

## 一维链状配合物[Cd(FA)(pyim)(H<sub>2</sub>O)]的合成、晶体结构和荧光性质

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### Synthesis, Crystal Structure and Luminescent Property of One-Dimensional Chain Complex [Cd(FA)(pyim)(H<sub>2</sub>O)]

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**Abstract:** A one-dimensional zigzag chain complex of Cd(FA)(pyim)(H<sub>2</sub>O) (**1**) (H<sub>2</sub>FA=4,4'-(hexafluoroisopropylidene)bis(benzoic acid) and pyim=2-(2-pyridyl)imidazole) was hydrothermal synthesized from Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) and 2-(2-pyridyl)imidazole. Single-crystal X-ray analysis revealed that the zigzag chains of **1** are linked into three-dimensional supramolecular networks by both O—H···O hydrogen-bonds and  $\pi\cdots\pi$  stacking interactions. The crystal is of monoclinic, space group  $P2_1/n$  with  $a=0.856\ 34(10)$  nm,  $b=1.020\ 49(12)$  nm,  $c=2.809\ 0(3)$  nm,  $\beta=98.115(2)^\circ$ ,  $V=2.430\ 2(5)$  nm<sup>3</sup>,  $D_c=1.820$  g·cm<sup>-3</sup>,  $Z=4$ ,  $F(000)=1\ 320$ ,  $Goof=1.009$ ,  $R_1=0.047\ 0$ ,  $wR_2=0.115\ 5$ . In addition, complex **1** exhibits strong photoluminescent emission at room temperature. CCDC: 733837.

**Key words:** cadmium(II) complex; crystal structure; flexible carboxylate ligand; photoluminescent property

Great interest has been focused on the rapidly expanding field of the construction of novel functional metal-organic frameworks (MOFs) owing to their variety of intriguing architectures and topologies and their potential applications in magnetism, electric conductivity, molecular adsorption, heterogeneous catalysis, nonlinear optics and fluorescent materials<sup>[1-3]</sup>. The self-assembly of multidentate organic ligands and metal ions has resulted in many coordination polymeric frameworks whose structures are influenced by the subtle

interplay of many factors like the geometric preference of metal ions, the size and shapes of organic building blocks, templates, and solvent systems. Hence, the selection or design of suitable ligands containing certain features, such as flexibility and versatile binding modes, is crucial to the construction of metal-organic coordination polymers, and the combination of both  $\pi\cdots\pi$  interactions and hydrogen bonding has proved to be particularly useful for the assembly of polymeric structures<sup>[4,5]</sup>. The assemblies of extended

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solids from bent arenedicarboxylate linkers are considerably less studied despite that they would likely offer new topologies with channels and, consequently, a great potential for the design and synthesis of functional materials. Recently, several microporous metal organic coordination polymers assembled from a bent ligand 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) ( $H_2FA$ ) have been reported<sup>[6-9]</sup>. These materials display potential applications in hydrogen storage, separation, catalysis and magnetism. We focus on the construction of novel complexes based on the bent ligand and mixed *N*-containing ligands. Herein, we present a novel zigzag chain complex of **1**, in which the mixed ligand is 2-(2-pyridyl)imidazole.

## 1 Experimental

### 1.1 Materials and general methods

All reagents for syntheses and analyses were purchased from commercial sources and used as received without further purification. Elemental analyses (C, H and N) were performed on a Vario EL III elemental analyzer. The IR spectrum as a KBr disk was recorded on a Nicolet Avatar 360 FTIR spectrometer. The emission/excitation spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. Thermal gravimetric analyses (TGA) were performed on a Netzsch STA-409PC instrument in flowing  $N_2$  with a heating rate of  $20\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ .

### 1.2 Synthesis of complex

The ligand pyim was synthesized by modification of the preparation due to Radziszewski<sup>[10]</sup>. A solution of 20 g (190 mmol) of pyridine-2-carboxaldehyde and 20 mL of 95% ethanol was cooled to  $0\text{ }^\circ\text{C}$  and added to a solution of 27 mL of 40% aqueous glyoxal in 20 mL of 95% ethanol, also at  $0\text{ }^\circ\text{C}$ . The mixture was stirred in an ice bath, and 64 mL of cold aqueous  $NH_3$  (30%) was added as quickly as possible while maintaining the temperature of the entire mixture below about  $5\text{ }^\circ\text{C}$ . The stirring solution gradually turned brown and allowed to warm to room temperature after 1 h. The volume was reduced by gentle warming under vacuum, and the remaining solution was extracted several times with ethyl ether. The ether extracts were combined and dried

thoroughly ( $Na_2SO_4$ ), and the ether was removed under vacuum to yield brown oil which was distilled under vacuum. The clear yellow oil so obtained was solidified and recrystallized from ethyl acetate, to get a light yellow needles with a yield of 9 g (33%), m.p.  $136\text{ }^\circ\text{C}$ .

The single crystals of **1** were prepared by hydrothermal reaction. A mixture containing  $Cd(NO_3)_2\cdot 4H_2O$  (30.8 mg, 0.1 mmol),  $H_2FA$  (39.2 mg, 0.1 mmol), pyim (14.5 mg, 0.1 mmol) and  $LiOH\cdot H_2O$  (8.4 mg, 0.2 mmol) in 15 ml deionized water was sealed in a 25 mL Teflon lined stainless steel container and heated at  $140\text{ }^\circ\text{C}$  for 3 d. Colorless pillar crystals of **1** were collected by filtration and washed with water and ethanol several times with a yield of 57%. Anal. Calcd. For  $C_{25}H_{17}F_6N_3O_5Cd$  (%): C, 45.10; H, 2.57; N, 6.31. Found (%): C, 45.01; H, 2.63; N, 6.33. IR spectrum: 3 385, 3 059, 2 957, 1 609, 1 579, 1 520, 1 387, 1 344, 1 210, 1 142, 1 087, 1 019, 935, 854, 725, 662, and  $585\text{ cm}^{-1}$ .

### 1.3 X-ray crystallography

A colorless pillar single crystal of **1** with  $0.28\text{ mm}\times 0.22\text{ mm}\times 0.14\text{ mm}$  was carefully selected under a polarizing microscope and glued at the tip of a thin glass fiber with cyanoacrylate (super glue) adhesive. Single crystal structure determination by X-ray diffraction was performed on a Bruker Smart Apex II CCD diffractometer equipped with a normal focus, 3 kW sealed tube X-ray source (Mo  $K\alpha$  radiation,  $\lambda = 0.071\,073\text{ nm}$ ) operating at 50 kV and 30 mA. A total of 4 517 reflections were collected in the range ( $2.13^\circ \leq \theta \leq 25.00^\circ$ ,  $-10 \leq h \leq 10$ ,  $-12 \leq k \leq 12$ ,  $-22 \leq l \leq 33$ ), of which 12 237 are unique ( $R_{int}=0.082\,3$ ) and 4 106 with  $I>2\sigma(I)$  were used in the refinement of the structure of **1**. Data processing was accomplished with the SAINT processing program<sup>[11]</sup>. Empirical absorption correction was applied. The structure was solved by the direct method and refined by full-matrix least squares on  $F^2$  using the SHELX 97 software<sup>[12,13]</sup>. All of the non-hydrogen atoms were refined anisotropically<sup>[13]</sup>. The hydrogen atoms were added according to the theoretical model. The crystal parameters date collection and refinement results for complex **1** is shown in Table 1. The selected bond distances and angles are listed in Table 2.

CCDC: 733837

**Table 1** Crystal data and structure refinement for complex **1**

Formula	C <sub>25</sub> H <sub>17</sub> F <sub>6</sub> N <sub>3</sub> O <sub>3</sub> Cd	Absorption coefficient / mm	0.989
Formula weight	665.82	<i>F</i> (000)	1 320
Temperature / K	293(2)	$\theta$ range / (°)	2.13~25.50
Crystal system	Monoclinic	Limiting indices	$-10 \leq h \leq 10, -12 \leq k \leq 12, -22 \leq l \leq 33$
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	Reflections collected	12 237
<i>a</i> / nm	0.856 34(10)	Independent reflections ( <i>R</i> <sub>int</sub> )	4 517 (0.082 3)
<i>b</i> / nm	1.020 49(12)	Reflections observed [ <i>I</i> > 2σ( <i>I</i> )]	4 106
<i>c</i> / nm	2.809 0(3)	Data / restraints / parameters	4 517 / 1 / 361
$\beta$ / (°)	98.115(2)	Goodness-of-fit on <i>F</i> <sup>2</sup>	1.009
<i>V</i> / nm <sup>3</sup>	2. 430 2(5)	<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.047 0, 0.115 5
<i>Z</i>	4	Largest difference peak and hole / (e <sup>−</sup> ·nm <sup>−3</sup> )	1 294, −2 396
<i>D</i> <sub>c</sub> / (g·cm <sup>−3</sup> )	1.820		

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

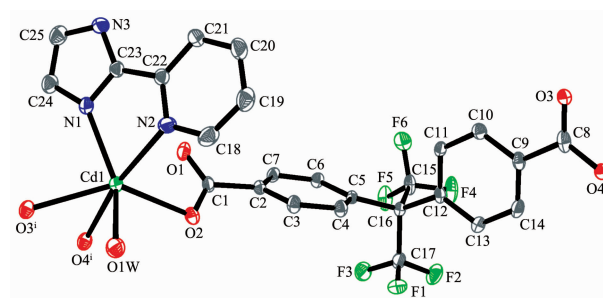
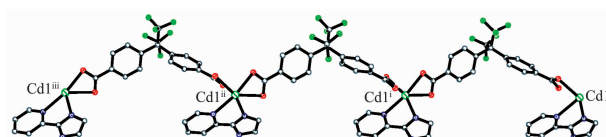
Cd1-N1	0.227 5(3)	Cd1-O2	0.229 0(3)	Cd1-O1W	0.232 6(4)
Cd1-O4 <sup>i</sup>	0.234 2(3)	Cd1-N2	0.241 5(3)	Cd1-O3 <sup>i</sup>	0.245 4(3)
N1-Cd1-O2	129.90(11)	O1W-Cd1-N2	92.86(13)	N1-Cd1-O1W	136.90(13)
O4 <sup>i</sup> -Cd1-N2	168.46(11)	O2-Cd1-O1W	84.12(13)	N1-Cd1-O3 <sup>i</sup>	84.78(10)
N1-Cd1-O4 <sup>i</sup>	114.92(10)	O2-Cd1-O3 <sup>i</sup>	138.23(9)	O2-Cd1-O4 <sup>i</sup>	86.43(10)
O1W-Cd1-O3 <sup>i</sup>	81.46(13)	O1W-Cd1-O4 <sup>i</sup>	89.21(12)	O4 <sup>i</sup> -Cd1-O3 <sup>i</sup>	54.50(9)
N1-Cd1-N2	70.61(11)	N2-Cd1-O3 <sup>i</sup>	137.04(11)	O2-Cd1-N2	82.49(11)

Symmetry code: <sup>i</sup>  $x+1/2, -y+3/2, z+1/2$ .

## 2 Results and discussion

The crystallographic analysis reveals that **1** is a one-dimensional zigzag chain complex. As shown in Fig.1, each Cd(II) atom is six-coordinated by three oxygen atoms from two different carboxylate groups, one water molecule and two nitrogen atoms of 2-(2-pyridyl)imidazole ligand to form a distorted octahedral geometry. The Cd-O bond lengths are in the range of 0.229 0(3)~0.245 4(3) nm, the Cd-N bond lengths are 0.227 5(3)~0.241 5(3) nm and the coordination angles around Cd atom are in the range of 54.50(9)°~168.46(11)°. Two carboxylate groups of FA<sup>2−</sup> ligand adopt monodentate and chelate coordination modes and link to the Cd(II) atoms, giving a one-dimensional zigzag chain structure. The dihedral angle between two phenyl rings of the bent FA<sup>2−</sup> ligand is 81.2°. The separation of neighboring Cd(II) atoms in chain is about 1.42 nm as illustrated in Fig.2. The packing structure of **1** shows a three-dimensional supramolecular network derived from chains formed via intermolecular O–H···O hydrogen

bonds and weak  $\pi \cdots \pi$  stacking interactions. Interestingly, there are small fluoro-lined cavities (about 0.032 nm<sup>3</sup>) in the 3D architecture, which indicates that **1** could potentially accommodate hydrogen-bonded H<sub>2</sub>O

Symmetry code: <sup>i</sup>  $x+1/2, -y+3/2, z+1/2$ **Fig.1** ORTEP drawing of **1** showing the labeling of atoms with thermal ellipsoids at 30% probabilitySymmetry code: <sup>i</sup>  $-1/2+x, 3/2-y, -1/2+z$ ; <sup>ii</sup>  $-1+x, y, -1+z$ ;  
<sup>iii</sup>  $-3/2+x, 3/2-y, -3/2+z$ **Fig.2** 1D zigzag chain representation for complex **1**

molecules to generate O-H $\cdots$ F interaction.

Thermal gravimetric analysis (TGA) was carried out to examine the thermal stability of **1**. The results show that complex **1** is stable in air at ambient temperature. The samples were heated up in flowing N<sub>2</sub> with a heating rate of 20 °C · min<sup>-1</sup>. For **1**, the weight loss corresponding to the release of one coordination water molecule is observed from 90 to 150 °C. The anhydrous complex begins to decompose at 300 °C. The framework collapsed in the temperature range 300~800 °C before the final formation of a metal oxide.

Luminescent compounds are of great current interest because of their various applications in chemical sensors, photochemistry, and electroluminescent display<sup>[14,15]</sup>. Thus, the photoluminescent properties of **1** in the solid state have been investigated at room temperature. As illustrated in Fig.3, the intense broad emission bands at 420 nm ( $\lambda_{\text{ex}}$ =371 nm) for **1**. For excitation wavelengths between 280 and 480 nm, there is no obvious emission observed for free pyim ligand under the same experimental conditions, while free H<sub>2</sub>FA ligand presents a photoluminescence emission at 382 nm ( $\lambda_{\text{ex}}$ =342 nm). Therefore, the fluorescent emission of **1** may be proposed to originate from the coordination of FA<sup>2-</sup> to the cadmium atom (ligand-to-metal charge transition, LMCT). The enhancement of luminescence may be attributed to ligand chelation to the metal center, which effectively increases the rigidity

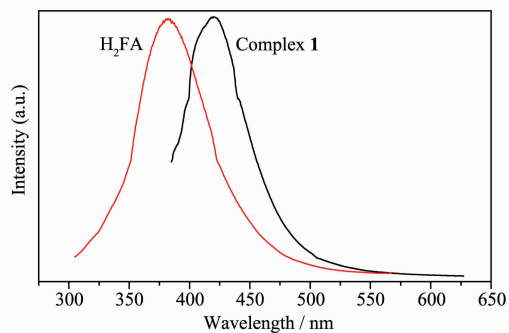


Fig.3 Photoluminescent spectra of **1** and free H<sub>2</sub>FA ligand in the solid state at room temperature

of the ligand and reduces the loss of energy by radiationless decay. These observations indicate that **1** may be candidates for potential photoactive materials.

### 3 Conclusion

In this paper, by using the bent linker 4,4' - (hexafluoroisopropylidene) bis (benzoic acid), whose central atom is an *sp*<sup>3</sup> carbon, a new Cd(II) complex has been obtained and displays strong photoluminescent emission at room temperature.

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