



CORPUS PUBLISHERS

Advance Research in Organic and Inorganic Chemistry (AROIC)

ISSN: 2833-3594

Volume 5 Issue 1, 2024

Article Information

Received date : March 05, 2024

Published date: March 14, 2024

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DOI: 10.54026/AROIC/1016

Keywords

Metal-organic frameworks; Phenyl-
carboxylate; Crystal engineering;
Functional chemistry; Porous materials

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Short Communication

A 5-fold Interpenetrated and Porous Dia-net Metal-Organic Framework Constructed from Long and Linear Phenyl-carboxylate Linkers

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Abstract

Interpenetration regulation is of great significance for both the crystal engineering and functional chemistry of MOFs. The combination of long and linear ditopic organic linkers with single or small metal node is effective to produce interpenetration metal-organic framework. Here, a 5-fold interpenetrated and porous *dia*-net metal-organic framework of $[\text{Cd}(\text{tpdc})_2]\cdot 3\text{DMF}$ (Cd-MOF, $\text{H}_2\text{tpdc} = 2',5'$ -dimethylterphenyl-4,4''-dicarboxylate) was synthesized under solvothermal reaction, which was structurally characterized by single X-ray crystal diffraction, coupled with thermal and luminescence properties study. The compound crystallises in monoclinic $P2_1/c$ space group with cell parameters of $a = 15.7789(4) \text{ \AA}$, $b = 24.8437(7) \text{ \AA}$, $c = 26.3720(4) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 96.5583(19)^\circ$, $\gamma = 90^\circ$, and $V = 23967 \text{ \AA}^3$. There are 1D channels and porosity of 57.5% for the Cd-MOF, which is a rare example of MOFs with coexistence of high-degree interpenetration and high porosity. The MOF can thermally stable up to 360°C , with light blue luminescent emission at 360 nm under a ultraviolet radiation.

Introduction

Metal-organic frameworks (MOFs) represent a large family of crystalline and porous coordination compounds constructed from metal noded linked by various organic linkers into extended networks [1]. They exhibit unprecedented structure designability, much larger porosity, rich dynamics, quite wide properties and functions over traditional porous materials like inorganic zeolite, porous carbon and porous organic polymers. The pursuing of high porosity and accessible surface area, based on rational design of the metal node, organic linker and topology net, was one of the persistent tasks in the area. Usually, long linear linkers or large size triangular or quadrangular linkers were used to increase the porosity, yet such a choice always led to interpenetration and lower porosity [2]. A numbers of research in recent years have also shown that interpenetration is not random but controllable, depending on the rational introduce of auxiliary functional groups, careful alteration of the template molecules, stoichiometric ratios, temperature, solvent, reaction time, and pressure of the reaction system [3]. Zaworotko M. J. et al. achieved the interpenetration regulation of mixed-ligands pillared-layered MOFs by adjusting the temperature and reactant concentration [4]. Xu Q. et al. reported that the interpenetration control by varying the temperature from the same raw materials, which was able to selectively prepare non-interpenetrated or 2-fold interpenetrated MOFs based on the same framework [5]. For the same system, further reduction of the solution concentration and shortening of the reaction time enabled the preparation of mesoporous MOFs. It is particularly interesting to note that some recent works have shown that single-crystal-to-single-crystal structural transitions between different interpenetrated MOFs under external stimulus [6]. Therefore, the study of interpenetration regulation is of great significance for both the crystal engineering and functional chemistry of MOFs.

We have a long experience in the construction, solid-state structure transformation and post-synthetic modification of MOFs [7-10]. The family of diamond (*dia*) net MOFs have attracted our great interest, as they exhibited high structure flexibility and recently be found to be special precursor to for MOF liquid or glass [11,12], considering their topology similarity to SiO_2 . In our wide design, synthesis and properties exploration of *dia*-net MOFs, a typical long and linear phenyl-carboxylate linker of 2',5'-dimethylterphenyl-4,4''-dicarboxylate (H_2tpdc) was used. As a result, a 5-fold interpenetrated and porous *dia*-net MOF of $[\text{Cd}(\text{tpdc})_2]\cdot 3\text{DMF}$ (Cd-MOF) was generated under solvothermal reaction, which was structurally characterized by single X-ray crystal diffraction, coupled with preliminary thermal and luminescence properties.

Synthesis Method

The Cd-MOF crystals were prepared by dissolving $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ (0.1 mmol, 30.8 mg) and H_2tpdc (0.1 mmol, 34.7 mg) in a solution of dimethylformamide (DMF, 15 mL), followed by stirring for 10 minutes. The product was then transformed and placed in a 25 mL Teflon-lined steel bomb and heated at 393 K for 72 h. The reaction bomb was cooled to room temperature at a rate of 10 K/h. Colourless block crystals were collected and washed with dried DMF, with yield of 40~55% based on Cd. The crystals are insoluble in DMF, DMA, methanol, ethanol, ethylene chloride, acetone, aromatic alkanes and other conventional solvents. The crystals tend to lose its crystalline with destroyed morphology after long-time exposure to air or under higher humidity. Elemental analyses (%): $\text{CdC}_{53}\text{H}_{53}\text{N}_3\text{O}_{11}$. Calcd: C 62.38, H 5.23, N 4.11. Found: C 61.54, H 5.30, N 3.98. IR spectrum (KBr , cm^{-1}): 3241(m, br), 2360(vw, br), 1653(w, sh), 1587(s, sh), 1533(w, sh), 1398(vs, sh), 1110(vw, sh), 855(m, sh), 781(sm, sh), 720(vw, sh), 517(vw, sh).

Crystal Structure

X-ray single-crystal diffraction analysis reveals that the Cd-MOF crystallises in the $P2/c$ space group of the monoclinic crystal system (Table 1). Each asymmetric unit of the compound contains one Cd^{2+} ion and one tpdc^{2-} ligand anion, leading to an electrically neutral framework. The Cd ion adopts a triangular dodecahedral coordination configuration with eight oxygen atoms from chelated carboxylate groups in four different tpdc^{2-} linkers (Figure 1a). For the ligands, one tpdc^{2-} interlinked two Cd^{2+} ions using a coordination fashion of $\mu_2\text{-}\eta^2\text{:}\eta^2$ (Figure 1b). As a result, each Cd^{2+} ion acts as a single-metal node that extended by four linear ligands into a three dimensional, four-connected and dia type network (Figure 1c). Within each single framework, the distance between neighbouring metal nodes is 19.8 Å, while the minimum distance between two non-neighbouring metal nodes that connected at the same metal node is 29.4 Å with the distance is 36.2 Å. Because of the existence of a huge void within a single dia topological network as well as the small size of single Cd metal node, interpenetration will inevitably formed. Indeed, five framework weave together in a paralleled fashion along the same translation direction (Figure 1d). Despite the occurrence of 5-fold interpenetration, there was still quite high solvent assemble porosity of 57.5%, calculated by the Platon software. Such high porosity mainly arises from the fact that there was one-dimensional penetrating channels with a window size of $5.6 \times 5.6 \text{ \AA}^2$ along the crystallographic a direction.

Table 1: Crystallographic data of the MOF.

Compound	Cd-MOF
Empirical formula	$\text{C}_{31}\text{H}_{37}\text{N}_3\text{CdO}_7$
Formula weight	676.05
Temperature / K	100(2)
Radiation / Å	0.71073 (Cu Ka)
Crystal system	Monoclinic
Space group	$P2/c$
a / Å	15.7789(4)
b / Å	24.8437(7)
c / Å	26.3720(4)
$\alpha / ^\circ$	90
$\beta / ^\circ$	96.5583(19)
$\gamma / ^\circ$	90
V/ Å ³	10270.3(4)
Z	2
F(000)	2618
Dc./ g cm ⁻³	0.836
μ / mm^{-1}	1.22
Reflns. coll.	72081
Unique reflns.	20790
R_{int}	0.036
$\sigma R_1 [I \geq 2\sigma(I)]$	0.174
wR^2 (all data)	0.469
GOF	1.18
Void	57.50%

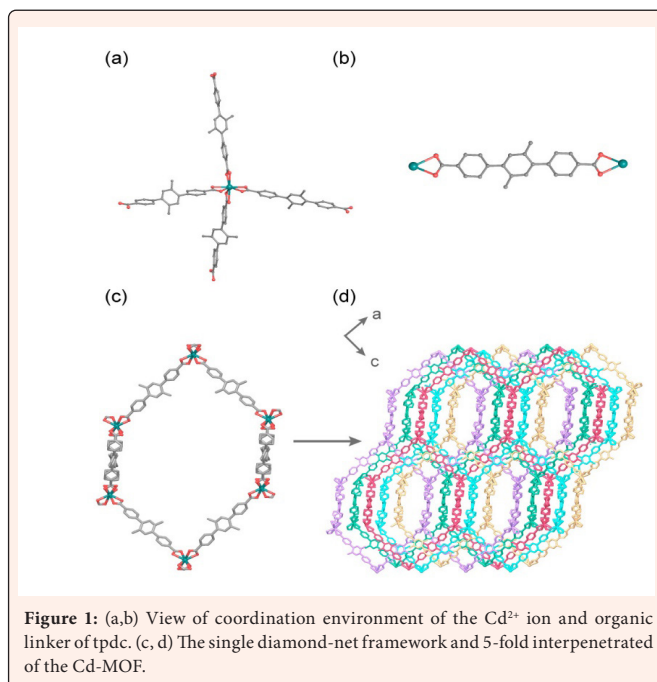


Figure 1: (a,b) View of coordination environment of the Cd^{2+} ion and organic linker of tpdc . (c, d) The single diamond-net framework and 5-fold interpenetrated of the Cd-MOF.

Thermal and fluorescence properties

The results of thermogravimetric analysis of Cd-MOF (Figure 2, under nitrogen flow rate of 15 mL/min, temperature increase rate of 10 °C/min) show a first stage weight loss of 21.7% (theoretical value of 22.9%) corresponding to the release of three guest DMF molecules in the temperature range from 25-360 °C. The second step rapid weight loss of 55.1% is due to the collapse of the structural framework along with the decomposition of the organic linkers. Subsequently, a smooth curve was observed above 500 °C and till 800 °C, with a weight residue of about 21.7%, corresponding to final product of CdO. Coordination polymer with a d^{10} configuration (such as Zn^{2+} or Cd^{2+}) usually exhibit photoluminescence. Therefore, the solid-state luminescence of Cd-MOF has been measured. Under an excitation wavelength of 330 nm, the strongest emission spectrum of the MOF is located at 360 nm, which is red-shifted by 34 nm compared to the solid-state fluorescence of free ligand H_2tpdc . Such results suggest charge transfer between ligand and the metal center is negligible and the luminescence properties of Cd-MOF is dominated by the intraligand $\pi\text{-}\pi^*$ electron transition.

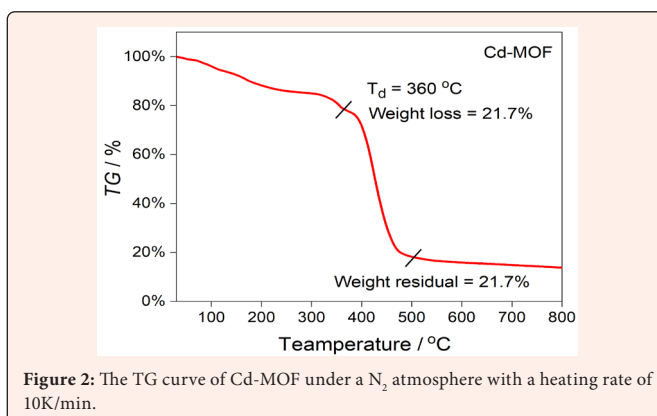


Figure 2: The TG curve of Cd-MOF under a N_2 atmosphere with a heating rate of 10K/min.

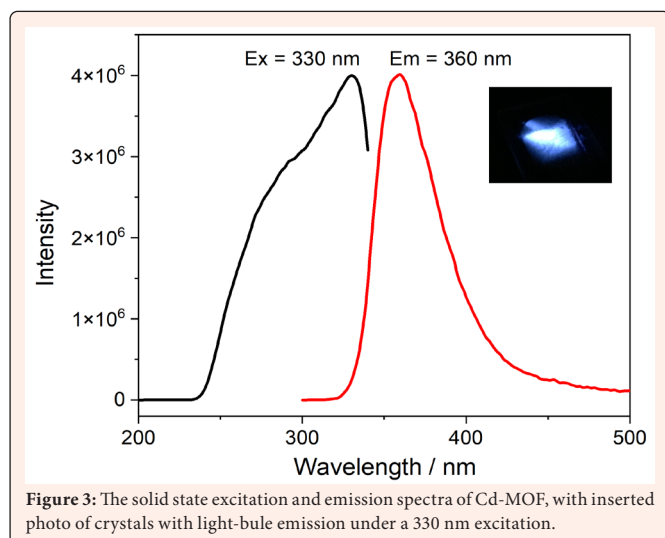


Figure 3: The solid state excitation and emission spectra of Cd-MOF, with inserted photo of crystals with light-blue emission under a 330 nm excitation.

Conclusion

With the rational choice of a long and linear ditopic organic linkers, coupled with a single $[Cd(COO)_4]$ metal node, a 5-fold interpenetrated dia-net MOF with large void fraction of 57.5% was synthesized under solvothermal reaction, and provide an interesting new example of balance in high-degree interpenetration and high porosity for MOFs. According to our research advance in multiple phase evolution involving liquid and glass states, presented compound is a potential suitable candidate to acquire new MOF glass and relative study is on going.

Acknowledgment

This work was supported by the Key Research and Development Program of Shaanxi Province (No. 2022GY-180), and the Scientific Research Project of Education Department of Shaanxi Province (No. 22JC014), the Open Foundation of Key Laboratory of Auxiliary Chemistry and Technology for Chemical Industry, Ministry of Education, and Shaanxi Collaborative Innovation Center of Industrial Auxiliary Chemistry and Technology (No. KFKT2023-07).

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