

## 含 $\pi$ - $\pi$ 相互作用的 Cu(I) 配位聚合物的合成、 表征、晶体结构及发光性能

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**摘要:** 合成了 2 个铜(I)的配位聚合物  $\{[\text{Cu}_2(4\text{-bpo})_2(\text{CH}_3\text{CN})_2(\text{PPh}_3)_2](\text{BF}_4)_2\}_n$  (**1**) 和  $\{[\text{Cu}(4\text{-bpo})(\text{CH}_3\text{CN})(\text{dppe})_{0.5}]\text{BF}_4\}_n$  (**2**) ( $\text{PPh}_3$ =triphenylphosphine,  $\text{dppe}$ =1,2-bis(diphenylphosphino)ethane, 4-bpo=2,5-bis(4-pyridyl)-1,3,4-oxadiazole), 对其进行了红外、 $^1\text{H}$  NMR、 $^{19}\text{F}$  NMR、 $^{11}\text{B}$  NMR、元素分析等相关表征, 并利用 X-射线单晶衍射仪测定了化合物的结构。晶体结构研究表明配位聚合物 **1** 和 **2** 通过  $\pi\cdots\pi$  相互作用连接成为不同的二维超分子的网状结构: 在配合物 **1** 中, 一维链状结构通过  $\pi\cdots\pi$  相互作用连接成为二维双层结构和二维网络结构; 在配合物 **2** 中, 一维梯形链状结构通过  $\pi\cdots\pi$  相互作用组装成不同二维和三维网络结构。此外, 还研究了配合物的固态发光性能, 显示其存在 TLCT/MLCT 电荷跃迁。

**关键词:** 铜(I)配位聚合物; 晶体结构;  $\pi\cdots\pi$  作用; 荧光性质

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## Copper(I) Coordination Polymers with Extended $\pi\cdots\pi$ Interactions: Syntheses, Structures, Characterization and Luminescent Properties

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**Abstract:** Two copper(I) coordination polymers,  $\{[\text{Cu}_2(4\text{-bpo})_2(\text{CH}_3\text{CN})_2(\text{PPh}_3)_2](\text{BF}_4)_2\}_n$  (**1**),  $\{[\text{Cu}(4\text{-bpo})(\text{CH}_3\text{CN})(\text{dppe})_{0.5}]\text{BF}_4\}_n$  (**2**) ( $\text{PPh}_3$ =triphenylphosphine,  $\text{dppe}$ =1,2-bis(diphenyl phosphino)ethane, 4-bpo=2,5-bis(4-pyridyl)-1,3,4-oxadiazole), have been synthesized and characterized by IR,  $^1\text{H}$  NMR,  $^{19}\text{F}$  NMR,  $^{11}\text{B}$  NMR, elemental analysis and X-ray crystal structure analysis. The structural analysis shows that complexes **1** and **2** consist of diverse and interesting 2D supramolecular structures formed by inter-chain interactions. For **1**,  $\pi$ -stacking interactions result in the construction of 1D bilayer chain and 2D supramolecular network. Compound **2** exhibits a 1D ladder-like chain and a 1D+1D $\rightarrow$ 2D/3D supramolecular structure formed by  $\pi$ -stacking interactions. Solid-state emission spectra of complexes **1** and **2** have been studied, displaying the existence of ILCT/MLCT excited states. CCDC: 1043971, **1**; 1043972, **2**.

**Key words:** copper(I) coordination polymers; crystal structures;  $\pi\cdots\pi$  interaction; luminescent properties

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## 0 Introduction

The design and construction of coordination polymers with novel topologies and structural motifs have been one of the most active research subjects in the field of coordination chemistry due to their properties in catalysis<sup>[1-4]</sup>, separation<sup>[5-7]</sup>, molecular recognition<sup>[8-10]</sup> and photoluminescence<sup>[11-15]</sup>. So far, some coordination polymer networks can be obtained by the change of reaction-influencing factors such as inorganic counter ions, organic ligands and metal-to-ligand ratio<sup>[16-18]</sup>. In particular, changing organic ligands with variable bridging lengths, conformation and flexibility is a powerful and synthetically convenient way of structural modifying of coordination polymers<sup>[19-21]</sup>. Use of a mono-ligand system can result in the formation of new coordination polymers<sup>[22-25]</sup>, but a mixed-ligand system containing two or three types ligands provides more changeable to form much more complicated and fantastic topological types of two-, and three-dimensional nets<sup>[26-31]</sup>.

Currently, the research on weak interactions have grown rapidly and have directed much attention toward the construction of supramolecular structures<sup>[32-36]</sup>, especially deliberate design of coordination polymers<sup>[37-42]</sup>. The extent of the  $\pi \cdots \pi$  stacking interactions of copper(I) compounds containing pyridyl ligands has result in the observation of fascinating structures and luminescent properties<sup>[43-45]</sup>, but predicting and designing supramolecular networks of copper(I) coordination polymers formed by inter-chain weak interactions, such as  $\pi \cdots \pi$  stacking interactions, is relatively difficult. It appears that the design of copper (I) coordination polymers with supramolecular structures are challenging but important. Herein, we report the synthesis, structure, characterization and luminescent properties of copper(I) coordination polymers  $\{[\text{Cu}_2(4\text{-bpo})_2(\text{CH}_3\text{CN})_2(\text{PPh}_3)_2](\text{BF}_4)_2\}_n$  (**1**) and  $\{[\text{Cu}(4\text{-bpo})(\text{CH}_3\text{CN})(\text{dppe})_{0.5}]\text{BF}_4\}_n$  (**2**) ( $\text{PPh}_3$ =triphenylphosphine,  $\text{dppe}$ =1,2-bis(diphenylphosphino)ethane, 4-bpo=2,5-bis(4-pyridyl)-1,3,4-oxadiazole), indicating diverse and interesting 1D chain, 2D layer and 3D extended supramolecular structures constructed by inter-chain

weak interactions. In addition, solid-state emission spectra of complexes **1** and **2** are also observed.

## 1 Experimental

### 1.1 General methods and materials

All chemicals were of AR grade and were used as received without further purification. Ligand 2, 5-bis(4-pyridyl)-1,3,4-oxadiazole (4-bpo) was prepared according to references<sup>[46-48]</sup>. IR spectra were recorded as KBr pellets on a Nicolet 6700 spectrometer in the range 4 000 ~450  $\text{cm}^{-1}$ . Elemental analyses were measured with a Carlo ERBA 1106 analyzer.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{19}\text{F}$  NMR spectra were recorded on a Bruker 400 spectrometer at 400.15, 128.3 and 376.5 MHz, respectively. The luminescent spectra of **1** and **2** were measured at room temperature at a FL3-P-TCSPEC fluorescence spectrophotometer.

### 1.2 Synthesis of $\{[\text{Cu}_2(4\text{-bpo})_2(\text{CH}_3\text{CN})_2(\text{PPh}_3)_2](\text{BF}_4)_2\}_n$ (**1**)

A mixture of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$  (0.031 6 g, 0.1 mmol) and 4-bpo (0.022 4 g, 0.1 mmol) in 5 mL  $\text{CH}_3\text{CN}/\text{DMF}$  was stirred at room temperature for 0.5 h and then  $\text{PPh}_3$  (0.026 2 g, 0.1 mmol) was added. The reaction mixture was allowed to stir for 0.5 h at room temperature. The vapor diffusion of diethyl ether into the solution gave yellow block crystals. The complex was obtained by filtration, washed with diethyl ether and dried *in vacuo*. Yield: 40%. Anal. Calcd. for  $\text{C}_{64}\text{H}_{52}\text{B}_2\text{Cu}_2\text{F}_8\text{N}_{10}\text{O}_2\text{P}_2$ (%): C, 56.70; H, 3.87; N, 10.33. Found(%): C, 56.43; H, 4.05; N, 10.09. IR ( $\text{cm}^{-1}$ ): 3 451 (br), 3 059 (w), 2 271 (w), 1 613 (m), 1 566 (m), 1 540 (w), 1 480 (s), 1 436 (s), 1 422 (m), 1 054 (vs), 839 (m), 746 (s), 697(s), 520 (s).  $^1\text{H}$  NMR ( $\text{CD}_3\text{SOCD}_3$ , 25  $^\circ\text{C}$ , TMS):  $\delta$  2.08 (6H,  $-\text{CH}_3$ ), 6.95~10.35 (46H,  $\text{PPh}_3$ +bipy).  $^{19}\text{F}$  NMR ( $\text{CD}_3\text{SOCD}_3$ , 25  $^\circ\text{C}$ , TMS):  $\delta$  -148.3.  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{SOCD}_3$ , 25  $^\circ\text{C}$ , TMS):  $\delta$  -1.32.

### 1.3 Synthesis of $\{[\text{Cu}(4\text{-bpo})(\text{CH}_3\text{CN})(\text{dppe})_{0.5}]\text{BF}_4\}_n$ (**2**)

The synthesis of **2** was similar to that of **1** using  $\text{dppe}$  (0.019 9 g, 0.050 mmol) instead of  $\text{PPh}_3$ . Yield: 49%. Anal. Calcd. for  $\text{C}_{27}\text{H}_{23}\text{BCuF}_4\text{N}_5\text{OP}$ (%): C, 52.74; H, 3.77; N, 11.39. Found(%): C, 52.37; H, 3.81; N, 11.27. IR ( $\text{cm}^{-1}$ ): 3 450 (br), 3 031 (w), 2 253 (w), 1 616

(w), 1 565 (w), 1 538 (w), 1 480 (m), 1 457 (w), 1 424 (s), 1 060 (vs), 838 (m), 744 (m), 715(m), 504 (s).  $^1\text{H}$  NMR ( $\text{CD}_3\text{SOCD}_3$ , 25  $^\circ\text{C}$ , TMS):  $\delta$  2.07(3H,  $-\text{CH}_3$ ), 2.20~2.42 (2H,  $\text{P}-\text{CH}_2-$ ), 7.07~9.98 (18H,  $\text{PPh}_2+\text{bipy}$ ).  $^{19}\text{F}$  NMR ( $\text{CD}_3\text{SOCD}_3$ , 25  $^\circ\text{C}$ , TMS):  $\delta$  -148.3.  $^{11}\text{B}$  NMR ( $\text{CD}_3\text{SOCD}_3$ , 25  $^\circ\text{C}$ , TMS):  $\delta$  -1.33.

#### 1.4 X-ray crystallography

Diffraction data for complexes **1** and **2** were collected on a Bruker APEX CCD diffractometer with graphite monochromated Mo  $K\alpha$  radiation ( $\lambda=0.071\ 073$  nm) using the  $\varphi$ - $\omega$  technique at room temperature. The crystal structures were solved by direct methods and refined by full-matrix least-squares on  $F^2$  using SHELXTL<sup>[49]</sup>. All hydrogens were generated geometri-

cally, assigned fixed isotropic thermal parameters, and included in structure factor calculations. During the structure refinement of **1**, an unidentifiable and badly disordered solvent molecule (probably  $\text{H}_2\text{O}$ ) was omitted by the SQUEEZE option in PLATON. The crystal of **2** was very small and had very weak high angle data, the data was of poor quality (The ratio of data completeness is 0.93, but the molecule structure can be determined). The details of the crystal data are ruled out in Table 1, and selected bond lengths and angles for complexes **1** and **2** are summarized in Table 2.

CCDC: 1043971, **1**; 1043972, **2**.

Table 1 Crystal data and structure refinement details of complexes **1** and **2**

Complex	<b>1</b>	<b>2</b>
Empirical formula	$\text{C}_{64}\text{H}_{52}\text{B}_2\text{Cu}_2\text{F}_8\text{N}_{10}\text{O}_2\text{P}_2$	$\text{C}_{27}\text{H}_{23}\text{BCuF}_4\text{N}_5\text{OP}$
Formula weight	1 355.80	614.82
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
$a$ / nm	1.182 60(6)	1.270 2(8)
$b$ / nm	1.579 24(9)	1.358 0(9)
$c$ / nm	1.945 02(11)	1.638 9(10)
$\alpha$ / ( $^\circ$ )	81.977(4)	90
$\beta$ / ( $^\circ$ )	77.069(4)	83.061(13)
$\gamma$ / ( $^\circ$ )	78.070(4)	90
$V$ / $\text{nm}^3$	3.447 3(3)	2.806(3)
$Z$	2	4
$D_c$ / ( $\text{g}\cdot\text{cm}^{-3}$ )	1.306	1.455
$\mu$ / $\text{mm}^{-1}$	0.733	0.892
$F(000)$	1 384	1 252
$\theta$ range / ( $^\circ$ )	1.90~27.64	1.92~25.00
Reflections collected	32 713	14 034
Independent reflections	15 570 ( $R_{\text{int}}=0.046$ 4)	4 936 ( $R_{\text{int}}=0.084$ 4)
Data / restraints / parameters	15 570 / 4 / 813	4 936 / 0 / 362
Goodness-of-fit on $F^2$	1.003	1.072
Final $R$ indices [ $I>2\sigma(I)$ ]	$R_1=0.081$ 4, $wR_2=0.236$ 8	$R_1=0.053$ 0, $wR_2=0.088$ 0
$R$ indices (all data)	$R_1=0.164$ 7, $wR_2=0.290$ 1	$R_1=0.140$ 5, $wR_2=0.099$ 2

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

<b>1</b>					
Cu(1)-N(1)	0.199 0(5)	Cu(1)-P(1)	0.222 22(16)	Cu(2)-N(6)	0.206 0(4)
Cu(1)-N(3)	0.206 4(5)	Cu(2)-N(2)	0.203 2(6)	Cu(2)-P(2)	0.221 88(15)
Cu(1)-N(10)A	0.209 8(4)	Cu(2)-N(7)	0.205 7(4)		

Continued Table 2

N(1)-Cu(1)-N(3)	98.93(19)	N(3)-Cu(1)-P(1)	113.36(13)	N(7)-Cu(2)-N(6)	116.16(18)
N(1)-Cu(1)-N(10)A	103.97(19)	N(10)A-Cu(1)-P(1)	105.45(12)	N(2)-Cu(2)-P(2)	119.81(15)
N(3)-Cu(1)-N(10)A	110.82(19)	N(2)-Cu(2)-N(7)	99.13(19)	N(7)-Cu(2)-P(2)	111.57(13)
N(1)-Cu(1)-P(1)	123.79(16)	N(2)-Cu(2)-N(6)	104.97(19)	N(6)-Cu(2)-P(2)	105.56(13)
<b>2</b>					
Cu(1)-N(5)	0.197 6(4)	Cu(1)-N(1)	0.206 6(4)	N(4)-Cu(1)B	0.204 7(4)
Cu(1)-N(4)A	0.204 7(4)	Cu(1)-P(1)	0.221 68(16)		
N(5)-Cu(1)-N(4)A	102.90(17)	N(4)A-Cu(1)-N(1)	117.92(15)	N(4)A-Cu(1)-P(1)	109.17(10)
N(5)-Cu(1)-N(1)	101.23(17)	N(5)-Cu(1)-P(1)	121.35(13)	N(1)-Cu(1)-P(1)	104.93(11)

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

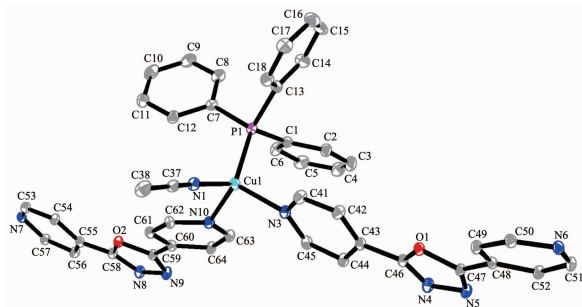
## 2 Results and discussion

### 2.1 Structural description

#### 2.1.1 $\{[\text{Cu}_2(4\text{-bpo})_2(\text{CH}_3\text{CN})_2(\text{PPh}_3)_2](\text{BF}_4)_2\}_n$ (**1**)

Single-crystal analysis shows, as shown in Fig. S1, that the general structure having two different Cu(I) centers present in the asymmetric unit. Both Cu1 and Cu2 are coordinated by two  $\text{N}_{\text{pyridyl}}$  atoms from 4-bpo, one  $\text{N}_{\text{acetonitrile}}$  atom from  $\text{CH}_3\text{CN}$  and one P atom from  $\text{PPh}_3$ , to yield a distorted tetrahedral geometry (Fig.1 and Fig.S1). The Cu-N bond lengths (0.199 0(5)~0.209 8(4) nm) and Cu-P bond lengths (0.221 88(15) and 0.222 22(16) nm) are within the normal ranges<sup>[50]</sup> and the metal ions are separated by the Cu1...Cu2 distances of 1.320 7 and 1.352 3 nm. Corresponding N-Cu-N bond angles range from  $98.93(19)^\circ$  to  $116.16(18)^\circ$ , while the N-Cu-P bond angles are in the range of  $105.45(12)^\circ$ ~ $123.79(16)^\circ$ .

In the solid state, the Cu1 and Cu2 centers are linked to each other by 4-bpo through both terminal



Hydrogen atoms are omitted for clarity

Fig.1 Coordination environments of the Cu(I) atoms (Cu1) in **1** with displacement ellipsoids drawn at the 10% probability level

N-donors into 1D “W”-shape chain, as shown in Fig. 2, which contains two different individual “links”. The neighboring chains are anti-parallel to each other with the nearest inter-chain Cu...Cu distance of 0.669 9 nm. These one-dimensional chains further stack together via intermolecular  $\pi \cdots \pi$  interactions to produce infinite 1D bilayer architecture (Fig.3a). In 1D bilayer architecture, two distinct types of inter-chain  $\pi \cdots \pi$  stacking interactions are observed: (a) the closest approach between the oxadiazole and pyridyl rings from two distinct 4-bpo is 0.334 2 nm, with the centroid...centroid distances of 0.3674 and 0.377 2 nm and dihedral angles of  $2.70^\circ$  and  $13.90^\circ$ ; (b) the center-to-center distances of two parallel pyridyl rings from the two neighboring 4-bpo molecules are 0.385 4 and 0.391 9 nm. The ordered-layer-lattice  $\text{BF}_4^-$  is located between these 1D bilayer chains (Fig.3b). Moreover, 1D “W”-shape chain extend to generate a 2D network by intermolecular  $\pi \cdots \pi$  stacking interactions (Fig.4). The oxadiazole ring from 4-bpo in 2D supramolecular network parallel to phenyl rings attached to phosphorus with a centroid-to-centroid distance of 0.379 8 nm and an offset dihedral angle of  $15.63^\circ$ , showing the existence of significant  $\pi \cdots \pi$  stacking interactions.



Hydrogen atoms are omitted for clarity; Symmetry code: A:  $x, y-1, z-1$

Fig.2 A view of the 1D  $[\text{Cu}_2(\text{PPh}_3)_2(4\text{-bpo})_2(\text{CH}_3\text{CN})_2]_n$  chain

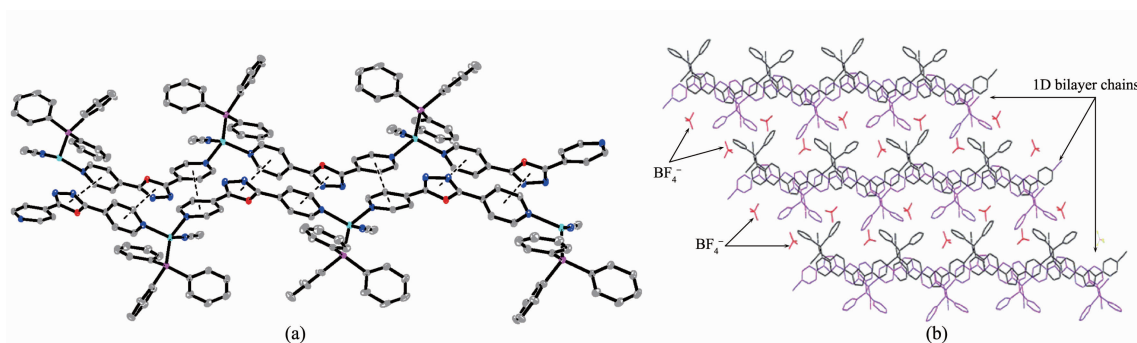


Fig.3 (a) Bilayer architecture in **1** formed by the 4-bpo-bridged Cu(I) coordination polymer chain and intermolecular  $\pi \cdots \pi$  stacking interaction; (b) Ordered-layer-lattice  $\text{BF}_4^-$  in **1** located between 1D bilayer chains

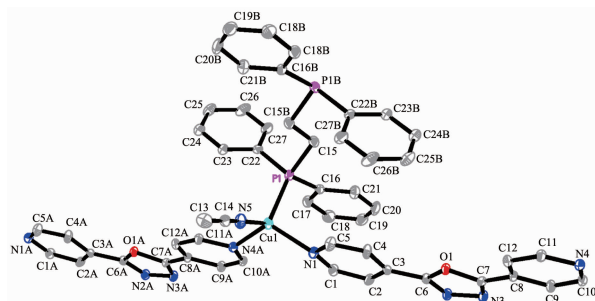
The 2D  $\pi$ -stacking structure also involves intermolecular C-H $\cdots\pi$  interactions, with CH/ $\pi$  distances of 0.271~0.299 nm and angles of 145°~166°, respectively, and the weak interactions of C-H $\cdots$ N and C-H $\cdots$ F hydrogen bonds (Table S1).

#### 2.1.2 $[\text{Cu}(\text{4-bpo})(\text{CH}_3\text{CN})(\text{dppe})_{0.5}]\text{BF}_4$ (**2**)

Single-crystal analysis shows, as shown in Fig.5, that the structure of **2** consists of a 1D ladder-like chain structure, based on the basis of the 4-bpo-bridged Cu(I) coordination polymer chain and the dppe connector (T-shaped motifs). Different from **1**, the fundamental building unit contains one independent Cu(I) center, one pair of symmetry-related 4-bpo and a dppe spacer. The  $\text{Cu}^+$  ion adopts a distorted tetrahedral geometry via coordinating to two  $\text{N}_{\text{pyridyl}}$  atoms of two 4-bpo ligands, one  $\text{N}_{\text{acetonitrile}}$  atom of  $\text{CH}_3\text{CN}$  and one P atom of one dppe ligand. The Cu-N bond lengths (0.197 6(4)~0.206 6(4) nm) and Cu-P bond lengths (0.221 68(16) nm) are within the normal ranges<sup>[51]</sup>. Corresponding N-Cu-N bond angles range from

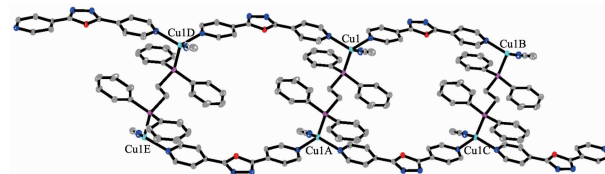
101.23(17)° to 117.92(15)°, while the N-Cu-P bond angles are in the range of 104.93(11)° to 121.35(13)°.

In the solid state, the 4-bpo ligand in **2** adopts a bidentate bridging mode to connect with two copper(I) atoms. The adjacent Cu(I) centers are linked by two terminal N-donors of 4-bpo ligand to form infinite Cu-4-bpo chains (Cu $\cdots$ Cu 1.358 0 nm) along the b axis; the neighbouring chains are further linked by dppe ligand to generate a ladder-like chains with the Cu $\cdots$ Cu distance of 0.724 8 nm (Fig.6). These 1D ladder-like chains are further interlinked parallel with the ab plane to generate a 2D network through intermolecular  $\pi \cdots \pi$  stacking interactions. In the 2D net, the planes of pyridyl and oxadiazole are approximately parallel with a centroid-to-centroid distance of 0.377 9 nm and an offset dihedral angle of 5.25°, revealing the existence of  $\pi \cdots \pi$  stacking interactions (Fig.7a). Similarly, the packing structure involves  $\pi \cdots \pi$  interactions parallel with the ac plane, being analogous to that of **1** (Fig.7b). In 2D supramolecular network, the oxadiazole ring from 4-bpo parallel to phenyl rings attached to phosphorus with a centroid-



Hydrogen atoms are omitted for clarity; Symmetry codes: A: x, y-1, z; B: 2-x, -y, -z

Fig.5 Coordination environments of the Cu(I) atoms in **2** with displacement ellipsoids drawn at the 10% probability level



Hydrogen atoms are omitted for clarity; Symmetry codes: A: 2-x, -y, -z; B: x, y-1, z; C: 2-x, -1-y, -z; D: x, 1+y, z; E: 2-x, -1+y, -z

Fig.6 1D ladder-like network formed by the 4-bpo-bridged Cu(I) coordination polymer chain and the dppe connector in **2**



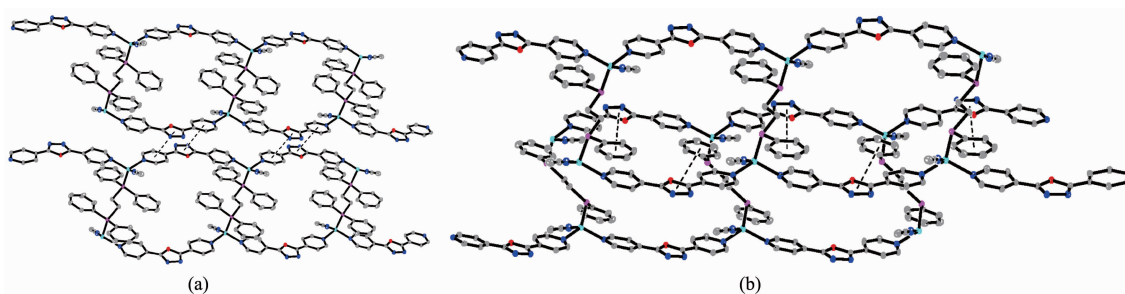


Fig.7 2D supramolecular network formed by intermolecular  $\pi\cdots\pi$  interactions parallel with the *ab* (a) or *ac* (b) plane in **2**

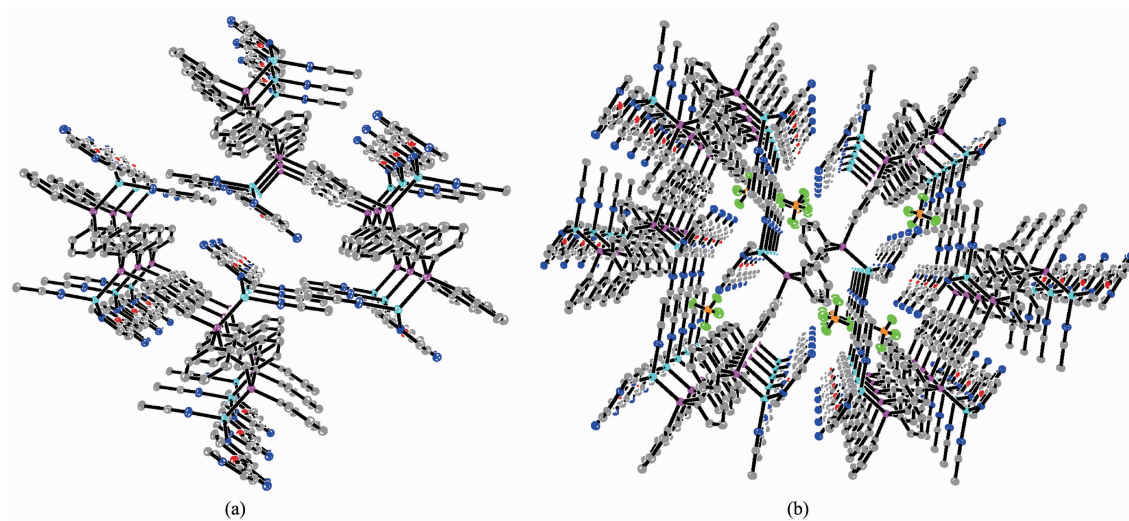


Fig.8 (a) 3D framework of **2**; (b) Ordered-layer-lattice  $\text{BF}_4^-$  in **2** located between 3D networks

to-centroid distance of 0.368 8 nm and an offset dihedral angle of  $5.64^\circ$ , which is shorter than the corresponding values in complex **1**. In other words, adjacent 1D ladder-like chains in the *ab* plane interact with each other by one kind of intermolecular  $\pi\cdots\pi$  stacking interactions (Fig.7a) to form two-dimensional (2D) supramolecular net, which are further linked by the other kind of intermolecular  $\pi\cdots\pi$  stacking interactions (Fig.7b) to form a three-dimensional (3D) supramolecular structure (Fig.8a). Moreover, the ordered-layer-lattice  $\text{BF}_4^-$  is located between these 3D networks (Fig.8b). In the 3D network, and C-H $\cdots$ F and C-H $\cdots$ N hydrogen bonds are also observed (H $\cdots$ F 0.241 nm, C $\cdots$ F 0.329 nm; H $\cdots$ N 0.238 nm, C $\cdots$ N 0.333 nm).

## 2.2 Luminescent properties

Coordination compounds constructed from  $d^{10}$  metal centers and conjugated organic ligands are promising candidates for hybrid luminescent materials with potential applications such as dye-sensitized

solar cells, light-emitting or electrochemical devices and so on. As shown in Fig.9, Solid-state emission spectra of complexes **1** and **2** were recorded at room temperature, showing that excitation of the microcrystalline samples affords different fluorescent emissions, with the maximum peaks occurring at 582 nm for **1** ( $\lambda_{\text{ex}}=400$  nm) and 440 for **2** ( $\lambda_{\text{ex}}=380$  nm). Moreover, the maximal emission of 4-bpo ligands is observed at

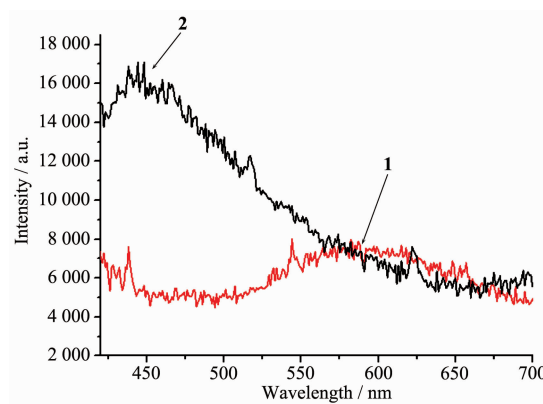


Fig.9 Emission spectra of complexes **1** and **2** in the solid state at room temperature

417 nm ( $\lambda_{\text{ex}}=370$  nm) according to references<sup>[52-53]</sup>. With regard to compound **1**, the significant red shift of the emission band (165 nm) compared with that of 4-bpo may be assigned to metal-to-ligand charge transfer (MLCT)<sup>[54-55]</sup>. For **2**, the very similar profiles of their emission peaks, in comparison with that of the free 4-bpo, indicate that their photoluminescent mechanism may be properly ascribed to intraligand (IL)  $\pi \rightarrow \pi^*$  transition<sup>[56-57]</sup>.

### 3 Conclusions

In this work, we have presented a new family of coordination polymers formulated as  $[\text{Cu}_2(4\text{-bpo})_2(\text{CH}_3\text{CN})_2(\text{PPh}_3)_2](\text{BF}_4)_2$  (**1**) and  $[\text{Cu}(4\text{-bpo})(\text{CH}_3\text{CN})(\text{dppe})_{0.5}](\text{BF}_4)_n$  (**2**), respectively. These polymers show different supramolecular architectures: **1** consists of 1D “W”-shape/bilayer chains and 2D  $\pi$ -stacking net; **2** shows the existence of 1D ladder-like chain, 2D network and 3D supramolecular structure. All these results undoubtedly reveal that the diverse structures of coordination polymers mainly depend on the  $\text{Cu}^+$  ions with 4-bpo, readily interacting with different flexible/angular ligands ( $\text{PPh}_3$  and dppe) to result in a variety of supramolecular (1D or 2D) networks. Moreover, the extended supramolecular networks of the lower-dimensional coordination polymers can be well modified by the secondary interactions such as intermolecular  $\pi \cdots \pi$  stacking interactions. Solid-state emission spectra of complexes **1** and **2** were observed at room temperature, showing that their photoluminescent mechanism may be properly attributed to ILCT or MLCT.

Supporting information is available at <http://www.wjhxxb.cn>

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