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Synthesis, structure and luminescent property of a new 3D porous metal–organic framework with rutile topology

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Abstract

A new 3D porous metal–organic framework (MOF), Cd(CTC)(HPDA)·(H_2O) (**1**) (CTC = *cis*,*cis*-1,3,5-cyclohexanetricarboxylate and PDA = 1,3-propanediamine) has been synthesized by using an organic amine, PDA, as a template. X-ray crystallography reveals that two cadmium centers are coordinated by six different carboxylate groups to construct a dinuclear octahedral secondary building unit (SBU), and these octahedral SBUs are further interconnected by the cyclohexane rings of CTC to generate a 3D network with quadrangular channel dimensions of ca. 10×17 Å^2. In this structure, the dinuclear octahedral SBU can be defined as a 6-connected node, and CTC ligating with three SBUs can act as a 3-connected node. So the resulting structure of **1** is a binodal (3,6)-connected net with rutile topology. Additionally, polymer **1** exhibits intense fluorescence at 364 nm with the excitation peak at 240 nm in the solid state at room temperature.

Keywords: Metal–organic framework; Fluorescence; 1,3-Propanediamine; *cis*,*cis*-1,3,5-Cyclohexanetricarboxylate; Rutile topology; Template

1. Introduction

Metal–organic frameworks (MOFs) have attracted much attention because of their enormous varieties of interesting molecular topologies and wide potential applications as functional materials [1–14]. However, it is still a challenging task to explore successful synthetic strategies for the preparation of the MOFs that have expected applications and intriguing structures, because these preparations are affected by many factors, such as solvent system, template, and reaction temperature [15–17]. Recently, Yaghi et al. successfully synthesized a series of Zn–BTC (BTC = 1,3,5-benzenetricarboxylate) frameworks by employing different solvents and organic bases, and found that the dimensionality of the resulting Zn–BTC framework is mainly dependent on the solvent media and the strength of organic base [18]. Additionally, Zaworotko et al. presented two very interesting Zn–BTC compounds by self-assembly of triangular, square, and tetrahedral molecular building blocks (MBBs) in the presence of different solvents, benzene and chlorobenzene [19]. In previous studies, our group has successfully prepared some novel MOFs by utilizing various organic bases, and found that they play different roles in the formation of various types of structures: an agent to deprotonate O-donor ligands, a template to construct new architectures, and a ligand to coordinate to the metal ion [20–23]. As a sequel, we use an organic amine, PDA (PDA = 1,3-propanediamine), as a template, and report here the crystal structure and luminescent property of a new 3D porous MOF with rutile topology, Cd(CTC)(HPDA)·(H_2O) (**1**) (CTC = *cis*,*cis*-1,3,5-cyclohexanetricarboxylate), constructed from 6-connected dinuclear octahedral cadmium–carboxylate SBUs (SBU = secondary building unit) and 3-connected CTC ligands.

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2. Experimental

2.1. Materials and measurements

All reagents and solvents were commercially available and used as received without further purification. A Perkin-Elmer TGA 7 thermogravimetric analyzer and a Perkin-Elmer DTA 1700 differential thermal analyzer were used to obtain thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves in air with a heating rate of 10 °C min^{-1}. Powder X-ray diffraction (XRD) data were collected on a Siemens D5005 diffractometer with CuKα radiation ($\lambda = 1.5418$ Å). Analyses for C, H, and N were carried out on a Perkin-Elmer 2400 element analyzer, and the inductively coupled plasma (ICP) analysis on a Perkin-Elmer Optima 3300 DV ICP spectrometer. The infrared (IR) spectra were recorded (400–4000 cm^{-1} region) on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. Fluorescence spectroscopy data were recorded on a LS55 luminescence spectrometer.

2.2. Preparation of Cd(CTC)(HPDA)·(H_2O) (**1**)

A mixture of $CdCl_2 \cdot 2.5\,H_2O$ (0.01 g, 0.05 mmol), H_3CTC (0.02 g, 0.1 mmol), DMF (DMF = *N*,*N*-dimethylformamide, 8.0 mL), EG (EG = ethylene glycol, 3.0 mL) and H_2O (2.0 mL) was stirred in air for 2 h, and then a DMF solution (0.5 mL) of PDA (0.05 mL) was slowly diffused into the above mixture solution at 65 °C for five days. The resulting colorless block-shaped single crystals of **1** were collected in 62% yield based on cadmium. The complex was insoluble in common organic solvents such as acetone, methanol, ethanol, dichloromethane, acetonitrile, chloroform, and DMF. Elemental analysis and ICP analysis for $C_{12}H_{22}N_2O_7Cd$ (418.73): C 34.47, H 5.11, N 6.72, Cd 26.88% (calcd: C 34.42, H 5.30, N 6.69, Cd 26.85%). FT-IR(KBr): $\bar{v}$ = 3419(s), 2937 (w), 2362 (w), 1653 (w), 1558 (s), 1516 (s), 1406 (s), 1352 (m), 1215 (w), 1066 (m), 981 (w), 919 (m), 773 (w), 719 (w), 694 (w), 586 (w), 538 (w) cm^{-1}.

2.3. X-ray crystallography

A colorless block-shaped crystal of **1** was selected for X-ray structural analysis on a Bruker SMART CCD diffractometer at 298 K. The complex crystallized in the space group $P2_1/c$, monoclinic, dimensions $0.32 \times 0.30 \times 0.18$ mm^3. A total of 7601 reflections were collected in the range of $2.34 < \theta < 25.00$, of which 2614 were unique. The final $R_1(wR_2)$ value 0.0245 (0.0670) for 2283 independent reflections [$I > 2\sigma(I)$]. The structure was solved and refined by full-matrix least-squares on F^2 values (SHELXL-97) [24]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at calculated positions. The crystallographic data and selected bond lengths and angles for polymer **1** are listed in Tables 1 and 2, respectively.

Table 1
Crystal data for **1**

Empirical formula	$C_{12}H_{20}N_2O_7Cd$
F_w	416.70
Cryst syst	Monoclinic
Space group (No.)	$P2_1/c$(14)
a (Å)	9.7538(14)
b (Å)	17.423(3)
c (Å)	10.0230(15)
β (°)	118.697(2)
V (Å^3)	1494.1(4)
Z	4
T (K)	298(2)
λ (Å)	0.71073
ρ_{calc} (g/cm^3)	1.853
μ (mm^{-1})	1.499
$R_1{}^a(I > 2\sigma(I))$	0.0245
$wR_2{}^b$	0.0670

$^aR_1 = \sum \| F_o| - |F_c\| / |F_o|$, $^bwR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

Table 2
Selected bond lengths (Å) and bond angles (°) for **1**

Bond lengths (Å)	
Cd(1)–O(5)#1	2.252(2)
Cd(1)–N(1)	2.330(3)
Cd(1)–O(3)#2	2.384(3)
Cd(1)–O(4)#2	2.449(3)
Cd(1)–O(2)	2.467(3)
Cd(1)–O(2)#3	2.515(3)
Cd(1)–O(1)	2.527(3)
Bond angles (°)	
O(5)#1–Cd(1)–N(1)	107.52(10)
O(5)#1–Cd(1)–O(3)#2	141.07(9)
N(1)–Cd(1)–O(3)#2	90.90(11)
O(5)#1–Cd(1)–O(4)#2	93.87(9)
N(1)–Cd(1)–O(4)#2	83.39(10)
O(3)#2–Cd(1)–O(4)#2	53.60(9)
O(5)#1–Cd(1)–O(2)	126.18(9)
N(1)–Cd(1)–O(2)	101.20(10)
O(3)#2–Cd(1)–O(2)	80.91(9)
O(4)#2–Cd(1)–O(2)	134.46(8)
O(5)#1–Cd(1)–O(2)#3	79.75(9)
N(1)–Cd(1)–O(2)#3	172.21(9)
O(3)#2–Cd(1)–O(2)#3	84.79(10)
O(4)#2–Cd(1)–O(2)#3	99.15(9)
O(2)–Cd(1)–O(2)#3	71.74(9)
O(5)#1–Cd(1)–O(1)	87.83(9)
N(1)–Cd(1)–O(1)	82.87(11)
O(3)#2–Cd(1)–O(1)	129.17(9)
O(4)#2–Cd(1)–O(1)	166.02(10)
O(2)–Cd(1)–O(1)	51.60(8)
O(2)#3–Cd(1)–O(1)	94.81(9)

Symmetry transformations used to generate equivalent atoms: #1 $x-1, y, z$; #2 $-x+1, y-1/2, -z+1/2$; #3 $-x+1, -y, -z+1$.

3. Results and discussion

3.1. Synthesis

Polymer **1** was synthesized under mild conditions in the presence of an organic amine, PDA. In a typical synthesis, a mixture of $CdCl_2 \cdot 2.5H_2O$ with H_3CTC was prepared with a mole ratio of 2:1 in DMF/EG/H_2O, then a DMF solution of PDA was allowed to diffuse into the above mixture at 65 °C to deprotonate the acid and initiate the copolymerization process. After keeping the reaction solution for five days, colorless block shaped crystals of **1** were collected in 62% yield based on cadmium. It is notable that PDA plays a template role in this structure, because the control reaction without using PDA or using another base (such as triethylamine (TEA) or ethylenediamine (EDA)) instead will not result in compound **1** under the same conditions, and only some very little unknown crystals or white powder which should be cadmium hydroxide have been obtained. Additionally, the experiments without EG will also result in white powder of cadmium hydroxide.

3.2. Description of the structure

X-ray crystallography reveals that **1** crystallizes in the monoclinic system, space group $P2_1/c$ (No. 14). The basic building unit of **1** contains two cadmium centers, six CTC ligands, and two coordinated HPDA. As shown in Fig. 1, each Cd(II) center is coordinated by six oxygen atoms from four different carboxylate groups of CTC and one nitrogen atom from terminal HPDA molecule, and each CTC ligand coordinates to four cadmium ions through its three carboxylate groups in the unidentate, chelating bidentate and chelating/bridging bidentate coordination fashions, respectively. In this structure, the distances of Cd–O (2.252–2.527 Å) are similar to normal Cd–OCO distances (2.251–2.879 Å) [25], and the bond angles of O(N)–Cd–O(N) are from 51.60(8)° to 172.21(9)°.

As shown in Fig. 2, two cadmium centers are coordinated by six different carboxylate groups to construct a dinuclear octahedral SBU, and these octahedral SBUs are further interconnected by the cyclohexane rings of CTC to generate a 3D network with quadrangular channel dimensions of ca. 10×17 Å^2 (measured between opposite atoms) viewed along the [100] direction. In this structure, the vacancies of each asymmetric unit are filled with one coordinated HPDA molecule and one guest H_2O which connects to the framework via hydrogen bonds (O7···O6 2.657 Å, O7···N2 2.796 Å and O7···O4 3.004 Å).

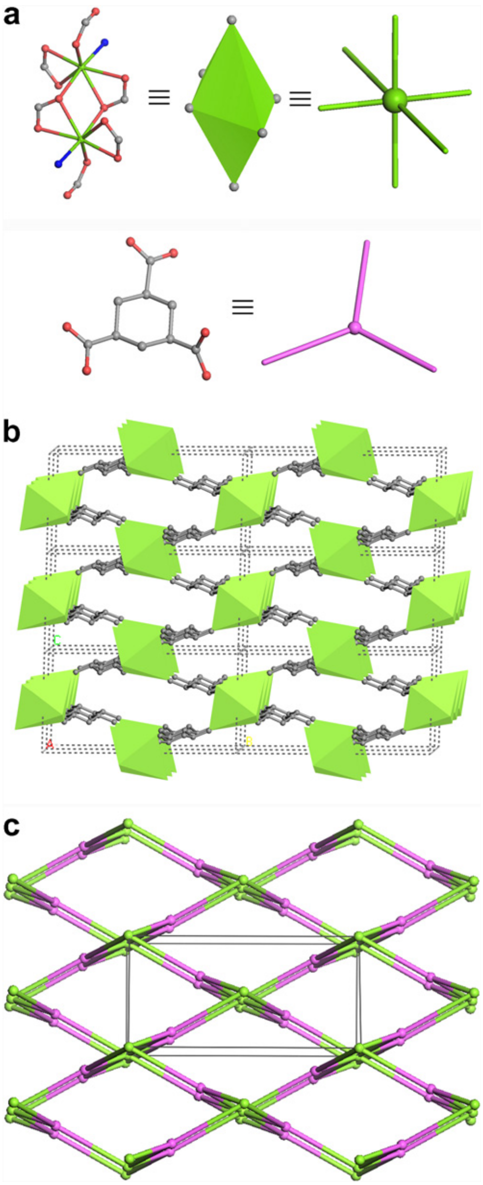

Fig. 2. (a) Simplified views of 6- and 3-connected building blocks in **1**. The color code: Cd, green; N, blue; O, red; C, gray. (b) Perspective view of the framework along the [100] direction. (c) The (3,6)-connected net of **1** with rutile topology (TiO_2). Black lines represent the unit cell of rutile topology. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

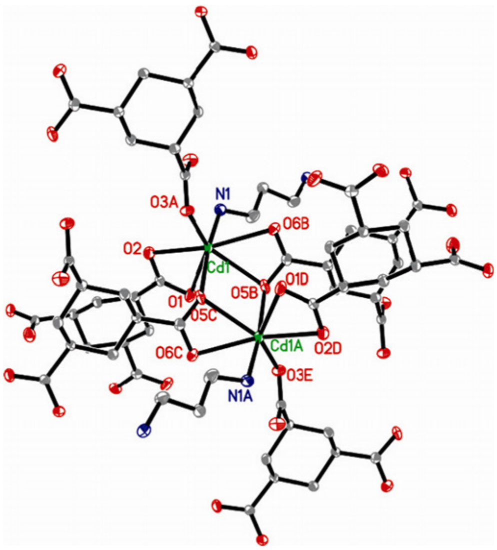

Fig. 1. ORTEP drawing (at a 30% probability level) of the coordination environment of cadmium ions in **1**.

A better insight into the nature of **1** can be achieved by the application of topological approach [26–29]. As discussed above, the dinuclear octahedral SBU is defined as a 6-connected node. Similarly, CTC ligating with three SBUs can act as a 3-connected node. According to the simplification principle, the resulting structure of **1** is a binodal

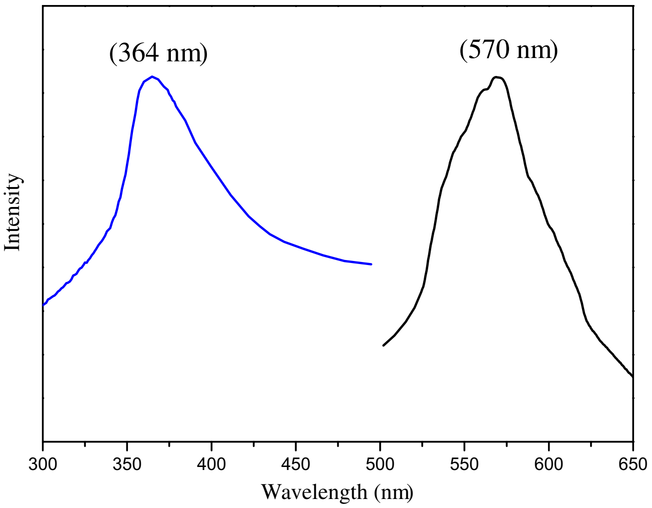

Fig. 3. Fluorescence emission spectra of the free CTC ligand (black line) and polymer **1** (blue line) in the solid state at room temperature. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(3,6)-connected net, and its Schläfli symbol is $(4{\cdot}6^2)_2(4^2{\cdot}6^{10}{\cdot}8^3)$ (the first symbol for 3-connected CTC and the second one for 6-connected dinuclear octahedral SBU), which is a deformed version of the idealized rutile structure (Fig. 2c) [30,31].

3.3. IR spectrum

The IR spectrum of **1** shows the presence of vibrational bands at 1585–1519 cm^{-1}, which are characteristic of the asymmetric stretching of the carboxylic groups of CTC. The absorptions at 1406 cm^{-1} are due to the symmetric vibrations of the carboxylic groups of CTC. The lack of the characteristic bands of the carboxylic groups of any protonated forms (1730–1680 cm^{-1}) [32–34] indicates the complete deprotonation of H_3CTC after the reaction. The broad band at 3419 cm^{-1} belongs to the typical band of the guest H_2O molecules, and the band at 1066 cm^{-1} is attributed to the vibration of $\upsilon_{C\text{–}N}$ of PDA.

3.4. Thermogravimetric analysis

The differential thermal analysis (DTA) for **1** has two endothermic peaks at 131.7 and 419.4 °C, correspondingly, the thermogravimetric analysis (TGA) curve shows two stages ranging from 30 to 250 °C, and from 350 to 476 °C. The weight loss of 22.06% between 30 and 250 °C corresponds to the loss of one guest H_2O and one coordinated HPDA of each asymmetric unit (calculated 22.25%). The polymer is stable between 250 and 350 °C, and the decomposition of **1** began at about 370 °C. The residue was CdO (experimental: 30.67% and calculated: 30.58%). To further study its stability, the polymer is calcined at 100 °C for 1 h. However, the intensity of diffraction peaks of the polymer become very weak and many reflections cannot be observed in the XRD pattern, implying the mostly decomposition of the structure.

3.5. Photoluminescent property

The solid-state excitation–emission spectrum of **1** has been studied at room temperature (Fig. 3). The strongest emission peak for the free H_3CTC is at 570 nm with the excitation peak at 396 nm. It is attributed to the $\pi^* \rightarrow n$ transitions [35]. Compared with the free H_3CTC, polymer **1** exhibits a blue-shift emission peak at 364 nm with the excitation peak at 240 nm. The emission peak of **1** can be assigned to the emission of ligand-to-metal-charge-transfer (LMCT) [36]. The strong fluorescent emission of **1** makes it a potentially useful photoactive material.

4. Conclusion

A new 3D porous MOF with rutile topology and quadrangular channel dimensions of ca. 10×17 Å^2, $Cd(CTC)(HPDA){\cdot}(H_2O)$ (**1**), has been synthesized by utilizing an organic amine, PDA, as a template. Furthermore, the polymer **1** possesses an intense luminescent property at room temperature. We believe that those polymers with potential properties and charming topologies will be further synthesized by using different organic amines as templates.

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Appendix A. Supplementary data

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary Publication No. CCDC-615742. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2007.01.064.

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