CRYSTAL GROWTH & DESIGN

Communication

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New Lithium Ion Clusters for Construction of Porous MOFs

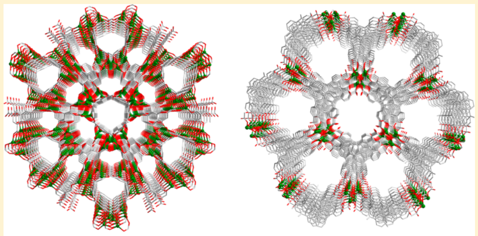
Andrew Clough,[†] Shou-Tian Zheng,[†] Xiang Zhao,[†] Qipu Lin,[‡] Pingyun Feng,[‡] and Xianhui Bu*,[†]

[†]Department of Chemistry and Biochemistry, California State University, Long Beach, CA 90840, United States

[‡]Department of Chemistry, University of California, Riverside, CA 92521, United States

Ⓢ *Supporting Information*

ABSTRACT: Two novel types of lithium clusters, Li_4 tetramer and Li_2 dimer, have been created as the building blocks of MOFs. The assembly of such unprecedented clusters with two types of tricarboxylate ligands leads to two highly open frameworks, one of which exhibits a very high CO_2 uptake capacity among Li-based MOFs. The work reveals the interesting and unprecedented structural chemistry of lithium ions.



Lithium carboxylate metal-organic frameworks

Crystalline porous materials (CPM), and metal−organic frameworks (MOF) in particular, have been extensively explored for various applications.[1−5] Unlike other types of porous materials, MOFs can be made from a large selection of inorganic and organic building blocks. One of the most significant successes is the use of the lightweight elements, especially, B^{3+}, Mg^{2+}, and Al^{3+}, which has culminated in the discovery of a Mg form of MOF-74 with the unsurpassed uptake capacity for CO_2.[6,7]

Compared to MOFs based on other lightweight elements, significantly fewer Li-MOFs (MOFs based on pure Li nodes) are currently known, even though some progress has been made.[8−10] This is apparently due to lithium's unique combination of hard Lewis acidity and low +1 charge. Other metal ions with a low +1 oxidation state (such as Cu^+ and Ag^+) are much softer than Li^+ and often derive their relatively rich coordination chemistry through their soft acid property.[11]

Clearly, synthetic strategies for making Li-MOFs are more likely to succeed if they properly address the unique property of Li^+. In our previous work, we used two strategies based on charge-complementarity of either organic or inorganic building blocks. In the first case, ligands with neutral and −1 charges are used together to lower the average negative charge of ligands to −0.5 [e.g., Li(4,4-bpy)(im), im = imidazolate]. In the second case, which led to the synthesis of boron imidazolate frameworks (BIFs) [e.g., $LiB(im)_4$], B^{3+} is used to compensate for the low +1 oxidation state of Li^+.[12] In both cases, the negative charge on the ligand does not exceed −1.

This work deals with Li-MOFs made from carboxylates, which are potentially more negative, depending on the number of carboxyl groups per ligand and the degree of deprotonation. The literature already contains a number of Li−carboxylate−MOFs, but the generally observed structural pattern is that Li^+ tends to form polymeric Li−O chains or layers (with carboxyl groups). So far, no discrete Li clusters have been observed in the Li−carboxylate system. Because MOFs constructed from discrete inorganic nodes are often more porous than those containing polymeric inorganic building blocks, for the simple reason that organic spacers are usually larger than inorganic spacers, the development of new lithium clusters in the Li−carboxylate system is of considerable interest.

Metal clusters, in general, are highly desirable in the design of a porous network because in addition to greatly increasing the materials diversity, clustering can enhance framework stability through the increased number of connectivity between inorganic and organic units and the formation of higher-connected nets.[13] For lithium, the clustering is even more desirable, for at least two reasons. The first is that Li usually has a low connectivity of 3 or 4 in its monomeric form and the formation of clusters is expected to have a more pronounced effect on the framework stability (compared to monomeric Li-MOFs).

The second reason is that clustering of metal ions (e.g., Cu_2^{4+}, In_3O^{7+}, $[Zn_4O]^{6+}$) can help increase the overall positive charge of the inorganic node. For Li^+, the clustering could provide a new route for synthesizing Li-MOF from more negative carboxylate ligands. The challenge is, however, that known lithium clusters are generally formed with anionic species [e.g., $Li_4(PhO)_4$] and are neutral.[9] We are thus very interested in synthetic possibilities that can lead to positive lithium clusters.

In this work, we have created such an interesting system by using highly negative organic anions, BTC^{3-} and BTB^{3-}, to promote the clustering of lithium ions. Indeed, such a method is effective, and we have observed the formation of a highly unusual lithium cluster, square-planar Li_4 tetramer as well as a Li_2 dimer. It is worth noting that despite their simple compositions, no Li-BTC or Li-BTB MOFs are known prior to this work, even though some Li-dicarboxylate MOFs have been reported.[10] These two Li-MOFs exhibit highly open

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architecture, and Li-BTB exhibits a high CO_2 uptake capacity among known Li-MOFs.

CPM-45 crystallizes in the noncentrosymmetric cubic $I\bar{4}3d$ space group.[14] Its most novel feature is the square-planar Li_4 cluster (Figure 1a). It is worth noting that square-planar clusters are also known for divalent metal ions such as Co^{2+}; however, these known square-planar clusters contain an oxo (O^{2-}) or hydroxyl (OH^-) species at the center that helps to assemble metal ions together. The Li_4 tetramer reported here is different and consists of only four lithium ions. From the viewpoint of self-assembly, such a metal-only tetramer is expected to be more difficult to form.

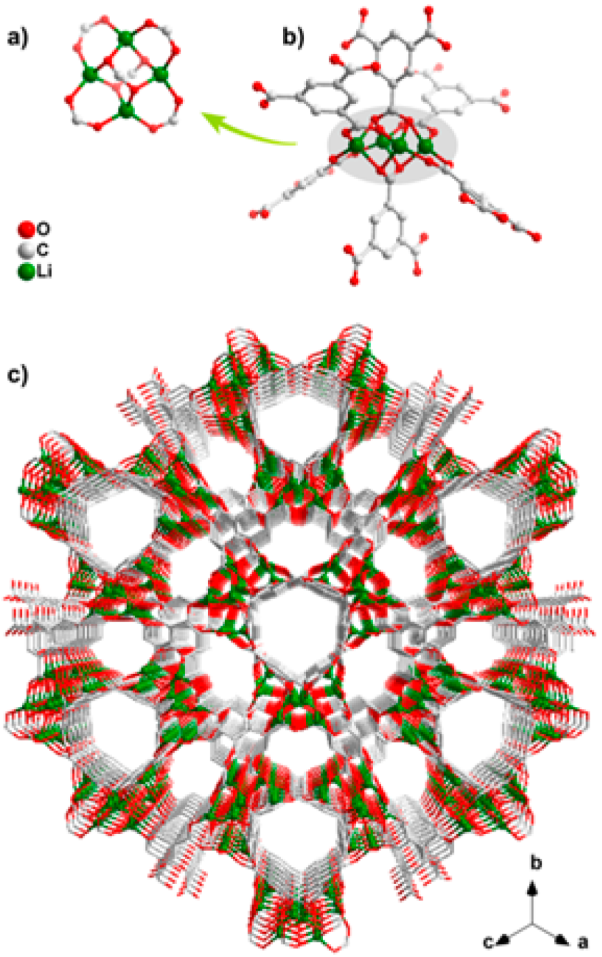

Figure 1. An illustration of CPM-45 framework. (a) representation of the square Li_4 SBU. (b) Coordination mode between Li_4 SBU and its adjacent six BTC ligands. (c) View of 3D framework showing open channels.

Each edge of the square (i.e., two Li sites at the corners) is bridged by a −COO carboxyl group, which gives a neutral $Li_4(COO)_4$ unit. In comparison with the $Li_4(PhO)_4$ cubane cluster (with tetrahedral Li_4) in which each Li site has only one free coordination site after the cluster formation, the $Li_4(COO)_4$ unit in CPM-45 still has two remaining coordination sites per Li for a total of 8 coordination sites. Very elegantly, it only takes two additional −COO groups, located above and below the Li_4 square, to complete all these 8 coordination sites, resulting in the dinegative $[Li_4(COO)_6]^{2-}$ building blocks (Figure 1a). In $[Li_4(COO)_6]^{2-}$, four edge-connected BTC ligands alternate above and below the Li_4 plane, while two face-connected BTC ligands are orthogonally oriented to each other.

It can be said that Li_4 clusters mimic monomeric 6-connected M^{4+} ions, which are rarely observed in MOFs. The resulting (3,6)-connected net in CPM-45 forms open channels along the cubic [111] direction (Figure 1c). The free volume accessible to guest species (i.e., solvents as well as charge-balancing species) is as high as 50.4%, as calculated with the PLATON program, most of which, however, are occupied by $NH_2(CH_3)_2^+$ serving as an extra-framework charge balancing species. The remaining void space (about 12%) is presumably occupied by disordered solvent molecules.

The unprecedented Li_4 tetramer in the Li-BTC system highlights the potentially rich cluster chemistry of Li-MOFs, which is further proven with the discovery of the unprecedented Li_2 in the Li-BTB system.

Similar to the Li_4 tetramer in CPM-45, each Li_2 dimer in CPM-46 also acts as a 6-connected node linked by tritopic BTB ligands to form a new (3,6)-connected 3D framework with 1D open channels along the *c* axis (Figure 2). Four out of six carboxylic groups around each Li_2 SBU are protonated (i.e., COOH), and they bond to Li^+ ions in the monodentate mode, while the remaining two carboxylic groups are deprotonated (i.e., COO−) and they bond to Li^+ ions in the bidentate mode, leading to the formation of the dimeric Li_2 SBU in CPM-46 (Figure 2a). Prior to this work, though various dimeric metal SBUs have been employed to create a large number of MOFs, dimeric Li_2-based MOF remained unknown. CPM-46 also exhibits a porous framework with 46% void space.[15] It is worth noting that CPM-45 and CPM-46 represent two types of unknown (3,6)-connected framework topologies with the point symbols of $\{6^{12}.8^3\}\{6^3\}_2$ and $\{6^8.8^7\}\{6^3\}_2$, respectively (details in Figure S10 of the Supporting Information).[16]

Inspired by the open architecture of CPM-45 and CPM-46, gas sorption studies were carried out. For CPM-45 with the negative framework, the gas adsorption experiments showed no adsorption, likely due to the pore blocking effect of extra-framework charge balancing cations. Since CPM-46 has a neutral framework with no extra-framework cations, further gas sorption experiments were performed with CPM-46. CPM-46 was activated by refluxing the crystals in acetonitrile for 48 h to exchange solvents and then degassed at 80 °C for 24 h under vacuum prior to the gas adsorption measurement (Figure S3 of the Supporting Information). As shown in Figure 3, the sorption isotherms obtained with CO_2 at 195 K revealed a typical type I adsorption curve. The CO_2 sorption increases abruptly at very low pressures and reaches a maximum uptake

Table 1. Summary of Crystal Data and Refinement Results[a]

compound	formula	sp gr	*a*/*b* (Å)	*c* (Å)	*R*(*F*)
CPM-45	$[NH_2(CH_3)_2]_2[Li_4(BTC)_2]\cdot$solvent	$I\bar{4}3d$	21.1288(4)	21.1288(4)	0.0834
CPM-46	$[Li_2(H_2BTB)_2]\cdot$solvent	*R*32	28.0967(8)	22.9666(14)	0.0677

[a] H_3BTC = 1,3,5-benzenetricarboxylic acid; H_3BTB = 1,3,5-tri(4-carboxyphenyl)benzene.

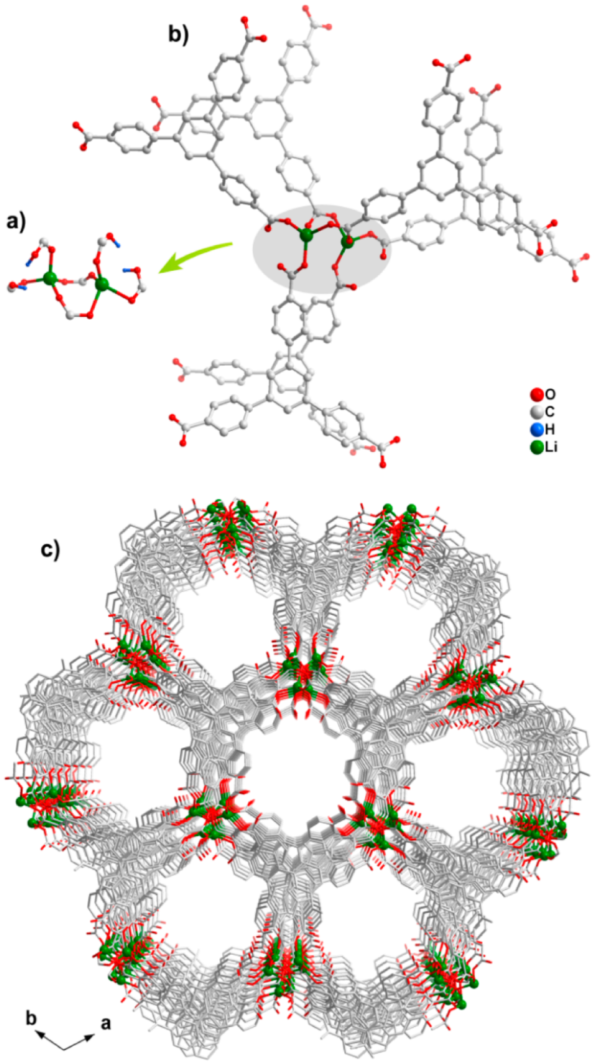

Figure 2. CPM-46 framework. (a) Representation of the dimeric Li_2 SBU. (b) Coordination mode between Li_2 SBU and its adjacent six BTB ligands. (c) View of 3D framework along the [001] direction, showing 1D hexagonal channels.

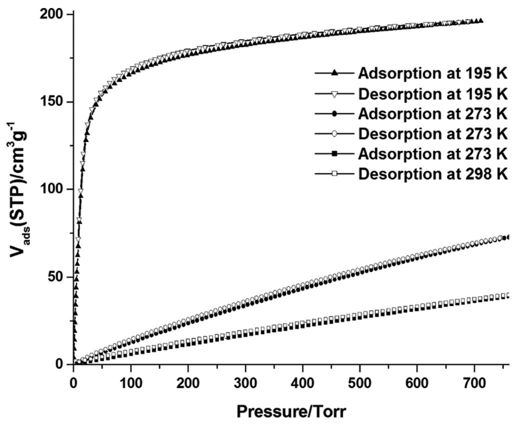

Figure 3. CO_2 sorption isotherms of CPM-46 at different temperatures.

of 196 cm^3/g at 1 atm. The sorption isotherm data were fitted to the BET equation to give a BET surface area of 592 m^2/g. Calculations from fitting the adsorption data to the Dubinin–Radushkevich equation gave a microporous surface area and a pore volume of 1784.2 m^2/g and 0.359 cm^3/g, respectively. Additionally, at atmospheric pressure, the CO_2 uptakes of CPM-46 at 273 and 298 K reach 72.5 cm^3/g and 39.3 cm^3/g, respectively, which is, to our knowledge, the highest among known Li-MOFs.

In summary, two novel types of lithium clusters, Li_4 tetramer and Li_2 dimer, have been created as the building blocks of MOFs. The assembly of such unprecedented clusters with two types of tricarboxylate ligands leads to two highly open frameworks. This work reveals the interesting structural chemistry of lithium ions never before observed.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic details, tables of crystallographic information, structural details, thermogravimetric curve, and powder XRD patterns. This information is available free of charge via the Internet at http://pubs.acs.org/.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: xianhui.bu@csulb.edu.

Notes

The authors declare no competing financial interest.

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(14) Synthesis for CPM-45: 0.020 g $LiNO_3$ and 0.030 g H_3BTC were weighed into a Teflon-lined stainless steel reaction autoclave. Added to the autoclave were 2.0 g CH_3CN, 1.0 g DMA, and 2.0 g MeOH, and the mixture was stirred for 1 h. The autoclave was then sealed and placed in an oven at 160 °C for 5 days. After cooling at RT for 24 h, colorless crystals were obtained. Synthesis for CPM-46: A mixture of $Zn(Ac)_2 \cdot 4H_2O$ (0.019 g), LiCl (0.020 g), and H_3BTB (0.025 g) was stirred in a mixed solution of CH_3CN/H_2O/p-murea (2.00 g/0.30 g/1.00 g) for 1 h and then transferred into a vial (23 mL). The vial was kept at 100 °C for 2 days, and then cooled to room temperature. After being washed with ethanol, the colorless crystals were obtained.

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