

苯基多羧酸及含氮配体构筑的三维框架结构锌配位聚合物的合成、晶体结构和荧光性质

汪鹏飞^{*1} 方 勤² 吴国志¹ 汪 新¹

(¹池州学院材料与化学工程系, 化学材料与工程实验中心, 池州 247000)

(²国家非金属矿深加工产品质量监督检验中心, 池州 247000)

摘要: 以醋酸锌、5-溴-1,2,4-苯基三羧酸(BTCAH₃)和 4,4'-联吡啶(4,4'-bipy)为原料, 在水热条件下合成了 1 个三维框架结构化合物[Zn₃(BTCA)₂(4,4'-bipy)₂](**1**), 利用红外光谱、元素分析、热重、X-粉末衍射以及 X-单晶衍射对该化合物进行了表征。化合物 **1** 是单斜晶系, C2/c 空间群。在化合物 **1** 中, 锌离子通过 BTCA³⁻配体的羧酸氧原子形成一个具有 3-节点、4-连接的三维框架结构。4,4'-联吡啶配体在框架结构中连接锌离子。另外, 研究了该化合物的热稳定性和固体荧光性质。

关键词: 金属有机框架; 晶体结构; 多羧酸配体; 荧光性质

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Synthesis, Crystal Structure and Luminescent Property of a Three-Dimensional Framework Zinc Coordination Polymer Constructed from the Benzenemulticarboxylic Acid and N-donor Ligands

WANG Peng-Fei^{*1} FANG Qin² WU Guo-Zhi¹ WANG Xin¹

(¹Center of Chemical Materials and Engineering Experiment, Department of Materials and Chemical Engineering, Chizhou College, Chizhou, Anhui 247000, China)

(²National Center of Supervision & Inspection on Nonmetallic Mineral Equipment Quality, Chizhou Anhui 247000, China)

Abstract: A novel coordination polymer, [Zn₃(BTCA)₂(4,4'-bipy)₂](**1**) (BTCAH₃=5-bromobenzene-1,2,4-tricarboxylic acid, 4,4'-bipy=4,4'-bipyridine) has been synthesized utilizing Zn(OAc)₂·2H₂O, the rigid 5-bromobenzene-1,2,4-tricarboxylic acid and 4,4'-bipy under the hydrothermal reaction. Compound **1** was characterized by infrared spectroscopy, elemental analysis, thermogravimetric analysis and single crystal X-ray diffraction analysis. In **1**, the Zn(II) ions are linked through the carboxylate oxygen atoms of the BTCA³⁻ anions, forming a three-dimensional framework structure with 3-nodal and 4-connected net with Schläfli symbol of (4·7·8⁴)₂(4·7⁴·8)₂(7⁴·8²). The 4,4'-bipy ligand coordinates the Zn(II) ions in the framework. In addition, the thermal stability and luminescent properties of compound **1** were also investigated in this paper. CCDC: 811925.

Key words: metal-organic frameworks; crystal structure; multicarboxylate ligand; luminescent property

0 Introduction

Coordination polymers (CPs) assembled through

the coordination bonds between metal ions and multifunctional organic ligands are of current interest due to not only their intrinsic topological structures,

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*通讯联系人。E-mail: wangpfchem@gmail.com

but also their potential applications in catalysis^[1-3], gas storage/separation^[4-5], ion exchange^[6-7], sensing^[8], optics^[9-10], magnetism^[11-13], and so on. Most of these compounds, the structural diversities were exhibited by changing the synthetic strategy of CPs, solvent, ligand to metal salts ratio, the reaction temperature, the pH value of reaction system, the counter ions, ligand substituent^[14-17]. As a class of important organic ligands, the rigid benzenemulticarboxylic acids provide reliable coordination modes, forming many coordination polymers with new topologies and useful properties, such as benzene-dicarboxylic acids, benzene-tricarboxylic acids and benzene-tetracarboxylic acids^[18-19]. However, the metal coordination polymers based the benzenemulticarboxylic acids with the halogen substitution groups have not been well documented^[20-22]. The 1,2,4-benzenetricarboxylic acid (H_3btc) has proven to be a good candidate for construction of novel coordination polymers because of its rigidity in conformation as well as varieties in coordination modes and numbers^[23-25]. On the other hand, the combination of benzenemulticarboxylate ligands with N-donor auxiliary ligands is a good choice for the construction of novel coordination polymers. To further understand the ability of the benzenemulticarboxylate containing the halogen substitution groups producing new metal coordination polymers. In this study, we have selected the 5-bromobenzene-1,2,4-tricarboxylic acid ($BTCAH_3$) ligand and the ancillary ligand 4,4'-bipy to assemble new metal coordination polymers with interesting structure and physical properties. This paper presents the synthesis, crystal structure, thermal stability and luminescent properties of a new three-dimensional coordination polymer $[Zn_3(BTCA)_2(4,4'-bipy)_2](1)$.

1 Experimental

1.1 Materials and methods

All commercially available chemicals are of reagent grade and used as received without further purification. IR (KBr pellets) spectra were recorded in the 400~4 000 cm^{-1} range using a Bruker Spectrum One FTIR spectrometer. Elemental analyses were carried out on PE 240C Elemental Analyzer.

Thermogravimetric analyses (TGA) were performed with a Perkin Elmer Pyris 1 TGA instrument in the range of 30~800 $^{\circ}C$ under a nitrogen flow at a heating rate of 10 $^{\circ}C \cdot min^{-1}$. Powder X-ray diffraction patterns were performed on a Bruker D8 diffractometer using Cu $K\alpha$ radiation ($\lambda=0.154\ 056\ nm$). Luminescent spectra for polycrystalline samples were measured at room temperature on a Perkin Elmer LS 55 fluorescence spectrometer.

$[Zn_3(BTCA)_2(4,4'-bipy)_2](1)$: A mixture of $Zn(OAc)_2 \cdot 2H_2O$ (33 mg, 0.15 mmol), $BTCAH_3$ (29 mg, 0.1 mmol), 4,4'-bipy (16 mg, 0.1 mmol) in H_2O (10 mL) was placed in a perr Teflon-lined stainless steel vessel (25 mL), and then the vessel was sealed and heated at 160 $^{\circ}C$ for 3 d. After being slowly cooled to room temperature, colorless needle-like crystals of **1** were collected (yield: 45%, based on Zn). Anal. Calcd. for $C_{38}H_{20}Br_2N_4O_{12}Zn_3$ (%): C 42.24, H 1.87, N 5.18; Found (%): C 42.04, H 1.98, N 5.03. IR spectrum (cm^{-1}): 3 414 (w), 1 603 (s), 1 482 (m), 1 377 (s), 1 217 (w), 1 061 (w), 1 007 (w), 919 (w), 815 (m), 731 (w), 632 (w), 562 (w). The positions of experimental diffraction peaks accord with the simulated PXRD patterns well, which indicate the phase purity of the as-synthesized sample (Fig.S2)

1.2 Crystallographic studies

Suitable single crystal of **1** with dimensions 0.12 mm×0.08 mm×0.05 mm was selected and mounted in air onto thin glass fibres. **1** was measured at room temperature on a Bruker SMART APEX II CCD diffractometer with graphic-monochromatic Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ nm$). The data were collected in the θ range 1.85° to 26.00°, using a narrow-frame method with scan widths of 0.30° in ω and exposure of 10 s per frame. Numbers of collected and unique reflections of **1** are 1 0307 and 3 818 ($R_{int}=0.060\ 1$). The data were integrated using Siemens SAINT program^[26], with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path through the detector faceplate. Absorption corrections were applied. The structure was solved by directed methods and refined on F^2 by full-matrix least squares using SHELXS-97^[27] and SHELXL-97^[28]. All the non-hydrogen atoms were

refined anisotropically. All the hydrogen atoms were put in calculated positions. All hydrogen atoms were refined isotropically with isotropic parameters related to the non-hydrogen atoms to which they are bonded.

Crystallographic and refinement details of **1** are listed in Table 1. Selected bond lengths and angles are given in Table 2.

CCDC: 811925.

Table 1 Crystallographic data for compound **1**

Empirical formula	C ₃₈ H ₂₀ Br ₂ N ₄ Zn ₃ O ₁₂	<i>V</i> / nm ³	3.884 9(9)
Formula weight	1 080.51	<i>Z</i>	4
Crystal system	Monoclinic	<i>D_c</i> / (g·cm ⁻³)	1.847
Space group	<i>C2/c</i>	<i>F</i> (000)	2128
<i>a</i> / nm	1.5445(2)	Goodness of fit on <i>F</i> ²	1.077
<i>b</i> / nm	1.8419(2)	<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>)) ^a	0.039 4, 0.111 5
<i>c</i> / nm	1.4954(2)	<i>R</i> ₁ , <i>wR</i> ₂ (All data) ^a	0.047 8, 0.113 8
β / (°)	114.044(3)	(Δρ) _{max} , (Δρ) _{min} / (e·nm ⁻³)	941, -996

$$^a R_1 = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|; wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$$

Table 2 Selected bond lengths (nm) and angle (°) for compound **1**

C(7)-O(1)	0.1251(4)	C(9)-O(6)	0.126 1(5)	Zn(2)-O(4)	0.193 2(2)
C(7)-O(2)	0.1239(4)	Zn(1)-N(1)	0.215 2(3)	Zn(2)-O(1)C	0.195 2(3)
C(8)-O(3)	0.1242(4)	Zn(1)-O(2)	0.213 6(3)	Zn(2)-O(6)F	0.190 9(3)
C(8)-O(4)	0.1261(4)	Zn(1)-O(3)	0.212 0(2)	C(9)-O(5)	0.122 4(5)
Zn(2)-N(2)	0.2022(3)				
O(3)E-Zn(1)-O(3)	86.92(13)	O(3)-Zn(1)-N(1)E	90.73(10)	N(1)E-Zn(1)-N(1)	95.31(17)
O(3)E-Zn(1)-O(2)	106.08(10)	O(2)-Zn(1)-N(1)E	88.30(11)	O(6)F-Zn(2)-O(4)	100.29(12)
O(3)-Zn(1)-O(2)	80.68(10)	O(2)E-Zn(1)-N(1)E	85.57(11)	O(6)F-Zn(2)-O(1)C	125.62(13)
O(3)E-Zn(1)-O(2)E	80.68(10)	O(3)E-Zn(1)-N(1)	90.73(10)	O(4)-Zn(2)-O(1)C	108.37(12)
O(3)-Zn(1)-O(2)E	106.08(10)	O(3)-Zn(1)-N(1)	164.81(11)	O(6)F-Zn(2)-N(2)	110.27(14)
O(2)-Zn(1)-O(2)E	170.90(14)	O(2)-Zn(1)-N(1)	85.57(11)	O(4)-Zn(2)-N(2)	121.08(13)
O(3)E-Zn(1)-N(1)E	164.81(11)	O(2)E-Zn(1)-N(1)	88.30(11)	O(1)C-Zn(2)-N(2)	93.10(13)

^aSymmetry transformations used to generate equivalent atoms: A: $-x+3/2, -y+3/2, -z$; B: $-x+3, -y+1, -z+1$; C: $-x+2, -y+1, -z+1$;

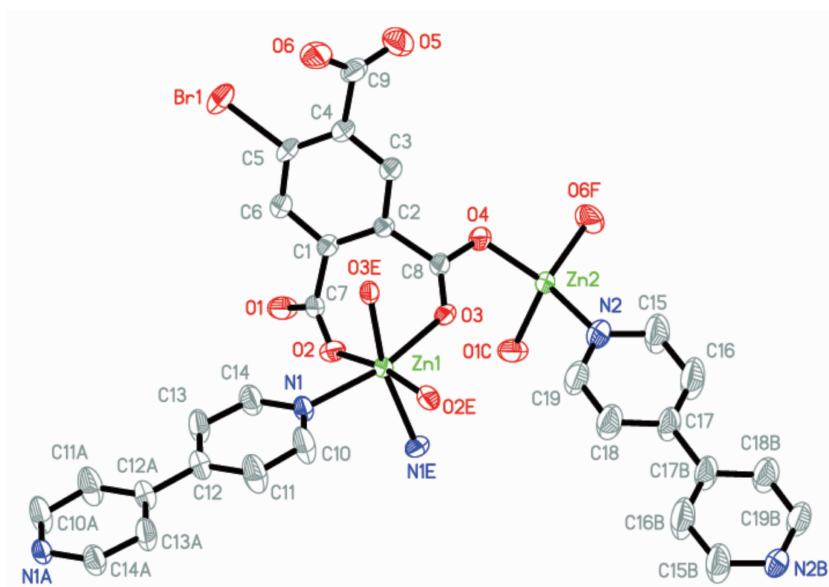
D: $x-1/2, -y+1/2, z-1/2$; E: $-x+2, y, -z+1/2$; F: $x+1/2, -y+1/2, z+1/2$

2 Results and discussion

2.1 Description of crystal structure

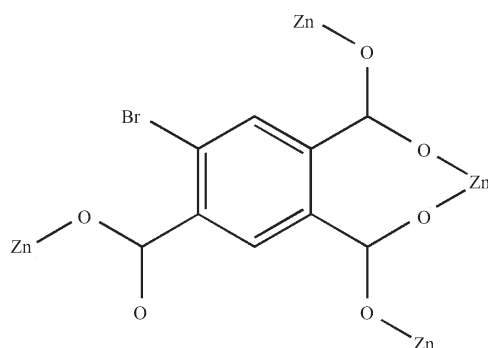
Compound **1** crystallizes in a monoclinic space group *C2/c*. The asymmetric unit consists of one and a half Zn(II) ions, one BTCA³⁻, one 4,4'-bipy molecule, as shown in Fig.1. Zn1 is six coordinated with octahedral coordination geometry defined by two nitrogen atoms from two different 4, 4'-bipy ligands, four carboxylate oxygen atoms from two different BTCA³⁻. Zn2 has a tetrahedral coordination environ-

ment surrounded by three carboxylate oxygen atoms from three different BTCA³⁻ and one nitrogen atom from the 4,4'-bipy ligand. Zn-O bond distances are in the range of 0.190 9 (3)~0.213 6 (3) nm, and Zn-N bond distances are 0.202 2 (3) and 0.215 2 (3) nm, respectively. The completely deprotonated BTCA³⁻ ligand displays a kind of coordination mode, as illustrated in Scheme 1, which adopts μ₅ bridging mode to link four different Zn atoms. The Zn1 and Zn2 atoms are linked by the oxygen atoms of the carboxylate group, forming to a three dimensional



50% thermal ellipsoids. All H atoms are omitted for clarity. Symmetry code: A: $-x+3/2, -y+3/2, -z$; B: $-x+3, -y+1, -z+1$; C: $-x+2, -y+1, -z+1$; D: $x-1/2, -y+1/2, z-1/2$; E: $-x+2, y, -z+1/2$; F: $x+1/2, -y+1/2, z+1/2$

Fig.1 Building unit of **1** in ORTEP view

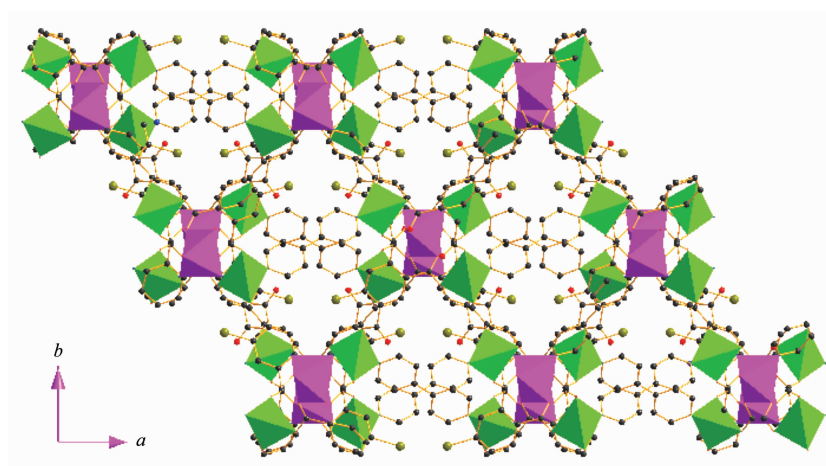


Scheme 1 Coordination mode of the BTCA³⁻ anion in **1**

framework structure (Fig.2). The 4,4'-bipy ligand coordinates the Zn atoms in the framework structure.

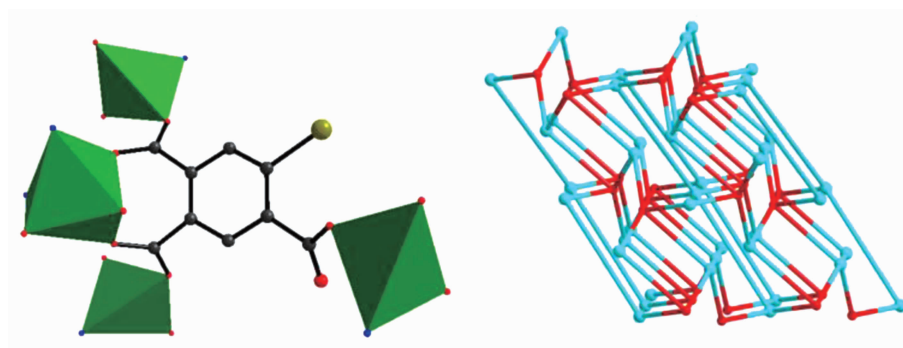
In order to better understand the structure of **1**, a topological analysis is performed using TOPOS 4.0 program^[29-31]. Each BTCA³⁻ anion is linked to four Zn (II) ions (Fig.3a), and each Zn1 and Zn2 atoms are linked to two and three BTCA³⁻ anion, respectively. Hence, the BTCA³⁻ anion can be viewed as 4-connected node, both Zn1 and Zn2 atoms can be regarded as 3-connector by omitting the 4,4'-bipy ligands (Fig.3b). According to the simplification principle, the resulting structure of **1** is a 3-nodal and 4-connected net with Schläfli symbol of $(4 \cdot 7 \cdot 8^4)_2(4 \cdot 7^4 \cdot 8)_2(7^4 \cdot 8^2)$.

It is worthwhile to note that the a three-dimensional coordination polymer $[Zn_6(btc)_4(4,4'-bipy)_5]_n$ through the reaction based on the $Zn(NO_3)_2 \cdot 6H_2O$, 1,2,4-benzenetricarboxylic acid (H_3btc) and 4,4'-bipy has been reported by Long and co-workers^[32], the structures of the two compounds are completely different, although they were synthesized under similar hydrothermal conditions expect that the 5-bromobenzene-1,2,4-tricarboxylic acid ($BTCAH_3$) instead of H_3btc . The halogen substitution group may play an important role in the formation of the target product. In order to understand the role of 4,4'-bipy in the formation of **1**. The reaction mixture of the absent 4,4'-bipy has been synthesized under the



Color codes: ZnO_4N_2 , pink; ZnO_3N , bright green

Fig.2 Structure of **1** packing along the *c* axis



Color codes: BTCA^{3-} , red; Zn(II) ions, blue

Fig.3 (a) Connection mode of each BTCA^{3-} ligand to the Zn(II) ions; (b) Schematic representation of the topology of **1**

above condition, only the colorless solution is obtained. According to the experimental result, the 4,4'-bipy is found to be essential in the formation of **1**.

2.2 IR spectrum

In the IR spectra of **1**, the features at $1\,603\text{ cm}^{-1}$ are attributed to the asymmetric stretching vibrations of the two carboxylate groups, and the strong vibration appearing around $1\,482$ and $1\,377\text{ cm}^{-1}$ corresponding to symmetric stretching vibrations of the carboxylate groups. The absence of the characteristic bands in the range of $1\,760\sim 1\,680\text{ cm}^{-1}$ attributed to protonated carboxylate groups in the compound indicates complete deprotonation upon reaction with Zn^{2+} in the compound, in agreement with the single crystal X-ray diffraction analysis^[33], comparable with those observed in the IR spectrum of the BTCAH_3 free ligand ($1\,720$

cm^{-1}).

2.3 Thermogravimetric analysis

To investigate the thermal stability of the compound, thermal analysis was carried out at the rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ under nitrogen atmosphere. As shown in Fig.S3, compound **1** is stable up to $400\text{ }^\circ\text{C}$, which reveals the strong coordinated bonds as well as the rigid framework structure in **1**. Above this temperature, the framework started to collapse accompanied by the decomposition of the organic components, leading to the formation of a stoichiometric amount of ZnO (Obsd. 41.50% , Calcd. 38.80%). Relatively high thermal stabilities of coordination polymers are also found in the other framework structures compounds containing the rigid multicarboxylate ligands with N-donor auxiliary ligands^[34-36].

2.4 Luminescent property

The metal-organic hybrid coordination polymers with d^{10} electronic configuration of metal centers are promising candidates for photoactive materials with potential applications^[37-39]. The luminescent properties of compound **1** and the free BTCAH₃ ligand are studied in the solid state at room temperature. As illustrated in Fig.4, the intense broad emission bands at 484 nm ($\lambda_{\text{ex}}=370$ nm) for **1**. The free organic BTCAH₃ ligand shows intense emission bands at 550 nm ($\lambda_{\text{ex}}=380$ nm). The ligand emission peak could be probably attributed to the π^*-n or $\pi^*-\pi$ transition^[40-42]. Obviously, the emission arising from the free ligand is not observed. The absence of ligand-based emission suggested energy transfer from the ligand to the central metal ions during luminescence. Thus, the luminescence could be assigned to the emission of ligand-to-metal charge-transfer (LMCT)^[9-10].

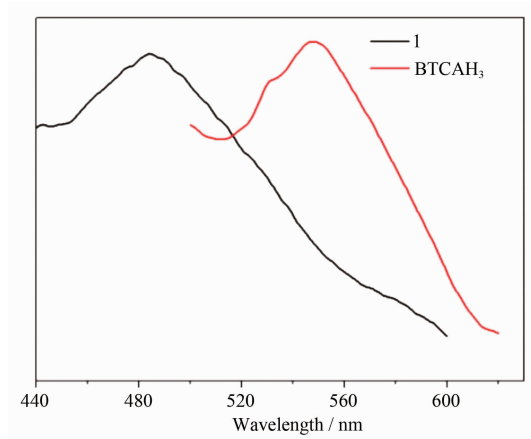


Fig.4 Solid-state emission spectrum of **1**

3 Conclusions

In summary, this paper reports a new Zn(II) coordination polymer, $[\text{Zn}_3(\text{BTCA})_2(4,4'\text{-bipy})_2]$ (**1**) under hydrothermal reaction. The compound was characterized by single crystal X-ray diffraction, IR spectroscopy, elemental analysis, thermogravimetric analysis and luminescent property. Compound **1** possesses a three-dimensional framework structure, which is a novel example 3-nodal and 4-connected net with $(4\cdot7\cdot8^4)_2(4\cdot7^4\cdot8)_2(7^4\cdot8^2)$ topological network. In addition, the thermal stability and luminescent properties of **1** were investigated. Further work is in

progress to explore new inorganic-organic hybrid materials based on the 5-bromobenzene-1,2,4-tricarboxylic acid ligand with interesting structures and functional properties.

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