen atoms are from carboxylate groups, and hydrogen atoms are from imidazoles. In the 2D supramolecular layers, there exist two types of rings (ring A and ring B). The 14-membered ring A is formed by two carboxylate groups, two imidazole rings and two Zn(II) ions

through two hydrogen bonds, and the ring B is formed by four terephthalates, two imidazole rings and four Zn(II) ions through two hydrogen bonds.

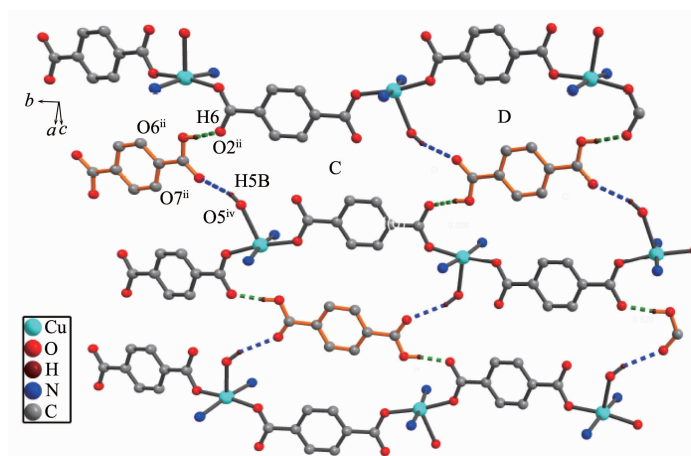
2.3 Structure of Coordination Polymer [Cu(L)₂(TP)]_n (**2**)

Similar to **1**, 1D zigzag polymeric chain of **2** is formed via Cu(II) and bridging terephthalates as depicted in Fig.2a. Each penta-coordinated Cu(II) adopts a distorted square pyramidal geometry, where the equatorial position is occupied by two oxygen donors from two different carboxyls (Cu-O being 0.197(2) nm and 0.198(2) nm, respectively) and two nitrogen donors from two different benzimidazyls (Cu-N being 0.197(3) nm and 0.198(3) nm, respectively), and the apical site is occupied by the water molecule (Cu-O_{water} being 0.234(2) nm). The bond angles of O(1)-Cu(1)-O(4) and N(1)-Cu(1)-N(3) are 170.5(9) $^\circ$ and 171.2(1) $^\circ$, respectively, and the other bond angles around Cu(II) center are from 87 $^\circ$ to 100 $^\circ$. These values are comparable



All hydrogen atoms are omitted for clarity; Symmetry code: i $1/2-x, -1/2+y, 3/2-z$

Fig.2a 1D coordination polymeric chain of **2**



1-butylbenzimidazole and all hydrogen atoms except those participating in the O-H...O hydrogen bonds were omitted for clarity; Symmetry code:

ii $1/2-x, 3/2+y, 1/2-z$; iii $-x, 2-y, 1-z$; iv $1/2-x, 3/2+y, 3/2-z$

Fig.2b 2D supramolecular layer by hydrogen bonds in **2**

with analogous data in other derivatives of Cu(II)^[12]. In **2** the dihedral angle of two adjacent benzene rings from terephthalates is 17.7° , and the dihedral angle of two benzimidazole rings linked on same copper ion is 9.1° . The distance of adjacent Cu-Cu in **2** is 0.107(1) nm, and it is somewhat shorter than that of Zn-Zn (0.110 (4) nm) in **1**. The bond angle of Cu-Cu-Cu in **2** is $165.6 (4)^\circ$, and it is larger than that of Zn-Zn-Zn ($121.4(2)^\circ$) in **1**.

An interesting feature in the crystal packing of **2** is that 1D polymeric chains are connected together by free terephthalic acid through the two types of O-H...O hydrogen bonds^[16] to form 2D supramolecular layers as shown in Fig.2b (the data of hydrogen bonds being given in Table 3). In first type of hydrogen bond (O(6)-H(6)...O(2)), the hydrogen atom is from free terephthalic acid and the oxygen atom is from the terephthalate of polymeric chain. In second type of

hydrogen bond (O(5)-H(5B)...O(7)), the hydrogen atom is from coordinating water molecule and the oxygen atom is from free terephthalic acid. In the 2D supramolecular layers, there exist two types of rings (ring C and ring D). The ring C is constructed by two terephthalates, two Cu(II) ions and two coordinating water molecules from two different polymeric chains, and two carboxyls from two different free terephthalic acid through four hydrogen bonds. The ring D is constructed by one terephthalate, two Cu(II) ions, one coordinating water molecule and one carboxyl from another terephthalate of polymeric chain, and one free terephthalic acid through two hydrogen bonds.

2.4 Fluorescent emission spectra of **L**, **1** and **2**

The fluorescent emission spectra of **L**, **1** and **2** in CH₂Cl₂ solution ($5.0 \mu\text{mol} \cdot \text{L}^{-1}$) at room temperature (298 K) are indicated in Fig.3. For complex **1** and **2**, the maximum emission bands are at 330~340 nm, and

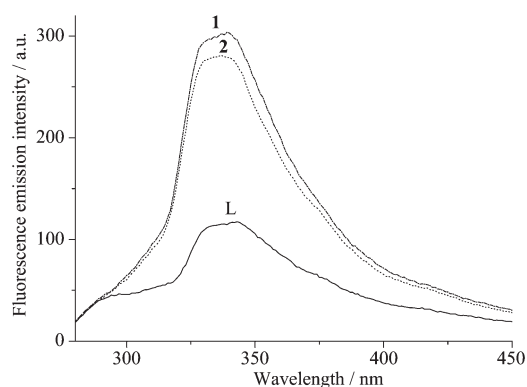


Fig.3 Emission spectra of L, **1** and **2**

their fluorescence emission spectra are stronger than that of corresponding ligand (L), which may be assigned to the result of ligand-to metal-charge-transfer (LMCT). These results show that the metal complexes might be good candidates for potential photoactive materials^[17-18].

3 Conclusions

In summary, the two Zn (II) and Cu (II) 1D coordination polymers have been prepared, and structurally characterized by X-ray diffraction analysis. In the crystal packings of **1** and **2** the 2D supramolecular layers are formed by the C-H \cdots O or O-H \cdots O hydrogen bonds, respectively. The resultant structures of the complexes will provide interesting experimental data for supramolecular chemistry and crystal engineering. Further studies on new metal complexes from ligand 1-butylbenzimidazole and analogous ligands are under way.

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