

Reversible and selective solvent adsorption in layered metal–organic frameworks by coordination control



Xinbo Yin^a, Haohong Chen^b, Yuna Song^c, Yang Wang^a, Qiaowei Li^{d,*}, Lijuan Zhang^{a,*}

^a Laboratory of Advanced Materials, Fudan University, 2205 Songhu Road, Shanghai 200438, China

^b Key Laboratory of Transparent Opto-functional Inorganic Materials, Shanghai Institute of Ceramics, Chinese Academy of Science, 1295 Dingxi Road, Shanghai 200050, China

^c School of Chemistry, Beijing Institute of Technology, 5 Zhongguancun South Street, Beijing 100081, China

^d Department of Chemistry, Fudan University, 220 Handan Road, Shanghai 200433, China

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ABSTRACT

With various functionalities in the framework and high thermal stability, metal–organic frameworks (MOFs) have been extensively studied for the applications in adsorption and separation. In last decade, synthesizing new MOFs with desired structures and improved chemical stability to meet these applications has drawn great attention. In this report, by using an organic ligand with azolate moiety, benzobis(imidazole) (H_2BBI), we synthesized two new 2D layered MOF structures with distinct topologies. Framework **1** $\{[Zn_2Cl_2(BBI)(MSM)_2]_n\}$, MSM = methylsulfonylmethane, constructed from tetrahedral Zn(II) and BBI, maintains its structure in organic solvents, such as methanol and benzene, and even in water. Meanwhile, framework **2** $\{[Cd_2Cl_2(BBI)(DMSO)_2]_n\}$, DMSO = dimethyl sulfoxide) differs from framework **1**, and is assembled from trigonal bipyramidal Cd(II) and square planar BBI. By removing the DMSO molecules coordinated to Cd(II) (25 weight% of the structure), **2** could transform to **3** $\{[Cd_2Cl_2(BBI)]_n\}$, which was further characterized by high-resolution powder X-ray diffraction. The solvent-free **3** retains the original connectivity within each layer, and is capable of reversible and selective adsorption of DMSO molecules. The bistable four- and five-coordinated geometry exchange of Cd(II) is the origin of this adsorption with improved selectivity and capacity.

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1. Introduction

Metal–organic frameworks (MOFs), bearing their great properties in gas adsorption and separation, and catalysis, have attracted much attention over the world [1–5]. As a result, an increasing number of chemically tunable MOFs with high porosities have been synthesized [6–10]. The interaction between the guest molecules and framework on the interface is the key to achieve small molecule adsorption and separation with improved capacity and selectivity [11–14]. Recently, by introducing specific modules in the pores, such as crown ethers, we designed MOFs capable of recognizing specific incoming molecules, such as paraquat cations [15]. This is done by organizing stereoelectronically selective unit as part of the organic ligand. On the other hand, the interaction could also happen between the backbone and the solvent molecules that participate in the reaction. For example, with solvent – ligand interactions, a lanthanide MOF prepared by Song et al. [16] shows luminescent turn-on upon exposed to *N,N*-dimethylformamide (DMF) vapor. The pores in this framework not only

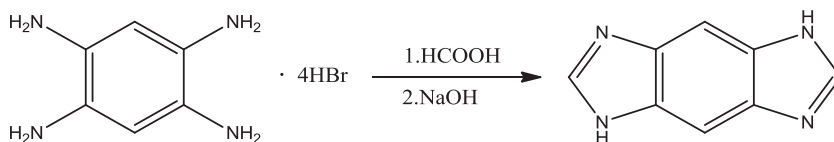
provide sites for solvent sensing, but also act as reservoirs for the small molecule inclusion.

This interaction specificity could also be controlled by the coordination mode of the metals in the frameworks. Not only does the family of metal ions contribute to the versatility of MOFs, but also provides coordination sites for the guests, resulting in stronger framework–guest interactions. The most extensively investigated metal ions in MOF synthesis are Zn, Cu, Co, Cd, and so forth [17–22]. For example, Zn(II) in tetrahedral geometry could adapt into structure with zeolitic topology, together with imidazolate [23]; while Cu(II), together with carboxylates, could be assembled into MOFs with paddle-wheel building units [24]. What is more, in some cases, the coordination number of metal ion in the framework could be modified by removing terminal ligand without losing the structural integrity. This provides specific adsorption sites for further incoming guests [25].

Improving the thermal and chemical stability of MOFs is essential for their potential applications. Imidazole ligands with functionalities, such as benzimidazole, are frequent choices for MOF synthesis [26]. Studies demonstrated that MOFs from these ligands with azolate moieties show higher chemical and thermal stability compared to other MOFs constructed from carboxylates and/or pyridyl ligands [23]. Due to the fact that the angle of

* Corresponding authors.

E-mail addresses: qwli@fudan.edu.cn (Q. Li), zhanglijuan@fudan.edu.cn (L. Zhang).



Scheme 1. Synthetic route to H₂BBI.

metal–imidazole–metal is in coincidence with the Si–O–Si angle (145°) [26], these MOFs resemble zeolites. The chemical stabilities of these MOFs were proved by structural intact in water, benzene, and even aqueous solution of sodium hydroxide [23].

To further explore the chemistry between this ligand with azolate moiety and various metals, and study the specific interactions between the resulting framework and the guests, we prepared benzo-bis(imidazole) (H₂BBI, Scheme 1) as the organic ligand for MOF synthesis. This planar ligand features four N atoms that could coordinate with metal ions. We report two 2D layered metal–organic frameworks, **1** {[Zn₂Cl₂(BBI)(MSM)₂]_n, MSM = methylsulfonylmethane} and **2** {[Cd₂Cl₂(BBI)(DMSO)₂]_n, DMSO = dimethyl sulfoxide}, with different topologies. Compared with framework **2**, improved chemical stability of framework **1** was confirmed by its structural intact in H₂O, methanol, and benzene. Furthermore, DMSO molecules coordinated to Cd(II) in framework **2** could be removed upon heating. This activated material, termed as **3**, shows adsorption of DMSO solvent with high capacity and efficiency (25 wt% of the structure). The single crystal structure of **2**, and the modeling structure of **3** supported by the high-resolution powder X-ray diffraction indexing, reveal that the coordination environment change of the Cd(II) from five-coordinated to four-coordinated is essential in achieving reversible and selective adsorption of DMSO. This metal–DMSO bond association and dissociation happen in between the layers, and do not affect the connectivity within the layers.

2. Experimental section

2.1. Materials and methods

The organic ligand was prepared according to the description reported previously [27]. All other chemicals were commercial products of reagent grade, and were used without further purifications. IR spectra were collected by an IR Prestige-21 spectrophotometer as KBr pellets between 4000 and 450 cm⁻¹. Thermogravimetric analysis (TGA) was obtained by a Perkin–Elmer TGA analyzer from room temperature to 800 °C under N₂ flow with a heating rate of 10 °C min⁻¹. The elemental analysis was measured by Vario EL analyzer. Powder X-ray diffraction (PXRD) data were collected on a Bruker AXS D8 Advance diffractometer operated at 1600 W power (40 kV, 40 mA) using Cu Kα₁ radiation. Simulated PXRD pattern was calculated using Mercury 3.0 from the corresponding single crystal structural data. High-resolution PXRD data for structure indexing was collected on a Huber G670 imaging plate Guinier camera equipped with Cu target (Cu Kα₁, 40 kV, 30 mA) and Ge monochromator.

2.2. Synthesis of the organic ligand H₂BBI

1,2,4,5-Benzenetetraamine tetrahydrobromic acid (3.25 g, 7.03 mmol) and formic acid (100 mL) were heated with reflux at 100 °C for 36 h. After the reflux, the mixture was treated with sodium hydroxide to make the solution neutral. After concentrating the solution to limited volume by rotovap, the final brown solid (900 mg, 80% yield) was collected by filtration.

2.3. Synthesis of framework 1 [Zn₂Cl₂(BBI)(MSM)₂]_n

A mixture of H₂BBI (15.0 mg, 9.48 × 10⁻² mmol), ZnCl₂ (129.4 mg, 9.49 × 10⁻¹ mmol), and DMSO (3.0 mL) was stirred for 20 min in air at room temperature, before they were transferred and sealed in a 5-mL teflon-lined stainless steel autoclave, and heated in a 150 °C oven for 5 days. Colorless block crystals were obtained after cooling to room temperature. The chemical structure of **1** was characterized by single crystal X-ray diffraction, combined with elemental analysis and TGA. Elemental analysis (%) calcd. For: C, 26.40; H, 2.93; N, 10.27; and S, 11.74. Found: C, 27.00; H, 3.42; N, 10.28; and S, 12.35. IR spectra of **1** (KBr, cm⁻¹): 3394(s), 3093(w), 2993(w), 2908(w), 2351(w), 1778(w), 1620(w), 1477(vs), 1375(vs), 1294(s), 1242(vs), 1205(s), 1163(s), 1004(vs), 960(s), 864(w), 844(vs), 840(s), 713(w), 640(s), 443(s).

2.4. Synthesis of framework 2 [Cd₂Cl₂(BBI)(DMSO)₂]_n

A mixture of H₂BBI (5.0 mg, 3.16 × 10⁻² mmol), CdCl₂·2.5H₂O (75.3 mg, 3.30 × 10⁻¹ mmol), DMSO (1.0 mL) and DMF (1.0 mL) was added into a 5-mL glass vial. After being sonicated for 20 min at room temperature, homogeneous solution was obtained. The vial was capped tightly and placed in an isothermal oven at 85 °C. After 5 days, colorless spindle-like crystals were collected. Elemental analysis (%) calcd. For: C, 23.72; H, 2.64; N, 9.22; and S, 10.54. Found: C, 22.54; H, 2.90; N, 8.85; and S, 10.65. IR spectra of **2** (KBr, cm⁻¹): 3412(s), 2991(w), 2908(w), 2349(w), 1753(w), 1625(s), 1490(vs), 1473(vs), 1448(s), 1361(vs), 1292(w), 1242(vs), 1197(s), 1153(s), 1008(vs), 950(s), 860(w), 850(vs), 835(vs), 707(w), 640(s), 406(s).

2.5. X-ray crystallography

Crystals coated with Paratone oil on Cryoloop pins were mounted on a Bruker SMART Apex (II) single X-ray diffractometer equipped with a CCD area detector and operated at 1500 W power (50 kV, 30 mA) to generate Mo Kα radiation (λ = 0.71073 Å) at room temperature. Absorption corrections were applied using the multi-scan technique. The structures were solved by the direct method and refined by full-matrix least-square techniques using the SHELXL-97 program package [28]. The results of the structural analysis were summarized in Table 1. Further details of the crystal structure determination have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication CCDC 943569-943570.

3. Results and discussions

3.1. Description of the crystal structures

3.1.1. Structure of 1

The framework **1** crystallizes in orthorhombic system, and possesses a *Pbca* space group. Each Zn(II) is four-coordinated, with two N atoms from two BBI, one O atom from MSM, and one Cl atom from (Fig. 1a). MSM was not present as the starting reagent in the reaction, but was formed due to the decomposition of DMSO under high temperature. MSM formation in similar systems was observed

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