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Versatile Flexible Azolate-based Metal-Organic Frameworks Possessing Different Bridging Ligands

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Research Article

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ABSTRACT

Many MOF structures, especially three-dimensional ones are usually rigid mainly due to the utilization of rigid ligands such as terephthalic acid, making the robust framework difficult to remain the integrity under structure variations or against acidic/basic media. In order to solve the problem as well as enhance the chemical and thermal inertness of MOFs, we have designed to synthesize MOF structures using the semirigid ligand, 3,3',5,5'-tetramethyl-4,4'-bipyrazole (H_2Me_4bpz), as the two pyrazolate (pz) rings can rotate around its C-C chemical bond so that can release some of the pressure caused by structure variations. We chose $CuCl_2$ and $ZnSO_4$ as the metal source and successfully synthesized two novel porous MOFs through solvothermal reaction with H_2Me_4bpz .

INTRODUCTION

Crystal 1 is a Zn-based two-dimensional MOF possessing one-dimensional channel with *hcb* topology, while Crystal 2 is a Cu-based three-dimensional MOF with Cl^- as bridging ligand. In addition, the counterions of the metal salts also take part in the construction of the framework, resulting in versatile MOF structures. Metal-organic frameworks (MOFs) are gaining tremendous attention in recent years owing to their extremely high surface area, tunable porosity, facile synthesis and good stability^[1]. With numerous combinations of metal ions or metal clusters as nodes and organic linkers as struts, MOFs can be designed into infinite number of structures with open channels^[2], discrete cages and cagelike polyhedral^[3], or functional groups throughout the whole framework^[4], thus have been developed extensively for versatile applications in various fields, such as gas adsorption, catalysis, sensing, energy storage utilizations and biomedical applications^[5-8]. But there are still many drawbacks to be resolved in the MOF structures: 1) many MOF structures, especially three-dimensional ones are usually rigid mainly due to the employment of rigid ligands such as terephthalic acid, making the robust framework difficult to sustain the integrity under volume change conditions or structure variations; 2) some polycarboxylato-based MOFs are unstable with poor water stability and chemical stability against acidic or basic media, making them easily to be broken in the harsh conditions of industrial applications^[9].

MOF STRUCTURES

In order to solve the problem as well as enhance the chemical and thermal inertness of MOFs, we have designed to synthesize MOF structures using semirigid ligand. The ditopic ligand 3,3',5,5'-tetramethyl-4,4'-bipyrazole (H_2Me_4bpz) is a promising candidate as the two pyrazolate (pz) rings can rotate around its C-C chemical bond so that can release some of the pressure caused by structure variations in the framework, and the metal-azolate bonds can also increase the stability of the framework^[10]. As shown in **Figure 1**, H_2Me_4bpz has two coordination modes (mode I, mode II), as the two N atoms in diagonal positions coordinate with metals in the former usually resulting in three-dimensional structures, while four of the N atoms all coordinate with metal ions in the latter and result preferably in planar structures^[11]. A variety of MOF structures have been synthesized through chemical reactions between H_2Me_4bpz with different metal ions such as Cu^{2+} , Zn^{2+} , Co^{2+} , Cd^{2+} and Ag^+ , in different modes mentioned above^[12-14]. In addition, we have also successfully discovered a 2D wavy layered Ni-based MOF using H_2Me_4bpz as ligand (named Ni- Me_4bpz) and investigated its electrochemical property as lithium ion battery anode material. The results showed that the flexibility

of the ligand and the 2D layered construction greatly improved the chemical stability during the electrochemical test, after which the XRD pattern still exists [15].

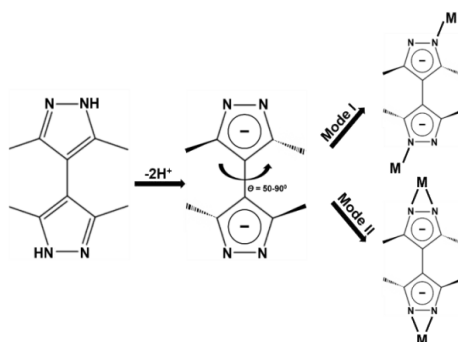


Figure 1. Different coordination modes of deprotonated ligand H_2Me_4bpz .

VERSATILITY in MOFs

On the other hand, the counter ions of the metal salts as well as the solvent molecules can also actively take part in the configuration of MOF structures, leading to different type of versatility in MOFs [16]. Here in this respect, we choose $CuCl_2$ and $ZnSO_4$ as the metal source because not only can Cu^{2+} and Zn^{2+} coordinate with H_2Me_4bpz , but also the Cl^- and SO_4^{2-} have been successfully served as the bridging ligands in many frameworks [17]. As a result, two new MOFs have been synthesized using the above flexible azolate ligand and metal salts. Crystal 1 is a Zn-based two-dimensional MOF possessing one-dimensional channel with *hcb* topology, while Crystal 2 is a Cu-based three-dimensional MOF with Cl^- as bridging ligand. The status of ligand H_2Me_4bpz in both crystals is in mode I. All the chemicals were commercial products of reagent grade, and were used without further purification. The synthesis of the H_2Me_4bpz ligand was according to our previous report [15], and the two crystals were synthesized through a simple hydrothermal method. Synthesis of Crystal 1: 5.0 mg (2.6×10^{-2} mmol) of H_2Me_4bpz and 6.9 mg (2.6×10^{-2} mmol) of $ZnSO_4 \cdot 7H_2O$ were added to a 10 ml glass vial and dissolved in 1 ml of dimethylacetamide (DMAc). After sonicating for 20 min, the vial was capped tightly and placed in an oven at 90 °C for 4 days. Colorless block crystals were collected. Synthesis of Crystal 2: 5.0 mg (2.6×10^{-2} mmol) of H_2Me_4bpz and 4.4 mg (2.6×10^{-2} mmol) of $CuCl_2 \cdot 2H_2O$ were added to a 10 ml glass vial and dissolved in 2 ml of a mixture of water, ethanol and dimethylformamide (1:1:1). After sonicating for 20 min, the vial was capped tightly and placed in an oven at 85 °C for 4 days. Blue crystals were collected. The crystal was coated with Paratone oil on a Cryoloop pin and mounted on a Bruker SMART Apex(II) single X-ray diffractometer equipped with a CCD area detector, which was operated at 1500 W power (50 kV, 30 mA) to generate Mo $K\alpha$ radiation ($\lambda=0.071073$ nm) at room temperature. The crystal structure was analyzed and solved by the direct method and refined by full-matrix least-square techniques with the help of the SHELXL-97 program package. Further details of the crystal structure determination were deposited at the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication (Crystal 1, 1430112; Crystal 2, 1430113).

As shown in **Figure 2**, in the framework of Crystal 1, the Zn(II) ion is four coordinated with two N atoms from two deprotonated Me_4bpz ligands, and two O atoms from two SO_4^{2-} . The bond lengths of Zn1-N1 and Zn1-O1 are 1.909 and 2.003 Å, respectively, indicating that the Zn(II) ion is in a distorted octahedron geometry. The ligand provides two N atoms coordinating with two Zn ions which are in the diagonal positions. In addition, in order to lower the energy level of the framework, the two pyrazolate (pz) rings rotate with a dihedral angle of 69.3°. Interestingly, the SO_4^{2-} also takes part in the constitution of the framework as bridging ligand, each coordinating with two Zn ions using two O atoms, which are in the same chemical situation. From **Figure 2b**, channels can be seen from the *c*-axis as a result of the stacking layers.

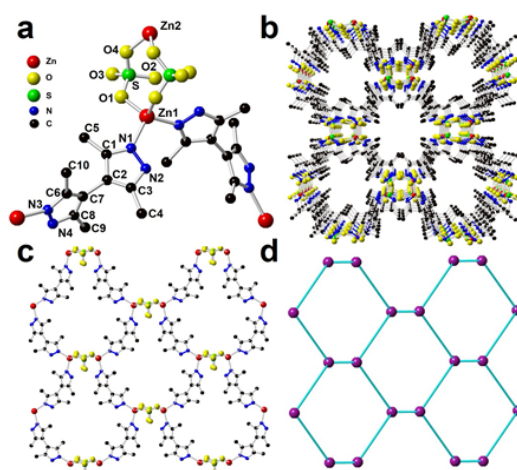


Figure 2. Structure of Crystal 2. (a), coordination mode; (b), stacking layers of 3D supermolecule configuration; (c), single layer of planar structure. (Zn: red, N: blue, C: black, S: green, O: yellow); (d), topological structure.

As shown in **Figure 2c**, the ligand H_2Me_4bpz and four-coordinated Zn ions as well as SO_4^{2-} constitute closed six-membered

rings, consisting of 40 atoms in total in each 2D layer, where four edges are made up by the ligand and two by SO_4^{2-} in each six-membered ring. The lengths for the long edge and short edge are 9.438 Å and 4.412 Å, respectively (Zn-Zn). When the Zn(II) ion and the $\text{H}_2\text{Me}_4\text{bpz}$ ligands are regarded as vertexes and edges, a *hcb* topology is obtained (Figure 2d). From the side direction of Crystal 1 as shown in Figure 3, each 2D layer composed of six-membered rings is packed by hydrogen bond forming a 3D super molecule configuration with 1D porous channels. The distance between each layer is 7.788 Å (Zn-Zn).

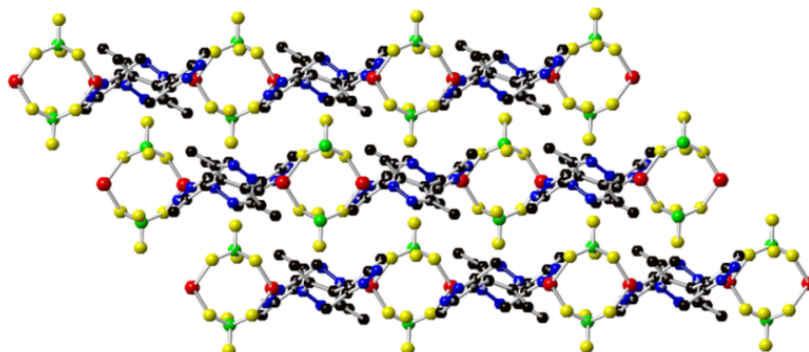


Figure 3. Crystal 1: layered structure from *a/b*-axis.

Different from Crystal 1, Crystal 2 is a three-dimensional framework with $\text{H}_2\text{Me}_4\text{bpz}$ and Cl⁻ as the bridging ligand. As shown in Figure 4a, the Cu^{2+} coordinates with two Cl⁻ and two N atoms from two ligands, same as in Crystal 1 in mode I, the bond lengths of Cu1-Cl1 and Cu1-N1 are 2.557 and 1.936 Å, respectively. The dihedral angle of the two pyrazolate (pz) rings is 79.9°, which is larger than Crystal 1. Specially, apart from the $\text{H}_2\text{Me}_4\text{bpz}$ ligand, each Cl⁻ coordinates with two Cu ions from two different planes which is different from SO_4^{2-} in Crystal 1 (Figure 4b). With the participation of Cl⁻ in the construction of the framework, the interconnected 2D planes bridge into 3D porous structures (Figure 4c). From the *c*-axis, it can be seen that there are two types of pores in Crystal 2. One is in the triangle shape while the other is in hexagon shape with the length of side about 9.497 Å. The detailed information about Crystal 1 and Crystal 2 is summarized in Table 1.

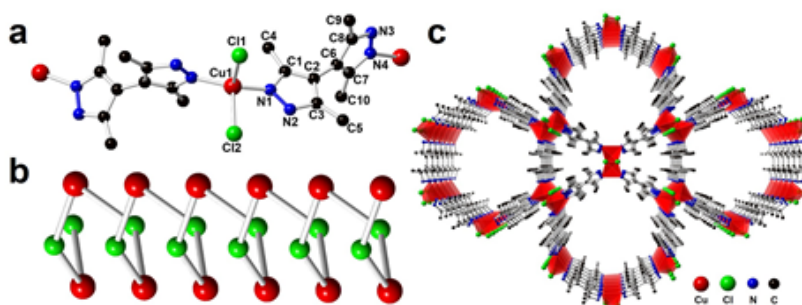


Figure 4. Structure of Crystal 2. (a), Cu^{2+} coordination mode; (b), Cl⁻ coordination mode; (c), pore structure of 3D configuration. (Cu: red, N: blue, C: black, Cl: green).

Table 1. The detailed information about Crystal 1 and Crystal 2.

Identification code	Crystal 1	Crystal 2
Empirical formula	$\text{C}_{10}\text{H}_{14}\text{N}_4\text{O}_5\text{SZn}$	$\text{C}_{60}\text{H}_{72}\text{Cl}_6\text{Cu}_6\text{N}_{24}\text{O}_6$
Formula weight	367.68	1819.42
Temperature	296(2) K	296(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Monoclinic, C2/c	Hexagonal, P6322
Unit cell dimensions	a=19.761(18) Å alpha=90 deg b=15.382(14) Å beta=129.435 deg c=15.167(14) Å gamma=90 deg	a=21.313(5) Å alpha=90 deg b=21.313(5) Å beta=90 deg c=6.585(3) Å gamma=120 deg
Volume	3561(6) Å ³	2590.5(15) Å ³
Z, calculated density	8, 1.372 mg/m ³	1, 1.166 mg/m ³
Absorption coefficient	1.518 mm ⁻¹	1.411 mm ⁻¹
<i>F</i> (000)	1504	924
Crystal size	0.12 x 0.12 x 0.11 mm	0.12 x 0.12 x 0.10 mm
Theta range for data collection	1.88-17.14°	1.10-26.44°
Limiting indices	-16 ≤ <i>h</i> ≤ 16 -9 ≤ <i>k</i> ≤ 12 -12 ≤ <i>l</i> ≤ 12	-25 ≤ <i>h</i> ≤ 26 -26 ≤ <i>k</i> ≤ 21 -8 ≤ <i>l</i> ≤ 6
Reflections collected/unique	3595/1068 [R(int)=0.1325]	13907/1798 [R(int)=0.1367]

Completeness to theta	17.14, 99.8%	26.44, 99.7%
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	1068/14/190	1798/0/85
Goodness-of-fit on F^2	1.664	0.730
Final R indices [$I > 2\sigma(I)$]	$R_1=0.0976$, $wR_2=0.2755$	$R_1=0.0476$, $wR_2=0.1298$
R indices (all data)	$R_1=0.1457$, $wR_2=0.3052$	$R_1=0.1006$, $wR_2=0.1597$
Largest diff. peak and hole	0.865 and -0.623 e. \AA^{-3}	0.988 and -0.503 e. \AA^{-3}

CONCLUSION

In summary, we have successfully synthesized two novel MOF structures using $\text{H}_2\text{Me}_4\text{bpz}$ ligand and different salts as metal source, as well as the counterions (SO_4^{2-} , Cl^-) as bridging ligands, through a facile solvothermal method. The as-obtained frameworks display unique structure morphologies as a result of the combination of metal ions, $\text{H}_2\text{Me}_4\text{bpz}$ ligand and diverse counterions. The semirigid ligand $\text{H}_2\text{Me}_4\text{bpz}$ delivered different dihedral angle of the two pyrazolate (pz) rings in order to adapt to the 2D or 3D framework under the lowest energy level as well as to resist the structure variations.

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