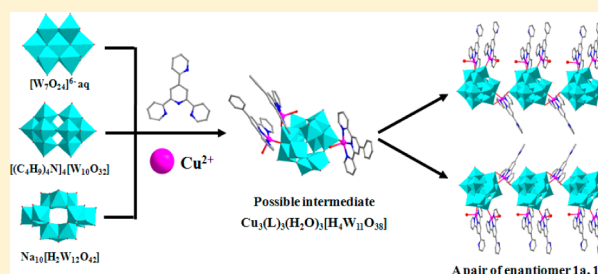


Symmetry Breaking of  $\alpha$ -[H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>]<sup>6-</sup> Depends on the Transformation of IsopolyoxotungstatesYing-Nan Chi,<sup>†</sup> Pan-Pan Shen,<sup>†</sup> Feng-Yun Cui,<sup>‡</sup> Zheng-Guo Lin,<sup>†</sup> Shi-Lu Chen,<sup>\*,†</sup> and Chang-Wen Hu<sup>\*,†</sup><sup>†</sup>Key Laboratory of Cluster Science Ministry of Education, Beijing Key Laboratory of Photoelectronic/Electrophotonic, School of Chemistry, Beijing Institute of Technology Beijing 100081, People's Republic of China<sup>‡</sup>Beijing Entry-Exit Inspection and Quarantine Bureau, Beijing 100026, People's Republic of China

## Supporting Information

**ABSTRACT:** Two enantiotopic 1D chain compounds, [Cu<sub>3</sub>(L1)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>(H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>)<sub>2</sub>·4H<sub>2</sub>O (**1a,b**; L1 = 2-(4,6-bis-(pyridin-2-yl)pyridin-2-yl)pyridine), crystallizing in the chiral space group *P*<sub>2</sub><sub>1</sub><sub>2</sub><sub>1</sub> were prepared and spontaneously resolved in the absence of any chiral source. Interestingly, compounds **1a,b** can be prepared from a [W<sub>7</sub>O<sub>24</sub>]<sup>6-</sup> aqueous solution, [(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>4</sub>[W<sub>10</sub>O<sub>32</sub>], or Na<sub>10</sub>[H<sub>2</sub>W<sub>12</sub>O<sub>42</sub>], but when [H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>]<sup>6-</sup> aqueous solution was the starting material, the achiral compound [CuL1]<sub>2</sub>[H<sub>4</sub>W<sub>12</sub>O<sub>40</sub>]·5H<sub>2</sub>O (**2**) was obtained. When a terpyridine ligand (L2) having a coordination mode similar to that of L1 was used, the mesomeric dimer [Cu<sub>3</sub>(L2)<sub>3</sub>(H<sub>2</sub>O)(H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>)<sub>2</sub>·4H<sub>2</sub>O (**3**) was obtained from [W<sub>7</sub>O<sub>24</sub>]<sup>6-</sup> aqueous solution or Na<sub>10</sub>[H<sub>2</sub>W<sub>12</sub>O<sub>42</sub>], but from [H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>]<sup>6-</sup> aqueous solution only compound [Cu<sub>2</sub>(L2)<sub>2</sub>Cl<sub>2</sub>]<sub>2</sub>[W<sub>10</sub>O<sub>32</sub>] (**4**) was isolated. It is notable that in compounds **1a,b** and **3** the symmetry of the  $\alpha$ -[H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>]<sup>6-</sup> cluster is broken by asymmetric coordination with metal–organic units in a similar mode. As the asymmetric subunit based on a tridecorated [H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>]<sup>6-</sup> cluster can be obtained from several isopolyoxotungstate sources except for [H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>]<sup>6-</sup>, we speculate that the symmetry breaking of  $\alpha$ -[H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>]<sup>6-</sup> depends on the transformation of isopolyoxotungstates. Furthermore, during the transformation a possible reaction intermediate as the precursor for **1a,b**, compound [Cu<sub>3</sub>(L1)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>(H<sub>4</sub>W<sub>11</sub>O<sub>38</sub>)] (**5**), has been presented and characterized by density functional theory (DFT) calculations.



## INTRODUCTION

The ongoing attention and research on chiral polyoxometalates (POMs) are driven from their unique structures as well as their application in asymmetric catalysis, nonlinear optics, and molecular recognition.<sup>1,2</sup> To synthesize chiral POMs, two synthetic strategies have been developed. The first is based on the use of chiral species including chiral organic molecules,<sup>3</sup> chiral metal–organic units,<sup>4</sup> or chiral POMs<sup>5,6</sup> as structure-directing agents, where the chirality of substances can be transferred to the whole structure. Thanks to the contributions by Hill,<sup>3a</sup> Hasenkopf,<sup>1a,2d,5</sup> Wang,<sup>1b,3b,c,6</sup> Kortz,<sup>3d,4b</sup> and Cronin,<sup>3c</sup> this method has been well developed. The second is using achiral starting materials to spontaneously yield a conglomerate (50:50 racemic mixtures of two enantiomorphs) or a pseudoracemate. Due to the absence of external chiral influence, the second method faces more difficulties and challenges.

Spontaneous chiral resolution upon crystallization without any chiral auxiliary is one of the oldest and most fascinating resolution methods. Although a large number of achiral organic molecules are known to crystallize into chiral crystallites,<sup>7</sup> the examples of POMs are still infrequent for the following reasons. First, to date, spontaneous resolution is still poorly understood and it is difficult to predict whether a given achiral source can undergo chiral crystallization. Second, most POM clusters

possess high symmetry, which is the opposite of chiral molecules in lack of symmetry. On the basis of the examples contributed by several groups, it is found that breaking the symmetry of achiral organic molecules<sup>8,9</sup> or POM precursors<sup>10,11</sup> during the assembly process should be a key factor. The symmetry of organic molecules can be broken by the formation of a helical structure with metal ions<sup>8</sup> or by the limitation of free rotation of a covalent bond.<sup>9</sup> In this subfield, flexible organic molecules with various conformations are usually adopted. As for POMs, in order to break the symmetry easily, lacunary or substituted POMs with relatively low symmetry are often used.<sup>10,11</sup> For example, two lacunary [PW<sub>11</sub>O<sub>39</sub>]<sup>7-</sup> units are connected by Hf<sup>4+</sup> ions to form two enantiomerically pure [Hf(PW<sub>11</sub>O<sub>39</sub>)<sub>2</sub>]<sup>10-</sup> clusters.<sup>10a</sup> The symmetries of the monosubstituted Keggin POMs [SiW<sub>11</sub>CuO<sub>39</sub>]<sup>6-</sup> and [PW<sub>11</sub>NaO<sub>39</sub>]<sup>6-</sup> are destroyed by asymmetric coordination with metal–organic units.<sup>11a,b</sup> However, the generation of an asymmetric conformation does not always lead to the formation of enantiomeric crystals. In more cases, the right-handed and left-handed POMs or POM-based compounds simultaneously exist in the same unit cell, canceling their chirality and giving a mesomeric compound.<sup>12</sup>

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Statistically, only 5–10% of racemates can form conglomerate crystals, indicating that heterochiral interactions are more facile than homochiral interactions.<sup>13</sup> Therefore, the promotion of homochiral interactions vs heterochiral interactions is also essential for the achievement of conglomerates.

In our experiment, the pair of enantiomers  $[\text{Cu}_3(\text{L1})_3(\text{H}_2\text{O})_2(\text{H}_2\text{W}_{12}\text{O}_{40})]\cdot 4\text{H}_2\text{O}$  (**1a,b**; L1 = 2-(4,6-bis(pyridin-2-yl)pyridin-2-yl)pyridine) were initially isolated by using  $[(\text{C}_4\text{H}_9)_4\text{N}]_4[\text{W}_{10}\text{O}_{32}]$  as the starting material. According to a previous study, in addition to  $[\text{W}_{10}\text{O}_{32}]^{4-}$ ,  $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$  as well as  $[\text{W}_7\text{O}_{24}]^{6-}$  can work as the precursor for the formation of  $\alpha$ - $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$ .<sup>14</sup> Therefore,  $\text{Na}_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}]$  and aqueous  $[\text{W}_7\text{O}_{24}]^{6-}$  were also adopted as isopolyoxotungstate sources in the present study, and subsequently chiral **1a,b** were equally obtained. The chirality of compounds **1a,b** was revealed to derive from the asymmetrical coordination on the  $\alpha$ - $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$  cluster. However, when aqueous  $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$  was used directly, the achiral compound  $[\text{CuL1}]_2[\text{H}_4\text{W}_{12}\text{O}_{40}]\cdot 5\text{H}_2\text{O}$  (**2**) was obtained. These results imply that the symmetry breaking of  $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$  is related to the transformation of isopolytungstates. This speculation has been proved again by the following successful preparation of the compounds  $[\text{Cu}_3(\text{L2})_3(\text{H}_2\text{O})\text{-(H}_2\text{W}_{12}\text{O}_{40})_2]\cdot 4\text{H}_2\text{O}$  (**3**) and  $[\text{Cu}_2(\text{L2})_2\text{Cl}_2]_2[\text{W}_{10}\text{O}_{32}]$  (**4**) (L2 = terpyridine). To explain why asymmetrical decoration can be achieved in the high-symmetry  $\alpha$ - $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$ , a possible reaction intermediate as a precursor for compounds **1a,b**,  $\text{Cu}_3(\text{L1})_3(\text{H}_2\text{O})_3[\text{H}_4\text{W}_{11}\text{O}_{38}]$  (**5**), has been presented and characterized by density functional theory (DFT) calculations.

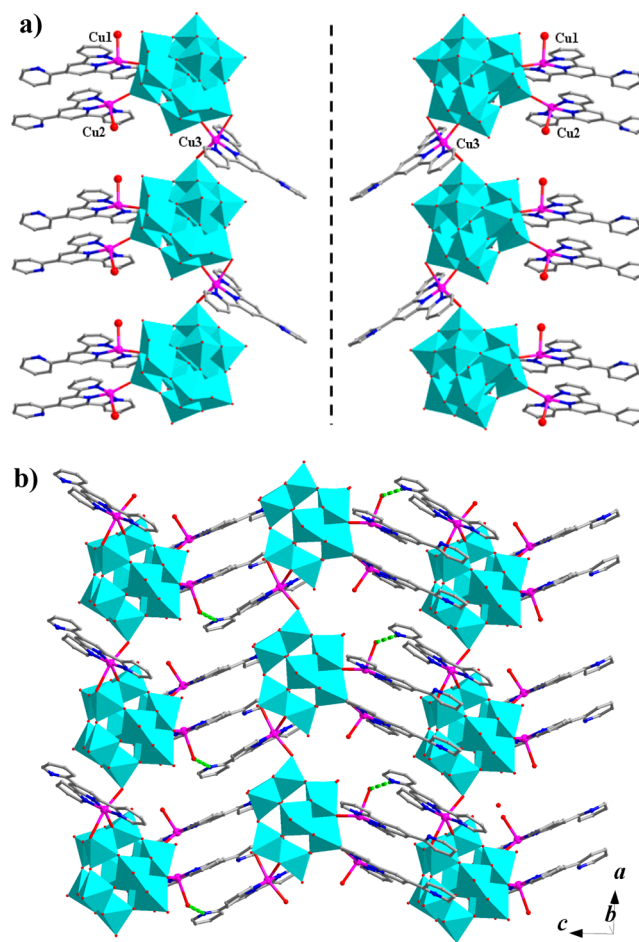
## RESULTS AND DISCUSSION

**Synthesis.** In the hydrothermal synthesis of compounds **1–4**, the pH values were all adjusted from 2.0 to 7.0 and parallel experiments were done more than three times. The crystals of compounds **1a,b** have been observed using  $[\text{W}_7\text{O}_{24}]^{6-}$  aqueous solution or  $\text{Na}_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}]$  as a precursor when the pH was at 2.0, 3.0, 4.0, 5.0, 6.0, and 7.0. It was further found that the yields of **1a,b** were low at pH 2.0 and 3.0, while high yield and good reproducibility were obtained in the pH range 4.0–7.0. Moreover, no crystals of compound **2** were observed, even when the pH was 2.0. When  $[(\text{C}_4\text{H}_9)_4\text{N}]_4[\text{W}_{10}\text{O}_{32}]$  is used as the starting material, the yield and reproducibility of **1a,b** are obviously not as good as those for the two other W sources. The low yield is perhaps caused by the poor solubility of  $[(\text{C}_4\text{H}_9)_4\text{N}]_4[\text{W}_{10}\text{O}_{32}]$  in water. However, single crystals suitable for X-ray diffraction were obtained in this synthetic system. The crystals of compound **2** were observed at pH 2.0, 2.5, 3.0, 3.5, but the yields at pH 2.5, 3.0, and 3.5 were very low. However, in the pH range 4.0–7.0, a large amount of yellow-green powder was obtained instead of crystals and a PXRD experiment displayed that the yellow-green powder is a phase different from that of compounds **1** and **2**. After a few rounds, we realized that a low pH value is beneficial to the preparation of **2**; therefore, the pH value was decreased to 1.5, at which point high-quality crystals were isolated in relatively good yield.

Crystals of compound **3** have been isolated by using  $[\text{W}_7\text{O}_{24}]^{6-}$  aqueous solution at pH 4.0 and 5.0 or by using  $\text{Na}_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}]$  at pH 4.0, 5.0, 6.0, and 7.0. When  $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$  aqueous solution was the starting material, compound **4** was synthesized at pH 3.0, 4.0, 5.0, and 6.0. Surprisingly, although  $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$  was used as the precursor, compound **4** is based on the  $[\text{W}_{10}\text{O}_{32}]^{4-}$  cluster. In addition, the control experiments show that the use of

$[(\text{C}_4\text{H}_9)_4\text{N}]_4[\text{W}_{10}\text{O}_{32}]$  cannot give rise to **4**. We have thought for some time that the  $\text{Cl}^-$  anion in HCl might play some role in the isolation of compound **4**; thus, we used  $\text{HNO}_3$  to adjust the pH value. However, no meaningful results were obtained by using  $\text{HNO}_3$ .

**Structures.** Compounds **1a,b** can be prepared under hydrothermal conditions by the reaction of  $\text{Cu}(\text{CH}_3\text{COO})_2\cdot \text{H}_2\text{O}$ , ligand L1, and  $\text{Na}_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}]$ ,  $[(\text{C}_4\text{H}_9)_4\text{N}]_4[\text{W}_{10}\text{O}_{32}]$ , or aqueous  $[\text{W}_7\text{O}_{24}]^{6-}$ . Single-crystal analyses reveal that the enantiomers **1a,b** both crystallize in the chiral space group  $P2_12_12_1$  and their Flack parameters are 0.005(12) and  $-0.004(13)$ , respectively. Their unit-cell dimensions, volumes, related bond distances, and angles are only slightly different. Therefore, compound **1a** is selected as an example to describe below. An asymmetric unit of **1a** contains one  $\alpha$ - $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$  cluster, two  $[\text{CuL1}(\text{H}_2\text{O})]^{2+}$  units, and one  $[\text{CuL1}]^{2+}$  unit as well as four lattice water molecules (Figure 1 and Figure S1



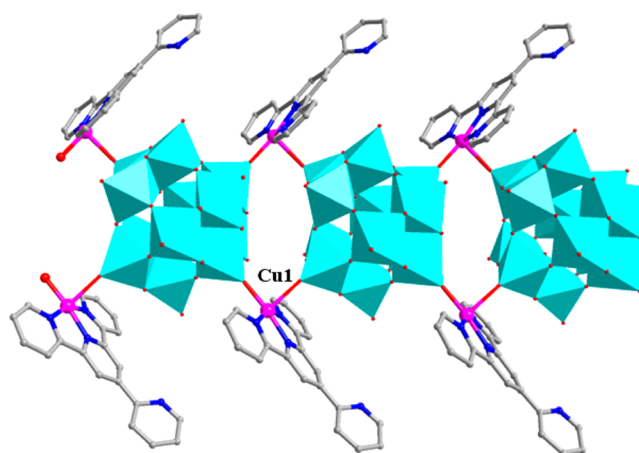
**Figure 1.** (a) Polyhedral and ball-and-stick representation of the 1D chain in compounds **1a,b**. Color code: W (bluish green octahedra); Cu (pink); O (red); C (gray); N (blue). (b) 2D supramolecular network formed by hydrogen bonds in the *ac* plane. The green dashed lines represent hydrogen-bond interactions.

(Supporting Information)). The structure of  $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$  is identical with that of reported  $\alpha$ -metatungstate compounds.<sup>15</sup> In the polyoxanion, four trimetallic  $\text{W}_3\text{O}_{13}$  subunits are linked together by sharing corners; however, its center is occupied by two protons instead of a heteroatom in a tetrahedral environment.

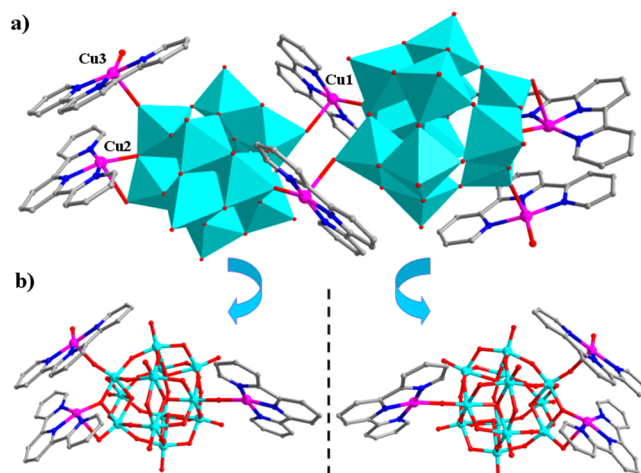
There are three crystallographically independent Cu(II) ions in **1a**. The Cu1 and Cu2 ions each coordinate to three N atoms from one L1 ligand, one O atom from the  $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$  cluster, and one water molecule, adopting distorted-square-pyramidal geometries. The Cu3 center exhibits a distorted-octahedral geometry with three N atoms from one L1 and three O atoms from two adjacent POMs. The  $[\text{Cu}_3(\text{L1})]^{2+}$  units act as bridges to connect  $\alpha\text{-}[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$  polyoxoanions into a 1D chain along the *a* axis, while two  $[\text{CuL1}(\text{H}_2\text{O})]^{2+}$  units are anchored to one side of the POM-based chain (Figure 1a). Although there are four N atoms in L1, only three N atoms in chelating positions participate in coordination. The uncoordinated N atoms from  $[\text{Cu}_3(\text{L1})]^{2+}$  units connect with coordinated water molecules from the neighboring 1D chain through a hydrogen bond ( $\text{N}\cdots\text{O}_w = 2.924 \text{ \AA}$ ) to construct a 2D network on the *ac* plane (Figure 1b). The 2D supermolecular networks are further assembled into a 3D supermolecular framework by hydrogen bonds ( $\text{O}_w\cdots\text{O}_{\text{POM}} = 2.846 \text{ \AA}$ ). As none of the building blocks in **1a,b**, i.e.  $\alpha\text{-}[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$ ,  $[\text{CuL1}(\text{H}_2\text{O})]^{2+}$ , and  $[\text{CuL1}]^{2+}$ , have chiral features, the structural chirality should be derived from the metal–organic units asymmetrically coordinated on the  $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$  cluster. It is noted that the structure of  $\alpha\text{-}[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$  is very close to that of the Keggin-type POMs. In most previous cases, the chirality of Keggin-type POMs is induced by chiral species<sup>2c,3b,16</sup> or a helical motif.<sup>17</sup> There are also two pairs of chiral monosubstituted Keggin-type POMs recently obtained by asymmetrical coordination of POM with metal–organic units.<sup>11a,b</sup> In comparison with the two examples of monosubstituted Keggin-type POMs, the most remarkable feature of **1a,b** is that the  $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$  cluster has a high symmetry. Compounds **1a,b** represent the first example of chiral isopolyoxotungstates spontaneously isolated without any chiral auxiliary. There is no observable color or shape difference between **1a** and **1b** (Figure S2 (Supporting Information)); therefore, manual separation between them cannot be carried out.

When we used the aqueous solution of  $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$  as the starting material, compound **2** instead of **1** was obtained. Single-crystal analysis shows that **2** crystallizes in the centrosymmetric space group *C2/c* and consists of one  $[\text{H}_4\text{W}_{12}\text{O}_{40}]^{4-}$  and two  $[\text{Cu}(\text{L1})]^{2+}$  units and five lattice water molecules. As shown in Figure 2, there is only one crystallographically independent Cu(II) ion, which coordinates with three N atoms from one L1 ligand and two terminal O atoms from two different  $[\text{H}_4\text{W}_{12}\text{O}_{40}]^{4-}$  clusters, exhibiting a distorted-square-pyramidal geometry. In **2**, each POM as a quadridentate inorganic ligand that connects with four Cu(II) centers and each Cu(II) links two adjacent  $[\text{H}_4\text{W}_{12}\text{O}_{40}]^{4-}$  to construct a 1D chain (Figure 2). Because the  $[\text{H}_4\text{W}_{12}\text{O}_{40}]^{4-}$  cluster in **2** is symmetrically decorated by four  $[\text{Cu}(\text{L1})]^{2+}$  units through coordination bonds, the symmetrical center of the POM cluster is maintained and the final structure is achiral.

To explore the reason chirality appears in **1a,b** but disappears in **2**, ligand L2 was adopted, which is simplified from L1 by removing the uncoordinated 2-pyridine and keeping the essential terpyridine part. Consequently, compound **3** was isolated by the reaction of  $\text{Cu}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}$  (L2) and  $\text{Na}_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}]$  or aqueous  $[\text{W}_7\text{O}_{24}]^{6-}$ . However, from  $[(\text{C}_4\text{H}_9)_4\text{N}]_4[\text{W}_{10}\text{O}_{32}]$ , no crystal was obtained. Single-crystal X-ray diffraction analysis reveals that compound **3** is a conventional achiral dimer (Figure 3a) and crystallizes in the achiral space group *P2<sub>1</sub>/c*.



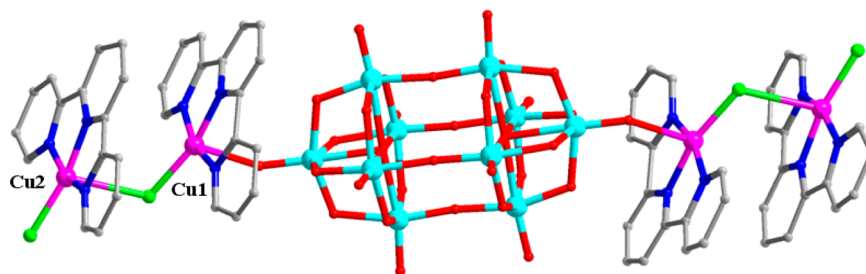
**Figure 2.** Polyhedral and ball-and-stick representation of the 1D chain in compound **2**. Color code: W (bluish green octahedra); Cu (pink); O (red); C (gray); N (blue).



**Figure 3.** (a) Dimeric structure in compound **3**. (b) Ball-and-stick representation of two enantiotopic subunits in **3**. Color code: W (bluish green); Cu (pink); O (red); C (gray); N (blue).

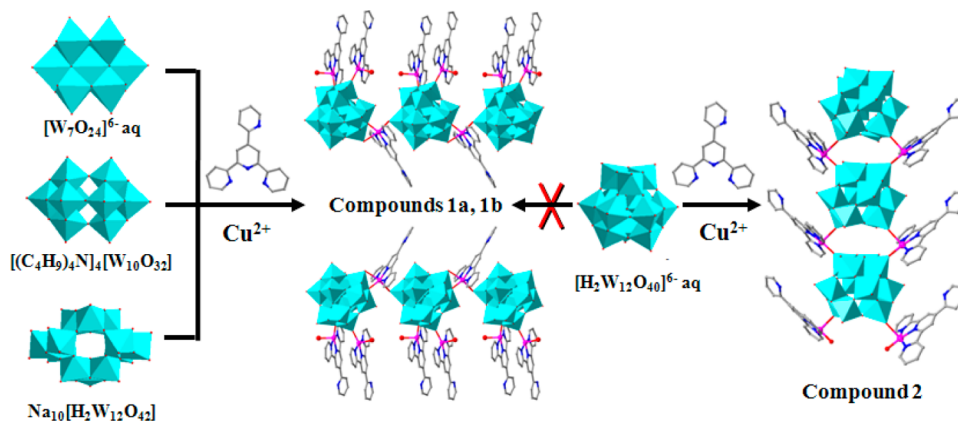
In **3**, there are three crystallographically independent Cu(II) ions which all adopt distorted-square-pyramidal geometries. Cu1 coordinates to three N atoms from the L2 ligand and two terminal O atoms from two adjacent  $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$  clusters, Cu2 coordinates to three N atoms from the L2 ligand and two O atoms from one  $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$  group, and Cu3 is surrounded by three N atoms from one ligand, two O atoms from one polyanion, and one water molecule. It is worth mentioning that compound **3** is composed of two enantiotopic  $[\text{Cu}_3(\text{L2})_3(\text{H}_2\text{O})(\text{H}_2\text{W}_{12}\text{O}_{40})]$  subunits induced by metal–organic units asymmetrically coordinating on the  $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$  cluster (Figure 3b). However, **3** is a mesomeric compound, as two enantiotopic subunits are fused into a dimer and such an arrangement leads to the existence of an inversion center.

When an aqueous solution of  $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$  was used instead of  $\text{Na}_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}]$  or aqueous  $[\text{W}_7\text{O}_{24}]^{6-}$ , compound **4** was synthesized under the similar conditions. Single-crystal X-ray diffraction analysis displays that **4** crystallizes in the space group *P $\bar{1}$*  and consists of one decatungstate polyoxoanion  $[\text{W}_{10}\text{O}_{32}]^{4-}$  and four  $[\text{Cu}(\text{L2})\text{Cl}]^+$  units (Figure 4). The structure of  $[\text{W}_{10}\text{O}_{32}]^{4-}$  itself is identical with that of the

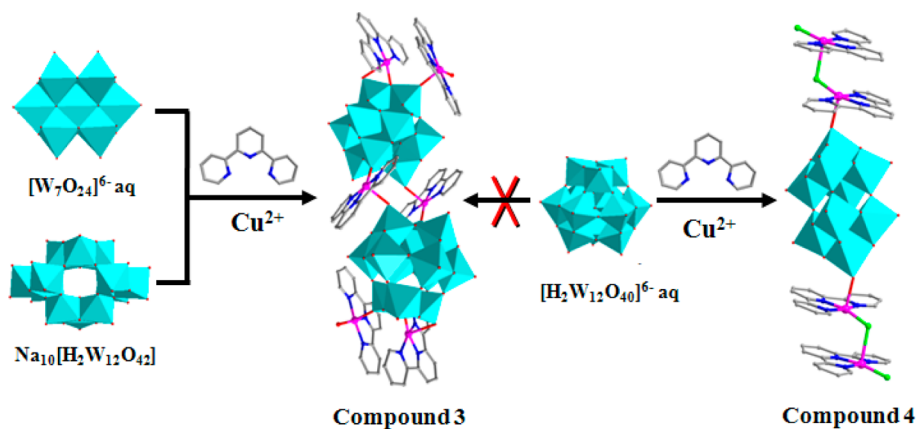


**Figure 4.** Ball-and-stick representation of compound 4. Color code: W (bluish green); Cu (pink); O (red); C (gray); N (blue); Cl (green).

**Scheme 1. Isopolyoxotungstate Precursor Influence on the Formation of Chiral Compounds 1a,b**



**Scheme 2. Isopolyoxotungstate Precursor Influence on the Formation of Compound 3**

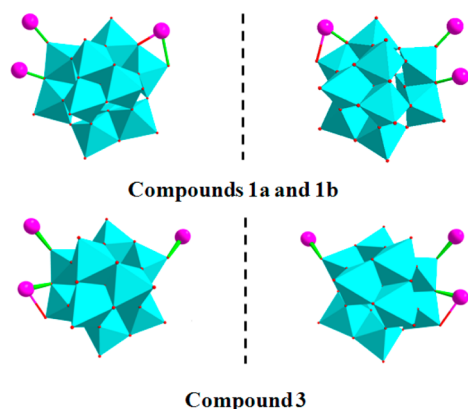


reported compounds.<sup>18</sup> The decatungstate cluster could be viewed as a dimer of two defect Lindqvist  $W_5O_{18}$  units which are linked by four corner-sharing O atoms.

There are two crystallographically independent five-coordinated Cu(II) ions in 4. The Cu1 ion is coordinated by three N atoms from one L2, one O terminal atom from  $[W_{10}O_{32}]^{4-}$ , and one chloride atom. The coordination environment of Cu2 is completed by three N atoms from one L2 and two chloride atoms. The two copper centers are bridged by one  $\mu_2$ -Cl to form a dinuclear cluster, and  $[W_{10}O_{32}]^{4-}$  links two dinuclear clusters into a polynuclear structure. In this structure there is an inversion center in the center of decatungstate. Interestingly, although the starting material is  $[H_2W_{12}O_{40}]^{6-}$ , 4 is a compound based on  $[W_{10}O_{32}]^{4-}$ . In addition, the control experiments display that the use of  $[(C_4H_9)_4N]_4[W_{10}O_{32}]$  cannot give rise to 4. In general, the compounds containing decatungstate polyanion were synthesized by using

$[(C_4H_9)_4N]_4[W_{10}O_{32}]$  or  $Na_2WO_4$  as the starting material.<sup>19</sup> Recently, we have reported a supramolecular assembly composed of  $[W_{10}O_{32}]^{4-}$  and a Cu/O/W heterometallic cluster which was prepared by using  $[(C_4H_9)_4N]_2[W_6O_{19}]$  as the starting material.<sup>18b</sup> To the best of our knowledge, compound 4 is the first example of decatungstate obtained by using  $[H_2W_{12}O_{40}]^{6-}$  as precursor.

As shown in Schemes 1 and 2, compounds 1a,b and 3 could be prepared from several kinds of isopolyoxotungstate sources, except for  $[H_2W_{12}O_{40}]^{6-}$ . It is interesting to find that the  $[Cu_3(L1)_3(H_2O)_2(H_2W_{12}O_{40})]$  subunit in 1a,b and the  $[Cu_3(L2)_3(H_2O)(H_2W_{12}O_{40})]$  subunit in 3 have very similar structures (Figure 5). Moreover, in these two cases the symmetry of  $\alpha$ - $[H_2W_{12}O_{40}]^{6-}$  is broken by the asymmetric coordination with three  $[Cu(L)(H_2O)_n]^{2+}$  units ( $n = 0, 1$ ). This implies that the symmetry breaking of  $[H_2W_{12}O_{40}]^{6-}$  depends on the transformation of isopolytungstates.



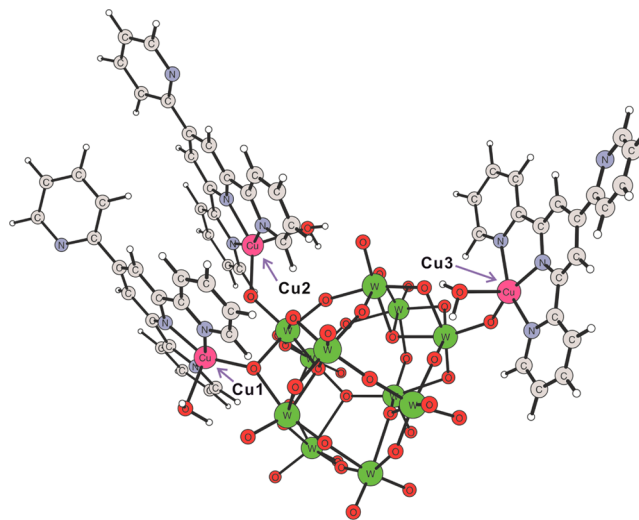
**Figure 5.** Asymmetric decoration mode between  $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$  and Cu ions in compounds **1a,b** and **3**. The ligands coordinating to coppers are omitted for clarity. Color code: W (bluish green octahedra); Cu (pink).

A comparison of compounds **1a,b** and **3** should promote our understanding of homochiral and heterochiral interactions. Although **1a,b** and **3** have similar asymmetric subunits, their structures are very different: namely, **1a,b** are a pair of enantiomeric chains and **3** is a mesomeric dimer. The structural differences may originate from the difference in ligands. In comparison to L2, L1 has one extra uncoordinated 2-pyridyl ring which may play a crucial role in the formation of a conglomerate vs a mesomer. On one hand, the uncoordinated N atoms in L1 participate in hydrogen bonding, which might facilitate homochiral interactions in the crystal packing.<sup>20</sup> On the other hand, the large steric hindrance of L1 probably leads to the assembly of homochiral subunits into a 1D chain, while the relatively small steric hindrance of L2 may facilitate the assembly of two enantiomeric subunits into a dimer.

An interesting question is emerging: that is, how the high symmetry of  $\alpha\text{-}[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$  is able to be destroyed in the absence of any chiral auxiliary. The answer may be sought from previous and present experiments. As the transformation of isopolyoxotungstate is necessary for the symmetry breaking of  $\alpha\text{-}[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$ , the thought arises that the reaction may proceed through the same intermediate that is formed by the coordination between some sort of isopolyoxotungstate cluster and metal–organic units. What is the necessary species in the transformation from  $[\text{W}_7\text{O}_{24}]^{6-}$ ,  $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ , or  $[\text{W}_{10}\text{O}_{32}]^{4-}$  to  $\alpha\text{-}[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$ ? According to previous studies,  $[\text{W}_7\text{O}_{24}]^{6-}$ ,  $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ , and kinetically unstable  $[\text{W}_{10}\text{O}_{32}]^{4-}$  can all convert into a metastable  $\psi$ -metatungstate anion which is subsequently transformed, via  $\beta\text{-}[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$ , into a thermodynamically stable  $\alpha\text{-}[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$  anion (Figure S3 (Supporting Information)).<sup>15</sup> Nowadays,  $\psi$ -metatungstate can be unambiguously detected in aqueous solution and is shown to be a nonsymmetry isopolyoxotungstate cluster containing 11 W atoms,<sup>21</sup> but its structure is not quite clear. The isopolyoxotungstate containing 11 W atoms reminds us of the  $[\text{H}_4\text{W}_{11}\text{O}_{38}]^{6-}$  cluster, which was characterized by single-crystal X-ray diffraction in 1988<sup>22</sup> and also appeared as a subunit in  $[\text{H}_4\text{W}_{22}\text{O}_{74}]^{12-}$ ,  $[\text{H}_{10}\text{W}_{34}\text{O}_{116}]^{18-}$ , and  $[\text{H}_{12}\text{W}_{36}\text{O}_{120}]^{12-}$ .<sup>23</sup> Due to the low  $\sigma_v$  symmetry of the  $[\text{H}_4\text{W}_{11}\text{O}_{38}]^{6-}$  cluster, the asymmetrical decoration is thought to be realized quite easily. Therefore, a speculation is made here that a  $[\text{H}_4\text{W}_{11}\text{O}_{38}]^{6-}$  cluster coordinated by three  $[\text{CuL}(\text{H}_2\text{O})]$  units (referred to as compound **5**) might be the crucial reaction intermediate working as a possible precursor for the thermodynamically

stable  $\alpha\text{-}[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$  cluster under hydrothermal conditions (Figure S4 (Supporting Information)). However, it should be mentioned that great efforts have been made for the capture of this intermediate, but without success.

**DFT Calculations of Compound 5.** As discussed above, the possible precursor for compounds **1a,b** is speculated to be compound **5**, in which three  $[\text{CuL}(\text{H}_2\text{O})]$  metal–organic units coordinate with the oxygen atoms of  $[\text{H}_4\text{W}_{11}\text{O}_{38}]^{6-}$ . To explore the possible structure, theoretical modeling of deprotonated compound **5** (Figure 6) with diverse multi-



**Figure 6.** DFT-optimized structure of deprotonated compound **5** in the quartet state.

licities has been performed with the unrestricted density functional theory (UDFT) method as implemented in the Jaguar 7.6 package.<sup>24</sup> Since each open-shell  $\text{Cu}^{2+}$  ion has one unpaired spin population, the coupling between three copper ions in antiferromagnetic and ferromagnetic modes should lead to four spin states for **5**: i.e., one quartet state and three doublet states (see Table 1). The structures of **5** at these four spin states have all been optimized using the B3LYP functional<sup>25</sup> coupled with the LACVP\* basis set<sup>26</sup> and confirmed to be energetic minima by frequency analysis (their Cartesian coordinates are given in the Supporting Information), indicating the possible existence of compound **5**. It turns out that these four spin states of compound **5** have very similar optimized geometries. It can further be seen that the three metal–organic units at compound **5** have orientations similar to those in compounds **1a,b**, implying that compound **5** may be an alternative precursor for compounds **1a,b**. It is worth stressing that compound **5** may have a very short lifetime in the real solution, although its geometry optimized here has been shown to be a minimum on the potential energy surface.

The energetics of compound **5** in the four spin states show that the complexes (i.e., entries 2 and 4 in Table 1) formed by the antiferromagnetic coupling between the two copper ions ligated by the terminal oxygens of POM (Cu2 and Cu3 in Table 1) are slightly more stable than those derived from ferromagnetic coupling (entries 1 and 3 in Table 1). Furthermore, a reversal of spin direction at the copper bound by the bridging oxygen of POM (Cu1) hardly changes the energy of the complex (see entries 1 and 3 in Table 1). However, it is worth mentioning that energy differences of this amount are within the uncertainty of the method. Therefore, it

Table 1. Properties of Compound 5 Optimized by DFT Calculations

| entry | compd | multiplicity | spin/charge <sup>a</sup> |            |             | energy (kcal/mol) |
|-------|-------|--------------|--------------------------|------------|-------------|-------------------|
|       |       |              | Cu1                      | Cu2        | Cu3         |                   |
| 1     | 5-1   | 4            | 0.64/0.67                | 0.63/0.82  | 0.60/0.84   | 0.0               |
| 2     | 5-2   | 2            | 0.64/0.67                | -0.66/0.82 | 0.60/0.85   | -1.2              |
| 3     | 5-3   | 2            | -0.64/0.69               | 0.63/0.82  | 0.60/0.85   | -0.4              |
| 4     | 5-4   | 2            | 0.64/0.72                | 0.64/0.84  | -0.66/-0.88 | -0.9              |

<sup>a</sup>See Figure 6 for the definition of Cu1, Cu2, and Cu3.

is not safe to say which state definitely is the ground state. In the real solution, compound 5 probably exists as a mixture of the four spin states.

## CONCLUSION

In this work, five organic–inorganic hybrid compounds based on isopolyoxometalates have been synthesized under hydrothermal conditions and their structural characterization has also been performed. Compounds 1a,b have been synthesized as a conglomerate of two enantiomerically pure crystals without any chiral auxiliary. Compound 3 is obtained as a mesomeric dimer consisting of two enantiotopic subunits. Noticeably, the symmetry of the  $\alpha$ -[H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>]<sup>6-</sup> cluster in compounds 1a,b and 3 is broken by asymmetric coordination of metal–organic units and the obtained subunits based on [H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>]<sup>6-</sup> are structurally similar. The control experiments display that the symmetry breaking of [H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>]<sup>6-</sup> is closely relevant to the transformation of isopolyoxotungstates. The possible reaction intermediate 5 acting as a precursor for compounds 1a,b is presented as being based on a [H<sub>4</sub>W<sub>11</sub>O<sub>38</sub>]<sup>6-</sup> cluster and metal–organic units. The structural speculation of 5 has been supported by our DFT calculations. This investigation will help us further understand how the symmetry of POMs is broken when using achiral sources.

## EXPERIMENTAL SECTION

**General Methods and Materials.** All common laboratory chemicals were reagent grade, purchased from commercial sources and used without further purification. Ligand L1 was prepared by the published procedure,<sup>27</sup> and [n-(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>4</sub>[W<sub>10</sub>O<sub>32</sub>], Na<sub>10</sub>[H<sub>2</sub>W<sub>12</sub>O<sub>42</sub>], [W<sub>7</sub>O<sub>24</sub>]<sup>6-</sup> aqueous solution, and [H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>]<sup>6-</sup> aqueous solution were synthesized according to the literature.<sup>28–31</sup> IR spectra were obtained (as KBr pressed pellets) using a Nicolet 170SXFT/IR spectrometer in the range 400–4000 cm<sup>-1</sup>. X-ray powder diffraction (XRPD) of samples was collected on a Japan Rigaku D/max instrument equipped with graphite-monochromated Cu K $\alpha$  radiation ( $\gamma = 0.154060$  nm). The C, H, and N elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. The metal contents of compounds 1–4 were measured by inductively coupled plasma (ICP) on a JY-ULTIMA2 analyzer. TG analyses were carried out under a nitrogen atmosphere between 40 and 800 °C at a heating rate of 10 °C/min on a DTG-60AH simultaneous thermal analyzer.

**Synthesis of [Cu<sub>3</sub>(L1)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>(H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>)]·4H<sub>2</sub>O (1a,b).** *Method A.* [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>4</sub>[W<sub>10</sub>O<sub>32</sub>] (0.1 mmol), Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O (0.2 mmol), and L1 (0.1 mmol) were added in water (8 mL). The resulting solution was stirred and the pH value was adjusted to 4.0, 5.0, or 6.0 with 1 M HCl. The solution was then transferred to a Teflon-lined autoclave (15 mL) and kept at 160 °C for 72 h. After the mixture was slowly cooled to room temperature, green sticklike crystals were filtered off, washed with distilled water, and dried at room temperature to give a yield of 5% based on L1.

*Method B.* Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O (0.2 mmol) and L1 (0.05 mmol) were added to 8 mL of a [W<sub>7</sub>O<sub>24</sub>]<sup>6-</sup> aqueous solution (about 0.1 mmol). The resulting solution was stirred, and the pH value was

adjusted to 4.0, 5.0, 6.0, or 7.0 with 1 M HCl. The solution was then transferred to a Teflon-lined autoclave (15 mL) and kept at 180 °C for 72 h. After the mixture was slowly cooled to room temperature, green cluster crystals were filtered off, washed with distilled water, and dried at room temperature to give a yield of 23% based on L1.

*Method C.* Na<sub>10</sub>[H<sub>2</sub>W<sub>12</sub>O<sub>42</sub>] (0.1 mmol), Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O (0.2 mmol), and L1 (0.05 mmol) were added to water (8 mL). The resulting solution was stirred, and the pH value was adjusted to 4.0, 5.0, 6.0, or 7.0 with 1 M HCl. The solution was then transferred to a Teflon-lined autoclave (15 mL) and kept at 160 °C for 72 h. After the mixture was slowly cooled to room temperature, green clusters were filtered off, washed with distilled water, and dried at room temperature to give a yield of 11% based on L1. Anal. Calcd for C<sub>60</sub>H<sub>56</sub>N<sub>12</sub>Cu<sub>3</sub>W<sub>12</sub>O<sub>46</sub>: C, 17.66; H, 1.37; N, 4.12; Cu, 4.74; W, 54.85. Found: C, 17.75; H, 1.32; N, 4.28; Cu, 4.54; W, 55.11. IR (KBr, cm<sup>-1</sup>): 3422 (m), 2965 (w), 2925 (w), 1616 (w), 1558 (w), 1473 (m), 1457 (w), 1418 (w), 1318 (w), 1265 (w), 1164 (w), 1050 (w), 947 (s), 885 (m), 811 (m), 665 (w), 584 (w), 443 (s).

**Synthesis of [Cu<sub>1</sub>]<sub>2</sub>[H<sub>4</sub>W<sub>12</sub>O<sub>40</sub>]<sub>2</sub>·5H<sub>2</sub>O (2).** Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O (0.2 mmol) and L1 (0.05 mmol) were added to 6 mL of a [H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>]<sup>6-</sup> aqueous solution (about 0.1 mmol). The resulting solution was stirred, and the pH value was adjusted to 1.5 or 2.0 with 1 M HCl. The solution was then transferred to a Teflon-lined autoclave (15 mL) and kept at 180 °C for 72 h. After the mixture was slowly cooled to room temperature, green blocklike crystals were filtered off, washed with distilled water, and dried at room temperature to give a yield of 10% based on L1. Anal. Calcd for C<sub>40</sub>H<sub>42</sub>N<sub>8</sub>Cu<sub>2</sub>W<sub>12</sub>O<sub>45</sub>: C, 13.01; H, 1.14; N, 3.04; Cu, 3.46; W, 60.05. Found: C, 13.15; H, 1.27; N, 3.12; Cu, 3.29; W, 60.85. IR (KBr, cm<sup>-1</sup>): 2929 (w), 2958 (w), 1605 (w), 1560 (w), 1474 (m), 1414 (w), 1315 (w), 1239 (w), 1180 (w), 937 (s), 872 (m), 765 (s), 724 (w), 662 (w).

**Synthesis of [Cu<sub>3</sub>(L2)<sub>3</sub>(H<sub>2</sub>O)(H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>)]<sub>2</sub>·4H<sub>2</sub>O (3).** *Method A.* Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O (0.2 mmol) and L2 (0.05 mmol) were added to 8 mL of a [W<sub>7</sub>O<sub>24</sub>]<sup>6-</sup> aqueous solution (about 0.1 mmol). The resulting solution was stirred and the pH value was adjusted to 4.0 or 5.0 with 1 M HCl. The solution was then transferred to a Teflon-lined autoclave (15 mL) and kept at 180 °C for 72 h. After the mixture was slowly cooled to room temperature, blue striplike crystals were filtered off, washed with distilled water, and dried at room temperature to give a yield of 22% based on L2.

*Method B.* Na<sub>10</sub>[H<sub>2</sub>W<sub>12</sub>O<sub>42</sub>] (0.1 mmol), Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O (0.2 mmol), and L1 (0.05 mmol) were added to water (8 mL). The resulting solution was stirred, and the pH value was adjusted to 4.0, 5.0, 6.0, or 7.0 with 1 M HCl. The solution was then transferred to a Teflon-lined autoclave (15 mL) and kept at 160 °C for 72 h. After the mixture was slowly cooled to room temperature, blue striplike crystals were filtered off, washed with distilled water, and dried at room temperature to give a yield of 18% based on L2. Anal. Calcd for C<sub>90</sub>H<sub>82</sub>N<sub>18</sub>Cu<sub>6</sub>W<sub>24</sub>O<sub>86</sub>: C, 14.24; H, 1.08; N, 3.32; Cu, 5.04; W, 58.29. Found: C, 14.35; H, 1.27; N, 3.48; Cu, 4.84; W, 59.05. IR (KBr, cm<sup>-1</sup>): 3450 (w), 1601 (s), 1575 (w), 1499 (s), 1477 (s), 1451 (s), 1409 (w), 1330 (w), 1253 (w), 1172 (w), 1022 (s), 954 (w), 935 (m), 878 (s), 765 (s), 662 (w), 434 (s).

**Synthesis of [Cu<sub>2</sub>(L2)<sub>2</sub>Cl<sub>2</sub>]<sub>2</sub>[W<sub>10</sub>O<sub>32</sub>] (4).** Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O (0.2 mmol) and L2 (0.05 mmol) were added to 6 mL of a [H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>]<sup>6-</sup> aqueous solution (about 0.1 mmol). The resulting solution was stirred, and the pH value was adjusted to 3.0, 4.0, 5.0, or 6.0 with 1 M HCl. The solution was then transferred to a Teflon-lined autoclave (15 mL) and kept at 180 °C for 72 h. After the mixture was

Table 2. Crystallographic Data for Compounds 1–4<sup>a</sup>

|   | 1a  | 1b  | 2  | 3   | 4   |
|---|---|---|--|---|---|
| formula   | C <sub>60</sub> H <sub>42</sub> N <sub>12</sub> Cu <sub>3</sub> W <sub>12</sub> O <sub>43</sub> | C <sub>60</sub> H <sub>48</sub> N <sub>12</sub> Cu <sub>3</sub> W <sub>12</sub> O <sub>43</sub> | C <sub>40</sub> H <sub>28</sub> N <sub>8</sub> Cu <sub>2</sub> W <sub>12</sub> O <sub>45</sub> | C <sub>90</sub> H <sub>66</sub> N <sub>18</sub> Cu <sub>6</sub> W <sub>24</sub> O <sub>82</sub> | C <sub>74</sub> H <sub>44</sub> N <sub>12</sub> Cu <sub>4</sub> W <sub>10</sub> O <sub>32</sub> |
| <i>M<sub>r</sub></i>                            | 4021.84   | 4021.84   | 3673.98  | 7569.07   | 3679.53   |
| cryst syst                                      | orthorhombic  | orthorhombic  | monoclinic   | monoclinic  | triclinic   |
| space group                                     | <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>   | <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>   | <i>C</i> 2/ <i>c</i>   | <i>P</i> 2 <sub>1</sub> / <i>c</i>  | <i>P</i> $\bar{1}$  |
| <i>a</i> (Å)                                    | 12.1527(9)  | 12.145(2)   | 25.7827(12)  | 18.1203(9)  | 10.6480(10)   |
| <i>b</i> (Å)                                    | 25.226(2)   | 25.160(5)   | 10.1372(5)   | 13.3697(7)  | 12.2469(11)   |
| <i>c</i> (Å)                                    | 27.992(2)   | 28.001(5)   | 25.3918(12)  | 28.7433(15)   | 15.3821(14)   |
| $\alpha$ (deg)                                  | 90  | 90  | 90   | 90  | 84.306(2)   |
| $\beta$ (deg)                                   | 90  | 90  | 110.1410(10)   | 90.6890(10)   | 72.7310(10)   |
| $\gamma$ (deg)                                  | 90  | 90  | 90   | 90  | 77.7570(10)   |
| <i>V</i> (Å <sup>3</sup> )                      | 8581.3(11)  | 8556.3(3)   | 6230.7(5)  | 6962.9(6)   | 1870.5(3)   |
| <i>Z</i>  | 4   | 4   | 4  | 2   | 1   |
| <i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> ) | 3.099   | 3.123   | 3.917  | 3.610   | 3.267   |
| <i>F</i> (000)                                  | 7220  | 7245  | 6520   | 6740  | 1668  |
| Flack param                                     | 0.005(12)   | −0.004(13)  |  |   |   |
| no. of rflns collected                          | 42786   | 38653   | 18009  | 33704   | 9296  |
| no. of unique rflns                             | 15078   | 12615   | 7055   | 12163   | 6424  |
| no. of obsd rflns                               | 52949   | 38691   | 18613  | 42876   | 11836   |
| <i>R</i> <sub>int</sub>                         | 0.0404  | 0.0684  | 0.0251   | 0.0328  | 0.0215  |
| <i>R</i> 1( <i>I</i> > 2σ( <i>I</i> ))          | 0.0313  | 0.0413  | 0.0268   | 0.0280  | 0.0483  |
| w <i>R</i> 2( <i>I</i> > 2σ( <i>I</i> ))        | 0.0802  | 0.0933  | 0.0846   | 0.0712  | 0.1688  |
| <i>R</i> 1(all data)                            | 0.0383  | 0.0504  | 0.0337   | 0.0369  | 0.0724  |
| w <i>R</i> 2(all data)                          | 0.1096  | 0.0980  | 0.1113   | 0.0752  | 0.2625  |
| GOF on <i>F</i> <sup>2</sup>                    | 1.158   | 1.036   | 1.088  | 1.047   | 1.029   |

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|; wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}.$$

slowly cooled to room temperature, blue striplike crystals were filtered off, washed with distilled water, and dried at room temperature to give a yield of 10% based on L2. Anal. Calcd for C<sub>60</sub>H<sub>44</sub>N<sub>12</sub>Cl<sub>4</sub>Cu<sub>2</sub>W<sub>10</sub>O<sub>32</sub>: C, 20.27; H, 1.24; N, 4.73; Cu, 6.91; W, 49.96. Found: C, 20.05; H, 1.27; N, 4.68; Cu, 6.78; W, 50.11. IR (KBr, cm<sup>-1</sup>): 3087 (w), 1599 (m), 1577 (w), 1475 (s), 1447 (s), 1409 (w), 1328 (m), 1305 (w), 1252 (m), 1166 (m), 1022 (s), 994 (m), 974 (s), 964 (s), 933 (m), 909 (m), 888 (s), 802 (s), 771 (s), 651 (w).

**X-ray Crystallography.** Single crystals of compounds 1–4 were mounted on a Bruker-AXS CCD diffractometer equipped with a graphite-monochromated Mo K $\alpha$  radiation source ( $\lambda = 0.07103$  Å) at 298 K. The absorption corrections were performed with the SADABS program. The structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The H atoms on C and N atoms were fixed at calculated positions. The H atoms on water in compound 1b were located from the difference Fourier map and the H atoms on water in compounds 1a, 2, and 3 could not be found from the residual peaks and were directly included in the final molecular formula. Although only one water molecule was found in compounds 1a,b by single-crystal X-ray diffraction, according to the TG result we believe that there are four lattice water molecules in 1. The H atoms were isotropically refined. All calculations were performed using the SHELXTL-97 program.<sup>32</sup> The crystallographic details of 1–4 are summarized in Table 2.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Figures, tables, and CIF files giving X-ray crystallographic data for 1–4, some structural figures, X-ray powder diffraction patterns, digital photos, IR spectra, TG analysis curves, and Cartesian coordinates of optimized structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Authors

\*S.-H.C.: e-mail, [shlchen@bit.edu.cn](mailto:shlchen@bit.edu.cn).

\*C.-W.H.: e-mail, [cwhu@bit.edu.cn](mailto:cwhu@bit.edu.cn); tel, +86-10-68912631; fax, ++86-10-68912631.

### Notes

The authors declare no competing financial interest.

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