Absolute helicity induction in three-dimensional homochiral frameworks†

Jian Zhang and Xianhui Bu*

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Three Co(II) isomers assembled from D-, or L-, or DL-camphorate together with achiral isonicotinate exhibit a clear relationship between chirality and helicity even though chiral molecules are not in the backbone of the helix: the absolute sense of helix made of achiral components is controlled by chains of metal and enantiopure chiral ligands running perpendicular to helix in two enantiomeric forms.

Helicity and homochirality are intimately associated with the living processes even though their origin remains unclear.[1] Enzymes, nucleic acids, and other biopolymers made up of L-amino acids or D-sugars *etc.* have acquired a definite handedness.[2] The research on the relationship between chirality of molecular building blocks and helicity of polymeric structures could ultimately lead to a better understanding on the origin of asymmetry in living systems.

Chirality and absolute helicity are often closely linked with each other in the same structure, although they are two distinct concepts.[3] Chirality includes molecular chirality (molecules with chiral structures) and spatial chirality (resulting from crystallization-based spatial organization of molecular building blocks) whereas helicity is a special form of one-dimensional chirality. The control of the absolute helicity is well-known in 1-D polymers such as DNA in which the handedness of D-sugars leads to the right-handed helicity.

Crystalline porous materials have undergone tremendous development in recent years.[4–8] In particular, homochiral framework materials have attracted a significant amount of interest because of their potential applications in enantioselective catalysis, separation *etc.*[9–14] Recently developed metal–organic framework materials (MOFs) have shown great promise for the synthetic design of homochiral framework materials because it is possible to take advantage of the molecular chirality of organic components, in addition to the spatial chirality that often results from the self-assembly-based process.[9a] In addition to their potential enantioselective applications, one particular reason we are interested in homochiral MOFs is that they can integrate both molecular chirality and absolute helicity, in a way that mimics the chiral and helical features of well-known biopolymers such as DNA. It is felt that the integrated chiral and helical features of MOFs may provide fresh opportunities and model systems for probing the relationship between chirality and helicity in biopolymers.

In this context, absolute asymmetric assembly of achiral precursors into homohelical structures is especially intriguing. While it is not uncommon to generate chiral and helical structures through the spatial organization of achiral components, the resulting bulk materials are generally racemic.[15,16] To produce homohelical materials in the bulk sample is not a trivial task. Two driving forces have been shown to be able to induce the absolute homo-helicity. One is the internal induction in which the chirality of the molecular building block forms an inherent part of the helical backbone (*e.g.*, the helicity of DNA based on D-sugars).[1] The second one is the external induction in which the chiral source is not part of the helical backbone (*e.g.*, the formation of homohelical structure upon ligation of a chiral ligand).[17]

Herein, we report two homochiral cobalt camphorate frameworks $[Co_2(\text{D-Cam})(int)_2(H_2O)]_n$ (**1D**, int = isonicotinate) and $[Co_2(\text{L-Cam})(int)_2(H_2O)]_n$ (**1L**) based on enantiopure D- or L-Cam ligand (H_2Cam = camphoric acid). For comparative purpose, we have also prepared one isomeric structure $[Co_2(\text{DL-Cam})(int)_2(H_2O)]_n$ (**1R**, R denotes racemic) using racemic DL-Cam ligand.

Even though all these structures contain chiral molecules, the helices are actually constructed from achiral units (*i.e.*, cobalt and isonicotinate ligand) while chiral molecules (*i.e.*, D-cam or L-cam) and cobalt form chains that intersect helices from a perpendicular direction in **1D** and **1L**. Therefore, in this case, the molecular chirality of D- or L-camphorates serves as an external chiral source to interact with the helix made of achiral building blocks. The most interesting aspect in these structures is the observed correlation between molecular chirality and absolute helicity. D- or L-Cam ligand results in homohelical arrangement of achiral components: right-handed helix (*P*-helix) in **1D** (similar to DNA where D-sugars lead to *P*-helix) and left-handed helix (*M*-helix) in **1L** (Fig. 1(a) and (b)). Interestingly, the use of racemic ligands leads both right- and left-handed helices in **1R** (Fig. 3(d)).

All three compounds were synthesized under similar hydrothermal conditions except with different optical isomer of camphoric acid.‡ They have the same formula and are therefore isomeric. The structures are characterized by single-crystal X-ray diffraction.§ **1D** and **1L** are two enantiomorphic forms based on D- or L-Cam ligand, respectively, while **1R** has an achiral and non-centrosymmetric crystal structure based on racemic DL-Cam ligand.

All three frameworks are based on a 6-connected dinuclear Co^{2+} unit which is surrounded by four isonicotinate ligands, two Cam ligand and one terminal aqua ligand (Fig. 2(a)). In each compound, the chiral camphorate ligand acts as μ_4-bridging ligand and links the dinuclear Co units into a homochiral chain (Fig. 1 and Fig. 3(b) and (c)).

Department of Chemistry and Biochemistry, California State University, Long Beach, 1250 Bellflower Boulevard, CA 90840 Long Beach, USA. E-mail: xbu@csulb.edu

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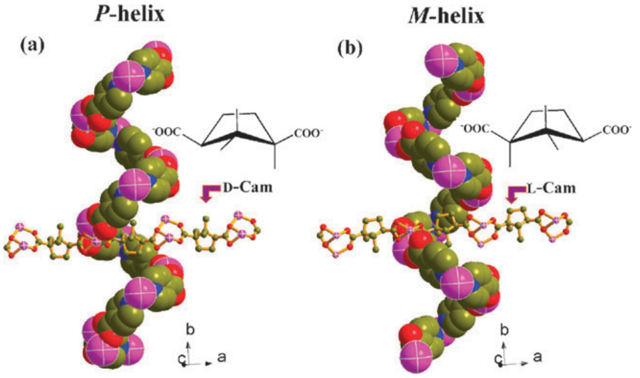

Fig. 1 The linear chain formed from D-camphorate and cobalt runs perpendicular to the *P*-helix formed from isonicotinate-cobalt in **1D** (a) and its mirror image in **1L** (b). For color code, see Fig. 2(a).

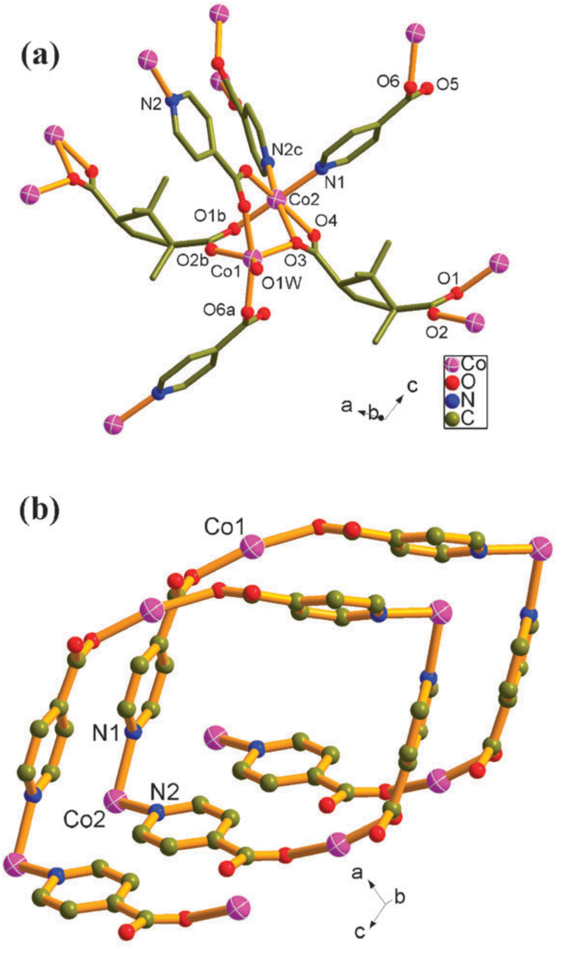

Fig. 2 (a) Crystal structure of **1D** showing the atom-labeling scheme. Hydrogen atoms were omitted for clarity (symmetry codes: $a = x, y, -1 + z$; $b = 1 + x, y, z$; $c = 2 - x, -0.5 + y, 1 - z$); (b) the right-handed single-stranded 2_1 helix along the *b* axis based on achiral isonicotinate ligands in **1D**.

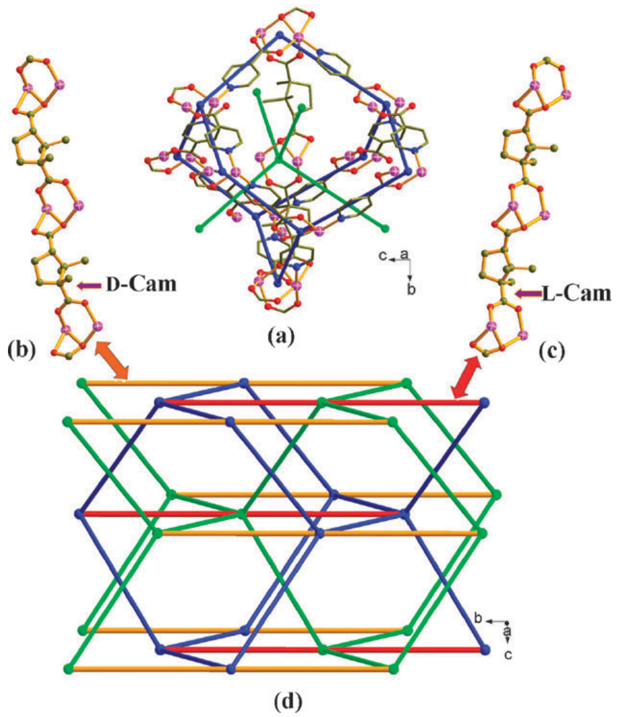

Fig. 3 (a) The building block of the diamond-type net formed by int ligands and dinuclear Co units (blue lines) and its interpenetrating sublattice (green lines) in **1R**. In the line representation, the dinuclear Co units are shown in single nodes (blue and green) and the int ligands are shown as lines (blue and green). (b) The D-Cam-Co linear chain in **1R**. (c) The L-Cam-Co linear chain in **1R**. (d) Topological representation of the 6-connected $4^8{\cdot}6^7$ net in **1R**, which shows two interpenetrating diamond nets (blue net and green net) linked by adjacent parallel D-Cam-Co (yellow) and L-Cam-Co (red) linear chains.

In **1D**, two crystallographically independent Co^{2+} ions are linked by two independent int ligands into a right-handed 2_1 helix along the *b* axis (Fig. 2(b)), while the enantiopure D-Cam ligands bridge the Co^{2+} ions into a linear chain parallel to the *a* axis (Fig. 1(a)). The three-dimensional framework of **1D** (or **1L**) can be simplified into the primitive cubic lattice (pcu net).[18]

In **1R**, the achiral isonicotinate ligands link dinuclear Co units to form an interpenetrating diamond structures (Fig. 3(a)) and two diamond sub-lattices are covalently joined together by the racemic DL-Cam ligands into an unusual 6-connected network with short Schläfli symbol of $4^8{\cdot}6^7$ (Fig. 3(d)).[18]

Unlike in **1D** (or **1L**) with only one handed helix, adjacent parallel D-Cam-Co chains and L-Cam-Co chains in **1R** induce the formation of edge-sharing right- and left-handed double-stranded 2_1 helices along the *b* axis (Fig. 3(d)). It is apparent that homochiral chains made of chiral molecular building blocks are closely associated with the sense of the helix formed of achiral components.

In summary, we present here a comparative study of three polymeric isomers in which the chirality of enantiopure ligands dictates the absolute sense of helix made of the achiral components. It is of particular interest to note that unlike 1-D helix such as DNA in which chiral molecules form the backbone of the helix and control the helical sense as an internal driving force, the chiral molecules used here (D- or L-camphorate) serve as the external driving force in the control of helicity.

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Notes and references

‡ *Synthesis* of $[Co_2(\text{D-Cam})(\text{int})_2(H_2O)]_n$ (**1D**): Hydrothermal reaction of D-H_2Cam (0.1005 g, 0.50 mmol), int (0.1283 g, 1.00 mmol), and $CoCO_3$ (0.1157 g, 1.00 mmol) in mixed H_2O (5 mL)/ethylene glycol (2 mL) solution was performed at 160 °C for 3 days, and the mixture was then cooled to room temperature. Purple crystals of **1D** were obtained (yield: 80% based on camphoric acid).

Synthesis of $[Co_2(\text{L-Cam})(\text{int})_2(H_2O)]_n$ (**1L**): Hydrothermal reaction of L-H_2Cam (0.0513 g, 0.25 mmol), int (0.0656 g, 0.50 mmol), and $CoCO_3$ (0.0704 g, 0.59 mmol) in mixed H_2O (5 mL)/ethylene glycol (2 mL) solution was performed at 160 °C for 3 days, and the mixture was then cooled to room temperature. Purple crystals of **1L** were obtained (yield: 78% based on camphoric acid).

Synthesis of $[Co_2(\text{DL-Cam})(\text{int})_2(H_2O)]_n$ (**1R**): Hydrothermal reaction of DL-H_2Cam (0.1003 g, 0.50 mmol), int (0.1244 g, 1.00 mmol), and $CoCO_3$ (0.1203 g, 1.00 mmol) in mixed H_2O (5 mL)/ethylene glycol (2 mL) solution was performed at 160 °C for 3 days, and the mixture was then cooled to room temperature. Purple crystals of **2** were obtained (yield: 85% based on camphoric acid).

§ *Crystal data* for **1D**: $C_{22}H_{24}Co_2N_2O_9$, M_r = 578.29, monoclinic, space group $P2_1$, a = 8.9543(1), b = 13.3217(2), c = 10.5371(1) Å, β = 110.195(1)°, V = 1179.66(2) $Å^3$, Z = 2, T = 293(2) K, D_c = 1.625 g cm^{-3}, R(int) = 0.0499, 11 273 reflections collected, Flack parameter = 0.013(18), $R1$ ($wR2$) = 0.0406 (0.0900) and S = 0.950 for 3719 reflections with $I > 2\sigma(I)$.

Crystal data for **1L**: $C_{22}H_{24}Co_2N_2O_9$, M_r = 578.29, monoclinic, space group $P2_1$, a = 8.9412(1), b = 13.2661(2), c = 10.5045(2) Å, β = 110.289(1)°, V = 1168.68(3) $Å^3$, Z = 2, T = 293(2) K, D_c = 1.643 g cm^{-3}, R(int) = 0.0227, 5545 reflections collected, Flack parameter = 0.01(2), $R1$ ($wR2$) = 0.0394 (0.1082) and S = 1.156 for 2981 reflections with $I > 2\sigma(I)$.

Crystal data for **1R**: $C_{22}H_{24}Co_2N_2O_9$, M_r = 578.29, orthorhombic, space group $Pca2_1$, a = 19.6658(9), b = 8.9899(4), c = 13.6956(6) Å, V = 2421.29(19) $Å^3$, Z = 4, T = 293(2) K, D_c = 1.586 g cm^{-3}, R(int) = 0.0745, 15 438 reflections collected, Flack parameter = 0.03(2), $R1$ ($wR2$) = 0.0450 (0.0889), and S = 0.929 for 2998 reflections with $I > 2\sigma(I)$.

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