



Assembly of new polyoxometalate-templated metal-organic frameworks based on flexible ligands

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ABSTRACT

Four new polyoxometalate(POM)-templated metal-organic frameworks based on flexible ligands, namely, $[\text{Cu}_6(\text{bip})_{12}(\text{PMo}_{12}\text{O}_{40})_2(\text{PMo}^{\text{V}}\text{Mo}_{11}^{\text{V}}\text{O}_{40}\text{O}_2)] \cdot 8\text{H}_2\text{O}$ (**1**), $[\text{Cu}_3\text{Cu}_3^{\text{II}}(\text{bip})_{12}(\text{PMo}_{12}\text{O}_{40})_2(\text{PMo}_{12}\text{O}_{34})] \cdot 8\text{H}_2\text{O}$ (**2**), $[\text{Ni}_6(\text{bip})_{12}(\text{PMo}_{12}\text{O}_{40})(\text{PMo}_{11}^{\text{V}}\text{Mo}^{\text{V}}\text{O}_{40})_2\text{Cl}] \cdot 6\text{H}_2\text{O}$ (**3**), $[\text{Co}_3^{\text{II}}\text{Co}_2^{\text{III}}(\text{H}_2\text{bib})_2(\text{Hbib})_2(\text{PW}_9\text{O}_{34})_2(\text{H}_2\text{O})_6] \cdot 6\text{H}_2\text{O}$ (**4**) (bip = 1,3-bis(imidazolyl)propane, bib = 1,4-bis(imidazolyl)butane) have been obtained under hydrothermal condition and characterized by single-crystal X-ray diffraction analyses, elemental analyses, and thermogravimetric (TG) analyses. The studies of single crystal X-ray indicate that compounds **1–3** crystallize in the trigonal space group *P*-3, and compound **4** crystallizes in the triclinic space group *P*-1. Compounds **1** and **3** represent 3D frameworks, and POMs as the guest molecules are incorporated into the cages which are composed of the ligands and metals, while compounds **2** and **4** show 3D frameworks by hydrogen bonds. This compounds provide new examples of host-guest compounds based on flexible bis(imidazole) ligands. In addition, the electrochemical property and the catalytic property of compound **1** have also been investigated.

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1. Introduction

Polyoxometalates (POMs), one kind of metal oxide clusters, have attracted more and more people's interest because of their properties, such as catalytic activity, photochemistry, magnetism, and electrochemistry [1–6]. Metal-organic frameworks (MOFs) have recently become one of the most focus of material due to their structural diversities and the applications to gas storage and separation, catalysis, chirality, and photoluminescence. Especially MOFs can be modified with organic ligands and metal centers [7–14].

Currently, the design and synthesis of modified POMs with metals and organic components are the research focus by reason of their stable properties as well as structural diversity [15–24], especially, POMs are an optimal choice of chemical species for incorporation into the pores of MOFs, because these metal oxide clusters can be engaged in a very rich and wide variety of multielectron reversible redox reactions. The research of the POM-templated host-guest hybrid compounds is one of the focuses in recent years. These frameworks are more stable than MOFs and can be recycled simply by filtration. Constructing POM-templated host-guest hybrid compounds provides a good way to combine the inorganic component with the organic component together [25–27]. One of the challenging

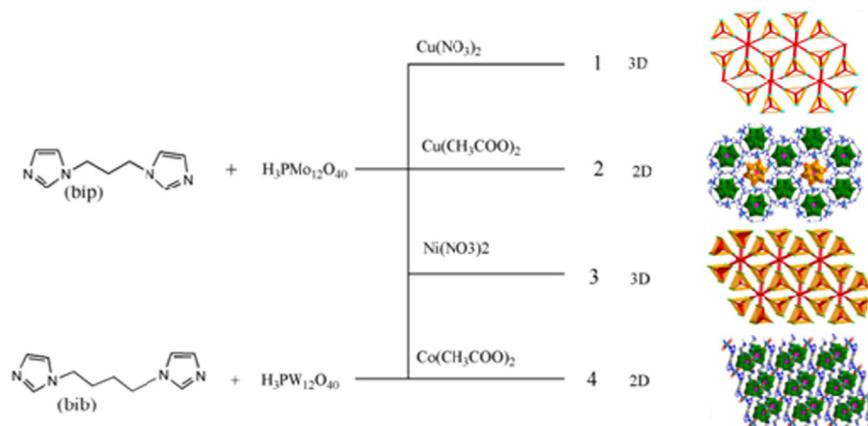
tasks in polyoxometalates chemistry is to find some novel organic units and then link them up into larger clusters, or to one-, two-, and even three-dimensional extended frameworks.

The organic ligands are extremely important because changing the organic ligands can control and adjust the topologies of MOFs. The flexible N-containing polydentate ligands are excellent candidates for the construction of novel structures and topologies. According to the previous literatures, many N-donor ligands, which can bridge metal nodes to construct MOFs, for example, 1,4-bis(imidazol-1-yl)-butane, 1,2-bis(tetrazol-5-yl)ethane, 1,4-bis(imidazol-1-yl-methylene)-benzene, 1,3-bis(benzimidazol)propane, 1,3-bis(tetrazol-5-yl)propane, 1,4-bis(tetrazol-5-yl)butane have been widely reported [28–31]. So far, much work is focused on the construction of MOFs based POMs by N-containing polydentate ligands [32–35]. However, the examples of POMs templated MOFs based on 1,3-bis(imidazolyl)propane are rare.

So we choose these two ligands, 1,3-bis(imidazolyl)propane (bip) and 1,4-bis(imidazol)butane (bib) to construct new structures. Four new compounds based on flexible bidentate ligands, namely, $[\text{Cu}_6(\text{bip})_{12}(\text{PMo}_{12}\text{O}_{40})_2(\text{PMo}^{\text{V}}\text{Mo}_{11}^{\text{V}}\text{O}_{40}\text{O}_2)] \cdot 8\text{H}_2\text{O}$ (**1**), $[\text{Cu}_3\text{Cu}_3^{\text{II}}(\text{bip})_{12}(\text{PMo}_{12}\text{O}_{40})_2(\text{PMo}_{12}\text{O}_{34})] \cdot 8\text{H}_2\text{O}$ (**2**), $[\text{Ni}_6(\text{bip})_{12}(\text{PMo}_{12}\text{O}_{40})(\text{PMo}_{11}^{\text{V}}\text{Mo}^{\text{V}}\text{O}_{40})_2\text{Cl}] \cdot 6\text{H}_2\text{O}$ (**3**), $[\text{Co}_3^{\text{II}}\text{Co}_2^{\text{III}}(\text{H}_2\text{bib})_2(\text{Hbib})_2(\text{PW}_9\text{O}_{34})_2(\text{H}_2\text{O})_6] \cdot 6\text{H}_2\text{O}$ (**4**) (bip = 1,3-bis(imidazolyl)propane, bib = 1,4-bis(imidazol)butane) have been synthesized under hydrothermal condition (Scheme 1). The electrochemical behaviors and catalytic properties of compound **1** have been investigated.

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Scheme 1. Experimental routes for compounds 1–4.

2. Experimental

2.1. Materials and general methods

All of the raw material were purchased commercially and used without purification. C, H and N elements were analyzed on a Perkin–Elmer 2400 CHN elemental analyzer. FT-IR spectra (KBr pellets) were taken on a Nicolet 170SX spectrophotometer. The thermogravimetric analysis (TGA) was carried out on a STA449C integration thermal analyzer with a heating rate of 10 °C/min from room temperature to 1000 °C at nitrogen atmosphere. Electrochemical measurements were performed with a CHI660b electrochemical workstation. A conventional three-electrode system was used. Ag/AgCl electrode was used as a reference electrode and a Pt wire as the counter electrode. The title compound bulk-modified carbon paste electrode (CPE) was used as the working electrode.

2.2. Synthesis of compound 1

A mixture of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.1 mmol), bip (0.1 mmol), $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ (0.1 mmol), and H_2O (10 mL) was placed in an 25 mL teflon reactor, the pH value was adjusted to 5–6 by 1 mol/L NaOH, and kept under autogenous pressure at 140 °C for 4 days. After slow cooling to room temperature, blue crystals were filtered and washed with distilled water (yield 72% based on Cu). Elemental analysis results for $\text{C}_{108}\text{H}_{160}\text{N}_{48}\text{Cu}_6\text{P}_3\text{Mo}_{36}\text{O}_{130}$ (8138.83): Calcd. C 15.924, H 1.966, N 8.257. Found. C 15.134, H 1.957, N 7.931. IR data (KBr pellet, cm^{-1}): 645(m), 733(w), 804(s), 869(w), 943(s), 1052(s), 1108(s), 1238(s), 1291(m), 1365(m), 1404(m), 1451(w), 1531(s), 3128(m).

2.3. Synthesis of compound 2

Compound 2 was prepared similarly to that of compound 1, except that $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.1 mmol) was replaced by $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$. Light blue crystals were filtered and washed with distilled water (yield 78% based on Cu). Elemental analysis results for $\text{C}_{108}\text{H}_{160}\text{N}_{48}\text{Cu}_6\text{P}_3\text{Mo}_{36}\text{O}_{122}$ (8010.83): Calcd. C 16.178, H 1.997, N 8.388. Found. C 15.348, H 1.989, N 7.905. IR data (KBr pellet, cm^{-1}): 650(m), 720(w), 791(s), 860(w), 962(s), 1050(s), 1200(w), 1401(m), 1450(m), 1531(m), 1550(m), 3128(m).

2.4. Synthesis of compound 3

Compound 3 was prepared similarly to that of compound 1, except that $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.1 mmol) was replaced by $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and the pH value was adjusted by 1 mol/L NaOH

and 1 mol/L HCl. Blue crystals were filtered and washed with distilled water (yield 45% based on Ni). Elemental analysis results for $\text{C}_{108}\text{H}_{156}\text{N}_{48}\text{Ni}_6\text{P}_3\text{Mo}_{36}\text{O}_{126}\text{Cl}$ (8077.27): Calcd. C 16.045, H 1.931, N 8.320. Found. C 15.198, H 1.924, N 7.921. IR data (KBr pellet, cm^{-1}): 648(m), 736(w), 801(s), 866(w), 943(s), 1046(m), 1105(m), 1232(m), 1294(m), 1374(w), 1451(w), 1525(w), 1587(m), 3125(w).

2.5. Synthesis of compound 4

A mixture of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 6\text{H}_2\text{O}$ (0.1 mmol), bib (0.1 mmol), $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ (0.1 mmol), and H_2O (10 mL) was placed in an 25 mL teflon reactor, the pH value was adjusted to 5.26 by 1 mol/L NaOH, and kept under autogenous pressure at 110 °C for 3 days. After slow cooling to room temperature, purple crystals were filtered and washed with distilled water (yield 89% based on Co). Elemental analysis results for $\text{C}_{40}\text{H}_{86}\text{N}_{16}\text{Co}_5\text{P}_2\text{W}_{18}\text{O}_{80}$ (5737.14): Calcd. C 8.367, H 1.499, N 3.904. Found. C 8.145, H 1.491, N 3.846. IR data (KBr pellet, cm^{-1}): 570(m), 700(m), 721(s), 823(s), 885(s), 981(w), 1038(w), 1050(w), 1100(m), 1400(m), 1600(s), 1550(w), 3000 (m).

2.6. Synthesis of 1-CPE

The compound 1 modified CPE (1-CPE) was fabricated as follows: A mixture of 0.1 g graphite powder and 0.01 g compound 1 was grind together with an agate mortar and then was added 0.1 mL of mineral oil with stirring. Then the mixture was packed into a glass tube with a 1.5 mm inner diameter. Electrical contact was established with a copper wire on the back of the electrode.

2.7. X-ray crystallographic study

Diffraction data for compounds 1–4 were collected on a Bruker Smart Apex CCD diffractometer by graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda=0.71073 \text{ \AA}$) at room temperature. The structures were solved by direct methods and refined on F2 by full-matrix least-squares using SHELXTL-97 on a legend computer [36]. All non hydrogen atoms were refined anisotropically. Hydrogens were located in calculated positions and refined by using a riding model. The crystal and structure refinement data for 1–4 are summarized in Table S1. Selected bond lengths (\AA) and angles ($^\circ$) for 1–4 are listed in Table S3. CCDC reference number 1013483, 1013482, 1013484, 1013481 contain the crystallographic data for compounds 1–4.

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