

Synthesis of a new porous anionic Metal-Organic framework constructed of Terephthalic acid

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ABSTRACT

A Zinc-based porous anionic metal-organic framework, $[\text{Me}_2\text{NH}_2]_2 [\text{Zn}_3(\text{BDC})_4] \cdot 8\text{DMF}$ **1** (DMF = N,N'-dimethylformamide, BDC = 1,4-benzenedicarboxylate), with space group $C2/c$, $a = 33.299$ (3) Å, has been solvothermally synthesized with dimethylammonium cations template and characterized by X-ray Diffraction. Compound **1** contains isolated zinc tetrahedral and octahedra connected by the organic linker (BDC) forming a anionic porous network. Disordered positively charged ions and solvent molecules are present in the pore, compensating for the negative charge of the framework. These positively charged molecules could be exchanged with alkali-metal ions, as is evident by an ICP-MS study. The H_2 storage capacity of the parent framework can be measured.

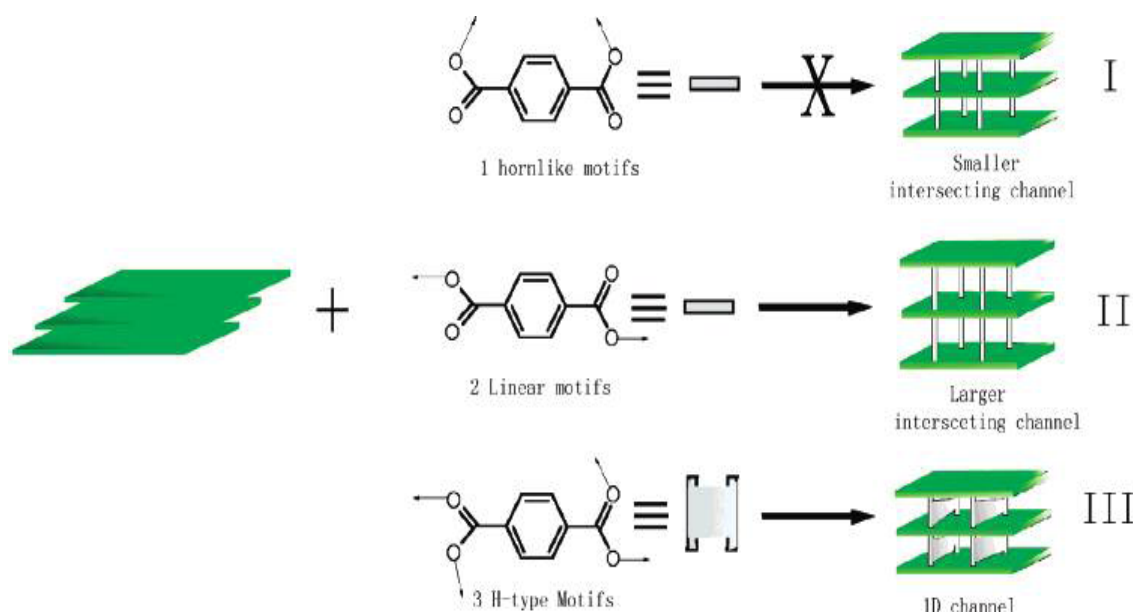
1. INTRODUCTION

Metal-organic frameworks (MOFs) have recently emerged as an important class of porous materials for their amenability to design and the flexibility with which their pores can be functionalized (Yaghi 2005). A wide range of metal centers and multifunctional organic ligands are used to construct metal-organic frameworks (MOFs) and coordination polymers (CPs), which could be tailored for specific uses such as gas storage, ion exchange, separation, catalysis, and sensing and detection. One of the advantages of this particular class of materials is that the structural topologies and properties can be tuned by altering synthetic parameters such as the solvent and temperature, in addition to the metal ions and organic linkers (Parise 2010). Usually, the synthesis of MOFs is straightforward, using well-soluble salts as the source for the metal component, e.g. metal nitrates, sulfates or acetates. The organic ingredients, which mostly are mono-, di-, tri- and tetracarboxylic acids, are supplied in a polar organic solvent, typically an amine (triethylamine) or amide (diethylformamide, dimethylformamide). After combination of these inorganic and organic components under stirring, the metal-organic structures are formed by self-assembly at temperatures starting at room temperature and up to solvothermal conditions at 200 °C within a few hours (Czaja 2009). Aromatic polycarboxylates are widely used as bridging ligands in the construction of inorganic/organic hybrid nanoporous materials, because

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they are sterically rigid and chemically robust, leading to frameworks of high thermal stability approaching that of purely inorganic zeolites. The presence of two potentially coordinating oxygen atoms in the carboxylic acid group, on the one hand, is beneficial for thermal stability and, on the other hand, leads to several possible coordination modes (monodentate, bridging, chelating), resulting in a low degree of structure predictability compared to aromatic nitrogen-donor ligands. Multiple coordination modes are often observed within the same structure, and several examples have been reported where as many as three different coordination modes occur within the same polycarboxylate ligand (Jacobson 2005). Below, we describe the methods to construct 3D layer-pillared homoligand coordination polymers by reassembling a BDC acid with its layered coordination polymer. Compound **1** is an example of a layered metal-BDC coordination polymer that can be prepared in good yield and then reacted with its BDC ligand, acting as a pillar, to create a 3D layer-pillared porous phase, as shown in **Scheme 1**. The scheme shows that BDC ligands are more successful in creating 3D pillared structures than the organic amines in the other reports. This scheme may also be useful in the synthesis of specific products and the investigation of the self-assembly mechanism of layer-pillared coordination polymers, including whether layered intermediates are necessary precursors to layer-pillared structures (Zhoa 2006)



Scheme 1 Coordination Mode of BDC and the Layer-Pillared Structures Expected

2. EXPERIMENTAL SECTION

2.1 Materials and Physical Techniques. Compound **1** was synthesized under solvothermal conditions using Teflon-lined Parr stainless steel autoclaves. The starting materials include zinc nitrate hydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99.9%, metal basis, Sigma-Aldrich], 1,4-benzenedicarboxylic acid ($\text{C}_8\text{H}_6\text{O}_4$, BDC, 95%, Sigma-Aldrich), and N,N-dimethylformamide ($\text{C}_3\text{H}_7\text{NO}$, DMF, 99%, Sigma-Aldrich) were used without any further purification.

2.2 $[\text{NH}_4(\text{CH}_3)_2]_2 [\text{Zn}_3 (\text{BDC})_4] \cdot 8\text{DMF}$. A typical synthesis involves the use of a mixture of 0.5 mmol of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.304 g) and 0.5 mmol of BDC (0.490 g). The mixture was dissolved in 8 ml of DMF and stirred for 1 h to achieve homogeneity [molar ratio of metal salt: ligand = 1:1]. The resultant solution was heated for 5 days at 180 °C. The product was obtained as a yellow block-shaped microcrystal (yield: 50% based on zinc), recovered by filtration, and subsequently washed with DMF.

2.3 Ion-Exchange Experiments. Saturated solutions of LiNO_3 and NaNO_3 in DMF were separately added to the as-synthesized compound **1** (80-90 mg in each vial). The saturated salt solutions were decanted and replaced by a fresh solution every 24 h for 5 days. The ion-exchanged samples were filtered and washed with DMF before being stored under fresh DMF for 3 days. At this time, they were once again filtered and washed prior to being tested for their metal content using ICP technique.

3. Results and Discussion

Compound **1** consists of zinc tetrahedral and octahedral connected by the organic ligands forming an overall three dimensional network. The asymmetric unit of **1** consists of two crystallographically independent zinc metal centers. The coordination number of zinc(II) is strongly influenced by the symmetry, steric requirements, and mode of coordination of the linker. The nature of the solvent and structure-directing agent also plays a major role in the zinc coordination behavior (Fig 1).

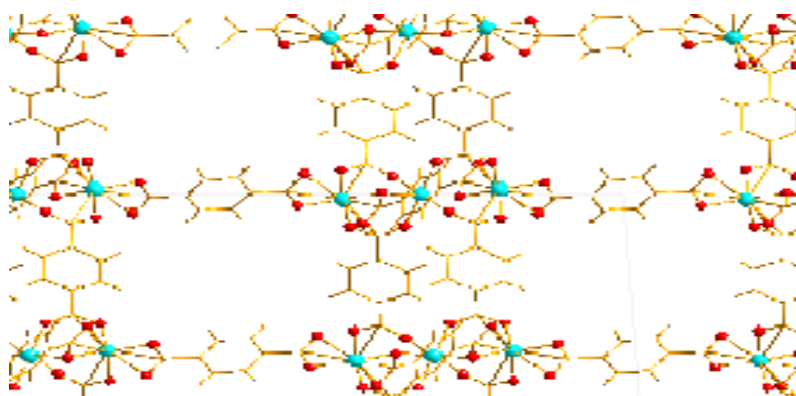


Fig 1. View of the Framework of **1**

The presence of the cationic species within the pore makes **1** a suitable candidate for ion-exchange studies with alkalimetal cations. Compound **1** undergoes partial ion exchange with alkalimetal cations like Li^+ and Na^+ . The powder XRD of an ion-exchanged material shows a pattern similar to that of the as-synthesized compound **1**, indicating that the basic framework remains unchanged upon ion exchange (Fig 2).

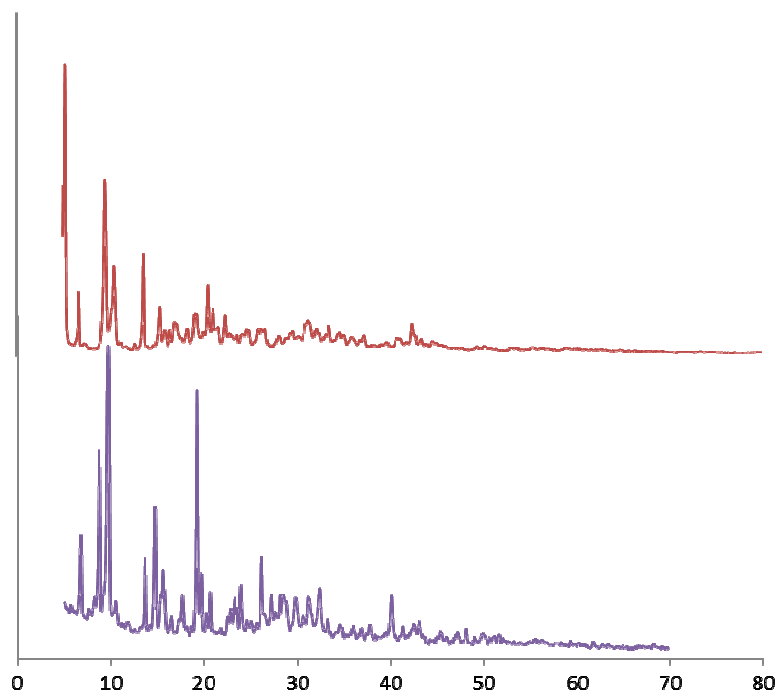


Fig 2. Powder XRD pattern of ion-exchanged compound **1** with Li^+ (Red: compound **1**, Purple: the exchanged compound with Li^+).

CONCLUSION

A three-dimensional zinc-based anionic framework was synthesized using solvothermal techniques. **1** consists of isolated zinc tetrahedra and octahedral forming a network encompassing large pores, which contain solvent molecules and counterions.

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