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"Design and Synthesis of Novel Porous Metal-Organic Frameworks (MOFs) Toward High Hydrogen Storage Capacity"
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<u>Statement of Objectives:</u>

1. Synthesize viable porous MOFs for high H_2 storage at ambient conditions to be assessed by measuring H_2 uptake.
2. Develop a better understanding of the operative interactions of the sorbed H_2 with the organic and inorganic constituents of the sorbent MOF by means of inelastic neutron scattering (INS, to characterize the H_2-MOF interactions) and computational studies (to interpret the data and predict novel materials suitable for high H_2 uptake at moderate temperatures and relatively low pressures).
3. Synergistically combine the outcomes of objectives 1 and 2 to construct a made-to-order inexpensive MOF that is suitable for super H_2 storage and meets the DOE targets - 6% H_2 per weight (2kWh/kg) by 2010 and 9% H_2 per weight (3kWh/kg) by 2015.

The ongoing research is a collaborative experimental and computational effort focused on assessing H_2 storage and interactions with pre-selected metal-organic frameworks (MOFs) and zeolite-*like* MOFs (ZMOFs), with the eventual goal of synthesizing made-to-order high H_2 storage materials to achieve the DOE targets for mobile applications. We proposed in this funded research to increase the amount of H_2 uptake, as well as tune the interactions (i.e. isosteric heats of adsorption), by targeting readily tunable MOFs:

1)- Anionic open MOFs (i.e. ZMOFs) allow the addition of new sorption sites for H_2 in the void space (via post-synthesis modification *aka* ion exchange), an approach that is not feasible in neutral MOFs, and thus tunability of H_2 interactions by systematic evaluation of the extra-framework cations, a feature unique to anionic MOFs.

2)- Isoreticular compounds: a) allow the ability to easily modify the intra-framework constituents, assess their effect on H_2 sorption, and provide a direct comparison of the modified constituent(s) effects; our recently introduced **rht**-MOFs are excellent candidates for this method since **rht** is the only possible network for 3,24-connected nodes; b) permit systematic studies on the effect of pore volume on the amount of H_2 sorbed, since the ligands can be simply expanded while maintaining the same network topology.

3)- Model compounds can be used to assess the effect of pore size and functionality on H_2 sorption; molecular squares/boxes (MBs) are the systems of choice, because: a) they have been and can be synthesized from a variety of linkers (with myriad functionalities) and metals; b) to study the effects on H_2 sorption, their discrete nature and reduced unit cell (limited number of atoms) are ideally suited to molecular simulations studies; and c) the information gained from these MB systems can be implemented to design 3D MOFs (e.g. pillared 4.4 square grids, SGs) containing the desired attributes toward a material with strong H_2-framework interactions, an attribute suitable for storing H_2 at room temperature and moderate pressures.

Accordingly, we divided our research objectives into 5 subgroups: 1) Anionic MOFs (ZMOFs serve as the exemplary platforms) allow the facile exchange of extra-framework cations, where the impact of charge and/or polarizability on the isosteric heats of adsorption can be assessed; several ZMOF platforms have been synthesized with various metals and ligands. 2) The isoreticular system provided by the 3,24-connected **rht**-MOFs allows tuning of inorganic and organic components and permits to evaluate the effects of functionalization, pore size, and pore volume for direct and systematic comparison in a similar class of networks. 3) Molecular boxes allow for simplified studies on the effect of pore size and functionalization on H_2 sorption energetics. 4) We expand the MB approach to generate open pillared 3D structures with a combination of small windows, high

surface area, and large volume for higher uptake at higher pressures. 5) Computational studies allow us to elucidate the impact of each component on the energetics of sorption and predict novel materials to be made. The collaborative effort has a final objective of the eventual design and synthesis of an advanced material for super H_2 storage.

A. Description of Accomplishments
A.1. Anionic MOFs

- *Anionic ZMOFs are unique frameworks that allow for the addition of extra H_2 sorption sites in the void space for a systematic evaluation of the effect of extra-framework cations on H_2 sorption.*

Anionic ZMOFs, our recent discovery, can be designed and synthesized from pre-selected angular, hetero-functional ligands (e.g. 4,5-imidazoledicarboxylic acid, H_3ImDC) and high-coordinate single-metal ions (e.g. 6-8 coordinate metals, like In^{3+}). One ZMOF analogous to zeolite RHO, In-HImDC **rho**-ZMOF, has a unit cell containing 48 In^{3+} ions and 96 HImDC ligands to give an overall framework formula of ($[In_{48}(HImDC)_{96}]^{48-})_n$, where the negatively charged framework is neutralized by 48 dimethylammonium (DMA) cations, generated *in situ* by the degradation of DMF solvent molecules. The ability to completely exchange the extra-framework cations of DMA-**rho**-ZMOF was proven. Recently, the DMA-**rho**-ZMOF was used as a platform for ion exchange with Li^+ or Mg^{2+} to probe the effect of the charged environment on enhancing the H_2 interactions. Synchrotron single-crystal X-ray diffraction (SCD) for Mg-**rho**-ZMOF indicated that the Mg^{2+} counterions were hexa-aqua (i.e., $[Mg(H_2O)_6]^{2+}$, octahedral geometry, coordinated by six water molecules), and were found near each of the 4-membered ring (4MR) windows of the framework (12 per α-cage) (Fig. 1a). It was expected that the water molecules coordinate to the naked Mg ions (from $Mg(NO_3)_2$ salt) during the exchange process, as the exchange solvent is a mixture of water and ethanol. Thus, the relatively larger complex, $[Mg(H_2O)_6]^{2+}$, though too large for the 6MR and 4MR windows, must be small enough to diffuse through the 8MR windows of **rho**-ZMOF. This led us to explore other octahedral complexes for diffusion into **rho**-ZMOF. Commercially available or readily obtained complexes are an obvious choice, especially complexes with polar groups or groups with H-bonding potential, as further structure analysis revealed that the $[Mg(H_2O)_6]$ cations interact with the framework in the 4MR windows via H-bonding from the terminal aqua ligands surrounding each cation, which aided in localization and structure determination, beneficial in understanding structure-H_2 interactions and relationships. Thus, we chose to explore the diffusion potential of $[Co(NH_3)_6]^{3+}$ (Fig. 1b) from the commercially available $[Co(NH_3)_6]Cl_3$ salt, which possesses polar groups capable of H-bonding with **rho**-ZMOF.
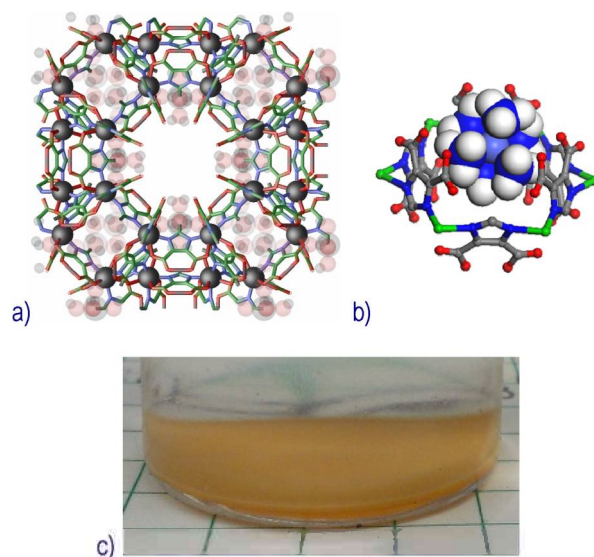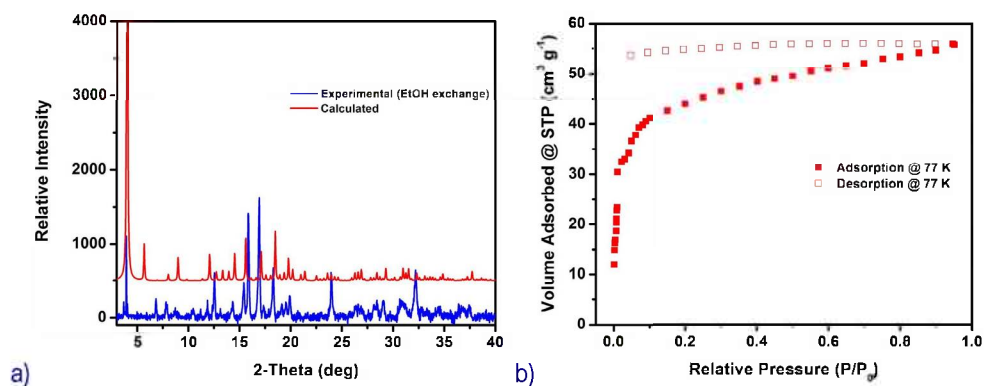

Fig. 1. a) A fragment of the single-crystal structure of **rho**-ZMOF viewed along the 8MR window. Framework H atoms and free solvent molecules were omitted for clarity; In = green, C = gray, N = blue, O = red, Co = light blue, H = white. The *in situ* generated DMA cations, resulting in colorless crystals, can be exchanged with b) $[Co(NH_3)_6]^{3+}$ to give c) orange crystals.

Comparison of the experimental [Co(NH$_3$)$_6$]-**rho**-ZMOF powder X-ray diffraction (PXRD) pattern to the calculated pattern for **rho**-ZMOF indicates they are in good agreement (Fig. 2a), signifying retention of the **rho**-ZMOF structural integrity upon exchange of [Co(NH$_3$)$_6$]$^{3+}$. Synchrotron SCD for [Co(NH$_3$)$_6$]-**rho**-ZMOF indicated that the Co^{3+} complex counterions were found near each of the 6MR and 8MR windows of the framework. Unfortunately, these windows, the 6MR and 8MR, are the primary access to the interior cavities of the **rho**-ZMOF structure, and localization of the cobalt complex here (vs. the 4MR windows in [Mg(H$_2$O)$_6$]-**rho**-ZMOF) could lead to pore blocking.

To confirm retention of permanent porosity in the new [Co(NH$_3$)$_6$]$^{3+}$-exchanged **rho**-ZMOF, we performed a series of gas sorption studies. Using similar activation conditions to the original **rho**-ZMOF, we found a lack of porosity, as initial tests on our NOVA instrument showed a 0 m^2/g surface area. These results suggested that either the framework had collapsed, was no longer porous, or different activation conditions must be determined; it should be noted that determining appropriate activation conditions is key in unlocking and maximizing porosity in such materials, especially MOFs. One of the most efficient ways to accomplish this goal is to screen several conditions (e.g., adjust soaking solutions, soaking temperature, evacuation temperature, evacuation rate) for the highest BET. With this method, we found the optimal conditions included soaking in absolute ethanol for 8 days and evacuation at 25°C for 24h.

As shown in Fig. 2b, it is apparent from the nitrogen sorption isotherm that the cation-exchanged material, [Co(NH$_3$)$_6$]-**rho**-ZMOF, is porous, though there is pronounced hysteresis. This result is indicative of slow/hindered diffusion through the pores, which is expected considering the complexes sitting in the [normally] accessible windows of **rho**-ZMOF. Nonetheless, mini N$_2$ isotherm (10^{-3}) on the AS-6B Instrument result in a calculated Langmuir surface area of 240 m^2/g, a BET surface area of 140 m^2/g, and a pore volume (at 0.95) of 0.086 cc/g. This data is in agreement with the screening performed on our Quadrasorb-SI, as well (i.e., reproducible). To study H$_2$ uptake in [Co(NH$_3$)$_6$]-**rho**-ZMOF, we performed hydrogen sorption at 760 Torr and 77 and 87 K, resulting in 0.43 and 0.32 wt% uptake, respectively. Note than no hysteresis was observed in either of the hydrogen isotherms (Fig. 2c), and they exhibit typical Type I behavior for microporous materials. This difference can be expected due to the smaller kinetic diameter of H$_2$ compared to N$_2$ gas molecules. The corresponding isosteric heats of adsorption (Qst) results (Fig. 2d) were very irregular, and these measurements will be repeated on the AS-1. However, if the low points are disregarded, the average is approximately 5 kJ/mol. This value is lower than expected, and lower than the isosteric heats of adsorption derived from the analogous isotherms at 77K and 87K for Li-**rho**-ZMOF (9.12kJ/mol), Mg-**rho**-ZMOF (8.87 kJ/mol), and DMA-**rho**-ZMOF (7.97 kJ/mol).
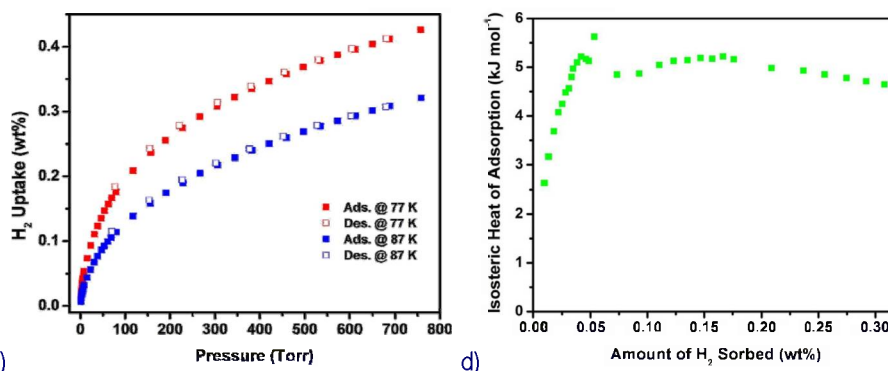
Fig. 2. a) Calculated (rho-ZMOF) and experimental ([Co(NH₃)₆]-**rho**-ZMOF) PXRD patterns. b) Nitrogen sorption isotherms for [Co(NH₃)₆]-**rho**-ZMOF. c) Hydrogen sorption isotherms for [Co(NH₃)₆]-**rho**-ZMOF. d) Isosteric heats of adsorption for hydrogen in [Co(NH₃)₆]-**rho**-ZMOF.

A similar cobalt complex salt, [Co(NH₃)₆Cl]Cl₂, also was commercially available, which possesses a coordinated Cl⁻. The substitution of one ammine ligand for a chloride not only changes the charge on the complex from 3+ to 2+, but also changes the symmetry and polarity within the octahedral complex, [Co(NH₃)₆Cl]²⁺ (Fig. 3a). These subtle changes could substantially change the potential interactions with hydrogen (or other gas) molecules within the pores. Ion exchange under similar conditions results in a color change associated with the formation of the new [Co(NH₃)₆Cl]-**rho**-ZMOF (Fig. 3b). SCD, PXRD, and sorption studies are currently underway.
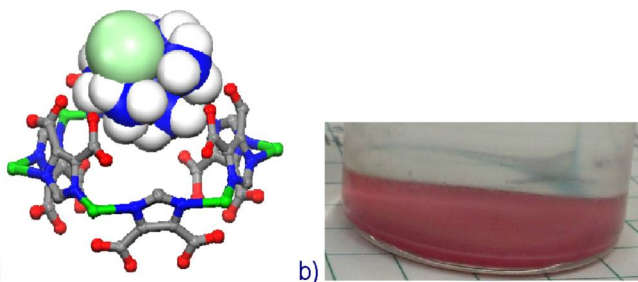

Fig. 3. The *in situ* generated DMA cations, resulting in colorless crystals, can be exchanged with a) [CoCl(NH₃)₅]²⁺ to give b) pink crystals. Framework H atoms and free solvent molecules were omitted for clarity; In = green, C = gray, N = blue, O = red, Co = light blue, Cl = light green, H = white.

A.2. Isoreticular SBB-MOFs

- *The uniqueness of the SBB approach is ideal for the practice of isoreticular chemistry, and for studies on the effect of functionalization, pore size, surface area, and pore volume on H₂ uptake.*

Recently, our groups established a new design strategy which exploits polyhedral metal-organic, supermolecular building blocks (SBBs), generated *in situ*, as building units to construct high-connectivity (12- and 24-connected based) MOFs. Such SBBs offer the potential to significantly increase the scale of MOFs (*aka* scaled-up or SUMOFs) and offer an unprecedented level of structural control (i.e., crystal engineering) and fine-tunability beyond even that seen with MOFs sustained by MBBs. For a uninodal 12-connected MOF the targeted blueprint is the **fcu** net (an edge transitive net, suitable targets in crystal chemistry) whose vertex figure is the cuboctahedron. Such a polyhedron holds the geometrical attributes that an SBB would need for the assembly of an MOF having an augmented **fcu** like net. This relationship between the SBB and a specific net illustrates how SBBs, when rigidly linked, are uniquely suited for a particular net. Furthermore, they offer new horizons in terms of scale and chemical functionality. Accordingly, we reported the first examples of MOFs based on the assembly of cuboctahedra as SBBs (as opposed to discrete molecules or ions). The novel anionic cuboctahedron of formula [M₆(BDC)₁₂]¹²⁻ (Fig. 4a), sustains 12-connected **fcu** nets when using tetracarboxylate organic linkers, specifically bis-isophthalates (e.g., 3,3'5,5'-azobenzenetetracarboxylic acid), through rigid cross-linking at each of the 12 vertices of the cuboctahedral SBB. Our analysis of the RCSR database and other 12-connected edge

transitive nets, led us to the (4,12)-connected **ftw** net, which is an ideal target in crystal chemistry and can be targeted using our cuboctahedral SBB (12-connected) and a square (4-connected) cross-linker (Fig. 4a). Our previous experience and success with alkoxy linkers, and the potential for flexibility and rotation leading to better crystallization and structure adjustment, led us to design and synthesize 5,5',5'',5'''-((benzene-1,2,4,5-tetrayltetrakis(methylene))tetrakis(oxy))tetraisophthalic acid (Fig. 4b), a tetra-isophthalate (octacarboxylate) capable of planarity of the terminal isophthalates (which form the SBB) resulting in the desired quatrefoil-like (square core) organic ligand, for the construction of **ftw**-MOFs.
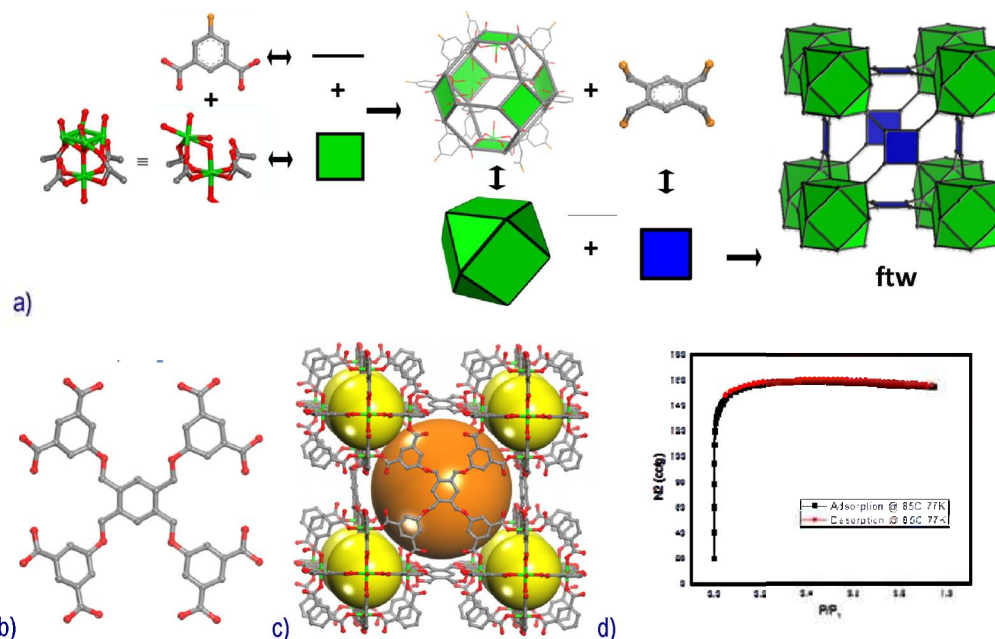

Fig. 4. a) Scheme showing the design, from the $[M_{12}(BDC)_{12}]$ MOP, of the prototypal cuboctahedral SBB and cross-linking with square linkers to form MOFs from the **ftw** net, **ftw**-MOFs. b) The quatrefoil-like organic ligand, 5,5',5'',5'''-((benzene-1,2,4,5-tetrayltetrakis(methylene))tetrakis(oxy))tetraisophthalic acid. c) A fragment of the single-crystal structure of **ftw**-MOF-1. H atoms and free solvent molecules were omitted for clarity; M = green, C = gray, N = blue, O = red, van der Waals spheres for the cuboctahedron SBB cavity and larger interior cavity are in yellow and orange, respectively. d) N_2 sorption isotherms for **ftw**-MOF-1 at 77K.

Indeed, solvothermal reaction between the quatrefoil ligand and $Co(NO_3)_2 \cdot 6H_2O$ in the presence of excess water affords a new homogeneous crystalline material, phase and purity confirmed by comparisons between experimental and calculated PXRD patterns. A pink polyhedral crystal of the as-synthesized compound was characterized by SCD as $[Co_4(PTetMOl)(H_2O)_x]_n$, **ftw**-MOF-1 (Fig. 4c). The crystal structure of **ftw**-MOF-1 is built from $[Co_{12}(PTetMOl)_{12}]$ cuboctahedron SBBs (12-connected) that are cross-linked by the ligand core (4-connected) to give the underlying (4,12)-connected **ftw** net. In this case, the square paddlewheel-like $Co_2(O_2CR)_4$ MBB is composed of divalent metal ions, Co(II), in two different coordination geometries/environments. Each Co1 assumes octahedral geometry (CoO_6), where the equatorial plane is occupied by four monodentate carboxylate oxygen atoms from four different ligands and an H_2O molecule occupies the axial position. The second position is occupied by a crystallographically disordered Co(II) cation, Co2, that bridges the axial H_2O and two of the four carboxylate moieties, resulting in bis-monodentate coordination. Sorption studies confirm the permanent microporosity of **ftw**-MOF-1, as evidenced by the fully reversible type I nitrogen sorption isotherm (Fig. 4d). Hydrogen sorption studies are underway.

In summary, we have demonstrated that polyhedral SBBs are indeed amenable to crystal engineering approaches that facilitate the generation of nets that cannot be readily accessed through the choice of regular MBBs. Furthermore, the use of SBBs inherently affords a high degree of fine-tunability for MOFs and guarantees a larger scale for the resulting material. Work is in progress to evaluate hydrogen sorption properties of this unique class of materials.

A.4. Pillared 3D MOFs

- *Methods for designing and synthesizing pillared 3D MOFs, like pillared square and Kagomé lattices (sql and kgm), are well-established, and are amenable to modifications utilizing information gained from the studies on molecular boxes to develop a material for high H_2 uptake.*

We have instituted a plan which targets select well-established MOFs based upon 2D topologies (e.g., square or Kagomé lattices, **sql** or **kgm**) and attempts to extend their familiar pore shapes (e.g., squares, triangles, hexagons) into 3D frameworks in an effort to develop a series of microporous materials capable of storing H_2 with the express goal of discerning the impact of pore size and functionalization on storage capacity and isosteric heats of adsorption. Simultaneous studies on MBBs will guide the incorporation of particular pore sizes and functional groups into the framework constituents in an effort to design and synthesize a 3D pillared MOF with high H_2 uptake and isosteric heats of adsorption. 2D **sql**-MOFs or **kgm**-MOFs based on the assembly of dimetal tetracarboxylate square paddlewheel MBBs, $M_2(O_2CR)_4L_2$, and dicarboxylate ligands (e.g., benzenedicarboxylates or BDCs) are well-established. It has been shown that, to improve sorption properties, surface area, and H_2 uptake (depending on the size and/or functionality of the ligand/pillar), these layered materials can be pillared through three approaches: (1) ligand-to-ligand cross-linking at the 5-position of the BDC; (2) metal-to-metal cross-linking through the MBBs; (3) ligand-to-metal cross-linking through the 5-position of the BDC and the MBB. As such, we designed a suitable flexible ligand, 1,3-bis-[3,5-bis(carboxy)phenoxy]propane (Fig. 5a), H_4L, one that links BDC at the 5-position to cross-link $Cu_2(O_2CR)_4$ paddlewheels and corresponding neighboring **kgm**-MOF layers, resulting in two novel cross-linked Kagomé (**kgm**) nets, depending on reaction conditions: an **acs** net sustained by trigonal prismatic pseudo-SBBs and a hitherto unprecedented partially pillared Kagomé topology.
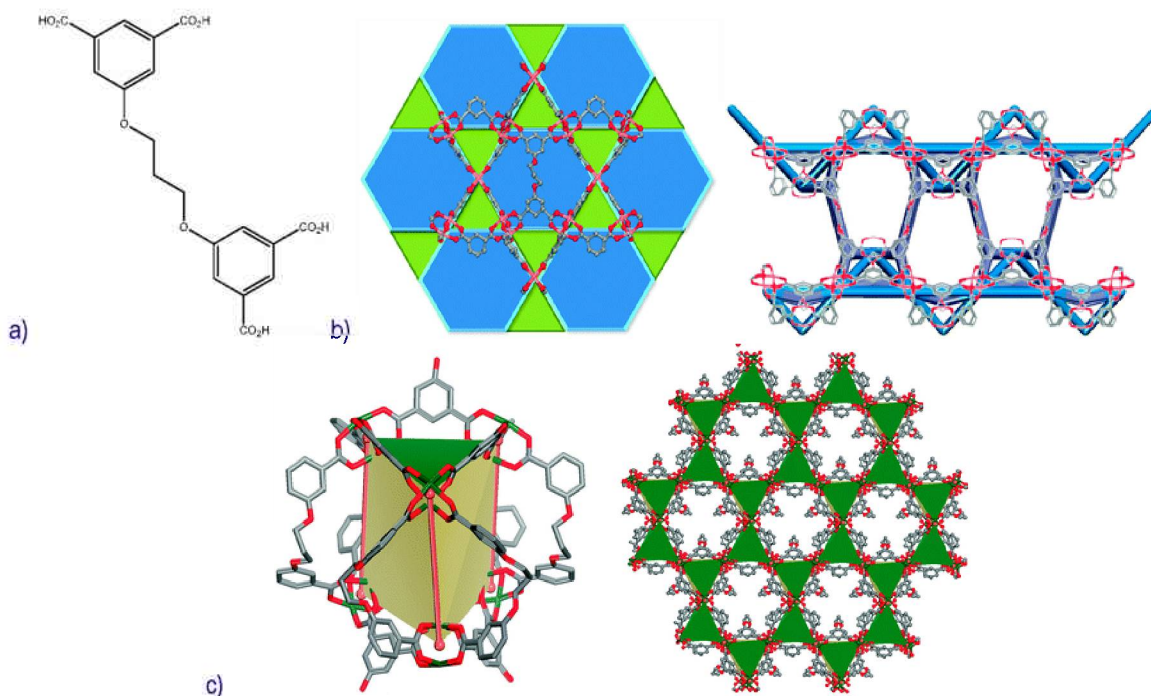

Fig. 5. a) The 1,3-bis-[3,5-bis(carboxy)phenoxy]propane organic ligand. b) Illustrations of the Kagomé like layers in compound **1** reveal that one-third of the **L** ligands cross-link across the hexagonal cavity within the layer (left) whereas two-thirds cross-link between adjacent layers to generate the observed pillared 3D structure (right). c) The trigonal prismatic pseudo-SBB in **2** is generated through triple cross-linking of triangles of squares (left), meaning that Kagomé layers are eclipsed as viewed down the c-axis (right).

Solvothermal reaction of $Cu(NO_3)_2 \cdot 2.5H_2O$ and H_4L in N,N-dimethylacetamide with pyridine afforded $[Cu_6(L)_3 \cdot 5H_2O \cdot (C_5H_5N)]_n$, **1**. The bulk purity of **1** was confirmed by comparing the calculated and experimental X-ray powder diffraction patterns. The crystal structure of **1** is illustrated in Fig. 5b and it reveals that it is a new type of Kagomé lattice sustained by partially cross-linked $Cu_2(O_2CR)_4$ paddlewheel MBBs. Two types of L are present in the crystal structure, La and Lb. La serves as a pillaring ligand whereas Lb cross-links four of the six paddlewheels that make the hexagonal cavity of the Kagomé lattice (Fig. 5b). A truncated pyramidal cavity with a height of 7.3 Å from copper atom on the top to the centre of the bottom exists in **1**. A second hourglass-like cavity/channel (13.0 Å × 17.6 Å) runs along the a-axis in between the cavities. This partially pillared Kagomé lattice has four 4-connected nodes since there are two independent square paddlewheels and two independent ligands. **1** exhibits a new topology with Schläfli symbol $(4.6^4.8)_2(4^2.6^4)(6^4.8^2)_2(6^6)$ and 76% void space after axial ligands and solvent molecules are removed (as calculated by PLATON).

Switching the solvent system to DMF and HNO_3 afforded $[Cu_6(L)_3(H_2O)_6]_n$, **2**. The bulk purity of **2** was confirmed by comparing calculated and experimental X-ray powder diffraction patterns. The flexibility of L facilitates triple cross-linking of the triangles of $Cu_2(O_2CR)_4$ paddlewheels of a Kagomé lattice and the crystal structure of **2** reveals how in effect this creates trigonal prismatic pseudo-SBBs (Fig. 5c). Each trigonal prism is connected through its vertices to afford an **acs** net. The Kagomé layers are necessarily eclipsed and if viewed down the c-axis the presence of hexagonal cavities is revealed (Fig. 5c). The trigonal prismatic cavity has an equilateral triangle length of ∼9.3 Å between the centroids of the paddlewheels and a height of ∼11.7 Å. This cavity can accommodate a sphere of ∼10.7 Å. With axial ligands and solvent molecules removed **2** exhibits 65% void space as calculated by PLATON. Sorption studies are currently underway.

- ## MOFs based on the assembly of trimeric clusters and tetracarboxylates

Our research group reported a porous MOM with **s**quare-**oc**tahedral (**soc**) topology assembled from indium trimer building blocks. The framework incorporates high surface area, high charge density, and narrow pores leading to a high hydrogen uptake (up to 2.6wt% at 78K and 1.2atm), that is considerably larger than many MOFs reported to date. The potential of this class of compounds was emphasized in our original proposal and its promise has been realized by studies on the In-azobenzenetetracarboxylate **soc**-MOF (Fig. 6).
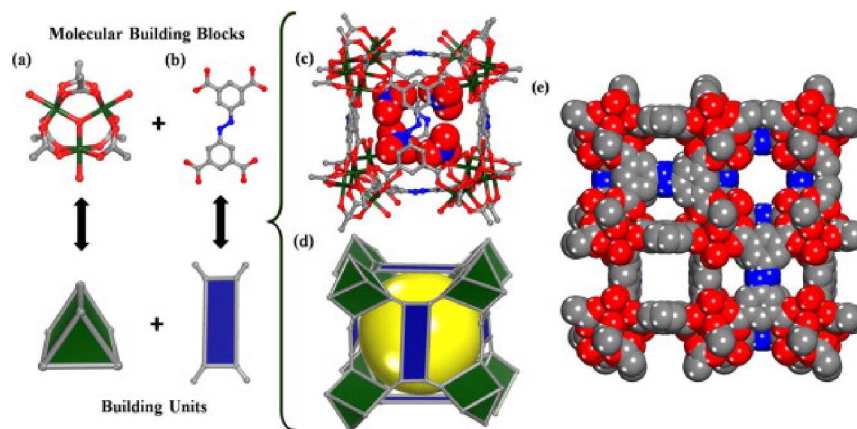

Fig. 6. X-ray crystal structure of indium **soc**-MOF: (a) ball-and-stick view of oxygen centered indium-carboxylate trimer, TMBB, $In_3O(CO_2)_6(H_3O)_3$, which can be viewed as a 6-connected node having trigonal-prismatic geometry, (b) the organic linker, 3,3'5,5'-azobenzenetetracarboxylic acid, which can be viewed as a 4-connected node with rectangular-planar geometry, (c) ball-and-stick, and (d) polyhedral representations of the cuboidal cage of **soc**-MOF-1 (color scheme: carbon = gray, oxygen = red, nitrogen = blue, indium = dark green). Hydrogen atoms and water molecules, and are omitted for clarity. Nitrate anions are depicted without disorder in space filling format. (e) space filling representation of the framework viewed along the y-direction.

To study the effect of functionalization on the H_2 uptake capacity and strength of interaction (among others) we chose to exploit the isoreticular nature of MOF systems, where suitable and analogous ligand design is readily achieved through organic chemistry. One can envision numerous tetracarboxylic acids analogous to the original

3,3'5,5'-azobenzenetetracarboxylic acid (Fig. 7a), which might be used to target the **soc**-MOF platform. Our previous experience and success with alkoxy linkers, and the potential for flexibility at the trapezoidal windows of [and possibly access to] the highly charged nitrate-encapsulating cage, led us to design and synthesize 5-((3,5-dicarboxybenzyl)oxy)isophthalic acid (Fig. 7b).
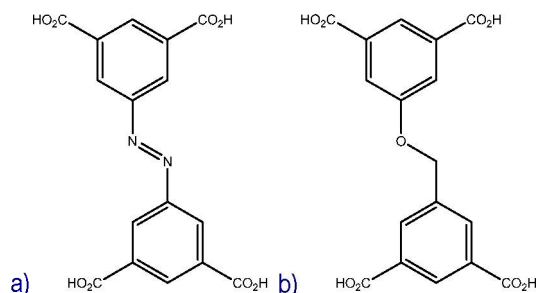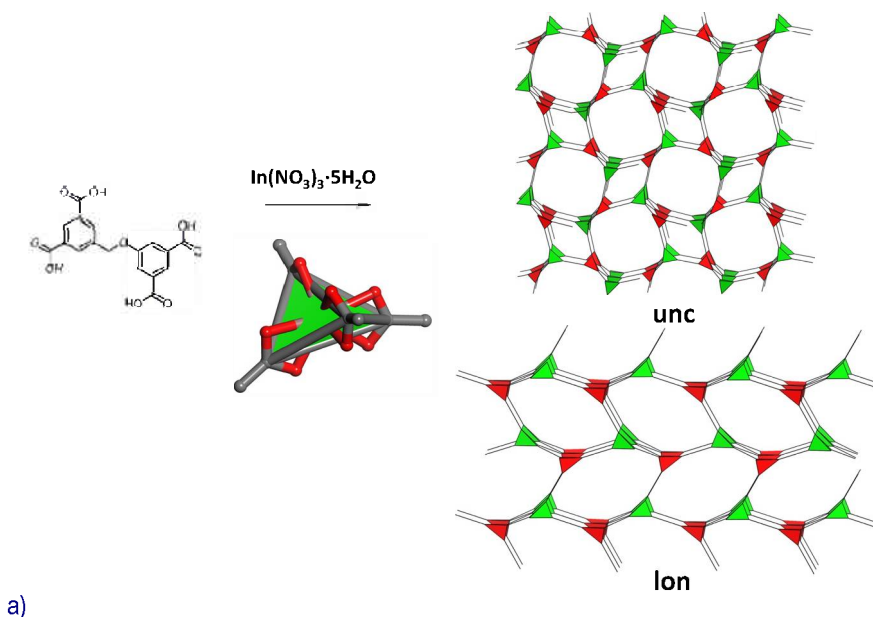
Reactions between indium salts and 5-((3,5-dicarboxybenzyl)oxy)isophthalic acid have thus far not yielded the desired In-trimer, which would result in the isoreticular **soc**-MOF. Instead, reactions have produced the well-known 8-coordinate, tetracarboxylate single-metal ion [In(O$_2$CR)$_4$], where the oxygen atoms from four individual carboxylates chelate each indium ion (Fig. 8a). PXRD studies (Fig. 8b) have revealed two independent phases, depending on reaction conditions, and SCD studies confirm the presence of a MOF having the tetrahedron-based lonsdaleite topology (**lon**-MOF) and another matching the tetrahedron-based **unc** (**unc**-MOF). In each case the MBB [In(O$_2$CR)$_4$] is anionic {i.e., [In(O$_2$CR)$_4$]$^{1-}$}, resulting in anionic MOFs with cation exchange potential, a feature that has proven effective in enhancing H$_2$ uptake and interactions (see above). Ion exchange and sorption studies are currently underway, as well as continued pursuit of the **soc**-MOF analogue.
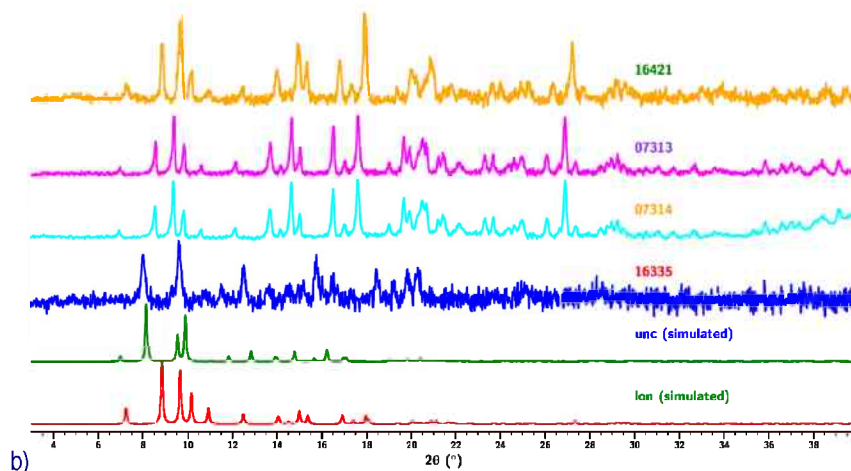
b)

Fig. 8. The organic ligand, 5-((3,5-dicarboxybenzyl)oxy)isophthalic acid, can be reacted with indium salts to give [In(O2CR)4] tetrahedral MBBs and corresponding tetrahedron-based **lon**-MOFs and **unc**-MOFs. b) The calculated and experimental PXRD patterns of our **lon**-MOFs and **unc**-MOFs.

A.5. Computational Studies

- *We have developed a supercomputing application that supports potential energy functions not previously utilized in studying H_2 interactions with MOFs, in particular many-body polarization.*

Hydrogen sorption in [Mg(H2O)6]-**rho**-ZMOF was simulated using Grand Cannonical Monte Carlo, which holds chemical potential, volume and temperature constant and allows parameters to fluctuate. The crystal structure was taken from the CSD database which included all atoms except the hydrogen atoms on the six water molecules coordinated to Mg^{2+} (octahedral geometry) and one of the ligand hydrogen atoms. These were inserted manually and geometry optimized. The structure was held rigid during simulation (Fig. 9).
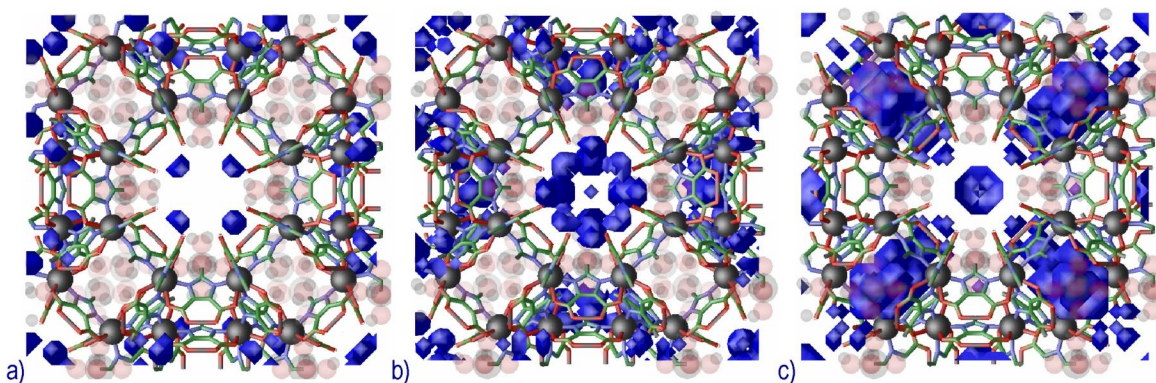

a)   b)   c)

Fig. 9. Dipole occupancy for molecular hydrogen in the unit cell of [Mg(H2O)6]-**rho**-ZMOF: a) 0.49 Debye, b) 0.40 Debye, and c) 0.13 Debye.

Three energy terms were used in the simulation van der Waals/repulsion, modeled with Universal Force Field (UFF) parameters; charge/quadropole, modeled with partial charges located on atomic centers; and induced dipole, modeled with Thole/Applequist point polarizabilities. Sorption using three hydrogen sorbate potential parameters, each of which included different sets of energy terms: the Buch van der Waals/dispersion only model, the BSS van der Waals and charge/quadropole model, and the BSSP van der Waals, charge/quadropole and induced dipole model.

These models produced respectively 20, 30,110% of the experimental results (see Fig. 10a). Some possible reasons for the discrepancies investigated were:

- Insertion of H_2 into closed pores during simulation – failed to locate such pores
- Insertion past dynamically hindered region – only likely region (hexagonal opening) found had a ~7 angstrom diameter window, which made it an unlikely barrier
- Atomic partial charges too high – did not account for over sorption of the Buch van der Waals model, cutting back the charges to 75% still had the polarizable model over sorbing by about 30%.
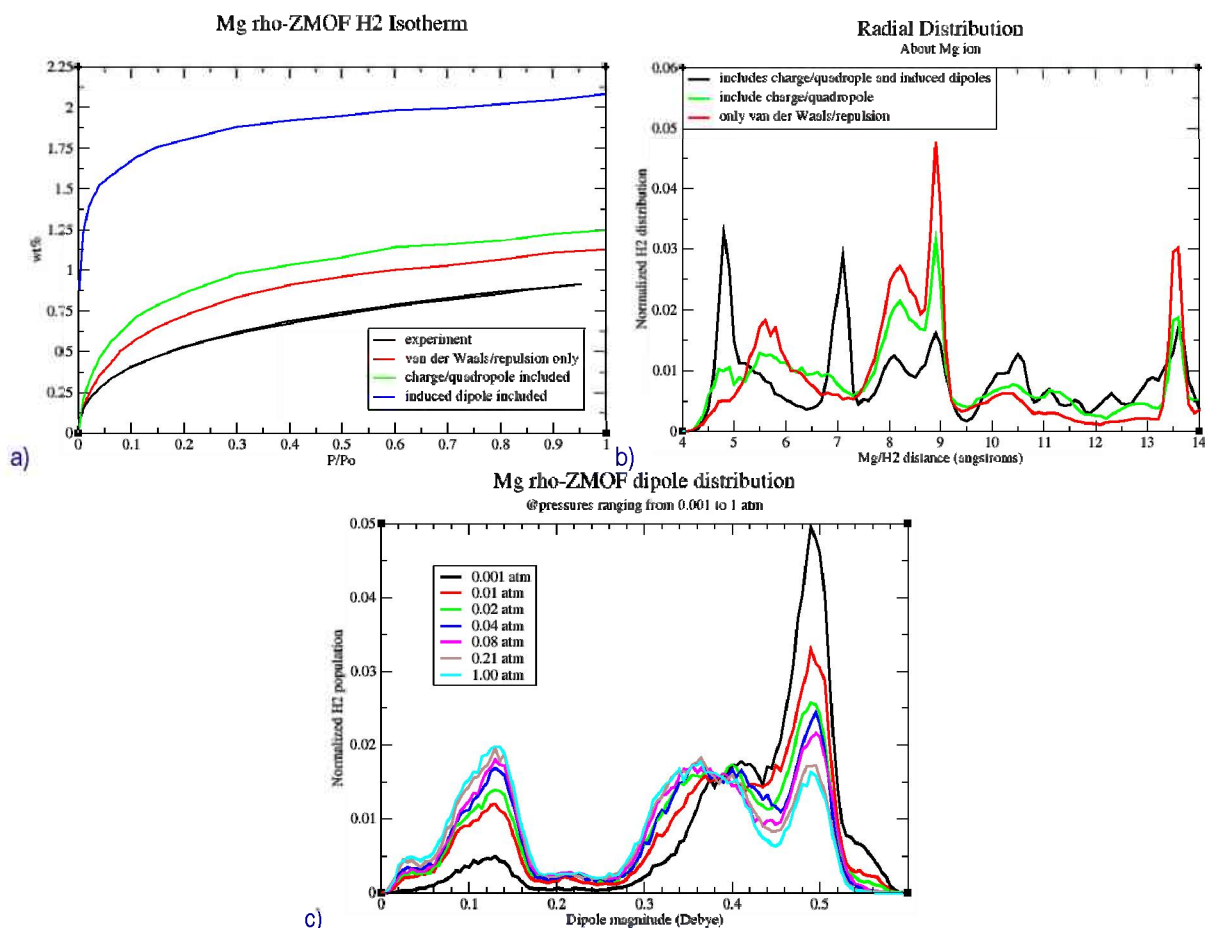

Fig. 10. a) Hydrogen sorption istherms using Buch van der Waals/dispersion only model (red), the BSS van der Waals and charge/quadropole model (green), and the BSSP van der Waals, charge/quadropole, and induced dipole model (blue) compared to the experimental (black). b) and c) Distribution of induced molecular hydrogen dipoles in [Mg(H_2O)$_6$]-**rho**-ZMOF.

B. List of Papers

Published:

- Perman, J. A.; Cairns, A. J.; Wojtas, L.; Eddaoudi, M.; Zaworotko, M. J. "Cocrystal controlled solid-state synthesis of a rigid tetracarboxylate ligand that pillars both square grid and Kagomé lattice layers" *CrystEngComm,* **2011**, *13*, 3130-3133.
- Moellmer, J.; Celer, E. B.; Luebke, R.; Cairns, A. J.; Staudt, R.; Eddaoudi, M.; Thommes, M. "Insights on Adsorption Characterization of Metal-Organic Frameworks: A Benchmark Study on the Novel *soc*-MOF" *Microporous and Mesoporous Materials* **2010**, *129*(3), 345-353.

- Qiu, W.; Perman, J. A.; Wojtas, L.; Eddaoudi, M.; Zaworotko, M. J. "Structural diversity through ligand flexibility: two novel metal–organic nets via ligand-to-ligand cross-linking of 'paddlewheels'" *Chem. Commun.*, **2010**, *46*, 8734-8736.
- Alkordi, M. H.; Brant, J. A.; Wojtas, L.; Kravtsov, V. Ch.; Cairns, A. J.; Eddaoudi, M. "Zeolite-like Metal-Organic Frameworks (ZMOFs) Based on the Directed Assembly of Finite Metal-Organic Cubes (MOCs)" *J. Am. Chem. Soc.* **2009**, *131*, 17753-17755.
- Perman, J. A.; Dubois, K.; Nouar, F.; Zoccali, S.; Wojtas, L.; Eddaoudi, M.; Larsen, R. W.; Zaworotko, M. J. "Cocrystal Controlled Solid-State Synthesis of a Thermally Stable Nicotinate Analogue That Sustains an Isostructural Series of Porous Metal-Organic Materials" *Cryst. Growth Des.* **2009**, *9*, 5021-5023.
- Sava, D. F.; Kravtsov, V. Ch.; Eckert, J.; Eubank, J. F.; Nouar, F.; Eddaoudi, M. "Exceptional Stability and High Hydrogen Uptake in Hydrogen-Bonded Metal-Organic Cubes Possessing ACO and AST Zeolite-like Topologies" *J. Am. Chem. Soc.* **2009**, *131*, 10394-10396.
- Nouar, F.; Eckert, J.; Eubank, J. F.; Forster, P.; Eddaoudi, M. "Zeolite-like Metal-Organic Frameworks (ZMOFs) as Hydrogen Storage Platform: Lithium and Magnesium Ion-Exchange and H_2-(rho-ZMOF) Interaction Studies" *J. Am. Chem. Soc.* **2009**, *131*, 2864-2870.
- Perman, J. A.; Zaworotko, Michael J. "Synthesis and Crystal Structure of a Polymorph of the DMF Solvate of the Dicoppertetracarboxylate Paddlewheel Complex Cu_2(p-aminobenzoate)$_4$(DMF)$_2$" *J. Chem. Crystallogr.* **2009**, *39*, 78-82.
- Belof, J. L.; Stern, A. C.; Space, B. "A Predictive Model of Hydrogen Sorption for Metal-Organic Materials" *J. Phys. Chem. C* **2009**, *113*, 9316-9320.
- Belof, J. L.; Stern, A. C.; Space, B. "An Accurate and Transferable Intermolecular Diatomic Hydrogen Potential for Condensed Phase Simulation" *J. Chem.Theory Comput.* **2008**, *4*, 1332-1337.

C. List of People Working on the Project

In the Final Year, funds were requested in support of the equivalent of one full-time graduate student for each of three PIs located at USF, and one post-doctoral fellow (2months). The following students were supported:

Student	type	months supported for the coverage dates of the present report
George Norton	graduate	12
Hasnaa Mouttaki	graduate	12
Belof John,	graduate	12
Jason Perman	graduate	12
Dr. Jarrod F. Eubank	post-doc	2.0

D. Planned Activities for Next Year
End of funding = No planned activities
E. Updated List of Other Support
Current
- NSF-CAREER: "Molecular Building Block Approach to Zeolite-*like* Metal-Organic Frameworks (ZMOFs)" NSF, USF. $550,000 – Period of performance: 04/01/06-03/31/11. Level of commitment: 1.7 months. The project is centered upon generation and implementation of novel design strategies for the construction of ZMOFs and their potential use in separation of large molecules, selective catalysis, and host-guest chemistry for sensory applications. This project does not involve, in any way, the sorption/storage of hydrogen gas.

F. Unexpended Funds

We do not anticipate any unexpended funds over 4% to be left over at the end of the current budget period. All funds for graduate students and the post-doc have been allocated for the remaining three months, and thus will be expended accordingly. All funds for supplies have already been exhausted.