Microporosity Enhancement in a One-Dimensional Imidazolium Caged Metal-Organic Framework by Highly Selective Postsynthetic Removal of Inner Yttrium Clusters

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A one-dimensional (1D) metal-organic caged framework (**YMOF-Y**) was obtained via self-assembly of yttrium cations with a U-shape imidazolium based ligand and the structure was elucidated by single-crystal X-ray diffraction analysis. The **YMOF-Y** has a unique 1D chain structure composed of octa-imidazolium based cages. Inside the cage, an inner Y_4 cluster connected to yttrium cations of the cage through formate anions is present. The microporosity and flexibility of **YMOF-Y** can be improved by an unprecedented postsynthetic removal of the Y_4 clusters from the cage by washing with alkali metal solutions. The removal of the Y_4 cluster is reflected in a significant change in the properties of the metal-organic framework (MOF), as confirmed by carbon dioxide sorption measurements and variable temperature powder X-ray diffraction analysis.

Keywords: Metal-organic framework, Microporous materials, Postsynthetic modification, Selective removal, Imidazolium-based framework

Metal-organic frameworks (MOFs) are crystalline materials having a permanent porosity composed of a metal (or a metal cluster) and an organic bridging ligand coordinated to each other.¹ Compared to other porous materials (activated carbon, zeolite, mesoporous silica), MOFs are unique in terms of porosity that can be easily tuned² and hence find various applications in gas storage,³ separation/purification,⁴ sensing,⁵ catalysis,⁶ drug delivery,⁷ and so on. Especially, introduction of diverse functional groups-via preorganization⁸ or postsynthetic modification9-into organic linkers enables to tailor the properties of MOFs. Among various functional groups found in the MOFs, imidazolium-containing organic linkers have been successfully utilized as heterogeneous precursors of N-heterocyclic carbenes, providing MOF¹⁰ for various applications such as in catalysis,¹¹ gas sorption,¹² and processes requiring high proton conductivity.¹³

Sumby and coworkers reported five different onedimensional (1D) chained MOFs that consist of various metal ions (Mg, Mn, Co, Zn, and Cu) and a U-shaped imidazolium ligand.¹⁴ Two distinct topologies were generated differing in the coordination geometry and coordination number of the metals: 1D porous undulating chains with a paddle-wheel cluster (Zn and Cu) and nonporous "polymeric caged" structures with a trimeric cluster (Mg, Mn, and Co).

Herein, we report a new caged 1D polymer MOF (**YMOF-Y**) of previously unknown topology composed of U-shaped imidazolium linkers and yttrium metal ions with a high coordination number (8 and 10).¹⁴ Cavities in the original **YMOF-Y**

are occupied by Y_4 metal clusters; however, a porous structure could be generated by the postsynthetic leaching out the clusters using alkali metal solutions. To the best of our knowledge, this is the first example of a selective metal cluster removal from a preformed MOF.

The parent **YMOF-Y** was synthesized by a solvothermal reaction, in which $Y(OAc)_3 \cdot 4H_2O$ and 1,3-bis(3-carboxyphenyl) imidazolium chloride (**H**₂**L-Cl**, [C₁₇H₁₃N₂O₄]Cl) were dissolved in MeOH and the solution was subsequently treated with formic acid. Keeping the mixture at 50 °C for 3–4 h, followed by removal of any solids by filtration and another 14 h at elevated temperature afforded colorless needle shaped crystals, that could be purified by washing with *N*,*N*-dimethylformamide (DMF) (Figure 1).

The crystal structure of **YMOF-Y** was determined by singlecrystal X-ray crystallography analysis, and the formula of **YMOF-Y** ($Y_4(C_{17}H_{11}N_2O_4)_4(Cl)_4(formate)_9(Y_2O_{0.5})$) was confirmed by both X-ray structural and elemental analysis. **YMOF-Y** shows a 1D chain structure in which cages composed of yttrium cations coordinated to carboxylate groups of the imidazole ligands are bridged by formate anions (**for-1**, Figure 2(a)). The cage contains eight yttrium ions, eight imidazolium ligands, and eight formate anions (**for-2**, Figure 2 (a)). The yttrium cations form two square planar clusters, four cations and four bridging formate anions each, positioned in the up and down sides of the cage. Each yttrium atom exhibits a coordination number of eight with two bidentate carboxylate groups from two different imidazolium units and four oxygen atoms from four formate molecules as ligands. In the cavity inside the cage, an yttrium cluster bearing four yttrium cations is present. Each yttrium cation in the cluster is coordinated by four oxygen atoms from four formate bridges, two other yttrium atoms, two chloride atoms, and two water molecules, resulting in coordination number of 10. The yttrium cluster is connected to the clusters forming the cage by six formate connectors (**for-3**, Figure 2(a)). The 1D chain is surrounded by four other chains, and the cages in the chains form a body-centered cubic lattice. Close packing of the neighboring chains is possible due to π - π interactions between parallel displaced aromatic rings of the imidazolium ligands (Figure 2(b) and (c)).

Since the inner yttrium cluster is held in place exclusively by interaction with formate anions and not with the imidazolium ligand, we speculated that it could be leached out with solutions containing alkali metals. Removal of the cluster



Figure 1. Reported topology types of 1D chain MOFs containing Ushape imidazolium-containing linkers and metal ions of various coordination geometries and coordination numbers. Selective removal of the Y_4 inner clusters of **YMOF-Y** by postsynthetic modification.

would make the inner space of the cage accessible for other molecules, expanding the scope of potential applications of **YMOF**. Hence, **YMOF-Y** was soaked in 0.3 M solutions of alkali metal (Li, Na, and K) nitrates in DMF/H₂O (DMF: $H_2O = 9:1$ mixture for lithium and sodium nitrate, DMF: $H_2O = 8:2$ mixture for potassium nitrate) at 100 °C for 24 h providing new crystalline solids (**YMOF-Li**, **YMOF-Na**, and **YMOF-K**). As evidenced by powder X-ray diffraction (PXRD) the original basic framework was retained in these solids, *i.e.*, the diffraction patters of **YMOF-Y**, **YMOF-Li**, **YMOF-Na**, and **YMOF-Na**, and **YMOF-Na**, and **YMOF-Na**, and **YMOF-Na**.

The removal of the yttrium clusters from the cages was first demonstrated by XRD analysis of **YMOF-Li**. Even though the exact assignment of each atom was not possible due to distortions of water and nitrate molecules, electron density mapping inside the cage clearly showed an empty void in place of the cluster (Figures 3(a) and S7). Unfortunately, the XRD analysis of **YMOF-Na** and **YMOF-K** afforded only the connectivity information due to their low crystallinity.

To further confirm the successful removal of the inner yttrium clusters, NMR studies, elemental, inductively coupled plasma optical emission spectrometry (ICP-OES), and thermogravimetric analysis (TGA) were carried out. The ¹H NMR spectrum of digested **YMOF-Y** indicated presence of the imidazolium ligand and formate in approximately 1:2.25 ratio, as expected from the chemical formula obtained from single crystal X-ray crystallography analysis. In the ¹H NMR spectra of postsynthetically modified YMOFs, this ratio increased to 1:1.5, which corresponds to removal of six formate molecules pro a cage unit. Since PXRD analysis before and after postsynthetic modification (PSM) indicates that for-1 and for-2 are intact, this result strongly suggests that the **for-3**, holding the Y_4 clusters in the cage, have been exchanged with solvent molecules during the postsynthetic modification process. Molecular formulas obtained from elemental analysis corresponded to structures in which approximately 88% of the inner clusters were removed and residual nitrate anions were present (Table S1). In the TGA thermograms of YMOF-Y and YMOFs, the ratio between the organic and the residual inorganic (metal oxide part, Y_2O_3) components was also examined and it was found that the contribution from inorganic components was reduced after



Figure 2. Single-crystal structure of **YMOF-Y**. (a) Cage unit structure and dimensions, (b) π - π interaction between 1D-chains, and (c) packing mode (viewed along the *c*-axis); C (gray), O (red), N (blue), Y (cyan), Cl (green), all H atoms were omitted.



Figure 3. (a) Overlayed X-ray crystal structures of the cage units in **YMOF**s (red: **YMOF-Y** [red dots represent yttrium ions], blue: **YMOF-Li**). (b) CO₂ sorption isotherms of **YMOF-Y** (black) and **YMOF-Li** (red) at 195 K (circle) and 273 K (triangle) (adsorption: filled, desorption: blank).

PSM (Figures S15 and S16). In addition, alkali metal ions were detected only in a trace amount by ICP-OES analysis (Table S4), which rules out the possibility of transmetallation of yttrium with alkali metal cations and indicates that a majority of yttrium cations were replaced by solvent molecules (water). Based on these results, we conclude that the Y_4 clusters and **for-3** formate molecules were indeed removed from the cage upon treatment with the alkali metal solutions. To the best of our knowledge, this is the first example of a selective cluster removal from a MOF.

In order to study the effect of inner cluster removal on the YMOF properties, gas sorption measurements were carried out. Since the cluster removal makes the void inside the cage accessible for guest molecules, we expected to observe an increase in adsorption capacity of PSM MOFs as compared to the parent YMOF-Y. Hence, acetone-exchanged YMOFs were activated at 80 °C for 6 h under dynamic vacuum and then treated with gaseous CO2. Indeed, PSM MOFs adsorbed CO₂ at 195 K with an uptake of 42 mL/g and reversible isotherms, while YMOF-Y exhibited an uptake of 17 mL/g under the same conditions (Figure 3(b)) and the process was irreversible (Figure S14). In addition, the zero-coverage isosteric heats (Q_{st}) of adsorption for CO₂ in YMOF-Y and YMOF-Li were calculated to be 12.0 kJ/mol and 26.2 kJ/mol, respectively.¹⁵ Therefore, upon inner cluster removal the uptake increased approximately 2.5 times and the adsorption process became reversible. At 273 K, the adsorption capacity of YMOF-Li dropped significantly (Figure 3), but still remained higher than that of the parent YMOF-Y.

These results clearly demonstrate that the microporosity enhancement due to inner cluster removal makes the **YMOF** a more effective CO₂ adsorbent. In order to gain a deeper insight into the sorption mechanism in these **MOF**s, unit cell parameters of **YMOF-Y** and **YMOF-Li** were measured at various temperatures. At 195 K, no significant difference from the structures measured at 100 K was observed. On the other hand, at 298 K there was a slight expansion (~0.18 Å, Table 1) along the *a* and *b* axes in **YMOF-Y**. No such expansion was detected in **YMOF-Li**, rendering these unit cell dimensions (*a* and *b*) similar in both **MOF**s. At the same temperature, significant contraction of **YMOF-Y** and

Table 1. Single crystal X-ray diffraction (SC-XRD) data ofYMOF-Y and YMOF-Li at 100 K and 298 K.

	Temperature (K)	Space group	Unit cell parameter (Å)	
			а	С
YMOF-Y	100	I4/m	24.0654	17.1973
	298	I4/m	24.2426	16.8874
YMOF-Li	100	I4/m	24.2479	16.6760
	298	I4/m	24.2682	17.1850

expansion of **YMOF-Li** along the c axis were observed (by 0.31 Å and 0.51 Å, respectively). Although this unit cell dimension remained significantly different in both MOFs, the difference was smaller in magnitude than at 100 K. Therefore, it can be concluded that as the temperature increases, the unit cell parameters of YMOF-Y and YMOF-Li become more similar, which may account for the large difference in CO₂ uptake in both YMOFs at 195 K and the much smaller one at 298 K. In addition, these results suggest that in the **YMOF** system sorption of CO₂ is strongly associated with a movement along the c axis and that the size of the channels can be tuned by choice of temperature in a flexible manner to afford a reversible adsorption/desorption behavior. Further studies of the temperature-dependence of the channel size in activated **YMOF-Y** by means of variable temperature powder X-ray diffraction (VT-PXRD) (synchrotron radiation, $\lambda = 1.2$) showed that as the temperature increases, the peaks related to the expansion along the *a* and b axes shift to lower angles [from approximately 7.5° (211) plane] and 8.0° [(002) and (220) planes by $0.02-0.03^{\circ}$ as the temperature changes from 170 K to 298 K; Figure 4]. Recently, a similar phenomenon was observed by the Kitagawa group,¹⁶ that reported gas separation and storage utilizing flexible 2D MOF showing a temperature-dependent pore aperture contraction. The flexible MOF with a square lattice (sql) network enables the separation of O₂ from argon with high efficiency utilizing the change in the size of the inlet of a cage due to the temperature-dependent motion of a ligand. We believe that the YMOFs can also be potential candidates for such applications.



Figure 4. VT-PXRD patterns of activated YMOF-Y at 170–298 K.

In summary, we synthesized a novel 1D chain yttrium based MOF composed of cages containing an Y_4 cluster that could be removed from the cavity through postsynthetic leaching out with alkali metal solutions. The removal of the inner cluster enhances the microporosity of **YMOF**, resulting in a significant increase of CO₂ adsorption capacity. Since the pore size in the 1D chain is temperature-dependent, the adsorption properties of both parent and PSM **MOF**s can be further influenced by the choice of temperature, making the **YMOF**s suitable candidates for gas separation application.

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Supporting Information. Additional supporting information may be found online in the Supporting Information section at the end of the article.

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