

# Metal ions directed self-assembly based on rigid polycarboxylate ligand 5-tert-butyl isophthalic acid and flexible N-heterocyclic ligand 1,4-bis(2-methylimidazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene

Yajuan Mu <sup>a,\*</sup>, Yungen Ran <sup>b</sup>, Guifang Qin <sup>a</sup>, Xiaoli Ma <sup>a</sup>, Lijing Hao <sup>a</sup>, Zhidong Wei <sup>a</sup>, Yanyan Niu <sup>a</sup>, Hongxiao Lü <sup>a</sup>

<sup>a</sup> College of Traditional Chinese Medicine, Hebei University, Baoding 071000, PR China

<sup>b</sup> Henan Provincial Engineering Research Center for Radiation Processing, Zhengzhou 450015, PR China

## ARTICLE INFO

### Article history:

Received 18 May 2013

Accepted 1 September 2013

Available online 8 September 2013

### Keywords:

Cadmium coordination polymer

Zinc coordination polymer

1,4-Bis(2-methylimidazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene

5-Tert-butyl isophthalic acid

Crystal structures

## ABSTRACT

Two new complexes  $\{[\text{Cd}(\text{bmimx})_{0.5}(\text{tbip})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\}_n$  (**1**) and  $[\text{Zn}(\text{bmimx})(\text{tbip})]_n$  (**2**) (bmimx = 1,4-bis(2-methylimidazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene, H<sub>2</sub>tbip = 5-tert-butyl isophthalic acid) based on mixed ligands have been hydrothermally synthesized by varying the metal ions. Structural analysis reveals that complex **1** displays a 2D layer structure with a 4<sup>4</sup>-sql topology; complex **2** exhibits a 3D 4-fold interpenetrated framework with *sra* topology. The structural differences between **1** and **2** indicate that metal ions have significant effects on the formation of the final architectures. In addition, the thermal stabilities and photoluminescent properties of the two complexes were also investigated.

© 2013 Elsevier B.V. All rights reserved.

The design and construction of coordination polymers with fascinating topological structures and potential applications as functional solid materials have aroused great interest of chemists [1–3]. From the viewpoint of crystal engineering, the intrinsic geometric preferences of metal centers and various coordination sites of bridging ligands are the critical factors in determining the supramolecular architectures [4–8]. Recent research has revealed that metal-directed self-assembly is one of the most useful strategies for generating intriguing supramolecular architectures [9–15], because it not only has the advantage in rational bottom-up construction for its regulated coordination geometry, but also has a profound effect on physical and chemical properties of molecular architectures. Some remarkable examples of metal-directed approaches have been documented, such as metal-directed stereoselective syntheses of homochiral complexes [16], metal-assisted ligand-centered redox potential [17], metal-regulated mixed-ligand metal-organic frameworks [18], metal-tuned fluorescent properties of complexes [19], and so on.

On the other hand, due to the diversity of the connecting modes and the high structural stability, mixed ligands of rigid polycarboxylate and flexible N-heterocyclic ligands have received considerable attention in creating new structurally defined supramolecular architectures [20–23]. This is because rigid polycarboxylate ligands not only have various coordination modes, which are beneficial to forming unique

architectures, but also have strong coordinating ability to metal ions, which can lead to good thermal stabilities of the architectures and increase the possibility of their functionalization. Meanwhile, the flexible N-heterocyclic ligands have strong collaborative coordination ability with rigid polycarboxylate ligands, which can change their conformations to meet the coordination requirement of the metal ions. Considering the advantages of rigid polycarboxylate and flexible N-heterocyclic mixed ligands, in this report, rigid polycarboxylate ligand 5-tert-butyl isophthalic acid (H<sub>2</sub>tbip) and flexible N-heterocyclic ligand 1,4-bis(2-methylimidazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene (bmimx) are selected. Then we employed metal-directed approach, two complexes, namely,  $\{[\text{Cd}(\text{bmimx})_{0.5}(\text{tbip})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\}_n$  (**1**) and  $[\text{Zn}(\text{bmimx})(\text{tbip})]_n$  (**2**), were successfully synthesized. Structural determinations show that the structure spans from 2D layer to 3D 4-fold interpenetrated framework, indicating that metal ions play an essential role in the formation of the frameworks. Herein we report the synthesis, crystal structures as well as the photoluminescent properties of the two complexes.

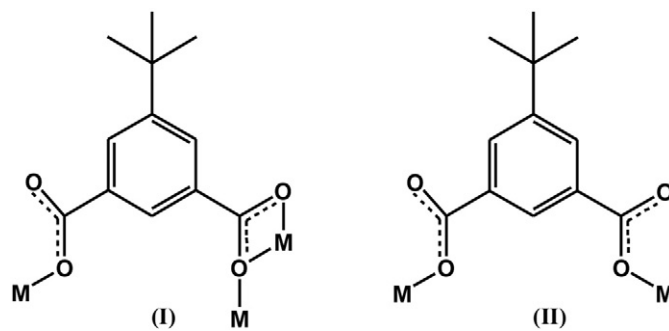
The reaction of  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  or  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with H<sub>2</sub>tbip/bmimx under hydrothermal condition led to the formation of complex **1** or **2**, respectively [24]. The compositions were confirmed by elementary analysis and IR spectra, and the phase purities of the bulk samples for luminescent/thermal measurements were identified by powder X-ray diffraction (PXRD) (please see Fig. S1 in the Supplementary material).

The results of the crystallographic analysis [25] revealed that **1** crystallizes in triclinic system with *P*-1 space group. The asymmetric unit of complex **1** consists of one Cd(II) atom, half bmimx ligand,

\* Corresponding author. Tel./fax: +86 312 5078519.

E-mail address: [muyajuan1027@163.com](mailto:muyajuan1027@163.com) (Y. Mu).

one  $\text{tbip}^{2-}$  ligand, one coordinated water molecule and one lattice water molecule. As shown in Fig. 1a, each Cd(II) atom is in a severely distorted octahedral environment finished by four carboxylate oxygen atoms from three  $\text{tbip}^{2-}$  ligands, one water molecule and one nitrogen atom from one  $\text{bmimx}$  ligand. The distances of Cd–O/N bonds range from 2.215(2)–2.487(2) Å, which are similar to other Cd-based complexes [26]. Each  $\text{tbip}^{2-}$  ligand links three Cd(II) atoms, in which one carboxylate group possesses a  $\mu_1-\eta^0:\eta^1$  mode and the other adopts a  $\mu_2-\eta^1:\eta^2$  fashion (type I in Scheme 1). The Cd(II) atoms are connected by  $\text{tbip}^{2-}$  ligands to give rise to a 1D double-chain structure (Fig. 1b), which is composed of the centrosymmetric  $\text{Cd}_2$  dinuclear unit linked by  $\mu_2$ -O of two carboxylate groups. The four atoms (Cd – O – Cd – O) of the dinuclear unit are completely coplanar, and Cd–Cd and O–O



Scheme 1. The coordinated mode of the  $\text{H}_2\text{tbip}$  ligand.

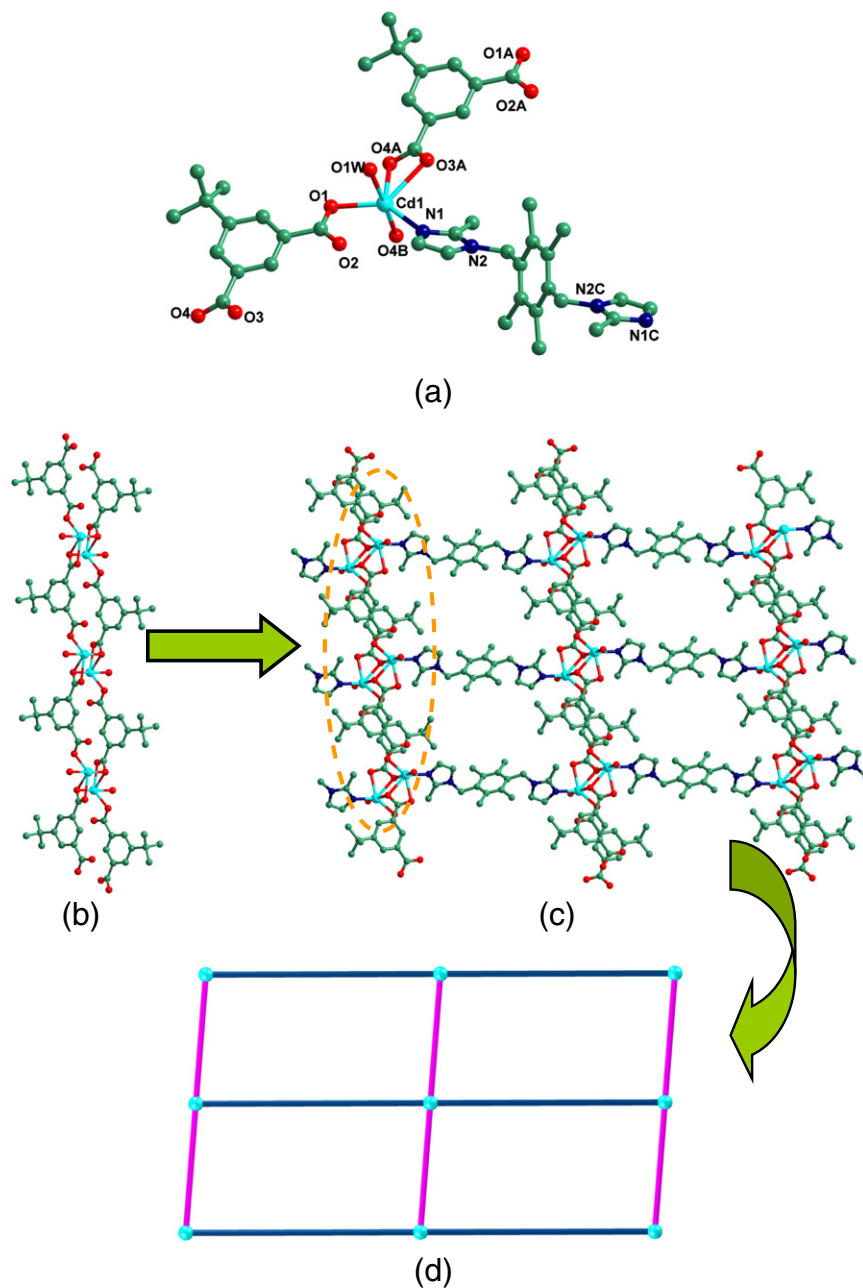


Fig. 1. (a) Coordination environment around the Cd(II) center in **1**. Hydrogen atoms and solvent molecules are omitted for clarity. Symmetry code: A =  $x, 1 + y, z$ ; B =  $1 - x, -y, -z$ ; C =  $-x, 1 - y, 1 - z$ . (b) The 1D [Cd– $\text{tbip}$ ] double-chain. (c) The 2D layered structure. (d) The  $4^4\text{-sql}$  topology of complex **1**.

Download English Version:

<https://daneshyari.com/en/article/1301935>

Download Persian Version:

<https://daneshyari.com/article/1301935>

[Daneshyari.com](https://daneshyari.com)