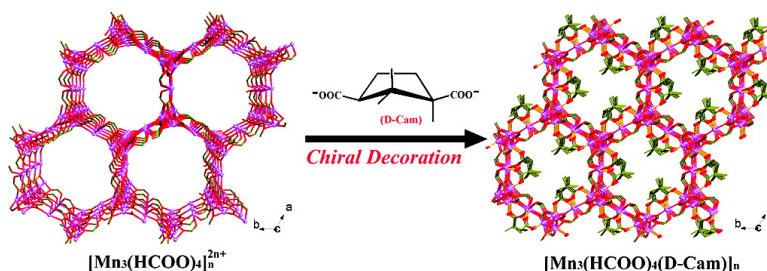


Manganese and Magnesium Homochiral Materials: Decoration of Honeycomb Channels with Homochiral Chains

Jian Zhang, Shumei Chen, Henry Valle, Matthew Wong, Cristina Austria, Maria Cruz, and Xianhui Bu

J. Am. Chem. Soc., **2007**, 129 (46), 14168-14169 • DOI: 10.1021/ja076532y • Publication Date (Web): 30 October 2007

Downloaded from <http://pubs.acs.org> on February 13, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 21 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



Manganese and Magnesium Homochiral Materials: Decoration of Honeycomb Channels with Homochiral Chains

Jian Zhang, Shumei Chen, Henry Valle, Matthew Wong, Cristina Austria, Maria Cruz, and Xianhui Bu*

Department of Chemistry and Biochemistry, California State University, Long Beach, 1250 Bellflower Boulevard, Long Beach, California 90840

Received August 31, 2007; E-mail: xbu@csulb.edu

Hybrid organic–inorganic coordination assembly, which may incorporate functionality from both inorganic and organic components, is currently an active research area.^{1–3} However, despite impressive progress in the past decade, there remain a number of challenges, two of which are highlighted here. One is the control of the dimensionality in inorganic connectivity.^{2–5} Inorganic components in the majority of coordination polymers are isolated metal cations or clusters, and only a very limited number of 3-D inorganic connectivity (within organic–inorganic hybrids) are known.^{3,4} The 3-D inorganic connectivity is desirable for properties resulting from cooperative phenomenon such as magnetism^{3c} and conductivity.^{2d}

The second challenge relates to homochiral open-framework materials that have potential enantioselective applications.^{6–8} While the crystallization of chiral crystals from achiral precursors is not uncommon, the bulk sample tends to be a racemate, except in some rare cases when a particular chiral form is preferentially formed.⁷ For enantioselective applications, it is desirable to develop new synthetic procedures to produce enantiopure open-framework materials.

In known 3-D homochiral crystalline inorganic–organic hybrids, enantiopure ligands generally serve as structural building units to cross-link inorganic units into covalent frameworks, and chiral ligands are essential for the 3-D framework connectivity. The framework dimensionality in terms of the covalent connectivity would generally be lowered (to two-, one-, or zero-dimension) without cross-linking chiral ligands.

Here we present two isostructural homochiral materials (**1** and **2**) in which homochiral features serve as decoration on 3-D metal–oxygen frameworks. The most interesting feature is that the 1-D homochiral chains can be considered not as a part of the 3-D framework but as decorative ligands to strengthen the existing 3-D metal–oxygen framework. Compounds **1** and **2** are also among rare inorganic–organic hybrids that contains 3-D inorganic connectivity (here, 3-D Mn–O or Mg–O network). It is worth noting that the 3-D inorganic connectivity among homochiral inorganic–organic hybrids is rare. Some metal carboxylates with 3-D M–O–M connectivity are known, but they are not homochiral.^{2c,3a,5a}

Compounds **1** and **2** are among a total of five homochiral framework materials prepared in this work. These five compounds possess homochiral connectivity (i.e., the connectivity between enantiopure ligands and metal centers) in one-, two-, and three-dimensions. Such diverse homochiral features highlight the versatility of the synthetic system reported here. While **1**, **3**, **4**, and **5** are based on the magnetic Mn²⁺ cations, we also prepared **2** to demonstrate that the synthetic chemistry reported here can be extended to other metal species such as Mg²⁺.

Homochiral materials reported here are based on D-camphoric acid (D-H₂Cam) (Table 1). Figure 1a shows an unusual [Mn₃(HCOO)₄]_n²ⁿ⁺ 3-D framework in **1** with 3-D Mn–O–Mn con-

nectivity and open honeycomb channels. The organic chains based on enantiopure D-Cam ligands are attached to the wall of the channels, generating an unprecedented framework with 3-D inorganic M–O connectivity and decorative 1-D chiral chains (Figure 1a–e). Each Mn²⁺ site in **1** has distorted octahedral geometry. There are three independent Mn²⁺ ions. Mn1 and Mn2 are connected by HCOO[−] ligands to form a 3₂ helix along the *c*-axis. Each 3₂ helix is connected to three adjacent helices by Mn3. Such connectivity results in the formation of the [Mn₃(HCOO)₄]_n 3-D framework with open channels along the *c*-axis (Figure 1a). The diameter of the cylindrical channel is about 14 Å.

The simplification of the 3-D network in **1** by connecting all the Mn²⁺ sites gives a distorted eta net (or (8,3)-a net)⁹ where the Mn1 centers behave as 3-connected nodes (Figure 1b). In this net, the linkage between the 3₂ helices with the same handedness gives rise to a 3-D network. All four independent HCOO[−] ligands use μ₂-O atoms to bridge Mn²⁺ ions, resulting in a 3-D Mn–O–Mn framework. Thermal analysis results show compound **1** has relatively high stability with no weight loss under 400 °C. Magnetic susceptibility measurements reveal dominant antiferromagnetic behavior, and the magnetic data above 25 K can be fitted to the Curie–Weiss law with $C = 11.18 \text{ cm}^3 \text{ K mol}^{-1}$ and $\theta = -61.13 \text{ K}$.

The large space of each hexagonal channel accommodates three columns of the D-Cam ligands with all chiral C centers of the D-Cam ligands directed toward the center of the channel. Such exposed chirality centers are particularly desirable for chiral recognition, but unfortunately, no additional solvent-accessible space is present within the honeycomb channels because channels are already filled with columns of homochiral ligands.

By employing different solvents, three other homochiral compounds **3–5** were obtained. Unlike compound **1** with 1-D homochiral connectivity (attached to 3-D M–O–M framework), compounds **3** and **4** exhibit 2-D homochiral connectivity while compound **5** has 3-D homochiral connectivity. The *n*-D homochiral connectivity means that metal cations or metal clusters are joined together by enantiopure ligands in *n*-dimensions. The dimensionality of homochiral connectivity may be equal to or lower than the overall framework dimensionality because of the additional cross-linking by achiral ligands.

It can be useful to indicate the dimensionality of metal/chiral ligand connectivity and the dimensionality of metal/achiral ligand connectivity using the C^{*n*}A^{*m*} scheme first proposed here, where C and A represent chiral and achiral connectivity, respectively, and *n* and *m* represent dimensionality of chiral and achiral connectivity (Table 1). The C^{*n*}A^{*m*} scheme is similar to the previously reported I^{*n*}O^{*m*} scheme that shows inorganic and organic connectivity in inorganic–organic hybrids.^{2a}

Compound **3** has a homochiral 2-D layered structure with dinuclear Mn units bridged by the D-Cam ligands and belongs to the C²A⁰-type structure (Figure 2a). Each Mn(II) site in **3** has square

Table 1. A Summary of Crystal Data and Refinement Results^a

	formula	space group	a (Å)	b (Å)	c (Å)	β (°)	R (F)	Flack parameter	C ⁿ A ^m type
1	[Mn ₃ (HCOO) ₄ (D-Cam)] _n	P3 ₂	15.128(1)	15.128(1)	7.716(1)	90	0.0662	0.09(5)	C ¹ A ³
2	[Mg ₃ (HCOO) ₄ (D-Cam)] _n	P3 ₂	14.872(1)	14.872(1)	7.333(1)	90	0.0751	0.02(7)	C ¹ A ³
3	[Mn ₂ (D-Cam) ₂ (DMA) ₂] _n	P2 ₁	9.670(1)	13.269(1)	13.274(1)	108.63(1)	0.0847	0.2(3)	C ² A ⁰
4	[Mn ₃ (HCOO) ₂ (D-Cam) ₂ (DMF) ₂] _n	P2 ₁	8.872(1)	13.708(1)	14.441(1)	97.75(1)	0.0646	0.01 (1)	C ² A ¹
5	[Mn ₂ (D-Cam) ₂] _n	P2 ₁	6.868(1)	12.566(2)	12.782(2)	103.46(1)	0.0389	-0.04(2)	C ³ A ⁰

^a D-H₂Cam = D-camphoric acid; DMF = *N,N'*-dimethylformamide; DMA = *N,N'*-dimethylacetamide; CCDC-655527–655531 (1–5).

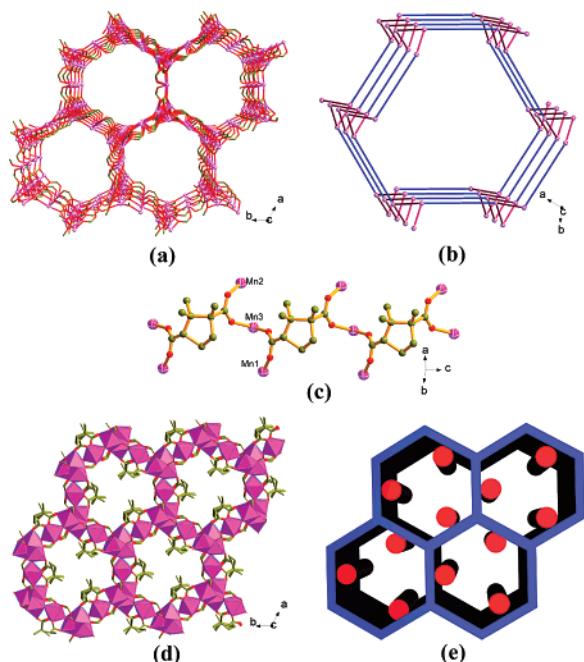


Figure 1. (a) The [Mn₃(HCOO)₄]_n²⁺ 3-D framework with 3-D Mn–O–Mn connectivity and open channels along the *c*-axis. (b) Topological representation of the eta net in 1. (c) The D-Cam ligands link trinuclear Mn(II) centers into the 1-D homochiral chain in 1. (d) The 3-D I³O¹ (or C¹A³) framework of 1, showing the 3-D Mn–O–Mn connectivity (polyhedron) and the attached homochiral chains. (e) Schematic representation of the honeycomb-like 3-D frameworks with attached 1-D homochiral chains.

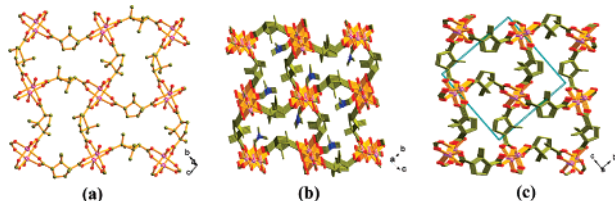


Figure 2. (a) The 2-D homochiral layer in 3. (b) The 3-D C²A¹ framework of 4. (c) The 3-D C³A⁰ framework of 5.

pyramidal geometry, and the Mn dimers are bridged by four bidentate carboxylate groups from four D-Cam ligands into a paddle-wheel. The DMA molecule affords one oxygen atom to complete the five-coordinate geometry of the Mn(II) center.

Compound 4 consists of homochiral layers linked by 1-D achiral chains and therefore has a C²A¹ 3-D framework (Figure 2b). The D-Cam ligands act as μ_4 -linkers and connect the trinuclear Mn units to form a homochiral (4,4) layer parallel to the *bc* plane. Both DMF and HCOO[−] ligands afford μ_2 -O atoms to connect Mn(II) centers to form a 1-D Mn–O–Mn chain along the *a*-axis. The homochiral layer and achiral Mn–O–Mn chain share the common trinuclear Mn units resulting in a 3-D C²A¹ homochiral framework ($n + m = 3$).

Compound 5 is formed between Mn²⁺ ions and D-Cam ligands and has the 3-D homochiral connectivity (C³A⁰) (Figure 2c). It

consists of Mn²⁺ chains bridged by homochiral D-Cam ligands. There are two independent Mn²⁺ centers, and both of them are coordinated by five carboxylate oxygen atoms from four D-Cam ligands in a distorted square pyramidal geometry. Mn1 and Mn2 atoms are bridged by two carboxylate groups from two independent D-Cam ligands to form a chain with corner-sharing [MnO₅] square pyramids. Each carboxylate-bridged Mn chain is further linked to four neighboring chains by D-Cam ligands, to generate a 3-D homochiral framework. Such framework can be described as the PtS net by considering Mn²⁺ as tetrahedral nodes and D-Cam as planar 4-connected nodes.

In conclusion, we have synthesized five framework solids that exhibit homochiral connectivity in one-, two-, and three-dimensions. The overall framework connectivity of these materials ranges from two- to three-dimensions by also considering achiral connectivity. Compounds 1 and 2 are unusual because of the presence of 3-D inorganic metal–oxygen frameworks coupled with the decoration of their honeycomb channels by columns of homochiral chains.

Acknowledgment. We thank the support of this work by the NIH (2 S06 GM063119-05), NSF-MRI, NIH-RISE, and the SCAC award (Summer 2007) of CSULB.

Supporting Information Available: Detailed synthesis conditions, additional structural diagrams, thermal analysis data, experimental and simulated X-ray powder diffraction patterns, magnetic data, and CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705. (b) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334.
- (2) (a) Cheetham, A. K.; Rao, C. N. R.; Feller, R. K. *Chem. Commun.* **2006**, 4780. (b) Guillou, N.; Gao, Q. M.; Forster, P. M.; Chang, J. S.; Park, S. E.; Férey, G.; Cheetham, A. K. *Angew. Chem., Int. Ed.* **2001**, *40*, 2831. (c) Forster, P. M.; Cheetham, A. K. *Angew. Chem., Int. Ed.* **2002**, *41*, 457. (d) Férey, G.; Millange, F.; Morcrette, M.; Serre, C.; Doublet, M.-L.; Greneche, J.-M.; Tarascon, J.-M. *Angew. Chem., Int. Ed.* **2007**, *46*, 3259.
- (3) (a) Livage, C.; Forster, P. M.; Guillou, N.; Tafoya, M. M.; Cheetham, A. K.; Férey, G. *Angew. Chem., Int. Ed.* **2007**, *46*, 5877. (b) Serre, C.; Millange, F.; Surble, S.; Greneche, J.-M.; Férey, G. *Chem. Mater.* **2004**, *16*, 2706. (c) Guillou, N.; Livage, C.; Drillon, M.; Férey, G. *Angew. Chem., Int. Ed.* **2003**, *42*, 5314. (d) Livage, C.; Egger, C.; Férey, G. *Chem. Mater.* **2001**, *13*, 410.
- (4) Gutschke, S. O. H.; Price, D. J.; Powell, A. K.; Wood, P. T. *Angew. Chem., Int. Ed.* **2001**, *40*, 1920.
- (5) (a) Wang, Z.; Zhang, B.; Fujiwara, H.; Kobayashi, H.; Kurmoo, M. *Chem. Commun.* **2004**, 416. (b) Dybtsev, D. N.; Chun, H.; Yoon, S. H.; Kim, D.; Kim, K. *J. Am. Chem. Soc.* **2004**, *126*, 32.
- (6) (a) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982. (b) Kesaneli, B.; Linn, W. *Coord. Chem. Rev.* **2003**, *246*, 305. (c) Anokhina, E. V.; Go, Y. B.; Lee, Y.; Vogt, T.; Jacobson, A. *J. Am. Chem. Soc.* **2006**, *128*, 9957.
- (7) (a) Lin, Z.; Slawin, A. M. Z.; Morris, R. E. *J. Am. Chem. Soc.* **2007**, *129*, 4880. (b) Ezuhara, T.; Endo, K.; Aoyama, Y. *J. Am. Chem. Soc.* **1999**, *121*, 3279.
- (8) (a) Vaidhyanathan, R.; Bradshaw, D.; Rebilly, J.-N.; Barrio, J. P.; Gould, J. A.; Berry, N. G.; Rosseinsky, M. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 6495. (b) Dybtsev, D. N.; Yutkin, M. P.; Peresypkina, E. V.; Virovets, A. V.; Serre, C.; Férey, G.; Fedin, V. P. *Inorg. Chem.* **2007**, *46*, 6843. (c) Zhang, J.; Bu, X. *Angew. Chem., Int. Ed.* **2007**, *46*, 6115.
- (9) Rosi, N. L.; Kim, J.; Eddaoudi, M.; Chen, B.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, *127*, 1504.

JA076532Y