



A multifunctional reduced molybdophosphate-based 3D metal–organic framework induced by a rigid triazole and a flexible bis(triazole) mixed ligand



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ABSTRACT

A novel reduced molybdophosphate-based metal–organic framework (MOF) $\text{Zn}[(\text{MoO}_2)_6(\text{HPO}_4)_2(\text{PO}_4)_2(\text{OH})_3]_2[\text{Zn}_2(\text{L}^1)][\text{Zn}(\text{HL}^2)_2]_2 \cdot 10\text{H}_2\text{O}$ (**1**) ($\text{L}^1 = 1,6\text{-bis}(1,2,4\text{-triazol-1-yl})\text{hexane}$, $\text{L}^2 = 1,2,4\text{-triazol}$) has been hydrothermally synthesized and structurally characterized. Compound **1** is constructed from the $[\text{Zn}(\text{P}_4\text{Mo}_6)_2]$ -based 2D layer and μ_2 -bridging L^1 ligands, which shows a (2,3,8)-connected three-dimensional framework with $\{[4 \cdot 6^2]2[4^4 \cdot 6^2 \cdot 8^{18} \cdot 12^4]\{4\}^2\}$ topology. **1** represents the first 3D P_4Mo_6 -based MOF constructed by mixed N-donor ligands. The electrocatalytic and photocatalytic activities of compound **1** have been investigated.

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In recent years, metal–organic frameworks (MOFs) are of great interest in the fields of coordination polymers and materials, not only because of their structural diversity and novelty, but also owing to their multiple potential applications, such as catalysis, magnetism, separation and gas adsorption [1]. An attractive branch is the introduction of polyoxometalates (POMs) to MOFs, aiming for generation of various multifunctional hybrid materials, known as POMOFs [2]. At present, most of the reported POMOFs rest on the classical polyanions, such as Keggin- and Wells–Dawson type anions [3]. The reduced molybdenum phosphate $[\text{P}_4\text{Mo}_6\text{O}_{28}(\text{OH})_3]^{9-}$ (abbreviated as $[\text{P}_4\text{Mo}_6]$) as an important member of the POM family may represent an ideal building block, which may combine with transition metals and organic ligands to construct novel POMOFs due to the following points: (i) it possesses many terminal and bridging oxygen atoms, which can provide more coordination sites and versatile coordination modes to coordinate with transition metal ions [4]; (ii) it owns high negative charges due to the reduced Mo^V centers, which may link more cationic units into complicated architectures [5]. However, the reports on $[\text{P}_4\text{Mo}_6]$ -based MOFs are quite rare, to our knowledge. Thus, grafting the $[\text{P}_4\text{Mo}_6]$ building blocks onto MOFs may be a great challenge and a meaningful work in the fields of POM chemistry and coordination chemistry.

As is known, the rational design and selection of suitable organic ligands is an effective strategy for the construction of POMOFs. Currently, most of the reported $[\text{P}_4\text{Mo}_6]$ -based complexes rested on rigid

organonitrogen ligands, such as 2,2'-bipyridine, 4,4'-bipyridine and 1,10-phenanthroline [6]. In order to extend this synthetic strategy, we introduce a flexible N-donor ligand 1,6-bis(1,2,4-triazol-1-yl)hexane (L^1) to the P_4Mo_6 -based transition metal complex system in this work. L^1 not only owns more N donors for enhancing the coordination ability, but also possesses flexible $-(\text{CH}_2)_n-$ spacer, which can bend and rotate easily to conform to the coordination environments of metal ions and POMs, and may result in novel POM-based complexes [7]. However, the flexible ligands usually tend to construct interpenetrating topologies [8]. Therefore, in order to avoid interpenetration, a second ligand may be necessary. In this work, a rigid 1,2,4-triazol (L^2) attracted our attention due to the following points: (i) it possesses three N donor coordination sites; (ii) its small size and rigid bone may avoid forming the interpenetrating structures and conduce to constructing new topologies. Up to now, POMOFs constructed from mixed organic ligands are very limited, especially for the $[\text{P}_4\text{Mo}_6]$ anion. Thus, we introduce the mixed triazole-based ligands to the $[\text{P}_4\text{Mo}_6]$ -based system, aiming for exploring whether the mixed ligands can lead to the new POMOFs without interpenetration. Fortunately, a novel $[\text{P}_4\text{Mo}_6]$ -based MOF $\text{Zn}[(\text{MoO}_2)_6(\text{HPO}_4)_2(\text{PO}_4)_2(\text{OH})_3]_2[\text{Zn}_2(\text{L}^1)][\text{Zn}(\text{HL}^2)_2]_2 \cdot 10\text{H}_2\text{O}$ (**1**) has been obtained in this work, which represents the first example of $[\text{P}_4\text{Mo}_6]$ -based MOFs constructed from mixed ligands. In addition, the electrochemical properties and photocatalytic activity of the title compound have been reported.

Compound **1** was prepared under hydrothermal conditions from heating a mixture of MoO_3 , $\text{ZnCl}_2 \cdot 6\text{H}_2\text{O}$, D,L- α -alanine, L^1 , L^2 and H_3PO_4 in 5 mL water at 160 °C for 4 days [9]. Single crystal X-ray

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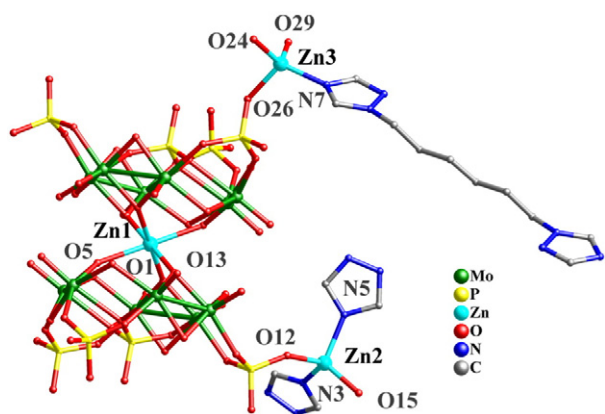


Fig. 1. Ball/stick view of the asymmetric unit of **1**. The hydrogen atoms and lattice water molecules are omitted for clarity.

structural analysis reveals that compound **1** crystallizes in a *Pi* space group [10], which contains a sandwich-type $\text{Zn}[\text{P}_4\text{Mo}_6]_2$ dimer, four Zn^{II} ions, one flexible L^1 , four rigid L^2 and ten lattice water molecules (Fig. 1). According to the valence bond calculations [11], all Mo atoms are in reduced oxidation state (+5), while Zn atoms are +2. The μ_2 -O atoms between non-bonding Mo atoms and partly uncoordinated O atoms from PO_4 groups are protonated.

In compound **1**, there are three crystallographically independent Zn^{II} ions (Fig. 1): Zn(1) is located in the $[\text{Zn}(\text{P}_4\text{Mo}_6)_2]$ dimer and bridges two $[\text{P}_4\text{Mo}_6]$ units through six μ_3 -O atoms [O(1), O(5), O(13)] to generate a centrosymmetrical $[\text{Zn}(\text{P}_4\text{Mo}_6)_2]$ dimer [with Zn(1)–O bond lengths of 2.130(5) Å, 2.151(5) Å and 2.175(5) Å, respectively], Zn(2) adopts a distorted $\{\text{ZnN}_2\text{O}_2\}$ tetrahedral configuration, which is coordinated by two N atoms [N(3) and N(5)] from two L^2 ligands [with Zn(2)–N distances of 2.019(9) Å and 2.003(10) Å, respectively], and two O atoms [O(12) and O(15)] from two PO_4 tetrahedra of two different $\text{Zn}[\text{P}_4\text{Mo}_6]_2$ units [with Zn(2)–O(12) and Zn(2)–O(15) bond distances of 1.915(7) Å and 1.898(6) Å, respectively]. Zn(3) is defined by three phosphate O atoms [O(24), O(26) and O(29)] from two different $\text{Zn}[\text{P}_4\text{Mo}_6]_2$ units with Zn–O distances of 1.925(6), 1.951(6) and 1.972(5) Å, and a nitrogen atom [N(7)] from one L^1 ligand [Zn(2)–N = 1.985(7) Å], showing a tetrahedral geometry.

As shown in Fig. 2a, each $[\text{Zn}(\text{P}_4\text{Mo}_6)_2]$ dimer was connected by two Zn(3) atoms to form an infinite inorganic chain along the *a* axis. The adjacent 1D chains were linked by $\text{Zn}_2(\text{L}^2)_2$ units to form a 2D layer (Fig. 2b). L^1 acts as a bridging ligand by providing two apical N donors to coordinate with Zn(3) atoms from different 2D networks. Thus, the 2D sheets are extended to a 3D framework by bridging L^1 ligands (Fig. 3, Fig. S1 and Fig. S2). Topologically, each $[\text{Zn}(\text{P}_4\text{Mo}_6)_2]$ dimer coordinates with four Zn(2) ions and four Zn(3) ions by the terminal O atoms of phosphate groups, which can be regarded as an 8-connected node (Fig. 2b, Fig. S3). Each Zn(2) ion can be considered as a 2-connected node, each Zn(3) ion acts as a 3-connected node, and the L^1 ligands act as linkers, thus the 3D framework of **1** can be described as a 2,3,8-connected net with the Schläfli symbol of $\{4 \cdot 6^2\}2\{4^4 \cdot 6^2 \cdot 8^{18} \cdot 12^4\}\{4\}^2$ (Fig. 2c).

As expected, the mixed ligands play a key role in the construction of the $[\text{P}_4\text{Mo}_6]$ -based high-dimensional MOF. In our previous work, when only L^1 was used in a P_4Mo_6 system, a 2D network $[\text{Cd}(\text{H}_2\text{O})_2][\text{Cd}(\text{H}_2\text{O})(\text{Hbth})]_2[\text{Cd}_{0.5}(\text{H}_2\text{O})(\text{bth})]_2[\text{Cd}(\text{PO}_4)_4(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_2(\text{MoO}_2)_{12}(\text{OH})_6] \cdot 4\text{H}_2\text{O}$ (**1'**) was obtained [12], in which the L^1 ligand with a monodentate mode only grafts onto the Cd– PO_4 chain of **1'**, and does not show contribution to the structural dimensionality. In order to explore the effect of a secondary ligand on the structure of the P_4Mo_6 -based complex, L^2 was introduced as the second ligand in this work. In the final structure of the title compound, though L^2 only adopts the monodentate mode coordinating with the Zn(2) ions, L^1

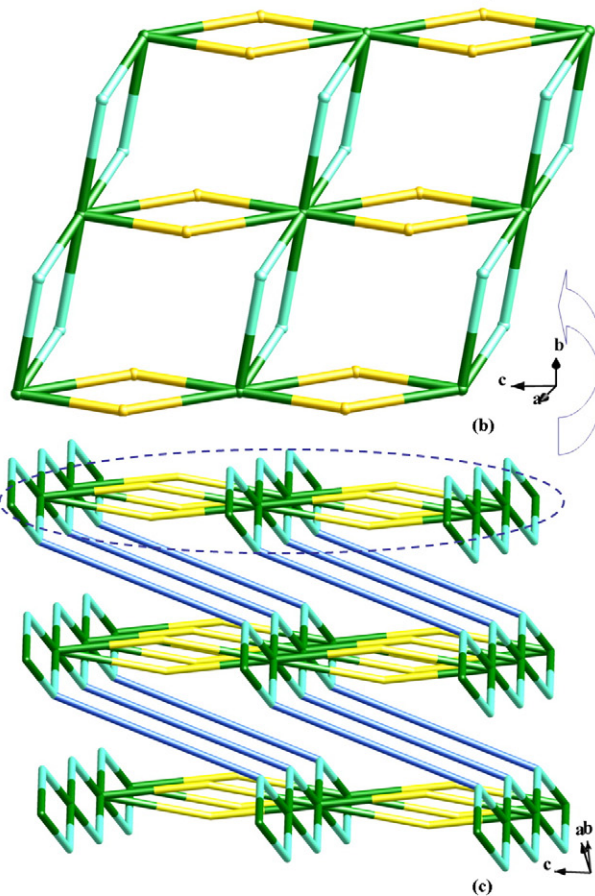
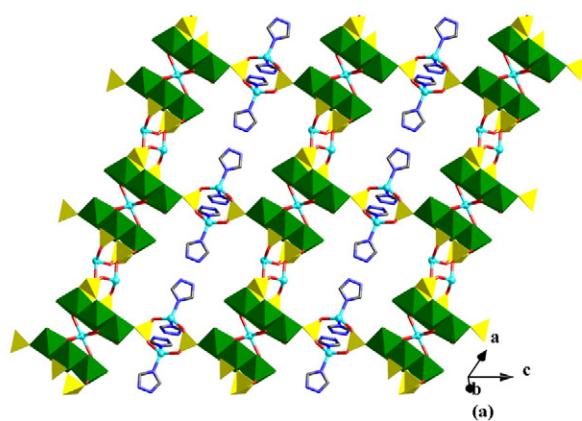


Fig. 2. (a) View of 2D network constructed by $[\text{Zn}(\text{P}_4\text{Mo}_6)_2]$ dimers and $\text{Zn}^{\text{II}}\text{-L}^2$ units in compound **1**. (b) Schematic view of the 2D layers. (c) The schematic view of the 3D framework.

acts as a bridging ligand to connect the Zn(3) ions of the adjacent $\text{P}_4\text{Mo}_6\text{-Zn-L}^2$ sheets, resulting in a 3D framework. In addition, the small steric effect of L^2 may contribute to the formation of the channels (Fig. 3). The result indicates that the introduction of the secondary ligand L^2 has a great effect on the coordination behavior of L^1 and the final structure of the title compound.

The cyclic voltammetric behaviors of compound **1** bulk-modified carbon paste electrode (**1**-CPE) in 0.1 mol/L H_2SO_4 + 0.5 mol/L Na_2SO_4 aqueous solution at different scan rates are presented in Fig. 4a. In the potential range of 450 to –250 mV, there are three pairs of reversible redox peaks, I–I', II–II' and III–III', with the mean peak potentials $E_{1/2} = (E_{\text{pc}} + E_{\text{pa}}) / 2$ of 243, 127 and –135 mV (scan rate: $200 \text{ mV} \cdot \text{s}^{-1}$), respectively, which should be ascribed to the redox of P_4Mo_6 [13]. The peak potentials change gradually following

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