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A metal–organic framework based on Wells–Dawson polyoxometalates $[As_2W_{18}O_{62}]^{6-}$ template

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ABSTRACT

A metal–organic framework based on Wells–Dawson polyoxometalate $[As_2W_{18}O_{62}]^{6-}$, $Co_2(bpy)_3(ox)(As_2W_{18}O_{62})\cdot 2(H_2bpy)\cdot 2H_2O$ (**1**) (bpy = 4,4′-bipyridine, ox = oxalate), has been synthesized hydrothermally by reacting $Co(NO_3)_2$, 4,4′-bipyridine, oxalate and $K_6As_2W_{18}O_{62}$. Single-crystal X-ray diffraction reveals that compound **1** contains a 3D cationic host framework composed of oxalate-bridged binuclear secondary building unit and 4,4′-bipyridine linkers. The channels of the 3D host framework are occupied by Wells–Dawson $[As_2W_{18}O_{62}]^{6-}$ templates. Thermogravimetric analysis shows the host framework keeps high thermal stability up to 450 °C. Furthermore, the electrochemistry property of **1** has been studied. The result indicates **1** has good electrocatalytic activity toward the reduction of nitrite.

Metal–Organic Frameworks (MOFs) have attracted a lot of interest because they are regarded as promising materials for applications in catalysis [1], magnetism [2], sorption [3] and molecular recognition [4]. Their structures and properties can be controlled by templates (molecules or ions) encapsulated in their channels [5]. Thus, the choice of templates is an important synthetic strategy to construct this type of porous materials [6]. Generally, organic amine cations are one class of common templates to prepare porous MOFs [7]. It is interesting that Keller's group has confirmed that polyoxometalates (POMs) can also be employed as templates to build MOFs [8]. POMs are early-transition metal-oxygen clusters with a wide range of size, high negative charges, redox and catalytic properties [9]. Especially, POMs, being nanosized metal-oxygen cluster anions, can act as effective templates to construct appropriate cationic host frameworks [10]. As template, POMs play two important roles in MOFs: (1) POMs can control and adjust size/shape and chemical functionalities of the pores; (2) POM guests can stabilize the three-dimensional host structure. For example, our group has reported NENU-n series compounds [11]. Among them, POM molecules are uniformly encapsulated in the pore of $Cu_3(BTC)_2$, resulting in the change of chemical functionalities and enhancement of thermal stability of the host framework. Such a series of compounds present corresponding applications in heterogeneous acid catalyst [12] and sorption [13]. However, rational design and construction of these types of materials remain a challenge because the oxophilic transition metal ions easily react with oxygen-enriched POMs to produce precipitate instead of crystallization. Much effort has been devoted to the synthesis of MOFs under the template effect of those smaller size discreet POMs, such as $[M_6O_{19}]^{n-}$ [14], $[XM_{12}O_{40}]^{n-}$ [15] and decavanadate clusters [16]. Nevertheless, as a kind of typical structure in POM chemistry, Wells–Dawson-type POMs have been rarely employed as templates to construct POM-templated MOFs [17] due to their high electronic and large bulk. Hence, we expect to obtain novel MOFs with distinctive structure topologies and properties by assembling the Wells–Dawson-type POMs into MOFs.

Versatile neutral rigid N-donors organic ligands are applied in the construction of MOFs [18]. 4, 4′-bipyridine, as a typical rigid N-donors organic ligand, has been extensively employed to construct porous MOFs through linking with transition metal ions [19]. As we know, most POM-templated MOFs are constructed by 4, 4′-bipyridine and another N-donors organic ligand [20]. However, POM-templated MOFs containing carboxyl ligands have been rarely reported [21], because it is difficult to get a cationic framework by using of electronegative carboxyl ligands. To overcome this obstacle, oxalate was used to chelate two metal ions to form a secondary building unit (SBU) in this work, which not only get a cationic SBU but also augment the size of the pores. The SBUs as nodes are jointed by 4, 4′-bipyridine to form the cationic framework.

In our previous work, we have obtained some POM-templated MOFs by hydrothermal technique [22]. It is interesting for us to question that the possibility whether the same framework could be constructed by utilizing another Wells–Dawson-type POMs in the pores. As expected, in such a way, an isomorphic framework was obtained, which confirms that the structure of MOFs could be controlled and tuned by POMs. In this paper, we report the synthesis, characterizations and properties of a 3D MOFs based on Wells–Dawson-type $[As_2W_{18}O_{62}]^{6-}$ template, $Co_2(4,4'\text{-bpy})_3(ox)(As_2W_{18}O_{62})\cdot 2(H_2bpy)\cdot 2H_2O$ (**1**). **1** was obtained by the hydrothermal reaction of $K_6As_2W_{18}O_{62}$, $C_2H_2O_4$, $Co(NO_3)_2$ and

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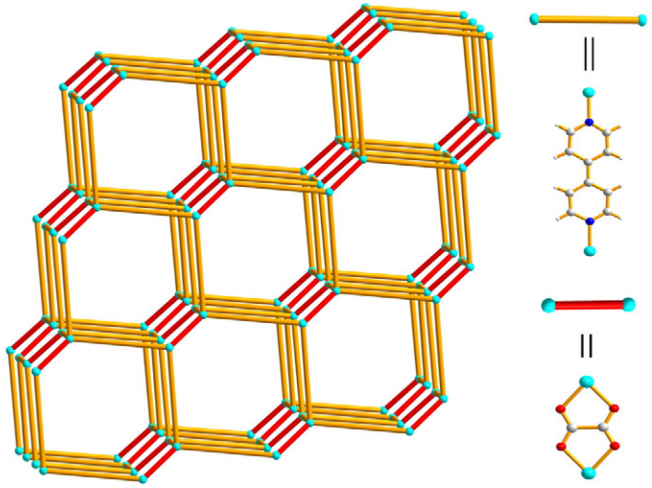

Fig. 1. View of the 3D network of compound **1** along the b axis.

4,4′-bipyridine [23]. Single crystal X-ray analysis shows that **1** consists of non-coordination $[As_2W_{18}O_{62}]^{6-}$ template and 3D host framework. The $[As_2W_{18}O_{62}]^{6-}$ exhibits α-Wells–Dawson structure and regularly occupies in channels of host framework. Moreover, the cyclic voltammetry (CV) of **1** has been discussed.

Compound **1** crystallizes in the *P*21/m space group, and the basic structure unit consists of a cationic framework moiety $[Co_2(bpy)_3(H_2O)_2(ox)]^{2+}$, a Wells–Dawson-type ployoxoanion $[As_2W_{18}O_{62}]^{6-}$, two bpy molecules, and two water molecules. The template $[As_2W_{18}O_{62}]^{6-}$ possesses Wells–Dawson-type structure and all of the bond lengths and bond angles are within the normal ranges and are consistent with those described in the literature. Meanwhile, the $[As_2W_{18}O_{62}]^{6-}$ alternately embed in the pore of host framework. The 3D host framework is constructed from oxalate-bridged binuclear superoctahedron SBUs and bpy linkers. Elemental and TG analysis confirm that the surplus anions charges are neutralized by the protoned bpy guests. Each Co^{II} cations coordinate with two oxygen atoms from an oxalate, three nitrogen atoms from three different bpy molecules and one oxygen atom from water molecule and exhibit a distorted octahedron geometry. The Co–O (ox) and Co–N (bpy) distances are 2.075(1)–2.104(1) Å and 2.111(1)–2.193(1) Å respectively, the Co–O (H_2O) distance is 2.142(1) Å. The bond distances of Co–N and Co–O are in the normal range. In the host framework, two Co^{II} cations are bridged by an oxalate molecule to form a binuclear secondary building unit. The connection of alternating binuclear Co units and bpy linkers results in an infinite 3D net (Fig. 1). The $[As_2W_{18}O_{62}]^{6-}$ anions occupy alternatively in the resulting square channels, which realize the immobilization of POMs in a host framework (Fig. 2). It is notable that the binuclear secondary building units play an important role as nodes in constructing the cationic framework. We successfully introduced the binuclear secondary building units into the host framework, which increased the size of the pores of the framework. The large pore provides enough space for the $[As_2W_{18}O_{62}]^{6-}$ template.

The IR spectrum of **1** (Figure S2 in supporting information) shows the characteristic bands at 1075, 967, 898, 771 cm^{-1} are attributed to the Wells–Dawson $As_2W_{18}O_{62}^{6-}$ polyoxoanion and the peaks at 1611, 1539, 1491, 1416 cm^{-1} are attributed to the ring-stretching vibrations of the bpy molecule. The bands at 1316 and 1357 cm^{-1} could be considered as ν_s(CO) and the resonances at 1643 cm^{-1} are assigned to ν_s(CO) of the oxalate ligand in a bis-bidentate bridging mode.

The thermal stability of **1** indicates that it can be stable up to 450 °C. The TGA curve (Figure S3 in supporting information) shows a loss weight of 4.03% below 200 °C. The value is much higher than 1.62% that is calculated for the loss weight of the lattice waters and coordination water molecules, which indicates that there are some guest molecules released. The second weight loss of 3.57% among the 350–450 °C region is due to the removal of the residual bpy guests. Upon further heating, it loses weight barely, indicating its high thermal stability. From 500 to 900 °C, the TGA trace shows a sharp decline to give a weigh loss of 13.12%, corresponding to the loss of all organic ligands and to sublimation of As_2O_5. The total weight loss is about 20.72%, which is accorded with the calculated value of 20.54%. The high thermal stability of **1** is due to the interplay between POMs and catinic host framework, which can provide a systematic route to construct high thermal stability MOFs.

To study the redox properties of compound **1**, the **1**-CPE was fabricated as described [24]. Fig. 3 shows the cyclic voltammetric behavior of **1**-CPE in 1 M H_2SO_4 solution in the potential range −800 to + 600 mv. In the voltammetric, it can be clearly seen that there are three pairs of redox peaks (I–I′, II–II′, and III–III′) which ascribe to the W center of $[As_2W_{18}O_{62}]^{6-}$ polyanion [25]. Moreover, there is an irreversible peak (IV) attributed to Co^{II}. The fact suggests that POMs are the activity center for electrochemical redox activity in CPEs. In addition, **1**-CPE is very stable. With the increase of scan rate, the increasing extent of anodic and cathodic peak currents are almost the same, and the peak potential change gradually. The approximate proportionally of the reduction peak current to the scan

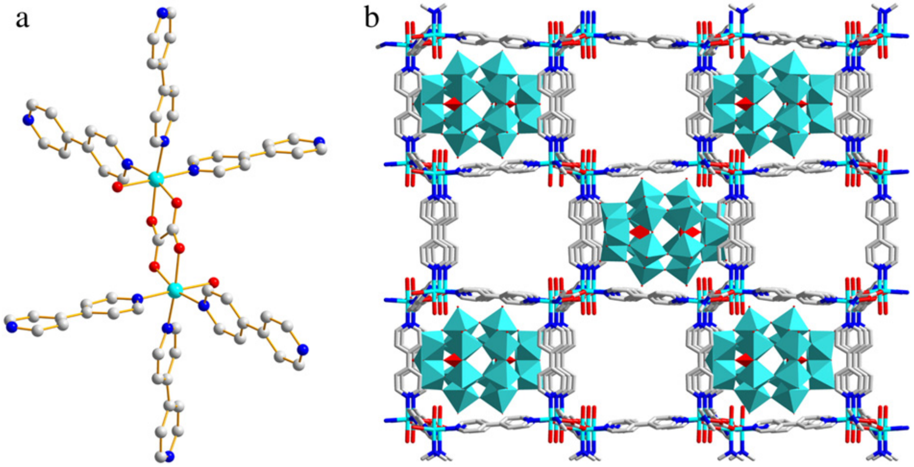

Fig. 2. a. A view of the SUB of the compound. b. A view of the 3D hosts framework and the embedded $[As_2W_{18}O_{62}]^{6-}$ polyanions (polyhedra).

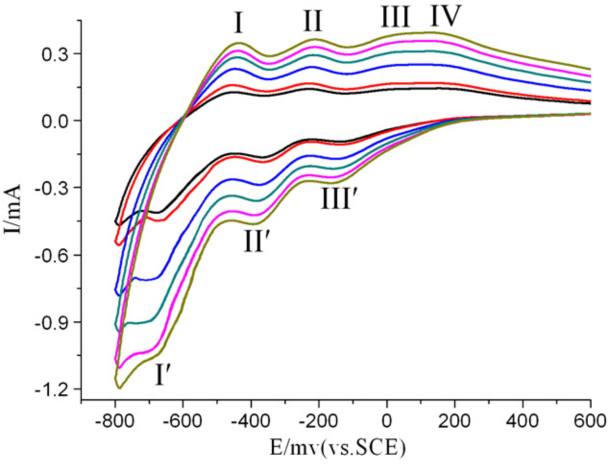

Fig. 3. Cyclic voltammograms of 1-CPE in a 1 M H_2SO_4 solution at different scan rate (from inner to outer: 80, 100, 200, 300, 400, and 500 $mV \cdot s^{-1}$).

rate up to 500 $mV \cdot s^{-1}$ indicates that the redox process is surface-controlled [26].

It is well-known that POMs can be employed in electrocatalytic reduction for nitrite [27]. Herein, **1**-CPE was tested for its activity in the reduction of nitrite. Fig. S4 (see supporting information) confirms that the electrocatalytic activity of POMs is maintained in **1**-CPE. With the addition of nitrite, all the three reduction peak currents increase, and the corresponding oxidation peak currents decrease, which indicates that the **1**-CPE has good electrocatalytic activity for reduction of nitrite.

In summary, a novel 3D MOFs has been constructed by incorporating of the nanosized $[As_2W_{18}O_{62}]^{6-}$ as template. The compound displays high thermal stability up to 450 °C and good electrocatalytic activity toward the reduction of nitrite. Research results confirm that the assembly of POM-templated MOFs can be controlled by a suitable POM template. In the future, we can imagine that more types of these MOFs could be constructed by using of other organic linkers or POM templates. In addition, based on our previous work, we believe that the present work can be extended to application in sorption and catalyst. These efforts are currently ongoing.

Acknowledgements

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Appendix A. Supplementary data

Further details of the crystal structure investigations for **1** could be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein–Leopoldshafen, Germany (fax: (+49)7247–808–666; e-mail: crystdata@fiz-karlsruhe.de) on quoting the depository number CCDC 834821. Supplementary material associated with the article can be found in the online version at doi:10.1016/j.inoche.2011.12.013.

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.inoche.2011.12.013.

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[23] Synthesis of $Co_2(4,4'\text{-bpy})_3(ox)(As_2W_{18}O_{62})_2(H_2bpy) \cdot 2H_2O$ (**1**): A mixture of $K_6As_2W_{18}O_{62}$ (0.5 g), $C_2H_2O_4$ (0.001 g), $Co(NO_3)_2$ (0.058 g), and 4,4′-bipyridine (0.14 g), was dissolved in water (8 ml) and ethanol (2 ml) at room temperature. After stirring for 30 min, the suspension was placed into a 15 ml Teflon-lined stainless-steel container and heated at 160 °C for 5 days. After slow cooling to room temperature, pink block crystals were filtered, washed with distilled water, and dried in desiccators at room temperature to give a yield of 64% based on $K_6As_2W_{18}O_{62}$. Elemental analysis (%). Anal. calcd. for $C_{42}H_{46}N_8Co_2As_2W_{18}O_{68}$ (5327.66): C, 9.42; H, 0.88; N, 2.09; Co, 2.21; As, 2.86; W, 61.98(%).

[24] Compound 1-modified carbon paste electrode 1-CPE was prepared as the following: 50 mg of graphite powder and 8 mg compound 1 were mixed and ground together by agate mortar and pestle to achieve a uniform mixture, and then it was added 0.6 mL nujol with stirring. The homogenized mixture was packed into a glass tube with 1.2 mm inner diameter, and the tube surface was wiped with paper. Electrical contact was established with copper rod through the back of the electrode.

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