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Enhanced CO₂ Capture in Metal-Organic and Covalent-Organic Frameworks

By

Robinson W Flaig

A dissertation submitted in partial satisfaction of the

requirements for the degree of

Doctor of Philosophy

in

Chemistry

in the

Graduate Division

of the

University of California, Berkeley.

Committee in charge:

Professor Omar M. Yaghi, Chair

Professor John Arnold

Professor Alessandra Lanzara

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Robinson W Flaig

Abstract

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Doctor of Philosophy in Chemistry

University of California, Berkeley

Professor Omar Yaghi, Chair

Global atmospheric carbon dioxide (CO₂) levels are rising. It is widely acknowledged by the scientific community that this phenomenon is contributing to climate change. Therefore, the need for effective CO₂ capture from both point sources (power plants, etc.) and direct air capture is urgent. Despite years of investigation, the development of scalable, cost-effective, and energy-efficient, carbon capture and sequestration (CCS) technologies remains an outstanding challenge. The most widely-employed technique to date is the use of aqueous monoethanolamine (MEA) solutions at CO₂ point sources. Flue gas from point sources is pumped through these solutions which capture the CO₂ by forming chemical bonds (e.g. ammonium carbamate formation) between the gas and the amine moieties in solution. Although a large amount of CO₂ can be captured using this technology, it is energetically inefficient. With one of the highest specific heat capacities among common solvents, water requires a significant amount of energy to bring to temperatures at which the MEA molecules release the previously-captured CO₂. The requisite energy is often produced at similar CO₂-producing point sources, limiting the effectiveness of this technique when employed.

For this reason and others, (e.g. instability of aqueous MEA solutions to other contaminants present in flue gas) many are considering alternative methods of CO₂ capture from point sources. One particularly potent method involves the use of amine-functionalized porous adsorbents in an analogous fashion to MEA solutions, as these materials frequently exhibit lower heat capacities, higher selectivities, and greater chemical tunability compared to their liquid-based counterparts.

Reticular chemistry, the process of assembling judiciously designed rigid molecular building blocks into predetermined ordered structures (networks) which are held together by strong bonds, has been widely applied to the synthesis of such porous adsorbents, most notably Metal-Organic Frameworks (MOFs) and Covalent Organic Frameworks (COFs). Much of the insight on the fundamental science which set the foundation for these materials as a potential next-generation of CO₂ adsorbents was

gleaned through development of many MOFs which demonstrate some of the highest CO₂ uptake capacities of any porous material. Recent work has focused on elucidation of MOF systems with practical CO₂ capture applications.

Recently, the Yaghi group designed a new MOF, IRMOF-74-III-CH₂NH₂ that selectively captures CO₂ in the presence of water under flue gas conditions. I followed up on this study with an augmented material, IRMOF-74-III-(CH₂NH₂)₂ which exhibited a 133% increase in CO₂ uptake in the pressure regime of interest to this application (e.g. <150 mbar). Upon further investigation, it was concluded that this drastic increase in CO₂ uptake was caused not only by the increase in the amine population in the framework, but also by a new chemical capture mechanism, the formation of elusive, relatively unstable, carbamic acid species upon reaction between framework-based amines and CO₂ under dry (<10% relative humidity) conditions. Interestingly, I discovered that CO₂ captured as carbamic acid moieties is removed with more facility than CO₂ captured as ammonium carbamates. The understanding gleaned by these fundamental studies has necessitated the assessment of the applicability of such systems, while exploring the potential of additional, potentially more promising, systems.

Currently the use of COFs for CO₂ capture is under investigation. Although only few have examined the behavior of COFs in such a manner, the potential advantages are quite apparent. Consisting of light atoms with high chemical and moisture stability, COFs have the potential to achieve high gravimetric uptake of CO₂ with enhanced cyclability under humid, flue-gas analogous, conditions. Specifically, I synthesized a COF analogue (COF-81) of IRMOF-74-III-(CH₂NH₂)₂. This material has already exhibited modest CO₂ adsorption capacity and formation of carbamic acid species under both dry and humid conditions. These observations warrant continued study of the material under flue gas conditions as the mechanistic tuning of the CO₂ capture mechanism would allow this highly stable material to achieve high CO₂ adsorption capacity accompanied by decreased regeneration energies.

Additionally, I developed a new, post-synthetically modified MOF material, MOF-808-Glycine. The parent material, MOF-808-P can be synthesized on gram scales and rendered CO₂-philic by incorporation of an economical, abundant amino acid, glycine. Herein, I demonstrate that the framework remains crystalline and porous after each post-synthetic modification and that MOF-808 can be loaded with high quantities of glycine. Furthermore, I show that MOF-808-Glycine has significantly improved CO₂ adsorption properties compared to MOF-808-P, and that the material chemisorbs CO₂, forming a mixture of carbamic acid and ammonium carbamate under dry (0% RH) conditions, and ammonium bicarbonate under humid (95%) conditions. This work represents a significant step toward real-world, large scale CO₂ adsorption using MOFs.

Dedication

This dissertation is dedicated to Erin Sullivan and the late Robin Wiessinger Jones.

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To my fiancé, Ms. Erin Sullivan, thank you for teaching me so many things that I could never learn in a classroom or a laboratory. Every day with you is a new adventure and I am so proud of you for all you have and have yet to accomplish. Of everything that happened during my time at UC Berkeley, meeting and falling in love with you was the most important event. I am overjoyed that I will spend the rest of my life with you.

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Chapter 1: Carbon Capture Using Metal-Organic Frameworks

Portions of this chapter have been adapted from:

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1.1 Introduction

Energy demands of the global society are being met largely by combustion of fossil fuels including coal, petroleum, and natural gas. A major greenhouse gas (GHG), carbon dioxide (CO_2), is a key by-product of such combustion. The immense quantity of CO_2 emissions has resulted in serious environmental issues, such as global warming, ocean acidification, extreme weather, and species extinction.^{1,2} Since the early 19th century, a steep and continuous increase has been observed in atmospheric CO_2 concentrations from approximately 280 ppm in the early 1800s to over 400 ppm in 2018. With little to no mitigative action, the Intergovernmental Panel on Climate Change (IPCC) has predicted that atmospheric CO_2 concentrations could reach 950 ppm by 2100.³⁻⁵ Elevated atmospheric CO_2 levels serve to directly increase the global mean temperature (around 1.9 °C at atmospheric CO_2 concentrations of 570 ppm) by absorbing outgoing longwave radiation (i.e. the greenhouse effect).³ Therefore, decreasing emissions and mitigating atmospheric CO_2 concentrations are imperative tasks that require drastic, immediate attention. With the understanding that fossil fuels will remain a major source of energy for the foreseeable future, the most straightforward strategy to reduce anthropogenic CO_2 emissions lies in removing CO_2 from point sources, such as the flue gas from fossil-fuel burning power plants. This can be accomplished using suitable carbon capture and storage (CCS) technologies. Key drawbacks in such technologies lie in the energy consumption associated with separation, purification, compression, transportation, and storage processes.⁶ This consumption is likely to be accompanied by further CO_2 emission, and thus will not adequately address the issue. Moreover, various adsorbents have been developed in order to capture and store CO_2 , but their high regeneration temperatures and/or limited CO_2 adsorption capacities still hinder the development of CCS technologies.^{2,6,7}

In the past decades, several classes of materials, including ionic liquids (ILs), zeolites, porous carbons, porous organic polymers, covalent organic frameworks (COFs) and metal-organic frameworks (MOFs), have been developed for CO_2 capture applications.⁸⁻¹⁶ In particular, MOFs signify a relatively new class of crystalline porous materials constructed from multimetallic units called secondary building units (SBUs) and organic linkers.¹⁷⁻²¹ By designing and functionalizing SBUs, linkers and pore environments, MOFs' physical and chemical properties can be finely tuned, making them promising materials for a variety of applications, such as gas storage and separation, heterogeneous catalysis, sensing, drug delivery, to mention a few.^{14-19,22-42} With respect to CO_2 capture, MOFs serve as promising adsorbents because of their unique advantages: 1) Predictable, functionalizable structures; it is possible to predict the structures of many MOFs and the structural designability and chemical tunability of the materials allow for incorporation of different types of accessible capture sites. 2) Hybrid structures; MOFs are highly compatible with other materials and can serve as precursors and/or templates to afford MOF composites or MOF derivatives with extraordinary physical and chemical properties. 3) The well-defined and tailorable structures of MOFs greatly facilitate the

understanding of structure-property relationships in MOF-based adsorbents. All of these attributes make MOFs ideally suited for CO₂ capture applications.

1.2 MOFs for CO₂ Capture

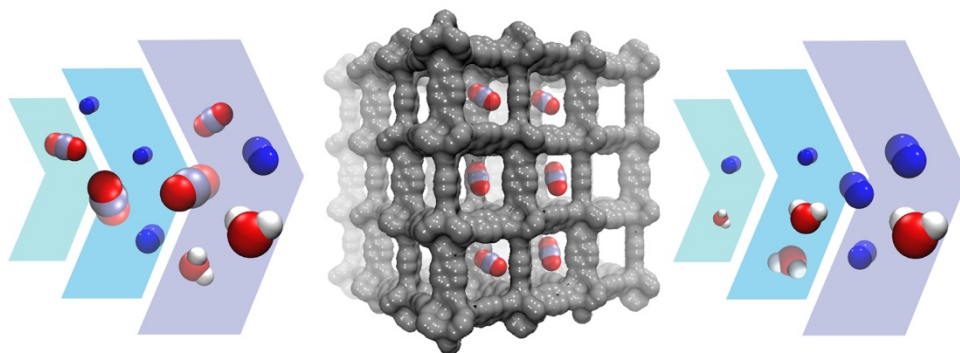


Figure 1.1 An illustration of a generic porous, framework material (center). The material is shown to selectively capture CO₂ from a mixed gas stream comprised of nitrogen, water, and CO₂ that would typically result from combustion of fossil fuels. Color code: framework material, grey; nitrogen, blue molecules; water, red and white molecules; and CO₂, grey and red molecules.

Since their inception over 20 years ago^{43,44}, MOFs have been targeted for CO₂ adsorption and capture applications due to their high porosity and chemical tunability.⁴⁵ To date, many reports focus on the study of CO₂ capture and increasing the capacity in MOFs. Generally, the interaction(s) between the framework and CO₂ adsorbate molecules play a critical role, as increasing the strength of such interactions augments the material's CO₂ uptake capacity, especially at low loading pressure. The methods employed to increase these interaction strengths stem from tailoring the frameworks' chemical and physical properties. This relies on the ability to alter the intrinsic properties of MOFs based on judicious design and synthesis of the framework via *de novo* process or by post-synthetic modification. In each case, the goal is to leverage MOFs' chemical tunabilities and compatibilities to adjust the affinity of the framework for CO₂ molecules. Additionally, post-synthetic modification has been widely applied recently as a means of achieving this adjustment with a high degree of precision. Specifically, MOFs are applied as selective CO₂ adsorbents that can capture CO₂ from mixed gas streams, especially post-combustion streams consisting of N₂, H₂O, and CO₂ (Figure 1.1). In this chapter, I will briefly explain each strategy and provide some examples of the employment of each.

CO₂ Binding Sites within MOFs

Traditional adsorbent materials including zeolites, silicas, polymers, activated carbons, take up CO₂ in a physisorptive manner through the use of weak interactions between CO₂ and the pore. Although MOFs also capture CO₂ by physisorption, their

ultrahigh surface areas give much higher uptake capacities compared to other materials. In addition, the advantage of being able to design MOFs that possess features such as open metal sites (OMSs) and Lewis basic sites (LBSs), provides for a better handle on their tailorability. Specifically, the interaction of CO₂ with these sites tends to result in excellent CO₂ adsorption capacity and/or preferential CO₂ adsorption over other gas molecules, such as N₂, CH₄, and H₂O. Needless to say, MOFs can employ multiple interactions in a single structure to achieve extraordinary CO₂ adsorption.

Open Metal Sites (OMSs)

Accessing OMSs on MOFs' multimetallic secondary building units (SBUs) is one of the most widely used strategies to improve their CO₂ capture properties. In general, OMSs are generated by treating a MOF with coordinated terminal ligands such as water, *N,N*-dimethyl formamide (DMF), and/or methanol, on the SBUs, under heat and/or vacuum to remove such ligands with retention of the overall structure. This often results in improved porosity in the activated material. These OMSs commonly serve as Lewis acid sites (LASs) that have been shown to coordinate CO₂. Such behavior at Lewis acidic OMSs endows many MOFs with high CO₂ affinities, especially at low adsorbate partial pressures.

The concept of designing OMSs and its implementation was reported in 1998 and 2000.^{46,47} In 2005, the CO₂ uptake of HKUST-1, having OMSs, was found to be about 10 mmol g⁻¹ at 42 bar and ambient temperature.⁴⁸ In HKUST-1, the room-temperature CO₂ adsorption isotherm appears as a typical Type I isotherm in which the most gas is adsorbed at low pressures, leading to a “knee” shaped behavior, indicative of high affinity of this MOF for CO₂ at low partial pressures. These conditions are interesting with respect to practical CO₂ adsorption from gas streams as the material will have large CO₂ capture working capacity. Following this work, a wide variety of MOFs bearing OMSs have been applied as CO₂ absorbents, including NU-1000, MIL-101, and M-MOF-74.^{49–68} Among these, the M-MOF-74 (M = Mg²⁺, Ni²⁺, Co²⁺, Zn²⁺) isorecticular series, composed of an array of one-dimensional hexagonal channels with OMSs at the SBUs, has become one of the most well-studied sets of MOFs for CO₂ capture due to their extraordinary CO₂ uptake capacities at low pressures.^{52,69} More importantly, the CO₂ adsorption of this series can be tuned based on the metal from which the MOF is constructed. The CO₂ uptake of Mg-MOF-74 (5.4 mmol g⁻¹ at 0.1 atm) is 2–4 times higher than those of the other isorecticular M-MOF-74 compounds at the same CO₂ loading pressures.⁷⁰ The zero-coverage isosteric heats of CO₂ adsorption (*Q*_{st}) of the frameworks details important information regarding the affinity of frameworks for CO₂. Applying this analysis to the M-MOF-74 isorecticular series, one concludes that Mg-MOF-74 exhibits the highest CO₂ affinity (47 kJ mol⁻¹), whereas Zn-MOF-74, Ni-MOF-74 and Co-MOF-74 exhibit initial affinities of 26, 37, and 41 kJ mol⁻¹, respectively.⁷⁰ This high affinity for CO₂ in Mg-MOF-74 stems from the increased ionic character of the Mg–O bond that imparts stronger charge-quadrupole interactions between the Mg OMSs and CO₂.

To further understand the mechanism of CO₂ adsorption on MOFs' OMSs, density function theory (DFT) calculations, neutron powder diffraction experiments, infrared and Raman spectroscopy, and *in situ* solid-state ¹³C nuclear magnetic resonance (NMR) measurements were performed.^{69,71-73} Generally, CO₂ molecules interact with OMS in an end-on fashion through lone pair electron donation.⁶⁹ These fairly strong interactions only marginally alter the intramolecular angles of adsorbed CO₂. Additionally, DFT calculations suggest that CO₂ adsorption on the OMSs in these materials is still largely physisorptive.⁷¹ This not only reduces the energy penalty for adsorbent regeneration, a key consideration in CO₂ capture, but also accelerates the adsorptive kinetics in MOFs.

With these studies in mind, MOFs were evaluated for potential application in selective adsorption processes. For example, temperature swing post-combustion CO₂ adsorption was studied in MOF-177 and Mg-MOF-74.⁷⁴ While MOF-177 exhibits only poor to modest selectivity, Mg-MOF-74 was marked by tremendous selectivity with an ideal adsorbed solution theory (IAST) selectivity factor of 148.1 at a typical flue gas temperature (~50 °C). In fact, the CO₂ selectivity of Mg-MOF-74 was even greater than that of the previously most studied zeolite NaX (87.4) under the same conditions. The methods in this study were applied to five different MOFs, targeting pre-combustion CO₂ capture, namely the selective capture of CO₂ in the presence of H₂.⁷⁵ Mg-MOF-74 has the highest CO₂/H₂ selectivity (859 at 5 bar) measured from an 80:20 H₂/CO₂ mixture at 313 K because of the greater polarizability of CO₂ compared to H₂ and the high concentration of OMSs in the MOF pore.

Lewis Basic Sites (LBSs)

While the use of SBU-based OMSs for CO₂ capture lead to promising results with respect to adsorption capacity and selectivity, another important component of MOFs, the organic linkers, can also augment these properties. For instance, incorporation of organic linkers bearing LBSs into MOFs has been shown to greatly enhance their CO₂ binding affinities. This strategy was inspired by the outstanding CO₂ uptake capacities of aqueous amine solutions such as industrial solutions of monoethanolamine (MEA).^{76,77} As an attempt to include Lewis basic amines into a MOF, 2-aminoterephthalic acid (NH₂-H₂BDC), was utilized in the synthesis of IRMOF-3, a MOF isorecticular to MOF-5.⁴⁸ At 298 K, and over a wide pressure range (from 0 to 12.3 bar), IRMOF-3 exhibits a higher CO₂ uptake capacity (0-14.7 mmol g⁻¹) than MOF-5 (0-14.0 mmol g⁻¹). This study indicated that greater CO₂ affinities can be achieved by introducing LBSs on the organic linkers. Similar phenomena were also observed in many isorecticular MOFs, such as NH₂-MIL-53, NH₂-UiO-66, and NH₂-MIL-125.⁷⁸⁻⁸¹ It is important to note here that many aromatic amines that have been incorporated into MOFs do not necessarily capture CO₂ in the same chemisorptive manner as aqueous amine solutions, given that aromatic amines lack the nucleophilicity of the alkylamines in solution. Recently, several functionalized IRMOF-74-III compounds were synthesized in hopes of capturing CO₂ in the presence of water (Fig. 1.2).^{82,83} The linker-based amine functional groups of IRMOF-74-III-CH₂NH₂ endowed the material with the highest CO₂ uptake capacity (3.2 mmol g⁻¹ at 800 torr) of

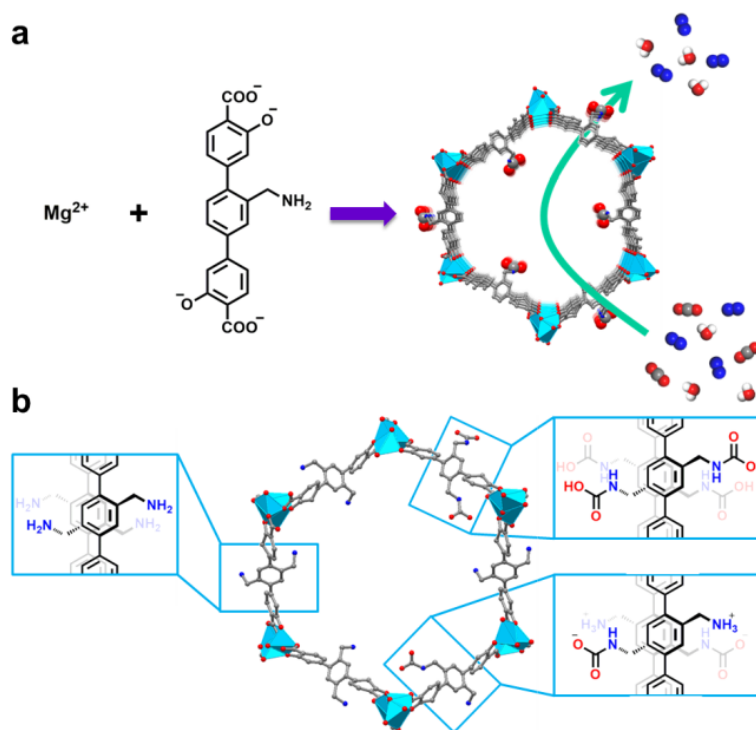


Figure 1.2 (a) Synthesis of IRMOF-74-III-CH₂NH₂ from Mg²⁺ and the amine-functionalized linker (2'-(aminomethyl)-3,3''-dioxido-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate) for selective, chemisorptive CO₂ capture from a CO₂/N₂/H₂O gas mixture. (b) View of modeled IRMOF-74-III-(CH₂NH₂)₂ structure down the crystallographic *c*-axis, depicting the three pore environments before (left pore wall) and after exposure to CO₂ under dry conditions to produce carbamic acids (upper right pore wall) and 95% relative humidity (RH) to give ammonium carbamates (bottom right pore wall). Color code: C, gray; O, red; N, blue; H, white; and Mg, cyan.

the series. In contrast to the aromatic amine cases detailed above, the alkylamines in IRMOF-74-III-CH₂NH₂ chemically bind CO₂, forming new, covalent species in the MOF. Solid-state cross-polarization magic angle spinning (CP-MAS) ¹³C NMR spectra indicated that the major chemisorption product in this material was a mixture of carbamic acid (RNHCOOH) and ammonium carbamate (RNHCOO⁻ + H₃NR). More importantly, since the CO₂ capture took place at the linker-based alkylamines instead of the OMSs, the influence of water was negligible with respect to the CO₂ adsorption performance of IRMOF-74-III-CH₂NH₂. Therefore, this MOF captured CO₂ with a high capacity and selectivity even under 65% relative humidity. Recently, this strategy has been improved by doubling the linker-based alkylamines in the framework, yielding IRMOF-74-III-(CH₂NH₂)₂.⁸² With two alkylamines per organic linker, the CO₂ adsorption capacity of the framework increased by more than 100% because the arrangement of the amines in the structure allowed for the formation of only carbamic acids under dry conditions. These carbamic acids are less stable and thus more easily removed, by vacuum or lower heat, than their ammonium carbamate counterparts which are formed when CO₂ is captured under humid conditions (Fig. 1.2b). Clearly, the strategy of amine-incorporation

onto MOF linkers can be improved to target particular chemisorption products with desirable properties for specific CO₂ capture applications.

Apart from amine-functionalized linkers, other nitrogenous linkers, including pyrimidines, triazines, and azoles, have also been utilized to synthesize MOFs bearing LBSs.^{84–98} In 2012, a new *rht*-type MOF, Cu-TDPAT, based on an LBS-rich hexacarboxylate ligand (H₆TDPAT) was reported.⁸⁵ Its CO₂ adsorption capacity (5.9 mmol g⁻¹ at 298 K and 1 atm, 10.1 mmol g⁻¹ at 273 K and 1 atm) and isosteric heat of adsorption (42 kJ mol⁻¹) were substantially higher than many previously reported *rht*-type MOFs. To investigate the interactions between Cu-TDPAT and CO₂, room-temperature IR spectroscopy was conducted after CO₂ loading showing the evolution of a distinct band at $\nu = 2335\text{ cm}^{-1}$ perhaps attributable to CO₂ adsorption at the LBSs.

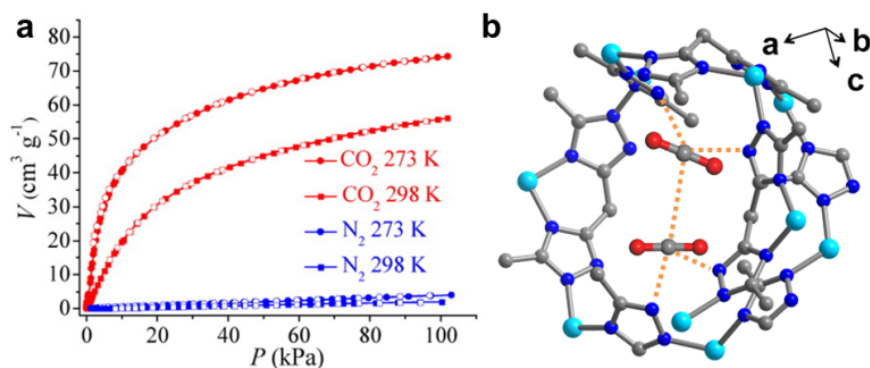


Figure 1.3 (a) CO₂ (red) and N₂ (blue) adsorption (solid) and desorption (open) isotherms at 273 K (circle) and 298 K (square) of MAF-23. (Reproduced with permission from ref. 96) (b) The perspective views of two CO₂ molecules adsorbed by the N···N claws of activated MAF-23. In this structure, four independent uncoordinated N atoms come from four different triazolate rings. Orange lines depict the interactions between two CO₂ molecules and the framework. H atoms are omitted for clarity. Color code: C, gray; N, blue; Zn, cyan; and O, red. Copyright 2008 American Chemical Society.

While LBS incorporation strategies are effective, MOF-CO₂ interactions remain mainly single site in nature. Reliance on such interactions can result in relative weak framework affinities for CO₂ or low reversibility.⁹⁶ As an alternative approach, MOFs can be designed such that their pores are decorated with multiple LBSs. The cooperation between these can endow the resultant MOFs with high CO₂ binding affinities, high selectivities, and reversible CO₂ adsorption. A flexible framework, MAF-23, was made from a chelating-bridging ligand (bis(5-methyl-1H-1,2,4-triazol-3-yl)methane, H₂btm)⁹⁶, where the available triazolate N-donors of the organic linker acted as CO₂ chelation sites. At 1 atm, MAF-23 exhibited a CO₂ uptake capacity of 3.3 and 2.5 mmol g⁻¹ at 273 and 298 K (Fig. 1.3a), with CO₂/N₂ selectivities calculated by Henry's law of 163 and 107 at 273 and 298 K, respectively. To elucidate the dynamic CO₂ adsorption behavior, the crystal structure of MAF-23 with different CO₂ loading levels was determined using single-crystal X-ray diffraction. From the data, two independent CO₂ molecules could be observed, located near the chelation sites of the organic linkers (Fig.1.3b).

The quantity and accessibility of MOFs' LBSs also play vital roles in the tunability of CO₂ uptake capacities in MOFs. A series of isorecticular copper-based MOFs, ZJNU-43, ZJNU-44 and ZJNU-45, based on three rigid organic linkers, 5,5'-(quinoline-5,8-diyl)-diisophthalate, 5,5'-(isoquinoline-5,8-diyl)-diisophthalate, and 5,5'-(quinoxaline-5,8-diyl)-diisophthalate, were constructed.⁹⁸ Although these MOFs had nearly identical surface areas, distinct differences were observed in their CO₂ uptake capacities. In ZJNU-43, the linker-based nitrogen atom is located at the α -position in the spacer of the organic linkers. Upon activation, ZJNU-43 adsorbed 4.6 mmol g⁻¹ CO₂ at 1 atm and 296 K. When the LBSs were shifted to the β -position in ZJNU-44, the CO₂ uptake capacity increased significantly (to 5.2 mmol g⁻¹) under the same conditions. When the number of the LBS at the α -position was doubled, the adsorption capacity of the resulting MOF, ZJNU-45, was only 4.8 mmol g⁻¹, slightly greater than ZJNU-43. Quantum chemical calculations indicated that CO₂ in the structures of ZJNU-43 and ZJNU-45 were trapped in narrow windows, stabilized by numerous weak hydrogen bonds between CO₂ and the H, N, and O atoms of the organic linkers. In contrast, the LBSs of ZJNU-44 pointed into the pores, allowing CO₂ to bridge the organic linkers. Ultimately, the calculated binding energies of CO₂ in the series of MOFs indicated the value of ZJNU-44 (-27.6 kJ mol⁻¹) was much larger than those of other two MOFs (-18.1 and -18.7 kJ mol⁻¹), explaining the high CO₂ adsorption capacity of ZJNU-44. These examples highlight the role of LBSs' orientation in MOF pores and its impact on CO₂ capture.

1.3 Post-synthetically Modified MOFs for CO₂ Capture

The intrinsic features of MOFs provide favorable conditions for CO₂ capture and separation. Nevertheless, in the *de novo* synthesis of MOFs, the introduction of certain specific adsorption sites or functional groups can be challenging due to poor solubility of the organic linkers, competitive reactions between functional groups and the target frameworks, or the sensitivity of frameworks to the alteration of either the metal ions/ligands or their coordination environment(s). In this context, post-synthetic strategies for the incorporation of desired functionalities into MOFs have been developed. Specifically, post-synthetic modification (PSM) can serve as a facile technique to introduce new CO₂ adsorptive sites into MOFs without significantly altering or damaging the underlying structure.⁹⁹ These techniques have been employed to accomplish the following: 1) introduction of additional functional groups, such as amine groups, or exchange of metals in the SBUs, 2) modification, insertion, or exchange of organic linkers, and 3) cation exchange in anionic MOFs.

Post-synthetically Modified MOF SBUs Applied to CO₂ Capture

In the case of SBU PSM, grafting alkylamine moieties onto OMSs serves as an effective means of improving the CO₂ uptake performances of MOFs based on the aforementioned strong affinities of alkylamines for Lewis acidic CO₂ molecules. As an example, the coordinatively unsaturated Cu^{II} sites in a water stable and triazolate-bridged MOF (Cu-BTT) were capped with ethylenediamine (en).⁶⁶ Although the pores of the

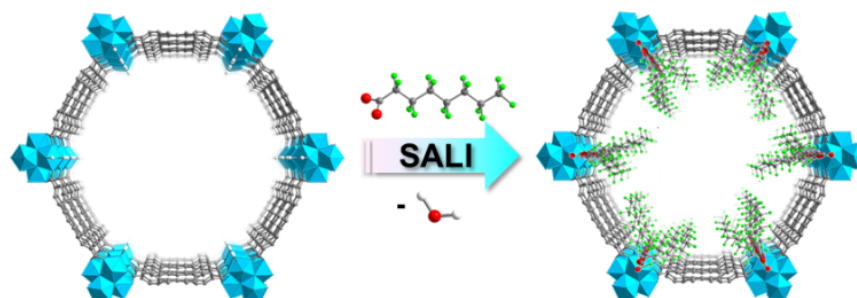


Figure 1.4 Solvent-assisted ligand incorporation (SALI) on NU-1000 as a result of the reaction between the hydroxyl groups on the Zr₆ SBU (turquoise polyhedra) and the carboxylate groups bearing the perfluorinated chain (2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanoate). Color code: C, gray; O, red; F, green; H, white; and Zr, cyan.

resultant material were occluded leading to relatively low CO₂ uptake at relatively high pressures, the CO₂ uptake at low pressures, CO₂/N₂ selectivity, and Q_{st} values dramatically increased compared to those associated with the pristine MOF. This technique was also successfully extended to other MOF systems.^{49,100–109} Among these, Mg-MOF-74, with a high concentration of OMSs and one of the highest CO₂ adsorption capacities at low CO₂ pressures (6.1 mmol g⁻¹ at 298 K and 0.15 bar),⁷⁰ has been identified as an ideal platform for post-synthetic amine functionalization. Unfortunately, its relatively narrow, one-dimensional channels (~11 Å) hinder effective diffusion of sterically bulky amines into the pores. For this reason, extended MOF-74-type structures such as Mg₂(dobpdc), Mg₂(dotpdc) and Mg₂(dondc) were utilized as substitutes for post-synthetic amine incorporation. All of the diamine-appended MOFs exhibited not only exceptional CO₂ adsorption capacities but also high CO₂ adsorption selectivity.^{49,101–104,107–109} Additionally, the thermal and chemical stabilities of the resultant materials under humid conditions were markedly enhanced, despite reduction of their Brunauer-Emmett-Teller (BET) surface areas and pore volumes.^{49,104–106} As an alternative to pore-expansion, the OMSs of Mg-MOF-74 were capped with a much smaller amine (hydrazine), yielding Mg-MOF-74(N₂H₄)_{1.8}.¹⁰⁵ The authors assumed that hydrazine would promote effective CO₂ adsorption in the MOF after PSM due to its small size, yet similar chemistry to other amines. Additionally, the distances between two adjacent amines were quite large. This inhibited the formation of weak hydrogen bonds and greatly enhanced the utility and availability of the grafted amines. Ultimately, the CO₂ uptake of Mg-MOF-74(N₂H₄)_{1.8} at 298 K and 0.4 mbar, the partial pressure of CO₂ in air, was 3.9 mmol g⁻¹ due to the high concentration (6.0 mmol g⁻¹) of surface-appended hydrazines. The Q_{st} calculated by the Clausius-Clapeyron equation and the Virial fitting method gave near zero-coverage values of 118 and 90 kJ mol⁻¹, respectively. These high heats of adsorption necessitate relatively high regeneration temperatures for such adsorbents. This interplay is an outstanding challenge in CO₂ capture; one desires strong chemical bonds between CO₂ molecules and the adsorbent to achieve selectivity, but strong bonds also typically require high adsorbent regeneration temperatures. As such, investigations into the modification of MOF SBUs with other CO₂-philic moieties were carried out. For example, a new functionalization technique, solvent assisted ligand

incorporation (SALI) was developed with the goal of introducing perfluorinated chains onto the Zr₆ SBU of NU-1000. In this case, the technique relied on acid-base chemistry between the hydroxyl groups on the Zr₆ SBU and the carboxylate group of the fluoroalkyl linker (Fig. 1.4).¹¹⁰ All the fluoroalkane-functionalized samples had higher CO₂ adsorption capacities and zero-uptake limits (Q_{st}^0) than those of the parent NU-1000, which can be attributed to the interactions between the C-F dipoles and the quadrupole of CO₂. More importantly, the Q_{st}^0 value for each sample was no greater than 35 kJ mol⁻¹, implying that these adsorbents could be easily regenerated.

Post-synthetic modification for enhanced CO₂ capture in MOFs is not limited to the modification of the metals' coordination environments. Post-synthetic exchange (PSE) of metal atoms in MOF SBUs is also a promising approach and can improve the CO₂ uptake capabilities and/or selectivities. The Zr(IV) ions of UiO-66 can be exchanged with Ti(IV) ions by immersing UiO-66(Zr₁₀₀) in a DMF solution of TiCl₄(THF)₂ for various lengths of time at 368 K to give UiO-66(Zr/Ti) with progressively higher Ti loadings.¹¹¹ The pore size distributions of the resultant frameworks as measured by N₂ adsorption experiments demonstrated that the size of the octahedral pores dramatically decreased as a result of the shorter Ti-O bonds compared to Zr-O bonds. The CO₂ adsorption capacity of UiO-66(Zr/Ti) increased from 2.2 (UiO-66(Zr₁₀₀)) to 4.0 mmol g⁻¹ (UiO-66(Ti₅₆)), which was ascribed to synergistic effects between the reduced pore size and framework density of the Ti-exchanged UiO-66. The highest Q_{st} value of the frameworks in this report was only about 38 kJ mol⁻¹, significantly lower than those of most amine-decorated MOFs. Though not mentioned in the original report, the working capacity of such materials might improve as their heats of adsorption are lower, but it comes at the cost of diminished framework CO₂ capacity. In order to stoichiometrically load new metal cations in MOFs, a new PSM strategy to exchange metal ions in a chromium-based MOF, porph@MOM-11 was devised. In porph@MOM-11, cationic porphyrin linkers serve as the pore walls.¹¹² Simple immersion of porph@MOM-11 into methanol (MeOH) solutions of different metal chlorides gave four PSM derivatives with different metal site occupancies. Due to the reduced pore sizes and the introduction of Cl⁻ and metal ions, the CO₂ volumetric uptake capacities (at 273 K and 1 atm) and Q_{st} values of each of the PSM variants were improved by 3.1-14.5% and 6.6-36.0%, respectively, in comparison to those of porph@MOM-11.

Modification, Insertion, or Exchange of MOFs' Organic Linkers for Enhanced CO₂ Capture

Apart from modification and exchange of metal centers, modification, insertion and exchange of the organic linkers in MOFs can also enhance the interactions between frameworks and CO₂. Organic linkers can be post-synthetically modified to introduce diverse CO₂-philic moieties.¹¹³⁻¹¹⁵ For example, alkylamines were tethered to Cr-MIL-101-SO₃H through a simple Brønsted acid-base reaction.¹¹³ The resultant Cr-MIL-101-SO₃H-TAEA (TAEA = tris(2-aminoethyl)amine) had a high CO₂ uptake capacity of 2.3 mmol g⁻¹ at 150 mbar and 313 K, and 1.1 mmol g⁻¹ at 0.4 mbar and 293 K. The Q_{st} value as calculated from a triple-site Langmuir model was 87 kJ mol⁻¹ at zero coverage, indicating

strong chemisorption of CO₂ in Cr-MIL-101-SO₃H-TAEA. UiO-66-allyl was also subjected to a plethora of post-synthetic functionalization reactions.¹¹⁴ Amongst the modified UiO-66 analogues, the amino alcohol-decorated MOF (UiO-66-aminoalcohol) exhibited the highest CO₂ uptake capacity (11.6 mmol g⁻¹ at 308 K and 20 bar), while only a negligible amount of N₂ was adsorbed under the same conditions, suggesting that UiO-66-aminoalcohol could be a promising candidate for CO₂/N₂ gas separation.

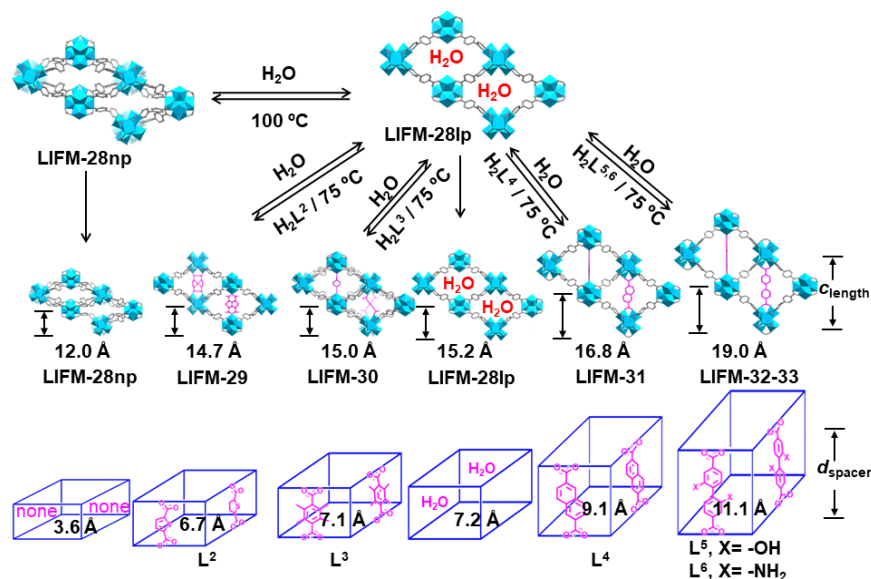


Figure 1.5 (Top) Reversible breathing behavior of LIFM-28 (LIFM-28np ↔ LIFM-28lp), and (middle) stepwise installation/removal of spacers (L²-L⁶) in an increasing expansion sequence to give LIFM-29-33. Each MOF in the series is composed of Zr SBUs (cyan polyhedra) linked together by organic linkers (gray lines). The spacers are highlighted in pink lines. (Bottom) Simplified MOF structures for this series highlighting the role of organic spacers. Color code: C, gray; O, red; and Zr, cyan. H and F atoms are omitted for clarity.

Insertion of organic linkers emerged as the second PSM technique with a goal of incorporating new organic linkers of similar or identical length, but bearing CO₂-philic moieties in MOFs.^{116,117} A bridging linker was post-synthetically incorporated into a MOF by a single crystal to single crystal (SCSC) transformation.¹¹⁶ By inserting 3,6-di(4-pyridyl)-1,2,4,5-tetrazine (bpta) linker into the zinc-based MOF, SNU-30, the honeycomb-like pores were divided into smaller channels along the *ab* plane of the framework, yielding SNU-31. This PSM slightly decreased the framework's void volume from 82.1% to 76.1%. Gas adsorption isotherms showed that N₂, H₂, CH₄ and CO₂ capacity of SNU-30 could reach up to 7.04 mmol g⁻¹ (77 K, 1 bar), 16.2 mmol g⁻¹ (77 K, 61 bar), 0.23 mmol g⁻¹ (298 K, 1 bar), and 1.16 mmol g⁻¹ (298 K, 1 bar), respectively. In contrast to SNU-30, SNU-31 displayed almost no adsorption capacity for N₂, H₂, and CH₄, whereas it exhibited moderate CO₂ uptake (0.6 mmol g⁻¹ at 1 bar) at 298 K. Another interesting example was found in the incorporation of five distinct linkers into a flexible MOF using a post-synthetic variable-spacer installation strategy (Fig. 1.5).¹¹⁷ Unlike the effects observed in rigid frameworks, the structural flexibility of LIFM-28 enabled the material's pore size to be finely tuned by the insertion of organic linkers with various lengths and

substituents.¹¹⁷ The resultant MOFs had functionalized pore environments, and improved thermal stabilities and BET surface areas. Due to these alterations, the CO₂ adsorption capacity and selectivity were greatly enhanced. The -NH₂ groups in LIFM-33 endowed it with the highest CO₂ uptake capacity (3.6 mmol g⁻¹) with a high Q_{st} of about 40 kJ mol⁻¹ based on the presence of strong NH₂-CO₂ interactions. The IAST calculation revealed that the CO₂/N₂ adsorption selectivity in LIFM-33 was about 30, demonstrably higher than that of parent MOF.

Linker exchange can also regulate MOFs' CO₂ capture performance while maintaining their crystallinity, stability, and porosity.¹¹⁸⁻¹²⁰ A family of water-stable UiO-66-AD_n frameworks modified by diverse flexible alkanedioic acids ((HO₂C(CH₂)_n-2CO₂H), n = 4, 6, 8 and 10) was reported.¹¹⁸ ¹H NMR spectra of digested MOFs demonstrated that the degree of linker substitution increased as the hydrocarbon chain in the substituting organic linker was elongated. Each terephthalate ligand of UiO-66 was substituted by two alkanedioic acid. Among the investigated frameworks, UiO-66-AD6 had the highest CO₂ uptake capacity and CO₂ desorption free energy due to the relatively strong interactions between CO₂ and the carboxyl groups of the flexible alkanedioic acid linker which was similar in length to the BDC linker of UiO-66. In this case, the linkers could also be replaced by metalated-ligands.¹¹⁹ The exchange process was carried out by incubating UiO-66 in aqueous solutions of 1,2,4,5-benzenetetracarboxylic acid (BTEC) or mellitic acid (MA) and various alkaline hydroxides, including LiOH, NaOH, and KOH. UiO-66-(COONa)₂-EX exhibited the highest CO₂/N₂ selectivity (33.3) while UiO-66-(COOLi)₄-EX had the highest CO₂ adsorption capacity (0.7 mmol g⁻¹ at 0.15 bar and 298 K). The authors attributed these effects to the mutual influence of the cations' polarizing abilities and reduced pore sizes.

With respect to ionic MOFs, CO₂ adsorption properties can be regulated by cation exchange.¹²¹⁻¹²⁴ A series of cation-exchanged ionic MOFs were prepared by soaking Bio-MOF-1 in DMF solutions of tetramethylammonium, tetraethylammonium, or tetrabutylammonium.¹²¹ Despite the observation of decreased BET surface areas and pore volumes in each cation-exchanged MOF, their CO₂ capacities and Q_{st} values improved compared to the parent Bio-MOF-1. This was attributed to strong interactions between CO₂ and the newly-inserted ammonium cations. The same team also exchanged the cations of Bio-MOF-1 with a series of guanidinium derivatives.¹²² When a guanidinium derivative with a high population of LBSs, diaminoguanidinium (DiAmGND⁺), was exchanged into bio-MOF-1, the MOF's CO₂ adsorption capacity and Q_{st} increased to 5.1 mmol g⁻¹ (at 273 K and 1 bar) and 29.4 kJ mol⁻¹, respectively. This was accompanied by only a slight decrease in both the pore volume and BET surface area of DiAmGND@bio-MOF-1. The authors speculated that the enhanced CO₂ uptake performance could be ascribed to the CO₂ affinity of aminated cations rather than the decreased pore size. It was demonstrated that Li⁺ exchange in an anionic MOF, [H₂N(Me)₂]₂[Zn₅(L)₃]·5.5DMF·3.5H₂O (L = 3,3',5,5'-biphenyltetracarboxylic acid), can be accomplished by SCSC transformation.¹²³ Impressively, both the guest H₂N(Me)₂⁺ counterions located in the pores and some coordinated metal ions (Zn²⁺) of the MOF were

replaced by Li^+ , resulting in a greatly increased BET surface area (from 342 to 1664 $\text{m}^2 \text{g}^{-1}$) and CO_2 adsorption capacity (from 1.7 to 6.6 mmol g^{-1} at 273 K and 1 bar).

1.4 Challenges and Opportunities in Developing MOFs for CO_2 Capture

Remarkable advances have been made toward CO_2 capture and separation in MOFs. In contrast to many other porous materials, MOFs have both high CO_2 capacities and outstanding CO_2 selectivities for capture in the presence of other gasses. This largely stems from MOFs' unique properties such as structural flexibility and the potential for framework post-synthetic modification. Many of these strategies have only recently been developed and further optimization promises to improve MOFs' CO_2 capture properties as more work is performed. However, many challenges regarding the preparation and application of MOFs with high CO_2 capture capacities remain unaddressed. For example, many MOFs still have low CO_2 selectivities in the presence of moisture/water/acidic gasses, even if their overall adsorption capacities are high. Additionally, under these conditions many MOFs chosen for studies lack the requisite stability for practical application. In the future, it would be necessary to choose MOFs which are known to have high chemical and thermal stability, as found for MOF-808.^{125,126} In this context, it is important to recall that CO_2 capture from large stationary sources such as the flue gas of power plants is regarded as one of the most promising avenues to mitigate rising atmospheric CO_2 concentrations. Generally, flue gas from power plants (CO_2 point sources) is composed of 15-16% carbon dioxide, 5-7% water vapor, 73-77% nitrogen, 3-4% oxygen and traces of acidic gasses such as H_2S , NO_x , SO_x .⁵¹ Consequently, during adsorption, gasses with higher polarities and/or binding energies such as H_2O or acidic gasses are preferentially adsorbed over CO_2 on the OMSs of MOFs. This has to be considered when selecting a MOF for CO_2 capture in the presence of water. Many pre- and post-synthetic strategies have been developed for improving the water and acid stabilities of those MOFs already under consideration.^{40,126-130}

Nevertheless, there are suites of MOFs as yet uninvestigated which may well be more appropriate for this application. Additionally, certain strategies can be accompanied by new issues such as dramatic reduction of the materials' specific surface areas and/or pore volumes. These issues are beginning to be addressed as we learn how to balance functionalization with maintaining crystallinity and porosity. Finally, for many MOFs, direct capture of CO_2 at low partial pressures remains a challenge due to relatively weak CO_2 -framework interactions. Although CO_2 adsorption capacities at low partial pressures can be improved by introducing CO_2 -philic moieties on MOFs' organic linkers, adsorbent regeneration energies also typically sharply increase.^{105,113} This can, of course be overcome by precisely tuning the chemistry between the frameworks and CO_2 . In the future, it is likely that high stability and high CO_2 adsorption capacity will be targeted in order to position MOFs as the next-generation of materials for practical CO_2 capture.

1.5 References for Chapter 1

- (1) Wang, Q.; Luo, J.; Zhong, Z.; Borgna, A. CO₂ Capture by Solid Adsorbents and Their Applications: Current Status and New Trends. *Energy Environ. Sci.* **2011**, *4*, 42–55.
- (2) Sanz-Pérez, E. S.; Murdock, C. R.; Didas, S. A.; Jones, C. W. Direct Capture of CO₂ from Ambient Air. *Chem. Rev.* **2016**, *116*, 11840–11876.
- (3) Mikkelsen, M.; Jørgensen, M.; Krebs, F. C. The Teraton Challenge. A Review of Fixation and Transformation of Carbon Dioxide. *Energy Environ. Sci.* **2010**, *3*, 43–81.
- (4) Zhang, L.; Zhao, Z.; Gong, J. Nanostructured Materials for Heterogeneous Electrocatalytic CO₂ Reduction and Their Related Reaction Mechanisms. *Angew. Chemie Int. Ed.* **2017**, *56*, 11326–11353.
- (5) Carbon dioxide: Projected Emissions and Concentrations, 2014 http://ipcc-data.org/observ/ddc_co2.html (accessed Apr 6, 2019).
- (6) D'Alessandro, D. M.; Smit, B.; Long, J. R. Carbon Dioxide Capture: Prospects for New Materials. *Angew. Chemie Int. Ed.* **2010**, *49*, 6058–6082.
- (7) Wang, J.; Huang, L.; Yang, R.; Zhang, Z.; Wu, J.; Gao, Y.; Wang, Q.; O'Hare, D.; Zhong, Z. Recent Advances in Solid Sorbents for CO₂ Capture and New Development Trends. *Energy Environ. Sci.* **2014**, *7*, 3478–3518.
- (8) Sneddon, G.; Greenaway, A.; Yiu, H. H. P. The Potential Applications of Nanoporous Materials for the Adsorption, Separation, and Catalytic Conversion of Carbon Dioxide. *Adv. Energy Mater.* **2014**, *4*, 1301873.
- (9) Cui, G.; Wang, J.; Zhang, S. Active Chemisorption Sites in Functionalized Ionic Liquids for Carbon Capture. *Chem. Soc. Rev.* **2016**, *45*, 4307–4339.
- (10) Zhang, Y.; Chan, J. Y. G. Sustainable Chemistry: Imidazolium Salts in Biomass Conversion and CO₂ Fixation. *Energy Environ. Sci.* **2010**, *3*, 408–417.
- (11) Sun, Q.; Wang, N.; Bing, Q.; Si, R.; Liu, J.; Bai, R.; Zhang, P.; Jia, M.; Yu, J. Subnanometric Hybrid Pd-M(OH)₂, M = Ni, Co, Clusters in Zeolites as Highly Efficient Nanocatalysts for Hydrogen Generation. *Chem* **2017**, *3*, 477–493.
- (12) Xie, Y.; Wang, T.; Liu, X.; Zou, K.; Deng, W. Capture and Conversion of CO₂ at Ambient Conditions by a Conjugated Microporous Polymer. *Nat. Commun.* **2013**, *4*, 1960.
- (13) Feng, X.; Ding, X.; Jiang, D. Covalent Organic Frameworks. *Chem. Soc. Rev.* **2012**, *41*, 6010.
- (14) Schoedel, A.; Ji, Z.; Yaghi, O. M. The Role of Metal–Organic Frameworks in a Carbon-Neutral Energy Cycle. *Nat. Energy* **2016**, *1*, 16034.
- (15) Trickett, C. A.; Helal, A.; Al-Maythaly, B. A.; Yamani, Z. H.; Cordova, K. E.; Yaghi, O. M. The Chemistry of Metal–Organic Frameworks for CO₂ Capture, Regeneration and Conversion. *Nat. Rev. Mater.* **2017**, *2*, 17045.
- (16) Wang, S.; Wang, X. Imidazolium Ionic Liquids, Imidazolyliene Heterocyclic Carbenes, and Zeolitic Imidazolate Frameworks for CO₂ Capture and Photochemical Reduction. *Angew. Chemie Int. Ed.* **2016**, *55*, 2308–2320.
- (17) Long, J. R.; Yaghi, O. M. The Pervasive Chemistry of Metal–Organic Frameworks. *Chem. Soc. Rev.* **2009**, *38*, 1213.

- (18) Zhou, H.-C.; Long, J. R.; Yaghi, O. M. Introduction to Metal–Organic Frameworks. *Chem. Rev.* **2012**, *112*, 673–674.
- (19) Zhou, H.-C. “Joe”; Kitagawa, S. Metal–Organic Frameworks (MOFs). *Chem. Soc. Rev.* **2014**, *43*, 5415–5418.
- (20) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O’Keeffe, M.; Yaghi, O. M. Modular Chemistry: Secondary Building Units as a Basis for the Design of Highly Porous and Robust Metal–Organic Carboxylate Frameworks. *Acc. Chem. Res.* **2001**, *34*, 319–330.
- (21) Lu, W.; Wei, Z.; Gu, Z.-Y.; Liu, T.-F.; Park, J.; Park, J.; Tian, J.; Zhang, M.; Zhang, Q.; Gentle, T.; Bosch, M.; Zhou, H.-C. Tuning the Structure and Function of Metal–Organic Frameworks via Linker Design. *Chem. Soc. Rev.* **2014**, *43*, 5561.
- (22) Suh, M. P.; Park, H. J.; Prasad, T. K.; Lim, D. Hydrogen Storage in Metal–Organic Frameworks. *Chem. Rev.* **2012**, *112*, 782–835.
- (23) Schneemann, A.; Bon, V.; Schwedler, I.; Senkovska, I.; Kaskel, S.; Fischer, R. A. Flexible Metal–Organic Frameworks. *Chem. Soc. Rev.* **2014**, *43*, 6062–6096.
- (24) Furukawa, H.; Cordova, K. E.; O’Keeffe, M.; Yaghi, O. M. The Chemistry and Applications of Metal–Organic Frameworks. *Science*. **2013**, *341*, 1230444–1230444.
- (25) Hu, Z.; Deibert, B. J.; Li, J. Luminescent Metal–Organic Frameworks for Chemical Sensing and Explosive Detection. *Chem. Soc. Rev.* **2014**, *43*, 5815–5840.
- (26) Liu, J.; Chen, L.; Cui, H.; Zhang, J.; Zhang, L.; Su, C.-Y. Applications of Metal–Organic Frameworks in Heterogeneous Supramolecular Catalysis. *Chem. Soc. Rev.* **2014**, *43*, 6011–6061.
- (27) Ramaswamy, P.; Wong, N. E.; Shimizu, G. K. H. MOFs as Proton Conductors – Challenges and Opportunities. *Chem. Soc. Rev.* **2014**, *43*, 5913–5932.
- (28) Doherty, C. M.; Buso, D.; Hill, A. J.; Furukawa, S.; Kitagawa, S.; Falcaro, P. Using Functional Nano- and Microparticles for the Preparation of Metal–Organic Framework Composites with Novel Properties. *Acc. Chem. Res.* **2014**, *47*, 396–405.
- (29) Zhu, L.; Liu, X.; Jiang, H.; Sun, L. Metal–Organic Frameworks for Heterogeneous Basic Catalysis. *Chem. Rev.* **2017**, *117*, 8129–8176.
- (30) Li, B.; Chrzanowski, M.; Zhang, Y.; Ma, S. Applications of Metal–Organic Frameworks Featuring Multi-Functional Sites. *Coord. Chem. Rev.* **2016**, *307*, 106–129.
- (31) He, H.; Perman, J. A.; Zhu, G.; Ma, S. Metal–Organic Frameworks for CO₂ Chemical Transformations. *Small* **2016**, *12*, 6309–6324.
- (32) Dhakshinamoorthy, A.; Li, Z.; Garcia, H. Catalysis and Photocatalysis by Metal Organic Frameworks. *Chem. Soc. Rev.* **2018**, *47*, 8134–8172.
- (33) Denny, M. S.; Moreton, J. C.; Benz, L.; Cohen, S. M. Metal–Organic Frameworks for Membrane-Based Separations. *Nat. Rev. Mater.* **2016**, *1*, 16078.
- (34) Gascon, J.; Corma, A.; Kapteijn, F.; Llabrés i Xamena, F. X. Metal Organic Framework Catalysis: Quo Vadis ? *ACS Catal.* **2014**, *4*, 361–378.
- (35) Horcajada, P.; Gref, R.; Baati, T.; Allan, P. K.; Maurin, G.; Couvreur, P.; Férey, G.; Morris, R. E.; Serre, C. Metal–Organic Frameworks in Biomedicine. *Chem. Rev.* **2012**, *112*, 1232–1268.
- (36) Kalmutzki, M. J.; Diercks, C. S.; Yaghi, O. M. Metal–Organic Frameworks for Water Harvesting from Air. *Adv. Mater.* **2018**, *30*, 1704304.

- (37) Diercks, C. S.; Liu, Y.; Cordova, K. E.; Yaghi, O. M. The Role of Reticular Chemistry in the Design of CO₂ Reduction Catalysts. *Nat. Mater.* **2018**, *17*, 301–307.
- (38) Jiang, J.; Yaghi, O. M. Brønsted Acidity in Metal–Organic Frameworks. *Chem. Rev.* **2015**, *115*, 6966–6997.
- (39) Kirchon, A.; Feng, L.; Drake, H. F.; Joseph, E. A.; Zhou, H. From Fundamentals to Applications: A Toolbox for Robust and Multifunctional MOF Materials. *Chem. Soc. Rev.* **2018**, *47*, 8611–8638.
- (40) Howarth, A. J.; Liu, Y.; Li, P.; Li, Z.; Wang, T. C.; Hupp, J. T.; Farha, O. K. Chemical, Thermal and Mechanical Stabilities of Metal–Organic Frameworks. *Nat. Rev. Mater.* **2016**, *1*, 15018.
- (41) Li, J.; Sculley, J.; Zhou, H. Metal–Organic Frameworks for Separations. *Chem. Rev.* **2012**, *112*, 869–932.
- (42) Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.; Long, J. R. Carbon Dioxide Capture in Metal–Organic Frameworks. *Chem. Rev.* **2012**, *112*, 724–781.
- (43) Li, H.; Eddaoudi, M.; Groy, T. L.; Yaghi, O. M. Establishing Microporosity in Open Metal–Organic Frameworks: Gas Sorption Isotherms for Zn(BDC) (BDC = 1,4-Benzenedicarboxylate). *J. Am. Chem. Soc.* **1998**, *120*, 8571–8572.
- (44) Li, H.; Eddaoudi, M.; O’Keeffe, M.; Yaghi, O. M. Design and Synthesis of an Exceptionally Stable and Highly Porous Metal–Organic Framework. *Nature* **1999**, *402*, 276–279.
- (45) Eddaoudi, M.; Li, H.; Yaghi, O. M. Highly Porous and Stable Metal–Organic Frameworks: Structure Design and Sorption Properties. *J. Am. Chem. Soc.* **2000**, *122*, 1391–1397.
- (46) Li, H.; Davis, C. E.; Groy, T. L.; Kelley, D. G.; Yaghi, O. M. Coordinatively Unsaturated Metal Centers in the Extended Porous Framework of Zn₃(BDC)₃·6CH₃OH (BDC = 1,4-Benzenedicarboxylate). *J. Am. Chem. Soc.* **1998**, *120*, 2186–2187.
- (47) Chen, B.; Eddaoudi, M.; Reineke, T. M.; Kampf, J. W.; O’Keeffe, M.; Yaghi, O. M. Cu₂(ATC)·6H₂O: Design of Open Metal Sites in Porous Metal–Organic Crystals (ATC: 1,3,5,7-Adamantane Tetracarboxylate). *J. Am. Chem. Soc.* **2000**, *122*, 11559–11560.
- (48) Millward, A. R.; Yaghi, O. M. Metal–Organic Frameworks with Exceptionally High Capacity for Storage of Carbon Dioxide at Room Temperature. *J. Am. Chem. Soc.* **2005**, *127*, 17998–17999.
- (49) McDonald, T. M.; Lee, W. R.; Mason, J. A.; Wiers, B. M.; Hong, C. S.; Long, J. R. Capture of Carbon Dioxide from Air and Flue Gas in the Alkylamine-Appended Metal–Organic Framework Mmen-Mg₂(Dobpdc). *J. Am. Chem. Soc.* **2012**, *134*, 7056–7065.
- (50) Farha, O. K.; Özgür Yazaydın, A.; Eryazici, I.; Malliakas, C. D.; Hauser, B. G.; Kanatzidis, M. G.; Nguyen, S. T.; Snurr, R. Q.; Hupp, J. T. De Novo Synthesis of a Metal–Organic Framework Material Featuring Ultrahigh Surface Area and Gas Storage Capacities. *Nat. Chem.* **2010**, *2*, 944–948.
- (51) Liang, L.; Liu, C.; Jiang, F.; Chen, Q.; Zhang, L.; Xue, H.; Jiang, H.; Qian, J.; Yuan, D.; Hong, M. Carbon Dioxide Capture and Conversion by an Acid-Base Resistant

- Metal-Organic Framework. *Nat. Commun.* **2017**, *8*, 1233.
- (52) Queen, W. L.; Hudson, M. R.; Bloch, E. D.; Mason, J. A.; Gonzalez, M. I.; Lee, J. S.; Gygi, D.; Howe, J. D.; Lee, K.; Darwish, T. A.; James, M.; Peterson, V. K.; Teat, S. J.; Smit, B.; Neaton, J. B.; Long, J. R.; Brown, C. M. Comprehensive Study of Carbon Dioxide Adsorption in the Metal–Organic Frameworks $M_2(\text{Dobdc})$ ($M = \text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$). *Chem. Sci.* **2014**, *5*, 4569–4581.
 - (53) Tan, C.; Yang, S.; Champness, N. R.; Lin, X.; Blake, A. J.; Lewis, W.; Schröder, M. High Capacity Gas Storage by a 4,8-Connected Metal–Organic Polyhedral Framework. *Chem. Commun.* **2011**, *47*, 4487.
 - (54) Mu, B.; Li, F.; Walton, K. S. A Novel Metal–Organic Coordination Polymer for Selective Adsorption of CO_2 over CH_4 . *Chem. Commun.* **2009**, No. 18, 2493.
 - (55) Hou, L.; Shi, W.-J.; Wang, Y.; Guo, Y.; Jin, C.; Shi, Q. A Rod Packing Microporous Metal–Organic Framework: Unprecedented Ukv Topology, High Sorption Selectivity and Affinity for CO_2 . *Chem. Commun.* **2011**, *47*, 5464.
 - (56) Zhang, Z.; Xiang, S.; Rao, X.; Zheng, Q.; Fronczek, F. R.; Qian, G.; Chen, B. A Rod Packing Microporous Metal–Organic Framework with Open Metal Sites for Selective Guest Sorption and Sensing of Nitrobenzene. *Chem. Commun.* **2010**, *46*, 7205.
 - (57) Tan, Y.; He, Y.; Zhang, J. Pore Partition Effect on Gas Sorption Properties of an Anionic Metal–Organic Framework with Exposed Cu^{2+} Coordination Sites. *Chem. Commun.* **2011**, *47*, 10647.
 - (58) Mallick, A.; Saha, S.; Pachfule, P.; Roy, S.; Banerjee, R. Selective CO_2 and H_2 Adsorption in a Chiral Magnesium-Based Metal Organic Framework (Mg-MOF) with Open Metal Sites. *J. Mater. Chem.* **2010**, *20*, 9073.
 - (59) Li, Y.-W.; Li, J.; Wang, L.; Zhou, B.; Chen, Q.; Bu, X. Microporous Metal–Organic Frameworks with Open Metal Sites as Sorbents for Selective Gas Adsorption and Fluorescence Sensors for Metal Ions. *J. Mater. Chem. A* **2013**, *1*, 495–499.
 - (60) Dietzel, P. D. C.; Besikiotis, V.; Blom, R. Application of Metal–Organic Frameworks with Coordinatively Unsaturated Metal Sites in Storage and Separation of Methane and Carbon Dioxide. *J. Mater. Chem.* **2009**, *19*, 7362.
 - (61) Yuan, D.; Zhao, D.; Sun, D.; Zhou, H.-C. An Isoreticular Series of Metal–Organic Frameworks with Dendritic Hexacarboxylate Ligands and Exceptionally High Gas-Uptake Capacity. *Angew. Chemie Int. Ed.* **2010**, *49*, 5357–5361.
 - (62) Loiseau, T.; Lecroq, L.; Volkringer, C.; Marrot, J.; Férey, G.; Haouas, M.; Taulelle, F.; Bourrelly, S.; Llewellyn, P. L.; Latroche, M. MIL-96, a Porous Aluminum Trimesate 3D Structure Constructed from a Hexagonal Network of 18-Membered Rings and μ^3 -Oxo-Centered Trinuclear Units. *J. Am. Chem. Soc.* **2006**, *128*, 10223–10230.
 - (63) Lee, Y.; Moon, H. R.; Cheon, Y. E.; Suh, M. P. A Comparison of the H_2 Sorption Capacities of Isostructural Metal–Organic Frameworks With and Without Accessible Metal Sites: $[\{\text{Zn}_2(\text{Abtc})(\text{DMF})_2\}_3]$ and $[\{\text{Cu}_2(\text{Abtc})(\text{Dmf})_2\}_3]$ versus $[\{\text{Cu}_2(\text{Abtc})\}_3]$. *Angew. Chemie Int. Ed.* **2008**, *47*, 7741–7745.
 - (64) Guo, Z.; Wu, H.; Srinivas, G.; Zhou, Y.; Xiang, S.; Chen, Z.; Yang, Y.; Zhou, W.; O’Keeffe, M.; Chen, B. A Metal–Organic Framework with Optimized Open Metal

- Sites and Pore Spaces for High Methane Storage at Room Temperature. *Angew. Chemie Int. Ed.* **2011**, *50*, 3178–3181.
- (65) Surblé, S.; Millange, F.; Serre, C.; Düren, T.; Latroche, M.; Bourrelly, S.; Llewellyn, P. L.; Férey, G. Synthesis of MIL-102, a Chromium Carboxylate Metal–Organic Framework, with Gas Sorption Analysis. *J. Am. Chem. Soc.* **2006**, *128*, 14889–14896.
 - (66) Demessence, A.; D'Alessandro, D. M.; Foo, M. L.; Long, J. R. Strong CO₂ Binding in a Water-Stable, Triazolate-Bridged Metal–Organic Framework Functionalized with Ethylenediamine. *J. Am. Chem. Soc.* **2009**, *131*, 8784–8786.
 - (67) Sumida, K.; Horike, S.; Kaye, S. S.; Herm, Z. R.; Queen, W. L.; Brown, C. M.; Grandjean, F.; Long, G. J.; Dailly, A.; Long, J. R. Hydrogen Storage and Carbon Dioxide Capture in an Iron-Based Sodalite-Type Metal–Organic Framework (Fe-BTT) Discovered via High-Throughput Methods. *Chem. Sci.* **2010**, *1*, 184.
 - (68) Li, J.-R.; Yu, J.; Lu, W.; Sun, L.-B.; Sculley, J.; Balbuena, P. B.; Zhou, H.-C. Porous Materials with Pre-Designed Single-Molecule Traps for CO₂ Selective Adsorption. *Nat. Commun.* **2013**, *4*, 1538.
 - (69) Kong, X.; Scott, E.; Ding, W.; Mason, J. A.; Long, J. R.; Reimer, J. A. CO₂ Dynamics in a Metal–Organic Framework with Open Metal Sites. *J. Am. Chem. Soc.* **2012**, *134*, 14341–14344.
 - (70) Caskey, S. R.; Wong-Foy, A. G.; Matzger, A. J. Dramatic Tuning of Carbon Dioxide Uptake via Metal Substitution in a Coordination Polymer with Cylindrical Pores. *J. Am. Chem. Soc.* **2008**, *130*, 10870–10871.
 - (71) Wu, H.; Simmons, J. M.; Srinivas, G.; Zhou, W.; Yildirim, T. Adsorption Sites and Binding Nature of CO₂ in Prototypical Metal–Organic Frameworks: A Combined Neutron Diffraction and First-Principles Study. *J. Phys. Chem. Lett.* **2010**, *1*, 1946–1951.
 - (72) Queen, W. L.; Brown, C. M.; Britt, D. K.; Zajdel, P.; Hudson, M. R.; Yaghi, O. M. Site-Specific CO₂ Adsorption and Zero Thermal Expansion in an Anisotropic Pore Network. *J. Phys. Chem. C* **2011**, *115*, 24915–24919.
 - (73) Dietzel, P. D. C.; Johnsen, R. E.; Fjellvåg, H.; Bordiga, S.; Groppo, E.; Chavan, S.; Blom, R. Adsorption Properties and Structure of CO₂ Adsorbed on Open Coordination Sites of Metal–Organic Framework Ni₂(Dhtp) from Gas Adsorption, IR Spectroscopy and X-Ray Diffraction. *Chem. Commun.* **2008**, *2*, 5125.
 - (74) Mason, J. A.; Sumida, K.; Herm, Z. R.; Krishna, R.; Long, J. R. Evaluating Metal–Organic Frameworks for Post-Combustion Carbon Dioxide Capture via Temperature Swing Adsorption. *Energy Environ. Sci.* **2011**, *4*, 3030.
 - (75) Herm, Z. R.; Swisher, J. A.; Smit, B.; Krishna, R.; Long, J. R. Metal–Organic Frameworks as Adsorbents for Hydrogen Purification and Precombustion Carbon Dioxide Capture. *J. Am. Chem. Soc.* **2011**, *133*, 5664–5667.
 - (76) Rochelle, G. T. Amine Scrubbing for CO₂ Capture. *Science*. **2009**, *325*, 1652–1654.
 - (77) MacDowell, N.; Florin, N.; Buchard, A.; Hallett, J.; Galindo, A.; Jackson, G.; Adjiman, C. S.; Williams, C. K.; Shah, N.; Fennell, P. An Overview of CO₂ Capture Technologies. *Energy Environ. Sci.* **2010**, *3*, 1645.
 - (78) Couck, S.; Denayer, J. F. M.; Baron, G. V.; Rémy, T.; Gascon, J.; Kapteijn, F. An Amine-Functionalized MIL-53 Metal–Organic Framework with Large Separation

- Power for CO₂ and CH₄. *J. Am. Chem. Soc.* **2009**, *131*, 6326–6327.
- (79) Yang, Q.; Wiersum, A. D.; Llewellyn, P. L.; Guillerm, V.; Serre, C.; Maurin, G. Functionalizing Porous Zirconium Terephthalate UiO-66(Zr) for Natural Gas Upgrading: A Computational Exploration. *Chem. Commun.* **2011**, *47*, 9603.
- (80) Kim, S.-N.; Kim, J.; Kim, H.; Cho, H.; Ahn, W. Adsorption/Catalytic Properties of MIL-125 and NH₂-MIL-125. *Catal. Today* **2013**, *204*, 85–93.
- (81) Si, X.; Jiao, C.; Li, F.; Zhang, J.; Wang, S.; Liu, S.; Li, Z.; Sun, L.; Xu, F.; Gabelica, Z.; Schick, C. High and Selective CO₂ Uptake, H₂ Storage and Methanol Sensing on the Amine-Decorated 12-Connected MOF CAU-1. *Energy Environ. Sci.* **2011**, *4*, 4522.
- (82) Flaig, R. W.; Osborn Popp, T. M.; Fracaroli, A. M.; Kapustin, E. A.; Kalmutzki, M. J.; Altamimi, R. M.; Fathieh, F.; Reimer, J. A.; Yaghi, O. M. The Chemistry of CO₂ Capture in an Amine-Functionalized Metal–Organic Framework under Dry and Humid Conditions. *J. Am. Chem. Soc.* **2017**, *139*, 12125–12128.
- (83) Fracaroli, A. M.; Furukawa, H.; Suzuki, M.; Dodd, M.; Okajima, S.; Gándara, F.; Reimer, J. A.; Yaghi, O. M. Metal–Organic Frameworks with Precisely Designed Interior for Carbon Dioxide Capture in the Presence of Water. *J. Am. Chem. Soc.* **2014**, *136*, 8863–8866.
- (84) An, J.; Geib, S. J.; Rosi, N. L. High and Selective CO₂ Uptake in a Cobalt Adeninate Metal–Organic Framework Exhibiting Pyrimidine- and Amino-Decorated Pores. *J. Am. Chem. Soc.* **2010**, *132*, 38–39.
- (85) Li, B.; Zhang, Z.; Li, Y.; Yao, K.; Zhu, Y.; Deng, Z.; Yang, F.; Zhou, X.; Li, G.; Wu, H.; Nijem, N.; Chabal, Y. J.; Lai, Z.; Han, Y.; Shi, Z.; Feng, S.; Li, J. Enhanced Binding Affinity, Remarkable Selectivity, and High Capacity of CO₂ by Dual Functionalization of a Rht-Type Metal–Organic Framework. *Angew. Chemie Int. Ed.* **2012**, *51*, 1412–1415.
- (86) Lin, R.-B.; Chen, D.; Lin, Y.; Zhang, J.; Chen, X. A Zeolite-Like Zinc Triazolate Framework with High Gas Adsorption and Separation Performance. *Inorg. Chem.* **2012**, *51*, 9950–9955.
- (87) Panda, T.; Pachfule, P.; Chen, Y.; Jiang, J.; Banerjee, R. Amino Functionalized Zeolitic Tetrazolate Framework (ZTF) with High Capacity for Storage of Carbon Dioxide. *Chem. Commun.* **2011**, *47*, 2011–2013.
- (88) Vaidhyanathan, R.; Iremonger, S. S.; Dawson, K. W.; Shimizu, G. K. H. An Amine-Functionalized Metal Organic Framework for Preferential CO₂ Adsorption at Low Pressures. *Chem. Commun.* **2009**, 5230–5232.
- (89) Li, J.; Tao, Y.; Yu, Q.; Bu, X.; Sakamoto, H.; Kitagawa, S. Selective Gas Adsorption and Unique Structural Topology of a Highly Stable Guest-Free Zeolite-Type MOF Material with N-Rich Chiral Open Channels. *Chem. - A Eur. J.* **2008**, *14*, 2771–2776.
- (90) Chen, Y.; Wang, H.; Li, J.; Lockard, J. V. In Situ Spectroscopy Studies of CO₂ Adsorption in a Dually Functionalized Microporous Metal–Organic Framework. *J. Mater. Chem. A* **2015**, *3*, 4945–4953.
- (91) McDonald, T. M.; D’Alessandro, D. M.; Krishna, R.; Long, J. R. Enhanced Carbon Dioxide Capture upon Incorporation of N,N'-Dimethylethylenediamine in the Metal–Organic Framework CuBTTri. *Chem. Sci.* **2011**, *2*, 2022.
- (92) Vaidhyanathan, R.; Iremonger, S. S.; Shimizu, G. K. H.; Boyd, P. G.; Alavi, S.; Woo,

- T. K. Direct Observation and Quantification of CO₂ Binding Within an Amine-Functionalized Nanoporous Solid. *Science*. **2010**, 330, 650–653.
- (93) Lin, J.; Zhang, J.; Chen, X. Nonclassical Active Site for Enhanced Gas Sorption in Porous Coordination Polymer. *J. Am. Chem. Soc.* **2010**, 132, 6654–6656.
- (94) Vaidhyanathan, R.; Iremonger, S. S.; Shimizu, G. K. H.; Boyd, P. G.; Alavi, S.; Woo, T. K. Competition and Cooperativity in Carbon Dioxide Sorption by Amine-Functionalized Metal-Organic Frameworks. *Angew. Chemie Int. Ed.* **2012**, 51, 1826–1829.
- (95) Qin, J.-S.; Du, D.-Y.; Li, W.-L.; Zhang, J.-P.; Li, S.-L.; Su, Z.-M.; Wang, X.-L.; Xu, Q.; Shao, K.-Z.; Lan, Y.-Q. N-Rich Zeolite-like Metal-Organic Framework with Sodalite Topology: High CO₂ Uptake, Selective Gas Adsorption and Efficient Drug Delivery. *Chem. Sci.* **2012**, 3, 2114.
- (96) Liao, P.; Zhou, D.; Zhu, A.; Jiang, L.; Lin, R.; Zhang, J.; Chen, X.-M. Strong and Dynamic CO₂ Sorption in a Flexible Porous Framework Possessing Guest Chelating Claws. *J. Am. Chem. Soc.* **2012**, 134, 17380–17383.
- (97) Lin, Q.; Wu, T.; Zheng, S.; Bu, X.; Feng, P. Single-Walled Polytetrazolate Metal-Organic Channels with High Density of Open Nitrogen-Donor Sites and Gas Uptake. *J. Am. Chem. Soc.* **2012**, 134, 784–787.
- (98) Song, C.; Hu, J.; Ling, Y.; Feng, Y.; Krishna, R.; Chen, D.; He, Y. The Accessibility of Nitrogen Sites Makes a Difference in Selective CO₂ Adsorption of a Family of Isostructural Metal-Organic Frameworks. *J. Mater. Chem. A* **2015**, 3, 19417–19426.
- (99) Cohen, S. M. Postsynthetic Methods for the Functionalization of Metal-Organic Frameworks. *Chem. Rev.* **2012**, 112, 970–1000.
- (100) Hu, Y.; Verdegaal, W. M.; Yu, S.; Jiang, H. Alkylamine-Tethered Stable Metal-Organic Framework for CO₂ Capture from Flue Gas. *ChemSusChem* **2014**, 7, 734–737.
- (101) Planas, N.; Dzubak, A. L.; Poloni, R.; Lin, L.; McManus, A.; McDonald, T. M.; Neaton, J. B.; Long, J. R.; Smit, B.; Gagliardi, L. The Mechanism of Carbon Dioxide Adsorption in an Alkylamine-Functionalized Metal-Organic Framework. *J. Am. Chem. Soc.* **2013**, 135, 7402–7405.
- (102) McDonald, T. M.; Mason, J. A.; Kong, X.; Bloch, E. D.; Gygi, D.; Dani, A.; Crocellà, V.; Giordanino, F.; Odoh, S. O.; Drisdell, W. S.; Vlasisavljevich, B.; Dzubak, A. L.; Poloni, R.; Schnell, S. K.; Planas, N.; Lee, K.; Pascal, T.; Wan, L. F.; Prendergast, D.; Neaton, J. B.; Smit, B.; Kortright, J. B.; Gagliardi, L.; Bordiga, S.; Reimer, J. A.; Long, J. R. Cooperative Insertion of CO₂ in Diamine-Appended Metal-Organic Frameworks. *Nature* **2015**, 519, 303–308.
- (103) Siegelman, R. L.; McDonald, T. M.; Gonzalez, M. I.; Martell, J. D.; Milner, P. J.; Mason, J. A.; Berger, A. H.; Bhowan, A. S.; Long, J. R. Controlling Cooperative CO₂ Adsorption in Diamine-Appended Mg₂(Dobpdc) Metal-Organic Frameworks. *J. Am. Chem. Soc.* **2017**, 139, 10526–10538.
- (104) Milner, P. J.; Martell, J. D.; Siegelman, R. L.; Gygi, D.; Weston, S. C.; Long, J. R. Overcoming Double-Step CO₂ Adsorption and Minimizing Water Co-Adsorption in Bulky Diamine-Appended Variants of Mg₂(Dobpdc). *Chem. Sci.* **2018**, 9, 160–174.
- (105) Liao, P.-Q.; Chen, X.-W.; Liu, S.-Y.; Li, X.-Y.; Xu, Y.-T.; Tang, M.; Rui, Z.; Ji, H.;

- Zhang, J.; Chen, X. Putting an Ultrahigh Concentration of Amine Groups into a Metal-Organic Framework for CO₂ Capture at Low Pressures. *Chem. Sci.* **2016**, *7*, 6528–6533.
- (106) Andirova, D.; Lei, Y.; Zhao, X.; Choi, S. Functionalization of Metal-Organic Frameworks for Enhanced Stability under Humid Carbon Dioxide Capture Conditions. *ChemSusChem* **2015**, *8*, 3405–3409.
- (107) Yeon, J. S.; Lee, W. R.; Kim, N. W.; Jo, H.; Lee, H.; Song, J. H.; Lim, K. S.; Kang, D. W.; Seo, J. G.; Moon, D.; Wiers, B.; Seop Hong, C. Homodiamine-Functionalized Metal-Organic Frameworks with a MOF-74-Type Extended Structure for Superior Selectivity of CO₂ over N₂. *J. Mater. Chem. A* **2015**, *3*, 19177–19185.
- (108) Lee, W. R.; Jo, H.; Yang, L.-M.; Lee, H.; Ryu, D. W.; Lim, K. S.; Song, J. H.; Min, D. Y.; Han, S. S.; Seo, J. G.; Yong, K. P.; Moon, D.; Seop Hong, C. Exceptional CO₂ Working Capacity in a Heterodiamine-Grafted Metal-Organic Framework. *Chem. Sci.* **2015**, *6*, 3697–3705.
- (109) Wu, D.; McDonald, T. M.; Quan, Z.; Ushakov, S. V.; Zhang, P.; Long, J. R.; Navrotsky, A. Thermodynamic Complexity of Carbon Capture in Alkylamine-Functionalized Metal-Organic Frameworks. *J. Mater. Chem. A* **2015**, *3*, 4248–4254.
- (110) Deria, P.; Mondloch, J. E.; Tylianakis, E.; Ghosh, P.; Bury, W.; Snurr, R. Q.; Hupp, J. T.; Farha, O. K. Perfluoroalkane Functionalization of NU-1000 via Solvent-Assisted Ligand Incorporation: Synthesis and CO₂ Adsorption Studies. *J. Am. Chem. Soc.* **2013**, *135*, 16801–16804.
- (111) Hon Lau, C.; Babarao, R.; Hill, M. R. A Route to Drastic Increase of CO₂ Uptake in Zr Metal Organic Framework UiO-66. *Chem. Commun.* **2013**, *49*, 3634.
- (112) Zhang, Z.; Gao, W.; Wojtas, L.; Ma, S.; Eddaoudi, M.; Zaworotko, M. J. Post-Synthetic Modification of Porphyrin-Encapsulating Metal-Organic Materials by Cooperative Addition of Inorganic Salts to Enhance CO₂/CH₄ Selectivity. *Angew. Chemie Int. Ed.* **2012**, *51*, 9330–9334.
- (113) Li, H.; Wang, K.; Feng, D.; Chen, Y.; Verdegaal, W.; Zhou, H.-C. Incorporation of Alkylamine into Metal-Organic Frameworks through a Brønsted Acid-Base Reaction for CO₂ Capture. *ChemSusChem* **2016**, *9*, 2832–2840.
- (114) Kronast, A.; Eckstein, S.; Altenbuchner, P. T.; Hindelang, K.; Vagin, S. I.; Rieger, B. Gated Channels and Selectivity Tuning of CO₂ over N₂ Sorption by Post-Synthetic Modification of a UiO-66-Type Metal-Organic Framework. *Chem. - A Eur. J.* **2016**, *22*, 12800–12807.
- (115) Hu, Z.; Zhang, K.; Zhang, M.; Guo, Z.; Jiang, J.; Zhao, D. A Combinatorial Approach towards Water-Stable Metal-Organic Frameworks for Highly Efficient Carbon Dioxide Separation. *ChemSusChem* **2014**, *7*, 2791–2795.
- (116) Park, H. J.; Cheon, Y. E.; Suh, M. P. Post-Synthetic Reversible Incorporation of Organic Linkers into Porous Metal-Organic Frameworks through Single-Crystal-to-Single-Crystal Transformations and Modification of Gas-Sorption Properties. *Chem. Eur. J.* **2010**, *16*, 11662–11669.
- (117) Chen, C.; Wei, Z.; Jiang, J.; Fan, Y.; Zheng, S.; Cao, C.; Li, Y.; Fenske, D.; Su, C. Precise Modulation of the Breathing Behavior and Pore Surface in Zr-MOFs by Reversible Post-Synthetic Variable-Spacer Installation to Fine-Tune the Expansion

- Magnitude and Sorption Properties. *Angew. Chemie Int. Ed.* **2016**, *55*, 9932–9936.
- (118) Hong, D. H.; Suh, M. P. Enhancing CO₂ Separation Ability of a Metal-Organic Framework by Post-Synthetic Ligand Exchange with Flexible Aliphatic Carboxylates. *Chem. - A Eur. J.* **2014**, *20*, 426–434.
 - (119) Hu, Z.; Faucher, S.; Zhuo, Y.; Sun, Y.; Wang, S.; Zhao, D. Combination of Optimization and Metalated-Ligand Exchange: An Effective Approach to Functionalize UiO-66(Zr) MOFs for CO₂ Separation. *Chem. Eur. J.* **2015**, *21*, 17246–17255.
 - (120) Sánchez-Laínez, J.; Veiga, A.; Zornoza, B.; Balestra, S. R. G.; Hamad, S.; Ruiz-Salvador, A. R.; Calero, S.; Téllez, C.; Coronas, J. Tuning the Separation Properties of Zeolitic Imidazolate Framework Core-Shell Structures via Post-Synthetic Modification. *J. Mater. Chem. A* **2017**, *5*, 25601–25608.
 - (121) An, J.; Rosi, N. L. Tuning MOF CO₂ Adsorption Properties via Cation Exchange. *J. Am. Chem. Soc.* **2010**, *132*, 5578–5579.
 - (122) Li, T.; Rosi, N. L. Screening and Evaluating Aminated Cationic Functional Moieties for Potential CO₂ Capture Applications Using an Anionic MOF Scaffold. *Chem. Commun.* **2013**, *49*, 11385.
 - (123) Liu, B.; Zhang, R.; Pan, C.; Jiang, H. Unprecedented Li⁺ Exchange in an Anionic Metal-Organic Framework: Significantly Enhanced Gas Uptake Capacity. *Inorg. Chem.* **2017**, *56*, 4263–4266.
 - (124) Park, H. J.; Suh, M. P. Enhanced Isosteric Heat, Selectivity, and Uptake Capacity of CO₂ Adsorption in a Metal-Organic Framework by Impregnated Metal Ions. *Chem. Sci.* **2013**, *4*, 685–690.
 - (125) Furukawa, H.; Gándara, F.; Zhang, Y.-B.; Jiang, J.; Queen, W. L.; Hudson, M. R.; Yaghi, O. M. Water Adsorption in Porous Metal-Organic Frameworks and Related Materials. *J. Am. Chem. Soc.* **2014**, *136*, 4369–4381.
 - (126) Yuan, S.; Feng, L.; Wang, K.; Pang, J.; Bosch, M.; Lollar, C.; Sun, Y.; Qin, J.; Yang, X.; Zhang, P.; Wang, Q.; Zou, L.; Zhang, Y.; Zhang, L.; Fang, Y.; Li, J.; Zhou, H.-C. Stable Metal-Organic Frameworks: Design, Synthesis, and Applications. *Adv. Mater.* **2018**, *30*, 1704303.
 - (127) Ding, N.; Li, H.; Feng, X.; Wang, Q.; Wang, S.; Ma, L.; Zhou, J.; Wang, B. Partitioning MOF-5 into Confined and Hydrophobic Compartments for Carbon Capture under Humid Conditions. *J. Am. Chem. Soc.* **2016**, *138*, 10100–10103.
 - (128) Zhang, W.; Hu, Y.; Ge, J.; Jiang, H.; Yu, S. A Facile and General Coating Approach to Moisture/Water-Resistant Metal-Organic Frameworks with Intact Porosity. *J. Am. Chem. Soc.* **2014**, *136*, 16978–16981.
 - (129) Nguyen, J. G.; Cohen, S. M. Moisture-Resistant and Superhydrophobic Metal-Organic Frameworks Obtained via Postsynthetic Modification. *J. Am. Chem. Soc.* **2010**, *132*, 4560–4561.
 - (130) Yang, S. J.; Park, C. R. Preparation of Highly Moisture-Resistant Black-Colored Metal Organic Frameworks. *Adv. Mater.* **2012**, *24*, 4010–4013.

Chapter 2: Custom Designed MTV-IRMOF-74-III for NMR Signal Amplification

Work in this Chapter was performed in a team including Alejandro M. Fracaroli, Louis S. Bouchard, and Omar M. Yaghi

2.1 Preface

To begin my graduate studies, I sought to append a homogeneous catalyst, $[\text{IrPy}(\text{COD})(\text{IMes})]\text{PF}_6$, (Py = pyridine; IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene; COD = cyclooctadiene) to the linkers of the IRMOF-74-III structure {IRMOF-74-III, $\text{Mg}_2(\text{DH}_3\text{PhDC})$, where $\text{H}_4\text{DH}_3\text{PhDC}$ = 2',5'-dimethyl-3,3'- dihydroxy-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid, Figure 2.1}, in a covalent, post-synthetic step. This catalyst had previously proven to affect nuclear magnetic resonance (NMR) signal amplification by reversible exchange (SABRE). Reports leading up to this work provided evidence that forming a heterogeneous SABRE catalyst drastically improved the applicability of the technique. In this chapter, I describe efforts toward forming a MOF-based heterogeneous SABRE catalyst and challenges with its implementation.

2.2 Introduction

Nuclear magnetic resonance (NMR) spectroscopy and magnetic resonance imaging (MRI) are powerful techniques for chemical structure analysis and tissue imaging, respectively. However, these techniques are plagued by low populations of nuclei in excited states under standard experimental conditions, necessitating increased scan times and high detection limits. Recent work has focused on bolstering the populations of these excited states and enhancing NMR/MRI signals using a strategy known as signal amplification by reversible exchange (SABRE).¹ In this technique, para-hydrogen, the singlet nuclear spin isomer of molecular hydrogen (denoted here as $p\text{-H}_2$), is used to enhance NMR/MRI signals up to 800 times via transfer of excited nuclear spin polarizations to target analytes.¹ This polarization transfer is typically mediated by mixing analytes in homogeneous solution with an organometallic iridium complex. Upon mixing, the compounds combine to form a transient, 6-coordinate iridium species consisting of the base ligand scaffold, analyte, and $p\text{-H}_2$.^{2,3} The synthesis of a heterogeneous SABRE catalyst has been previously reported⁴. In this work, polymeric microbeads with dangling organic functionalities terminating in pyridine moieties that ligate the SABRE catalyst were used as a solid support. However, in this approach only a fivefold enhancement in the pyridine signals was observed. One other example of heterogeneous SABRE also exists, but it has also only achieved a fraction of the 800-fold enhancement demonstrated by homogeneous SABRE catalysts.⁴

Metal-organic frameworks (MOFs) are an extensive class of extended crystalline materials composed of metal-containing secondary building units (SBUs) and organic linkers connected by strong bonds. Due to their permanent porosity, high specific surface area, and amenability to pore surface modification, much of the work on MOFs has focused on gas storage.^{6,7} In particular, hundreds of structures have been reported to efficiently store hydrogen with capacities up to 9 weight percent. Hydrogen uptake under the conditions of SABRE (e.g. 3.5 atm $p\text{-H}_2$ at room temperature)¹ has not been investigated *per se* in literature, however these reports demonstrate that MOFs may be useful for concentrating hydrogen, an inherent advantage over other solid supports.^{6,8,9}

MOFs show special promise because of their adjustable chemical functionality, which can be further increased by the preparation of multivariate MOFs (MTV-MOFs). The MTV approach has been shown to optimize properties of these porous crystalline materials via the introduction of heterogeneity.^{6,10} Typically, this heterogeneity is introduced into MOFs via incorporation of multiple linkers bearing different functionalities into the same MOF structure without changing the underlying topology, crystallinity, or porosity of the extended structures.¹¹ This approach can enhance MOF affinity for hydrogen relative to structures lacking designed heterogeneity.⁶

Covalent incorporation of highly reactive functionalities or catalytic sites into the pores of MOFs has been an outstanding challenge.¹²⁻¹⁵ Very often these active sites undergo chemical transformation when exposed to MOF synthesis conditions or prevent the formation of the desired extended structure altogether.¹⁶ In order to overcome this challenge, much focus has been placed on post-synthetic modification (PSM) to introduce reactive moieties into MOF structures.^{7,14,17-20} Recent work has led to the development of methods for *covalent* linker post-synthetic modification.^{7,21} One such PSM scheme installed a ligand scaffold for a chromium(III)-based ethylene polymerization catalyst onto the organic linker in IRMOF-III via imine condensation.²² Such work sets a precedent for covalent PSM as a viable method of catalyst introduction into the pore environments of MOFs.

The aim of this project is to design a heterogeneous catalyst for SABRE. The advantageous properties of MOFs such as permanent porosity, affinity for H₂, and amenability to functionalization, make them a prime candidate for the use of covalent bonds to post-synthetically bind a reactive iridium catalyst to perform NMR signal amplification. Although SABRE is a powerful analytical tool and can have important biological applications¹ such as tissue imaging, metabolite monitoring, and toxin detection, it is significantly limited by the fact that it must be performed using a homogeneous catalyst.² Homogeneous catalysis necessitates dissolution of the SABRE catalyst in the same media as the other reagents and analytes, a potentially toxic situation for *in vivo* application of the technique, which could be avoided using biocompatible MOFs such as IRMOF-74-III.²³ Also, the homogeneous nature of the iridium species means it is not readily reusable. Using a MOF as a solid support would improve the SABRE technique as it not only forms a heterogeneous (and thus separable, biocompatible, and reusable) catalyst, but the MOF itself can be used to enhance NMR signal by augmenting the local concentration of p-H₂. The MOF system reported here has been designed as crystalline, porous solid support for the SABRE catalyst.

2.3 Approach

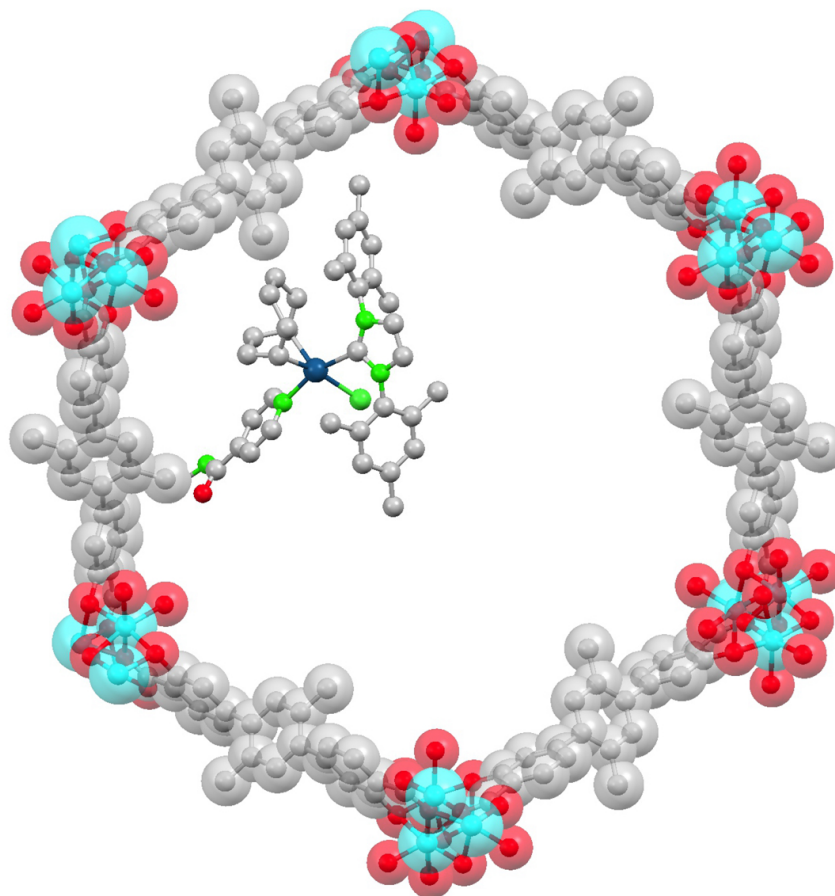
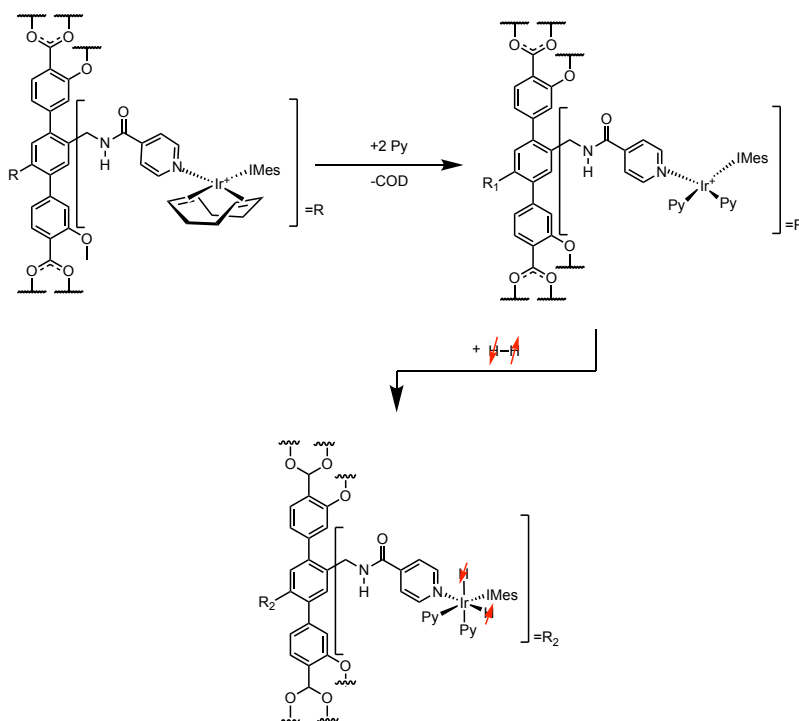


Figure 2.1. Schematic representation of covalently bound Ir SABRE catalyst in the pore of IRMOF-74-III. Color code: C, gray; O, red; N, green; Mg, light blue; and Ir, Navy.

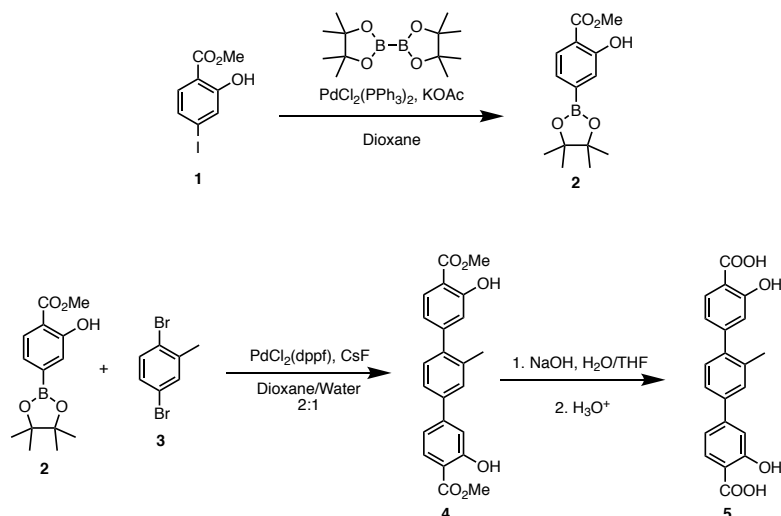
This work details efforts to covalently bind a variant of the SABRE catalyst, $[\text{IrPy}(\text{COD})(\text{IMes})]\text{PF}_6$, (Py = pyridine; IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene; COD = cyclooctadiene) to the linkers of the IRMOF-74-III structure {IRMOF-74-III, $\text{Mg}_2(\text{DH}_3\text{PhDC})$, where $\text{H}_4\text{DH}_3\text{PhDC}$ = 2',5'-dimethyl-3,3"- dihydroxy-[1,1':4',1"-terphenyl]-4,4"-dicarboxylic acid, Figure 2.1}, in a covalent, post-synthetic step. IRMOF-74-III was selected due to its large one-dimensional pores diagonally measuring 25 Å, which can accommodate the iridium catalyst while leaving enough free volume for the diffusion of $p\text{-H}_2$ and analyte.²⁴ The linkers of IRMOF-74-III have recently been functionalized with amine groups which can serve as sites for PSM. Nevertheless, post-synthetic incorporation of iridium catalysts into fully functionalized structures would likely lead to pore occlusion and issues with respect to analyte diffusion. This approach takes advantage of a multivariate MOF approach (MTV-MOF), to “dilute” the reactive functionalities in the IRMOF-74-III pores. It was demonstrated that it is possible to mix organic linkers with the same metrics during the MOF synthesis and obtain the same overall topology as the original IRMOF-74-III structure. Additionally, IRMOF-74-III is an

ideal candidate because the ratio of two different linkers incorporated into the MOF structure is the same as the ratio of these two linkers in the synthesis conditions.^{6,10} Thus a MTV-IRMOF-74-III system composed of 90% unfunctionalized linkers and 10% linkers with protected amines designed to be converted to free primary amines by post-synthetic modification was employed.⁷ Upon deprotection, these amino groups were coupled with isonicotinic acid (-inic; pyridine 4-carboxylic acid) using amide coupling conditions to install a pyridine moiety in the pore of the framework. Attempts were made to post-synthetically utilize the -inic moiety to coordinate and immobilize the iridium complex,⁴ leaving it available for interaction with p-H₂ and a target analyte, as is consistent with the SABRE mechanism (Scheme 2.1).

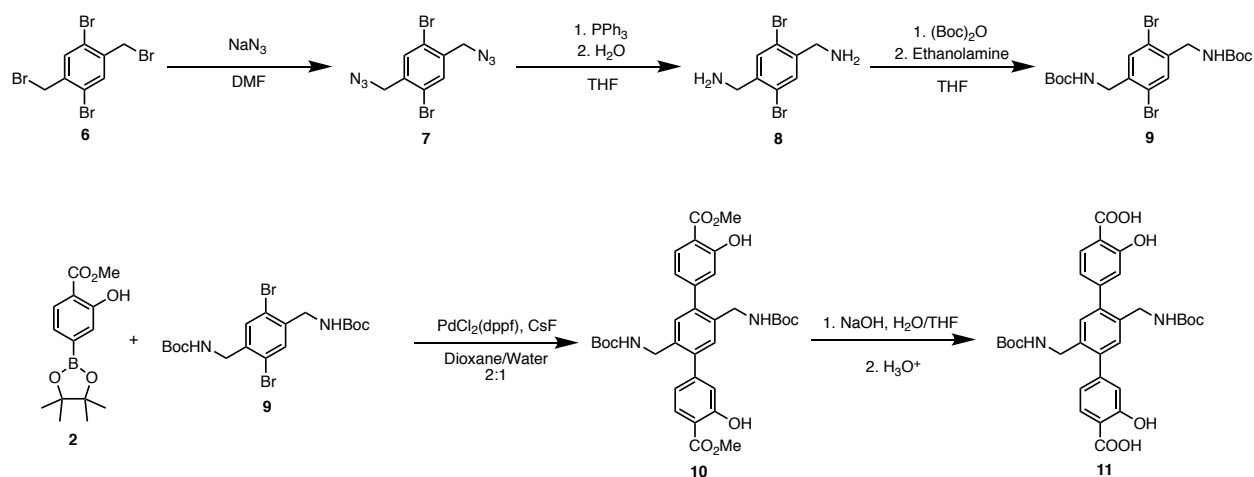


Scheme 2.1. Proposed heterogeneous SABRE effect in the IRMOF-74-III pore.^{2,3} This scheme involves (i) a dissociation of the η^4 -COD ligand with simultaneous association of analyte pyridine ligands, and (ii) oxidative addition of p-H₂ to the Ir center. After this scheme is complete, nuclear spins are transferred due to the close proximity of the p-hydride₂ ligands to the target analytes. Outer-sphere PF₆⁻ counterion and additional Ir catalyst (R₂) have been omitted from this figure for clarity. (Py = pyridine; IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene; COD = cyclooctadiene)

2.4 Organic Linker Synthesis



Scheme 2.2. Synthetic pathway for 3,3''-dihydroxy-2'-methyl-[1,1':4,1''-terphenyl]-4,4''-dicarboxylic acid **5**.



Scheme 2.3. Synthetic pathway for 2',5'-bis(((tert-butoxycarbonyl)amino)methyl)-3,3''-dihydroxy-[1,1':4,1''-terphenyl]-4,4''-dicarboxylic acid **11**.

The two terphenylene organic linkers, **5** and **11**, used to construct MTV-IRMOF-74-III were synthesized according to the synthetic routes provided in Schemes 2.1 and 2.2, respectively (Section 2.12.2). The methyl functionalized organic linker, **5**, was synthesized from the commercially available 2,5-dibromotoluene and methyl-2-hydroxy-4-iodobenzoate, according to reported procedures.²⁴ To prepare the di-amino functionalized organic linker, **11**, commercially available 1,4-dibromo-2,5-bis(bromomethyl)benzene was transformed via benzylic halide azidation to obtain the di-azido derivative (**7**). Subsequent Staudinger reduction and protection yielded the *t*-butoxycarbonyl (Boc) protected benzylic amine, **9**, which was coupled to methyl 2-

hydroxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate via a Suzuki–Miyaura coupling²⁵ to yield the methyl ester derivative of the IRMOF-74-III functionalized organic linker, **10**. The methyl ester was converted to the corresponding carboxylic acid via saponification with sodium hydroxide.

2.5 Metal-Organic Framework Synthesis and Post-Synthetic Modification

Synthesis of extended structures was accomplished by adhering to a previously reported procedure.²⁴ To realize the 10% MTV compound [MTV-IRMOF-74-III(CH₂NHBoc)_{0.1}] the methyl and di-amino functionalized organic linkers (**5** and **11** respectively), were added to the reaction mixture in the desired molar ratio (90:10). The solvothermal synthesis yielded faintly pale yellow microcrystalline spherulites, which were then washed according to previously published procedures in preparation for post-synthetic modification.²⁴ The product crystallinity was confirmed by powder X-ray diffraction (PXRD) measurements (section 2.12.7) of air-dried samples and linker ratios were confirmed by ¹H NMR spectroscopy studies on the materials digested in a DMSO-d₆/D₂O mixture brought to 50 mM in DCl (section 2.12.4). Analogous methods were employed to confirm the success of each subsequent PSM step.

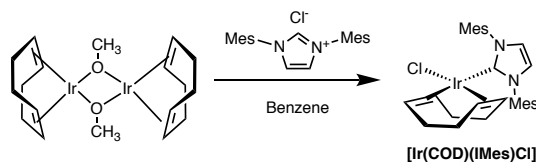
Interestingly, digested MOFs synthesized using the 90:10 linker **5**: linker **11** ratio were observed to quantitatively match the amounts of di-amino and methyl functionalized linkers added to the reaction mixture. The first PSM, quantitative –Boc deprotection, was accomplished using microwave thermolysis (section 2.12.4) in a ternary solvent mixture [2-ethyl-1-hexanol/ethylene glycol/water (9.1:0.5:0.5)]²⁴, yielding MTV-IRMOF-74-III(CH₂NH₂)_{0.1}. Installation of isonicotinic acid onto the exposed primary amine was accomplished via peptide coupling using *N,N,N',N'*-tetramethyl-*O*-(1*H*-benzotriazol-1-yl)uronium hexafluorophosphate (HBTU) (section 2.12.4).²⁶ The post synthetic modification loading efficiency was nearly quantitative as evidenced by ¹H NMR spectroscopy studies (section 2.12.4) on the digested materials, yielding MTV-IRMOF-74-III(CH₂NHInic)_{0.1}.

2.6 Synthesis and Covalent Attachment of SABRE Catalyst to MTV-IRMOF-74-III

Inspired by a previous approach to bind a variant of the SABRE catalyst to polymer microbeads⁴, a similar strategy was used to attach the iridium catalyst to the MOF interior. Thus, the post-synthetic incorporation of isonicotinic acid was designed as a method of decorating the MOF pore with a free pyridine ligand, just as polymer microbeads were decorated in a previous study of attachment of an iridium catalyst to a solid support.

Upon successful incorporation of isonicotinic acid, attempts were made to coordinate an iridium catalyst precursor [IrCl(COD)(IMes)] [IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene; cod = cyclooctadiene] to the pyridine moieties bedecking the pores under typical complexation conditions, as detailed below.

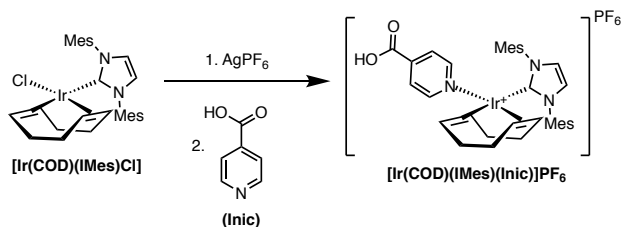
$[\text{IrCl}(\text{COD})(\text{IMes})]$ was prepared by reaction of bis(1,5-cyclooctadiene)di- μ -methoxydiiridium(I) with 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (Scheme 3)²⁷. The resultant complex was found to be air-stable for several months.



Scheme 2.4. Synthetic pathway for $[\text{IrCl}(\text{COD})(\text{IMes})]$.

The post-synthetic binding of the SABRE catalyst to the pyridine-functionalized MOF was tested by performing a ligand exchange reaction in two steps. First, chloride abstraction to yield the cationic complex was accomplished by adding $[\text{IrCl}(\text{COD})(\text{IMes})]$ to a THF solution of silver hexafluorophosphate (Scheme 2.5). Silver chloride precipitated out in the process, leading to the formation of a coordinatively unsaturated iridium center susceptible to ligation by the pyridyl nitrogen. After filtration from THF under N_2 to remove the precipitate, the iridium complex was added to a suspension of the MTV-IRMOF-74-III- $(\text{CH}_2\text{NHInic})_{0.1}$ compound also in THF. Although a color change in the bulk MOF (from bright orange to dark brown-orange) was observed in this trial, no quantifiable metalation of the pyridyl-functionalized MOF linkers was evident in the subsequent ^1H NMR spectrum of the digested MTV-IRMOF74-III after washing.

2.7 Molecular Screening of Metalation Conditions



Scheme 2.5. Synthetic pathway for $[\text{Ir}(\text{COD})(\text{IMes})(\text{Inic})]\text{PF}_6$ as a molecular analogue for metalation conditions in MTV-IRMOF-74-III.

To overcome the observed paltry loading of the iridium compound into post-synthetically modified MOFs, the reaction conditions were optimized using isonicotinic acid as a molecular analogue of the MTV-IRMOF-74-III- $(\text{CH}_2\text{NHInic})_{0.1}$ linker (Scheme 2.5). A variety of solvents were tested at both room temperature and 60°C . Among potential solvents, THF was chosen due to the non-coordinative nature of the solvent and its ability to effectively dissolve each precursor for the reaction. THF has also been shown to effectively perform other heterogeneous iridium catalyst transformations.⁴ Methanol was also chosen because it is a very weakly coordinating solvent and its polarity allows for facile diffusion into the MOF pore decorated with polar moieties such as pyridine.

Methanol has also been shown to be a highly compatible solvent for many post-synthetic modification procedures (e.g. the -Boc deprotection reported above) in IRMOF-74-III.²⁴ Toluene was tested because it was hypothesized to have a favorable π - π interaction with the aromatic organic linkers in the MTV-IRMOF-74-III structure, thus more likely to diffuse into the pores. Additionally, toluene also effectively dissolves isonicotinic acid and the [Ir(COD)(IMes)]PF₆ precatalyst.

Table 2.1. Evaluated reaction conditions for the screening of conditions to metalate Ir with isonicotinic acid.^a

Solvent	Temperature (°C)	Yield (%)
THF	25	65%
THF	60	39%
Methanol	25	69%
Methanol	60	35%
Toluene	25	50%
Toluene	60	27%

^a Reactions were conducted for 12 h. on 0.023 mmol scales.

Yield of the ligation reactions was monitored by ¹H NMR spectroscopy on the digested samples for the resultant materials. A summary of the results can be found in Table 2.1. It was found that performing the reaction in methanol at room temperature lead to higher complexation yields than other conditions. The decreased yield at higher temperature is likely due to thermal decomposition of starting materials. A possible mechanism for this decomposition would involve dissociation of the labile COD ligand, which is known in SABRE type mechanisms at room temperature (Scheme 2.1).^{2,3} Elevated temperatures could feasibly facilitate this dissociation.

2.8 Verification of [Ir(COD)(IMes)(Inic)]PF₆ Stability under MOF Digestion Conditions

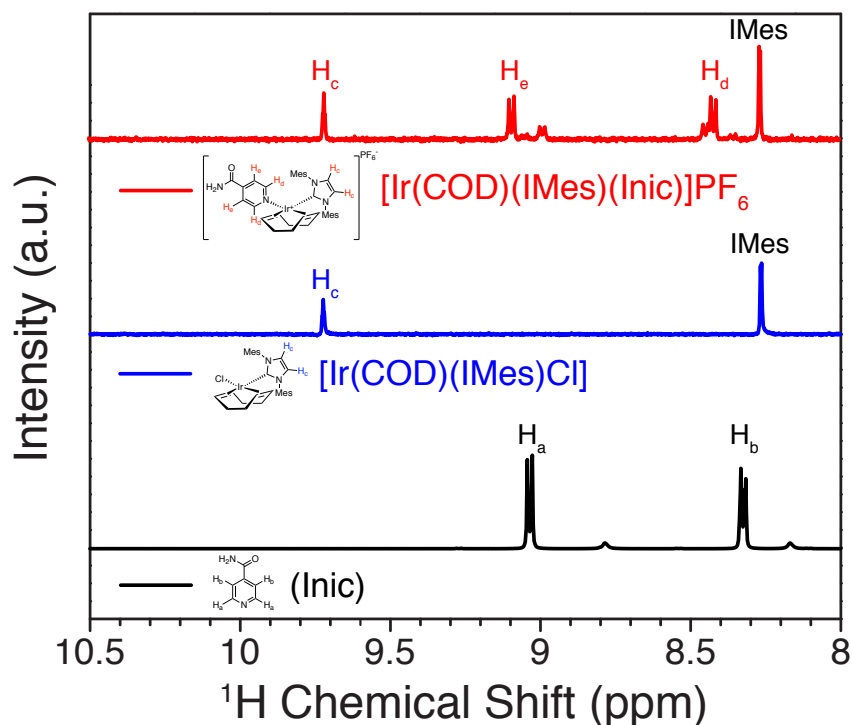


Figure 2.2. Pertinent region ($8 < \delta < 10.5$) of ^1H NMR spectra of isonicotinamide (black), [Ir(COD)(IMes)Cl] (blue), and [Ir(COD)(IMes)(Inic)]PF₆ (red) under MOF digestion conditions. From the product spectrum, it was calculated that more than 90% of the product remains unchanged when subjected to these conditions.

The starting material, [Ir(COD)(IMes)Cl], the product, [Ir(COD)(IMes)(Inic)]PF₆, and free isonicotinamide were exposed to the MOF digestion conditions mentioned earlier under inert N₂ atmosphere. The [Ir(COD)(IMes)(Inic)]PF₆ compound was generated according to literature conditions.⁴ Isonicotinamide was chosen as the pyridine analogue for this study to more accurately resemble the ligand as bound to the MOF linker. To verify the stability of the pyridine-iridium adduct to the MOF digestion conditions, ^1H NMR spectrum of each solution was obtained under inert atmosphere (Figure 2.2). In the spectrum of the product, [Ir(COD)(IMes)(Inic)]PF₆, the small doublet signals at $\delta=9.04$ ppm ($J=4$ Hz, free isonicotinamide ortho -H) and $\delta=8.33$ ppm ($J=4$ Hz, free isonicotinamide meta -H) correspond to the small amount of free, protonated isonicotinamide in solution. The presence of the larger doublet signals at $\delta=9.10$ ppm ($J=4$ Hz, Ir-bound isonicotinamide ortho -H) and $\delta=8.42$ ppm ($J=4$ Hz, Ir-bound isonicotinamide meta -H) suggest that most of the pyridine-iridium adduct remains intact.

2.9 Synthesis and Post-Synthetic Modification of Fully Functionalized MOF System

An alternative, fully amino-functionalized IRMOF-74-III, IRMOF-74-III(CH₂NH₂)₂, compound was evaluated to study the efficiency of the complexation reaction. This MOF was chosen instead of the previous MTV material to explore the possibility of increasing the Ir loading efficiency by increasing the number of pyridine units in the MOF interior. IRMOF-74-III-(CH₂NHBoc)₂ was synthesized via the previously described procedure, using only **11** as the organic linker. Successful MOF synthesis was confirmed by PXRD, and the ¹H NMR spectroscopy of samples digested in the solvent mixture mentioned above. The same procedures detailed above for -Boc deprotection and -inic loading post-synthetic steps were repeated. ¹H NMR spectroscopy studies of the digested IRMOF-74-III-(CH₂NHInic)₂ compound revealed complete conversion in both PSMs: -Boc deprotection of amines and isonicotinic acid loading. PXRD analysis of the resultant MOF showed nearly identical patterns to the parent MOF structure, indicating that the material remains crystalline along the PSM steps.

2.10 Metalation of IRMOF-74-III-(CH₂NHInic)₂

Metalation of IRMOF-74-III-(CH₂NHInic)₂ was attempted using the best conditions elucidated in the preliminary study mentioned above. After stirring the mixture of IRMOF-74-III-(CH₂NHInic)₂ and the hexafluorophosphate salts of the iridium complex at room temperature for 12 h, I proceeded to analyze the product(s) and yield of the reaction by measuring ¹H NMR spectra of the digested sample. The ¹H NMR spectrum of the product showed a doublet signal at $\delta=9.06$ ppm ($J=8$ Hz) ppm, and the doublet signal at $\delta=8.97$ ppm ($J=8$ Hz) correspond to free (Inic) ligand and (Inic) ligand bound to the iridium center respectively (Figure 2.3). The integration ratio of these doublets indicated a 7% metalation of the MOF structure.

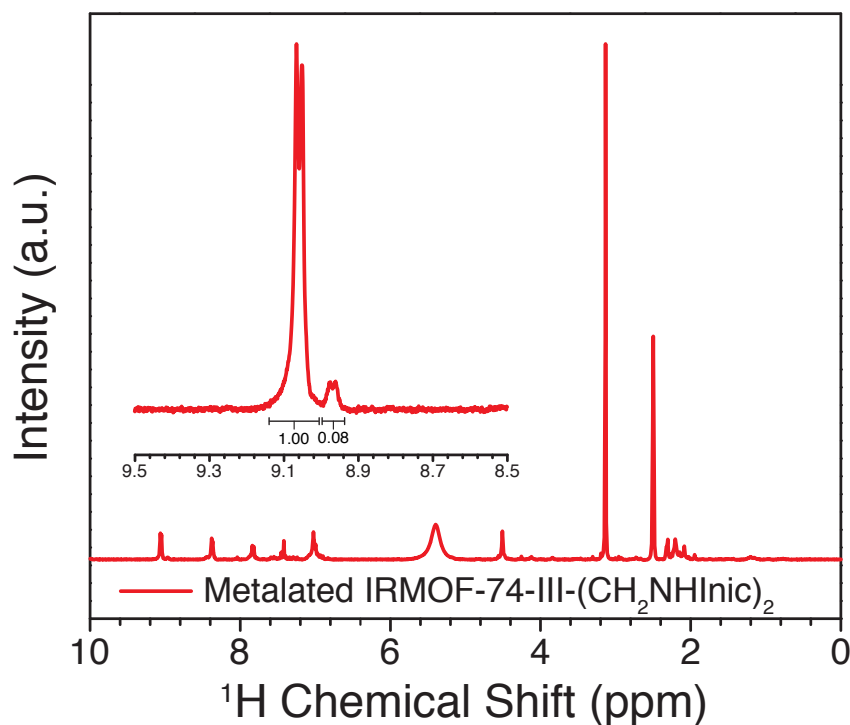


Figure 2.3. Representative ^1H NMR spectrum of successful metalation of IRMOF-74-III-(CH_2NHInic) $_2$ with 100% functionalized linker. (Inset) Pertinent region ($8.5 < \delta < 9.5$) of collected spectrum used to calculate metalation yield.

The low yield in the metalation step may be related to bulkiness of the iridium complex and the coincident hindered diffusion into the pores of the MOF, as also evidenced by the lack of quantitative metalation in the MTV system. It is also possible that the metalation was only successful on the surface of the MOF crystallites. A rough calculation of crystal surface area : volume ratio, estimated from the sizes ($100 \pm 25 \mu\text{m}$, measured by optical microscopy), implies that approximately 5% of the PSM-installed moieties exist on the surface of IRMOF-74-III(CH_2NHInic) $_2$. Therefore a 7% yield in metalation is inconclusive evidence of iridium precursor diffusion into the MOF pores and subsequent ligation by the available pyridine ligands.

2.11 Conclusion

Drawing inspiration from previous work in the field, successful synthesis of an MTV-IRMOF-74-III(CH_2NHBoc) $_{0.1}$ system with highly tunable linker ratios and sites readily available for post synthetic modification was accomplished. Capitalizing on facile, well-documented reactivity built into the protected primary amine moieties extending into the MOF pore, a pyridine ligand was installed onto the MOF linker. This installation was performed in hopes of coordinating a variant of an organometallic iridium catalyst to be utilized for heterogeneous solution NMR SABRE. Successful metalation was undetectable in the MTV system, but after further optimization and the use of a fully pyridine-functionalized IRMOF-74-III, we were able to observe meager metalation of the

IRMOF-74-III-(CH₂NHInic)₂ compound. Further attempts to improve the iridium SABRE catalyst loading into the pyridine functionalized MOFs were unsuccessful. These included attempts to use N,N-dimethyl formamide (DMF) as the solvent for the metalation reaction, as well as attempts to repeat the metalation procedure multiple times on the same material. Neither attempt increased the metalation yield in the fully-functionalized IRMOF-74-III-(CH₂NHInic)₂ compound and thus it was concluded that they would not be successful in the MTV system. Due to the inherent challenges facing the project such as the lack of optimization of the newly-developed SABRE technique and failure of attempts to incorporate optimized SABRE catalysts into MOFs using tethering techniques proven to be successful in both MOF and heterogeneous SABRE literature, I decided to move in a different direction.

2.12 Supporting Information for Chapter 2

2.12.1 General Considerations

Chemicals used in this work

Bis(1,5-cyclooctadiene)di- μ -methoxydiiridium(I) and Di-*tert*-butyl dicarbonate were acquired from Alfa Aesar and used as received. Bis(triphenylphosphine)palladium(II) dichloride, [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II), and cesium fluoride were acquired from Aldrich, stored under inert atmosphere, and used as received. 2,5-Dibromotoluene, N,N-diisopropylethylamine, bis(pinacolato)diboron, potassium acetate, sodium azide, triphenylphosphine, and ethanolamine were acquired from Aldrich used as received. Isonicotinic acid and 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride were acquired from Arcos Organics and used as received. Methyl 4-iodosalicylate was acquired from Boron Molecular, Inc. and used as received. N,N,N',N'-tetramethyl-O-(1H-benzotriazol-1-yl)uronium hexafluorophosphate (HBTU) was acquired from Nova Biochem Inc., stored in a refrigerator and used as received. 1,4-Dibromo-2,5-bis(bromomethyl)benzene was acquired from TCI America and used as received. Anhydrous solvents used in linker and MOF synthesis as well as reaction screening and optimization were obtained from Acros, EMD Chemicals, and Aldrich and stored in sealed bottles and used under inert atmosphere purge. Other common solvents and reagents such as ethanol, 2-ethyl-1-hexanol, and magnesium sulfate were obtained from other commercial sources and all chemicals in this work were used without further purification.

Analytical Techniques

Liquid-state ¹H and ¹³C{¹H} NMR spectra were acquired on Bruker AVB-400 (400 MHz), AV-300 (300 MHz), AV-500 (500 MHz), and AV-600 (600 MHz) spectrometers at 297–300 K. Chemical shifts were calculated using the solvent resonances as internal standards (¹H: 7.26 ppm for CHCl₃, 2.50 ppm for DMSO; ¹³C{¹H}: 77.00 ppm for CDCl₃,

39.51 ppm for DMSO-*d*₆). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet of doublets (dt), triplet (t), multiplet (m), and broad resonance (br).

FT-IR spectra were collected in-house using a Bruker ALPHA Platinum ATR-FT-IR Spectrometer equipped with a single reflection diamond ATR module.

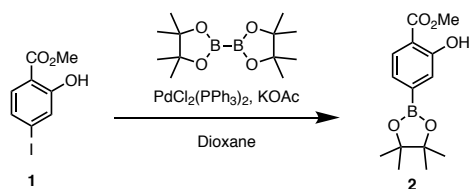
High Resolution Electrospray Ionization mass (HR-ESI) was acquired on an Finnigan LTQ FT (Thermo Electron Corporation) instrument, using either negative or positive modes and by direct injection of methanol solutions of the samples using syringe pump with a flow rate of 5 $\mu\text{L min}^{-1}$.

Powder X-ray diffraction data were collected using a Rigaku MiniFlex 600 instrument equipped with a copper X-ray source producing K_{α} radiation with a wavelength of 1.54056 Å. Samples were mounted on zero background sample holders by dropping powders from a wide-blade spatula and then leveling the sample with a razor blade. Data were collected using a $0.01^{\circ} 2\theta$ step scan from 2 – 30° .

Column chromatography was performed on silica gel purchased from Sorbent Technologies (standard grade, 60 Å, 40–63 μm). Analytical thin layer chromatography (TLC) was performed on Whatman 250 μm -thick silica gel 60 plates with a fluorescent indicator. Visualization of TLC spots was accomplished under UV light ($\lambda = 254 \text{ nm}$).

2.12.2 Organic Linker Synthesis

Synthesis of methyl-2-hydroxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (2)

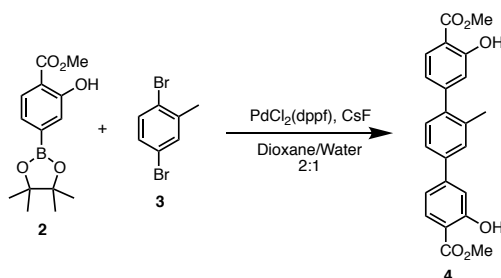


Scheme S2.1. Synthetic pathway for methyl-2-hydroxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate **2**.

A clean, oven dried 3-neck round bottom flask attached to a Schlenk line apparatus with equipped reflux condenser was charged with 25.0 g (89.9 mmol) of methyl-4-iodosalicylate (**1**), 25.1 g (98.9 mmol, 1.10 eq) of bis(pinacolato)diboron, 29.1 g (297 mmol, 3.30 eq) of potassium acetate, and 1.26 g (1.80 mmol, 0.0200 eq) of bis(triphenylphosphine) palladium(II) chloride. The flask and contents were then evacuated and refilled with inert house nitrogen atmosphere. This process was repeated three times to ensure an anhydrous and oxygen-free environment. 450 mL of 1,4 dioxane in a separate round bottom flask was deoxygenated by nitrogen gas bubbling for 30 min. and was subsequently added to the reaction mixture under N_2 . The reaction mixture was

then stirred and heated to 120° C by immersion in an oil bath until reflux for 16 h. Reaction progress was monitored via thin layer chromatography in a 10:1 hexanes: ethyl acetate mixture. The reaction mixture was then filtered through a plug of silica in a fritted filter to remove any remaining inorganic salts. The compound was purified by recrystallization from hot hexanes yielding compound **2** as pale yellow crystals (18.6g, 67.0 mmol, 67.7% yield). ¹H NMR (600 MHz, DMSO-*d*₆) δ 10.39 (s, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.23 – 7.16 (m, 2H), 3.88 (s, 3H), 1.28 (s, 12H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 169.33, 159.46, 129.70, 124.99, 123.41, 115.74, 84.44, 52.80, 24.98. MS (HR-ESI), *m/z* calcd. for C₁₄H₁₉BO₅ [M⁺]: 278.1326, found: 278.1330.

*Synthesis of dimethyl 3,3''-dihydroxy-2'-methyl-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate (**4**)*

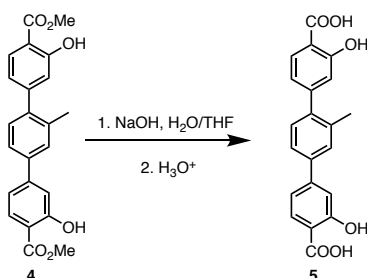


Scheme S2.2. Synthetic pathway for dimethyl 3,3''-dihydroxy-2'-methyl-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate **4**.

A clean, oven-dried, 3 neck round bottom flask attached to a Schlenk line apparatus with equipped reflux condenser was charged with 1.40 g (5.05 mmol) 3-hydroxy-4-(methoxycarbonyl) phenylboronic acid pinacol ester (**2**). The flask and its contents were then evacuated and refilled with inert house nitrogen atmosphere. This process was repeated three times to ensure an anhydrous and oxygen-free reaction environment. In a separate flask, 12.0 mL of anhydrous 1,4-dioxane and 6.00 mL of deionized water were combined and then bubbled with dried house N₂ for 30 min. to deoxygenate the resulting mixture. Under N₂ pressure, 0.330 mL (2.40 mmol, 2.10 eq) of 1,4-dibromo-2-methylbenzene (**3**), 2.46 g (16.190 mmol, 3.2 eq) of cesium fluoride, 0.0884 g (0.121 mmol, 0.0240 eq) [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II), and the 1,4-dioxane/deionized water mixture were added to the flask. The reaction mixture was heated to 90 °C using an oil bath and refluxed for 24 h. The resulting two-layer (top-dark opaque brown, bottom-transparent colorless) solution was tested for completion using thin layer chromatography (25:1 dichloromethane: ethyl acetate) which provided evidence of the presence of mono- and di-coupled products. The reaction mixture was poured into a 500 mL separatory funnel with ca. 80 mL of ethyl acetate. 20 mL of a saturated NH₄Cl solution were added to the mixture in the separatory funnel and the organic phase was collected. The aqueous phase was extracted with 20 mL of ethyl acetate and the combined organic phases were dried over anhydrous magnesium sulfate, filtered and evaporated to a brown powder. This crude product was purified by column chromatography (CH₂Cl₂:AcOEt 25:1) and the purified product was obtained in 46% yield (0.711 g). ¹H NMR (600 MHz, Benzene-*d*₆) δ 11.38 (d, *J* = 14.8 Hz, 2H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.45 (d, *J* = 1.8 Hz, 1H), 7.32 – 7.21 (m, 2H), 7.15 –

7.08 (m, 2H), 7.01 (dd, $J = 8.2, 1.8$ Hz, 1H), 6.71 (dd, $J = 8.1, 1.7$ Hz, 1H), 3.37 – 3.29 (m, 6H), 2.11 (s, 3H). ^{13}C NMR (151 MHz, Benzene- d_6) δ 170.72, 162.95, 162.42, 149.72, 148.52, 141.15, 139.56, 135.92, 130.62, 130.23, 129.97, 129.67, 128.35, 125.12, 120.54, 118.77, 118.26, 116.72, 116.38, 111.74, 111.53, 51.77, 20.41. MS (HR-ESI), m/z calcd. for $\text{C}_{23}\text{H}_{19}\text{O}_6[(\text{M}-\text{H})^-]$: 391.1187, found: 391.1182.

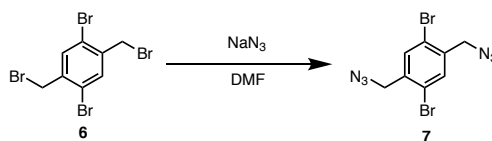
Synthesis of 3,3''-dihydroxy-2'-methyl-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid (5)



Scheme S2.3. Synthetic pathway for 3,3''-dihydroxy-2'-methyl-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid **5**.

A clean, oven dried, single-neck round bottom flask was charged with 2.7483 g (7.004 mmol) of (**4**) and 175 mL of anhydrous THF. The solution was sonicated and stirred until complete dissolution of the reactant was observed. In a separate flask, 2.8015 g (70.04 mmol, 10 eq) of anhydrous NaOH pellets were added to 175 mL of deionized water and the solution was stirred until the pellets were completely dissolved. The basic solution was subsequently added to the solution of (**4**) in THF to achieve a final NaOH concentration of 0.200 M and a final substrate concentration of 0.0200 M. The flask containing base and reactant was then attached to a Schlenk line apparatus with a reflux condenser equipped and was heated with an oil bath at 50 °C for 20 h. The reaction mixture was then cooled to room temperature and absence of starting material was confirmed by thin layer chromatography (1:1:1 dichloromethane: ethyl acetate: hexanes solvent mixture). The reaction mixture was acidified to pH 7 by addition of 8.584 mL of a 2M HCl solution. During acidification, a white solid formed in the reaction flask. The solid was collected by vacuum filtration to yield 2.4837 g of unfunctionalized linker (97% yield). ^1H NMR (600 MHz, DMSO- d_6) δ 11.40 (s, 2H), 7.85 (t, $J = 7.9$ Hz, 2H), 7.63 (s, 1H), 7.57 – 7.53 (m, 1H), 7.30 – 7.19 (m, 3H), 6.95 – 6.86 (m, 2H), 2.29 (s, 3H). ^{13}C NMR (151 MHz, DMSO- d_6) δ 171.85, 161.58, 161.44, 160.97, 148.16, 146.72, 140.34, 138.25, 135.53, 130.90, 130.23, 129.87, 129.11, 124.57, 120.22, 117.70, 117.38, 114.77, 111.99, 111.83, 20.21. MS (HR-ESI), m/z calcd. for $\text{C}_{21}\text{H}_{15}\text{O}_6[(\text{M}-\text{H})^-]$: 363.0874, found: 363.0869.

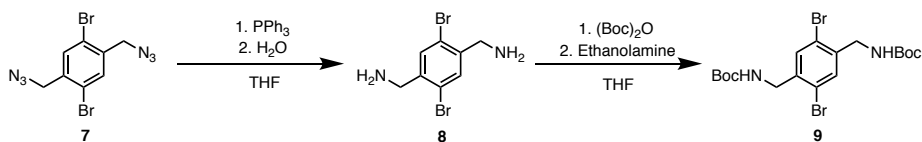
Synthesis of 1,4-bis(azidomethyl)-2,5-dibromobenzene (7)



Scheme S2.4. Synthetic pathway for 1,4-bis(azidomethyl)-2,5-dibromobenzene 7.

A clean, oven dried, 3-neck round bottom flask attached to a Schlenk line apparatus with equipped reflux condenser was charged with 2.37 g (5.62 mmol) of 1,4-dibromo-2,5-bis(bromomethyl)benzene (6) and 1.26 g (1.80 mmol, 4.00 eq) of sodium azide. The flask and its contents were evacuated and refilled with inert house nitrogen atmosphere. This process was repeated three times to ensure an anhydrous and oxygen-free reaction environment. 95 mL of anhydrous *N,N*-dimethylformamide was added to the reaction mixture under N_2 and the reaction mixture was then stirred and heated to 65 °C by immersion in an oil bath for 12 h. Reaction progress was monitored via thin layer chromatography (25:1 hexanes: ethyl acetate mixture) until the starting material was no longer detected. The reaction mixture was cooled to room temperature and then poured into a 500 mL separatory funnel. 60 mL of deionized water were added to the reaction mixture in the separatory funnel and the resultant solution was extracted three times with 50 mL of diethyl ether. The off-yellow organic phases were combined and washed with deionized water (30 mL, three times), and brine (20 mL, one time), dried over anhydrous magnesium sulfate, and evaporated until approximately 5 mL of ether remained. 20 mL of anhydrous THF was then added to the reaction mixture and the resultant solvent mixture was evaporated until approximately 5 mL of solvent remained. This process was repeated two more times when the reaction mixture was transferred to a new three neck round bottom flask in 120 mL of anhydrous THF where it was then bubbled with house nitrogen gas for 30 min. and left sealed and connected to a reflux condenser on a Schlenk line apparatus under nitrogen atmosphere for 12 h. Due to the potentially explosive nature of the resultant compound (C:N ratio in the chemical formula), the product was not isolated nor was any type of characterization performed and the product mixture was carried on to the next step in the synthetic procedure.

Synthesis of di-tert-butyl ((2,5-dibromo-1,4-phenylene)bis(methylene))dicarbamate (9)

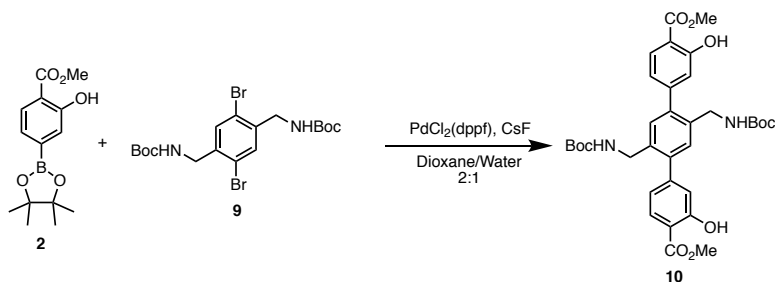


Scheme S2.5. Synthetic pathway for di-tert-butyl ((2,5-dibromo-1,4-phenylene)bis(methylene))dicarbamate 9.

A clean, oven dried three neck round bottom flask was charged with 3.25g (12.4 mmol, 2.20 eq) of triphenyl phosphine, 120 mL of anhydrous THF, and all of the 1,4-

bis(azidomethyl)-2,5-dibromobenzene (7) synthesized as mentioned above. The flask was connected to a reflux condenser on a Schlenk line apparatus under nitrogen atmosphere previously mentioned. The reaction mixture was heated to 60 °C and bubbles were noted indicating the evolution of N₂ gas, a product of the reaction. The reaction mixture was allowed to stir under heat for 5 h. at which point 5.01 mL (278 mmol, 49.5 eq) of deionized water were added and the reaction mixture was left at 60 °C for 12 h. Reaction progress was monitored via thin layer chromatography (10:1 hexanes: ethyl acetate mixture). After no presence of azide starting material was detected the reaction mixture was cooled to room temperature and 2.84 mL (12.4 mmol, 2.20 eq) di-*tert*-butyl dicarbonate [(Boc)₂O] was added under N₂ pressure. After 10 h., no sign of free amine was detected by thin layer chromatography using neat dichloromethane as the eluent, and 0.373 mL (6.19 mmol, 1.10 eq) ethanolamine was added under N₂ pressure. After three h., the THF was evaporated using a rotary-evaporator and the product mixture was collected as a yellow oil. This was then transferred to a 500 mL separatory funnel with 25 mL of deionized water and 100 mL of ethyl acetate. The aqueous phase was removed and the organic phase was washed with deionized water (20 mL, repeated three times) and brine (20 mL, one time) dried over anhydrous magnesium sulfate and evaporated to a white powder. This crude product was purified by column chromatography (CH₂Cl₂:AcOEt 25:1) and the purified product was obtained in 71% yield (2.78 g). ¹H NMR (600 MHz, Chloroform-*d*) δ 7.51 (s, 2H), 5.07 (t, *J* = 6.3 Hz, 2H), 4.31 (d, *J* = 6.4 Hz, 4H), 1.45 (s, 18H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 155.81, 138.97, 133.24, 122.38, 80.11, 44.35, 28.50. MS (HR-ESI), *m/z* calcd. for C₁₈H₂₆Br₂N₂O₄ [(M+Na)⁺]: 515.0157, Found: 515.0153.

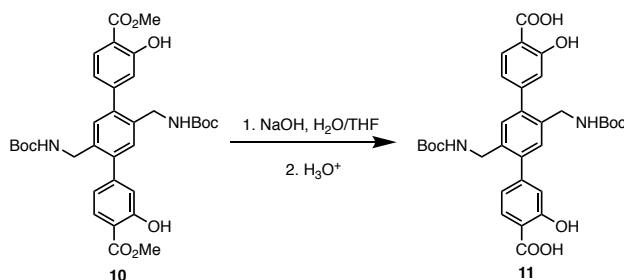
Synthesis of dimethyl-2',5'-bis(((tert-butoxycarbonyl)amino)methyl)-3,3''-dihydroxy-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate (10)



Scheme S2.6. Synthetic pathway for dimethyl-2',5'-bis(((tert-butoxycarbonyl)amino)methyl)-3,3''-dihydroxy-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate **10**.

A clean, oven dried, 3 neck round bottom flask attached to a Schlenk line apparatus with equipped reflux condenser was charged with 1.42 g (5.10 mmol) 3-hydroxy-4-(methoxycarbonyl) phenylboronic acid pinacol ester and 2.77 g (18.2 mmol, 3.57 eq) of cesium fluoride. The flask and its contents were then evacuated and refilled with inert house nitrogen atmosphere. This process was repeated three times to ensure an anhydrous and oxygen-free reaction environment. In a separate flask, 14.6 mL of anhydrous 1,4-dioxane and 7.30 mL of deionized water were combined and then bubbled with dried house N₂ for 30 min. to deoxygenate the resulting mixture. 1.200 g (2.43 mmol) of di-*tert*-butyl ((2,5-dibromo-1,4-phenylene)bis(methylene))dicarbamate were dissolved in the resultant solvent mixture under N₂ pressure and the solution was then added to the three neck round bottom flask containing the 3-hydroxy-4-(methoxycarbonyl) phenylboronic acid pinacol ester and cesium fluoride under N₂ pressure along with 0.0889 g (0.121 mmol, 0.0237 eq) [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II). The reaction mixture was heated to 90° C using an oil bath and refluxed for 24 h. The resulting two layer (top-dark opaque brown, bottom-transparent colorless) solution was tested for completion with thin layer chromatography (25:1 dichloromethane: ethyl acetate) which provided evidence of the presence of mono- and di-coupled products. The reaction mixture was poured into a 500 mL separatory funnel with ca. 80 mL of ethyl acetate. 20 mL of a saturated NH₄Cl solution were added to the mixture in the separatory funnel and the organic phase was collected. The aqueous phase was extracted with 20 mL of ethyl acetate and the combined organic phases were dried over anhydrous magnesium sulfate, filtered and evaporated to a brown powder. This crude product was purified by column chromatography (CH₂Cl₂:AcOEt 25:1) and the purified product was obtained in 46% yield (0.711 g). ¹H NMR (600 MHz, DMSO-*d*₆) δ 10.60 (s, 2H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 6.0 Hz, 2H), 7.25 (s, 2H), 7.00 – 6.94 (m, 4H), 4.11 (d, *J* = 6.0 Hz, 4H), 1.34 (s, 18H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 168.95, 159.70, 147.31, 138.60, 135.30, 129.92, 120.37, 117.69, 112.01, 77.85, 52.45, 40.86, 28.12. MS (HR-ESI), *m/z* calcd. for C₃₄H₄₀N₂O₁₀[(M+Na)⁺]: 659.2581, found: 659.2576.

Synthesis of 2',5'-bis(((tert-butoxycarbonyl)amino)methyl)-3,3''-dihydroxy-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid (**11**)

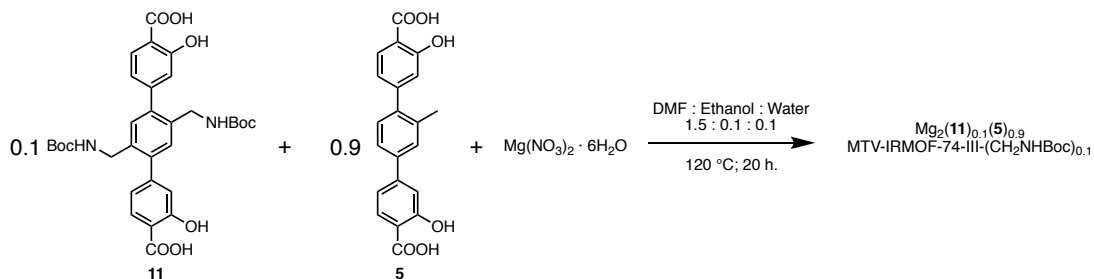


Scheme S2.7. Synthetic pathway for 2',5'-bis(((tert-butoxycarbonyl)amino)methyl)-3,3''-dihydroxy-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid **11**.

A single-neck round bottom flask was charged with 0.700 g (1.10 mmol) of difunctionalized linker methyl ester (**10**). 27.5 mL of anhydrous THF was added to the flask and the solution was sonicated and stirred until complete dissolution of the reactant. In a separate flask 0.440 g (11.0 mmol, 10.0 eq) of anhydrous NaOH pellets were added to 27.5 mL of deionized water and the solution was stirred until the pellets were completely dissolved. The basic solution was subsequently added to the solution of dimethyl 2',5'-bis(((tert-butoxycarbonyl)amino)methyl)-3,3''-dihydroxy-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate in THF to achieve a final NaOH concentration of 0.200 M and a final substrate concentration of 0.0200 M. The flask containing base and reactant was then attached to a Schlenk line apparatus with a reflux condenser equipped and was heated with an oil bath at 50 °C for 22 h. The reaction mixture was then cooled to room temperature and absence of starting material was confirmed by thin layer chromatography (1:1:1 dichloromethane: ethyl acetate: hexanes solvent mixture). The reaction mixture was acidified to pH 7 by addition of 1.157 mL of a 2M HCl solution. During acidification, a white solid formed in the reaction flask. 0.502 g of solid product was collected by vacuum filtration (75.0 % yield). ¹H NMR (600 MHz, DMSO-*d*₆) δ 14.00 (s, 2H), 11.35 (s, 2H), 7.86 (d, *J* = 7.9 Hz, 2H), 7.39 (t, *J* = 6.0 Hz, 2H), 7.26 (s, 2H), 6.95 (s, 2H), 4.12 (d, *J* = 5.9 Hz, 4H), 1.34 (s, 18H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 171.67, 160.85, 155.60, 147.39, 138.72, 135.30, 130.14, 128.47, 120.18, 117.40, 111.94, 77.85, 40.89, 28.14. MS (HR-ESI), *m/z* calcd. for C₃₂H₃₆N₂O₁₀ [(M+Na)⁺]: 631.2268, found: 631.2266.

2.12.3 Metal-Organic Framework Synthesis

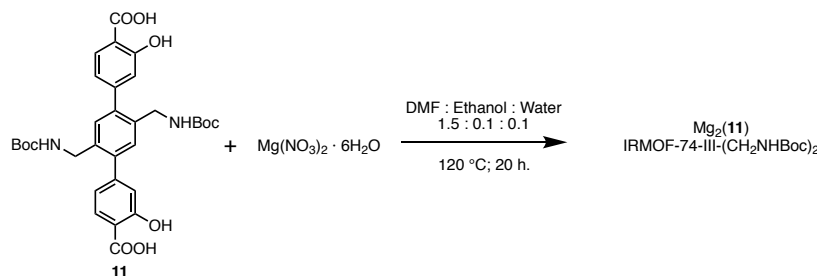
Synthesis of MTV-IRMOF-74-III-(CH₂NHBoc)_{0.1}



Scheme S2.8. Synthetic pathway for MTV-IRMOF-74-III-(CH₂NHBoc)_{0.1}.

In order to achieve the desired ratio of linkers in the MTV-MOF structure Mg(NO₃)₂ · 6H₂O (160 mg, 0.62 mmol), unfunctionalized linker (**5**) (62 mg, 0.17 mmol), functionalized linker (**11**) (11 mg, 0.019 mmol) and a solvent mixture containing 15 mL of N,N-dimethylformamide (DMF)/ethanol/water (9:0.5:0.5) were placed in a 20 mL capped vial, which was heated at 120 °C for 20 h. This yielded faintly pale yellow microcrystalline spherulites that were washed by removal of the mother liquor and immersion in 10 mL of fresh anhydrous DMF for 4 h. The supernatant was removed and replaced with another fresh 10 mL of anhydrous DMF. This process was repeated 3 times per day for 3 days to completely remove any unreacted materials from the interior of the MOF structures. All samples were dissolved in 0.51 mL DMSO-d₆/D₂O mixture brought to 50 mM in DCl and analyzed by ¹H NMR. Unfunctionalized linker (**5**) to functionalized linker (**11**) ratio was calculated from the ratio of integrations of proton signals at chemical shifts δ 2.3022 (Me-CH₃) to δ 1.3090 [(Boc-CH₃)₆]. To prepare the MOF for post-synthetic -Boc deprotection, the DMF supernatant was removed and replaced with 10 mL of anhydrous methanol. The methanol was removed and replaced with another 10 mL of fresh anhydrous methanol. This process was repeated 3 times per day for 3 days to completely remove any DMF from the open metal sites known to be present in the magnesium oxide rod SBUs in IRMOF-74-III.²⁴

Synthesis of IRMOF-74-III-(CH₂NHBoc)₂



Scheme S2.9. Synthetic pathway for IRMOF-74-III-(CH₂NHBoc)₂.

Mg(NO₃)₂ · 6H₂O (160 mg, 0.62 mmol) and **11** (114 mg, 0.188 mmol) were added to a 20-mL scintillation vial with 15 mL anhydrous DMF. The vial was sonicated for 10 minutes and 1.0 mL of ethanol was added to the homogeneous solution followed by 1.0 mL of deionized water. The vial was sonicated again for 10 minutes sealed. The vial containing the resultant clear solution was placed in an isothermal oven at 120 °C for 20 h. After cooling to room temperature, the supernatant solution was removed by syringe and the crystalline solid MOF compound was immersed in 10 mL of anhydrous DMF for 3 h. The liquid was then decanted and replaced with another 10 mL of anhydrous DMF. This process was repeated three times per day for 3 days after which time the procedure was repeated with methanol during 2 days to obtain the solid with washed interior. To determine the presence of functional groups in the MOF pores, I performed ¹H NMR of digested samples in 50 mM DCl in a DMSO-*d*₆/D₂O mixture (section S7). The resonance peaks at 1.35 ppm (d, 9H) and 4.14 ppm (s, 2H) corresponding to the Boc protecting group and benzyl amine (-CH₂-) respectively; confirm the presence of -CH₂NHBoc functional group in the framework. IR (ATR), $\bar{\nu}_{\text{max}}$ [cm⁻¹]: 3360 (br w), 2977 (w), 1682 (s), 1580 (s), 1505 (m), 1431 (s), 1367 (s), 1249 (br s), 1219 (m), 1157 (s), 1025 (s), 940 (m), 890 (m), 847 (m), 790 (m), 722 (m), 696 (m), 602 (m).

2.12.4 Post-Synthetic Modification

Thermal, Post-synthetic -Boc Deprotection of IRMOF-74-III Samples

Functionalized IRMOF-74-III crystals were subjected to solvent washing procedure described in section 2.12.3. The compounds were transferred using a glass pipette into a 10 mL reaction tube containing 3 mL of 2-ethyl-1-hexanol, 150 μ L of ethylene glycol and 150 μ L of deionized water. The heterogeneous mixture was subjected to 230 °C microwave heating using a CEM Discover microwave reactor equipped with an IR temperature sensor (300 PSI pressure limit, 300 W max power, no stirring, PowerMax setting off) for 10 minutes. The mixture was allowed to cool down to room temperature and the DMF and methanol solvent washing procedure was repeated. The obtained microcrystalline samples were analyzed by PXRD and ¹H NMR after digestion. For both MTV-IRMOF-74-III-(CH₂NH₂)_{0.1} and IRMOF-74-III-(CH₂NH₂)₂ the crystallites were recovered with 98% retention of original mass. The high degree of correspondence

between the sample patterns and those of the samples before the deprotection procedure indicated that the bulk materials remains crystalline with the same underlying topology after the post-synthetic deprotection (section 2.12.7). The successful Boc-deprotection was confirmed by the absence of the Boc resonance peak at 1.31 ppm in the ^1H NMR of digested samples in 50 mM DCl in a DMSO- d_6 /D $_2$ O mixture. IR (ATR), $\bar{\nu}_{\text{max}}$ [cm^{-1}]: IR (ATR), $\bar{\nu}_{\text{max}}$ [cm^{-1}]: 3360 (br w), 2977 (w), 1682 (br w), 1580 (s), 1431 (s), 1367 (s), 1249 (br s), 1219 (m), 1198 (m), 1157 (w), 1025 (s), 940 (m), 890 (m), 847 (m), 790 (m), 722 (m), 696 (m), 602 (m).

Peptide Coupling (Isonicotinic Acid Loading) in IRMOF-74-III Samples

A 20 mL scintillation vial equipped with a magnetic stir bar was charged with 13.9 mg (0.110 mmol) isonicotinic acid (pyridine-4-carboxylic acid) and 42.8 mg (0.110 mmol) *N,N,N',N'*-tetramethyl-*O*-(1*H*-benzotriazol-1-yl)uronium hexafluorophosphate (HBTU) and 10.0 mL anhydrous DMF. The resultant mixture was stirred for 3 min. until complete dissolution of the reactants was observed. A full batch of MTV-IRMOF-74-III-(CH $_2$ NH $_2$) $_{0.1}$ or IRMOF-74-III-(CH $_2$ NH $_2$) $_2$ microcrystalline spherulites was transferred from a 10 mL microwave tube used for amine deprotection to the scintillation vial. The resultant mixture was stirred for another 3 min. and then 0.0392 mL of *N,N*-diisopropyl ethylamine was added to the reaction mixture with constant stirring. Within 5 min. the reaction mixture changed from colorless and transparent in appearance to dark orange and transparent. The reaction mixture was stirred at room temperature for 12 h. The reaction was quenched by removal of the supernatant and immersion in 10 mL of fresh anhydrous DMF for 4 h. The supernatant was removed and replaced with another fresh 10 mL of anhydrous DMF. This process was repeated once every 4 h. for 3 days to remove excess reactants from the pores of the MOF. All samples were dissolved in 0.51 mL DMSO- d_6 /D $_2$ O mixture brought to 50 mM in DCl and analyzed by ^1H NMR. Quantitative reaction yields were calculated from the ratio of integrations of proton signals at chemical shifts δ = 9.0404 ppm (*opy*-C-H) and δ = 8.3922 ppm (*mpy*-C-H) to the proton signal at δ = 4.5024 ppm (linker -CH $_2$ -).

Screening Loading Catalyst into MTV-IRMOF-74-III-(CH $_2$ NHBoc) $_{0.1}$

A 20 mL 2 neck round bottom flask equipped with magnetic stir bar was charged with 60 mg (89 μmol) [Ir(COD)(IMes)Cl] and 25 mg (99 μmol) AgPF $_6$. The flask and its contents were attached to a Schlenk line apparatus and evacuated and refilled with inert house nitrogen atmosphere. This process was repeated three times to ensure an anhydrous and oxygen-free reaction environment. 10 mL of appropriate solvent was added and the reaction mixture was stirred for 12 h. at room temperature. The resultant solution was then filtered using a 0.45 μm syringe filter and added via syringe to a new 20 mL 2 neck round bottom flask charged with approximately a “half batch” of MTVIRMOF-74-III-(CH $_2$ NHInic) $_{0.1}$ equating to ca. 19 μmol of available pyridine ligands (as post-synthetically loaded isonicotinamide). The reaction mixture was allowed to stir at an appropriate temperature (either room temperature or 60 $^\circ\text{C}$) for 24 h. After this time,

stirring was halted and the mother liquor was removed under inert atmosphere via syringe and replaced with fresh reaction solvent and stirring was resumed. Post-synthetically metalated MTV-IRMOF-74-III structures were washed (via removal of supernatant and replacement with fresh designated reaction solvent) 3 times per day for 3 days and then with DMF 3 times per day for 3 days, all with constant stirring. It was noted that the color of the removed supernatant was a very pale orange upon each washing. All samples were dissolved in 0.51 mL DMSO- d_6 /D $_2$ O mixture brought to 50 mM in DCl and analyzed by ^1H NMR to test for a discrepancy in pyridyl proton chemical shifts at δ 9.0646 ppm and δ 8.3817 ppm. An identical procedure was applied to IRMOF-74-III-(CH $_2$ NHInic) $_2$ scaled up according to the additional amount of pyridine ligands present in the structure.

2.12.5 SABRE Pre-catalyst [IrCl(COD)(IMes)] Synthesis

The [IrCl(COD)(IMes)] compound was synthesized according to Scheme 2.4. A 25 mL Schlenk flask with an equipped magnetic stirbar was charged with 250 mg (0.38 mmol) bis(1,5-cyclooctadiene)di- μ -methoxydiiridium(I) and 257 mg (0.750 mmol) 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride. The flask and its contents were attached to a Schlenk line apparatus and evacuated and refilled with inert house nitrogen atmosphere. This process was repeated three times to ensure an anhydrous and oxygen-free reaction environment. 12.5 mL of benzene were added under nitrogen pressure. The resultant reaction mixture was stirred at room temperature for 8 h. and it was observed that the solution changed from dark brown and cloudy to bright yellow and transparent. The solution was evaporated to ca. 2 mL and then 10 mL of hexanes were added. This caused the solution to become turbid and brighter yellow. The solution was then evaporated again to ca. 2 mL and 10 mL hexanes were added. This process was repeated 2 more times and the resultant solution was filtered to yield 429 mg (88% yield) of a bright yellow semi-crystalline material. ^1H NMR (600 MHz, Benzene- d_6) δ 6.80 (d, J = 11.8 Hz, 2H), 6.11 (s, 1H), 4.70 (dt, J = 4.6, 1.9 Hz, 1H), 3.16 (dd, J = 5.3, 2.3 Hz, 1H), 2.58 (s, 3H), 2.11 (s, 3H), 2.04 (s, 3H), 1.85 (dtd, J = 10.1, 6.3, 5.2, 2.3 Hz, 1H), 1.80 – 1.72 (m, 1H), 1.41 – 1.31 (m, 2H), 1.31 – 1.19 (m, 2H), 0.89 (t, J = 7.0 Hz, 1H). ^{13}C NMR (151 MHz, Benzene- d_6) δ 138.66, 137.97, 136.78, 130.14, 128.35, 123.13, 83.44, 50.82, 34.12, 31.96, 29.37, 23.05, 21.06, 20.18, 18.29, 14.33.

2.12.6 Metalation Screening to form Molecular Analogue [Ir(COD)(IMes)(Inic)]PF₆

The [IrCl(COD)(IMes)] compounds as used to determine optimum MTV-MOF and MOF metalation conditions were synthesized according to Scheme 2.5 and Table 2.1. Generally, A 10 mL 2 neck round bottom flask equipped with magnetic stir bar was charged with 31 mg (46 μ mol) [Ir(COD)(IMes)Cl] and 13 mg (51 μ mol) AgPF₆. The flask and its contents were attached to a Schlenk line apparatus and evacuated and refilled with inert house nitrogen atmosphere. This process was repeated three times to ensure an anhydrous and oxygen-free reaction environment. 5 mL of appropriate solvent was added and the reaction mixture was stirred for 12 h. at room temperature. The resultant solution was then filtered using a 0.45 μ m syringe filter and added via syringe to a new 10 mL 2 neck round bottom flask charged with 5.2 mg of pyridine-4-carboxylic acid (isonicotinic acid) and the reaction mixture was allowed to stir at an appropriate temperature (either room temperature or 60°C, Table 2.1) for 12 h. All samples were dissolved in 0.51 mL DMSO-d₆/D₂O mixture brought to 50 mM in DCl and analyzed by ¹H NMR (Figure 2.2). Reaction yield was calculated from the ratio of integrations of protons at chemical shifts δ 8.7974 ppm (free *opy*-C-H) and 7.8612 ppm (free *mpy*-C-H) to protons at chemical shifts δ 7.9866 ppm (Ir-Bound *opy*-C-H) and 7.6710 ppm (IrBound *mpy*-C-H).

2.12.7 X-Ray Diffraction (XRD) Results

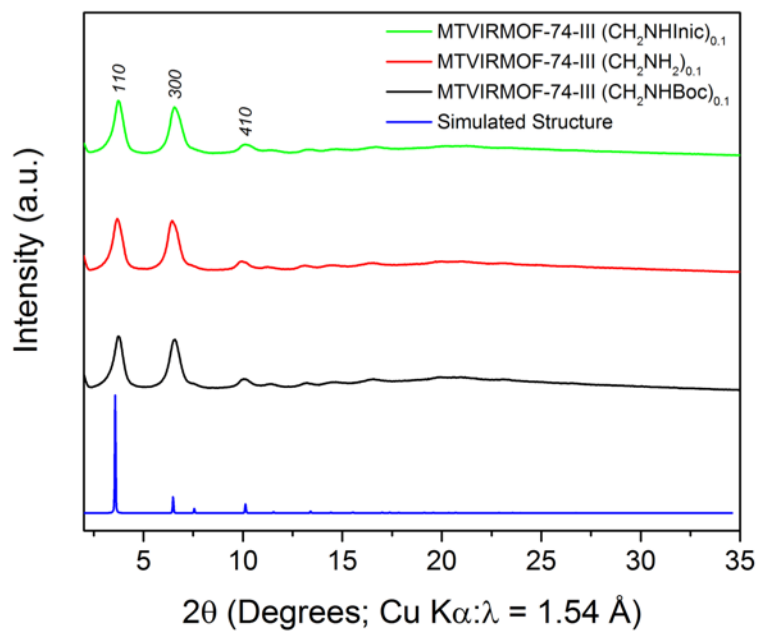


Figure S2.1. PXRD patterns of MTV-IRMOF-74-III structures before and after post synthetic modification.

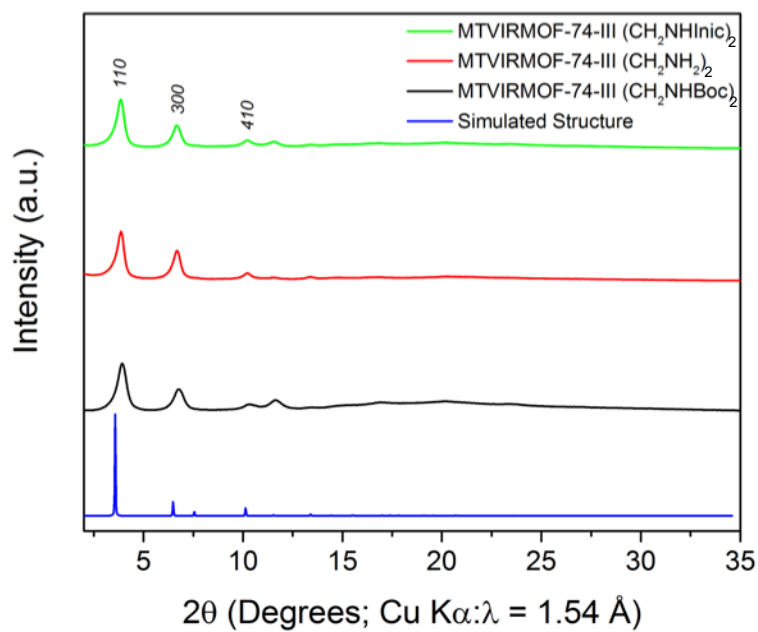


Figure S2.2. PXRD patterns of IRMOF-74-III structures before and after post synthetic modification.

2.13 References for Chapter 2

- (1) Adams, R. W.; Aguilar, J. A.; Atkinson, K. D.; Cowley, M. J.; Elliott, P. I. P.; Duckett, S. B.; Green, G. G. R.; Khazal, I. G.; López-Serrano, J.; Williamson, D. C. Reversible Interactions with Para-Hydrogen Enhance NMR Sensitivity by Polarization Transfer. *Science* **2009**, 323, 1708–1711.
- (2) Barskiy, D. a.; Kovtunov, K. V.; Koptug, I. V.; He, P.; Groome, K. a.; Best, Q. a.; Shi, F.; Goodson, B. M.; Shchepin, R. V.; Coffey, A. M.; Waddell, K. W.; Chekmenev, E. Y. The Feasibility of Formation and Kinetics of NMR Signal Amplification by Reversible Exchange (SABRE) at High Magnetic Field (9.4 T). *J. Am. Chem. Soc.* **2014**, 136, 3322–3325.
- (3) Crabtree, R. Iridium Compounds in Catalysis. *Acc. Chem. Res.* **1979**, 12, 331–337.
- (4) Shi, F.; Coffey, A. M.; Waddell, K. W.; Chekmenev, E. Y.; Goodson, B. M. Heterogeneous Solution NMR Signal Amplification by Reversible Exchange. *Angew. Chemie - Int. Ed.* **2014**, 53, 7495–7498.
- (5) Shi, F.; Coffey, A. M.; Waddell, K. W.; Chekmenev, E. Y.; Goodson, B. M. Nanoscale Catalysts for NMR Signal Enhancement by Reversible Exchange. *J. Phys. Chem. C.* **2015**, No. 119, 7525–7533.
- (6) Furukawa, H.; Cordova, K. E.; O’Keeffe, M.; Yaghi, O. M. The Chemistry and Applications of Metal-Organic Frameworks. *Science*. **2013**, 341, 974.
- (7) Cohen, S. M. Postsynthetic Methods for the Functionalization of Metal-Organic Frameworks. *Chem. Rev.* **2012**, 112, 970–1000.
- (8) Sumida, K.; Brown, C. M.; Herm, Z. R.; Chavan, S.; Bordiga, S.; Long, J. R. Hydrogen Storage Properties and Neutron Scattering Studies of Mg₂(Dobdc)-a Metal-Organic Framework with Open Mg²⁺ Adsorption Sites. *Chem. Commun.* **2011**, 47, 1157–1159.
- (9) Kim, H.; Rey, C.; Glimcher, M. J.; Res, J. B. M.; Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, T.; Kim, J.; Keffe, M. O.; Yaghi, O. M. Hydrogen Storage in Microporous Metal-Organic Frameworks. *Science*. **2002**, 73, 12–15.
- (10) 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*. **2010**, 327, 846–850.
- (11) Kong, X.; Deng, H.; Yan, F.; Kim, J.; Swisher, J.; Smit, B.; Yaghi, O. M.; Reimer, J. a. Mapping of Functional Groups in Metal-Organic Frameworks. *Science* **2013**, 341, 882–885.
- (12) Corma, A.; Garcia, H.; Xamena, F. Engineering Metal Organic Frameworks for Heterogeneous Catalysis. *Chem. Rev.* **2010**, 110, 4606–4655.
- (13) Lee, J.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. Metal-Organic Framework Materials as Catalysts. *Chem. Soc. Rev.* **2009**, 38, 1450–1459.
- (14) Gascon, J.; Corma, A.; Kapteijn, F.; Llabre i Xamena, F. X. Metal Organic Framework Catalysis : Quo Vadis? *ACS Catal.* **2014**, 4, 361–378.
- (15) Dhakshinamoorthy, A.; Alvaro, M.; Garcia, H. Metal-Organic Frameworks as Heterogeneous Catalysts for Oxidation Reactions. *Catal. Sci. Technol.* **2011**, 1, 856.
- (16) Lun, D. J.; Waterhouse, G. I. N.; Telfer, S. G. A General Thermolabile Protecting Group Strategy for Organocatalytic Metal-Organic Frameworks. *J. Am. Chem. Soc.*

- 2011**, 133, 5806–5809.
- (17) Tanabe, K. K.; Cohen, S. M. Postsynthetic Modification of Metal-Organic Frameworks-a Progress Report. *Chem. Soc. Rev.* **2011**, 40, 498–519.
 - (18) Fei, H.; Cohen, S. M. Metalation of a Thiocatechol-Functionalized Zr(IV)-Based Metal-Organic Framework for Selective C–H Functionalization. *J. Am. Chem. Soc.* **2015**, No. 137, 2191–2194.
 - (19) Manna, K.; Zhang, T.; Carboni, M.; Abney, C. W.; Lin, W. Salicylaldehyde-Based Metal-Organic Framework Enabling Highly Active Olefin Hydrogenation with Iron and Cobalt Catalysts. *J. Am. Chem. Soc.* **2014**, 136, 13182–13185.
 - (20) Gonzalez, M. I.; Bloch, E. D.; Mason, J. a.; Teat, S. J.; Long, J. R. Single-Crystal-to-Single-Crystal Metalation of a Metal-Organic Framework: A Route toward Structurally Well-Defined Catalysts. *Inorg. Chem.* **2015**, 2995–3005.
 - (21) Park, J.; Feng, D.; Zhou, H. Structure-Assisted Functional Anchor Implantation in Robust Metal – Organic Frameworks with Ultralarge Pores. *J. Am. Chem. Soc.* **2014**, No. 134, 1123–1129.
 - (22) Liu, B.; Jie, S.; Bu, Z.; Li, B.-G. A MOF-Supported Chromium Catalyst for Ethylene Polymerization through Post-Synthetic Modification. *J. Mol. Catal. A Chem.* **2014**, 387, 63–68.
 - (23) Bernini, M. C.; Fairen-Jimenez, D.; Pasinetti, M.; Ramirez-Pastor, A. J.; Snurr, R. Q. Screening of Bio-Compatible Metal-Organic Frameworks as Potential Drug Carriers Using Monte Carlo Simulations. *J. Mater. Chem. B* **2014**, 2, 766.
 - (24) Fracaroli, A. M.; Furukawa, H.; Suzuki, M.; Dodd, M.; Okajima, S.; Yaghi, O. M. Metal-Organic Frameworks with Precisely Designed Interior for Carbon Dioxide Capture in the Presence of Water. *J. Am. Chem. Soc.* **2014**, 136, 8863–8866.
 - (25) Miyaura, N.; Suzuki, A. Palladium-Catalyzed Cross-Coupling Reactions of Organoboron Compounds. *Chem. Rev.* **1995**, 95, 2457–2483.
 - (26) Dudash, J.; Jiang, J.; Mayer, S. C.; Joullié, M. M. Comparative Study of Selected Coupling Reagents in Dipeptide Synthesis. *Synth. Commun.* **1993**, 23, 349–356.
 - (27) Kownacki, I.; Kubicki, M.; Szubert, K.; Marciniec, B. Synthesis, Structure and Catalytic Activity of the First Iridium(I) Siloxide versus Chloride Complexes with 1,3-Mesitylimidazolin-2-Ylidene Ligand. *J. Organomet. Chem.* **2008**, 693, 321–328.

Chapter 3: The Chemistry of CO₂ Capture in an Amine-Functionalized Metal-Organic Framework under Dry and Humid Conditions

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3.1 Preface

Although IRMOF-74-III-(CH₂NH₂)₂ was successfully synthesized and characterized, it could not be adequately metalated in order to yield a heterogeneous SABRE catalyst. Therefore, I decided to apply the linker-based alkylamines in the framework to selective CO₂ capture, as had been demonstrated in a previous MOF, IRMOF-74-III-CH₂NH₂. In this case, I was interested in investigating whether or not doubling the number of linker-based alkylamines in a given framework would drastically improve the material's CO₂ uptake capacity. Notably, when moving from IRMOF-74-III-CH₂NH₂ to IRMOF-74-III-(CH₂NH₂)₂, I observed changes in both the CO₂ uptake capacity of the framework at capture-relevant pressures and the products resulting from chemisorptive CO₂ capture. These changes, outlined in this chapter, have interesting energetic consequences, furthered the understanding of chemisorptive CO₂ capture in MOFs, and will be relevant for the design of next-generation materials.

3.2 Introduction

Metal-organic frameworks (MOFs) are emerging as effective materials for selective CO₂ chemisorption with high uptake due to the ease with which they may be tuned by the pre- and post-synthetic modification of their building units.¹⁻³ To date, the most successful MOFs for CO₂ capture have included alkylamine-functionalized (R₁NHR₂, or RNH₂) pores. These alkylamines have been shown to selectively react with CO₂, forming covalent C-N bonds, yielding great low-pressure (<100 Torr) uptake and selectivity, yet only ammonium carbamate is reported as the product of CO₂ capture.⁴⁻¹⁰ Previously, it was demonstrated that the pores of IRMOF-74-III {Mg₂(3,3''-dioxido-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate)} can be designed and functionalized with one primary alkylamine covalently attached to each linker leading to enhanced CO₂ capture.⁵

Here, I report on a new, diamine-functionalized MOF system, IRMOF-74-III-(CH₂NH₂)₂ {Mg₂(2',5'-bis(aminomethyl)-3,3''-dioxido-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate)}, and demonstrate its framework chemistry with CO₂ under dry and humid conditions. This study contributes to the fundamental understanding of CO₂ capture in MOFs under conditions relevant to those required in practice. Although examples of carbamic acid formation in organic molecular crystals, surface modified silica, and porous silica are reported, control of the CO₂-binding chemistry has not been demonstrated.¹¹⁻¹⁵ I show that the equilibrium of chemisorbed CO₂ shifts at the time when CO₂ is introduced to the system from primarily carbamic acid to ammonium carbamate depending upon the absence or presence of water, respectively. Accordingly, understanding this chemistry is crucial to achieving control over which of the two chemisorption products are formed, as each species' unique properties may make it desirable for specific carbon capture applications.¹¹⁻¹⁵

3.3 Approach

The synthesis and characterization of organic linkers and extended structure, IRMOF-74-III-(CH₂NH₂)₂, was carried out according to modified and previously reported conditions (see Sections 3.9.2 and 3.9.3).⁵ Because the presence of free amines on the organic struts disrupts the synthesis of the extended structure, the two primary amine functional groups were incorporated into IRMOF-74-III as Boc-protected (–Boc = *tert*-butyloxycarbonyl) derivatives.¹⁶ The quantitative removal of the –Boc protecting groups from the framework structure by microwave irradiation (Section 3.9.4) was confirmed by solid state cross-polarization magic angle spinning nuclear magnetic resonance spectroscopy (CP-MAS NMR), and, Fourier transform infrared spectroscopy (FT-IR), as well as solution phase NMR of the acid-digested material (Sections 3.9.5, 3.9.6, and 3.9.7). Powder X-ray diffraction (PXRD) and nitrogen adsorption isotherm experiments confirmed that the framework maintained its structural integrity and porosity after post-synthetic deprotection of the –Boc groups (Sections 3.9.8 and 3.9.9).

3.4 CO₂ Sorption in IRMOF-74-III-(CH₂NH₂)₂

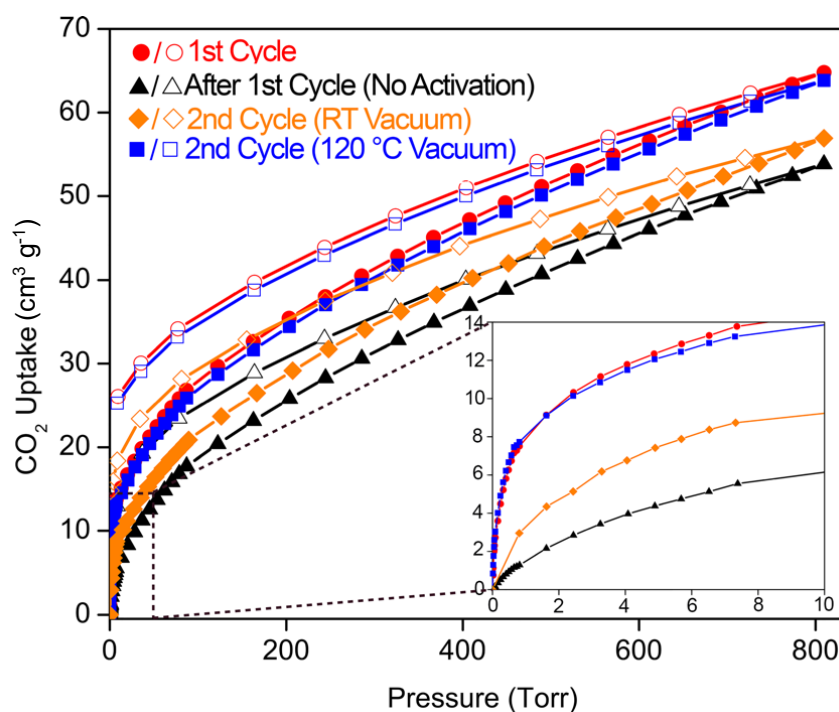


Figure 3.1. CO₂ isotherms (closed symbols = adsorption; open symbols = desorption) for IRMOF-74-III-(CH₂NH₂)₂. In red, after activation; in black, after first carbon dioxide isotherm (no activation); in orange, after room temperature activation 12 h; in blue, after 120 °C heating 2 h. (Inset) Expansion of the low pressure range.

To confirm that CO₂ binds in a chemisorptive fashion and that it can be removed, the CO₂ isotherms for IRMOF-74-III-(CH₂NH₂)₂ were measured at 25 °C (Figure 3.1). This compound shows similar capacity (67 cm³ g^{−1}) to the previously reported IRMOF-74-III–

CH₂NH₂ (75 cm³ g⁻¹) at 800 Torr, indicating similar physisorption behavior of the materials. In the low-pressure range (<100 Torr), however, the IRMOF-74-III-(CH₂NH₂)₂ compound significantly out-performs its monoamine counterpart, collecting 2.33 times the amount of CO₂ per gram of material at identical pressures (Section 3.9.10), indicative of enhanced chemisorption. The behavior of the material after different activation conditions was also studied (Figure 3.1). After the first CO₂ isotherm measurement, three separate experiments were conducted: first, a subsequent isotherm was measured without any activation of the material. Investigation of this isotherm reveals a *ca.* 17% drop in CO₂ uptake at 800 Torr, and a *ca.* 83% drop in CO₂ uptake at 0.8 Torr, compared to the as-synthesized material. This suggests that the amine moieties capture the CO₂ by covalent bond formation. The next isotherm was measured after activating the material under dynamic vacuum at 25 °C for 12 h. Investigation of this isotherm reveals a 12% drop in CO₂ uptake at 800 Torr, and a 61% drop in CO₂ uptake at 0.8 Torr. This indicates that only a portion of the amine-CO₂ bonds are broken simply by applying vacuum as shown in Fig. 3.2. Finally, an isotherm was measured after activating the material under vacuum for 2 h at 120 °C. This isotherm showed no drop in CO₂ uptake in both the high- and low-pressure regions, indicating full regeneration of the material.

3.5 Investigation of CO₂ Chemisorption in IRMOF-74-III-(CH₂NH₂)₂ using Solid State CP MAS NMR

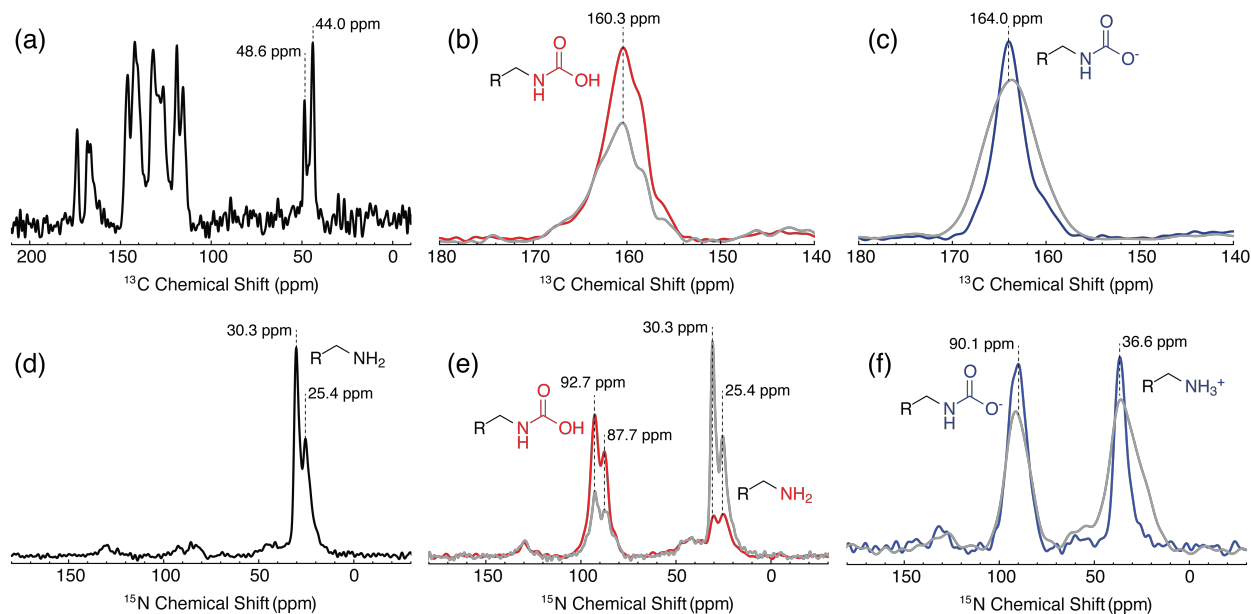


Figure 3.2. (a) ¹³C CP-MAS NMR for IRMOF-74-III-(CH₂NH₂)₂. (b) ¹³C CP-MAS NMR after exposure to 675 Torr ¹³CO₂ for 24 h (red) and after vacuum for 24 h (grey). (c) ¹³C CP-MAS NMR after exposure to 95% relative humidity (RH) N₂ atmosphere for 24 h followed by 675 Torr ¹³CO₂ for 24 h (blue), and after vacuum for 24 hours (grey). (d) ¹⁵N CP-MAS NMR for 50% ¹⁵N-enriched IRMOF-74-III-(CH₂NH₂)₂. (e) ¹⁵N CP-MAS NMR after exposure to 675 Torr ¹³CO₂ for 24 h (red) and after vacuum for 24 hours (grey). (f) ¹⁵N CP-MAS NMR after exposure to N₂ atmosphere at 95% RH for 24 h followed by 675 Torr ¹³CO₂ for 24 h (blue) and after vacuum for 24 h (grey).

The nature of the covalent bond being formed upon CO₂ chemisorption was examined by solid state ¹³C and ¹⁵N CP-MAS NMR of 50 % ¹⁵N-enriched IRMOF-74-III-(CH₂NH₂)₂ (Figure 3.2). The ¹³C spectrum (Figure 3.2a) shows the carbonyl phenoxide peaks at 173 and 166 ppm respectively, as well as the aromatic peaks between 110 ppm and 150 ppm. Of particular note is the CH₂ resonance with two features at 48.6 and 44.0 ppm. Though only one resonance here is expected, this pair of peaks was consistently observed with similar intensity ratios across several tested samples. Likewise, a pair of amine peaks is observed in the ¹⁵N spectrum at 30.3 and 25.4 ppm (Figure 3.2d), where only one amine resonance is expected. These two peaks are surmised to emanate from two distinct conformations of the linkers based on the torsional angle of the central phenyl ring, yielding two distinct amine positions with slightly different chemical shifts. In order to characterize the chemisorption products of CO₂, samples were exposed to 675 Torr of ¹³CO₂ (99% ¹³C atom basis) in a sealed dosing apparatus for 24 hours. (Section 3.9.5). The appearance of a highly intense peak in the ¹³C spectrum (Figure 3.2b, in red) with a maximum at 160.3 ppm and right-shoulder features at *ca.* 158 and 156 ppm confirmed that the ¹³CO₂ was adsorbed by reaction with the primary amines to form a new species. In contrast to our previous study in which a broad peak spanning 164-160 ppm was assigned to a mixture of carbamate and carbamic acid, this sharp, narrow peak is assigned as primarily carbamic acid. This assertion is consistent with chemical shifts observed and/or calculated for carbamic acid in various structural configurations in other solid CO₂ sorbents.^{5,12,14,17} The full-width-half-maximum linewidth of 350 Hz and asymmetric shape of this resonance suggest an inhomogeneous broadening arising from multiple overlapping carbamic acid sites, with each site likely varying slightly in its configuration and hydrogen bonding environment.

Further support of the assignment of this resonance as carbamic acid was gathered via ¹⁵N CP-MAS NMR (Figure 3.2d in red, Section 3.9.5). The presence of two residual amine peaks at 30.3 and 25.4 ppm was observed, indicating that complete saturation of the alkylamine moieties was not achieved upon exposure to ¹³CO₂ at 675 Torr. Two peaks at 92.7 and 87.7 ppm appear at the expense of the amine peaks, suggesting that this difference in chemical shift, arising from conformations of the linkers, carries over to the chemisorbed products as well. Critically, as no major peak is observed which can be assigned as ammonium, I assign these two downfield peaks as carbamic acid ¹⁵N sites. However, when the MOF was exposed to 95% relative humidity (RH) conditions prior to loading with ¹³CO₂, a significant new peak at 36.6 ppm is observed along with a peak at 90.1 ppm (Figure 3.2f, blue). Though these CP-MAS spectra are not quantitative with respect to integration, their similar magnitudes suggest that the species observed here is ammonium carbamate, with the peak at 36.6 ppm being ammonium. The assignment of the adsorbed species as ammonium carbamate is supported by the change in the ¹³C chemical shift maximum for the 95% RH-treated material to 164.0 ppm (Figure 3.2c, blue), consistent with previous reports of the ¹³C chemical shift of carbamate.^{12,14,17,18} While some small portion of this ¹³C signal may be attributable to bicarbonate, as has been discussed in studies of amine-tethered porous silicas,¹⁸ the ¹⁵N spectrum enables us to assert that the dominant amine-CO₂ chemisorption product in humid conditions is

ammonium carbamate. The peak splitting observed in the dry adsorption spectrum is lost upon exposure to 95% RH, suggesting that the inter-linker interaction required to produce the ion pair ammonium carbamate alters the torsional angle of the central phenyl ring on the linkers to result in one major structural conformation. This shift to ammonium carbamate from carbamic acid occurs as a function of the amount of water vapor present, with MOF samples exposed to atmospheric moisture (50% RH) exhibiting signal contributions from both carbamic acid and carbamate (Section 3.9.5).

To investigate the difference in thermal properties between ammonium carbamate and carbamic acid in IRMOF-74-III-(CH₂NH₂)₂ and their impact on regeneration of the material, vacuum was applied for 24 hours at room temperature to the NMR samples previously exposed to ¹³CO₂, and solid state CP-MAS NMR was performed. Under dry loading conditions, the ¹³C carbamic acid resonance at 160.3 ppm is significantly reduced after vacuum (Figure 3.2b, grey), and the ¹⁵N carbamic acid resonances at 92.7 and 87.7 ppm decrease as the two amine peaks at 30.3 and 25.4 ppm rise in intensity (Figure 3.2e, grey). For the sample exposed to both 95% RH and ¹³CO₂, room temperature vacuum activation appears much less effective (Figures 3.2c, 3.2f), with only minor loss of signal observed for the carbamate resonance in both the ¹³C and ¹⁵N spectra. This is consistent with the TGA-DSC-MS results discussed below, where the onset point of CO₂ desorption as carbamate occurs 18 °C higher than for carbamic acid.

3.6 Additional Evidence of Carbamic Acid and Ammonium Carbamate Formation in IRMOF-74-III-(CH₂NH₂)₂

For additional experimental support of these two species, FT-IR (Section 3.9.6), combined thermogravimetric analysis, differential scanning calorimetry, mass spectrometry (TGA-DSC-MS, Section 3.9.12), and breakthrough measurements (Section 3.9.13) were performed. Samples of IRMOF-74-III-(CH₂NH₂)₂, exposed to CO₂ were also analyzed using TGA-DSC-MS. The sample lost 12 mass % of CO₂ (*m/z* = 44) at relatively low temperature (onset at 47 °C) after exposure to dry CO₂. Humidified (95% RH) samples of IRMOF-74-III-(CH₂NH₂)₂ that were exposed to CO₂ exhibit a mass loss of 10 mass % corresponding to CO₂ (*m/z* = 44) and H₂O (*m/z* = 18) at higher temperature (onset at 65 °C). The results of the thermal analysis indicate CO₂ is more strongly bound as ammonium carbamate as opposed to carbamic acid under wet and dry conditions, respectively. Additionally, the decrease in mass loss under humid conditions supports the conclusion of two amines participating in ammonium carbamate formation versus one amine forming carbamic acid upon reaction with CO₂. The dynamic adsorption capacity, as measured by breakthrough, remained the same under dry (900 ± 10 s g⁻¹, 1.2 mmol g⁻¹) and 65% RH (890 ± 10 s g⁻¹, 1.2 mmol g⁻¹) conditions (Section 3.9.13). This appears counterintuitive given the TGA-DSC-MS results, but is justified by the fact that at 50% RH (Section 3.9.5) I observe a mixture of carbamate and carbamic acid in the solid state NMR. This mixture would likely be the result of initial carbamic acid generation, with subsequent proton transfer to form ammonium carbamates, and thus the kinetics of CO₂ capture would be dictated by the formation of the former species.

3.7 The Role of Amine Geometry in CO₂ Chemisorption in IRMOF-74-III-(CH₂NH₂)₂

Although the role of water is critical to this chemistry, initial examination in modeled IRMOF-74-III-(CH₂NH₂)₂ of the separation between primary amines points to geometric constraints within the pores as also being operative. To further understand the amine-amine distances and their contribution to this unique chemistry, I modeled the conformation of the linkers (Figure 3.3, Section 3.9.11) in IRMOF-74-III-(CH₂NH₂)₂.

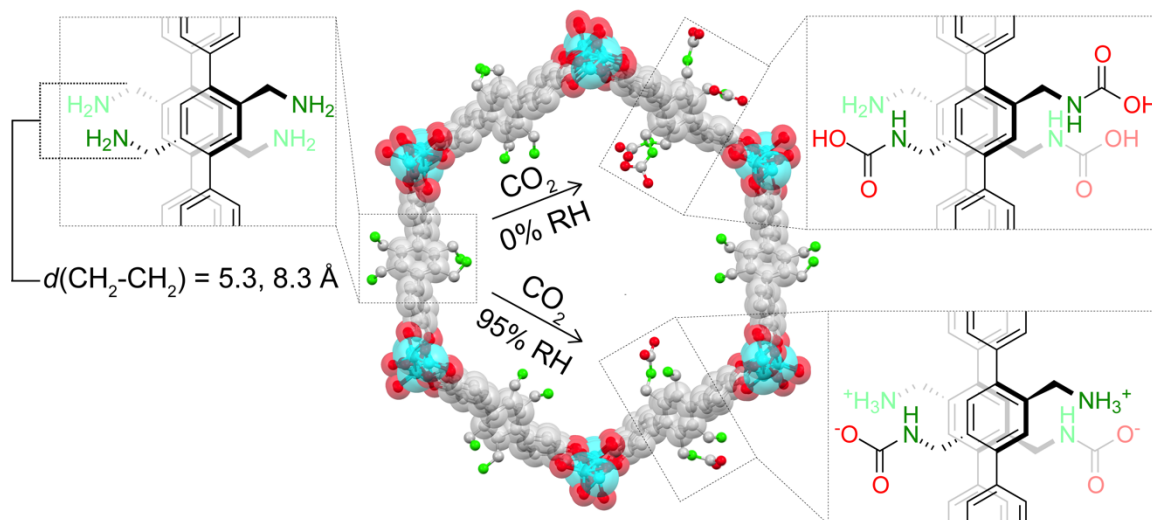


Figure 3.3. View of modeled IRMOF-74-III-(CH₂NH₂)₂ [staggered amine] structure down the crystallographic *c*-axis, depicting the three possible pore environments before (left pore wall) and after exposure to CO₂ under 95% RH (bottom right pore wall) and dry (upper right pore wall) conditions. Dashed boxes clarify the chemisorbed species upon reaction between linker-based alkylamine and CO₂ under the respective conditions. H atoms are omitted for clarity. Color code: C, gray; O, red; N, green; and Mg, blue.

Because the amines are introduced to the material as their -Boc protected counterparts, steric hindrance plays a significant role in their final orientation. When considering amine geometries that would facilitate formation of carbamic acids, two possible inter-methylene distances (staggered amine conformation), 5.3 Å and 8.3 Å, were of particular interest since similar inter-methylene distances have been found in molecular carbamic acids (5.982(4) Å, and 8.017(1) Å).^{11,15} The similarities between these distances and those in IRMOF-74-III-(CH₂NH₂)₂ support the notion of carbamic acid formation in the absence of a proton-transfer species (in the present case, water) which would generate ammonium carbamate.

3.8 Conclusion

I have delineated two distinct regimes for CO₂ capture in IRMOF-74-III-(CH₂NH₂)₂. I observed that the number of amines, their geometry, and the presence of water affect which products are formed as the result of CO₂ reaction with the covalently-tethered moieties. Understanding this chemistry lends insight into the mechanism by

which these materials capture CO₂ even in the presence of water. Additionally, the preferential formation of carbamic acid under dry conditions can lead to the development of strategies towards targeting this species as a product of CO₂ capture by alkylamine-tethered porous solids in the future.

3.9 Supporting Information for Chapter 3

3.9.1 General Considerations

Chemicals used in this work

Anhydrous *N,N*-dimethylformamide (DMF), and methanol were obtained from EMD Millipore Chemicals. Sodium azide, triphenylphosphine, anhydrous tetrahydrofuran (THF), di-*tert*-butyl dicarbonate (Boc₂O), magnesium nitrate hexahydrate, and 1,4-dioxane were purchased from Aldrich. Diethyl ether, cesium fluoride, [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II), sodium hydroxide, and 1,4-dioxane were purchased from Fischer Scientific. 1,4-Dibromo-2,5-bis(bromomethyl)benzene was purchased from Spectrum Chemical Manufacturing Group. Other common solvents and reagents (e.g. ethanol, ethanolamine, magnesium sulfate) were obtained from other commercial sources and all chemicals in this work were used without further purification. 3-hydroxy-4-(methoxycarbonyl) phenylboronic acid pinacol ester was synthesized according to published methods.⁶

Analytical Techniques

Liquid-state ¹H and ¹³C{¹H} NMR spectra were acquired on Bruker AVB-400 (400 MHz), and AV-300 (300 MHz) spectrometers at 297–300 K. Chemical shifts were calculated using the solvent resonances as internal standards (¹H: 7.26 ppm for CHCl₃, 2.50 ppm for DMSO; ¹³C{¹H}: 77.00 ppm for CDCl₃, 39.51 ppm for DMSO-*d*₆). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet of doublets (dt), triplet (t), multiplet (m), and broad resonance (br).

Solid state NMR spectra were collected using a 7.05 T magnet with a Tecmag Apollo spectrometer operating at 300.27 MHz for ¹H, 75.51 MHz for ¹³C, and 30.43 MHz for ¹⁵N. ¹³C chemical shifts were externally referenced to the downfield resonance of adamantane at 38.48 ppm, and ¹⁵N chemical shifts were externally referenced to glycine at 33.4 ppm. Experiments were performed using either a Doty 4-mm or Doty 5-mm triple resonance MAS probe operating in triple resonance ¹H/¹³C/¹⁵N mode. Magic angle spinning (MAS) was used to collect high-resolution NMR spectra at a spinning rate of 8 kHz. The magic angle was calibrated by maximizing the number and intensity of rotational echoes for the ⁷⁹Br resonance for KBr under MAS. ¹³C and ¹⁵N cross polarization (CP) experiments under the Hartmann-Hahn matching condition were performed with a ¹H 90° pulse time of 3.0 μs, and a contact time of 2 ms, using 80 kHz continuous-wave ¹H

decoupling during signal acquisition. Spectra were collected with 2048 scans and a recycle delay time of 4 s, and were processed without apodization except where specified.

Samples were activated under high vacuum using a Quantachrome Flovac Degasser initially at room temperature and then by heating at 120 °C for 8 h.

All nitrogen isotherms were measured using a Quantachrome Qudrasorb EVO instrument. Ca. 70 mg of guest free samples in 9 mm bulb gas cells were charged with argon to avoid air contamination and the cells were mounted on the instrument. A liquid nitrogen bath was used to maintain a temperature of 77 K for each measurement. Ultra-high-purity grade N₂ (Praxair, 99.999% purity) was used throughout the adsorption experiments. 46 adsorption and 16 desorption points were collected. The BET surface areas were estimated according to established procedures. Slight discrepancies in surface area measurements are likely caused by the same phenomena detailed in the study of IRMOF-74-III-(CH₂NH₂)⁶, which detail the presence of a H4 type hysteresis loop¹⁹ attributed to intercrystalline voids in the sample.²⁰

All CO₂ isotherms were measured immediately after activation procedures detailed above unless otherwise described. Measurements were performed using a Quantachrome Autosorb instrument. Ca. 70 mg of guest free samples in 9 mm bulb gas cells were charged with argon to avoid air contamination and the cells were mounted on the instrument. A water bath was used to maintain a temperature of 298 K for each measurement. CO₂ (Praxair, 99.998% purity) was used throughout the adsorption experiments. 55 adsorption and 12 desorption points were collected.

FT-IR spectra were collected in-house using a Bruker ALPHA Platinum ATR-FT-IR Spectrometer equipped with a single reflection diamond ATR module.

High Resolution Electrospray Ionization mass (HR-ESI) was acquired on an Finnigan LTQ FT (Thermo Electron Corporation) instrument, using either negative or positive modes and by direct injection of methanol solutions of the samples using syringe pump with a flow rate of 5 µL min⁻¹.

Powder X-ray diffraction data were collected using a Bruker D8-advance θ - θ diffractometer in parallel beam geometry employing Cu K α 1 line focused radiation at 1600 W (40 kV, 40 mA) power and equipped with a position sensitive detector with at 6.0 mm radiation entrance slit. Samples were mounted on zero background sample holders by dropping powders from a wide-blade spatula and then leveling the sample with a razor blade. Data were collected using a 0.01° 2 θ step scan from 2 - 35° with exposure time of 3 s per step.

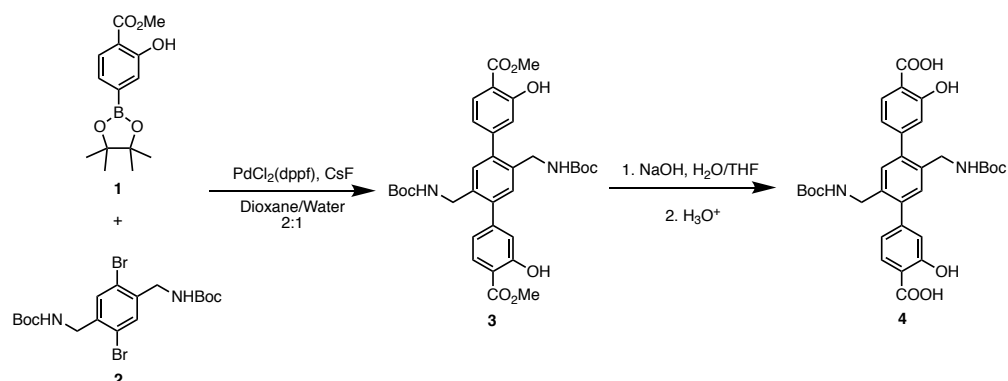
Column chromatography was performed on silica gel purchased from Sorbent Technologies (standard grade, 60 Å, 40-63 µm). Analytical thin layer chromatography

(TLC) was performed on Whatman 250 μm -thick silica gel 60 plates with a fluorescent indicator. Visualization of TLC spots was accomplished under UV light ($\lambda = 254 \text{ nm}$).

Coupled DSC-TGA studies were performed under a flow of CO_2 (20 ml min^{-1}) in a Netzsch Jupiter, STA 449 F5 apparatus. MS spectra were recorded on a Netzsch Aëolos QMS 403D.

3.9.2 Organic Linker Synthesis

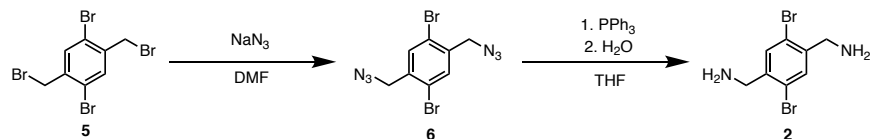
General Linker Synthesis



Scheme S3.1. General synthetic scheme for synthesis of organic linker **4**.

The synthesis of 3-hydroxy-4-(methoxycarbonyl)phenylboronic acid pinacol ester (**1**), was carried out according to the reported procedure⁶, on a multigram scale. The methyl ester of the desired organic linker was prepared by a two-fold Suzuki coupling of **1** and the dibromide **2** to give the corresponding dimethyl terphenyldicarboxylate derivative **3**. The dicarboxylic acid linker **4** was obtained by saponification of **3**. The general procedure is summarized in Scheme S3.1.

Synthesis of 2,5-dibromo-1,3-di-*t*-butylbenzylcarbamate (**2**)



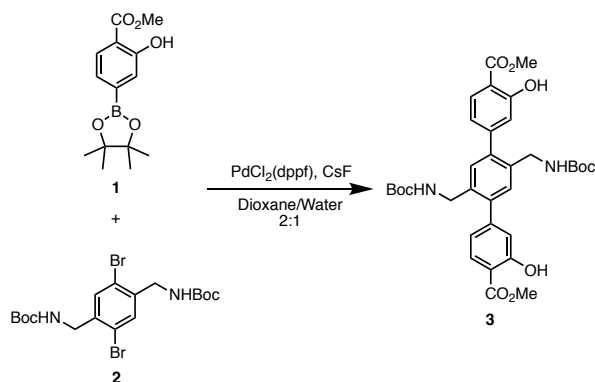
Scheme S3.2. Synthetic pathway for 2,5-dibromo-1,3-di-*t*-butylbenzylcarbamate **2**.

Commercially available 1,4-Dibromo-2,5-bis(bromomethyl)benzene (**5**, 1.6 g, 3.93 mmol), and sodium azide (1.0 g, 15.5 mmol) were added to a 250 mL three necked round bottom flask. The flask was evacuated and the atmosphere was replaced with dry nitrogen. This process was repeated three times to generate an air-free atmosphere in the reaction vessel. Anhydrous *N,N*-dimethylformamide (50 mL) was then added to the flask

under nitrogen and the solution was heated to 65 °C and stirred for 14 h. The reaction mixture was cooled to room temperature and then poured into a 250 mL separatory funnel. Diethyl ether (50 mL) was added to funnel and the mixture was then extracted with deionized water (3 × 50 mL) and brine (20 mL). The organic phase was dried over anhydrous magnesium sulfate, filtered, and evaporated to approximately 5 mL. THF (50 mL) was added to the concentrate and the resultant solution was evaporated until approximately 5 mL of solvent remained. This process was repeated two more times to give a light-yellow THF concentrate that was transferred to a three neck round bottom flask (RBF) for the next reaction without further purification [the product of the azidation reaction (**6**) was not isolated due to its potentially explosive nature].

THF (50 mL) was added to the RBF containing **6**, and the solution was degassed by bubbling with dry nitrogen for 30 minutes. Triphenylphosphine (2.3 g, 8.65 mmol) was added to the solution under nitrogen, and the reaction mixture was heated 60 °C and stirred for 2 h. Deionized water (4 mL) was then added and the reaction mixture was left to stir at the same temperature for 14 additional hours. The reaction mixture was cooled to room temperature and di-*tert*-butyl dicarbonate ((Boc)₂O, 2.0 mL, 8.66 mmol) was added under nitrogen. This mixture was stirred at room temperature for 8 h., and ethanolamine (0.3 mL, 4.97 mmol) was added. The reaction mixture was left to stir under nitrogen at room temperature for another 3 h before the THF was evaporated. The yellow oil obtained was then transferred to a 250 mL separatory funnel and ethyl acetate (75 mL) was added. The mixture was extracted with deionized water (3 × 20 mL) and brine (20 mL), dried over anhydrous magnesium sulfate and evaporated to give a solid that was then purified by column chromatography (CH₂Cl₂:AcOEt 25:1). The product 2,5-dibromo-1,3-di-*t*-butyl-benzylcarbamate (**2**) was obtained as a white powder in 70% yield (2.39 g). ¹H NMR (600 MHz, CDCl₃) δ [ppm]: 7.51 (s, 2H), 5.07 (t, *J* = 6.3 Hz, 2H), 4.31 (d, *J* = 6.4 Hz, 4H), 1.45 (s, 18H). ¹³C NMR (151 MHz, CDCl₃) δ [ppm]: 155.81, 138.97, 133.24, 122.38, 80.11, 44.35, 28.50. ESI-HRMS calculated for C₁₈H₂₆Br₂N₂O₄Na⁺: 515.0157, Found: 515.0153.

Synthesis of 2,5- Dimethyl 2',5'-bis(((tert-butoxycarbonyl)amino)methyl)-3,3''-dihydroxy-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate (3)

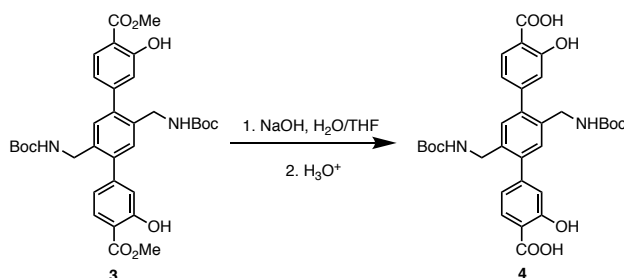


Scheme S3.3. Synthetic pathway for dimethyl 2',5'-bis(((tert-butoxycarbonyl)amino)methyl)-3,3''-dihydroxy-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate **3**.

The synthesis of dimethyl 2',5'-bis(((tert-butoxycarbonyl)amino)methyl)-3,3''-dihydroxy-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate (**3**) was accomplished via the two-fold Suzuki coupling outlined in scheme S3.1. A clean, oven dried, 3 neck round bottom flask attached to a Schlenk line apparatus with equipped reflux condenser was charged with 1.42 g (5.10 mmol) 3-hydroxy-4-(methoxycarbonyl) phenylboronic acid pinacol ester (**1**) and 2.77 g (18.2 mmol, 3.57 eq) of cesium fluoride. The flask and its contents were then evacuated and refilled with inert house nitrogen atmosphere. This process was repeated three times to ensure an anhydrous and oxygen-free reaction environment. In a separate flask, 14.6 mL of anhydrous 1,4-dioxane and 7.30 mL of deionized water were combined and then bubbled with dried house N₂ for 30 min. to deoxygenate the resulting mixture. 1.200 g (2.43 mmol) of di-*tert*-butyl ((2,5-dibromo-1,4-phenylene)bis(methylene))dicarbamate (**2**) were dissolved in the resultant solvent mixture under N₂ pressure and the solution was then added to the three neck round bottom flask containing the 3-hydroxy-4-(methoxycarbonyl) phenylboronic acid pinacol ester and cesium fluoride under N₂ pressure along with 0.0889 g (0.121 mmol, 0.0237 eq) [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II). The reaction mixture was heated to 90° C using an oil bath and refluxed for 24 h. The resulting two-layer (top-dark opaque brown, bottom-transparent colorless) solution was tested for completion with thin layer chromatography (25:1 dichloromethane: ethyl acetate) which provided evidence of the presence of mono- and di-coupled products. The reaction mixture was poured into a 500 mL separatory funnel with ca. 80 mL of ethyl acetate. 20 mL of a saturated NH₄Cl solution were added to the mixture in the separatory funnel and the organic phase was collected. The aqueous phase was extracted with 20 mL of ethyl acetate and the combined organic phases were dried over anhydrous magnesium sulfate, filtered and evaporated to a brown powder. This crude product was purified by column chromatography (CH₂Cl₂:AcOEt 25:1) and the purified product (**3**) was obtained in 46% yield (0.711 g). ¹H NMR (600 MHz, DMSO-*d*₆) δ 10.60 (s, 2H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.39

(t, $J = 6.0$ Hz, 2H), 7.25 (s, 2H), 7.00 – 6.94 (m, 4H), 4.11 (d, $J = 6.0$ Hz, 4H), 1.34 (s, 18H). ^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) δ 168.95, 159.70, 147.31, 138.60, 135.30, 129.92, 120.37, 117.69, 112.01, 77.85, 52.45, 40.86, 28.12. MS (HR-ESI), m/z calcd. for $\text{C}_{34}\text{H}_{40}\text{N}_2\text{O}_{10}[(\text{M}+\text{Na})^+]$: 659.2581, found: 659.2576.

Synthesis of 2',5'-bis(((tert-butoxycarbonyl)amino)methyl)-3,3''-dihydroxy-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid (4)



Scheme S3.4. Synthetic pathway for 2',5'-bis(((tert-butoxycarbonyl)amino)methyl)-3,3''-dihydroxy-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid **4**.

A single-neck round bottom flask was charged with 0.700 g (1.10 mmol) of dimethyl 2',5'-bis(((tert-butoxycarbonyl)amino)methyl)-3,3''-dihydroxy-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate (**3**). 27.5 mL of anhydrous THF were added to the flask and the solution was sonicated and stirred until complete dissolution of the reactant. In a separate flask 0.440 g (11.0 mmol, 10.0 eq) of anhydrous NaOH pellets were added to 27.5 mL of deionized water and the solution was stirred until the pellets were completely dissolved. The basic solution was subsequently added to the solution of dimethyl 2',5'-bis(((tert-butoxycarbonyl)amino)methyl)-3,3''-dihydroxy-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate in THF to achieve a final NaOH concentration of 0.200 M and a final substrate concentration of 0.0200 M. The flask containing base and reactant was then attached to a Schlenk line apparatus with a reflux condenser equipped and was heated with an oil bath at 50 °C for 22 h. The reaction mixture was then cooled to room temperature and absence of starting material was confirmed by thin layer chromatography (1:1:1 dichloromethane: ethyl acetate: hexanes solvent mixture). The reaction mixture was acidified to pH 7 by addition of 1.157 mL of a 2M HCl solution. During acidification, a white solid formed in the reaction flask. 0.502 g of solid product **4** was collected by vacuum filtration (75.0 % yield). ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ [ppm]: 14.00 (s, 2H), 11.35 (s, 2H), 7.86 (d, $J = 7.9$ Hz, 2H), 7.39 (t, $J = 6.0$ Hz, 2H), 7.26 (s, 2H), 6.95 (s, 2H), 4.12 (d, $J = 5.9$ Hz, 4H), 1.34 (s, 18H). ^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) δ [ppm]: 171.67, 160.85, 155.60, 147.39, 138.72, 135.30, 130.14, 128.47, 120.18, 117.40, 111.94, 77.85, 40.89, 28.14. ESI-HRMS calculated for $\text{C}_{32}\text{H}_{36}\text{N}_2\text{O}_{10}\text{Na}^+$: 631.2268, Found: 631.2266.

3.9.3 Synthesis of Metal-Organic Frameworks (MOFs)

General Notes for MOF Synthesis

Functionalized IRMOF-74-III was prepared according to the procedure reported in literature.⁵ $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (160 mg, 0.62 mmol) and the organic linker (114 mg, 0.188 mmol) were added to a 20-mL scintillation vial with 15 mL anhydrous DMF. The vial was sonicated for 10 minutes and 1.0 mL of ethanol was added to the homogeneous solution followed by 1.0 mL of deionized water. The vial was sonicated again for 10 minutes sealed. The vial containing the resultant clear solution was placed in an isothermal oven at 120 °C for 20 h. After cooling to room temperature, the supernatant solution was removed by syringe and the crystalline solid MOF compound was immersed in 10 mL of anhydrous DMF for 3 h. The liquid was then decanted and replaced with another 10 mL of anhydrous DMF. This process was repeated three times per day for 3 days after which time the procedure was repeated with methanol during 2 days to obtain the solid with washed interior. After this time, the -Boc protecting groups were quantitatively removed from the compounds following the procedure detailed in section 3.9.4. In order to avoid measuring CO_2 uptakes of the materials with protonated forms of the amino functionalities on the organic linkers, the MOFs were suspended in a 20% triethylamine solution in methanol for 30 min prior to activation. The solution within the pores of the resulting solid was removed under dynamic vacuum initially at room temperature and then by heating at 120 °C for 8 h. The guest free samples were analyzed by PXRD and their surface area was determined by nitrogen adsorption experiments.

Synthesis of IRMOF-74-III-(CH₂NHBoc)₂

The synthesis was accomplished according to the general procedure above, yielding 81% of off-white crystals. PXRD was collected on activated sample (guest free). The high degree of correspondence between the sample pattern and that of the simulated model indicates that the bulk material has the same crystal structure as the predicted by simulation (section 3.9.8). To determine the presence of functional groups in the MOF pores, I performed ¹H NMR of digested samples in 50 mM DCl in a DMSO-*d*₆/D₂O mixture (section 3.9.7). The resonance peaks at 1.35 ppm (d, 9H) and 4.14 ppm (s, 2H) corresponding to the Boc protecting group and benzyl amine (-CH₂-) respectively; confirm the presence of -CH₂NHBoc functional group in the framework. IR (ATR), $\bar{\nu}_{\text{max}}$ [cm⁻¹]: 3360 (br w), 2977 (w), 1682 (s), 1580 (s), 1505 (m), 1431 (s), 1367 (s), 1249 (br s), 1219 (m), 1157 (s), 1025 (s), 940 (m), 890 (m), 847 (m), 790 (m), 722 (m), 696 (m), 602 (m).

3.9.4 Thermal Post-synthetic -Boc Deprotection

General Procedure

Functionalized IRMOF-74-III crystals were subjected to solvent washing procedure described in Section 3.9.3. The compounds were transferred using a glass

pipette into a 10 mL reaction tube containing 3 mL of 2-ethyl-1-hexanol, 150 μ L of ethylene glycol and 150 μ L of deionized water. The heterogeneous mixture was subjected to 230 °C microwave heating using a CEM Discover microwave reactor equipped with an IR temperature sensor (300 PSI pressure limit, 300 W max power, no stirring, PowerMax setting off) for 10 minutes. The mixture was allowed to cool down to room temperature and the DMF and methanol solvent washing procedure was repeated. The obtained microcrystalline samples were analyzed by PXRD and ^1H NMR after digestion.

Thermal Post-synthetic -Boc Deprotection of IRMOF-74-III-(CH₂NHBoc)₂

The Boc protecting group was removed using microwave heating as described above. The yellow crystals of IRMOF-74-III-(CH₂NH₂)₂ were recovered in 98% yield. PXRD was collected on activated sample (guest free). The high degree of correspondence between the sample pattern and that of the sample before the deprotection procedure indicates that the bulk material remains crystalline and with the same underlying topology after the post-synthetic deprotection (Section 3.9.8). The successful Boc-deprotection was confirmed by the absence of the Boc resonance peak at 1.31 ppm in the ^1H NMR of digested samples (Section 3.9.7) in 50 mM DCl in a DMSO-*d*₆/D₂O mixture (Section 3.9.8). IR (ATR), $\bar{\nu}_{\text{max}}$ [cm⁻¹]: IR (ATR), $\bar{\nu}_{\text{max}}$ [cm⁻¹]: 3360 (br w), 2977 (w), 1682 (br w), 1580 (s), 1431 (s), 1367 (s), 1249 (br s), 1219 (m), 1198 (m), 1157 (w), 1025 (s), 940 (m), 890 (m), 847 (m), 790 (m), 722 (m), 696 (m), 602 (m).

3.9.5 Solid State NMR Experiments

CO₂ Gas Loading and NMR Sample Preparation

Each measured sample was packed into a Doty 4 mm or 5 mm zirconia rotor in an argon atmosphere glovebox. The packed, uncapped rotor was then quickly transferred to a home-built gas dosing apparatus and vacuum was applied for 2 hours. After this period, the sample was exposed to 675 torr (900 mbar) ¹³CO₂ gas (Sigma-Aldrich, 99% atom ¹³C) for 24 hours at room temperature. The pressure was monitored using an MKS Baratron capacitance manometer with a working range of 1-5000 torr. After exposure, the rotor was quickly capped and transferred to the magnet for NMR analysis to minimize any loss of CO₂. Significant CO₂ leakage, and correspondingly, changes to the ¹³C and ¹⁵N spectra (namely a loss of intensity from the carbamic acid resonance), was observed after several (12-24) of MAS NMR data acquisition. However, this loss was minimized by keeping the length of each NMR experiment to around 2 hours. Water-exposed MOF samples were prepared following the procedure detailed in Section 3.9.15. The water-exposed MOFs were then transferred to the gas dosing apparatus and exposed to ¹³CO₂ as described previously. The lab atmosphere was measured to be roughly 50 % RH using a chilled mirror setup described in Section 3.9.15. A packed rotor was left uncapped and exposed to the lab atmosphere for 24 hours before loading with ¹³CO₂ as described. These ¹³C and ¹⁵N CP-MAS spectra are shown in figures S3.2 and S3.3 respectively.

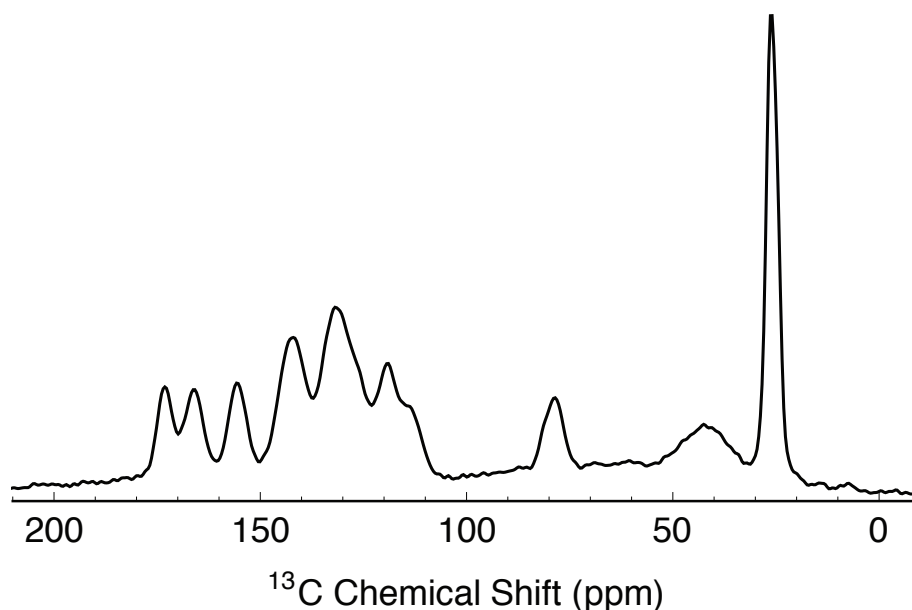


Figure S3.1. ¹³C CP-MAS NMR of activated IRMOF-74-III-(CH₂NHBoc)₂ processed with 25 Hz line broadening. Note the significant peaks at approximately 155, 80, 40 and 25 ppm corresponding to the -Boc group, which are not present in the ¹³C spectrum of the deprotected material.

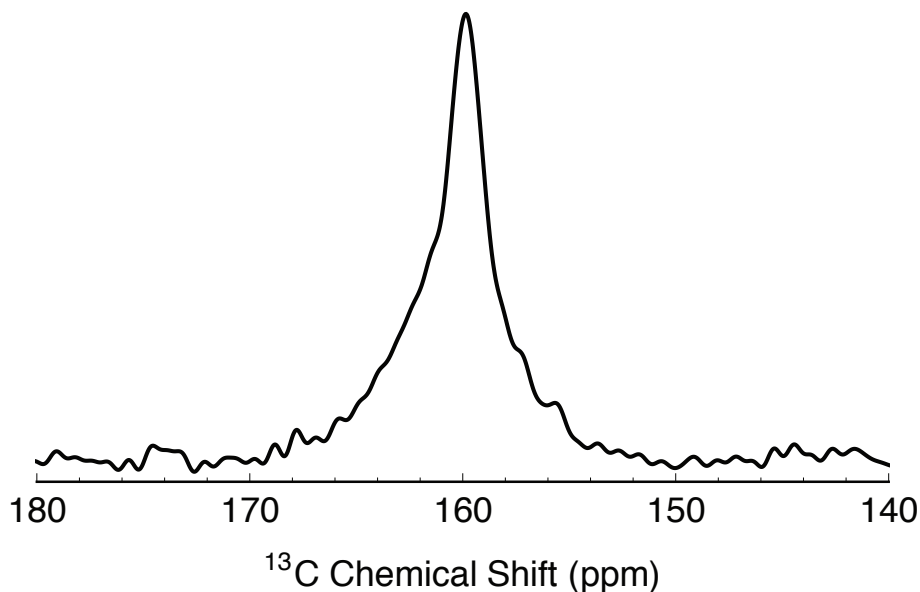


Figure S3.2. ^{13}C CP-MAS NMR of atmosphere-exposed (50% RH) IRMOF-74-III- $(\text{CH}_2\text{NH}_2)_2$ subsequently exposed to 675 mbar $^{13}\text{CO}_2$. Note the large peak with maximum at 160.3 ppm, however there is a loss of the right shoulder intensity between 160 and 155 ppm when compared to the dry spectrum (Figure 4.2 (b), red) and an increase in intensity for the left shoulder spanning through 164 ppm attributable to the increase in carbamate population.

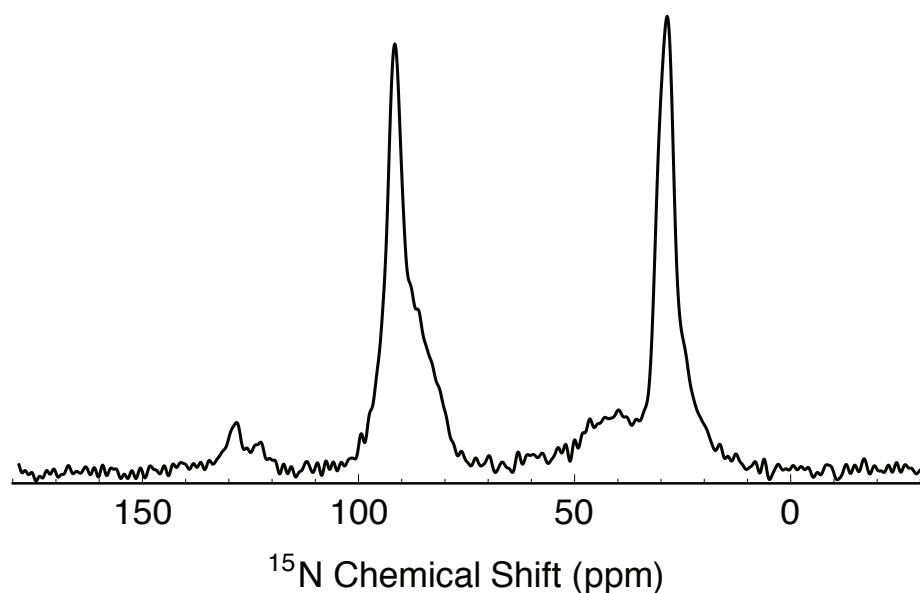


Figure S3.3. ^{15}N CP-MAS NMR of atmosphere-exposed (50% RH) IRMOF-74-III- $(\text{CH}_2\text{NH}_2)_2$ subsequently exposed to 675 mbar $^{13}\text{CO}_2$. The amine peak at 30 ppm has lost the splitting observed in the ^{15}N spectrum of the dry material. The broadening of the base of the resonance with a maximum at 91 ppm suggests that there is an increase in carbamate is formed in addition to carbamic acid, as well as a broad feature at around 40 ppm attributable to a small amount of ammonium.

3.9.6 FT-IR Spectra of Activated MOFs

Cleavage of the -Boc protecting groups was confirmed by the disappearance of the stretching frequencies at 1682 ($\nu_{\text{C=O}}$) and 1157 ($\nu_{\text{C-O}}$) cm^{-1} . After exposure to dry CO_2 the appearance of an absorption band at 1692 cm^{-1} in IRMOF-74-III- $(\text{CH}_2\text{NH}_2)_2$ indicated carbamic acid ($\nu_{\text{C=O}}$) formation, consistent with stretching frequencies previously reported.²¹ Further analysis of the FT-IR spectra revealed the absence of absorption bands typically assigned to carbamate moieties (1575 cm^{-1} [$\nu_{\text{C=O}}$]) after dry CO_2 loading.²¹

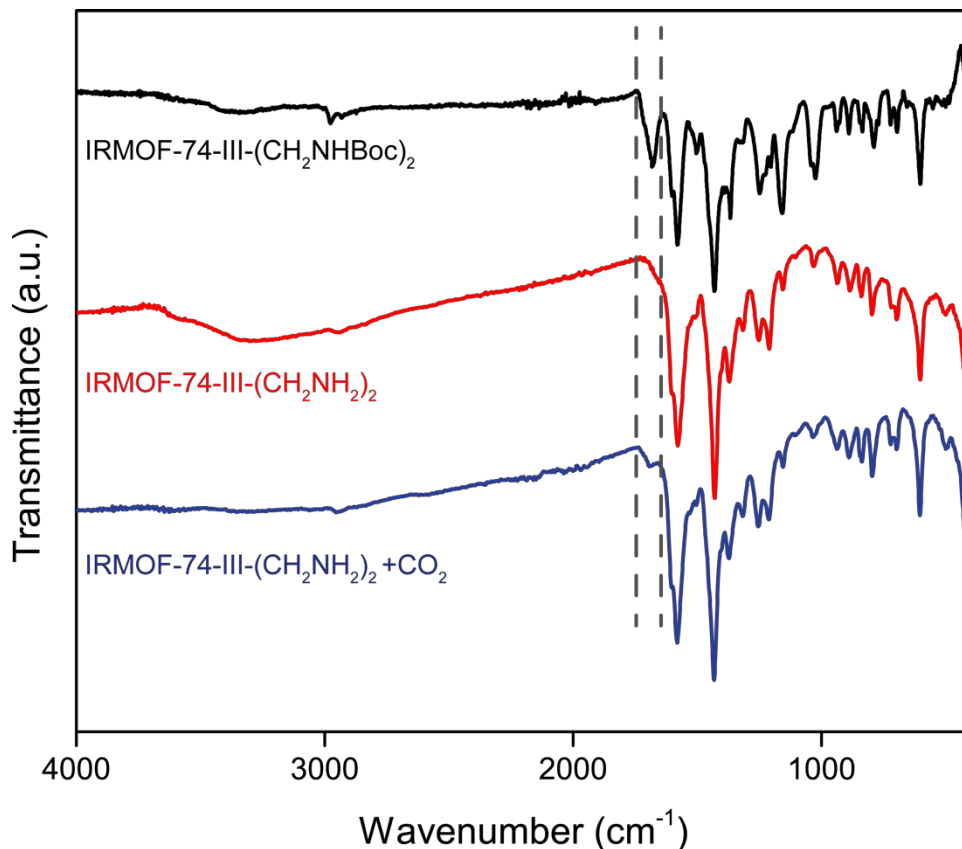


Figure S3.4. FT-IR (ATR) spectra of activated IRMOF-74-III- $(\text{CH}_2\text{NHBoc})_2$ (black curve) and IRMOF-74-III- $(\text{CH}_2\text{NH}_2)_2$ (red curve) showing -Boc group cleavage as evidenced by the disappearance of peaks at and 1682 and 1157 cm^{-1} . After exposure to dry CO_2 (blue curve) carbamic acid formation is observed as evidenced by the appearance of a small peak at and 1694 cm^{-1} .

3.9.7 Solution ^1H NMR of Digested Samples

General Procedure

Typically, for the digestion of the MOF samples ca. 10 mg of functionalized IRMOF-74-III were dried in air ca. 12 h after solvent washing with DMF. Then 0.5 mL of $\text{DMSO-}d_6$ and 10 μL of DCl in D_2O (35 wt. %), were added. The suspension was sonicated

1 min and left at room temperature until the solution clarified. The ^1H NMR spectra were recorded after 10 min.

Spectroscopic Results

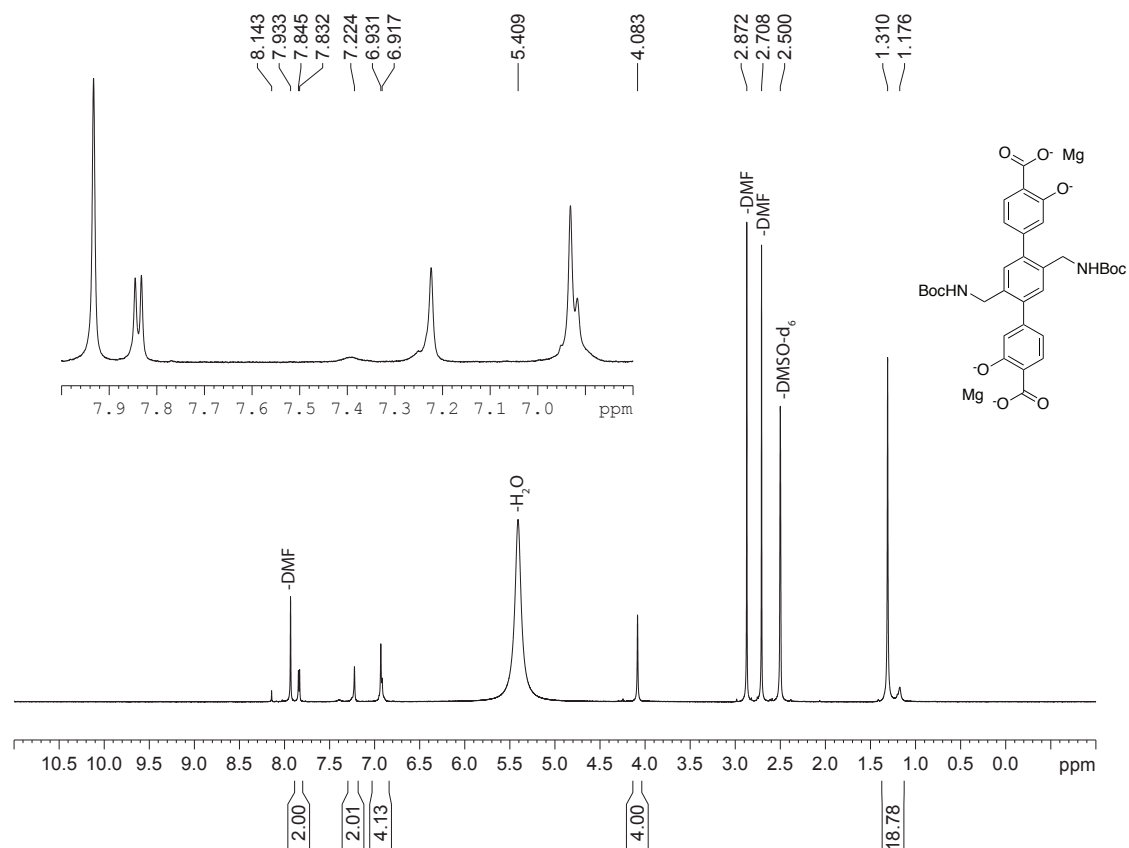


Figure S3.5. ^1H NMR spectra of IRMOF-74-III- $(\text{CH}_2\text{NHBoc})_2$ digested sample in 50 mM DCl/DMSO- d_6 /D $_2$ O mixture. (Inset) Expanded aromatic region in the spectra.

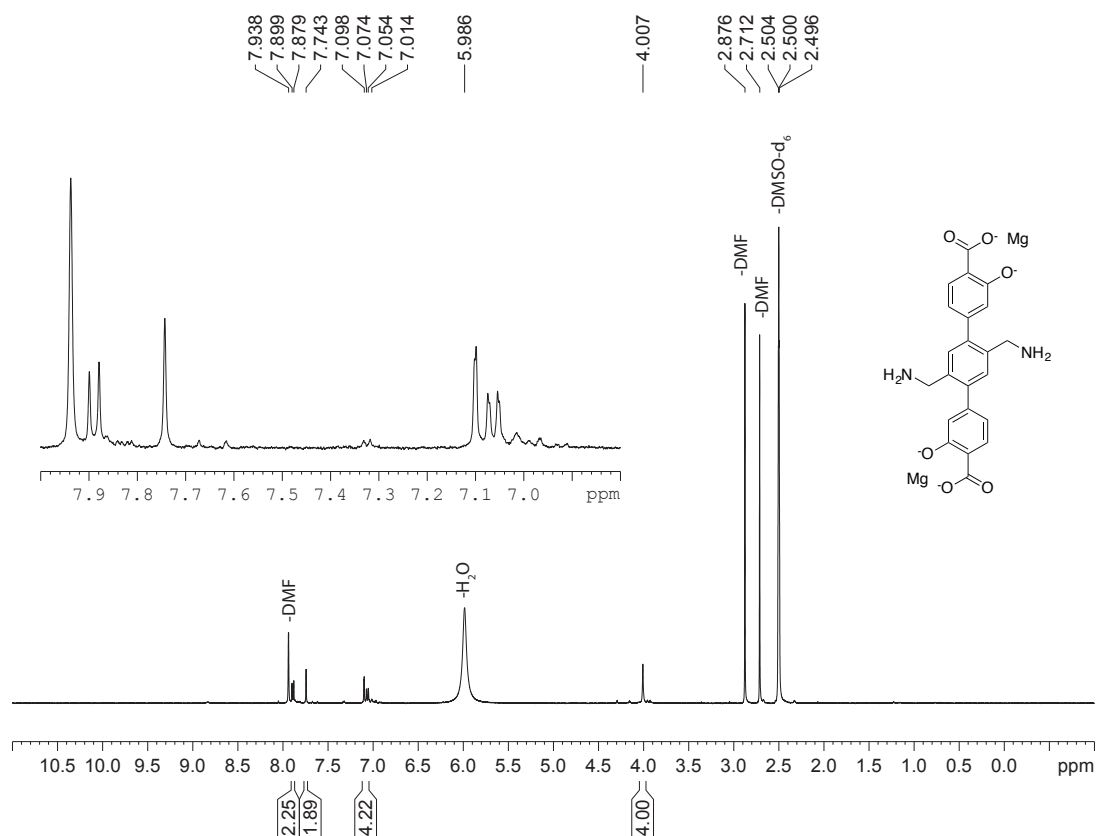


Figure S3.6. ^1H NMR spectra of IRMOF-74-III- $(\text{CH}_2\text{NH}_2)_2$ digested sample in 50 mM DCl/DMSO- d_6 /D $_2$ O mixture. (Inset) Expanded aromatic region in the spectra.

3.9.8 Powder X-ray Diffraction (PXRD) Characterization

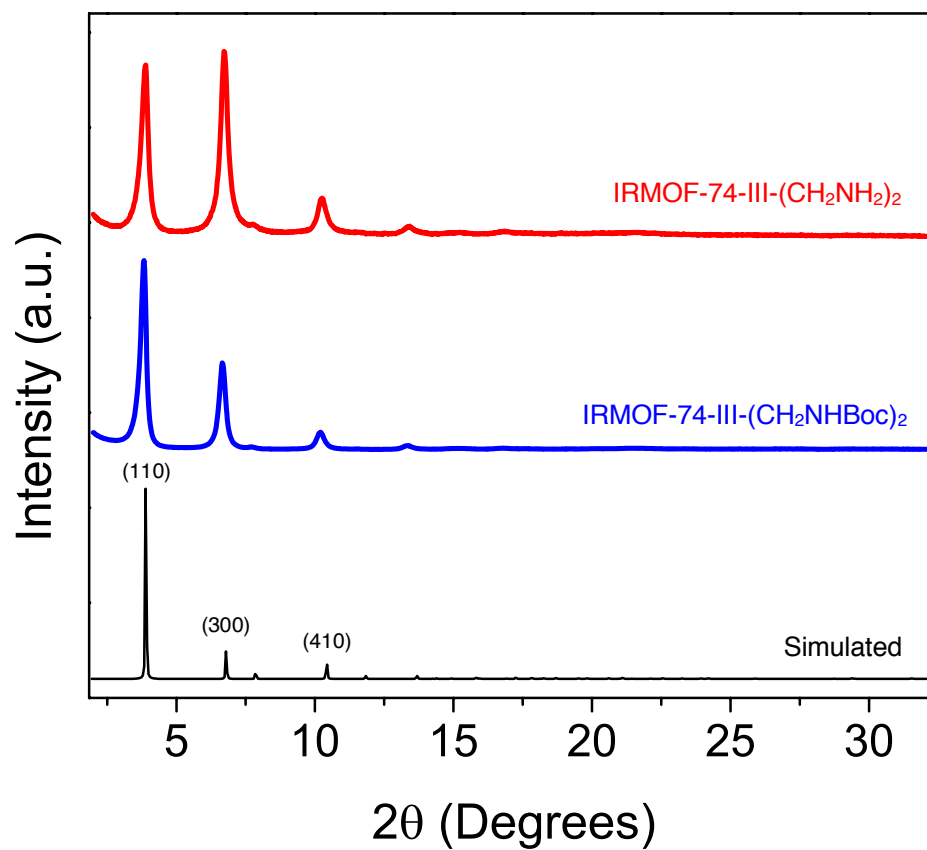


Figure S3.7. PXRD pattern of simulated IRMOF-74-III (black), activated IRMOF-74-III-(CH₂NHBoc)₂ (blue), and IRMOF-74-III-(CH₂NH₂)₂ (red).

3.9.9 Nitrogen Adsorption Measurements

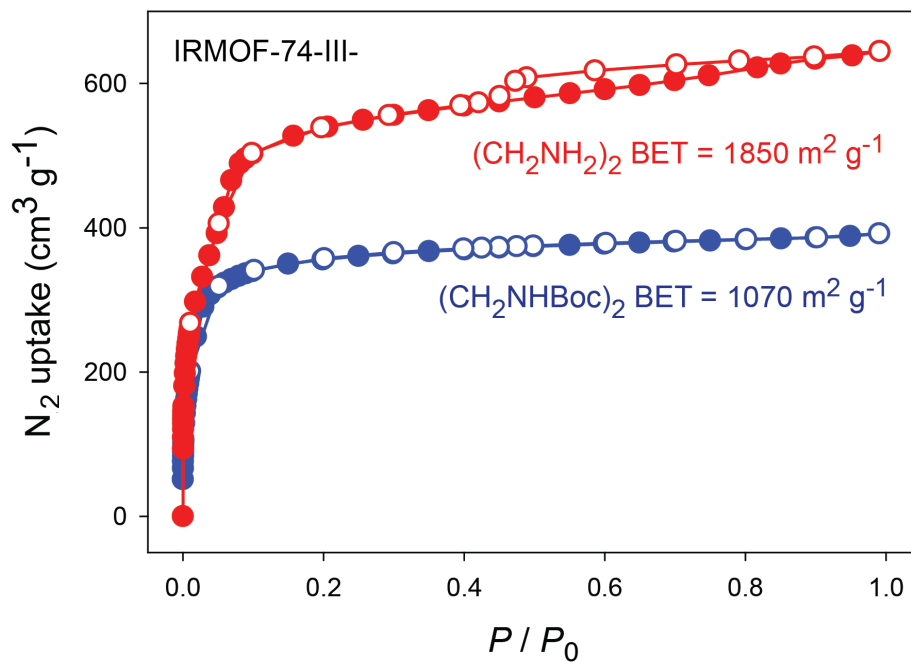


Figure S3.8. Nitrogen adsorption isotherms for IRMOF-74-III-(CH₂NHBoc)₂ (blue), and IRMOF-74-III-(CH₂NH₂)₂ (red) at 77 K. The inset text details the experimental BET surface areas for the two compounds.

3.9.10 Additional CO₂ Adsorption Measurements and Comparison to Previously-Reported Material

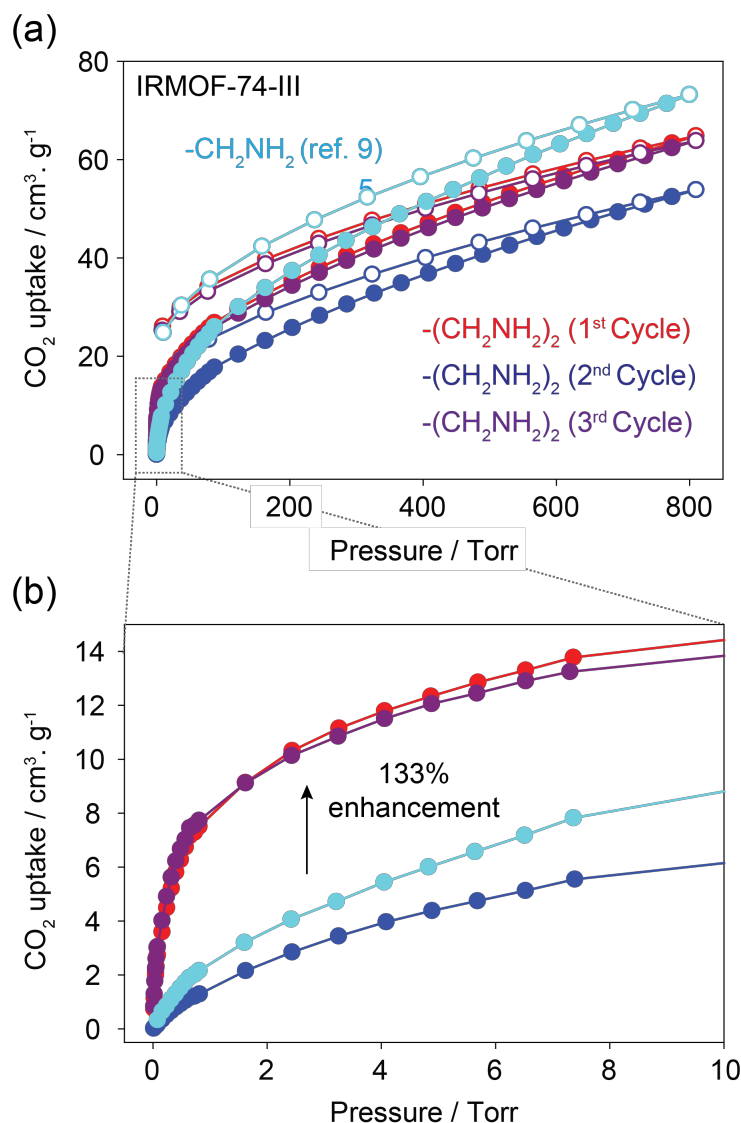


Figure S3.9. (a) Carbon dioxide isotherms for IRMOF-74-III-(CH₂NH₂)₂ and IRMOF-74-III-CH₂NH₂ at 25 °C. In red, after activation (first cycle); in blue, after first carbon dioxide isotherm (second cycle); and in purple, after 120 °C heating 2 h (third cycle) in cyan, carbon dioxide isotherm for IRMOF-74-III-CH₂NH₂ for comparison. (b) expansion of the low pressure range.

3.9.11 Modeling of IRMOF-74-III-(CH₂NH₂)₂ and Resultant Pertinent Atomic Distances

To model the inter-methylene distances in question in IRMOF-74-III-(CH₂NH₂)₂, I began with a crystal structure of Mg-IRMOF-74 previously published to establish O-Mg bond distances and inter-linker spacing for the material.²² I then constructed, from

scratch, a model of Mg-IRMOF-74-III in BIOVIA Materials Studio 8.0 using these distances as heuristics for the structure. The structure was optimized using the *Forcite* module in the software. From there, I modeled the amines in a staggered orientation (as logically follows from the argument with respect to steric hindrance mentioned previously) and re-optimized the structure. Finally, calculated PXRD patterns were generated using the *Reflex* module in the software. These patterns were used for comparisons in Section 3.9.8.

3.9.12 Thermogravimetric Analysis

Dry IRMOF-74-III-(CH₂NH₂)₂ Sample

IRMOF-74-III-(CH₂NH₂)₂ was loaded with CO₂ (see Section 3.9.5) prior to DSC-TGA analysis. About 7 mg of sample were filled into an aluminum sample holder. The samples were subjected to a heating rate of 10 °C min⁻¹ and a maximum temperature of 200 °C under a CO₂ (20 ml min⁻¹) atmosphere. A mass loss corresponding to 12 % is observed (Fig. S3.10), however an onset temperature for this mass loss could not be determined. The first derivative of the TGA curve coincides with the maximum of an endothermic effect in the DSC curve which is correlated to the loss of CO₂. The porous nature of IRMOF-74-III-(CH₂NH₂)₂ does not allow for the determination of a bond energy, due to ineffectual heating of the mostly voided activated sample. The thermal energy at 47 °C (center of the first derivative of the mass loss) correlates to approximately 89.6 kJ, which is in good agreement with calculated values for the activation energy of bond cleavage in carbamic acid.²³

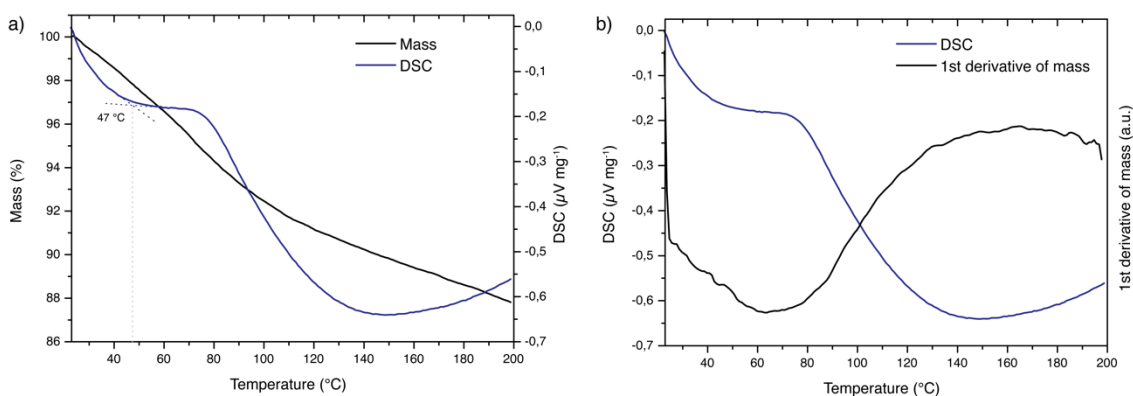


Figure S3.10. TGA-DSC measurement of a dry CO₂ loaded sample of IRMOF-74-III-(CH₂NH₂)₂. a) The blue line represents the DSC curve which shows an endothermic peak corresponding to the liberation of CO₂ centered around 80 °C. The onset at 47 °C correlates to the activation energy for the bond cleavage. b) The first derivative of the TG curve (black) shows one broad beak that correlates well with the endothermic peak in the DSC curve.

Humidified IRMOF-74-III-(CH₂NH₂)₂ Sample

20 mg of IRMOF-74-III-(CH₂NH₂)₂ was transferred into an aluminum sample holder, after humidification following the procedure detailed in Section 3.9.15 and subsequently exposed to CO₂ (flow-rate 40 ml min⁻¹) inside the STA 449 F5 for 24 hours. After CO₂ loading the sample was subjected to a heating rate of 10 °C min⁻¹ and a maximum temperature of 200 °C under a CO₂ atmosphere. The measurement shows a mass loss corresponding to 10 % with an onset at 65 °C (Fig. S3.11). The mass loss is attributed to both H₂O and CO₂ as evidenced by simultaneously recorded MS spectra. The first derivative of the TGA curve coincides with the maximum of an endothermic effect in the DSC curve which is correlated to the loss of CO₂ and the desorption of H₂O. The MS signals for CO₂ and H₂O both occur at the same temperature as the endothermic DSC peak. The fact that CO₂ is liberated at significantly higher temperatures (peak centered around 130 °C) indicates the presence of a different species (ammonium carbamate), which is in good agreement with the NMR measurements performed.

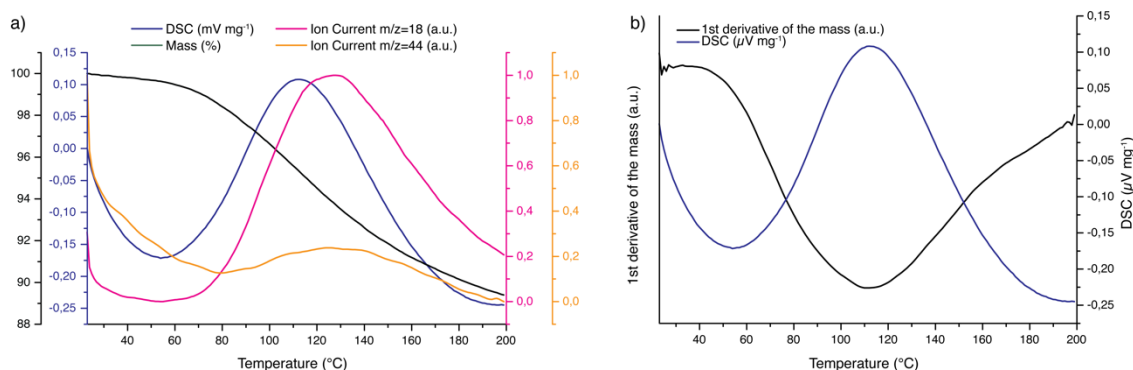


Figure S3.11. TGA-DSC-MS measurement of a humidified, CO₂ loaded sample of IRMOF-74-III-(CH₂NH₂)₂. a) The blue line represents the DSC curve which shows an endothermic peak corresponding to the liberation of CO₂ centered around 120 °C. The onset at 65 °C correlates to the activation energy for the bond cleavage (123 kJ). b) The first derivative of the TG curve (black) shows one broad peak that correlates well with the endothermic peak in the DSC curve.

3.9.13 Dynamic CO₂ Capture in the Presence of Water

To compare the dynamic capacity of IRMOF-74-III-(CH₂NH₂)₂ to the previously reported -CH₂NH₂ compound, CO₂ breakthrough experiments were conducted using dry (0% RH) and wet (65% RH) streams of 16% (v/v) CO₂ in nitrogen. A stainless steel column (10 cm length × 0.6 cm diameter) was packed with 240 mg (0.53 mmol) of IRMOF-74-III-(CH₂NH₂)₂ to be used as an adsorbent bed. The mixed gas streams were introduced to the column and the effluent gasses were monitored by a mass spectrometer. Breakthrough time was determined when the effluent CO₂ concentration reached 5% of the influent concentration, similar to other studies. Under exposure to the dry gas stream, the IRMOF-74-III-(CH₂NH₂)₂ adsorbent bed held CO₂ for 900 ± 10 s g⁻¹, which is equivalent to a kinetic CO₂ adsorption capacity of 1.2 mmol g⁻¹ (Figure S3.12). The

breakthrough experiment was repeated two times, and between each trial, the adsorbent bed was flushed with dry nitrogen gas and heated to 120 °C for 30 minutes to remove all CO₂ molecules chemisorbed to the surface. The kinetic adsorption capacity remained essentially unchanged when the material was exposed to the wet gas stream where the IRMOF-74-III-(CH₂NH₂)₂ adsorbent bed held CO₂ for $890 \pm 10 \text{ s g}^{-1}$, which is equivalent to a kinetic CO₂ adsorption capacity of 1.2 mmol g⁻¹. These results constitute a 34% increase in the dynamic capacity of the IRMOF-74-III-(CH₂NH₂)₂ material over its monoamine functionalized counterpart. Interestingly, when comparing the breakthrough performance of the material exposed to a wet gas mixture to that of the material exposed to a dry gas mixture, the breakthrough times are nearly identical as previously mentioned. However, the material requires a significantly greater amount of time for the effluent gas to match the CO₂ composition of the influent gas when the gas mixture is humidified. This supports the hypothesis that the mechanism of CO₂ uptake is altered in the presence of water and the kinetic consequence of using two amines to capture one molecule of CO₂ causes slower overall uptake.

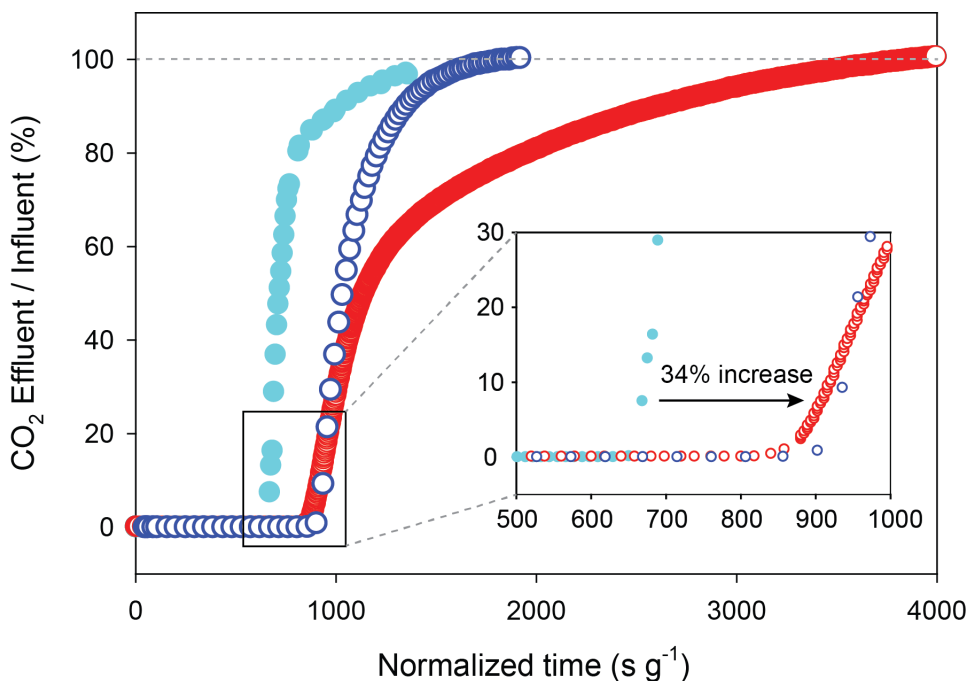


Figure S3.12. Breakthrough curves for IRMOF-74-III-(CH₂NH₂)₂ under dry conditions (dark blue empty markers) and wet conditions (red empty markers), and, for comparison, IRMOF-74-III-CH₂NH₂ under wet conditions (cyan filled markers).

3.9.14 Control Experiment Mitigating the Impact of Base Pre-Treatment

In order to fully neutralize the amine moieties in the MOF pores leaving them accessible to reaction with CO₂, the crystalline MOF powders were washed with a triethylamine in methanol solution as described in Section 3.9.2. To ensure that treatment of IRMOF-74-III-(CH₂NH₂)₂ with triethylamine-methanol solution would only affect the

primary amine moieties covalently bound to the organic struts of the material, I subjected an analogous compound, IRMOF-74-III-CH₃, to the same washing conditions. CO₂ uptake capacity was obtained by measuring isotherms at 298 K (25 °C, Figure S3.13) for IRMOF-74-III-CH₃ with and without base treatment. I observed no significant differences in the uptake behavior of the material regardless of whether or not triethylamine base was utilized in preparation of isotherm measurement, indicating that base treatment does not affect the underlying MOF structure, nor does it serve to alter the environment of the metal clusters present.

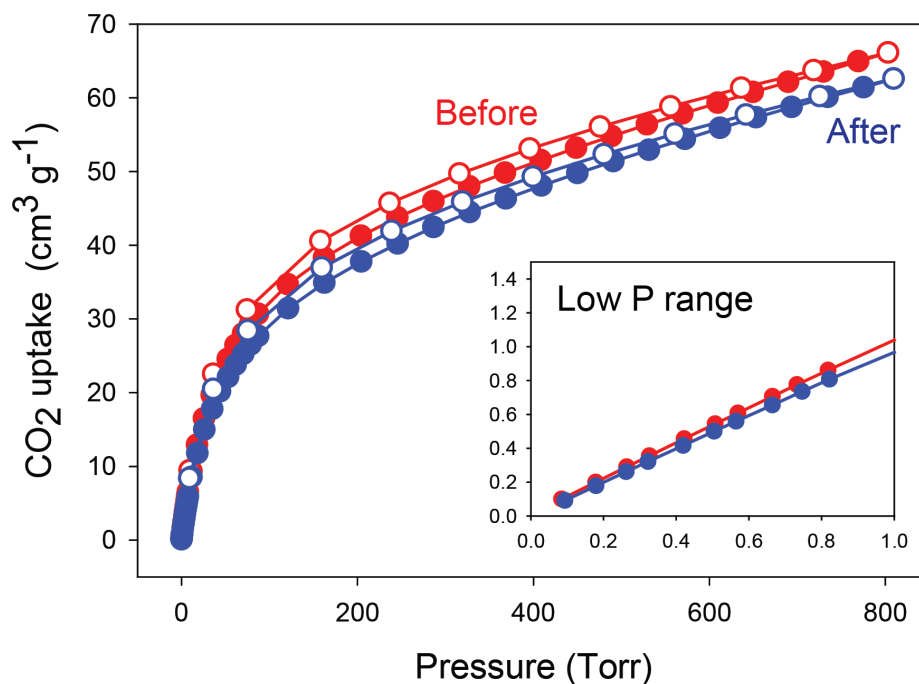


Figure S3.13. CO₂ isotherms for IRMOF-74-III-CH₃ at 25 °C. In red, before; in blue, after trimethylamine treatment. The inset shows that the low pressure uptake of carbon dioxide does not change upon treatment with triethylamine solution.

3.9.15 Humidification of IRMOF-74-III-(CH₂NH₂)₂ Samples

Samples of activated IRMOF-74-III-(CH₂NH₂)₂ were saturated with water vapor at a relative humidity (RH) values of RH = 95% by using a HygroCal100 Humidity Generator/Calibrator (Michell Inc, MA, USA) controlled humidity chamber. To generate uniform humidity across the chamber, the HygroCal 100 humidity generator is equipped with seven HygroSmart HS3 capacitive humidity sensors with $\pm 0.8\%$ accuracy. The bias error was eliminated by using an external standard reference precision dew-point meter (chilled mirror with $\pm 0.2^\circ\text{C}_{\text{dew-point}}$ accuracy). Ultimately, the humidity measurements were taken with the overall uncertainty of $\pm 1\%$.

For each humidification, ca 30 mg of activated MOF was transferred into the appropriate container (Al pan for TGA-DSC-MS, Rotor for CP-MAS-NMR) in a nitrogen-filled glove box and placed inside the sealed HygroCal100 humidity chamber in an uncapped 4 mL vial. To minimize atmospheric CO₂ interaction with the MOF during humidification, the chamber was purged with ultra-pure nitrogen (99.999%) and kept under 0-0.5% RH for at least 5 minutes. While nitrogen flowed through the humidity chamber, the vials were transferred to the chamber and after another 1-2 minutes the humidity value stabilized back to 0-0.5%. Then, the nitrogen flow was stopped and the water loading experiment commenced by increasing the relative humidity inside the chamber from 0-0.5% to 95% with transition period of less than 2 minutes. The samples were kept inside the humidity-controlled chamber for 24 hours to ensure that the samples were saturated with water at the specified RH values.

3.10 References for Chapter 3

- (1) Schoedel, A.; Ji, Z.; Yaghi, O. M. The Role of Metal–Organic Frameworks in a Carbon-Neutral Energy Cycle. *Nat. Energy* **2016**, *1*, 16034.
- (2) Belmabkhout, Y.; Guillerm, V.; Eddaoudi, M. Low Concentration CO₂ Capture Using Physical Adsorbents: Are Metal–Organic Frameworks Becoming the New Benchmark Materials? *Chem. Eng. J.* **2016**, *296*, 386–397.
- (3) Cohen, S. M. Postsynthetic Methods for the Functionalization of Metal–Organic Frameworks. *Chem. Rev.* **2012**, *112*, 970–1000.
- (4) McDonald, T. M.; Mason, J. A.; Kong, X.; Bloch, E. D.; Gygi, D.; Dani, A.; Crocellà, V.; Giordanino, F.; Odoh, S. O.; Drisdell, W. S.; Vlasisavljevich, B.; Dzubak, A. L.; Poloni, R.; Schnell, S. K.; Planas, N.; Lee, K.; Pascal, T.; Wan, L. F.; Prendergast, D.; Neaton, J. B.; Smit, B.; Kortright, J. B.; Gagliardi, L.; Bordiga, S.; Reimer, J. A.; Long, J. R. Cooperative Insertion of CO₂ in Diamine-Appended Metal–Organic Frameworks. *Nature* **2015**, *519*, 303–308.
- (5) Fracaroli, A. M.; Furukawa, H.; Suzuki, M.; Dodd, M.; Okajima, S.; Yaghi, O. M. Metal–Organic Frameworks with Precisely Designed Interior for Carbon Dioxide Capture in the Presence of Water. *J. Am. Chem. Soc.* **2014**, *136*, 8863–8866.
- (6) McDonald, T. M.; D’Alessandro, D. M.; Krishna, R.; Long, J. R. Enhanced Carbon Dioxide Capture upon Incorporation of N,N'-Dimethylethylenediamine in the Metal–Organic Framework CuBTTri. *Chem. Sci.* **2011**, *2*, 2022.
- (7) Planas, N.; Dzubak, A. L.; Poloni, R.; Lin, L.-C.; McManus, A.; McDonald, T. M.; Neaton, J. B.; Long, J. R.; Smit, B.; Gagliardi, L. The Mechanism of Carbon Dioxide Adsorption in an Alkylamine-Functionalized Metal–Organic Framework. *J. Am. Chem. Soc.* **2013**, *135*, 7402–7405.
- (8) Liao, P.; Chen, X.; Liu, S.; Li, X.; Xu, Y.; Tang, M.; Rui, Z.; Zhang, J.; Chen, X. Putting an Ultrahigh Concentration of Amine Groups into a Metal–Organic Framework for CO₂ Capture at Low Pressures. *Chem. Sci.* **2016**, 6528–6533.
- (9) Li, L.-J.; Liao, P.-Q.; He, C.-T.; Wei, Y.-S.; Zhou, H.-L.; Lin, J.-M.; Li, X.-Y.; Zhang, J.-P. Grafting Alkylamine in UiO-66 by Charge-Assisted Coordination Bonds for Carbon Dioxide Capture from High-Humidity Flue Gas. *J. Mater. Chem. A* **2015**, *3*, 21849–21855.
- (10) Gómora-Figueroa, A. P.; Mason, J. A.; Gonzalez, M. I.; Bloch, E. D.; Meihaus, K. R. Metal Insertion in a Methylamine-Functionalized Zirconium Metal–Organic Framework for Enhanced Carbon Dioxide Capture. *Inorg. Chem.* **2017**, *56*, 4308–4316.
- (11) Aresta, M.; Ballivet-Tkatchenko, D.; Dell’Amico, D. B.; Boschi, D.; Calderazzo, F.; Labella, L.; Bonnet, M. C.; Faure, R.; Marchetti, F. Isolation and Structural Determination of Two Derivatives of the Elusive Carbamic Acid. *Chem. Commun.* **2000**, *8*, 1099–1100.
- (12) Pinto, M. L.; Mafra, L.; Guil, J. M.; Pires, J.; Rocha, J. Adsorption and Activation of CO₂ by Amine-Modified Nanoporous Materials Studied by Solid-State NMR and ¹³CO₂ Adsorption. *Chem. Mater.* **2011**, *23*, 1387–1395.
- (13) Switzer, J. R.; Ethier, A. L.; Flack, K. M.; Biddinger, E. J.; Gelbaum, L.; Pollet, P.;

- Eckert, C. A.; Liotta, C. L. Reversible Ionic Liquid Stabilized Carbamic Acids: A Pathway Toward Enhanced CO₂ Capture. *Ind. Eng. Chem. Res.* **2013**, *52*, 13159–13163.
- (14) Mafra, L.; Čendak, T.; Schneider, S.; Wiper, P. V.; Pires, J.; Gomes, J. R. B.; Pinto, M. L. Structure of Chemisorbed CO₂ Species in Amine-Functionalized Mesoporous Silicas Studied by Solid-State NMR and Computer Modeling. *J. Am. Chem. Soc.* **2017**, *139*, 389–408.
- (15) Inagaki, F.; Matsumoto, C.; Iwata, T.; Mukai, C. CO₂-Selective Absorbents in Air: Reverse Lipid Bilayer Structure Forming Neutral Carbamic Acid in Water without Hydration. *J. Am. Chem. Soc.* **2017**, *139*, 4639–4642.
- (16) Lun, D. J.; Waterhouse, G. I. N.; Telfer, S. G. A General Thermolabile Protecting Group Strategy for Organocatalytic Metal-Organic Frameworks. *J. Am. Chem. Soc.* **2011**, *133*, 5806–5809.
- (17) Li, D.; Furukawa, H.; Deng, H.; Liu, C.; Yaghi, O. M.; Eisenberg, D. S. Designed Amyloid Fibers as Materials for Selective Carbon Dioxide Capture. *Proc. Natl. Acad. Sci.* **2014**, *111*, 191–196.
- (18) Chen, C.; Shimon, D.; Lee, J. J.; Didas, S. A.; Mehta, A. K.; Sievers, C.; Jones, C. W.; Hayes, S. E. Spectroscopic Characterization of Adsorbed ¹³CO₂ on 3-Aminopropylsilyl-Modified SBA15 Mesoporous Silica. *Environ. Sci. Technol.* **2017**, *51*, 6553–6559.
- (19) Doonan, C. J.; Morris, W.; Furukawa, H.; Yaghi, O. M. Isorecticular Metalation of Metal-Organic Frameworks. *J. Am. Chem. Soc.* **2009**, *131*, 9492–9493.
- (20) Vishnyakov, A.; Ravikovitch, P. I.; Neimark, A. V.; Bülow, M.; Wang, Q. M. Nanopore Structure and Sorption Properties of Cu-BTC Metal-Organic Framework. *Nano Lett.* **2003**, *3*, 713–718.
- (21) Masuda, K.; Ito, Y.; Horiguchi, M.; Fujita, H. Studies on the Solvent Dependence of the Carbamic Acid Formation from ω-(1-Naphthyl)Alkylamines and Carbon Dioxide. *Tetrahedron* **2005**, *61*, 213–229.
- (22) Dietzel, P. D. C.; Blom, R.; Fjellvåg, H. Base-Induced Formation of Two Magnesium Metal-Organic Framework Compounds with a Bifunctional Tetratopic Ligand. *Eur. J. Inorg. Chem.* **2008**, *2008*, 3624–3632.
- (23) Mora, J. R.; Tosta, M.; Domínguez, R. M.; Herize, A.; Barroso, J.; Córdova, T.; Chuchani, G. Joint Theoretical and Experimental Study of the Gas-Phase Elimination Kinetics of tert-Butyl Ester of Carbamic, N, N-Dimethylcarbamic, N-Hydroxycarbamic Acids and 1-(Tert-Butoxycarbonyl)-Imidazole. *J. Phys. Org. Chem.* **2007**, *20*, 1021–1031.

Chapter 4: Investigation of CO₂ Chemisorption in an Amine-Functionalized Covalent Organic Framework Under Dry and Humid Conditions

Work in this Chapter was performed in a team including Peter J. Waller, Hao Lyu, Lac Ha Nguyen, Hasan Celik, Nanette Jarenwattananon, and Omar M. Yaghi

4.1 Preface

After the discovery that chemisorption products could be selected based on humidity levels in IRMOF-74-III-(CH₂NH₂)₂, I sought to investigate this phenomenon in covalent organic frameworks (COFs). In doing so, I envisioned an alkylamine-functionalized material consisting only of light elements (C, H, N, O, etc.) that would be marked by high gravimetric CO₂ uptake. I also desired to observe whether or not the lack of metals in such a material would alter the chemisorption reaction mechanisms and shift the product distribution. In this chapter I detail the synthesis, characterization, post-synthetic modification, and framework chemistry of such a material, COF-81 and efforts to alleviate the issues intrinsic to the framework in the synthesis of an additional COF, COF-93.

4.2 Introduction

Covalent organic frameworks (COFs), a class of crystalline, porous, network solids constructed from small, light molecular building units by the formation of reversible bonds^{1,2}, can be functionalized with CO₂-philic amine, or alkylamine moieties.^{3,4} In contrast to metal-organic frameworks (MOFs), however, many of the most successful COFs for CO₂ capture applications lack such moieties apart from those contained in the compound's chemical linkage.⁵⁻¹⁴ Specifically, very few COFs have been applied to the selective capture of CO₂ from mixed gas streams, especially those containing significant amounts of water.¹⁵ Upon inspection of the linkages from which COFs are typically formed, namely boroxine anhydrides, boronate esters, imines, and hydrazones, the underlying reasoning for the apparent lack of COF application to such gas streams becomes obvious; the COF linkages are formed by condensation and thus are, in many cases, unstable under aqueous conditions.

Attempts have been made to improve the stability of COFs under a variety of conditions by post-synthetically modifying them either through organic transformation of their linkages, linker exchange, or a combination of the two methods.¹⁶⁻²³ COFs that are stable in acid, base, and boiling water can also be formed by performing imine condensations that are frequently applied to COF synthesis with an aldehyde linker possessing a vicinal hydroxy group.²⁴⁻²⁶ In these cases, imine condensation is followed by irreversible tautomerization, yielding β -ketoenamine linkages, which are significantly less susceptible to hydrolysis than their imine counterparts as demonstrated by the stability of the corresponding frameworks linked in this fashion.

With a water-stable, alkylamine-functionalized material in hand, one can determine the products of CO₂ chemisorption reactions under dry and humid conditions. Recently, I demonstrated that the discrepancy between two potential products, carbamic acids and ammonium carbamates, is measurable and has important consequences with respect to both adsorption capacity and adsorbent regeneration temperature.²⁷ Ideally, I envision a COF that can selectively capture CO₂ in the presence of water and form only

carbamic acid as the chemisorptive product (Figure 4.1), leading to higher adsorption capacity and lower requisite regeneration energy for the resultant material. In this chapter, I report that the major product of CO₂ chemisorption in a new material, COF-81, is carbamic acid under both dry *and* humid conditions. Unfortunately, COF-81 is plagued by side reactions intrinsic to its preparation and thus efforts to mitigate this issue via synthesis of a new compound, COF-93 are also detailed.

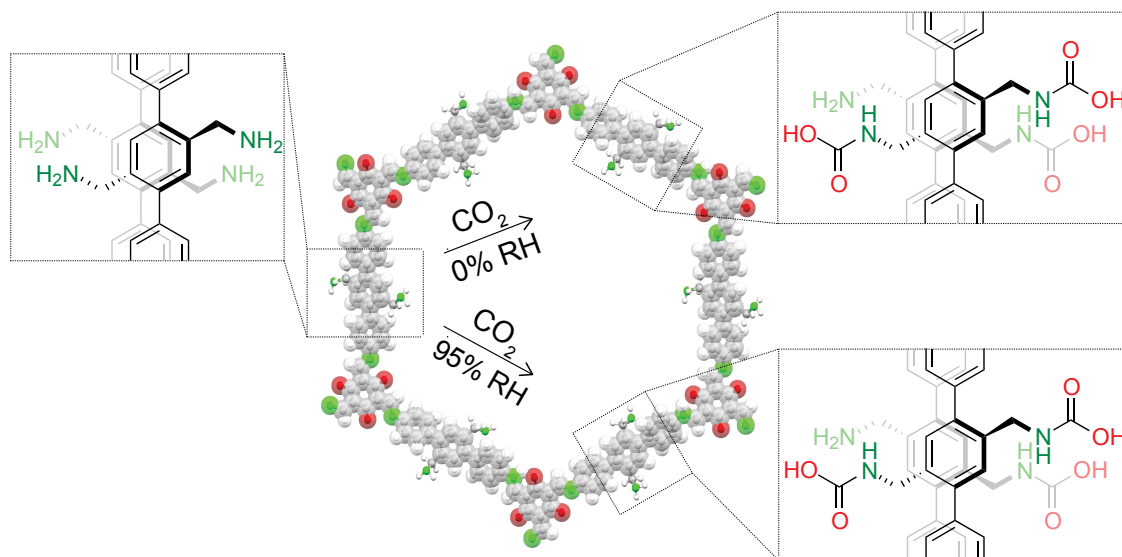
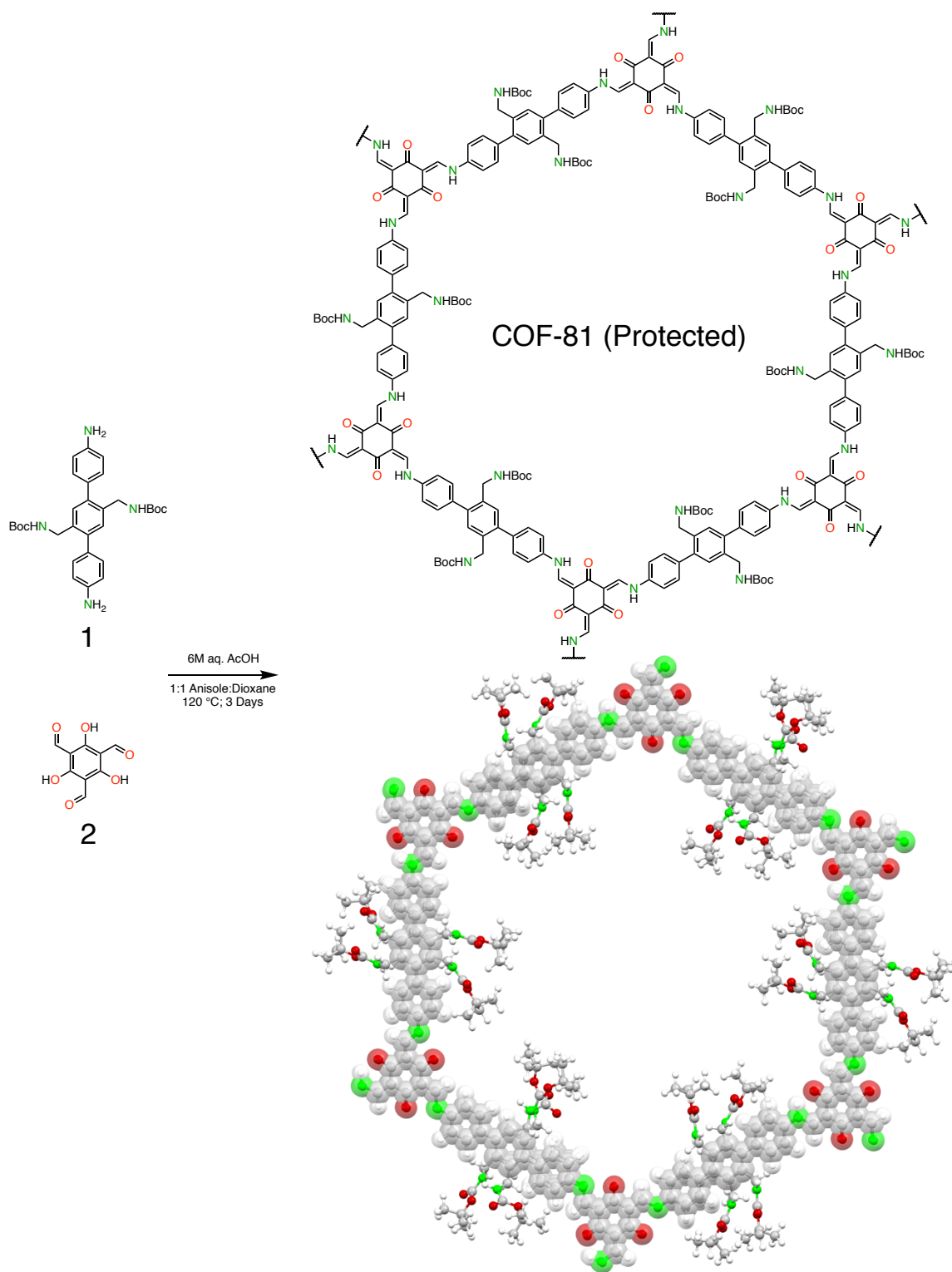


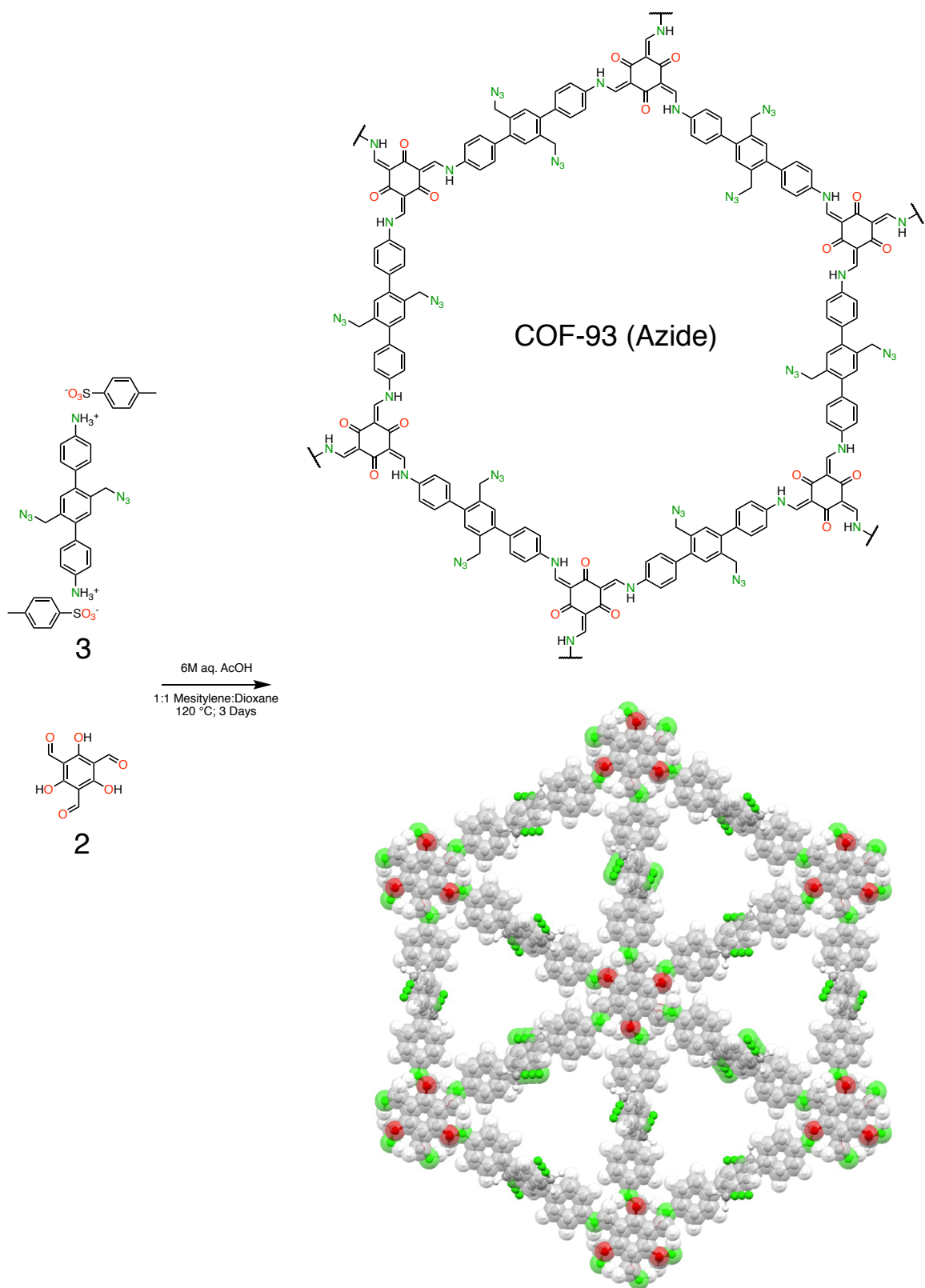
Figure 4.1. View of modeled, deprotected COF-81 [staggered amine] structure down the crystallographic *c*-axis, depicting the suspected pore environments before (left pore wall) and after exposure to CO₂ under 95% RH (bottom right pore wall) and dry (upper right pore wall) conditions. Note that under both dry and humid conditions, carbamic acid is the product of CO₂ chemisorption. Dashed boxes clarify the chemisorbed species upon reaction between linker-based alkylamine and CO₂ under the respective conditions. H atoms are omitted for clarity. Color code: C, gray; O, red; and N, green.

4.3 Approach

In this work, I sought to synthesize a diamine-functionalized COF system, COF-81 (Scheme 4.1), in which the chemisorptive capture of CO₂ under dry and humid conditions can be studied in a similar fashion to that in IRMOF-74-III-(CH₂NH₂)₂.²⁷ To accomplish this, I targeted a COF (COF-81) with an eclipsed, layered **hcb** topology that forms one-dimensional, mesoporous channels that are analogous to those in IRMOF-74-III-(CH₂NH₂)₂ (Scheme 4.1). I first developed a Boc-protected (-Boc = *tert*-butoxycarbonyl), alkylamine-functionalized COF linker (Sections 4.4 and 4.11.2) and a set of conditions from which COF-81 could be generated (Section 4.5). With this material in hand, I attempted to thermolytically liberate the Boc-protected alkylamines in the structure and characterize the resultant alkylamine-decorated COF-81 using the techniques listed above (Sections 4.5 and 4.11.4).



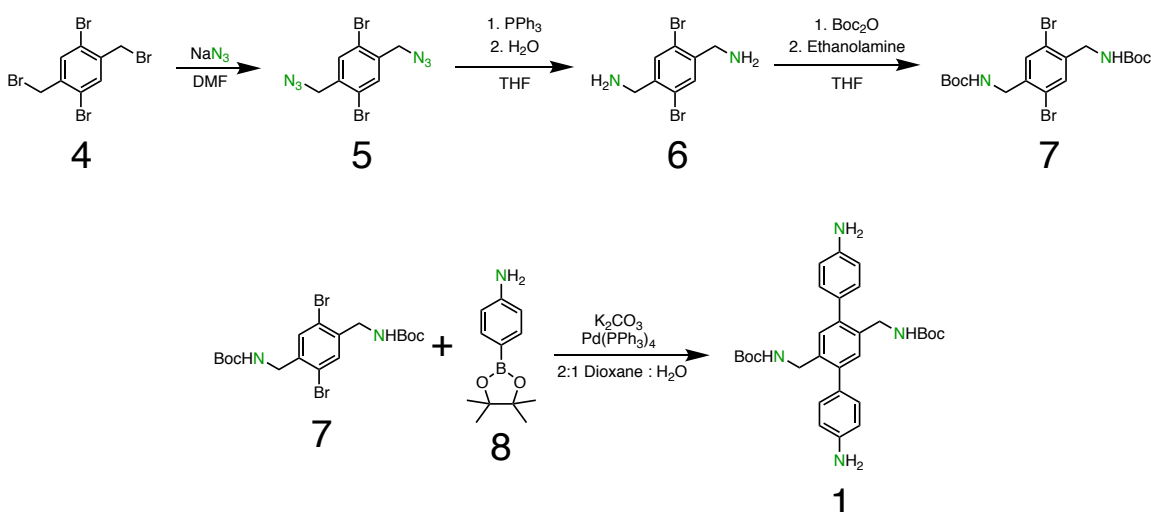
Scheme 4.1. Synthesis of Boc-protected COF-81. In the space-filling diagram, carbon, nitrogen, oxygen, and hydrogen atoms are represented as grey, green, red, and white spheres, respectively.



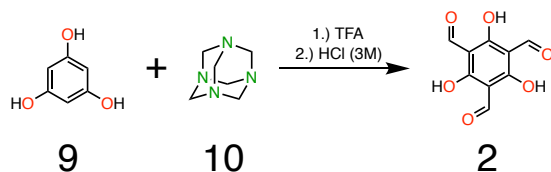
Scheme 4.2. Synthesis of azide-functionalized COF-93. In the space-filling diagram, carbon, nitrogen, oxygen, and hydrogen atoms are represented as grey, green, red, and white spheres, respectively.

Unfortunately, upon investigation via solid state ^{15}N CP-MAS NMR it was apparent that the amines in the material were not fully deprotected and that the deprotection procedure lead to the formation of new species in the pores of COF-81 (Section 4.8). To mitigate this issue, another material, COF-93, was targeted (Scheme 4.2, Section 4.9). Functionalized with alkyl azide functional groups as an alternative to -Boc-protected alkylamines, it was hypothesized that COF-93 can be decorated with alkylamines by post-synthetic Staudinger reduction instead of thermal deprotection.⁴ This strategy renders the formation of urea species in the pore impossible and thus allows for the formation of an alkylamine-functionalized COF to be studied for CO_2 chemisorption. A brief summary of the synthesis of COF-93 is included in this chapter.

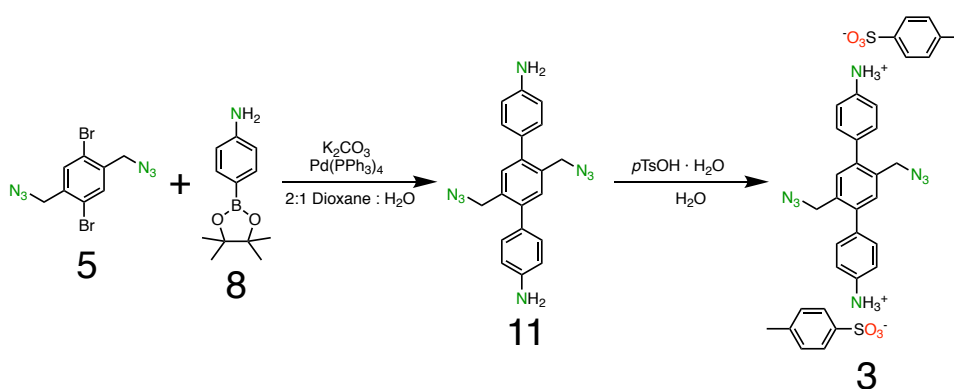
4.4 Organic Linker Synthesis



Scheme 4.3. Synthetic pathway for di-*tert*-butyl ((4,4''-diamino-[1,1':4',1''-terphenyl]-2',5'-diyl)bis(methylene))dicarbamate **1**.



Scheme 4.4. Synthetic pathway for 2,4,6-triformylphloroglucinol **2**.



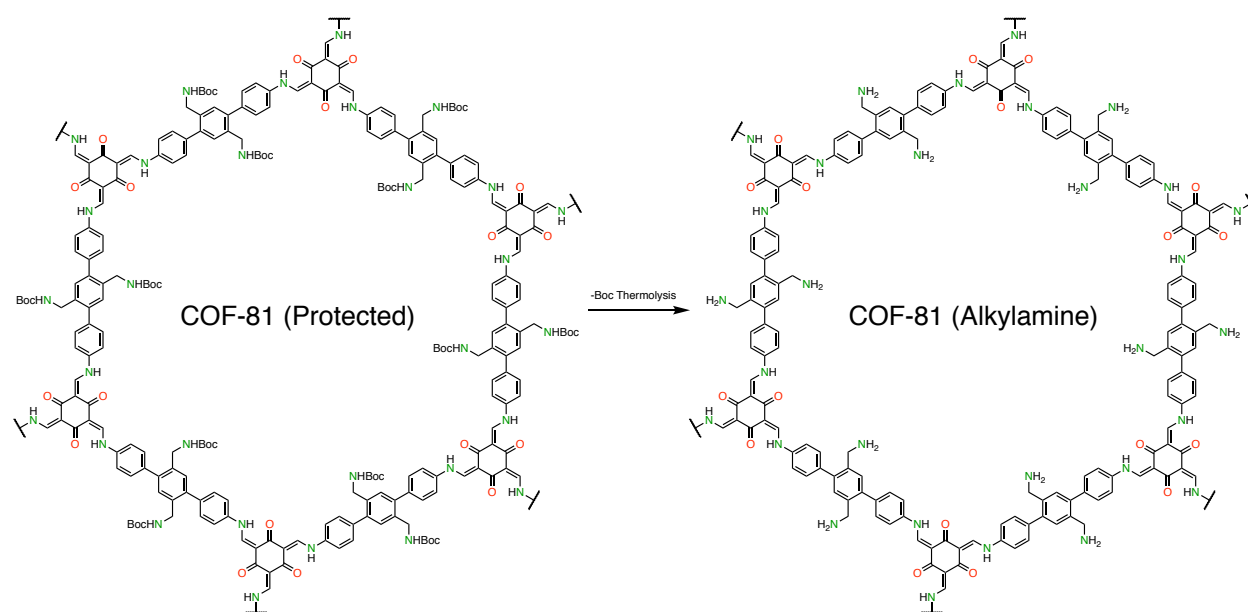
Scheme 4.5. Synthetic pathway for 2',5'-bis(azidomethyl)-[1,1':4',1''-terphenyl]-4,4''-diaminium 4-methylbenzenesulfonate **3**.

The terphenylene organic linker, di-*tert*-butyl ((4,4''-diamino-[1,1':4',1''-terphenyl]-2',5'-diyl)bis(methylene))dicarbamate (**1**), used to construct the Boc-protected COF-81 was synthesized according to the synthetic route provided in Scheme 4.3. As, the precursor to **1**, di-*tert*-butyl ((2,5-dibromo-1,4-phenylene) bis(methylene))dicarbamate (**7**) was synthesized according to previously reported methods.²⁷ With this compound in hand, the synthesis of **1** was realized by adopting and modifying a previously-reported Suzuki–Miyaura coupling procedure on an analogous compound.²⁸ Additionally, 2,4,6-triformylphloroglucinol (**2**) was synthesized in accordance with a previously reported procedure (Scheme 4.4).²⁹ Finally, 2',5'-bis(azidomethyl)-[1,1':4',1''-terphenyl]-4,4''-diaminium 4-methylbenzenesulfonate (**3**) used to construct the azide-functionalized COF-93 was synthesized according to the synthetic route provided in Scheme 4.5. Following the path detailed in Scheme 4.3, 1,4-bis(azidomethyl)-2,5-dibromobenzene (**5**) was generated. The product was then coupled to commercially available 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (**8**) via the aforementioned Suzuki–Miyaura coupling technique to yield 2',5'-bis(azidomethyl)-[1,1':4',1''-terphenyl]-4,4''-diamine (**11**).²⁸ Addition of *p*-toluenesulfonic acid monohydrate to **11** in a solution of deionized water according to reports of analogous procedures in the literature yielded 2',5'-bis(azidomethyl)-[1,1':4',1''-terphenyl]-4,4''-diaminium 4-methylbenzenesulfonate (**3**).³⁰ Detailed synthetic procedures for each organic linker in this work can be found in Section 4.11.2.

4.5 Synthesis and Post-Synthetic Modification of COF-81

Many COFs linked with β -ketoenamine functional groups have been reported. Typically, such frameworks are synthesized solvothermally in mixtures of mesitylene and 1,4-dioxane with additional small amounts aqueous acetic acid.^{24,31} Examples also exist where such frameworks have been synthesized in other solvents,²⁵ or by grinding the requisite linkers with *p*-toluenesulfonic acid and water and heating the resultant “paste” in order to form the extended structure.²⁶ After attempting to synthesize COF-81 under these and other, similar, conditions, I uncovered the procedure leading to optimum

framework crystallinity and porosity. COF-81 was synthesized solvothermally using a procedure inspired by previous reports of β -ketoenamine linked COFs²⁴, wherein di-*tert*-butyl ((4,4''-diamino-[1,1':4',1''-terphenyl]-2',5'-diyl)bis(methylene))dicarbamate (**1**) and 2,4,6-triformylphloroglucinol (**2**) were heated in a sealed Pyrex tube under vacuum at 120 °C for 3 days in a mixture of 1,4-dioxane, anisole, and 6 M aqueous acetic acid solution (Scheme 4.1, Section 4.11.3). The product's porosity and CO₂ affinity were investigated using nitrogen sorption (Section 4.11.8) and CO₂ sorption (Section 4.6) experiments, respectively. Solid state ¹³C and ¹⁵N CP-MAS NMR (Sections 4.8 and 4.11.5), FT-IR (Section 4.11.6), and powder X-Ray diffraction (PXRD, Section 4.11.7) experiments gave evidence of the structural and chemical nature of COF-81. To confirm that the target linkage was formed with retention of the -Boc protecting group, COF-81 was characterized using solid state cross-polarization magic angle spinning nuclear magnetic resonance spectroscopy (CP-MAS NMR), and, Fourier transform infrared spectroscopy (FT-IR) (Sections 4.11.5, and 4.11.6, respectively). Powder X-ray diffraction (PXRD), and nitrogen adsorption isotherm experiments confirmed that the framework was crystalline and permanently porous (Sections 4.11.7, and 4.11.8, respectively).



Scheme 4.6. General scheme illustrating post-synthetic -Boc thermolysis in COF-81 yielding alkylamine-functionalized COF-81.

The presence of free amine groups (not designed to be part of a covalent linkage) in a given MOF and/or COF synthetic mixture can greatly affect the resultant framework's structure, or prevent it from forming altogether. In the case of COF-81 the mechanism of β -ketoenamine linkage formation begins with a condensation between an amine and an aldehyde with subsequent tautomerization and thus the alkylamines on **1** would likely also condense with aldehyde groups on **2**. Therefore, as with IRMOF-74-III-(CH₂NH₂)₂ the primary amine functional groups were incorporated into COF-81 as Boc-protected derivatives.³² In order to cleave these protecting groups and thus liberate the

linker-based alkylamines in COF-81, microwave thermolysis was attempted in accordance with a previously reported procedure (Scheme 4.6, Section 4.11.4).²⁷ In contrast to IRMOF-74-III-(CH₂NH₂)₂, COF-81 did not remain crystalline after the post-synthetic modification reaction as evidenced by the disappearance of all reflections in PXRD patterns of the deprotected framework contrasted with the corresponding pattern associated with the parent material (Section 4.11.7). Interestingly, FT-IR indicated that the -Boc moieties were removed (Section 4.11.6).

With the understanding that -Boc groups are thermolabile and that the cleavage products are a COF-based alkylamine, isobutene, and CO₂, I achieved thermolysis under dynamic vacuum at 180 °C (Section 4.11.7).³² Initial evidence of -Boc group cleavage was provided by comparison of FT-IR spectra of the protected and heat-treated COF-81 structures (Section 4.11.6). Additionally, qualitative analysis of solid state ¹³C CP-MAS NMR measurements indicated that the majority of the -Boc groups had been removed (Section 4.11.5). This was demonstrated by the near disappearance of the dominant signal emanating from the framework attributed to the *tert*-butyl groups ($\delta = 27.6$ ppm) upon heat and vacuum treatment. Unfortunately, powder X-ray diffraction (PXRD) and nitrogen adsorption isotherm experiments indicated that the crystallinity and porosity of the framework both diminished significantly after the post-synthetic modification as demonstrated by the decreases in relative diffraction peak intensity and Brunauer–Emmett–Teller (BET) surface area (from 505 to 177 m² g⁻¹), respectively (Sections 4.11.7 and 4.11.8, respectively). Side reactions that occur during the post-synthetic modification of the material are likely responsible for such degradation (Section 4.8).

4.6 CO₂ Sorption in COF-81

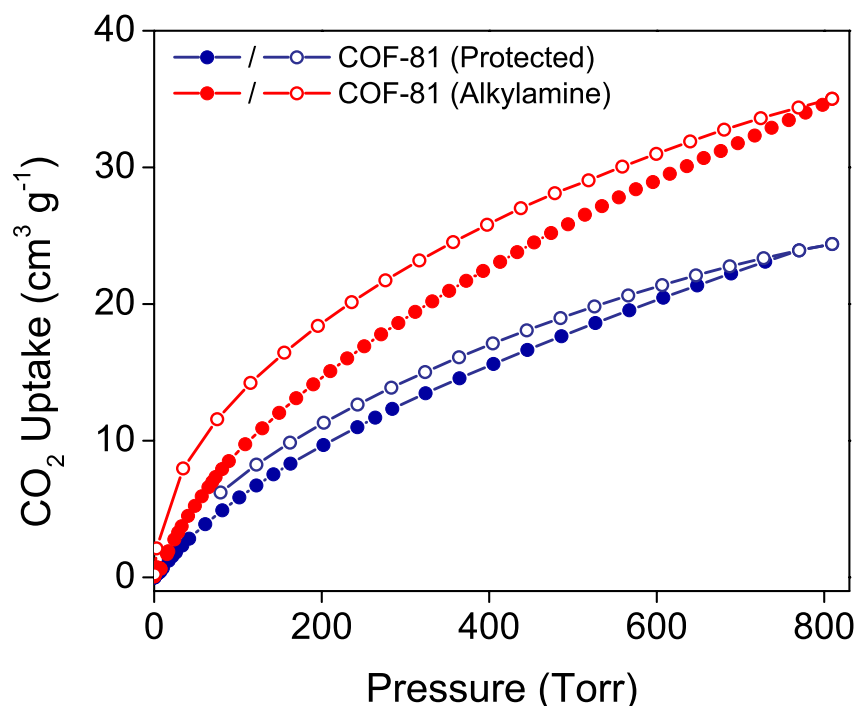


Figure 4.2. CO₂ isotherms (closed symbols = adsorption; open symbols = desorption) for COF-81. In navy, -Boc protected COF-81; in red, partially alkylamine-decorated COF-81 after thermolysis.

In spite of these drawbacks the framework chemistry of alkylamine-functionalized COF-81 with CO₂ was investigated using CO₂ sorption isotherms and solid state ¹³C CP-MAS NMR measurements with interesting results discussed below (Section 4.7). To investigate the adsorption properties of COF-81 before and after -Boc thermolysis, the CO₂ isotherms for COF-81 (Protected) and COF-81 (Alkylamine) were measured at 25 °C (Figure 4.2). The overall capacity of the deprotected COF-81 (35 cm³ g⁻¹) is comparable to other COFs applied to CO₂ adsorption applications. Upon thermolysis of the -Boc protecting groups, COF-81 collects 1.44 times the amount of CO₂ per gram of material at 800 torr compared to the protected COF-81 counterpart. Additionally, in the low-pressure range (<100 Torr) the alkylamine-decorated COF-81 significantly out-performs the protected counterpart, collecting 2.77 times the amount of CO₂ per gram of material at identical pressures, indicative of similarly enhanced chemisorption to previously reported materials.²⁷

4.7 Investigation of CO₂ Chemisorption in COF-81 using Solid State CP MAS NMR

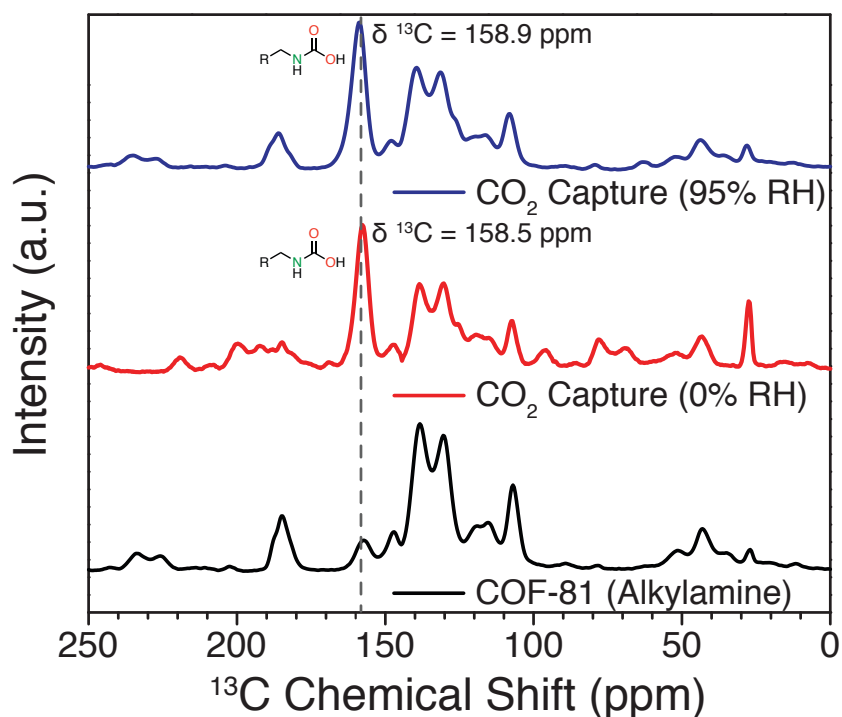


Figure 4.3. (bottom spectrum, black) ¹³C CP-MAS NMR for COF-81 (Alkylamine) after thermolytic deprotection. (middle spectrum, red) ¹³C CP-MAS NMR after exposure to 740 Torr ¹³CO₂ for 24 h. (top spectrum, navy) ¹³C CP-MAS NMR after exposure to 95% relative humidity (RH) N₂ atmosphere for 24 h followed by 740 Torr ¹³CO₂ for 24 h. The pertinent chemical shifts of chemisorbed products are given on the right of the newly-evolved signal and are highlighted with the dashed grey line centered between the two signals.

The augmented CO₂ adsorption capacity of COF-81 (Alkylamine) compared to that of COF-81 (protected) necessitated examination using solid state ¹³C CP-MAS NMR of the compounds before and after exposure to 740 Torr of ¹³CO₂ (99% ¹³C atom basis) in a sealed dosing apparatus for 24 hours (Section 4.11.5). The ¹³C spectrum of COF-81 (Alkylamine) shows the carbonyl peak at 184 ppm and the aromatic peaks between 100 ppm and 160 ppm. I attribute the peaks near 43 ppm to CH₂ resonances stemming from various chemical environments similar to those in IRMOF-74-III-(CH₂NH₂)₂.²⁷ Upon exposure to ¹³CO₂ under both dry (0% RH), and humid (95% RH) conditions an intense peak appeared in each subsequent ¹³C spectrum (Figure 4.3, in red and navy, respectively) with maxima at 158.5 and 158.9 ppm, respectively. The appearance of these chemical shifts has previously been used as evidence of carbamic acid formation with numerous examples supporting the claim.^{27,33–37} It is important to note here, that despite the evolution of carbamic acid as the result of chemisorption in COF-81 (Alkylamine) the relative intensity of the ¹³C CP-MAS NMR signal is significantly diminished compared to reports in other compounds. This is likely the result of the inhibited adsorption

performance detailed in Figure 4.2. This represents the first example, to my knowledge, of evolution of carbamic acid-like signals in a porous material under both dry and humid conditions. Further study will confirm the exact nature of the carbamic acid formation and if it is indeed persistent under a variety of conditions, but these preliminary results represent a path forward in efforts to target specific chemisorption products in one material.

4.8 Outstanding Challenges Regarding CO₂ Chemisorption in COF-81

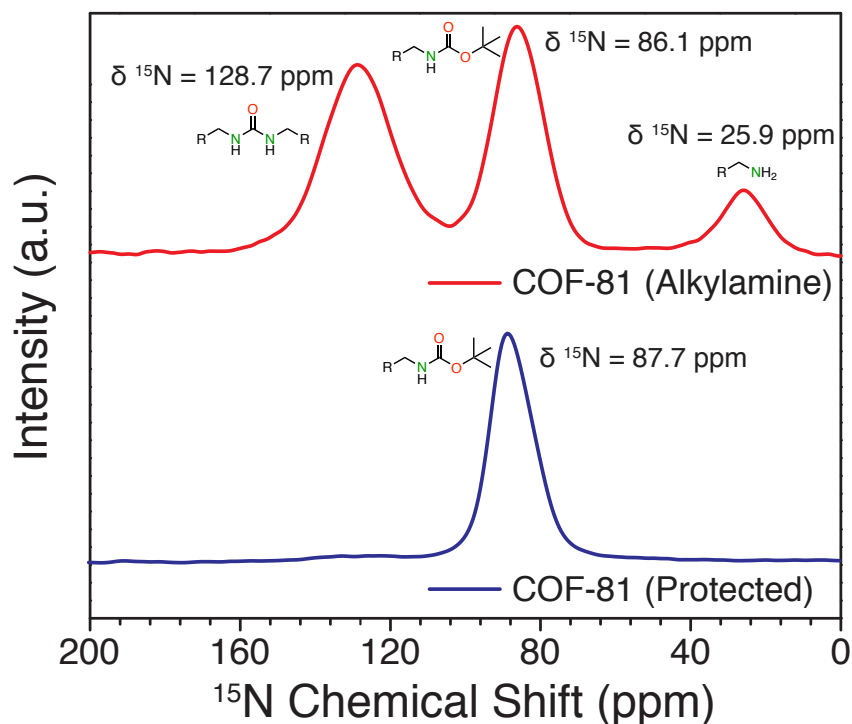


Figure 4.4. (bottom spectrum, navy) ¹⁵N CP-MAS NMR for 50% ¹⁵N-enriched COF-81 (Protected). (top spectrum, red) ¹⁵N CP-MAS NMR for 50% ¹⁵N-enriched COF-81 after thermolytic deprotection. The pertinent chemical shifts of the ¹⁵N-containing moieties are provided near their corresponding signals with representations of the corresponding moieties.

As was previously stated in Section 4.5, -Boc thermolysis in COF-81 resulted in diminished surface area and crystallinity of the resultant material. I speculate that this structural degradation was caused by the formation of strongly-bound urea species in the pores of COF-81 after thermolytic treatment as evidenced by the evolution of a new signal in the ¹⁵N CP-MAS NMR (of 50 % ¹⁵N-enriched COF-81) at $\delta = 128.73$ ppm in addition to the evolution of the free amine peak at $\delta = 25.87$ ppm (Figure 4.4).²⁷ As an additional consideration, ¹⁵N CP-MAS NMR experiments on COF-81 (Alkylamine) revealed that the -Boc groups had not been fully removed as evidenced by the remaining signal at $\delta = 86.1$ ppm after thermolytic treatment. Importantly, a similar, although very minor signal near $\delta = 128$ ppm was observed upon deprotection of IRMOF-74-III-

(CH₂NH₂)₂, indicating that this side product formation may be common in porous framework materials with similar functionalities and pore metrics.²⁷

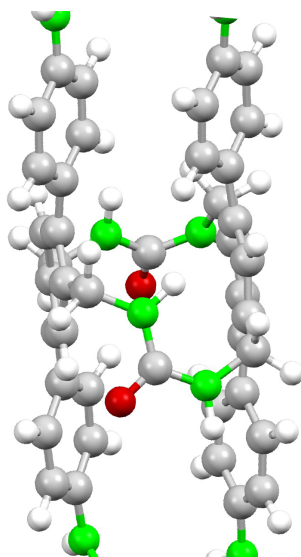


Figure 4.5. View of modeled, deprotected COF-81 (Alkylamine) structure perpendicular to the crystallographic *c*-axis, depicting the feasibility of interlayer urea formation as the result of side reactions during thermolytic deprotection. Color code: H, white; C, gray; O, red; and N, green.

Pore-based urea formation was further supported by modeling the deprotected COF-81 structure and adding the proposed urea moieties with subsequent convergent simulations indicating the feasibility of urea formation with respect to the pore metrics in deprotected COF-81 (Figure 4.5, Section 4.11.9). Additionally, previous reports have detailed conditions under which -Boc protected amines can be easily converted to ureas under similar conditions to those employed in this work.^{38,39}

The liberation of some alkylamines is likely responsible for the enhanced CO₂ uptake capacity and chemisorptive behavior detailed above, but the formation of side products as the result of -Boc cleavage and the relatively low abundance of free amines in COF-81 (Alkylamine) suggested that an alternative route was necessary to synthesize an alkylamine-functionalized COF.

4.9 Preliminary Synthesis of COF-93

With the promising chemisorption in COF-81, I proceeded to attempt to synthesize an azide-functionalized framework, COF-93 (Scheme 4.2). Due to divergent linker solubility, attempts to synthesize COF-93 under conditions similar to those used to generate COF-81 were unsuccessful, as were attempts to apply various synthetic conditions used to synthesize other β -ketoenamine-linked COFs. In each case, either no solid product, or an amorphous powder with no discernable peak intensity as measured by PXRD was formed. To ameliorate this issue, I converted the diamine-linker **11** to the

corresponding tosylate salt (**3**) using a modified literature procedure (Section 4.4, Section 4.11.2).³⁰ It has been previously demonstrated that porous, crystalline, β -ketoenamine-linked COFs can be synthesized from the corresponding ammonium tosylate salts.⁴⁰ Unfortunately, following this reported example did not yield crystalline material. Therefore, the most promising candidate to date resulted from a procedure in which COF-93 was synthesized solvothermally in a 1 : 1 : 0.1 (v/v/v) mixture of 1,4-dioxane, mesitylene, and 6 M aqueous acetic acid (Scheme 4.2, Section 4.11.3) COF-93 was found to crystallize in a staggered (ABC stacked) **hcb** topology, yielding smaller trigonal channels than those observed in COF-81 (Sections 4.11.7 and 4.11.9). In addition, the alkyl azide moieties on the COF linker appear to remain after COF synthesis as evidenced by FT-IR experiments (Section 4.11.6) Although only preliminary results on the properties of COF-93 have been gathered, I envision converting the azide moieties in COF-93 to alkylamines via a post-synthetic Staudinger reduction.⁴ Should such conversions be achieved in an optimized material, inter pore urea formation will likely be avoided and the framework chemistry of alkylamine-functionalized COF-93 with CO₂ will be investigated.

4.10 Conclusion

I demonstrated the synthesis and post-synthetic modification of a new COF, COF-81, to yield an alkylamine-decorated framework. This framework has a modest CO₂ uptake capacity, and can be used to chemisorb CO₂. Most promisingly, COF-81 (Alkylamine) reacts with CO₂ to form carbamic acids under dry and humid conditions, the first example of such behavior in a framework material. Finally, attempts to ameliorate the issues intrinsic to application of COF-81 were outlined in the synthesis of COF-93 which is still under investigation.

4.11 Supporting Information for Chapter 4

4.11.1 General Considerations

Chemicals used in this work

Anhydrous *N,N*-dimethylformamide (DMF), and methanol were obtained from EMD Millipore Chemicals. Sodium azide, triphenylphosphine, anhydrous tetrahydrofuran (THF), and di-*tert*-butyl dicarbonate (Boc₂O), were purchased from Aldrich. Potassium acetate was purchased from Fischer Scientific. *p*-toluenesulfonic acid monohydrate was purchased from EMD Millipore corporation. Tetrakis(triphenylphosphine)palladium(0) was purchased from Chem Impex Int'l Inc. 1,4-Dibromo-2,5-bis(bromomethyl)benzene was purchased from Spectrum Chemical Manufacturing Group. 4-Aminophenylboronic acid pinacol ester (**8**) was purchased from Frontier Scientific. Other common solvents and reagents (e.g. ethanol, ethanolamine, magnesium sulfate, acetic acid, diethyl ether, 1,4-dioxane, etc.) were obtained from other commercial sources and all chemicals in this work were used without further purification.

Analytical Techniques

Liquid-state ¹H and ¹³C{¹H} NMR spectra were acquired on a Bruker AV-600 (600 MHz) spectrometer at 297–300 K. Chemical shifts were calculated using the solvent resonances as internal standards (¹H: 2.50 ppm for DMSO; ¹³C{¹H}: 39.51 ppm for DMSO-*d*₆). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet of doublets (dt), triplet (t), multiplet (m), and broad resonance (br).

Solid state NMR spectra were collected using a 11.4 T magnet with a Bruker Avance I spectrometer operating at 500.23 MHz for ¹H, 125.75 MHz for ¹³C, and 50.69 MHz for ¹⁵N. ¹³C chemical shifts were externally referenced to the upfield resonance of adamantane at 29.46 ppm relative to TMS, and ¹⁵N chemical shifts were externally referenced to glycine at 33.4 ppm relative to neat NH₃. Experiments were performed using a Bruker 4-mm double resonance MAS probe (1H/X). Magic angle spinning (MAS) was used to collect high-resolution NMR spectra at a spinning rate of 12 kHz for each data set. The magic angle was calibrated by maximizing the number and intensity of rotational echoes for the ⁷⁹Br resonance for KBr under MAS. ¹³C and ¹⁵N cross polarization (CP) experiments under the Hartmann-Hahn matching condition were performed with a ¹H 90° pulse time of 4.25 μs, a 10.2 ms of acquisition time for both, 8 and 2 ms contact times and 2 and 4 s recycle delays, respectively. The two pulse phase modulated (TPPM) ¹H decoupling was used during signal acquisition. Spectra were zero-filled to 256 K points and were processed with 100 Hz line broadening. A multi-point baseline correction was applied to each spectra using Mestrelab MNova software suite.

Samples were activated under high vacuum using a Quantachrome Flovac Degasser initially at room temperature and then by heating at 120° for one day except where specified.

All nitrogen isotherms were measured using a Quantachrome Qudrasorb EVO instrument. Ca. 70 mg of guest free samples in 9 mm bulb gas cells were charged with argon to avoid air contamination and the cells were mounted on the instrument. A liquid nitrogen bath was used to maintain a temperature of 77 K for each measurement. Ultra-high-purity grade N₂ (Praxair, 99.999% purity) was used throughout the adsorption experiments. 46 adsorption and 16 desorption points were collected. The BET surface areas were estimated according to established procedures.

All CO₂ isotherms were measured immediately after activation procedures detailed above unless otherwise described. Measurements were performed using a Quantachrome Autosorb instrument. Ca. 70 mg of guest free samples in 9 mm bulb gas cells were charged with argon to avoid air contamination and the cells were mounted on the instrument. A water bath was used to maintain a temperature of 298 K for each measurement. CO₂ (Praxair, 99.998% purity) was used throughout the adsorption experiments. 55 adsorption and 12 desorption points were collected.

FT-IR spectra were collected in-house using a Bruker ALPHA Platinum ATR-FT-IR Spectrometer equipped with a single reflection diamond ATR module.

High Resolution Electrospray Ionization mass (HR-ESI) was acquired on an Finnigan LTQ FT (Thermo Electron Corporation) instrument, using either negative or positive modes and by direct injection of methanol solutions of the samples using syringe pump with a flow rate of 5 µL min⁻¹.

For qualitative assessment of crystallinity, diffraction data were collected on a Rigaku MiniFlex 600 instrument, using the Cu Kα1 line at 600 W (40 kV, 15 mA). Samples were mounted on stock Rigaku sample holders by dropping powders from a spatula and leveling with a razor blade. Data were collected using a 0.02° 2θ step scan from 2 – 30° at a rate of 4° per min, constituting an acquisition time of 9 min.

4.11.2 Organic Linker Synthesis

Synthesis of 2,5-dibromo-1,3-di-^tbutyl-benzylcarbamate (7)

The 2,5-dibromo-1,3-di-^tbutyl-benzylcarbamate starting material was made as reported (Scheme 4.3).²⁷

Synthesis of di-tert-butyl ((4,4''-diamino-[1,1':4',1''-terphenyl]-2',5'-diyl)bis(methylene))dicarbamate (1)

Di-tert-butyl ((4,4''-diamino-[1,1':4',1''-terphenyl]-2',5'-diyl)bis(methylene))dicarbamate (**1**) was synthesized by adopting and modifying a previously-reported Suzuki–Miyaura coupling procedure on an analogous compound (Scheme 4.3).²⁸ A clean, oven dried, 3 neck round bottom flask attached to a Schlenk line apparatus with equipped reflux condenser was charged with 1.071 g (2.167 mmol) of di-tert-butyl ((2,5-dibromo-1,4-phenylene)bis(methylene))dicarbamate, 1.139 g (5.199 mmol, 2.4 eq) of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (**8**), 1.647 g (11.92 mmol, 5.5 eq) of potassium carbonate, and 0.251 g (0.217 mmol, 0.1 eq) of tetrakis(triphenylphosphine)palladium(0). The flask and its contents were then evacuated and refilled with inert house nitrogen atmosphere. This process was repeated three times to ensure an anhydrous and oxygen-free reaction environment. In a separate flask, 24 mL of anhydrous 1,4-dioxane and 12 mL of deionized water were combined and then bubbled with dried house N₂ for 30 min. to deoxygenate the resulting mixture. The reaction mixture was heated to 115° C using an oil bath and refluxed for 3 d. After cooling to room temperature, deionized water was added. The resulting precipitate was collected via filtration and was washed with deionized water and methanol. The crude product was then triturated in chloroform overnight and filtered to yield pure **1** as a beige solid in 82% yield (0.92 g). ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.31 (t, *J* = 6.0 Hz, 2H), 7.12 (s, 2H), 7.03 (d, *J* = 8.0 Hz, 4H), 6.65 (d, *J* = 7.9 Hz, 4H), 5.18 (s, 4H), 4.13 (d, *J* = 6.1 Hz, 4H), 1.38 (s, 18H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 155.84, 147.74, 138.85, 134.75, 129.67, 128.27, 127.65, 113.60, 77.73, 41.22, 28.25. MS (HR-ESI), *m/z* calcd. for C₃₀H₃₈N₄O₄[(M+Na)⁺]: 541.2791, found: 541.2785.

Synthesis of 2,4,6-triformylphloroglucinol (2)

2,4,6-triformylphloroglucinol was made as reported (Scheme 4.4).²⁹

Synthesis of 2',5'-bis(azidomethyl)-[1,1':4',1''-terphenyl]-4,4''-diamine (11)

Scheme 4.5 depicts the synthesis of **11**. 1,4-bis(azidomethyl)-2,5-dibromobenzene (**5**) was made as reported on a 7.59 mmol scale with identical work up.²⁷ This compound was not isolated due to its potentially explosive nature. Instead, **5** was dissolved in a small amount (<5 mL) of diethyl ether in a clean, oven dried, 3 neck round bottom flask attached to a Schlenk line apparatus with equipped reflux condenser. To this mixture was added a mixture of 84 mL of anhydrous 1,4-dioxane and 42 mL of deionized water that had been deoxygenated by bubbling with dried house N₂ for 30 min. The flask was then charged with 3.991 g (18.216 mmol, 2.4 eq) of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (**8**), 5.769 g (41.745 mmol, 5.5 eq) of potassium carbonate, and 0.877 g (0.759 mmol, 0.1 eq) of tetrakis(triphenylphosphine)palladium(0) under a N₂ atmosphere. The reaction mixture was heated to 115° C using an oil bath and refluxed for 3 d. The reaction mixture was cooled to room temperature and then poured into a 1 L separatory funnel.

Toluene (500 mL) was added to funnel and the mixture was then extracted with deionized water (3 × 250 mL) and brine (100 mL). The organic phase was dried over anhydrous magnesium sulfate, filtered, and evaporated. To purify the crude product, the collected solid was dissolved in a minimal amount (ca. 10 mL) of toluene and heated until complete dissolution was observed. Then hexanes (ca. 600 mL) were added to the solution and the product was observed as a precipitate. This pale yellow solid was collected by filtration in 31% yield (0.861 g). ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.34 (s, 2H), 7.07 (d, *J* = 8.3 Hz, 4H), 6.69 – 6.61 (m, 4H), 5.26 (s, 4H), 4.42 (s, 4H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 148.25, 140.44, 132.44, 131.68, 129.61, 126.37, 113.76, 51.72. *m/z* calcd. for C₂₀H₁₈N₈ [(M+H)⁺]: 371.1734, found: 371.1734.

Synthesis of 2',5'-bis(azidomethyl)-[1,1':4',1''-terphenyl]-4,4''-diaminium 4-methylbenzenesulfonate (3)

2',5'-bis(azidomethyl)-[1,1':4',1''-terphenyl]-4,4''-diaminium 4-methylbenzenesulfonate (**3**) was synthesized by adopting and modifying a previously-reported procedure on an analogous compound (Scheme 4.5).³⁰ A clean 50 mL scintillation vial was charged with 0.700 g (1.89 mmol) of 2',5'-bis(azidomethyl)-[1,1':4',1''-terphenyl]-4,4''-diamine (**11**), 0.755 g (3.97 mmol) of *p*-toluenesulfonic acid monohydrate, and 40 mL of deionized water. The flask was then sealed and sonicated for 1 h. The prepared salt was filtered off and thoroughly washed with ethyl acetate three times in order to remove any unreacted acid and/or base. The product was isolated as a tan solid in 63% yield (0.849 g). ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.57 – 7.43 (m, 14H), 4.47 (s, 4H), 2.28 (s, 6H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 144.88, 140.04, 138.28, 138.12, 133.16, 132.59, 131.92, 130.29, 128.30, 125.54, 122.82, 51.37. *m/z* calcd. for C₂₀H₂₀N₈ [(M)²⁺]: 186.0900, found: 186.0901.

4.11.3 Synthesis of Covalent Organic Frameworks (COFs)

Synthesis of COF-81

COF-81 was synthesized by combining **1** (19.4 mg, 0.0375 mmol, 1 eq) with **2** (5.3 mg, 0.025 mmol, 0.67 eq) in a Pyrex tube. Solvent (1 mL 1,4-dioxane, 1 mL anisole) was added, and the resulting suspension was sonicated. Aqueous acetic acid (0.1 mL, 6 M AcOH) was added, the tube was flash frozen, and flame-sealed at a pressure of 150 mTorr. The tube was heated to 120 °C for 3 d. Then, the tube was broken open, and the solid was captured by filtration. The material was washed copiously with boiling THF, methanol, and acetone, and further washed with acetone via Soxhlet extraction for 1 d. The material was activated by applying vacuum at room temperature for 24 h, and then heated to 120 °C for 24 h.

Synthesis of COF-93

COF-93 was synthesized by combining **3** (26.8 mg, 0.0375 mmol, 1 eq) with **2** (5.3 mg, 0.025 mmol, 0.67 eq) in a Pyrex tube. Solvent (1 mL 1,4-dioxane, 1 mL mesitylene) was added, and the resulting suspension was sonicated. Aqueous acetic acid (0.1 mL, 6 M AcOH) was added, the tube was flash frozen, and flame-sealed at a pressure of 150 mTorr. The tube was heated to 120 °C for 3 d. Then, the tube was broken open, and the solid was captured by filtration. The material was washed copiously with boiling THF, methanol, and acetone, and further washed with acetone via Soxhlet extraction for 1 d. The as-synthesized material was not activated before characterization.

4.11.4 Thermal Post-synthetic -Boc Deprotection

Microwave Thermolysis

In targeting COF-81 (Alkylamine) ca. 15 mg of COF crystals were subjected to the solvent washing and activation procedure described in Section 4.11.3. The compound was transferred into a 10 mL reaction tube containing 3 mL of 2-ethyl-1-hexanol, 150 μ L of ethylene glycol and 150 μ L of deionized water. The heterogeneous mixture was subjected to 230 °C microwave heating using a CEM Discover microwave reactor equipped with an IR temperature sensor (300 PSI pressure limit, 300 W max power, no stirring, PowerMax setting off) for 10 minutes. The mixture was allowed to cool down to room temperature and the solvent washing procedure from section 4.11.3 was repeated. The obtained microcrystalline samples were analyzed by PXRD (Section 4.11.8) and FT-IR (Section 4.11.7).

Dynamic Vacuum Thermolysis

To yield COF-81 (Alkylamine) ca. 100 mg of COF crystals were subjected to the solvent washing and activation procedure described in Section 4.11.3. The compound was activated for an additional 48 h. at 180 °C. The obtained microcrystalline samples were analyzed by PXRD (Section 4.11.7) and FT-IR (Section 4.11.6).

4.11.5 Solid State NMR Experiments

CO₂ Gas Loading and NMR Sample Preparation

Each measured sample was packed into a Doty 4 mm or 5 mm zirconia rotor in an argon atmosphere glovebox. The packed, uncapped rotor was then quickly transferred to a home-built gas dosing apparatus and vacuum was applied for 24 hours. After this period, the sample was exposed to 710 torr ¹³CO₂ gas (Sigma-Aldrich, 99% atom ¹³C) for 24 hours at room temperature. The pressure was monitored using an MKS Baratron capacitance manometer with a working range of 2-1000 torr. After exposure, the rotor

was quickly capped and transferred to the magnet for NMR analysis to minimize any loss of CO₂. Water-exposed MOF samples were prepared following the procedure detailed in Section 4.11.10. The water-exposed MOFs were then transferred to the gas dosing apparatus and exposed to ¹³CO₂ as described above.

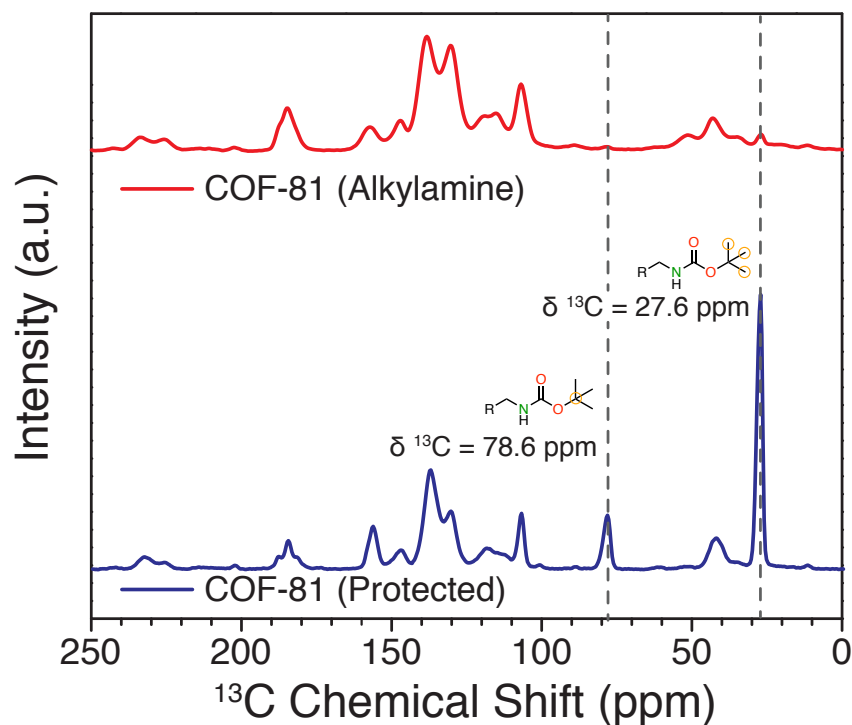


Figure S4.1. ¹³C CP-MAS NMR of activated COF-81 (Protected) (navy, bottom). Note the significant peaks at 78.6, and 27.6 ppm corresponding to the -Boc group, which are not present in the ¹³C spectrum of the deprotected material, COF-81 (Alkylamine) (red, top).

4.11.6 FT-IR Spectra of Activated COF-81 and Preliminary COF-93

Cleavage of the -Boc protecting groups by both microwave and vacuum thermolysis (Section 4.11.4) was confirmed by the disappearance of the stretching frequency at 1695 ($\nu_{C=O}$) cm^{-1} . The presence of alkyl azide moieties in COF-93 was confirmed by the stretching frequency at 2093 ($\nu_{N\equiv N}$) cm^{-1} .

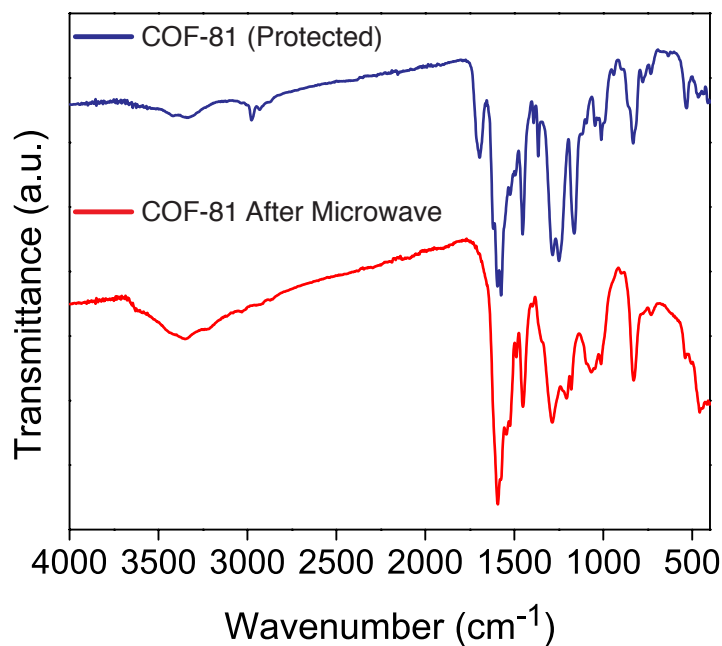


Figure S4.2. FT-IR (ATR) spectra of activated COF-81 (Protected) (navy, top) and COF-81 after microwave thermolysis (red, bottom) showing -Boc group cleavage as evidenced by the disappearance of the peak at 1695 cm^{-1} .

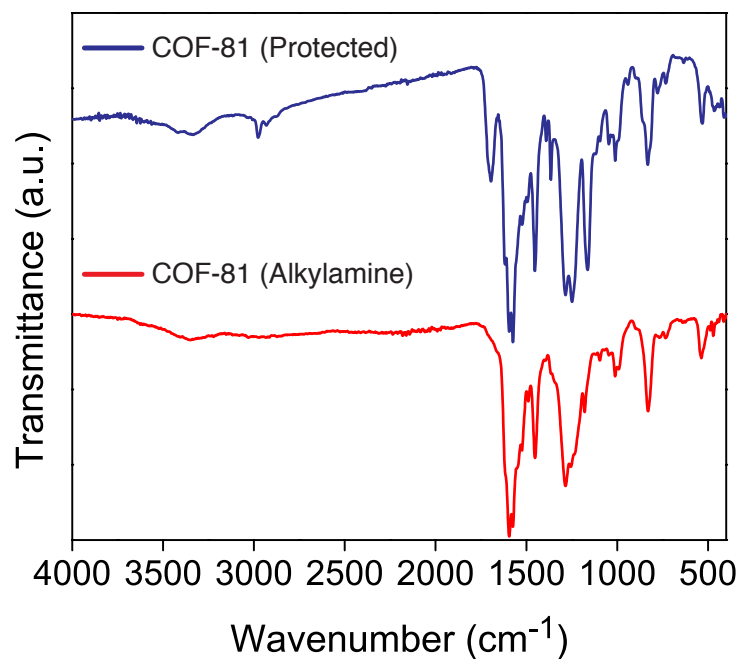


Figure S4.3. FT-IR (ATR) spectra of activated COF-81 (Protected) (navy, top) and COF-81 (Alkylamine) (red, bottom) resulting from vacuum thermolysis showing -Boc group cleavage as evidenced by the disappearance of the peak at 1695 cm⁻¹.

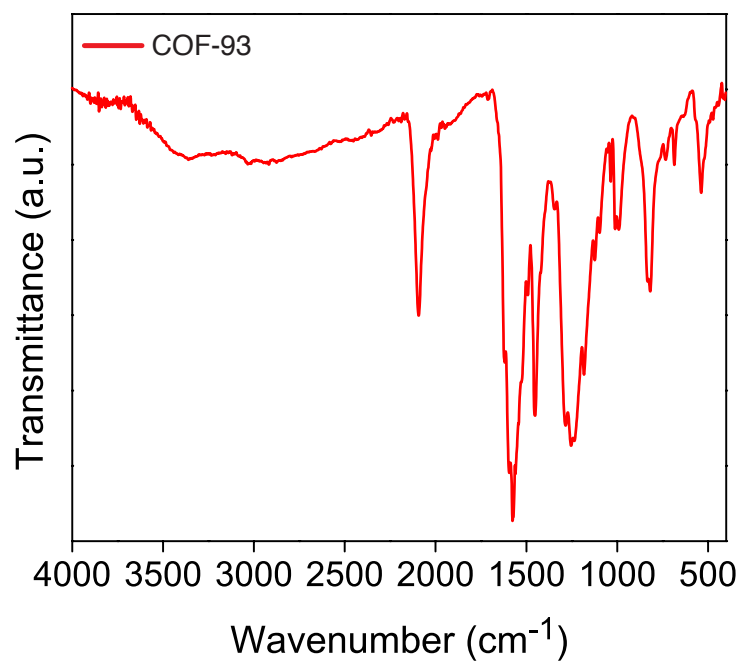


Figure S4.4. FT-IR (ATR) spectra of preliminary COF-93 (red) showing retention of azide groups after synthesis as evidenced by peak at 2093 cm⁻¹.

4.11.7 Powder X-ray Diffraction (PXRD) Characterization

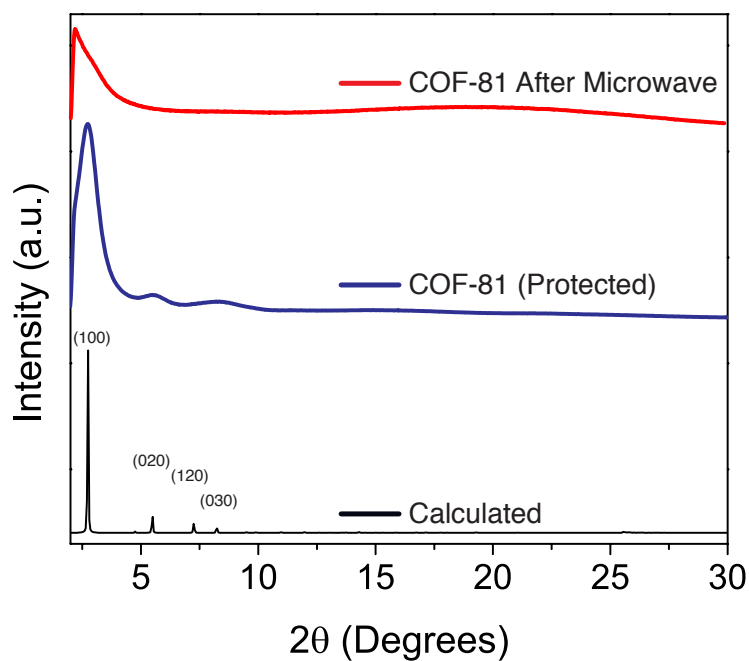


Figure S4.5. PXRD pattern of simulated COF-81 (black, bottom), activated COF-81 (Protected) (navy, middle), and COF-81 after microwave thermolysis (red, top).

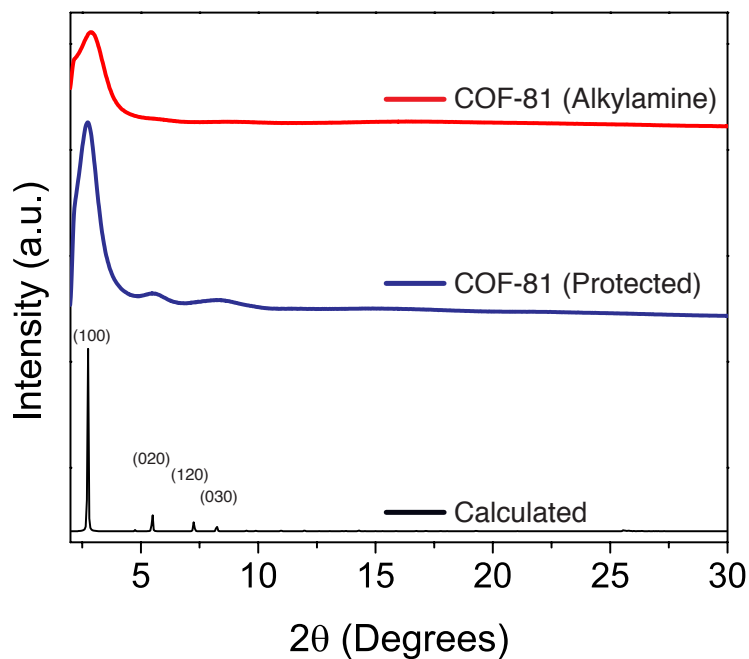


Figure S4.6. PXRD pattern of simulated COF-81 (black, bottom), activated COF-81 (Protected) (navy, middle), and activated COF-81 (Alkylamine) (red, top).

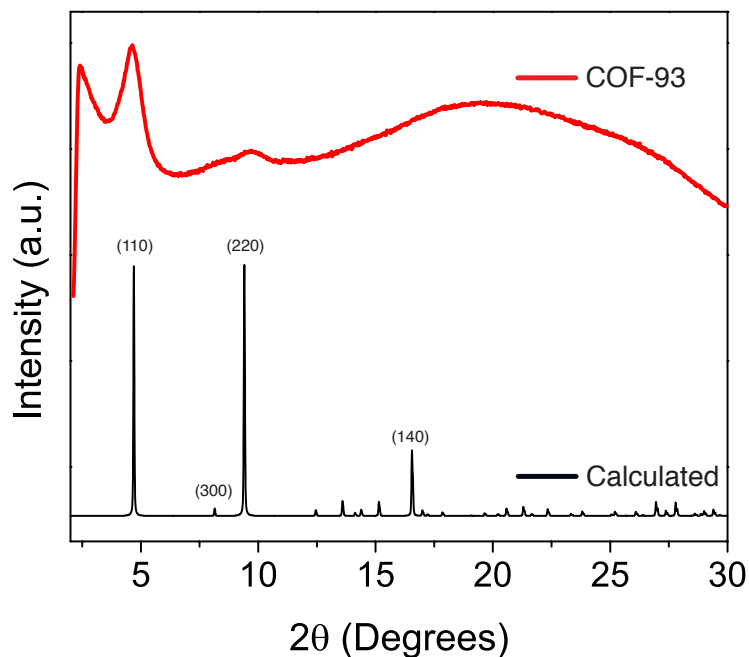


Figure S4.7. PXRD pattern of simulated COF-93 (black, bottom) and preliminary COF-93 (red, top).

4.11.8 Nitrogen Adsorption Measurements

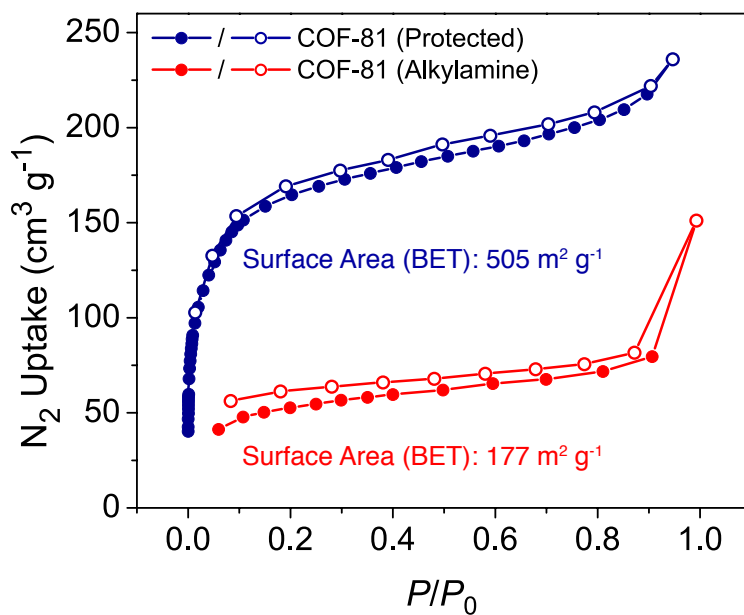


Figure S4.8. Nitrogen adsorption isotherms (closed symbols = adsorption; open symbols = desorption) for COF-81 (Protected) (navy), and COF-81 (Alkylamine) (red) at 77 K. The inset text details the experimental BET surface areas for the two compounds.

4.11.9 COF Modeling

To model COF-81 I began with a modeled crystal structure of TpPa-2 previously published to establish bond distances and inter-linker spacing for the material.²⁴ I then constructed, from scratch, a model of COF-81 in BIOVIA Materials Studio 8.0 using these distances as heuristics for the structure. The structure was optimized using the *Forcite* module in the software. From there, I modeled the amines in a staggered orientation (as logically follows from the argument with respect to steric hindrance mentioned previously) and re-optimized the structure. Finally, calculated PXRD patterns were generated using the *Reflex* module in the software. This process was also repeated after manually adding the urea moieties postulated to result from -Boc thermolysis (Section 4.8). Notably, the structure of COF-81 was largely unchanged upon urea formation supporting the side product hypothesis. These patterns were used for comparisons in Section 4.11.8. Similar methodology was used to construct a model of COF-93 except that the layers in the material were offset in an ABC manner as mentioned in the main text.

4.11.10 Humidification of COF-81 (Activated)

Samples of activated COF-81 were saturated with water vapor at a relative humidity (RH) values of RH = 95% by using a HygroCal100 Humidity Generator/Calibrator (Michell Inc, MA, USA) controlled humidity chamber. To generate uniform humidity across the chamber, the HygroCal 100 humidity generator is equipped with seven HygroSmart HS3 capacitive humidity sensors with $\pm 0.8\%$ accuracy. The bias error was eliminated by using an external standard reference precision dew-point meter (chilled mirror with $\pm 0.2^\circ\text{C}_{\text{dew-point}}$ accuracy). Ultimately, the humidity measurements were taken with the overall uncertainty of $\pm 1\%$.

For each humidification, ca 30 mg of activated COF was transferred into the NMR rotor in an argon-filled glovebox and placed inside the sealed HygroCal100 humidity chamber in an uncapped 4 mL vial. To minimize atmospheric CO₂ interaction with the COF during humidification, the chamber was purged with ultra-pure nitrogen (99.999%) and kept under 0-0.5% RH for at least 5 minutes. While nitrogen flowed through the humidity chamber, the vials were transferred to the chamber and after another 1-2 minutes the humidity value stabilized back to 0-0.5%. Then, the nitrogen flow was stopped and the water loading experiment commenced by increasing the relative humidity inside the chamber from 0-0.5% to 95% with a transition period of less than 2 minutes. The samples were kept inside the humidity-controlled chamber for 24 hours to ensure that the samples were saturated with water at the specified RH values.

4.12 References for Chapter 4

- (1) Waller, P. J.; Gándara, F.; Yaghi, O. M. Chemistry of Covalent Organic Frameworks. *Acc. Chem. Res.* **2015**, *48*, 3053–3063.
- (2) Diercks, C. S.; Yaghi, O. M. The Atom, the Molecule, and the Covalent Organic Framework. *Science*. **2017**, *355*, eaal1585.
- (3) Huang, N.; Krishna, R.; Jiang, D. Tailor-Made Pore Surface Engineering in Covalent Organic Frameworks: Systematic Functionalization for Performance Screening. *J. Am. Chem. Soc.* **2015**, *137*, 7079–7082.
- (4) Ji, W.; Xiao, L.; Ling, Y.; Ching, C.; Matsumoto, M.; Bisbey, R. P.; Helbling, D. E.; Dichtel, W. R. Removal of GenX and Perfluorinated Alkyl Substances from Water by Amine-Functionalized Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2018**, *140*, 12677–12681.
- (5) Furukawa, H.; Yaghi, O. M. Storage of Hydrogen, Methane, and Carbon Dioxide in Highly Porous Covalent Organic Frameworks for Clean Energy Applications. *J. Am. Chem. Soc.* **2009**, *131*, 8875–8883.
- (6) Kahveci, Z.; Islamoglu, T.; Shar, G. A.; Ding, R.; El-Kaderi, H. M. Targeted Synthesis of a Mesoporous Triptycene-Derived Covalent Organic Framework. *CrystEngComm* **2013**, *15*, 1524–1527.
- (7) Chandra, S.; Kandambeth, S.; Biswal, B. P.; Lukose, B.; Kunjir, S. M.; Chaudhary, M.; Babarao, R.; Heine, T.; Banerjee, R. Chemically Stable Multilayered Covalent Organic Nanosheets from Covalent Organic Frameworks via Mechanical Delamination. *J. Am. Chem. Soc.* **2013**, *135*, 17853–17861.
- (8) Li, Z.; Feng, X.; Zou, Y.; Zhang, Y.; Xia, H.; Liu, X.; Mu, Y. A 2D Azine-Linked Covalent Organic Framework for Gas Storage Applications. *Chem. Commun.* **2014**, *50*, 13825–13828.
- (9) Zeng, Y.; Zou, R.; Luo, Z.; Zhang, H.; Yao, X.; Ma, X.; Zou, R.; Zhao, Y. Covalent Organic Frameworks Formed with Two Types of Covalent Bonds Based on Orthogonal Reactions. *J. Am. Chem. Soc.* **2015**, *137*, 1020–1023.
- (10) Du, Y.; Calabro, D.; Wooller, B.; Kortunov, P.; Li, Q.; Cundy, S.; Mao, K. One Step Facile Synthesis of Amine-Functionalized COF-1 with Enhanced Hydrostability. *Chem. Mater.* **2015**, *27*, 1445–1447.
- (11) Stegbauer, L.; Hahn, M. W.; Jentys, A.; Savasci, G.; Ochsenfeld, C.; Lercher, J. A.; Lotsch, B. V. Tunable Water and CO₂ Sorption Properties in Isostructural Azine-Based Covalent Organic Frameworks through Polarity Engineering. *Chem. Mater.* **2015**, *27*, 7874–7881.
- (12) Gao, Q.; Bai, L.; Zhang, X.; Wang, P.; Li, P.; Zeng, Y.; Zou, R.; Zhao, Y. Synthesis of Microporous Nitrogen-Rich Covalent-Organic Framework and Its Application in CO₂ Capture. *Chinese J. Chem.* **2015**, *33*, 90–94.
- (13) Li, Z.; Zhi, Y.; Feng, X.; Ding, X.; Zou, Y.; Liu, X.; Mu, Y. An Azine-Linked Covalent Organic Framework: Synthesis, Characterization and Efficient Gas Storage. *Chem. Eur. J.* **2015**, *21*, 12079–12084.
- (14) Wang, L.; Dong, B.; Ge, R.; Jiang, F.; Xiong, J.; Gao, Y.; Xu, J. A Thiadiazole-

- Functionalized Covalent Organic Framework for Efficient CO₂ Capture and Separation. *Microporous Mesoporous Mater.* **2016**, 224, 95–99.
- (15) Zeng, Y.; Zou, R.; Zhao, Y. Covalent Organic Frameworks for CO₂ Capture. *Adv. Mater.* **2016**, 28, 2855–2873.
 - (16) Waller, P. J.; Lyle, S. J.; Osborn Popp, T. M.; Diercks, C. S.; Reimer, J. A.; Yaghi, O. M. Chemical Conversion of Linkages in Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2016**, 138, 15519–15522.
 - (17) Qian, C.; Qi, Q.-Y.; Jiang, G.-F.; Cui, F.-Z.; Tian, Y.; Zhao, X. Toward Covalent Organic Frameworks Bearing Three Different Kinds of Pores: The Strategy for Construction and COF-to-COF Transformation via Heterogeneous Linker Exchange. *J. Am. Chem. Soc.* **2017**, 139, 6736–6743.
 - (18) Zhang, G.; Tsujimoto, M.; Packwood, D.; Duong, N. T.; Nishiyama, Y.; Kadota, K.; Kitagawa, S.; Horike, S. Construction of a Hierarchical Architecture of Covalent Organic Frameworks via a Postsynthetic Approach. *J. Am. Chem. Soc.* **2018**, 140, 2602–2609.
 - (19) Wei, P.-F.; Qi, M.-Z.; Wang, Z.-P.; Ding, S.-Y.; Yu, W.; Liu, Q.; Wang, L.-K.; Wang, H.-Z.; An, W.-K.; Wang, W. Benzoxazole-Linked Ultrastable Covalent Organic Frameworks for Photocatalysis. *J. Am. Chem. Soc.* **2018**, 140, 4623–4631.
 - (20) Haase, F.; Troschke, E.; Savasci, G.; Banerjee, T.; Duppel, V.; Dörfler, S.; Grundei, M. M. J.; Burow, A. M.; Ochsenfeld, C.; Kaskel, S.; Lotsch, B. V. Topochemical Conversion of an Imine- into a Thiazole-Linked Covalent Organic Framework Enabling Real Structure Analysis. *Nat. Commun.* **2018**, 9, 2600.
 - (21) Waller, P. J.; AlFaraj, Y. S.; Diercks, C. S.; Jarenwattananon, N. N.; Yaghi, O. M. Conversion of Imine to Oxazole and Thiazole Linkages in Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2018**, 140, 9099–9103.
 - (22) Liu, H.; Chu, J.; Yin, Z.; Cai, X.; Zhuang, L.; Deng, H. Covalent Organic Frameworks Linked by Amine Bonding for Concerted Electrochemical Reduction of CO₂. *Chem* **2018**, 4, 1696–1709.
 - (23) Li, Z.; Ding, X.; Feng, Y.; Feng, W.; Han, B.-H. Structural and Dimensional Transformations between Covalent Organic Frameworks via Linker Exchange. *Macromolecules* **2019**, 52, 1257–1265.
 - (24) Kandambeth, S.; Mallick, A.; Lukose, B.; Mane, M. V.; Heine, T.; Banerjee, R. Construction of Crystalline 2D Covalent Organic Frameworks with Remarkable Chemical (Acid/Base) Stability via a Combined Reversible and Irreversible Route. *J. Am. Chem. Soc.* **2012**, 134, 19524–19527.
 - (25) Deblase, C. R.; Silberstein, K. E.; Truong, T. T.; Abruña, H. D.; Dichtel, W. R. B-Ketoenamine-Linked Covalent Organic Frameworks Capable of Pseudocapacitive Energy Storage. *J. Am. Chem. Soc.* **2013**, 135, 16821–16824.
 - (26) Karak, S.; Kandambeth, S.; Biswal, B. P.; Sasmal, H. S.; Kumar, S.; Pachfule, P.; Banerjee, R. Constructing Ultraporous Covalent Organic Frameworks in Seconds via an Organic Terracotta Process. *J. Am. Chem. Soc.* **2017**, 139, 1856–1862.
 - (27) Flaig, R. W.; Osborn Popp, T. M.; Fracaroli, A. M.; Kapustin, E. A.; Kalmutzki, M. J.; Altamimi, R. M.; Fathieh, F.; Reimer, J. A.; Yaghi, O. M. The Chemistry of CO₂ Capture in an Amine-Functionalized Metal–Organic Framework under Dry and

- Humid Conditions. *J. Am. Chem. Soc.* **2017**, *139*, 12125–12128.
- (28) Auras, F.; Ascherl, L.; Hakimiooun, A. H.; Margraf, J. T.; Hanusch, F. C.; Reuter, S.; Bessinger, D.; Döblinger, M.; Hettstedt, C.; Karaghiosoff, K.; Herbert, S.; Knochel, P.; Clark, T.; Bein, T. Synchronized Offset Stacking: A Concept for Growing Large-Domain and Highly Crystalline 2D Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2016**, *138*, 16703–16710.
 - (29) Chong, J. H.; Sauer, M.; Patrick, B. O.; MacLachlan, M. J. Highly Stable Keto-Enamine Salicylideneanilines. *Org. Lett.* **2003**, *5*, 3823–3826.
 - (30) Mirzaei, H. M.; Karimi, B. Sulphanilic Acid as a Recyclable Bifunctional Organocatalyst in the Selective Conversion of Lignocellulosic Biomass to 5-HMF. *Green Chem.* **2016**, *18*, 2282–2286.
 - (31) Sun, Q.; Aguila, B.; Perman, J.; Nguyen, N.; Ma, S. Flexibility Matters: Cooperative Active Sites in Covalent Organic Framework and Threaded Ionic Polymer. *J. Am. Chem. Soc.* **2016**, *138*, 15790–15796.
 - (32) Lun, D. J.; Waterhouse, G. I. N.; Telfer, S. G. A General Thermolabile Protecting Group Strategy for Organocatalytic Metal-Organic Frameworks. *J. Am. Chem. Soc.* **2011**, *133*, 5806–5809.
 - (33) Fracaroli, A. M.; Furukawa, H.; Suzuki, M.; Dodd, M.; Okajima, S.; Yaghi, O. M. Metal-Organic Frameworks with Precisely Designed Interior for Carbon Dioxide Capture in the Presence of Water. *J. Am. Chem. Soc.* **2014**, *136*, 8863–8866.
 - (34) Li, D.; Furukawa, H.; Deng, H.; Liu, C.; Yaghi, O. M.; Eisenberg, D. S. Designed Amyloid Fibers as Materials for Selective Carbon Dioxide Capture. *Proc. Natl. Acad. Sci.* **2014**, *111*, 191–196.
 - (35) Pinto, M. L.; Mafra, L.; Guil, J. M.; Pires, J.; Rocha, J. Adsorption and Activation of CO₂ by Amine-Modified Nanoporous Materials Studied by Solid-State NMR and ¹³CO₂ Adsorption. *Chem. Mater.* **2011**, *23*, 1387–1395.
 - (36) Mafra, L.; Čendak, T.; Schneider, S.; Wiper, P. V.; Pires, J.; Gomes, J. R. B.; Pinto, M. L. Structure of Chemisorbed CO₂ Species in Amine-Functionalized Mesoporous Silicas Studied by Solid-State NMR and Computer Modeling. *J. Am. Chem. Soc.* **2017**, *139*, 389–408.
 - (37) Forse, A. C.; Milner, P. J.; Lee, J.; Redfearn, H. N.; Oktawiec, J.; Siegelman, R. L.; Martell, J. D.; Dinakar, B.; Porter-Zasada, L. B.; Gonzalez, M. I.; Neaton, J. B.; Long, J. R.; Reimer, J. A. Elucidating CO₂ Chemisorption in Diamine-Appended Metal-Organic Frameworks. *J. Am. Chem. Soc.* **2018**, *140*, 18016–18031.
 - (38) Lee, S.; Matsushita, H.; Clapham, B.; Janda, K. D. The Direct Conversion of Carbamates to Ureas Using Aluminum Amides. *Tetrahedron* **2004**, *60*, 3439–3443.
 - (39) Spyropoulos, C.; Kokotos, C. G. One-Pot Synthesis of Ureas from Boc-Protected Amines. *J. Org. Chem.* **2014**, *79*, 4477–4483.
 - (40) Karak, S.; Kumar, S.; Pachfule, P.; Banerjee, R. Porosity Prediction through Hydrogen Bonding in Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2018**, *140*, 5138–5145.

Chapter 5: Selective, Chemisorptive CO₂ Capture in a Highly Stable, Amino Acid-Functionalized Metal Organic Framework

Work in this Chapter was performed in a team including Hao Lyu, Mohammad I. Hossain, Xiaokun Pei, Eugene A. Kapustin, Hasan Celik, T. Grant Glover, and Omar M. Yaghi

5.1 Preface

Previously in this dissertation, I have described work that lead to additional understanding for framework-CO₂ chemistry in IRMOF-74-III-(CH₂NH₂)₂ and COF-81. Although these results are scientifically interesting and may assist in the design of the next-generation of CO₂ adsorbent materials, I felt it was necessary to investigate a material that may be of practical use. In this Chapter, I show that MOF-808 can be functionalized with glycine to yield a CO₂ adsorbent with similar framework chemistry to the aforementioned materials. Specifically, this chapter details the first case of ammonium bicarbonate formation as the result of CO₂ chemisorption in a MOF. Finally, I highlight the ease with which this material can be generated and indicate that scalability may be possible in the future.

5.2 Introduction

Reticular chemistry, the process of linking geometrically defined units into robust crystalline structures through strong bonds, has been widely applied to CO₂ capture.¹⁻⁴ This has culminated in the development of thousands of metal-organic framework (MOF) and covalent organic framework (COF) structures proposed to be efficient CO₂ adsorbents.⁵⁻¹¹ The early investigations of MOFs as CO₂ absorbers focused primarily on the use of open metal sites present in the structures. Briefly, coordinatively unsaturated metal atoms in MOFs typically behave as Lewis acids, which can bind CO₂ through strong, non-covalent interactions. This is exemplified in the MOF-74 series of materials, whose constituents possess a high density of open metal sites with Mg-MOF-74 [Mg₂(DHBDC)(DMF)₂(H₂O)₂, DHBDC = 2,5- dihydroxy-1,4-benzenedicarboxylate] having the highest CO₂ uptake of any reticular material to date.^{12,13} For this reason, Mg-MOF-74 and similar compounds have been targeted as materials to be used for post-combustion CO₂ capture from flue gas streams (e.g. the exhaust of coal and natural gas-fired power plants).

Nevertheless, these open metal sites have proven to be poorly selective toward CO₂ in the presence of other Lewis bases often present, such as water which can coordinate such sites and deactivate them with respect to CO₂ adsorption.¹⁴⁻¹⁷ As water is omnipresent (5-7% concentration by volume)^{5,18} in flue gas, many framework materials including Mg-MOF-74 cannot be industrially applied at CO₂-producing “point sources”, such as the power plants described above. Some framework materials are intrinsically hydrophobic and can avoid this issue, but their CO₂ capture properties are difficult to tune.¹⁹ Overall, efforts to ameliorate this issue have largely focused on using MOFs as platforms with which to capture CO₂ in a chemisorptive fashion by forming chemical bonds between the gaseous molecule of interest and framework-based, CO₂-philic moieties, especially alkylamines.²⁰ In pursuit of this goal, MOFs with SBU-appended alkylamines²¹⁻²⁶ and linker-based alkylamines^{27,28} have been developed and extensively studied. In the majority of these cases, coadsorption of water either augments, or has no effect on dynamic CO₂ adsorption as measured by mixed-gas breakthrough experiments

that stand in as simulations of flue gas conditions. This is typically accompanied by a shift in chemisorptive mechanism from the formation of carbamic acid under dry conditions to the formation of ammonium carbamate under humid conditions. To date, the role of ammonium bicarbonate formation with respect to chemisorptive CO₂ capture in MOFs remains unexplored. Additionally, reports of these frameworks detail their stabilities under humid conditions, further justifying future application to real point-source CO₂ capture.

One major drawback of MOFs for CO₂ capture, however, is that they are fairly difficult to synthesize and prepare for real-world application. In almost every case, such compounds require many steps of organic synthesis and/or post-synthetic modification, either to append the alkylamines to the framework SBUs, or to liberate linker-based alkylamines after the framework has been formed such that they do not interfere with the parent framework's crystallinity and porosity. This effectively serves to limit the scale on which such compounds can be synthesized and thus applied. As an alternative, I envision a framework material that possesses high water, thermal, and acid stability, and can be formed on large scale. As the first step in this direction, I report in this chapter on the synthesis and CO₂ adsorption properties of MOF-808-Glycine ($[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{BTC})_2(\text{H}_2\text{NCH}_2\text{COO})_{3.5}(\text{H}_2\text{O})_{2.5}(\text{OH})_{2.5}]$, (BTC = 1,3,5-benzenetricarboxylate)) a post-synthetically modified version of the previously-reported MOF-808 $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{BTC})_2(\text{HCOO})_6]$ and MOF-808-P.^{29,30} Although MOF-808-Glycine lacks the high CO₂ adsorption capacity (under dry conditions) of some of the previously-referred to materials it has similar framework chemistry (e.g. chemisorption to form ammonium carbamates, carbamic acids and ammonium bicarbonates) and dynamic adsorption behavior (e.g. longer breakthrough times in the presence of water) as other MOFs previously studied for CO₂ capture. Additionally, to the best of my knowledge, MOF-808-Glycine is the first MOF to capture CO₂ as ammonium bicarbonates.^{26,31} This represents a transition from the typical ammonium carbamate formation and thus serves to improve the stoichiometry of the chemisorption reactions (from a 1:2 CO₂:alkylamine ratio to a 1:1 CO₂:alkylamine ratio). Notably, this ammonium bicarbonate formation occurs only in the presence of water and I speculate that this phenomenon increases the CO₂ capacity of the framework and is responsible for the increased breakthrough time under humid conditions which is beneficial with respect to practical implementation. Additionally, previous studies in aqueous solution have suggested that ammonium bicarbonates can be more easily regenerated than their ammonium carbamate counterparts.³² Therefore, MOF-808-Glycine deserves consideration at least as a proof of concept with respect to large-scale CO₂ capture implementation as it can be easily synthesized on multigram scales.³³

5.3 Approach

The synthesis and characterization of microcrystalline MOF-808-P and single crystals of MOF-808 were carried out according to previously reported conditions (see Section 5.9.2).^{29,30} With this material in hand, I sought to replace the accessible formate

ligands on the Zr secondary building units (SBUs) with glycine (Figure 5.1) in an analogous manner to previous reports in which these capping ligands are replaced with sulfate groups to endow hydrated MOF-808 and MOF-808-P with strongly acidic characteristics.^{30,34} I determined that glycine could indeed be incorporated into MOF-808 and MOF-808-P and that optimum loading was observed after a two-step process wherein the formate ligands were removed by treating the material with 1M HCl at 85 °C for 3 days yielding MOF-808-Formates Removed $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{BTC})_2(\text{H}_2\text{O})_6(\text{OH})_6]$ followed by submersion of the samples in a 2.66 M aqueous solution of glycine at 85 °C for an additional 3 days (Section 5.9.3). Before CO₂ sorption measurements, MOF-808-Glycine was washed with water and a NaOH Glycine buffer solution (pH = 10) in order to ensure that the glycine-based alkylamines were deprotonated and thus able to react with and chemisorb CO₂ (Sections 5.7 and 5.9.8). Similar treatment has been shown to be effective in previously-reported CO₂ chemisorptive MOFs.²⁸ After each synthetic and/or post-synthetic modification step, the resultant compounds were characterized using Fourier transform infrared spectroscopy (FT-IR), solution phase NMR of the acid-digested materials, solid state cross-polarization magic angle spinning nuclear magnetic resonance spectroscopy (CP-MAS NMR), and single crystal X-Ray diffraction (Sections 5.9.4, 5.9.5, 5.9.8, and 5.9.11). Finally, powder X-ray diffraction (PXRD) and nitrogen adsorption isotherm experiments confirmed that the frameworks maintained their structural integrity and porosity after each post-synthetic modification (Sections 5.9.6, and 5.9.7).

5.4 Structures of MOF-808, MOF-808-Formates Removed, and MOF-808 Glycine

The crystal structure of MOF-808 has been well studied and described previously.^{29,30,34} Briefly, MOF-808 with **spn** topology crystallizes in the cubic space group $\text{Fd}\bar{3}\text{m}$. Each inorganic secondary building unit (SBU) in MOF-808 contains six zirconium atoms that are connected to six BTC linkers, which are then connected to two other SBUs. Six formate ions that are disordered as both mono- and bidentate ligands balance the charge of the SBU and complete the coordination sphere of each Zr atom. MOF-808 also has small tetrahedral cage pores and large adamantane cage pores. The single crystal structure of MOF-808 used in this set of experiments can be found on the left side (top and bottom) of Figure 5.1. Upon acid treatment (Sections 5.3 and 5.9.3) the formate ions are removed from MOF-808 and postulated to be replaced with an equal number monodentate hydroxy and aquo ligands (Figure 5.1, middle top and bottom). Although X-ray crystallography cannot distinguish between such ligands, it is logical to assume that the hydroxy and aquo ligands are present in a 1:1 ratio because any other ratio would disturb the charge balance of the SBU metal oxide cluster. When glycine is added (Sections 5.3 and 5.9.3), crystallographic measurements reveal that 3.5 equivalents of the amino acid bind in a monodentate fashion, displacing enough equimolar amounts (3.5 equivalents) of hydroxy and aquo ligands in order to maintain charge balance in the structure. Upon close inspection of the resolved single crystal structure of MOF-808-Glycine (Figure 5.1, right top and bottom) one can observe that the glycine-based alkylamines point away from the inorganic SBU and into the pore of the MOF. I postulate

that this leaves them available to react with CO₂ in a chemisorptive fashion. Details of the single crystal experiments used to determine the structures of MOF-808, MOF-808-Formates Removed, and MOF-808-Glycine can be found in Section 5.9.11.

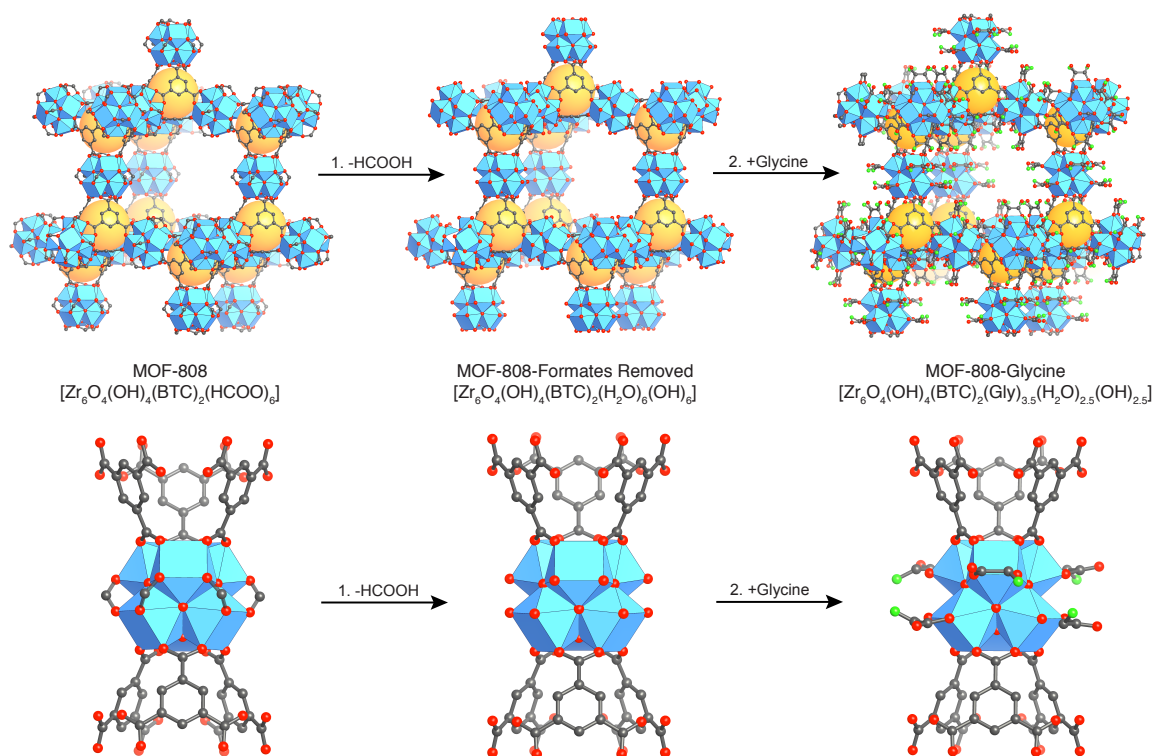


Figure 5.1. Post-synthetic modification scheme of MOF-808 to yield MOF-808-Formates Removed and MOF-808 Glycine. (Top) Fragments of the MOF-808 crystal structures obtained from single-crystal X-ray diffraction studies. (Bottom) Zoomed-in representations of MOF-808's SBUs at each step of the post-synthetic modification depicting the precise chemical and coordinative nature of the clusters. Upon formate ligand removal, the Zr sites are coordinated by equal amounts of crystallographically-indistinguishable water and hydroxy ligands. Upon glycine incorporation, these sites are occupied by glycine-based oxygen atoms with remaining sites still coordinated by water and hydroxide. C, O, and N atoms are represented by black, red, and green spheres, respectively; Zr coordination polyhedra are blue. Yellow spheres enclose the space within the tetrahedral cages. H atoms are omitted for clarity. Glycine = H₂NCH₂COOH; Gly = H₂NCH₂COO⁻

5.5 CO₂ Sorption in MOF-808-Glycine

To study the CO₂ adsorption properties of MOF-808-Glycine, CO₂ isotherms for the material were measured at 25 °C and compared to the parent compound, MOF-808-P, and the framework after the formate capping ligands had been removed, MOF-808-Formates Removed (Figure 5.1). MOF-808 glycine collects double the amount of CO₂ per gram of material compared to MOF-808-P and 1.74 times the amount of CO₂ per gram of material compared to MOF-808-Formates Removed. The miniscule increase in CO₂ uptake capacity of MOF-808-Formates Removed over MOF-808-P can be attributed to both increased surface area that facilitates physisorption (Section 5.9.7) and higher charge

density of the inorganic SBUs (Section 5.4). It should be noted, however, that only moderate uptake in the low-pressure range (<100 Torr) was observed which is in contrast to many MOFs that capture CO₂ in a chemisorptive fashion.^{23–25,27,28} Altogether, MOF-808 exhibited drastically increased CO₂ uptake capacity upon glycine incorporation. With such improvements resulting from the utilization of glycine as an alkylamine source, I decided to probe this chemistry further.

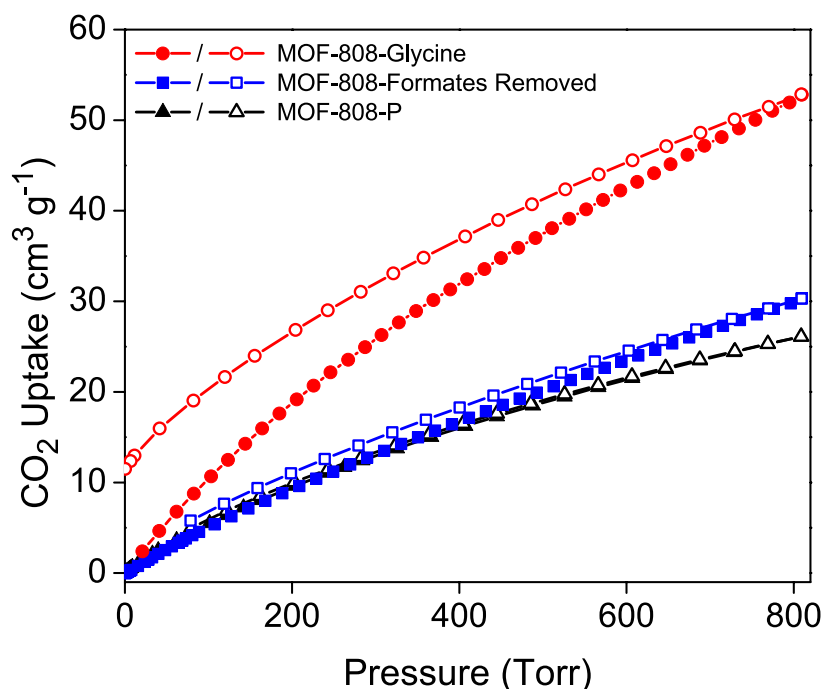


Figure 5.2. CO₂ isotherms (closed symbols = adsorption; open symbols = desorption) for the three frameworks reported in this chapter. In red circles, MOF-808-Glycine; in blue squares, MOF-808-Formates Removed; in black triangles, MOF-808-P.

5.6 Dynamic CO₂ Capture in the Presence of Water for MOF-808-Glycine

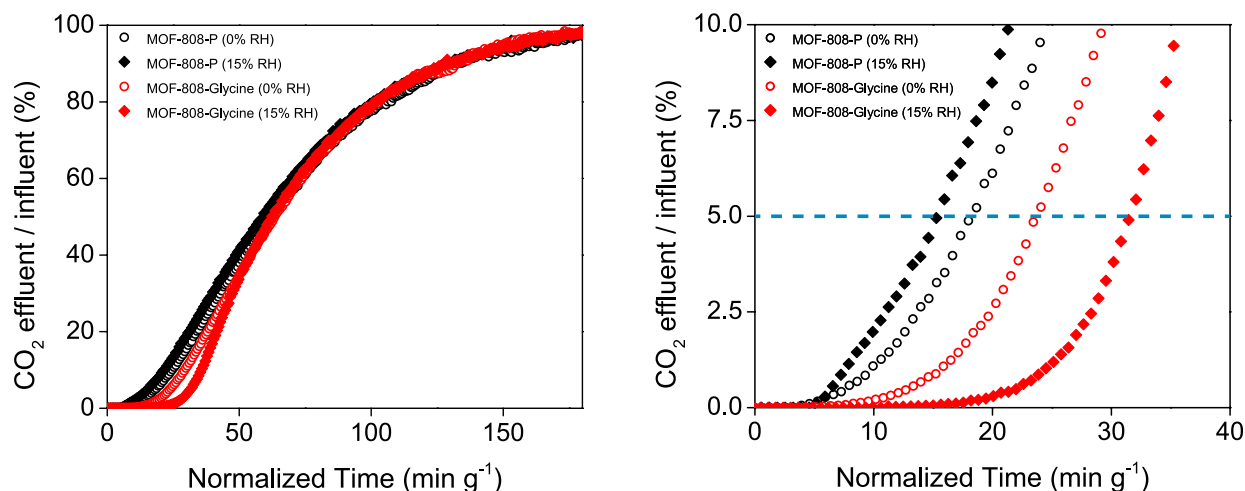


Figure 5.3. (left) Full MOF-808-P and MOF-808-Glycine breakthrough curve under dry (0% RH, empty circle markers) and humid conditions (15% RH, filled diamond markers). (right) Expansion of -ertinent breakthrough curve region for MOF-808-P and MOF-808-Glycine under dry and humid conditions. Breakthrough time (5% CO₂ effluent/influent) is highlighted as a light blue horizontal line.

To determine the dynamic adsorptive capacity of MOF-808-Glycine, breakthrough measurements were performed wherein a mixture of CO₂ and He (20/80, v/v) was passed through a *ca.* 130 mg bed of MOF-808-P and MOF-808-Glycine under dry (0% RH) and humid (15% RH) conditions (Figure 5.3, Section 5.9.10). The dynamic adsorption behavior of MOF-808-Formates Removed was not studied here because it has similar static adsorption behavior to MOF-808-P and is essentially an intermediate in the formation of MOF-808-Glycine. Notably, the bed containing MOF-808-Glycine retained CO₂ for longer times than MOF-808-P under both dry and humid conditions. Specifically, the breakthrough time, defined as the moment when the effluent analyte gas reaches 5% of its influent composition, for MOF-808-Glycine was 1.34 times longer than that for MOF-808-P under dry conditions and 2.06 times longer than MOF-808-P under humid conditions. This corresponds to dynamic adsorptive capacities of 6.82 cc g⁻¹ for MOF-808-P under dry conditions, 3.27 cc g⁻¹ for MOF-808-P under humid conditions, 7.79 cc g⁻¹ for MOF-808-Glycine under dry conditions, and 9.47 cc g⁻¹ for MOF-808-Glycine under humid conditions. Increased CO₂-MOF bed breakthrough time in the presence of water has previously been observed, and is typically accompanied by a shift in chemisorptive mechanism toward the formation of ammonium carbamates if other species had previously been observed in the product distribution.^{24,26} However, in light of the fact that practical CO₂ capture occurs in the presence of water (*ca.* 15% RH), and considering the drastic increase (21%) in dynamic CO₂ adsorption capacity in MOF-808-Glycine under humid *vs.* dry conditions, I believe that this material shows great promise as a practical CO₂ adsorbent. To confirm that this breakthrough time enhancement was accompanied by a shift in chemisorptive mechanism, I turned to solid state CP MAS NMR experiments.

5.7 Investigation of CO₂ Chemisorption in MOF-808-Glycine using Solid State CP MAS NMR

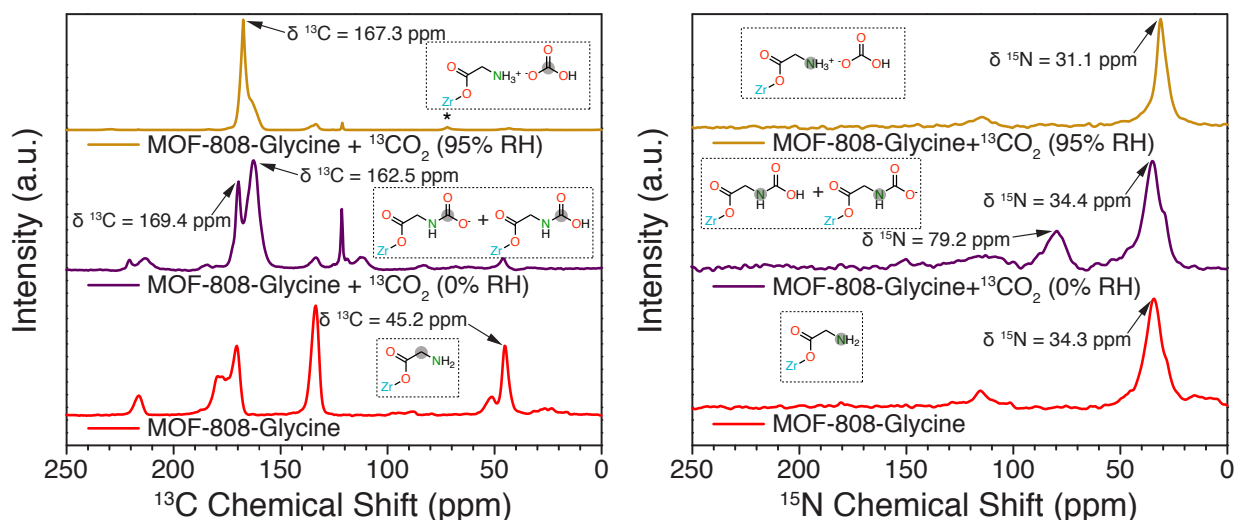


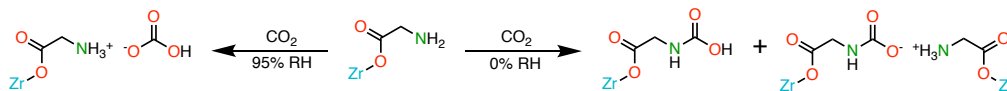
Figure 5.4. Summary of pertinent solid state ^{13}C (left plot) and ^{15}N (right plot) CP-MAS NMR spectra collected for MOF-808-Glycine. In red (bottom of both plots) are the spectra for activated MOF-808-Glycine. In purple (middle of both plots) are the spectra for MOF-808-Glycine after exposure to 740 Torr $^{13}\text{CO}_2$ for 24 h. In gold (top of both plots) are the spectra for MOF-808-Glycine after exposure to 95% relative humidity (RH) N_2 atmosphere for 24 h followed by 675 Torr $^{13}\text{CO}_2$ for 24 h. Signals of interest are denoted with arrows indicating either their ^{13}C or ^{15}N chemical shifts. The insets (dashed boxes) show the identity of the major species present in the structure at the conditions under which the experiment was run.

After observing the dynamic adsorption behavior of MOF-808-P and MOF-808-Glycine (Sections 5.6 and 5.9.9), I decided to probe the adsorptive chemistry between the glycine-based alkylamine and CO₂ by solid state ^{13}C and ^{15}N CP-MAS NMR of 98 % ^{15}N -enriched MOF-808-Glycine (Figure 5.4). In each measurement of MOF-808-P, MOF-808-Formates Removed, and MOF-808-Glycine, peaks at $\delta^{13}\text{C} = 170.2$ ppm and $\delta^{13}\text{C} = 133.4$ ppm are present (Section 5.9.8). These are attributed to the BTC carboxylates and aromatic carbons, respectively. After removing the formate ions from the SBUs of MOF-808, the signal at $\delta^{13}\text{C} = 162.2$ ppm is significantly attenuated (Section 5.9.8) and thus is not present in Figure 5.4. When ^{15}N enriched (98% atom basis) glycine was loaded onto the SBUs of MOF-808, two new signals appeared at $\delta^{13}\text{C} = 179.4$ ppm and $\delta^{13}\text{C} = 45.2$ ppm that are attributed to the carboxylate of glycine and the α -carbon in the molecule, respectively (Figure 5.4, left, in red). Notably, these signals are distinct from those observed for glycine in solution, or for crystalline or surface-adsorbed glycine.³⁵ I attribute this change in chemical shift to the coordination of glycine to the zirconium atom in MOF-808's SBUs (Section 5.4) as the electron-withdrawing nature of the metal would serve to deshield the nuclei in glycine and move their chemical shift signals downfield of those in the parent compound. The same phenomenon was observed with respect to the ^{15}N signal ($\delta^{15}\text{N} = 34.3$ ppm) from the amine nitrogen in glycine (Figure 5.4, right, in red).

After dosing MOF-808-Glycine with $^{13}\text{CO}_2$ (99% ^{13}C atom basis) under dry (0% RH) conditions (Section 5.9.8), three new, intense signals evolved in the resultant ^{13}C CP-MAS NMR spectrum at $\delta^{13}\text{C} = 169.4, 162.5,$ and 121.3 ppm (Figure 5.4 left, in purple). These signals are assigned to ammonium carbamate, carbamic acid, and free (not chemisorbed) CO_2 , respectively. This assignment is supported by the fact that these signals are very close to reported ^{13}C signals for the corresponding species, except that they have all been shifted downfield by *ca.* 3-5 ppm in accordance with the zirconium coordination detailed above.^{26,28} As further evidence of the signal at $\delta^{13}\text{C} = 162.5$ ppm belonging to a carbamic acid, this peak diminished after drawing vacuum on the sample at room temperature while the peak at $\delta^{13}\text{C} = 169.4$ ppm remained relatively unchanged (Section 5.9.8). This is in good agreement with previous studies on carbamic acids.^{28,36,37} The signal in the ^{15}N CP-MAS NMR spectrum at $\delta^{15}\text{N} = 79.2$ ppm corresponds to a mixture of the nitrogen atoms adjacent to the newly-formed carbonyl species and has also been accordingly shifted downfield.^{26,28}

Interestingly, when MOF-808-Glycine was dosed with $^{13}\text{CO}_2$ under humid (95% RH) conditions (Sections 5.9.8 and 5.9.10), a different product distribution was observed by solid state NMR. In the ^{13}C CP-MAS NMR spectrum (Figure 5.4, top left, in gold), one new, intense signal at $\delta^{13}\text{C} = 167.3$ ppm with a broad shoulder spanning from $\delta^{13}\text{C} = 164$ to 158 ppm. This signal is assigned to bicarbonate, in accordance with previous reports.³⁸ Additionally, a qualitative analysis of this spectrum compared to the ^{13}C spectrum measured under dry (0% RH) conditions reveals that this peak is much larger than either of those assigned to carbamic acid or ammonium carbamate when compared to the baseline signals such as the signal at $\delta^{13}\text{C} = 133.4$ ppm from the aromatic carbons in the BTC linker. This finding supports the data collected from breakthrough experiments which demonstrate that the dynamic adsorptive CO_2 capacity of MOF-808-Glycine is greater under humid conditions than under dry conditions. Additionally, the ^{15}N CP-MAS NMR spectrum of MOF-808-Glycine loaded with CO_2 under humid conditions shows that the amine signal has changed from $\delta^{15}\text{N} = 34.4$ ppm to $\delta^{15}\text{N} = 31.1$ ppm indicative of ammonium bicarbonate formation.³⁸ Finally, the signal at $\delta^{15}\text{N} = 79.2$ ppm, present in the MOF-808-Glycine sample dosed with $^{13}\text{CO}_2$ under dry conditions is absent, demonstrating that no nitrogen-carbonyl bonds are present in any observable quantity in the framework upon CO_2 chemisorption.

5.8 Conclusion



Scheme 5.1. Products of CO_2 chemisorption in MOF-808-Glycine (center) under dry (right) and humid (left) conditions as determined by this work.

I have developed a new porous solid, MOF-808-Glycine that is capable of CO_2 capture under dry and humid conditions. In taking advantage of the mechanistic

understanding I gleaned previously, I was able to design a framework that has a higher dynamic CO₂ adsorption capacity under humid (15 and 95% RH) conditions as compared to its capacity under dry (0% RH) conditions. This is due to the chemisorptive nature by which MOF-808-Glycine adsorbs CO₂ and forms different products depending upon the amount of water present at the time of adsorption. In spectroscopically probing this chemistry, I was able to determine two distinct chemisorptive mechanisms in MOF-808-Glycine (Scheme 5.1), one yielding ammonium bicarbonates, and the other yielding a mixture of ammonium carbamate and carbamic acid. Future work will include collecting binary adsorption data (water and CO₂) for MOF-808-Glycine and crystallographic determination of the structures of the ammonium carbamate, carbamic acid, and ammonium bicarbonate CO₂ chemisorption products. Also, comparing the relative desorption energetics of the ammonium carbamate/carbamic acid product mixture (dry conditions) to the ammonium bicarbonate products (humid conditions) will be of paramount importance. Finally, as this MOF can be made on a large scale, future work will address considerations regarding the applicability of this material to real-world CO₂ capture.

5.9 Supporting Information for Chapter 5

5.9.1 General Considerations

Chemicals used in this work

Anhydrous *N,N*-dimethylformamide (DMF), and formic acid (purity > 98%) were obtained from EMD Millipore Chemicals. Sodium hydroxide pellets, hydrofluoric acid (HF, 48 wt% in water), and hydrochloric acid (HCl, 37% in water) were obtained from Aldrich. Zirconium oxychloride octahydrate (ZrOCl₂ · 8H₂O, purity ≥ 98%) was obtained from Alfa Aesar. 1,3,5-Benzenetricarboxylic acid (H₃BTC) was obtained from TCI America. Glycine was obtained from Calbiochem. ¹⁵N (98% atom basis) enriched Glycine was obtained from Sigma Aldrich. Deuterated solvents were obtained from Cambridge Isotope Laboratories. Other common solvents and reagents (e.g. acetone) were obtained from other commercial sources and all chemicals in this work were used without further purification.

Analytical Techniques

Liquid-state ¹H and ¹³C{¹H} NMR spectra were acquired on a Bruker AV-600 (600 MHz) or a Bruker AV-300 (300 MHz) spectrometer at 297–300 K. Chemical shifts were calculated using the solvent resonances as internal standards (¹H: 2.50 ppm for DMSO; ¹³C{¹H}: 39.51 ppm for DMSO-*d*₆). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet of doublets (dt), triplet (t), multiplet (m), and broad resonance (br).

Solid state NMR spectra were collected using a 11.4 T magnet with a Bruker Avance I spectrometer operating at 500.23 MHz for ^1H , 125.75 MHz for ^{13}C , and 50.69 MHz for ^{15}N . ^{13}C chemical shifts were externally referenced to the upfield resonance of adamantane at 29.46 ppm relative to TMS, and ^{15}N chemical shifts were externally referenced to glycine at 33.4 ppm relative to neat NH_3 . Experiments were performed using a Bruker 4-mm double resonance MAS probe (1H/X). Magic angle spinning (MAS) was used to collect high-resolution NMR spectra at a spinning rate of 12 kHz for each data set. The magic angle was calibrated by maximizing the number and intensity of rotational echoes for the 79Br resonance for KBr under MAS. ^{13}C and ^{15}N cross polarization (CP) experiments under the Hartmann-Hahn matching condition were performed with a ^1H 90° pulse time of 4.25 μs , a 5 ms contact time, and 10.2 ms of acquisition time. A recycle delay of 2 and 3 s were used for ^{13}C and ^{15}N CP experiments, respectively. The two pulse phase modulated (TPPM) ^1H decoupling was used during signal acquisition. Spectra were zero-filled to 256 K points and were processed with 100 Hz line broadening. A multi-point baseline correction was applied to each spectra using Mestrelab MNova software suite.

Samples were activated under high vacuum using a Quantachrome Flovac Degasser initially at room temperature for 24 h. and then by heating at 120 °C for 24 h.

All nitrogen isotherms were measured using a Quantachrome Qudrasorb EVO instrument. Ca. 70 mg of guest free samples in 9 mm bulb gas cells were charged with argon to avoid air contamination and the cells were mounted on the instrument. A liquid nitrogen bath was used to maintain a temperature of 77 K for each measurement. Ultra-high-purity grade N_2 (Praxair, 99.999% purity) was used throughout the adsorption experiments. 46 adsorption and 16 desorption points were collected. The BET surface areas were estimated according to established procedures.

All CO_2 isotherms were measured immediately after activation procedures detailed above unless otherwise described. Measurements were performed using a Quantachrome Autosorb instrument. Ca. 70 mg of guest free samples in 9 mm bulb gas cells were charged with argon to avoid air contamination and the cells were mounted on the instrument. A water bath was used to maintain a temperature of 298 K for each measurement except where specified. CO_2 (Praxair, 99.998% purity) was used throughout the adsorption experiments. 55 adsorption and 12 desorption points were collected.

FT-IR spectra were collected in-house using a Bruker ALPHA Platinum ATR-FT-IR Spectrometer equipped with a single reflection diamond ATR module.

Powder X-ray diffraction data were collected using a Bruker D8-advance θ - θ diffractometer in parallel beam geometry employing Cu $\text{K}\alpha_1$ line focused radiation at 1600 W (40 kV, 40 mA) power and equipped with a position sensitive detector with at 6.0 mm radiation entrance slit. Samples were mounted on zero background sample holders by dropping powders from a wide-blade spatula and then leveling the sample with a

razor blade. Data were collected using a 0.01° 2θ step scan from $2 - 50^\circ$ with exposure time of 3 s per step.

5.9.2 Synthesis of MOF-808 and MOF-808-P

Single crystals of MOF-808 were synthesized and activated following the reported procedure.²⁹ Microcrystalline MOF-808-P was synthesized and activated following an alternative reported procedure.³⁰ All activated MOF-808 and MOF-808-P samples were stored in an argon atmosphere glovebox at room temperature until further use.

5.9.3 Post-synthetic Modification of MOF-808 and MOF-808-P

Formate Ligand Removal from MOF-808 SBUs

To remove the formate capping ligands surrounding the $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{BTC})_2(\text{HCOO})_6$ SBUs in MOF-808, 1 g of activated MOF-808-P was placed in a clean 150 mL jar with Teflon lid. To this jar ca. 135 mL of an HCl solution (1 M in deionized water) was added. The jar containing MOF-808-P and HCl was shaken gently and placed in an isothermal oven set at 85°C for 3 days. Initially, a turbid suspension of MOF-808 in the solution was observed. Over a period of 6-12 hours, the MOF settled onto the bottom of the jar and the supernatant was visibly clear. At this time, the majority (ca. 90 mL) of supernatant was decanted and replaced with fresh 1M HCl. This process was repeated two times per day over the three day period after which the jar was removed from the oven and cooled to room temperature. The solid was then washed three times per day (3 X 90 mL) for three days with deionized water and carried onto the glycine loading step. In order to characterize the product, MOF-808-Formates Removed, the water washing was carried out followed by an identical washing procedure with acetone. This solid was activated (Section 5.9.1) and then characterized as detailed in the following sections. To perform formate removal from single crystals of MOF-808, an identical procedure was applied to ca 50 mg of MOF crystals in a 4 mL scintillation vial.

Glycine Loading onto MOF-808-Formate Removed SBUs

A near-saturated (2.66 M) solution of glycine in deionized water was generated by dissolving 200 g of glycine in ca. 1L deionized water in a 1L Pyrex screw-capped media storage jar which was then sonicated and placed in an isothermal oven set at 85°C for 1 day. To load glycine onto the $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{BTC})_2(\text{HCOO})_6$ SBUs in MOF-808-Formates Removed, ca. 1 g of solvent-exchanged MOF-808-Formates Removed was placed in a clean 150 mL jar with Teflon lid. To this jar ca. 135 mL of the 2.66 M glycine solution was added. The jar containing MOF-808-Formates Removed and glycine solution was shaken gently and placed in the same isothermal oven set at 85°C for 3 days. Initially, a turbid suspension of MOF-808 in the solution was observed. Over a period of 6-12 hours, the MOF settled onto the bottom of the jar and the supernatant was visibly clear. At this time, the majority (ca. 90 mL) of supernatant was decanted and replaced with fresh glycine

solution. This process was repeated two times per day over the three day period after which the jar was removed from the oven and cooled to room temperature. The solid was then washed three times per day (3 X 90 mL) for three days with deionized water and three times per day (3 X 90 mL) for one day with a pH 10 buffer solution (3 X 90 mL) that was 0.05 M in glycine and 0.032 M in NaOH in deionized water. After the buffer wash, MOF-808-Glycine was washed for one day (3 X 90 mL) with acetone and further washed with acetone via Soxhlet extraction overnight. This solid was activated (Section 5.9.1) and then characterized as detailed in the following sections. To perform glycine loading onto single crystals of MOF-808, an identical procedure was applied to ca 50 mg of MOF crystals in a 4 mL scintillation vial. To load MOF-808-Formates Removed with ^{15}N enriched glycine, an analogous procedure was used with ^{15}N enriched (98% atom basis) glycine on a 20 mL (H_2O) scale.

5.9.4 FT-IR Spectra of Activated MOFs

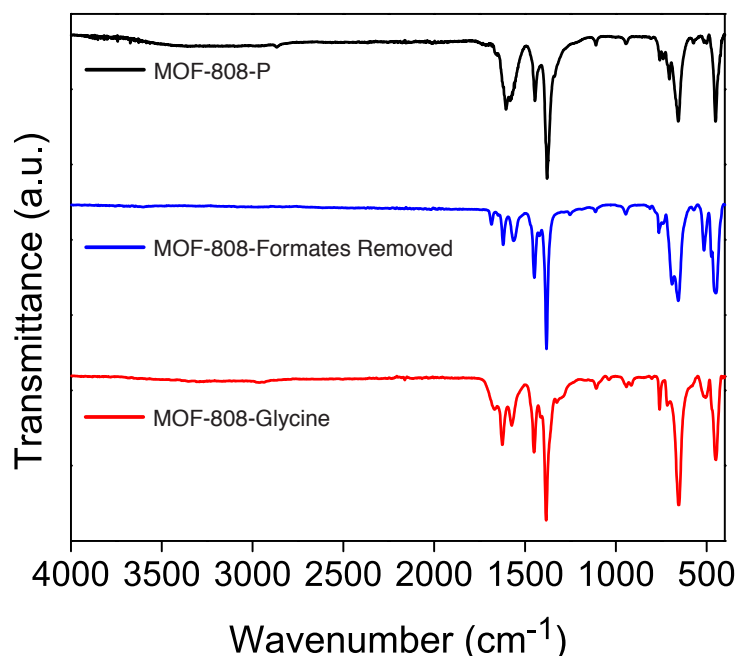


Figure S5.1. FT-IR (ATR) spectra of activated MOF-808-P (black, top), MOF-808-Formates Removed (blue, middle), and MOF-808-Glycine (red, bottom).

5.9.5 Solution ^1H NMR of Digested Samples

Typically, for the digestion of the MOF samples ca. 20 mg of activated, microcrystalline samples were placed in a 4 mL scintillation vial. Then 580 μL of $\text{DMSO-}d_6$, 20 μL of hydrofluoric acid (48 wt% in water), and 150 μL of DCl in D_2O (35 wt. %), were added. The suspension was sonicated 10 min and left at room temperature until the solution clarified after which time the ^1H NMR spectra were recorded. An identical procedure was performed on pure glycine to be used as a chemical shift reference.

Glycine: ^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ 3.51 (s, 2H).

MOF-808-P: ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 8.39 (s, 6H), 8.00 (s, 5H).

MOF-808-Formates Removed: ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 8.40 (s, 6H), 8.00 (s, 0.13H).

MOF-808-Glycine: ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 8.41 (s, 6H), 8.02 (s, 0.07H), 3.53 (s, 6.91H).

5.9.6 Powder X-ray Diffraction (PXRD) Characterization

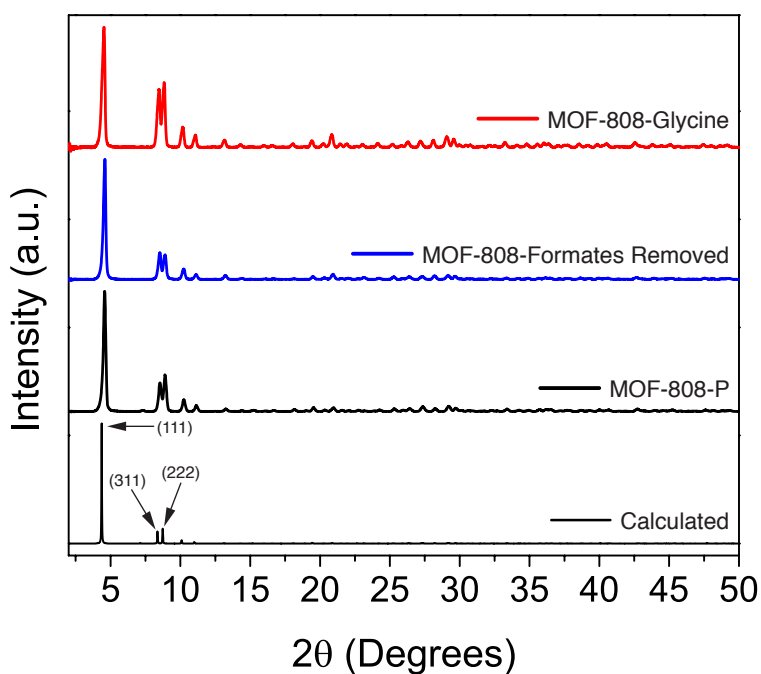


Figure S5.2. PXRD pattern of simulated MOF-808 (black, bottom), activated MOF-808-P (black, second from bottom), activated MOF-808-Formates Removed (blue, second from top), and activated MOF-808-Glycine (red, top).

5.9.7 Nitrogen Adsorption Measurements

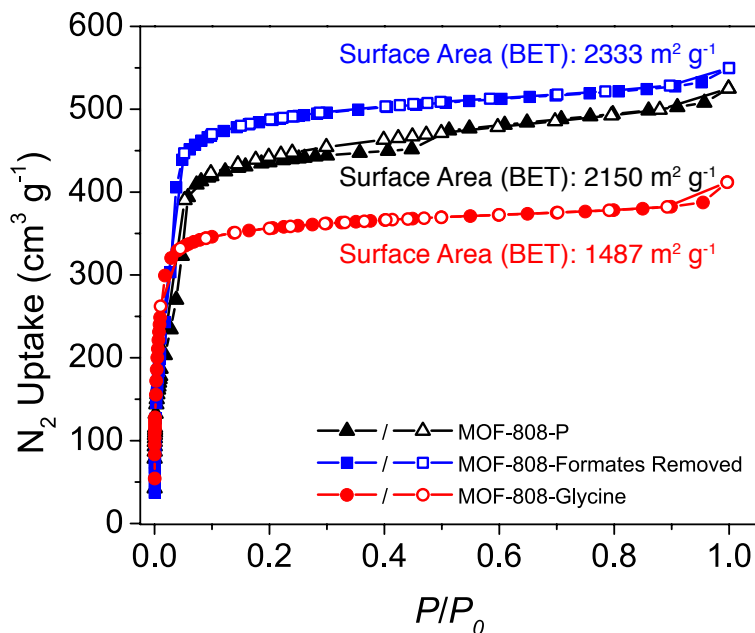


Figure S5.3. Nitrogen adsorption isotherms (closed symbols = adsorption; open symbols = desorption) for MOF-808-P (black triangles), MOF-808-Formates Removed (blue squares), and MOF-808-Glycine (red circles) at 77 K. The inset text details the experimental BET surface areas for the three compounds.

5.9.8 Additional Solid State NMR Experiments and Details

CO₂ Gas Loading and NMR Sample Preparation

Each measured sample was packed into a Doty 4 mm or 5 mm zirconia rotor in an argon atmosphere glovebox. The packed, uncapped rotor was then quickly transferred to a home-built gas dosing apparatus and vacuum was applied for 2 hours. After this period, the sample was exposed to 740 torr $^{13}\text{CO}_2$ gas (Sigma-Aldrich, 99% atom ^{13}C) for 24 hours at room temperature. The pressure was monitored using an MKS Baratron capacitance manometer with a working range of 2-1000 torr. After exposure, the rotor was quickly capped and transferred to the magnet for NMR analysis to minimize any loss of CO_2 . Water-exposed MOF samples were prepared following the procedure detailed in Section 5.9.10. The water-exposed MOFs were then transferred to the gas dosing apparatus and exposed to $^{13}\text{CO}_2$ as described previously. For vacuum experiments, the MOF-808-Glycine sample was kept in the solid state NMR rotor and evacuated in the same home-built gas dosing apparatus for 48 h. For 120 °C activation experiments, samples were removed from the solid state NMR rotor and activated according to the procedure detailed in section 5.9.1.

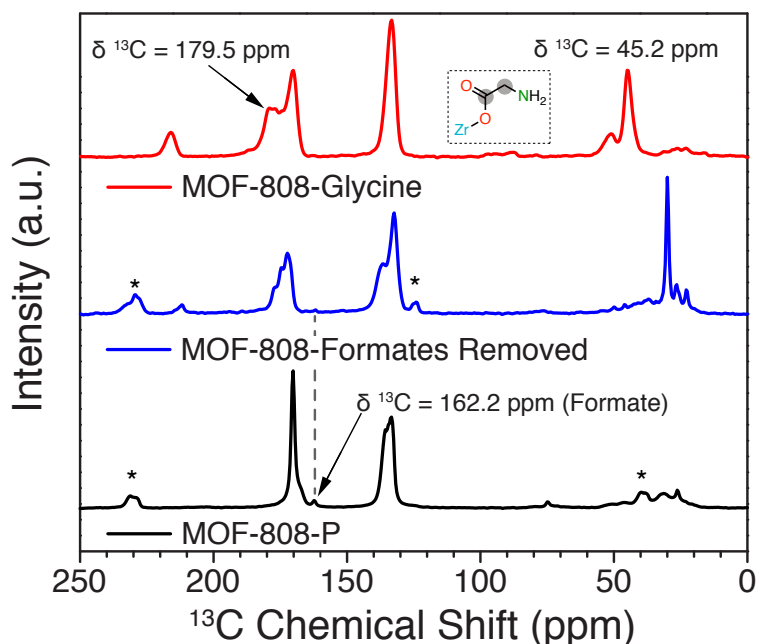


Figure S5.4. Summary of ^{13}C CP-MAS NMR spectra collected for MOF-808-P (black, bottom), MOF-808-Formates Removed (blue, middle), and MOF-808-Glycine (red, top). The signal at $\delta^{13}\text{C} = 162.2$ ppm (attributed to formate anions) is highlighted so as to view its relative disappearance throughout the post-synthetic modification process. In the spectrum for MOF-808-Formates Removed, the signal at $\delta^{13}\text{C} = 30.1$ ppm is attributed to residual acetone in the framework as the result of solvent exchange. The new peaks at $\delta^{13}\text{C} = 179.5$ and 45.2 ppm in the spectrum for MOF-808-Glycine are attributed to the carbonyl and α -carbons in glycine coordinated to zirconium, respectively. Spinning sidebands are denoted with stars above the corresponding signal.

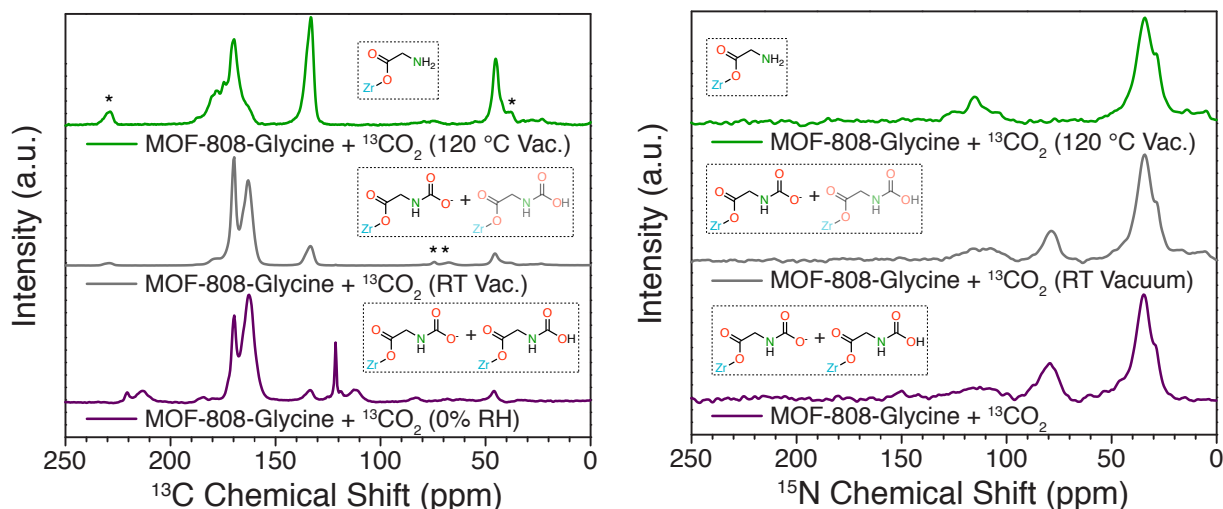


Figure S5.5. Summary of MOF-808-Glycine activation as measured by solid state ^{13}C (left plot) and ^{15}N (right plot) CP-MAS NMR. In purple (bottom of both plots) are the spectra for MOF-808-Glycine after exposure to 740 Torr $^{13}\text{CO}_2$ for 24 h. In grey (middle of both plots) are the spectra for MOF-808-Glycine+ $^{13}\text{CO}_2$ after evacuation on the home-built CO_2 dosing apparatus for 48 h denoting the relative attenuation of the carbamic acid peak at $\delta^{13}\text{C} = 162.5$ ppm. In green (top of both plots) are the spectra for reactivated (at 120°C for 24 h) MOF-808-Glycine indicating complete activation as evidenced by the disappearance of the peaks at $\delta^{13}\text{C} = 169.4$ and 162.5 ppm (left plot) and $\delta^{15}\text{N} = 79.2$ ppm (right plot) which were previously assigned to ammonium carbamate, carbamic acid, and the nitrogen atom adjacent to the carbonyl carbon, respectively.

5.9.9 Additional Breakthrough Experimental Details

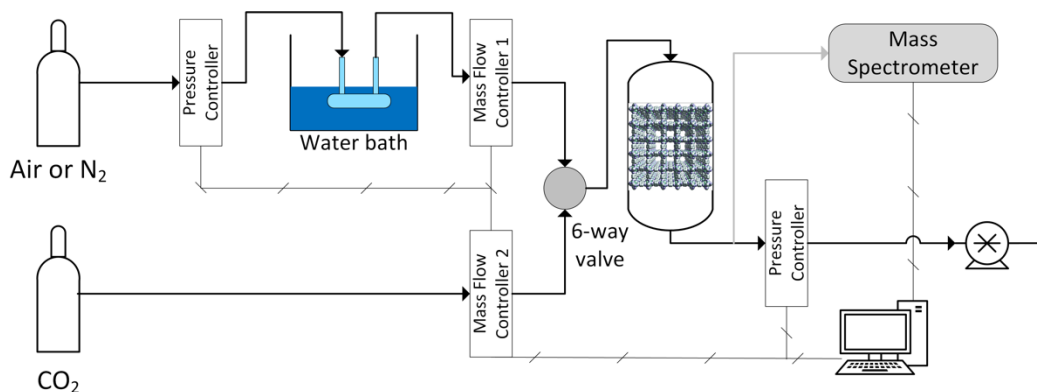


Figure S5.6. Schematic of the dynamic adsorption (breakthrough) instrument used in this experiment.

Dynamic column breakthrough experiments were performed using a custom built apparatus and a mass spectrometer (Figure S5.6). Helium was passed through a water saturator-cell, that was located in a temperature controlled water-bath. The pressure was controlled at approximately 120 kPa using a pressure controller (MKS Baratron type 640B) upstream of the saturator. A second He stream was mixed with the first stream and the mixed stream was passed through the adsorbent bed via a six-way valve. The bed

pressure was controlled at 760 Torr using another MKS pressure controller. Both stream 1 and 2 were controlled by MKS mass flow controllers (MFC 1 & MFC 2), and the adsorbate gas concentration fed to the adsorbent bed was determined by the combined flow rates of stream 1 and 2. The relative humidity of the stream was controlled by controlling the bath temperature and the flow rate of gas streams. The effluent gas from the adsorbent bed was sampled by an Agilent 5973 mass spectrometer. A SS tube with a length of 5 cm and an internal diameter of 0.51 cm was used as the adsorbent bed (1/4" tubing). Roughly 130 mg of each sample was used for the breakthrough experiments. The samples were regenerated at 120 °C under vacuum (0.03 mTorr) for 15 hours and then by flowing 1 sccm He for 12 hours at 760 torr. For humid runs, the samples were prehumidified by flowing He through a water bath and saturator to MFC 1 and dry He through MFC 2 for 12-15 hrs. Prior to the breakthrough run, CO₂/He (20/80) mixture gas with a flow rate of 5 sccm was introduced by switching the second He stream to a dry CO₂ via MFC 2 while the six-way valve was used to bypass the bed. To start the breakthrough run, the six-way valve then used to switch the mixed stream to flow through the adsorption bed. For the dry breakthrough run, the saturator-cell was bypassed and dry He was mixed directly with the second stream.

5.9.10 Humidification of MOF-808-Glycine Samples

Samples of activated MOF-808-Glycine were saturated with water vapor at a relative humidity (RH) values of RH = 95% by using a HygroCal100 Humidity Generator/Calibrator (Michell Inc, MA, USA) controlled humidity chamber. To generate uniform humidity across the chamber, the HygroCal 100 humidity generator is equipped with seven HygroSmart HS3 capacitive humidity sensors with $\pm 0.8\%$ accuracy. The bias error was eliminated by using an external standard reference precision dew-point meter (chilled mirror with $\pm 0.2^\circ\text{C}_{\text{dew-point}}$ accuracy). Ultimately, the humidity measurements were taken with the overall uncertainty of $\pm 1\%$.

For humidification, ca 70 mg ¹⁵N enriched MOF-808-Glycine was dosed with ¹³CO₂ and then reactivated as detailed in Section 5.9.8. Solid state NMR spectra of the activated sample indicated that it was nearly fully activated and that the glycine-based alkylamines were available to chemisorb further CO₂. The sample was transferred into a solid state NMR rotor in an argon-filled glove box and placed inside the sealed HygroCal100 humidity chamber in an uncapped 4 mL vial. To minimize atmospheric CO₂ interaction with the MOF during humidification, the chamber was purged with ultra-pure nitrogen (99.999%) and kept under 0-0.5% RH for at least 5 minutes. While nitrogen flowed through the humidity chamber, the vials were transferred to the chamber and after another 1-2 minutes the humidity value stabilized back to 0-0.5%. Then, the nitrogen flow was stopped and the water loading experiment commenced by increasing the relative humidity inside the chamber from 0-0.5% to 95% with transition period of less than 2 minutes. The samples were kept inside the humidity-controlled chamber for 24 hours to ensure that the samples were saturated with water at the specified RH values.

5.9.11 Single Crystal X-ray Diffraction Analyses

Single crystal X-ray diffraction data was collected using a Bruker D8 Venture diffractometer equipped with a microfocus X-ray ($I\mu S$) source. The diffractometer is also equipped with a PHOTON-II CMOS detector, and the radiation is monochromated using mirror optics.

Single crystal samples were mounted on MiTeGen® kapton loops and placed in a 100(2) K nitrogen cold stream from Cryostream system. The raw data were processed using Bruker APEX3 software package.¹ The data were first integrated with SAINT V8.38A and then corrected for absorption via SADABS 2016/2 routines.² The structures were solved by intrinsic phasing (SHELXT-2018/03) and refinement was accomplished using full-matrix least squares on F^2 (SHELXL-2018/03), in the Olex² software package.³⁻⁵ The resolution cut-off was based on the intensity statistics table (.prp file).

For structure refinement, MOF structures were first assigned and refined anisotropically. The refinement on the disordered μ_3 -O (O1A/O1B) and ligand-based oxygens (O2A/O2B) followed a previous report.⁴ The occupancies of the ligand and the neighboring coordinating water were determined via a free variable assignment, later fixed to a constrained value. Hydrogen atoms were placed at geometrically calculated positions. Refinement details can be found in the _refine_special_details sections of the corresponding cif files and also in the responses to the checkcif reports.

Table S5.1. Crystal data and structure refinement for MOF-808 single crystal.

Empirical formula	C _{1.77} H _{0.85} O _{2.67} Zr _{0.5}
Formula weight	110.35
Temperature/K	150
Crystal system	cubic
Space group	Fd-3m
a/Å	35.2563(14)
b/Å	35.2563(14)
c/Å	35.2563(14)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	43824(5)
Z	192
ρ _{calc} /cm ³	0.803
μ/mm ⁻¹	4.872
F(000)	10135.0
Crystal size/mm ³	0.045 × 0.045 × 0.045
Radiation	CuKα (λ = 1.54178 Å)
2Θ range for data collection/°	8.318 to 117.95
Index ranges	-37 ≤ h ≤ 34, -38 ≤ k ≤ 39, -31 ≤ l ≤ 39
Reflections collected	40361
Independent reflections	1525 [R _{int} = 0.0517, R _{sigma} = 0.0149]
Data/restraints/parameters	1525/12/76
Goodness-of-fit on F ²	1.144
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0482, wR ₂ = 0.1597
Final R indexes [all data]	R ₁ = 0.0523, wR ₂ = 0.1633
Largest diff. peak/hole / e Å ⁻³	1.74/-0.48

**Table S5.2 Crystal data and structure refinement for MOF-808-Formates
Removed single crystal.**

Empirical formula	C _{1.5} H _{2.08} O _{2.67} Zr _{0.5}
Formula weight	108.39
Temperature/K	150
Crystal system	cubic
Space group	Fd-3m
a/Å	35.3519(6)
b/Å	35.3519(6)
c/Å	35.3519(6)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	44181(2)
Z	192
ρ _{calc} /cm ³	0.782
μ/mm ⁻¹	4.822
F(000)	10064.0
Crystal size/mm ³	0.05 × 0.05 × 0.05
Radiation	CuKα (λ = 1.54178 Å)
2Θ range for data collection/°	8.294 to 130.042
Index ranges	-41 ≤ h ≤ 41, -39 ≤ k ≤ 41, -41 ≤ l ≤ 39
Reflections collected	48861
Independent reflections	1811 [R _{int} = 0.0657, R _{sigma} = 0.0170]
Data/restraints/parameters	1811/30/72
Goodness-of-fit on F ²	1.181
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0501, wR ₂ = 0.1621
Final R indexes [all data]	R ₁ = 0.0554, wR ₂ = 0.1691
Largest diff. peak/hole / e Å ⁻³	1.27/-0.47

Table S5.3. Crystal data and structure refinement for MOF-808-Glycine single crystal.

Empirical formula	Zr _{0.5} OHCN
Formula weight	45.83
Temperature/K	150
Crystal system	cubic
Space group	Fd-3m
a/Å	35.5627(4)
b/Å	35.5627(4)
c/Å	35.5627(4)
α /°	90
β /°	90
γ /°	90
Volume/Å ³	44976.4(15)
Z	192
ρ_{calc} /cm ³	0.325
μ /mm ⁻¹	4.334
F(000)	3862.0
Crystal size/mm ³	0.04 × 0.04 × 0.04
Radiation	CuK α (λ = 1.54178 Å)
2 Θ range for data collection/°	7.03 to 129.996
Index ranges	-27 ≤ h ≤ 33, -41 ≤ k ≤ 33, -39 ≤ l ≤ 30
Reflections collected	24803
Independent reflections	1843 [R_{int} = 0.0317, R_{sigma} = 0.0138]
Data/restraints/parameters	1843/22/77
Goodness-of-fit on F ²	1.091
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0480, wR_2 = 0.1415
Final R indexes [all data]	R_1 = 0.0517, wR_2 = 0.1456
Largest diff. peak/hole / e Å ⁻³	1.14/-0.67

5.10 References for Chapter 5

- (1) Furukawa, H.; Cordova, K. E.; O’Keeffe, M.; Yaghi, O. M. The Chemistry and Applications of Metal-Organic Frameworks. *Science*. **2013**, 341, 1230444–1230444.
- (2) Waller, P. J.; Gándara, F.; Yaghi, O. M. Chemistry of Covalent Organic Frameworks. *Acc. Chem. Res.* **2015**, 48, 3053–3063.
- (3) Diercks, C. S.; Yaghi, O. M. The Atom, the Molecule, and the Covalent Organic Framework. *Science*. **2017**, 355, eaal1585.
- (4) Cordova, K. E.; Yaghi, O. M. The ‘Folklore’ and Reality of Reticular Chemistry. *Mater. Chem. Front.* **2017**, 1, 1304–1309.
- (5) Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.-H.; Long, J. R. Carbon Dioxide Capture in Metal–Organic Frameworks. *Chem. Rev.* **2012**, 112, 724–781.
- (6) Zhang, Z.; Yao, Z.-Z.; Xiang, S.; Chen, B. Perspective of Microporous Metal–Organic Frameworks for CO₂ Capture and Separation. *Energy Environ. Sci.* **2014**, 7, 2868.
- (7) Zeng, Y.; Zou, R.; Zhao, Y. Covalent Organic Frameworks for CO₂ Capture. *Adv. Mater.* **2016**, 28, 2855–2873.
- (8) Trickett, C. A.; Helal, A.; Al-Maythaly, B. A.; Yamani, Z. H.; Cordova, K. E.; Yaghi, O. M. The Chemistry of Metal–Organic Frameworks for CO₂ Capture, Regeneration and Conversion. *Nat. Rev. Mater.* **2017**, 2, 17045.
- (9) Schoedel, A.; Ji, Z.; Yaghi, O. M. The Role of Metal–Organic Frameworks in a Carbon-Neutral Energy Cycle. *Nat. Energy* **2016**, 1, 16034.
- (10) Liu, J.; Wei, Y.; Zhao, Y. Trace Carbon Dioxide Capture by Metal–Organic Frameworks. *ACS Sustain. Chem. Eng.* **2019**, 7, 82–93.
- (11) Modak, A.; Jana, S. Advancement in Porous Adsorbents for Post-Combustion CO₂ Capture. *Microporous Mesoporous Mater.* **2019**, 276, 107–132.
- (12) Millward, A. R.; Yaghi, O. M. Metal–Organic Frameworks with Exceptionally High Capacity for Storage of Carbon Dioxide at Room Temperature. *J. Am. Chem. Soc.* **2005**, 127, 17998–17999.
- (13) Queen, W. L.; Hudson, M. R.; Bloch, E. D.; Mason, J. A.; Gonzalez, M. I.; Lee, J. S.; Gygi, D.; Howe, J. D.; Lee, K.; Darwish, T. A.; James, M.; Peterson, V. K.; Teat, S. J.; Smit, B.; Neaton, J. B.; Long, J. R.; Brown, C. M. Comprehensive Study of Carbon Dioxide Adsorption in the Metal–Organic Frameworks M₂(Dobdc) (M = Mg, Mn, Fe, Co, Ni, Cu, Zn). *Chem. Sci.* **2014**, 5, 4569–4581.
- (14) Huang, H.; Zhang, W.; Liu, D.; Zhong, C. Understanding the Effect of Trace Amount of Water on CO₂ Capture in Natural Gas Upgrading in Metal–Organic Frameworks: A Molecular Simulation Study. *Ind. Eng. Chem. Res.* **2012**, 51, 10031–10038.
- (15) Yu, J.; Balbuena, P. B. Water Effects on Postcombustion CO₂ Capture in Mg-MOF-74. *J. Phys. Chem. C* **2013**, 117, 3383–3388.
- (16) Burtch, N. C.; Jasuja, H.; Walton, K. S. Water Stability and Adsorption in Metal–Organic Frameworks. *Chem. Rev.* **2014**, 114, 10575–10612.
- (17) Li, P.; Chen, J.; Zhang, J.; Wang, X. Water Stability and Competition Effects Toward

- CO₂ Adsorption on Metal Organic Frameworks. *Sep. Purif. Rev.* **2015**, *44*, 19–27.
- (18) Granite, E. J.; Pennline, H. W. Photochemical Removal of Mercury from Flue Gas. *Ind. Eng. Chem. Res.* **2002**, *41*, 5470–5476.
 - (19) Nguyen, N. T. T.; Furukawa, H.; Gándara, F.; Nguyen, H. T.; Cordova, K. E.; Yaghi, O. M. Selective Capture of Carbon Dioxide under Humid Conditions by Hydrophobic Chabazite-Type Zeolitic Imidazolate Frameworks. *Angew. Chemie - Int. Ed.* **2014**, *53*, 10645–10648.
 - (20) Lin, Y.; Kong, C.; Chen, L. Amine-Functionalized Metal–Organic Frameworks: Structure, Synthesis and Applications. *RSC Adv.* **2016**, *6*, 32598–32614.
 - (21) McDonald, T. M.; D’Alessandro, D. M.; Krishna, R.; Long, J. R. Enhanced Carbon Dioxide Capture upon Incorporation of N,N'-Dimethylethylenediamine in the Metal–Organic Framework CuBTtri. *Chem. Sci.* **2011**, *2*, 2022.
 - (22) McDonald, T. M.; Lee, W. R.; Mason, J. A.; Wiers, B. M.; Hong, C. S.; Long, J. R. Capture of Carbon Dioxide from Air and Flue Gas in the Alkylamine-Appended Metal–Organic Framework Mmen-Mg₂(Dobpdc). *J. Am. Chem. Soc.* **2012**, *134*, 7056–7065.
 - (23) McDonald, T. M.; Mason, J. A.; Kong, X.; Bloch, E. D.; Gygi, D.; Dani, A.; Crocellà, V.; Giordanino, F.; Odoh, S. O.; Drisdell, W. S.; Vlaisavljevich, B.; Dzubak, A. L.; Poloni, R.; Schnell, S. K.; Planas, N.; Lee, K.; Pascal, T.; Wan, L. F.; Prendergast, D.; Neaton, J. B.; Smit, B.; Kortright, J. B.; Gagliardi, L.; Bordiga, S.; Reimer, J. A.; Long, J. R. Cooperative Insertion of CO₂ in Diamine-Appended Metal–Organic Frameworks. *Nature* **2015**, *519*, 303–308.
 - (24) Siegelman, R. L.; McDonald, T. M.; Gonzalez, M. I.; Martell, J. D.; Milner, P. J.; Mason, J. A.; Berger, A. H.; Bhowan, A. S.; Long, J. R. Controlling Cooperative CO₂ Adsorption in Diamine-Appended Mg₂(Dobpdc) Metal–Organic Frameworks. *J. Am. Chem. Soc.* **2017**, *139*, 10526–10538.
 - (25) Milner, P. J.; Siegelman, R. L.; Forse, A. C.; Gonzalez, M. I.; Runčevski, T.; Martell, J. D.; Reimer, J. A.; Long, J. R. A Diaminopropane-Appended Metal–Organic Framework Enabling Efficient CO₂ Capture from Coal Flue Gas via a Mixed Adsorption Mechanism. *J. Am. Chem. Soc.* **2017**, *139*, 13541–13553.
 - (26) Forse, A. C.; Milner, P. J.; Lee, J.; Redfearn, H. N.; Oktawiec, J.; Siegelman, R. L.; Martell, J. D.; Dinakar, B.; Porter-Zasada, L. B.; Gonzalez, M. I.; Neaton, J. B.; Long, J. R.; Reimer, J. A. Elucidating CO₂ Chemisorption in Diamine-Appended Metal–Organic Frameworks. *J. Am. Chem. Soc.* **2018**, *140*, 18016–18031.
 - (27) Fracaroli, A. M.; Furukawa, H.; Suzuki, M.; Dodd, M.; Okajima, S.; Yaghi, O. M. Metal–Organic Frameworks with Precisely Designed Interior for Carbon Dioxide Capture in the Presence of Water. *J. Am. Chem. Soc.* **2014**, *136*, 8863–8866.
 - (28) Flaig, R. W.; Osborn Popp, T. M.; Fracaroli, A. M.; Kapustin, E. A.; Kalmutzki, M. J.; Altamimi, R. M.; Fathieh, F.; Reimer, J. A.; Yaghi, O. M. The Chemistry of CO₂ Capture in an Amine-Functionalized Metal–Organic Framework under Dry and Humid Conditions. *J. Am. Chem. Soc.* **2017**, jacs.7b06382.
 - (29) Furukawa, H.; Gándara, F.; Zhang, Y.-B.; Jiang, J.; Queen, W. L.; Hudson, M. R.; Yaghi, O. M. Water Adsorption in Porous Metal–Organic Frameworks and Related Materials. *J. Am. Chem. Soc.* **2014**, *136*, 4369–4381.

- (30) Jiang, J.; Gándara, F.; Zhang, Y.-B.; Na, K.; Yaghi, O. M.; Klemperer, W. G. Superacidity in Sulfated Metal–Organic Framework-808. *J. Am. Chem. Soc.* **2014**, *136*, 12844–12847.
- (31) Chen, C.; Shimon, D.; Lee, J. J.; Mentink-Vigier, F.; Hung, I.; Sievers, C.; Jones, C. W.; Hayes, S. E. The “Missing” Bicarbonate in CO₂ Chemisorption Reactions on Solid Amine Sorbents. *J. Am. Chem. Soc.* **2018**, *140*, 8648–8651.
- (32) Zhang, R.; Liang, Z.; Liu, H.; Rongwong, W.; Luo, X.; Idem, R.; Yang, Q. Study of Formation of Bicarbonate Ions in CO₂ -Loaded Aqueous Single 1DMA2P and MDEA Tertiary Amines and Blended MEA–1DMA2P and MEA–MDEA Amines for Low Heat of Regeneration. *Ind. Eng. Chem. Res.* **2016**, *55*, 3710–3717.
- (33) Lyle, S. J.; Flaig, R. W.; Cordova, K. E.; Yaghi, O. M. Facilitating Laboratory Research Experience Using Reticular Chemistry. *J. Chem. Educ.* **2018**, *95*, 1512–1519.
- (34) Trickett, C. A.; Osborn Popp, T. M.; Su, J.; Yan, C.; Weisberg, J.; Huq, A.; Urban, P.; Jiang, J.; Kalmutzki, M. J.; Liu, Q.; Beak, J.; Head-Gordon, M. P.; Somorjai, G. A.; Reimer, J. A.; Yaghi, O. M. Identification of the Strong Brønsted Acid Site in a Metal–Organic Framework Solid Acid Catalyst. *Nat. Chem.* **2019**, *11*, 170–176.
- (35) Glycine. AIST:Spectra Database for Organic Compounds, SDBS.
- (36) Pinto, M. L.; Mafra, L.; Guil, J. M.; Pires, J.; Rocha, J. Adsorption and Activation of CO₂ by Amine-Modified Nanoporous Materials Studied by Solid-State NMR and ¹³CO₂ Adsorption. *Chem. Mater.* **2011**, *23*, 1387–1395.
- (37) Mafra, L.; Čendak, T.; Schneider, S.; Wiper, P. V.; Pires, J.; Gomes, J. R. B.; Pinto, M. L. Structure of Chemisorbed CO₂ Species in Amine-Functionalized Mesoporous Silicas Studied by Solid-State NMR and Computer Modeling. *J. Am. Chem. Soc.* **2017**, *139*, 389–408.
- (38) Chen, C.; Shimon, D.; Lee, J. J.; Didas, S. A.; Mehta, A. K.; Sievers, C.; Jones, C. W.; Hayes, S. E. Spectroscopic Characterization of Adsorbed ¹³CO₂ on 3-Aminopropylsilyl-Modified SBA15 Mesoporous Silica. *Environ. Sci. Technol.* **2017**, *51*, 6553–6559.

Chapter 6: Conclusion and Outlook

The development of metal-organic framework (MOF) and covalent organic framework (COF) materials has opened a door leading to a new set of promising adsorbents for CO₂ capture. Keys to the successful implementation of MOFs and COFs as CO₂ adsorbents lie in their chemical tunabilities that improve interactions with the gaseous molecule. These interactions are mostly between CO₂ and open metal sites (in MOFs) and/or Lewis basic sites. Exploration of these interactions has precipitated magnificent adsorption capacities and selective CO₂ capture in the presence of N₂, CH₄, and H₂O, among others. Furthermore, given the challenges involved with the introduction of certain functional groups into framework materials by *de novo* syntheses, various post-synthetic strategies have been developed. Large-scale application of MOFs and COFs to CO₂ capture remains subject to research to address further improvements of selectivity in the presence of water or acidic gases. It is incumbent upon researchers to choose the appropriate porous material for the desired performance.

The work in this dissertation describes the synthesis and characterization of new metal-organic framework (MOF) and covalent organic framework (COF) materials designed to assist in ushering in the next phase of development of porous materials for CO₂ capture applications. In presenting the design of these systems, I detail the complexity with which their constituent components must be considered. I stress the importance of this because the nature and crystallographic orientation of the organic moieties (typically alkylamines) used to chemisorb CO₂ plays a critical role in their framework chemistry with CO₂. I have also detailed extensive efforts to elucidate such chemistry, giving examples of framework-based alkylamines reacting with CO₂ to form carbamic acids, ammonium carbamates, and ammonium bicarbonates under a variety of conditions. Specifically, I have demonstrated that humidity plays a large role in the chemisorption product distribution in three newly-developed framework materials, IRMOF-74-III-(CH₂NH₂)₂, COF-81, and MOF-808-Glycine. I have also placed these new materials in the broader context of porous CO₂ adsorbents, highlighting their specific advantages and disadvantages.

To conclude, I caution the reader that none of the materials presented in this dissertation should be viewed as a “magic bullet” with which atmospheric CO₂ concentrations will be drastically and immediately reduced. Indeed, no current evidence would support a claim that one singular material exists that is capable of addressing the CO₂ problem and/or anthropogenic climate change. Instead, the work presented here should serve as a guideline and a starting point for future researchers. It is imperative that efforts to augment selective CO₂ capture focus on chemisorptive reactions. In studying reticular chemistry, I have stumbled upon an avenue by which to precisely probe and understand such reactions. In reviewing the work in this dissertation, it is likely that ideas regarding the development of future materials in which chemisorptive CO₂ reactions can be finely tuned will emerge. It is my sincerest hope that the understanding provided in this dissertation will prove useful as large-scale implementation of porous materials for CO₂ capture is brought to fruition in the coming years.