

# Synthesis, Structure and Photoluminescence of Two Zinc Carboxylate Polymers with Different Coordination Architectures

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The hydrothermal reaction of ZnO with benzene-1,4-dicarboxylic acid gave Zn·BDC·2H<sub>2</sub>O (**1**) and Zn·BDC·H<sub>2</sub>O (**2**) (BDC = benzene-1,4-dicarboxylate), respectively. Polymer **1** (C<sub>4</sub>H<sub>4</sub>O<sub>3</sub>Zn<sub>0.5</sub>) shows a one-dimensional zigzag chain structure built up from the alternate connection of tetrahedral ZnO<sub>4</sub> and BDC units. Polymer **2** (C<sub>4</sub>H<sub>3</sub>O<sub>2.5</sub>Zn<sub>0.5</sub>) possesses a three-dimensional framework containing infinite zigzag Zn···Zn···Zn pseudochains generated by five-coordinate zinc centers and a rectangular channel system including three groups of different straight channels along the [001], [010] and [60-1] directions. The two metal-organic polymeric compounds exhibit strong photoluminescent emission bands at 402 nm (λ<sub>ex</sub> = 260 nm) (for **1**) and at 344 nm and 385 nm (λ<sub>ex</sub> = 279 nm) (for **2**) in the solid state at room temperature.

**Keywords** metal-organic polymers, hydrothermal synthesis, structure, photoluminescence

## Introduction

The synthesis of metal-organic polymers has undoubtedly been a topic of special interest due to their host-guest interactions which have been tailored to a variety of industrial processes such as catalysis, adsorption and gas separation.<sup>1-5</sup> So far, many efforts have been dedicated to the exploration of metal-organic framework materials built up from metallic clusters and rigid organic building blocks. This strategy, as reported by the groups of Robson,<sup>6</sup> Yaghi<sup>7-11</sup> and others, utilizes rigid organic linkers for directly linking the metal clusters of known geometry to yield the desired extended networks, opening up the possibility of making metal-organic polymers with large voids and permanent porosity.

As known, polynuclear Zn—O—C clusters usually serve as large rigid network vertices joined by rigid carboxylate ligands to produce porous materials with robust structures. In this article, we assembled zinc ions and benzene-1,4-dicarboxylic acid into two polymeric structures, Zn·BDC·2H<sub>2</sub>O (**1**) and Zn·BDC·H<sub>2</sub>O (**2**) (BDC

= benzene-1,4-dicarboxylate), under hydrothermal conditions. Benzene-1,4-dicarboxylic acid has been a versatile ligand with the good binding ability as manifested by the formation of 1D, 2D and 3D polymeric structure systems.<sup>11-22</sup> Furthermore, X-ray crystal structure and photoluminescent properties of the two metal-organic polymers have been investigated.

## Experimental

### Materials and analyses

All chemicals were used as purchased without further purification. The infrared spectra were recorded within the 500—4000 cm<sup>-1</sup> region on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. Elemental analyses were conducted on a Perkin-Elmer 240C element analyzer. Thermogravimetric analyses (TGA) were performed on a NETZSCH STA 449C thermogravimetric analyzer under an atmospheric environment at a heating rate of 20 °C/min. The photoluminescent spectra were obtained on a Perkin-Elmer LS55 luminescence spectrometer.

### Preparation of Zn·BDC·2H<sub>2</sub>O (**1**) and Zn·BDC·H<sub>2</sub>O (**2**)

A mixture of zinc oxide (0.017 g, 0.2 mmol), benzene-1,4-dicarboxylic acid (0.033 g, 0.2 mmol) and distilled water (10 mL) with an empirical composition of 1:1:2778 was sealed in a Teflon-lined stainless steel autoclave and heated at 160 °C for 48 h under autogenous pressure to give colorless crystals of **1**. The resulting colorless crystals were collected by filtration, washed with distilled water and dried in air at ambient temperature to give a ca. 40% yield of **1** based on Zn. Anal. calcd for C<sub>4</sub>H<sub>4</sub>O<sub>3</sub>Zn<sub>0.5</sub>: C 36.23, H 3.02; found C 37.08, H 2.63.

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Received December 12, 2002; revised May 3, 2003; accepted June 4, 2003.

Project supported by the National Natural Science Foundation of China (No. 20128001).

Similar to the synthesis of **1**, the hydrothermal reaction of zinc oxide (0.017 g, 0.2 mmol), benzene-1,4-dicarboxylic acid (0.033 g, 0.2 mmol), glutamic acid (0.033 g, 0.2 mmol) and distilled water (10 mL) in a molar ratio of 1:1:1:2778 was performed at 160 °C for 48 h to give colorless crystals of **2**. The resulting colorless crystals were collected by filtration, washed with distilled water and dried in air at ambient temperature to give a ca. 68% yield of **1** based on Zn. Anal. calcd for  $C_4H_3O_{2.5}Zn_{0.5}$ : C 38.87, H 2.43; found C 39.68, H 2.94.

In addition, when we substituted lactamic acid or malic acid for glutamic acid, the formed compounds well correspond with polymer **2** on the basis of the powder X-ray diffraction.

### Crystallographic analyses

Crystallographic data for polymer **1** were recorded at room temperature on a Bruker-AXS Smart CCD diffractometer equipped with a normal-focus, 2.4 kW sealed tube X-ray source (graphite-monochromated Mo  $K\alpha$  radiation with  $\lambda = 0.071073$  nm) operating at 50 kV and 40 mA. Intensity data were collected in 1271 frames with increasing  $\omega$  (width of 0.3° and exposure time 30 s per frame). The structures were solved by direct methods and refined by full-matrix least-squares techniques against  $F^2$  using the SHELXTL-NT5.1 package.<sup>23</sup> All non-hydrogen atoms were refined anisotropically. The hydrogen atoms in all the phenylene groups were generated with idealized geometries and those of water molecules were found in the electron density map and refined isotropically. The data for polymer **2** were collected at room temperature on a Rigaku R-AXIS RAPID IP diffractometer. The structure was solved by Patterson methods and refined on  $F^2$  by full-matrix least-squares techniques using the SHELXTL-NT5.1 package.<sup>23</sup> Empirical absorption corrections ( $T_{\max} = 1.0872$  and  $T_{\min} = 0.8963$ ) and extinction corrections [extinction coefficient = 0.0117(12)] were applied. Anisotropic displacement parameters were refined for all non-hydrogen atoms. The hydrogen atoms of the phenylene groups and the water molecules were found in the electron density map and refined isotropically.

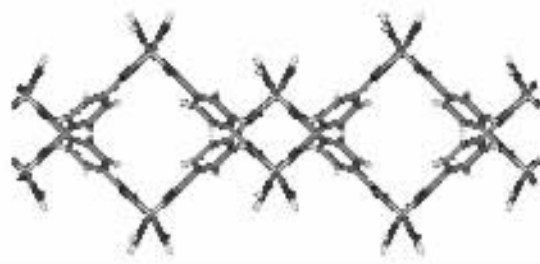
## Results and discussion

The elemental analysis for the two polymers shows that the contents of C, H and N in the polymers well correspond with the formula of  $Zn \cdot BDC \cdot 2H_2O$  and  $Zn \cdot BDC \cdot H_2O$ . The IR spectra reveal two strong bands of the carboxylic groups at 1630–1550  $cm^{-1}$  for the asymmetric vibration and at 1440–1300  $cm^{-1}$  for the symmetric vibration. The absence of the expected characteristic bands at around 1700  $cm^{-1}$  attributed to the protonated carboxylic groups indicates the complete deprotonated of BDC ligands on the reactions with Zn ions. Furthermore, the broad

bands for water molecules appear at around 3300  $cm^{-1}$ .

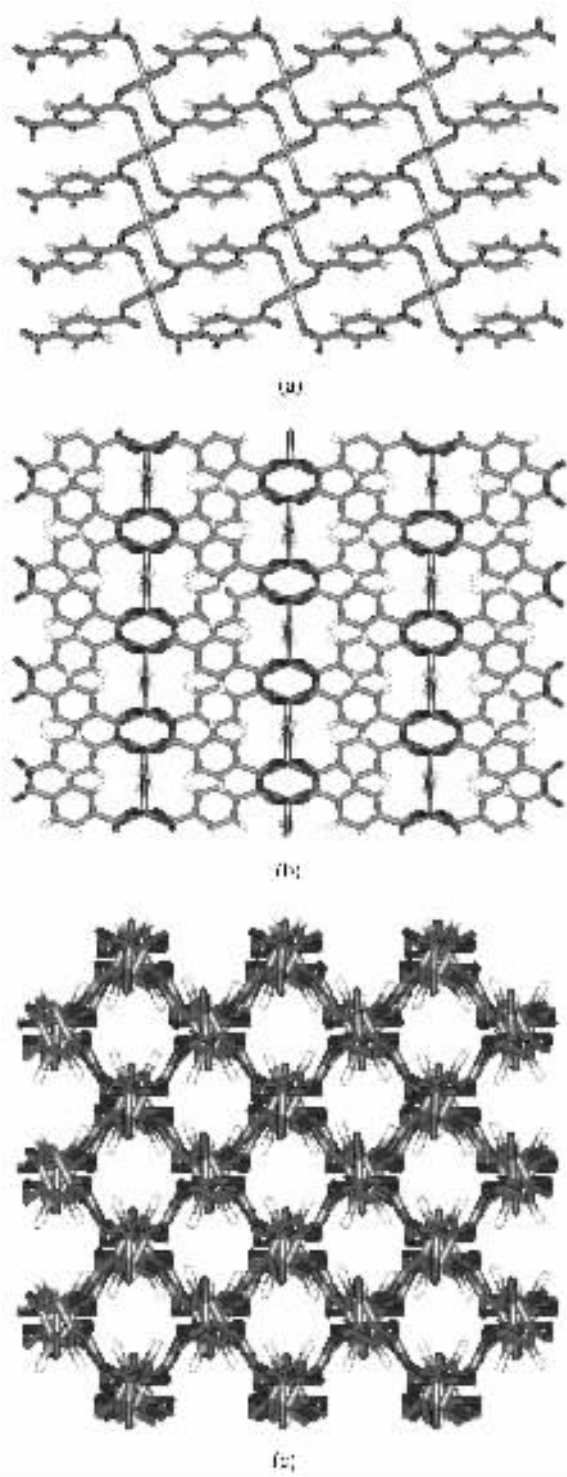
We prepared polymers **1** and **2** by the direct crystallization under hydrothermal conditions and determine their structures by single crystal X-ray diffraction although they were previously obtained through the addition of water to  $Zn \cdot BDC$  and their structures were solved by *ab initio* from powder X-ray diffraction data.<sup>18</sup>

Polymer **1** is a one-dimensional zigzag chain metal-organic polymer built up from the alternate connection of octahedral  $ZnO_4$  and BDC units (Fig. 1). Each Zn ion shares four oxygen atoms with two adjacent carboxylic groups of different BDC ligands and two terminal water molecules, whereas each BDC ligand adopts the bis-monodentate (*syn-anti*) coordination mode to contact two adjacent Zn ions, forming the zigzag chains (Fig. 1). To our knowledge, this is one of the rare examples<sup>19,20</sup> consisting of four-coordinated metal centers and two independent BDC ligands with entirely bis-monodentate and semi-chelating modes. The observed interatomic distances of the oxygen atoms associated with the hydrogen bonds range from 0.2717(5) nm to 0.2785(3) nm, indicative of strong hydrogen bonding interactions.



**Fig. 1** 1-D zigzag chains running along the crystallographic direction [001] for polymer **1**.

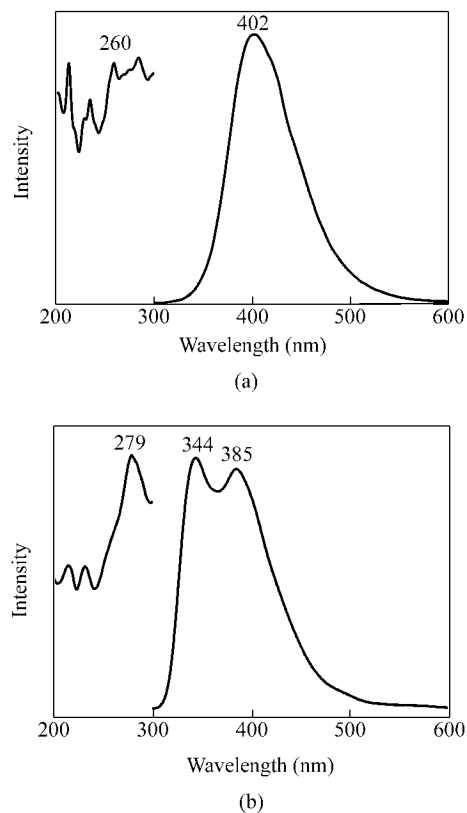
Polymer **2** has a three-dimensional framework based on infinite zigzag pseudochains of isolated polyhedra running along the [001] direction (Fig. 2a) connected by carboxylate moieties in the [100] direction (Fig. 2b). The Zn atom is located in the center of a capped square pyramid formed by four carboxylate oxygen atoms and one terminal water molecule.  $MO_4(OH_2)$  coordination environments have earlier been reported for a limited amount of compounds containing Zn and Mn.<sup>21</sup> The carboxylate bridges adopt a *syn-anti* conformation, which is far less common than the *syn-syn* conformation. There exists the same difference in bond distances between the *syn* and the *anti* oxygen donors [Zn—O(1) = 0.19498(16) nm and Zn—O(2) = 0.21814(16) nm]. This is just reflecting the strong hydrogen bonding interactions involving the carboxylic oxygen O(2) and the terminal water molecules [O(2)—O(1W) = 0.2642(2) nm]. Intriguingly, this open metal-organic polymeric framework contains a three-dimensional rectangular channel system including three types of straight channels along the [010] (Fig. 2a), [001] (Fig. 2b), and [60-1] (Fig. 2c) directions.



**Fig. 2** 3-D channel system of polymer **2** is shown approximately down the crystallographic direction (a) [010], (b) [001] and (c) [60-1], respectively.

The photoluminescent spectra of polymers **1** and **2** in the solid state at room temperature are shown in Fig. 3. The intense emissions occurring at 402 nm (Fig. 3a,  $\lambda_{\text{ex}} = 260$  nm) for **1**, at 344 nm and 385 nm (Fig. 3b,  $\lambda_{\text{ex}} = 279$  nm) for **2** are assigned to the ligand-to-metal charge-transfer (LMCT) band. Although  $\text{Zn}^{2+}$  ion has no empty 3d orbital, it has empty 4s orbital which can accept electrons from ligands (it is well-known that ZnO emits

light upon excitation and the emission is essentially a charge transfer process). In addition, similar emission band at about 430 nm has also been observed previously for other zinc-organic polymer compounds with either photoluminescent or non-photoluminescent ligands.<sup>24-26</sup>



**Fig. 3** Solid state photoluminescent spectra of (a) polymer **1** and (b) polymer **2** at room temperature.

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(E0212122 CHENG, B.; LU, Z. S.)