



Short communication

## Construction of two mixed-ligand coordination polymers presenting unusual polyrotaxane-like entanglements

Yongnian Yan<sup>a</sup>, Siyu Liu<sup>a</sup>, Mingming Guo<sup>a</sup>, Xianmin Guo<sup>a</sup>, Huadong Guo<sup>a,b,\*</sup><sup>a</sup> Department of Chemistry, Changchun Normal University, Changchun 130032, People's Republic of China<sup>b</sup> Central Laboratory, Changchun Normal University, Changchun 130032, People's Republic of China

## ARTICLE INFO

## Article history:

Received 6 July 2016

Received in revised form 16 July 2016

Accepted 22 July 2016

Available online 25 July 2016

## Keywords:

Coordination polymers

Polyrotaxane

Self-threading

Luminescence

## ABSTRACT

Two novel polyrotaxane-like coordination polymers,  $[\text{Ni}_4(\text{L})_4(\text{H}_2\text{O})_3(\text{bpp})_4] \cdot 3\text{H}_2\text{O}$  (**1**) and  $[\text{Cd}_4(\text{L})_4(\text{bpp})_3] \cdot 3\text{H}_2\text{O}$  (**2**) ( $\text{H}_2\text{L} = \text{Me}_2\text{Si}(\text{p}-\text{C}_6\text{H}_4\text{COOH})_2$ ,  $\text{bpp} = 1,3\text{-bis}(4\text{-pyridyl})\text{propane}$ ), have been synthesized and structurally characterized. Compound **1** features a 2D  $\rightarrow$  3D polyrotaxane array by the interlock of bi-layer networks. Compound **2** exhibits an unusual 3D polyrotaxane-like self-threading framework. In addition, compound **2** shows an emission at 485 nm when it was excited at 400 nm.

© 2016 Elsevier B.V. All rights reserved.

Over the past few decades, coordination polymers (CPs) have increased much attention not only because of their interesting structural diversity, but also for their potential applications as functional materials [1–2]. Many of these arrays are particularly intriguing because of the presence of independent motifs entangled together in different ways, such as polycatenanes, polyrotaxanes and polyknots, which have been well discussed in some comprehensive reviews by Robson and Batten [3]. Among versatile entangled systems, polyrotaxane, which can be described as the extended periodic version of rotaxane motifs, has received considerable attention for its mechanical links and potential applications in molecular machines or switches [4]. However, till now, most of the reported polyrotaxane-like CPs present 1D  $\rightarrow$  1D, 1D  $\rightarrow$  2D and 2D  $\rightarrow$  2D entangled associations, and the construction of polyrotaxane with high dimensional arrays such as 1D  $\rightarrow$  3D, 2D  $\rightarrow$  3D or self-penetration remains a challenging theme in entangled systems [5].

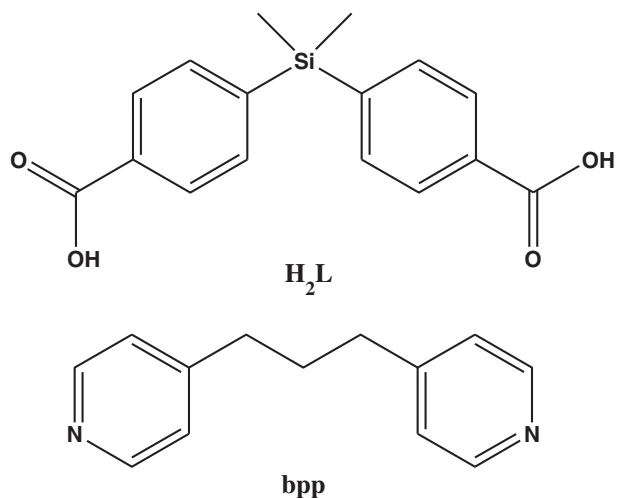
It is well known that the rational design and modification of mixed ligands from polycarboxylates and N-donor ligands is an effective approach to construct CPs, due to their ability to introduce functional groups and to easily modify architecture by changing one of units [6]. Meanwhile, as mentioned by Yang and Ma, in order to access the goal of polyrotaxane-like arrays, the basic design element is the construction of a molecule unit with loops, and insertion of a linear rod through those loops [7]. Basically, in this paper, we chose a long V-shaped dicarboxylic acid  $\text{Me}_2\text{Si}(\text{p}-\text{C}_6\text{H}_4\text{COOH})_2$  ( $\text{H}_2\text{L}$ ) as the building unit, which features two special characteristics: (1) Its long size favors the generation

of entangled framework. (2) Its bent conformation is beneficial for the construction of a loop or ring. Furthermore, the conformationally flexible ligand 1,3-bis(4-pyridyl)propane (bpp), which often shows a supra-molecular isomerism by altering the geometry of the ligand, has already proven to be a good candidate to give fascinating entanglements (Scheme 1). Thus it may be possible to yield new classes of entangled compounds through combining the two types of different precursors. Successfully, we reported here two novel coordination polymers,  $[\text{Ni}_4(\text{L})_4(\text{H}_2\text{O})_3(\text{bpp})_4] \cdot 3\text{H}_2\text{O}$  (**1**),  $[\text{Cd}_4(\text{L})_4(\text{bpp})_3] \cdot 3\text{H}_2\text{O}$  (**2**), which both display unusual polyrotaxane-like networks [8]. Their structures have been characterized by elemental analysis, IR spectroscopy, thermogravimetric analysis (TGA) and X-ray crystallography [9].

Compound **1** crystallizes in a triclinic space group  $P\bar{1}$ . In the asymmetric unit, there exist four crystallographically unique Ni(II) atoms, four  $\text{L}^{2-}$  anions, four bpp ligands, two  $\mu_2$ -bridged water molecules, one terminally coordinated water molecule and three uncoordinated water molecules. As shown in Fig. S1, all Ni(II) atoms adopt distorted octahedral geometry: Ni1, Ni2 and Ni3 are coordinated by two nitrogen atoms from two bpp ligands and four oxygen atoms from three  $\text{L}^{2-}$  anions and one  $\mu_2$ -bridged water molecule; while, Ni4 is coordinated by one nitrogen atom from one bpp ligand and five oxygen atoms from three  $\text{L}^{2-}$  anions, one  $\mu_2$ -bridged water molecule and one terminally coordinated water molecule. Ni(II) to O/N distances and bond angles are within the normal range (Table S1 in the supporting information). Two  $\text{L}^{2-}$  anions connect two Ni(II) atoms by two monodentate carboxylates; the other two  $\text{L}^{2-}$  anions connect four Ni(II) atoms through two *syn,syn*-bidentate carboxylates. The four bpp ligands present three kinds of conformation: two of them in the TT conformation connect two Ni(II) atoms, one in the GG' conformation connects two Ni(II)

\* Correspondence author.

E-mail address: [hdxmguo@163.com](mailto:hdxmguo@163.com) (H. Guo).



Scheme 1. The building units that were used.

atoms, while one in the TG conformation ligates with one Ni(II) atom as a dangling arm.

In compound **1**, two independent binuclear subunits formulated as  $[\text{Ni}_2(\mu\text{-COO})_2(\mu\text{-H}_2\text{O})]$  are formed, with the adjacent Ni1...Ni2 and Ni3...Ni4 distances of 3.538 Å and 3.528 Å, respectively. These dimers are connected by the organic ligands to give rise to a 2D bilayer network (Fig. 1a). Within the network, the neighboring dimers are separated by distances of 13.75 Å, 14.22 Å, 16.31 Å (by  $\text{L}^{2-}$  anions), 10.57 Å and 16.97 Å (through bpp ligands). Based on the concept of topology, the Ni(II) dimers can be regarded as nodes, and the organic ligands as linkers, thus the topology of the structure can be simplified as a uninodal 6-connected net with a point symbol of  $\{3^3 \cdot 4^{10} \cdot 5.6\}$  (Fig. 1b), which may be considered as two  $4^4$  sqf layers are bridged by the zigzag linkages in an “edge to edge” fashion. Normally, 6-connected nets adopt 3D topologies, and there are very few examples of 6-connected topologies having 2D structures. To the best of our knowledge, such a unique net has only been found in the complex  $[\text{Co}_2(\text{mip})_2(\text{bpp})_2(\text{H}_2\text{O})]_n$  ( $\text{H}_2\text{mip}$  refers to 5-methylisophthalate)

[10]. From the point of the topology, in compound **1**, these 6-connected networks do not entangle with each other, but after deep insight into the structure, a fascinating entangled mode-polyrotaxane comes into appearance. For every bilayer net, parts of the edges of each  $4^4$  sqf motif are occupied by the  $\{[\text{Ni}_2(\mu\text{-COO})_2(\mu\text{-H}_2\text{O})]_2[\text{L}]_2\}$  coordinative rings, which are threaded by the rod bpp ligands from the neighboring bilayer, and vice versa (Fig. 1c). Thus, each bilayer interlocks with two others from above and below to generate an unusual 2D → 3D polyrotaxane array (Fig. 1d).

Compound **2** crystallizes in a monoclinic space group  $C2/c$ . In the asymmetric unit, there exist two crystallographically unique Cd(II) atoms, two  $\text{L}^{2-}$  anions, 1.5 bpp ligands, and 1.5 uncoordinated water molecules. As shown in Fig. S2, Cd1 atom adopts a distorted pentagonal bipyramid geometry and is coordinated by two nitrogen atoms from two bpp ligands and five oxygen atoms from three  $\text{L}^{2-}$  anions; while, Cd2 atom is ligated by one nitrogen atom from one bpp ligand and five oxygen atoms from five  $\text{L}^{2-}$  anions to give a distorted octahedral geometry. Cd(II) to O/N distances and bond angles are within the normal range (Table S2 in the supporting information). One  $\text{L}^{2-}$  anion connects four Cd(II) atoms by one *syn,syn*-bidentate carboxylate and one *syn,syn,anti*-bidentate carboxylate. The other  $\text{L}^{2-}$  anion also connects four Cd(II) atoms by one *syn,anti*-bidentate carboxylate and one *syn,syn,anti*-bidentate carboxylate. Both bpp ligands act as a linker to bridge two Cd(II) atoms: one in TT conformation and the other in TG conformation.

In compound **2**, one Cd1 atom and Cd2 atom are combined one *syn,syn*-bidentate carboxylate and two *syn,syn,anti*-bidentate carboxylates to form a  $\text{Cd}_2$  dimer. Two such  $\text{Cd}_2$  dimers are bridged by two *syn,anti*-bidentate carboxylates to afford a linear  $\text{Cd}_4$  cluster. These clusters are further connected by eight  $\text{L}^{2-}$  anions and six bpp ligands to assemble a 3D framework. Within the framework, the neighboring  $\text{Cd}_4$  clusters are separated by distance of 17.78 Å, 18.63 Å (by bpp) and 13.12 Å (through  $\text{L}^{2-}$  anion). Based on the concept of topology, the  $\text{Cd}_4$  clusters can be regarded as eight-connected nodes (Fig. 2a and b), the organic ligands can be regarded as linear linkers, thus the whole structure can be simplified into a uninodal eight-connected **CsCl** network (Fig. 2c). If just evaluated topologically, the **CsCl** net is a non-penetrating framework, in spite of its high connectivity [11]. Unusually, a careful examination of the structure of **2** reveals that every two  $\text{Cd}_2$

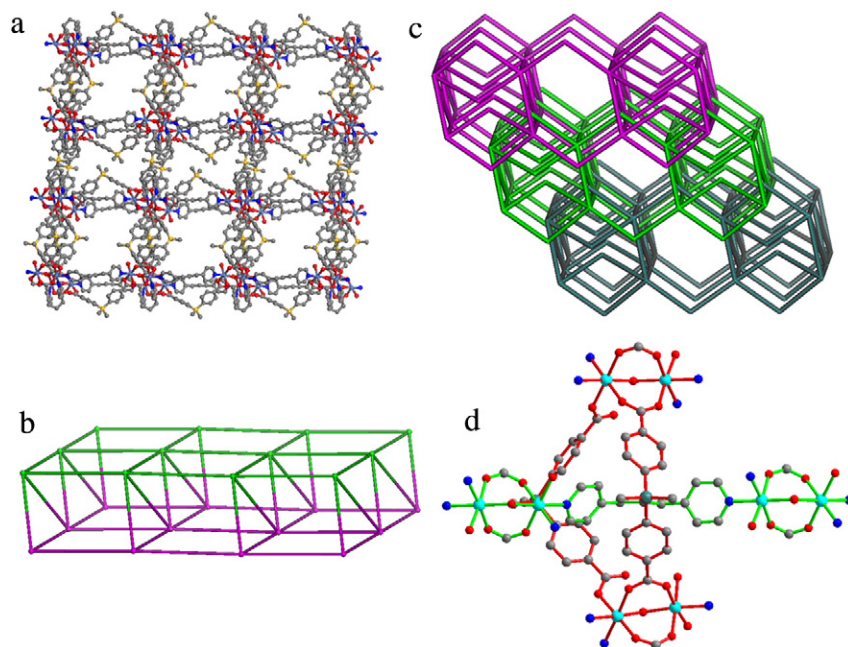


Fig. 1. (a) The perspective view of the 2D bilayer structure (The dangling bpp arms are omitted for clarity). (b) The schematic view of the 6-connected net. (c) The schematic view of the interlock of bilayer networks into a 2D → 3D polyrotaxane array. (d) The perspective view of rotaxane-like motif.

Download English Version:

<https://daneshyari.com/en/article/1301733>

Download Persian Version:

<https://daneshyari.com/article/1301733>

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