

Short communication

A new 3D cadmium coordination polymer containing 3-amino-1H-1,2,4-triazole: Synthesis, structure, and property

Bing Liu^{a,*}, Mei-Ting Wen^a, Mei-Lin Shen^b, Wei-Ni Miao^a, Ting-Ting He^a, Ling Xu^{b,*}^a College of Chemistry and Chemical Engineering, Shaanxi University of Sciences and Technology, Xi'an 710021, Shaanxi Province, PR China^b Key Laboratory of Macromolecular Science of Shaanxi Province, School of Chemistry & Chemical Engineering, Shaanxi Normal University, Xi'an 710062, Shaanxi Province, PR China

ARTICLE INFO

Article history:

Received 23 October 2017

Received in revised form 20 November 2017

Accepted 22 November 2017

Available online 2 December 2017

Keywords:

Coordination polymer

1,2,4-Triazole

Fluorescence

Crystal structure

ABSTRACT

Cadmium acetate ($\text{Cd}(\text{Ac})_2$) reacted with 3-amino-1H-1,2,4-triazole (Hatr) under hydrothermal conditions to produce a 3D framework, $[\text{Cd}_5(\text{atr})_7(\text{Ac})_3(\text{H}_2\text{O})_2]$ (**1**), which is constructed through the interweaving of the 2D (4'4) layers with the 1D zigzag $[\text{Cd}_3(\text{atr})_2(\text{H}_2\text{O})]$ chains. Compound **1** was isolated with high phase purity confirmed by PXRD. TGA indicates the thermal decomposition temperature of compound **1** at 343 °C, showing the framework of **1** has high thermal stability. The solid state fluorescence of **1** at ambient temperature exhibits a blue emission at 419 nm, assigned to intraligand $\pi \rightarrow \pi^*$ transition of 1,2,4-triazole ring, which is similar to that of free Hatr with emission at 427 nm. The temperature-dependent fluorescence of **1** shows a thermal quenching with 43.78% quenching rate at 200 °C, and the fluorescent intensity can be completely recovered as the temperature decreased to ambient temperature.

© 2017 Published by Elsevier B.V.

Coordination polymers (CPs) have made many progresses recently in many fields, such as gas storage and selective separation [1], chemosensor [2], light-emitting devices [3], catalysis [4], drug-delivery [5], gas/liquid detection [6], which aims at the structure constructions and the structure-property relationship [7]. A lot of work have been devoted to the structure design and controlled synthesis of CPs, attributing to understand the structure-property relationship [8]. However, at present, the preparation of a CP with predicted structure and desired property is still a challenge [9]. One of the strategies of CP structure construction is the rational selection of inorganic metal connectors and organic linkers [10]. The organic linkers containing the donor sites of N or O atoms are commonly used to tune the CP structure constructions [11]. The metal azolate frameworks have attracted much interest due to the rich π -electron aromatic N-heterocycles bind to soft transition metal showing charming structures and properties with high stabilities [12]. Compared to the famous diazole ligands of imidazole and pyrazole with simple coordination modes to fabricate the predictable structures, 1,2,4-triazole ligands with one more nitrogen donor exhibit less predictable coordination behaviors and relative weaker coordination abilities. With the bridging fashions of $\mu_3-1\kappa\text{N}:2\kappa\text{N}:4\kappa\text{N}$, $\mu_2-1\kappa\text{N}:2\kappa\text{N}$, $\mu_2-2\kappa\text{N}:4\kappa\text{N}$ [13], 1,2,4-triazole ligands demonstrate themselves as versatile linkers to construct "simple, high-symmetry" structures [14]. 3-amino-1H-1,2,4-triazole (Hatr) is a two-connecting neutral or three-connecting anionic (deprotonated) ligand in the constructions of coordination polymers, which vails to achieve open porous

CPs and new topological nets [15]. In this contribution, we present a 3D atr-containing cadmium CP, $[\text{Cd}_5(\text{atr})_7(\text{Ac})_3(\text{H}_2\text{O})_2]$ (**1**), which was synthesized under hydrothermal condition [16] and characterized by single crystal X-ray diffraction (SCXRD) (Table 1), powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), solid-state and temperature-dependent fluorescence, and FT-IR. Compound **1** shows interesting structure features, high thermal stability, blue fluorescence, and fluorescence thermal quenching.

1. Crystal structure

The single crystal analysis reveals **1**, $[\text{Cd}_5(\text{atr})_7(\text{Ac})_3(\text{H}_2\text{O})_2]$, is a 3D architecture, in whose asymmetric unit there are five cadmium atoms, seven atr[−] ligands, three Ac[−] anions, and two coordinated water molecules. Compound **1** crystallizes in orthorhombic noncentrosymmetric space group $P2_12_12_1$, whose structural flack factor is $-0.02(6)$, indicating the absolute structure is accurate [17]. Five cadmium atoms show two types of coordination geometries: five-coordinated Cd1, Cd2 and Cd5 atoms are in distorted CdN_5 and CdN_3O_2 square pyramids and a CdN_3O_2 triangular bipyramid respectively; six-coordinated Cd3 and Cd4 are in CdN_5O and CdN_3O_3 octahedra (Supporting information, Fig. S1). All the deprotonated atr[−] ligands adopt the same coordination mode of $\mu_3-1\kappa\text{N}:2\kappa\text{N}:4\kappa\text{N}$ (Supporting information, Scheme S1a). The Ac[−] anions exhibit three types of coordination modes: μ_3 -monodentate bridging/monodentate, μ_2 -monodentate bridging, and monodentate (Supporting information, Scheme S1b–d). Each Cd3 shapes a $[\text{Cd}(\text{H}_2\text{O})]$ subunit with O1W as a terminal ligand, which is further connected into a 1D $[\text{Cd}(\text{atr})(\text{H}_2\text{O})]$ chain along the

* Corresponding authors.

E-mail addresses: liubing@sust.edu.cn (B. Liu), xuling@snnu.edu.cn (L. Xu).

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

| Compound | 1 |
|---|--|
| Empirical formula | C ₂₀ H ₃₁ Cd ₅ N ₂₉ O ₈ |
| Fw | 1367.74 |
| Crystal system | orthorhombic |
| Space group | P2 ₁ 2 ₁ 2 ₁ |
| a/Å | 13.3148(7) |
| b/Å | 15.0801(5) |
| c/Å | 19.6590(4) |
| V/Å ³ | 3947.3(3) |
| Z | 4 |
| D _c (Mg m ⁻³) | 2.302 |
| μ/mm ⁻¹ | 2.734 |
| F(000) | 2632.0 |
| Crystal size/mm ³ | 0.20 × 0.10 × 0.05 |
| 2θ/° | 8.24 to 50.046 |
| Reflections collected | 13,449 |
| Independent reflections | 6627 [R _{int} = 0.0768, R _{sigma} = 0.1307] |
| S | 1.020 |
| Final R ₁ , wR ₂ [I > 2σ(I)] | R ₁ = 0.0682, wR ₂ = 0.1412 |
| R ₁ , wR ₂ (all data) | R ₁ = 0.1064, wR ₂ = 0.1631 |
| Δρ _{max} /min/e ⁻ Å ⁻³ | 1.82/−1.18 |
| Flack parameter | −0.02(6) |

$$R_1 = (\sum ||F_o| - |F_c|| / \sum |F_o|). \quad wR_2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum (w|F_o|^2)]^{1/2}.$$

a-direction by the atr⁻ ligands with N71 connecting neighboring [Cd(H₂O)] subunits in μ₂-1κN: 4κN mode (Fig. 1). Cd2 and Cd5 are alternately linked by the μ₂-atr⁻ ligands with N61 and Ac⁻ bridges into a [Cd₂(atr)(Ac)] chain along the *a*-direction, and its neighboring staggered chain is connected by the μ₂-atr⁻ ligands with N12 into a lattice-like chain (Fig. 1). These ladder-like chains fabricate with the [Cd(atr)(H₂O)] chain containing Cd3 through two groups of μ₂-atr⁻ bridges with N21 and N31 into a 2D (4'4) layer along the *ac*-plane (Fig. 1; the topological

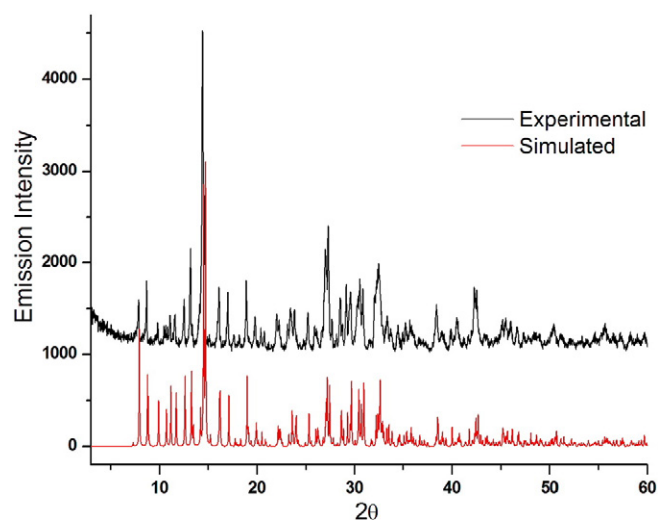


Fig. 2. Comparison of the simulated and experimental PXRD patterns of compound **1**.

network in Supporting information, Fig. S2). Cd4 also shapes a similar [Cd(H₂O)] subunit. Each Cd1 connects N44 and N51 of two atr⁻ ligands in almost coplanar mode with the dihedral angle of 3.364°. The two atr⁻ ligands continue to bind the [Cd(H₂O)] subunits into a 1D zigzag [Cd₃(atr)₂(H₂O)] chain along the *c*-direction (Fig. 1). The 2D (4'4) layers interweave with the zigzag [Cd₃(atr)₂(H₂O)] chains through the rest N sites of the atr⁻ ligands and the Ac⁻ to form a 3D architecture (Fig. 1).

Considering the structural features of **1**, the Cd₂(Ac) subunit that is formed by the μ₂-monodentate bridging Ac⁻ bridging Cd2 and Cd4

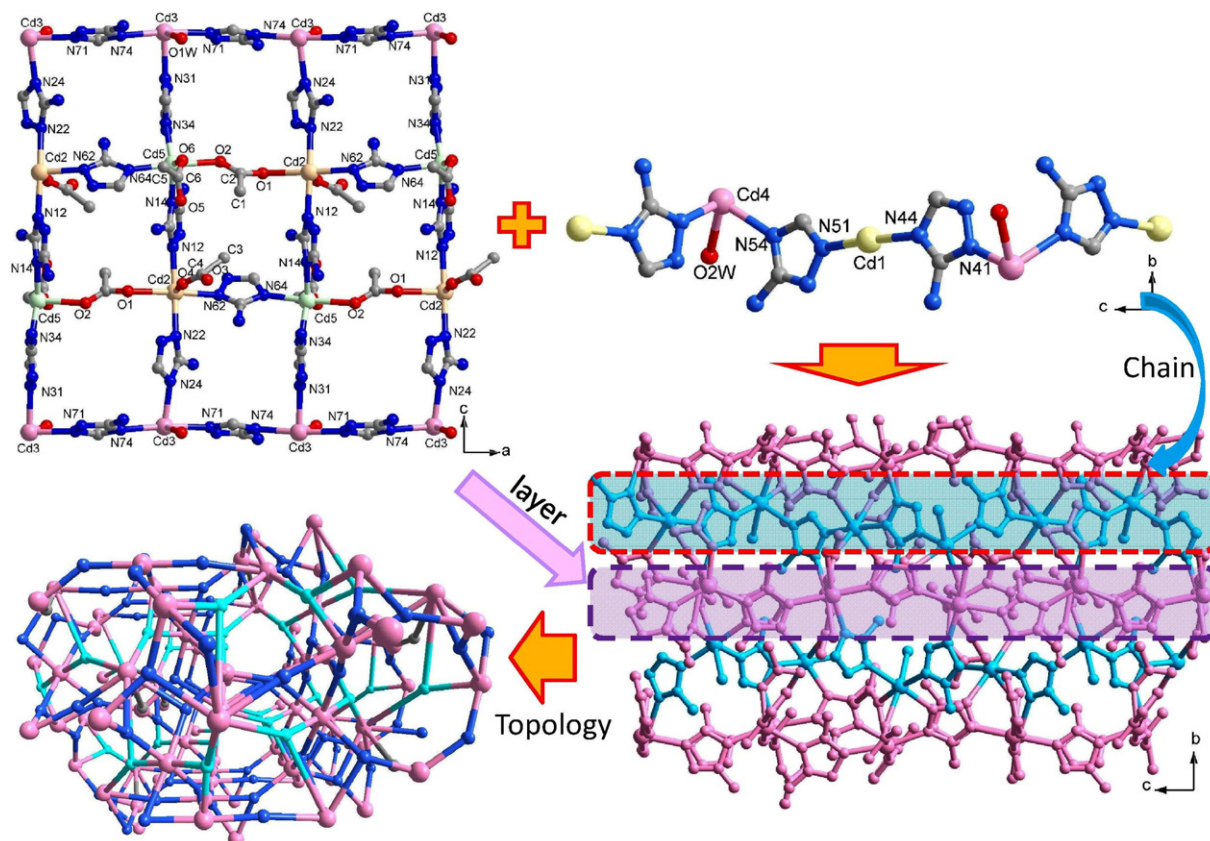


Fig. 1. The structural construction and the topological network of **1**.

Download English Version:

<https://daneshyari.com/en/article/7748694>

Download Persian Version:

<https://daneshyari.com/article/7748694>

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