Polyhedron 115 (2016) 54–60

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

# Temperature-controlled Cd(II)–phosphonate coordination polymers: Syntheses, crystal structures, and luminescent properties

Hui-Ling Sung [a,*], Cheng-Hua Lee [b], Jui-En Wu [b,c], Yuh-Sheng Wen [b], Tien-Wen Tseng [c,*], Zhi-Jia Hu [d], Tze-Min Her [d]

[a] *Division of Preparatory Programs for Overseas Chinese Students, National Taiwan Normal University, New Taipei City 244, Taiwan*
[b] *Institute of Chemistry, Academia Sinica, Taipei 115, Taiwan*
[c] *Department of Chemical Engineering, National Taipei University of Technology, Taipei 106, Taiwan*
[d] *Department of Chemical and Materials Engineering, Lunghwa University of Science and Technology, Taoyuan 333, Taiwan*

ARTICLE INFO

*Article history:*
Received 24 February 2016
Accepted 15 April 2016
Available online 29 April 2016

*Keywords:*
Cadmium
Coordination polymer
Phosphonate
Temperature effect
Ligands competition

ABSTRACT

Two temperature-controlled Cd(II)–phosphonate coordination polymers have been synthesized successfully. Compound $\{[Cd_2(H_4tpmb)(H_2O)_3]\}_n$ (**1**; $H_8tpmb$ = 1,2,4,5-tetrakis(phosphorylmethyl)benzene) produced at 80 °C adopts a three-dimensional network with a Cd:$H_2O$ ratio of 2:3, while compound $\{[Cd(H_6tpmb)(H_2O)_4]\cdot 4H_2O\}_n$ (**2**) synthesized at room temperature displays a zigzag one-dimensional chain structure with a Cd:$H_2O$ ratio of 1:4. The phosphonate ligand is partially deprotonation, being a form of $H_4tpmb^{4-}$ in **1** and $H_6tpmb^{2-}$ in **2**, where the former shows a $\mu_8$-bridging mode with a *cis,trans,cis,trans* conformation while the latter adopts a $\mu_2$-bridging mode with a *trans,cis,trans,cis* conformation. These results indicate that water molecules make higher competition in coordinating with the Cd(II) center of such materials at room temperature, while at 80 °C, the water molecules are more labile and the coordination of phosphonate to the Cd(II) center becomes dominant. This clearly illustrates a case of temperature-modulated complexation of phosphonate ligand and water molecule towards the Cd(II) center, which result in differences in ligand charges, ligand conformations, and coordination modes, leading to drastic variations of network topologies.

## 1. Introduction

Metal–organic frameworks (MOFs) [1], which can be considered to be analogous to coordination polymers [2], are typically composed of metallic centers and organic ligands. Because MOFs can be prepared with a wide variety of architectures [3], they have attracted considerable attention, since desirable structures can be obtained starting from simply constructed starting molecules via spontaneously processes such as self-assembly [4], self-organization [5] as well as self-adaptation reactions [6]. Among these processes, self-adaptation is an essential and effective process for generating desirable molecules, since this can be achieved by the adjustment of various reaction factors such as the concentration [7], pH [8], reaction time or the solvent used [9], as well as temperature used in the process [10]. For example, it has been reported that self-assembly products with different structures can be formed by controlling the amount of water in the solvent system [9h]. In other cases, by adjusting the reaction time, products with different structures can be generated through a self-adaptation process.

Inspired by efficient ligand design strategies, the phosphonate ligand with its multi-coordination atoms and flexible binding phosphonate group represent a good candidate for a ligand, given its specific geometry and the fact that it can exist in different forms [11]. To the best of our knowledge, coordination polymers containing this kind of profuse variability phosphonate ligand so far are rare [11]. Herein we report on two novel Cd(II) coordination polymers based on a tetra-phosphonate ligand, 1,2,4,5-tetrakis(phosphorylmethyl)benzene ($H_8tpmb$) [12,13], which comprises four flexible phosphonate groups attached to a benzene core via freely rotatable methylene (–$CH_2$–) joints and thus can form five possible conformations (Scheme 1). Self-assembly reactions using this ligand are found to be significantly temperature dependent.

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* Corresponding authors.
*E-mail addresses:* hlsung@ntnu.edu.tw (H.-L. Sung), f10403@ntut.edu.tw (T.-W. Tseng).

http://dx.doi.org/10.1016/j.poly.2016.04.019
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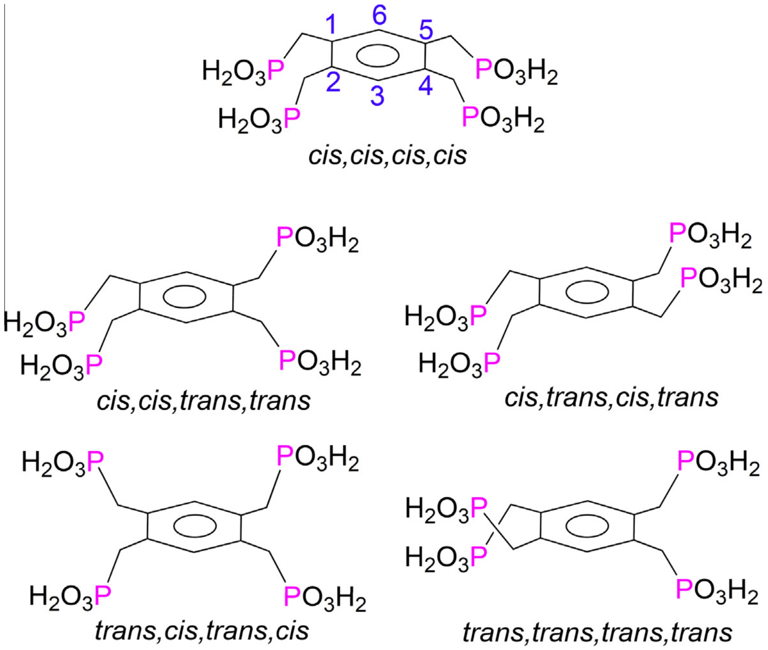

**Scheme 1.** Five possible conformations of the $H_8$tmpb ligand.

## 2. Experimental

### 2.1. Materials and instruments

Ligand $H_8$tpmb was prepared via a procedure as previously reported [12]. Other chemicals were purchased commercially and used as received without further purification. Thermogravimetric analyses were performed under nitrogen with a Perkin-Elmer TGA-7 TG analyzer. The powder X-ray diffraction patterns (PXRD) were recorded on a MPD Philips Analytical diffractometer at 40 kV, 30 mA for Cu Kα (λ = 1.5406 Å) with a step size of 0.02° in θ and a scan speed of 1 s per step size. Elemental analyses (C, H, N) were carried out on a Perkin-Elmer 2400 CHN elemental analyzer. The solid-state photoluminescence measurements were recorded on a Hitachi F4500 spectrometer.

### 2.2. Synthesis of $\{[Cd_2(H_4tpmb)(H_2O)_3]\}_n$ **1**

A mixture of $H_8$tpmb (11.6 mg, 0.025 mmol) and $Cd(ClO_4)_2{\cdot}6H_2O$ (42.0 mg, 0.10 mmol) was dissolved in 6 mL water solution. The resulting solution was kept at 80 °C for 3 h. The white acicular crystals were collected by filtration, washed with water/EtOH and dried in air. The yield is 48% (0.012 mmol). *Anal.* Calc. for $C_{20}H_{20}Cd_4O_{30}P_8$: C, 16.52; H, 2.50. Found: C, 16.31; H, 2.90%. IR (KBr, $cm^{-1}$): 3404(s), 2917(w), 2304(m), 1618(m), 1508(m), 1422 (m), 1387(m), 1260(s), 1202(s), 1122(vs), 1091(vs), 1126(m), 1020(vs), 929(vs), 753(m), 612(s), 555(s).

### 2.3. Synthesis of $\{[Cd(H_6tpmb)(H_2O)_4]{\cdot}4H_2O\}_n$ **2**

A mixture of $H_8$tpmb (11.6 mg, 0.025 mmol in 5 mL water) and $Cd(ClO_4)_2{\cdot}6H_2O$ (42.0 mg, 0.10 mmol in 1 mL water) was kept in room temperature for 16 days. The white block-shaped crystals were collected by filtration, washed with water/EtOH and dried in air. The yield is 72% (0.018 mmol). *Anal.* Calc. for $C_{10}H_{32}CdO_{20}P_4$: C, 16.95; H, 4.55. Found: C, 17.13; H, 4.50%. IR (KBr, $cm^{-1}$): 3534(s), 2919(m), 2301(m), 1627(m), 1508(m), 1422(vs), 1265(s), 1247(s), 1209(s), 1172(vs), 1093(vs), 973(vs), 931(vs), 822(m), 557(s).

### 2.4. Crystallography

Data collections for **1** and **2** were performed on a Bruker Smart CCD diffractometer and on a Bruker APEX2 CCD diffractometer, respectively, equipped with a graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Starting models for structure refinement were found using direct methods [14], and the structural data were refined by full-matrix least-squares methods on $F^2$ using the WINGX [15] and SHELX-97 [16] program packages. Non-hydrogen atoms were found from the different Fourier maps and refined with anisotropic displacement parameters. Carbon-bound hydrogen atoms were assigned by geometrical calculation and refined as a riding model. Oxygen-bound hydrogen atoms were first located on difference Fourier maps, and then fixed at the calculated positions and were included in the final refinement. Isotropic displacement parameters of all hydrogen atoms were derived from the parent atoms. The crystallographic data of **1** and **2** are summarized in Table 1. The selected bond lengths and angles are listed in Table S1, and the hydrogen bonding distances and angles are listed in Table S2.

## 3. Results and discussion

### 3.1. Syntheses

Compound $\{[Cd_2(H_4tpmb)(H_2O)_3]\}_n$ (**1**) was synthesized by reacting $Cd(ClO_4)_2{\cdot}6H_2O$ and $H_8$tpmb in aqueous solution at 80 °C (Scheme 2), while compound $\{[Cd(H_6tpmb)(H_2O)_4]{\cdot}4H_2O\}_n$ (**2**) was obtained at room temperature.

### 3.2. Crystal structure of compound **1**

A single-crystal X-ray diffraction analysis revealed that compound **1** crystallizes in the triclinic space group $P\bar{1}$, and the asymmetric unit is comprised of two Cd(II) centers, one $H_4tpmb^{4-}$ ligand, and three coordinated water molecules. Both the two crystallographically independent Cd(II) centers adopt an octahedral $\{CdO_6\}$ coordination geometry, made up of four phosphonate groups derived from four $H_4tpmb^{4-}$ ligands and two coordination