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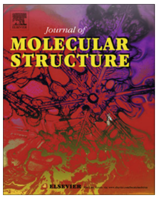


Constructions of two photoluminescent 3D coordination polymers comprising of hydroxide-bridged cadmium chain and polynuclear cadmium macrocycle using phenylsuccinic acid

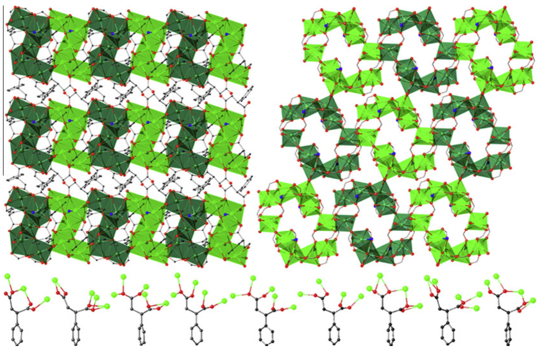
Sheng Hu *, Peng Zhang, Fang-Yong Yu, Dian-Rong Lin, Mei-Xian Chen

School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, China

HIGHLIGHTS

- Two new 3D cluster-based coordination polymers have been synthesized and characterized.
- Novel cadmium hydroxide chains and polynuclear cadmium macrocycles have been successfully introduced.
- Flexible phenylsuccinate ligand exhibits changeable coordination modes and side group effect.
- The luminescent properties of these compounds were investigated at room temperature.

GRAPHICAL ABSTRACT



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ABSTRACT

Two new coordination polymers $[Cd_5(OH)_2(psa)_4(bpe)(H_2O)_2]_n$ (**1**) and $[Cd_5(psa)_5(bpp)(H_2O)_2]_n$ (**2**) (H_2psa = phenylsuccinic acid, bpe = 1,2-bis(4-pyridyl)ethylene, bpp = 1,3-bis(4-pyridyl)propane) have been synthesized by methods of hydrothermal reaction and their crystal structures determined. In **1**, psa ligands act as changeable bridges bound to Cd atoms, resulting in the formation of a sublayer based on cadmium hydroxide chains comprising of $Cd_5(OH)_2$ units. The adjacent layers are pillared by bpe linkers forming a 3D condensed structure. **2** has a 3D structure based on cadmium carboxylate sublayer with polynuclear cadmium macrocycles, pillared by bpp ligands. The structure versatility indicates that the phenyl side groups of psa ligands play a crucial role in modulating the cluster-based coordination polymers. A discussion of the crystal structures, as well as the coordination behavior of psa ligand is provided. IR, elemental analysis and XRPD confirmed the phase purity of the bulk materials. The photoluminescent properties of **1** and**2** in the solid state are also investigated.

1. Introduction

The design and construction of novel polymeric or cluster-based metal–organic frameworks (MOFs) are currently attracting interest not only for their potential applications in magnetism, catalysis, gas storage and optical properties, but also for their fascinating topologies and intriguing structural diversity [1]. The main strategy used in this area is crystal engineering approach, which provides a facile way to imitate the structure of natural minerals by replacement of the bonds with organic bridges so as to control the assembly of various frameworks [2]. Utilization of polynuclear clusters as building blocks to construct high dimensional frameworks has been proven to be a very practicable route, owing to the fact that their large surface areas that can readily accommodate the steric demands of more organic linkers [3]. Furthermore, the coordination polymers constructed with polynuclear clusters should be more stable and exhibit more properties than those non-cluster frameworks with the same connectivity [4]. However,

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* Corresponding author. Fax: +86 20 39322231.
E-mail address: husheng@gdut.edu.cn (S. Hu).

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to establish precise principles of constructing desirable cluster-based MOFs remains a big challenge, owing to the design and synthesis of these coordination architectures are highly influenced by a few factors such as the coordination nature of the metal ion, the structural characteristics of the organic ligand, the metal–ligand ratio, the solvent quality and the other reaction conditions [5]. Therefore, the design and synthesis of new cluster-based coordination architectures for functional materials are focused on choosing versatile functional building-blocks, organic ligands and appropriate reaction conditions [6].

A novel monoligand can lead to the formation of new coordination polymers, but a mixed-ligand assembly system [7] consisting of two or three types ligands provides more variability to construct more fantastic structures. So, one primary ligand should to be elaborately selected in the assembly system. Aliphatic polycarboxylic acids, being very flexible when they involve long carbon chains, have been widely used for the synthesis of coordination polymers [8]. In contrast, the research on phenylsuccinic acid (denoted H_2psa hereafter) is still limited [9]. The H_2psa ligand exhibits an interesting phenyl ring side group, which is expected to modulate and influence the orientation relationship and coordination abilities of the two carboxylate groups. So it can be applied as a configurationally asymmetric bridging ligand leading to more interesting coordination polymers.

The secondary ligands chosen are classical long pillars [10] 1,2-bis(4-pyridyl)ethylene (bpe) and 1,3-bis(4-pyridyl)propane) (bpp). Although the two ligands all contain two peripheral pyridines symmetrically, their separation lengths and steric conformations are different, which may offer different link modes. In this research, two coordination polymers $[Cd_5(OH)_2(psa)_4(bpe)(H_2O)_2]_n$ (**1**) and $[Cd_5(psa)_5(bpp)\cdot 2H_2O]_n$ (**2**) with different cluster-based building blocks were obtained as their single crystals. The details of structures show the side group effects of the psa ligands on the conformations of frameworks. Furthermore, the auxiliary bipyridine ligands display some influences on the structures. The control experiments were carried out by not using the auxiliary bipyridine ligands above had failed to obtain any single-crystal product under identical conditions, presumable because the bipyridine ligands play vital roles in stabilizing the solid structures.

2. Experimental section

2.1. Materials and measurements

(*RS*)-phenylsuccinic acid and other chemicals were obtained from commercial sources and were used without further purification. The C, H and N microanalyses were carried out with an Elementar Vario-EL CHNS elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Bio-Rad FTS-7 spectrometer. X-ray powder diffraction (XRD) intensities for **1** and **2** were measured at 293 K on a Rigaku D/max-IIIA diffratometer (Cu Kα, $\lambda = 1.54056$ Å). The crushed single-crystalline powder samples were prepared by crushing the crystals and scanned from 3° to 60° with a step of 0.1°/s. Calculated patterns of **1** and **2** were generated with Mercury (Hg) program, available free of charge via the Internet at http://www.iucr.org. The emission/excitation spectra of **1** and **2** were measured on a Fluoro-Max-4 VPF-100 fluorescence spectrophotometer (HORIBA Jobin Yvon).

2.2. Synthesis

2.2.1. $[Cd_5(OH)_2(psa)_4(bpe)(H_2O)_2]_n$ (**1**)

$Cd(NO_3)_2\cdot 6H_2O$ (0.689 g, 2.0 mmol) was dissolved in H_2O (6 ml) at ambient temperature, followed by the addition of (*RS*)-phenylsuccinic acid (0.194 g, 1.0 mmol), 1,2-bis(4-pyridyl)ethylene (0.182 g, 1.0 mmol), NaOH (0.08 g, 2.0 mmol) in H_2O (8 ml) with vigorous magnetic stirring in a 25 ml Parr Teflon-lined stainless steel vessel. The mixture was heated for 3 days at 180 °C and then cooled to room temperature at a rate of 10 °C/h. After cooling to room temperature, colorless block-like crystals were obtained in the yield of 80% (based on phenylsuccinic acid). The phase purity of the bulk materials was confirmed by comparison of its powder diffraction pattern with that calculated from the single crystal study (Fig. S1, ESI). Elemental analysis for **1** $C_{52}H_{48}Cd_5N_2O_{20}$, Calcd: C, 39.45; H, 3.06; N, 1.77. Found: C, 39.51; H, 3.09; N, 1.75. IR data (KBr) (400–4000 cm^{-1}): 3421s, 3060m, 3023m, 1599s, 1573s, 1424s, 1407s, 1317w, 1296w, 1276s, 1237w, 1220w, 1088w, 1064m, 1031w, 1011m, 964m, 946m, 891m, 875m, 840m, 828s, 798w, 727m, 697s, 635m, 597m, 571m, 551s, 502w.

2.2.2. $[Cd_5(psa)_5(bpp)(H_2O)_2]_n$ (**2**)

Complex **2** was prepared as for **1** by using 1,3-bis(4-pyridyl)propane (0.198 g, 1.0 mmol) in place of 1,2-bis(4-pyridyl)ethylene (0.182 g, 1.0 mmol). Colorless block-like crystals were obtained in the yield of 70% (based on phenylsuccinic acid). The phase purity of the bulk materials was confirmed by comparison of its powder diffraction pattern with that calculated from the single crystal study (Fig. S2, ESI). Elemental analysis for $C_{63}H_{58}Cd_5N_2O_{22}$, Calcd: C, 43.06; H, 3.33; N, 1.59. Found: C, 43.11; H, 3.37; N, 1.62. IR data (KBr) (400–4000 cm^{-1}): 3423s, 3061m, 3026m, 2941s, 2863m, 1950w, 1608s, 1573s, 1500m, 1424s, 1277m, 1222s, 1069m, 1012s, 944w, 883w, 841m, 812s, 737m, 699s, 605m, 571m, 513s.

2.3. X-ray crystallography

Single crystals of **1** and **2** suitable for X-ray analysis were obtained directly from the above hydrothermal syntheses. The diffraction data for complexes **1** and **2** were recorded on a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 296 K (for **1**) and 293 K (for **2**). Processing data were accomplished by use of the program *SAINT*; an absorption correction based on symmetry equivalent reflections was applied using the *SADABS* program [11]. The structures were solved by direct methods and refined by the full-matrix least-squares method on F^2 with *SHELXTL* program package [12]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The CCDC reference numbers are 934021 and 934022 for crystals **1** and **2**. The crystallographic details and selected bond lengths are provided in Tables 1 and 2, respectively. The selected bond angles are provided in Tables S1.

3. Results and discussion

3.1. Structural description of **1**

Colorless block-like crystals of compound **1** were synthesized as a single phase by the hydrothermal reaction of $Cd(NO_3)_2\cdot 6H_2O$, NaOH, phenylsuccinic acid and 1,2-bis(4-pyridyl)ethylene. X-ray structural analysis shows that the asymmetric unit contains six crystallographically unique Cd atoms, two μ_3-OH^-, four psa ligands, one bpe ligand and two coordination water molecules (Fig. 1a). Cd1, Cd3, Cd4 and Cd6 atoms localize in general positions, while Cd2 and Cd5 lie in special position (SOF = 0.5). The structure of **1** is built around cadmium hydroxide chains comprising of $Cd_5(OH)_2$ units. Each cluster can also be regarded as two $[Cd_3(\mu_3\text{-}OH)_2]$ triangles sharing a common Cd vertex (Cd2 or Cd5). Each triangle has a central μ_3-OH^- core, and they are held together by bridging carboxylates around the periphery. The two $[Cd_3(\mu_3\text{-}OH)]$ triangles within the pentanuclear cluster are completely symmetrical and