

IV.H.6 Synthetic Design of New Metal-Organic Framework Materials for Hydrogen Storage

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Objectives

- Design and synthesize new metal-organic framework materials using lightweight chemical elements to help improve gravimetric hydrogen storage capacity.
- Develop new synthetic strategies to generate novel active binding sites on metal ions and ligands to enhance solid-gas interactions for increased uptake near ambient conditions.
- Develop synthetic methods to create porous frameworks with novel architectural features such as partitioned pore space for the optimum size match with hydrogen molecule.

Technical Barriers

- Lithium ion usually has a low coordination number of 4 and the generation of open metal sites in the absence of cluster or chain formation would reduce its connectivity and may also destabilize the framework.
- Lithium ion has strong solvation energy in many polar solvents. The identification of best solvents that promote crystallization and generation of reversible solvent binding sites is challenging.
- To achieve pore space partition often requires the co-assembly of multiple components of inorganic building blocks, which are formed in situ and difficult to control.

Abstract

Crystalline porous materials such as zeolites have played an important role in energy-related applications due to the unique coupling between their geometrical features and chemical functionalities. The overall objective of this project is to develop synthetic strategies to synthesize new

porous materials with new geometrical features and chemical functionalities useful for hydrogen storage applications.

The project places a strong emphasis on the use of lightweight elements (lithium in particular) as the structural building block. Lithium is the lightest metallic element and also possesses desirable binding affinity for dihydrogen molecule if active binding sites can be created. Compared with other metallic ions used for the construction of porous materials, lithium is unique in its synthetic and structural chemistry, because of its small ionic radius, low oxidation state, and high solvation enthalpy. Therefore, innovative synthetic methods need to be developed to realize lithium based porous materials. In this work, synthetic strategies are being developed that aim to match the unique characteristics of lithium with proper charge and coordination geometry of organic ligands. One method seeks to create zeolite-type porous materials by using charge-complementary polyhedral nodes (e.g., through the integration between Li^+ and a higher valent element such as Mg^{2+} and B^{3+}). Another method uses lithium ions as the sole polyhedral node, but integrates charge-complementary ligands to create porous zeolite-like frameworks. Other strategies being studied for enhancing hydrogen storage capacity include a comparative study of the related lightweight ion Mg^{2+} , the creation of high-density binding sites on ligands, and partition of pore-space for better size match with hydrogen molecules.

Progress Report

A highly stable porous material constructed from lithium aryloxide clusters.

In order to further enhance the adsorption property, an emergent and promising strategy is to introduce lightweight elements into the framework, which may lead to an increase in the gravimetric uptake capacity. A new porous material based on Li_4O_4 cubane cluster has been realized. While $\text{Li}_4(\text{OPh})_4$ type clusters linked by neutral ligands are well-known in the literature, none is porous, mainly because phenol-type ligands used for the formation of lithium clusters also block the pore space. Our success was through the use of a very unique ditopic ligand 4-pyridinol (also called 4-hydroxypyridine). Because 4-pyridinol serves dual roles (i.e., cluster formation and intercluster crosslinking), this strategy eliminates the pore-blocking effect of the aryloxide ligand, leading to the accessible porosity. The synthesized material exhibits a zeolite topology and possesses large pore channels (Figure 1). Considering that it is based on low-valent lithium framework, this material has an unbelievably high

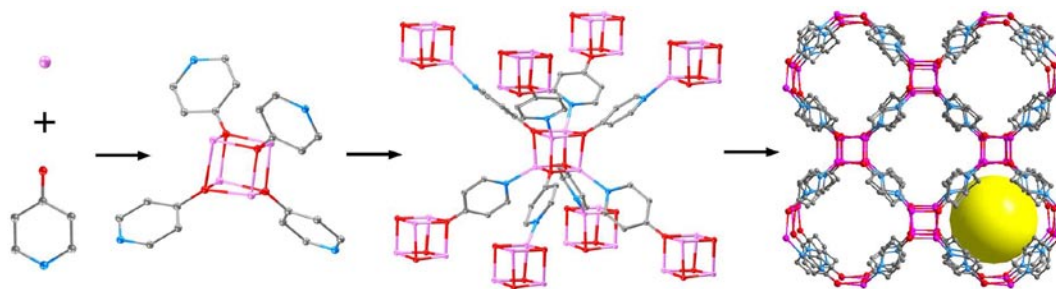


FIGURE 1. Illustration of the self-assembly process from molecular species Li^+ and 4-pyridinol to Li_4O_4 cubane clusters, and finally to three-dimensional (3-D) framework. (purple: Li; red: O; blue: N; grey: C)

thermal stability up to at least 500°C . Its Brunauer-Emmett-Teller and Langmuir surface areas reach $440.3\text{ m}^2/\text{g}$ and $632.5\text{ m}^2/\text{g}$, respectively and its hydrogen storage capacity is $1.4\text{ wt}\% \text{ H}_2$ at 77 K-1 atm . While these numbers are modest compared to the best metal-organic framework materials (MOFs) based on some other metal ions, they are nevertheless the highest among lithium-based MOFs, demonstrating the significant potential of this system [1].

Lithium zeolitic imidazolate frameworks (Li-ZIF) constructed with charge-complementary ligands

A versatile synthetic method capable of generating a large family of Li-based porous materials has been developed. This method is based on the use of mixed charge-complementary ligands (mono-negative L^- and neutral L^0 , L = ligand) specifically chosen to mimic SiO_2 composition and to create $\text{Li}^+\text{L}^-\text{L}^0$ -type lithium-based zeolitic imidazolate frameworks. We have so far synthesized four types of 3-D framework materials with the general SiO_2 -type framework composition of LiL^0L^- .

A porous tetragonal magnesium-carboxylate framework with nanotubular channels

Because highly negative tetraanionic ligands can increase the metal-to-ligand ratio (for the simple reason of charge balance), which has the potential to increase the density of active metal sites and gas uptake capacity as shown by MOF-74 [2], the use of tetraanionic ligands should have a great potential for developing high-capacity porous materials. In this work, we sought to mimic the tetraanionic ligand used in MOF-74 ($\text{Mg}_2(\text{dobdc})$, $\text{H}_4\text{dobdc} = 2,5$ -dihydroxyterephthalic acid) by investigating the reaction of Mg^{2+} with a tetracarboxylate (biphenyl-3,3',5,5'-tetracarboxylic acid or H_4bptc) (Figure 2) and were able to synthesize a new Mg-MOF (denoted CPF-1) from a solvent mixture of *N*-ethylformamide (NEF) and water.

CPF-1 is built from 4_1 -helical inorganic chains (space group: $I4_122$), connected to each other with a tetracarboxylate to form one-dimensional (1-D) cylindrical nanotubular channels with tetragonal symmetry, in contrast with the 1-D

hexagonal channels in MOF-74 (Figure 2). We were able to achieve a higher density of solvent sites on Mg^{2+} sites with each Mg^{2+} bonded to two solvent molecules. However, solvent sites on two adjacent Mg^{2+} sites are oriented toward each other, which leads to the bridging mode for the coordinated solvent molecules. This apparently complicates the sample activation due to the more difficult removal of coordinated solvent molecules. The present measurement data show that its storage capacity ($1.3\text{ wt}\% \text{ H}_2$ at 77 K-1 atm , $84\text{ cm}^3/\text{g}$ of CO_2 at 273 K-1 atm) is lower than that of MOF-74-Mg, and is the second highest among known Mg-MOFs [2,3], demonstrating the potential of the synthesis strategy for further advancing the hydrogen uptake capacity.

Single-walled metal-organic channels with high density of open nitrogen-donor sites and gas uptake

In addition to uncoordinated metal sites, unused functional groups of the organic ligands can play a key role in gas adsorption of MOF materials. Thus, having available the largest number of exposed functional sites (on either metals or non-metals) would likely contribute to the enhanced gas sorption properties.

Of particular interest are functional groups such as aromatic $-\text{N}(\text{H})-$ donors found in metal azolate frameworks. Despite the fact that the use of triazoles and tetrazoles has led to some MOF compounds, it is still an ongoing challenge to create porous frameworks in which the largest possible number of N-donor sites are left uncoordinated to metals (called open donor sites, in analogy with open metal sites).

For the purpose of increasing the percentage of open donor sites, individual triazole or tetrazole ligands are less effective, because at least two N-donor sites will be needed for the framework connectivity, and the maximum percentage of open donor sites would be only 33% for a triazole and 50% for a tetrazole framework. Hence, we are especially interested in ligands containing multiple triazole and tetrazole groups (i.e., polytriazole or polytetrazole such as 1,3,5-tris(2*H*-tetrazol-5-yl)benzene or H_3BTT in short), and such a ligand can achieve a high connectivity if they only use one N-donor site (per triazole or tetrazole group) for

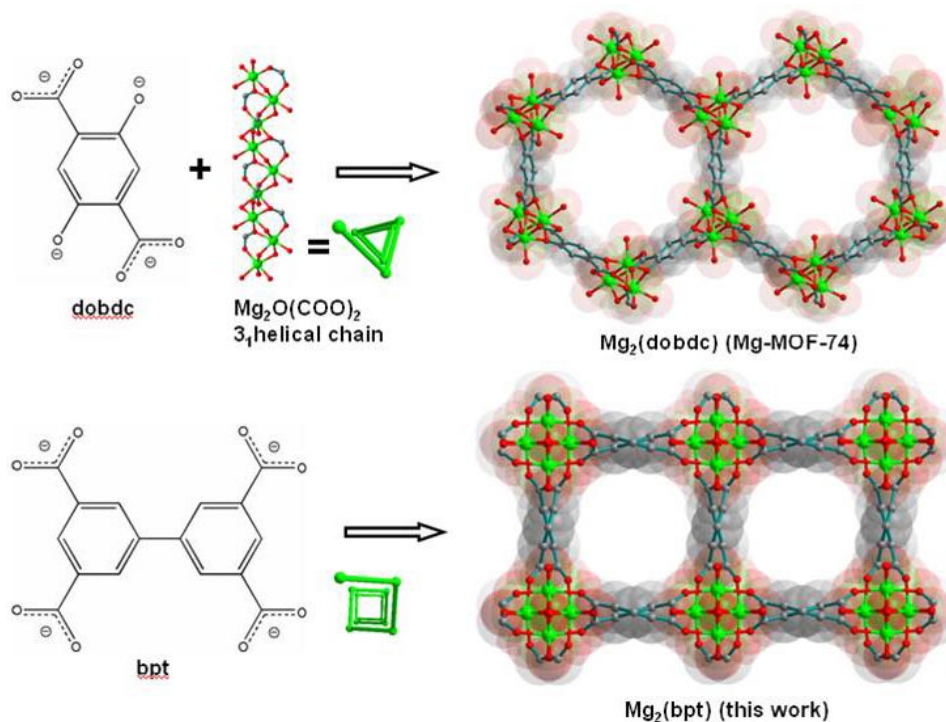


FIGURE 2. A comparison between two MOFs based on tetraanionic ligands. (top) Mg₂(dobdc) (Mg-MOF-74) and (bottom) CPF-1.

bonding with metals. The highest percentage of open donor sites would be 67% for a triazole and 75% for a tetrazole, assuming each ligand uses just one N-donor site for the framework formation. However, such a high percentage of open donor sites have not yet been achieved.

In this work, by using a urea derivative (1,3-dimethylpropyleneurea) as the co-solvent in *N,N*-dimethylacetamide (DMA), an interesting porous framework (denoted CPF-6) with 1-D square single-atom-walled channel system has been prepared (Figure 3). This material has a highly porous 3-D framework with a large percentage (67%) of N-donor sites unused for bonding with metals. Even though it does not have any open metal sites, it exhibits high gas storage capacity (ca. 1.9 wt% H₂ at 77 K-1 atm, 98 cm³/g CO₂ at 273 K-1 atm). The high percentage of open N-donor sites, coupled with the low-framework density resulting from single-walled channels is believed to contribute to the high gas uptake capacity.

Future Directions

To develop high-capacity hydrogen storage materials, we will need to further develop synthetic methods to synthesize porous materials that combine multiple features including lightweight building block, active binding sites, and high stability. A systematic study of solvent systems that can bind reversibly to metal ions such as Li⁺ without adversely

affecting the crystallization process is important. Also important is to create a stable support system for Li⁺ with active binding sites. The application of the pore partition strategy to the lightweight building units would make it possible to integrate advanced architectural features with desirable chemical compositions and functionality.

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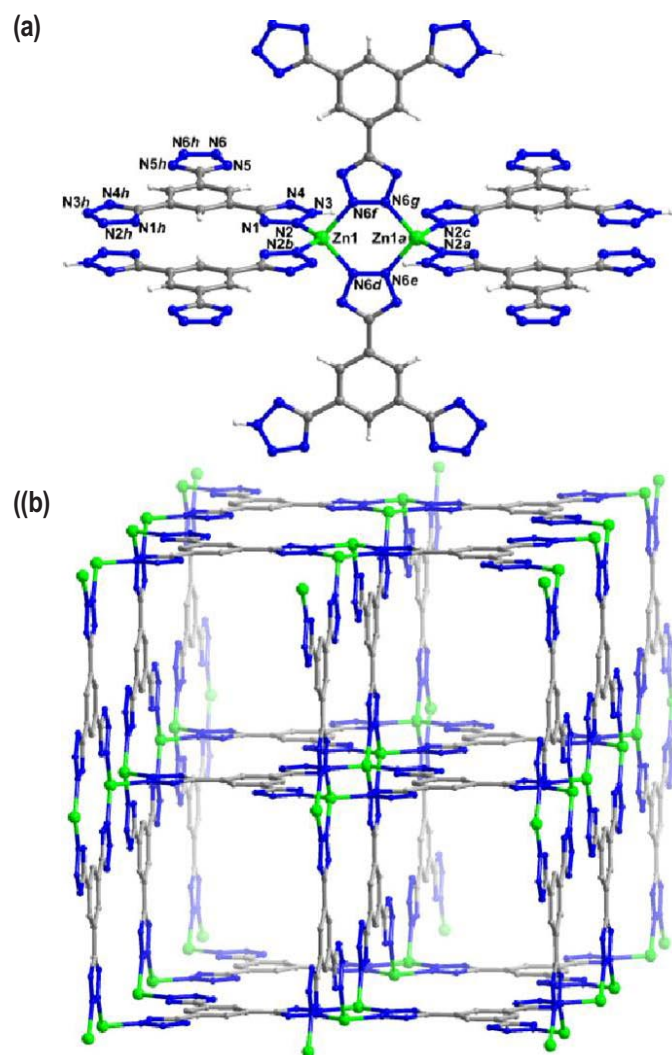


FIGURE 3. (a) View of the zinc dimer bridged by two tetrazolate groups (in bidentate fashion) and completed by four other tetrazolate groups (in unidentate fashion), (b) the 3-D extended network showing large channels.

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