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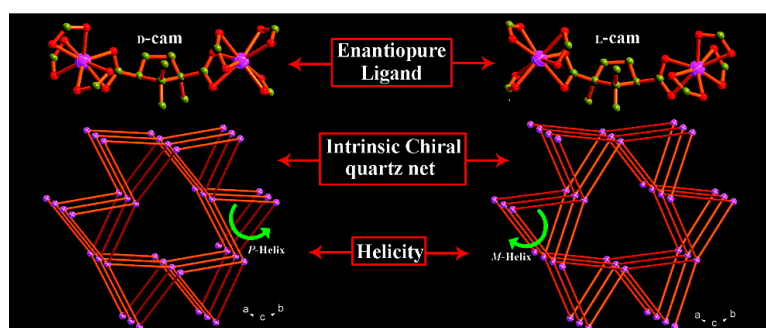
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Integrated Molecular Chirality, Absolute Helicity, and Intrinsic Chiral Topology in Three-Dimensional Open-Framework Materials

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Homochirality and helicity are two essential features of life and are integral to various biological functions. Biopolymers such as proteins and DNA have acquired a definite helical sense (e.g., right-handed α-helix) associated with the chirality of their molecular building blocks (e.g., L-amino acids or D-sugars). Such biopolymers exhibit dual homochiral features with both molecular chirality and absolute helicity (Scheme 1).

Helicity is also common in the nonliving world, as evidenced by the ubiquity of quartz. There is even speculation that biological homochirality may be linked to the interactions between biomolecules and resolved inorganic chiral solids such as quartz.[1] Unlike 1-D polymeric DNA, intertwined helices in quartz are embedded in a 3-D net that is intrinsically chiral.[2] Also unlike biopolymers such as DNA, quartz does not possess a chiral molecular building block and is known to exist in both D- and L-forms. Similarly, several metal−organic or chalcogenide materials are known to adopt the quartz topology.[3] Prior to this work, the bulk products of such quartz-type materials tended to be racemic and the handedness of the helix could not be controlled to be homohelical.

Materials with an intrinsically chiral topology[2] such as quartz and zeolite β have attracted interest for decades because of their obvious potential in enantioselective applications. However, the current inability to prepare zeolite β with reasonable enantiomeric excess prevents its industrial application in chiral catalysis.[4] There is clearly an urgent need to prepare homochiral framework materials with an intrinsically chiral topology.[2]

Recent successes with metal−organic frameworks (MOFs) have resulted in some very interesting chiral materials.[5−8] With few exceptions,[9] bulk homochiral MOFs contain enantiopure molecular building blocks (e.g., chiral carboxylates) with a framework topology (e.g., diamond) that is not intrinsically chiral,[6−8] a situation opposite to that in quartz or zeolite β. Despite decades of research, there are few examples of 3-D open-framework materials in which an intrinsically chiral topology[2] (e.g., quartz and zeolite β) coexists with the chirality of enantiopure framework building blocks. It is of great interest to explore 3-D framework materials that integrate molecular chirality and intrinsic chiral topology; not only could

Scheme 1. Unusual Integrated Homochirality Features
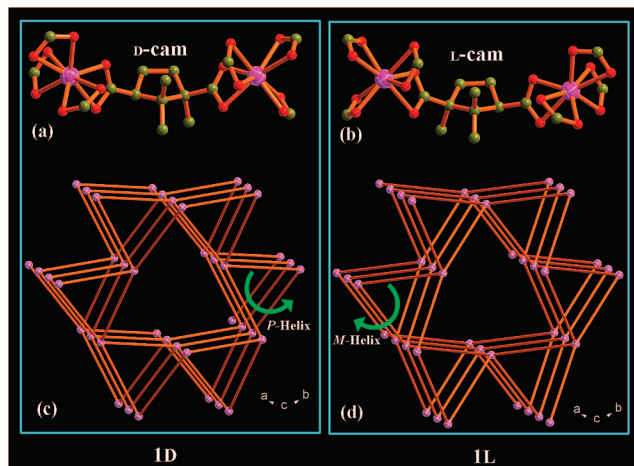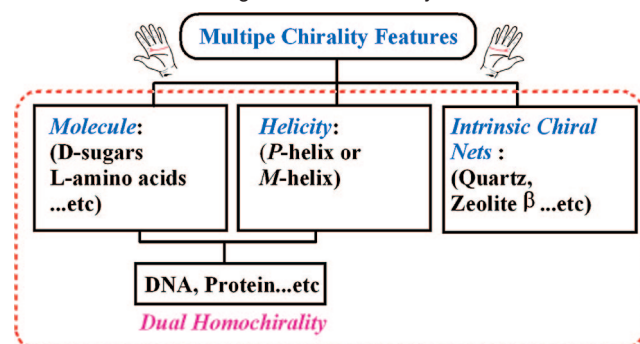
Figure 1. Absolute helicity control and coexistence of 3-D chiral quartz net (c and d; here the balls represent In^{3+} centers and the rods represent camphorate ligands) with enantiopure chiral building blocks (a and b) in **1D** and **1L**, respectively.

such study lead to functional framework materials for efficient chiral recognition processes, but it also may help to provide fresh opportunities for better understanding the origin of asymmetry in the living system.

Here we describe unusual integrated homochirality features in six new 3-D framework materials (**1D**, **1L**, and **2−5**) containing enantiopure building blocks embedded in intrinsically chiral topological nets, of which quartz net is the most well-known. Each material has three homochiral features: 3-D intrinsically homochiral net,[2] homohelicity, and enantiopure molecular chirality (Scheme 1). It is shown here that the absolute helicity can be controlled by the chirality of molecular building blocks.

In **1D**, **1L** and **2**, the enantiopure monomers coexist with the 3-D intrinsically chiral topology of quartz (denoted qtz) net. For each structure, the basic coordination chemistry of the In^{3+} site is four-connected despite its eight-coordinate geometry, because each In^{3+} site is bonded to four carboxylate ligands and each carboxylate group chelates to just one In^{3+} site (Figure 1a,b). The negative framework $[In(cam)_2]_n^{n-}$ in each crystal (Figure 1c,d) is balanced by guest organic ions (Table 1).

A striking feature in **1D** and **1L** is the helicity induction effect of the enantiopure ligands, resulting in the formation of the homohelical quartz topology. **1D** and **1L** are built from enantiopure D- and L-camphoric acid, respectively. In both structures, the absolute helicity is controlled by the handedness of the enantiopure ligand. D-Camphorate leads to the right-handed (*P*-helix) quartz net in **1D** (denoted *P*-D form), whereas L-camphorate leads to the left-handed (*M*-helix) quartz net in **1L** (denoted *M*-L form). The chirality and helicity of compound **1D** are comparable to DNA, because both adopt the *P*-D form.

Table 1. Crystal Data and Refinement Results

	formula[a]	space group	a (Å)	b (Å)	c (Å)	$R(F)$	Flack param	chiral nets[b]	helicity[c]
1D	(TMA)[In(D-cam)$_2$]·2H$_2$O	$P3_121$	12.7624(2)	12.7624(2)	17.6291(5)	0.0495	−0.01(7)	qtz	*P*-helix
1L	(TMA)[In(L-cam)$_2$]·2H$_2$O	$P3_221$	12.9913(3)	12.9913(3)	17.3911(1)	0.0688	0.05(9)	qtz	*M*-helix
2	(choline)[In(D-cam)$_2$]·2H$_2$O	$P3_121$	12.8708(1)	12.8708(1)	17.2433(4)	0.0513	−0.02(6)	qtz	*P*-helix
3	Co(D-Cam)$_{1/2}$(bdc)$_{1/2}$(tmdpy)	$P3_121$	10.4498(5)	10.4498(5)	31.896(2)	0.0457	0.01(4)	qzd	*P*-helix
4	Ni(D-cam)(H$_2$O)$_2$	$P2_12_12_1$	7.2182(7)	12.175(1)	14.182(2)	0.0454	0.00(4)	srs	*M*-helix
5	Mg(L-ma)(H$_2$O)$_2$·(H$_2$O)	$P4_3$	7.943(1)	7.943(1)	12.8125(2)	0.0460	0.10(6)	srs	*M*-helix

[a] D-H$_2$Cam = D-camphoric acid; bdc = 1,4-benzenedicarboxylate; tmdpy = 4,4′-trimethylenedipyridine; L-H$_2$ma = L-malic acid; TMA = (CH$_3$)$_4$N$^+$; choline = [(CH$_3$)$_3$NCH$_2$CH$_2$OH]$^+$. [b] For definitions of three-letter abbreviations, see Reticular Chemistry Structure Resource (http://rcsr.anu.edu.au/). [c] *M* = minus (left-handed) helicity; *P* = plus (right-handed) helicity.
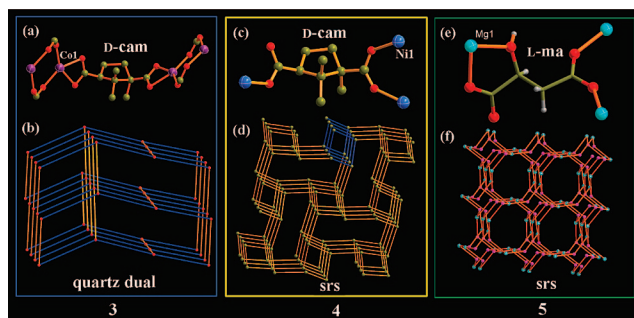
Figure 2. Coexistence of the enantiopure building block (a) and chiral qzd net (b) in **3**, and of the enantiopure building block (c and e) and chiral srs net (d and f) in **4** and **5**.

In addition to the chiral quartz type, other intrinsically chiral nets (quartz dual and srs) have also been made in this work by using D-camphoric acid (D-cam) or L-malic acid (L-ma) (compounds **3**−**5**). In **3**, the enantiopure building blocks coexist with the 3-D homochiral topology of the quartz dual (denoted qzd, maximum symmetry $P6_222$) net. The framework of **3** is built by cross-linking dinuclear cobalt sites with two different carboxylate linkers: chiral D-cam ligands and achiral 1,4-benzenedicarboxylate (BDC) ligands (Supporting Information, Figure S3). Each carboxylate group of the BDC ligand bridges two symmetry-related Co sites to form a linear chain. Unlike the BDC ligand, in which each carboxylate group bridges two Co sites, each carboxlyate group of the D-cam ligand chelates to only one cobalt site (Figure 2a). In this mode, the D-cam ligands link the dinuclear Co units into a right-handed 3_1 helix along the c axis (Supporting Information, Figure S4b). The linear BDC−Co chains and helical D-cam−Co 3_1 chains share the common dinuclear cobalt unit, resulting in the formation of a 3-D framework (Figure 2b; Supporting Information, Figure S5) with the dinuclear Co unit serving as the planar four-connected node.

In **4** and **5**, the enantiopure ligands (D-cam in **4** and L-ma in **5**) coexist with the 3-D intrinsically chiral topology of the (10,3)-a (also denoted srs, maximum symmetry $I4_132$) net.[10,11] In **4**, the octahedral Ni centers are doubly linked by one μ_2-aqua ligand and one μ_2-bridging carboxylate group from the D-cam ligand into a 1-D chain (Supporting Information, Figure S7a). Two remaining sites of each octahedral Ni site are occupied by a terminal H$_2$O ligand and one O atom from the monodentate carboxylate group of a bridging D-cam ligand (Figure 2c). The above 1-D Ni−carboxylate chain is further linked to four neighboring chains by the chiral five-rings of the D-cam ligands, to generate a 3-D homochiral framework with srs topology (Figure 2d; Supporting Information, Figure S7). In this srs net, all helices exhibit the same left-handedness (denoted as -γ*).[11]

In **5**, both metal center and L-ma ligand act as three-connected nodes (Figure 2e), although the Mg^{2+} center is six-coordinate through coordination to four oxygen atoms from three L-ma ligands and two terminal aqua ligands. Each L-ma ligand links three Mg^{2+}

centers, leading to the formation of the 3-D homochiral [Mg(L-ma)(H$_2$O)$_2$]$_n$ framework with srs topology (Figure 2f; Supporting Information, Figure S8). Along the c axis, there are 1-D channels filled by the guest water molecules. Here, the L-ma ligands induces absolute left-handed helicity in the srs net and controls the homochirality of the srs net (-γ*).

In conclusion, we report here a series of 3-D open-framework materials with unusual integration of molecular chirality, absolute helicity, and 3-D intrinsic chiral net. The helicity of the intrinsically chiral net can be dictated by enantiopure framework building units, in a manner mimicking the chirality−helicity relationship in biopolymers. Three-dimensional framework materials with integrated homochiral features have the potential for enhanced chiral recognition and enantioselectivity. The exploration of such multi-chirality materials and chirality−helicity relationship could lead to new insights into the generation and control of helicity and homochirality in both solid-state materials and biopolymers.

Supporting Information Available: Experimental details, additional crystallographic figures, TGA diagram, magnetic properties of **3**, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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