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Zn(II) Porous Material Assembled from V-Shaped Dicarboxylate Ligand and N-Donor Ancillary Ligand

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A new porous metal-organic framework, $[Zn(fipbb)(bpp)]_n$ (1) (H_2fipbb = (4,4′-(hexafluoroisopropylidene)bis(benzoic acid) and bpp = 1,3-bis(4-pyridyl)propane), constructed from mixed flexible co-liagnds, has been synthesized under mild condition and characterized by elemental analysis, IR and single-crystal X-ray diffraction analysis. Compound 1 exhibits (4,4) grid network containing multi-helical chains. Furthermore, two adjacent layers are displaced by about one half of the polymer period along the direction of extension and stacked with iterative sequence of ABAB. This result revealed that the coordination mode of fipbb and metal ion play important roles in controlling the resulting coordination framework.

Keywords crystal structure, helical chain, porous network, Zn complex

1. INTRODUCTION

Presently, the design and synthesis of new materials "on demand" is becoming increasingly significant. Keeping this in mind, new outstanding possibilities are presented in the area of the synthesis of organo-inorganic polymeric materials, where a particularly promising method to attaching to the predesign of a material is a building-block approach.[1–5] Thus far, porous coordination polymers have centered on the assembly of linear rigid polycarboxylates, especially dicarboxylates and d-block metal ions, as these metal ions have low coordination number and are easily connected to form kinds of frameworks.[6–8] Yaghi et al. have successfully constructed plenty of metal-organic frameworks (MOFs) using the self-assembly of d-block metal ions and rigid dicarboxylates.[9–11] In contrast to the rigid ligands, the conformation of flexible ones is variable; thus, they can meet the coordination geometrical requirement of metal ions through changing their conformation, which may provide more possibility for the construction of novel architectures.

On the other hand, supramolecuar networks with helicity are highly fascinating. The chiral nature in helical arrangement may also be associated with enantioselectivity, models of biological systems and optoelectronic materials. Therefore, the exploit of new systems possessing specific helicity has been an intensive research field just now. It has been proved that by the appropriate assembly of metal ions and longer and flexible organic ligand, multifarious discrete helicates and coordination polymers consisting of infinite helices can be rationally achieved.[12–15] In recent years, the employment of mixed flexible ligands during the self-assembly process has gradually become an effective approach, which is expected to obtain networks with more diverse structural motifs compared to using only one type of ligands. Thus, the auxiliary ligands containing an N-donor, such as biprydidyl-like ligand, are introduced into the reactions systems so as to tune up metal coordinated sites.[16] Taking all the above discussion into account, we focus our attention on a V-shaped flexible 4,4′-(hexafluoroisopropylidene)bis(benzoic acid)(H_2fipbb) dicarboxylate ligand, whose has been employed to build novel coordination polymer considering the following viewpoints; (i) the rotate randomly backbones gives the potential ability to construct helical assembly; and (ii) the potential longer molecular backbones of such building blocks may lead to the formation of porous MOFs with channels. Fortunately, we have successfully synthesized a new coordination polymer, $[Zn(fipbb)(bpp)]_n$ (**1**) (bpp = 1,3-bis(4-pyridyl)propane), which is 2D open grid structure containing three types of helical chains.

2. EXPERIMENTAL

Materials and Physical Measurements

All the reagents and solvents for synthesis and analysis were commercially available and used directly. Elemental analyses for carbon, hydrogen and nitrogen were performed on a Vario EL III elemental analyzer. The infrared spectra (4000 ∼ 600 cm^{-1}) were recorded by using KBr pellet on an AVATAR-370 (Nicolet) IR spectrometer (Japan). The crystal determination was performed on a Bruker SMART APEX II CCD diffractometer (Germany) equipped with graphite-monochromatized MoKα radiation ($\lambda = 0.71073$ Å) (Germany).

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TABLE 1
Crystallographic data for **1**

Empirical formula	$C_{30}H_{22}F_6N_2O_4Zn$
Formula weight	653.87
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	C2/c
Unit cell dimensions	a= 12.4777(19) Å
	b= 17.797(3) Å
	c= 13.250(2) Å
	β = 105.063(2)°
Volume, Z	2841.3(8)Å^3, 4
Calculated density (Kg/m^3)	1.529
Crystal size (mm^3)	0.25×0.21×0.15
θ Range for data collection (°)	2.04–25.20
Reflections collected	7021
Independent reflection	2545
Final R indices [$I > 2\sigma$ (I)]	R_1= 0.0320, wR_2= 0.1082
R indices (all data)	R_1= 0.0379, wR_2= 0.1143

Synthesis of the Complex

To an methane aqueous solution (10 mL) containing H_2fipbb (0.2 mmol) was added $Zn(NO_3)_2{\cdot}4H_2O$ (0.12 mmol) in water at 30°C. The pH of the resulting solution was adjusted to 6 using dilute NaOH (0.1 mol/L) and kept at 105°C for two hours to prepare compound **1**. From that solution, colourless crystals suitable for X-ray measurements were obtained. Yield: 58%. Anal. calc. (%) for $C_{30}H_{22}F_6N_2O_4Zn$: C, 55.10; N, 4.28; H, 3.39; Found: C, 55.15; N, 4.26; H, 3.37. IR (KBr cm^{-1}): 3118 (m), 2903 (w), 1615 (s), 1539 (s), 1398 (s), 1371 (s), 1248 (m), 1220 (w), 1182 (w), 1032 (m), 1021 (w), 982 (w), 832 (s).527(m).

Crystallographic Data Collection and Structure Determination

Single-crystal data were collected at 298(2) K on a Bruker Smart Apex II diffractometer equipped with graphite-monochromated Mo Kα radiation. The structure was solved using direct methods and successive Fourier difference synthesis (SHELXS-97),[17] and refined using the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97).[18] Metal atoms in all the complexes were located from the E-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses. All other hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atoms. The final agreement factor values are R_1= 0.032, wR_2= 0.1082, w= $1/[\sigma^2(F_0)^2 + (0.08P)^2]$ where$P$= $(F_0^2 + 2F_c^2)/3$. A summary of the crystallographic data is given in Table 1. Selected bond distances and angles and hydrogen-bonding geometric data are given in Table 2 and Table 3, respectively.

TABLE 2
Selected bond lengths (Å) and angles (°) for **1**

Zn(1)-O(1)	1.9447(17)	O(1)-Zn(1)-N(1)	114.61(8)
Zn(1)-N(1)	2.0677(19)	N(1)-Zn(1)-N(1)	101.75(10)
O(1)-Zn(1)-O(1)	133.11(12)	C(8)-O(1)Zn(1)	110.69(16)

3. RESULTS AND DISCUSSION

In compound **1**, X-ray single-crystal structure determination reveals that the asymmetric unit consists of one crystallographically Zn(II) ion, one Hfipbb dianion and one bpp ligand, as illustrated in Figure 1. All carboxylic groups of H_2fipbb are deprotonated, in agreement with the IR data in which no characteristic absorption bands of the -COOH group at 1700–1750 cm^{-1} are observed. For complex **1**, the difference between the asymmetric and symmetric stretches, $\Delta\nu_{as}(COO^-)$–$\nu_{as}(COO^-)$, are on the order of 200 cm^{-1} indicating that carboxyl groups are either free or coordinated to the metal in a mono-dentate fashion, consistent with the observed X-ray crystal structures of **1**. The Zn has a tetrahedron coordination environment to construct from two O atoms (O1 and O1A) from two separated fipbb ligands, and two N atoms (N1 and N2) from two different

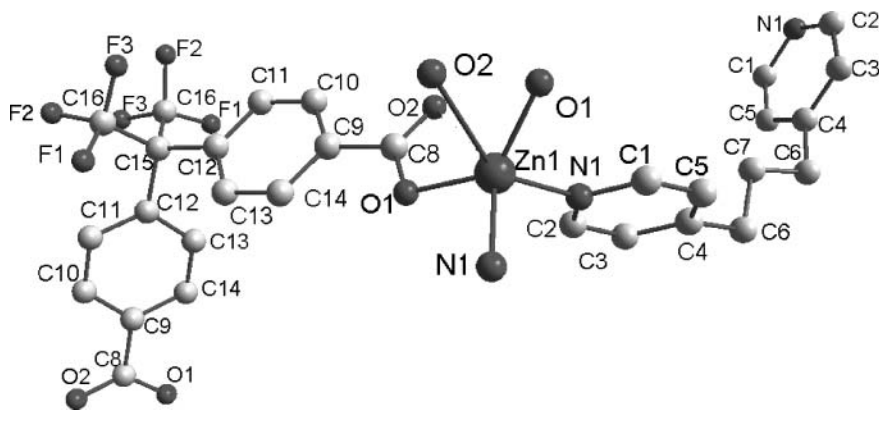


FIG. 1. Coordination environment of Zn(II) in **1**.

TABLE 3
Selected H-bonding geometric data (Å, °) for **1**

D–H···A	D···A	D–H···A	symmetry codes
C1–H1···O1	3.0773(3)	113(6)	
C6–H6B···O2	3.4840(2)	155(4)	1/2 + x,1/2 + y,z
C118–H11···F1	2.9413(7)	107(8)	

bpp ligands. The Zn-O and Zn-N distances are good agreed with related Zn-carboxylate polymers.[15] The Zn unit show in Figure 2a is further extended through the connection of bpp ligands, and results in the formation of a helical chain along the a axis and the pitch of the screw is 9.3 Å. The bpp molecule exhibits a TG conformation in the compound. As exhibited in Figure 2b, the flexible V-shaped fipbb dianion ligand joins adjacent Zn1 atoms and leads to another helical chain along the b direction and the pitch of the screw is 13.5 Å, the torsion dihedral angle of phenyl rings of fipbb is 69.5(3)°. As shown in Figure 2c, the adjacent bpp and fipbb connect Zn1 center atoms into a new helical chain the pitch of the screw is 22.8 Å. The entire 2D network of compound 1 is archiral due o the phenomenon that the left-handed screws (L-heix) and the right-handed ones (R-helix) arrange alternatively in the bc plane.

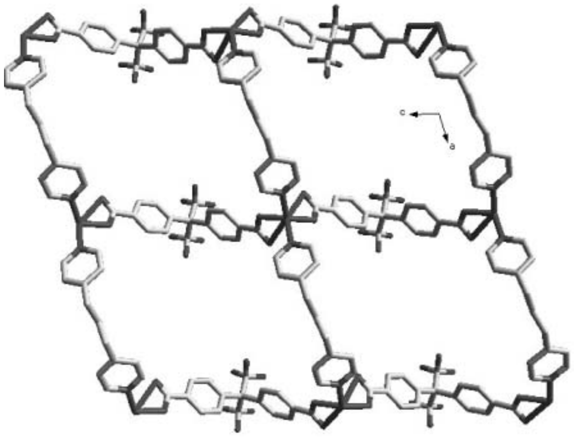
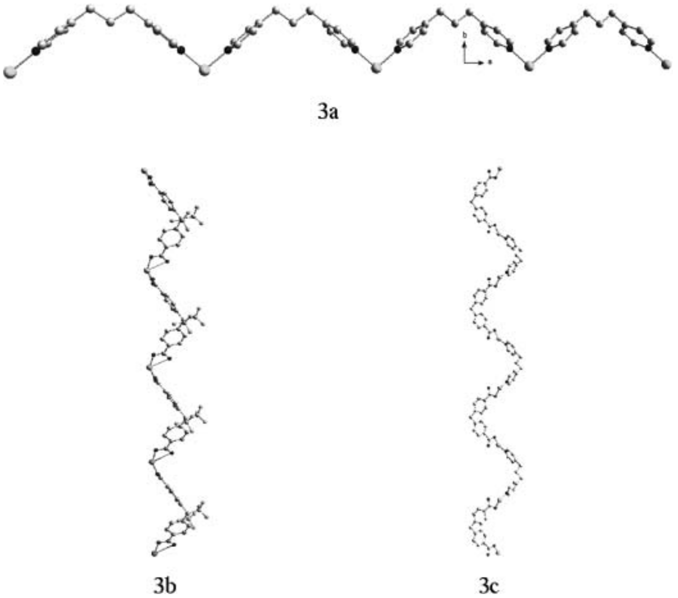


FIG. 3. Corrugated 2D grid network in **1**.

Significantly the bent fipbb and bpp moieties link Zn atoms alternatively, which results into an undulating sheet net wth a rhombic window, as shown in Figure 3. A relative coordination polymer $\{[\mathrm{Co_4(OH)(fipbb)(Hfipbb)(bpp)_2}].\mathrm{H_2O}\}_n$ exhibits a three-dimensional pillared helical layer open networks with six-connected self-interpenetrating topology based on a mixed binuclear paddle-wheel cluster and tetranuclear cobalt(II) steplike cluster.[13] The structural difference between the $\{[\mathrm{Co_4(OH)(fipbb)(Hfipbb)(bpp)_2}].\mathrm{H_2O}\}_n$ and compound **1** in the prescience of same linkages indicate that the metal ions can modulate the resulting structure, this result may be ascribed to the radium difference of metal ions. The dimensions of the net are 14.13 × 15.71 Å^2, corresponding to the distance between neighboring centers of Zn subunits at their corner. The covalent skeleton of this 2D sheet can be also described as a unique helical tubular double layer in which the left and right helical chains appear alternatively by sharing Zn subunits. By reducing multidimensional structures to simple node-and-connection reference nets, it plays an essential role in structural simplification. The di-connector bpp ligands and fipbb occupy the opposite sides and connect the center metal ions, extending the structural motif into grid 2D framework (Figure 3). Thus, Zn atoms are depicted as four–connected node, the framework can be represented simply by connecting the Zn nodes according to the connectivity defined by the bpp and fipbb ligands with (4,4) topology. Furthermore, two adjacent layers are displaced by about one half of the polymer period along the direction of extension and stacked with iterative sequence of ABAB, as shown in Figure 4. The 2D sheets are further extended comparable C...H—O and C...H—F interactions (see Table 3) to shape a 3D supramolecular



3a

3b

3c

FIG. 2. A viewing illustration of the three types of single-stranded helical chains in **1**.

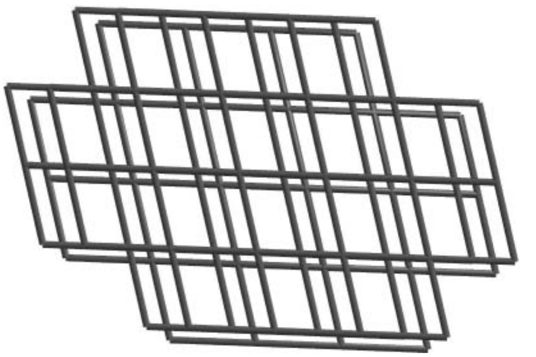


FIG. 4. Schematic illustration of stacked with iterative sequence of ABAB fashion.

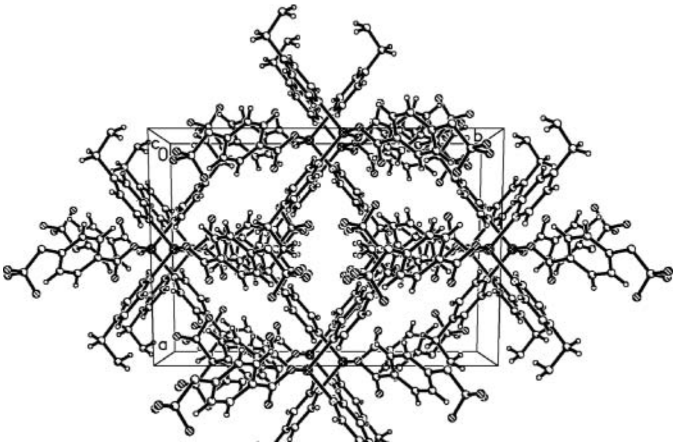


FIG. 5. A perspective viewing of 3D supramolecular framework in **1**.

network. There exists big void space in the resulting structure (Figure 5).

4. CONCLUSIONS

Assembly of Zn(II) salt with V-shaped dicarboxylate in the presence of flexible N-donor ligand leads to a new porous coordination polymer containing muti-helical chains. This result revealed that the coordination mode of fipbb and metal ion play important roles in controlling the resulting coordination framework. It is believed that the preliminary result presented herein provide a promising access to the rational design and synthesis of MOF material with specific structure and properties.

Supplementary Material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 737937 Copies of this information may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: t44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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