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Achieve to easier opening of channels in anionic nanoporous metal–organic framework by cation exchange process

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ABSTRACT

A zinc-based metal–organic framework {$(HDMA)_2[Zn_3(BDC)_4]\cdot DMF\cdot H_2O$} (**1**) ($BDC^{2-}$ is 1,4-benzenedicarboxylate, DMF is N,N-dimethylformamide and $HDMA^+$ is dimethylammonium), with C2/c space group, $a = 33.299$ (3), $b = 9.790$ (4), $c = 18.185$ (5) Å, $\alpha = \gamma = 90.00°$, $\beta = 93.420$ (6)° and $V = 5918$ (3) Å^3, was synthesized by solvothermal technique. Compound **1** was characterized by single crystal X-ray diffraction. It contains isolated zinc tetrahedra and octahedra by the organic linker BDC^{2-} forming an anionic porous network with 2D channels. Positively charged ions and solvent molecules are present in the pores compensating for the negative charge of the framework. This positively charged molecule could be exchanged with metal ions, as it is evident by ICP, TGA and NMR studies. Unlike type V nitrogen adsorption isotherm curve of **1** at 77 K, replacement of the organic cation with smaller Li^+ leads to a type I adsorption isotherm.

1. Introduction

Crystalline porous metal–organic frameworks (MOFs) have been widely studied because of their diverse structures and chemical compositions [1–5]. The design of MOFs can take advantage of both the diversity of organic linkers and specific physical properties of the inorganic core structural units [6–8]. A broad range of metal centers and multifunctional organic ligands are used to construct MOFs that can be tailor-made for specific purposes such as gas storage [9–15]. In the past decade, adjustment of the chemical properties of MOFs is an in progress challenge in the area of material chemistry [16–22]. Sometimes the exchange of metal ions or organic cations within anionic MOFs can modify the chemical properties of a MOF [23–28]. In few cases, post-synthesis modifications of pre-constructed MOFs by replacement of the organic cation with smaller inorganic cation have been performed to tune the pore size and provide desired surface chemistries in MOFs [29,30]. Incorporating lithium ions into MOFs has attracted considerable attention because of the potential for producing high heats of adsorption for H_2 [31,32]. Utilization of anionic MOFs in tuning CO_2 and CH_4 adsorption of MOFs has been studied too [33,34]. The Zn^{2+}/1,4-benzenedicarboxylic acid reaction system is very sensitive to the variation of water content and the solvents employed in the starting mixture. Small changes in the synthesis of zinc terephthalates leads to new compounds, which demonstrates the large structural variability of this system [35]. Thus, many different structures for example $[HDMA]_2[Zn_2(BDC)_3(DMA)_2]\cdot 6DMF$ ($HDMA^+$: dimethylammonium and DMA: dimethylamine) [34], $Zn(BDC)\cdot DMF\cdot H_2O$ (MOF-2) [36], $Zn_3(BDC)_3\cdot 6CH_3OH$ (MOF-3) [37] and $Zn_4O(BDC)_3$ (MOF-5) [38] were synthesized in the last few years. In our previous work on synthesis of anionic MOFs, we prepared single crystals of $[HDMA]_2[Zn_2(BDC)_3(DMA)_2]\cdot 6DMF$ in the presence of terephthalodinitrile [34], in this work, we replaced terephthalodinitrile with 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (4-bpdb) and prepared single crystals of {$(HDMA)_2[Zn_3(BDC)_4]\cdot DMF\cdot H_2O$} (**1**), ($HDMA^+$: dimethylammonium, BDC^{2-}: 1,4-benzenedicarboxylate and DMF: N,N-dimethylformamide). In addition to synthesis and structural characterization, ion exchange process and gas adsorption analyses of **1** and the ion exchanged samples were studied too. It should be also mentioned that Biemmi et al. [35] described the same framework but with $HDEA^+$ ($HDEA^+$: diethylammonium) charge balancing cations and Sun et al. [39] reported a pillared 3D structure with the same framework composition of $[Zn_3(BDC)_4]\cdot 2HPIP$ (HPIP is partly protonated piperazine).

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2. Experimental

2.1. Materials and physical techniques

All reagents for the synthesis and analysis were commercially available and used as received. Microanalyses were carried out using a Heraeus CHN–O– Rapid analyzer. The amounts of metal ions in each sample were measured by ICP analyses. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. ^{1}H NMR spectra were measured in d$_6$-DMSO with a BRUKER DRX-500 AVANCE spectrometer at 500 MHz and all chemical shifts are reported in δ units downfield from Me$_4$Si. The thermal behavior was measured with a PL-STA 1500 apparatus with the rate of 10 °C min^{-1} in a static atmosphere of nitrogen. Crystallographic measurements were made using a Bruker APEX area-detector diffractometer. The intensity data were collected using graphite monochromated Mo-K$_\alpha$ radiation. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2. The molecular structure plot and simulated XRD powder pattern based on single crystal data were prepared using Mercury software. X-ray powder diffraction (XRD) measurements were performed using a Philips diffractometer of X'pert Company with monochromated Cu-K$_\alpha$ radiation. N_2 (at 77 K) isotherms were measured up to 1 bar using approximately 0.2 g sample on a volumetric BELSORP-max apparatus by high-purity gas (N_2: 99.999%). Prior to the N_2 adsorption measurement, the sample was degassed under reduced pressure at 373 K.

2.2. Synthesis of $[HDMA]_2[Zn_3(BDC)_4]\cdot DMF\cdot H_2O$ (**1**) and preparation of its single crystals

Colorless crystals of **1** were prepared by dissolving 0.5 mmol 1,4-benzenedicarboxylic acid (H_2BDC), 0.5 mmol $Zn(NO_3)_2\cdot 6H_2O$ and 0.25 mmol 4-bpdb (1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene) in 8 ml DMF. After preparing a colloidal solution by stirring at room temperature, it was transferred to the teflon-lined steel autoclave and heated at 125 °C. After 50 h, the teflon-lined steel autoclave was slowly cooled to room temperature with the rate of 0.01 °C min^{-1}. The resulting product was washed with DMF and stored in it, d.p. = above 300 °C, yield: 80% (based on final product). Anal. calc. For $C_{39}H_{41}N_3O_{18}Zn_3$: C, 45.21; H, 3.40; N, 4.05 found; C, 45.19; H, 4.49; N, 3.98%. Fig. S1 shows the IR spectrum of **1**. The XRD pattern of this anionic MOF after exposure to the air for 3 weeks indicated that although the crystals of **1** were lost their transparency in the air, they were stable and no destruction process occurred for them (Fig. S2).

2.3. Postsynthetic cation exchange process of **1** with Cu^{2+}, Li$^+$ and Na$^+$ ions

In order to study the cation exchange process in a crystal-to-crystal transformation, initially we examined the stability of compound **1** crystallinity in various solvents such as methanol, ethanol, acetone, distilled water, acetonitrile, tetrahydrofuran (THF) and N,N-dimethylformamide (DMF), but this MOF only retained its crystallinity in DMF. Thus, crystals of **1** were immersed in a saturated DMF solution of $Cu(NO_3)_2$, $3H_2O$, $LiNO_3$ and $NaNO_3$ at room temperature. The crystals were soaked for 10 days and during this time, the saturated solutions were refreshed three times daily. Unfortunately, the crystallinity of these samples was not maintained during these cation exchange processes and we could not determine the structures of these cation-exchanged samples by single crystal X-ray crystallography. After decanting the metal ion saturated solutions, the cation-exchanged samples were rinsed and soaked in DMF for 3 days to remove residual $Cu(NO_3)_2$, $3H_2O$, $LiNO_3$ and $NaNO_3$ from the frameworks. The results of ICP analysis for these three samples are summarized in Table 1. Fig. S3 shows the IR spectra of **2**–**4** MOF materials.

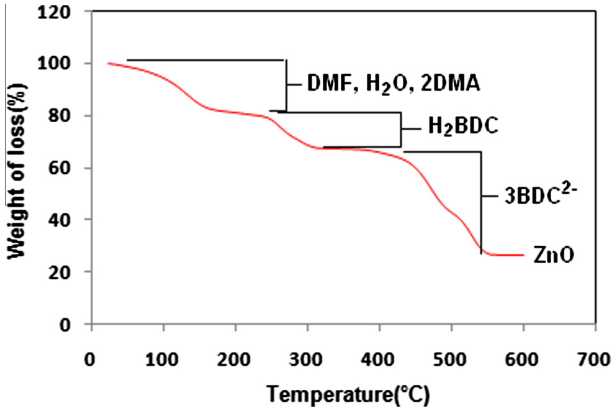

Fig. 1. TGA diagram of compound **1** in a static atmosphere of nitrogen.

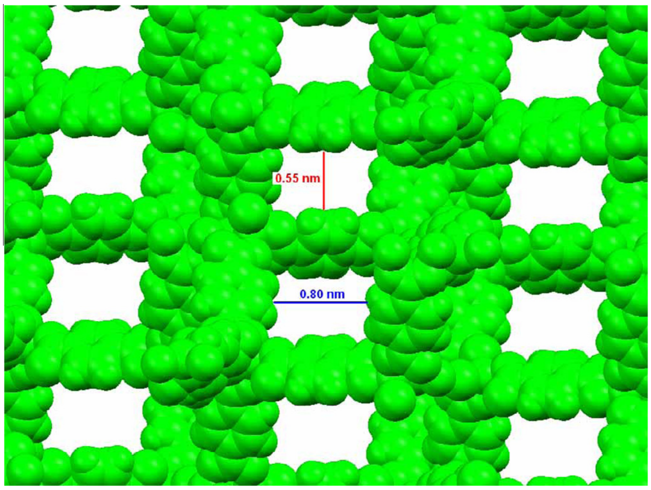

Fig. 2. Showing the existence of one-dimensional channels along the crystallographic *b* axis in an anionic nanoporous MOF of **1**.

Table 1
Results of the ICP analyses obtained for MOF materials of **2–4**.

	Amount of M^{2+} or M$^+$ ion (mg)	Amount of Zn^{2+} ion (mg)	Amount of M^{2+} or M$^+$ ion (mmol)	Amount of Zn^{2+} ion (mmol)	The ratio of M^{2+}:Zn^{2+} or M$^+$:Zn^{2+}	The expected ratio in cation exchange with DMA$^+$
2 (M^{2+}:Cu^{2+})	7.0182	5.8257	0.11	0.089	3.722:3	1:3
3 (M$^+$:Li$^+$)	0.508	6.2202	0.0732	0.0951	2.31:3	2:3
4 (M$^+$:Na$^+$)	1.517	7.1555	0.066	0.1094	1.81:3	2:3