

Two new homometallic coordination polymers based on a carboxylate-functionalized salen ligand

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ABSTRACT

Two new homometallic coordination polymers **1** and **2** have been prepared by the directly one-step hydrothermal reactions of a carboxylate-functionalized salen ligand with Zn(II) and Co(II) ions, respectively. **1** exhibits a 3D open framework built by $[Zn_4(\mu_4-O)(\text{carboxylate})_8]$ units and double Zn-salen ligands, while **2** shows a 1D chain structure constructed by cobalt ions and the ligand derived from the hydrolysis to one C=N bond of salen ligand. The preliminary fluorescence measurements of **1–2** show the influence of structure on the property.

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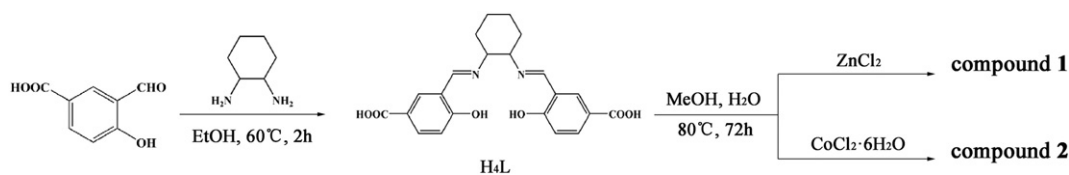
Metal–organic frameworks (MOFs) have received much attention due to not only their versatile intriguing architectures and topologies tuned by metal ions and organic ligands, but also their properties for potential applications in various areas, such as catalysis, ion exchange, gas separation and storage, luminescence, magnetism and even in toxic gas removal [1]. Among the researches, design and construction of new MOFs with diverse structures have been drawing considerable attention. There is no doubt that organic ligands play a vital role in tuning the structural topology and functionality of MOFs. Salen complexes have also gained a great deal of recent interests thanks to their remarkable physical–chemical properties and biological activities, especially the extensive applications in catalytic chemistry [2]. It is not surprising that salen-based ligands have grown to be among the most widely explored ligands for coordination complexes owing to their easily-prepared, stronger nitrogen donated and modular designed. Considering the superiorities of both MOF materials and salen complexes, considerable impetus towards using salen complexes as ligands to construct MOFs has been provided [3]. Introducing functional groups such as carboxylate and pyridyl groups into the para- or meta-positions to the OH group of salen ligands [4] has been proved to be an effective strategy for constructing salen-based MOFs. A series of MOFs based on the carboxylate-functionalized salen ligand have been reported. For example, Cui et al. synthesized chiral nanoporous MOFs based on dicarboxyl-functionalized chiral Ni(salen) and Co(salen) ligands with square-planar Cd_4 units [5], whereas Kitagawa et al. prepared an achiral Zn-MOF using M-salphdc (M = Cu(II), Co(II), and Ni(II)); salphdc = N,N-

phenylenebis(salicylideneimine)dicarboxylic acid) as linkers [4a]. Lin et al. reported a family of isorecticular chiral MOFs constructed from $[Zn_4(\mu_4-O)(O_2CR)_6]$ secondary building units and systematically elongated Mn-salen-derived dicarboxylic acid struts [6]. Commonly, the assembly process of salen-based MOFs contains two steps: Firstly, functionalized salen ligand coordinates to a metal center (M1) forming a metalloligand M-salen; and secondly, M-salen ligands acting as linkers react with another metal center (M2) acting as nodal units to form heterometallic MOFs. Therefore, to our knowledge, salen-based homometallic MOFs are rare [7]. Herein, we report the syntheses and characterizations of two new homometallic coordination polymers (**1** and **2**) that were formed directly from the one step reaction of salen-derived dicarboxylate-bridging ligands (H_4L) and transition metal ions (M = Co and Zn).

As shown in Scheme 1, the reaction of $ZnCl_2$ with the H_4L in $H_2O/MeOH$ at 80 °C for 72 h [8b] afforded purple block single crystals of **1**. Single-crystal X-ray diffraction [9] reveals that **1** crystallizes in the *P6mm* space group and possesses a 3D open framework based on a tetranuclear SBU. There are two distinct zinc coordination environments in **1**: one (Zn1) is located in the center of the salen ligand and is coordinated in a distorted square-planar geometry with two nitrogen atoms and two oxygen atoms from the H_4L ligand to form a metalloligand ZnL, while the other (Zn2) exhibits a distorted tetragonal pyramid geometry defined by one central μ_4-O atom, two oxygen atoms from one bidentate carboxylate group and two oxygen atoms respectively from two monodentate carboxylate groups. Four Zn2 centers are held together by a central μ_4-O atom adopting a tetrahedral geometry with Zn–O bond lengths ranging from 1.931 (9) to 1.986 (0) Å, and eight carboxylate groups from eight ZnL ligands coordinate to the four

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Scheme 1. Synthesis of compounds **1** and **2**.

Zn₂ centers to form a [Zn₄(μ₄-O)(carboxylate)₈] SBU (Fig. 1). In **1**, each antiparallel double ZnL ligands are linked to two Zn₄ SBUs, and each Zn₄ SBU is connected with eight ZnL ligands generating a 3D porous framework with square channels of 13.009 × 18.717 Å² along the *c*-axis. Calculations using PLATON show that **1** has about 27% of the total volume available for guest inclusion.

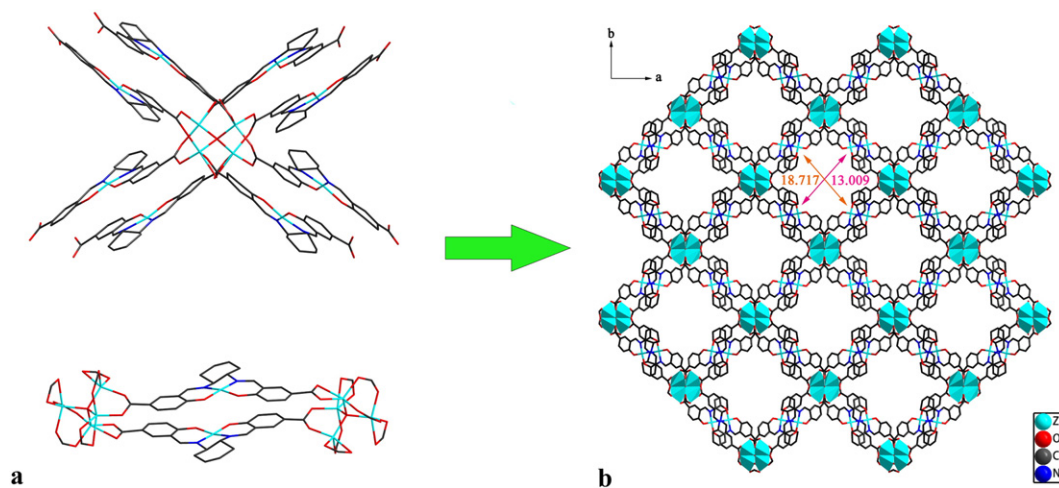
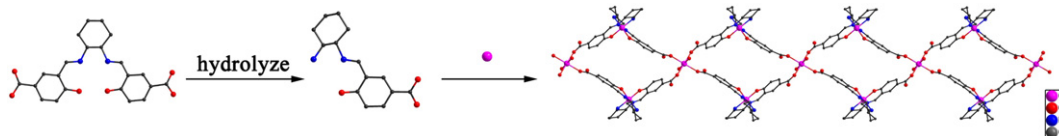
The preparation process of **2** [8c] is similar to **1** except that CoCl₂·6H₂O is adopted instead of ZnCl₂ (Scheme 1). Detailed analysis of the single-crystal X-ray diffraction data [9] reveals that **2** adopts a 1D chain structure and crystallizes in the space group *P*-1. In **2**, there happens the hydrolysis to one C=N bond of each H₄L ligand, so that each Co(III) (calculated by bond valences) center adopts an octahedral geometry by coordinating to two pairs of N₂O donor from two hydrolyzed H₄Ls, which planes are perpendicular to each other (Fig. S4). Moreover, each hydrolyzed H₄L ligand uses one monodentate carboxylate group to bind adjacent Co(II) center to form 1D coordination polymeric chains (Fig. 2). Two H₂O molecules serve as terminal ligands to complete the octahedral coordination geometry of the Co(II) center. The hydrogen atoms linked to the amine of hydrolyzed H₄L ligand in the polymeric chains are pointing outward and are well positioned to form strong hydrogen bonds with the uncoordinated deprotonated carboxylate oxygen atoms (O···N, 2.889 (1) Å) of adjacent chains leading to a 2D network (Fig. S5). Further, the inter π···π interactions between layers drive the 2D network into a 3D framework (Fig. S5).

The IR spectrum of H₄L (Fig. S1.1) displays a band at 1208 cm⁻¹ assigned to the -Ph-O asymmetric stretch vibration. In **1** (Fig. S1.2) and **2** (Fig. S1.3), this band shifts to the 1184 and 1192 cm⁻¹ respective-

ly, indicating the participation in coordination. Besides, the red-shift Δν (ν(C=N)-ν(C=N)) of 20 cm⁻¹, suggests the coordination of the azomethine group and center metals, which softens the intensity of C=N vibration. The characteristic absorption bands at 1400–1600 cm⁻¹ are owing to the aromatic C=C vibration.

The thermal gravimetric analyses (TGAs) of **1** and **2** were performed to investigate their thermal behavior (Fig. S2). The TGA of compound **1** reveals that the lattice water molecules are lost at the temperature 35–114 °C (obsd 13.78%, calcd 12.83%). Then the compound is stable up to 332 °C. In the temperature range of 315–480 °C, two continuous weight losses (51.19%) are observed due to the decomposition of the salen ligands, which is in agreement with the calculated value 51.34%. For **2**, the first weight loss is 9.11% (calcd 8.12%) in the temperature range from 47 to 161 °C, which corresponds to the release of lattice and coordinated water molecules in the structure. Then the compound is stable up to 250 °C. At higher temperature, two continuous weight losses of about 72.16% occur from 250 to 480 °C assigned to the losses of the salen ligands (calcd 73.75%).

Preliminary fluorescence of **1–2** together with H₄L is measured at room temperature. As shown in Fig. 3, **1** exhibits an intense emission band at 447 nm, in the solid state upon excitation at 370 nm, along with the blue shift. That may be assigned to the π*–π or π*–n transition of intraligand because of the difficulty for Zn(II) ion (d¹⁰ configuration) to oxidize or reduce [12]. And the emission spectrum of **2** consists of a broad band with a maximum at about 556 nm (λ_{ex} = 380 nm), and appears red-shifted compared to the free H₄L ligand, which is presumably due to the intermolecular interactions (such as π–π stacking) between

Fig. 1. (a) View of the local connections' tetranuclear zinc units and H₄L ligands. (b) Projection diagram of **1** down the *c* axis showing the 3D porous framework.Fig. 2. View of the forming process of 1D chain in **2**.

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