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Chiral Frameworks

Chiralization of Diamond Nets: Stretchable Helices and Chiral and Achiral Nets with Nearly Identical Unit Cells**

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Current interest in homochiral solids is rapidly expanding because of their potential applications in enantioselective processes.[1–7] For inorganic oxides such as zeolites in which the basic structural building units such as $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ or secondary building units such as the double four-membered rings in $[Si_4Al_4O_{16}]^{4-}$ are achiral, the chirality must come from the spatial organization (usually helices) of achiral units. Zeolite β (polymorph A) is a rare chiral porous aluminosilicate, but its pure enantiomer has not yet been prepared because of the stacking disorder.[8] The desire to create materials of the zeolite β type has motivated researchers to use chiral molecules (such as amines[9] or metal complexes[10]) as templates to induce the chirality. However, chiral species used for this purpose tend to racemize under hydrothermal conditions or have a tendency to direct the synthesis of low-dimensional structures.

Recent successes with metal–organic framework materials (MOFs)[11] have opened up new routes towards the synthesis of homochiral solids, even from achiral precursors.[12] Many MOFs have been found to adopt framework topologies commonly known in simple inorganic solids.[13] Unfortunately, the most common chiral net (quartz) is rarely adopted by these framework solids, whereas the achiral diamond net frequently occurs. Considering the ubiquity of the diamond net, a method for its conversion into the chiral net should be of general interest. Furthermore, the method developed for *chiralization* of the diamond net may be extensible to other four-connected nets such as those represented by zeolites.

Homochiral solids can be constructed from enantiopure ligands.[1–5,14–16] However, despite intensive research on chiral framework materials, homochiral 3D frameworks with the four-connected topology remain rare. Furthermore, comparative studies on the structure-directing effects of both enantiopure and racemic ligands should be of particular interest, because such studies can uncover important factors regulating the crystallization process of homochiral solids. Because the crystallization processes involving enantiopure and racemic ligands have fundamental differences owing to the differing symmetry requirements, it can be expected that the homochiral 3D frameworks prepared from enantiopure ligands usually have different topological features from those prepared from the corresponding racemate. This work, however, offers a rare example of homochiral and achiral solids that have nearly identical unit cells and crystal structures.

Herein we report five new homochiral materials and one achiral 3D material synthesized from D- or DL-camphoric acid (D- or DL-H_2cam) and 4,4′-trimethylenedipyridine (tmdpy). These materials are prepared by employing strategies (such as lower temperature and shorter reaction time, or higher temperature and longer reaction time) that allow the formation of crystals with different degrees of thermodynamic stability. These materials exhibit three distinct topological features: homochiral threefold interpenetrating diamond net (crystals **1**, **2**, **3**, **6**), homochiral fourfold interpenetrating diamond net (crystal **4**), and achiral fourfold interpenetrating diamond net (crystal **5**; see Table 1 for summary of compound formulas and crystallographic parameters).

The flexibility of helices allows the single-crystal to single-crystal transformation from [Cd(D-cam)(tmdpy)]·2 H_2O (**1**) to anhydrous α-[Cd(D-cam)(tmdpy)] (**2**) at 100 °C and subsequent polymorphic displacive phase transition into β-[Cd(D-cam)(tmdpy)] (**3**) at 140 °C. Two homochiral solids, β-[Cd(D-cam)(tmdpy)] (**3**) and γ-[Cd(D-cam)(tmdpy)] (**4**), have the same topological type and yet contain lattice interpenetration of a different order. An unusual discovery is that the chirality of the 3D framework can be readily switched between chiral (γ-[Cd(D-cam)(tmdpy)] (**4**), space group $P2_1$) and achiral ([Cd(DL-cam)(tmdpy)] (**5**), space group $Pna2_1$) forms with negligible changes in all six unit cell parameters.

In all six structures, the basic coordination chemistry is the same. Each M^{2+} site is four-connected despite its octahedral coordination, as each M^{2+} atom is bonded to two tmdpy ligands and two D-cam ligands. Each D-cam ligand bridges two M^{2+} sites (similar to dicoordinate oxygen sites in zeolites; Figure 1 a–c, Figure 2 a, b). Such structural features are characteristic of the zeolite-type net with the AX_2 formula. Therefore, all materials reported herein possess the four-connected 3D framework. Each sublattice can be represented topologically as the diamond net (Figure 1 and Figure 2).

Among these six phases, **1**, **2**, **3**, and **6** exhibit similar chiral diamond nets, incorporating stretchable helical substructures. All four phases crystallize in the chiral space group $P2_12_12_1$ with one M^{2+} (Cd or Zn) atom, one D-cam ligand, and one tmdpy ligand in the asymmetric unit (Table 1). Each D-cam ligand bridges two M^{2+} atoms to form a 2_1 helix along the *c* axis (Figure 1 a–c). The flexibility of the chiral framework is

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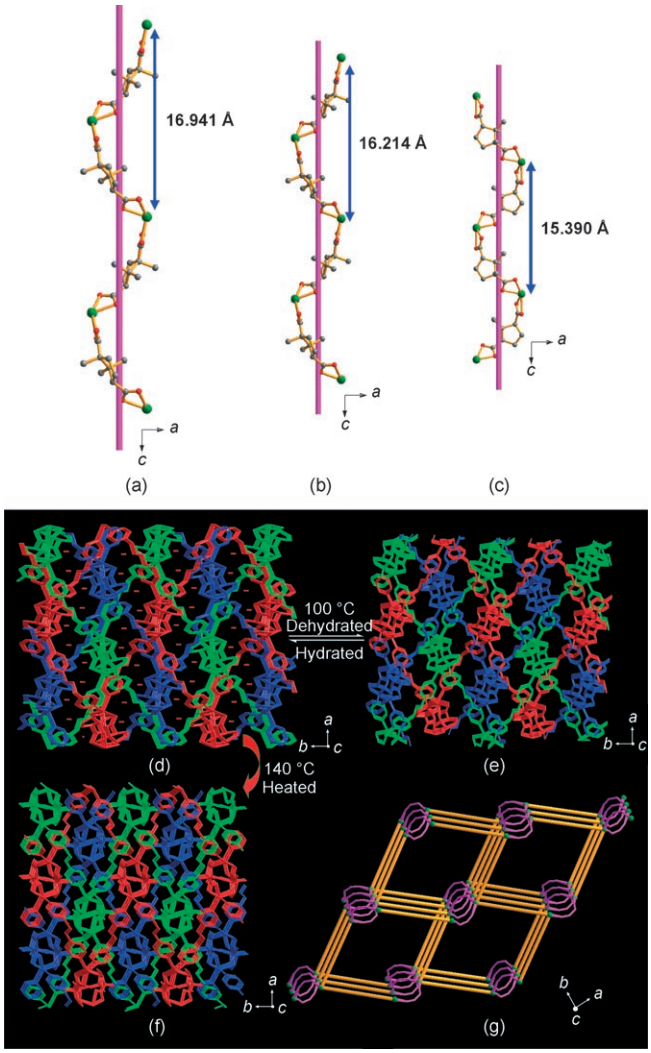

Figure 1. Top: Ball-and-stick diagrams showing the progressive contraction of the 2_1 helix from **1** (a) to **2** (b) to **3** (c). O red, C gray, Cd green. Bottom: Topological diagrams showing the phase transformation from **1** (d) to **2** (e) and from **1** (d) to **3** (f). The simplified topological representation of the chiral diamond net in **1**, **2**, **3**, and **6** is shown in (g). In (d), (e), and (f), blue, red, and green represent three interpenetrating lattices.

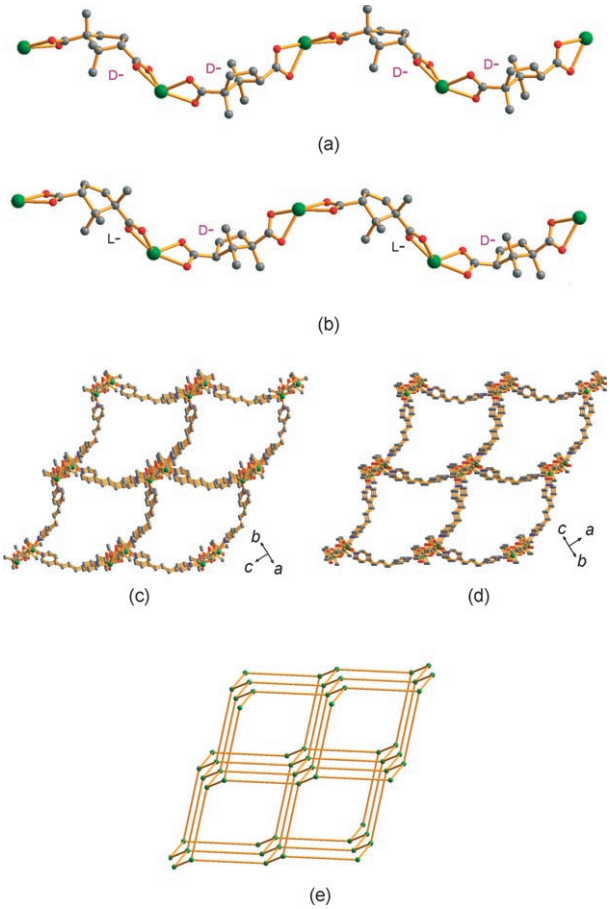

Figure 2. Ball-and-stick diagrams showing two chains in homochiral **4** (a) and achiral **5** (b). The 3D framework of **4** and **5** is shown in (c) and (d), respectively. The simplified topological representation of the diamond net in **4** and **5** is shown in (e). O red, C gray, Cd green.

shown by the separation between adjacent tetrahedral nodes that are closely associated with the compression or stretching of the helices during phase transformations. The helical chains are further linked through tmdpy to generate a 3D framework (Figure 1 d–f).

The hydrated phase (**1**) was synthesized by the diffusion process at room temperature. The α-[Cd(D-cam)(tmdpy)] phase (**2**) was obtained by single-crystal to single-crystal transformation of the hydrated phase (**1**) heated at 100 °C. The loss of two water molecules from **1** to **2** leads to a 4.3 % shrinkage of the helices and a 2.8 % decrease in the volume of the unit cell.

The X-ray powder diffraction shows that the α phase (**2**) can undergo a displacive phase transition to give **3**, accompanied by an additional 5.1 % shrinkage of the helices and 3.6 % decrease in the unit cell volume. From **1** to **3**, the total contraction of the helices is as large as 1.6 Å, more than 9 % of

Table 1: Crystallographic data and refinement results.

	Formula	Space group	*a* [Å]	*b* [Å]	*c* [Å]	*β* [°]	*R*(*F*)	Flack parameter
1	[Cd(D-cam)(tmdpy)]·2 H_2O	$P2_12_12_1$	9.8411(2)	14.5031(2)	16.9409(3)	90	0.0314	−0.04(2)
2	[Cd(D-cam)(tmdpy)]	$P2_12_12_1$	9.7425(10)	14.8831(18)	16.2144(19)	90	0.1135	−0.03(3)
3	[Cd(D-cam)(tmdpy)]	$P2_12_12_1$	11.004(3)	13.376(3)	15.390(4)	90	0.0275	−0.05(2)
4	[Cd(D-cam)(tmdpy)]	$P2_1$	13.2420(6)	12.5161(7)	14.2033(7)	90.00(2)	0.0396	−0.01(4)
5	[Cd(DL-cam)(tmdpy)]	$Pna2_1$	14.1592(3)	13.2142(2)	12.5186(3)	90	0.0655	0.10(9)
6	[Zn(D-cam)(tmdpy)]·H_2O	$P2_12_12_1$	9.736(5)	14.977(8)	16.268(9)	90	0.0713	0.03(3)

the helical pitch. Thus, the two-step phase transition is related to the flexibility of the homochiral framework.

Hydrothermal synthesis of **3** and **4** demonstrates the effect of relative crystal stability over the crystallization process. The cell volume of **4** is 3.9% larger than that of polymorphic **3**, suggesting that **4** may be thermodynamically less stable. Indeed, the time-dependent synthetic studies suggest that under the same reaction conditions, the shorter reaction time (36 h) leads to **4** whereas the longer reaction time gives rise to **3**. Furthermore, the temperature-dependent synthesis shows that **4** is favored at lower temperature (100 °C) whereas **3** is favored at higher temperature (160 °C).

Unlike the homochiral threefold diamond net in **1**, **2**, **3**, and **6**, structures **4** and **5** have fourfold interpenetrating frameworks with chiral and achiral diamond nets, respectively. Compound **4** was prepared from enantiopure D-cam and crystallized in the chiral space group $P2_1$ whereas **5** was prepared from racemic DL-cam and crystallized in achiral and polar space group $Pna2_1$. A polar group such as $Pna2_1$ contains one or more polar directions whose opposite ends are not related by symmetry. A polar group can contain mirror symmetry, but does not have a center of inversion. It is therefore a subset of non-centrosymmetric groups. In comparison, a chiral (that is, enantiomorphous) group can not have any inversion axes including mirror symmetry and a center of inversion.

For **4**, a total of five crystals were randomly picked for single-crystal X-ray diffraction. The Flack parameters are −0.01(4), 0.03(5), 0.06(5), 0.05(6), and 0.06(6), respectively, when the same set of positional coordinates are refined against five *hkl* data sets, which indicates that there is no racemization of the enantiopure ligand during the hydrothermal synthesis.

The most interesting observation about **4** and **5** is the nearly identical unit cell parameters between the chiral **4** and achiral **5** forms. This demonstrates that it is possible to replace every other enantiopure D-cam ligand with the opposite L-cam ligand and yet still maintain the same crystal structure. There is essentially no change in all six unit cell parameters (cell volume change $< 0.5\%$). It is worth noting that crystals obtained from enantiopure ligands and racemates generally have differing crystal structures because of the differing symmetry requirements (that is, forbiddance of inversion axes in homochiral crystals). To our knowledge, there is no prior example of homochiral and achiral 3D four-connected framework solids with nearly identical unit cell parameters.

Because homochiral **4** and achiral **5** have essentially identical unit cell constants and crystal structures, their unambiguous identification through X-ray powder diffraction proved to be impossible. In fact, it is also not possible to distinguish them by using single-crystal X-ray diffraction without a full data collection because of the near identicalness of the unit cell constants. Fortunately, **4** and **5** can be readily distinguished through the full data analysis. Despite the orthorhombic metric symmetry of **4**, the intensity data for **4** show monoclinic symmetry ($R_{int} = 3.4\%$ for the monoclinic cell with 12.516 Å as the *b* axis and $R_{int} > 19\%$ when assuming orthorhombic symmetry or monoclinic symmetry with two other choices of the *b* axis.). In comparison, the intensity data for **5** shows true orthorhombic symmetry ($R_{int} = 4.1\%$). The final confirmation of structural differences between **4** and **5** comes from full-matrix refinements.

In conclusion, a total of five homochiral materials and one achiral 3D framework material have been prepared by matching synthetic conditions with the relative stability of crystalline phases. The structural variations in these phases are related to the flexibility of the helices. It is shown that the achiral diamond net can be chiralized by using enantiopure chiral ligands as linkers between tetrahedral nodes. The coexistence of the achiral and homochiral diamond-type structures with essentially identical unit cell parameters raises an intriguing prospect about the possible direct conversion of achiral nets into homochiral nets through judicious ligand design and substitution.

Experimental Section

1: A solution of tmdpy (0.0510 g) in ethanol (4 mL) was layered onto a solution of $Cd(NO_3)_2{\cdot}4H_2O$ (0.151 g), Na_2CO_3 (0.0258 g), and D-camphoric acid (0.0570 g) in distilled water (5 mL). Slow diffusion over several days yielded colorless crystals.

2: A single crystal of **2** was obtained by heating a single crystal of **1** at 100 °C for 10 min in air.

3: $Cd(NO_3)_2{\cdot}4H_2O$ (0.1545 g), Na_2CO_3 (0.0518 g), tmdpy (0.1023 g), D-camphoric acid (0.1075 g), and distilled water (8.0229 g) were mixed in a 23-mL teflon cup, and the mixture was stirred for 20 min. The vessel was then sealed and heated at 140 °C for 3 days. The autoclave was allowed to cool to room temperature. Transparent colorless crystals were obtained in 78% yield. Compound **3** can also be synthesized at a higher temperature (160 °C) over 3 days. Alternatively, a polycrystalline sample of **3** can be prepared by heating crystals of **1** in air at 140 °C for 20 min.

4: $Cd(NO_3)_2{\cdot}4H_2O$ (0.1453 g), Na_2CO_3 (0.0502 g), tmdpy (0.0983 g), D-camphoric acid (0.0995 g), and distilled water (8.2459 g) were mixed in a 23-mL teflon cup, and the mixture was stirred for 20 min. The vessel was then sealed and heated at 140 °C for 36 h. The autoclave was allowed to cool to room temperature. Colorless crystals were obtained in 56% yield. Compound **4** can also be prepared at a lower temperature (100 °C) over 2 days.

5: This phase was synthesized in an analogous procedure to **4** except that DL-camphoric acid was used in place of D-camphoric acid. $Cd(NO_3)_2{\cdot}4H_2O$ (0.1503 g), Na_2CO_3 (0.0495 g), tmdpy (0.0992 g), DL-camphoric acid (0.10033 g), and distilled water (8.3002 g) were mixed in a 23-mL teflon cup, and the mixture was stirred for 20 min. The vessel was then sealed and heated at 140 °C for 36 h. The autoclave was allowed to cool to room temperature. Colorless crystals were prepared in 85% yield.

6: $Zn(NO_3)_2{\cdot}6H_2O$ (0.1535 g), Na_2CO_3 (0.0487 g), tmdpy (0.1003 g), D-camphoric acid (0.1023 g), and distilled water (8.0233 g) were mixed in a 23-mL teflon cup, and the mixture was stirred for 20 min. The vessel was then sealed and heated at 140 °C for 72 h. The autoclave was allowed to cool to room temperature. Colorless crystals were obtained in 64% yield.

CCDC-641511–641516 (**1**–**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

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