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“Pinwheel” Subunit-Directed A Polyoxometalate-Based Hybrid Compound $[\text{Cu}(\text{bimb})_2]_2[\beta\text{-Mo}_8\text{O}_{26}]$ with Both Helices and Chiral Layers†

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Abstract

A new polyoxometalate-based hybrid compound, $[\text{Cu}(\text{bimb})_2]_2[\beta\text{-Mo}_8\text{O}_{26}]$ (**1**) (bimb = 1,3-bis(1-imidazoly)benzene), has been synthesized and characterized by single crystal X-ray diffraction, IR spectrum, elemental analyses and powder X-ray diffraction. Structural analysis reveals that the structure of **1** consists of a pair of chiral “pinwheel” subunits, and such “pinwheel” subunits direct formation of enantiomorphous chiral layers, in which the left- and right-handed helical chains are arranged regularly along the [001] direction, respectively. To our knowledge, compound **1** represents the first example of octamolybdate-based compound with both chiral and helical structural features. In addition, the photocatalytic experiment indicates that the title compound presents a good degradation activity and may be a potential photocatalyst to decompose the Methylene Blue dye.

Introduction

Inorganic-organic hybrid compounds as a type of new generation of solid state materials¹ have various structures as well as wide ranging applications from catalysis to material science^{2,3}, and the syntheses of inorganic-organic hybrid compounds through crystal engineering sprung up rapidly in virtue of the quick development of characterization techniques⁴. In this field, it is considerably attractive to exploit inorganic-organic compounds containing helical and/or chiral structures⁵⁻¹¹. Up to now, thanks to the work of chemists, many novel helical and/or chiral compounds have been rationally designed and synthesized through the assembly of ligands and metal cations.¹²⁻²⁵ In contrast, only a few hybrid compounds containing polyoxometalates (POMs) and organic ligands/metal coordination complexes have been reported to possess helical and/or chiral features²⁶. From the structural point of view, the incorporation of POMs into helical or chiral character system leading to the formation of the helical compounds based on POMs is very interesting, since there exists a correlation between structural complexity and multi-functionality in coordination compounds²⁷. These facts have provided a powerful impetus for the creation of helical and/or chiral compounds based on POMs²⁸⁻²⁹. An excellent example is the first inorganic double helixes self-assembled from simple starting materials under hydrothermally conditions reported by Haushalter and Zubieta *et al.* in 1993³⁰. Subsequently, thanks to the pioneering work of Wang and Lu, a few inorganic-organic double helixes based on POMs have been reported³¹⁻³⁵. In the very recently, by choosing V-shaped bimb ligands, Cu²⁺ cations and isopolymolybdates as starting materials, a helical compound [Cu(H₂O)(bimb)]₂[β-Mo₈O₂₆] (**2**) has been hydrothermally synthesized by us³⁶ (Scheme 1). It is well known that the solvents of

reaction system have an important influence on the final structures of the compounds³⁷. In order to investigate the effect of solvent system on the helical structures, in this work we chose the identical reagent and synthetic method with that of compound **2**, except that the C₂H₅OH instead of H₂O solvent is introduced into the reaction system of **1**. Fortunately, we obtain a new compound, [Cu(bimb)₂]₂[β-Mo₈O₂₆] (**1**) (bimb = 1,3-bis(1-imidazolyl)benzene) (Scheme 1). In particular, the structure of **1** consists of a pair of enantiomorphous “pinwheel” subunits and such “pinwheel” subunits direct formation of the novel structure of **1** with both helical and chiral features. Furthermore, the photocatalytic properties of **1** towards photodecomposition of Methylene Blue (MB) were investigated in detail.



Scheme 1. Illustration of the structure motifs of **1** and **2** (compound **1** is reported in this work and **2** was reported previously³⁶).

Experimental

Materials and methods

All chemicals were of reagent grade and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer,

and that of Cu and Mo were carried out with a Leaman inductively coupled plasma (ICP) spectrometer. The FT-IR spectrum were recorded from KBr pellets in the range 4000–400 cm^{-1} with a Nicolet AVATAR FT-IR360 spectrometer. The X-ray powder diffraction (XRPD) patterns were recorded with a Siemens D5005 diffractometer with Cu-K α ($\lambda = 1.5418 \text{ \AA}$) radiation. The UV-vis absorption spectra were recorded on a 756 CRT UV-vis spectrophotometer.

Synthesis of [Cu(bimb)₂]₂[β -Mo₈O₂₆] (1)

A mixture of (NH₄)₆Mo₇O₂₄·4H₂O (0.37 g, 0.3 mmol), CuCl₂·2H₂O (0.16 g, 0.9 mmol), bimb (0.12 g, 0.6 mmol), H₂C₂O₄ (0.06 g, 0.5 mmol) and C₂H₅OH (15 mL) was stirred for 1 h. Then the solution was sealed in a 25 mL Teflon-lined auto autoclave and heated at 160 °C for 3 days with a starting pH = 3.5 adjusted by 1mol/L HCl. After slow cooling to room temperature, purple crystals of **1** were filtered, washed with distilled water and dried at room temperature (41% yield based on Mo). Elemental analysis: C₄₈N₁₆H₄₀Cu₂Mo₈O₂₆ (**1**) (2151.53). Anal. Calcd for **1**: H, 1.85; C, 26.77; N, 10.41; Cu, 5.94; Mo, 35.69 (%). Found: H, 1.84; C, 26.79; N, 10.44; Cu, 5.91; Mo, 35.63 (%).

X-ray Crystallography

Single-crystal X-ray diffraction data for **1** was recorded on a Bruker Apex CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71069 \text{ \AA}$). Absorption corrections were applied using multi-scan technique. All the structures were solved by Direct Method of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program within WINGX.³⁸ The hydrogen atoms of bimb ligands were generated geometrically for compound **1**. The detailed crystallographic data and structure refinement parameters are summarized in Table 1.

Crystallographic data for the structure reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC Number: CCDC 1416556.

Table 1 Crystal data and structure refinements for compound **1**.

Compound	1
Formula	C ₄₈ N ₁₆ H ₄₀ Cu ₂ Mo ₈ O ₂₆
Formula weight	2151.53
Crystal system	Monoclinic
Space group	<i>P</i> 2(1)/ <i>n</i>
<i>a</i> /Å	12.816(5)
<i>b</i> /Å	17.289(5)
<i>c</i> /Å	16.132(5)
β /°	111.716(5)
<i>V</i> /Å ³	3320.8(19)
<i>Z</i>	2
<i>D</i> _{calcd} /g cm ⁻³	2.152
T/K	293(2)
μ /mm ⁻¹	2.174
Refl. Measured	23654
Refl. Unique	8107
<i>R</i> _{int}	0.0336
GoF on <i>F</i> ²	1.023
<i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> ≥2σ(<i>I</i>)]	0.0311/0.0881
$R_1 = \frac{\sum F_o - F_c }{\sum F_o }$. $wR_2 = \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]}^{1/2}$	

Results and Discussion

Synthesis. As compounds [Cu(bimb)₂]₂[β-Mo₈O₂₆] (**1**) in present work and [Cu(H₂O)(bimb)]₂[β-Mo₈O₂₆] (**2**) reported by us in previous work³⁶ were synthesized under the identical reaction conditions, except that the C₂H₅OH instead of H₂O solvent is introduced into the reaction system of **1**, we deduce that the structural distinction of **1** and **2** arise from the difference of the solvents of reaction system. In **2**, the Cu atoms are coordinated by one H₂O molecule, two β-Mo₈ clusters and two bimb ligands. In contrast to H₂O molecule, the coordination ability of C₂H₅OH molecule towards Cu atoms is

much lower. By introducing the C₂H₅OH instead of H₂O solvent into the reaction system of **1**, it can effectively reduce the coordination competition between bimb/POM and H₂O molecule towards Cu atom. Consequently, the Cu atoms are coordinated by four bimb ligands and a β -Mo₈ cluster forming a chiral “pinwheel” subunit. Such chiral “pinwheel” subunit finally direct formation of a novel POM-based hybrid compound **1** with both helices and chiral layers (see details in the section of **Description of the structure**). Therefore, this work offers practical evidence that the solvents of reaction system play an important influence on the final structures of the compounds once more.

Description of the structure of **1**

Single-crystal X-ray diffraction analysis reveals that **1** crystallizes in the monoclinic space group *P2(1)/n* (No. 14), and consists of two Cu²⁺ cations, one [Mo₈O₂₆]⁴⁻ polyanion (abbreviated as Mo₈) and two pairs of mirror symmetry bimb ligands (bimb1/bimb#1 and bimb2/bimb#2, see Fig. S1a). The valence sum calculations of **1** show that all Mo and Cu atoms are in the +VI and +II oxidation state³⁹, respectively. This result is consistent with structural analyses and charge balance. The Mo₈ clusters in **1** are a typical β -octamolybdate, which exhibits the most compact structure of eight edge-sharing [MoO₆] octahedra with two [Mo₄O₁₃] subunits stacking together⁴⁰ and each β -Mo₈ cluster as a bidentate inorganic linker, provides its a pair of symmetric terminal oxygen atoms bonding to two Cu(1) atoms, see Fig. S1b. There is one crystallographically independent Cu²⁺ cation, and the Cu(1) atom is penta-coordinated in a square pyramid geometry achieved by one oxygen atom from a β -Mo₈ cluster and four nitrogen donors from four bimb ligands (Fig. S1c). The bond lengths and angles around the Cu ions are in the

ranges of 1.965(3)–2.038(3) Å (Cu–N), 1.958(3)–2.315(2) Å (Cu–O), 94.27(11)–172.00(11)° (N–Cu–N) and 89.37(10)–171.96(12)° (N–Cu–O).

Compound **1** is the first example of octamolybdate-based compound with both chiral and helical structural features. Such intriguing structure can be described in detail as follows: There are two crystallographically independent bimb molecules (bimb1 and bimb2). In each bimb molecule, one of the imidazole groups has been rotated to different plane with the intramolecular aromatic ring and the other imidazole group (Fig. 1a and 1c), and the torsion angles of aromatic rings and rotated imidazole groups for two crystallographically independent bimb molecules are different. Such rotation may play a key role in promoting the formation of intriguing structure. Consequently, the two crystallographically independent bimb molecules (bimb1 and bimb2) are respectively interconnected by Cu centers in a “head-tail” mode (Fig. 1b and 1d) to form a pair of enantiomorphous chiral “pinwheel” subunits (Fig. 1e). The adjacent same chiral “pinwheel” subunits are interconnected by sharing Cu(II) cations to generate left-handed or right-handed chiral layers (Fig. 1f). Further, the two types of chiral layers, one left-handed and the other right-handed, are linked together by bi-dentate β -Mo₈ inversion centers leading to a mesomeric 3D inorganic-organic framework (Fig. 2a). Note that, there exist left- or right-handed helical chains in the two types of chiral layers, respectively. Both the right- and left-handed helical chains show an identical screw-pitch of *ca.* 16.289 Å and are constructed by the {CuON₄} coordination fragments and bimb molecules in a fashion of corner sharing nitrogen atoms of bimb molecules (Fig. 2b-2d). Meanwhile, the left- and right-handed helical chains are arranged regularly along the

crystallographic 2_1 screw axis in the [001] direction to construct 1D helical channels, respectively. The cross-section dimension of each channel is *ca.* $5.2 \times 6.5 \text{ \AA}^2$ (Fig. S2).

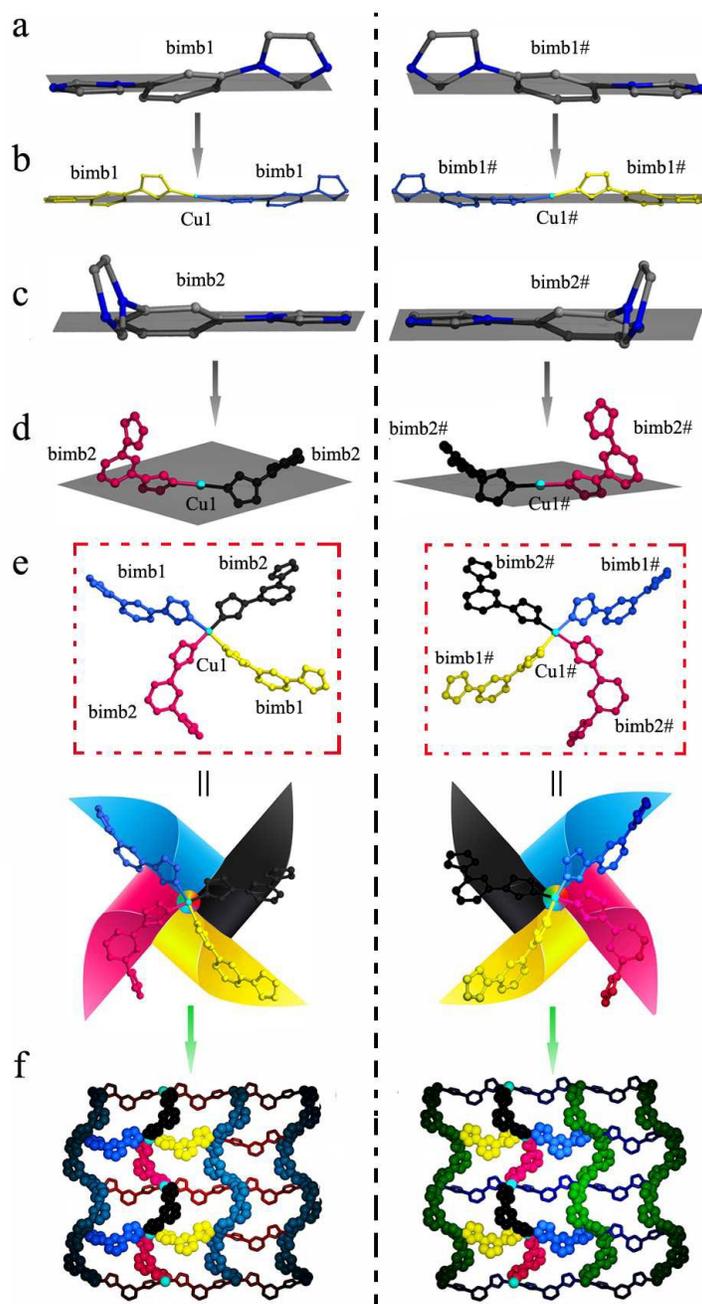


Fig. 1. View of the structural motifs in **1**: two crystallographically independent bimb molecules (a and c), the “head-tail” connected mode of two bimb molecules and a Cu center (b and d), chiral “pinwheel” subunits (e) and chiral 2D layers (f).

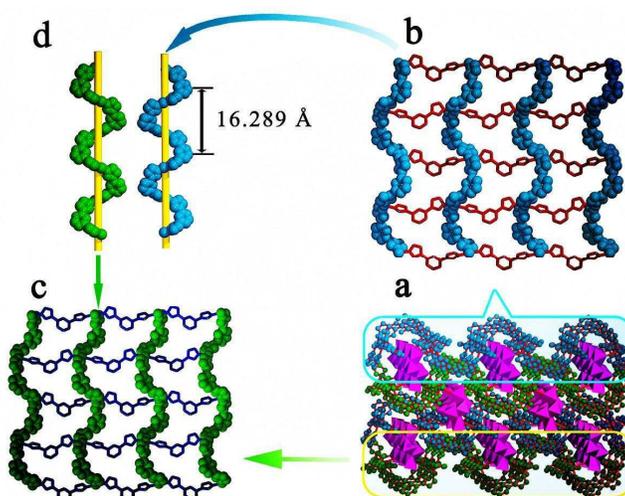


Fig. 2. View of the 3D organic-inorganic framework (a), the left- and right-handed helical chains in the two types of chiral layers (b–d).

Analyses of IR spectrum and PXRD patterns.

The IR spectrum of compound **1** (Fig. S3) exhibits the characteristic peaks of the β - Mo_8 cluster at 938, 894, 767, 676 and 568 cm^{-1} , which are attributed to $\nu(\text{Mo}=\text{O}_t)$, $\nu_{as}(\text{Mo}-\text{O}_b-\text{Mo})$ and $\nu_{as}(\text{Mo}-\text{O}_c-\text{Mo})$, respectively. The bands in the region of 1632 to 1089 cm^{-1} could be ascribed to the character peaks of the bimb ligands.

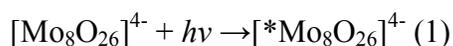
The PXRD patterns for **1** are presented in the Fig. S4. The diffraction peaks of both simulated and experimental patterns match well indicating the phase purity of the compound is good.

Photocatalytic Properties.

To investigate the photocatalytic activities of compound **1** as catalysts, the photodecomposition of methylene blue (MB) was evaluated under UV irradiation through a typical process: 50 mg of compound **1** was mixed with 100 mL of a $1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ (C_0) solution of MB in a beaker through ultrasonic dispersion for 10 min. The mixture was stirred for 0.5 h until that the equilibrium in the surface adsorption on the particles of

compound **1** was reached. Then, the mixture was continuously stirred under UV irradiation from a 125 W high-pressure Hg lamp. At 15, 30, 45, 60, and 75 minute, 3 mL of the sample was removed from the beaker, followed by several centrifugation steps to remove the compound **1** and a clear solution was obtained for UV/Vis analysis.

The results show that the absorbance of the reaction solution decreased as the irradiation time was increased, which indicate that **1** has good catalytic effectiveness (Fig. 3a). The decomposition rate of MB (K) can be expressed as $K = (I_0 - I_t)/I_0$, where I_0 represents the UV-vis absorption intensity of MB at the initial time ($t = 0$) and I_t is the intensity at a given time (t). The concentrations of MB (C) against reaction times (t) of **1** are shown in (Fig. 3b). It can be seen that the photocatalytic activities increase from 13% (without any catalyst, see Fig. S5) to 88% (with compound **1**, see Fig. 3a) after 75 minute of irradiation⁴¹. The possible photocatalytic mechanisms can be deduced as follows: during the photocatalytic reaction, $[\text{*Mo}_8\text{O}_{26}]^{4-}$ (*POM) abstract electrons from water molecules and hold the electrons (Equations (1) and (2)). The reduced POM (POM^-) is quite stable, but is rapidly re-oxidized in the presence of O_2 through Equation (3). The main function of O_2 in the POM reactions seems to be the re-oxidation (regeneration) of the catalyst. The re-oxidation step accompanies the generation of superoxides. These cycles occur continuously whilst the system is exposed to UV light. Furthermore, the MB dye is also excited by UV light to generate *MB molecules, as shown in Equation (4). Finally, after several photo-oxidation cycles, degradation of the MB dye by hydroxyl radicals and superoxides occurs (Equation (5))⁴².



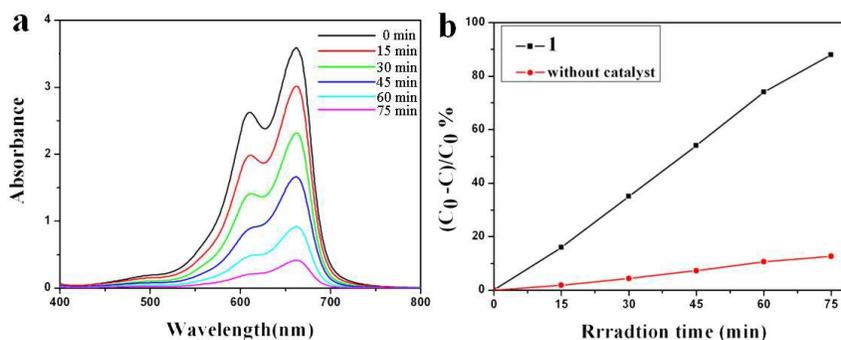
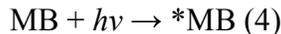
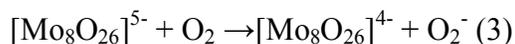


Fig. 3. (a) Absorption spectra of the MB aqueous solution during the photodegradation under 250 W Hg-lamp irradiation with compound **1** (b) Conversion rate of MB (K) vs the irradiation time (t).

Conclusion

In summary, as a continuous work, we have constructed a novel octamolybdate-based hybrid compound utilizing the identical reaction system with our previous work, except that $\text{C}_2\text{H}_5\text{OH}$ was used as solvent instead of H_2O . Thanks to the much weaker coordination ability of $\text{C}_2\text{H}_5\text{OH}$ molecules and Cu cations compared to that of other molecules (organic ligand, polyoxometalate and H_2O) and Cu ions. The Cu cations are five-coordination forming a pair of enantiomorphous chiral “pinwheel” subunits. Finally, the “pinwheel” subunit directed formation of the compound **1** with both chiral and helical structural features. To some extent, our attempts offer practical evidence that the solvents of reaction system may play an important influence on the final structures of the compounds, which provide a useful example for understanding step by step the influences of various factors on the assembly processes of polyoxometalate-based hybrid materials.

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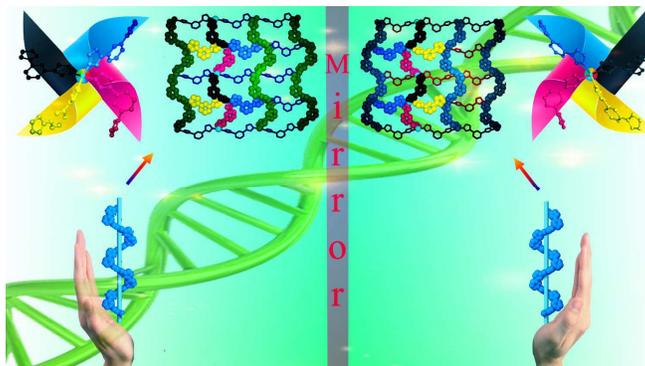
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“Pinwheel” Subunit-Directed A Polyoxometalate-Based Hybrid Compound $[\text{Cu}(\text{bimb})]_2[\beta\text{-Mo}_8\text{O}_{26}]$ with Both Helixes and Chiral Layers†

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An unprecedented hybrid octamolybdate-based compound with both chiral and helical structure, consisting of a pair of enantiomorphous chiral “pinwheel” subunits, has been synthesized, and its photocatalytic properties have been also investigated.