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Chiral Polyoxometalate-Induced Enantiomerically 3D Architectures: A New Route for Synthesis of High-Dimensional Chiral Compounds

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Chiral polyoxometalates (POMs) have become a topic of intense interest owing to their intriguing potential applications in medicine and asymmetric catalysis.¹ However, only a handful of chiral compounds containing polyoxoanions have been reported.² Furthermore, despite considerable efforts, attempts to prepare enantiomerically high-dimensional frameworks constructed from POM units have met with only limited success. Most reported chiral POMs are discrete. Therefore, the synthesis of chiral POMs with 3D frameworks is one of the most challenging issues in synthetic chemistry and material science.

In theory, there are two synthetic strategies to approach chiral POM-based frameworks. The first is based on direct connection of POM clusters with chiral organic ligands or metal–organic moieties. Prominent work on this approach has been performed by the groups of Pope, Hill, Yamase, and Kortz.^{3–8} Recently, our group obtained the first chiral POM-based 3D architectures from this approach, which is constructed from $[\text{BW}_{12}\text{O}_{40}]^{5-}$ clusters and copper–amino acid complexes.^{9,10} The second approach is to link suitable discrete chiral polyoxoanions by simple metal cations or metal–organic segments,¹¹ thereby making the chirality of the polyoxoanion transfer to the whole framework. To our knowledge, most work reported to date has focused on the first approach, while the second method has never been developed. Aiming at further exploring the possible ways of synthesizing chiral POMs, we attempted to produce chiral POM-based 3D frameworks from the second strategy. Herein, we report the synthesis of two novel chiral 3D architectures based on polyoxoanions, $\text{L}-(\text{Zn}(\text{H}_2\text{O})_3)_3[\text{MnMo}_9\text{O}_{32}] \cdot 4\text{H}_2\text{O}$ (**L-1**) and $\text{D}-(\text{Zn}(\text{H}_2\text{O})_3)_3[\text{MnMo}_9\text{O}_{32}] \cdot 4\text{H}_2\text{O}$ (**D-1**), by using the second strategy.

We adopted a typical synthesis procedure for compounds **L-1** and **D-1**. Compounds **L-1** and **D-1** were isolated by the reaction of $\text{K}_3(\text{NH}_4)_3[\text{MnMo}_9\text{O}_{32}]^{12}$ with Zn^{2+} ions¹³ and separated manually.¹⁴ Single-crystal X-ray diffraction analyses¹⁵ reveal that the structures of compounds **L-1** and **D-1** are enantiomers. The structures of **L-1** and **D-1** exhibit a similar unique 3D chiral framework assembled from $[\text{MnMo}_9\text{O}_{32}]^{6-}$ clusters and $\{\text{Zn}(\text{H}_2\text{O})_3\}$ groups. **L-1** and **D-1** crystallize in the chiral space group $R\bar{3}2$. The polyoxoanions $[\text{MnMo}_9\text{O}_{32}]^{6-}$ in **L-1** and **D-1** are a typical Waugh heteropolymolybdate (Figure 1) with D_3 symmetry,^{14a} which consist of a central MnO_6 octahedron sharing edges with nine distorted MoO_6 octahedra. The Mo–O bond lengths range from 1.703(8) to 2.233 (7) Å. The central Mn–O distances are 1.882–(6)–1.887(6) Å, and the O–Mn–O angles are in the range of 86.2–(4)–169.6(3)°.

In **L-1** and **D-1**, all the zinc atoms have the same coordination sphere and exhibit distorted square pyramidal structure. Each Zn^{2+} cation in **1** is coordinated by three water molecules and two terminal oxygen atoms from two $[\text{MnMo}_9\text{O}_{32}]^{6-}$ polyoxoanions ($\text{Zn}-\text{OW}$

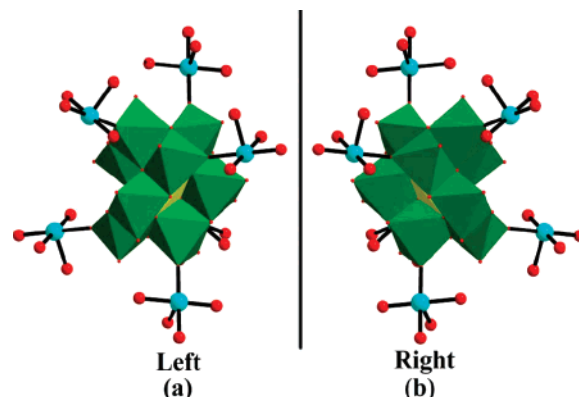


Figure 1. The combined polyhedral and ball-and-stick representation of **L-1** (a), **D-1** (b); O red, Zn blue, Mn yellow, Mo green.

1.939(9)–2.15(3) Å; $\text{Zn}-\text{O}'$ 2.052(7)–2.055(7) Å). Each $[\text{MnMo}_9\text{O}_{32}]^{6-}$ cluster acts as a hexadentate ligand and coordinates to six zinc cations through its terminal oxygen atoms (Figure 1), thus generating a novel 3D framework with α -Po topology that possesses channels along the $[0\ 1\ 1]$ direction of approximately 12.3×9.3 Å (Figure 2a). The large channels allow an identical network to penetrate it, giving rise to a 2-fold interpenetrating net (Figure 2b). Observed chirality of compounds **L-1** and **D-1** can be understood in terms of chirality transfer from the Waugh polyoxoanion to the whole framework.

To examine the chiroptical and stable activities of compounds **L-1** and **D-1** in the solution state, the CD spectra of compounds **L-1** and **D-1** in water were investigated (Figure 3). The CD spectra of compounds **L-1** and **D-1** are mirror images of one another, which indicated that the two compounds are enantiomers. The CD spectra of compounds **L-1** and **D-1** show different Cotton effects in the wavelength range of 170–194 nm compared with that of $\text{K}_3(\text{NH}_4)_3[\text{MnMo}_9\text{O}_{32}]$ (Figure 3, inset). The spectrum of $\text{K}_3(\text{NH}_4)_3[\text{MnMo}_9\text{O}_{32}]$ exhibits several weak Cotton effects in the range of 174–200 nm, while the spectra of compounds **L-1** and **D-1** display strong Cotton effects at 187, 182, 177, and 172 nm and 186, 183, 177, and 172 nm, respectively. The CD and UV/vis spectra of compounds **L-1** and **D-1** are virtually unchanged with time, indicating that both compounds are stable in aqueous solution.

In conclusion, we have successfully developed a new way to synthesize POM-based chiral 3D architectures, and two novel enantiomerically chiral 3D architectures, $\text{L}-(\text{Zn}(\text{H}_2\text{O})_3)_3[\text{MnMo}_9\text{O}_{32}] \cdot 4\text{H}_2\text{O}$ and $\text{D}-(\text{Zn}(\text{H}_2\text{O})_3)_3[\text{MnMo}_9\text{O}_{32}] \cdot 4\text{H}_2\text{O}$ have been produced. They are the first examples of POM-based chiral 3D frameworks consisting of only inorganic components. With a

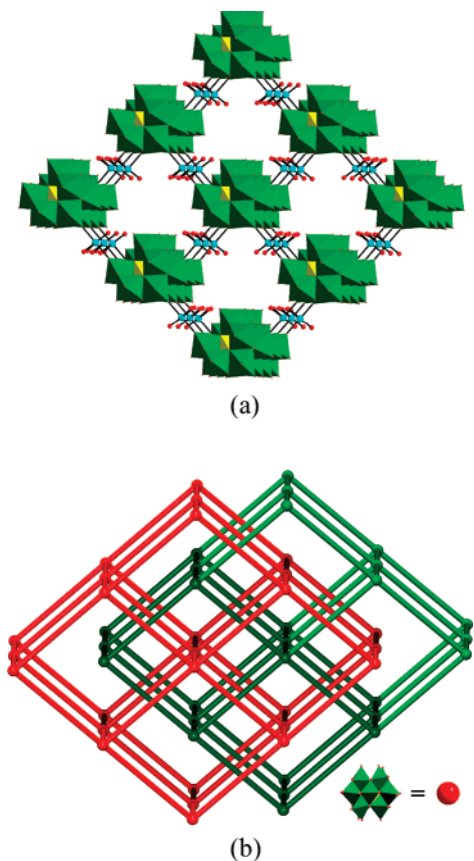


Figure 2. The 3D framework structure of L-1, which is composed of Zn²⁺ covalently linked to Waugh polyoxoanions (a) as a combined polyhedral and ball-and-stick representation; O red, Zn blue, Mn yellow, Mo green; (b) a schematic view of the 3D interpenetrating network of L-1.

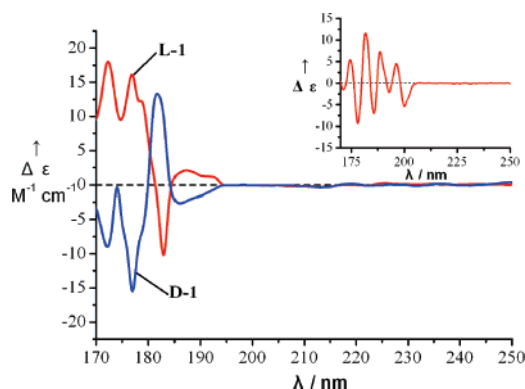


Figure 3. CD spectra in aqueous solution of L-1 and D-1, and their precursor, K₃(NH₄)₃[MnMo₉O₃₂] (inset).

judicious choice of chiral polyoxoanion, this approach provides a promising route for high-dimensional chiral structures based on polyoxoanions that may come in useful in the areas of asymmetric catalysis, separation, and even medicine.

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Supporting Information Available: X-ray crystallographic files for compounds L-1 and D-1 in CIF format and additional figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (13) Synthesis of compound 1: K₃(NH₄)₃[MnMo₉O₃₂] (0.5 g) and was dissolved in water (40 mL). The pH value of the mixture was carefully adjusted with a dilute HCl solution (1 M) to approximately 3.00. A solution of ZnCl₂·2H₂O (2.7310g, 0.02 mol) in water (10 mL) was added with stirring, and then, the mixture was heated to 80 °C for 1 h. After cooling to room temperature, the filtrate was kept at room temperature, and slow evaporation for two days resulted in the red crystals. Elemental analysis (%) calcd for mixture of L-1 and D-1: Zn, 10.48; H, 1.30; Mn, 2.90; Mo, 46.55. Found: Zn, 10.54; H, 1.40; Mn, 2.95; Mo 46.40. IR (KBr pellet): 1483(w), 946(s), 906(s), 847(w); 684(m), 591(m), 539(m), 496(m), 427(m).
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- (15) Crystal data for L-1 ((Zn(H₂O)₃)₃[MnMo₉O₃₂]·4H₂O): *M_r* = 1860.72, trigonal, space group *R*32, *a* = 15.6460(4), *b* = 15.6460(4), *c* = 12.5656(7) Å, *V* = 2633.91(18) Å³, *Z* = 3, *ρ*_{calcd} = 3.480 g cm⁻³, *R*_{int} = 0.0223, final *R*1 = 0.0469 (*wR*₂ = 0.1406) for 1479 independent reflections [*I* > 2σ(*I*)]. Crystal data for D-1 ((Zn(H₂O)₃)₃[MnMo₉O₃₂]·4H₂O): *M_r* = 1860.72, trigonal, space group *R*32, *a* = 15.6562(4), *b* = 15.6562(4), *c* = 12.5757(7) Å, *V* = 2669.53(18) Å³, *Z* = 3, *ρ*_{calcd} = 3.472 g cm⁻³, *R*_{int} = 0.0230, final *R*1 = 0.0477 (*wR*₂ = 0.1427) for 1482 independent reflections [*I* > 2σ(*I*)]. Data were collected on a Bruker Smart-Apex CCD diffractometer with Mo Kα (λ = 0.71073 Å) at 293 K using the ω scan technique. Empirical absorption corrections were applied. The Flack parameters of 0.04(7) and 0.02(8) for L-1 and D-1 indicate that the absolute configurations are correct. CSD-418004 (L-1) and CSD-418005 (D-1) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49 7247 808 666; e-mail: crysdata@Wz-karlsruhe.de).

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