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Unprecedented Li^+ Exchange in an Anionic Metal–Organic Framework: Significantly Enhanced Gas Uptake Capacity

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Supporting Information

ABSTRACT: We herein report the first example of Li^+ exchanged with both the guest $H_2N(Me)_2^+$ cations located in the channels and the coordinated metal ions from an anionic metal–organic framework (MOF), leading to significant enhancement of the pore volume and gas sorption abilities of the exchanged MOF. Furthermore, both MOFs before and after Li^+ exchange show good selective adsorption for CO_2 over CH_4.

Metal–organic frameworks (MOFs), owing to their adjustable pore sizes and controllable pore-surface properties, present a diversity of applications in clean energy, such as hydrogen and methane storage and CO_2 capture.[1] Particularly given the increasingly serious global warming, the effective capture and removal of CO_2 from industrial flue gas is becoming an important environmental issue.[2] In view of the problems existing in CO_2 capture, recent studies have demonstrated that MOFs could be a promising physical adsorbent for CO_2, being an alternative to the existing benchmark materials for CO_2 capture at low concentration and moderate temperature.[3] In order to enhance the CO_2 adsorption capacity and selectivity of MOFs, some strategies, such as creating high internal surface areas and large pore volumes,[4] increasing the coordinatively unsaturated open metal sites or nitrogen-enriched Lewis basic sites,[5] and functionalizing by postsynthetic modification,[6] have been adopted. In this regard, the introduction of light metal ions such as Li^0/Li^+ into MOFs might be an effective approach to improving the gas uptake capacity. For example, lithium-doped MIL-53 was reported to exhibit nearly double the H_2 uptake capacity of pristine MOF.[7] Eddaoudi et al.[8] investigated the enhanced isosteric heat of H_2 adsorption in a Li^+-exchanged Li-ρ-ZMOF. Yang et al.[9] synthesized an interpenetrated anionic MOF by exchanging dications with Li^+ cations to modulate the hysteretic H_2 adsorption behavior and determined the precise Li^+ position in the Li^+-exchange framework as important evidence for the basis of modulated H_2 uptake. In summary, chemical reduction and cation exchange are two methods to incorporate Li^+ into MOFs that act as effective strategies to modulating H_2 adsorption in most previous studies.[10]

More recently, the incorporation of Li^+ cations into MOFs for enhancing the CO_2 adsorption capacity and selectivity has aroused widespread concern.[11] In this contribution, we report the synthesis, structure, and exchange reactions of two MOFs, $[H_2N(Me)_2]_2[Zn_5(L)_3]\cdot 5.5DMF\cdot 3.5H_2O$ (**1**) and $[Li(H_3O)_2]$-$[Zn_4Li(L)_3]\cdot 6CH_3OH$ (**1-Li**), of a $Zn_5(CO_2)_{12}/Zn_4Li(CO_2)_{12}$ cluster-based anionic framework, together with the gas (N_2, H_2, CH_4, and CO_2) sorption properties of their desolvated forms. Notably, **1-Li** presents an unprecedented example in which the exchange interaction of Li^+ ions take place in both the guest $H_2N(Me)_2^+$ ions and the coordinated metal atoms of the host framework. In addition, the pore volume and gas uptake capbility of **1-Li** show significant enhancement compared to the pristine **1**.

Compound **1** crystallizes in the monoclinic space group $C2/c$, showing a 3D anionic porous framework constructed from an irregular linear pentanuclear Zn^{2+} cluster and L^{4-} ligand. The asymmetric unit of **1** consists of two and a half Zn^{2+} ions and one and a half L^{4-} ions (Figure S1). All Zn^{2+} centers adopt distorted tetrahedral coordination geometries via bonding to single O centers from four carboxylate groups. L^{4-} adopts μ_6^- and μ_7^-, two kinds of bridging coordination modes (Figure S2). Interestingly, five linearly arranged Zn^{2+} ions are bridged by eight carboxylate groups, in which each outer Zn ion (Zn2) is further coordinated by two carboxylate O atoms from two carboxylate groups to generate a $Zn_5(CO_2)_{12}$ cluster (Figure 1a), presenting a new zinc carboxylate based Zn^{II} cluster. Furthermore, the $Zn_5(CO_2)_{12}$ cluster as a secondary building unit (SBU) incorporates eight carboxylate groups from six μ_7-L^{4-} infinitely to form 2D layers that run parallel to the *ab* plane and shows narrow 1D channels along the *c* axis that are occupied by $H_2N(Me)_2^+$ cations decomposed from *N*,*N*-dimethylformamide (Figure 1b). The 2D layers are further linked by μ_6-L^{4-} ligands to give a 3D anionic framework (Figure 1c), and a 1D large channel B is formed with a cylindrical aperture of ca. 12.322 Å (the distance of C22···C22, including the van der Waals radii of the atoms). The void space of **1** is 55.3%, estimated by *PLATON* after excluding the $H_2N(Me)_2^+$ cations and free solvents.[12]

To establish the influence of the cationic species on the adsorption properties, Li^+-ion exchange was performed. To this end, crystals of as-synthesized **1** were immersed in a saturated solution of $LiNO_3$ in methanol at room temperature for 10 days, and the $LiNO_3$ solution was refreshed daily. Subsequently, the cation-exchanged crystals of **1-Li** were rinsed and soaked in methanol for 3 days to remove residual $LiNO_3$ from the framework. Powder X-ray diffraction (PXRD) of **1-Li** clearly revealed that the framework structure remained intact after the cation-exchange process (Figure S3). Elemental analysis of a bulk

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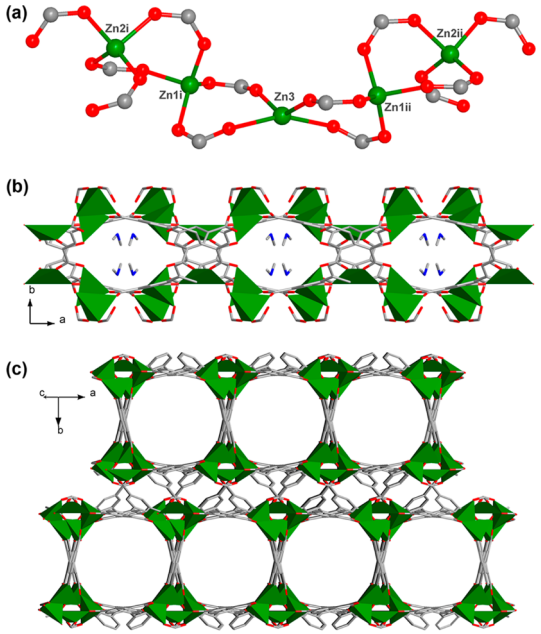

Figure 1. (a) $Zn_5(CO_2)_{12}$ cluster (symmetry codes: i, −1 + *x*, *y*, *z*; ii, 1 − *x*, *y*, 1.5 − *z*), (b) view of the 2D layer along the *c* axis in which the channels are filled by $H_2N(Me)_2^+$ cations, and (c) view of the 3D structure.

sample of **1-Li** confirmed that no N element was detectable in the Li^+-exchanged material, indicating that $H_2N(Me)_2^+$ had been totally replaced by Li^+ and H_3O^+ within the pores of the framework. Moreover, inductively coupled plasma results demonstrated that the molar ratio between Li and Zn within **1-Li** was approximately 0.5. Especially, the single-crystal structure of **1-Li** can be obtained by single-crystal X-ray diffraction analysis (Table S1 and CIF). Significantly, in the structure of **1-Li**, not only was $H_2N(Me)_2^+$ replaced by Li^+ but also the Zn^{2+} ion located in the center of the $Zn_5(CO_2)_{12}$ cluster was exchanged with Li^+ ion. This unprecedented cation-exchange process occurring to both the guest and host framework is attributed to two reasons: first, as shown in Figure 2, in the $Zn_5(CO_2)_{12}$

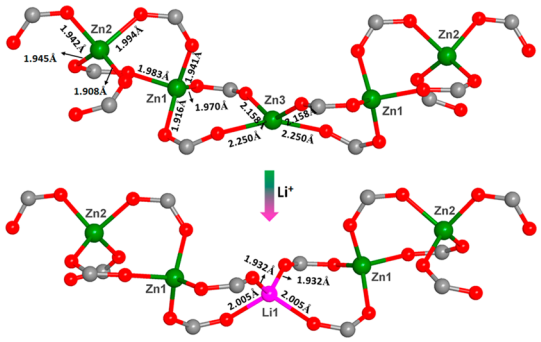

Figure 2. Bond lengths of the Zn−O and Li−O bonds in the $Zn_5(CO_2)_{12}$ and $Zn_4Li(CO_2)_{12}$ clusters.

cluster, the Zn3 atom possessing the longer Zn−O bond is more "active" than the other four Zn^{II} atoms; second, the Li^+ ion is four-coordinated in most of the Li-based MOFs[13] and the four-coordinated Zn3 atom is exactly suitable for metal-ion exchange. Although many Li^+-exchanged MOFs have been reported,[7−11] only one of their structures was successfully determined by single-crystal X-ray diffraction.[9] Herein, **1-Li** presents the first example of Li^+ exchange with both the guest $H_2N(Me)_2^+$ ions and the coordinated metal ions of the host framework, for which the structure is decided by single-crystal data.

The methanol-exchanged sample **1** and Li^+-exchanged sample **1-Li** are stable upon heating to 150 °C under high vacuum (10^{-5} mbar) for 8 h and give fully desolvated samples, maintaining their structural integrity, as confirmed by the PXRD results (Figures S5 and S6). The N_2 sorption isotherm of **1** measured at 77 K shows an uptake of 136 $cm^3\ g^{-1}$ at 1 atm (Figure 3a),

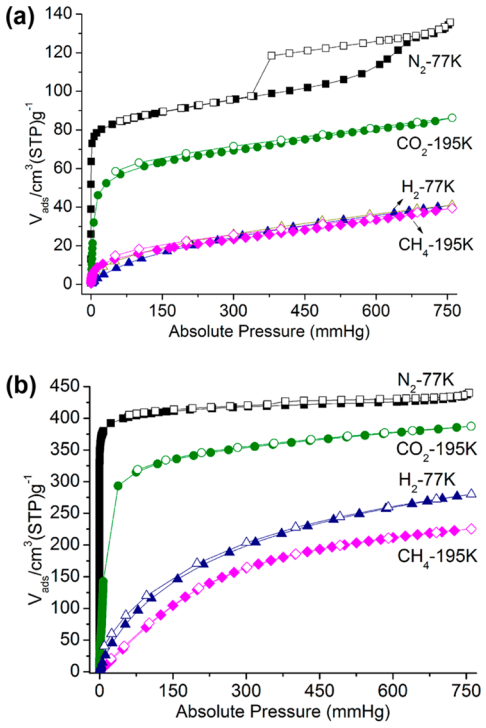

Figure 3. N_2, H_2, CO_2, and CH_4 adsorption (filled) and desorption (open) isotherms of **1** (a) and **1-Li** (b) measured at 77 and 195 K.

corresponding to Brunauer−Emmett−Teller (BET) and Langmuir surface areas of 342 and 383 $m^2\ g^{-1}$, respectively. However, the isotherm of **1-Li** displays significantly higher N_2 uptake, with a maximum uptake of 440 $cm^3\ g^{-1}$ (Figure 3b). A comparison of the N_2 isotherms for **1** and **1-Li** presents a change in the isotherms from type V in **1** to type I in **1-Li**. This behavior might be due to fact that the existence of small Li^+ cations in channels of **1-Li** is not a barrier for the entrance of N_2 molecules, but the presence of large $H_2N(Me)_2^+$ cations would block the channels of **1**.[9,14] The BET and Langmuir surface areas of **1-Li** are up to 1664 and 1780 $m^2\ g^{-1}$, respectively, indicating that the adsorption capacity of **1-Li** is 3.9 times greater than that of **1**. The total pore volumes for **1** and **1-Li** calculated from the maximum N_2 adsorption are 0.21 and 0.68 g cm^{-3}, respectively. The experimental pore-size-distribution curves based on the nonlocal density functional theory model demonstrate almost the same pore-size distribution of **1** and **1-Li** (Figure S7), consistent with their similar structures. The H_2 sorption of **1-Li** exhibits a very much enhanced uptake capacity compared to that of **1**. As shown in Figure 3, the H_2 uptakes of **1** and **1-Li** at 77 K and 1 atm are 41 $cm^3\ g^{-1}$ (0.37 wt %) and 280 $m^3\ g^{-1}$ (2.50 wt %), respectively. The uptake of **1-Li** is nearly 5.8 times higher than that of **1**, indicating a high H_2 adsorption capacity of **1-Li**. It is worth noting that such a remarkable enhancement of the H_2 uptake is

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Table 1. Adsorption Data for 1 and 1-Li

		77 K[b]	195 K[b]		273/298 K[b]			
	BET[a]	H_2	CO_2	CH_4	CO_2	CH_4	$Q_{st}(CO_2)$[c]	$S(CO_2/CH_4)$[d]
1	342	41	86	40	37/24	30/17	23.0	11
1-Li	1664	280	388	226	148/85	35/21	20.1	9

[a]Surface area, $m^2\ g^{-1}$. [b]Adsorptive capability, $cm^3\ g^{-1}$. [c]Isosteric heat of adsorption, kJ mol^{-1}. [d]Selectivity sorption at 298 K.

the largest compared with known methods utilized for modulation of the H_2 sorption.[1c,10,15]

The above results regarding enhanced N_2 and H_2 uptake capacities of **1-Li** encourage us to examine their potential applications for CO_2 and CH_4 sorption at different temperatures (Table 1). At low temperature (195 K), the CO_2 and CH_4 uptakes of **1** are 86 and 40 $cm^3\ g^{-1}$. In sharp contrast, those values of **1-Li** reach 388 and 226 $cm^3\ g^{-1}$, respectively, at 195 K. The CO_2 and CH_4 uptakes at ambient temperature have been further investigated (Figure 4). For **1**, the CO_2 uptakes are 37 $cm^3\ g^{-1}$ at

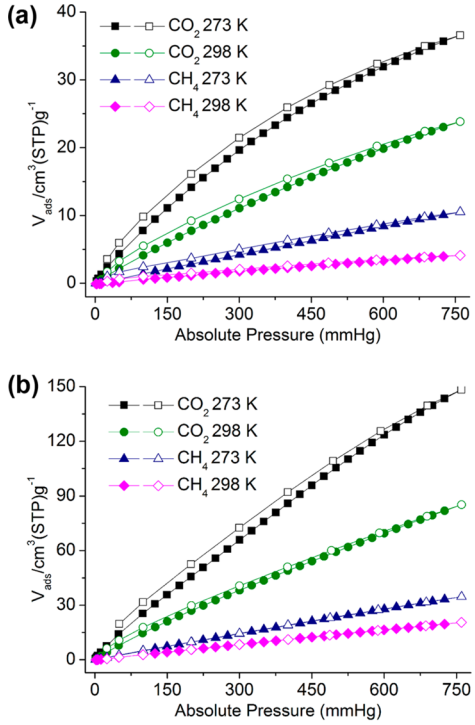

Figure 4. Sorption isotherms of CO_2 and CH_4 at 273 and 298 K for **1** (a) and **1-Li** (b). Solid and open symbols represent adsorption and desorption isotherms, respectively.

273 K and 24 $cm^3\ g^{-1}$ at 298 K at 1 atm, whereas the CH_4 uptakes are 30 and 17 $cm^3\ g^{-1}$ at 273 and 298 K, respectively. Significantly, the CO_2 isotherms of **1-Li** at 273 and 298 K reach maxima of 148 and 85 $cm^3\ g^{-1}$, respectively. In comparison, the CH_4 uptakes are 35 and 21 $cm^3\ g^{-1}$ at 1 atm, respectively, suggesting a highly selective uptake for CO_2 over CH_4. To predict the CO_2/CH_4 selectivity in **1** and **1-Li** for a CO_2/CH_4 binary mixture, the ideal adsorbed solution theory[16] was employed on the basis of the adsorption curves of CO_2 and CH_4 at 298 K (Figures S8 and S9). For CO_2/CH_4 mixtures with typical feed compositions of landfill gas (CO_2/CH_4 = 50/50), the CO_2/CH_4 selectivities of **1** and **1-Li** are 11 and 9, respectively. The values are comparable to functionalized MOFs with high selectivity results.[17] In addition, the isosteric heat (Q_{st}) of CO_2 adsorption was calculated by the virial equation from the sorption isotherms at 273 and 298 K (Figures S10 and S11). The initial Q_{st} values of CO_2 are 23.0 and 20.1 kJ mol^{-1} for **1** and **1-Li**, respectively, suggesting that the affinity of $H_2N(Me)_2^+$ cations toward CO_2 is slightly larger than that of Li^+ cations, which is probably due to the stronger intermolecular interaction between $H_2N(Me)_2^+$ and CO_2.[10b,11d,18]

In summary, through postsynthetic ion exchange, we have achieved Li^+ exchange with both the guest $H_2N(Me)_2^+$ ions located in the pores and the coordinated metal centers of the host framework based on an anionic MOF. Furthermore, the pore volume and gas uptake capacity of the Li^+-exchanged MOF have been greatly improved. The results presented in this study might open an avenue to improvement of the pore volume and gas uptake capacity in MOFs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b00538.

Experimental details, additional structures, PXRD data, thermogravimetric analysis curve, and sorption data fittings (PDF)
CIF file for **1** (CIF)
CIF file for **1-Li** (CIF)

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Notes

The authors declare no competing financial interest.

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