

基于 1,1'-苯乙炔-3,3',5,5'-四羧酸的配位聚合物: 水热合成、结构和荧光性质

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摘要: 合成并表征了配合物 **1**, $[\text{Zn}_2(\text{EBTC})(\text{BPDO})(\text{DMSO})(\text{H}_2\text{O})_2]_n$, 其中 EBTC 为 1,1'-苯乙炔-3,3',5,5'-四羧酸根, BPDO 为 4,4'-二吡啶基 1,1'-二氧化物, DMSO 为二甲亚砜。 **1** 沿着 *b* 轴的方向具有类似于三腿梯子状的链状结构, 链与链之间通过氢键作用和 π - π 堆积作用形成了三维超分子结构。在室温条件下 **1** 表现出了荧光性质。

关键词: 配位聚合物; 氢键作用; 溶剂热合成; 荧光性质

中图分类号: O614.24^{*1}

文献标识码: A

文章编号: 1001-4861(2011)03-0542-05

Solvothermal Synthesis, Crystal Structure and Photoluminescence Property of a Coordination Polymer Based on 1,1'-Ethynebenzene-3,3',5,5'-tetracarboxylate

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Abstract: A novel Zn^{2+} coordination polymer, $[\text{Zn}_2(\text{EBTC})(\text{BPDO})(\text{DMSO})(\text{H}_2\text{O})_2]_n$ (**1**) (EBTC=1,1'-ethynebenzene-3,3',5,5'-tetracarboxylate; BPDO=4,4'-bipyridine 1,1'-dioxide) has been synthesized and characterized. **1** has the three-leg-ladder-like architecture along the crystallographic *a*-axis direction, in which the adjacent three-leg-ladder-like chains are linked together to build 3D supermolecules via intermolecular hydrogen bond and $\pi \cdots \pi$ stacking interactions. It displays fluorescent emission at room temperature. CCDC: 806016.

Key words: coordination polymer; hydrogen bond interaction; solvothermal synthesis; photoluminescence property

0 Introduction

Coordination polymers have been flourishing in the recent years^[1]. The majority of the numerous coordination polymers reported are normally constructed by linking metal ions with multidentate bridging ligands, and a great numerous of one-, two- and three-dimensional (1D, 2D and 3D) coordination polymers have been synthesized through the judicious selection

of versatile organic ligands, appropriate metal ions and reaction conditions^[2-5]. Aromatic polycarboxylates have been found to be favorable ligands since the multipotential oxygen donors after deprotonation can adopt different coordination modes and lead to diverse coordination networks as well as interesting optical, magnetic and hydrogen storage properties^[6-8].

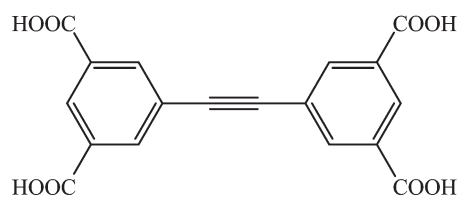
Up to now, even if many metal carboxylate frameworks have been reported in literatures, the

收稿日期: 2010-09-10。收修改稿日期: 2010-11-25。

国家自然科学基金资助项目(No.20871068)。

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coordination chemistry of the 1,1'-ethynebenzene-3,3',5,5'-tetracarboxylate acid (H₄EBTC, Scheme 1) remains largely unexplored^[9-10]. Most recently, we have successfully synthesized one microporous cupric MOFs based on H₄EBTC, which exhibits excellent uptake of H₂, CH₄, CO₂ and C₂H₂^[9]. Taking advantages of structures and properties of H₄EBTC and BPDO, we expect to design and synthesize new functional metal-organic frameworks. Herein we present the solvothermal synthesis, crystal structure and photoluminescence property of a novel Zn²⁺ coordination polymer [Zn₂(EBTC)(BPDO)(DMSO)(H₂O)₂]_n (**1**) based on the molecular building blocks (MBBs).



Scheme 1 Structure of H₄EBTC

1 Experimental

1.1 Materials and measurements

All commercially available chemicals were of analytical grade and used as received without further purification. Elemental analyses (C, H, S and N) were carried out on a Perkin-Elmer 240 analyzer. The FTIR spectra were obtained on a VECTOR TM 22 spectrometer with KBr pellets in the 400~4 000 cm⁻¹ region. TGA-DTA diagrams were recorded by a CA Instruments DTA-TGA 2960 type simultaneous analyzer heating from 293 to 1073 K in nitrogen atmosphere at a rate of 20 K · min⁻¹. Powder X-ray diffraction (PXRD) data were recorded on a Shimadzu XRD-6000 diffracto-

meter with Cu Kα (λ=0.154 056 nm) radiation at room temperature with a scan speed of 5° · min⁻¹ and a step size of 0.02° in 2θ. Photoluminescence spectra in the solid state were recorded with a Hitachi 850 fluorescence spectrophotometer.

1.2 Preparation of complex 1

Zn(NO₃)₃ · 6H₂O (15 mg, 50.4 mmol), H₄EBTC, (5.0 mg, 0.014 mmol), DMF (0.15 mL), DMSO (0.15 mL) and BPDO (1.3 mg, 0.007 mmol) were heated at 65 °C for 24 h to give a pellucid solution, then 0.4 mL water was added to the clear solution, and the mixture was heated at 120 °C for 12 h. Colorless block-shaped [Zn₂(EBTC)(BPDO)(DMSO)(H₂O)₂]_n was achieved after slowly cooling down to room temperature (yield *ca.* 36% based on Zn(NO₃)₃ · 6H₂O). Elemental analysis calcd. for C₃₀H₂₄N₂O₁₃SZn₂ (%): C 45.96, H 3.06, N 3.57, S 4.08; Found(%): C 46.20, H 3.10, N 3.59, S 4.11. Selected IR data (cm⁻¹): 3 408(b), 1 573(s), 1 363(s), 1 492(s), 1 010(w), 721(w).

1.3 X-ray crystallography

Single crystal X-ray diffraction data were collected on a Bruker Smart Apex II CCD diffractometer at 153 K using graphite monochromated Mo Kα radiation (λ=0.071 073 nm). The structure was solved by direct method and refined with full-matrix least squares technique using the SHELXTL package^[11]. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were put in calculated positions. Main data of collection and refinement details of **1** are summarized in Table 1. Selected bond lengths and angles are listed in Table 2. Hydrogen bond distances and angle are listed in Table 3.

CCDC: 806016.

Table 1 Crystal data and structure refinement for complex 1

Empirical formula	C ₃₀ H ₂₄ N ₂ O ₁₃ SZn ₂	β / (°)	78.124(10)
Formula weight	783.31	Volume / nm ³	1.438
Temperature / K	153(2)	Z	2
Wavelength / nm	0.071 073	F(000)	796
Crystal system	Triclinic	Crystal size / mm	0.3×0.26×0.21
Space group	P $\bar{1}$	θ range for data collection / (°)	2.0~26.0
a / nm	0.833 2(8)	Goodness-of-fit on F ²	1.08
b / nm	1.019 9(9)	Final R indices (I>2σ(I))	R ₁ =0.052 9, wR ₂ =0.208 3
c / nm	1.745 1(15)		

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

Zn1-O1	0.194 9(4)	Zn1-O4 ⁱ	0.202 9(5)	Zn1-O13	0.199 4(5)
Zn1-O11	0.203 4(5)	Zn1-O3 ⁱ	0.249 0(54)	Zn2-O7 ⁱⁱ	0.199 8(4)
Zn2-O5 ⁱ	0.202 6(4)	Zn2-O9	0.207 3(5)	Zn2-O8	0.199 4(4)
Zn2-O12	0.223 2(5)				
O1-Zn1-O13	114.59(19)	O1-Zn1-O4 ⁱ	101.91(18)	O13-Zn1-O4	125.9(2)
O1-Zn1-O11	105.51(19)	O4-Zn1-O11	104.9(2)	O13-Zn1-O11	102.3(2)
O8-Zn2-O7 ⁱⁱ	137.61(18)	O8-Zn2-O5 ⁱ	113.64(18)	O7-Zn2-O5 ⁱ	108.59(18)
O8-Zn2-O9	89.58(18)	O7-Zn2-O9	94.65(19)	O5-Zn2-O9	89.11(19)
O8-Zn2-O12	94.26(18)	O7-Zn2-O12	84.46(2)	O5-Zn2-O12	86.71(18)
O9-Zn2-O12	175.20(17)				

Symmetry codes: ⁱ $x, 1+y, z$; ⁱⁱ $-x, 1-y, -z$.

Table 3 Hydrogen bond distances and angles

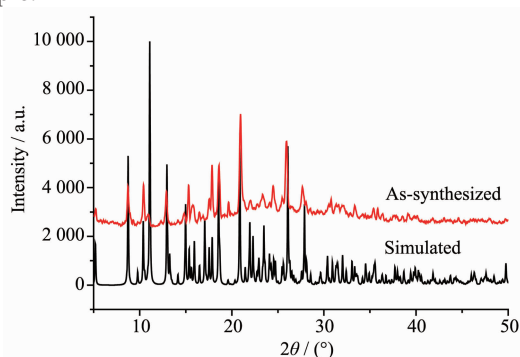
D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H-A}) / \text{nm}$	$d(\text{D-A}) / \text{nm}$	$\angle \text{DHA} / (^\circ)$
O11-H11A...O10 ⁱⁱⁱ	0.0850	0.1910	0.273 2(8)	163.00
O11-H11B...O5 ^{iv}	0.0850	0.2240	0.296 1(7)	142.00
O12-H12A...O6 ^v	0.0850	0.2060	0.273 6(7)	136.00
O12-H12B...O10 ^{vi}	0.0850	0.1850	0.269 8(7)	177.00

Symmetry codes: ⁱⁱⁱ $1-x, 2-y, 1-z$; ^{iv} $-x, -y, 1-z$; ^v $x, 1+y, z$; ^{vi} $-1+x, -1+y, z$.

2 Results and discussion

2.1 IR spectra and PXRD data

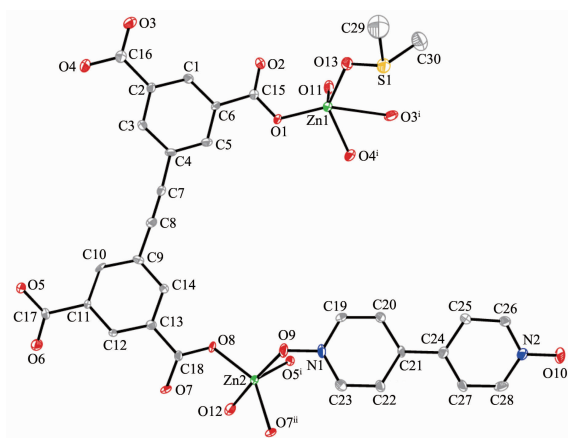
IR spectra of **1** showing strong absorption bands around 1 362, 1 578 and 1 627 cm^{-1} can be assigned to coordinated carboxylate groups^[12]. The broad and strong absorption bands in the range of 3 350~3 500 cm^{-1} correspond to the presence of water molecules in **1**. The experimental and stimulated powder X-ray diffraction (PXRD) patterns are given in Fig.1, which are consistent with each other to indicate the good purity of sample.

Fig.1 Experimental and simulated PXRD patterns of **1**

2.2 Crystal structure description

Crystal of **1** belongs to triclinic system with space

group $P\bar{1}$. Its asymmetric unit consists of two different Zn^{2+} ions, one deprotonated EBTC^{4-} , one BPDO, one coordinated DMSO molecule and two coordinated H_2O molecules as shown in Fig.2. Two crystallographically independent Zn^{2+} ions exhibit different coordination geometries. Zn1 is coordinated by five oxygen atoms from H_2O (O11), DMSO (O13) and EBTC^{4-} (O1, O3ⁱ and O4ⁱ) to form a distorted trigonal bipyramidal coordination environment with $\tau=0.543$ ($\tau=(\beta-\alpha)/60$, α and β are the bigger bond angles around Zn1 center, which are 125.9(2)° and 158.5(2)°, respectively. Usually, $\tau=0$ for ideal square pyramid and $\tau=1$ for ideal trigonal bipyramid^[13], in which O4ⁱ, O11 and O13 atoms are lying on the equatorial plane and O1 and O3ⁱ atoms are on the axial positions. The Zn-O distances are in the range of 0.194 9(4)~0.203 4(5) nm. Zn2 coordinates five oxygen atoms from H_2O (O12), BPDO (O9) and EBTC^{4-} (O5ⁱ, O7ⁱⁱ and O8), where a distorted trigonal bipyramidal coordination geometry with $\tau=0.627$ was formed (α and β are 137.61 (18)° and 175.20 (17)°, respectively^[13]). The distorted trigonal bipyramidal geometry of Zn2 atoms is composed of O5ⁱ, O7ⁱⁱ, O8, O12 and O9 atoms with O5ⁱ, O7ⁱⁱ and O8 atoms lying the equatorial

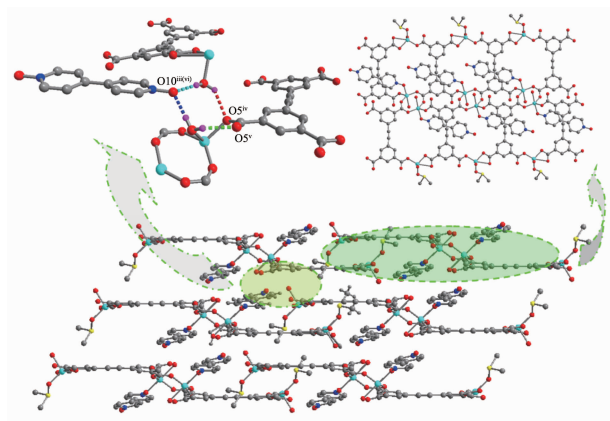


Symmetry codes: $i: x, 1+y, z$; $ii: -x, 1-y, -z$

Fig.2 ORTEP plot of **1** showing the local coordination environment of Zn1 and Zn2 ions with thermal ellipsoids at 50% probability

plane and the axial positions being occupied by O12 and O9 atoms. The Zn-O distances around Zn2 are in the range of 0.199 4(4)~0.223 2(5) nm.

As illustrated in Fig.3, each EBTC⁴⁻ ligand bridges five Zn²⁺ ions via four carboxylate groups in monodentate and bidentate coordination modes, respectively. The oxygen atoms (O2, O6) of EBTC⁴⁻ are uncoordinated. The two neighboring trigonal bipyramids comprising of Zn2 atoms are connected through two carboxylate groups (O7ⁱⁱ, O8) into a 8-membered ring dinuclear subunit with Zn-Zn distance of 0.343 1 nm. Each dinuclear Zn2 subunit is coordinated by four EBTC⁴⁻ ligands, and every Zn1-type coordination polyhedron is connected by two EBTC⁴⁻ ligands to form three-leg-ladder-like architecture along the crystallographic *b*



Symmetry codes: $iii: 1-x, 2-y, 1-z$; $iv: -x, -y, 1-z$; $v: x, 1+y, z$; $vi: -1+x, -1+y, z$

Fig.3 Perspective view of stacking along *b* direction

axis direction.

The adjacent three-leg-ladder-like chains are linked together to build 3D supermolecules via intermolecular hydrogen bond interactions between O10/O5ⁱ and O11 with O11-H11A...O10 0.273 2 (8) nm, O11-H11B...O5ⁱ 0.296 1(7) nm in the *ac* plane as well as between O10 and O12 with O12-H12B...O10 0.269 8(7) nm along the *b* direction. Besides the intermolecular hydrogen bond interactions, **1** also has intramolecular hydrogen bond interaction between O12 and O6 with O12-H12A...O6 0.273 6 (7) nm in the *ac* plane (Table 3). Moreover it is worth noting that a shorter contact of 0.356 8 nm between the center of the ethynyl fragment and the center of the phenyl ring is observed in the *ac* plane (Fig.4). Therefore, it is highly probable that there exists $\pi \cdots \pi$ stacking interactions between the superimposed phenyl ring and the ethynyl fragment. Moreover, slipped $\pi \cdots \pi$ interactions are also found between the offset face-to-face phenyl rings in the *ac* plane due to its centroid-centroid distance of 0.365 3 nm. In the meanwhile, shorter distances of 0.333 5 nm within adjacent BPDO molecules with dihedral angle of 11.768° and 0.328 0 nm between the BPDO and the EBTC⁴⁻ ligands with dihedral angle of 12.697° are also observed in the *ac* plane, respectively. They can be considered as aromatic interactions which are intermediate between slipped $\pi \cdots \pi$ interactions and edge-on C-H... π interactions^[14].

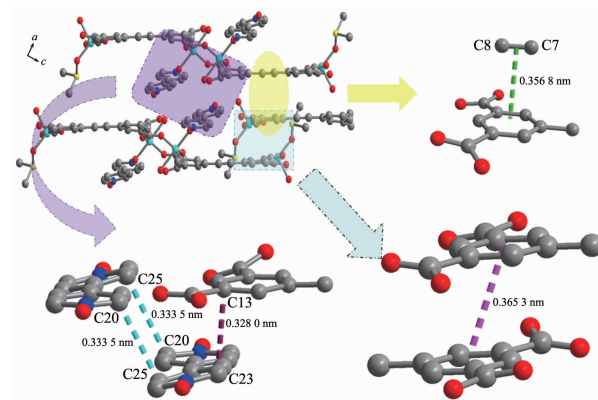


Fig.4 Perspective view of $\pi \cdots \pi$ stacking interactions along the *b* direction

2.3 Thermal analysis

Thermal gravimetric analysis (TGA) experiment was conducted to determine the thermal stability of **1**,

which is an important aspect for metal-organic frameworks. As shown in Fig.5, **1** shows three steps of weight loss. The first weight loss of 4.5% in the temperature of 40~100 °C corresponds to the liberation of two coordinated water molecules (calculated as 4.6%). The second weight loss of 9.2% in the temperature of 100~200 °C is attributed to the removal of coordinated DMSO molecule (calculated as 9.7%). The third weight loss of 22.0% is assigned to the loss of coordinated BPDO ligand (calculated as 21.7%). The coordination framework is collapsed when the temperature is higher than 440 °C.

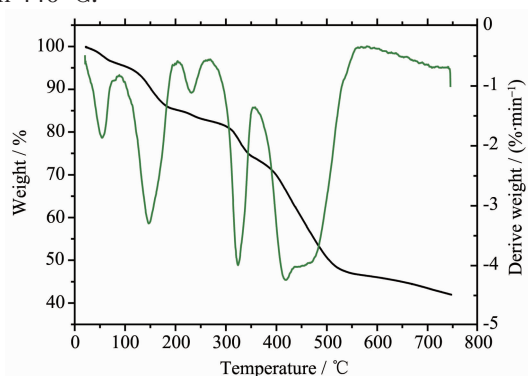


Fig.5 TGA plot of **1** in the temperature range of 25~750 °C

2.4 Photoluminescence

The luminescent property of **1** was investigated in the solid state at room temperature (25 °C), as depicted in Fig.6. It displays fluorescent emission bands at about 431 nm upon excitation at 365 nm. This band is probably assigned to the π - π^* fluorescent emission since similar emission is observed at 420 nm upon excitation at 342 nm for H₄EBTC. Compared with the emission of H₄EBTC, the emission band of **1** is shift to

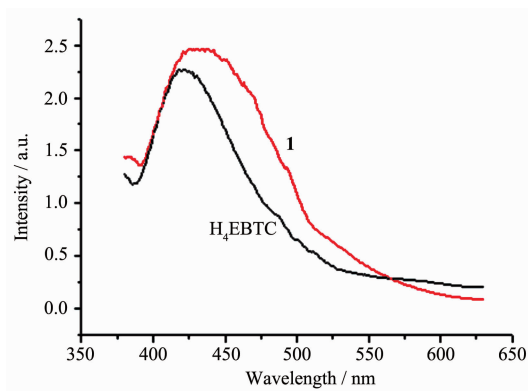


Fig.6 Emission spectra of **1** in the solid state at ambient temperature

low energy region. Due to its remarkable luminescence, it appears to be good candidate of novel hybrid inorganic-organic optic materials.

Acknowledgments: We thank the Nature Science Foundation of China for financial support (Grant No. 20871068) and the Center of Analysis and Determining of Nanjing University for their assistances. We also appreciate Dr. WANG Fang-Ming and Dr. KANG Ling-Chen for their kind help.

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