

## 两个基于双咪唑基配体的 Co(II)/Cu(I)配合物的合成、 晶体结构及荧光性质

李秀梅<sup>\*1</sup> 杨佳琦<sup>2</sup> 潘亚茹<sup>1</sup> 刘 博<sup>\*2</sup> 周 实<sup>2</sup>

(<sup>1</sup> 通化师范学院化学学院, 通化 134002)

(<sup>2</sup> 吉林师范大学环境友好材料制备与应用省部共建教育部重点实验室, 四平 136000)

**摘要:** 以  $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ / $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ 、1,4-双(咪唑基-1-基)丁烷(bib)/1,4-双(咪唑基-1-基)苯(bix)和 4,4'-(1,3-苯基双(亚甲基氧基))二苯甲酸( $\text{H}_2\text{pmda}$ )为原料,在水热条件下反应,得到了 2 个配合物  $\{[\text{Co}(\text{bib})_3](\text{ClO}_4)_2\}_n$  (**1**)和  $\{[\text{Cu}_3(\text{bix})_4](\text{ClO}_4)_3\}_n$  (**2**)( $\text{H}_2\text{pmda}$  未参与反应),对它们进行了元素分析、红外光谱、荧光光谱、单晶和粉末 X 射线衍射表征。配合物 **1** 属于三方晶系,  $R\bar{3}$  空间群,  $a=b=1.393\ 37(5)\ \text{nm}$ ,  $c=1.740\ 54(13)\ \text{nm}$ ,  $V=2.926\ 5(3)\ \text{nm}^3$ ,  $M_r=828.59$ ,  $D_c=1.410\ \text{g}\cdot\text{cm}^{-3}$ ,  $F(000)=1\ 293$ ,  $\mu=0.639\ \text{mm}^{-1}$ ,  $Z=3$ ,  $R_1=0.061\ 1$ ,  $wR_2=0.193\ 7(I>2\sigma(I))$ 。配合物 **2** 也属于三方晶系,  $P\bar{3}$  空间群,  $a=b=2.334\ 41(15)\ \text{nm}$ ,  $c=0.715\ 11(9)\ \text{nm}$ ,  $V=3.374\ 9(5)\ \text{nm}^3$ ,  $M_r=1\ 561.28$ ,  $D_c=1.536\ \text{g}\cdot\text{cm}^{-3}$ ,  $F(000)=1\ 602$ ,  $\mu=1.131\ \text{mm}^{-1}$ ,  $Z=2$ ,  $R_1=0.043\ 9$ ,  $wR_2=0.109\ 0(I>2\sigma(I))$ 。单晶结构分析表明配合物 **1** 为含有 36 元环的二维网状结构,配合物 **2** 为含有 84 元环的二维网状结构,并通过氢键或  $\pi$ - $\pi$  堆积使它们扩展成超分子结构。此外,还研究了 2 个配合物的荧光性质。

**关键词:** 水热合成; 晶体结构; 钴(II)配合物; 铜(I)配合物; 荧光性质

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## Syntheses, Crystal Structures and Photoluminescent Properties of Two Co(II)/Cu(I) Coordination Polymers Based on Bis(imidazol) Ligands

LI Xiu-Mei<sup>\*1</sup> Yang Jia-Qi<sup>2</sup> PAN Ya-Ru<sup>1</sup> LIU Bo<sup>\*2</sup> ZHOU Shi<sup>2</sup>

(<sup>1</sup> Faculty of Chemistry, Tonghua Normal University, Tonghua, Jilin 134002, China)

(<sup>2</sup> Key Laboratory of Preparation and Applications of Environmental Friendly Materials (Jilin Normal University),  
Ministry of Education, Siping, Jilin 136000, China)

**Abstract:** Two coordination polymers,  $\{[\text{Co}(\text{bib})_3](\text{ClO}_4)_2\}_n$  (**1**) and  $\{[\text{Cu}_3(\text{bix})_4](\text{ClO}_4)_3\}_n$  (**2**), (bib=1,4-bis(imidazol-1-yl)-butane, bix=1,4-bis(imidazol-1-ylmethyl)benzene) have been hydrothermally synthesized by using  $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ / $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ , 1,4-bis(imidazolyl-1-yl)butane/1,4-bis(imidazolyl-1-yl) benzene and 4,4'-(1,3-phenylenebis(methyleneoxy))dibenzoic acid ( $\text{H}_2\text{pmda}$ ) as raw materials and structurally characterized by elemental analysis, IR spectrum, fluorescence spectrum, single-crystal and powder X-ray diffraction. Complex **1** crystallizes in trigonal system, space group  $R\bar{3}$  with  $a=b=1.393\ 37(5)\ \text{nm}$ ,  $c=1.740\ 54(13)\ \text{nm}$ ,  $V=2.926\ 5(3)\ \text{nm}^3$ ,  $M_r=828.59$ ,  $D_c=1.410\ \text{g}\cdot\text{cm}^{-3}$ ,  $F(000)=1\ 293$ ,  $\mu=0.639\ \text{mm}^{-1}$  and  $Z=3$ . The final  $R_1=0.061\ 1$  and  $wR_2=0.193\ 7$  for 1 274 observed reflections with  $I>2\sigma(I)$ . Complex **2** belongs to trigonal system too, space group  $P\bar{3}$  with  $a=b=2.334\ 41(15)\ \text{nm}$ ,  $c=0.715\ 11(9)\ \text{nm}$ ,  $V=3.374\ 9(5)\ \text{nm}^3$ ,  $M_r=1\ 561.28$ ,  $D_c=1.536\ \text{g}\cdot\text{cm}^{-3}$ ,  $F(000)=1\ 602$ ,  $\mu=1.131\ \text{mm}^{-1}$  and  $Z=2$ . The final  $R_1=0.043\ 9$  and  $wR_2=0.109\ 0$  for 3 167 observed reflections with  $I>2\sigma(I)$ . Structural analyses reveal that complex **1** shows 2D network structure with 36-membered ring and complex **2** possesses 2D network structure

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\*通信联系人。E-mail: lixm20032006@163.com, 112363305@qq.com

with 84-membered ring. The intermolecular hydrogen bonding or  $\pi$ - $\pi$  stacking interactions extend the complexes **1** and **2** into supramolecular architectures. Furthermore, we also studied the fluorescence properties of the complexes. CCDC: 1950200, **1**; 1950184, **2**.

**Keywords:** hydrothermal synthesis; crystal structure; Co(II) complex; Cu(I) complex; luminescence

## 0 Introduction

The design and synthesis of metal-organic coordination polymers relied on the selection of ligands and metal ions has become a very attractive research field. This is motivated not only by the intriguing structural diversity but also by the demand of applying functional materials into the fields of catalysis, porosity, magnetism, luminescence and nonlinear optics<sup>[1-3]</sup>. In general, grids with various sizes and shapes can be synthesized by choosing suitable single metal ions and organic ligands such as carboxylates and N-donor groups<sup>[4-6]</sup>. Self-assembly is a complex process, highly influenced by many factors, such as the coordination geometry of metal ions, the nature of organic ligands, solvent system, temperature, pH value of the solution, the ratio between metal salt and ligand, the templates and the counter anions<sup>[7-14]</sup>. These factors have been well-studied, but there are other forces such as hydrogen-bonding,  $\pi$ - $\pi$  interactions, metal-metal interactions that can greatly influence the supramolecular topology and its dimensionality<sup>[15-17]</sup>. Therefore, these considerations made us investigate new coordination structures with 4,4'-(1,3-phenylene-bis(methyleneoxy)) dibenzoic acid ( $H_2$ pmda), and bridging ligands (bib/bix). In this manuscript, we reported the syntheses, crystal structures, IR and fluorescence properties of two new complexes, namely  $\{[Co(bib)_3](ClO_4)_2]_n$  (**1**) and  $\{[Cu_3(bix)_{4.5}](ClO_4)_3]_n$  (**2**). Complexes **1** and **2** all exhibit intense purple luminescence, and appears to be good candidates for novel hybrid inorganic-organic photoactive materials.

## 1 Experimental

### 1.1 General procedures

All reagents were purchased commercially and used without further purification. Elemental analyses

(C, H and N) were measured on a Vario EL (III) Elemental Analyzer. IR spectrum was recorded in a range of 4 000~400  $cm^{-1}$  on a Nicolet 6700 spectrometer using a KBr pellet. The fluorescence spectra were performed on an F-7000 photospectrometer (Hitachi, High-Tech, Science, Japan). The powder X-ray diffraction (PXRD) studies were performed with a Bruker D8 Discover instrument (Cu  $K\alpha$  radiation,  $\lambda = 0.154\ 184\ nm$ ,  $U=40\ kV$ ,  $I=40\ mA$ ) over the  $2\theta$  range of  $5^\circ\sim 50^\circ$  at room temperature.

### 1.2 Synthesis

$\{[Co(bib)_3](ClO_4)_2]_n$  (**1**):  $H_2$ pmda (0.075 6 g, 0.2 mmol),  $Co(ClO_4)_2\cdot 6H_2O$  (0.2 mmol, 0.075 g), bib (0.038 g, 0.2 mmol) and 18 mL  $H_2O$  were mixed, and the pH value of the mixture was adjust to about 8 with 40% NaOH. Then it was sealed in a Teflon-lined stainless steel vessel, heated to 120  $^\circ C$  for 7 days, and followed by slow cooling to room temperature. Pink block crystals were obtained. Unfortunately,  $H_2$ pmda ligand did not participate in the coordination. Yield: 34%. Anal. Calcd. for  $C_{30}H_{42}Cl_2CoN_{12}O_8$  (%): C, 43.49; H, 5.11; N, 20.29. Found(%): C, 43.00; H, 4.99; N, 19.95. IR ( $cm^{-1}$ ): 3 126m, 2 952w, 1 657w, 1 605w, 1 521s, 1 465w, 1 443w, 1 404w, 1 373m, 1 303w, 1 280m, 1 236s, 1 096s, 936m, 870w, 834m, 772m, 743w, 729w, 667m, 623m.

$\{[Cu_3(bix)_{4.5}](ClO_4)_3]_n$  (**2**):  $H_2$ pmda (0.075 6 g, 0.2 mmol),  $Cu(ClO_4)_2\cdot 6H_2O$  (0.2 mmol, 0.08 g), bix (0.048 g, 0.2 mmol) and 18 mL  $H_2O$  were mixed, and the pH value of the mixture was adjust to about 6 with 40% NaOH. Then it was sealed in a Teflon-lined stainless steel vessel, heated to 120  $^\circ C$  for 7 days, and followed by slow cooling to room temperature. Pale yellow block crystals were obtained. Unfortunately,  $H_2$ pmda ligand did not participate in the coordination. Yield: 23%. Anal. Calcd. for  $C_{63}H_{63}Cl_3Cu_3N_{18}O_{12}$ (%): C, 48.46; H, 4.07; N, 16.15. Found (%): C, 48.01; H, 3.71; N,

15.85. IR ( $\text{cm}^{-1}$ ): 3 448w, 3 128m, 2 948w, 1 655w, 1 618w, 1 521s, 1 450m, 1 430w, 1 401w, 1 351w, 1 302w, 1 279m, 1 237s, 1 181w, 1 126w, 1 081s, 1 023w, 978w, 942w, 869w, 824w, 815w, 764w, 742m, 714s, 653m, 624s, 517w, 436w.

### 1.3 Structure determination

Single-crystal X-ray diffraction data for **1** with dimensions of 0.45 mm×0.35 mm×0.34 mm and **2** with dimensions of 0.30 mm×0.22 mm×0.18 mm were recorded on a Bruker D8 QUEST CMOS diffractometer

with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.071\ 073\ \text{nm}$ ) at 293 K. The structures were solved with the direct method of SHELXS-97 and refined with full-matrix least-squares techniques using the SHELXL-97 program<sup>[18-19]</sup>. The non-hydrogen atoms of the complexes were refined with anisotropic temperature parameters. The hydrogen atoms attached to carbons were generated geometrically. Selected bond lengths and bond angles are listed in Table 1.

CCDC: 1950200, **1**; 1950184, **2**.

Table 1 Selected bond lengths (nm) and bond angles ( $^\circ$ ) for **1** and **2**

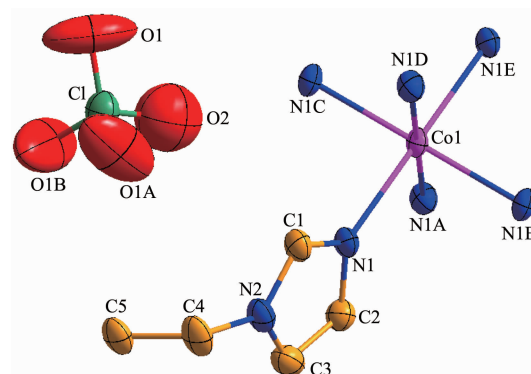
<b>1</b>					
Co(1)-N(1)	0.218 2(2)	Co(1)-N(1A)	0.218 2(2)	Co(1)-N(1B)	0.218 2(2)
Co(1)-N(1C)	0.218 2(2)	Co(1)-N(1D)	0.218 2(2)	Co(1)-N(1E)	0.218 2(2)
N(1)-Co(1)-N(1B)	90.82(9)	N(1)-Co(1)-N(1E)	89.18(9)	N(1B)-Co(1)-N(1E)	180.000(1)
N(1)-Co(1)-N(1C)	180.0	N(1B)-Co(1)-N(1C)	89.18(9)	N(1E)-Co(1)-N(1C)	90.82(9)
N(1)-Co(1)-N(1A)	90.82(9)	N(1B)-Co(1)-N(1A)	90.82(9)	N(1E)-Co(1)-N(1A)	89.18(9)
N(1C)-Co(1)-N(1A)	89.18(9)	N(1)-Co(1)-N(1D)	89.18(9)	N(1C)-Co(1)-N(1D)	89.18(9)
N(1E)-Co(1)-N(1D)	90.82(9)	N(1C)-Co(1)-N(1D)	90.82(9)	N(1A)-Co(1)-N(1D)	180.00(9)
<b>2</b>					
Cu(1)-N(5)	0.196 5(2)	Cu(1)-N(5A)	0.196 5(2)	Cu(1)-N(5B)	0.196 5(2)
Cu(2)-N(1)	0.196 4(3)	Cu(2)-N(1C)	0.196 4(3)	Cu(2)-N(1D)	0.196 4(3)
Cu(3)-N(4)	0.197 4(2)	Cu(3)-N(4E)	0.197 4(2)	Cu(3)-N(4F)	0.197 4(2)
N(5A)-Cu(1)-N(5B)	119.955(7)	N(5A)-Cu(1)-N(5)	119.955(7)	N(5B)-Cu(1)-N(5)	119.955(6)
N(1C)-Cu(2)-N(1)	119.819(14)	N(1D)-Cu(2)-N(1C)	119.819(14)	N(1)-Cu(2)-N(1C)	119.819(14)
N(4)-Cu(3)-N(4E)	119.990(3)	N(4)-Cu(3)-N(4F)	119.990(3)	N(4E)-Cu(3)-N(4F)	119.990(3)

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

## 2 Results and discussion

### 2.1 Description of the structure

Single crystal X-ray analysis reveals that complex **1** crystallizes in trigonal system with  $P\bar{3}$  space group. The asymmetric unit of complex **1** is composed of one-sixth crystallographically Co(II) ion, half bib ligand, and one-third free  $\text{ClO}_4^-$  (Fig.1). Each Co(II) ion is six-coordinated and attach to six nitrogen atoms from six different bib ligands, forming the cation  $[\text{Co}(\text{bib})_3]^{2+}$ , while the two  $\text{ClO}_4^-$  anions play the role of balancing the charge. The geometry around each Co(II) center is slightly distorted octahedron coordination sphere

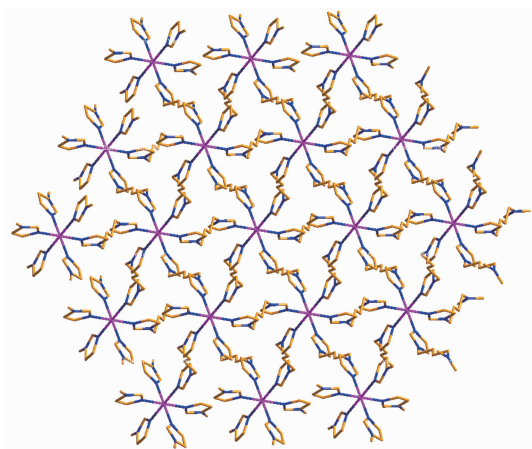


Symmetry codes: A:  $1-y, x-y-1, z$ ; B:  $2-x+y, 1-x, z$ ; C:  $2-x, -y, 2-z$ ; D:  $1+y, 1-x+y, 2-z$ ; E:  $x-y, x-1, 2-z$

Fig.1 View of coordination environment (at 30% probability level) of Co(II) ion of **1**

because the angles in a range of  $89.18(9)^\circ \sim 180.00(9)^\circ$ . The Co-N bond distance is  $0.218\ 2(2)$  nm and similar to those in analogous complexes<sup>[20-21]</sup>.

In complex **1**, the bib ligand takes *trans*-conformation bridging mode with a dihedral angle between the two imidazole rings of  $0^\circ$ . As depicted in Fig.2, three Co(II) ions are bridged by six nitrogen atoms of bib ligands to give crystallographically isosceles triangle trimers with Co...Co distance of  $1.411\ 9$  nm, which are further connected to a two-dimensional network with a 36-membered ring, and to the best of our knowledge, this structure is relatively rare. Single crystal X-ray diffraction reveals that  $[\text{Co}(\text{bib})_3]^{2+}$  and  $\text{ClO}_4^-$  units form 3D supramolecular architectures (Fig.3) through two hydrogen bonds:  $\text{C}(1) \cdots \text{H}(1) \cdots \text{O}(2)$  ( $\text{C}(1) \cdots \text{O}(2)$   $0.323\ 5(17)$  nm) and  $\text{C}(3) \cdots \text{H}(3) \cdots \text{O}(1)$  ( $\text{C}(3) \cdots \text{O}(1)$   $0.315\ 6(8)$  nm), undoubtedly stabilizing the 3D structure of complex **1**.



$\text{ClO}_4^-$  ions are omitted for clarity

Fig.2 View of 2D network structure with 36-membered ring of complex **1**

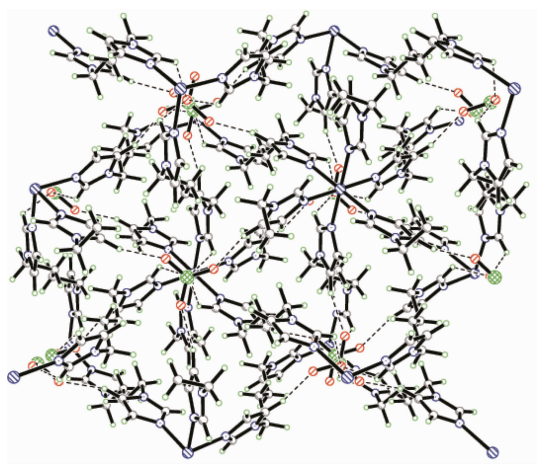
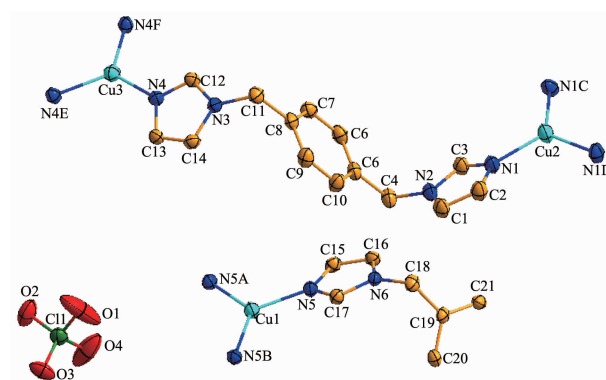


Fig.3 Three-dimensional supramolecular structure of **1** through hydrogen bonds

A single-crystal X-ray diffraction study reveals that complex **2** crystallizes in trigonal system with  $R\bar{3}$  space group and features a 2D network structure. The coordination environment of Cu(I) ion in **2** is shown in Fig.4. The Cu(I) ion is three-coordinated by three nitrogen atoms from three different bix ligands to furnish a slightly distorted plane triangle coordination architecture, which has been reported relatively rarely<sup>[22]</sup>. The bond distances of Cu-N in complex **2** are in a range of  $0.196\ 4(3) \sim 0.197\ 4(2)$  nm and the coordination angles around the Cu(I) ion are in a range of  $119.819(14)^\circ \sim 119.990(3)^\circ$ , which further proves that the plane triangle structure of Cu(I) ion. It is worth pointing out that Cu(II) ion took place redox reaction, and turned into Cu(I) ion, which may be the magic of hydrothermal reactions.

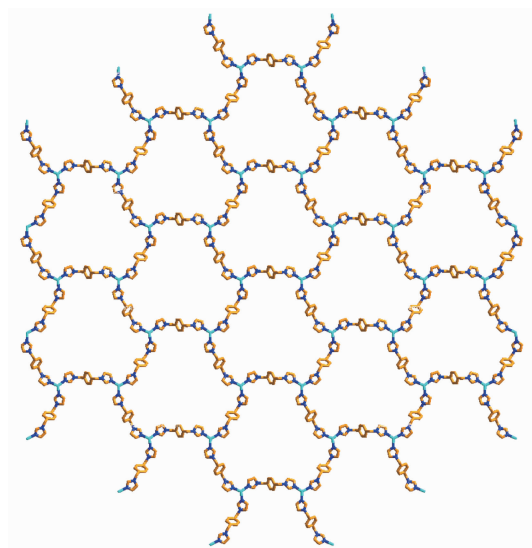


Symmetry codes: A:  $1-y, x-y, z$ ; B:  $1-x+y, 1-x, z$ ; C:  $-y, x-y, z$ ; D:  $-x+y, -x, z$ ; E:  $-y, x-y-1, z$ ; F:  $1-x+y, -x, z$

Fig.4 View of coordination environment (at 30% probability level) of Cu(I) ion of **2**

In the crystal structure of complex **2**, the bix ligand adopts a *trans*-conformation bridging mode with a dihedral angle between two imidazole rings of  $28.81^\circ$  and link the Cu(I) ions to form a two-dimensional network structure with 84-membered ring, as shown in Fig.5.

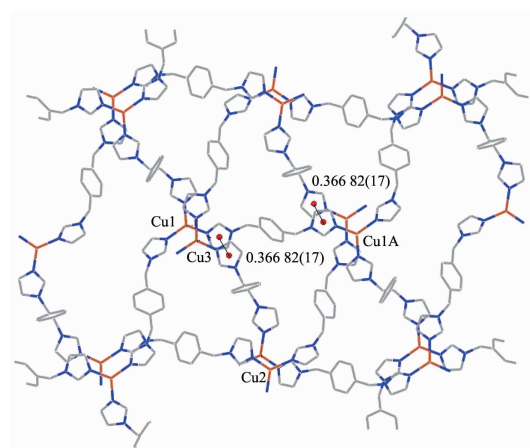
Hydrogen bonding interactions are frequently chief in the synthesis of supramolecular structure. Single crystal X-ray reveals that  $[\text{Cu}_3(\text{bix})_{4.5}]^{3+}$  and  $\text{ClO}_4^-$  units form 3D supramolecular architectures through two hydrogen bonds:  $\text{C}(12) \cdots \text{H}(12\text{A}) \cdots \text{O}(1)$  ( $\text{C}(12) \cdots$



$\text{ClO}_4^-$  ions are omitted for clarity

Fig.5 Two-dimensional network structure with 84-membered ring along  $c$  axis of complex **2**

$\text{O}(1) \cdots \text{O}(4) 0.334\ 9(7)\text{ nm}$ ) and  $\text{C}(20)\text{--H}(20\text{A})\cdots\text{O}(4)$  ( $\text{C}(20)\cdots\text{O}(4) 0.348\ 4(5)\text{ nm}$ ). In addition, there are  $\pi\text{--}\pi$  interactions (Fig.6) in complex **2** between imidazole rings of bix ligands. The centroid-to-centroid distance between adjacent ring is  $0.366\ 82(17)\text{ nm}$  for  $\text{N}(3)\text{C}(12)\text{N}(4)\text{C}(13)\text{C}(14)$  and  $\text{N}(5)\text{C}(15)\text{C}(16)\text{N}(6)\text{C}(17)$  (Symmetry code:  $y, -x+y, 1-z$ ) imidazole rings. The perpendicular distance is  $0.338\ 23(12)\text{ nm}$  and the dihedral angle is  $0.00(17)^\circ$ . Thus, through hydrogen bonds and  $\pi\text{--}\pi$  interactions, a three-dimensional

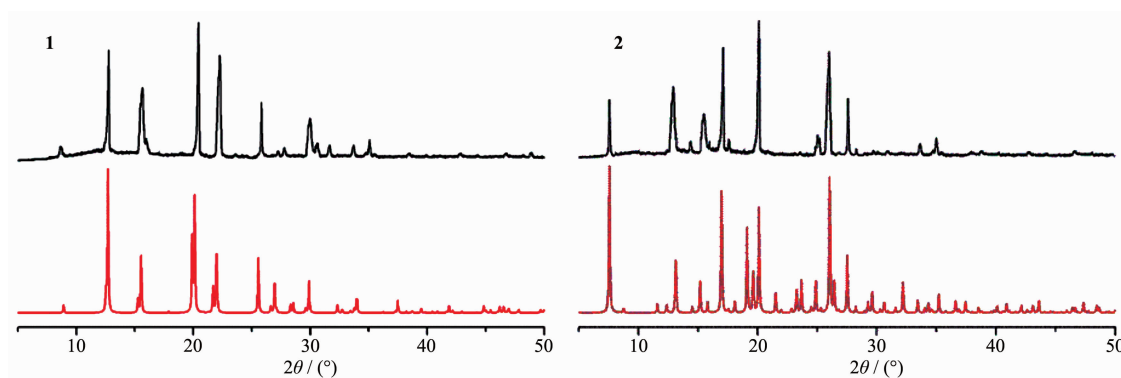


Symmetry codes: A:  $1-y, x-y, z$

Fig.6 View of  $\pi\text{--}\pi$  interactions in **2**

supramolecular architecture is formed and plays an important role in stabilizing complex **2**.

To investigate whether the analyzed crystal structure is truly representative of the bulk materials, X-ray powder diffraction (PXRD) analysis has been performed for the complex at room temperature (Fig. 7). The main peak positions observed are in good agreement with the simulated ones. Although minor differences can be found in the positions, widths, and intensities of some peaks, the bulk synthesized materials and analyzed crystal can still be considered as homogeneous. The differences may be due to the preferred orientation of the powder samples<sup>[23-24]</sup>.



Bottom: simulated; Top: experimental

Fig.7 PXRD patterns of complexes **1** and **2**

## 2.2 Photoluminescent properties

Metal-organic coordination polymers and conjugated organic linker have been studied because of their fluorescent properties and potential

applications as fluorescent-emitting materials, chemical sensors and electroluminescent displays<sup>[25]</sup>. Therefore, in the present work, the photoluminescent properties of bib, bix, complexes **1** and **2** have been

investigated in the solid state at room temperature, as depicted in Fig.8. The free ligands bib and bix showed photoluminescence with the emission maximum at 408 nm ( $\lambda_{\text{ex}}=348$  nm) and 450 nm ( $\lambda_{\text{ex}}=350$  nm), respectively, which can be assigned to intraligand ( $\pi \rightarrow \pi^*$ ) transition<sup>[26]</sup>. Compared with the free bib ligand, a wide range of the emission with maximum peaks at *ca.* 438 nm upon excitation at *ca.* 350 nm for complex **1** was observed, which was red-shift. This emission band can be tentatively attributed to a ligand-to-metal charge transfer (LMCT)<sup>[27]</sup>. While the emission peak of complex **2** ( $\lambda_{\text{em}}=434$  nm,  $\lambda_{\text{ex}}=350$  nm) was blue-shift as compared to the free ligand bix. Therefore, this emission band may be assigned as ligand-to-ligand charge transfer (LLCT) transitions<sup>[28-29]</sup>. The fluorescence emissions of the complexes make them potentially useful photoactive materials.

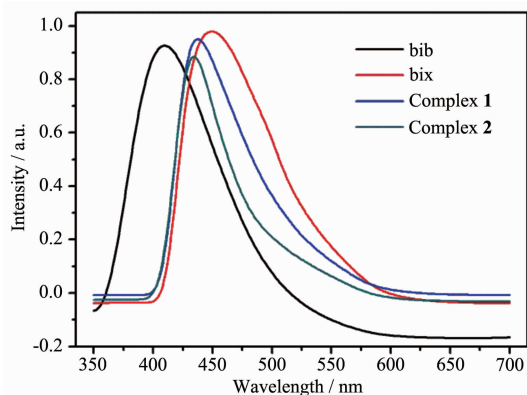


Fig.8 Solid-state emission spectra of the ligands, complexes **1** and **2** at room temperature

### 3 Conclusions

In general, we have prepared two new complexes with bib/bix ligands. The bib/bix ligands adopt bridging mode, and link neighboring Co(II)/Cu(I) ions to generate 2D network structure. Furthermore, the 3D supramolecular architectures are formed by hydrogen bonding or  $\pi$ - $\pi$  interactions. They all exhibit intense purple luminescence. These materials will give new impetus to the construction of novel functional material with potentially useful physical properties.

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