

Microporous Frameworks

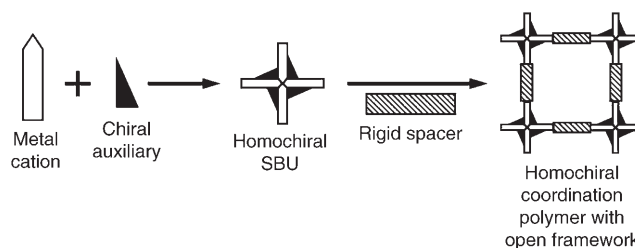
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A Homochiral Metal–Organic Material with Permanent Porosity, Enantioselective Sorption Properties, and Catalytic Activity**

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Metal–organic porous materials are receiving growing attention^[1] because of their potential applications in gas storage,^[2]

separation,^[3] and many other areas.^[4] Although catalysis is one of the most promising applications of such materials, only a handful of examples have been reported to date.^[5] Furthermore, despite considerable efforts, attempts to synthesize robust, homochiral metal–organic porous materials capable of enantioselective separation and/or catalysis have met with only limited success.^[6,7] Most homochiral metal–organic frameworks are not robust enough to show permanent porosity, nor porous enough to be useful for selective sorption or catalytic transformation of organic molecules. Therefore, the synthesis of robust homochiral metal–organic frameworks with potential for application is still challenging. For the synthesis of homochiral metal–organic open frameworks, two general approaches have been taken: 1) use of a rigid homochiral organic ligand as a spacer to link adjacent metal centers or secondary building units (SBUs),^[5b–d,7] and 2) use of a homochiral ligand as an auxiliary pendant which does not directly participate in the formation of a framework backbone, but forces the framework to adopt a specific chiral topology.^[3d] Herein, we introduce another rational approach to the synthesis of homochiral metal–organic frameworks. A metal ion and a readily available homochiral organic ligand are used to form homochiral SBUs, which in turn, are linked together by rigid spacers to build a network structure, in a one-pot reaction (Scheme 1).^[8] With a judicious choice of



Scheme 1. Our approach to the synthesis of homochiral metal–organic frameworks.

metal ion, homochiral organic molecule, and rigid polytopic linker (that is, a connector with more than one metal coordination site), this approach allows us to synthesize metal–organic open frameworks with stable chiral pores. Herein, we report a new homochiral metal–organic material that has permanent porosity, size- and enantioselective sorption properties, and catalytic activity.^[9]

A dimethylformamide (DMF) solution of $\text{Zn}(\text{NO}_3)_2$, L-lactic acid (L- H_2lac), and 1,4-benzenedicarboxylic acid (H_2bdc) in a 2:1:1 ratio was heated in a teflon-lined stainless steel vessel at 110 °C for 2 days to produce large rod-shaped colorless crystals. Single-crystal X-ray analysis of these crystals revealed a 3D metal–organic framework structure formulated as $[\text{Zn}_2(\text{bdc})(\text{L-lac})(\text{dmf})] \cdot (\text{DMF})$ (**1**·DMF). The phase purity of the bulk product was independently confirmed by powder X-ray diffraction (XRD) and elemental analysis.

The lactate ligand in **1** coordinates to the Zn^{2+} ions in the framework as a dianion owing to the deprotonation of the hydroxy group;^[10] therefore, the whole framework is charge neutral. There are two crystallographically independent Zn^{2+}

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ions in the polymeric structure, and both of them have a coordination number five and an uncommon trigonal-bipyramidal coordination environment (Figure 1). The first Zn^{2+} ion is coordinated by a deprotonated hydroxy group of a

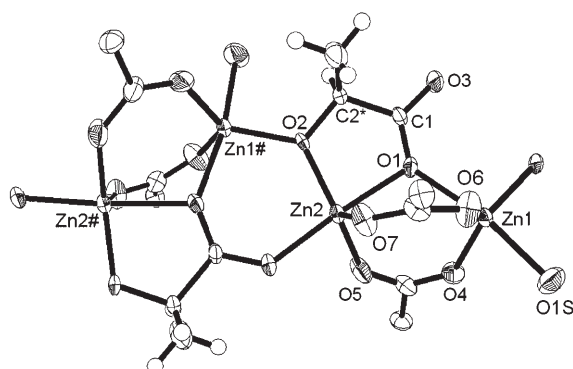


Figure 1. Section of the X-ray crystal structure of **1**-DMF, showing the coordination environments of the Zn^{2+} ions and their connectivity with lactate anions. Thermal ellipsoids are set at 50% probability. The chiral C atom of the lactic acid is marked by an asterisk. The following translation was applied: #) $-0.5+x, 0.5-y, 2-z$.

lactate ligand, a carboxylate oxygen atom of another lactate ligand, and the oxygen atom of a DMF molecule. The second Zn^{2+} ion is chelated by one lactate ligand (by the carboxylic and hydroxy oxygen atoms) and coordinated to a carboxylic oxygen atom of another lactate ligand. In addition, the two Zn^{2+} ions are linked to each other by two bridging benzenedicarboxylate ligands (Figure 1). Overall, each lactate dianion connects four Zn^{2+} ions.

The Zn^{2+} ions and lactate ligands form 1D chiral chains running along the *a* axis (Figure 2). These chains act as SBUs, which are further interlinked by benzenedicarboxylate spacers in the other two directions to form a 3D coordination polymer of **1** with an open architecture.^[11] The pores of roughly 5 Å diameter are interconnected in three directions. The chiral centers of the *L*-lactate moieties are exposed within the voids. In short, the pores in **1** have a homochiral environment.

In the as-synthesized material, the pores are occupied by coordinated DMF ligands, as well as guest DMF molecules that can readily be removed at elevated temperatures. A thermogravimetric analysis on the crystalline product of **1**-DMF indicates an approximately 30% loss of weight between 110–200 °C, which is roughly equivalent to the total weight of the coordinated and uncoordinated solvent DMF molecules. Heating the as-synthesized material at a lower temperature (for example, 90 °C) in vacuo for 3 h leads to a 10% weight loss, which corresponds to a partial removal of the guest molecules from the pores. The crystalline nature of the partially evacuated material $\mathbf{1}(\text{DMF})_x$ ($x \approx 0.4$) was confirmed by powder XRD measurements, in which no significant shift or broadening of peaks was observed compared to the diffractogram of the as-synthesized form. However, heating **1** above 90 °C for a prolonged period of time (several days) induces partial collapse of the framework,

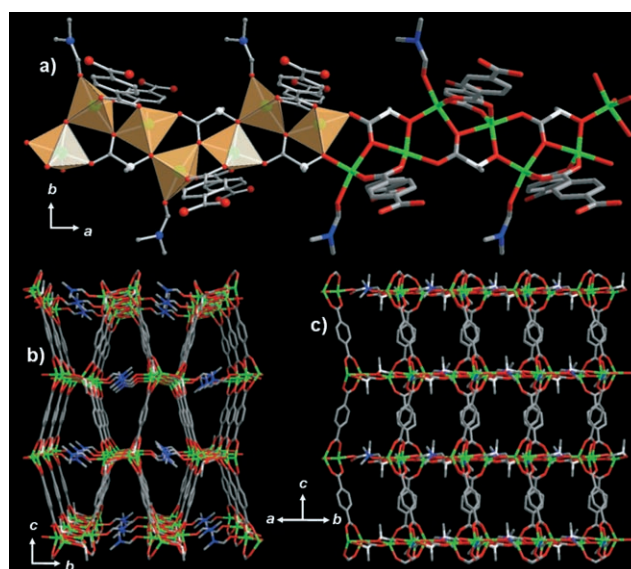


Figure 2. a) A view of the 1D chiral chains (as both ball-and-stick/polyhedra and wire models; polyhedra represent the Zn coordination environments) in the structure of **1**-DMF. b) Perspective view of the structure of **1**-DMF along the *a* axis. c) Projection of the structure of **1**-DMF in the (110) plane. Hydrogen atoms and guest molecules are omitted for clarity. Zn green, N blue, O red, C gray; chiral C atoms of the lactic acid ligand are shown in white.

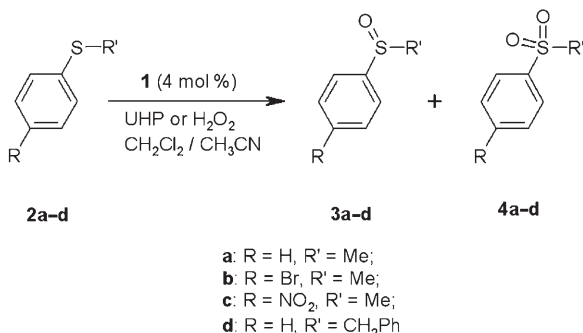
judging from the peak broadening and appearance of new peaks in powder XRD patterns. This outcome is probably due to the slow detachment of coordinated DMF ligands. These results suggest that the coordinated DMF molecules do not play a direct role in the formation of the metal–organic architecture, but do prevent the porous structure from collapsing.^[12]

The permanent porosity of the partially evacuated material ($\mathbf{1}(\text{DMF})_{0.4}$) was established by reversible gas-sorption experiments using H_2 at 78 K, which revealed an unsaturated type I isotherm characteristic of microporous materials (see Supporting Information). The corresponding Langmuir surface area was estimated to be $190 \text{ m}^2 \text{ g}^{-1}$, which is similar to typical microporous zeolites, but rather small compared to other metal–organic porous materials.^[13] This low surface area may be attributed to the incomplete evacuation of guest DMF molecules from the pores in **1**. Nevertheless, the sustainability of the open architecture of **1** is unambiguously demonstrated by the gas-sorption experiments.^[7] The guest DMF molecules in **1**-DMF can be smoothly exchanged with other solvent or guest molecules in solution without causing structural collapse, demonstrating the porosity of **1** with respect to guest exchange. The corresponding solvent-accessible volume of the microporous metal–organic framework in **1** was estimated to be as high as 41%, assuming the guest-free structure $[\text{Zn}_2(\text{bdc})(\text{L-lac})(\text{dmf})]$.^[14]

The most valuable properties of the homochiral porous material **1** arise from the unique combination of its porosity and chirality. Having the importance of enantiopure sulfonides both as efficient synthetic auxiliaries and as valuable

pharmaceuticals in mind,^[15] we examined the enantioselective sorption of several substituted thioether oxides (**3a–d**, see Scheme 2) in the homochiral porous material **1**. The crystalline, partially evacuated material **1**-(DMF)_{0.4} was stirred in a CH₂Cl₂ solution containing a racemic mixture of sulfoxides for 16 h, collected, and thoroughly washed with methanol to extract adsorbed guest molecules. Material **1** showed a remarkable sorption capability towards the sulfoxides with smaller substituents, such as H, Me (**3a**), and Me, Br (**3b**)—0.68 and 0.18 molecules, respectively, per formula unit of [Zn₂(bdc)(L-lac)(dmf)]. The enantiomeric excess (*ee*) values for the adsorbed guests were found to be 20% for **3a** and 27% for **3b**, with the *S* enantiomer in excess for both cases. However, sulfoxides with larger substituents (**3c** and **3d**) were not included in the pores of **1** in any significant amount. Such size- and enantioselective guest inclusion clearly indicates that **1** has a robust framework structure with pores of uniform size and chiral environment.^[17] After the sorption experiments, the porous matrix of **1** could be regenerated by extracting the adsorbed guest molecules and reused in the next cycles of sorption experiments, without appreciable loss of its sorption capability.^[18] Although the enantioselectivity is modest, these results suggest that **1** may be useful for the separation or purification of such compounds.

The metal–organic porous material **1** is also capable of mediating highly size- and chemoselective catalytic oxidation of thioethers **2** to sulfoxides **3** by urea hydroperoxide (UHP) or H₂O₂ (Scheme 2, Table 1). Paralleling the sorption behavior described above, thioethers **2a** and **2b** with smaller substituents exhibited reasonable conversion (64 and 58%, respectively; Table 1, entries 1 and 2) and high selectivity (92



Scheme 2. Oxidation of sulfides catalyzed by **1**.

Table 1: Oxidation of sulfides **2a–d** catalyzed by **1**.^[a]

Entry	Sulfide	Oxidant (equiv)	1 /Sulfide	Solvent	Conversion [%] ^[b]	Selectivity [%] ^[c]
1	2a	UHP (2)	1:2	CH ₂ Cl ₂	64	92
2	2b	UHP (2)	1:2	CH ₂ Cl ₂	58	83
3	2c	UHP (2)	1:2	CH ₂ Cl ₂	7	90
4	2d	UHP (2)	1:2	CH ₂ Cl ₂	3	[d]
5	2a	H ₂ O ₂ 30% (3)	1:3	CH ₃ CN	92	100
6	2a	H ₂ O ₂ 90% (3)	1:3	CH ₂ Cl ₂ /CH ₃ CN 10:1	100	87
7	2b	H ₂ O ₂ 90% (3)	1:3	CH ₂ Cl ₂ /CH ₃ CN 10:1	85	100
8	2b	H ₂ O ₂ 90% (3)	1:50	CH ₂ Cl ₂ /CH ₃ CN 10:1	58	100

[a] Reaction conditions: sulfide concentration 0.05 mol L⁻¹, room temperature, 16 h. [b] Calculated as ([sulfone] + [sulfoxide]) / ([sulfide] + [sulfoxide] + [sulfone]). [c] Calculated as [sulfoxide] / ([sulfoxide] + [sulfone]). [d] Not measured.

and 83%, respectively) after 16 h of catalytic reaction, whereas thioethers **2c** and **2d** with bulkier substituents exhibited very poor conversion (only a few percent; Table 1, entries 3 and 4). The remarkable size selectivity in the catalytic reaction implies that the reaction primarily occurs inside the uniform micropores of the framework solid **1** and, therefore, attests to the heterogeneous nature of the catalysis.^[19] Furthermore, upon using H₂O₂ instead of UHP and varying the solvent composition, the conversion and selectivity reached a quantitative level (Table 1, entries 5–8).^[20] We also found that each formula unit of **1** can perform at least 30 catalytic cycles without loss of oxidation selectivity. To our knowledge, the metal–organic porous material **1** is the first example of its kind that exhibits such a remarkable catalytic activity in sulfoxidations. The mechanism of the catalytic reaction is currently under investigation.^[21]

Despite the good conversion we, unfortunately, failed to observe any asymmetric induction in the catalytic sulfoxidations. The origin of the failure remains to be investigated in conjunction with the reaction mechanism. However, enantioenriched sulfoxides can be obtained by enantioselective sorption of the resulting racemic mixture by the chiral pores of **1**, which occurs simultaneously with the catalytic process. For example, after catalytic oxidation of **2a** using a comparable amount of **1** (Table 1, entry 1), we observed that (*S*)-**3a** was preferentially adsorbed with 20% *ee* in the pores of crystalline **1**, leaving the corresponding *R* enantiomer in excess in the solution phase. Thus, the homochiral metal–organic microporous material **1** provides a unique opportunity to produce enantioenriched sulfoxides in a one-pot process, through the size-selective catalytic oxidation of thioethers, using cheap and environment-friendly H₂O₂, and the enantioselective separation of the products. With improved enantioselectivity, this method may offer promise for the synthesis of enantiopure sulfoxides, as an alternative to the traditional asymmetric oxidation methods using soluble transition-metal catalysts.^[15,22]

In conclusion, we have described a new approach to the synthesis of homochiral metal–organic porous materials starting from readily available chemicals. We successfully produced a 3D homochiral microporous framework that has permanent porosity, size- and enantioselective guest-sorption properties, as well as remarkable catalytic activity with size- and chemoselectivity, and high conversion in the oxidation of thioethers to sulfoxides. Studies to elucidate the mechanism

of the catalytic reaction and the origin of the enantioselectivity in guest-sorption are in progress.

Experimental Section

Synthesis: A DMF solution (10 mL) containing Zn(NO₃)₂·6H₂O (300 mg, 1 mmol), H₂bdc (83 mg, 0.5 mmol), and L-H₂lac (49 mg, 0.5 mmol) in a teflon-lined steel bomb was heated at 110°C for 2 days. Colorless rod-shaped crystals were collected, washed with DMF, and Et₂O, and dried in vacuo for 3 min to yield **1**-DMF (240 mg, 86%). Elemental analysis (%) calcd for [Zn₂(bdc)(L-lac)-

(dmf)]·0.9DMF·0.1H₂O: C 38.31, H 4.14, N 5.08; found: C 38.38, H 4.23, N 5.08. X-ray data for **1**·DMF: C₁₇H₂₂N₂O₉Zn₂, *M*_r = 529.11, orthorhombic, *P*2₁2₁1 (No. 19), *a* = 10.299(2), *b* = 11.824(2), *c* = 20.372(4) Å, *V* = 2480.81(90) Å³, *Z* = 4, *T* = 223 K, ρ_{calcd} = 1.417 g cm⁻³, $\mu(\text{MoK}\alpha)$ = 1.977 mm⁻¹, *R*₁ = 0.0474, *wR*₂ = 0.1339 (*I* > 2 σ (*I*)), GoF = 1.116, Flack = 0.06(2). See Supporting Information for further details. CCDC-281753 (**1**·DMF) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Enantioselective sorption experiments: A racemic sulfoxide (**3a-d**, 0.1 mmol) was dissolved in CH₂Cl₂ (2 mL), and the partially evacuated material **1**·(DMF)_{0.4} (heated at 90°C for 3 h in vacuo before use, 40 mg, 0.17 mmol of zinc atoms) was added to the solution. After stirring the mixture for 16 h at room temperature, the crystalline adsorbent was collected by filtration and flushed with hexane (1 mL), which does not wash out the adsorbed compounds. After the adsorbed sulfoxide was extracted with methanol (2 × 5 mL), the solvent was removed in vacuo, and the resulting sulfoxide was purified by passing it through a short column (SiO₂, hexane/EtOAc) to remove DMF. The enantiomeric excess was measured by ¹H NMR spectroscopy with the chiral shift reagent Eu(hfc)₃ (hfc = 3-(heptafluoropropylhydroxymethylene)-(+)-camphorate) in CCl₄, as described in reference [16].

Typical catalytic sulfoxidation experiment: A mixture of a sulfide (**2a-d**, 0.1 mmol), the partially evacuated material **1**·(DMF)_{0.4} (0.004 to 0.1 mmol zinc atoms), and an oxidant (UHP or H₂O₂, 1–3 equiv with respect to the sulfide) dissolved in CH₂Cl₂ (2 mL) or CH₂Cl₂:CH₃CN (10:1, 2 mL) was stirred at room temperature for 16 h. Then, the solid catalyst was collected by filtration, and the adsorbed sulfoxide was extracted with methanol (2 × 5 mL). The extract and filtrate were combined, the volatiles were removed in vacuo, and the sulfide, sulfoxide, and sulfone were purified by column chromatography (SiO₂, hexane/EtOAc). The composition of the reaction products and the enantiomeric excess were measured by ¹H NMR spectroscopy with the chiral shift reagent Eu(hfc)₃ in CCl₄, as described in reference [16].

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- [10] The Zn–O distances between Zn^{2+} ions and the hydroxy oxygen atom of the lactate anion in **1** (1.969 and 1.939 Å) clearly support the deprotonation of the OH group.
- [11] A number of porous metal–organic frameworks based on 1D SBUs have been described. For recent examples, see: N. L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O’Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 1504–1518, and references therein.
- [12] Similar collapse of porous structures was observed upon removal of coordinated DMF ligands in: H. Chun, D. Kim, D. N. Dybtsev, K. Kim, *Angew. Chem.* **2004**, *116*, 989–992; *Angew. Chem. Int. Ed.* **2004**, *43*, 971–974.
- [13] Typically, the specific surface areas of metal–organic microporous materials are in the range of 1000–3000 m^2g^{-1} ; see ref. [2] for recent examples. However, the highest Langmuir surface area obtained to date for metal–organic frameworks is 5650 m^2g^{-1} ; see ref. [1k] and H. K. Chae, D. Y. Siberio-Pérez, J. Kim, Y. Go, M. Eddaoudi, A. J. Matzger, M. O’Keeffe, O. M. Yaghi, *Nature* **2004**, *427*, 523–527.
- [14] A. L. Spek, PLATON, a multipurpose crystallographic tool, Utrecht University, Utrecht, The Netherlands, **2001**.
- [15] Recent reviews on chiral sulfoxides: a) H. B. Kagan in *Catalytic Asymmetric Synthesis* (Ed.: I. Ojima), 2nd ed., Wiley-VCH, New York, **2000**, chap. 6, p. 327; b) I. Fernandez, N. Khier, *Chem. Rev.* **2003**, *103*, 3651–3706, and references therein; c) H. J. Federsel, *Chirality* **2003**, *15*, S128–S142.
- [16] K. P. Bryliakov, E. P. Talsi, *Angew. Chem.* **2004**, *116*, 5340–5342; *Angew. Chem. Int. Ed.* **2004**, *43*, 5228–5230.
- [17] The material $[\text{Zn}_2(\text{bdc})(\text{L-lac})(\text{dmf})_x]$ ($x < 1$) with partially removed coordinating DMF ligands showed poorer sorption of **3b** (about 0.05 molecules per formula unit of $[\text{Zn}_2(\text{bdc})(\text{L-lac})(\text{dmf})]$), along with a lower *ee* value (12% in favor of the *S* enantiomer).
- [18] After the sorption experiment, the crystalline material **1** was washed thoroughly with CH_2Cl_2 (5 portions, 4–5 mL each) to remove traces of sorbed sulfoxide, collected by filtration, and dried in air for 1 h, before use in the next cycles of sorption experiments. The amount of sorbed **3b** in **1** in the second cycle was found to be the same, 0.18 molecules per formula unit of $[\text{Zn}_2(\text{bdc})(\text{L-lac})(\text{dmf})]$.
- [19] The heterogeneous nature of the catalysis was further confirmed in that no conversion was observed in the reaction of **2b** with UHP in the supernatant solution, removed after stirring with **1** in CH_2Cl_2 for 16 h.
- [20] Without a catalyst, H_2O_2 and UHP do not oxidize the sulfides into sulfoxides or sulfones, as no conversion was observed after 18 h of reaction of **2b** (10 mg, 0.05 mmol) with UHP (10 mg, 2 equiv) in CH_2Cl_2 , or with H_2O_2 (90%, 3 equiv) in $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{CN}$ (10:1). Also see: M. Palucki, P. Hanson, E. N. Jacobsen, *Tetrahedron Lett.* **1992**, *33*, 7111–7114.
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