Journal of Inorganic and General Chemistry
ZAAC
Zeitschrift für anorganische und allgemeine Chemie
DOI: 10.1002/zaac.201900219
ARTICLE

A New Three-dimensional Metal-organic Framework based on Dinuclear Rare Earth Cluster and Olsalazine

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Abstract. A new microporous metal organic frameworks $Eu_2(olz)_3$·7(DMF), based on olsalazine, has been successfully designed and synthesized. Eu-olz has three-dimensional structure with dinuclear rare earth cluster and drug molecule olsalazine as ligand, and features as low toxic MOF materials. The Eu-olz exhibits weak fluorescent emission which can be ascribed to the luminescence of the organic ligand.

Introduction

Metal-organic frameworks (MOFs), is a fascinating class of porous crystal materials with high specific surface area and regular channels, which are formed by self-assembly of metal ions/clusters and organic ligand through coordination bonds.[1] Due to the structural topology and permanent channel properties, MOFs have shown great potential in many fields, such as gas adsorption and separation,[2] photocatalysis/electrocatalysis,[3] drug delivery and cancer therapy,[4] and fluorescence sensing,[5] etc.

The research on metal-organic framework has experienced rapid development over the past decade.[6] Numerous works focus on new MOFs synthesis and thousands of structures reported, the majority of them are composed of transition metal ions and rigid organic ligands derived from non-renewable petrochemical products.[7] MOFs as adsorbent materials have good thermal stability, chemical stability and suitable pore size, which are needed for applications in fluorescent probe and electrocatalysis.[8] However, there has been increasing trends in developing low-toxic MOFs,[9] due to the costs and safety considerations towards their potential industrial and biological applications. A few pioneering works have explored the low-toxic MOFs, including the Bio-MOF series,[10] the MIL series[9c,11] edible MOFs with r-cyclodextrin as ligands[9a,12] Zn-ZIF-8,[13] Zr-UiO series,[14] and Fe-MOF series.[4c,15] However, only very few of the low-toxic MOFs utilized bioactive molecule as the sole ligand.[16] For example, Hf-porphyrin MOF for photodynamic therapy ,[17] Mg-gallate metal-organic framework for antioxidant carrier,[18] medi-MOF-1 with Zn^{2+} and the pharmaceutical ingredient curcumin.[19]

Olsalazine is an anti-inflammatory prodrug, widely used in the treatment of acute and chronic ulcerative colitis,[20] and also shown the ability to inhibit the development of colorectal cancer.[21] Olsalazine contains azo group, salicylic acid groups, and the rigid benzene ring. The geometry structure of the salicylic acid groups in olsalazine is similar with the dobpdc (dobpdc^{4-} = 4,4′-dioxidobiphenyl-3,3′-dicarboxylate) ligand of the well-known MOF-74 series,[22] but is slightly longer than dobpdc ligand due to the azo group. The pioneering work by Long group have reported the development of novel olsalazine-based M-MOF-74 analogues (M = Mg, Fe, Co, Ni and Zn) MOFs as drug delivery and calcium-olsalazine MOF for pH-triggered release of olsalazine.[23] Other groups also reported several three-dimensional olsalazine-based MOFs with transition metal ions.[24] However, the study on olsalazine-based MOFs with rare earth metal ions is still scarce.

Herein, a new three-dimensional MOF based on rare earth ions and olsalazine was synthesized. A new Eu^{III}-MOF, $Eu_2(olz)_3$·7(DMF) (1), was successfully synthesized via the solvothermal reaction of $Eu(NO_3)_3$·$6H_2O$ and 3,3′-azobis(6-hydroxy-benzoic acid) disodium salt (olsalazine, olz, Figure 1). The MOF has regular channels, and also exhibits the characteristic emission of Eu^{III}.

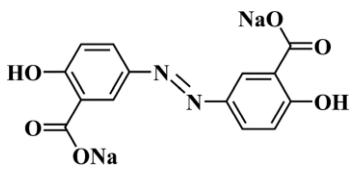

Figure 1. The structural formula of Olsalazine sodium.

Experimental Section

Materials and Method: All chemicals are purchased commercially and are not further purified. Power X-ray diffraction patterns were recorded on a Bruker D8 Advanced diffractometer equipped with Cu-K_α radiation (λ = 1.542 Å) at a scan rate of 5°·min^{-1} and a scan range of 3–50°. The thermal stability of Eu-olz was analyzed by thermogravimetric analyzer (TGA, Pyris Diamond I, Perkin–Elmer Corporation). The chemical structure of Eu-olz was analyzed by FT-IR spec-

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Supporting information for this article is available on the WWW under **http://dx.doi.org/10.1002/zaac.201900219** or from the author.

trometer (Nicolet 5700, Thermo Electron Corp., USA). Fluorescence measurements were taken on a F4600 fluorescence spectrometer. UV/Vis absorption spectroscopy was measured by HITACHI U-3900.

Synthesis of $Eu_2(olz)_3$·$(DMF)_7$ (1): 0.1 mmol (45 mg) $Eu(NO_3)_3$·$6H_2O$ and 0.043 mmol (15 mg) Olsalazine sodium were dissolved in 7.5 mL DMF and 3.75 mL H_2O, then 75 µL concentrated hydrochloric acid was added under the fume hood, and the mixture was taken to and sealed in 50 mL Teflon-lined autoclave, which was heated at 75 °C for 24 h. After cool down to room temperature, the mixture was washed by DMF and ethanol several times. And then the gold crystals were obtained.

X-ray Collection and Structure Determination: Single crystal diffraction data were collected on an CrystalClear-SM Expert 2.0 r5 (Rigaku, 2010) diffractometer with an Atlas detector using graphite monochromatic Mo-K_α radiation (λ = 0.71073 Å) at 293 K. The structure of crystal was solved by direct methods and refined with full-matrix least-squares on F2 with the SHELXL-97 program package. All non-solvent H-atoms were placed on calculated positions. Crystallographic data are summarized in Table 1.

Table 1. The crystal data of $Eu_2(olz)_3$·7(DMF).

	$Eu_2(olz)_3$·7(DMF)
Empirical formula	$C_{65}H_{60}Eu_2N_{14}O_{25}$
Formula weight	1741.19
Temperature /K	98(2)
Space group	*C*2/*m*
a /Å	24.010(2)
b /Å	15.2540(13)
c /Å	11.4526(9)
α /°	90.00
β /°	117.096(8)
γ /°	90.00
Volume /Å^3	3734.1(5)
Z	2
Crystal density /g·cm^{-3}	1.549
Adsorption coefficient /mm^{-1}	1.750
F(000)	1748
Crystal size /mm^3	0.25 × 0.15 × 0.14
GOF	0.998
R_1, wR_2 [$I > 2\sigma(I)$] [a]	0.0238, 0.0772
R_1, wR_2 (all data) [a]	0.0243, 0.0779

a) $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. b) $wR_2 = [\Sigma w(|F_o| - |F_c|^2)/\Sigma wF_o^2]^{1/2}$.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-1946450 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

Supporting Information (see footnote on the first page of this article): The PXRD, TG, IR and PL of the MOF are provided in the supporting information.

Result and Discussion

The purity of Eu-olz was verified based on single-crystal X-ray diffraction, PXRD and TGA. The single-crystal XRD analysis shows that Eu-olz crystallizes in the space group *C*2/*m* with the unit cell parameters of *a* = 24.010(2) Å, *b* = 15.2540(13) Å, *c* = 11.4526(9) Å, *α* = 90.00°, *β* = 117.096(8) °, *γ* = 90.00°. The unit cell volume is 3734.1(5) Å^3.

The Eu^{III} ion adopts eight-coordinate mode in the framework, each Eu^{III} ion is connected with five deprotonated carboxylate oxygen atoms from five ligands and three solvent molecules (Figure 2a). Every two Eu^{III} ion centers share four deprotonated carboxylate oxygen atoms from four ligands, forming a dual-core Eu^{III} ion cluster structure (Figure 2a). For the ligand olz, unlike the coordination mode in MOF-74 series where both the deprotonated carboxylate oxygen atoms and the hydroxyl groups are coordinated with metal ions,[23a] three

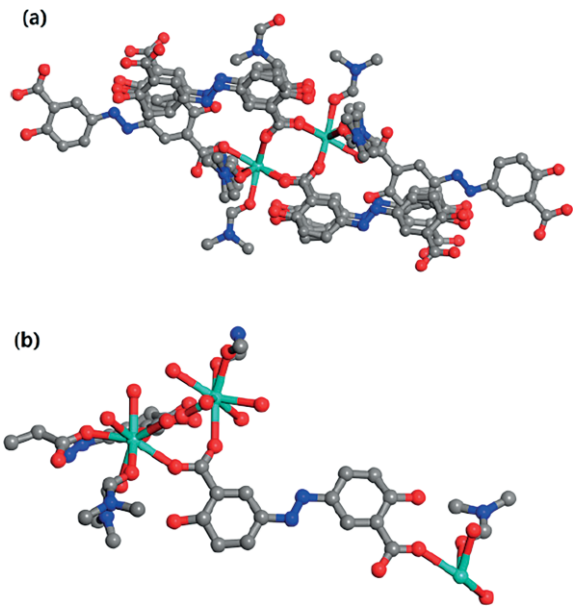

Figure 2. (a) A dual-core cluster in Eu-olz, Eu = green, O = red, C = black, N = blue, respectively. (b) The azo bond in 3,3-azo (6-hydroxybenzoic acid) disodium salt.

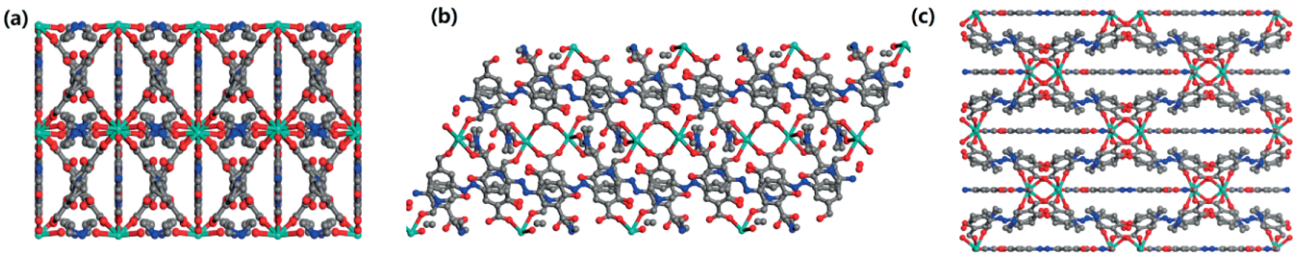

Figure 3. (a, b, c) The structure of Eu-olz along the *a*, *b* and *c* axis, respectively.

deprotonated carboxylate oxygen atoms in the ligand are coordinated with three Eu^{III} ions, while the other one deprotonated carboxylate oxygen atoms remains uncoordinated, and the two hydroxyl groups also remain exposed (Figure 2b). The Eu-olz features three-dimensional structure with micropores along *a* and *c* axes (Figure 3).

The thermal stability of the Eu-olz was carried out by thermal gravimetric analyses with a heating rate 2 K/min under N_2 atmosphere (Figure S4, Supporting Information). The TGA suggests that the release of guest and coordinated DMF molecules occurs before 200 °C, then the framework began to decompose at about 250 °C. After that, the total framework collapsed and left metal oxides eventually. Furthermore, the UV/Vis absorption spectroscopy of Eu-olz was conducted (Figure 4). The adorption peak before 300 nm can be ascribed to the organic ligand absorbing energy through the π-π* electronic transition. Eu-olz exhibits significant absorption at 200–500 nm, which is in accordance with the gold color of the MOF.

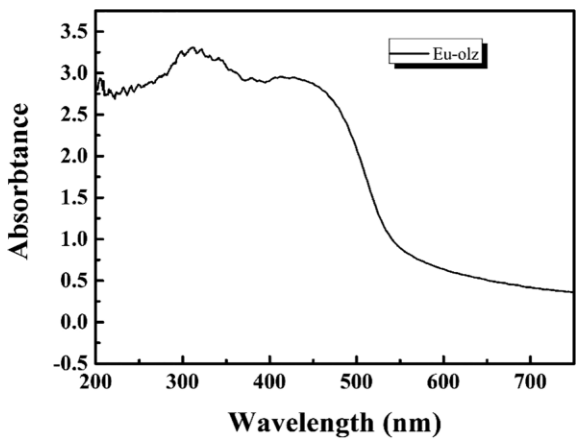

Figure 4. UV/Vis absorption spectrum of Eu-olz.

The Eu-olz exhibits very weak fluorescent emission, which can be ascribed to the luminescence of the organic ligand (Figure S6, Supporting Information).

Conclusions

In summary, the new microporous metal organic framework $Eu_2(olz)_3{\cdot}7(DMF)$ was successfully designed and synthesized. Eu-olz has three-dimensional structure with dinuclear rare earth cluster and drug molecule olsalazine as ligand, and features as low toxic MOF materials. The Eu-olz exhibits weak fluorescent emission which can be ascribed to the luminescence of the organic ligand.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (51602301) and the Natural Science Foundation of Zhejiang Province (No. LY19E020007, LD18F050001 and LY18E020008).

Keywords: Metal-organic framework; Crystal structure; Rare earths; Olsalazine drug molecule; Fluorescent emission

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Received: September 7, 2019
Published Online: November 8, 2019

