

Article

# One-Dimensional Helical Homochiral Metal-Organic Framework Built from 2,2'-Dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic Acid

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**Abstract:** A homochiral metal-organic framework (MOF) based on enantiopure (*R*)-2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid was synthesized. X-ray crystal diffraction studies revealed that the MOF adopts a one-dimensional infinite right-handed helical tubular structure along the *a*-axis, which serves as a host for the inclusion of guest dimethylformamide (DMF) molecules.

**Keywords:** homochiral metal-organic framework; chiral ligand; helix structure; one-dimensional network

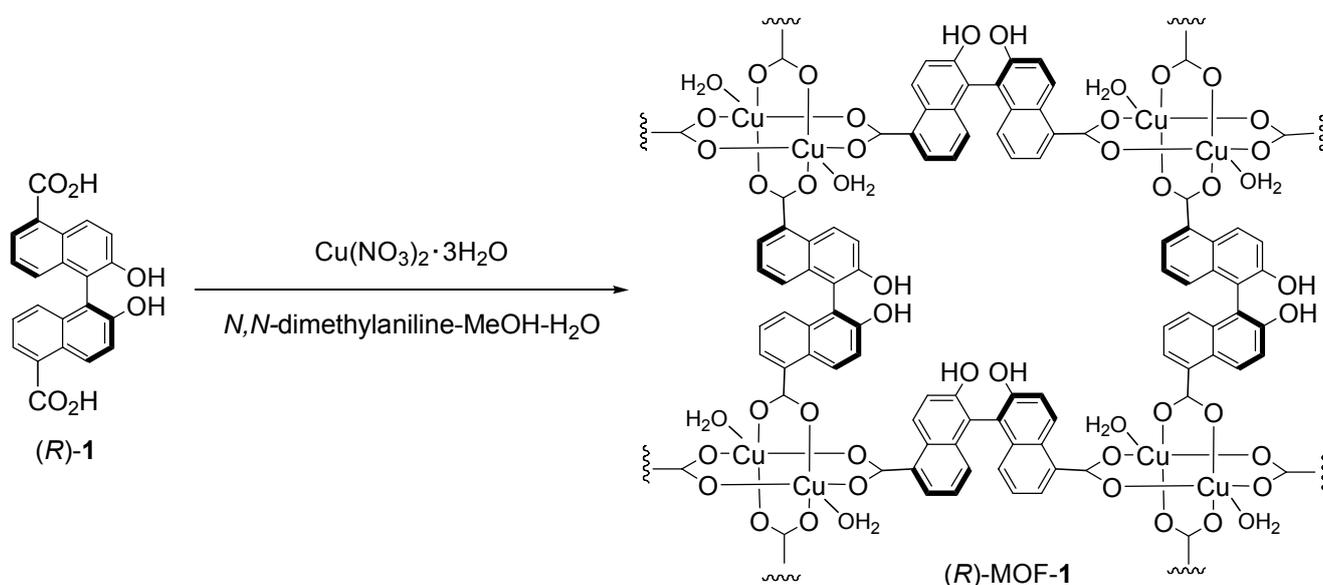
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## 1. Introduction

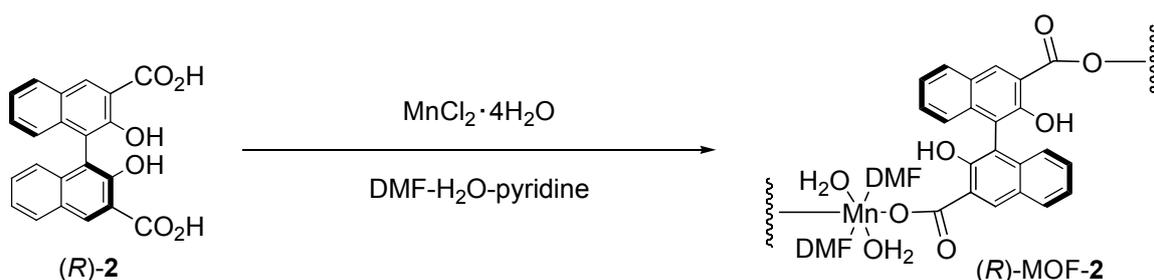
The field of metal-organic frameworks (MOFs) has grown explosively in recent years [1-8]; numerous studies have been reported owing to the potential applications of MOFs in gas storage [9-15], separation [16-23], luminescent materials [24-32], and heterogeneous catalysis [33-41]. While several MOFs have been discovered so far, only a few examples of chiral MOFs for enantiomer separations or heterogeneous asymmetric catalysis have been investigated [42]. We recently reported the synthesis of a

novel two-dimensional homochiral MOF, (*R*)-MOF-1, from (*R*)-2,2'-dihydroxy-1,1'-binaphthyl-5,5'-dicarboxylic acid (**1**) (Scheme 1) and its application as an effective catalyst for the asymmetric ring-opening reaction of epoxide with amine [43] and the alcoholic kinetic resolution of styrene oxide under heterogeneous conditions [44]. The helical structures of MOFs have also attracted considerable attention because of not only their intriguing structures, but also their potential applications in chiral recognition, nonlinear optical materials, and asymmetric catalysis. Over the past two decades, several MOFs containing single-, double-, and multi-stranded helices have been constructed and recently reviewed [45]. For example, one-dimensional helical metal-organic framework built from a chiral octahydrobinaphthalene-derived dicarboxylic acid showed the intense broad photoluminescence emission in the solid state [46]. Tridentate chiral Schiff base ligands has been found to form 1D helical framework which allow highly enantioselective separation of racemic secondary alcohols by inclusion crystallization [47]. Chiral binaphthylbisbipyridine-based copper (I) coordination polymer gels for use as catalysts in 1,3-dipolar Huisgen cycloaddition reactions are also reported [48]. Herein, we report the synthesis and X-ray crystal structure of the one-dimensional helical homochiral MOF, (*R*)-MOF-2, constructed from (*R*)-2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid (**2**) (Scheme 2).

**Scheme 1.** Synthesis of (*R*)-MOF-1.



**Scheme 2.** Synthesis of (*R*)-MOF-2.



## 2. Experimental Section

**General:**  $^1\text{H-NMR}$  spectra were recorded on a JEOL JNM-GSX 400 spectrometer with tetramethylsilane (TMS) as the internal standard. IR spectra were recorded with a JASCO FT-IR 4100 spectrometer. Thermogravimetric (TG) analyses were performed on a Rigaku TG8120 instrument. Solid-state circular dichroism (CD) spectra were recorded as KBr pellets on a JASCO J-820 CD system.

**Synthesis of enantiopure 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid (2):** (*R*)- and (*S*)-2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid (**2**) were synthesized according to the procedure previously reported by D. J. Cram *et al.* [49].

**Synthesis of  $[\text{Mn}_2((R)\text{-1})_2(\text{DMF})_4(\text{H}_2\text{O})_4]\cdot 2\text{DMF}$ :** A mixture of (*R*)-2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid (**2**) (78 mg, 0.2 mmol) and  $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$  (40 mg, 0.2 mmol) was dissolved in DMF (1 mL) and  $\text{H}_2\text{O}$  (2 mL), and then pyridine (1 mL) was added to the solution. The solution was stirred for 30 min at room temperature and then left for 3 days. Pale yellow prisms were obtained, filtered, and dried at room temperature to give (*R*)-MOF-2 (132 mg). IR (KBr pellet,  $\text{cm}^{-1}$ ): 3,402, 2,931, 1,655, 1,559, 1,505, 1,457, 1,392, 1,336, 1,309, 1,242, 1,101, 932, 874, 810, 755, 702.

**X-ray analysis:** X-ray single-crystal diffraction data for (*R*)-MOF-2 were collected on a Rigaku RAXIS RAPID imaging plate diffractometer using  $\text{Cu K}\alpha$  radiation. Crystal data: Formula  $\text{C}_{62}\text{H}_{74}\text{Mn}_2\text{N}_6\text{O}_{22}$ , Formula weight 1365.17, Space group  $P2_1(\#4)$ ,  $a = 10.9585(3)$ ,  $b = 25.2165(8)$ ,  $c = 11.8505(9)$  Å,  $\beta = 96.629(7)^\circ$ ,  $V = 3252.8(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho = 1.394$  g/cm<sup>3</sup>,  $2\theta_{\text{max}} = 136.4^\circ$ ,  $R1 = 0.0514$  (for 8372 reflections with  $I > 2\sigma(I)$ ),  $wR2 = 0.1315$  (for 11,652 reflections), GOF = 0.985, Flack parameter = 0.009(4) (calculated using 5,571 Friedel pairs). The structure was solved by SHELXS97 and refined by SHELXL97. The absolute structure was deduced from the Flack parameter.

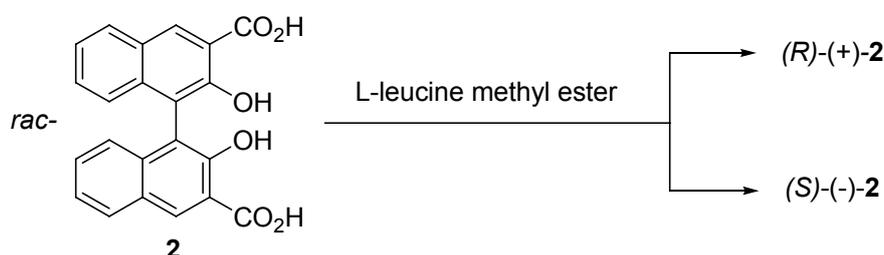
**CCDC:** 838075. See <http://www.rsc.org/suppdata/cc/...../> for crystallographic data in cif or other electric formats.

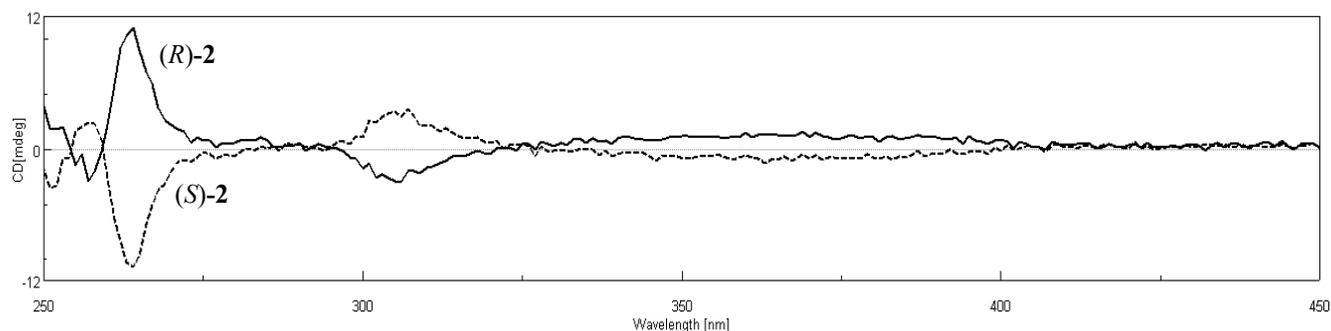
## 3. Results and Discussion

### 3.1. Synthesis of Chiral MOF

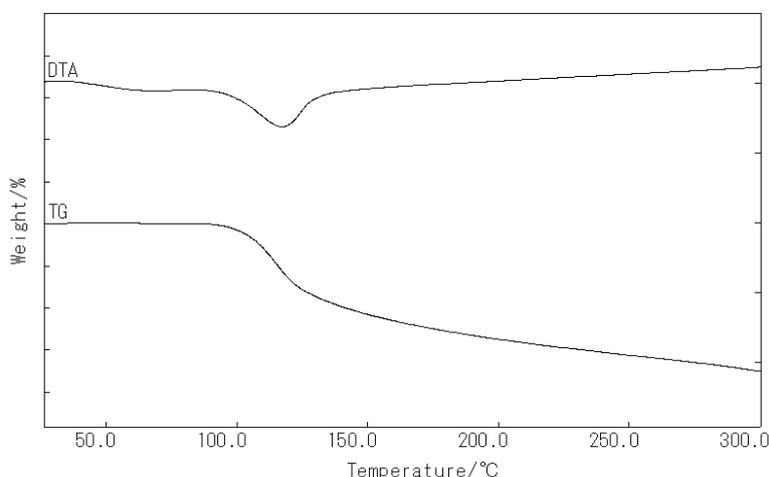
Chiral ligand (*R*)-2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid (**2**) was prepared in good yield by the diastereomeric complexation of *rac*-**2** with L-(+)-leucine methyl ester (Scheme 3). The CD spectra of (*R*)-(+)-**2** and (*S*)-(−)-**2** in  $\text{CHCl}_3$  are shown in Figure 1.

**Scheme 3.** Optical resolution of *rac*-**2**.



**Figure 1.** CD spectra of (*R*)- and (*S*)-**2** in CHCl<sub>3</sub>.

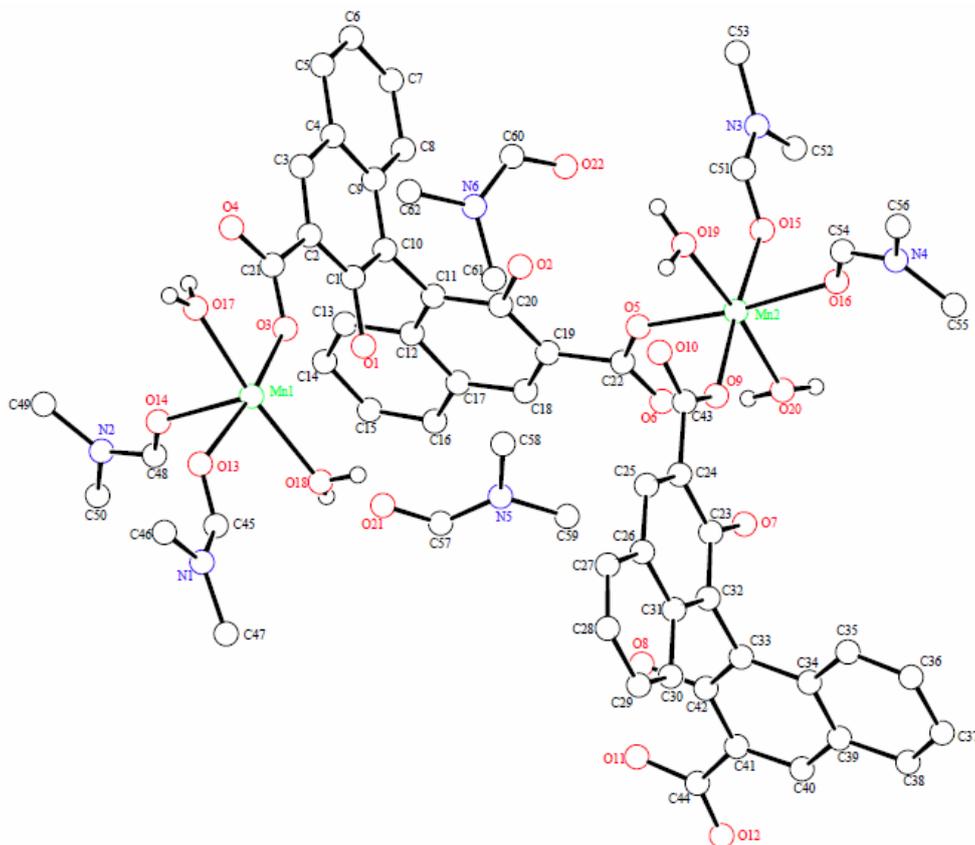
New homochiral (*R*)-MOF-**2** [Mn<sub>2</sub>((*R*)-**1**)<sub>2</sub>(DMF)<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>]·2DMF was synthesized by the reaction of (*R*)-(+)-**2** and MnCl<sub>2</sub>·4H<sub>2</sub>O in the presence of pyridine in DMF at room temperature. The product was characterized by IR spectroscopy, CD spectroscopy, thermogravimetric analysis (TGA), and X-ray analysis. The IR spectra of (*R*)-MOF-**2** exhibited peaks of νOH and νCO<sub>2</sub><sup>-</sup> at 3,401 and 1,559 cm<sup>-1</sup>, respectively. TGA showed that (*R*)-MOF-**2** loses 34.3% of its total weight in the range of 26–300 °C, which is ascribed to the loss of six DMF and four water molecules per formula unit (calculated at 37.4% of the total weight) (Figure 2).

**Figure 2.** TG trace of (*R*)-MOF-**2**.

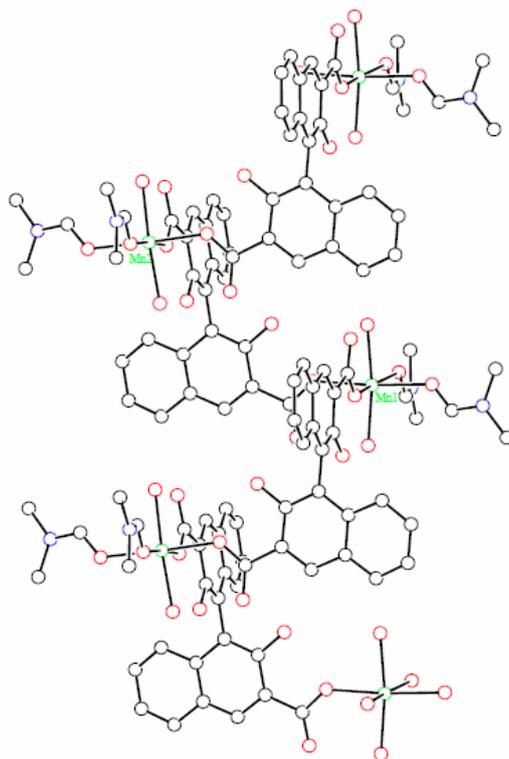
### 3.2. Crystal Structure of (*R*)-MOF-**2**

X-ray diffraction measurement revealed that (*R*)-MOF-**2** crystallizes in a chiral space group of *P*2<sub>1</sub>. An asymmetric unit of (*R*)-MOF-**2** contains two Mn<sup>2+</sup> ions, two (*R*)-**2**<sup>2-</sup> groups, four DMF molecules, four water molecules, and two DMF guest molecules, as shown in Figure 3. The Mn<sup>2+</sup> ion is coordinated by two (*R*)-**2**<sup>2-</sup> groups, two DMF molecules, and two water molecules. The sixth coordination site of Mn1, although vacant in Figure 3, is occupied by O11 of the (*R*)-**2** group lying in the next unit cell in the direction of *a*-axis. A helical chain composed of –Mn–(*R*)-**2**–Mn–(*R*)-**2**– is thus formed in the right-handed form and extends along the *a*-axis as shown in Figure 4. The guest molecules are bound to the water molecules by the hydrogen bonds of O21–H...O18 and O22–H...O19.

**Figure 3.** Structure of (*R*)-MOF-2 in an asymmetric unit and atomic numbering system. Hydrogen atoms, excluding those of water, are omitted for clarity.

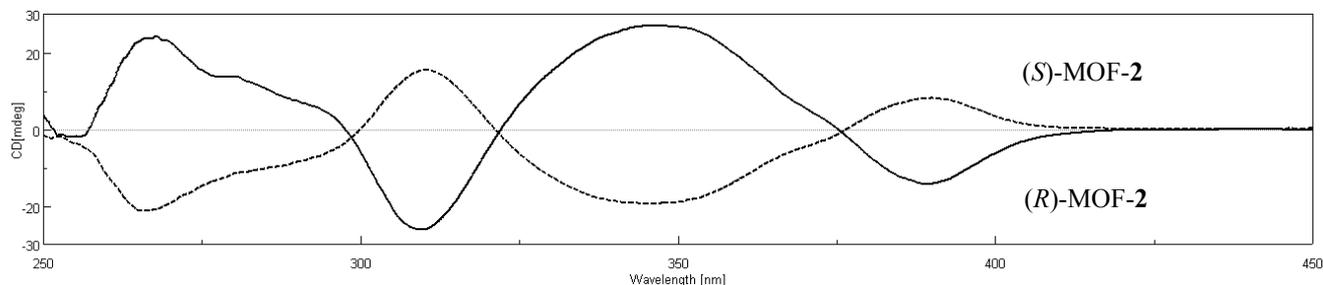


**Figure 4.** Right-handed helical structure in the crystal of (*R*)-MOF-2. The *a*-axis of the crystal is oriented vertically. All hydrogen atoms and guest molecules are omitted for clarity.



We also prepared (*S*)-MOF-2 using (*S*)-2 as the chiral ligand. As shown in Figure 5, the solid-state CD spectra of (*R*)- and (*S*)-MOF-2 synthesized from (*R*)- and (*S*)-2, respectively, are mirror images of each other, thus indicating that the helices built from (*R*)- and (*S*)-2 are enantiomeric.

**Figure 5.** Solid-state CD spectra of (*R*)- and (*S*)-MOF-2 in KBr pellet.



#### 4. Conclusions

We have synthesized a one-dimensional helical homochiral MOF (MOF-2) using  $\text{MnCl}_2$  and  $C_2$  symmetric chiral ligands (*R*)- and (*S*)-2 as the building blocks. We are currently studying its potential applications in heterogeneous asymmetric catalysis and enantioselective separations.

#### Acknowledgment

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