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基于吡啶酰胺类配体一维带状配位聚合物的合成、结构及荧光性质

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摘要: 通过吡啶酰胺类配体 3,5-二(4-吡啶酰胺基)吡啶(4-DPBA)与相应金属盐反应,合成了 3 个配位聚合物{[Zn(4-DPBA)$_2$(NO$_3$)$_2$]·4DMF}$_n$ (**1**),{[Cd(4-DPBA)$_2$(NO$_3$)$_2$]·4DMF}$_n$ (**2**)和{[Cu(4-DPBA)$_2$(DMF)$_2$](ClO$_4$)$_2$·7DMF·2H$_2$O}$_n$ (**3**),并用红外光谱、元素分析、粉末及单晶 X-射线衍射等方法对其进行了表征。结果表明配合物 **1** 和 **2** 是同构的,由平行的一维带状链通过氢键连接而成二维层状结构,而配合物 **3** 是由 3 种不同取向的一维带状链构成二维多层结构。这 3 个配合物最终均通过氢键连接形成三维超分子结构。研究了配合物 **1** 和 **2** 的荧光性质。

关键词: 吡啶酰胺类配体; 一维带状链; 荧光性质
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One-Dimensional Ribbon-Like Chain Coordination Polymers with Pyridyl and Amide-Containing Ligand: Synthesis, Structure and Luminescence Property

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Abstract: Three new coordination polymers {[Zn(4-DPBA)$_2$(NO$_3$)$_2$]·4DMF}$_n$ (**1**), {[Cd(4-DPBA)$_2$(NO$_3$)$_2$]·4DMF}$_n$ (**2**) and {[Cu(4-DPBA)$_2$(DMF)$_2$](ClO$_4$)$_2$·7DMF·2H$_2$O}$_n$ (**3**) were synthesized by reactions of pyridyl and amide-containing ligand *N*,*N*′-di(pyridin-4-yl)-pyridine-3,5-dicarboxamide (4-DPBA) with corresponding metal salt. All the complexes were characterized by FTIR, elemental, powder and single crystal X-ray diffraction analyses. The results show that complexes **1** and **2** are isostructural and have two-dimensional (2D) layer structure with parallel one-dimensional (1D) ribbon-like chains linked by hydrogen bonds, while complex **3** possesses 2D networks with three different orientations of 1D chains connected by hydrogen bonds. All the complexes show three-dimensional (3D) supramolecular structures through hydrogen bonding interactions. The photoluminescent property of complexes **1** and **2** was investigated. CCDC: 879335, **1**; 879366, **3**.

Key words: pyridyl- and amide-containing ligand; 1D ribbon-like chain; luminescence property

Coordination polymers (CPs) with transition metal centers are currently of great interest because of their intriguing structures and possible applications as functional materials in catalysis, gas sorption, magnetism and luminescence etc[1-5]. In the past years, various one-dimensional (1D) CPs, such as beeline, ladder, zigzag and ribbon, have been designed and synthesized by the strategy of crystal engineering[6].

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Compared with high dimensional structures, the 1D CPs have relatively simple construction, and can show stable porosity and solvent storage properties like the two- (2D) and three-dimensional (3D) frameworks[7]. Studies on the structural diversity and properties of 1D CPs have been widely carried out in recent years[8].

On the other hand, metal centers and anions have remarkable influence on the structure and property of CPs. Metal ions with d^{10} configuration, like Zn(Ⅱ) and Cd(Ⅱ), have attracted great attention owing to their interesting property in photoluminescence[9], while the Cu(Ⅱ) can display coordination numbers from four to eight, thus providing diverse central coordination sites in the construction of versatile CPs[10]. Meanwhile, the regulation of structures via changing anions is useful, for example, Seward et al. have reported the influence of different counteranions on the 1D structures constructed by the reactions of $AgCF_3CO_2$, $AgNO_3$, $AgPF_6$ with 2,2′,3″-tripyridylamine, and demonstrated that the crystal structures depend on the coordination fashion of the anions[11]. Therefore, changing metal centers and anions are effective methods to design and synthesize new CPs.

In our previous studies, we have reported four new CPs with 1D ribbon-like and 2D layer structures by using a V-shaped ligand containing pyridine and amide moieties, *N*,*N*′-di(pyridin-3-yl)pyridine-3,5-dicarboxamide (3-DPBA)[12]. The rigid and highly conjugated backbone of 3-DPBA is favorable for generation of remarkable photoactive properties, and pronounced photoluminescence have been observed in the Zn(Ⅱ) and Cd(Ⅱ) complexes of 3-DPBA[13]. As a continuation of our previously work, we synthesized another ligand, *N*,*N*′-di(pyridin-4-yl)pyridine-3,5-dicarboxamide (4-DPBA), and three new metal complexes $\{[Zn(4\text{-}DPBA)_2(NO_3)_2]\cdot 4DMF\}_n$ (**1**), $\{[Cd(4\text{-}DPBA)_2(NO_3)_2]\cdot 4DMF\}_n$ (**2**) and $\{[Cu(4\text{-}DPBA)_2(DMF)_2](ClO_4)_2\cdot 7DMF\cdot 2H_2O\}_n$ (**3**) (DMF=*N*,*N*-dimethylformamide) were obtained. The structures of the complexes were determined by single-crystal X-ray diffraction analysis and the photoluminescence property of complexes **1** and **2** was studied.

1 Experimental

1.1 Materials and instruments

All commercially available chemicals are of reagent grade and were used as received without further purification. Solvents were purified according to the standard methods. Elemental analyses were performed on an Elementar Vario MICRO Elemental Analyzer at the analysis center of Nanjing University. Infrared spectra were recorded on a Bruker Vector22 FTIR Spectrophotometer in the range of 400~4 000 cm^{-1} by using KBr pellets. Powder X-ray diffraction (PXRD) measurements of the complexes were performed on a Bruker D8 Advanced X-ray diffractometer using Cu $K\alpha$ radiation (λ=0.154 18 nm), and the X-ray tube was operated at 40 kV and 40 mA. The data were collected in the 2θ range of 5.00°~50.00° with a step of 0.02°. The luminescent spectra for the solid state samples were recorded at room temperature on an Aminco Bowman Series **2** spectrophotometer with a xenon arc lamp as the light source. In the measurements of the emission and excitation spectra, the pass width is 5.0 nm.

1.2 Synthesis of the ligand

Ligand 4-DPBA was prepared according to the literature method reported for the synthesis of 3-DPBA [12]. Yield: 93%. IR (KBr pellet,cm^{-1}): 3 388, 3 261, 3 176, 3 090, 1 681, 1 600, 1 520, 1 334, 1 251, 1 209, 1 118, 1 095, 1 026, 1 005, 890, 827, 729, 660, 587, 538. ^{1}HNMR (DMSO-d_6): 7.80 (d, 4H), 8.53 (d, 4H), 8.86 (t, 1H), 9.31 (d, 2H), 10.98 (s, NH). Anal. Calcd. for $C_{17}H_{13}O_2N_5$ (%): C, 63.98; H, 4.10; N, 21.95. Found (%): C, 63.83; H, 4.19; N, 21.84.

1.3 Synthesis of the complexes

1.3.1 Preparation of $\{[Zn(4\text{-}DPBA)_2(NO_3)_2]\cdot 4DMF\}_n$ (**1**)

A solution of 4-DPBA (16 mg, 0.05 mmol) in DMF (3 mL) was added to a DMF solution (3 mL) of $Zn(NO_3)_2\cdot 6H_2O$ (14.9 mg, 0.05 mmol). The solution was stirred for 15 min, then filtered. The filtrate was diffused by diethyl ether at room temperature for several days, during which time colorless crystals appeared. Yield: 72%. Anal. Calcd. for $C_{46}H_{54}ZnN_{16}O_{14}$

(%): C, 49.31; H, 4.86; N, 20.01. Found(%): C, 49.32; H, 4.89; N, 20.12. IR (KBr pellet, cm^{-1}): 3 265 (m), 1 690 (s), 1 659 (s), 1 601 (s), 1 515 (s), 1 425 (m), 1 383 (m), 1 337 (m), 1 305 (m), 1 255 (m), 1 211 (m), 1 102 (w), 1 015 (w), 846 (m), 661 (w), 545 (w), 594 (w).

1.3.2 Preparation of $\{[Cd(4\text{-}DPBA)_2(NO_3)_2]\cdot 4DMF\}_n$ (**2**)

The complex was synthesized by the same method used for preparation of **1** except that $Zn(NO_3)_2\cdot 6H_2O$ was replaced by $Cd(NO_3)_2\cdot 6H_2O$. Yield: 67%. Anal. Calcd. for $C_{46}H_{54}CdN_{16}O_{14}$ (%): C, 47.32; H, 4.66; N, 19.20. Found (%): C, 47.22; H, 4.76; N, 19.16. IR (KBr pellet, cm^{-1}): 3 310 (s), 1 691 (m), 1 658 (s), 1 601 (s), 1 514 (m), 1 429 (m), 1 386 (m), 1 338 (m), 1 307 (m), 1 254 (w), 1 214 (m), 1 091 (w), 1 011 (w), 844 (m), 661 (w), 588 (w).

1.3.3 Preparation of $\{[Cu(4\text{-}DPBA)_2(DMF)_2](ClO_4)_2\cdot 7DMF\cdot 2H_2O\}_n$ (**3**)

A mixture containing $Cu(ClO_4)_2\cdot 6H_2O$ (18.5 mg, 0.05 mmol), 4-DPBA (16 mg, 0.05 mmol), 9 mL DMF and 1 mL H_2O was sealed in a Teflon lined stainless steel container and heated at 90 ℃ for 3 d. The solution was filtered into the tube after cooling to room temperature. Blue crystals were obtained by the slow diffusion of diethyl ether into the filtrate in a week. Yield: 58%. Anal. Calcd. for $C_{61}H_{91}CuCl_2N_{19}O_{22}$ (%): C, 46.44; H, 5.82; N, 16.88. Found(%): C, 46.54; H, 5.78; N, 16.68. IR (KBr pellet, cm^{-1}): 3 419 (s), 1 655 (s), 1 601 (s), 1 517 (m), 1 430 (m), 1 335 (m), 1 304 (w), 1 256 (w), 1 211 (m), 1 098 (s), 1 026 (m), 838 (m), 738 (w), 664 (w), 623 (m), 601 (w), 541 (m).

1.4 Structure determination

Crystallographic data of complexes **1** and **2** were collected at 293 K on a Bruker SMART Apex Ⅱ CCD area-detector diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ=0.071 073 nm) using ω-φ scan technique. The diffraction data were integrated by using the SAINT program[14], which was also used for intensity corrections for Lorentz and polarization effects. Semi-empirical absorption correction was applied using SADABS program[15]. The crystallographic data for **3** were collected on a Rigaku RAXIS-RAPID Ⅱ imaging plate area detector with Mo Kα radiation (λ=0.071 075 nm) at 200 K using MicroMax-007HF microfocus rotating anode X-ray generator and VariMax-Mo optics. The structures of **1** and **3** were solved by direct methods and all non-hydrogen atoms were refined anisotropically on F^2 by full-matrix least-squares using the SHELXL-97 crystallographic software package[16]. All the hydrogen atoms, except those of water molecule in **3** which were located from Fourier map directly, were generated geometrically and refined isotropically using the riding model. Details of the crystal parameters, data collection, and refinements for **1** and **3** are summarized in Table 1, and selected bond lengths and angles with estimated standard deviations are listed in Table 2.

CCDC: 879335, **1**; 879366, **3**.

Table 1　Crystal data and structure refinements for complexes 1 and 3

Complexes	**1**	**3**
Empirical formula	$C_{46}H_{54}ZnN_{16}O_{14}$	$C_{61}H_{91}CuCl_2N_{19}O_{22}$
Formula weight	1 120.42	1 576.97
Crystal system	Orthorhombic	Trigonal
Space group	*Fddd*	$P3_221$
a / nm	1.459 0(3)	1.451 8(2)
b / nm	1.765 5(4)	1.451 8(2)
c / nm	4.022 4(8)	3.342 9(6)
T / K	293(2)	200(2)
V / nm^3	10.361(4)	6.101 7(16)
Z	8	3
D_c / ($g\cdot cm^{-3}$)	1.436	1.287
Flack parameter		0.04(2)

Continued Table 1

μ / mm^{-1}	0.555	0.412
F(000)	4672	2 487
Reflections collected	12 329	44 709
Unique reflections	2 306	7 155
R_{int}	0.055 4	0.082
Observed reflections	2 063	5 550
Parameters refined	185	534
GOF	1.125	1.014
R_1 ($I>2\sigma(I)$)	0.063 1	0.070 7
R_1 (all data)	0.068 2	0.086 7
wR_2 ($I>2\sigma(I)$)	0.162 9	0.186 9
wR_2 (all data)	0.167 1	0.203 3

Table 2 Selected bond lengths (nm) and angles (°) for complexes 1 and 3

1					
Zn1-N1	0.216 4(3)	Zn1-O2	0.217 0(5)		
N1-Zn1-N1$^{\#1}$	89.76(14)	N1$^{\#1}$-Zn1-N1$^{\#2}$	90.29(14)	N1-Zn1-N1$^{\#2}$	177.57(15)
N1-Zn1-O2$^{\#1}$	88.79(7)	N1-Zn1-O2	91.21(7)		
3					
Cu1-N31	0.202 6(3)	Cu1-N51$^{\#2}$	0.203 3(3)	Cu1-O21	0.243 5(3)
N31-Cu1-N31$^{\#1}$	89.14(17)	N31-Cu1-N51$^{\#2}$	90.32(13)	N31-Cu1-N51$^{\#3}$	175.57(14)
N51$^{\#2}$-Cu1-N51$^{\#3}$	90.56(19)	O21-Cu1-N51$^{\#3}$	88.09(13)	O21$^{\#1}$-Cu1-N51$^{\#3}$	87.96(13)
O21-Cu1-N31	96.28(12)	O21$^{\#1}$-Cu1-N31	87.73(12)	O21-Cu1-O21$^{\#1}$	174.39(15)

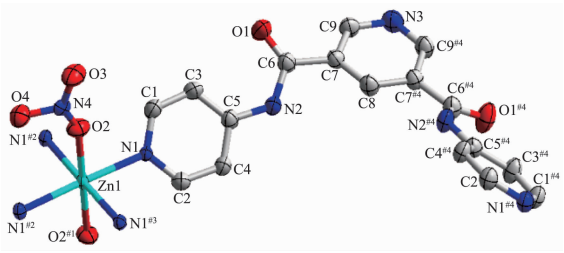
Symmetry codes: **1**: $^{\#1}$ 5/4−x, 1/4−y, z; $^{\#2}$ 5/4−x, y, 5/4−z; **3**: $^{\#1}$ 2−x, 1−x+y, 2/3−z; $^{\#2}$ x, −1+y, z; $^{\#3}$ 2−x, −x+y, 2/3−z.

2 Results and discussion

2.1 Crystal structure description

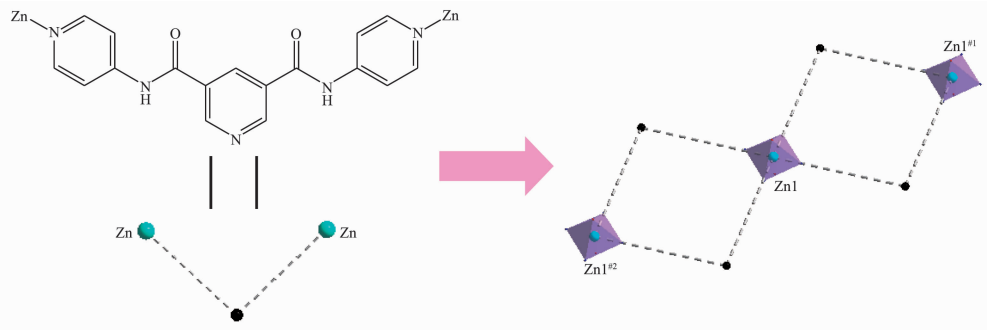
2.1.1 {[Zn(4-DPBA)$_2$(NO$_3$)$_2$]·4DMF}$_n$ (**1**) and {[Cd(4-DPBA)$_2$(NO$_3$)$_2$]·4DMF}$_n$ (**2**)

The crystallographic data indicate that complex **2** crystallizes in the orthorhombic space group *Fddd* and has cell parameters of a=1.482 0(2), b=1.732 4(2) and c=4.050 9(5) nm, which are almost the same as those of complex **1** (Table 1). The results of crystallographic analysis revealed that complexes **1** and **2** have the same backbone structures, however, the refinements of complex **2** did not give convergent result, probably due to the disorder of anions and/or solvent molecules. Therefore, only the structure of **1** is described here in detail. The asymmetric unit of **1** contains one Zn(Ⅱ) atom located at specific position with a quarter occupancy, one half nitrate anion, one half 4-DPBA ligand and one DMF molecule. It is clearly seen from Fig.1a that each Zn(Ⅱ) atom is six-coordinated in a distorted octahedral coordination environment by two oxygen atoms from two nitrate ions and four nitrogen atoms from four different 4-DPBA ligands. The Zn1-N and Zn1-O bond distances are 0.216 4(3) and 0.217 0(5) nm, respectively (Table 2). In complex **1**,



Symmetry code: $^{\#1}$ 5/4−x, 1/4−y, z; $^{\#2}$ 5/4−x, y, 5/4−z; $^{\#3}$ x, 1/4−y, 5/4−z; $^{\#4}$ 9/4−x, 1/4−y, z; Hydrogen atoms and free DMF molecules were omitted for clarity

Fig.1(a) Coordination environment of Zn(Ⅱ) in **1** with ellipsoids drawn at the 30% probability level



Symmetry code: #1 1+*x*, *y*, *z*; #2 −1+*x*, *y*, *z*

Fig.1(b)　Schematic representation of 4-DPBA and 1D chain linked by Zn(Ⅱ) and 4-DPBA in **1**

two Zn(Ⅱ) atoms and two 4-DPBA ligands form a 32-membered M_2(4-DPBA)$_2$ macrocyclic ring[13], and further assemble into an infinite 1D ribbon-like chain through Zn-N coordination interactions, with Zn⋯Zn separation of 1.459 0(5) nm (Fig.1b). It is noteworthy that nitrate anions participate in the coordination as well as the formation of 2D network from 1D chains via C–H⋯O hydrogen bonding interactions (Fig.1c). In addition, there are N–H⋯O hydrogen bonds

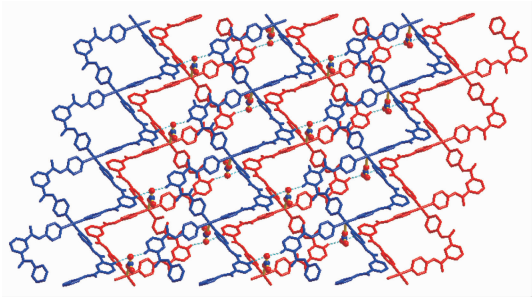


Fig.1(c)　2D network in **1** connected by C–H⋯O hydrogen bonds indicated by dashed lines

Table 3　Parameters of hydrogen bonds for complexes 1 and 3

D–H⋯A	*d*(D-H) / nm	*d*(H⋯A) / nm	*d*(D⋯A) / nm	∠DHA / (°)
1				
N2–H2⋯O5#1	0.086	0.215	0.299 2(6)	166
C9–H9⋯O3	0.093	0.262	0.350 6(9)	158
C1–H1⋯O1#2	0.093	0.255	0.337 9(5)	149
C8–H8⋯O5#1	0.093	0.246	0.314 9(6)	131
3				
N5–H2⋯O23#1	0.088	0.192	0.278 7(7)	168
N3–H1⋯O22#2	0.088	0.201	0.287 9(5)	169
C4–H4⋯O22#2	0.095	0.257	0.317 4(7)	122
C6–H5⋯O13#3	0.095	0.253	0.341(2)	153
C53–H11⋯O23#1	0.095	0.248	0.323(8)	136
C56–H13⋯O24#4	0.095	0.256	0.327(1)	131
C12–H20⋯O5#5	0.098	0.258	0.351 8(8)	160
C13–H23⋯O14#3	0.098	0.216	0.311(3)	162
C12–H18⋯O14#3	0.098	0.284	0.347 5(5)	124
C14–H25⋯O11#3	0.098	0.253	0.349(1)	166
C15–H29⋯O3	0.098	0.257	0.341 4(8)	144
C15–H31⋯O24	0.098	0.255	0.343(1)	149
C25–H42⋯O23#2	0.095	0.252	0.336(2)	148
C19–H43⋯O23#6	0.098	0.225	0.289(2)	121
C19–H44⋯O22	0.098	0.230	0.324(2)	162

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

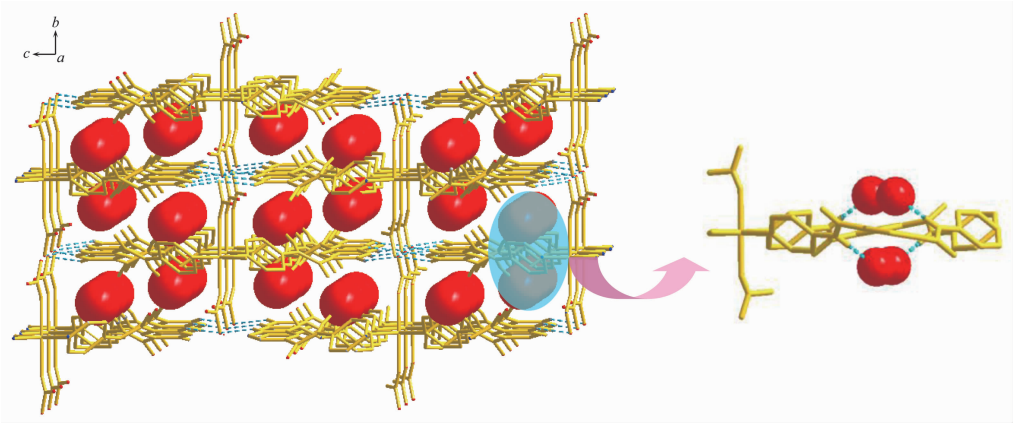
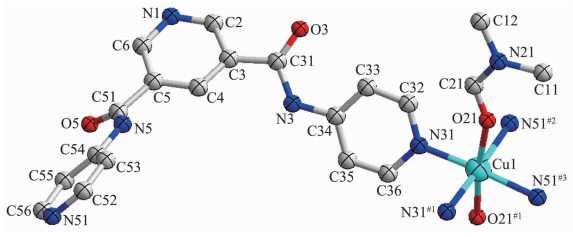


Fig.1(d) 3D framework of **1** linked by N–H···O hydrogen bonds indicated by dashed lines and DMF solvent molecules (represented as red balls) with space filling mode located between two layers

between the DMF molecules and amide groups of the 2D network, which lead to the formation of 3D framework of **1** (Fig.1d). The hydrogen bonding data are summarized in Table 3.

2.1.2 $\{[Cu(4\text{-}DPBA)_2(DMF)_2](ClO_4)_2\cdot 7DMF\cdot 2H_2O\}_n$ (**3**)

When a perchlorate salt of $Cu(ClO_4)_2$, instead of nitrate ones in **1** and **2**, was utilized to react with 4-DPBA, complex **3** was obtained. X-ray structural analysis indicates that **3** crystallizes in trigonal space group $P3_221$ with flack parameter of 0.04(2), and has a different supramolecular structure from that of **1** and **2**. As shown in Fig.2a, each Cu(Ⅱ) in **3** is six-coordinated by four nitrogen atoms from four distinct 4-DPBA ligands and two oxygen atoms from two DMF molecules. There are two kinds of Cu1-N bonds with different bond distances, namely Cu1-N31 of 0.202 6(3) nm and Cu1-N51 of 0.203 3(3) nm, while the bond length of Cu1-O is 0.243 5(3) nm, and the coordination angles around the Cu1 range from 87.73 (12)° to 175.57(14)° (Table 2). Complex **3** also adopts the 1D ribbon-chain structure composed of $M_2(4\text{-}DPBA)_2$ macrocyclic rings just like **1** and **2**, and perchlorate anions locate alongside the chains, connecting them through C–H···O hydrogen bonds to give 2D layers (Fig.2b). Unlike the unique extending direction of 1D chains in **1** and **2**, in **3** the 1D chains show three



Symmetry code: #1 2–*x*, 1–*x*+*y*, 2/3–*z*; #2 *x*, –1+*y*, *z*; #3 2–*x*, –*x*+*y*, 2/3–*z*; Hydrogen atoms, perchlorate anions, free water and DMF molecules were omitted for clarity

Fig.2(a) Coordination environment of Cu(Ⅱ) in **3** with ellipsoids drawn at the 30% probability level

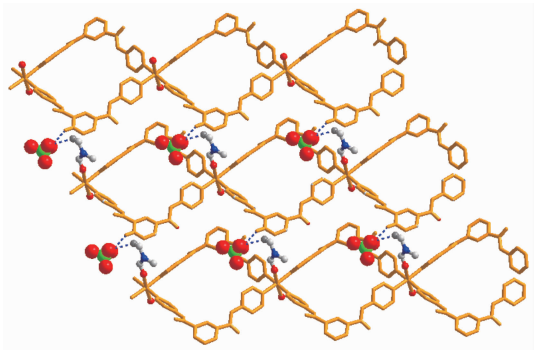


Fig.2(b) 2D layer structure of **3** with 1D chains linked by ClO_4^- anions

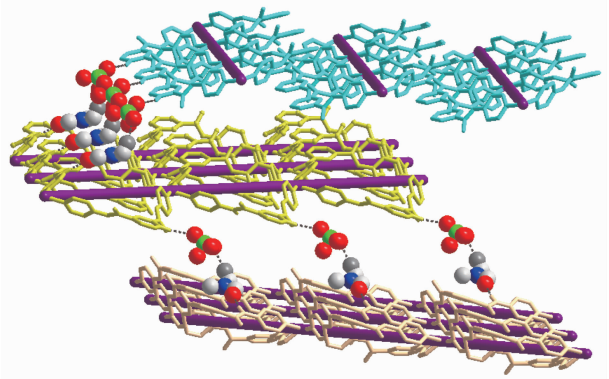


Fig.2(c) View of three different orientations of 1D chains and 3D structure of **3** connected by N–H···O and C–H···O hydrogen bonds indicated by dashed lines

different spreading orientations, with an angle of 120° to each other to give different 2D networks. Furthermore, the 2D layers in 3 are held together by DMF solvent molecules via N–H⋯O and C–H⋯O hydrogen bonds to form 3D architecture (Fig.2c and Table 3).

2.2 Comparison and discussion

The results of structural analysis indicate that all the complexes of **1**~**3** possess the same coordination mode, namely each metal center connects four different 4-DPBA ligands and each 4-DPBA ligand in turn links two metal atoms using its two terminal pyridine groups while the central pyridine group of 4-DPBA is free of coordination. The metal centers are six coordinated from four 4-DPBA ligands and two oxygen atoms from NO_3^- in **1** (**2**) or DMF in **3**. It is noteworthy that the Cu-O bond is much longer than the Cu-N bond in **3** due to the Jahn-Teller effect[17]. In addition, the nitrate anions coordinate with metal centers in **1** (**2**) while the DMF is free of coordination, however, in the case of **3**, the perchlorate anion does not participate the coordination but the DMF coordinates with the Cu(Ⅱ). The results show that the coordination ability of the anion is important in formation of CPs.

Interestingly, the previously reported complex $[Cd(3\text{-DPBA})(DMF)(NO_3)_2]\cdot DMF$ (**4**), obtained by reaction of 3-DPBA with $Cd(NO_3)_2\cdot 6H_2O$, has 2D network structure[12] rather than the 1D chain of **2**. In **4**, the Cd(Ⅱ) is seven-coordinated with distorted pentagonal bipyramid geometry, and all the three pyridine groups of the 3-DPBA ligand coordinate with the Cd(Ⅱ), however, the central pyridine group in 4-DPBA does not take part in the coordination in **1**~**3**. The results imply that the subtle difference in ligands, such as the different coordination sites in 3-DPBA and 4-DPBA, can have remarkable influence on the formation and structure of the complexes.

2.3 PXRD analysis

To confirm that the crystal structure is the representative of the bulk sample, PXRD measurements were carried out for **1** and **3** at room temperature. The experimental and simulated PXRD patterns for each complex are shown in Fig.3, which demonstrate that the diffraction peaks of simulated and experimental patterns match well. The results indicate the phase purity of **1** and **3**.

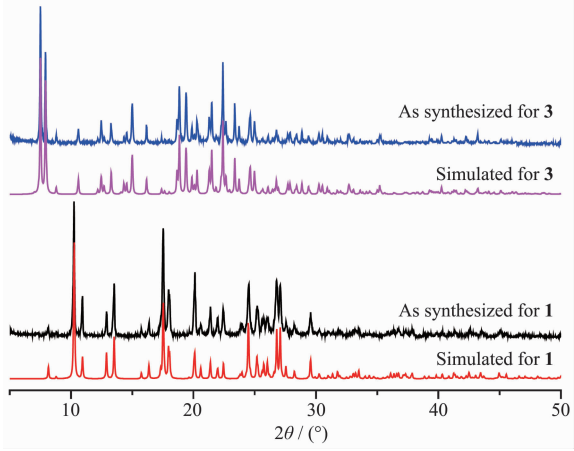


Fig.3　PXRD patterns for complexes **1** and **3**

2.4 Photoluminescence property

CPs with d^{10} transition metal centers and extended conjugated ligands are particularly interested in view of potential candidates as photoactive materials[18]. Therefore, we studied photoluminescence property of complexes **1** and **2**, as well as the 4-DPBA ligand. As shown in Fig.4, intense emission bands were observed at 412 nm (λ_{ex}=363 nm) for **1**, 402 nm (λ_{ex}=351 nm) for **2** and 423 nm for 4-DPBA (λ_{ex}=338 nm). Compared to 4-DPBA, the emission bands of **1** and **2** are respectively 11 and 21 nm blue-shifted, which can be tentatively ascribed to the influence of the coordination of metal atom to the ligand[19]. The similar emissions between the ligand and the complexes are probably contributed by the π-π^*

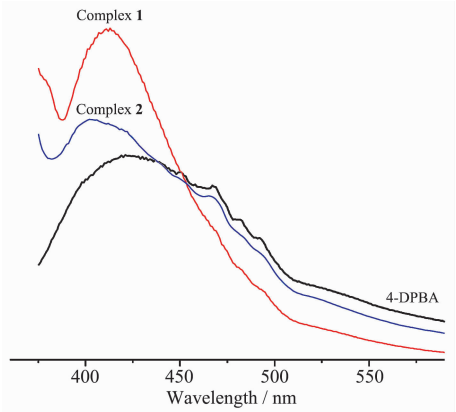


Fig.4　Emission spectra of complexes **1**, **2** and 4-DPBA in the solid state at room temperature

intraligand fluorescence[20].

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