

Spontaneous resolution of a 3D chiral polyoxometalate-based polythreaded framework consisting of an achiral ligand†

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Two enantiomerically 3D chiral POM-based architectures have been constructed based on the achiral ligand bbi, $[V_{10}O_{26}]^{4-}$ polyoxoanion and mixed valence Cu(I/II) without a chiral auxiliary, and they represent the first examples of enantiomerically 3D POM-based compounds using achiral ligands.

The design and construction of chiral polyoxometalates (POMs) is currently of great interest because of their intriguing potential applications, for instance in medicine and asymmetric heterogeneous catalysis.¹ To date, only a limited number of chiral POM-based compounds have been observed, and most of them are discrete or low-dimensional structures.² The rational synthesis of chiral high-dimensional frameworks constructed from POM units is still a great challenge.

In general, chiral compounds can be obtained by two routes. The first method is based on the use of chiral species (chiral organic linkers or chiral metal complexes) as structure directing agents.³ This method has been developed for the formation of chiral POM-based compounds. Recently, thanks to the work of Pope, Hill, Yamase, and Kortz, much prominent work has been performed using this approach,⁴ and our group has obtained two chiral POM-based 3D architectures from this approach.⁵ One of them is constructed from $[BW_{12}O_{40}]^{5-}$ clusters and copper–proline acid complexes.^{5a} The chirality of the amino acid is transferred to the whole framework through the bonding of the metal centers to the POM cluster. The other was achieved using a typical Waugh heteropolymolybdate $[MnMo_9O_{32}]^{6-}$ as a chiral polyoxoanion building block,^{5b} thereby making the chirality of the polyoxoanion transfer to the whole framework.

The second approach to creating chiral compounds is based on the use of achiral ligands under spontaneous resolution without any chiral auxiliary,⁶ which yields a conglomerate. A conglomerate is a mechanical and racemic mixture of chiral crystals, in which each crystal is enantiopure and crystallizes in a chiral space group.⁷ Using this method to synthesize chiral POM-based 3D architectures is more difficult given the following considerations: (i) How is a chiral molecular unit generated from achiral components without a chiral auxiliary? (ii) It is much more difficult to achieve interlinking of the chiral molecular units into a homochiral

structure of higher dimensionality and to induce spontaneous resolution. (iii) How can the high symmetry of the POM be destroyed and the structure be crystallised in a non-centrosymmetric space group? Therefore, the search for suitable achiral organic molecules, metal cations, and POM building units to be applied in the construction of chiral 3D frameworks is one of the most challenging issues in synthetic chemistry and materials science.

Based on the previous literature,⁸ we chose the flexible ligand 1,1'-(1,4-butanediyl)bis(imidazole) (bbi) as a achiral ligand to synthesize chiral POM-based 3D frameworks. Fortunately, compounds $[Cu(bbi)_2V_{10}O_{26}][Cu(bbi)_2 \cdot H_2O]$ (L-1 and D-1) can be isolated by hydrothermal methods‡ and separated manually. Single-crystal X-ray diffraction analyses§ reveal that the structures of compounds L-1 and D-1 are enantiomers. Their unit-cell dimensions, volumes, related bond distances, and angles are only slightly different. To the best of our knowledge, they represent the first example of enantiomerically pure chiral 3D POM-based polythreaded frameworks which are constructed from achiral ligands under spontaneous resolution without any chiral auxiliary. Each of them contains one $[V_{10}O_{26}]^{4-}$ polyoxoanion, three kinds of Cu cations and six kinds of bbi ligands (bbi1, bbi2, bbi3, bbi4, bbi5 and bbi6) in the crystallographically independent unit (Fig. S1, S2†). The bbi3–6 ligands are imposed on the crystallographically twofold symmetry. The $[V_{10}O_{26}]^{4-}$ polyoxoanion is an oblate spherical mixed valence structure, which has eight vertex-sharing V(V)O₄ tetrahedra forming a cyclic octavanadate and two V(IV)O₅ tetragonal pyramids positioned above and below as crowns of cyclic octavanadate with V–O distances similar to those in the reported complexes (Fig. S3†).⁹ Due to the strong Jahn–Teller effect of the d⁹ electronic configuration,¹⁰ the Cu1(II) center adopts a distorted octahedral geometry which is completed by four nitrogen atoms from two bbi1 and two bbi2 ligands, and two terminal oxygen atoms from different $[V_{10}O_{26}]^{4-}$ polyoxoanions (Fig. S6a†), while Cu2(I) is linearly coordinated by two nitrogen atoms from the bbi3 and bbi4 ligands. Cu3(I) exhibits a similar coordination environment to Cu2(I) except that the two nitrogen atoms are from the bbi5 and bbi6 ligands. The bbi1 and bbi2 units act as bis-monodentate bridging ligands, and coordinate to Cu1 ions to generate a 2D waved (4,4) sheet which is pillared by $[V_{10}O_{26}]^{4-}$ polyoxoanions to extend to a distorted 3D α -Po topology framework (Fig. 1, Fig. S4†). It is interesting that there exists a flower-like subunit in which two bbi1 and two bbi2 ligands act as petals and the $[V_{10}O_{26}]^{4-}$ polyoxoanion acts as the stamen (Fig. S5†). This kind of connection mode results in the formation of two kinds of channels (A and B) along the *c* axis. Cu2 and Cu3

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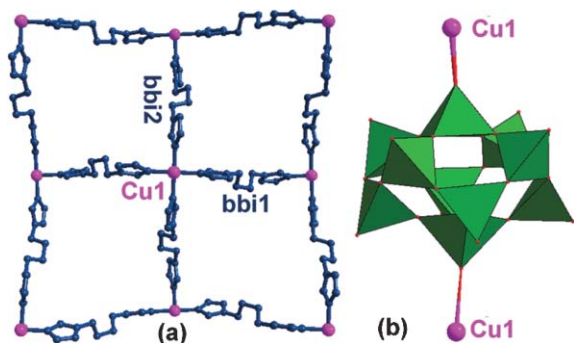


Fig. 1 (a) Ball-stick representation of the (4,4) sheet formed by bbi ligands and Cu(II). (b) Polyhedral and ball-stick representation of each $[V_{10}O_{26}]^{4-}$ polyoxoanion linking two CuI cations.

are coordinated by the bbi3 and bbi4, and bbi5 and bbi6 ligands respectively to form two kinds of distorted helical chains. Two Cu2–bbi chains pass through channel A, and two Cu3–bbi chains are inserted in channel B along the crystallographic *c* axis (Fig. 2). As a result, the unusual chiral 3D polythreaded framework has been formed, by two helical chains threading through a distorted α -Po skeleton (Fig. S7a†). Polythreaded structures which have been defined by Ciani and co-workers are characterized by the presence of closed loops, as well as of elements that can thread through the loops, and can be considered as extended periodic analogues of molecular rotaxanes and pseudorotaxanes.¹¹ A few coordination compounds exhibiting polythreaded network architectures have been reported.¹² However, a 3D chiral polyoxometalate-based polythreaded framework has not been observed. On further study of the structure, there are Cu–O interactions between Cu^I ions and two terminal oxygen atoms from the $[V_{10}O_{26}]^{4-}$ polyoxoanions (Fig. S6b†). So the overall structures of L-1 and D-1 are 3D (3,4,6)-connected frameworks based on Cu^I ions as three-connected nodes, $[V_{10}O_{26}]^{4-}$ polyoxoanions as four-connected nodes and Cu^{II} ions as six-connected nodes (Fig. S6†). The Schläfli symbols for L-1 and D-1 are $(6.8^2)_2(6^5.8)$ $(4^4.6^8.8^3)$ (Fig. S7b†).

Even though spontaneous resolution was discovered as early as in 1848 by Louis Pasteur,¹³ it is still a rare phenomenon and cannot be predicted *a priori* because the laws of physics determining the processes are not yet fully understood.¹⁴ What is the reason that L-1 and D-1 can be constructed from achiral bbi ligands and high symmetry $[V_{10}O_{26}]^{4-}$ polyoxoanions by spontaneous resolution upon crystallization without any enantiopure

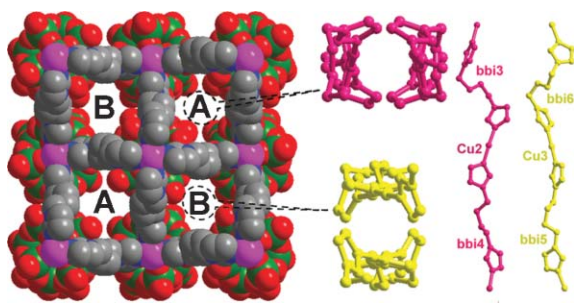


Fig. 2 Space-filling representation of the two kinds of channels in the α -Po framework (left), and view of the two kinds of Cu(I)–bbi helical chains in the channels along the different directions (right) in D-1.

chiral auxiliary? Further study into the nature of these intricate architectures reveals that the bbi ligands in these compounds adopt two conformations. The bbi1, bbi2, bbi4, and bbi5 adopt a TGT conformation, and the bbi3 and bbi6 adopt GTG conformation (T = *trans*, G = *gauche*, Fig. S2†). Each Cu^I is linked linearly by the bbi ligands with different GTG and TGT conformations to generate conformationally chiral chains with a C_2 axis (left-handed helices in L-1, right-handed helices in D-1) (Fig. 3a). In addition, $[V_{10}O_{26}]^{4-}$ polyoxoanions are linked by two Cu^{II} ions *via* covalent linkages and two Cu^I ions through Cu–O interactions (Fig. S6b†). The asymmetrical coordination mode without mirror or inversion symmetry between the $[V_{10}O_{26}]^{4-}$ polyoxoanions and the Cu cations not only destroys the symmetry of the $[V_{10}O_{26}]^{4-}$ polyoxoanions but also generates the $[Cu^II Cu^I_2 V_{10}O_{26}]_{\infty}$ chain with a 2-fold screw axis passing through the Cu^{II} ions and the center of the $[V_{10}O_{26}]^{4-}$ polyoxoanions (Fig. 8a†). Four distorted helical chains with conformational chirality are linked by the $[Cu^II Cu^I_2 V_{10}O_{26}]_{\infty}$ chain *via* Cu–O interactions, which are related by the 2-fold screw axis and hence of the same chirality. As a result, the POM-based chiral units $[Cu^II Cu^I_2 (bbi)_2 V_{10}O_{26}]_{\infty}$ are formed (left-handed in L-1, right-handed in D-1) (Fig. 3b, Fig. S8†). The adjacent POM-based chiral units are extended into the whole framework by the bbi1 and bbi2 ligands with the same conformation (TGT) bridging Cu^{II} cations (Fig. S9†). All chiral units are related by translation or 2-fold rotation, so the whole structure is homochiral and spontaneous resolution occurs. The generation of the crystals of L-1 and D-1 represents two new examples of induction and transfer of chirality in the absence of chiral auxiliaries, a progression from simple achiral species to homochiral chains, to POM-based homochiral units $[Cu^II Cu^I_2 (bbi)_2 V_{10}O_{26}]_{\infty}$ and finally to whole chiral crystals. Obviously, the twist of the bbi ligands induces the initial generation of the chirality of the distorted helical chains, and the asymmetrical coordination mode destroys the high symmetry of the POMs. Chiral preservation in the whole structure is achieved *via* non-covalent Cu–O interactions between the Cu^I ions and the $[V_{10}O_{26}]^{4-}$ polyoxoanions. The non-covalent interactions, such as Cu–O interactions, may play a crucial role in the process of spontaneous resolution.

The CD spectra in DMSO have been investigated and display strong Cotton effects at 234 and 258 nm for L-1, and 233 and

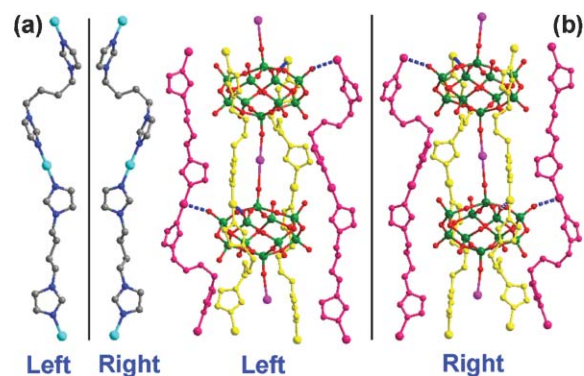


Fig. 3 (a) View of bbi–Cu(I) distorted helical chains (left-handed helix in L-1, right-handed helix in D-1). (b) Ball-stick representation of the chiral subunit $[Cu^II Cu^I_2 (bbi)_2 V_{10}O_{26}]_{\infty}$ (left in L-1, right in D-1; dashed lines represent Cu(I)–O interactions).

259 nm for D-1, respectively (Fig. S10–S11†). However, electro-spray ionization mass spectra of L-1 and D-1 in DMSO show that they decompose to some small fragments (Fig. S12†). The interesting results from the CD spectra indicate these small fragments retain their chirality, which may suggest there exist stable interactions among small fragments in solution.

In summary, we have prepared and characterized two enantiomerically 3D chiral POM-based architectures based on the achiral ligand bbi, $[V_{10}O_{26}]^{4-}$ polyoxoanion and mixed valence Cu(I/II) without a chiral auxiliary. To our knowledge, compounds L-1 and D-1 represent the first example of enantiomerically 3D POM-based compounds using achiral ligands, and they are also unique 3D chiral POM-based polythreaded frameworks which are constructed from two helical chains threading through the distorted α -Po skeleton. The successful isolation of this species not only provides an intriguing example of enantiomerically pure architectures but also may open up possibilities for synthesizing new chiral POM-based materials with particular functions by using achiral ligands.

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Notes and references

† Synthesis of compound 1: A mixture of NH_4VO_3 (0.117 g, 1 mmol), bbi (0.095 g, 0.5 mmol), $Cu(NO_3)_2 \cdot 3H_2O$ (0.121 g, 0.5 mmol) and H_2O (10 mL) was adjusted to approximately pH 5 with dilute Et_3N solution and hydrochloric acid and stirred for 1 h, and then transferred to and sealed in a 25 mL Teflon-lined stainless steel container, which was heated at 150 °C for 72 h and then cooled to room temperature at a rate of 10 °C h^{-1} . Black crystals of 1 were collected in 42.6% yield based on $Cu(NO_3)_2 \cdot 3H_2O$. Elemental analysis (%) calcd for compound 1: C, 25.35; H, 3.08; N, 11.83. Found: C, 25.41; H, 3.01; N, 11.89%. IR (cm^{-1}): 3121 (w), 1635 (m), 1522 (m), 1450 (w), 1278 (w), 1233 (w), 1104 (m), 890 (s), 828 (s), 655 (s).

§ Crystal data for $C_{40}H_{58}N_{16}Cu_3V_{10}O_{27}$ (L-1): orthorhombic, space group I_{222} , $M_r = 1895.04$, $a = 23.0670(10)$ Å, $b = 23.1760(10)$ Å, $c = 24.9480(9)$ Å, $V = 13337.2(9)$ Å³, $Z = 8$, $\mu = 2.353$ mm⁻¹, $D_c = 1.888$ Mg m⁻³, $F(000) = 7544$, $T = 293(2)$ K, 37072 reflections collected, 13213 unique with $R_{int} = 0.0596$, $R1 = 0.0539$, $wR2 = 0.1121$ ($I > 2\sigma(I)$), GOF = 1.045. Crystal data for $C_{40}H_{58}N_{16}Cu_3V_{10}O_{27}$ (D-1): orthorhombic, space group I_{222} , $M_r = 1895.04$, $a = 23.0670(14)$ Å, $b = 23.1760(14)$ Å, $c = 24.9480(14)$ Å, $V = 13337.2(9)$ Å³, $Z = 8$, $\mu = 2.353$ mm⁻¹, $D_c = 1.888$ Mg m⁻³, $F(000) = 7544$, $T = 293(2)$ K, 33818 reflections collected, 11790 unique with $R_{int} = 0.0841$, $R1 = 0.0549$, $wR2 = 0.1107$ ($I > 2\sigma(I)$), GOF = 1.006. Data collection was performed on a Bruker Smart Apex CCD diffractometer (Mo K α , $\lambda = 0.71073$ Å). Empirical absorption corrections were applied. The Flack parameters of 0.017(17) and 0.02(2) for L-1 and D-1 indicate that the absolute configurations are correct. CCDC 658057 (L-1) and CCDC 658056 (D-1). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b714413j

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