

三维配合物 $[\text{Zn}_2(\text{OH})(\text{pyim})(\text{BIPA})]_n$ 的水热合成、 晶体结构和荧光性质研究

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Hydrothermal Synthesis, Crystal Structure and Photoluminescence of a Novel Three-Dimensional Zinc(II) Complex: $[\text{Zn}_2(\text{OH})(\text{pyim})(\text{BIPA})]_n$

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Abstract: Hydrothermal reaction between 5-bromoisophthalic acid (H_2BIPA) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at the presence of the second ligand of 2-(2-pyridyl)imidazole (Hpyim) yields a new 3D metal-organic coordination polymer $[\text{Zn}_2(\text{OH})(\text{pyim})(\text{BIPA})]_n$ (**1**), which has been characterized by single-crystal X-ray diffraction, elemental analysis, IR spectrum and thermal analysis. Complex **1** presents an α -Po net with $4^{12}6^3$ topology constructed from tetranuclear clusters and displays strong luminescent emission at room temperature. CCDC: 763940.

Key words: Zinc(II) complex; crystal structure; multicarboxylate ligand; luminescence

Metal-organic frameworks (MOFs) are rapidly increasing not only because of their tremendous potential applications in functional materials, nanotechnology and biological recognition, but also because of their intriguing variety of architectures and topologies^[1-5]. The ability to rationally design and modify the crystal structure of MOF materials is the key to increase the potential for commercial applications^[6]. Recently, Yaghi et al. have successfully developed a secondary building unit (SBU) strategy to direct the assembly of MOFs, which has been widely used for understanding and predicting structural topologies^[7-8]. The use of secondary

building blocks is attractive in part because of their steric requirements and rigidity, which dramatically reduce the number of possible network topologies arising for a given node-linker combination^[9]. Metal-carboxylate based clusters, where metals are locked into their positions, have been synthesized in situ and successfully used as rigid directional secondary building units to design and construct stable open metal-organic assemblies^[10]. For example, a family of highly porous MOFs has been constructed using $\text{Zn}_4\text{O}(\text{COO})_6$ as the SBU^[11]. Multicarboxylate ligands are often selected as multifunctional organic linkers to

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build metal clusters because of their abundant coordination modes to metal ions, resulting from completely or partially deprotonated sites, allowing for various structural topologies, and also because they can be regarded not only as H-bond acceptors and but also as donors depending upon the number of deprotonated carboxylic groups^[12-14].

In addition, a careful selection of the properties of the second ligands, such as shape, functionality, flexibility, angle and symmetry, is a key step for the rational design of structures and specific chemical and physical properties^[15-16]. In previous studies^[17-18], we focused our attention on the construction of metal organic frameworks with metal salts and flexible bis (imidazol) ligands, for example, 1,4-bis(imidazol-1-yl)butane, 1,2-bis(imidazol-1-ylmethyl)benzene, 1,3-bis(imidazole-1-ylmethyl)benzene and so on. In comparison with the above-mentioned ligands, 2-(2-pyridyl)imidazole (Hpyim) is asymmetry ligand, which can act as both chelate and bridging ligand. Therefore, 2-(2-pyridyl)imidazole is introduced into the reaction systems, a novel coordination polymer $[\text{Zn}_2(\text{OH})(\text{pyim})(\text{BIPA})]_n$ (**1**) was synthesized under hydrothermal conditions. Moreover, the infrared spectra, thermogravimetric analyses, and luminescent properties of the complex have been investigated in detail.

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. The ligand Hpyim was synthesized by modification of the preparation due to Radziszewski^[19]. 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 single crystals of **1** were prepared by hydrothermal reaction. A mixture containing $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (59.5 mg, 0.2 mmol), H_2BIPA (39.2 mg, 0.1 mmol), Hpyim (14.5 mg, 0.1 mmol) and NaOH (12.0 mg, 0.3 mmol) in 15 mL deionized water was sealed in a 25 mL Teflon lined stainless steel container and heated at $160\text{ }^\circ\text{C}$ for 3 d. Colorless pillar crystals of **1** were collected by filtration and washed with water and ethanol several times with a yield of 63%. IR spectrum (cm^{-1}): 3 442, 3 055, 2 931, 1 581, 1 554, 1 519, 1 433, 1 383, 1 367, 1 283, 1 249, 1 142, 1 121, 1 089, 1 047, 958, 859, 834, 811, 769, 743, 682, 649, 624 and 546.

1.3 X-ray crystallography

A colorless block single crystal of **1** with $0.24\text{ mm}\times 0.18\text{ mm}\times 0.16\text{ mm}$ 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 ($\text{Mo K}\alpha$ radiation, $\lambda = 0.071\text{ }073\text{ nm}$) operating at 50 kV and 30 mA. Data processing was accomplished with the SAINT processing program^[20]. 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^[21-22]. All of the non-hydrogen atoms were refined anisotropically^[22]. The hydrogen atoms were added according to the theoretical model. The crystal parameters data collection and refinement results for complex **1** is shown in Table 1. The selected bond distances and angles are listed in Table 2.

CCDC: 763940.

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

Formula	$\text{C}_{16}\text{H}_{10}\text{BrN}_3\text{O}_2\text{Zn}_2$	Absorption coefficient / mm	4.996
Formula weight	534.92	$F(000)$	2096
Temperature / K	293(2)	θ range / ($^\circ$)	1.89~25.00
Crystal system	Monoclinic	Limiting indices	$-22 \leq h \leq 23, -14 \leq k \leq 16, -13 \leq l \leq 17$

Continued Table 1

Space group	$C2/c$	Reflections collected	8 211
a / nm	1.997 3(4)	Independent reflections (R_{int})	2 997 (0.098 1)
b / nm	1.365 7(4)	Reflections observed [$I > 2\sigma(I)$]	2 110
c / nm	1.490 0(3)	Data / restraints / parameters	2 997 / 0 / 238
β / ($^\circ$)	119.312(6)	Goodness-of-fit on F^2	1.067
V / nm ³	3.544 1(15)	$R1, wR2$ [$I > 2\sigma(I)$]	0.060 6, 0.136 8
Z	8	Largest difference peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	1 001, -737
D_c / ($\text{g} \cdot \text{cm}^{-3}$)	2.005		

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

Zn(1)-O(5)	0.187 7(5)	Zn(1)-O(3) ⁱⁱⁱ	0.198 7(5)	Zn(2)-N(1)	0.197 6(5)
Zn(1)-N(2) ⁱ	0.195 4(6)	Zn(2)-O(5)	0.194 7(5)	Zn(2)-O(4) ⁱⁱⁱ	0.205 3(5)
Zn(1)-O(2) ⁱⁱ	0.194 1(5)	Zn(2)-O(1)	0.196 2(4)	Zn(2)-N(3)	0.240 4(8)
O(5)-Zn(1)-O(2) ⁱⁱ	107.3(2)	O(5)-Zn(2)-O(1)	127.1(2)	O(5)-Zn(2)-N(3)	82.3(2)
O(5)-Zn(1)-N(2) ⁱ	118.5(2)	O(5)-Zn(2)-N(1)	114.7(2)	O(1)-Zn(2)-N(3)	91.2(2)
O(2) ⁱⁱ -Zn(1)-N(2) ⁱ	114.6(3)	O(1)-Zn(2)-N(1)	113.4(2)	N(1)-Zn(2)-N(3)	73.7(2)
O(5)-Zn(1)-O(3) ⁱⁱⁱ	102.4(2)	O(5)-Zn(2)-O(4) ⁱⁱⁱ	95.1(2)	O(4) ⁱⁱⁱ -Zn(2)-N(3)	170.0(2)
O(2) ⁱⁱ -Zn(1)-O(3) ⁱⁱⁱ	103.7(3)	O(1)-Zn(2)-O(4) ⁱⁱⁱ	98.0(2)		
N(2) ⁱ -Zn(1)-O(3) ⁱⁱⁱ	108.7(2)	N(1)-Zn(2)-O(4) ⁱⁱⁱ	98.9(2)		

Symmetry code: ⁱ $2-x, y, 5/2-z$; ⁱⁱ $3/2-x, 1/2-y, 2-z$; ⁱⁱⁱ $3/2-x, -1/2+y, 3/2-z$.

2 Results and discussion

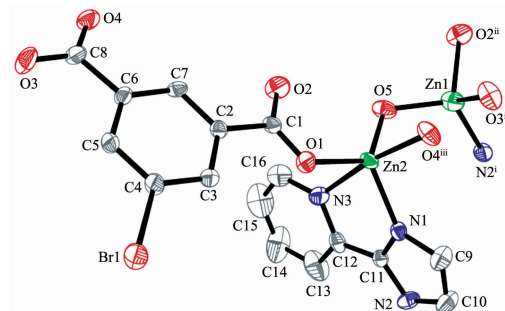
2.1 IR spectra

The IR spectral data show features attributable to the carboxylate stretching vibrations of the complex. The absence of bands in the range of $1\,760\sim1\,680\text{ cm}^{-1}$ indicates the complete deprotonation of the H_2BIPA ligand. The characteristic bands of the carboxylate groups appear in the range $1\,550\sim1\,620\text{ cm}^{-1}$ for the asymmetric stretching and $1\,370\sim1\,470\text{ cm}^{-1}$ for the symmetric stretching, and the value of $\Delta\nu[\nu_{\text{as}}(\text{COO}^-)-\nu_{\text{s}}(\text{COO}^-)]$ reveals that the carboxylate groups are coordinated in monodentate and bidentate-bridging fashions, which is consistent with the results of the X-ray analysis. The IR spectra of complex **1** contain characteristic peaks of hydroxyl group at $3\,442\text{ cm}^{-1}$. Also observed were the bands for the pym ligand at $1\,519\text{ cm}^{-1}$ for **1**, shows The C=N stretching vibration of imidazolyl group^[23].

2.2 Crystal structure

Colorless block crystals of the title complex were obtained from the reaction of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, H_2BIPA and Hpyim, and its structure was determined by a

single-crystal X-ray diffraction study. Complex **1** crystallizes in the monoclinic with space group $C2/c$. As depicted in Fig.1, the structure of **1** contains two different types of Zn(II) atoms, one unique BIPA anion, one pym anion and one hydroxyl group. Within the unit, there are four-coordinated and five-coordinated Zn(II) centers, which are bounded to two carboxylate groups. The four-coordinated Zn1 atom adopts a distorted tetrahedral geometry with two oxygen atoms from two BIPA anions, one nitrogen atom from pym anion and one hydroxyl group. The five coordinated Zn2

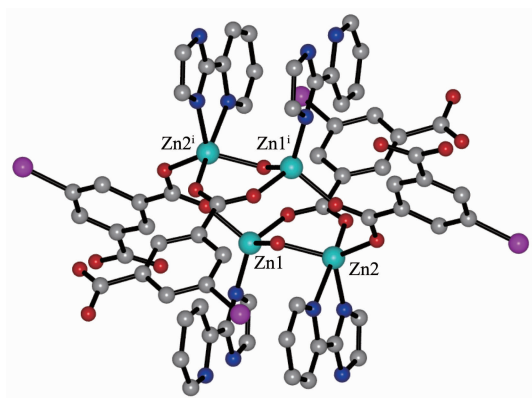


Symmetry code: ⁱ $2-x, y, 5/2-z$; ⁱⁱ $3/2-x, 1/2-y, 2-z$; ⁱⁱⁱ $3/2-x, -1/2+y, 3/2-z$

Fig.1 ORTEP drawing of **1** showing the labeling of atoms with thermal ellipsoids at 30% probability

atom is coordinated by two nitrogen atoms from pyim anion, two oxygen atoms from two different BIPA anions and one hydroxyl group to adopt a square-pyramidal coordination geometry. The Zn-O and Zn-N distances are in the range of 0.187 7(5)~0.205 3(5) nm and 0.195 4(6)~0.240 4(8) nm, respectively, which are similar to the reported Zn-O and Zn-N distances in other Zn(II) coordination polymers^[24].

The Zn1 and Zn2 atoms are bridged by a carboxylate group and a hydroxyl group with Zn1...Zn2 separation of 0.322 nm to form a dinuclear unit, which is further linked by carboxylate group into a tetranuclear cluster (Fig.2). The tetranuclear clusters are connected through the BIPA anions to generate an infinite 2D lattice network (Fig.3). Each BIPA anion acts as a μ_3 -bridge linking three zinc atoms with



Symmetry code: $1/2 - x, 1/2 - y, 2 - z$

Fig.2 Representation of Zn_4 unit linked by four carboxylate groups and two hydroxyl groups in **1**

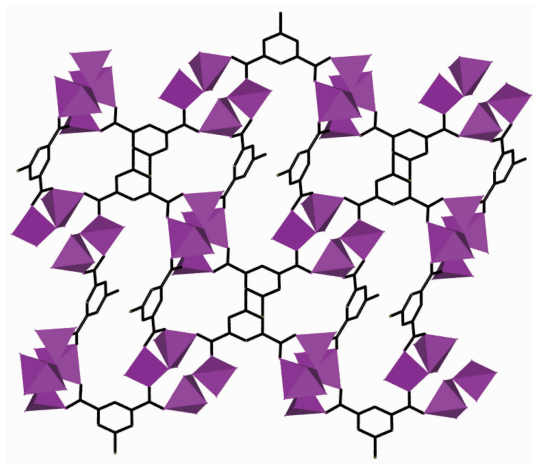


Fig.3 Polyhedral representation of the 2D layer connected by BIPA anions in **1**

monodentate and bidentate-bridging coordination modes. The 2D networks are further pillared by rod-like pyim anions to form a 3D supramolecular architecture with Zn...Zn separation of 0.584 nm.

The Zn_4 cluster is surrounded by four BIPA anions and four pyim anions, while two pyim anions doubly connect two clusters, which means that each cluster is linked by six other neighboring ones. From the topology view, the tetranuclear cluster was taken as a single node, this 3D frame is classified to be an α -Po net with $4^{12}6^3$ topology (Fig.4).

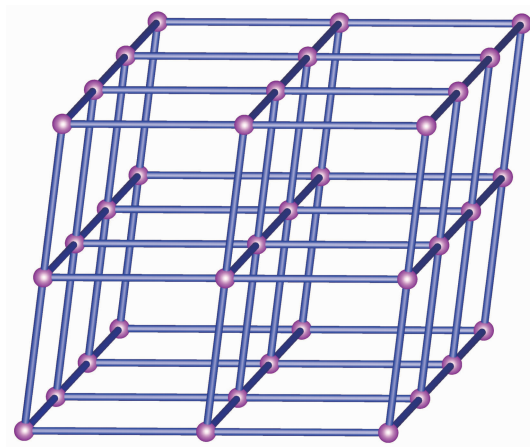


Fig.4 Schematic representation of the α -Po topology of **1**

2.3 Thermogravimetric analyses

Thermal gravimetric analyses (TGA) were carried out to examine the thermal stability of **1**. The samples were heated up in flowing N_2 with a heating rate of $20\text{ }^\circ\text{C}\cdot\text{min}^{-1}$. The TGA curve of **1** indicates that there is no significant loss up to about $320\text{ }^\circ\text{C}$. Then a sharp weight-loss step was observed between 320 and $500\text{ }^\circ\text{C}$, which can be attributed to the decomposition of organic ligands.

2.4 Luminescent properties

Luminescent complexes are of great current interest because of their various applications in chemical sensors, photochemistry, and electroluminescent display^[25-26]. Thus, the photoluminescent properties of **1** in the solid state have been investigated at room temperature. As illustrated in Fig.5, the intense emission bands at 447 nm ($\lambda_{\text{ex}}=330\text{ nm}$) for **1** are observed. The neutral Hpyim exhibit fluorescent emission bands at 505 nm ($\lambda_{\text{ex}}=370\text{ nm}$). In comparison

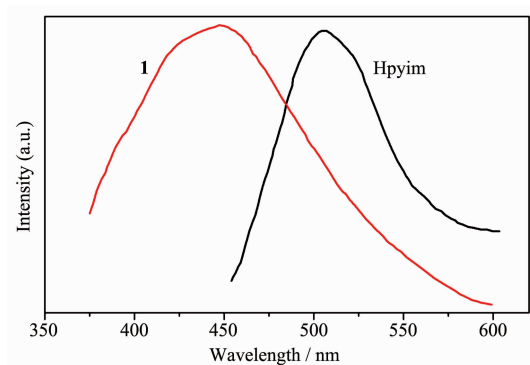


Fig.5 Photoluminescent spectrum of **1** and neutral hpyim in the solid state at room temperature

with the free ligands, the emission maximum of **1** has changed. It is possible that a combination of several factors together^[27], including charge-transfer transition between pym anions and metal centers, pym anions coordinating to the metal centers, which effectively increases the rigidities of the ligands and reduces the loss of energy by radiationless decay, and a change in the HOMO and LUMO energy levels of deprotonated BIPA anions. These observations indicate that the condensed polymeric materials may be excellent candidates for potential photoactive materials, since they are thermally stable and insoluble in common polar and nonpolar solvents.

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