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A new pillared-layer 3D coordination polymer involving *in situ* generated formate

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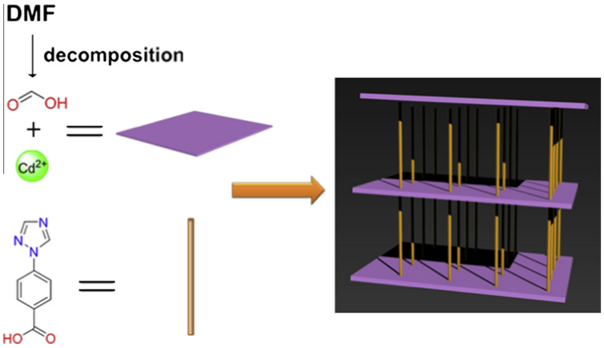
HIGHLIGHTS

- The 3D polymer is constructed by pillared-layer structures.
- The polymer contains *in situ* generated formate from the decomposition of solvent DMF.
- The compound displays fluorescence property.

GRAPHICAL ABSTRACT

A new pillared-layer 3D coordination polymer, $[Cd(cpt)(HCOO)]_n$ (**1**), has been constructed based on 1-(4-carboxyphenyl)-1,2,4-triazole) ligand (Hcpt). It is noteworthy that the polymer contains a novel 2D metal-formate layer by *in situ* generating formate ligands from decomposition of DMF. Additionally, the fluorescence property of **1** was discussed.



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ABSTRACT

A new Cd-based coordination polymer, $[Cd(cpt)(HCOO)]_n$ (**1**), has been synthesized from 1-(4-carboxyphenyl)-1,2,4-triazole) ligand (Hcpt). The structure was characterized through X-ray crystallography, elemental analysis, and IR spectrum. Compound **1** presents a three-dimensional (3D) pillared-layer structure constructed by metal-formate layers and cpt^- ligands. Moreover, the unusual formate anions are generated *in situ* from the decomposition of DMF precursors. The fluorescence property of **1** in solid state was also researched.

Introduction

Since the first man-made coordination polymer, Prussian Blue, was found in early eighteenth century, coordination polymers (CPs) have been attracting significant attention and becoming a research hotspot with massive potential applications, such as gas storage and chemical separations [1], heterogeneous catalysis [2], drug delivery [3], sensor devices [4], and magnetism [5]. For researchers in crystal engineering and supramolecular chemistry, how to synthesize CPs with predesigned structures and ideal functionalities become an ultimate goal. In order to solve this problem, an effective strategy, the so called pillared-layer method

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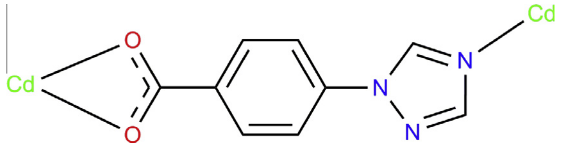

Fig. 1. Schematic representation of the observed coordination mode of cpt$^-$ ligand in **1**.

was created, which has been becoming a pretty useful guiding principle to synthesize new kinds of CPs [6,7]. The creative work brings us fresh perspectives and knowledge about using a controlled measure to predict, design and synthesize of the target compounds. By survey of the various structures of CPs, one can see that most of them were constructed beforehand by introducing multidentate chelating ligands to capture metal ions to form the 2D layers, rare studies have focused on the O-donor from *in situ* generated formate to assemble layers. As we know, the formate anion is a three-atom bridge that has its own unique characteristics, such as minor steric hindrance, strong coordination ability and flexible coordination mode [7]. Thus these features make small-volume formate molecules have strong coordination ability and provide more chances to chelate center metal ions to construct metal-formate 2D layers. Given the above consideration, we selected 1-(4-carboxyphenyl)-1,2,4-triazole (Hcpt) (see SI) as multidentate ligand bearing O-donor and N-donor at the same time to give chelating and the bridging coordination modes (see Fig. 1). We also elaborately used *N,N-dimethylformamide* (DMF) as solvent which often decomposes to *in situ* generate formate under solvothermal conditions [8] and favors for the construction of metal-formate layers. With these points in mind, we successfully constructed a novel Cd^{II}-based coordination polymer, $[Cd(cpt)(HCOO)]_n$ (**1**). Compound **1** presents a novel 3D pillared-layer structure. Furthermore, the crystal structure, topological analyses and fluorescence property of **1** have also been researched.

Experiment section

Materials and methods

All purchased chemicals were of analytical grade and used without further purification.

Elemental analyses (C, H, and N) were performed on a Perkin–Elmer 2400 analyzer. IR spectra were recorded on a Nicolet-5700 FT-IR spectrophotometer with KBr pellets in the 4000–400 cm^{-1} region. The powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Advance diffractometer with Cu Kα radiation (λ = 1.5418 Å) and a graphite monochromator at room temperature. Simulation of the PXRD spectra were carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program available free of charge via the Internet at http://www.ccdc.cam.ac.uk. The photoluminescence spectra were measured on a Perkin Elmer LS-55 spectrofluorometer.

Synthesis of $[Cd(cpt)(HCOO)]_n$ (1)

A mixture of $Cd(NO_3)_2{\cdot}4H_2O$ (0.0308 g, 0.1 mmol), Hcpt (0.0189 g, 0.1 mmol) and $DMF/CH_3CN/H_2O$ (8 mL, 6:1:1, v/v/v) was placed in a tightly capped 20 mL vial under ultrasonic irradiation to produce a clear solution, which was then heated at 85 °C for 3 days and cooled to room temperature at a rate of 10 °C h^{-1}. Colorless block shaped crystal of **1** were collected in 56% yield (based on Cd). The resulting crystals were rinsed with DMF three times and then dried at room temperature. Elemental analysis for $C_{10}H_7CdN_3O_4$ (Mr = 345.60) (**1**): calcd: C 34.75, H 2.04, N 12.16%; found: C 34.68, H 2.09, N 12.47%. The phase purity of the bulk crystals was proved by their powder X-ray diffraction (PXRD) pattern (Fig. S1).

X-ray crystallography

Single-crystal X-ray diffraction for complex **1** were collected on a Bruker SMART-1000 CCD diffractometer at room temperature with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation in the ω scan mode. The diffraction profiles were integrate by the program *SAINT* [9]. All the structures were solved by direct methods using the *SHELXS* program of the *SHELXTL* package and refined by full-matrix least-squares methods with *SHELXL* program [10]. All non-hydrogen atoms were refined with anisotropic displacement parameters, while the hydrogen atoms on ligands were placed in idealized positions with isotropic thermal parameters. The command "omit −3.00 50.04" was used to omit some disagreeable reflections during the refinement of the compound **1** (see Table 1).

Results and discussion

Crystal structure description

Single-crystal X-ray diffraction analysis reveals that **1** crystallizes in the orthorombic space group *Pbcm*, and has a 3D pillared-layer framework containing deprotonated HCOO$^-$ *in situ* generated from the decomposition of solvent DMF. As shown in Fig. 2a, two asymmetric Cd^{2+} ions have two kinds of coordination modes, which are, the hexa-coordinated distorted octahedron geometry (Cd1^{2+}) and the octa-coordinated distorted geometry (Cd2^{2+}). The Cd1^{2+} is coordinated with four bidentate oxygen atoms deriving from four different HCOO$^-$ and two monodentate nitrogen atoms originating from two different cpt$^-$ ligands. The Cd2^{2+} is coordinated with four bidentate oxygen atoms deriving from two different HCOO$^-$ and four monodentate oxygen atoms originating from two different cpt$^-$ ligands. The selected bond lengths and angles are listed in Table S1 (SI). All cpt$^-$ ligands possess the same coordination mode: the carboxylate group chelates one Cd^{2+} ion, while the N-donor of the five-membered triazole heterocyclic ring bridges another Cd^{2+} ion. The HCOO$^-$ have the same coordination mode, which adopts both chelating and bridging coordination modes with two O-donors chelating the Cd1^{2+} ion and bridging the different Cd1^{2+} and Cd2^{2+} ions at the same time

Table 1
Crystal data and structure refinement for compound **1**.

Empirical formula	$C_{10}H_7CdN_3O_4$
Formula weight	345.59
Crystal system	Orthorombic
Space group	Pbcm
a/Å	6.8232(4)
b/Å	13.2372(11)
c/Å	23.2008(17)
α/°	90
β/°	90
γ/°	90
V/Å^3	10,932(3)
Z	8
D_{calc}/g/cm^3	2.191
R_{int}	0.0381
R_1 [$I > 2\theta(I)$]	0.0279
wR_2 [$I > 2\theta(I)$]	0.0529
R_1 (all data)	0.0407
wR_2 (all data)	0.0588
GOF	1.089