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Short communication

An unprecedented molybdenum oxide based helical MOF with peroxidase-like activity synthesized by surfactant-thermal method

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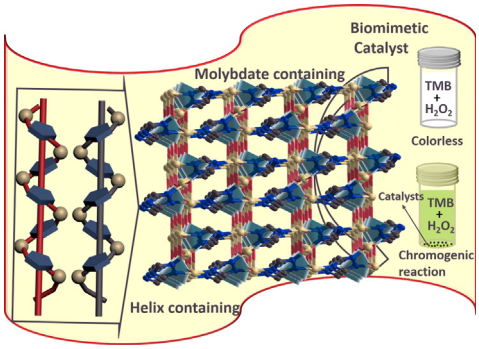
GRAPHICAL ABSTRACT

A surfactant-thermal method synthesis a new 3D molybdate-based MOF containing helical structure, which as peroxidase-like catalyst exhibit good catalytic activity around physiological pH, low detection limit and fast response towards the detection of H_2O_2.



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ABSTRACT

Here, a new three-dimensional molybdate-based metal-organic framework (MOF), $[Zn_3(MoO_4)_2(trz)_2(H_2O)_2]$ (**1**), (trz = 1,2,4-triazole) was successfully prepared by the surfactant-thermal method for the first time. Single crystal X-ray diffraction analysis reveals that the new compound possesses twofold meso-helical structure fabricated by Zn ions and trz ligand, and the inorganic MoO_4-Zn nets insert into the helix arrays. In addition, Zn ions as their common junction stabilize the whole framework. As a kind of new peroxides mimic enzyme, the new compound can effectively catalyze the oxidation of the substrate 3,3′,5,5′-tetramethylbenzidine (TMB) in the presence of H_2O_2, accompanied by a obvious color varvation of solution (1 min responsed time). Moreover, the result of colorimetric sensing of H_2O_2 is that the H_2O_2 detection limit is 0.25 μM, and the linear range is 1 to 80 μM.

H_2O_2 detection has aroused widespread concerns as its production may affect many biochemistry reactions in the body that is critical for human health [1–3]. At present, the most common method for H_2O_2 detection involves the use of horseradish peroxidase (HRP) catalyzing the peroxidase substrate 3,3′,5,5′-tetramethylbenzidine (TMB), and producing a color reaction under mild and favorable conditions [4]. The defects of nature enzymes such as inactivation, as well as time-consuming and expensive preparation [5,6] motivate us to develop

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efficient methods for detecting and quantifying the amount of H_2O_2 molecules. In this context, stable metal-organic frameworks (MOFs) have been widely studied as peroxidase-like catalyst [7,8], because the catalytically active metal centres can be integrated into the framework, or loaded into the pores [9]. The combination of molybdenum oxide moieties with MOFs (molybdate-based MOFs) can exhibit great interest because they can merge the merits of molybdate to generate diversified structures (nanocage, catenane, helix and so on) with special properties. What's more, molybdenum in its high oxidation state with higher reacting ability tends to form mononuclear/polynuclear anionic metal-oxygen clusters, which are considered as charge-balancing anions for the cationic coordination polymers, to extend novel products into higher dimensional frameworks [10].

Currently, hydrothermal, solvothermal and ionothermal methods are the common ways for the synthesis of solid crystal materials [11–13]. However, significant limitations associated with the use of solvents, such as low the boiling point or high cost, have posed a limitation on further exploring novel structures. Thus, new synthetic strategies are required for preparing crystalline MOFs with novel structures and interesting properties. Surfactants with thermal stability and industrial abundance have been widely applied in controlling the sizes and shapes of nanocrystals and the pore sizes and phases of porous materials [14,15], so using surfactants as reaction media to synthesize novel crystalline materials (surfactant-thermal method) is highly expected. Recently, several crystalline chalcogenides [16,17] and MOFs [18–26] have been synthesized by surfactant-thermal method. However, the use of surfactants as solvents to grow molybdate-based crystal material has remained unexplored. Herein, polyethylene glycol 400 (PEG-400) as the surfactant solvent, $H_3PMo_{12}O_{40}$ as molybdate source, $Zn(NO_3)_2$ as heteroatom, and 1,2,4-triazole as organic linker, an unprecedented molybdate-based MOFs, $[Zn_3(MoO_4)_2(trz)_2(H_2O)_2]$ (**1**), was successfully isolated, in which mononuclear MoO_4 as charge-balancing anions is integrated into the cationic coordination polymers.

The title compound was prepared by the reaction from a mixture of $H_3PMo_{12}O_{40}$, 1,2,4-trz, $Zn(NO_3)_2$, NH_4VO_3 in PEG 400 at 170 °C for 4 days [27]. Note that when PEG 400 was replaced by other solvents such as distilled water, methanol and *N*,*N*-dimethylformamide, no crystals were obtained for all the reaction systems. Single-crystal X-ray diffraction analysis [28] reveals that compound **1** crystallizes in the monoclinic space group *P21/n* (No. 14) and consists of two $[MoO_4]^{2-}$ anion, three Zn cations, two trz ligands and two coordination water molecules (Fig. S1a). Two crystallographic independent Zn ions (Zn1 and Zn2) all adopt distorted octahedron geometries completed by two N atoms from trz ligand, four O atoms form $[MoO_4]^{2-}$ anion and crystal water (Fig. S1b). In turn, MoO_4 anion connects with four Zn ions (Fig. S1c), and the deprotonated trz ligands link with three Zn cations (Fig. S1d). Bond valence sum calculations show that all Mo atoms are in +VI oxidation states and Zn ions are in +II oxidation states (Table S1), which was confirmed by crystal color, charge neutrality and coordination environments. Bond lengths are in range of 2.140–2.540 Å for Zn—O bonds and 2.176–2.190 Å for Zn—N bonds. The new compound exhibits a three-dimensional molybdate-based MOF containing the infinite helical Zn-trz arrays and MoO_4-Zn inorganic network. The most important structural feature is that there are two kinds of helical channels constructed by Zn cations and trz ligand. More specifically, Zn cations link with trz ligand forming twofold meso-helixes, in which the left- and right-handed helixes are fabricated along the same route of [Zn1-trz-Zn2-trz-Zn1]n (Figs. 1 and S2). The pitch of helix is 8.907 Å along *a* axis, which is consistent with the unit length of *a* axis. Then the left- and right-handed helical chains are connected together by sharing $Zn(trz)_2$ fragment forming one dimensional double helix tunnel arrays.

Without regard for trz ligand, $[MoO_4]^{2-}$ anion and Zn cations form a two dimensional network along *b* axis as shown in Fig. 2a, in which each $[MoO_4]^{2-}$ anion connect with four Zn cations (three Zn1 and one Zn2 cations). Finally, two-dimensional MoO_4-Zn networks interlude into the helical tunnels using Zn cations as their common vertexes generating the

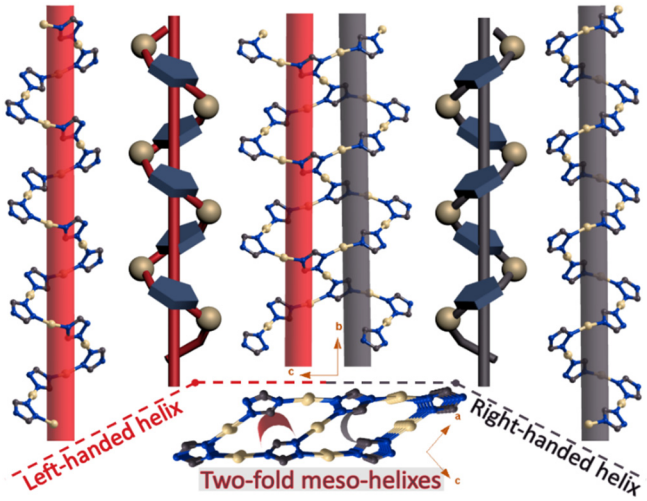

Fig. 1. Representation of the twofold meso-helixes formed by finite left-/right-handed helix conformation along *a* axis, and extended to the helical layer further.

final MoO_4-containing MOF (Figs. 2b–d and S3). Note that the $[MoO_4]^{2-}$ anion not only as linker connect to the adjacent 2D helical array, but also stabilize the three-dimensional framework. From the topological view, the title compound exhibits a unique (4, 6, 7)-connected 3D framework with an unprecedented $\{3{\cdot}4{\cdot}5^3{\cdot}6\}^2\{3^3{\cdot}4^2{\cdot}5^8{\cdot}6^8\}^2\{3^4{\cdot}4^2{\cdot}5^4{\cdot}6^5\}$ topology (Fig. S2d). In this simplification, the 4-connected nodes are $[MoO_4]^{2-}$ anion, the 6-connected nodes are Zn2 cations and the 6-connected nodes are Zn1 cations.

The morphology of as-synthesized MoO_4-based MOF was characterized by the scanning electron microscopy (SEM), which was discussed in supporting information (Fig. S4). The bulk samples of the compound were characterized using Fourier transform infrared spectroscopy (FT-IR), and their phase purities were verified by the well matched powder X-ray diffraction (PXRD) patterns of the as-synthesized samples and the simulated ones (Figs. S5 and S6). TG analysis of **1** (Fig. S7) indicates that the weight loss before 150 °C attributed to the loss of water molecules, then the whole framework completely collapsed after 260 °C. Because the molybdenum oxide moieties was introduced into the Zn-based MOF, compound **1** may be endowed superior catalytic ability. As we all know, the excellent chemical stability is beneficial for the new compound as catalytic material. Compound **1** is stable in aqueous solutions in the pH range of 3–12 at room temperature for 24 h, as confirmed by PXRD and IR measurements (Figs. 3a and S8). Moreover, **1** is also stable after soaking in common organic solvents such as methanol (MeOH), ethanol (EtOH), acetonitrile (MeCN), dimethylformamide (DMF) or dimethylacetamide (DMA) for 12 h at room temperature (Fig. 3b).

To investigate the peroxidase-like activity of the MoO_4-based MOF, the catalytic oxidation of the peroxidase substrate TMB in the presence of hydrogen peroxide was examined. As shown in Fig. 4a, when compound **1** was introduced into the solution with H_2O_2 and TMB, a chromogenic reaction was observed after incubation, which is consistent with reported results [29]. With the increasing reaction time, the absorbance intensity is raised rapidly, and achieves 0.43 at 5 min. Note that compound **1** as peroxidase-like catalyst exhibit rapid catalytically rate in only 1 min to observe color change by naked eye, which is superior to reported compounds in 90 min [28]. In addition, the absorbance of reaction solution under different conditions show that the solutions exhibit no absorbance change both in the absence and presence of H_2O_2, indicating that no oxidation reaction occurs without catalyst (Fig. 4b).

Similar to HRP and other enzyme mimics, compound **1** exhibits pH- and temperature-dependent catalytic activities. Thus, pertinent