

## Design of Stratified Functional Nanoporous Materials for CO<sub>2</sub> Capture and Conversion

J. Karl Johnson (PI), [karlj@pitt.edu](mailto:karlj@pitt.edu) and Nathaniel L. Rosi (Co-PI), [nrosi@pitt.edu](mailto:nrosi@pitt.edu)

We propose a combined theoretical and experimental approach for developing new functional nanoporous materials that have tailored properties for controlling adsorption, diffusion, and reactions. The ultimate goal of our work is the selective capture and catalytic conversion of CO<sub>2</sub> to useful products within a nanoporous solid sorbent. The sorbents we will design will be based on functionalizable metal organic frameworks (MOFs). We will synthesize stratified MOFs having multiple layers where each layer contains task-specific functional groups. **Our hypothesis is that a combination of computational theory and advanced experimental synthesis can be used to design task-specific nanoporous MOFs for highly-efficient capture and conversion of CO<sub>2</sub> to formic acid.** Our proposal addresses the BESAC Grand Challenge # 2, "How do we design and perfect atom- and energy-efficient synthesis of revolutionary new forms of matter with tailored properties?" This is addressed through the interplay between theory and experiments aimed at designing new materials at the atomic level. The major advantages of our proposed approach over extant methods for CO<sub>2</sub> reduction are: (1) Tailorable selectivity of the MOF to capture CO<sub>2</sub> and exclude undesirable gases such as H<sub>2</sub>O and N<sub>2</sub>. (2) The ability to functionalize the MOF pores with moieties to chemically bind the CO<sub>2</sub> for hydrogenation. (3) The ability to include catalytic metal centers inside MOFs. (4) The ability to tailor functional groups for stabilizing the HCOOH product. (5) Increased effective concentration of CO<sub>2</sub> and H<sub>2</sub> within the pore due to strong adsorption. (6) Increased efficiency by combining CO<sub>2</sub> separation and conversion into a single unit.

**Methods:** We will use a wide variety of quantum mechanical and classical statistical mechanical modeling techniques to design functional groups for CO<sub>2</sub> binding, HCOOH binding, and separation of H<sub>2</sub>O/N<sub>2</sub>/CO<sub>2</sub> mixtures. These include periodic density functional theory, semi-empirical methods, post-Hartree-Fock methods, molecular dynamics, grand canonical Monte Carlo, hybrid-MC, and coarse graining methods. Experiments will use UiO-66 as the MOF platform for preparing multi-layered stratified MOFs. The functional groups in each layer will be addressed and modified via sequential post-synthetic modification steps to create layers with unique, yet complementary functions.

**Project Objectives:** (1) Use a hierarchy of computational methods to design sets of functional groups that can chemically bind CO<sub>2</sub> and that can be incorporated into MOFs. (2) Experimentally test the most promising functional groups for binding CO<sub>2</sub>. (3) Computationally design sets of functional groups that can bind HCOOH over a range of energies to prevent the reverse reaction, yet allow easy release. (4) Synthesize and test a variety of candidate HCOOH binding functional groups. (5) Systematically study the stability of the MOFs in the presence of varying concentrations of formic acid. (6) Develop computational methods for fast screening of transport through MOFs having flexible functional groups. (7) Computationally design functional groups that will yield high transport selectivity for separation of CO<sub>2</sub>/H<sub>2</sub>O/N<sub>2</sub> mixtures. (8) Synthesize MOFs with candidate functional groups for separating gas mixtures. (9) Develop computational techniques that can model diffusion of gas molecules across the interface between layers in stratified MOFs. (10) Develop methods for synthesis of stratified MOFs having three or more layers, with each layer containing different functional groups. (11) Selectively introduce functional groups to the different layers using various post-synthetic MOF modification strategies. (12) Measure pure fluid isotherms for multi-layered stratified MOFs to confirm that layer ordering changes the adsorption phenomena of the stratified MOF compared to the single component MOF counterparts. (13) Compute reaction pathways for CO<sub>2</sub> reduction on prototypical CO<sub>2</sub> hydrogenation catalysts. Use these calculations to identify the kinetically limiting steps in the reaction. (14) Use the kinetic information computed for CO<sub>2</sub> hydrogenation on existing catalysts to design new catalysts that incorporate functional groups to bind CO<sub>2</sub> in the correct geometry and with the correct electronic interactions to reduce the reaction barrier for CO<sub>2</sub> conversion to formic acid.

## **Design of Stratified Functional Nanoporous Materials for CO<sub>2</sub> Capture and Conversion**

Applicant/Institution:

J. Karl Johnson  
University of Pittsburgh  
Pittsburgh, PA 15260

J. Karl Johnson (PI), 412-624-5644, [karlj@pitt.edu](mailto:karlj@pitt.edu)  
Nathanial L. Rosi (Co-PI), 412-624-3987, [nrosi@pitt.edu](mailto:nrosi@pitt.edu)  
Department of Chemical Engineering & Department of Chemistry  
Administrative Point of Contact:

Ms. Laurie Mejia  
University of Pittsburgh  
Office of Research  
123 University Place  
Pittsburgh, PA 15213  
412-624-7400  
[LAM15@pitt.edu](mailto:LAM15@pitt.edu)

FOA Number: DE-FOA-0000768

DOE/Office of Science Program Office: Chemical Sciences, Geosciences, & Biosciences (CSGB) Division

DOE/Office of Science Program Office Technical Contact: Mark R Pederson

DOE Grant Number: DE-SC0004484

Research areas: Selective carbon-dioxide/gas separation, storage and capture; Reactivity and catalysis

**Basic Energy Sciences Impact: This proposal addresses BESAC Grand Challenge # 2, “How do we design and perfect atom- and energy-efficient synthesis of revolutionary new forms of matter with tailored properties?” This grand challenge is addressed through the development of computational and experimental tools for atomic-level control of adsorption, separation, and chemical conversion of small molecules within functional nanoporous materials, with the ultimate goal of capturing and converting CO<sub>2</sub> to a valuable chemical.**

## Project Overview

We propose a combined theoretical and experimental approach for developing new functional nanoporous materials that have tailored properties for controlling adsorption, diffusion, and reactions. The ultimate goal of our work is the selective capture and catalytic conversion of CO<sub>2</sub> to useful products within a nanoporous solid sorbent. The sorbents we will design will be based on functionalizable metal organic frameworks (MOFs). The unique approach we take is that we will synthesize stratified MOFs having multiple layers, shown schematically in Figure 1, where each layer contains task-specific functional groups. Thus, each MOF particle will act as a miniature separation column and reaction vessel.

As a specific target for CO<sub>2</sub> reduction, we consider the conversion of CO<sub>2</sub> to HCOOH through the reaction



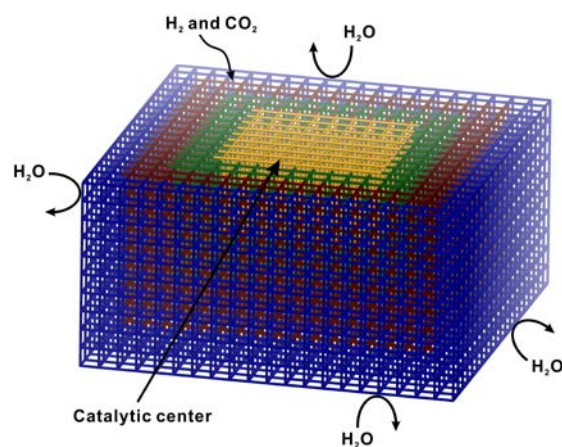
Reaction (1) can be considered a prototypical initial step in the reduction of CO<sub>2</sub>.<sup>1-3</sup> Formic acid is a viable feedstock for a host of value-added products, including fine chemicals<sup>4</sup> and liquid hydrocarbons.<sup>5</sup> One of the challenges of producing HCOOH from CO<sub>2</sub> via Reaction (1) is that it is thermodynamically disfavored at standard conditions and therefore HCOOH must be stabilized in some way to achieve reasonable conversions.<sup>2</sup> One of the most widely-used methods of increasing the conversion is by reacting the HCOOH product with a base, producing a formate salt or formamide.<sup>2</sup> A recent method for stabilizing formic acid is to use ionic liquids containing amine functionalities.<sup>3,6-9</sup> **Our hypothesis is that a combination of computational theory and advanced experimental synthesis can be used to design task-specific nanoporous MOFs for highly-efficient capture and conversion of CO<sub>2</sub> to formic acid.** The major advantages of our proposed approach over extant methods for CO<sub>2</sub> reduction are: (1) Tailorable selectivity of the MOF to capture CO<sub>2</sub> and exclude undesirable gases such as H<sub>2</sub>O and N<sub>2</sub>. This can be accomplished through the use of stratified or layered MOFs with different functional groups in each layer and choosing these groups to achieve the desired separation.<sup>10</sup> (2) The ability to functionalize the MOF pores with moieties such as amines to chemically bind the CO<sub>2</sub>, holding it in the correct orientation for hydrogenation. The ultimate goal is to design an enzyme-mimic site that dramatically increases the reactivity of CO<sub>2</sub>. (3) The ability to include catalytic metal centers inside the MOF,<sup>11-13</sup> as recently demonstrated by various groups, including Hupp and coworkers<sup>14,15</sup> and Lin and coworkers,<sup>16-20</sup> provides additional routes to controlling chemical reactions within the MOFs. (4) The ability to tailor functional groups for stabilizing the HCOOH product, preventing the thermodynamically favored reverse reaction, while not binding the product state so strongly as to require an unacceptable amount of heat or pressure driving force to remove the product (through temperature or pressure swing adsorption, for example). (5) Adsorption of CO<sub>2</sub> and H<sub>2</sub> within a microporous material leads to an increase in the effective “pressure” experienced by the reactants inside the pores (through increased density) that is known to shift the chemical equilibrium toward the product by Le Chatelier’s principle.<sup>21,22</sup> (6) Combining CO<sub>2</sub> separation and conversion into a single unit will result in significant efficiency increases and cost reduction through process intensification.

We propose to use both quantum mechanical and classical statistical mechanical atomistic modeling to design functional groups and compute properties of functionalized MOFs and to use this

information to help guide experimental efforts to synthesize families of stratified (layered) MOFs having different functional moieties in each layer. The computational work will be carried out by Johnson's group and the experiments will be performed by Rosi's group. As an example, consider a stratified MOF with four layers, shown schematically in Figure 1. The first layer could be designed to repel water through addition of highly hydrophobic groups, as we have already demonstrated.<sup>10,23</sup> The second layer could be selective for CO<sub>2</sub> and H<sub>2</sub>, while rejecting N<sub>2</sub> and other contaminants. The third layer could preferentially bind the HCOOH product in order to shift the conversion toward products. The fourth layer could contain functional moieties that bind CO<sub>2</sub> strongly and in close proximity to catalytic metal sites. Thus, the catalytic sites, which might be sensitive to water and other contaminants, will be protected by the outer strata of the MOF. Moieties that stabilize the formic acid product could be added in proximity to the catalytic sites to improve the conversion, effectively shifting the equilibrium toward the product by removal of HCOOH as soon as it is synthesized.

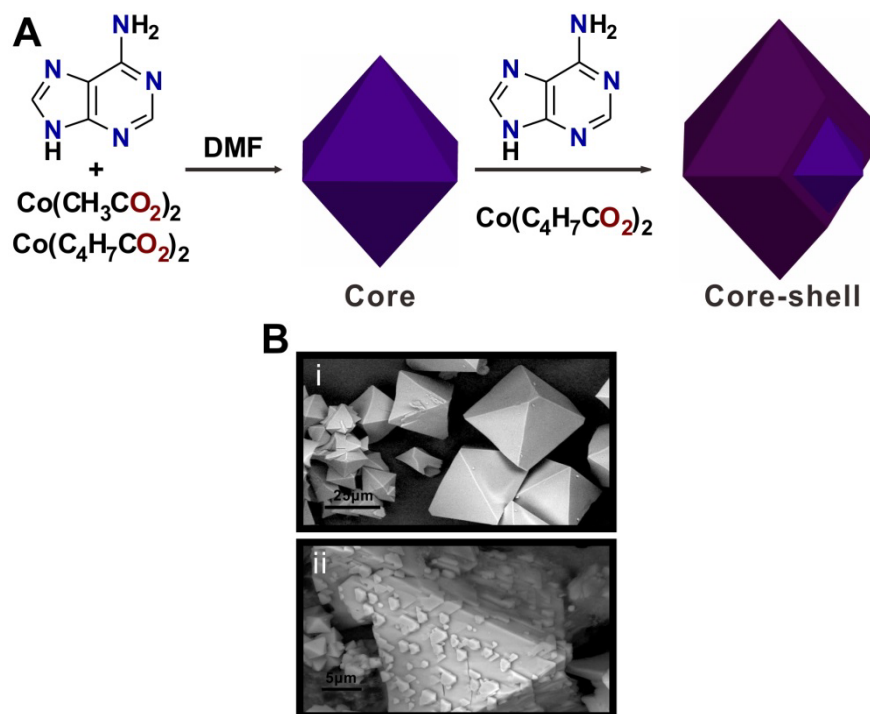
The success of the proposed work critically depends on the ability to synthesize layered MOF structures having different functionalities in each layer, as shown schematically in Figure 1. Rosi's group has recently demonstrated the feasibility of making functional layered MOFs.<sup>10</sup> Rosi's group synthesized an isorecticular series of cobalt-adeninate bio-MOFs known as **bio-MOF-11** through **bio-MOF-14**. These four MOFs are functionalized with acetate, propionate, butyrate, and valerate, respectively; Rosi's group measured gas adsorption and Johnson's group provided modeling to help interpret the results.<sup>23</sup> They found that **bio-MOF-11** has high capacity for CO<sub>2</sub>, good CO<sub>2</sub>/N<sub>2</sub> selectivity, but is not water stable. In contrast, **bio-MOF-14** has much lower capacity for CO<sub>2</sub>, higher CO<sub>2</sub>/N<sub>2</sub> selectivity, and robust water stability, thanks to the hydrophobic nature of the valerate functional groups.<sup>23</sup> Note that high CO<sub>2</sub> capacity, high CO<sub>2</sub>/N<sub>2</sub> selectivity, and water stability are all needed for a viable CO<sub>2</sub> capture material, since flue gas contains significant amounts of water vapor. Rosi's group was able to synthesize a core-shell MOF having an inner core of **bio-MOF-11** and an outer shell of **bio-MOF-14**. The synthetic scheme is shown in Figure 2A and images of the product core-shell materials in Figure 2B. The resulting material showed both high CO<sub>2</sub> capacity and water stability. Adsorption isotherms for CO<sub>2</sub> and N<sub>2</sub> in the pure **bio-MOF-11** and **bio-MOF-14** and for the core-shell material are shown in Figure 3. Also shown in Figure 3 are isotherms for the core-shell material after grinding the crystals to destroy the protective **bio-MOF-14** shell and allow N<sub>2</sub> greater access to the core. These isotherms demonstrate conclusively the functionality of the core-shell MOF and the role of the individual layers. This provides a proof-of-concept that we are able to synthesize layered MOFs showing desired characteristics in each layer.

Another critical factor in the success of this proposal is the ability to use computational approaches to design functional groups that can bind CO<sub>2</sub>. Amine functional groups have the potential to chemically bind CO<sub>2</sub> forming zwitterions, carbamic acids, or carbamates. Johnson's group has computed the energetics and kinetics for these product states for the CO<sub>2</sub>/monoethanol amine (MEA) system<sup>24</sup> and for a series of substituted MEA molecules.<sup>25</sup> These same product states could be formed



**Figure 1.** Schematic of a cross-section of a stratified MOF having four different layers, denoted by the different colors of the lattice framework, each containing different functional groups. The first layer is hydrophobic and excludes water, while allowing target molecules to enter.

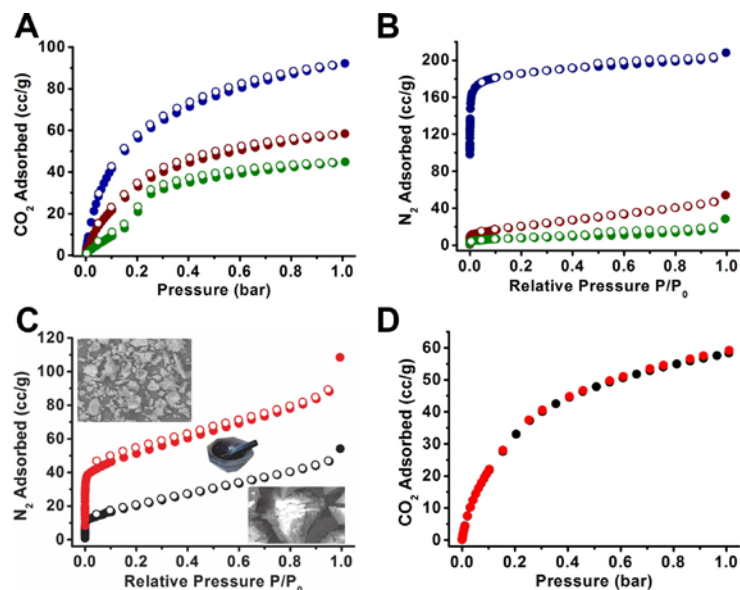
with bidentate functional groups within MOFs. As a proof-of-concept we have designed a diamine azide moiety that could be incorporated into a MOF by carrying out density functional theory (DFT) calculations on a series of molecules. Our figure of merit in the design was the ability of the moiety to form chemical bonds with CO<sub>2</sub>, as measured by the binding energy and characterized by the bend angle of the CO<sub>2</sub>. We found that the length of the aliphatic chains was crucial in designing structures that allowed strong bonds to form. The zwitterion and the carbamic acid products for the most promising candidate structure identified are shown in Figure 4, parts (a) and (b), respectively. The moiety has two NH<sub>2</sub> groups spaced so that they can both interact with CO<sub>2</sub>, one group binding the C atom and the other group contributing hydrogen bonds. The H-bonds, shown as dashed lines in Figure 4, along with distances in Å shown as the red numbers, are critical to stabilizing the structure. We found that other structures having different placement and different length of the aliphatic chains produced binding energies that were significantly less favorable due to reduced hydrogen bonding. The binding energies for the structures shown in Figure 4 are both close to 50 kJ/mol.



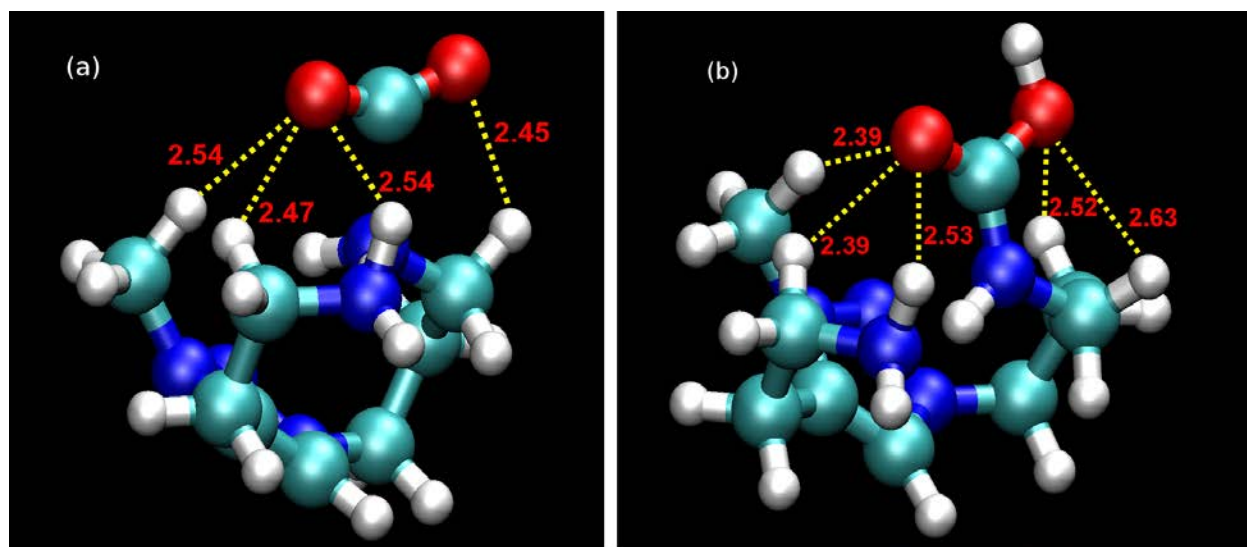
**Figure 2.** Synthetic scheme for the preparation of the core-shell crystal (A). SEM images of the core crystal (Bi) and core-shell crystal with multiple shell layers grown (Bii).

There are many other possible moieties for binding CO<sub>2</sub> in addition to the specific diamine azide molecule shown in Figure 4. We propose to use a variety of computational tools to screen candidate structures for their potential to bind CO<sub>2</sub> and chemically react to form initial states that are likely to lead to kinetically favorable pathways for HCOOH formation. We aim to tailor functional groups both chemically and geometrically to design promising structures for experimental synthesis and testing. The computational approach will include the development of a set of descriptors to assess the performance of various functional moieties, allowing for the rational design of tailored functional groups. Experimental work will be carried out concurrently with exchange of information between both groups such that computations will guide experiments and at the same time experiments will provide accuracy checks and will guide calculations. This close collaboration between theory and experiment will

accelerate discovery of principles for designing atom- and energy-efficient materials with tailored properties.



**Figure 3.** CO<sub>2</sub> (A) and N<sub>2</sub> (B) adsorption isotherms at 273 K and 77 K, respectively (core, navy; core-shell, dark red; **bio-MOF-14**, green). N<sub>2</sub> (C) and CO<sub>2</sub> (D) adsorption isotherms at 273 K and 77 K before (black) and after (red) grinding.



**Figure 4.** Bidentate diamine azide functional group binding CO<sub>2</sub> in (a) a zwitterion and (b) carbamic acid configuration. The binding energies for the zwitterion and carbamic acid are both about 50 kJ/mol as computed from DFT. The hydrogen bonds, shown as dashed lines with distances in Å shown as the red numbers, are critical to stabilizing the structure.

The ultimate goal of this work is to design an enzyme-mimic site that will facilitate the hydrogenation of CO<sub>2</sub> by lowering the barrier further. Enzymatic reduction of CO<sub>2</sub> to formic acid has been studied in the literature.<sup>26,27</sup> Formate dehydrogenase can be used to convert CO<sub>2</sub> to formic acid. Dehydrogenase enzymes can be made to function in reverse in the presence of electron donors, such as



excess NADH (nicotinamide adenine dinucleotide).<sup>27-29</sup> We note in passing that photocatalytic reduction of CO<sub>2</sub> has been widely studied.<sup>30-40</sup> Our approach is to focus on the catalysis of CO<sub>2</sub> hydrogenation with the assumption that the H<sub>2</sub> required for the process can be developed through renewable means, such as photocatalytic splitting of H<sub>2</sub>O. We propose to use computational methods to develop a first approximation to an enzyme-like structure that lowers the barrier for CO<sub>2</sub> hydrogenation. We envision using relatively simple functional groups, such as that shown in Figure 4, to bind CO<sub>2</sub> and hold it in place with hydrogen bonds or Lewis acid/Lewis base interactions,<sup>41-44</sup> such that it can interact with a catalytic complex *in situ* to lower the barrier of hydrogenation. In this way we can use chemical and physical binding of CO<sub>2</sub> to increase the reaction rate.

### Scope of Work

We here briefly delineate the broad scope of the work we aim to accomplish over the three-year duration of the proposal. The work is divided into five general tasks. These tasks are not all sequential. Some of them will be carried-out concurrently, while others will best be carried-out by making use of results from a previous task. **We note that the experimental work could start a year after the computational work if required by budget constraints, so as to decouple the funding of the computational and experimental parts of the proposal.**

**Task 1:** Design and synthesis of functionalized MOFs that chemically bind CO<sub>2</sub>. As described above, this will involve use of a variety of computational techniques to screen functional groups and searching for appropriate guiding principles for tailoring functional groups to bind CO<sub>2</sub> in a variety of different ways, e.g., zwitterion, carbamic acid, carbamate, etc. This task also encompasses synthesis and modification of MOFs, accompanied by characterization and analysis. This task is iterative, with a continuous feedback-loop between calculations and experiments.

**Task 2:** Design and synthesis of functionalized MOFs that bind HCOOH over a range of energies. The ability to bind HCOOH after it is synthesized is important to increasing the conversion of the reaction. However, binding formic acid too strongly will lower the reaction rate and make product recovery energetically expensive. This task will focus on designing families of functional groups that can be incorporated into MOFs that have a variety of binding mechanisms and adsorption energies. The purpose is to facilitate optimization by tuning of the binding energy.

**Task 3:** Design and synthesis of functionalized MOF for separation of CO<sub>2</sub>/H<sub>2</sub>O/N<sub>2</sub> mixtures. Computational work will suggest functional groups to be used for rejecting H<sub>2</sub>O while allowing transport of target analytes such as CO<sub>2</sub> and H<sub>2</sub>. Experimental work will involve the synthesis and characterization of various MOFs having different functional groups. Accuracy of the modeling will be assessed and iterations made as necessary.

**Task 4:** Design and synthesis of stratified MOFs having different functional groups in each layer. This task will involve synthesis of multi-layered MOFs with different functional groups or combinations of functional groups in each layer. New modeling techniques will be required to estimate the selectivity of stratified MOFs.

**Task 5:** Computational study of enzyme-mimic catalytic hydrogenation of CO<sub>2</sub>. Many studies have demonstrated that CO<sub>2</sub> can be catalytically hydrogenated to HCOOH. A fairly wide variety of transition metal complexes have been widely used as catalysts for CO<sub>2</sub> hydrogenation, with Ru complexes perhaps the most commonly used.<sup>1-3,7-9,45-49</sup> This task is exploratory and only computational in nature. Experimental work and additional computational work is envisioned for a future phase of this project. We will model the catalytic reaction mechanism for CO<sub>2</sub> conversion to HCOOH on selected target catalytic complexes, based on the most promising materials reported in the literature. We will then model interactions between CO<sub>2</sub>-binding moieties, such as that shown in Figure 4, and the catalytic center.

**Projected Outcomes:**

1. Fundamental atomistic-level elucidation of the interactions between CO<sub>2</sub> and classes of functional materials that strongly bind CO<sub>2</sub>. Identification of electronic, Lewis acid/base, and steric interactions that lead to favorable binding.
2. Atomistic description of the diffusion pathways, selectivity mechanisms, and adsorption sites within functionalized layered MOFs.
3. Development of design strategies and methods for synthesizing multi-layered MOFs (> two layers) having tailored functional groups in each layer.
4. Control of functional group placement and distribution within MOF layers for optimization of properties.
5. Realization of multi-functional MOFs having cooperative properties and functions.
6. Description of kinetic pathways for catalytic reduction of CO<sub>2</sub> to HCOOH on tailored functional materials, leading to better insights on atomic-level control of chemical reactions.

**Project Objectives:**

- Use a hierarchy of computational methods to design sets of functional groups that can chemically bind CO<sub>2</sub> and that can be incorporated into MOFs.
- Experimentally test the most promising functional groups for binding CO<sub>2</sub> by synthesizing functionalized MOFs and measuring CO<sub>2</sub> adsorption isotherms and IR spectra (collaboration with NETL).
- Computationally design sets of functional groups that can bind HCOOH over a range of energies to prevent the reverse reaction, yet allow easy release.
- Synthesize and test a variety of candidate HCOOH binding functional groups by measuring formic acid adsorption isotherms and IR spectra.
- Systematically study the stability of the MOFs in the presence of varying concentrations of formic acid using powder X-ray diffraction and gas adsorption of the materials after exposure to formic acid.
- Develop computational methods for fast screening of transport through MOFs having flexible functional groups with the aim of predicting transport (combined adsorption & diffusion) selectivity.
- Computationally design functional groups that will yield high transport selectivity for separation of CO<sub>2</sub>/H<sub>2</sub>O/N<sub>2</sub> mixtures.
- Synthesize MOFs with candidate functional groups for separating gas mixtures. Measure the pure fluid adsorption isotherms as a function of time to assess kinetic effects. Use ideal adsorbed solution theory to estimate transport selectivity.
- Develop computational techniques that can model diffusion of gas molecules across the interface between layers in stratified MOFs.
- Develop methods for synthesis of stratified MOFs having three or more layers, with each layer containing different functional groups.
- Selectively introduce functional groups to the different layers using various post-synthetic MOF modification strategies.
- Measure pure fluid isotherms for multi-layered stratified MOFs to confirm that layer ordering changes the adsorption phenomena of the stratified MOF compared to the single component MOF counterparts.
- Compute reaction pathways for CO<sub>2</sub> reduction on prototypical CO<sub>2</sub> hydrogenation catalysts. Use these calculations to identify the kinetically limiting steps in the reaction.



- Use the kinetic information computed for CO<sub>2</sub> hydrogenation on existing catalysts to design new catalysts that incorporate functional groups to bind CO<sub>2</sub> in the correct geometry and with the correct electronic interactions to reduce the reaction barrier for CO<sub>2</sub> conversion to formic acid.

### Changes in Overall Research Direction

In broad terms, the overall research direction remains focused on capture and reduction of CO<sub>2</sub>. We have changed focus from photocatalytic reduction to chemical reduction using H<sub>2</sub>. We will defer the problem of how to produce H<sub>2</sub> in a sustainable way to future work, but we recognize that it will likely involve photocatalytic processes. We are using what we have learned in the initial study to tune the direction of our research toward more fruitful avenues.

### Unexpended Funds

No unexpended funds will remain at the end of the current project period.

### Progress Report

The accomplishments from our previous award have laid the groundwork for the new work proposed here. As a result of the previous award we have published seven papers in peer-reviewed journals,<sup>23,50-55</sup> including one paper recently published in *Physical Review Letters*<sup>52</sup> and one paper just accepted for publication in the *Journal of the American Chemical Society*.<sup>54</sup> In addition, we have several manuscripts in preparation, including one on chemical reactions in MOFs containing metal porphyrins,<sup>56</sup> work on selective adsorption of CO<sub>2</sub> in an amine-functionalized MOF,<sup>57</sup> and one joint with the Lewis group at WVU on conformational effects of photoexcitations in MOFs functionalized with azobenzene groups.<sup>58</sup> Our calculations on reactions in metal porphyrin-containing MOFs serves as an initial guide to our proposed work on CO<sub>2</sub> hydrogenation (see Task 5). We carried out plane wave DFT calculations on styrene epoxidation within the pores of ZnMn-RPM, which was studied experimentally by Hupp et al.<sup>14</sup> We have used both DFT-based molecular dynamics (DFT-MD) and the “Nudged Elastic Band” (NEB)<sup>59-62</sup> transition state finding method to characterize the reaction pathways for oxygen transfer from the oxygen carrier, 2-(*tert*-butylsulfonyl)iodosylbenzene, to the Mn center in the MOF and the subsequent epoxidation of styrene by the transfer of the oxygen from Mn to the C=C double bond of styrene. Results from the DFT-MD calculations for oxygen transfer from the oxygen carrier to the ZnMn-RPM are shown in Figure 5. Both the DFT-MD and the NEB calculations (not shown) demonstrate that the spin state is very important in the energetics of the oxygen transfer and the same is true for the styrene epoxidation step. In the latter case there is a crossover in energy going from the triplet to the quintet state as oxygen is transferred from the Mn to the C=C bond, as shown from our NEB calculations in Figure 6. The physics of spin transitions are not accounted for in DFT so our DFT-MD results are qualitative, at best. However, multireference problems do not appear to be significant for this system.<sup>63</sup> Importantly, we should not encounter spin or multireference problems on the systems we propose to study in this work.

Our work in progress on computing the adsorption and diffusion of CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>, and H<sub>2</sub> in an amine-functionalized MOF<sup>57</sup> provides a foundation upon which to build for this current proposal. We have computed diffusion barriers for gas molecules from classical potentials and from DFT calculations, both with and without vdW corrections applied to the DFT functionals. We have found that the vdW corrections are very important for getting the adsorption potential correct, but that the relative barrier heights are less sensitive to vdW interactions. As an example we show in Figure 7 the barriers computed for CH<sub>4</sub> diffusion through the amine-MOF as computed from standard generalized gradient DFT (PW91), vdW-corrected DFT (DFT-TS), and from classical Lennard-Jones potentials (LJ-model).<sup>57</sup> We have also assessed the importance of framework flexibility in these calculations.

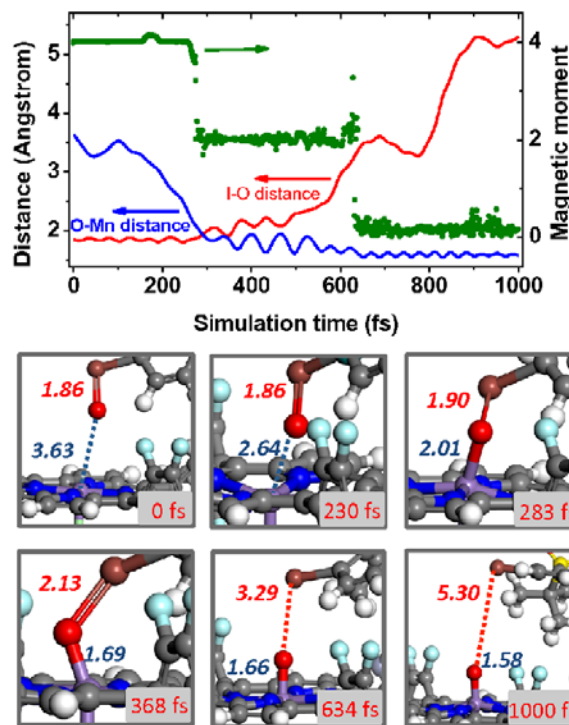


Figure 5. Oxygen transfer in ZnMn-RPM. The two red and blue curves in the upper plot represent the change of I-O (iodine-oxygen) and O-Mn distance (left axis) as a function of simulation time, during the DFT-MD simulation (at 500 K) for the oxidation of ZnMn-RPM using PBE functional. The green dots represent magnetic moment (right axis) for each configuration. Six snapshots extracted from DFT-MD trajectories are shown in the lower panels at the times indicated. The I-O (red text) and O-Mn (blue text) bond distances are shown.

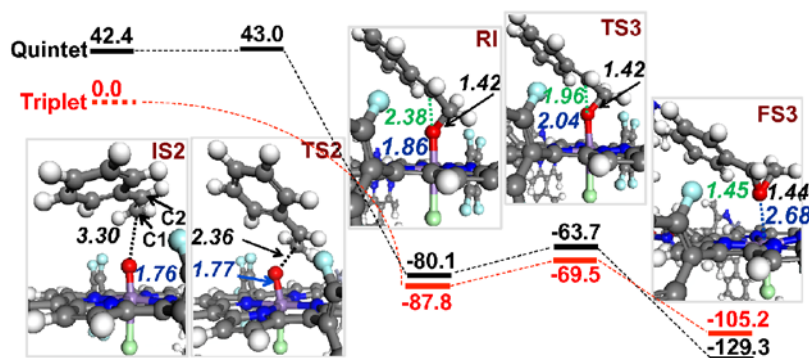


Figure 6. Relative energies of initial state (IS2), radical intermediate (RI), two transition states (TS2 and TS3), and final state (FS2) for the epoxidation of styrene, obtained from NEB calculations. The bond distances of O-Mn (in blue), O-C1 (in red), and O-C2 (in green) are shown for the quintet state.

We have modeled the adsorption geometry, energetics, and vibrational modes of CO<sub>2</sub> in a spin-crossover porous coordination polymer containing transition metals (Figure 8).<sup>53</sup> These calculations have been used to develop the basis for the work proposed in this renewal by elucidating fundamental

interactions between molecules and surfaces, chemical reactions within catalytically active MOFs, and guest-host interactions with CO<sub>2</sub>.

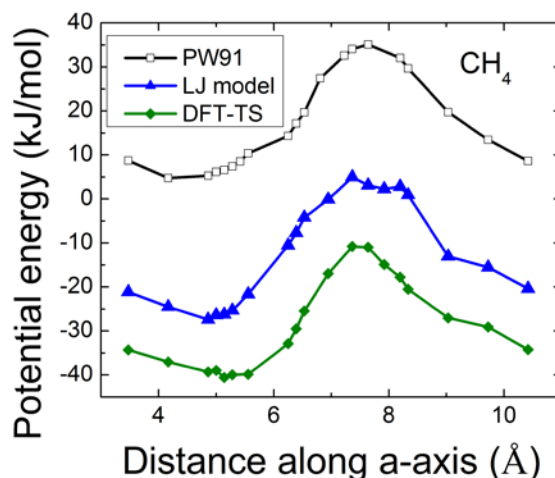


Figure 7. Potential energy barrier (diffusion barrier) for CH<sub>4</sub> moving through the pores of an amine functionalized MOF. The potential energy curves are computed from a standard generalized gradient approximation functional (PW91) shown by the open squares and black line, from a classical Lennard-Jones potential (blue triangles, blue line), and from vdW-corrected DFT (DFT-TS), shown as green diamonds and the green line. Lines are to guide the eye.

#### Computational Methods:

Recent developments in computational methods for screening MOFs for specific applications have made it possible to predict new MOFs that have desired properties, such as the ability to store methane at high volumetric densities,<sup>64</sup> to capture CO<sub>2</sub>,<sup>65-70</sup> or to separate other gas mixtures.<sup>71,72</sup> Wilmer and co-workers have demonstrated that one can enumerate all possible MOFs that can be synthesized from a given combination of metal ligand clusters and organic linkers. They have predicted almost 140,000 different MOFs.<sup>64</sup> Sholl et al. screened 1163 MOFs for CO<sub>2</sub>/N<sub>2</sub> separation.<sup>71</sup> In addition to screening very large numbers of MOFs, there are also developments in screening functional groups within MOFs for their interactions with target molecules. Examples include screening about 20 different groups for ammonia capture,<sup>73,74</sup> and about 15 different groups for CO<sub>2</sub> capture.<sup>67-69</sup> Note that it is much more difficult to screen functional groups because the modeling requires higher-level quantum mechanical methods for predicting chemical interactions, whereas screening MOFs for adsorption capacity and selectivity can be accomplished with empirical pair potentials in the limit of only physisorption interactions.

The computational arm of the proposed work will initially involve screening interactions between various adsorbate molecules and a pool of potential functional groups. This will involve a variety of different computational techniques, ranging from accurate quantum chemical post-Hartree-Fock methods, to efficient DFT methods, to mixed quantum-statistical mechanical methods, such as COSMOtherm, to classical statistical mechanics methods. The Johnson group has proven expertise with these methods. Effective use of computations will require close collaboration between the modeling and experimental teams. The Johnson group has extensive experience in working closely with experimental groups to identify fundamental chemical and physical processes and to design new materials. His group, working with Sholl et al., made the first predictions that transport of gases through carbon nanotubes would be extremely fast.<sup>75,76</sup> These predictions were later validated experimentally.<sup>77,78</sup> Johnson's group has worked with a number of different experimental groups on

studies of MOFs,<sup>53,79-82</sup> including our recent work with Rosi's group.<sup>23</sup> We have employed grand canonical Monte Carlo (GCMC) methods to predict adsorption isotherms and mixture selectivities, and van der Waals corrected density functional theory (DFT) methods to compute binding energies, geometries, and vibrational spectra. The Johnson group has had a long-standing collaboration with the Yates group (UVA) employing a combination of theory and experiments to attack problems involving adsorption, transport, and reactions of molecules on surfaces and nanoporous materials.<sup>35,83-92</sup> We also have close collaborations with experimental groups at the National Energy Technology Laboratory (NETL) dealing with CO<sub>2</sub> adsorption and interactions with nanoporous materials.<sup>53,93,94</sup> One powerful tool for comparing experiments and modeling is infrared spectrometry (IR). We have used computed IR frequencies and intensities to identify the atomic-level details of interactions that give rise to experimentally observed IR shifts.<sup>53,85,86,91-94</sup>

Two examples are shown in Figure 8. In the left panel we show joint work with the Yates group. They identified an unusual IR stretching frequency for H<sub>2</sub>O adsorbed inside single-walled carbon nanotubes (SWNTs), but experiments alone were unable to identify the exact origin of this mode. DFT and classical calculations performed by the Johnson group found that the mode was due to unusual H-bonding for the ring-like water confined inside the SWNTs.<sup>85</sup> The second example, shown in the right panel in Figure 8, is a collaboration with NETL and identified the origin of distinct shifts in the  $\nu_2$  and  $\nu_3$  IR bands of CO<sub>2</sub> adsorbed in spin-crossover pillared Hofmann compounds. Calculations showed that the shifts are due to the structure of CO<sub>2</sub> adsorbed in the compounds combined with changes in the lattice constant with spin state changes.<sup>53</sup> These methods can be applied to the present work through collaborations with NETL scientists. The Johnson group has previously used DFT-based screening methods to identify candidate materials for hydrogen storage<sup>95-103</sup> and CO<sub>2</sub> capture.<sup>104,105</sup> This expertise will aid in screening functional groups in this work.

We will use a combination of approaches to screen functional moieties to bind CO<sub>2</sub>. The first level of screening will be carried out with the COSMOtherm approach, which is much faster than ab initio modeling, even though it employs quantum mechanical information in building the model. The basic idea is that interactions between moieties can be approximately computed from the conductor-like screening model for real solvents (COSMO-RS) formalism,<sup>106,107</sup> which only requires computation of the so-called " $\sigma$ -profile" or polarization charge density of the individual molecules from quantum

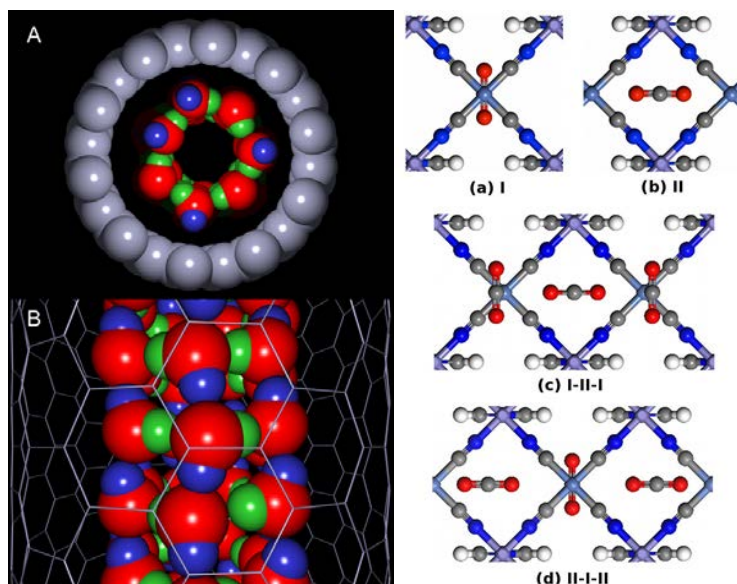


Figure 8. Left: Snapshot from a molecular simulation of water adsorbed inside a (10, 10) SWNT at 123 K. (A) End view. (B) Side view. Red: oxygen, blue: hydrogens H-bonded to adjacent rings, green: hydrogens having intra-ring H-bonds. Right: (a)-(b) Two different orientations I (perpendicular) and II (parallel) for isolated CO<sub>2</sub> adsorbed in the low spin Fe(pyrazine)M(CN)<sub>4</sub> structure. (c)-(d) Two possible configurations of CO<sub>2</sub> molecules at a loading of 1.5 molecules per unit cell, denoted I-II-I and II-I-II.

mechanics. The mixture interactions are computed from statistical mechanics. Hence, the COSMOtherm approach does not require the calculation of any mixture interactions from first principles. We have successfully used this approach in the past to predict the solubility of CO<sub>2</sub> in various oligomers.<sup>108,109</sup> We can also compute interactions between functional groups and target analytes from cluster (gas phase) quantum chemistry codes such as Gaussian<sup>110</sup> or TURBOMOLE, utilizing both DFT and more accurate wave function methods such as MP2 and CCSD(T). The Johnson group has used this approach extensively in the past.<sup>24,25,41-44,111</sup> The next level of theory we will use is DFT. We will use both cluster and periodic DFT approaches, as appropriate. The cluster calculations will be bench-marked against accurate MP2 and CCSD(T) calculations to choose the appropriate functional and basis set. We expect that van der Waals (vdW) interactions will be important for many of the CO<sub>2</sub>-functional group interactions we will encounter. We will therefore employ vdW corrected DFT methods such as Grimme's formalism<sup>112</sup> and the Tkatchenko-Scheffler approach<sup>113</sup> in our calculations. Johnson's group has previously used these methods, along with the Langreth functional,<sup>114-118</sup> to attack a number of different problems where van der Waals interactions are important.<sup>50-55</sup> Periodic plane wave DFT methods will be used to compute geometric and electronic properties of MOFs, including the use of DFT-MD to compute the conformational properties of the functional groups within the MOFs as we have previously done.<sup>23</sup>

Tight-binding formalisms are efficient, but less accurate methods for computing structural, electronic, and dynamic properties of periodic systems. Fireball is an ab initio tight-binding formalism that makes use of slightly excited numerical atomic-like orbitals for very efficient and fast calculations.<sup>119</sup> However, while Fireball can efficiently handle systems containing hundreds or thousands of atoms, in its current form it is limited to a small number of distinct atom *types*. This is because integrals are pre-calculated on a numerical grid, hence many different atom types result in prohibitively large grids, because the number of integrals grows as  $N^3$  where  $N$  is the number of atom types in the system.<sup>119</sup> Another method that is more accurate, but also more computationally demanding is CP2K, which uses the QUICKSTEP mixed Gaussian and plane wave approach to performing DFT calculations.<sup>120</sup> This is an alternative to Fireball since it is more efficient than most DFT methods. The Johnson group has previously used VASP<sup>121-123</sup> to compute structural, energetic, and vibrational properties of adsorbate/adsorbent systems.<sup>53,83-86</sup> However, VASP is not efficient, nor does it run well in highly parallel environments. Nevertheless, this will be useful for benchmark calculations, since it is robust and has an excellent library of pseudopotentials. We will benchmark our CP2K and Fireball (if possible) calculations against select calculations with VASP. Other codes, such as PWscf/QuantumEspresso and FHI-aims will be explored and used if these are better suited to the problems to be solved.

We have previously used a combination of computational screening and experiments to tune the heats of reaction for CO<sub>2</sub> reacting with monoethanolamine (MEA) derivatives.<sup>25</sup> We computed the heats of reaction for MEA and 10 different substituted MEA analogs. We used CH<sub>3</sub>, NH<sub>2</sub>, OH, OCH<sub>3</sub> and F substitution groups at both the  $\alpha$ - and  $\beta$ -carbon positions in MEA to construct the 10 substituted MEA molecules. The heats of reaction for carbamate formation and for carbamic acid formation were computed. The carbamate reaction requires two amine molecules, denoted RNH<sub>2</sub>, and involves a proton transfer from the amine molecule to which the CO<sub>2</sub> is bound to a neighboring RNH<sub>2</sub> molecule, as shown in Reaction (2):



The carbamic acid reaction only requires a single amine molecule and involves an intramolecular proton transfer from N to the O of CO<sub>2</sub> after it binds to the NH<sub>2</sub> group, as shown in Reaction (3):



We have tested our computational approach by comparing our calculated value of  $\Delta H$  with experimental values for  $\alpha$  and  $\beta$   $\text{CH}_3$  substituted MEA, as measured by our collaborators at GE; these values are reported in Table 1.<sup>25</sup> We found excellent agreement between our predictions and the experiments, giving us confidence in the predictions for the other eight substituted MEA species. The goal of our work was to design a substitution group that would change the thermodynamics such that formation of carbamic acid would be favored over carbamate. In MEA the heat of reaction highly favors carbamate formation. We found that a good descriptor for the heat of reaction was the relative basicity of the amine and that the reaction becomes more exothermic (large magnitude) as the basicity of the amine increases for both Reactions (2) and (3). More importantly, we found that the slope of  $\Delta H$  vs. basicity is much steeper for Reaction (2) than Reaction (3), which allowed us to predict that a substituted MEA having a small basicity would favor carbamic acid formation. The correlations between  $\Delta H$  and basicity for the reactions are shown in Figure 9. The correlations predict that the carbamate and carbamic acid heats of reaction should be about equal for a species that has a relative basicity of 272 and that carbamic acid formation would be favored for basicities lower than this value. This is seen to be the case for  $\alpha$ -F-MEA, for which  $\Delta H(\text{carbamate}) = -0.5$  kcal/mol and  $\Delta H(\text{carbamic acid}) = -4.1$  kcal/mol. This work is proof-of-concept that we are able to tune reaction enthalpies through the use of electron donating and electron withdrawing groups, which affect the relative basicity of the amine.<sup>25</sup>

We have previously used umbrella sampling in conjunction with weighted histogram analysis<sup>124,125</sup> to compute reaction barriers for  $\text{CO}_2$  forming carbamates and zwitterions with MEA.<sup>24</sup> For the work proposed here we will primarily use techniques such as NEB<sup>59-61</sup> to identify reaction pathways and barrier heights.

Table 1: Comparison of calculated and experimentally determined heats of reaction (kcal/mol) for carbamate formation with substituted MEA.

Species	Calculated $\Delta H$	Experimental $\Delta H$
MEA	-16.3	$-17.3 \pm 1.3$
$\alpha$ - $\text{CH}_3$ -MEA	-13.3	$-12.9 \pm 1.2$
$\beta$ - $\text{CH}_3$ -MEA	-15.4	$-15.6 \pm 1.3$

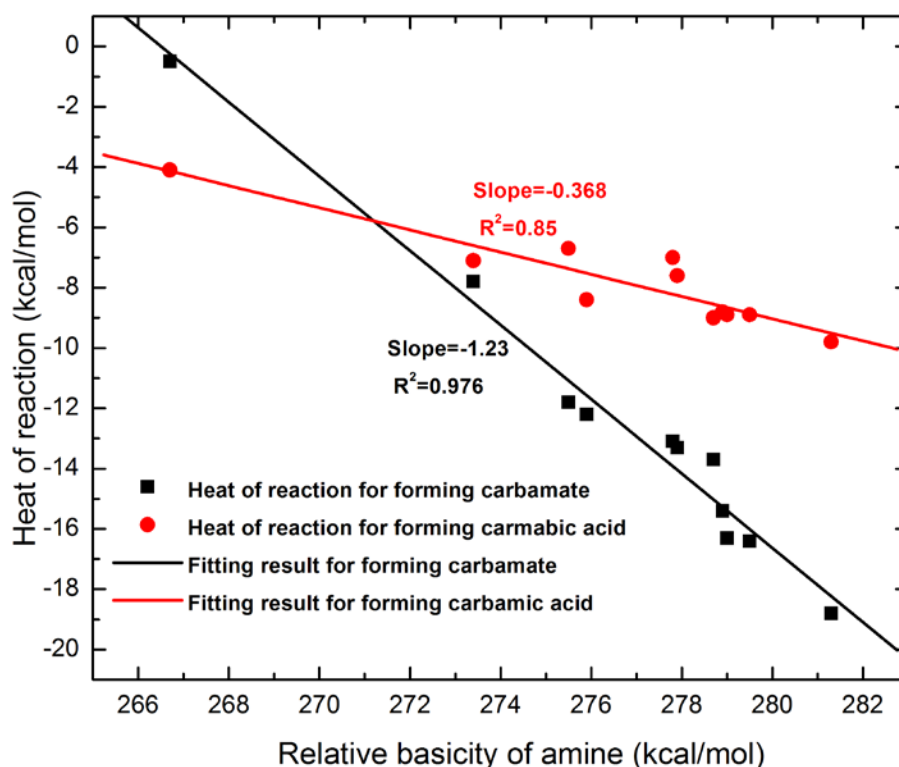


Figure 9. Heats of reaction for forming carbamate and carbamic acid as a function of the relative basicity of the substituted MEA.

In addition to quantum mechanical methods, we will use classical statistical mechanics to compute adsorption and diffusion of gases within the functional MOFs. We have extensive experience in computing these properties in nanoporous materials.<sup>23,53,55,76,79-82,85,86,88,93,94,126-140</sup> The classical calculations will provide information that cannot readily be obtained from electronic structure calculations because of system sizes and time-scale issues. We will be able to compute adsorption isotherms in various MOFs. These can be compared with experimental adsorption isotherms to shed light on the atomic-level details that give rise to macroscopically-observed phenomena. We will also explore kinetic effects through computing diffusivities of gas-phase molecules through the MOFs.

Traditional methods for computing adsorption isotherms, such as GCMC cannot be used for calculating the adsorption in materials with flexible functional groups, as we have found to be the case for bio-MOF-14.<sup>23</sup> One potential solution to this problem is to use hybrid-Monte Carlo (HMC) to accurately account for the conformational degrees of freedom of the functional groups. We have previously used HMC techniques for modeling ring polymers within the path integral formalism to simulate the thermodynamic properties of quantum fluids, including adsorption of quantum fluids in narrow pores with an HMC GCMC approach.<sup>136,141-144</sup> We will explore the use of HMC and other techniques for developing methods for dealing with the flexibility issues inherent in using functional groups having long chain lengths.

### Experimental Methods:

Over the last 15 years, Rosi and his group have been deeply involved in the design, synthesis, and characterization of novel MOF materials.<sup>10,23,145-158</sup> Recently, their focus has been on the preparation of MOFs for selective CO<sub>2</sub> capture,<sup>10,23,146,147</sup> design and preparation of mesoporous



MOFs,<sup>145,158</sup> and the development of NIR-emitting MOFs for biological applications.<sup>148,156,157,159</sup> In the last year and in collaboration with the Johnson group, they have begun to explore straightforward methods for increasing the functional complexity of MOF materials. They have designed and prepared MOF materials that are highly selective for CO<sub>2</sub> capture and also highly stable in water, two properties that are essential for an adsorbent for practical CO<sub>2</sub> capture applications.<sup>136</sup> In recent work shown in Figure 2, they have prepared core-shell MOF materials that consist of a water-stable and CO<sub>2</sub>-selective shell encasing a core with a high capacity for storing CO<sub>2</sub>.<sup>10</sup> The shell acts to protect the water-sensitive core and also selectively filter CO<sub>2</sub> to the core. In short, the core-shell architecture combines the merits of its components. In order to increase the complexity of MOF materials, the Rosi group recently developed a post-synthetic MOF modification strategy that relies on strain-promoted ‘click’ chemistry.<sup>158</sup> This proof-of-principle work was performed using mesoporous bio-MOF-100 as the MOF scaffold. Post-synthetic modification (PSM) of MOF ligands will be important for constructing the proposed stratified MOFs; many PSM methods have been reported<sup>16,158,160-167</sup> and we will utilize some of these in this work. In submitted yet unpublished work, Rosi’s group has also recently demonstrated that short ligands in bio-MOF-100 structures can be replaced with long ligands in a single-crystal to single-crystal fashion.<sup>168</sup> Similar ligand exchange processes have been reported by the groups of Seth Cohen<sup>169,170</sup> and Joseph Hupp.<sup>171</sup> Ligand exchange represents another PSM method that will be used in constructing the stratified MOFs. In summary, Rosi’s group has a wealth of synthetic experience in preparing and modifying complex MOF materials. They have either submitted or published key papers describing the preparation of core-shell MOF structures, ligand exchange PSM, and PSM of MOF ligands. In this proposal, they will combine these areas of expertise and apply them to a new MOF system in order to prepare a new class of concentrically-multilayered and multifunctional MOF materials: so-called stratified MOFs.

We define stratified MOFs as MOFs having a functionalized core surrounded by two or more layers of uniquely functionalized MOF layers (Figure 1). We emphasize that core-shell MOFs have been prepared; we can denote these as AB materials having an A core surrounded by a B shell.<sup>172-180</sup> There is at least one example of a more complicated ABA material, with an A core, a B interior shell, and then an A exterior shell.<sup>178</sup> **More sophisticated structures with multiple levels of stratification, for example ABC, ABCD, or ABCDE, have not been reported. In the proposed work, we will develop new strategies for achieving these hierarchically ordered MOF materials.**

There are two key requirements for the MOF platform to be used in this study: the ability to be functionalized and water stability. We have therefore chosen to use the water stable UiO-66<sup>181</sup> family of MOFs as the MOF platform for these studies. UiO-66 consists of Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> clusters linked together by twelve benzenedicarboxylate (BDC) linkers as shown in Figure 10. There exists many potential ways of incorporating functional groups into the cavities of the UiO-66 type MOFs. First, isostructural analogues of UiO-66 can be prepared with a variety of functionalized BDC linkers,<sup>182,183</sup> including 2-amino-BDC, for example. Second, UiO-66 prepared with amino-BDC linkers can be post-synthetically modified,<sup>184</sup> which allows for introduction of more complex functional groups. Third, recent studies show that ligand exchange can also be used to post-synthetically introduce new functionalized BDC ligands into the UiO-66 structure.<sup>170</sup> These three strategies, taken together, allow one to address the functionality of the UiO-66 system in a highly versatile fashion. In summary, the UiO-66 MOF platform is ideal because i) UiO-66 is stable in a variety of solvents, including water;<sup>181,185</sup> ii) rigorous studies have shown that the amino-BDC variant is also water stable;<sup>185</sup> and iii) multiple routes are available for introducing various functional groups.

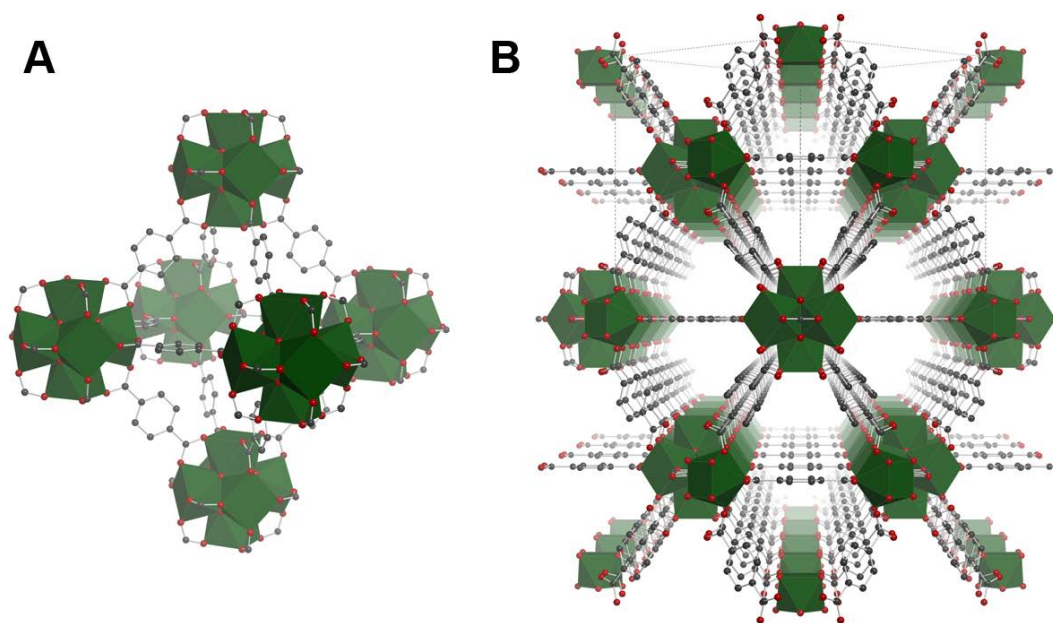


Figure 10. Crystal structure of UiO-66. (A) The octahedral cavity within the structure and (B) a perspective view of the 3-D crystal lattice (color codes:  $\text{Zr}^{4+}$ , green; C, black; O, red; H, omitted for clarity).

The principal goal of the experimental part of the proposed work is to prepare stratified MOFs consisting of multiple MOF layers surrounding a central MOF core. The MOF core and the MOF layers encapsulating the core will each be decorated with a different functional group and in some cases, a layer or the core may be functionalized with a mixture of different functional groups. The layers surrounding the core will serve to either selectively adsorb or reject certain small molecules. The core will be decorated with i) a functional group that serves to bind and activate  $\text{CO}_2$  for eventual reduction with dihydrogen to form formic acid and ii) a functional group that serves to trap the formic acid upon formation to prevent back-reaction.<sup>9</sup> The synthesis of such stratified MOFs will begin with preparation of the core UiO-66 type MOF. Johnson's group will use theory to identify the  $\text{CO}_2$ -associating and the formic acid trapping functional groups. Several routes will be investigated to incorporate a mixture of these two identified functional groups into the MOF core. These routes are detailed below and illustrated in Figure 11.

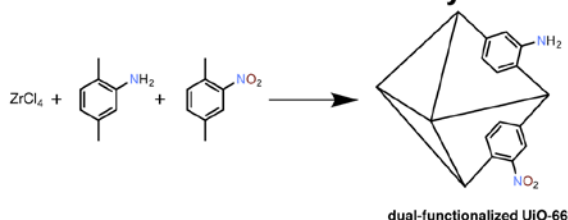
**Route 1:** If the two functional groups are relatively simple (e.g.  $-\text{NH}_2$  and  $-\text{NO}_2$ ),<sup>183</sup> their dual incorporation into the core MOF should be fairly trivial: a 'divariate' core can be prepared by performing the UiO-66 synthesis with a 1:1 mixture of 2-aminobenzenedicarboxylic acid and 2-hydroxybenzenedicarboxylic acid.<sup>186-189</sup> The resulting core would essentially be a solid-state mixture of the two ligands. Synthetic conditions could be tuned to adjust the ratio between the two ligands as needed.  $^1\text{H}$  NMR spectroscopy of the dissolved core would be used to verify the ligand ratio.

**Route 2:** If the two functional groups are complex and cannot be incorporated onto the ligands prior to MOF synthesis, post-synthetic modification of amino-BDC ligands can be utilized.<sup>163</sup> The functional groups of interest will be decorated with an acyl chloride, for example. The amino groups and the acyl chlorides can react together to liberate HCl and covalently tether the functional group of choice to the MOF through an amide linkage. We note that studies have confirmed that UiO-66 is stable in 0.1 M HCl,<sup>185</sup> so the produced HCl from the PSM reactions should not negatively impact the UiO-66 structure. To incorporate two different functional groups ( $\text{R}_1$  and  $\text{R}_2$ ), we will react the core amino-functionalized MOF with a mixture of two different acyl chlorides, each attached to our selected

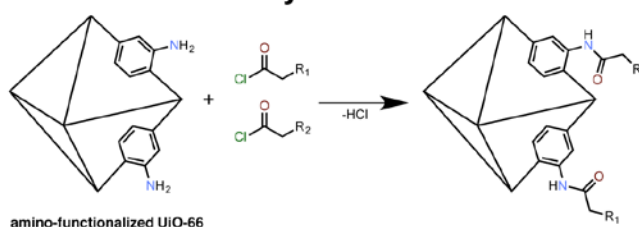
functional groups. To obtain the desired ratio of functional groups, we may need to adjust reactant ratios. Again,  $^1\text{H}$  NMR spectroscopy of the dissolved core would be used to verify the ligand ratio.

**Route 3:** We will also investigate solvent-assisted ligand exchange pathways to introduce more complicated functional groups into the MOF core.<sup>169-171</sup> For example, theory may identify a simple functional group ( $-\text{NH}_2$ ) and a complex functional group  $\text{R}_3$  as the ideal two functional groups. A MOF core can first be prepared with 100% amino-BDC. Then, the core can be soaked in a solution of  $\text{R}_3$ -functionalized benzenedicarboxylic acid, heated to promote ligand exchange, and then cooled.  $^1\text{H}$  NMR spectroscopy of the dissolved core would be used to verify the ligand ratio after ligand exchange; the concentration of  $\text{R}_3$ -functionalized benzenedicarboxylic acid, the temperature, and the reaction time can all be tuned to optimize the degree of ligand exchange so that we achieve the desired 50/50 ratio of  $-\text{NH}_2$  to  $\text{R}_3$ .

### Route 1: Direct Mixed-Linker Synthesis



### Route 2: Post-Synthetic Modification



### Route 3: Post-Synthetic Ligand Exchange

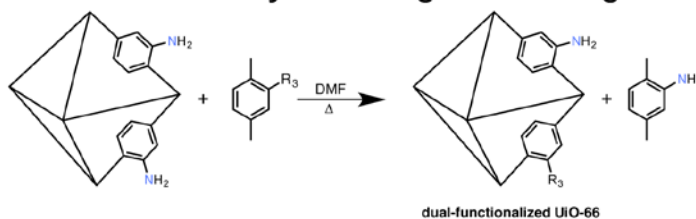


Figure 11. Potential pore functionalization strategies. The octahedron represents a fragment of a UiO-66 type MOF, where the edges are the linkers and the vertices are the  $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{COO})_{12}$  clusters. In each case, the ligands are represented only by the functionalized benzene ring; the carboxylates at the 1 and 4 positions are omitted.

After we have successfully prepared our desired dual-functional group core UiO-66 variant, we will begin to grow additional MOF shells around the core. Core-shell MOF materials have been prepared by us, as shown in Figure 2,<sup>10</sup> and others,<sup>172-180</sup> but to our knowledge, core-shell MOF materials based on the UiO-66 structure type have not been prepared. Our initial experiments will focus on preparing a simple UiO-66 core having only one type of ligand (e.g., amino-BDC) and growing onto this core a UiO-66 shell containing only BDC. Matzger and coworkers performed similar studies on MOF-5 isorecticular analogues, showing that the core and shell could be distinguished from one another by the orange color

of the amino-BDC ligand.<sup>178</sup> We will use this simple system to optimize the shelling process. Once the synthetic process is optimized, we will begin growing layers onto our dual-functionalized UiO-66 core. Briefly, our approach will be: i) prepare core, ii) wash and rinse core with DMF to remove any unreacted starting materials, iii) disperse core in shell growth solution containing  $\text{Zr}^{4+}$  source and functionalized benzenedicarboxylic acid of choice, iv) wash, rinse, and repeat for subsequent layers. We realize that small defects may form in the core after PSM. However, we do not expect that these defects will significantly impact shell growth, as we have shown in our previous work that the unit cell parameters of the core and the shell do not need to be perfectly identical to ensure shell growth.<sup>10</sup> The MOF layers surrounding the core can be functionalized using either pre-functionalized ligands for the synthesis or via PSM of amino-BDC ligands, provided that free amino groups are not exposed in the core (we would need to avoid functionalizing the core via PSM when targeting shell functionalization via PSM). The outer MOF layer will be constructed using hydrophobic ligands that will prevent or significantly limit water adsorption, such as 1,4-naphthalenedicarboxylate,<sup>182</sup> 2-methyl-benzenedicarboxylate,<sup>190</sup> post-synthetically modified amino-BDC linkers functionalized with long hydrophobic aliphatic chains,<sup>191</sup> and other hydrophobic groups identified by Johnson's group.

**MOF Characterization:** Each prepared stratified MOF will be rigorously characterized using a suite of characterization methods available in Rosi's laboratory and in user facilities at UPitt. The composition of each stratified MOF will be determined using  $^1\text{H}$  NMR. The MOF samples will be dissolved in deuterated HCl prior to analysis. The linker ratios will be extracted from the  $^1\text{H}$  NMR spectra and will allow accurate determination of composition of the stratified MOFs. Although based on experience and literature precedent,<sup>181</sup> we expect to form very small MOF crystallites, in the event we are able to grow large MOF crystals, we will slice these crystals and study the compositions of the different layers using microscopic attenuated total reflection (ATR) IR.<sup>175</sup> The crystalline structure of the stratified MOFs will be revealed using powder X-ray diffraction and subsequent comparison of the powder data to diffraction patterns of UiO-66. The shelling process will also be monitored using SEM, a tool we have found useful in imaging the shell formation at different stages of growth and in confirming that the shell is actually growing onto the core crystallites.<sup>10</sup> SEM images can also provide useful qualitative information about shell growth: if the shell crystal growth clearly aligns with the edges and faces of the core crystallites this is potentially a sign of epitaxial shell growth on the core. SEM will also yield information about the extent of shell growth and whether the shell completely covers the core. If the shell does not completely cover the core, we will need to increase the shell growth time or have multiple shell growth cycles to ensure complete coverage. We note that non-complete coverage would result in undesired open pathways for analyte diffusion to the core that do not pass through the MOF shells. The stratified MOFs will be characterized using gas adsorption, where each relevant fluid (water,  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{CO}_2$ , and  $\text{HCOOH}$ ) will be studied. Adsorption kinetics will be monitored by measuring uptake as function of time. *In situ* FTIR studies will be performed in parallel to both monitor adsorbate diffusion and interaction with the different layers. These studies will be performed in collaboration with Dr. Chris Matranga at NETL, with whom we have active collaborations.

The core MOF and each MOF layer will also be prepared as single phase MOFs. For the MOFs with mixed ligand compositions,  $^1\text{H}$  NMR of dissolved samples will be used to determine composition. For MOFs with only one ligand, composition will be determined via elemental analysis. The stability of each of these pure phase MOFs in formic acid will be studied and evaluated (see below). In addition, isotherms for all the relevant fluids will be collected, including water,  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2$ , and formic acid. Adsorption kinetics will be determined by measuring the adsorption as a function of time. In addition, *in situ* FTIR studies will be performed on the MOFs during fluid adsorption and desorption to monitor, measure, and understand the interactions between the MOF functional groups and the adsorbates. These studies will be particularly useful for  $\text{CO}_2$  and formic acid. By studying the single phase MOFs, we will understand and demonstrate how each layer performs its given function. For example, if we design

an outer layer to be water resistant, we would measure water isotherms<sup>182,192</sup> on the pure phase MOF whose composition was identical to the outer layer. After water vapor adsorption studies, the integrity of the materials will be evaluated using i) powder X-ray diffraction to determine retention of crystallinity and ii) N<sub>2</sub> adsorption studies to confirm retention of porosity and surface area. If the MOF adsorbs a negligible amount of water, we will move forward with that MOF composition for the outer layer. If it adsorbs a significant amount of water, we will prepare a new MOF composition with new hydrophobic functional groups that would prevent water adsorption. Again, water adsorption isotherms would be collected, and this general iterative process would be repeated until we arrive at a composition for the outer layer that results in negligible water adsorption. A similar process will be used to optimize the adsorptive properties of the intermediate layer and the core. The intermediate layer would be optimized to exclude N<sub>2</sub> at room temperature and atmospheric pressure, while allowing the passage of CO<sub>2</sub> and H<sub>2</sub>. The core would be optimized to strongly associate and adsorb CO<sub>2</sub> (to some functional groups) and formic acid (to other functional group). Adsorption isotherms of the optimized stratified MOF would be expected to reveal the following behavior: negligible water and N<sub>2</sub> adsorption yet significant CO<sub>2</sub> adsorption.

We will rigorously study the stability of each MOF layer in the presence of different amounts of formic acid. To our knowledge, the stability of UiO-66 structures has not been studied after exposure to formic acid. For a comprehensive study, 20 different formic acid solutions will be prepared in increments of 5% v/v formic acid/solvent, where the solvent will be water, DMF, or other simple organic solvents. Samples of the single component MOFs having the same composition of each layer will be soaked in the solutions for various time periods, and after soaking the crystallinity of these samples will be studied using powder X-ray diffraction and the porosity will be measured using N<sub>2</sub> adsorption at 77 K. If the MOFs are stable in the formic acid solution, we expect no loss or change in crystallinity and no loss in surface area. We note that the pK<sub>a</sub> of formic acid is 3.77 while the pK<sub>a</sub>'s of benzenedicarboxylic acid are 3.51 and 4.82. Therefore, we should expect that formate could potentially displace one of the carboxylates upon prolonged exposure to formic acid, but displacement of the second carboxylate would be less favored. In our MOF core design, we incorporate functional groups that will trap the produced formic acid. We expect that capture of the formic acid by these functional groups would prevent any significant MOF degradation by produced formic acid. After catalysis, the formic acid would be removed quickly from the framework via either or both heating and vacuum. Therefore, since formate is not an extremely strong base and since the produced formic acid will be trapped by a functional group and thereafter rapidly removed from the framework, we expect negligible framework decomposition after exposure to formic acid.

**Future Aims:** After we have successfully completed the proposed work, in the next phase of the project we aim to incorporate CO<sub>2</sub> reduction catalysts into the core of the stratified MOFs and measure, study, and optimize catalytic activity. Our design strategy described herein was chosen to be compatible with future installation of prototypical ruthenium(II) CO<sub>2</sub> reduction catalysts.<sup>46</sup> One potential way of incorporating such catalysts into the core of these UiO-66 MOF platforms is via post-synthetic ligand exchange. For example, we will replace BDC in the core with the BDC/catalyst complex shown in Figure 12.

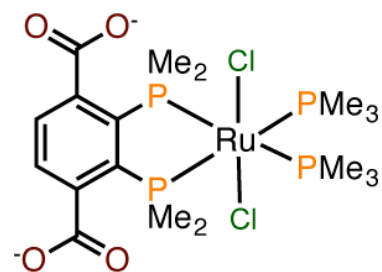


Fig. 12. BDC-catalyst complex.

## Detailed Statement of Work

We give details of the projected work here and identify which students will focus on which tasks. We are requesting support for four graduate students. They are identified here as SJ1, SJ2 for the two students in Johnson's group, and SR1, SR2 for the students in Rosi's group. Each sub-task is assigned to one or more of the students.

**Task 1:** Design and synthesis of functionalized MOFs that chemically bind CO<sub>2</sub>.

**Task 1.1 (SJ1):** Use COSMOtherm to screen a library of functional groups (to be developed by all team members) for interactions with CO<sub>2</sub>.

**Task 1.2 (SJ2):** Test accuracy and assess usefulness of the COSMOtherm screening by computing binding energies using DFT and wavefunction methods.

**Task 1.3 (SJ1 & SJ2):** Further refine and modify the family of promising functional groups by using chemical insight to perturb the best structures to improve binding energies, e.g., by adding Lewis acid/base sites.

**Task 1.4 (SR1):** Synthesize a small set of candidate functional moieties for incorporation into the MOFs via PSM.

**Task 1.5 (SR2):** Synthesize MOFs and incorporate functional groups via PSM.

**Task 1.6 (SR1 & SR2):** Measure CO<sub>2</sub> adsorption isotherms and IR spectra (through collaboration with NETL, with whom we have on-going collaborations) to characterize the adsorption and binding states of CO<sub>2</sub> in the various MOFs.

**Task 1.7 (SJ1):** Compute binding energies and compute vibrational frequencies using periodic DFT.

**Task 1.8 (SJ2):** Compute adsorption isotherms from GCMC simulations, developing ad-hoc potentials for chemically bound CO<sub>2</sub> as necessary, e.g., with Morse potentials.

**Task 1.9 (All):** Compare experiments and simulations, iterate and refine modeling as needed.

**Task 2:** Design and synthesis of functionalized MOFs that bind HCOOH over a range of energies.

**Task 2.1 (SJ1):** Use COSMOtherm to screen a library of functional groups for interactions with HCOOH. Identify functional groups that span a range of binding energies.

**Task 2.2 (SJ2):** Test accuracy and assess usefulness of the COSMOtherm screening by computing binding energies using DFT and wavefunction methods.

**Task 2.3 (SJ1 & SJ2):** Refine the library of promising functional groups by using chemical insight to perturb the best structures to both increase and decrease the binding energy to produce a ranked list of groups by binding energy.

**Task 2.4 (SR1):** Synthesize a small set of candidate functional groups for incorporation into the MOFs via PSM, choosing groups from the list that show weak binding and other groups with predicted strong binding.

**Task 2.5 (SR2):** Synthesize MOFs and incorporate functional groups via PSM.

**Task 2.6 (SR1 & SR2):** Measure HCOOH adsorption isotherms and IR spectra (through collaboration with NETL) to characterize the adsorption and binding states of HCOOH in the various MOFs.

**Task 2.7 (SR1 & SR2):** Examine MOF stability in HCOOH.

**Task 2.8 (SJ1):** Compute binding energies and compute vibrational frequencies using periodic DFT.

**Task 2.9 (SJ2):** Compute adsorption isotherms from GCMC simulations, developing ad-hoc potentials for chemically bound HCOOH as necessary, e.g., with Morse potentials.

**Task 2.10 (All):** Compare experiments and simulations, iterate and refine modeling as needed.

**Task 3:** Design and synthesis of functionalized MOF for separation of CO<sub>2</sub>/H<sub>2</sub>O/N<sub>2</sub> mixtures.

**Task 3.1 (SJ1):** For rigid functional groups, use high-throughput screening methods to estimate charges, structure, and adsorption isotherms for the target gases.

**Task 3.2 (SJ1 & SJ2):** For flexible functional groups no rapid screening methods exist. Develop methods that account for the entropy and dynamics of the flexible functional groups. This could include DFT-MD, Boltzmann weighting of structures, coarse-graining methods, hybrid Monte Carlo, etc.

**Task 3.3 (SJ1 & SJ2):** Refine the library of promising functional groups by using chemical insight to perturb the best structures.

**Task 3.4 (SJ1 & SJ2):** Use modeling to identify the most promising candidates for separation of CO<sub>2</sub>/H<sub>2</sub>O/N<sub>2</sub> mixtures.

**Task 3.5 (SR1 & SR2):** Synthesize MOFs with the most promising candidate functional groups.

**Task 3.6 (SR1 & SR2):** Measure adsorption isotherms as a function of time for the pure gases to characterize the kinetics of uptake of each of the gases in the MOFs. Include adsorption isotherms of H<sub>2</sub> to test that its adsorption is not significantly impeded.

**Task 3.7 (SJ1 & SJ2):** Compare results from modeling with experiments and refine modeling methods as needed. Compute IAST isotherms and estimate

**Task 3.8 (All):** Iterate on functional group design and synthesis as needed to achieve acceptable results.

**Task 4:** Design and synthesis of stratified MOFs having different functional groups in each layer.

**Task 4.1 (SJ1):** Develop coarse-grained methods for estimating transport of guest molecules across the interface of two adjacent layers in a stratified MOF.

**Task 4.2 (SJ2):** Carry out atomically-detailed calculations of guest molecule diffusion across model interfaces of two adjacent layers in a stratified MOF. Select a variety of interface configurations and check sensitivity.

**Task 4.3 (SR1):** Optimal stratified MOF synthetic procedures will be determined by first preparing simple amino-BDC UiO-66 cores surrounded by an intermediate BDC UiO-66 layer and a final amino-BDC UiO-66 layer.

**Task 4.4 (SR1):** Using optimized conditions from Task 4.3, prepare dual-functionalized core UiO-66 MOFs and coat with layers to produce stratified MOF.

**Task 4.5 (SR2):** Characterize structure and composition of stratified MOFs using <sup>1</sup>H NMR, SEM, and powder X-ray diffraction.

**Task 4.4 (SR1 & SR2):** Use time-dependent adsorption isotherm measurements to explore the kinetics and equilibrium of various pure gases adsorbing in layered MOFs.

**Task 4.5 (SR1 & SR2):** Use IR measurements, taken at various times, to explore the kinetics and equilibrium of various pure gases adsorbing in layered MOFs.

**Task 4.6 (SJ1 & SJ2):** Compare simulation results with experiments and revise the modeling as needed.

**Task 5:** Computational study of enzyme-mimic catalytic hydrogenation of CO<sub>2</sub>.

**Task 5.1 (SJ1):** Compute reaction pathways for CO<sub>2</sub> reduction on prototypical transition metal complexes.

**Task 5.2 (SJ2):** Develop possible enzyme-mimic structures that bind CO<sub>2</sub> in close proximity to the catalyst center and with advantageous geometries to facilitate hydrogenation.

**Task 5.3 (SJ1 & SJ2):** Refine the enzyme-mimic structures and employ different functional groups to develop alternate candidate complexes. Compute reaction pathways and barriers.



## References

- (1) Leitner, W. "Carbon Dioxide as a Raw Material: The Synthesis of Formic Acid and Its Derivatives from CO<sub>2</sub>", *Angewandte Chemie International Edition in English*, **34**, 2207-2221 (1995).
- (2) Jessop, P. G.; Ikariya, T.; Noyori, R. "Homogeneous Hydrogenation of Carbon Dioxide", *Chemical Reviews*, **95**, 259-272 (1995).
- (3) Wesselbaum, S.; Hintermair, U.; Leitner, W. "Continuous-Flow Hydrogenation of Carbon Dioxide to Pure Formic Acid using an Integrated scCO<sub>2</sub> Process with Immobilized Catalyst and Base", *Angewandte Chemie International Edition*, **51**, 8585-8588 (2012).
- (4) Mura, M. G.; Luca, L. D.; Giacomelli, G.; Porcheddu, A. "Formic Acid: A Promising Bio-Renewable Feedstock for Fine Chemicals", *Advanced Synthesis & Catalysis*, **354**, 3180-3186 (2012).
- (5) Case, P. A.; van Heiningen, A. R. P.; Wheeler, M. C. "Liquid hydrocarbon fuels from cellulosic feedstocks via thermal deoxygenation of levulinic acid and formic acid salt mixtures", *Green Chemistry*, **14**, 85-89 (2012).
- (6) Martindale, B. C. M.; Compton, R. G. "Formic acid electro-synthesis from carbon dioxide in a room temperature ionic liquid", *Chemical Communications*, **48**, 6487-6489 (2012).
- (7) Zhang, Z.; Xie, Y.; Li, W.; Hu, S.; Song, J.; Jiang, T.; Han, B. "Hydrogenation of Carbon Dioxide is Promoted by a Task-Specific Ionic Liquid", *Angewandte Chemie International Edition*, **47**, 1127-1129 (2008).
- (8) Zhang, Z.; Hu, S.; Song, J.; Li, W.; Yang, G.; Han, B. "Hydrogenation of CO<sub>2</sub> to Formic Acid Promoted by a Diamine-Functionalized Ionic Liquid", *ChemSusChem*, **2**, 234-238 (2009).
- (9) Yasaka, Y.; Wakai, C.; Matubayasi, N.; Nakahara, M. "Controlling the Equilibrium of Formic Acid with Hydrogen and Carbon Dioxide Using Ionic Liquid", *The Journal of Physical Chemistry A*, **114**, 3510-3515 (2010).
- (10) Li, T.; Sullivan, J. E.; Rosi, N. L. "Design and Preparation of a Core-Shell Metal-Organic Framework for Selective CO<sub>2</sub> Capture", *J. Am. Chem. Soc.*, Submitted (2013).
- (11) Ma, L.; Abney, C.; Lin, W. "Enantioselective catalysis with homochiral metal-organic frameworks", *Chemical Society reviews*, **38**, 1248-1256 (2009).
- (12) Lee, J.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. "Metal-organic framework materials as catalysts", *Chemical Society reviews*, **38**, 1450-1459 (2009).
- (13) Ma, L.; Lin, W. In *Functional Metal-Organic Frameworks: Gas Storage, Separation and Catalysis*; Schröder, M., Ed.; Springer Berlin Heidelberg: 2010; Vol. 293, p 175-205.
- (14) Farha, O. K.; Shultz, A. M.; Sarjeant, A. A.; Nguyen, S. T.; Hupp, J. T. "Active-Site-Accessible, Porphyrinic Metal-Organic Framework Materials", *Journal of the American Chemical Society*, **133**, 5652-5655 (2011).
- (15) Shultz, A. M.; Farha, O. K.; Hupp, J. T.; Nguyen, S. T. "A Catalytically Active, Permanently Microporous MOF with Metalloporphyrin Struts", *Journal of the American Chemical Society*, **131**, 4204-4205 (2009).
- (16) Wu, C.-D.; Hu, A.; Zhang, L.; Lin, W. "A Homochiral Porous Metal-Organic Framework for Highly Enantioselective Heterogeneous Asymmetric Catalysis", *Journal of the American Chemical Society*, **127**, 8940-8941 (2005).
- (17) Wang, J.-L.; Wang, C.; Lin, W. "Metal-Organic Frameworks for Light Harvesting and Photocatalysis", *ACS Catalysis*, **2**, 2630-2640 (2012).
- (18) Wang, C.; Wang, J.-L.; Lin, W. "Elucidating Molecular Iridium Water Oxidation Catalysts Using Metal-Organic Frameworks: A Comprehensive Structural, Catalytic, Spectroscopic, and Kinetic Study", *Journal of the American Chemical Society*, **134**, 19895-19908 (2012).
- (19) Wang, C.; deKrafft, K. E.; Lin, W. "Pt Nanoparticles@Photoactive Metal-Organic Frameworks: Efficient Hydrogen Evolution via Synergistic Photoexcitation and Electron Injection", *Journal of the American Chemical Society*, **134**, 7211-7214 (2012).

- (20) Ma, L.; Falkowski, J. M.; Abney, C.; Lin, W. "A series of isorecticular chiral metal–organic frameworks as a tunable platform for asymmetric catalysis", *Nat Chem*, **2**, 838-846 (2010).
- (21) Turner, C. H.; Brennan, J. K.; Lisal, M.; Smith, W. R.; Johnson, J. K.; Gubbins, K. E. "Simulation of chemical reaction equilibria by the reaction ensemble Monte Carlo method: a review", *Molecular Simulation*, **34**, 119-146 (2008).
- (22) Santiso, E. E.; George, A. M.; Turner, C. H.; Kostov, M. K.; Gubbins, K. E.; Buongiorno-Nardelli, M.; Sliwinska-Bartkowiak, M. "Adsorption and catalysis: The effect of confinement on chemical reactions", *Applied Surface Science*, **252**, 766-777 (2005).
- (23) Li, T.; Chen, D.-L.; Sullivan, J. E.; Kozlowski, M. T.; Johnson, J. K.; Rosi, N. L. "Systematic modulation and enhancement of CO<sub>2</sub> : N<sub>2</sub> selectivity and water stability in an isorecticular series of bio-MOF-11 analogues", *Chemical Science*, **4**, 1746-1755 (2013).
- (24) Xie, H.-B.; Zhou, Y.; Zhang, Y.; Johnson, J. K. "Reaction Mechanism of Monoethanolamine with CO<sub>2</sub> in Aqueous Solution from Molecular Modeling", *J. Phys. Chem. A*, **114**, 11844-11852 (2010).
- (25) Xie, H.-B.; Johnson, J. K.; Perry, R. J.; Genovese, S.; Wood, B. R. "A Computational Study of the Heats of Reaction of Substituted Monoethanolamine with CO<sub>2</sub>", *J. Phys. Chem. A*, **115**, 342-350 (2011).
- (26) Yadav, R. K.; Baeg, J.-O.; Oh, G. H.; Park, N.-J.; Kong, K.-j.; Kim, J.; Hwang, D. W.; Biswas, S. K. "A Photocatalyst–Enzyme Coupled Artificial Photosynthesis System for Solar Energy in Production of Formic Acid from CO<sub>2</sub>", *Journal of the American Chemical Society*, **134**, 11455-11461 (2012).
- (27) Lu, Y.; Jiang, Z.-y.; Xu, S.-w.; Wu, H. "Efficient conversion of CO<sub>2</sub> to formic acid by formate dehydrogenase immobilized in a novel alginate–silica hybrid gel", *Catalysis Today*, **115**, 263-268 (2006).
- (28) Obert, R.; Dave, B. C. "Enzymatic Conversion of Carbon Dioxide to Methanol: Enhanced Methanol Production in Silica Sol–Gel Matrices", *Journal of the American Chemical Society*, **121**, 12192-12193 (1999).
- (29) Kuwabata, S.; Tsuda, R.; Yoneyama, H. "Electrochemical conversion of carbon dioxide to methanol with the assistance of formate dehydrogenase and methanol dehydrogenase as biocatalysts", *Journal of the American Chemical Society*, **116**, 5437-5443 (1994).
- (30) Abou Asi, M.; He, C.; Su, M.; Xia, D.; Lin, L.; Deng, H.; Xiong, Y.; Qiu, R.; Li, X.-z. "Photocatalytic reduction of CO<sub>2</sub> to hydrocarbons using AgBr/TiO<sub>2</sub> nanocomposites under visible light", *Catalysis Today*, **175**, 256-263 (2011).
- (31) Izumi, Y. "Recent advances in the photocatalytic conversion of carbon dioxide to fuels with water and/or hydrogen using solar energy and beyond", *Coordination Chemistry Reviews*, **257**, 171-186 (2013).
- (32) Jeyalakshmi, V.; Mahalakshmy, R.; Krishnamurthy, K. R.; Viswanathan, B. "Titania based catalysts for photoreduction of carbon dioxide: Role of modifiers", *Indian Journal of Chemistry Section a-Inorganic Bio-Inorganic Physical Theoretical & Analytical Chemistry*, **51**, 1263-1283 (2012).
- (33) Koci, K.; Matejka, V.; Kovar, P.; Lacny, Z.; Obalova, L. "Comparison of the pure TiO<sub>2</sub> and kaolinite/TiO<sub>2</sub> composite as catalyst for CO<sub>2</sub> photocatalytic reduction", *Catalysis Today*, **161**, 105-109 (2011).
- (34) Lee, D.-S.; Chen, H.-J.; Chen, Y.-W. "Photocatalytic reduction of carbon dioxide with water using InNbO<sub>4</sub> catalyst with NiO and Co<sub>3</sub>O<sub>4</sub> cocatalysts", *Journal of Physics and Chemistry of Solids*, **73**, 661-669 (2012).
- (35) Mandeltort, L.; Büttner, M.; Yates, J. T., Jr.; Choudhury, P.; Xiao, L.; Johnson, J. K. "Carbon-Chlorine Bond Scission in Li-Doped Single-Walled Carbon Nanotubes: Reaction of CH<sub>3</sub>Cl and Lithium", *J. Phys. Chem. C*, **114**, 17148-17158 (2010).

- (36) Liu, G.; Hoivik, N.; Wang, K.; Jakobsen, H. "Engineering TiO<sub>2</sub> nanomaterials for CO<sub>2</sub> conversion/solar fuels", *Solar Energy Materials and Solar Cells*, **105**, 53-68 (2012).
- (37) Richardson, P. L.; Perdigoto, M. L. N.; Wang, W.; Lopes, R. J. G. "Manganese- and copper-doped titania nanocomposites for the photocatalytic reduction of carbon dioxide into methanol", *Applied Catalysis B-Environmental*, **126**, 200-207 (2012).
- (38) Wang, C.; Thompson, R. L.; Baltrus, J.; Matranga, C. "Visible Light Photoreduction of CO<sub>2</sub> Using CdSe/Pt/TiO<sub>2</sub> Heterostructured Catalysts", *Journal of Physical Chemistry Letters*, **1**, 48-53 (2010).
- (39) Wang, Y.; Li, B.; Zhang, C.; Cui, L.; Kang, S.; Li, X.; Zhou, L. "Ordered mesoporous CeO<sub>2</sub>-TiO<sub>2</sub> composites: Highly efficient photocatalysts for the reduction of CO<sub>2</sub> with H<sub>2</sub>O under simulated solar irradiation", *Applied Catalysis B-Environmental*, **130**, 277-284 (2013).
- (40) Xia, X.-H.; Jia, Z.-H.; Yu, Y.; Liang, Y.; Wang, Z.; Ma, L.-L. "Preparation of multi-walled carbon nanotube supported TiO<sub>2</sub> and its photocatalytic activity in the reduction of CO<sub>2</sub> with H<sub>2</sub>O", *Carbon*, **45**, 717-721 (2007).
- (41) Kilic, S.; Michalik, S.; Wang, Y.; Johnson, J. K.; Enick, R. M.; Beckman, E. J. "Effect of Grafted Lewis Base Groups on the Phase Behavior of Model Poly(dimethyl siloxanes) in CO<sub>2</sub>", *Industrial & Engineering Chemistry Research*, **42**, 6415-6424 (2003).
- (42) Baradie, B.; Shoichet, M. S.; Shen, Z.; McHugh, M. A.; Hong, L.; Wang, Y.; Johnson, J. K.; Beckman, E. J.; Enick, R. M. "Synthesis and Solubility of Linear Poly(tetrafluoroethylene-co-vinyl acetate) in Dense CO<sub>2</sub>: Experimental and Molecular Modeling Results", *Macromolecules*, **37**, 7799-7807 (2004).
- (43) Tapriyal, D.; Wang, Y.; Enick, R. M.; Johnson, J. K.; Crosthwaite, J.; Thies, M. C.; Paik, I. H.; Hamilton, A. D. "Poly(vinyl acetate), poly((1-O-(vinylloxy) ethyl-2,3,4,6-tetra-O-acetyl-β-d-glucopyranoside) and amorphous poly(lactic acid) are the most CO<sub>2</sub>-soluble oxygenated hydrocarbon-based polymers", *The Journal of Supercritical Fluids*, **46**, 252-257 (2008).
- (44) Kilic, S.; Wang, Y.; Johnson, J. K.; Beckman, E. J.; Enick, R. M. "Influence of tert-amine groups on the solubility of polymers in CO<sub>2</sub>", *Polymer*, **50**, 2436-2444 (2009).
- (45) Motokura, K.; Kashiwame, D.; Miyaji, A.; Baba, T. "Copper-Catalyzed Formic Acid Synthesis from CO<sub>2</sub> with Hydrosilanes and H<sub>2</sub>O", *Organic Letters*, **14**, 2642-2645 (2012).
- (46) Jessop, P. G.; Ikariya, T.; Noyori, R. "Homogeneous catalytic hydrogenation of supercritical carbon dioxide", *Nature*, **368**, 231-233 (1994).
- (47) Fujita, E.; Muckerman, J. T.; Himeda, Y. "Interconversion of CO<sub>2</sub> and formic acid by bio-inspired Ir complexes with pendent bases", *Biochimica et Biophysica Acta (BBA) - Bioenergetics*, **in press**.
- (48) Tanaka, R.; Yamashita, M.; Nozaki, K. "Catalytic Hydrogenation of Carbon Dioxide Using Ir(III)-Pincer Complexes", *Journal of the American Chemical Society*, **131**, 14168-14169 (2009).
- (49) Federsel, C.; Jackstell, R.; Beller, M. "State-of-the-Art Catalysts for Hydrogenation of Carbon Dioxide", *Angewandte Chemie International Edition*, **49**, 6254-6257 (2010).
- (50) Chen, D.-L.; Al-Saidi, W. A.; Johnson, J. K. "Noble gases on metal surfaces: Insights on adsorption site preference", *Physical Review B*, **84**, 241405 (2011).
- (51) Chen, D.-L.; Al-Saidi, W. A.; Johnson, J. K. "The role of van der Waals interactions in the adsorption of noble gases on metal surfaces", *Journal of Physics: Condensed Matter*, **24**, 424211 (2012).
- (52) Chen, D.-L.; Mandeltort, L.; Saidi, W. A.; Yates, J. T., Jr.; Cole, M. W.; Johnson, J. K. "Is there a Difference in Van Der Waals Interactions between Rare Gas Atoms Adsorbed on Metallic and Semiconducting Single-Walled Carbon Nanotubes?", *Physical Review Letters*, **110**, 135503 (2013).
- (53) Culp, J. T.; Chen, D.-L.; Liu, J.; Chirdon, D.; Kauffman, K.; Goodman, A.; Johnson, J. K. "Effect of Spin-Crossover-Induced Pore Contraction on CO<sub>2</sub>-Host Interactions in the Porous Coordination Polymers [Fe(pyrazine)M(CN)<sub>4</sub>] (M = Ni, Pt)", *European Journal of Inorganic Chemistry*, **2013**, 511-519 (2013).

- (54) Mandeltort, L.; Chen, D.-L.; Saidi, W. A.; Johnson, J. K.; Cole, M. W.; Yates, J. T., Jr. "Experimental and Theoretical Comparison of Gas Desorption Energies on Metallic- and Semiconducting Single Walled Carbon Nanotubes", *J. Am. Chem. Soc.*, in press. (2013).
- (55) Bucior, B. J.; Chen, D.-L.; Liu, J.; Johnson, J. K. "Porous Carbon Nanotube Membranes for Separation of H<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/CH<sub>4</sub> Mixtures", *The Journal of Physical Chemistry C*, **116**, 25904-25910 (2012).
- (56) Chen, D.-L.; Johnson, J. K. "Porphyrinic Metal-Organic Framework as Catalyst for Styrene Epoxidation Reaction: A First Principle Study", In preparation (2013).
- (57) Chen, D.-L.; Liu, J.; Johnson, J. K. "Atomic-Scale Modeling on Selective Adsorption and Diffusion of CO<sub>2</sub> in Amine Functionalized Metal-Organic Framework ", in preparation (2013).
- (58) Chen, D.-L.; Barry Haycock
- James, P. L.; Johnson, J. K. "Theoretical Modeling of CO<sub>2</sub> Adsorption on Azobenzene Functionalized Metal-Organic Framework", in preparation (2013).
- (59) Henkelman, G.; Jónsson, H. "Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points", *J. Chem. Phys.*, **113**, 9978 (2000).
- (60) Henkelman, G.; Uberuaga, B. P.; Jónsson, H. "A climbing image nudged elastic band method for finding saddle points and minimum energy paths", *J. Chem. Phys.*, **113**, 9901 (2000).
- (61) Sheppard, D.; Terrell, R.; Henkelman, G. "Optimization methods for finding minimum energy paths.", *J. Chem. Phys.*, **128**, 134106 (2008).
- (62) Jónsson, H.; Mills, G.; Jacobsen, K. W.; Berne, B. J.; Ciccotti, G.; Coker, D. F. "Nudged elastic band method for finding minimum energy paths of transitions", *Eds.; World Scientific: Singapore*, 385-404 (1998).
- (63) Kepenekian, M.; Calborean, A.; Vetere, V.; Le Guennic, B.; Robert, V.; Maldivi, P. "Toward Reliable DFT Investigations of Mn-Porphyrins through CASPT2/DFT Comparison", *Journal of Chemical Theory and Computation*, **7**, 3532-3539 (2011).
- (64) Wilmer, C. E.; Leaf, M.; Lee, C. Y.; Farha, O. K.; Hauser, B. G.; Hupp, J. T.; Snurr, R. Q. "Large-scale screening of hypothetical metal-organic frameworks", *Nature Chemistry*, **4**, 83-89 (2012).
- (65) Wilmer, C. E.; Farha, O. K.; Bae, Y.-S.; Hupp, J. T.; Snurr, R. Q. "Structure-property relationships of porous materials for carbon dioxide separation and capture", *Energy & Environmental Science*, **5**, 9849-9856 (2012).
- (66) Wilmer, C. E.; Snurr, R. Q. "Towards rapid computational screening of metal-organic frameworks for carbon dioxide capture: Calculation of framework charges via charge equilibration", *Chemical Engineering Journal*, **171**, 775-781 (2011).
- (67) Amrouche, H.; Aguado, S.; Pérez-Pellitero, J.; Chizallet, C. I.; Siperstein, F.; Farrusseng, D.; Bats, N.; Nieto-Draghi, C. "Experimental and Computational Study of Functionality Impact on Sodalite–Zeolitic Imidazolate Frameworks for CO<sub>2</sub> Separation", *J. Phys. Chem. C*, **115**, 16425-16432 (2011).
- (68) Torrisi, A.; Mellot-Draznieks, C.; Bell, R. G. "Impact of ligands on CO<sub>2</sub> adsorption in metal-organic frameworks: First principles study of the interaction of CO<sub>2</sub> with functionalized benzenes. II. Effect of polar and acidic substituents", *The Journal of Chemical Physics*, **132**, 044705-044713 (2010).
- (69) Torrisi, A.; Mellot-Draznieks, C.; Bell, R. G. "Impact of ligands on CO<sub>2</sub> adsorption in metal-organic frameworks: First principles study of the interaction of CO<sub>2</sub> with functionalized benzenes. I. Inductive effects on the aromatic ring", *The Journal of Chemical Physics*, **130**, 194703-194713 (2009).
- (70) Han, S.; Huang, Y.; Watanabe, T.; Dai, Y.; Walton, K. S.; Nair, S.; Sholl, D. S.; Meredith, J. C. "High-Throughput Screening of Metal–Organic Frameworks for CO<sub>2</sub> Separation", *ACS Comb. Sci.*, **14**, 263-267 (2012).

- (71) Watanabe, T.; Sholl, D. S. "Accelerating Applications of Metal–Organic Frameworks for Gas Adsorption and Separation by Computational Screening of Materials", *Langmuir*, **28**, 14114–14128 (2012).
- (72) Sikora, B. J.; Wilmer, C. E.; Greenfield, M. L.; Snurr, R. Q. "Thermodynamic analysis of Xe/Kr selectivity in over 137 000 hypothetical metal-organic frameworks", *Chemical Science*, **3**, 2217–2223 (2012).
- (73) Kim, K. C.; Yu, D.; Snurr, R. Q. "Computational screening of functional groups for ammonia capture in metal-organic frameworks", *Langmuir*, **29**, 1446–1456 (2013).
- (74) Yu, D.; Ghosh, P.; Snurr, R. Q. "Hierarchical modeling of ammonia adsorption in functionalized metal-organic frameworks", *Dalton Transactions*, **41**, 3962–3973 (2012).
- (75) Ackerman, D. M.; Skoulidas, A. I.; Sholl, D. S.; Johnson, J. K. "Diffusivities of Ar and Ne in Carbon Nanotubes", *Molecular Simulation*, **29**, 677–684 (2003).
- (76) Skoulidas, A. I.; Ackerman, D. M.; Johnson, J. K.; Sholl, D. S. "Rapid Transport of Gases in Carbon Nanotubes", *Phys. Rev. Lett.*, **89**, 185901 (2002).
- (77) Holt, J. K.; Park, H. G.; Wang, Y.; Stadermann, M.; Artyukhin, A. B.; Grigoropoulos, C. P.; Noy, A.; Bakajin, O. "Fast Mass Transport Through Sub-2-Nanometer Carbon Nanotubes", *Science*, **312**, 1034–1037 (2006).
- (78) Majumder, M.; Chopra, N.; Andrews, R.; Hinds, B. J. "Nanoscale hydrodynamics - Enhanced flow in carbon nanotubes", *Nature*, **438**, 44–44 (2005).
- (79) Liu, J.; Lee, J. Y.; Pan, L.; Obermyer, R. T.; Simizu, S.; Zande, B.; Sankar, S. G.; Li, J.; Johnson, J. K. "One-dimensional adsorption and diffusion in Zn(tbp)", *Molecular Simulation*, **37**, 640–646 (2011).
- (80) Liu, J.; Lee, J. Y.; Pan, L.; Obermyer, R. T.; Simizu, S.; Zande, B.; Li, J.; Sankar, S. G.; Johnson, J. K. "Adsorption and Diffusion of Hydrogen in a New Metal–Organic Framework Material: [Zn(bdc)(ted)0.5]", *The Journal of Physical Chemistry C*, **112**, 2911–2917 (2008).
- (81) Liu, J.; Culp, J. T.; Natesakhawat, S.; Bockrath, B. C.; Zande, B.; Sankar, S. G.; Garberoglio, G.; Johnson, J. K. "Experimental and Theoretical Studies of Gas Adsorption in Cu<sub>3</sub>(BTC)<sub>2</sub>: An Effective Activation Procedure", *The Journal of Physical Chemistry C*, **111**, 9305–9313 (2007).
- (82) Pan, L.; Sander, M. B.; Huang, X.; Li, J.; Smith, M.; Bittner, E.; Bockrath, B.; Johnson, J. K. "Microporous Metal Organic Materials: Promising Candidates as Sorbents for Hydrogen Storage", *Journal of the American Chemical Society*, **126**, 1308–1309 (2004).
- (83) Büttner, M.; Choudhury, P.; Karl Johnson, J.; Yates, J. T., Jr. "Vacancy clusters as entry ports for cesium intercalation in graphite", *Carbon*, **49**, 3937–3952 (2011).
- (84) Büttner, M.; Xiao, L.; Mandeltort, L.; Johnson, J. K.; Yates, J. T., Jr. "Enhancement of Adsorption Inside Single Walled Carbon Nanotubes—Li Doping Effect on n-Heptane van der Waals Bonding", *J. Phys. Chem. C*, **113**, 4829–4838 (2009).
- (85) Byl, O.; Liu, J.-C.; Wang, Y.; Yim, W.-L.; Johnson, J. K.; Yates, J. T., Jr. "Unusual Hydrogen Bonding in Water-Filled Carbon Nanotubes", *Journal of the American Chemical Society*, **128**, 12090–12097 (2006).
- (86) Kim, S.; Byl, O.; Liu, J.-C.; Johnson, J. K.; Yates, J. T., Jr. "Spectroscopic Measurement of Diffusion Kinetics through Subnanometer and Larger Al<sub>2</sub>O<sub>3</sub> Particles by a New Method: The Interaction of 2-Chloroethylethyl Sulfide with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>", *The Journal of Physical Chemistry B*, **110**, 9204–9210 (2006).
- (87) Kondratyuk, P.; Wang, Y.; Johnson, J. K.; Yates, J. T., Jr. "Observation of a One-Dimensional Adsorption Site on Carbon Nanotubes: Adsorption of Alkanes of Different Molecular Lengths", *The Journal of Physical Chemistry B*, **109**, 20999–21005 (2005).
- (88) Kondratyuk, P.; Wang, Y.; Liu, J.; Johnson, J. K.; Yates, J. T., Jr. "Inter- and Intratube Self-Diffusion in n-Heptane Adsorbed on Carbon Nanotubes", *The Journal of Physical Chemistry C*, **111**, 4578–4584 (2007).

- (89) Mandeltort, L.; Choudhury, P.; Johnson, J. K.; Yates, J. T., Jr. "Methyl Radical Reactivity on the Basal Plane of Graphite", *The Journal of Physical Chemistry C*, **116**, 18347-18357 (2012).
- (90) Mandeltort, L.; Choudhury, P.; Johnson, J. K.; Yates, J. T., Jr. "Reaction of the Basal Plane of Graphite with the Methyl Radical", *The Journal of Physical Chemistry Letters*, **3**, 1680-1683 (2012).
- (91) Yim, W. L.; Byl, O.; Yates, J. T., Jr.; Johnson, J. K. "Vibrational behavior of adsorbed CO<sub>2</sub> on single-walled carbon nanotubes", *J. Chem. Phys.*, **120**, 5377-5386 (2004).
- (92) Yim, W.-L.; Byl, O.; Yates, J. T., Jr.; Johnson, J. K. "Dimensional Effects on the LO-TO Splitting in CF<sub>4</sub>: First-Principles and Infrared Absorption Studies", *Journal of the American Chemical Society*, **127**, 3198-3206 (2005).
- (93) Matranga, C.; Chen, L.; Bockrath, B.; Johnson, J. K. "Displacement of CO<sub>2</sub> by Xe in single-walled carbon nanotube bundles", *Physical Review B*, **70**, 165416 (2004).
- (94) Matranga, C.; Chen, L.; Smith, M.; Bittner, E.; Johnson, J. K.; Bockrath, B. "Trapped CO<sub>2</sub> in Carbon Nanotube Bundles", *The Journal of Physical Chemistry B*, **107**, 12930-12941 (2003).
- (95) Dai, B.; Sholl, D. S.; Johnson, J. K. "First-Principles Investigation of Adsorption and Dissociation of Hydrogen on Mg<sub>2</sub>Si Surfaces", *The Journal of Physical Chemistry C*, **111**, 6910-6916 (2007).
- (96) Alapati, S. V.; Johnson, J. K.; Sholl, D. S. "Stability analysis of doped materials for reversible hydrogen storage in destabilized metal hydrides", *Physical Review B*, **76**, 104108 (2007).
- (97) Dai, B.; Sholl, D. S.; Johnson, J. K. "First-Principles Study of Experimental and Hypothetical Mg(BH<sub>4</sub>)<sub>2</sub> Crystal Structures", *The Journal of Physical Chemistry C*, **112**, 4391-4395 (2008).
- (98) Alapati, S. V.; Johnson, J. K.; Sholl, D. S. "Large-scale screening of metal hydride mixtures for high-capacity hydrogen storage from first-principles calculations", *J. Phys. Chem. C*, **112**, 5258-5262 (2008).
- (99) Dai, B.; Rankin, R. B.; Johnson, J. K.; Allendorf, M. D.; Sholl, D. S.; Zarkevich, N. A.; Johnson, D. D. "Influence of Surface Reactions on Complex Hydride Reversibility", *The Journal of Physical Chemistry C*, **112**, 18270-18279 (2008).
- (100) Kim, K. C.; Dai, B.; Johnson, J. K.; Sholl, D. S. "Assessing nanoparticle size effects on metal hydride thermodynamics using the Wulff construction", *Nanotechnology*, **20**, 204001 (2009).
- (101) Kulkarni, A. D.; Wang, L.-L.; Johnson, D. D.; Sholl, D. S.; Johnson, J. K. "First-Principles Characterization of Amorphous Phases of MB<sub>12</sub>H<sub>12</sub>, M = Mg, Ca", *The Journal of Physical Chemistry C*, **114**, 14601-14605 (2010).
- (102) Kim, K. C.; Kulkarni, A. D.; Johnson, J. K.; Sholl, D. S. "Examining the robustness of first-principles calculations for metal hydride reaction thermodynamics by detection of metastable reaction pathways", *Physical Chemistry Chemical Physics*, **13**, 21520-21529 (2011).
- (103) Kim, K. C.; Kulkarni, A. D.; Johnson, J. K.; Sholl, D. S. "Large-scale screening of promising metal hydrides for hydrogen storage system from first-principles calculations based on equilibrium reaction thermodynamics", *PhysChemChemPhys*, **13**, 7218-7229 (2011).
- (104) Zhang, B.; Duan, Y.; Johnson, K. "Density functional theory study of CO<sub>2</sub> capture with transition metal oxides and hydroxides", *The Journal of Chemical Physics*, **136**, 064516-064513 (2012).
- (105) Duan, Y.; Zhang, B.; Sorescu, D. C.; Johnson, J. K.; Majzoub, E. H.; Luebke, D. R. "Density functional theory studies on the electronic, structural, phonon dynamical and thermo-stability properties of bicarbonates MHCO<sub>3</sub>, M = Li, Na, K", *Journal of Physics: Condensed Matter*, **24**, 325501 (2012).
- (106) Eckert, F.; Klamt, A. "Fast solvent screening via quantum chemistry: COSMO-RS approach", *Aiche Journal*, **48**, 369-385 (2002).
- (107) Klamt, A.; Eckert, F. "COSMO-RS: a novel and efficient method for the a priori prediction of thermophysical data of liquids (vol 172, pg 43, 2000)", *Fluid Phase Equilibria*, **205**, 357-357 (2003).

- (108) Miller, M. B.; Chen, D.-L.; Luebke, D. R.; Johnson, J. K.; Enick, R. M. "Critical Assessment of CO<sub>2</sub> Solubility in Volatile Solvents at 298.15 K", *Journal of Chemical and Engineering Data*, **56**, 1565-1572 (2011).
- (109) Miller, M. B.; Chen, D.-L.; Xie, H.-B.; Luebke, D. R.; Johnson, J. K.; Enick, R. M. "Solubility of CO<sub>2</sub> in CO<sub>2</sub>-philic oligomers; COSMOtherm predictions and experimental results", *Fluid Phase Equilibria*, **287**, 26-32 (2009).
- (110) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Wallingford CT, 2009.
- (111) Diep, P.; Jordan, K. D.; Johnson, J. K.; Beckman, E. J. "CO<sub>2</sub>-Fluorocarbon and CO<sub>2</sub>-Hydrocarbon Interactions from First-Principles Calculations", *The Journal of Physical Chemistry A*, **102**, 2231-2236 (1998).
- (112) Grimme, S. "Semiempirical GGA-type density functional constructed with a long-range dispersion correction", *Journal of Computational Chemistry*, **27**, 1787-1799 (2006).
- (113) Tkatchenko, A.; Scheffler, M. "Accurate Molecular Van Der Waals Interactions from Ground-State Electron Density and Free-Atom Reference Data", *Phys. Rev. Lett.*, **102**, 073005 (2009).
- (114) Dion, M.; Rydberg, H.; Schroder, E.; Langreth, D. C.; Lundqvist, B. I. "Van der Waals density functional for general geometries", *Physical Review Letters*, **92** (2004).
- (115) Dion, M.; Rydberg, H.; Schroder, E.; Langreth, D. C.; Lundqvist, B. I. "Van der waals density functional for general geometries (vol 92, art no 246401, 2004)", *Physical Review Letters*, **95** (2005).
- (116) Lee, K.; Kelkkanen, A. K.; Berland, K.; Andersson, S.; Langreth, D. C.; Schröder, E.; Lundqvist, B. I.; Hyldgaard, P. "Evaluation of a density functional with account of van der Waals forces using experimental data of H<sub>2</sub> physisorption on Cu(111)", *Phys. Rev. B*, **84**, 193408 (2011).
- (117) Lee, K.; Murray, É. D.; Kong, L.; Lundqvist, B. I.; Langreth, D. C. "Higher-accuracy van der Waals density functional", *Phys. Rev. B*, **82**, 081101 (2010).
- (118) Dion, M.; Rydberg, H.; Schröder, E.; Langreth, D. C.; Lundqvist, B. I. "Van der Waals Density Functional for General Geometries", *Phys. Rev. Lett.*, **92**, 246401 (2004).
- (119) Lewis, J. P.; Jelinek, P.; Ortega, J.; Demkov, A. A.; Trabada, D. G.; Haycock, B.; Wang, H.; Adams, G.; Tomfohr, J. K.; Abad, E.; Drabold, D. A. "Advances and applications in the FIREBALL ab initio tight-binding molecular-dynamics formalism", *Phys. Status Solidi B-Basic Solid State Phys.*, **248**, 1989-2007 (2011).
- (120) Vande Vondele, J.; Krack, M.; Mohamed, F.; Parrinello, M.; Chassaing, T.; Hutter, J. "Quickstep: Fast and accurate density functional calculations using a mixed Gaussian and plane waves approach", *Computer Physics Communications*, **167**, 103-128 (2005).
- (121) Kresse, G.; Furthmüller, J. "Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set", *Physical Review B*, **54**, 11169-11186 (1996).
- (122) Kresse, G.; Furthmüller, J. "Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set", *Computational Materials Science*, **6**, 15-50 (1996).
- (123) Kresse, G.; Hafner, J. "Ab initio molecular dynamics for liquid metals", *Physical Review B*, **47**, 558-561 (1993).



- (124) Kumar, S.; Bouzida, D.; Swendsen, R. H.; Kollman, P. A.; Rosenberg, J. M. "The Weighted Histogram Analysis Method for Free-Energy Calculations on Biomolecules .1. The Method", *J. Comput. Chem.*, **13**, 1011-1021 (1992).
- (125) Souaille, M.; Roux, B. "Extension to the weighted histogram analysis method: combining umbrella sampling with free energy calculations", *Comput. Phys. Commun.*, **135**, 40-57 (2001).
- (126) Liu, J.; Keskin, S.; Sholl, D. S.; Johnson, J. K. "Molecular Simulations and Theoretical Predictions for Adsorption and Diffusion of CH<sub>4</sub>/H<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> Mixtures in ZIFs", *The Journal of Physical Chemistry C*, **115**, 12560-12566 (2011).
- (127) LaBrosse, M. R.; Johnson, J. K. "Defect and Nondefect Interstitial Channel Availability in Carbon Nanotube Bundles: Comparison of Modeling with Experiments", *The Journal of Physical Chemistry C*, **114**, 7602-7610 (2010).
- (128) Liu, J.; Johnson, J. K. "Prediction of CH<sub>4</sub>/H<sub>2</sub> Mixture Selectivity in Zn(tbip) from Computer Simulations", *J Low Temp Phys*, **157**, 268-276 (2009).
- (129) Rankin, R. B.; Liu, J.; Kulkarni, A. D.; Johnson, J. K. "Adsorption and Diffusion of Light Gases in ZIF-68 and ZIF-70: A Simulation Study", *The Journal of Physical Chemistry C*, **113**, 16906-16914 (2009).
- (130) Keskin, S.; Liu, J.; Johnson, J. K.; Sholl, D. S. "Atomically detailed models of gas mixture diffusion through CuBTC membranes", *Microporous and Mesoporous Materials*, **125**, 101-106 (2009).
- (131) Liu, J.; Rankin, R. B.; Karl Johnson, J. "The importance of charge–quadrupole interactions for H<sub>2</sub> adsorption and diffusion in CuBTC", *Molecular Simulation*, **35**, 60-69 (2009).
- (132) Keskin, S.; Liu, J.; Rankin, R. B.; Johnson, J. K.; Sholl, D. S. "Progress, Opportunities, and Challenges for Applying Atomically Detailed Modeling to Molecular Adsorption and Transport in Metal–Organic Framework Materials", *Industrial & Engineering Chemistry Research*, **48**, 2355-2371 (2008).
- (133) LaBrosse, M. R.; Shi, W.; Johnson, J. K. "Adsorption of Gases in Carbon Nanotubes: Are Defect Interstitial Sites Important?", *Langmuir*, **24**, 9430-9439 (2008).
- (134) Keskin, S.; Liu, J.; Johnson, J. K.; Sholl, D. S. "Testing the Accuracy of Correlations for Multicomponent Mass Transport of Adsorbed Gases in Metal–Organic Frameworks: Diffusion of H<sub>2</sub>/CH<sub>4</sub> Mixtures in CuBTC", *Langmuir*, **24**, 8254-8261 (2008).
- (135) Chen, H.; Johnson, J. K.; Sholl, D. S. "Transport Diffusion of Gases Is Rapid in Flexible Carbon Nanotubes", *The Journal of Physical Chemistry B*, **110**, 1971-1975 (2006).
- (136) Garberoglio, G.; DeKlaven, M. M.; Johnson, J. K. "Quantum Sieving in Single-Walled Carbon Nanotubes: Effect of Interaction Potential and Rotational–Translational Coupling", *The Journal of Physical Chemistry B*, **110**, 1733-1741 (2006).
- (137) Skoulidas, A. I.; Sholl, D. S.; Johnson, J. K. "Adsorption and diffusion of carbon dioxide and nitrogen through single-walled carbon nanotube membranes", *The Journal of Chemical Physics*, **124**, 054708-054707 (2006).
- (138) Garberoglio, G.; Skoulidas, A. I.; Johnson, J. K. "Adsorption of Gases in Metal Organic Materials: Comparison of Simulations and Experiments", *The Journal of Physical Chemistry B*, **109**, 13094-13103 (2005).
- (139) Chen, L.; Johnson, J. K. "Formation of Odd-Numbered Clusters of CO<sub>2</sub> Adsorbed on Nanotube Bundles", *Physical Review Letters*, **94**, 125701 (2005).
- (140) Shi, W.; Johnson, J. K. "Gas Adsorption on Heterogeneous Single-Walled Carbon Nanotube Bundles", *Physical Review Letters*, **91**, 015504 (2003).
- (141) Wang, Q.; Johnson, J. K.; Broughton, J. Q. "Path integral grand canonical Monte Carlo", *The Journal of Chemical Physics*, **107**, 5108-5117 (1997).
- (142) Wang, Q.; Challa, S. R.; Sholl, D. S.; Johnson, J. K. "Quantum Sieving in Carbon Nanotubes and Zeolites", *Physical Review Letters*, **82**, 956-959 (1999).

- (143) Zhao, X.; Johnson, J. K.; Rasmussen, C. E. "Surface tension of quantum fluids from molecular simulations", *The Journal of Chemical Physics*, **120**, 8707-8715 (2004).
- (144) Garberoglio, G.; Johnson, J. K. "Hydrogen Isotope Separation in Carbon Nanotubes: Calculation of Coupled Rotational and Translational States at High Densities", *ACS Nano*, **4**, 1703-1715 (2010).
- (145) An, J.; Farha, O. K.; Hupp, J. T.; Pohl, E.; Yeh, J. I.; Rosi, N. L. "Metal-adeninate vertices for the construction of an exceptionally porous metal-organic framework", *Nature communications*, **3**, 604 (2012).
- (146) An, J.; Geib, S. J.; Rosi, N. L. "High and Selective CO<sub>2</sub> Uptake in a Cobalt Adeninate Metal-Organic Framework Exhibiting Pyrimidine- and Amino-Decorated Pores", *Journal of the American Chemical Society*, **132**, 38-39 (2010).
- (147) An, J.; Rosi, N. L. "Tuning MOF CO<sub>2</sub> Adsorption Properties via Cation Exchange", *Journal of the American Chemical Society*, **132**, 5578-5579 (2010).
- (148) An, J.; Shade, C. M.; Chengelis-Czegan, D. A.; Petoud, S. p.; Rosi, N. L. "Zinc-Adeninate Metal-Organic Framework for Aqueous Encapsulation and Sensitization of Near-infrared and Visible Emitting Lanthanide Cations", *Journal of the American Chemical Society*, **133**, 1220-1223 (2011).
- (149) An, J. Y.; Fiorella, R. P.; Geib, S. J.; Rosi, N. L. "Synthesis, Structure, Assembly, and Modulation of the CO<sub>2</sub> Adsorption Properties of a Zinc-Adeninate Macrocyclic", *Journal of the American Chemical Society*, **131**, 8401-8403 (2009).
- (150) An, J. Y.; Geib, S. J.; Rosi, N. L. "Cation-Triggered Drug Release from a Porous Zinc-Adeninate Metal-Organic Framework", *Journal of the American Chemical Society*, **131**, 8376-8377 (2009).
- (151) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. "Systematic design of pore size and functionality in isorecticular MOFs and their application in methane storage", *Science*, **295**, 469-472 (2002).
- (152) Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. "Hydrogen storage in microporous metal-organic frameworks", *Science*, **300**, 1127-1129 (2003).
- (153) Rosi, N. L.; Eddaoudi, M.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. "Infinite secondary building units and forbidden catenation in metal-organic frameworks", *Angewandte Chemie-International Edition*, **41**, 284-+ (2001).
- (154) Rosi, N. L.; Eddaoudi, M.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. "Advances in the chemistry of metal-organic frameworks", *Crystengcomm*, 401-404 (2002).
- (155) Rosi, N. L.; Kim, J.; Eddaoudi, M.; Chen, B. L.; O'Keeffe, M.; Yaghi, O. M. "Rod packings and metal-organic frameworks constructed from rod-shaped secondary building units", *Journal of the American Chemical Society*, **127**, 1504-1518 (2005).
- (156) White, K. A.; Chengelis, D. A.; Gogick, K. A.; Stehman, J.; Rosi, N. L.; Petoud, S. "Near-Infrared Luminescent Lanthanide MOF Barcodes", *Journal of the American Chemical Society*, **131**, 18069-18071 (2009).
- (157) White, K. A.; Chengelis, D. A.; Zeller, M.; Geib, S. J.; Szakos, J.; Petoud, S.; Rosi, N. L. "Near-infrared emitting ytterbium metal-organic frameworks with tunable excitation properties", *Chemical Communications*, 4506-4508 (2009).
- (158) Liu, C.; Li, T.; Rosi, N. L. "Strain-Promoted "Click" Modification of a Mesoporous Metal-Organic Framework", *Journal of the American Chemical Society*, **134**, 18886-18888 (2012).
- (159) Imaz, I.; Rubio-Martinez, M.; An, J.; Sole-Font, I.; Rosi, N. L.; Maspoch, D. "Metal-biomolecule frameworks (MBioFs)", *Chemical Communications*, **47**, 7287-7302 (2011).
- (160) Tanabe, K. K.; Allen, C. A.; Cohen, S. M. "Photochemical activation of a metal-organic framework to reveal functionality", *Angew Chem Int Ed Engl*, **49**, 9730-9733 (2010).

- (161) Tanabe, K. K.; Cohen, S. M. "Postsynthetic modification of metal-organic frameworks--a progress report", *Chemical Society reviews*, **40**, 498-519 (2011).
- (162) Wang, Z.; Cohen, S. M. "Tandem modification of metal-organic frameworks by a postsynthetic approach", *Angew Chem Int Ed Engl*, **47**, 4699-4702 (2008).
- (163) Wang, Z. Q.; Cohen, S. M. "Postsynthetic modification of metal-organic frameworks", *Chemical Society reviews*, **38**, 1315-1329 (2009).
- (164) Wang, Z. Q.; Tanabe, K. K.; Cohen, S. M. "Accessing Postsynthetic Modification in a Series of Metal-Organic Frameworks and the Influence of Framework Topology on Reactivity", *Inorg. Chem.*, **48**, 296-306 (2009).
- (165) Gadzikwa, T.; Farha, O. K.; Malliakas, C. D.; Kanatzidis, M. G.; Hupp, J. T.; Nguyen, S. T. "Selective Bifunctional Modification of a Non-catenated Metal-Organic Framework Material via "Click" Chemistry", *Journal of the American Chemical Society*, **131**, 13613-13615 (2009).
- (166) Lun, D. J.; Waterhouse, G. I. N.; Telfer, S. G. "A General Thermolabile Protecting Group Strategy for Organocatalytic Metal-Organic Frameworks", *Journal of the American Chemical Society*, **133**, 5806-5809 (2011).
- (167) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. "A homochiral metal-organic porous material for enantioselective separation and catalysis", *Nature*, **404**, 982-986 (2000).
- (168) Li, T.; Kozlowski, M. T.; Doud, E. A.; Blakely, M. N.; Rosi, N. L. "Stepwise Ligand Exchange for the Preparation of a Family of Mesoporous MOFs", *J. Am. Chem. Soc.*, submitted (2013).
- (169) Kim, M.; Cahill, J. F.; Fei, H.; Prather, K. A.; Cohen, S. M. "Postsynthetic Ligand and Cation Exchange in Robust Metal-Organic Frameworks", *Journal of the American Chemical Society*, **134**, 18082-18088 (2012).
- (170) Kim, M.; Cahill, J. F.; Su, Y.; Prather, K. A.; Cohen, S. M. "Postsynthetic ligand exchange as a route to functionalization of 'inert' metal-organic frameworks", *Chemical Science*, **3**, 126-130 (2012).
- (171) Takaishi, S.; DeMarco, E. J.; Pellin, M. J.; Farha, O. K.; Hupp, J. T. "Solvent-assisted linker exchange (SALE) and post-assembly metallation in porphyrinic metal-organic framework materials", *Chemical Science*, **4**, 1509-1513 (2013).
- (172) Bres, E. F.; Ferlay, S.; Dechambenoit, P.; Leroux, H.; Hosseini, M. W.; Reyntjens, S. "Investigations on crystalline interface within a molecular composite crystal by microscopic techniques", *Journal of Materials Chemistry*, **17**, 1559-1562 (2007).
- (173) Ferlay, S.; Hosseini, M. W. "Crystalline molecular alloys", *Chemical Communications*, 788-789 (2004).
- (174) Furukawa, S.; Hirai, K.; Nakagawa, K.; Takashima, Y.; Matsuda, R.; Tsuruoka, T.; Kondo, M.; Haruki, R.; Tanaka, D.; Sakamoto, H.; Shimomura, S.; Sakata, O.; Kitagawa, S. "Heterogeneously Hybridized Porous Coordination Polymer Crystals: Fabrication of Heterometallic Core-Shell Single Crystals with an In-Plane Rotational Epitaxial Relationship", *Angewandte Chemie-International Edition*, **48**, 1766-1770 (2009).
- (175) Furukawa, S.; Hirai, K.; Takashima, Y.; Nakagawa, K.; Kondo, M.; Tsuruoka, T.; Sakata, O.; Kitagawa, S. "A block PCP crystal: anisotropic hybridization of porous coordination polymers by face-selective epitaxial growth", *Chemical Communications*, 5097-5099 (2009).
- (176) Hirai, K.; Furukawa, S.; Kondo, M.; Meilikhov, M.; Sakata, Y.; Sakata, O.; Kitagawa, S. "Targeted functionalisation of a hierarchically-structured porous coordination polymer crystal enhances its entire function", *Chemical Communications*, **48**, 6472-6474 (2012).
- (177) Hirai, K.; Furukawa, S.; Kondo, M.; Uehara, H.; Sakata, O.; Kitagawa, S. "Sequential Functionalization of Porous Coordination Polymer Crystals", *Angewandte Chemie-International Edition*, **50**, 8057-8061 (2011).
- (178) Koh, K.; Wong-Foy, A. G.; Matzger, A. J. "MOF@MOF: microporous core-shell architectures", *Chemical Communications*, 6162-6164 (2009).

- (179) MacDonald, J. C.; Dorrestein, P. C.; Pilley, M. M.; Foote, M. M.; Lundburg, J. L.; Henning, R. W.; Schultz, A. J.; Manson, J. L. "Design of layered crystalline materials using coordination chemistry and hydrogen bonds", *Journal of the American Chemical Society*, **122**, 11692-11702 (2000).
- (180) Shekhah, O.; Hirai, K.; Wang, H.; Uehara, H.; Kondo, M.; Diring, S.; Zacher, D.; Fischer, R. A.; Sakata, O.; Kitagawa, S.; Furukawa, S.; Woll, C. "MOF-on-MOF heteroepitaxy: perfectly oriented Zn-2(ndc)(2)(dabco) (n) grown on Cu-2(ndc)(2)(dabco) (n) thin films", *Dalton Transactions*, **40**, 4954-4958 (2011).
- (181) Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K. P. "A New Zirconium Inorganic Building Brick Forming Metal Organic Frameworks with Exceptional Stability", *Journal of the American Chemical Society*, **130**, 13850-13851 (2008).
- (182) Cmarik, G. E.; Kim, M.; Cohen, S. M.; Walton, K. S. "Tuning the adsorption properties of UiO-66 via ligand functionalization", *Langmuir*, **28**, 15606-15613 (2012).
- (183) Kandiah, M.; Nilsen, M. H.; Usseglio, S.; Jakobsen, S.; Olsbye, U.; Tilset, M.; Larabi, C.; Quadrelli, E. A.; Bonino, F.; Lillerud, K. P. "Synthesis and Stability of Tagged UiO-66 Zr-MOFs", *Chemistry of Materials*, **22**, 6632-6640 (2010).
- (184) Garibay, S. J.; Cohen, S. M. "Isorecticular synthesis and modification of frameworks with the UiO-66 topology", *Chemical Communications*, **46**, 7700-7702 (2010).
- (185) DeCoste, J. B.; Peterson, G. W.; Jasuja, H.; Glover, T. G.; Huang, Y.-g.; Walton, K. S. "Stability and degradation mechanisms of metal-organic frameworks containing the Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> secondary building unit", *Journal of Materials Chemistry A*, **1**, 5642-5650 (2013).
- (186) Chun, H.; Dybtsev, D. N.; Kim, H.; Kim, K. "Synthesis, X-ray Crystal Structures, and Gas Sorption Properties of Pillared Square Grid Nets Based on Paddle-Wheel Motifs: Implications for Hydrogen Storage in Porous Materials", *Chemistry – A European Journal*, **11**, 3521-3529 (2005).
- (187) Kleist, W.; Jutz, F.; Maciejewski, M.; Baiker, A. "Mixed-Linker Metal-Organic Frameworks as Catalysts for the Synthesis of Propylene Carbonate from Propylene Oxide and CO<sub>2</sub>", *European Journal of Inorganic Chemistry*, **2009**, 3552-3561 (2009).
- (188) Deng, H.; Doonan, C. J.; Furukawa, H.; Ferreira, R. B.; Towne, J.; Knobler, C. B.; Wang, B.; Yaghi, O. M. "Multiple Functional Groups of Varying Ratios in Metal-Organic Frameworks", *Science*, **327**, 846-850 (2010).
- (189) Fukushima, T.; Horike, S.; Inubushi, Y.; Nakagawa, K.; Kubota, Y.; Takata, M.; Kitagawa, S. "Solid Solutions of Soft Porous Coordination Polymers: Fine-Tuning of Gas Adsorption Properties", *Angewandte Chemie International Edition*, **49**, 4820-4824 (2010).
- (190) Jasuja, H.; Zang, J.; Sholl, D. S.; Walton, K. S. "Rational Tuning of Water Vapor and CO<sub>2</sub> Adsorption in Highly Stable Zr-Based MOFs", *J. Phys. Chem. C*, **116**, 23526-23532 (2012).
- (191) Nguyen, J. G.; Cohen, S. M. "Moisture-Resistant and Superhydrophobic Metal–Organic Frameworks Obtained via Postsynthetic Modification", *Journal of the American Chemical Society*, **132**, 4560-4561 (2010).
- (192) Schoenecker, P. M.; Carson, C. G.; Jasuja, H.; Flemming, C. J. J.; Walton, K. S. "Effect of Water Adsorption on Retention of Structure and Surface Area of Metal–Organic Frameworks", *Industrial & Engineering Chemistry Research*, **51**, 6513-6519 (2012).