

Three POM-based MOFs containing Ag/3-pttz frameworks with 1D to 3D features



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ABSTRACT

Three new polyoxometalate-based metal–organic framework compounds $[\text{Ag}_7(3\text{-pttz})_4(\text{PMo}_{12}\text{O}_{40})] \cdot \text{H}_2\text{O}(\mathbf{1})$, $[\text{Ag}_6(3\text{-Hpttz})_2(3\text{-pttz})_2(\text{SiMo}_{12}\text{O}_{40})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}(\mathbf{2})$ and $[\text{Ag}_6(3\text{-Hpttz})_6(\text{PMo}_{12}\text{O}_{40})_2] \cdot 2\text{H}_2\text{O}(\mathbf{3})$ (3-Hpttz = 5-(3-pyridyl)-1H-tetrazole) are synthesized hydrothermally by changing the polyoxoanions and the pH values in the same metal–organic system (Ag/pttz), and structurally characterized by IR spectra, elemental analyses and single crystal X-ray diffraction. Compound **1** exhibits a three-dimensional (3D) Ag/3-pttz host framework with larger channels. The discrete $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ anions, acting as inorganic templates, are embedded in the channels. In compound **2**, the Ag/3-pttz motif displays a two-dimensional (2D) stair-like layer, which is linked by $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$ anions to construct a 3D framework. In compound **3**, the Ag/3-pttz motif shows a 1D ribbon-like chain, some of $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ anions in a “shoulder-to-shoulder” mode link two ribbon-like polymers to form a 1D “quadrangular prism-like” chains, and the others of $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ anions bond to chains and become pendants of the quadrangular prism, projecting toward two sides. Therefore, compound **3** displays a scarce 1D “quadrangular prism with pendants” structure. In addition, the electrochemical behavior and electrocatalytic activity of compound **1** as an example were investigated.

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1. Introduction

The designs and syntheses of polyoxometalate-based (POM) metal–organic frameworks (MOFs) have attracted considerable attention in the field of materials chemistry and crystal engineering owing to their potential applications in catalysis, medicine, nanotechnology, as well as their fascinating architectures and topological frameworks [1]. The reported works indicate that polyoxometalates are a kind of multiple functional metal oxide clusters in the crystal engineering of POM-based MOFs. Firstly, they are multidentate inorganic ligands due to their larger size and multiple coordination sites, so they can connect more than one metal cation to form high-connected and high dimensional POM-based MOFs. Secondly, POMs can control and adjust the sizes, shapes and dimensions of MOFs due to their various sizes, shapes, electronic density, and oxo-rich surfaces. Furthermore, MOFs can also conquer the inherent drawbacks of POMs (such as low specific surface area and instability under the reaction conditions) to optimize the traditional POM materials. The introduction of POM building

blocks to MOF is not merely a strategy to obtain charming structures, but also an effective method to construct multifunctional hybrid materials [2,3].

The final structures of POM-based MOFs are commonly influenced by various factors, such as pH value in the reaction, coordination geometries of metal ions, electronic charge, sizes and shapes of POMs and coordination modes, steric hindrance, and flexibility of ligands. Therefore, from the crystal engineering point of view, the rational design and control of self assembly processes is still a very challenging work to realize the targeted syntheses of POM-based MOFs. The rigid ligand 5-(3-pyridyl)-1H-tetrazole (3-Hpttz) in its anionic form is an attractive multidentate ligand for the design of POM-based MOFs owing to their smaller steric hindrance, more donor atoms and flexible coordinate modes (Scheme 1). So it is a good candidate for acting as useful organic linkers for the connection of the POM units [4–6]. Additionally, a rational selection of the metal centers is also crucial. The silver ion can display various coordination geometries including linear, T-type, Y-type, “seesaw”, “square pyramidal” and “trigonal bipyramidal” [5,6]. Therefore, it fits into the abundant coordination mode of the 3-Hpttz ligand and can be chosen as the bridging linker in POM-based MOFs [5,6]. Among the different types of POMs, the Keggin POMs, have

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widely been regarded as an important molecular building unit for constructing inorganic–organic coordination polymers due to its unique structure and electronic characteristics [6–8].

Considering aforementioned points, we selected Keggin POMs, transition metal Ag(I) cation, and organic ligand 3-Hpttz to construct the POMs-based MOFs in different pH value. As expected, three new compounds were obtained: $[\text{Ag}_7(3\text{-pttz})_4(\text{PMo}_{12}\text{O}_{40})_2] \cdot \text{H}_2\text{O}$ (**1**), $[\text{Ag}_6(3\text{-Hpttz})_2(3\text{-pttz})_2(\text{SiMo}_{12}\text{O}_{40})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (**2**), $[\text{Ag}_6(3\text{-Hpttz})_6(\text{PMo}_{12}\text{O}_{40})_2] \cdot 2\text{H}_2\text{O}$ (**3**), (3-Hpttz = 5-(3-Pyridyl)-1H-tetrazole). Compounds **1**, **2** and **3** provide good examples of reasonable design and controllable assembly of POM-based coordination polymers.

2. Experimental

2.1. Materials and methods

5-(3-Pyridyl)-1H-tetrazole (abbreviated as 3-Hpttz) was prepared according to literature procedures [9]. All reagents for the syntheses were purchased from commercial and used as received. All title compounds were synthesized in poly(tetrafluoroethylene)-lined stainless steel autoclaves under autogenous pressure. Elemental analyses of C, H and N were performed with an EA1110 CHNS-O CE elemental analyzer. IR (KBr pellet) spectra were recorded on a Nicolet Magna 750FTIR spectrometer. Thermogravimetric analyses were performed on a METTLER TGA/SDTA851 microanalyzer under nitrogen atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$. The powder X-ray diffraction (PXRD) patterns were measured on a Rigaku DMAX2500 powder diffractometer at 40 kV and 100 mA using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$). Cyclic voltammetry measurements were carried out on a CHI 660B electrochemical station using a conventional three-electrode single compartment cell at room temperature. The working electrode was a modified CPE (carbon paste electrode). Platinum gauze was used as the counter electrode and Ag/AgCl was used as the reference electrode. Compound **1**-modified carbon paste electrode (**1**-CPE) was fabricated as follows: 600 mg of graphite powder and 65 mg compound **1** were mixed, and ground together by an agate

mortar and pestle to achieve an even, dry mixture. Paraffin oil (0.7 mL) was then added to the mixture and stirred. The mixture was further packed into a graphite tube (3 mm inner diameter).

2.2. Synthesis of compounds **1**–**3**

2.2.1. $[\text{Ag}_7(3\text{-pttz})_4(\text{PMo}_{12}\text{O}_{40})_2] \cdot \text{H}_2\text{O}$ (**1**)

A mixture of MoO_3 (0.8 mmol), AgNO_3 (0.3 mmol), 3-Hpttz (0.2 mmol), KH_2PO_4 (0.1 mmol) was dissolved in 8.0 mL of HNO_3 aqueous solution (0.25 M) and stirred for half an hour at the pH value of 2.3. Then the mixture was sealed in an 18 mL Teflon-lined reactor and heated at 165°C for 3 days. Yellow columnar crystals of compound **1** were obtained, filtered, washed with water and dried at room temperature (yield: ~50% based on Mo). *Anal.* Calc. for $\text{C}_{24}\text{H}_{18}\text{Ag}_7\text{Mo}_{12}\text{N}_{20}\text{O}_{41}\text{P}$: C, 9.06; H, 0.57; N, 8.81. Found: C, 8.89; H, 0.66; N, 8.96%. IR (solid KBr pellet, v/cm^{-1}): 3443(m), 1608(m), 1454(m), 1424(m), 1386(m), 1061(vs), 956(vs), 875(vs), 795(vs), 674(s), 499(s).

2.2.2. $[\text{Ag}_6(3\text{-Hpttz})_2(3\text{-pttz})_2(\text{SiMo}_{12}\text{O}_{40})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (**2**)

The compound **2** (yellow and sheet) was synthesized by the same procedure as **1** except for the replacement of KH_2PO_4 with Na_2SiO_3 at the pH value of 3.1. (Yield: ~60% based on Mo). *Anal.* Calc. for $\text{C}_{24}\text{H}_{26}\text{Ag}_6\text{Mo}_{12}\text{N}_{20}\text{O}_{44}\text{Si}$: C, 9.22; H, 0.84; N, 8.97. Found: C, 9.09; H, 0.91; N, 9.13%. IR (solid KBr pellet, v/cm^{-1}): 3452(s), 3408(m), 1612(s), 1457(m), 1431(m), 1384(s), 1180(w), 1038(w), 938(m), 951(vs), 901(vs), 796(vs), 707(s), 673(m), 620(m), 533(m), 506(m).

2.2.3. $[\text{Ag}_6(3\text{-Hpttz})_6(\text{PMo}_{12}\text{O}_{40})_2] \cdot 2\text{H}_2\text{O}$ (**3**)

The compound **3** (yellow and block) was synthesized by the same procedure as **1** except for the replacement 8.0 mL of 0.25 M HNO_3 with 8.0 mL of 0.5 M HNO_3 at the pH value of 1.1. (Yield: 45% based on Mo). *Anal.* Calc. for $\text{C}_{10}\text{H}_6\text{Ag}_4\text{Mo}_4\text{N}_{12}\text{O}_{13}$: C, 9.12; H, 0.46; N, 12.76. Found: C, 8.89; H, 0.56; N, 13.06%. IR (solid KBr pellet, v/cm^{-1}): 3447(m), 3039(m), 1608(m), 1608(m), 1564(m), 1455(m), 1386(m), 1254(w), 1153(w), 1061(vs), 956(vs), 877(vs), 794(vs), 671(s), 499(s).

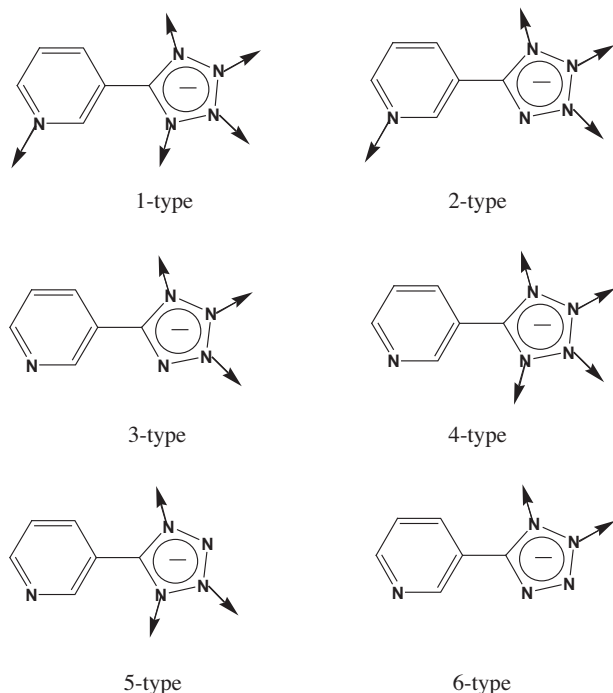
2.3. X-ray crystallography

Single-crystal X-ray diffraction analyses of **1**–**3** were carried out on a Rigaku Mercury CCD diffractometer equipped with a graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. Structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 by using the SHELX-97 program package. All non-hydrogen atoms were located with successive Fourier difference syntheses and refined anisotropically. All hydrogen atoms of the organic ligands were generated geometrically (C–H, 0.93 $\text{\AA}$). For the compounds **1**, the hydrogen atoms attached to water molecules were located in difference Fourier map. But the water H atoms of compounds **2** and **3** were not located. A summary of crystallographic data and other pertinent information for **1**–**3** is provided in Table 1. Selected bond lengths and angles are listed in Tables S1–S3. Weak coordination interactions $[\text{Ag} \cdots \text{O} = 2.634\text{--}2.862 \text{ \AA}]$ are observed within the title compounds. The weak coordination bonds are also discussed in extending the dimensionality of compounds. Consequently, they are listed in Tables S1–S3.

3. Results and discussion

3.1. Description of the crystal structures

Compound **1** was obtained at the pH value of 2.6. Crystallographic structure analysis reveals that compound **1** (Fig. 1a) is



Scheme 1. Coordination modes of the 3-pttz ligand in title compounds.

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