Final Scientific/Technical Report

1. DOE Award # and name of the recipient (Institution)

Award#: DE-SC0002235.

University of California at Riverside

2. Project title and name of the PI

Title of the project: "Low-Density and High Porosity Hydrogen Storage Materials Built from Ultra-Light Elements"

PI: Pingyun Feng; University of California at Riverside

3. Date of the report and research period covered by the report

Date of the report: January 10, 2014

Period covered by the report: Sept. 15, 2009 to Sept. 14, 2012

4. **A brief description of accomplishments. This can follow any format you think is useful and appropriate to indicate your progress. Please limit this section to no more than 5 pages.**

A total of 22 publications resulted from this DOE support. As summarized below, a number of significant advances have been achieved, opening up new opportunities for the synthetic development of novel porous materials and their energy-related applications including gas storage and separation and catalysis.

Figure 1. Illustration of the self-assembly process from (a) molecular species Li⁺ and 4-pyridinol to (b) Li₄O₄ cubane clusters, and finally to (c) 3-D framework. (purple: Li; red: O; blue: N; grey: C)

4.1 Lithium-based Metal-Organic Frameworks

Lithium is the lightest metallic element. Compared with other metal ions (such as Co, Ni, Cu, and Zn) commonly used for the construction of porous metal-organic framework (MOF) materials, lithium is unique in its synthetic and coordination chemistry, because of its atomic properties such as low oxidation state and hard Lewis acidity. In this work, we devised a synthetic strategy specifically tailored to address these unique properties of Li⁺ and have created a series of Li-MOFs, some with an impressive thermal stability that is even higher than most well-known MOFs based on transition metal ions.

Neutral lithium aryloxide Li₄(OPh)₄(Solvent)₄ (Ph= phenyl) clusters are well known in the literature. There are also examples in which such neutral clusters are linked by ditopic neutral ligands such as dioxane into 3-D frameworks. However, these known Li-

Figure 2. Simulated (black) and experimental X-ray diffraction patterns for as-synthesized sample (blue) and samples after thermal treatment at different temperatures: 300 °C (cyan), 400 °C (green), 500 °C (yellow), 520 °C (orange) and 550 °C (red).

cluster-based frameworks are not porous because there are four *dangling* aryl groups attached to each Li-cubane cluster and they block the pore access. They are also not thermally stable because the linkage between neutral clusters and ligands tends to be weak. With our method, we were able to generate porosity by converting aryl groups from the *pendent* mode to the *bridging* mode, which frees up the pore space, and we were also able to enhance the stability of the framework by embedding 50% donor atoms (oxygen) of the bridging ligand (4-pyridinol) within the cluster.

Our method is based on the use of a ligand that combines the *cluster-forming* ability of aryloxide and the *crosslinking* ability of dioxane. While a family of such ligands exists, the simplest one with such integrated features is the ditopic ligand *4-pyridinol* (also called 4-hydroxypyridine). Because 4-pyridinol serves the dual roles (i.e., cluster formation through hydroxy group and intercluster crosslinking using pyridal group), this strategy naturally turns the aryl group into a bridging group, which helps eliminate its pore-blocking effect. This material exhibits the zeolite ACO-type topology and possesses large channels (Figure 1). Considering that it is based on monovalent lithium framework, this material has an unbelievably high thermal stability up to at least 500°C (Figure 2), apparently due to the embedding of crosslinking donor atoms inside the cubane cluster. Its BET and Langmuir surface areas reach 440.3 m²/g and 632.5 m²/g, respectively. While the surface area is modest compared to the best porous materials, it is nevertheless the highest among lithium-based coordination polymers, demonstrating the significant potential of our synthesis method. Depending on synthetic conditions, in particular solvents, such Li₄O₄ cubane clusters can also form porous hydrogen-bonded networks.

4-pyridinol

4.2 Magnesium-based Metal-Organic Frameworks

In addition to lithium, magnesium is another metallic element whose low atomic weight has attracted considerable attention. The interest in Mg has been further heightened by the discovery that the magnesium form of MOF-74 currently exhibits the highest CO₂ uptake capacity among all known porous materials. Still, compared to MOFs based on other divalent metals such as Zn and Cu, the chemistry of Mg-MOFs is much less well understood and so far there are much fewer examples of Mg-MOFs. Prior to our work, magnesium-based structural building blocks such as trimeric Mg₃(OH) were unknown, even though corresponding transition metal trimers such as Co₃(OH) are common.

Because highly negative 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, the use of tetraanionic (or even more negative) ligands should have a great potential for developing high-capacity porous materials. MOF-74 is a somewhat special case, because its tetraanionic ion comes from two carboxyl and two hydroxyl groups. Since the deprotonation of the -OH group under common MOF synthesis conditions is less common, tetracarboxylates may provide a more general alternative.

In this work, we sought to mimic the tetraanionic ligand used in MOF-74 ($\text{Mg}_2(\text{dobdc})$, H_4dobdc = 2,5-dihydroxyterephthalic acid) by studying the reaction of Mg^{2+} with a tetracarboxylate (biphenyl-3,3',5,5'-tetracarboxylic acid or H_4bptc) (Figure 4) and were able to synthesize a new Mg-MOF (denoted CPF-1, **CPF** = *Crystalline Porous Framework*) from a solvent mixture of *N*-ethylformamide (NEF) and water (note: we found that *the formation of Mg-MOF is highly sensitive to the type of solvent or solvent mixture*). CPF-1 is built up from 4₁-helical inorganic chains (space group: $I4_122$), connected to each other with the tetracarboxylate to form 1D cylindrical nanotubular channels with tetragonal symmetry, in contrast with the 1D hexagonal channels in MOF-74 (Figure 3). Its storage capacity (1.29 wt% H_2 at 77 K-1atm, 84cm³/g of CO_2 at 273K-1atm) is quite high compared to most known MOFs. To our knowledge, the gas uptake capacity of CPF-1 is the second highest among known Mg-MOFs (only behind Mg-MOF-74). One reason for the lower performance of CPF-1 (compared to MOF-74) is that two adjacent open metal sites in CPF-1 bond to the same solvent molecule, which makes it more difficult to remove the solvent molecule.

Figure 3. A comparison between two MOFs based on tetraanionic ligands. (top) $\text{Mg}_2(\text{dobdc})$ (Mg-MOF-74) and (bottom) $\text{Mg}_2(\text{bpt})$ (this work).

4.3 High Gas Uptake in Porous Frameworks with High Density of Open Donor Sites

In **Sections 4.1 and 4.2**, the primary focus is on the control of the framework composition and topology by exploring less well-studied and perhaps more challenging inorganic building blocks such as Li and Mg frameworks. In the following, we highlight some specific synthetic successes in creating functional sites that could enhance host-guest interactions.

4.3.1 Open Nitrogen-Donor Sites from Polytetrazole

In addition to uncoordinated metal sites, unused functional groups of organic ligands can play a key role in gas adsorption. Various studies in the literature have shown that gas molecules can interact with both metal sites and organic ligands of the porous frameworks. 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.

Obviously, the binding affinity between framework sites and gas molecules can vary greatly depending on framework compositions or the nature of gas molecules. Of particular interest are functional groups such as aromatic -N(H)- donors in metal azolate frameworks (an azole is a type of heterocyclic molecules with at least two donor atoms such as nitrogen). Despite the fact that the use of triazoles and tetrazoles has led to some MOFs, 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(2H-tetrazol-5-yl)benzene or H₃BTT 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 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, in the literature examples such as Cu-BTT or Mn-BTT, 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 (ZnHBTT, denoted CPF-6) with 1D square single-atom-walled channel system has been prepared (Figure 4). 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. 98cm³/g CO₂ at 273K-1atm and 1.89wt% H₂ at 77K-1atm). 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.

Figure 4. (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.

4.3.2 High CO₂ and H₂ Uptake in an Anionic Framework with Amino-Decorated Cages

We synthesized an exceptional anionic porous metal-organic framework, $[(\text{CH}_3)_2\text{NH}_2][\text{Zn}_3(\text{DATRZ})(\text{BDC})_3] \cdot x\text{DMF}$ (denoted CPF-13, **DATRZ** = 3,5-diamino-1,2,4-triazole, **BDC** = 1,4-benzenedicarboxylate, **DMF** = N,N-dimethylformamide), that integrates multiple desirable features such as nanoscopic polyhedral cages, framework functionalization by amino-groups, and charged framework (Figure 5). These features contribute to the high gas uptake capacity of CPF-13. CPF-13 was obtained in high yield as octahedral crystals via solvothermal reaction between $\text{Zn}(\text{NO}_3)_2$, DATRZ and BDC in DMF at 90°C. It shows the type I adsorption isotherm typical of materials of permanent microporosity. The Langmuir and BET surface areas were 1008 and 642 m^2/g , respectively. A micropore volume of 0.350 cm^3/g and the median pore size of 4.62 Å were also calculated. The uptake of H_2 at 1 atm and 77 K reaches 2.0 wt% (223.9 cm^3/g). Impressively, CPF-13 exhibits a very high CO_2 uptake capacity of 116 cm^3/g (5.2 mmol/g) at 273 K and 1 atm (Figure 6). At 298 K and 1 atm, CPF-13 has a CO_2 uptake of 81 cm^3/g (3.62 mmol/g). Although the CO_2 uptake of CPF-13 is lower than the neutral Mg-MOF-74 (8.48 mmol /g at 298 K), to our knowledge, CPF-13 has the highest CO_2 uptake among charged MOFs under ambient conditions. In particular, the CO_2 uptake capacity of CPF-13 is higher than CPM-6, another well-known MOF with an anionic framework. We have further found that CPF-13 exhibits high CO_2/N_2 and CO_2/CH_4 selectivity (Figure 6).

Figure 5. A nanoscopic cage enclosed by paddlewheel Zn dimers, BDC and DATRZ ligands.

Figure 6. (Left) H_2 and N_2 adsorption isotherms at 77K. (Right) Adsorption isotherms for CO_2 at 273K and 298K, CH_4 at 273K, and N_2 at 273K.

5. A list of papers (mark as published, in press, or submitted) in which DOE support is acknowledged. Include an excerpt of the acknowledgement section. Instructions regarding BES acknowledgement protocol are contained in the attached document "Acknowledgement of support and delineating BES-funding in publications".

5.1 Zhang, J.; Chen, S.; Nieto, R. A.; Wu, T.; Feng, P.; Bu, X. "A Tale of Three Carboxylates: Cooperative Asymmetric Crystallization of Three-Dimensional Microporous Framework from Achiral Precursors", *Angew. Chem. Int. Ed.* 2010, 49, 1267-1270. (published)

We thank the support of this work by NIH (X. B. 2 S06 GM063119-05), NSF (X. B. DMR-0846958), and DOE (P. F. 004407-002). NIH for synthesis, NSF for structure analysis, DOE for property characterizations including stability and gas sorption analysis.

5.2 Zheng, S.; Wu, T.; Zhang, J.; Chow, M.; Nieto, R.; Feng, P.; Bu, X. "Porous Metal Carboxylate Boron Imidazolate Frameworks", *Angew. Chem. Int. Ed.* 2010, 49, 5362-5366. (published)

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5.3 Zheng, S.; Li, Y.; Wu, T.; Nieto, R.; Feng, P.; Bu, X. "Porous Lithium Imidazolate Frameworks Constructed with Charge-Complementary Ligands", *Chem. Eur. J.* 2010, 16, 13035-13040. (published)

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5.5 Zheng, S.; Bu, J. T.; Li, Y.; Wu, T.; Zuo, F.; Feng, P.; Bu, X. "Pore Space Partition and Charge Separation in Cage-within-Cage Indium-Organic Frameworks with High CO₂ Uptake", *J. Am. Chem. Soc.* 2010, 132, 17062-17064. (published)

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5.22 Zheng, S.; Mao, C.; Wu, T.; Lee, S.; Feng, P.; Bu, X. Generalized Synthesis of Zeolite-Type Metal-Organic Frameworks Encapsulating Immobilized Transition Metal Clusters, *J. Am. Chem. Soc.* 2012, 134, 11936-11939. (published)

The Research at CSULB was supported by the National Science Foundation under Award No. DMR-0846958 (synthesis of samples, crystallographic and topological studies). The research at UCR was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE-SC0002235 (XRD and stability studies, gas sorption studies). Acknowledgement is made to the donors of the ACS Petroleum Research Fund for partial support of a portion of the synthetic studies (X. B. 50635-UR10).