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Short communication

Two new Keggin-type polyoxometalate-based entangled coordination networks constructed from metal-organic chains with dangling arms

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ABSTRACT

Two new polyoxometalate(POM)-based entangled coordination networks with chemical formula of $[Mn_2(H_2O)_2(BBPTZ)_5][SiW_{12}O_{40}]$ (1) and $[Ni_2(H_2O)_2(BBPTZ)_5][SiMo_{12}O_{40}]\cdot 6H_2O$ (2) (BBPTZ = 4.4′-bis(1,2,4-triazol-1-ylmethyl)biphenyl), were prepared in a hydrothermal reaction system. Compounds **1–2** were characterized by elemental analyses, IR spectroscopy, thermogravimetric analysis, powder X-ray diffraction and single-crystal X-ray diffraction. In compound **1**, dangling arms thread in quadrangular window of the adjacent 2-D layers, thus resulting in a rare 2-D → 3-D polythreading motif. Compound **2** exhibits a rare 2-D → 3-D zipper-closing motif. Using the degradation of methylene blue (MB) as the model, the photocatalytic activities of compounds **1–2** were investigated. Both compounds show efficient catalytic activity for the degradation of MB with the order of 2 > 1. It is found that the POM species of compounds **1–2** play the main role in the photocatalytic degradation process.

The design and synthesis of new organic-inorganic hybrid materials, especially polyoxometalate(POM)-based compounds modified by different transition-metals (TMs) and organic ligands, have attracted considerable attention over recent years, owing to not only their chemical and structural diversities but also their promising applications, such as adsorption, luminescence, catalysis, molecular recognition and electronic and magnetic materials [1]. In the field of catalysis, uniform dispersal of POM units within MOFs skeleton at the molecular level can improve POMs' specific surface area (SSA) to increase the catalytic activity, and they can be easily recycled after catalytic reactions [2]. In this aspect, POMs, as one type of unique nano-sized metal-oxo clusters, can be regarded as "building blocks" with their terminal or bridging oxides coordinating with metal cations [3]. Especially, Keggin-type POMs are best choice because of the following reasons: (i) the best chemically-tunable clusters with multiple components, negative charges and chemical modifications; (ii) having excellent catalytic properties, such as strong Brønsted acidity; (iii) their tuned acidic and redox properties [4]. Moreover, transition metal (TM) cations are important nodes due to their explicit coordination geometries and strong coordination ability to connect with POMs and organic ligands. However, the choice and design of organic ligands are of great importance for exploring new POM-based coordination networks [5–10]. From viewing coordination modes of organic ligands, the monodentate N-donor ligands such as pyridine and imidazole groups have been employed due to their definite coordination modes with TM ions [5]. By comparison, the multi-dentate ligands such as triazole and tetrazole ligands have also been extensively explored in recent years considering their relatively high coordination activities with TM ions and various coordination modes [6–8]. Thus, the introduction of $—(CH_2)_n—$ and/or phenyl spacers between two terminal multi-dentate N-donor groups can generate flexible ligands with various coordination modes so as to construct more complicated and variable structural topologies [6–8]. Therefore, we chose a rigid and flexible double-triazole-containing ligand, namely 4,4′-bis(1,2,4-triazol-1-ylmethyl)biphenyl (BBPTZ) (see Scheme 1), and have successfully synthesized three new POM-based coordination networks [9] and a POM-encapsulating cationic MOF with wavelike channels [10]. As a continuing work of this reaction system, we introduce the metal ions Mn^{2+} and Ni^{2+} by changing pH to isolate two new Keggin-type polyoxometalate-based entangled coordination networks with the molecular formulas $[Mn_2(H_2O)_2(BBPTZ)_5][SiW_{12}O_{40}]$ (1) and $[Ni_2(H_2O)_2(BBPTZ)_5][SiMo_{12}O_{40}]\cdot 6H_2O$ (2) [11]. Interestingly, both compounds contain similar 2-D layers which are formed by Keggin-type POMs and ladder-like chains with dangling arms. Compound **1** exhibits a rare 2-D → 3-D polythreading network due to dangling arms threading in quadrangular window of the adjacent 2-D layers, but dangling arms of the adjacent 2-D layers are parallel with each other to display a rare 2-D → 3-D zipper-closing network for compound **2**. Due to the excellent catalytic property of Keggin-type POMs, the photocatalytic properties of two compounds were also investigated.

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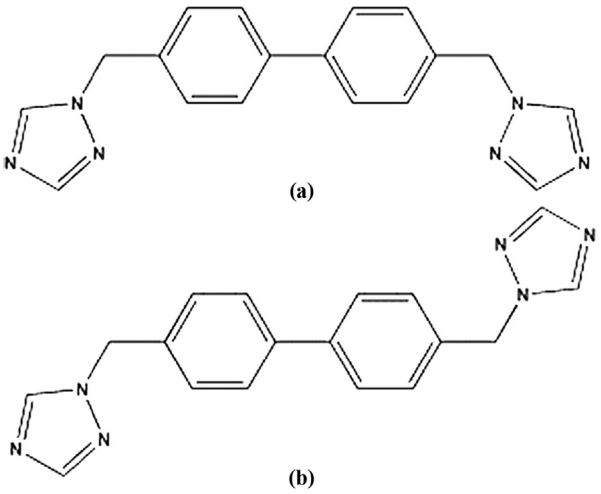

Scheme 1. Two configurations of BBPTZ (4,4′-bis(1,2,4-triazol-1-ylmethyl)biphenyl).

Single-crystal X-ray diffraction analyses [14] shows that compound **1** crystallizes in the monoclinic space group P2(1)/c. In **1**, the basic structural unit contains cationic $[Mn_2(H_2O)_2(BBPTZ)_5]^{4+}$ and the Keggin-type polyoxoanion $[SiW_{12}O_{40}]^{4-}$ (SiW_{12}) and two lattice water molecules (Fig. 1a and Fig. S1). In the cationic $[Mn_2(H_2O)_2(BBPTZ)_5]^{4+}$ unit, there is only one crystallographically independent Mn^{2+} center, which possesses a six-coordinated mode with four nitrogen atoms derived from four different BBPTZ ligands, one terminal oxygen atom originated from SiW_{12} polyoxoanions, and one coordinated water molecules (Fig. 1a and Fig. S1). The bond distances of Mn—N vary from 2.204(2) Å to 2.244(2) Å, and Mn—O are 2.192(1) Å and 2.237(1) Å. The bond angles of N(O)—Mn—N(O) are in the range of 84.1(5)–173.9(6)°. It is interesting that the BBPTZ ligands can be regarded as three different types labeled with L_a, L_b and L_c as shown in Fig. 1a and Fig. S2. Although apical nitrogen atom of each triazole group on the L_a and L_b ligands displays a monodentate coordination mode with one Mn center, two rigid phenyl centers of L_a and L_b ligands with trans-configuration exhibit two different orientation (Fig. 1a and Fig. S2). For L_c ligand, apical nitrogen atom of one triazole group exhibits a monodentate coordination mode with one Mn center and the other triazole group is not coordinated with any atom (Fig. 1a and Fig. S2). Based on above coordination mode, the Mn atoms are connected via *trans*-L_a ligands to form an undulating 1-D chain and the *trans*-L_b can be viewed as the "middle rail" that connects the adjacent 1-D chains to form a ladder-like chain (Fig. 1). Meanwhile, each Mn center also connects one S-type L_c ligand acted as "dangling arm" and L_c ligands protrude upper and lower sides of the ladder (Fig. 1). Further, the adjacent ladder-like chains are connected by the terminal O atom of the polyoxoanions to construct a 2-D network with quadrangle-like cavities, in which L_c ligands having an effectual length of about 16.3 Å are alternately appeared (Fig. 2 and Fig. S3). Such a 2-D network possesses two types of meshes (A and B) (Fig. 2). The A mesh is formed by four Ni centers, two L_a-type BBPTZ ligands and two L_b-type BBPTZ (Fig. 2a). The B mesh is constructed by four Ni centers, two L_a-type BBPTZ ligands and two SiW_{12} polyoxoanions (Fig. 2a). The sizes of two types of meshes are 15.33(1) × 16.31(5) Å and 14.67(1) × 16.31(5) Å, respectively (Fig. 2b). As a result, each B mesh is threaded by two dangling arms of above and below 2-D layers, thus resulting in a rare 2-D → 3-D polythreading motif (Fig. 3). In the packing arrangement, dangling arms of adjacent 2-D nets are extended in different directions, so that these adjacent 2-D nets are not parallel with each other, but these interval 2-D layers are parallel with each other (Fig. 3).

Single-crystal X-ray diffraction analysis [14] reveals compound **2** crystallizes in the triclinic space group P-1, and the crystallographically asymmetric unit consists of one Keggin-type polyoxoanion $[SiMo_{12}O_{40}]^{4-}$ ($SiMo_{12}$), two Ni^{2+} ion, three BBPTZ bridging ligands, two monoprotonated BBPTZ ligand, two coordinated water molecules and six lattice water molecule (Fig. 4a and Fig. S4). The cationic metal-organic fragment $[Ni_2(H_2O)_2(BBPTZ)_5]^{4+}$ contains one crystallographically independent Ni^{2+} center, which adopts a hexa-coordinated mode with four nitrogen atoms derived from four BBTZ ligands, one terminal oxygen atom originated from $SiMo_{12}$ polyoxoanions and one coordinated water molecules (Fig. 4a and Fig. S4). The bond lengths of Ni—N range from 1.968(2) to 2.018(2) Å and the N—Ni—N bond angles vary from 86.7(6) to 172.8(7)°. The bond distance of Ni—O(12) is 2.478(1) Å, which can be viewed as weak coordination bonds between

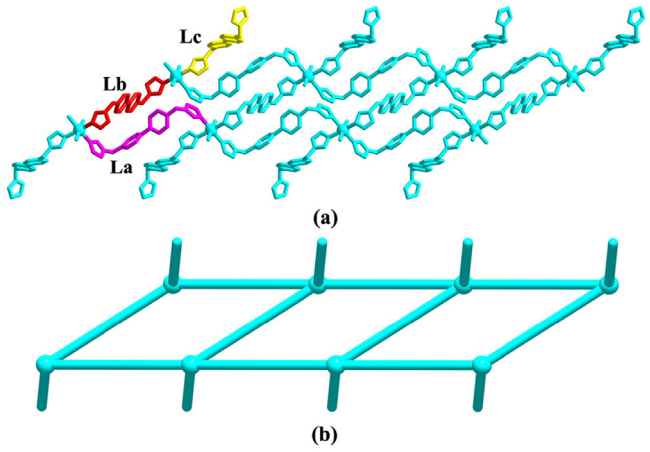

Fig. 1. (a) Ball-and-stick and (b) schematic views of the 1-D ladder-like chain with dangling arms in **1** formed by one Mn^{2+} center and BBPTZ ligands with three different kinds of structural configurations.

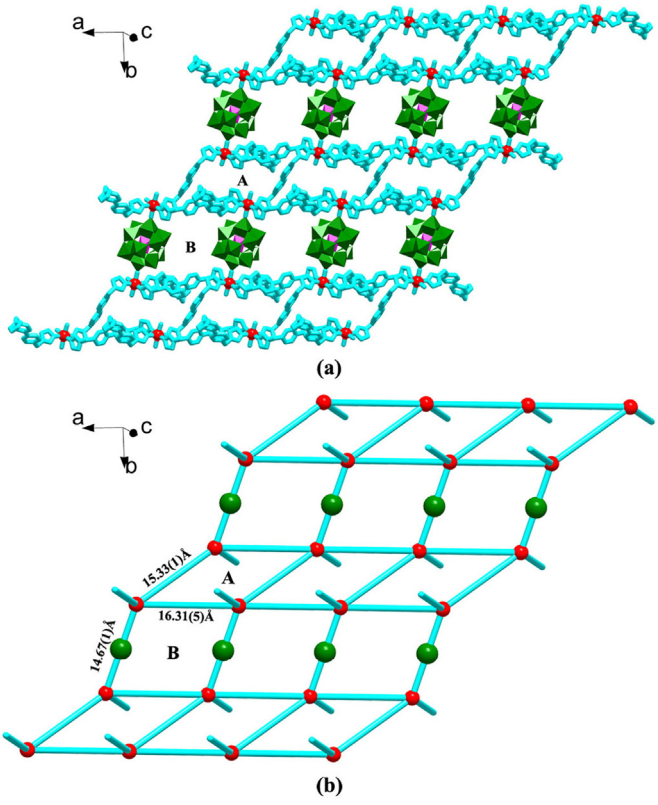

Fig. 2. (a) Structural views and (b) schematic views of 2-D network motif based on Keggin-type POM clusters and the ladder-like chains in **1** with two types of meshes (A and B).