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# A two-fold interpenetrating metal-organic framework based on tetranuclear zinc-carboxylate clusters

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## ABSTRACT

A novel two-fold interpenetrating 3D framework consisting of unprecedented tetranuclear Zn(II)-carboxylate units has been synthesized. The tripodal semi-rigid tricarboxylate ligand and 4,4-bipy link the tetranuclear units into a 3,8-connected *tfz-d* topological network.

## Introduction

Metal-organic frameworks (MOFs) have been of great interest in supramolecular chemistry and crystal engineering owing to their intriguing structural topologies and potential application as functional materials [1–4]. Much effort has been devoted to the rational design and synthesis of the cluster-based MOFs since metal clusters are much better than single metal ions at maintaining specific geometries and imparting physical properties to MOFs [2]. The metal clusters usually are used as secondary building units (SBUs), which are extended into the desirable MOFs by bridging organic ligands. The judicial selection of organic ligands containing appropriate coordination sites linked by a spacer with specific positional orientation plays an important role in the construction of MOFs [3]. In the context, carboxylate ligands are promising because of their versatile coordination modes and high stability, allowing for the synthesis of charge-neutral binuclear, trinuclear, even higher nuclear clusters as SBUs to generate rigid and high porous MOFs [4], moreover, the counterion effect in self-assembly process may be mitigated. 1,3,5-benzenetricarboxylae and its rigid derivates have been extensively employed to link metal clusters into high dimensional frameworks containing channels or cavities [5]. Their rigid scaffold may provide the constrained and proper binding directions to stable SBUs. Thus, it is possible to design and predict structures of the final products through the rigid carboxylate ligands and cluster-based SBUs. It was known that the flexible spacer between carboxylate groups may freely rotate or bent to meet for the requirement of coordination geometry around metal centers, complicating the control and modification of target products, but novel MOFs with specific structures and functions can be produced [6].

In the construction of MOFs based on SBUs, the combinational use of carboxylate and dipyridyl ligands represents a promising approach [7–10]. The mixed ligands may play different roles in the structural construction of final products. Generally, the bridging carboxylate ligands may link di- or polynuclear SBUs into charge-neutral 1D chains or 2D networks, the bridging pyridyl ligands further extend the metal-carboxylate frameworks into higher dimensional architectures [8]. However, due to the presence of many subtle factors in assembly process, controlling synthesis of cluster-based MOFs from mixed bridging ligands is still a challenge despite the fact that a few of layer-pillared MOFs based on dinuclear SBUs have been reported [9]. In our continuous study of porous MOFs from carboxylate ligands, we are interested in deprotonated 5-(4-carboxyphenoxy)isophthalic acid ($H_3$cpip), its two carboxylate groups are predisposed at 120° in phenyl ring, while phenylcarboxylate group may be twisted to conform to specific conformation and steric hindrance of metal clusters, resulting in cluster-based MOFs with interesting structures and properties, but MOFs from cpip were seldom explored in comparison with the rigid tricarboxylate ligands [10]. Herein, we report the synthesis, structure and photoluminescence of a two-fold interpenetrating metal-organic framework consisting of tetranulcear Zn(II)-carboxylate clusters, $[Zn_4(OH)_2(cpip)_2(4,4'\text{-bipy})]_n$ (**1**), in which cpip links tetranuclear units into a 2D layer, which is pillared by 4,4′-bipy to generate a two-fold interpenetrating 3D network.

The complex **1** was synthesized through the hydrothermal reaction of cpip, 4,4′-bpy and $Zn(OAc)_2{\cdot}2H_2O$ at 160 °C in the presence

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of NaOH (see Supplementary material). The phase purity of **1** was confirmed by XRPD (Fig. S1, Supplementary material). The measured peaks are in good agreement with those calculated from X-ray single crystal diffraction data. Thermogravimetric analysis (TGA) under $N_2$ revealed that the complex is stable up to 413 °C (Fig. S2, Supplementary material).

Single crystal X-ray diffraction analysis shows that complex **1** crystallizes in the triclinic space group *P-1* [11] and is a two-fold interpenetrating 3D framework consisting of tetranuclear Zn(II)-carboxylate units. As shown in Fig. 1, there are two crystallographically independent Zn(II) ions, which display different coordination geometries. Zn(1) is in a distorted octahedral geometry and is coordinated by two chelating carboxylate oxygen atoms, two $\mu_2,\eta_2$-carboxylate oxygen atom and two$\mu_3$-OH. While Zn(2) is in a distorted tetrahedral geometry and is coordinated by two oxygen atoms from different $\mu_2,\eta_2$-carboxylate, one pyridyl nitrogen atom and one $\mu_3$-OH. It should be mentioned that Zn(2)-O bond distances [1.917(3)–1.966(4) Å] are shorter than Zn(1)-O bond distances [2.072(3)–2.175(3) Å]. Interestingly, the two Zn(II) are bridged by two $\mu_2,\eta_2$-carboxylate from different cpip and one $\mu_3$-OH to form a dinuclear subunit. The Zn(1)···Zn(2) distance in the subunit is 3.0971(8) Å. Two $\mu_3$-OH further connect two symmetry-related dinuclear subunits into a $[Zn_4(\mu_3\text{-}OH)_2]$ SBU. The Zn(1)···Zn(2) distance bridged by $\mu_3$-OH is 3.1399(13) Å. Zn(1)···Zn(1A) and Zn(2)···Zn(2A) separations in the SBU are 3.140 and 5.948 Å, respectively. To our knowledge, this type of SBU is still rare to date in the Zn(II)-carboxylate coordination complexes although many MOFs containing the tetrahedral oxo-centred tetranuclear Zn(II)-carboxylate clusters are reported [12]. cpip serves as a $\mu_5$-bridge through its two $\mu_2,\eta_2$-carboxylate and one chelating carboxylate groups (Scheme 1), the twisting angle between two phenyl rings is 76.5°. Two 1,3-positioned carboxylate groups in cpip link two adjacent tetranuclear SBUs into a 1D chain, further connection by 5-positioned phenylcarboxylates generate a 2D layer (Fig. 2). *exo*-Bidentate 4,4′-bipy serves as a pillar between the adjacent layers (Fig. 3). Zn(II)···Zn(II) distance across the 4,4′-bipy is 11.061 Å. The large void in the 3D network results in the formation of a two-fold interpenetrating framework owing to the absence of large guest molecules to fill the void. To have a better insight into the 3D structure, topological analysis is given. Taking the $[Zn_4(\mu_3\text{-}OH)_2]$ SBU as one node, each SBU becomes a 8-connected node, cpip and 4,4′-bipy can be regarded as independent three-connected and two-connected vertex, respectively. The interlinkage of eight SBUs with six cpip and two 4,4-bipy generates a 3,8-connected *tfz-d* topology (Fig. 4) [10a], its point symbol is {4^3}2{4^6.6^18.8^4}.

The luminescent property of complex **1** has been studied in the solid state at room temperature. As illustrated in Figs. 5, 1 shows the emission maxima at 428 and 447 nm upon the excitation at 307 and 338 nm, respectively. The free ligand $H_3$cpip exhibits the strongest emission peak at 375 nm upon excitation at 330 nm in the solid state at room temperature (Fig. S3, Supplementary material). In comparison with the emission peak of $H_3$cpip, the main luminescent emission peaks are red-shifted. The emission of complex **1** is neither ligand-to-metal charge transfer (LMCT) nor metal-to-ligand charge transfer (MLCT), and may be assigned to the ligand chelating or bridging effect due to the coordination of Zn(II), changing the rigidity and conjugation of cpip [5b,12b].

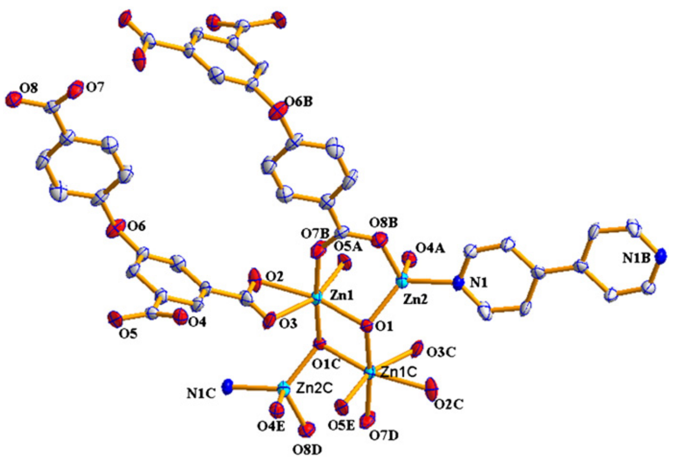
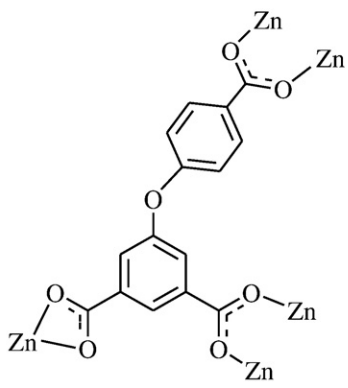


**Fig. 1.** The coordination environment of tetranuclear Zn(II) unit in **1** with thermal ellipsoids at 50% probability.



**Scheme 1.** The coordination mode of cpip in **1**.

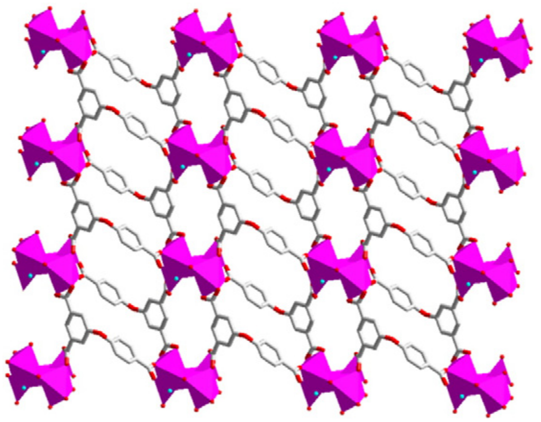


**Fig. 2.** View of 2D $[Zn_4(\mu_3\text{-}OH)_2(cpip)_2]_n$ layer in **1**.

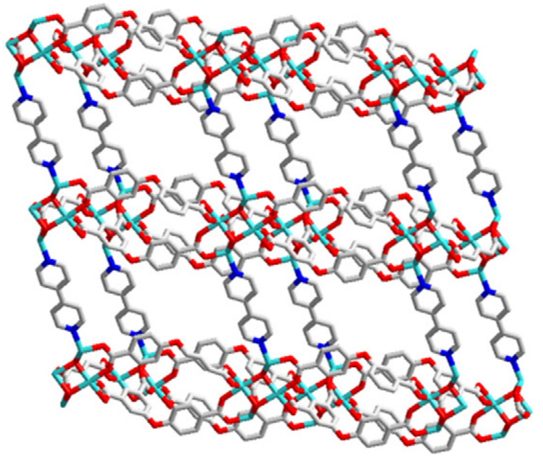


**Fig. 3.** 2D layers pillared by 4,4′-bipy into a 3D network in **1**.