

Structural Elucidation And Electrochemiluminescence On A 3D Cadmium (II) MOF With 5-C Topology

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Abstract

A novel cadmium (II) based MOF, $[\text{Cd}(\mu\text{-ppza})]_n$ (**1**) ($\text{H}_2\text{ppza} = 3\text{-(pyridin-4-}y\text{)-1}H\text{-pyrazole-5-carboxylic acid}$) was synthesized under solvothermal condition. The single-crystal X-ray diffraction reveals that the title MOF **1** exhibits a 3D structure bridged through the carboxylic group, which has a 5-c $\{4^6.6^4\}$ topological structure. Furthermore, MOF **1** exhibits good electrochemiluminescence (ECL) behavior.

1 Introduction

In the last two decades, the design and synthesis of metal-organic frameworks (MOFs) has attracted more and more attentions due to their a unique structure and potential applications in the fields of magnetism[1, 2], ectrochemiluminescence[3, 4], supercapacitors[5–7], *etc.* Generally, to obtain metal organic framework materials with interesting topological structure and performance, many influencing factors should be considered, such as metal ions, organic ligand, temperature, pH value, *etc.*, among which the selected ligand is crucial in the construction system. Because it can modulate the coordination mode and the flexibility of molecular skeleton to construct metal-organic framework materials[8]. Among the candidate organic ligands, pyrazole carboxylic acid ligands have excellent coordination abilities and flexible coordination modes in the assembly of MOFs structure. Pyrazole carboxylic acid ligands can not only be acted as hydrogen bond donors, but also be as a acceptors to bring its topological structures have many diversities, so this type of ligand is widely used to construct MOFs with intriguing topological structures and outstanding performances[9].

Electrochemiluminescence (ECL) is a phenomenon that the luminescent body forms excited species on the electrode surface through high-energy electron transfer reaction, and then rapidly returns to the ground state through energy relaxation. It is an analytical technology combining electrochemical methods and chemiluminescence methods[10], and has been received considerable attention. As we know that, the Ir-, Ru- and Re- based complexes in the field of ECL has been used widely, but they are precious metals, so it limited their applications[11–14]. Therefore, it is a good choice to use transition metal complexes as ECL materials for the wide range and inexpensive. As our continuing work, our group have reported a series of transition metal framework based on pyrazole carboxylic ligands with excellent ECL performace [15, 16]. Thus, the use of transition metal ions and organic ligands to synthesize MOFs with highly luminescent efficiency has become an urgent issue.

In this work, we taken 3-(pyridin-2-*y*)-1*H*-pyrazole-5-carboxylic acid (H_2ppza) as ligand and synthesized a new MOF $[\text{Cd}(\mu\text{-ppza})]_n$ (**1**) under the hydrothermal condition which possessed 3D structure. Herein, we illustrate the synthesis, crystal structure, topology and the electrochemiluminescent performance of the title MOF.

2 Experimental

2.1 Materials and Methods

All the reagents and solvents were purchased from commercial grade and used without purification. 3-(pyridin-4-yl)-1*H*-pyrazole-5-carboxylic acid (H₂ppza) was prepared according to the literature[7]. Elemental analyses (C, H, and N) were made with a Thermo Quest Flash EA1112 microanalyzer. IR spectra were recorded with a Spectrum One Perkin-Elmer FT-IR spectrophotometer (KBr disc) from 4000 to 400 cm⁻¹. The thermogravimetry (TGA) was taken on a Netzsch STA 409PC differential thermal analyzer by heating the crystalline sample from 25 to 900°C at a rate of 20°C min⁻¹ in air.

2.2 Synthesis

Synthesis of [Cd(μ-ppza)]_n (1)

A mixture of CdCl₂ (0.0228 g, 0.1 mmol), H₂ppza (0.0189 g, 0.1 mmol), MeOH (5 mL) and H₂O (10 mL) was put into a Teflon-lined autoclave. The reaction mixture was heated at 150°C for 72 h, followed by slow cooling to room temperature and phase pure colorless crystals of **1** were obtained by manual separation (yield: 68.21% based on CdCl₂). Anal. Calcd. (%) for C₈H₁₄CdN₄O₈ (*M_r* = 406.63): C, 36.05; H, 1.67; N, 14.02. Found: C, 35.98%; H, 1.75%; N, 13.97%. IR (KBr, ν, cm⁻¹): 3433(s), 2922(w), 1716(w), 1613(m), 1558(s), 1501(m), 1455(w), 1415(s), 1330(s), 1038(s), 1170(s), 1113(s), 1059(w), 1020(m), 831(m), 795(m), 699(w).

2.3 X-ray crystallography

Single-crystal X-ray diffraction measurement for **1** was performed using a SuperNova diffractometer. using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) with the ω-θ scan technique at 293 K. The structure was solved with SHELXS-97 employing by direct methods, and refined by full matrix least squares on *F*² with SHELXS-2014 [17]. All non-hydrogen atoms were refined with anisotropic thermal parameters. H atoms linked to C were placed at the geometric positions and refined with an isotropic displacement parameter. Detailed data collection and refinements were summarized in Table S1. Selected bond lengths and angles were listed in Table S2. Crystallographic data has been deposited with the Cambridge Crystallographic Data Center (CCDC numbers: **2123339**).

3 Results And Discussion

3.1 Crystal structure of [Cd(μ-ppza)]_n (1)

MOF **1** crystallizes in the triclinic system with the *P*-1 space group, and each asymmetric unit consists of one Cd (II) ion and one completely deprotonated (Hppza)²⁻ as shown in Figure 1. Figure 2 displays the coordination environment of Cd(II) ions, each Cd (II) is coordinated with five (Hppza)²⁻ ions forming a distorted octahedron. In the octahedron, three O atoms of carboxyl group, two N atoms from pyrazole rings and one N atom from the pyridine ring, where the Cd-N and Cd-O bond lengths fall in 2.268(3)-2.403(3) Å and 2.265(3)-2.639(3) Å, respectively. Each ligand in **1** is completely deprotonated and all N

and O atoms participate in coordination, meanwhile the carboxylate O atom chelates the metal center with the N atom from the adjacent pyrazole, and the other carboxylate O atoms bridge two metal Cd(II) centers and the N atom on pyridine also acts as a bridge to connect the other two Cd(II) atoms. It is precisely because of this unique chelating-bridging coordination mode that makes **1** has a three-dimensional structure, seen in Figure 3. Additionally, there exists a twisted ribbon structure in **1**, which formed by a four-membered ring Cd₂O₂ and a six-membered ring Cd₂O₄C₂, and the adjacent Cd...Cd distances are 3.973 (3) Å and 5.721 (9) Å. Considering from the principle of topology, With each Cd₂O₂ taken for a node, and the ligand for a line, MOF **1** can be simplified as a 5-c net with {4⁶.6⁴} Schläfli symbol (Figure 4).

3.2 Electrochemiluminescence for [Cd(μ-ppza)]_n (**1**)

Electrochemiluminescence (ECL) is the process where species generated at electrodes undergo electron-transfer reactions to form excited states that emit light. ECL has become a powerful tool with near zero background, excellent sensitivity, fast response and wide dynamic range. Up to now, most of the coordination polymers used as electrochemiluminescent groups contain noble metals such as Ru, Ir, and Re. Due to their high cost, the application of these coordination polymers has been limited. Therefore, the use of transition metal complexes as ECL materials is a potential choice[18]. Based on this point of view, we studied the electrochemiluminescence properties of complex **1**.

In this paper, we tested the ECL behavior of the title MOF in DMF solution and the results were showed in Figure 5. The electrochemical properties of **1** was measured in a standard three-electrode system, where the reference electrode is Ag/AgCl, Pt electrode is used as auxiliary electrode, glassy carbon electrode is used as working electrode, and the co-reactant is 0.1 mol/L K₂S₂O₈. In order to understand the redox properties of the complex, we also carried out a cyclic voltammetry test on the MOF **1**. From Figure S1, it is obviously to find that the oxidation peak in the cathodic current at -0.8 V and the reduction peak at -1.24 V. The ECL intensity of **1** is approximately to 1150 a.u. which is higher than reported[19], and much more stable. Taken the Ru(bpy)₃³⁺ as the standard[20], the ECL yield of title complex is 0.25. This good ECL performance may due to the intersecting 3D structure of MOF **1**, and its luminescence properties are mainly affected by the central metals, as well as the Cd...Cd interactions providing channels for carrier transferring[21]. Hence, as the good ECL performance, the title MOF with interesting topological structure can be used to design OLED devices for the future.

3.3 TGA and PXRD

Figure S2 gives the TGA curve of MOF **1**, which can be seen a long stage, and implies that the **1** is very stable before 500°C. After 500°C, the MOF skeleton began to collapse, the weight loss is about 80% at 580°C, and the last remaining maybe CdO. To confirm whether successful formation of the final products, the X-ray powder diffraction (PXRD) was tested in Figure S3. The PXRD pattern reveals that the peak positions of the obtained crystalline sample of MOF **1** matched well with the simulated.

4 Conclusions

In summary, by the use of 3-(pyridin-4-yl)-1*H*-pyrazole-5-carboxylic acid as a ligand, one novel 3D Cd(II) MOF (**1**) has been successfully synthesized by solvothermal method. Single-crystal X-ray diffraction reveals MOF **1** displays a 3D structure with a 5-c topology. The electrochemiluminescent properties of **1** has been studied, show that **1** could be anticipated as good candidates for obtaining solid state photoluminescent materials or OLED materials. And we wish that our research would attract more crystallographers' attentions on the filed of electrochemiluminescence.

Declarations

Acknowledgements

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Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figures

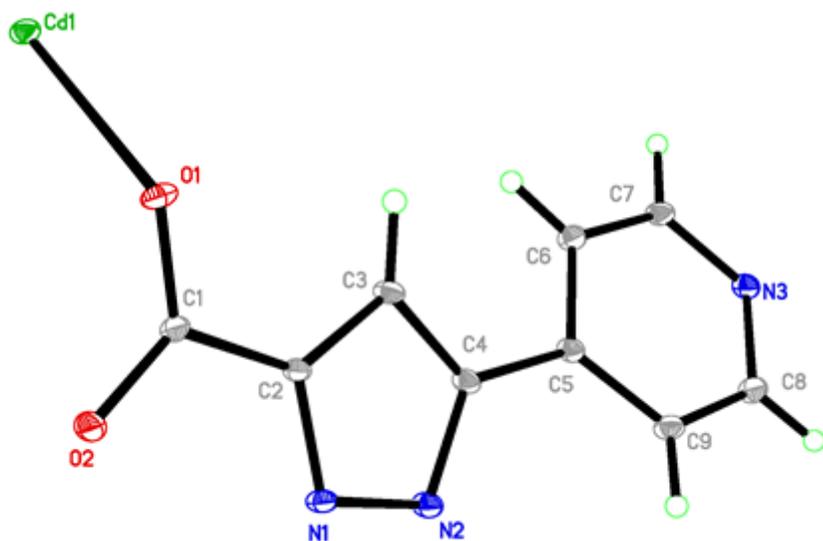


Figure 1

The asymmetry of 1 with thermal ellipse at the 30% probability level.

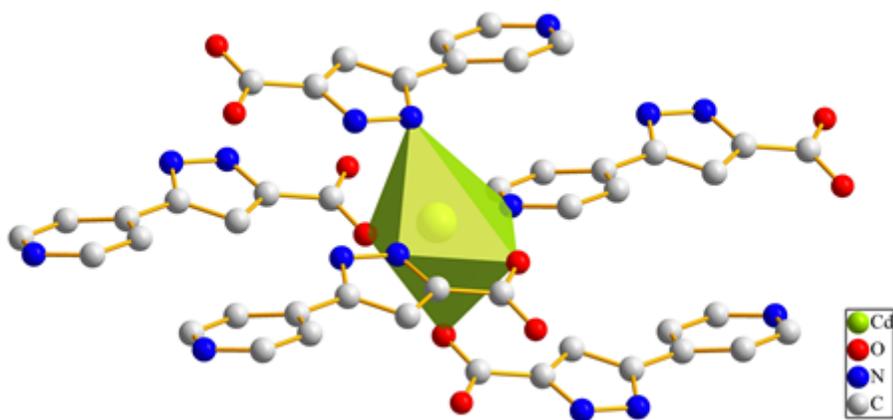


Figure 2

The coordination environment of Cd(II), all hydrogen atoms were omitted for clarity

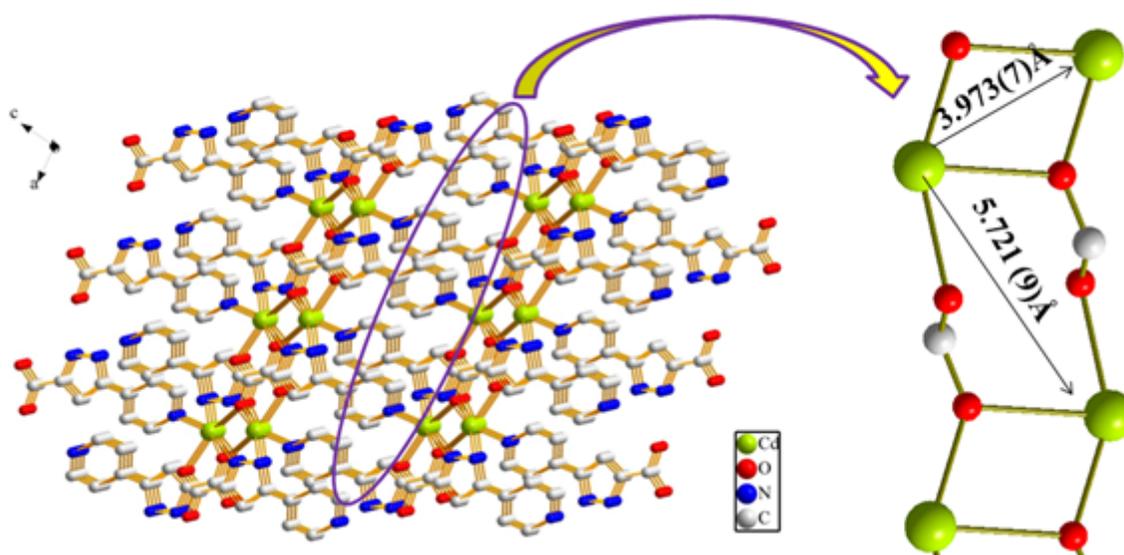


Figure 3

3D structure in MOF 1 with a twisted ribbon

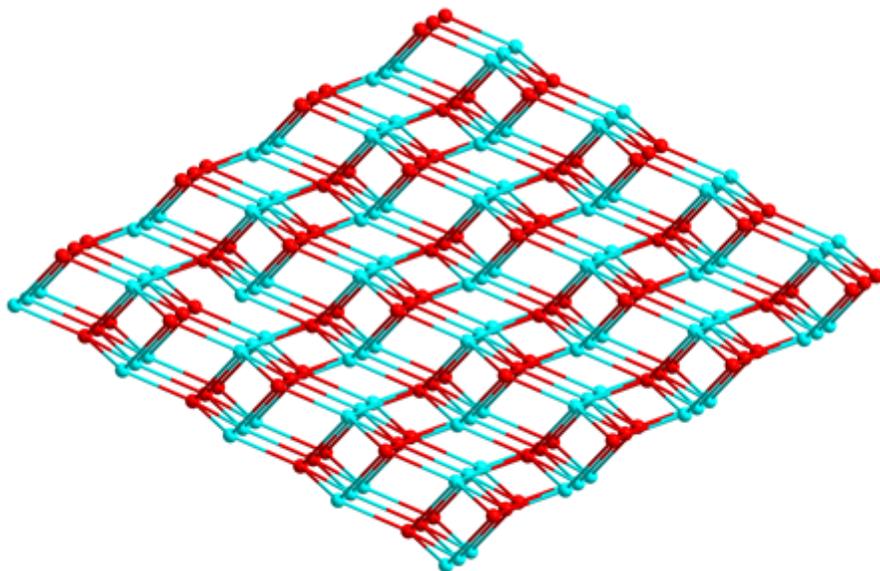


Figure 4

The topological structure of MOF 1 with {46.64} Schläfli symbol

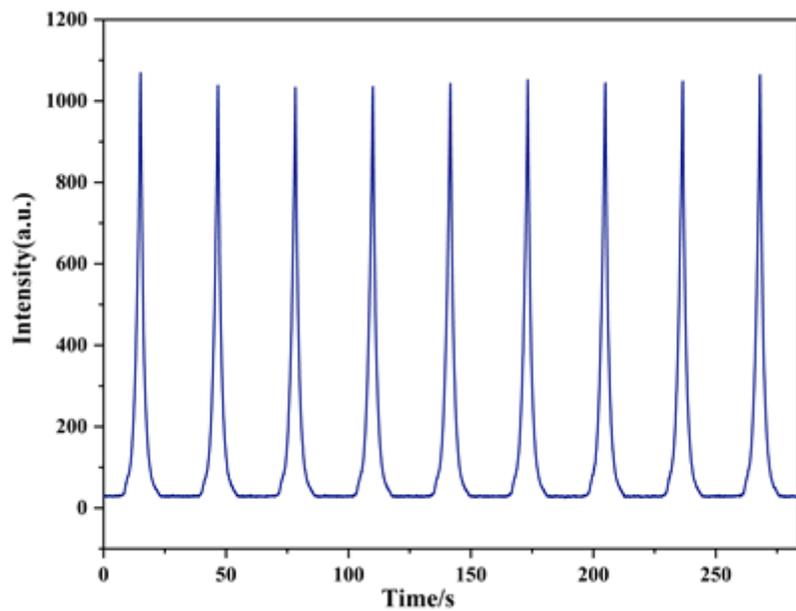


Figure 5

ECL intensity of MOF 1

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