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Nanoscale Chiral Rod-like Molecular Triads Assembled from Achiral Polyoxometalates

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Chiral polyoxometalates (POMs), or chiral compounds containing POMs, have attracted particular attention in recent years,[1] due to their unique structures, remarkable properties, and potential applications in materials science, biology, pharmacy, and asymmetric catalysis.[2] Thanks to the prominent work of Pope, Hill, Yamase, Kortz, Wang, and other groups,[3−9] several synthetic strategies have now been developed to obtain chiral POM architectures and are summarized in an excellent review.[1] For example, one can construct chiral POM skeletons by bond length alteration, structure distortion, the formation of lacunae, replacement with other metals, or decorating with organic ligands to remove the symmetric center or mirror in POMs.[3,4] Another powerful method is directly introducing chiral functional groups including organic ligands, metal−organic moieties, or even cluster-based building blocks to the surface of POMs *via* chemical modification, or to their counterions.[5−9] The enantiopure crystals can be obtained via either enantioselective synthesis with enantiopure chiral species or spontaneous resolution upon crystallization without any chiral auxiliary. Recently, Hasenknopf et al. afforded a way to resolve racemic hybrid POMs by chiral recognition with peptides.[10] However, enantiomerically pure chiral POM crystals by the *covalent* assembly of achiral POM clusters is still rarely reported in the literature. Herein, we provide a method to synthesize enantiopure chiral POM nanorods, compounds **1** and **2** (Figure 1), by assembling achiral Lindqvist and Anderson anions into a triad *via* organic ligands with rotatable covalent bonds. Such chiral molecular nanorods have special interest in fabricating novel supramolecular assemblies and nanoarchitectures with unique physical properties, including ferroelectric and NLO properties.[11]

Inspired by the outstanding work of Hasenknopf, Gouzerh, and Cronin et al.,[12,13] we feel that POMs can be bridged *via* covalent functionalization with organic ligands,[14] in a more controlled manner, into various nanoarchitectures by a flexible synthetic strategy, in which the organic linker between the POMs is designed to be bifunctional. In this work, we utilized TRIS (tromethamine, $(HOCH_2)_3CNH_2$), in combination with Anderson-type POMs, to make POM building blocks with remote amino groups, which are easily bonded onto Lindqvist hexamolybdate anions to form imido derivatives.[15−17]

Compounds **1** and **2** are obtained conveniently by the well-developed DCC (DCC = *N*,*N*′-dicyclohexylcarbo-diimide) protocol to prepare organoimido-substituted POMs,[17] in which Anderson-type heteropolyoxomolybdates containing two pendant amino groups act as the imido-releasing reagents. When a mixture of $(Bu_4N)_2[Mo_6O_{19}]$, $(Bu_4N)_3[MMo_6O_{18}\{(OCH_2)_3CNH_2\}_2]$ ($M = Mn^{III}$, Fe^{III}), and DCC was refluxed in anhydrous acetonitrile at the molar ratio of 2:1:2, the organic-POM-segment-bridged hexamolybdate nanorod is formed by a one-step reaction, which essentially belongs to mono-organoimido-substituted derivatives. As we reported previously,[18] dumbbell-like POM-organic hybrid nanorods can be synthesized directly from the reaction of $(Bu_4N)_4[\alpha\text{-}Mo_8O_{26}]$ and aromatic diamine dihydrochlorides with DCC. Yet, by making use of POM clusters with remote amino groups, instead of common organic amines, as starting material, the present synthetic strategy extends the type of bridge between two hexamolybdates from simple organic compounds to organically derivatized POM clusters. This method can be applied especially to the assembly of hybrid organic−POM nanotriads.

Single-crystal X-ray diffraction studies show that both enantiopure compounds **1** and **2** are isolated by spontaneous resolution on crystallization in the absence of any outside chiral influence, which crystallize in chiral space group $P3_121$ and $P3_221$, respectively. Their cell parameters, related bond distances, and angles are almost the same, except for the difference of the central heteroatom in Anderson-type heteropolyoxometalates and that they were two kinds of chiral crystal grains. In both crystals, there are a half triad anion of $[Mo_6O_{18}NC(OCH_2)_3MMo_6O_{18}(OCH_2)_3CNMo_6O_{18}]^{7-}$ ($M = Mn^{III}$ (**1**), Fe^{III} (**2**)), three and a half cations of $(Bu_4N)^+$, and one acetonitrile solvent molecule in the asymmetric unit.

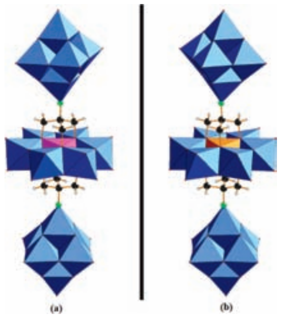

Figure 1. Combined polyhedral and ball-and-stick representation of cluster anions of (−)-**1** (a), (+)-**2** (b): Mn, purple; Fe, orange; N, green; O, red; C, black; Mo, blue.

As shown in Figure 1, two monosubstituted hexamolybdates are bridged by one diimido ligand of an Anderson-type POM to form a chiral triad with crystallographically imposed C_2 symmetry. Both of the chiral triads have similar features to those of reported organoimido hexamolybdates.[15−19] The Mo−N bonds show substantial triple-bond character, proven by the short bond length (1.71 Å for **1** and 1.72 Å for **2**) and nearly linear Mo−N−C angle (178.55° for **1** and 177.11° for **2**).[20] The structure of the Anderson segment of compounds **1** and **2** is the same with that of starting material $(Bu_4N)_3[MMo_6O_{18}\{(OCH_2)_3CNH_2\}_2]$. Two central oxo atoms and two nitrogen atoms of the two organoimido-substituted hexamolybdate clusters are almost located on the axis line of the triad through the central heteroatom of the Anderson cluster, which is almost perpendicular to the two equatorial Mo_4O_4 planes of two hexamolybdate clusters and the Mo_6M plane ($M = Mn^{III}$, Fe^{III}) of the Anderson cluster. These two equatorial Mo_4O_4 planes are nearly

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parallel to the Mo_6M plane with a dihedral angle of 3.5° for **1** and 3.4° for **2**, respectively. Therefore, the whole anion cluster can be viewed as a nanorod by the assembly of two types of POMs with a length of *ca*. 2.77 nm.

The highest possible symmetry of the triad nanorod is C_{2h}; however, due to the asymmetric rotation about the C−N single bond, two hexamolybdate units are in fact staggered relative to one another along the long axis of the nanorod with an intermediate stagger (dihedral) angle of *ca*. 21°, resulting in their symmetry lowering to C_2. Thus the structure is chiral, and due to increased hindrance of the bulky and heavy POMs to rotation at the C−N single bond, the chiral conformation is stabilized, and spontaneous resolution occurs during the crystallization process. Apparently, the chirality genesis of such nanorods is similar to that of the well-known binaphthalene systems.[21] The chiral triads in the crystal are arranged around a 3-fold screw axis and form a helical chain-like pattern along the *c* axis (Figure 1S).

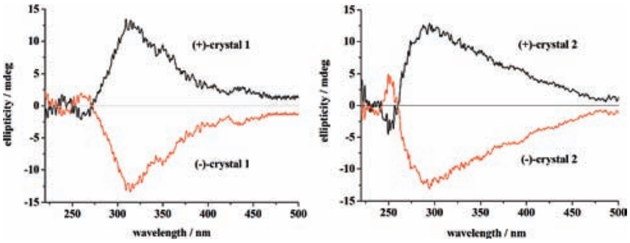

Figure 2. Solid state CD spectra of two kinds of enantiopure crystal grains of **1** (left) and **2** (right) in KBr. A mixture of a single crystal (∼100 μg) and 100 mg of KBr was ground well and compacted into a disk with a radius of 10 mm for the measurement.

To examine the chiroptical of compounds **1** and **2**, the solid-state circular dichroic (CD) spectra of compounds **1** and **2** were determined by mixing enantiopure crystal grains in KBr. These enantiomers show considerable optical activity in the solid state and afford approximately mirror-image CD spectra of one another (Figure 2). The crystals are designated as (+) and (−) crystals by the sign of ellipticity at $\lambda \approx 317$ nm for **1** and 313 nm for **2**, respectively.

Infrared spectra of the title compounds show similar characteristic absorption bands of mono-organoimido hexamolybdates and Anderson-type heteropolyoxomolybdates. The very strong peaks located at 948 and 788 cm^{-1} for **1** and at 950 and 791 cm^{-1} for **2** are assigned to the stretching vibrations of the $Mo-O_t$ groups and the $Mo-O_b-Mo$ of $[Mo_6O_{18}N]$, which are shifted to lower wavenumbers compared to that of the parent hexamolybdate cluster owing to the modification by one organoimido ligand. The $Mo-O_t$ and $Mo-O_b-Mo$ stretching vibrations of $[MMo_6O_{18}\{(OCH_2)_3C\}_2]$ are found at 943, 922, and 903 cm^{-1} in **1** and at 942, 923, and 904 cm^{-1} in **2**, respectively, which are almost the same as that of the parent Anderson-type heteropolyoxomolybdates. In addition, the strong shoulder peak near 975 cm^{-1} around the $Mo-O_t$ stretching is attributed to the Mo−N bond stretching vibration,[20] which is typical for mono-organoimido substitution.[22] Both of the C−O stretching vibrations of **1** and **2** appear at 1064 cm^{-1}, which have an obvious blue shift. It implies that these C−O bonds are stronger than that of the parent Anderson-type heteropolyoxomolybdates owing to the inductive effect of the incorporated electron-withdrawing hexamolybdate, which is consistent with the crystal structure data of shortened C−O bond lengths.

In summary, we have successfully synthesized two nanoscale POM-organic hybrid chiral molecular rods that are assembled from two types of POMs, Lindqvist and Anderson, through strong covalent linkages with a bifunctional organic ligand. The enantiopure crystals of these compounds have been obtained by spontaneous resolution upon crystallization in the absence of any chiral source. The present work provides a new approach to make chiral nanoarchitectures deriving from achiral POMs in a controllable manner. Potential applications of such chiral nanorods in asymmetric catalysis as well as ferroelectric and NLO materials are under study in our laboratory.

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Supporting Information Available: Synthetic details, characterization data, including elemental analysis, ESI-MS, IR, UV/vis, ^1H NMR, solid CD, and X-ray crystallography with CIF files, for compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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