Journal of Solid State Chemistry 260 (2018) 46–51

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

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

Modular construction, magnetic property, and luminescent sensing of 3D Mn(II) and Cd(II) coordination polymers based on *p*-terphenyl-2,2″,5″,5‴-tetracarboxylate acid

Liming Fan[a,*], Yujuan Zhang[a], Jiang Wang[a], Li Zhao[a], Xiaoqing Wang[a], Tuoping Hu[a], Xiutang Zhang[b,*]

[a] *Department of Chemistry, College of Science, North University of China, Taiyuan 030051, China*
[b] *Advanced Material Institute of Research, College of Chemistry and Chemical Engineering, Qilu Normal University, Jinan 250013, China*

ARTICLE INFO

Keywords:
Terphenyltetracarboxylate
Modular construction
Structural diversity
Magnetic property
Luminescent sensing

ABSTRACT

Two 3D modular designed coordination polymers, namely, $\{[H_2N(CH_3)_2]_2[Mn(TPT)]\}_n$ (**1**), and $\{[Cd(TPT)_{0.5}(bib)]\cdot 0.5H_2O\}_n$ (**2**) (H_4TPT = *p*-terphenyl-2,2″,5″,5‴-tetracarboxylate acid, and bib = 1,3-bis((imidazol-1-yl) benzene) have been synthesized and structural characterized by EA, IR, TG, PXRD. Single-crystal X-ray diffraction analyses reveal that complex **1** is a 3D 4-connected $\{4^2.6^3.8\}$–**sra** net with the tiling modular being $[4^2.6^2.8^2]$ = $[4a.4b.6^2.8a.8b]$ (transitivity is 2451). While complex **2** is a 3D (4,4)-connected $\{6^4.8^2\}\{6^6\}_2$–**bbf** net with tiling modular is $[6.8^2]+[6^3.8]$ = [6 c.8a.8b]+[6a.6b.6 c.8a] (transitivity is 2352). The variable-temperature susceptibility of **1** has been investigated. Besides, complex **2** exhibits highly sensitive sensing of Fe^{III} ions in DMF solution.

1. Introduction

The design of coordination polymers (CPs) have attracted widespread research interests for their various potential applications as functional materials [1–5]. In general, such materials are constructed from organic linkers and inorganic nodes, depending on many factors, such as, metal ions, pH value, counteranions, metal-ligand ratios, template agents [6–12]. Numerous facts have proved that the organic linkers are the permanent leading roles in the construction of CPs, for they can determine the structural diversity, and greatly affect the properties [13–17]. Therefore, the design and rational selection of organic ligands are important in building those resultant CPs.

Polycarboxylates, have been widely used in the assembly of CPs, for their strong coordination abilities, numerous coordination modes, and the stable backbones. Among them, the tetracarboxylates, such as, 1,2,4,5-benzenetetracarboxylic acid, 3,3′,5,5′-biphenyltetracarboxylic acid, terphenyl-3,3″,5,5″-tetracarboxylic acid, quaterphenyl-3,3‴,5,5‴-tetracarboxylic acid, 1,3-di(2′,4′-dicarboxyphenyl)benzene, terphenyl-2,5,2′,5′-tetracarboxylic acid, show excellent performances in constructing diverse CPs with fascinating structures and outstanding properties [18–27]. Thus, we have reasons to believe that the modular building blocks of tetracarboxylates play important roles in the assembly of CPs. Besides, the introduction of N-donor ancillary linkers usually greatly effect the coordination modes of polycarboxylates as well as the final structures, due to the steric effects as well as synergistic effects of N-donors [28–30].

Inspired by the above-mentioned points, we designed two novel coordination polymers, $\{[H_2N(CH_3)_2]_2[Mn(TPT)]\}_n$ (**1**), and $\{[Cd(TPT)_{0.5}(bib)]\cdot 0.5H_2O\}_n$ (**2**), by using tetracarboxylate of *p*-terphenyl-2,2″,5″,5‴-tetracarboxylate acid (H_4TPT) with or without the help of 1,3-bis((imidazol-1-yl) benzene (bib) (Scheme 1). Two CPs exhibit interesting 3D modular nets with the tilings of $[4^2.6^2.8^2]$ = $[4a.4b.6^2.8a.8b]$ for **1**, and $[6.8^2]+[6^3.8]$ = [6c.8a.8b]+[6a.6b.6c.8a] for **2**, respectively. The variable-temperature susceptibility of **1** has been investigated. Besides, the luminescent sensing of complex **2** was also investigated here.

2. Experimental

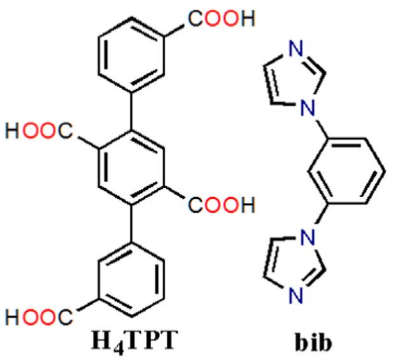
2.1. Materials and methods

All chemical reagents were purchased from Jinan Camolai Trading Company, and were used as received without further purification. Elemental analyses of C, N, and H were performed on an EA1110 CHNS-0 CE elemental analyzer. IR (KBr pellet) spectra were recorded on a Nicolet Magna 750FT-IR spectrometer. Thermogravimetric mea-

---

* Corresponding authors.
E-mail addresses: limingfan@nuc.edu.cn (L. Fan), xiutangzhang@163.com (X. Zhang).

https://doi.org/10.1016/j.jssc.2018.01.018
Received 3 December 2017; Received in revised form 19 January 2018; Accepted 21 January 2018



Scheme 1. Selected organic ligands in the assembly of **1** and **2**.

surements were carried out in a nitrogen stream using a Netzsch STA449C apparatus with a heating rate of 10 °C min^{-1}. X-Ray powder diffraction (PXRD) were carried out on a RIGAKU DMAX2500 apparatus. Variable temperature magnetic susceptibility measurement was performed on the Quantum Design SQUID MPMS XL-7 instruments. Fluorescent data were collected on the Hitachi F-4600 FL Spectrophotometer.

2.2. Syntheses of complexes 1 and 2

2.2.1. Synthesis of {[H$_2$N(CH$_3$)$_2$]$_2$[Mn(TPT)]}$_n$ (1)

A mixture of H$_4$TPT (40.6 mg, 0.1 mmol), MnSO$_4$·H$_2$O (33.8 mg, 0.2 mmol), NaOH (8.0 mg, 0.2 mmol), 12 mL H$_2$O and 2 mL DMF were added into a 25 mL stainless steel autoclave and heated at 170 °C for 3 days, and then cooled to room temperature at a descent rate of 10 °C/h. The orange crystals were collected by filtration, washed with mother liquor and ethanol for three times, and then dried at room temperature to give **1** in 39% (based on H$_4$TPT). Anal. (%) calcd. for C$_{26}$H$_{26}$MnN$_2$O$_8$: C, 56.84; H, 4.77; N, 5.10. Found: C, 56.39; H, 4.79; N, 5.07. IR (KBr pellet, cm^{-1}): 3098 (s), 1548 (vs), 1469 (w), 1396 (vs), 1257 (m), 1126 (m), 1086 (m), 1026 (m), 914 (w), 769 (s), 697 (m) (Fig. S1, See ESI).

2.2.2. Synthesis of {[Cd(TPT)$_{0.5}$(bib)]·0.5H$_2$O}$_n$ (2)

A mixture of H$_4$TPT (40.6 mg, 0.1 mmol), bib (42.2 mg, 0.2 mmol), CdSO$_4$·8/3H$_2$O (51.3 mg, 0.2 mmol), NaOH (8.0 mg, 0.2 mmol), 12 mL H$_2$O and 2 mL DMF were added into a 25 mL stainless steel autoclave and heated at 170 °C for 3 days, and then cooled to room temperature at a descent rate of 10 °C/h. The orange crystals were collected by filtration, washed with mother liquor and ethanol for three times, and then dried at room temperature to give 2 with a yield of 46% (based on H$_4$TPT). Anal. (%) calcd. for C$_{46}$H$_{32}$Cd$_2$N$_8$O$_9$: C, 51.85; H, 3.03; N, 10.52. Found: C, 51.48; H, 3.12; N, 10.47. IR (KBr pellet, cm^{-1}): 3123 (m), 2107 (m), 1864 (m), 1653 (vs), 1521 (s), 1375 (s), 1304 (s), 1211 (m), 1181 (m), 1017 (m), 857 (m), 812 (m), 708 (m) (Fig. S2, See ESI).

2.3. X-ray crystallography

Single crystals of 1 and 2 with appropriate dimensions were chosen under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corporation) before being mounted on a glass fiber for data collection. Intensity data collection was carried out on a Siemens SMART diffractometer equipped with a CCD detector using MoKα monochromatized radiation (λ = 0.71073 Å). The absorption correction was based on multiple and symmetry-equivalent reflections in the data set using the SADABS program. The structures were solved by direct methods and refined by full-matrix least-squares using the SHELXTL package [31–33]. Anisotropic thermal parameters were applied to all non-hydrogen atoms. And all hydrogen atoms attached to C and N atoms were placed geometrically [34]. For 1, the dimethylammonium ions are disordered and were refined with split positions and the occupancy ratios of 69:31 for N1, C1, C2 and N1′, C1′, C2′, and 47:53 for N2, C3, C4 and N2′, C3′, C4′, respectively. In 2, the carboxyl O atoms are disordered with the occupancy ratios of 41.9:58.1 for O1–O4 and O1′–O4′. Crystallographic data for 1 and 2 are given in Table 1. Selected bond lengths and angles for 1 and 2 are listed in Table S1.

Table 1
The crystal data, experimental conditions, and structure refinement parameters of **1** and **2**.

Complex	**1**	**2**
Empirical formula	C$_{26}$H$_{26}$MnN$_2$O$_8$	C$_{46}$H$_{32}$Cd$_2$N$_8$O$_9$
Formula weight	549.43	1065.60
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$/n	$P2_1$/c
a [Å]	15.681(12)	9.4757(5)
b [Å]	9.295(7)	15.6375(8)
c [Å]	18.891(14)	14.3292(7)
β [°]	111.205(13)	93.9480(10)
V [Å^3]	2567(3)	2118.21(19)
Z	4	2
Dc/(g cm^{-3})	1.422	1.671
F(000)	1140	1064
μ(Mo Kα)/mm^{-1}	0.566	1.072
θ range (deg)	2.60–26.37	1.93–25.01
Temperature (K)	296(2)	298(2)
R_{int}	0.0488	0.0179
Refinement method	Full-matrix least-squares on F^2	
Goodness-of-fit on F^2	1.098	1.096
R_1, wR_2 [$I > 2\sigma(I)$][a,b]	0.1015, 0.3201	0.0258, 0.0682
R_1, wR_2 (all data)[a,b]	0.1222, 0.3386	0.0282, 0.0697
CCDC number	1588778	1588779

[a] $R_1 = \Sigma||Fo|-|Fc|/\Sigma||Fo|$.
[b] $wR_2 = \{[\Sigma w(Fo^2-Fc^2)^2/\Sigma w(Fo^2)^2]\}^{1/2}$.

3. Result and discussion

3.1. Structure descriptions

3.1.1. Crystal Structure of {[H$_2$N(CH$_3$)$_2$]$_2$[Mn(TPT)]}$_n$ (1)

Structural analysis reveals that complex **1** is a 3D framework which crystallizes in monoclinic system $P2_1/n$, and its asymmetric unit contains one Mn$^{\mathrm{II}}$ ion, one TPT^{4-} ligand, and two dimethylammonium ions for charge balancing (Fig. 1) [35]. Each Mn$^{\mathrm{II}}$ ion is located in a distorted {MnO$_6$} octahedral geometry, completed by six O atoms from two (κ^1-κ^0)-μ_1 carboxyl groups and two (κ^1-κ^1)-μ_1 chelating carboxyl groups. The bond lengths of Mn–O span from 2.082(6) Å to 2.326(7) Å, and the bond angles around Mn$^{\mathrm{II}}$ ions are in the range of 56.9(3)–163.3(3)°, respectively.

The H$_4$TPT is completely deprotonated and coordinated with four Mn$^{\mathrm{II}}$ ions by adopting (κ^1-κ^1)-(κ^1-κ^0)-(κ^1-κ^1)-(κ^1-κ^0)-μ_4 coordination mode (Mode I, Scheme 2), in which the carboxyl groups attaching

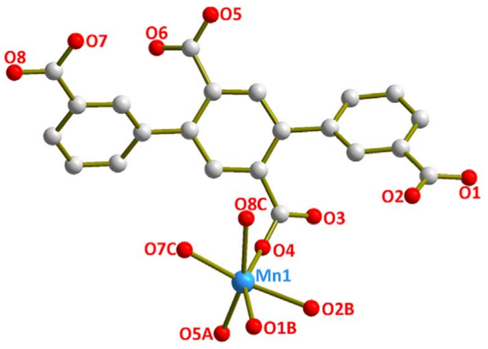


Fig. 1. The coordination environment of Mn(II) ion in **1** (Symmetry codes: A: −1/2+x, 3/2−y, −1/2+z; B: −x, 2−y, 1−z; C: 1−x, 2−y, 1−z.).