

# A thermally stable and homochiral **j<sub>sm</sub>**-type metal–organic framework: Syntheses, structure and properties



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## ABSTRACT

A novel 3D homochiral framework, [Co(L)(BYBP)<sub>0.5</sub>] (**1**), has been synthesized by the solvothermal reaction of a much longer ligand, 4,4'-di(4-pyridyl)-biphenyl (BYBP, 15.7 Å) which is more than twice the length of 4,4'-bipy, and an achiral flexible V-shaped ligand, 4,4'-dicarboxydiphenylamine (H<sub>2</sub>L) (Scheme 1). The resultant complex was characterized by IR spectroscopy, thermal analysis, single crystal X-ray diffraction, in situ variable-temperature power X-ray diffraction and circular dichroism (CD). The results indicated that complex **1** is a rare homochiral 3-fold **j<sub>sm</sub>** net. Its thermal stability was investigated and **1** keeps its crystal structure up to 375 °C. Magnetic susceptibility measurements indicate that **1** exhibits antiferromagnetic behavior.

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## 1. Introduction

Over recent decades, metal–organic frameworks (MOFs) have received increasing attention because of their intriguing aesthetic architectures and topological features, as well as their promising applications as functional materials, which have stimulated the interest of chemists in recent years [1–3]. Achiral molecules have now been investigated for the assembly into homochiral porous networks at a solid–liquid interface. This has implications for practical processes such as separations, but also for understanding how homochirality – crucial in biological systems – arises from achiral or racemic species [4]. Previous research indicated that some supramolecular interactions, such as hydrogen bonds or  $\pi$ – $\pi$  interactions, may be the driving force and contribute to the occurrence of symmetry breaking [5]. Without the driving force of supramolecular interactions, symmetry breaking is rarely seen in the crystallization of three-dimensional (3D) framework materials [6]. For building chiral frameworks, the helix gives a good opportunity to transmit chiral information, and flexible multidentate organic bridging ligands may be efficient candidates to improve the helix elements for generating chiral MOFs [7]. Various parameters, such as ligand, solvent, temperature and pH value of the solution [8–11], can affect the rational synthesis and control the porosity and topology of new coordination polymers. The introduction of longer ligands has largely widened the pore size, but interpenetration

takes place at the same time, which greatly reduces the porosity and the space of the architecture [12]. Otherwise, interpenetration is not considered as negative as it has been sought after previously [13–15]. In this work, the solvothermal reaction of H<sub>2</sub>L, and Co(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O in the presence of BYBP resulted in the formation of black octahedron crystals, namely [Co(L)(BYBP)<sub>0.5</sub>] (**1**).

## 2. Experimental

### 2.1. Materials and general methods

The reagents and solvents employed were commercially available and used as received. IR absorption spectra of the compounds were recorded in the range 400–4000 cm<sup>−1</sup> on a Nicolet (Impact 410) spectrometer with KBr pellets (5 mg of sample in 500 mg of KBr). C, H and N analyses were carried out with a Perkin–Elmer 240C elemental analyzer. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å), in which the X-ray tube was operated at 40 kV and 40 mA. The as-synthesized samples were characterized by thermogravimetric analysis (TGA) on a Perkin Elmer thermogravimetric analyzer Pyris 1 TGA up to 1023 K using a heating rate of 10 K min<sup>−1</sup> under a N<sub>2</sub> atmosphere. The circular dichroism (CD) spectrum of **1** was recorded at room temperature with a Jasco J-810(S) spectropolarimeter (KBr pellets). Temperature dependent magnetic susceptibility data were obtained on a MPMS XL-7 SQUID magnetometer under an applied field of 2000 Oe over the temperature range 2–300 K.

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## 2.2. Synthesis of [Co(L)(BYBP)<sub>0.5</sub>] (1)

A mixture of Co(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (29.1 mg, 0.1 mmol), BYBP (30.8 mg, 0.1 mmol), H<sub>2</sub>L (25.7 mg, 0.1 mmol) and 0.5 mL of 3% NaOH solution was dissolved in 6 mL of EtOH/H<sub>2</sub>O (1:1, v/v). The final mixture was placed in a Parr Teflon-lined stainless steel vessel (15 mL) under autogenous pressure and heated at 95 °C for 3 days. Black octahedral crystals were obtained, which were washed with the mother liquid and then dried under ambient conditions (Yield: 36% based on H<sub>2</sub>L). *Anal.* Calcd for C<sub>25</sub>H<sub>16</sub>O<sub>4</sub>N<sub>2</sub>Co: C, 64.23; H, 3.40; N, 5.99; Found C, 63.92; H, 3.50; N, 5.81%. IR (KBr, cm<sup>-1</sup>): 3135(w), 1596(s), 1553(s), 1504(s), 1449(m), 1375(s), 1263(s), 1239(s), 1131(s), 1061(w), 960(w), 934(w), 822(m), 781(s), 729(s), 651(m), 537(m).

## 2.3. Crystal structure determination

X-ray crystallographic data of **1** were collected at room temperature using epoxy-coated crystals mounted on a glass fiber. All measurements were made on a Bruker Apex Smart CCD diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structure of compound **1** was solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using full-matrix least-squares procedures based on  $F^2$  values [14]. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on their parent atoms. Relevant crystallographic data are presented in Table 1, while selected bond lengths and angles are given in the Supporting information, Table S1.

## 3. Results and discussion

### 3.1. Structure description of [Co(L)(BYBP)<sub>0.5</sub>] (1)

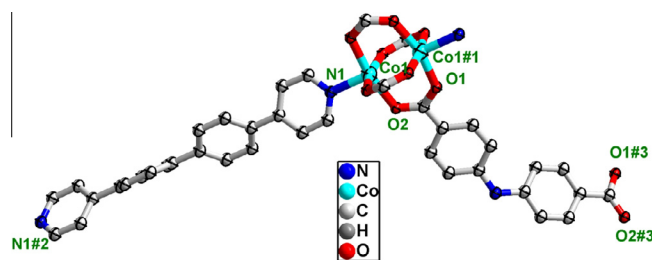
Single-crystal X-ray diffraction revealed that complex **1** crystallizes in the tetragonal chiral space group  $I4_122$ .<sup>1</sup> The asymmetric unit of **1** contains half an independent Co(II) cation, half L<sup>2-</sup> and one quarter BYBP. As shown in Fig. 1, each cobalt atom is five-coordinated by four oxygen atoms from L<sup>2-</sup> and one nitrogen atom from a BYBP ligand. Each pair of Co(II) ions are bridged by four carboxylate groups to generate a well-known paddle-wheel SBU. The axial position of each Co(II) ion, with a square pyramidal coordination geometry, is coordinated by the BYBP molecule.

The H<sub>2</sub>L and BYBP ligands show an interesting conformation, as shown in Scheme 1, the C $\cdots$ N<sub>core</sub> $\cdots$ C angle of the H<sub>2</sub>L ligands is 126°, which is defined by the central nitrogen atom and the carbon atoms of the carboxyl groups. On the other hand, the dihedral angle between the two phenyl rings of the H<sub>2</sub>L ligands is about 50°. For the linear BYBP ligands, the dihedral angle between two adjacent phenyl rings or pyridine rings are all almost 45°.

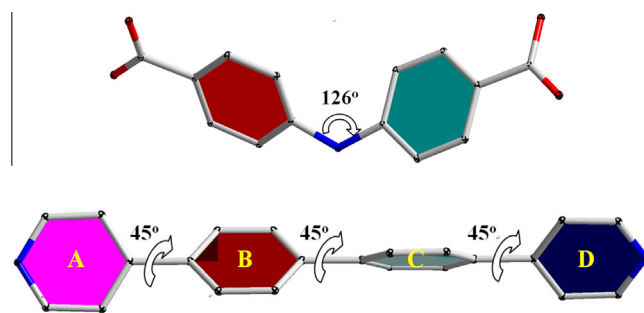
The six L<sup>2-</sup> linker assembly with six Co<sub>2</sub>(COO)<sub>4</sub> units result in a twisted chair-form metalocyclic ring, which shows a large dimension of about 38.9  $\times$  15.9 Å (Fig. 2). These chair-form metalocyclic rings are connected to each other to form a diamond structure. Furthermore, the diamond structures are connected to each other forming a 3D framework with large channels (Fig. 3a). When the paddle-wheel SBUs are simplified as nodes and the bridging L<sup>2-</sup>

**Table 1**  
Crystallographic data for compound **1**.

Formula	C <sub>25</sub> H <sub>16</sub> CoN <sub>2</sub> O <sub>4</sub>
Formula weight	467.33
Crystal system	tetragonal
Space group	$I4_122$
<i>a</i> (Å)	15.9669(7)
<i>b</i> (Å)	15.9669(7)
<i>c</i> (Å)	16.9298(13)
$\alpha$ (°)	90
$\beta$ (°)	90
$\gamma$ (°)	90
<i>V</i> (Å <sup>3</sup> )	4316.1(5)
<i>Z</i>	8
<i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	1.438
$\mu$ (Mo K $\alpha$ )(mm <sup>-1</sup> )	0.83
<i>F</i> (000)	2136.0
<i>R</i> <sub>int</sub>	0.0288
Observed data [ $I > 2\sigma(I)$ ] [ $I > 2\sigma(I)$ ]	1911
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ $I > 2\sigma(I)$ ]	0.0399, 0.0806
<i>S</i>	0.989
Minimum and Maximum Resd dens (e Å <sup>-3</sup> )	-0.13, 0.29



**Fig. 1.** Coordination environment of the Co(II) ion in **1**. The hydrogen atoms are omitted for clarity. Symmetry codes: (#1) 2-x, 1-y, z; (#2) 1-x, -y, z; (#3) x, 1.5-y, 1.25-z.



**Scheme 1.** Conformational structures of the BYBP and H<sub>2</sub>L ligands.

ligands are simplified as the linkers, a uninodal four-connected **dia** topology can be rationalized.

The L<sup>2-</sup> ligands bridging Co<sub>2</sub>(COO)<sub>4</sub> units form infinite left-handed helical chains along the *b*-axis, co-generated helices are derived with adjacent helical chains, which makes the diamond network exhibit a chiral 3-D metal-organic framework (Fig. 4). The helical chains have a pitch of 50.7894(4) Å and the nearest Co $\cdots$ Co distance through the L<sup>2-</sup> ligand is 14.0535(9) Å.

BYBP molecules link Co<sub>2</sub>(COO)<sub>4</sub> units and are inserted into the diamond net, leading to the formation of a complicated 3-D network for **1** with large open channels along the *a* and *b* axes (Fig. 3b). When the paddle-wheel SBUs are simplified as nodes and the bridging L<sup>2-</sup> and BYBP ligands are simplified as the linkers,

<sup>1</sup> Crystallographic data of **1** were collected on a Bruker Apex Smart CCD diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) using the  $\omega$ -scan technique. Crystal data and structural parameters for **1**: [C<sub>25</sub>H<sub>16</sub>O<sub>4</sub>N<sub>2</sub>Co], Mr = 467.33, Tetragonal, space group  $I4_122$ , *a* = 15.9669, *b* = 15.9669, *c* = 16.9298 Å, *V* = 4316.12 Å<sup>3</sup>, *Z* = 8, *D<sub>c</sub>* = 1.438 g cm<sup>-3</sup>,  $\mu$ (Mo K $\alpha$ ) = 0.830 mm<sup>-1</sup>, 1911 independent reflections (*R*<sub>int</sub> = 0.0399), final *R*<sub>1</sub> [ $I > 2\sigma(I)$ ] = 0.0288 and final *wR*<sub>2</sub> = 0.0806.

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