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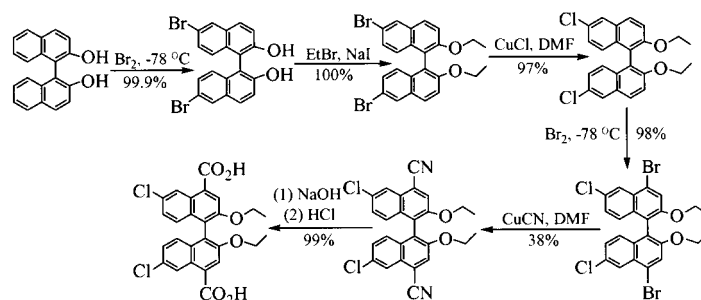
Rational Design of Homochiral Solids Based on Two-Dimensional Metal Carboxylates**

Yong Cui, Owen R. Evans, Helen L. Ngo,
Peter S. White, and Wenbin Lin*

The design and construction of metal–organic coordination networks (MOCNs) have received significant attention in recent years, mostly motivated by the potential of generating tailor-made functional materials through molecular engineering of the constituent building blocks using the tools of modern synthetic chemistry.^[1] Indeed many MOCNs have been reported to exhibit interesting properties, which include functional-group or size-selective sorption,^[2] catalysis,^[3] gas storage,^[4] molecular recognition,^[5] and second harmonic generation.^[6] Among these, the synthesis of MOCNs with permanent porosity is by far the most fruitful, and many metal–carboxylate coordination networks with extremely large surface areas have been constructed, based on the secondary building unit (SBU) concept that has been extensively used in zeolite synthesis.^[7] Compared to zeolites and the recently developed MCM-type mesoporous materials,

MOCNs are built with weaker metal–ligand coordination bonds and are inherently less stable. It is thus imperative to incorporate functions that are not possible with inorganic oxide materials into MOCNs. Our recent success with crystal engineering of nonlinear-optical (NLO) materials based on MOCNs provides such an example.^[6] Another unique feature of MOCNs is the ability to design chiral pores and functionalities, which may be exploited in heterogeneous asymmetric catalysis and enantioselective separations.^[8] With a few exceptions,^[3b,c,9] the chiral MOCNs reported to date were synthesized from simple achiral components.^[10] The chirality of such MOCNs originates from the spatial disposition of their building blocks and is not amenable to fine tuning.^[1d] Moreover, the bulk materials of such MOCNs tend to be racemic and cannot be exploited for chirotechnology.^[11] A more straightforward approach to chiral solids relies on the use of metal ions or metal clusters as nodes, and chiral multifunctional ligands to link these nodes. Herein we report the rational synthesis of chiral two-dimensional (2D) networks, based on enantiopure dicarboxylate bridging ligands and metal–organic SBUs.

As illustrated in Scheme 1, enantiopure atropisomeric 6,6'-dichloro-2,2'-diethoxy-1,1'-binaphthylene-4,4'-dicarboxylic



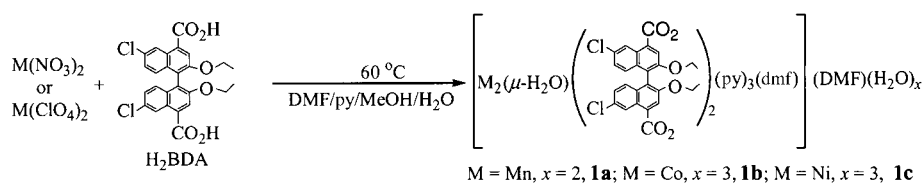
Scheme 1. Synthesis of 6,6'-dichloro-2,2'-diethoxy-1,1'-binaphthylene-4,4'-dicarboxylic acid (H₂BDA).

acid (H₂BDA), was prepared in six steps in good overall yield (35.7%), from the readily available chiral 1,1'-bi-2-naphthol (BINOL). Homochiral metal carboxylates with the general formula of $[M_2(\mu\text{-H}_2\text{O})(\text{bda})_2(\text{py})_3(\text{dmf})] \cdot (\text{DMF}) \cdot (\text{H}_2\text{O})_x$ (M = Mn, $x = 2$, **1a**; M = Co, $x = 3$, **1b**; M = Ni, $x = 3$, **1c**) were obtained in moderate yields (31–42%), by treatment of metal nitrate or perchlorate salts with H₂BDA in a mixture of N,N'-dimethylformamide (DMF), MeOH, and pyridine (py) at 60 °C (Scheme 2). Compounds **1a–c** are stable in air, and insoluble in water and common organic solvents. The IR spectra of **1a–c** exhibited bands at 1660–1320 cm⁻¹ characteristic of carboxylate groups. Thermogravimetric analyses (TGA) show that **1a** loses 12.8% of its total weight on heating to 220 °C, which corresponds to the loss of three water molecules and two DMF molecules per formula unit (expected 12.7%). TGA indicate that **1b** and **1c** experience 13.7% and 13.3% weight losses by 220 °C, corresponding to the loss of four water molecules and two DMF molecules for both **1b** and **1c** (expected 13.9%). The formulations of **1a–c** are supported by microanalysis results.

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[**] We acknowledge financial support from NSF (DMR-9875544). We thank Dr. Gary Enright for the X-ray powder diffraction patterns. W.L. is an Alfred P. Sloan Fellow, an Arnold and Mabel Beckman Young Investigator, a Cottrell Scholar of Research Corp, and a Camille Dreyfus Teacher-Scholar.

Supporting information for this article is available on the WWW under <http://www.angewandte.com> or from the author.



Scheme 2.

A single-crystal X-ray diffraction study^[12] performed on (*S*)-**1a** reveals an infinite 2D coordination network that crystallizes in the chiral space group $P2_12_12_1$. The asymmetric unit of **1a** consists of two Mn centers, two BDA groups, three pyridine molecules, two DMF molecules, and three water molecules. Each BDA ligand contains one bridging carboxylate group and one monodentate carboxylate group. The basic building unit for **1a** is a dimanganese carboxylate moiety (Figure 1), where the Mn1 and Mn2 centers are bridged by

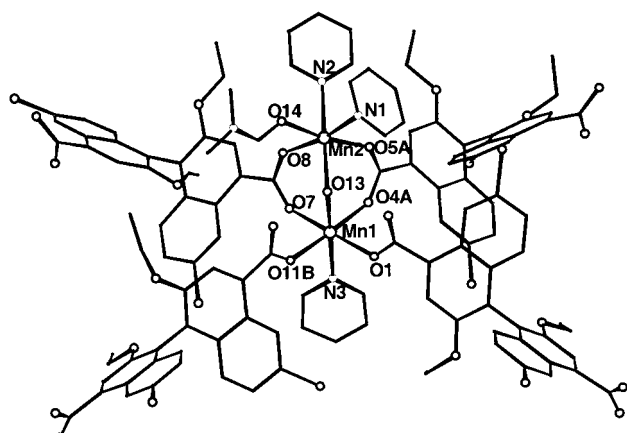


Figure 1. Coordination environment for the $[\text{Mn}_2(\mu\text{-H}_2\text{O})(\text{bda})_2(\text{py})_3\text{-(dmf)}]$ building block in **1a**. Only one part of the disordered ethyl group of the BDA anion is shown, and the DMF and water guest molecules are omitted.

two carboxylate groups of two different BDA ligands and one water molecule, with a $\text{Mn1} \cdots \text{Mn2}$ distance of 3.710(1) Å. The water molecule bridges the Mn centers in a slightly unsymmetrical fashion with the $\text{Mn1}-\text{O13}$ distance of 2.334(3) Å and the $\text{Mn2}-\text{O13}$ distance of 2.230(3) Å. There are two monodentate carboxylate groups of two other BDA ligands around the dimeric core (Figure 1). The remainder of the coordination environments of the Mn1 and Mn2 centers is completed by three pyridine molecules and one DMF molecule. Both Mn1 and Mn2 adopt a slightly distorted octahedral coordination geometry; the Mn1 center coordinates to two bridging carboxylate O atoms and two monodentate carboxylate O atoms of four BDA groups, one bridging water molecule, and one pyridine molecule, while the Mn2 center coordinates to two bridging carboxylate O atoms of two BDA groups, one bridging water molecule, one DMF molecule, and two pyridine molecules. The *cis*-bond angles around the Mn1 center range from 85.9(2) to 96.3(2)°, while the *cis*-bond angles around the Mn2 center range from 82.0(2) to 101.6(2)°. The dihedral angles between the two binaphthyl subunits of the DBA ligands are 93.9 and 94.2°.

The dimanganese cores are linked by four *exo*-tridentate BDA ligands to four adjacent dimanganese cores to result in a 2D neutral rhombohedral grid in the *bc* plane with a (4,4) topology (Figure 2a). The short and long diagonals of the rhombohedral grid run along the *b* and *c* axis,

respectively. The carboxylate groups on the 4,4'-positions of BDA ligands behave as rigid linear linkers, and allow the formation of 2D rhombohedral grids. A space-filling representation of **1a** (Figure 2b) clearly demonstrates the formation of chiral cavities. Interestingly, the ethoxy-protected

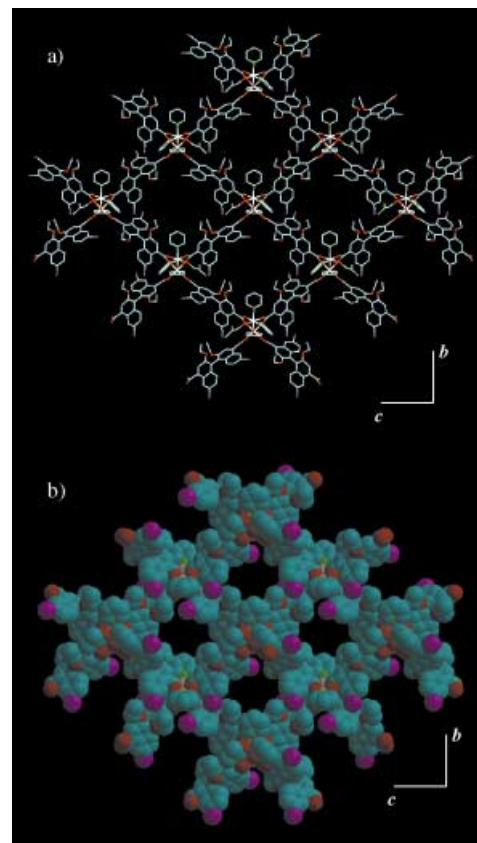


Figure 2. a) A view of 2D rhombohedral grid of **1a** down the *a* axis; b) A space-filling model of **1a**, viewed down the *a* axis. The DMF and water guest molecules are omitted for clarity.

BINOL functionalities point towards the open cavities. It is important to note that BINOL is well established in the organic community as a beneficial chiral auxiliary for a variety of highly enantioselective homogeneous asymmetric catalyses.^[13] The ability to place such a useful chiral auxiliary inside an open channel of well-characterized, crystalline, porous MOCN represents a major step towards the rational synthesis of crystalline chiral porous materials. Unfortunately, a careful examination of the structure of **1** shows that the 2D grids stack on top of each other in a staggered arrangement along the *a* axis (Figure 3). The adjacent layers are shifted by $\frac{1}{2}b$ and $\frac{1}{2}c$ along the *b* and *c* axes, respectively, and have a layer-to-layer separation of 7.45 Å ($\frac{1}{2}a$). Such a staggered arrange-

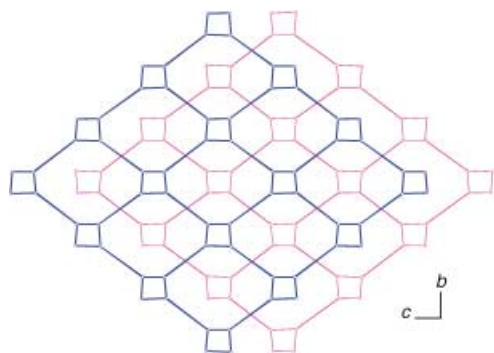


Figure 3. A schematic showing the staggered arrangement of adjacent 2D rhombohedral grids of **1a**. The dimanganese cores are represented by smaller quadrangles (comprised of the four carbon atoms of the four coordinating carboxylate groups), while the BDA linkers are represented by the longer lines.

ment positions the dimanganese core from an adjacent layer in the open cavity of the 2D rhombohedral grid. Consequently, compound **1** has a minimal void space, which is occupied by one DMF and two water guest molecules. Finally, the bridging water molecule forms strong intramolecular hydrogen bonds with the uncoordinated oxygen atoms of two monodentate carboxylate groups of the BDA ligands, as indicated by O...O distances of 2.613(1) and 2.647(1) Å.

A single-crystal X-ray structure determination reveals that (*S*)-**1b** is isostructural to (*S*)-**1a**,^[12] while cell parameter determinations and powder X-ray diffraction studies establish that (*S*)-**1c** is also isostructural to (*S*)-**1a**.^[14] The phase purity for the bulk samples of **1a–c** has been established by comparison of their observed and simulated X-ray powder diffraction patterns. We have also prepared Co compound **1b** using the (*R*)-enantiomer of 6,6'-dichloro-2,2'-diethoxy-1,1'-binaphthyl-4,4'-dicarboxylic acid. Solid-state (circular dichroism) CD spectra of compound **1b** made from (*R*)- and (*S*)-H₂DBA are exact mirror images of each other, and demonstrate that when compound **1b** is made from either (*R*)- or (*S*)-H₂BDA, supramolecular enantiomers result. Solid-state CD spectra of compound (*S*)-**1a** and (*S*)-**1c** are similar to that of (*S*)-**1b**.

In conclusion, we have developed a rational synthetic approach toward homochiral solids, based on 2D coordination networks and using enantiopure dicarboxylate ligands and dimetal SBUs as the building blocks.

Experimental Section

Full experimental details are given in the Supporting Information. Synthesis of **1a–c**: A mixture of Co(ClO₄)₂·6H₂O, Mn(NO₃)₂·6H₂O, or Ni(NO₃)₂·6H₂O (0.005 mmol) and H₂BDA (0.005 mmol) was placed in a small vial containing DMF (2.5 mL), H₂O (0.5 mL), MeOH (0.5 mL), and pyridine (0.5 mL). The vial was sealed, heated at 60 °C for 16 h, and allowed to cool to room temperature. The crystals which were suitable for X-ray diffraction were collected by filtration, washed with diethyl ether, and dried in air. Yield: **1a**, 0.058 g, 42%; **1b**, 0.050 g, 37%; **1c**, 0.035 g, 31%. IR and analytical data: **1a**: elemental analysis (%) calcd for C₇₃H₇₁Mn₂N₅O₁₇: C 56.86, H 4.64, N 4.54; found: C 56.09, H 4.17, N 3.90; IR: $\tilde{\nu}$ = 3442 (m), 2978 (w), 2926 (w), 1653 (s), 1642 (m), 1624 (s), 1578 (s), 1492 (m), 1445 (ms), 1401 (s), 1323 (s), 1222 (ms), 1117 (m), 1091 (ms), 1060 (m), 1045 (m), 906 (w), 868 (w), 822 (w), 800 (m), 744 (ms), 698 (m), 678 (w), 625 (w) cm⁻¹. **1b**: elemental analysis (%) calcd for C₇₃H₇₃Co₂N₅O₁₈: C 55.91, H 4.69, N 4.47; found: C 55.52, H 4.14, N 3.88; IR: $\tilde{\nu}$ = 3433 (m), 2978 (w), 2927 (w), 1657

(ms), 1641 (m), 1627 (s), 1580 (s), 1492 (m), 1445 (ms), 1402 (s), 1322 (s), 1222 (ms), 1117 (m), 1091 (ms), 1060 (m), 1042 (m), 907 (w), 868 (w), 822 (w), 799 (m), 740 (ms), 700 (m), 630 (w) cm⁻¹. **1c**: elemental analysis (%) calcd for C₇₃H₇₃Ni₂N₅O₁₈: C 55.93, H 4.69, N 4.47; found: C 54.15, H 4.31, N 3.90; IR: $\tilde{\nu}$ = 3447 (m), 2980 (w), 2928 (w), 1655 (ms), 1642 (m), 1628 (s), 1579 (s), 1491 (m), 1445 (ms), 1402 (s), 1322 (s), 1222 (ms), 1118 (m), 1091 (ms), 1060 (m), 1042 (m), 907 (w), 868 (w), 822 (w), 799 (m), 750 (ms), 699 (m), 631 (w) cm⁻¹.

Received: October 15, 2001 [Z18062]

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- [12] X-ray single-crystal diffraction data for both **1a** and **1b** were collected on a Siemens SMART CCD diffractometer. Crystal data for **1a**: orthorhombic, space group *P*₂₁₂₁₂, *a* = 14.891(1), *b* = 19.906(1), *c* = 24.500(1) Å, *V* = 7262.3(4) Å³, *Z* = 4, ρ_{calcd} = 1.41 g cm⁻³, $\mu(\text{MoK}\alpha)$ = 0.567 mm⁻¹. Least-squares refinement based on 17348 reflections with *I* > 2σ(*I*) and 851 parameters led to convergence, with a final *R*1 = 0.072, *wR*2 = 0.193, and *GOF* = 1.09. Flack parameter = 0.04(2). Crystal data for **1b**: orthorhombic, space group *P*₂₁₂₁₂, *a* = 14.710(5), *b* = 18.992(1), *c* = 24.783(1) Å, *V* = 7286.6(3) Å³, *Z* = 4, ρ_{calcd} = 1.42 g cm⁻³, $\mu(\text{MoK}\alpha)$ = 0.687 mm⁻¹. Least-squares refinement based on 15985 reflections with *I* > 2σ(*I*) and 855 parameters led to convergence, with a final *R*1 = 0.104, *wR*2 = 0.233, and *GOF* = 1.14. CCDC-177733 (**1a**) and CCDC-177734 (**1b**) contains the supplement-

tary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/contents/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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Inorganic Chemistry Goes Protein Size: A Mo₃₆₈ Nano-Hedgehog Initiating Nanochemistry by Symmetry Breaking**

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Marc Schmidtman, and Andreas Dress

*Dedicated to Professor Dieter Fenske
on the occasion of his 60th birthday*

Nature's evolution from the primordial Earth through to the present overwhelming variety of macroscopic forms and functionalities, the formation of which is directed by their molecular "counterparts", that is, by nanosized biomolecules, should stimulate thoughts about the potential of material systems in general as well as related basic first principles or natural laws.^[1] We refer to processes based on reservoir systems containing appropriate building blocks, the linking of which can lead to an overwhelming or even infinite variety of molecular forms including those showing symmetry breaking. This process is particularly valid on entering the nanocosmos size category.^[2] The nanocosmos as such, does not show the variety-limiting translational symmetry restriction of macroscopic crystalline materials but offers—in contrast to the microcosmos with its small molecules—the possibility that (several) larger arrays with local symmetries are not in agreement with the overall symmetry—a situation well known for spherical viruses (see Figure 1 and ref. [3])—can occur. This increases the options for the generation of an extreme structural versatility. Thus, the appropriate building units must display a certain type of flexibility as prerequisite for linking versatility (of course not coming close to that of amino



Figure 1. A drawing of a $T=3$ icosadeltahedron—as model for the topologically identical coat protein subunits of the Tomato Bushy Stunt Virus (TBSV)—showing its arrangement of three quasi-equivalent sets of 60 icosahedrally related subunits (lobes/proteins). The orange lobes pack about the icosadeltahedron's exact fivefold axes, whereas the blue and green lobes alternate about its local sixfold axes (reproduced with permission from ref. [3]).

acids), a condition well fulfilled by molybdenum oxide based fragments/aggregates. These special entities, abundant as (virtual) building units in a potential "dynamic library",^[4,5] can, by a type of "split-and-link process", adapt their size and shape depending upon slight alterations of the relevant boundary conditions;^[6-8] evident reasons for this "molybdate" specific quality are listed in footnote ref. [9]. This versatility could lead us, to use a term from J.-M. Lehn lectures, to the category "Multiple Expression of Molecular Information", a statement also supported by the variety of giant clusters obtained from relevant "libraries".^[6-8] Here we report the formation of a rather unusual giant molybdenum oxide based nanocluster, the size of hemoglobin (diameter approximately 6 nm), and containing 368 metal (1880 non-hydrogen) atoms formed by the linking of 64 {Mo₁}-, 32 {Mo₂}-, and 40 {Mo-(Mo₃)}-type units by a remarkable symmetry-breaking process which is nicely recognizable at the cluster surface. The understanding of the present process will be the starting point for the synthesis of quite a number of other "size comparable" clusters and reactions of these. Here we refer to a far-reaching step into the nanocosmos with perspectives for nanochemistry through symmetry breaking, molecular topology, and surface sciences with catalytical and topological relevance. Symmetry breaking will be referred to in relation to transitions from positive to negative surface areas which can be considered as model for nature's patternings or breaking monotony.

By reducing a molybdate solution which is acidified with sulfuric acid, the deep-blue compound **1** containing the giant mixed-valence cluster anion **1a** (Figure 2) is obtained which was characterized by elemental analysis (including redox titrations to determine the (formal) number of Mo^V centers), thermogravimetry (to determine the actual crystal-water content which is important for the analyses), bond valence

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 [**] Financial support by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the European Union (HPRN-CT 1999-00012) and the GK is gratefully acknowledged.