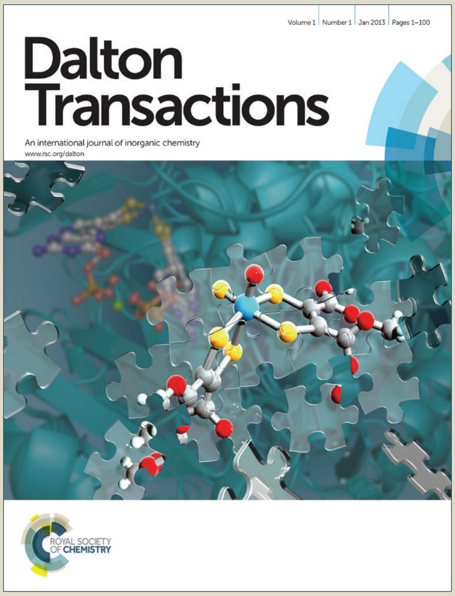
# Dalton Transactions



# Coexistence of Interconnected and Interweaved Double Helixes in an Octamolybdate-based Compound: Synthesis, Structure, and Photocatalytic Properties†

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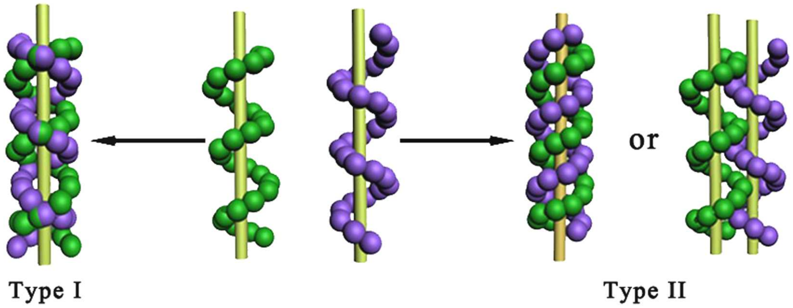
By choosing V-shaped ligands, $Cu^{2+}$ cations and isopolymolybdates as starting materials, a novel double helical compound $[Cu(H_2O)(bimb)]_2[\beta\text{-}Mo_8O_{26}]$ (**1**) (bimb = 1,3-bis(1-imidazoly)benzene), has been hydrothermally synthesized and characterized by elemental analyses, single-crystal X-ray diffraction, powder X-ray diffraction and IR spectrum. A structural feature is that compound **1** represents the first example of the helical compound based on polyoxometalates, which possesses an unprecedented helical disposition, namely coexistence of both interconnected and interweaved double helixes in one structure. The photocatalytic properties of compound **1** were also investigated in details and the result of photocatalytic experiments shows that compound **1** can be used as a stable photocatalyst toward the decomposition of organic pollutant methylene blue.

## Introduction

The DNA is prevalent in nature and is the foundation of the genetic code. Since the discovery of the double-stranded helical structure of DNA[1], many chemists have put great efforts on the rational design and synthesis of artificial helical compounds[2], because of their importance in multidisciplinary areas such as biological systems, asymmetric catalysis and optical devices.[3]

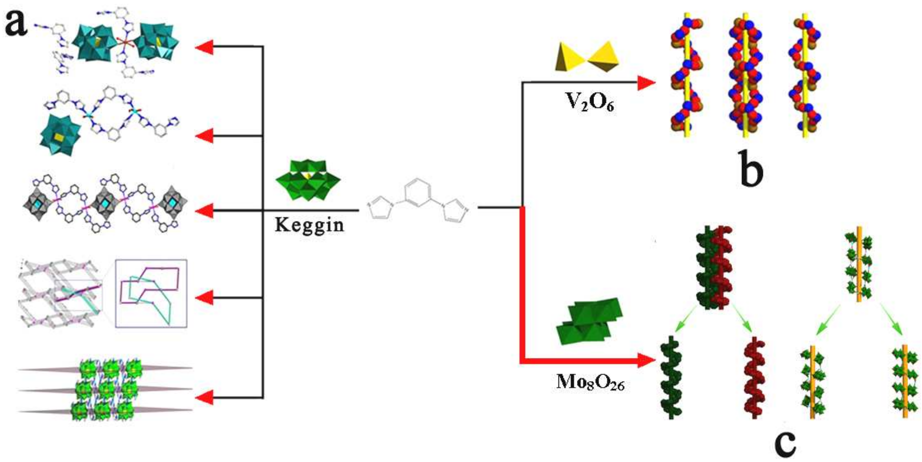
Polyoxometalates (POMs),[4] a unique class of metal-oxide clusters, have many properties that make them attractive for applications in magnetism, materials science, and catalysis.[5] From the structural point of view, the incorporation of POMs into helical system leading to the formation of the helical compounds based on POMs is very interesting, since there exists a correlation between structural complexity and multi-functionality in coordination compounds[6]. These facts have provided a powerful impetus for the creation of helical compounds based on POMs[7]. Among them, some compounds with intriguing double helixes have been obtained in recent years. 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 1993[8]. Subsequently, thanks to the pioneering work of Wang and Lu, a few inorganic-organic double helixes based on POMs have been reported.[9-12] Nevertheless, investigation on the preparation of double helical compounds based on POMs is still a current challenge. For the sake of comparison, herein we try to sort the known double helical compounds based on POMs into two types according to the entangled styles of helixes (Scheme 1): (I) Interconnected double helixes, a pair of intertwined right- and/or left-handed helixes with entanglement nodes; (II)

Interweaved double helixes, a pair of intertwined/interdigitated right- and/or left-handed helixes without entanglement nodes. As far as we know, only about ten and six compounds respectively belonging to type I and II have been reported till now (see table S1, ESI). Furthermore, these compounds are ascribed to either type I or type II and no double helical compounds based on POMs consisting of both types of double helixes in one structure have been structurally characterized. The synthesis of such compounds will provide actual models for investigating the nature of POMs within helical system.



**Scheme 1**. Schematic representation of the two types of double helical structures (I and II).

According to the literature[13], the use of V-shaped ligands as structure directing agents is an effective approach to obtain helical compounds with ease. The bimb molecule (bimb = 1,3-bis(1-imidazoly)benzene), is a readily available bridging ligand with the V-shaped motif, and it had been chosen by us to react with different POM reaction systems for preparing the POM-based helical compounds. First, we introduced bimb ligands into the reaction systems of two types of Keggin POMs ($H_5BW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$) respectively, obtaining five new compounds[14] (Scheme 2a). Unfortunately, single-crystal X-ray diffraction analyses reveal that all of these compounds don’t contain any helixes. After carefully analyzing theses structures, we found that the Keggin polyanions with a $T_d$ symmetry showing a high symmetrical globular surface may be unfavorable to formation of helical structures. Choosing some low symmetrical POMs such as isopolyvanadates and isopolymolybdates may be conducive to the formation of helical structures according to the literature[15]. Taking these points into account, by choosing the bimb ligands, isopolyvanadates and other reagent, we have obtained a novel double helical compound [Co(bimb)$V_2O_6$] very recently[16] (Scheme 2b). As a continuance of our work, we choose $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ isopolymolybdates, $CuSO_4\cdot 5H_2O$ salts, bimb ligands and have hydrothermally synthesized a new double helical compound based on POMs, $[Cu^{II}(H_2O)(bimb)]_2[\beta\text{-}Mo_8O_{26}]$ (**1**) (bimb = 1,3-bis(1-imidazoly)benzene). Compound **1** represents the first example of the double helical compound based on POMs that possesses two types of double helixes, namely both interconnected and interweaved double helixes (Scheme 2c). Furthermore, the photocatalytic properties of **1** towards photodecomposition of Methylene Blue were investigated in detail.



**Scheme 2**. View of the structures of the compounds obtained us, which are constructed by the bimb ligands and different POM systems: (a) Keggin system, five different architectures without any helical structures, (b) $V_2O_6$ system, a interconnected double helical chain, (c) $Mo_8O_{26}$ system, both interconnected and interweaved double helixes. The $V_2O_6$ and $Mo_8O_{26}$ are the abbreviations of $[V_2O_6]^{2-}$ and $[Mo_8O_{26}]^{4-}$, respectively.

## 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. The FT-IR spectra 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$\alpha$ ($\lambda$ = 1.5418 Å) radiation. A CHI 760D electrochemical workstation was used for control of the electrochemical measurements and data collection. UV-vis absorption spectra were recorded on a 756 CRT UV-vis spectrophotometer.

### Synthesis of $[Cu(H_2O)(bimb)]_2[\beta\text{-}Mo_8O_{26}]$ (1)

A mixture of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.37 g, 0.3 mmol), $CuCl_2\cdot 2H_2O$ (0.16 g, 0.9 mmol), bimb (0.12 g, 0.6 mmol), $H_2C_2O_4$ (0.06 g, 0.5 mmol) and $H_2O$ (15 mL) was stirred for 1 h. Then the solution was sealed in a 23 mL Teflon-lined auto autoclave and heated at 160 °C for 3 days with a starting pH = 3.5 adjusted by 1 M HCl. After slow cooling to room temperature, blue block crystals of **1** were filtered, washed with distilled water and dried at room temperature. The reproducibility of the compound is good and the yield of the compound is high (*ca.* 46% yield based on Mo). Elemental analysis: $C_{24}N_8H_{24}Cu_2Mo_8O_{28}$ (**1**) (1767.1). Anal. Calcd for **1**: H, 1.36; C, 16.31; N, 6.34; Cu, 7.19; Mo, 43.43 (%). Found: H, 1.41; C, 16.23; N, 6.28; Cu, 7.08; Mo, 43.55 (%).

### X-ray Crystallography

Single-crystal X-ray diffraction data for **1** was recorded on a Bruker Apex CCD diffractometer with graphite-monochromated MoK$_\alpha$ radiation ($\lambda$ = 0.71069 Å). Absorption corrections were applied using multi-scan technique. All the structures were solved by Direct Method of SHELXS-97[17a] and refined by full-matrix least-squares techniques using the SHELXL-97 program[17b] within WINGX[17c]. The hydrogen atoms of bimb ligands were generated geometrically for compound **1**, while the hydrogen atoms of water molecules can not be found from the residual peaks and were directly included in the final molecular formula. 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 1012514.

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

| Compound | **1** |
|---|---|
| Formula | $C_{24}N_8H_{24}Cu_2Mo_8O_{28}$ |
| Formula weight | 1767.1 |
| Crystal system | Monoclinic |
| Space group | $P2(1)/n$ |
| $a$/Å | 13.526(5) |
| $b$/Å | 11.743(5) |
| $c$/Å | 13.885(5) |
| $\beta$/° | 107.129(5) |
| $V$/Å$^3$ | 2107.6(14) |
| $Z$ | 4 |
| $D_{calcd}$/g cm$^{-3}$ | 2.778 |
| T/K | 293(2) |
| $\mu$/mm$^{-1}$ | 3.389 |
| Refl. Measured | 15247 |
| Refl. Unique | 5255 |
| $R_{int}$ | 0.0170 |
| GoF on $F^2$ | 1.042 |
| $R_1/wR_2$ [$I\geq2\sigma(I)$] | 0.0170/0.0426 |

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

## Results and Discussion

### Description of the structure of 1

Single-crystal X-ray diffraction analysis reveals that **1** crystallizes in the monoclinic space group *P*2(1)/n (No. 14), and consists of one crystallographically $Cu^{2+}$ cations, one $[\beta\text{-}Mo_8O_{26}]^{4-}$ polyanion (abbreviated as $\beta$-$Mo_8$), two bimb ligands and one coordination water molecule. The Cu(1) atom is six-coordination in an elongated octahedral geometry, which coordinated by four oxygen atoms from one water molecule, three oxygen atoms from two $\beta$-$Mo_8$ clusters and two nitrogen donors from two bimb ligands, displaying Jahn–Teller (JT) elongation axes with the two JT bonds being at least 0.4 Å longer than the other four bonds (Fig. 1). 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). All of these bond lengths and angles are within the normal ranges observed in other Cu(II)-containing complexes[18].

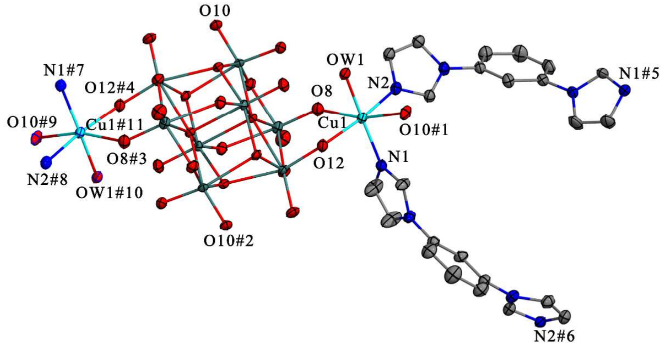


**Fig. 1**. ORTEP diagram (at 50% probability level) of the basic building blocks and the coordination environments for the $\beta$-$Mo_8$ cluster and $Cu^{2+}$ ions in **1** (symmetry codes: #1: -0.5+x, 1.5-y, -0.5+z; #2: 1-x, 2-y, 2-z; #3: 1-x, 2-y, 2-z; #4 1-x, 2-y, 2-z; #5 0.5-x, -0.5+y, 0.5-z; #6 0.5-x, 0.5+y, 0.5-z; #7 1-x, 2-y, 2-z; #8 1-x, 2-y, 2-z; #9 1.5-x, 0.5=y, 2.5-z; #10 1-x, 2-y, 2-z; #11 1-x, 2-y, 2-z; The H atoms of coordinated water and bimb molecules are omitted for clarity.)

Compound **1** is the first example of the 3D helical compound based on POMs, which shows an unprecedented helical disposition, namely coexistence of both interconnected and interweaved double helixes in one structure (Scheme 1, table S1). Such intriguing structure can be described in detail as follows: on the one hand, in the crystal structure, there are 1D helical channels with cross-section dimensions *ca.* 8.5 × 7.8 $Å^2$ (Fig. S1a). The channels are formed through the twining double helixes that consist of a pair of interweaved right- and left-handed helical chains (Fig. 2a). Each helical chain is constructed by the $\{Cu(H_2O)O_3N_2\}$ octahedra and bimb molecules in a fashion of corner sharing nitrogen atoms of bimb molecules. The interweaved right- and left-handed helical chains are running along the [001] direction with an identical screw-pitch of *ca.* 11.743 Å (Fig. 2a). There are extensive edge to face stacking $\pi\cdots\pi$ interactions between the bimb molecules respectively from adjacent right- and left-handed helical chains (Fig. S2). Consequently, an inorganic-organic supramolecular layer is formed by the $\pi\cdots\pi$ interactions (Fig. 3a, 3a$^*$). On the other hand, the $\beta$-$Mo_8$ clusters and $\{Cu(H_2O)O_3N_2\}$ octahedra are connected to each other by corner-sharing oxygen atoms of $\beta$-$Mo_8$ clusters to form left- and right-handed helixes with an identical pitch of *ca.* 10.959 Å. Furthermore, the left- and right-handed helixes are interconnected together through sharing copper and oxygen atoms to achieve double helixes running along the [001] direction (Fig. 2b). Furthermore, of the neighboring double helixes are connected together by corner-sharing copper and oxygen atoms to achieve an inorganic layer with cavities *ca.* 6.7 × 8.4 $Å^2$ (Fig. 3c, 3c$^*$). The interconnected double helixes in the inorganic layer are arranged regularly along their screw axes to construct 1D helical channels with cross-section dimensions *ca.* 3.0 × 5.5 $Å^2$ (Fig. S1b). Finally, the inorganic-organic and inorganic layers (Fig. 3a and 3c) are linked together through sharing copper atoms to achieve a 3D inorganic-organic framework (Fig. 3b). The topological analysis of the structure has been performed by considering each {$\beta$-$Mo_8$} polyanion and {$Cu(H_2O) N_2O_3$} octahedron as a 4-connected node, respectively. Hence, the 3D framework of **1** can be simplified as a (4, 4)-connected net with a $(6^4 8^2)(6^5 8^1)$ topology (Fig. S3).

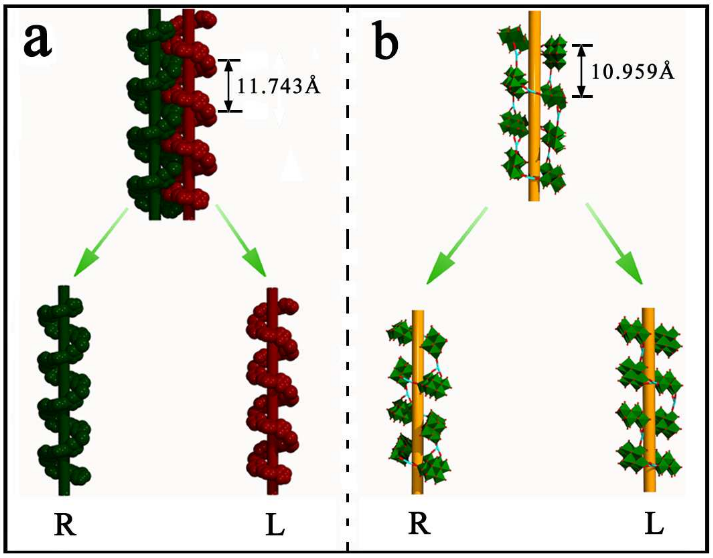


**Fig. 2**. Detailed view of the two pair of entangled double helical chains in **1** (For clarity, only the backbones of the helical chains are shown).

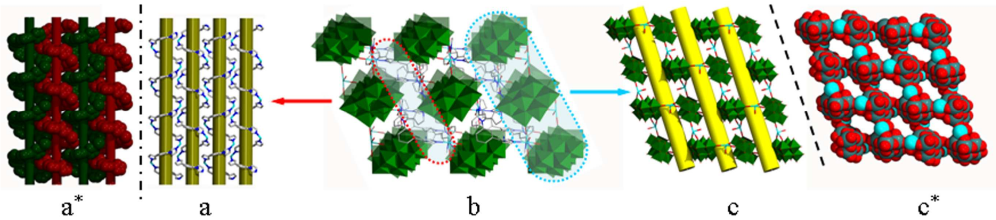


**Fig. 3**. (a) A wires/sticks model of the 2D supramolecular layer. ($a^*$) A space-filling model of the fourfold entangled. (b) Projection of the 3D framework. (c) Polyhedral view of the 2D network. ($c^*$) A space-filling model of the 2D inorganic with 6.7 × 8.4 $Å^2$ channels layer (Color code: $\beta$-$Mo_8$ polyhedral cluster, green; Cu cation, blue.)

### Analyses of IR spectrum and PXRD patterns.

The IR spectrum of compound **1** (Fig. S4) exhibits the characteristic peaks of the $\beta$-Mo$_8$ cluster at 932, 842 and 702 cm$^{-1}$, which are attributed to $v$(Mo=O$_t$), $v_{as}$(Mo–O$_b$–Mo) and $v_{as}$(Mo–O$_c$–Mo), respectively[19]. The bands in the region of 1612 to 1063 cm$^{-1}$ could be ascribed to the character peaks of the bimb ligands[14-15]. The broad band at 3416 cm$^{-1}$ is associated with the water molecules[20]. The PXRD (powder X-ray diffraction) experiments evidenced the good phase purity of compound **1** as the diffraction peaks of both simulated and experimental patterns match well (see Fig. S5, ESI).

### Photocatalytic Properties.

The use of POMs as photocatalysts to decompose waste organic molecules so as to purify the water resources has attracted great attention in recent years.[21] In this work, methylene blue (MB), which is typically difficult to decompose in wastewater,[22] was selected for evaluating the photocatalytic activities of the compound **1** toward the decomposition of organic pollutants. The typical experiment process is as follows: prior to photocatalytic experiment, the powder of 150 mg **1** was mixed together with 90 mL of 10.0 mg/L MB solution in a beaker by ultrasonic dispersion for 0.5 h. The mixture was stirred for 2 h to reach the surface-adsorption equilibrium on the particles of **1**. Then, the mixture was stirred continuously under ultraviolet (UV) irradiation of a 250 W high pressure Hg lamp at a distance of 4–5 cm between the liquid surface and the lamp. Took a sample from the mixture every 15 min and then removed the catalyst of compound **1** from this sample by several centrifugations to achieve a clear solution 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. 4a). 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. 4b). It can be seen that the photocatalytic activities increase from 23% (without any catalyst) to 87% (with compound **1**) after 1.5 h of irradiation. The possible photocatalytic mechanisms can be deduced as follows: during the photocatalytic reaction, $[^*Mo_8O_{26}]^{4-}$ (*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)).[23]

$[Mo_8O_{26}]^{4-} + h\nu \rightarrow [^*Mo_8O_{26}]^{4-}$ (1)

$[^*Mo_8O_{26}]^{4-} + H_2O \rightarrow [Mo_8O_{26}]^{5-} + H^+ + OH^\cdot$ (2)

$[Mo_8O_{26}]^{5-} + O_2 \rightarrow [Mo_8O_{26}]^{4-} + O_2^-$ (3)

$MB + h\nu \rightarrow {}^{*}MB$ (4)

$^{*}MB + OH^{\cdot} + O_2^{-} \rightarrow$ intermediate products $\rightarrow$ degradation (5)

Furthermore, to investigate the stability of the compound **1** as a photocatalyst, the PXRD pattern of compound **1** after the photocatalytic reaction was done. As shown in (Fig. 5), both simulative PXRD patterns and the experimental patterns after photocatalytic reaction mach well each other, although there were slight difference in reflection intensities of some peaks attributable to the different orientation of the crystals in the powder sample. This result suggests that the compound **1** can be used as a stable photocatalyst.

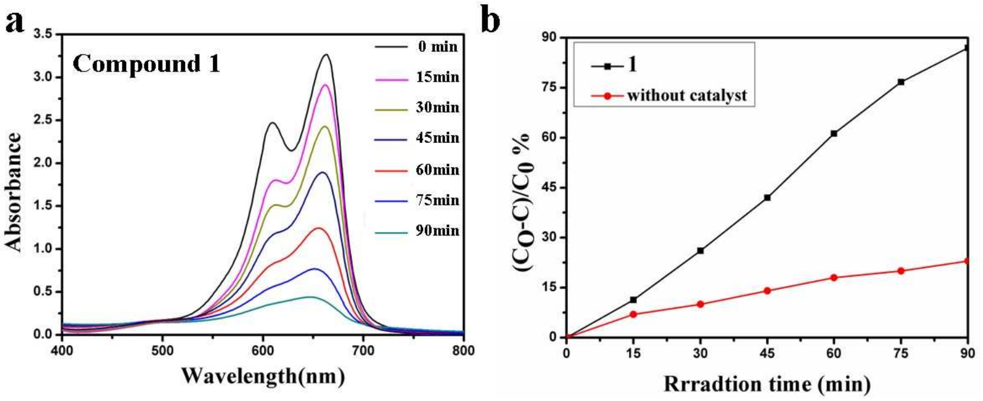


**Fig. 4.** (a) Absorption spectra of the MB aqueous solution during the photodegradation under 250 W Hg-lamp irradiation. (b) Conversion rate of MB (K) *vs* the irradiation time (t).

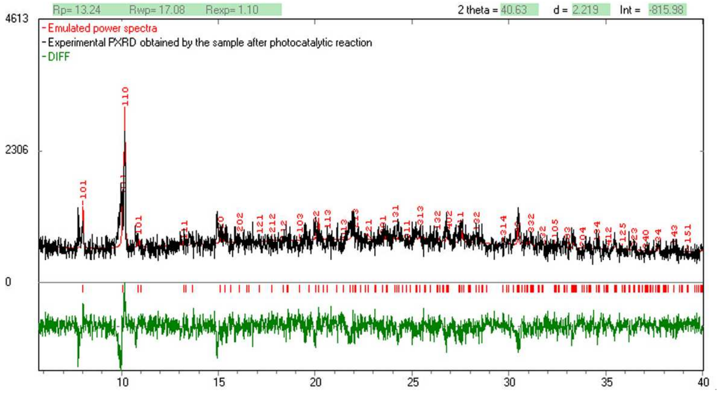


**Fig. 5** Output of a calculated powder X-ray patterns by *POWDER CELL*.

## Conclusion

In summary, a new compound based on POMs has been synthesized under hydrothermal conditions, in which there exist both interconnected and interweaved double helixes. As a continuance of our previous work, the successful isolation **1** not only provides intriguing example of POM-based helical compound showing an unprecedented helical disposition, but also confirms that compared with high symmetrical Keggin polyanions, the isopolyvanadate or isopolymolybdate polyoxoanions, thanks to their low symmetrical structures, cooperating with the V-shaped ligand bimb, are conducive to the formation of helical structures.

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## References

(1) J. D. Watson and F. C. H. Crick, *Nature*, 1953, **171**, 737.

(2) (a) J. M. Lehn, A. Rigault, J. Siegel, J. Harrowfield, B. Chevrier and D. Moras, *Proc. Natl. Acad. Sci. U.S.A.*, 1987, **84**, 2565; (b) V. Berl, I. Huc, R. G. Khoury, M. J. Krische and J. M. Lehn, *Nature*, 2000, **407**, 720; (c) Y. Cui, S. J. Lee and W. Lin, *J. Am. Chem. Soc.*, 2003, **125**, 6014; (d) X. M. Chen and G. F. Liu,

*Chem. Eur. J.*, 2002, **8**, 4811; (e) P. Grosshans, A. Jouaiti, V. Bulach, J. Planeix, M. W. Hosseini and J. F. Nicoud, *Chem. Commun.* 2003, 1336; (f) X. J. Luan, Y. Y. Wang, D. S. Li, P. Liu, H. M. Hu, Q. Z. Shi and S. M. Peng, *Angew. Chem., Int. Ed.*, 2005, **44**, 3864.

(3) (a) T. Nakano and Y.Okamoto, *Chem. Rev.* 2001, **101**, 4013; b) M. Albrecht, *Chem. Rev.*, 2001, **101**, 3457; (c) Y. Song, J. Yu, Y. Li, G. Li and R. Xu, *Angew. Chem., Int. Ed.*, 2004, **43**, 2399.

(4) (a)M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, Berlin, 1983; (b) C. L. Hill, *Chem. Rev.*, 1998, **98**, 1;(c) K. Fukaya and T. Yamase, *Angew. Chem., Int. Ed.*, 2003, **42**, 654; (d) C. D. Wu, C. Z. Lu, H. H. Zhuang and J. S. Huang, *J. Am. Chem. Soc.*, 2002, **124**, 3836; (e) M. I. Khan, E. Yohannes and R. J. Doedens, *Angew. Chem., Int. Ed.*, 1999, **38**, 1292; (f) P. J. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed.*, 1999, **38**, 2638; (g) E. Burkholder and J. Zubieta, *Chem. Commun.*, 2001, 2056; (h) D. L. Long, E. Burkholder and L. Cronin, *Chem.Soc.Rev.*, 2007, **36**, 105; (i) D. Y. Du, J. S. Qin, S. L. Li, Z. M. Su and Y. Q. Lan, *Chem. Soc. Rev.*, 2014, **43**, 4615; (j) W. W. He, S. L. Li, H. Y. Zang, G. S. Yang, S. R. Zhang, Z. M. Su and Y. Q. Lan, *Coord. Chem. Rev.*, 2014 DOI: http://dx.doi.org/doi:10.1016/j.ccr.2014.03.022.

(5) (a) A. Muller, S. Q. N. Shah, H. Bogge and M. Schmidtmann, *Nature*, 1999, **397**, 48; (b) P. Kogerler and L. Cronin, *Angew. Chem., Int. Ed.*, 2005, **44**, 844; (c) L. Xu, M. Lu, B. B. Xu, Y. G. Wei, Z. H. Peng and D. R. Powell, *Angew. Chem., Int. Ed.*, 2002, **41**, 4129. (d) J. Zhou, J. W. Zhao, Q. Wei, J. Zhang and G. Y. Yang, *J.*

*Am. Chem. Soc.*, 2014, **136**, 5065. (e) L. Huang, S. S. Wang, J. W. Zhao, L. Cheng, and G. Y. Yang, *J. Am. Chem. Soc.*, 2014, **136**, 7637.

(6) D. Hagrman, P. J. Hagrman and J. Zubieta, *Angew. Chem. Int. Ed.* 1999, **38**, 3165.

(7) D. Y. Du, L. K. Yan, Z. M. Su, S. L. Li, Y. Q. Lan and E. B. Wang, *Coord. Chem. Rev.*, 2013, **257**, 702.

(8) V. Soghomonian, Q. Chen, R. C. Haushalter, J. Zubieta and C. J. O'Connor, *Science*, 1993, **259**, 1596.

(9) (a)C. Z. Lu, C. D. Wu, S. F. Lu, J. C. Liu, Q. J. Wu, H. H. Zhuang and J. S. Huang, *Chem. Commun.*, 2002, 152.

(10) C. D. Wu, C. Z. Lu, X. Lin, D. M. Wu, S. F. Lu, H. H. Zhuang and J. S. Huang, *Chem. Commun.*, 2003, 1284.

(11) X. L. Wang, C. Qin, E. B. Wang and Z. M. Su, *Chem. Commun.*, 2007, 4245.

(12) H. Y. An, E. B. Wang, D. R. Xiao, Y. G. Li, Z. M. Su, and L. Xu, *Angew. Chem. Int. Ed.*, 2005, **44**, 1.

(13) L. Han and M. C. Hong, *Inorg. Chem. Commun.*, 2005, **8**, 406.

(14) (a) T. T. Yu, K. Wang, H. Y. Ma, H. J. Pang and S. B. Li, *RSC Adv.*, 2014, **4**, 2235; (b) D. Wu, K. Wang, H. R. Ma, H. J. Pang, T. T. Yu, Z. F. Zhang, S. B. Li and H. Liu, *Solid State Sci.*, 2014, **35**, 39.

(15) (a) D. H. Xiao, Y. Xu, Y. Hou, E. B. Wang, S. T. Wang, Y. G. Li, L. Xu and C. W. Hu, *Eur. J. Inorg. Chem.*, 2004, 1385; (b) D. R. Xiao, Y. Hou, E. B. Wang, Y. G. Li, J. Lu, L. Xu and C. W. Hu, *J. Mol. Struct.*, 2004, **691**, 123;(c) Y. Q. Lan, S. L. Li, K. Z. Shao, X. L. Wang, X. R. Hao and Z. M. Su, *Dalton Trans.*, 2009, 940;

(d) C. D. Wu, C. Z. Lu, S. F. Lu, H. H. Zhuang and J. S. Huang, *Dalton Trans.*, 2003, 3192; e) J. Q. Sha, M. T. Li, J. W. Sun, Y. N. Zhang, P. F. Yan and G. M. Li, *Dalton Trans.*, 2013, **42**, 7803.

(16) S. B. Li, W. L. Sun, K. Wang, H. Y. Ma, H. J. Pang, H. Liu and J. X. Zhang, *Inorg. Chem.*, 2014, **53**, 4541.

(17) (a) G. M. Sheldrick, SHELXS-97, Programs for X-ray Crystal Structure Solution,University of Göttingen: Göttingen, Germany, 1997; (b) G. M. Sheldrick, SHELXL-97, Programs for X-ray Crystal Structure Refinement, University of Göttingen: Göttingen, Germany, 1997; (c) L. J. Farrugia, WINGX, A Windows Program for Crystal Structure Analysis; University of Glasgow; Glasgow, UK, 1988.

(18) J. Q. Sha, J. Peng, Y. Zhang, H. J. Pang, A. X. Tian, P. P. Zhang and H. Liu, *Cryst Growth Des.*, **2009**, 9, 1708.

(19) W. G. Klemperer and W. *J.* Shum, *Am. Chem. Soc.*, **1976**, 98, 8291.

(20) J. X. Meng, Y. Lu, Y. G. Li, H. Fu, and E. B. Wang, *Cryst. Growth Des.*, 2009, **9**, 4116.

(21) H. X. Li, X. Y. Zhang, Y. N. Huo and J. Zhu, *Environ. Sci. Technol.*, 2007, **41**, 4410.

(22) (a) T. Tsumura, N. Kojitan, I. Izumi, N. Iwashita, M. Toyoda and M. J.Inagaki, *Mater. Chem.*, 2002, **12**, 1391; (b) D. S. Muggli, L. Ding and M. J. Odland, *Catal. Lett.*, 2002, **78**, 23; (c) R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki and Y.Taga, *Science*, 2001, **293**, 269; (d) H. Lin and P. A. Maggard, *Cryst. Growth Des.*, 2010, **10**, 1323.

(23) C. H. Wu and J. M. Chern, *Ind. Eng. Chem. Res.*, 2006, **45**, 6450.