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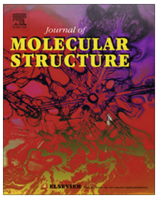

A Yb(III)–Zn(II) heterometallic coordination polymer with interesting three-fold 1D *pseudo*-nanotube architectures

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H I G H L I G H T S

- A Yb(III)–Zn(II) heterometallic complex was synthesized.
- Complex **1** presents a three-fold 1D *pseudo*-nanotube architectures.
- Photoluminescence property of the complex has also been investigated.

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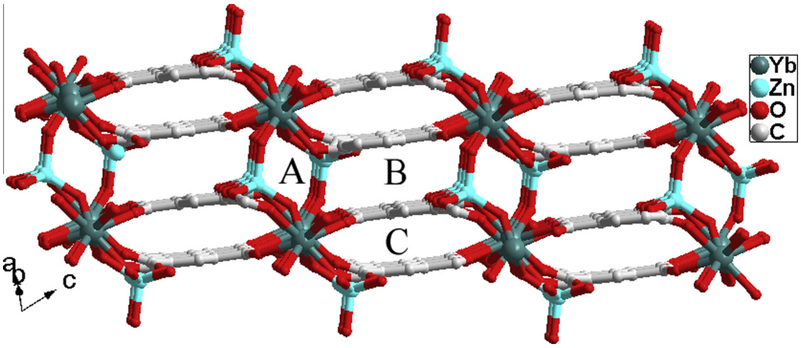

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A heterometallic coordination polymer formulated as $[YbZn(btc)(OH)_2(H_2O)]\cdot H_2O$ (**1**), where H_3btc = 1,3,5-benzenetricarboxylic acid has been synthesized under hydrothermal condition. Single crystal analysis reveals that complex **1** presents a three-dimensional (3D) structure containing three-fold 1D *pseudo*-nanotube architectures. The complex has also been characterized by IR, PXRD, TG and elemental analysis. Moreover, solid-state photoluminescence property of the complex has also been investigated at room temperature.

Introduction

Coordination polymers have been attracting considerable attention as a new class of metal organic hybrid functional material in recent years [1–5]. Reaction of metal ion and organic ligand under certain condition affords numerous coordination polymers with interesting structures and potential applications in many fields such as gas adsorption, photoluminescence, and selective catalysis as well as molecular delivery [6–9]. The assemble process of metal ion and ligand, structure and functional behavior of the result coordination polymer greatly depend on coordination geometry of metal ion and linking behavior of organic ligand. Elaborate selection of metal ion as node and organic ligand as linker is a widely used strategy for the construction of coordination polymer material [10,11]. However, many factors as reaction temperature, solvent, pH value, metal-to-ligand ratio and so on affect deeply on the final outcomes [12–15]. Thus, rational design of the assemble process and scrupulous tuning of the experiment conditions are extremely important to realize the structural control and functional tuning of coordination polymer materials.

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The structure and property of coordination polymer is greatly affected by nature of the metal ion involved in it. Many complexes with intriguing structure and property have been synthesized with single kind of metal ion [16–18]. However, complexes with different kinds of metal ions are less studied. On the other hand, 1,3,5-benzenetricarboxylic acid (H_3btc) is a very popular linker in the construction of coordination polymer due to its rigid structure, good coordination ability and various coordination modes [19–21]. In our previous work, we have synthesized two heterometallic coordination polymer based on H_3btc ligand with main-transition metal ions [22]. Now, taking into account of the good coordination behavior and excellent properties of lanthanide metal ions, we expand our work to construction of coordination polymers based on H_3btc ligand and lanthanide-transition metal ions system.

Herein, we report the synthesis and crystal structure of a novel heterometallic coordination polymer through reaction of Yb(III)/Zn(II) salts and H_3btc ligand under hydrothermal condition, namely $[YbZn(btc)(OH)_2(H_2O)]\cdot H_2O$ (**1**) which has been characterized by IR spectrum, XRPD, TGA (see the Supporting Information). Single crystal X-ray diffraction analysis reveals that complex **1** holds a three-dimensional (3D) structure containing three-fold 1D *pseudo*-nanotube architectures. Luminescent property of this complex has also been studied.

Table 1
Crystal data and structure refinement parameters for compound **1**.

Complex	1
Empirical formula	$C_9H_9O_{10}ZnYb$
Formula weight	515.61
Crystal system	Triclinic
Space group	*P*-1
a/Å	6.8438(8)
b/Å	9.0585(7)
c/Å	10.4859(16)
α/°	67.830(11)
β/°	75.258(12)
γ/°	76.952(9)
Volume/Å^3	576.05(12)
Z	2
ρ_{calc}/mg/mm^3	2.949
F (000)	478
Reflns collected/unique	6070/2369
μ (mm^{-1})	10.205
GOF on F^2	1.068
Final *R* indexes [I ⩾ 2σ (I)]	$R_1 = 0.0326$, $wR_2 = 0.0749$
Final *R* indexes [all data]	$R_1 = 0.0384$, $wR_2 = 0.0776$

Table 2
Selected bond lengths (Å) and angles (°) for complex **1**.

Bond lengths			
Yb1–O1	2.305(5)	Yb1–O1W	2.359(5)
Yb1–O2^1	2.312(5)	Zn1–O3^5	1.996(5)
Yb1–O5^2	2.408(5)	Zn1–O6^2	2.021(5)
Yb1–O4^3	2.314(5)	Zn1–O8	1.944(6)
Yb1–O8^4	2.278(6)	Zn1–O7	1.953(6)
Yb1–O7	2.380(6)	Yb1–O7^1	2.376(6)
Bond angles			
O1–Yb1–O2^1	140.89(16)	O1W–Yb1–O7	142.80(19)
O1–Yb1–O5^2	74.94(17)	O4^3–Yb1–O7	143.06(18)
O1–Yb1–O4^3	117.97(18)	O4^3–Yb1–O1W	70.70(18)
O1–Yb1–O7^1	73.72(19)	O8^4–Yb1–O1	139.79(19)
O1–Yb1–O7	76.5(2)	Zn1–O7–Yb1^1	122.0(3)
O1–Yb1–O1W	70.66(17)	Zn1–O7–Yb1	114.7(3)
O2^1–Yb1–O5^2	118.18(17)	O8–Zn1–O3^5	105.1(2)
O2^1–Yb1–O4^3	75.89(17)	O8–Zn1–O6^2	108.0(2)
O2^1–Yb1–O7	73.62(19)	O8–Zn1–O7	116.4(3)
O2^1–Yb1–O1W	143.51(17)	O7–Zn1–O3^5	110.9(2)
O7–Yb1–O5^2	72.68(17)	O7–Zn1–O6^2	118.3(2)

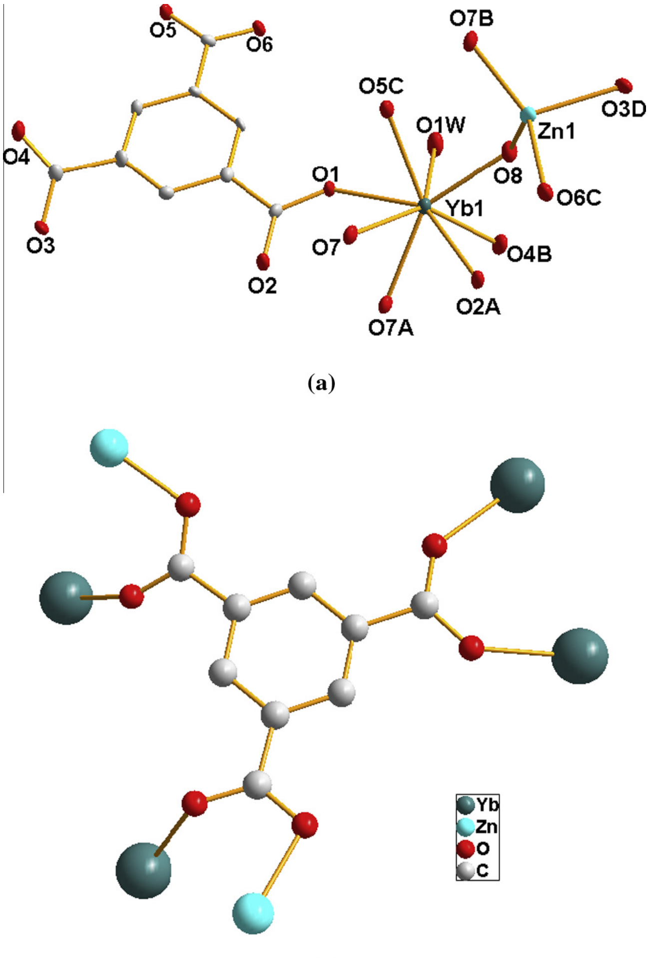
Experimental section

Materials required and general methods

All the starting materials and solvents were commercially purchased and used as received without further purification. Elemental analysis (C, H, N) was carried out on an Elementar Vario EL III analyzer. Infrared (IR) spectrum was recorded on PerkinElmer Spectrum One with a sample prepared as KBr pellet in the range 4000–400 cm^{-1}. The thermogravimetric analysis (TGA) was carried out with a NETZSCH STA 449C unit, at a heating rate of 10 °C/min under a nitrogen atmosphere. Fluorescence spectroscopy of the compound was performed on an Edinburgh Analytical instrument FLS920. This instrument is equipped with an Edinburgh Xe900 xenon arc lamp as exciting light source. X-ray Powder diffraction (XRPD) pattern of the sample was recorded by a X-ray diffractometer (Rigaku D/Max 2200PC) with a graphite monochromator and Cu Kα radiation at room temperature while the voltage and electric current are held at 40 kV and 20 mA.

Synthesis of compound 1

$[YbZn(btc)(OH)_2(H_2O)]\cdot H_2O$ (**1**). Complex **1** was isolated by mixing $Yb(NO_3)_3\cdot 5H_2O$ (0.1 mmol), $Zn(NO_3)_2\cdot 6H_2O$ (0.1 mmol), H_3btc (0.2 mmol), and NaOH (0.45 mmol) in 8 mL water and stirred for



(a)

(b)

Fig. 1. (a) The coordination environment of Yb(III) and Zn(II) ions in **1**. (b) Coordination mode of the btc^{3-} ligand. Hydrogen atoms and unligated water molecules are omitted for clarity. Symmetry codes: (A) $-x, 2-y, 1-z$; (B) $x, -1+y, 1+z$; (C) $x, y, 1+z$; (D) $1+x, -1+y, 1+z$.