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$_2$N(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. 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. 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. 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, increasing the coordinatively unsaturated open metal sites or nitrogen-enriched Lewis basic sites, and functionalizing by postsynthetic modification, have been adopted. In this regard, the introduction of light metal ions such as 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.

Eddaoudi et al. investigated the enhanced isosteric heat of H$_2$ adsorption in a Li$^+$-exchanged Li$^+$-μ-ZMOF. Yang et al. 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.

More recently, the incorporation of Li$^+$ cations into MOFs for enhancing the CO$_2$ adsorption capacity and selectivity has aroused widespread concern. In this contribution, we report the synthesis, structure, and exchange reactions of two MOFs, [H$_2$N(Me)$_2$]$_2$[Zn$_6$(L)$_3$]$\cdot$5.5DMF·3.5H$_2$O (1) and [Li(H$_2$O)$_2$]-[Zn$_5$Li$(L)_3$]$\cdot$6CH$_3$OH (1-Li), of a Zn$_5$(CO$_2$)$_{12}$/Zn$_4$Li(CO$_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$_2$N(Me)$_2^+$ ions and the coordinated metal atoms of the host framework. In addition, the pore volume and gas uptake capability 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 Li$^+$ ligand. The asymmetric unit of 1 consists of two and a half Zn$^{2+}$ ions and one and a half Li$^+$ ions (Figure S1). All Zn$^{2+}$ centers adopt distorted tetrahedral coordination geometries via bonding to single O centers from four carboxylate groups. Li$^+$ 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$^{2+}$ cluster. Furthermore, the Zn$_5$(CO$_2$)$_{12}$ cluster as a secondary building unit (SBU) incorporates eight carboxylate groups from six μ$_6$-L$^-$ ligands to give a 3D anionic framework (Figure 1c), and a 1D large channel B is formed with a cylindrical aperture of ca. 12.32 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$_2$N(Me)$_2^+$ cations and free solvents.

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 sample of 1-Li corroborated the presence of Li$^+$ in the framework. Consequently, compound 1-Li was subjected to CO$_2$ and CH$_4$ uptake experiments at various pressures and temperatures, providing the possibility of using MOF 1-Li for CO$_2$ capture.

In conclusion, this work demonstrates the power of Li$^+$ incorporation into MOFs for enhancing their CO$_2$ capture characteristics and suggests the potential of this approach for practical applications in CO$_2$ management.
sample of 1-Li confirmed that no N element was detectable in the Li+-exchanged material, indicating that H2N(Me)2+ had been totally replaced by Li+ and H3O+ 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 H2N(Me)2+ replaced by Li+ but also the Zn2+ ion located in the center of the Zn5(CO2)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 Zn5(CO2)12 cluster, the Zn3 atom possessing the longer Zn−O bond is more "active" than the other four ZnII atoms; second, the Li+ ion is four-coordinated in most of the Li-based MOFs13 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.7 Herein, 1-Li presents the first example of Li+ exchange with both the guest H2N(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 N2 sorption isotherm of 1 measured at 77 K shows an uptake of 136 cm3 g−1 at 1 atm (Figure 3a), corresponding to Brunauer–Emmett–Teller (BET) and Langmuir surface areas of 342 and 383 m2 g−1, respectively. However, the isotherm of 1-Li displays significantly higher N2 uptake, with a maximum uptake of 440 cm3 g−1 (Figure 3b). A comparison of the N2 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 N2 molecules, but the presence of large H2N(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 m2 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 N2 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 H2 sorption of 1-Li exhibits a very much enhanced uptake capacity compared to that of 1. As shown in Figure 3, the H2 uptakes of 1 and 1-Li at 77 K and 1 atm are 41 cm3 g−1 (0.37 wt %) and 280 m3 g−1 (2.50 wt %), respectively. The uptake of 1-Li is nearly 5.8 times higher than that of 1, indicating a high H2 adsorption capacity of 1-Li. It is worth noting that such a remarkable enhancement of the H2 uptake is...
the largest compared with known methods utilized for modulation of the H2 sorption.1c,10,15

The above results regarding enhanced N2 and H2 uptake capacities of 1-Li encourage us to examine their potential applications for CO2 and CH4 sorption at different temperatures (Table 1). At low temperature (195 K), the CO2 and CH4 uptakes of 1 are 86 and 40 cm3 g−1. In sharp contrast, those values of 1-Li reach 388 and 226 cm3 g−1, respectively, at 195 K. The CO2 and CH4 uptakes at ambient temperature have been further investigated (Figure 4). For 1, the CO2 uptakes are 37 cm3 g−1 at 273 K and 24 cm3 g−1 at 298 K at 1 atm, whereas the CH4 uptakes are 30 and 17 cm3 g−1 at 273 and 298 K, respectively. Significantly, the CO2 isotherms of 1-Li at 273 and 298 K reach maxima of 148 and 85 cm3 g−1, respectively. In comparison, the CH4 uptakes are 35 and 21 cm3 g−1 at 1 atm, respectively, suggesting a highly selective uptake for CO2 over CH4. To predict the CO2/CH4 selectivity in 1 and 1-Li for a CO2/CH4 binary mixture, the ideal adsorbed solution theory16 was employed on the basis of the adsorption curves of CO2 and CH4 at 298 K (Figures S8 and S9). For CO2/CH4 mixtures with typical feed compositions of landfill gas (CO2/CH4 = 50/50), the CO2/CH4 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 (Qst) of CO2 adsorption was calculated by the virial equation from the sorption isotherms at 273 and 298 K (Figures S10 and S11). The initial Qst values of CO2 are 23.0 and 20.1 kJ mol−1 for 1 and 1-Li, respectively, suggesting that the affinity of H2N(Me)2+ cations toward CO2 is slightly larger than that of Li+ cations, which is probably due to the stronger intermolecular interaction between H2N(Me)2+ and CO2.10b,11d,18

In summary, through postsynthetic ion exchange, we have achieved Li+ exchange with both the guest H2N(Me)2 cations 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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