

Design and Synthesis of Ultramicroporous Zinc-azolate-based MOFs for Selective CO₂ Capture

विद्या वाचस्पति की
उपाधि की अपेक्षाओं की आंशिक पूर्ति में प्रस्तुत शोध प्रबंध

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Indian Institute of Science Education and Research, Pune
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Dedicated to

My Father

Late Dr. Ravindra Nath Singh



CERTIFICATE

Certified that the work incorporated in the thesis entitled “*Design and Synthesis of Ultramicroporous Zinc-azolate-based MOFs for Selective CO₂ Capture*” submitted by **Piyush Singh** was carried out by the candidate, under my supervision. The work presented here or any part of it has not been included in any other thesis submitted previously for the award of any degree or diploma from any other university or institution.

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I declare that this written submission represents my idea in my own words and where others' ideas have been included; I have adequately cited and referenced the original sources. I declare that I have acknowledged collaborative work and discussions wherever such work has been included. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that violation of the above will be cause for disciplinary action by the Institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.

The work reported in this thesis is the original work done by me under the guidance of Dr/Prof. R. Vaidhyanathan.

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Date: 07-08-2025

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Synopsis

Global warming remains a significant challenge, primarily caused by greenhouse gases such as CO₂, CH₄, and N₂O, which trap heat in the atmosphere. Since the industrial revolution, CO₂ levels have risen from approximately 270 ppm to 424 ppm due to human activities, leading to rising temperatures, glacier melts, and extreme weather events. Carbon Capture and Storage (CCS) has emerged as a crucial strategy to mitigate these effects. While conventional CO₂ capture relies on energy-intensive liquid amines, solid sorbents such as zeolites, porous carbons, silica gels and metal organic frameworks (MOFs) offer more efficient alternatives. MOFs gain a special interest owing to their easy structural and chemical designability. Many MOFs have been investigated for carbon capture; of these, the ultramicroporous (< 6 Å) ones are quite effective. CALF-20, an ultramicroporous Zn-triazolato-oxalate MOF, has been demonstrated at industrial scale to capture multi tons of CO₂ per day from flue gas. Its strong metal–ligand bonds, high selectivity and steam stability make it a promising candidate for humid CO₂ separation. However, CALF-20's pore space limits further enhancement of its intrinsic capacity and also its capture capacity at extremely low CO₂ pressures is insufficient. In this thesis we focus on developing design principles for zinc-azolate MOFs to achieve superior CO₂ capture characteristics. Also, adhering to simple gram-scale synthesizability as a key requirement. Thus the thesis contributes to the development of next-generation MOFs with enhanced low-pressure CO₂ capture is essential in supporting global decarbonization efforts.

Chapter 1: Introduction

Global warming, caused by the continuous rise in atmospheric greenhouse gases, has become a critical threat to our planet, with global surface temperatures increasing by approximately 1.4 °C from 1880 to 2024. Alarmingly, 2024 marked the first year the average temperature rise crossed the 1.5 °C limit set by the Paris Agreement. Among greenhouse gases, CO₂ is the most significant contributor due to its high concentration and long atmospheric lifetime, primarily emitted from the power and industrial sectors. To mitigate these emissions, Carbon Capture and Storage (CCS) is considered a promising approach, though its current implementation is limited by the high energy

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demand of traditional amine-based capture systems. Solid adsorbents, particularly



those relying on physisorption, offer a more energy-efficient alternative, with Metal–Organic Frameworks (MOFs) emerging as leading candidates due to their tunable porosity, high surface area, and chemical versatility. Recent studies highlight that ultra-microporous MOFs (pore size < 6 Å) exhibit remarkable potential for CO₂ separation under practical conditions, as exemplified by CALF-20, a zinc–triazole–oxalate-based MOF. Building on this progress, this thesis focuses on the design and development of new zinc–triazolate ultra-microporous MOFs with an emphasis on scalable synthesis, hydrolytic stability, and efficient CO₂ capture under low partial pressures and humid environments.

Chapter 2: Structure-Property Discernments from a Hydrophobic Zinc-Diaminotriazole-Formate Metal Organic Framework (MOF) Exhibiting Superior CO₂/H₂O Binary

Efficient and selective capture of CO₂ under humid conditions is essential for the development of practical carbon capture technologies. Ultramicroporous metal–organic frameworks (MOFs) are particularly promising due to their strong host–guest interactions, which enhance CO₂ selectivity. A well-known example is CALF-20, a Zn–triazolate-based ultramicroporous MOF that has demonstrated excellent CO₂ capture performance; however, its uptake significantly decreases beyond 40% relative

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humidity (RH), limiting its use in higher humidity environment. To address this limitation, we report the synthesis and characterization of a new MOF, IISERP-MOF16 (Zn-Damtz-Formate)), featuring a formate-pillared layered structure with 3,5-diamino-1,2,4-triazole (Damtz) linkers. This framework, synthesized via a solvothermal method on a gram scale, is structurally analogous to CALF-20 but incorporates diamino basic functional groups and formate linkers to enhance hydrophobicity and CO₂ affinity. Gas adsorption studies reveal that IISERP-MOF16 exhibits a acceptable CO₂ uptake of 40.2 cm³/g at 298 K and 1 bar, with a moderate isosteric heat of adsorption (Q_{st}) of 32 kJ mol⁻¹ and an IAST-predicted CO₂/N₂ selectivity of 67 for a 15:85 (v/v) mixture. Importantly, dynamic vapor sorption measurements indicate that IISERP-MOF16 retains over 20% of its initial CO₂ uptake at 70% RH, a level at which CALF-20 shows negligible adsorption. The material also demonstrates excellent stability, recyclability, and easy regeneration under various conditions, aligning well with industrial requirements. This study highlights a rational design strategy for developing MOFs with enhanced performance in humid environments. (Figure 1).

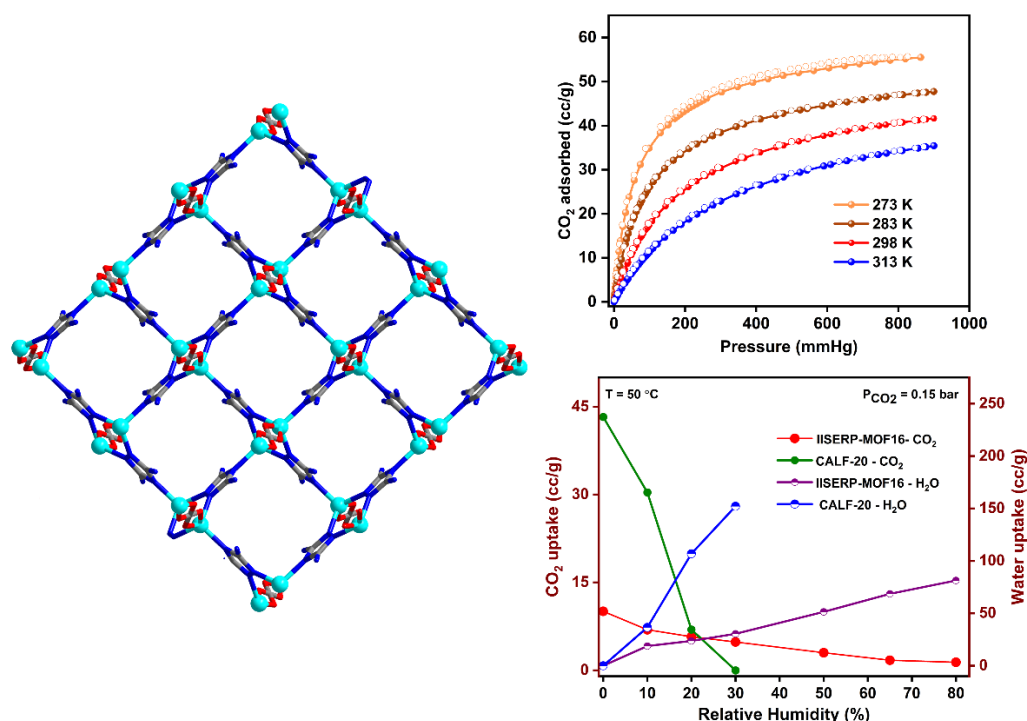


Figure 1: Crystal structure of IISERP-MOF16, CO₂ adsorption isotherms at different temperatures, and competitive CO₂-H₂O adsorption behavior.

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Chapter 3: Preferential CO₂ adsorption by an ultra-microporous 3D zinc-aminotriazolato-acetate MOF

Ultramicroporous MOFs enable tight packing of the active functional groups, directly impacting the selective guest–framework interactions. MOFs with pores simultaneously lined by methyl and amine may serve as the ultimate humid CO₂ sorbent. However, structural complexity prevents taking full advantage even in a simple zinc-triazolato-acetate layered-pillared MOF (Figure 2).

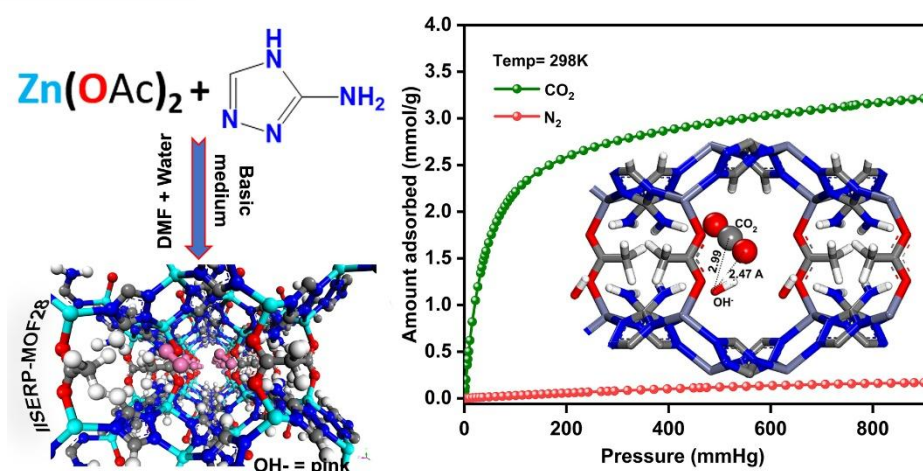


Figure 2: Synthetic route to IISERP-MOF28, its single-crystal structure, gas adsorption isotherms at 298 K, and the positioning of CO₂ molecules within the pores as revealed by computational modeling.

Chapter 4: CO₂-specific gate opening transforms a dense cation-filled zinc-aminotriazolato-oxalate framework into an ultra-microporous MOF

CALF-20, a zinc-triazolato-oxalate MOF, $[\text{Zn}_2(\text{tz})_2(\text{Ox})]\cdot\text{solvent}$, is an industrially practiced ultramicroporous MOF sorbent. In CALF-20, some interesting structural transformations occur during its humid CO₂ capture. Even though its structure is simple, the design of superior sorbents based on its structure is still not straightforward. Hence, a broader investigation of these Zn-triazolato-oxalate frameworks with a new outlook is necessary. Herein, we report a Zn-aminotriazolato-oxalate MOF (**IISERP-MOF35**, $[(\text{CH}_3)_2\text{NH}_2]_2[\text{Zn}_5(\text{Atz})_4(\text{Ox})_4]\cdot 2\text{H}_2\text{O}$), which has a unique framework that does not resemble the ubiquitous layered-pillared topology prevalent among CALF-20 and related zinc-triazolato-oxalate systems. The **IISERP-**

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MOF35's CO₂-specific gate opening at lower partial pressures makes it intriguing. Comparing it to our earlier reported flexible Zn-aminotriazolato-oxalate MOF (**IISERP-MOF32**), [Zn₂(Atz)₂(Ox)]·solvent, which had a CALF-20-like layered-pillared topology, reveals valuable structure–property insights. Despite its markedly different structures and compositions, this new dense 3D framework has the same structural feature as that in the layered-pillared **IISERP-MOF32**, which is responsible for the gate opening. Further comparison with the existing frameworks in this system advocates that the structural motif identified here could help in the futuristic design of creating open frameworks predesigned for guest-assisted flexibility ([Figure 3](#)).

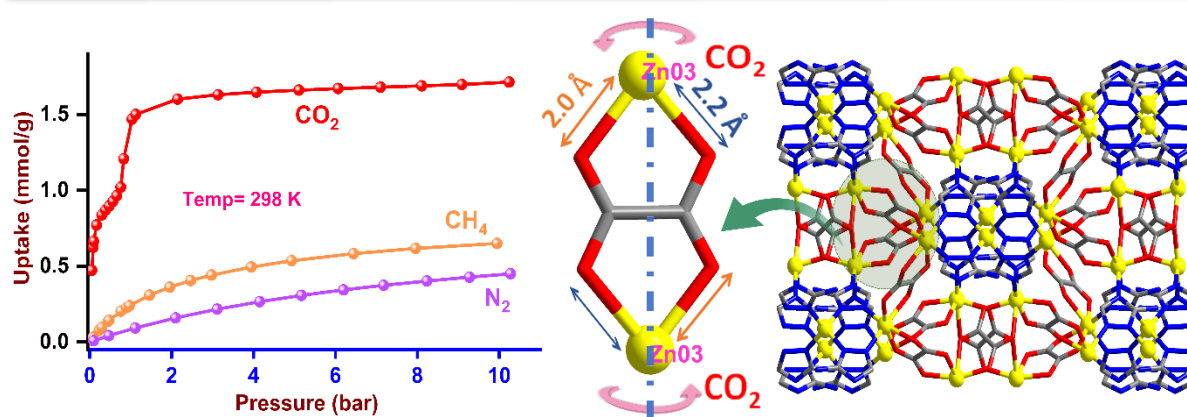


Figure 3: Crystal structure of **IISERP-MOF35** showing diagonally positioned, slightly elongated Zn–O bonds that facilitate CO₂-specific spindle-like rotation of oxalate units, leading to gate-opening behavior observed in gas adsorption isotherms.

Chapter 5: Ultra-Microporous Zinc-Diaminotriazolate-Oxalate Metal Organic Framework with Nonlayered-Pillared Structure Showing High Carbon Dioxide Uptakes at Low Partial Pressures

We report a zinc-diaminotriazolato-oxalate metal–organic framework (**IISERP-MOF36**, **1**) inspired by the exceptional CO₂ selectivity demonstrated by its triazolate analogue, CALF-20. Unlike the CALF-20 family, **1** adopts a nonlayered, pillared structure, despite their similar composition. The 1D ultramicroporous channels in this MOF enhance strong interactions with the carbon dioxide CO₂. Additionally, the t-shaped orientation of CO₂ molecules within the pores promotes cooperative CO₂–CO₂ interactions, resulting in superior low-pressure CO₂ uptake compared to that of

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CALF-20. This suggests that **1** has potential as a sorbent in applications such as the natural gas combined cycle or direct air capture. However, despite its structural and compositional similarities to CALF-20, **1** exhibits reduced hydrophobicity due to subtle differences in the pore environment. These findings open possibilities for designing advanced sorbents combining the best characteristics of both of these MOFs ([Figure 4](#)).

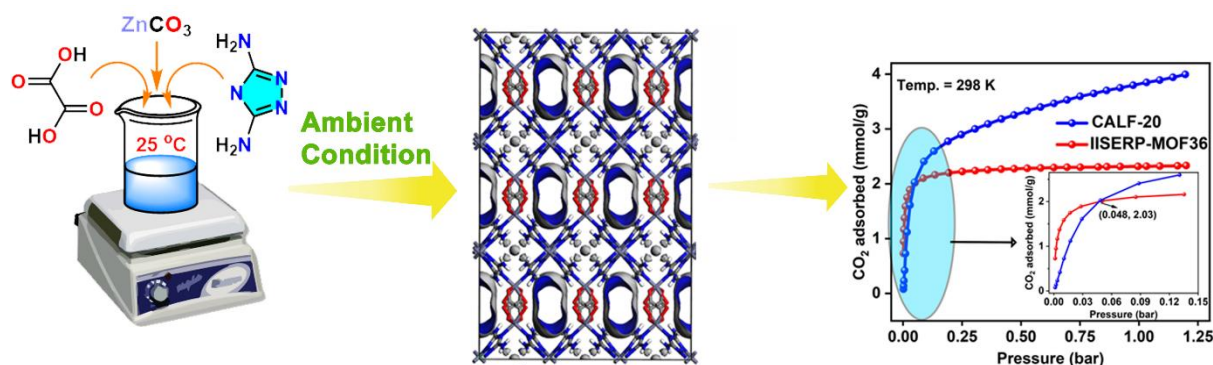


Figure 4: Synthesis scheme of IISERP-MOF36 under ambient conditions and its crystal structure featuring narrow channels, which exhibit a sharp CO₂ uptake at low partial pressures compared to CALF-20.

Abbreviation

Abbreviation	Full Name
Å	Angstrom
AcOH	Acetic Acid
ACN	Acetonitrile
Atz	3-amino-1,2,4-triazolate
B.E.	Binding Energy
BET	Brunauer–Emmett–Teller
CIF	Crystallographic Information File
CCS	Carbon Capture and Storage
Datz	3,5-amino-1,2,4-triazolate
DAC	Direct air capture
DCM	Dichloromethane
DFT	Density Functional Theory
DMF	Dimethylformamide
DSC	Differential Scanning Calorimetry
DSL	Dual Site Langmuir
FWHM	Full Width at Half Maximum
G	Gram
GCMC	Grand Canonical Monte Carlo
HCl	Hydrochloric Acid
HOA	Heat of Adsorption
IAST	Ideal Adsorption Solution Theory
FT-IR	Fourier Transform Infrared Spectroscopy
K	Kelvin
MD	Molecular Dynamics
MeOH	Methanol
mg	Milligram
min	Minutes
mmol	Millimoles
MSD	Mean Square Displacement
NLDFT	Non-local Density Functional Theory
PSA	Pressure Swing Adsorption
PXRD	Powder X-Ray Diffraction
RDF	Radial Distribution Function
RH	Relative Humidity
RT	Room Temperature
SCXRD	single-crystal X-ray diffraction
Sp. Gr.	Space Group
SSL	Single Site-Langmuir
TGA	thermogravimetric analysis (TGA)
THF	Tetrahydrofuran
Tz	1,2,4-triazolate
Um-MOF	Ultra-microporous Metal Organic Framework
VT	variable temperature

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Chapter 3

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Chapter 4

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Chapter 5

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Publications

Included in the Thesis:

1. [Piyush Singh](#), Checkers R. Marshall, Himan Dev Singh, Pragalbh Shekhar, Chitvan Jain, Yashraj Kumar Singh and Ramanathan Vaidhyanathan, Structure-Property Discernments from a Hydrophobic Zinc-Diaminotriazole-Formate Metal Organic Framework (MOF) Exhibiting Superior CO₂/H₂O Binary (Manuscript under preparation).
2. [Piyush Singh](#), Himan Dev Singh, Abhijith Hari Menon and Ramanathan Vaidhyanathan, Preferential CO₂ adsorption by an ultra-microporous zinc-aminotriazolato-acetate MOF, *Chem. Commun.*, **2023**, 59, 5559-5562.
3. [Piyush Singh](#), Himan Dev Singh, Pragalbh Shekhar, Praveen Nasa, Deepak Rase, Chitvan Jain, Yashraj Kumar Singh, and Ramanathan Vaidhyanathan, CO₂-Specific Gate Opening Transforms a Dense Cation-Filled Zinc Aminotriazolato-Oxalate Framework into an Ultramicroporous MOF, *Cryst. Growth Des.*, **2024**, 24, 8838–8846.
4. [Piyush Singh](#), Himan Dev Singh, Pragalbh Sekhar, Chitvan Jain, Ping Song, Mahsa Loloei, Michael Edwin, Yan Gao, Nima Mousamifaid and Ramanathan Vaidhyanathan, An Ultra-Microporous Zinc-Diaminotriazolate-Oxalate MOF with Non-layered-pillared Structure Showing High CO₂ Uptakes at Low Partial-pressures Synthesized under Ambient Condition, *Chem. Mater.*, **2025**, 37, 2496–2505.

Not included in the Thesis:

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Chapter 1

**Introduction to Carbon Capture and
Metal Organic Frameworks (MOFs)
for the CO₂ Capture**

1.1 Introduction

Global warming presents a major challenge to Earth's climate stability, driven largely by the greenhouse effect, a process where certain gas molecules trap heat that would otherwise escape into space.¹ When sunlight reaches Earth, it's absorbed and re-emitted as infrared radiation. Among these greenhouse gases, carbon dioxide (CO₂) is the most significant contributor to climate change due to its high concentration and long atmospheric lifetime.^{2,3} Although other gases like methane (CH₄), chlorofluorocarbons (CFCs) and nitrous oxide (N₂O) also contribute to the greenhouse effect, their overall impact is relatively lower because they are present in much smaller amounts.⁴ Since the onset of the Industrial Revolution, atmospheric CO₂ levels have risen dramatically from about 270 parts per million (ppm) to approximately 424 ppm in 2023 mainly as a result of anthropogenic emission including the burning of fossil fuels, deforestation, and industrial operations. The elevated concentration of CO₂ in the atmosphere is a major driver of global warming, leading to accelerated glacier melt, rising global temperatures, and an increased frequency of extreme weather phenomena, issues that have become a growing concern worldwide.^{1,4,5,6,7} In response to these climate challenges, the Paris Agreement sets a target to restrict global temperature rise to well below 2°C, with an aspirational limit of 1.5°C. Achieving this objective necessitates significant reductions in greenhouse gas emissions and reaching net-zero emissions by the year 2050.^{8,9} Achieving these targets demands comprehensive decarbonization of both energy and industrial sectors. According to the International Energy Agency's 2022 report, global CO₂ emissions reached 36.3 gigatonnes (Gt) in 2021,⁵ with the power sector emitting 14.3 Gt and the industrial sector 9.3 Gt together responsible for about 65% of total emissions (Figure 1.1). The coal-fired plants contribute around 10.5 Gt in 2021.^{10,11} To address these challenges, carbon capture and sequestration (CCS) technologies are essential, allowing CO₂ emissions from coal plants and other industrial sources to be effectively captured and stored, supporting global efforts to reduce emissions and mitigate climate change.¹²⁻

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1.2 What is CCS

One crucial technology for lowering greenhouse gas emissions and halting climate change is carbon capture and storage, or CCS. It functions by absorbing carbon

dioxide (CO₂) emissions from energy production and industrial processes and keeping them from escaping into the environment. The three main steps of the CCS process are capture, transport, and storage.

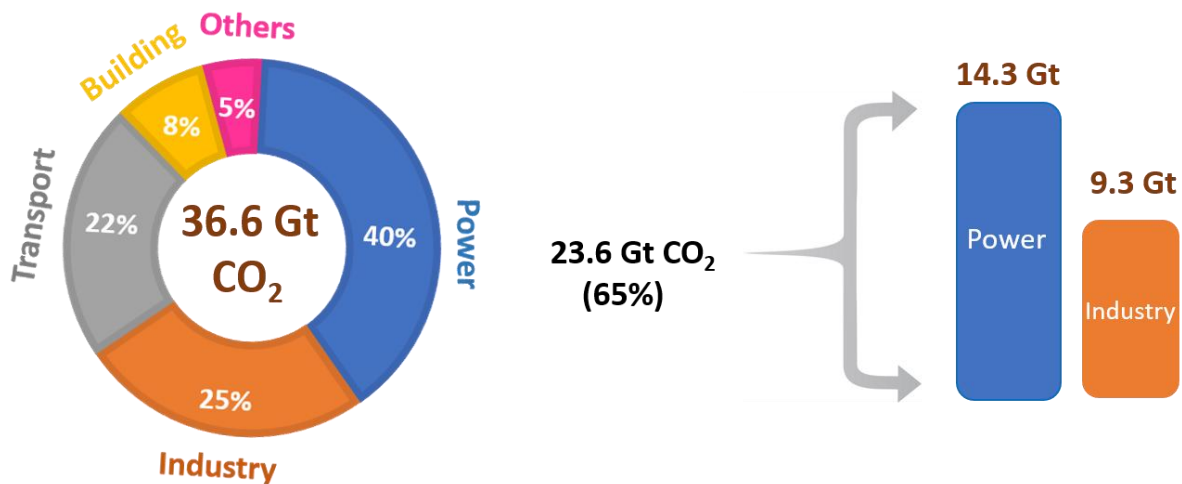


Figure 1.1 Global CO₂ emissions in 2021 totalled 36.6 Gt, with the power and industrial sectors collectively responsible for 65% of total Gt CO₂ emissions.

In the capture phase, CO₂ present in the flue gas is separated from other gases emitted by major sources such as coal and natural gas power plants, as well as industrial facilities like cement and steel production. After capture, the CO₂ is compressed for efficient transport, typically through pipelines, to designated storage locations. The final step involves injecting the compressed CO₂ deep underground into geological formations¹⁵ where it can be securely stored for long periods, effectively isolating it from the atmosphere geo-sequestration.

1.2.1 Challenge associated with CCS

Although Carbon Capture and Storage (CCS) technology is considered one of the most effective methods for mitigating carbon dioxide (CO₂) emissions^{4,15,16} it faces several significant challenges that hinder its widespread adoption. One of the primary obstacles is the high cost of implementation.¹⁷⁻¹⁹ The expenses associated with capturing CO₂ from point sources, such as power plants and industrial facilities, remain

substantial due to the energy-intensive processes required for capturing, transporting, and storing CO₂.^{15,17,18,19} This financial burden can make many CCS projects economically unviable without supportive policies or market incentives.¹⁹ Another challenge is the limited scale of CCS deployment.¹⁸⁻¹⁹ Currently, there are only about 30 operational CCS facilities worldwide, with a combined capacity to capture approximately 42.6 million tonnes per annum (mtpa) of CO₂, which accounts for merely 0.1% of global annual CO₂ emissions estimated at 36 gigatonnes per annum (gtpa). Despite the first CCS projects being initiated in the 1970s and 1980s, the pace of large-scale implementation has been very slow.^{10,11} The International Energy Agency (IEA) has indicated that to effectively address global decarbonization goals, approximately 6.2 gigatonnes of CCS capacity will need to be operational by 2050.¹¹ Given the current scale of deployment, significant acceleration in CCS implementation is essential to make a meaningful contribution to reducing global emissions.^{18,19}

1.2.2 Current trends in CCS

Despite present obstacles including high costs and limited large-scale deployment, carbon capture and storage (CCS) has a bright future. Recent years have seen tremendous advancements, particularly in the creation of cutting-edge materials like metal-organic frameworks, porous polymers, zeolites and ionic liquids, which are intended to increase capture efficiency and lower prices.²⁰⁻²² Since CO₂ capture alone accounts for nearly 70% of the total CCS cost²¹. Although the projected figure is expected to decrease with future materials optimization, there are significant practical considerations associated with other steps in a Carbon Capture and Storage (CCS) system. For instance, the quantities of CO₂ captured are too large for reuse by any chemical industry, making the sustainable storage of CO₂ essential for the successful development of CCS. Thus, improving the capture step is essential, to reduce expenses by lowering the overall energy penalty associated with the process. An efficient capture process can significantly reduce the energy required for CO₂ separation, making CCS more viable on a large scale. Researchers are also exploring innovative storage methods, such as deep saline aquifers and basaltic rocks, which can securely store CO₂ and convert it into stable carbonates.^{23,24}

1.3 Methods for CO₂ capture: Carbon dioxide (CO₂) capture strategies are generally grouped into three major categories based on the point of origin of the gas being captured. These are:

1. Post-combustion capture, which involves removing CO₂ from the exhaust gases produced after burning fossil fuels.
2. Pre-combustion capture, where CO₂ is extracted from fuel gases before combustion, often during the gasification of coal or reforming of natural gas.
3. Direct air capture (DAC), a method that captures CO₂ directly from the atmosphere, even at very low concentrations.

1.3.1 Post-Combustion Carbon Capture Process

Post-combustion carbon capture is a widely used method for separating carbon dioxide (CO₂) from flue gas generated by burning fossil fuels such as coal, natural gas, or oil in power plants and industrial facilities. Flue gas typically contains about 10-15% CO₂, 80–85% nitrogen (N₂), along with small amounts of water vapor and trace pollutants like sulfur oxides (SO_x) and nitrogen oxides (NO_x).^{7,15,25,26,27,28} One of the key advantages of this approach is that it can be retrofitted to existing infrastructure with minimal changes to the combustion system.²⁹ Before the capture process begins, the flue gas passes through air pollution control units that remove acidic components such as SO_x and NO_x. It is then treated with scrubbers and electrostatic precipitators to eliminate moisture and fine particulates, which could otherwise degrade the performance of the capture solvents.^{30,31} Chemical absorption is the predominant method used in most post-combustion carbon capture systems for industrial power plants, with amine-based scrubbing emerging as the most widely adopted technique for capturing CO₂.^{7,26, 32,33} The cleaned gas consisting mostly of nitrogen and about 15% CO₂ enters an absorber column containing amine-based solvents like monoethanolamine (MEA), which chemically react with CO₂. The resulting CO₂-rich solvent is then directed to a regeneration unit, where heat is applied to release the captured CO₂ and regenerate the solvent (Figure 1.2). The purified CO₂ is cooled, dried, and compressed for either geological storage³⁴ or industrial use, such as

enhanced oil recovery, while the regenerated solvent is recycled back to the absorber to maintain continuous operation.

Although this technology is mature and scalable, challenges remain, including the high energy demand for solvent regeneration, equipment corrosion due to the chemical solvents, and solvent degradation over time.³⁵ To mitigate these issues, solid sorbents have emerged as a promising alternative, relying on physical adsorption with weaker CO₂ interactions that allow easier and less energy-intensive regeneration.^{35,37} Zeolites such as 13X are commonly employed in pressure swing adsorption systems for gas purification because of their thermal stability, low corrosiveness, and high CO₂ selectivity.^{38,39,40} However, their strong affinity for water vapor limits performance under humid conditions and necessitates regeneration at elevated temperatures, increasing operational costs.³⁶ Despite these limitations, solid sorbents present an energy-efficient and durable option for post-combustion CO₂ capture.

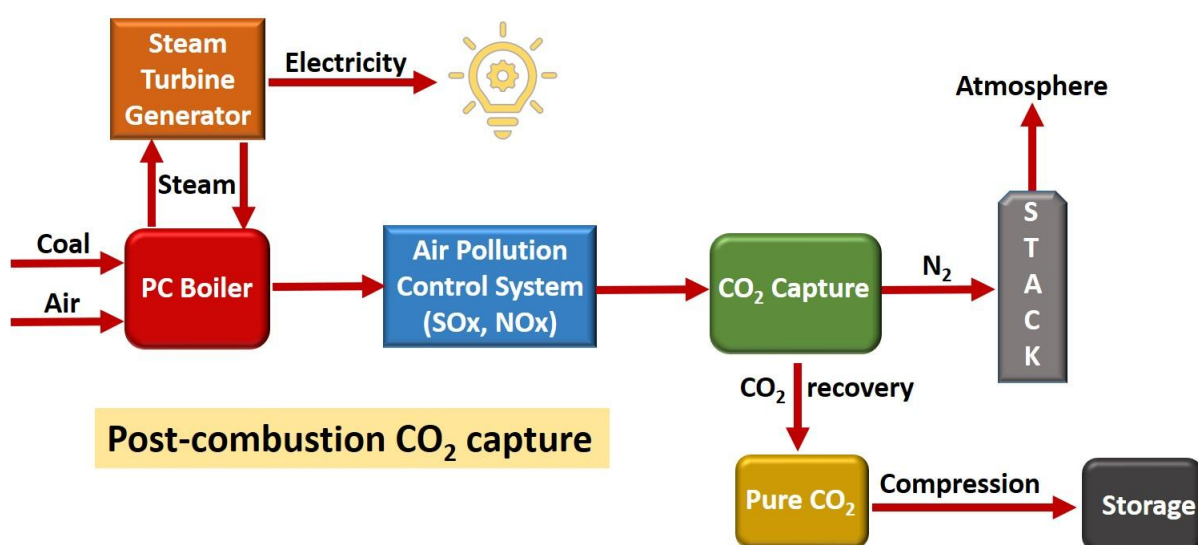


Figure 1.2: Schematic of a post-combustion CO₂ capture system for fossil fuel-based power generation

1.3.2 Pre-Combustion Carbon Capture Process

Pre-combustion carbon capture is a technique that involves removing carbon dioxide (CO_2) from fuel sources like coal or biomass before they are burned to generate energy.⁴¹ This is commonly done through a process called gasification, where the fuel is partially oxidized with steam and oxygen (or air) at high temperatures and pressures, producing a synthesis gas (syngas) that mainly contains hydrogen (H_2) and carbon monoxide (CO), along with some CO_2 and other gases (Figure 1.3).⁴²⁻⁴⁴ The syngas is then treated with steam in a water-gas shift reaction, converting CO into additional H_2 and CO_2 .⁴⁵ This results in a gas mixture rich in hydrogen and carbon dioxide, typically around 60% H_2 and 40% CO_2 . To make use of hydrogen as a clean fuel, CO_2 must be effectively separated from this mixture.^{46,47} Pressure swing adsorption (PSA), which employs porous materials like zeolites or activated carbon to selectively collect CO_2 under high pressure, is one of the most popular techniques in industry for this separation.⁴⁸⁻⁵¹ After CO_2 is removed, the remaining hydrogen can be used directly as a fuel or stored for future applications, such as in fuel cell vehicles. This process not only supports cleaner energy production but also helps in reducing greenhouse gas emissions.

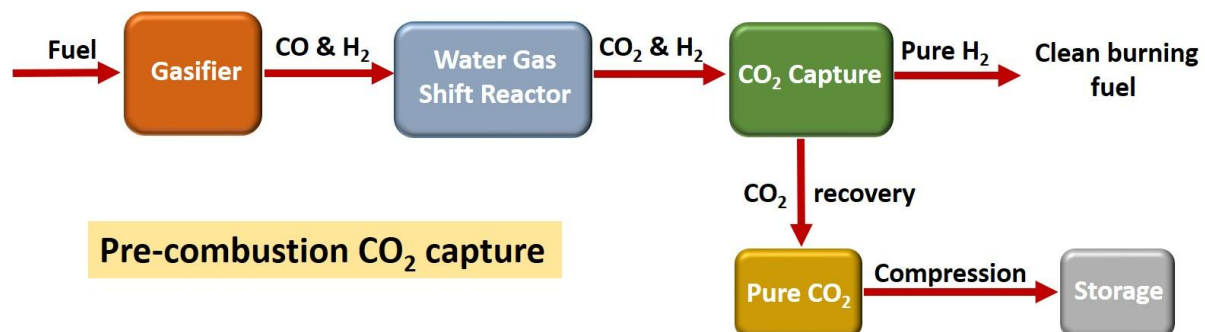


Figure 1.3: Schematic illustration of the pre-combustion CO_2 capture process, where CO_2 is removed from syngas before combustion.

1.3.3 Direct Air Capture Process

Direct Air Capture (DAC) is a carbon removal technology that extracts carbon dioxide (CO_2) directly from ambient air rather than from point sources like power plants.^{52,53} Originally proposed by Lackner in 1999, DAC has become an important tool for

achieving net-zero emissions⁵⁴. It operates by passing large volumes of air through systems equipped with solid or liquid sorbents that selectively capture CO₂, which can then be compressed, stored underground, or used in chemical processes or fuel synthesis (Figure 1.3). One key benefit of DAC is its geographical flexibility it

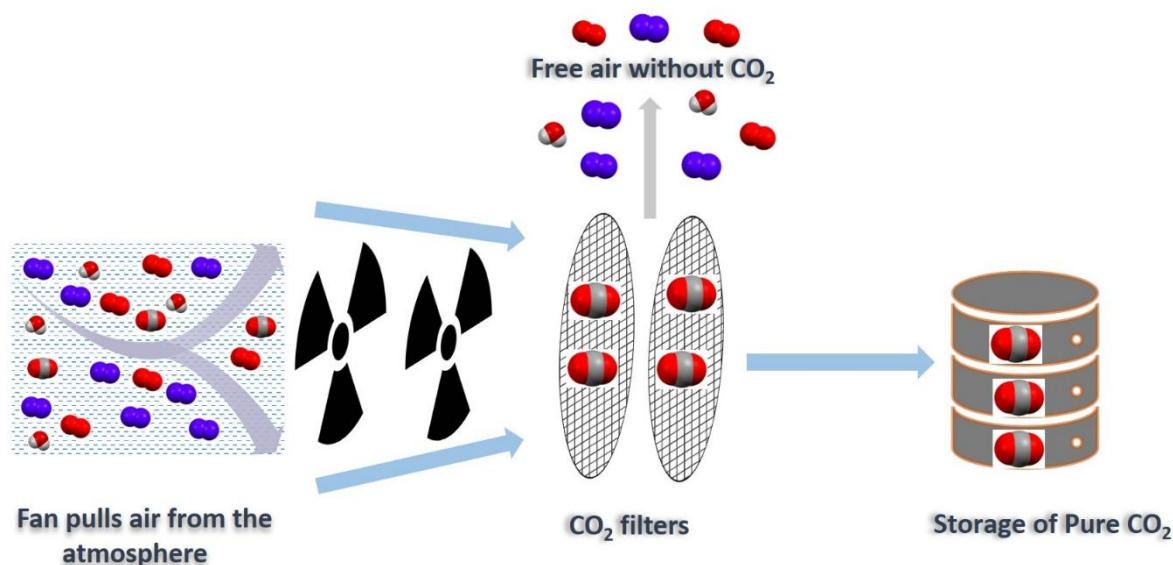


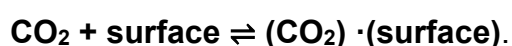
Figure 1.3: Schematic representation of a direct air capture (DAC) system for atmospheric CO₂ removal.

can be deployed in various locations since ambient air is relatively clean compared to industrial emissions, containing fewer acidic gases like NO_x and SO_x.^{55,56} However, DAC systems need sorbents with good selectivity and absorption at low partial pressures because of the low atmospheric concentration of CO₂ (~400 ppm). High CO₂ capacity, superior selectivity over N₂ and O₂, moisture and thermal stability, quick kinetics, ease of handling, and regeneration under moderate conditions are all characteristics of the perfect sorbent.^{52,57,58} While amine-functionalized materials show promise, physisorbents such as zeolites and MOFs often exhibit lower performance under these dilute and humid conditions.⁵⁵ DAC is also energy-intensive; capturing CO₂ from air requires about 19-22 kJ/mol, nearly four times more energy than post-combustion capture (4.6-5.6 kJ/mol) from flue gas containing 10-15% CO₂.⁵⁹ As of now, there are 18 DAC facilities worldwide, collectively capturing only about 0.01

million tonnes of CO₂ per year, underscoring that the technology is still in its infancy and remains costly, estimated at 2-6 times above the target of USD 100 per tonne of CO₂ removed.⁶⁰ On going research is focused on lowering costs through better contactor designs, improved sorbents, and efficient regeneration strategies. Mobile DAC units powered by renewable energy are also being explored to increase scalability and reduce the overall carbon footprint.⁶⁰

1.4 Solid Sorbents for Carbon Capture

Capturing carbon dioxide from flue gas mixtures can be effectively accomplished using solid porous materials through the physisorption process. This approach relies on weak intermolecular forces such as van der Waals interactions, hydrogen bonding, and dipole–dipole attractions which allow CO₂ molecules to reversibly adhere to the surface of the sorbent.⁶¹ The interaction can be expressed by the equilibrium:



The overall capture process involves two fundamental steps: the adsorption of CO₂ onto the sorbent and its subsequent desorption during regeneration. These two steps together complete one full CO₂ capture cycle. To maintain continuous operation and minimize energy usage, various cyclic regeneration techniques have been implemented, including Pressure Swing Adsorption (PSA), Vacuum Swing Adsorption (VSA) and Temperature Swing Adsorption (TSA). Solid sorbents have gained increasing attention as an alternative to traditional liquid amine-based absorbents due to several favourable attributes. These include lower energy requirements for regeneration, ease of handling, higher adsorption efficiency, better selectivity for CO₂, and a smaller environmental footprint.⁶²⁻⁶⁴ For this purpose, a variety of porous materials have been investigated, including metal-organic frameworks (MOFs), covalent-organic frameworks (COFs), hydrogen-bonded organic frameworks (HOFs), activated carbons, zeolites, porous polymers, and molecular cages.⁶²⁻⁶⁴ However, several of these materials have constraints such as lower stability in humid or oxygen-containing environments and limited CO₂ selectivity in the presence of other gases.^{62,65} Among them, MOFs stand out due to their high surface areas, tunable pore structures, and the possibility of incorporating functional sites that enhance CO₂

adsorption.^{65,66} Current research is focused on improving both the moisture resistance and selectivity of these materials to assure their efficacy in real industrial situations.

1.5 Brief Introduction to MOF

Metal–Organic Frameworks (MOFs), are an emerging class of crystalline porous materials composed of metal ions or clusters coordinated to multifunctional organic ligands.^{67,68} These hybrid networks are characterized by their exceptionally high surface areas, well-defined porosity, and structural modularity.⁶⁸ The rational selection of metal nodes and organic linkers allows for the systematic tuning of pore size, shape, and chemical functionality (Figure 1.4), enabling their deployment in a wide range of applications including gas storage^{69–84}, gas separations^{85–96}, water harvesting^{97–101}, heterogeneous catalysis^{102–111}, chemical sensing^{112–116}, proton conductivity^{117–127} and targeted drug delivery^{128–132}. The inherent crystallinity of MOFs facilitates detailed structural elucidation through single-crystal or powder X-ray diffraction techniques, offering insights into their topological diversity and functional characteristics.⁶⁷ In 2025, the Nobel Prize in Chemistry was awarded to **Prof. Susumu Kitagawa**, **Prof. Richard Robson**, and **Prof. Omar M. Yaghi** for the development of metal-organic frameworks, highlighting the profound impact of MOF research and reticular chemistry on modern materials science. Unlike traditional porous solids such as zeolites, MOFs exhibit superior design flexibility due to the broad spectrum of available metal ions (e.g., Zn^{2+} , Cu^{2+} , Al^{3+} , Cr^{3+}) and organic linkers bearing carboxylate, azolate, or phosphonate functionalities.¹³³ As a result, over 100,000 unique MOF structures have been reported in the Cambridge Structural Database, underscoring the rapid expansion of this field. Synthetic methodologies such as solvothermal, microwave-assisted, mechanochemical, and sonochemical techniques have been extensively employed to obtain MOFs with controlled particle size, morphology, and crystallinity.¹³⁴

Tunable pore size is one of the most important properties of different MOFs. Based on pore dimensions, MOFs can be broadly categorized into ultra-microporous (<6 Å), microporous (6–20 Å), and mesoporous (>20 Å) frameworks.^{67,68} Among these, ultra-microporous MOFs have gained particular interest for selective CO_2 capture due to their ability to discriminate between CO_2 and larger gas molecules like N_2 via size-exclusion and strong host–guest interactions. Despite their great potential, a major

challenge in using MOFs for selective CO₂ capture from flue gas or low-concentration sources lies in developing cost-effective materials that are stable under humid condition, varying pH, and reusable over multiple cycles, while also being scalable.

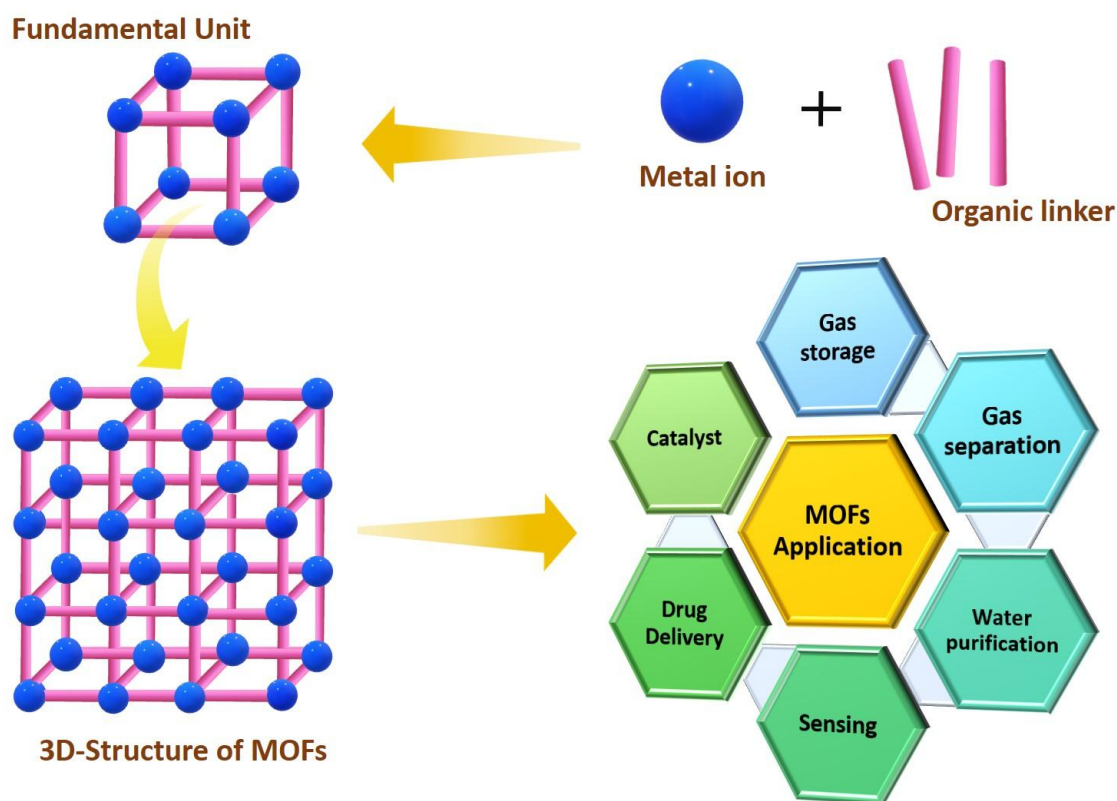


Figure 1.4: Schematic representation of MOF construction and their key application.

While CALF-20 is a notable example, its limited performance under high humidity highlights the continued need to design MOFs that meet all these criteria. Some of the important ultra-microporous MOFs having potential in industrial carbon capture applications have been discussed below.

1.6 CO₂ Capture Using Ultra-Microporous MOFs

Ultra-microporous metal–organic frameworks (Um-MOFs), defined by pore apertures below 6 Å, have attracted considerable interest as solid sorbents for selective CO₂ capture.^{37,85,94,95,135,136} Their narrow pores impart molecular sieving features and

enable improved interactions between the framework and guest molecules, especially CO₂, which has a small kinetic diameter and a significant quadrupole moment.^{93,137,138} These interactions result in high selectivity and adsorption efficiency, making Ultra-Microporous MOFs an ideal candidate for selective CO₂ capture from a mixture of gases. Over the past decade, a wide variety of Um-MOFs have been reported, many of which have been studied for CO₂ capture applications.^{37,85,92-95,136} Among these Um-MOFs, azolate-based metal-organic frameworks (MOFs) are of significant interest due to the ability of nitrogen-rich azole ligands to strongly coordinate with metal ions such as Zn, Co, Ni, Mn, and Fe via sp²-hybridized nitrogen atoms. Upon deprotonation, these ligands generate azolates that enable the construction of stable, multidimensional frameworks. Ultramicroporous azolate MOFs (Um-MOFs) are particularly promising for gas separation applications, owing to their structural rigidity, high stability, and strong metal-ligand interactions. Their compact design promotes the creation of ultramicroporous networks, boosting CO₂ collection through size exclusion and electrostatic interactions.^{37,93, 139-142} The success of CALF-20, a zinc triazolate-oxalate ultramicroporous framework, has further demonstrated the practical viability of this approach. CALF-20 represents the first MOF to be scaled for industrial CO₂ capture by Svante, owing to its excellent cycling stability, moisture resistance, and selective CO₂ adsorption.³⁷ Motivated by this success, in this thesis, our focus was to design and synthesize new azolate-based Um-MOFs with a combination of short linkers like oxalic acid, acetate and formate group. In the following sections, selected azolate-based Um-MOFs, along with other representative ultra-microporous frameworks, are discussed in detail with a focus on their CO₂ adsorption behaviour and structure property relationships.

1.6.1 Zinc-Based Ultra-Microporous MOFs Constructed from Triazolate and Oxalate Ligands

CALF-15 a zinc-aminotriazolato-oxalate MOF

In 2009, Vaidhyanathan et al.^{93, 143} reported the synthesis of an ultra-microporous metal-organic framework, Zn₂(Atz)₂(ox), constructed via a solvothermal reaction involving zinc carbonate, 3-amino-1,2,4-triazole (Atz), and oxalic acid. The structure comprises 2D Zn-Atz layers that are pillared by oxalate linkers, resulting in a three-

dimensional porous framework with cubic-like ultra-micropores (~ 4.0 Å) lined with accessible amine groups (Figure 1.5A-B). The framework exhibited a BET surface area of $782 \text{ m}^2/\text{g}$ and showed steep CO_2 adsorption at low pressures, achieving an uptake of 4.35 mmol/g at 273 K and 1.2 bar , while showing negligible adsorption of N_2 , Ar , and H_2 , attributed to size exclusion and strong host-guest interactions (Figure 1.5C).

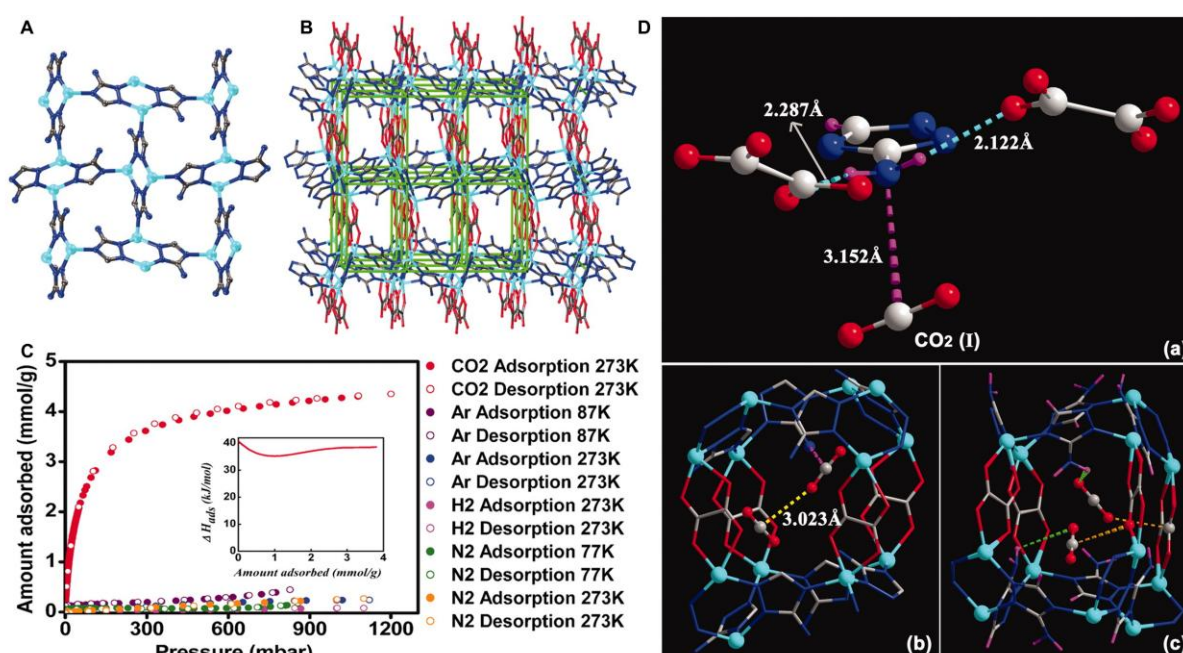


Figure 1.5: (A) Two-dimensional arrangement of Zn^{2+} dimers bridged by 3-amino-1,2,4-triazolate (Atz) ligands. (B) Three-dimensional structure of $\text{Zn}_2(\text{Atz})_2(\text{ox})$, where Zn-Atz layers are pillared by oxalate linkers. (C) Gas adsorption isotherms of CO_2 , Ar , H_2 , and N_2 measured at different temperatures; the inset shows the isosteric heat of CO_2 adsorption calculated using the Virial method. (D) Single-crystal X-ray structure of CO_2 -loaded $\text{Zn}_2(\text{Atz})_2(\text{ox})$ at 173 K , illustrating distinct CO_2 binding sites and cooperative $\text{CO}_2 \cdots \text{CO}_2$ interactions. Atom color: Zn – cyan, O – red, N – blue, C – grey.

Notably, single-crystal X-ray diffraction studies at 173 K directly visualized the positioning of CO_2 molecules within the pores (Figure 1.5D). Two CO_2 molecules were located per pore: one near the $-\text{NH}_2$ group with $\sim 80\%$ occupancy and another adjacent

to the oxalate linker with ~50% occupancy. These interactions were stabilized through hydrogen bonding, electrostatic attractions, and dispersion forces. The isosteric heat of adsorption (ΔH_{ads}) was calculated to be ~40.8 kJ/mol at zero loading and remained above 35 kJ/mol throughout the isotherm, indicating strong guest–guest (CO_2 - CO_2) cooperative interactions. Computational studies employing grand canonical Monte Carlo (GCMC), density functional theory (DFT), and molecular dynamics (MD) simulations closely matched the experimental findings, positioning this MOF as a model system for low-pressure CO_2 capture.

In continuation of previous studies, Vaidhyanathan and co-workers investigated a family of layered-pillared Um-MOFs with the general formula ZnAtzOx , IISERP-MOF32¹⁴⁴, synthesized via solvothermal reactions involving zinc carbonate, 3-amino-1,2,4-triazole (Atz), and oxalic acid, using different solvent systems. Despite sharing a common six-connected cubic topology, the frameworks exhibited distinct gas adsorption behaviours (Figure 1.6 A). Notably, one polymorph (referred to as compound 2) showed exceptional rigidity and ultra-microporosity, accompanied by a gate-opening mechanism upon exposure to CO_2 (Figure 1.6B-C). This resulted

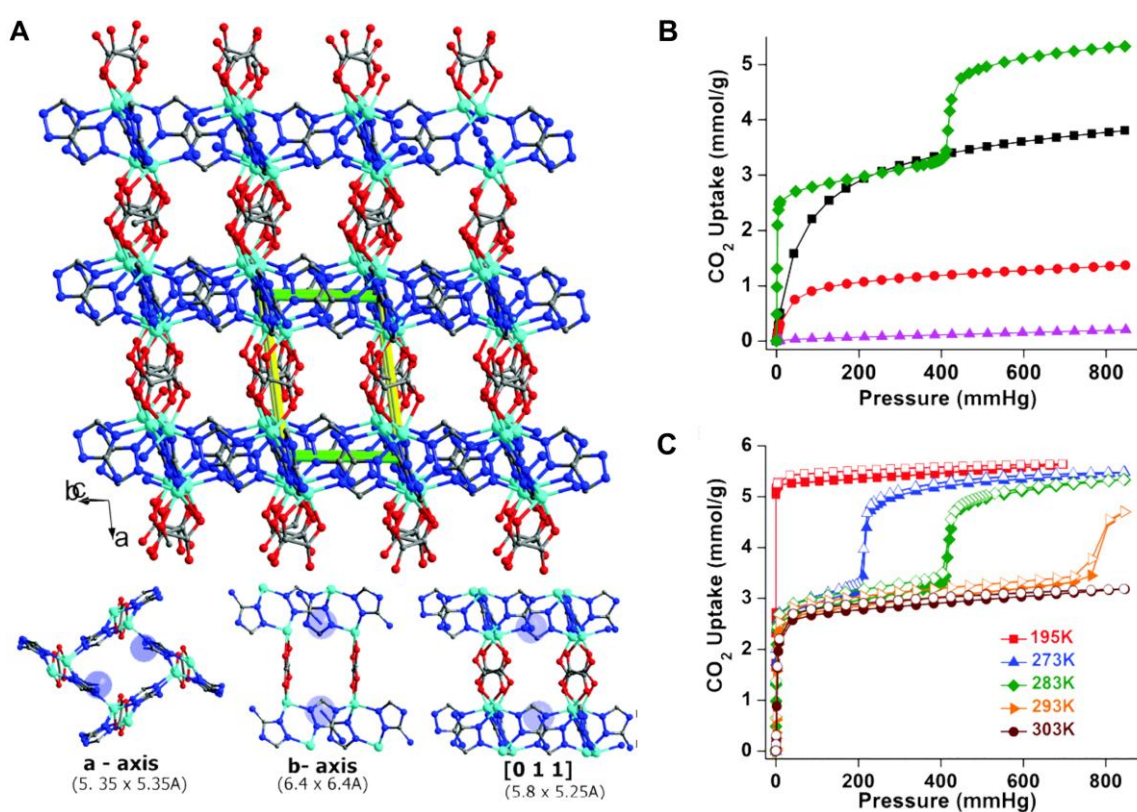


Figure 1.6: (A) Three-dimensional structure of $\text{Zn}_2(\text{Atz})_2(\text{ox})$ synthesized using a water/n-butanol solvent mixture, showing oxalate-pillared Zn-Atz layers that generate ultra-microporous channels along all three crystallographic axes (van der Waals radii not considered). Atom color scheme: Zn – cyan, O – red, N – blue, C – grey. (C) Comparison of CO_2 uptake at 283 K for the various polymorphic forms of $\text{Zn}_2(\text{Atz})_2(\text{ox})$; color code: green – phase 2, black – phase 1, red – phase 3, pink – phase 4 (B) CO_2 adsorption isotherms at different temperatures for phase 2. (Adapted from ref. 144 with permission from © 2016 from Royal Society of Chemistry).

in a 42% enhancement in CO_2 uptake, while retaining high selectivity over N_2 . The gate-opening was attributed to symmetrically aligned, elongated Zn-O bonds (~ 2.2 Å) within the oxalate linkers, which facilitated a subtle rotational motion often described as “molecular swivelling.” In situ PXRD measurements demonstrated that this transition occurred without any structural phase change, indicating a localized, reversible framework flexibility.

To probe the adsorption mechanism further, the authors employed a dual-site Langmuir-Freundlich model, revealing two energetically distinct CO_2 binding sites: one near the free amine ($-\text{NH}_2$) groups with an enthalpy of adsorption ($\Delta H_{\text{ads}} \approx 46$ kJ/mol), and a second site attributed to CO_2 - CO_2 cooperative interactions ($\Delta H_{\text{ads}} \approx 32$ kJ/mol). These findings emphasize the role of framework dynamics and multiple binding sites in enhancing CO_2 uptake at low pressures.

CALF-20 a zinc-triazolato-oxalate MOF: In 2021, Shimizu and co-workers reported CALF-20³⁷ (Calgary Framework-20), a zinc-based ultramicroporous metal–organic framework (MOF) with the formula $\text{Zn}_2(\text{Tz})_2(\text{ox})$, synthesized from 1,2,4-triazole (Tz) and oxalic acid (ox). The structure features 1,2,4-triazolate-bridged Zn(II) layers pillared by oxalate anions, forming a rigid three-dimensional framework with a calculated void volume of $\sim 38\%$ (Figure 1.7A-B). CALF-20 is isostructural with the previously reported $\text{Zn}_2(\text{Atz})_2(\text{ox})$, but incorporates triazole ligands in place of aminotriazole, which enhances its water resistance.

CALF-20 exhibits superior CO₂ capture efficacy at low partial pressure, with an uptake of 4.07 mmol g⁻¹ at 1.2 bar and 293 K (Figure 1.7C), with minimal N₂ adsorption, yielding a CO₂/N₂ selectivity of 230 for a 10:90 mixture. Water sorption isotherms recorded at different temperatures exhibit a characteristic S-shaped profile, with minimal water uptake observed below 40% relative humidity (RH). This behaviour

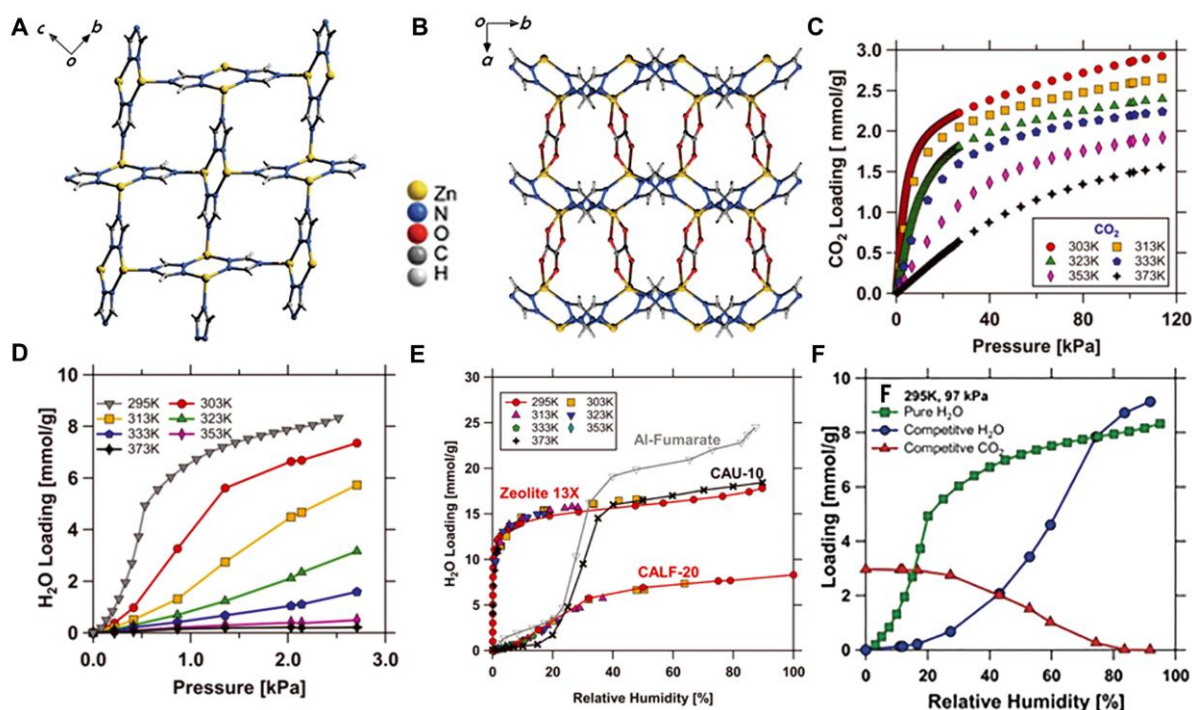


Figure 1.7: (A) Top-down view of the two-dimensional zinc-triazolate coordination layers. (B) Three-dimensional framework of CALF-20 formed by pillaring the zinc-triazolate layers with oxalate linkers. (C) CO₂ adsorption isotherms of structured CALF-20 measured at various temperatures. (D) Water vapor adsorption isotherms on structured CALF-20 measured across a temperature range of 295 K to 373 K (E) Water sorption isotherms of zeolite 13X, CAU-10, Al fumarate, and structured CALF-20 at 295 K. (F) Competitive CO₂ (red triangles) and H₂O (blue circles) adsorption at varying RH levels. Pure H₂O uptake (green squares) is shown for comparison.

underscores the material's weak interaction with water compared to other leading CO₂ sorbents (Figure 1.7D-E). Furthermore, CALF-20 has demonstrated exceptional chemical and hydrothermal stability, retaining structural integrity and adsorption

capacity even after 45,000 cycles of steam exposure. Competitive separation studies using structured CALF-20 adsorbents have demonstrated not only a strong preference for CO₂ physisorption over N₂ but also a notable suppression of water uptake by CO₂, particularly at relative humidity (RH) levels below 40% (Figure 1.7F). Grand Canonical Monte Carlo (GCMC) simulations corroborated these findings, revealing that CO₂ preferentially adsorbs at the center of the ultra-micropores through predominantly dispersion-driven interactions (~85%), with minor contributions from electrostatics. The absence of strong hydrogen-bonding donor or acceptor sites within the framework accounts for its exceptionally low water affinity, an uncommon and highly desirable feature for physisorbent materials. However, when RH exceeds 40%, water molecules begin to compete with CO₂ for adsorption sites, leading to a significant reduction in CO₂ uptake. As a result, pre-dehumidification of flue gas to maintain RH below 40% is essential for ensuring optimal CO₂ capture performance of this material.

To address the moisture sensitivity of CALF-20 under humid flue gas conditions, Farha and co-workers recently reported three new methyl-functionalized zinc-triazolate-based MOFs- NU-220, CALF-20M-w, and CALF-20M-e¹⁴⁵. Structural analysis revealed that NU-220 adopts a distinct topology, while CALF-20M-w and CALF-20M-e are isostructural with CALF-20, with solvent-dependent synthesis leading to subtle variations in pore size and layer orientation (Figure 1.8A-D). The incorporation of hydrophobic methyltriazolate linkers was designed to improve the materials' performance under high relative humidity (RH). These methylated frameworks exhibited CO₂ uptake values ranging from 1.81 to 2.13 mmol g⁻¹ at 0.15 bar (typical CO₂ partial pressure in flue gas), which corresponds to approximately 69–78% of the CO₂ adsorption capacity of CALF-20 under identical conditions (Figure 1.8E). This indicates that methyl functionalization has a limited impact on CO₂ uptake under dry conditions. Importantly, under 70% RH, CALF-20M-w and CALF-20M-e retained more than 20% of their CO₂ capacity, whereas the parent CALF-20 showed negligible uptake (Figure 1.8F-G). Furthermore, these frameworks exhibited excellent thermal and hydrolytic stability, maintaining crystallinity and porosity after prolonged exposure to humid environments and elevated temperatures.

Grand Canonical Monte Carlo (GCMC) simulations and radial distribution function (RDF) analyses revealed that methyl substitution inhibits the formation of water clusters and increases the Zn-H₂O distance, thereby suppressing water adsorption and preserving CO₂ selectivity. However, the incorporation of methyl groups also increases the overall material cost and slightly reduces the CO₂ uptake compared to CALF-20, which may limit the industrial scalability and cost-effectiveness of these materials for large-scale CO₂ capture applications. Nevertheless, this methyl-functionalization strategy represents a meaningful step toward enhancing the moisture stability of triazolate-based MOFs for humid post-combustion CO₂ capture.

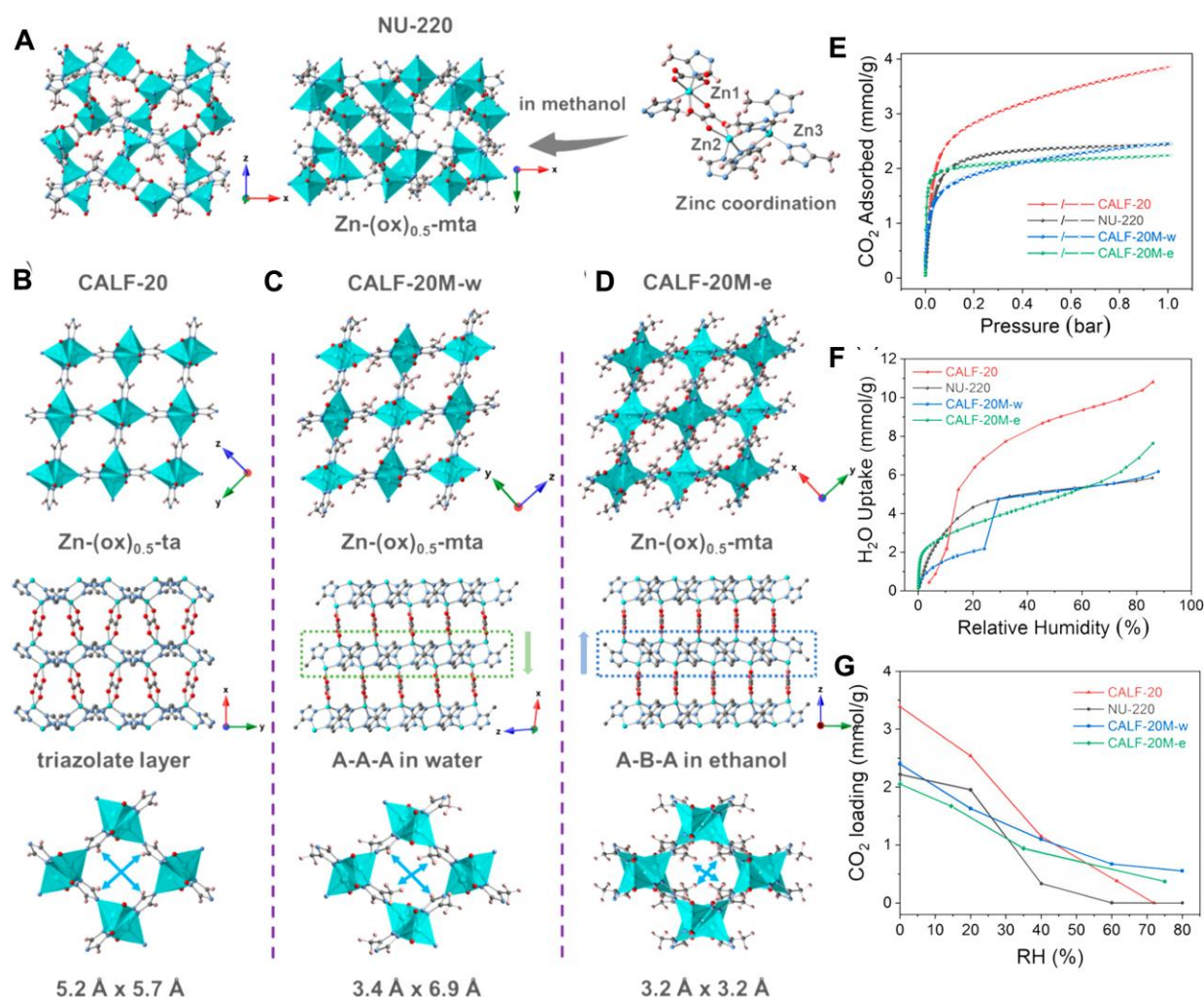


Figure 1.8: (A) Crystal structure of NU-220 highlighting the zinc coordination environment. (B-D) Structural representations of CALF-20, CALF-20M-w, and CALF-

20M-e, showing the zinc–triazolate layers, the arrangement of oxalate-pillared layers, and the resulting one-dimensional ultramicroporous channels. Atom color scheme: carbon (gray), nitrogen (blue), oxygen (red), zinc (cyan), and hydrogen (pink). (E-F) CO₂ adsorption isotherm for CALF-20, NU-220, CALF-20M-w, and CALF-20M-e at 298 K and water isotherms at 298 K. (G) Amount of CO₂ captured under different humidities for CALF-20, NU-220, CALF-20M-w, and CALF-20M-e. (Adapted from ref. 145 with permission from © 2024, American Chemical Society). "

1.6.2 Zinc–Aminotriazole–Phosphate-Based Ultramicroporous MOFs:

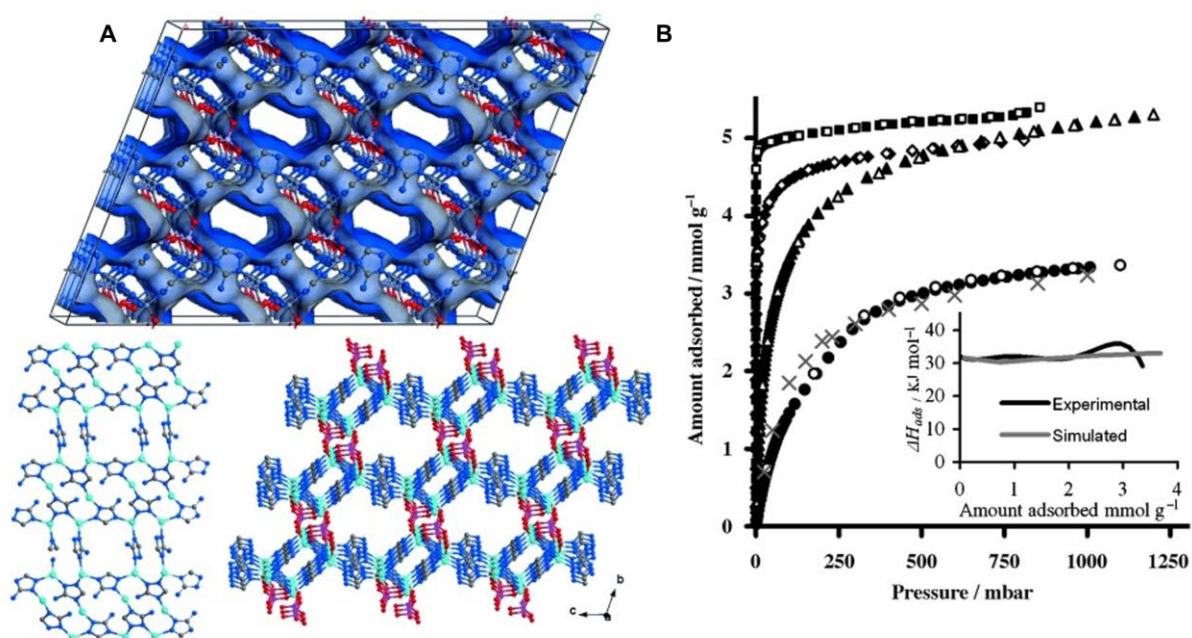


Figure 1.9: (A) Structure of $\{Zn_3(Atz)_3(PO_4)\}$ showing the 3D Zn-Atz framework pillared by phosphate groups with Atz ligands. Color code: C (gray), N (blue), O (red), P (purple), Zn (light blue). (B) Gas sorption isotherms for $\{Zn_3(Atz)_3(PO_4)\}$: CO₂ (273 K ○, 195 K, ◇), N₂ (□) and H₂ (▲) at 77 K, with simulated CO₂ isotherm at 273 K. Inset shows simulated vs. experimental CO₂ enthalpy of adsorption as a function of loading. (Adapted from ref. 146 with permission from © 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

Following their successful development of the zinc aminotriazolato-oxalate MOF, $\{Zn_2(Atz)_2(ox)\}$, which demonstrated strong CO₂ adsorption (~40 kJ/mol) and well-

defined binding sites, Vaidhyanathan and co-workers in 2013 synthesized another framework, $\{Zn_3(Atz)_3(PO_4)\} \cdot (H_2O)_{3.5}$, using a solvothermal reaction involving $ZnCO_3$, 3-amino-1,2,4-triazole, H_3PO_4 , and NH_4OH ¹⁴⁶. This new MOF features cationic Zn-Atz layers pillared by phosphate groups, forming a 3D porous structure with larger amine-lined channels than its oxalate-based analogue (Figure 1.9A). However, despite the increased pore size and retention of amine functionalities, this material showed lower CO_2 uptake and heat of adsorption (~ 32 kJ/mol) than $\{Zn_2(Atz)_2(ox)\}$ (Figure 1.9B). Structural analysis revealed that the amine groups do not effectively project into the pores due to the buckled, antiparallel arrangement of the Zn-Atz layers, thereby diminishing their contribution to CO_2 binding.

To understand the unexpected reduction in CO_2 uptake, a combination of grand canonical Monte Carlo (GCMC), molecular dynamics (MD), and density functional theory (DFT) simulations was employed. These computational models, previously validated on $\{Zn_2(Atz)_2(ox)\}$, accurately reproduced the experimental isotherms and binding sites for the phosphate-pillared framework. Interestingly, simulations indicated slightly higher CO_2 uptake at low pressures, likely due to the cooperative interactions among CO_2 molecules within the pores. This study highlights the complex interplay between framework geometry and functionality, showing that higher degrees of amination do not always correlate with stronger adsorption. Instead, spatial arrangement and intermolecular CO_2 - CO_2 interactions play a crucial role in enhancing binding.

1.6.3 Fluorinated Zinc-Triazolate–Ultramicroporous MOFs

Zhang and coworkers¹⁴⁷ developed a series of metal–organic frameworks (MOFs) engineered for robust CO_2 capture under realistic post-combustion conditions, including high humidity and the presence of acidic gases. Their approach involved functionalizing triazolate-based linkers with electron-donating groups, particularly amino moieties, to enhance the frameworks' chemical and thermal resilience. The synthesized MOFs, $ZnF(TZ)$, $ZnF(aTZ)$, $ZnF(daTZ)$, and $ZnF(dmTZ)$ were obtained using microwave-assisted solvothermal methods, yielding phase-pure, highly crystalline materials confirmed by PXRD and SEM analyses (Figure 1.10A-B). Thermal stability up to $440^\circ C$ was observed, with $ZnF(daTZ)$ showing the highest

tolerance due to stronger metal–ligand coordination enhanced by amino substitution. All frameworks exhibited excellent chemical stability, retaining crystallinity and porosity even after prolonged exposure to boiling water and a broad pH range (1–12). CO₂ adsorption isotherms collected at 195 K displayed Type I profiles, confirming permanent microporosity. Analysis of CO₂ adsorption at 273 K indicated that these MOFs possess an ultramicroporous nature, with pore sizes in the range of 4.2 to 6.0 Å highly favorable for kinetic CO₂ selectivity over larger gas molecules such as N₂.

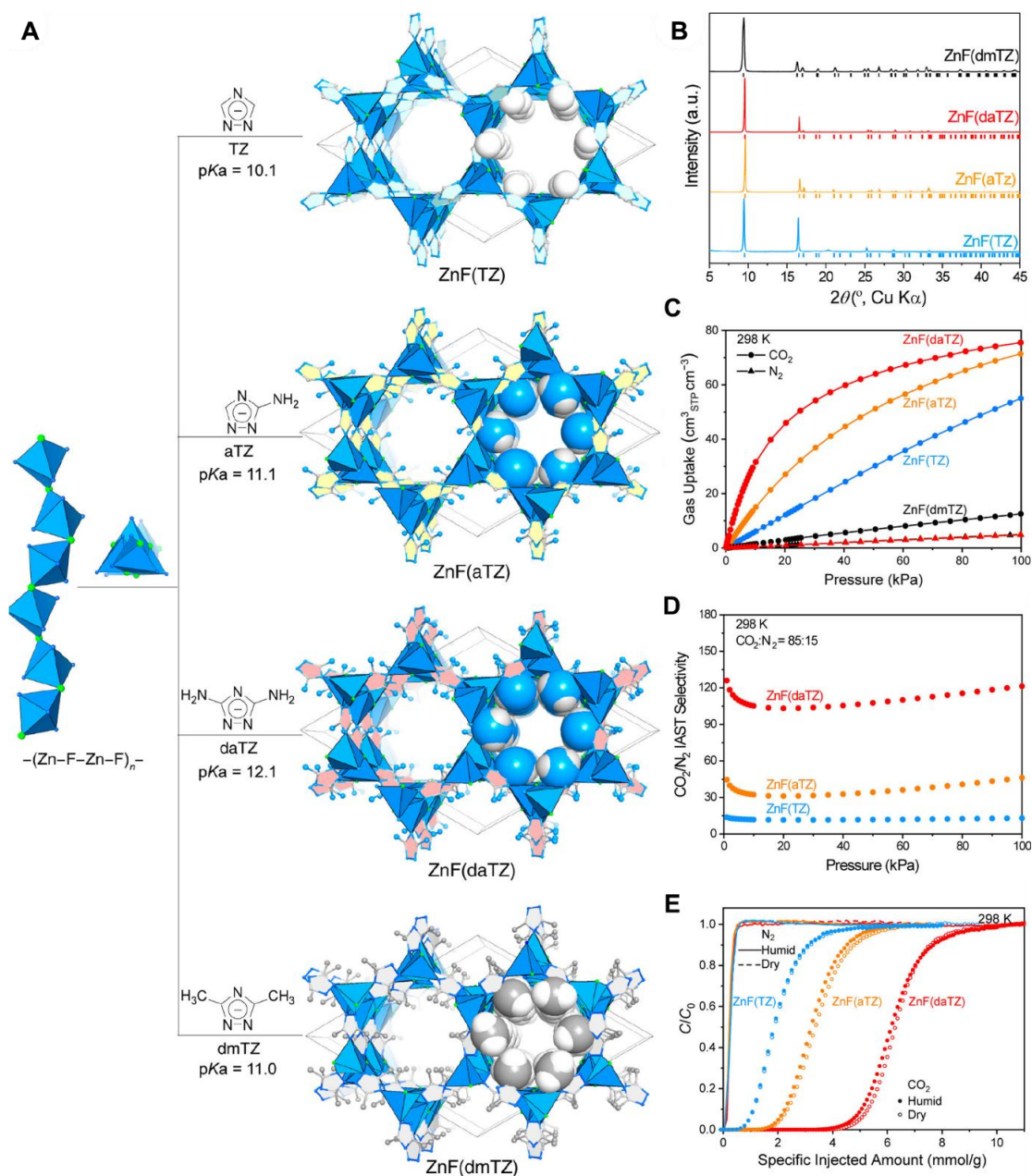


Figure 1.10: Figure. (A) Representative crystal structures of the synthesized metal-triazolate frameworks: ZnF(TZ), ZnF(aTZ), ZnF(daTZ), and ZnF(dmTZ), illustrating variations introduced by functional groups on the triazolate linkers. (B) Powder X-ray diffraction (PXRD) patterns of the as-synthesized MOFs, confirming phase purity and crystallinity. (C) CO₂ adsorption isotherms at 298 K for all frameworks, indicating the effect of functional groups on adsorption capacity. (D) IAST-predicted CO₂/N₂ selectivity for a 15:85 gas mixture at 298 K, relevant to flue gas composition (E) Breakthrough curves under dry and humid (~99% RH) conditions, showing the dynamic CO₂ capture performance and moisture tolerance of ZnF(daTZ). (Adapted from ref. 147 with permission from © 2020, American Chemical Society).

Among the series, ZnF(daTZ), containing two amino substituents, showed the highest CO₂ uptake (1.8 mmol/g at 298 K) and the strongest CO₂ binding affinity, with an initial heat of adsorption exceeding 30 kJ/mol (Figure 1.10C). This highlights the role of amine functionalities in promoting host–guest interactions. Ideal Adsorbed Solution Theory (IAST) calculations showed a CO₂/N₂ selectivity of approximately 120 for ZnF(daTZ) in a 15:85 gas mixture, greatly exceeding its unsubstituted equivalent (Figure 1.10D). Breakthrough studies at both dry and humid environments (33%, 53%, and 99% RH) showed no decrease in separation ability, with slightly better CO₂ retention under humid conditions (Figure 1.10D).

1.6.4 Fluorinated MOFs for Efficient Low-Pressure CO₂ Capture

A prominent type of ultramicroporous metal-organic frameworks (MOFs) studied, for efficient CO₂ capture, particularly under humid conditions, are fluorinated anion-pillared frameworks. Zaworotko and co-workers⁸⁵ reported several notable examples including SIFSIX-2-Cu, SIFSIX-2-Cu-i, and SIFSIX-3-Zn. These MOFs were synthesized via slow diffusion methods at room temperature, using hexafluorosilicate (SiF₆²⁻) as the anionic pillar and neutral nitrogen donor ligands such as 4,4'-dipyridylacetylene (dpa) or pyrazine (Figure 1.11A-C). SIFSIX-2-Cu, composed of Cu²⁺ and dpa ligands, forms a 3D primitive cubic framework with large square channels of ~13.05 Å, while its interpenetrated analogue, SIFSIX-2-Cu-i, crystallized using a similar method in different solvents, features a reduced pore size of ~5.15 Å

due to two-fold interpenetration. SIFSIX-3-Zn, synthesized using pyrazine and ZnSiF_6 , forms a non-interpenetrated primitive cubic network with even narrower pores of ~ 3.84 Å just above the kinetic diameter of CO_2 .

These materials exhibit very good CO_2 capture capabilities at low partial pressure. SIFSIX-2-Cu adsorbs 1.84 mmol/g of CO_2 at 298 K and 1 bar, whereas SIFSIX-2-Cu-i demonstrates a much higher uptake of 5.41 mmol/g under the same conditions (Figure 1.11D-E). The significant enhancement in CO_2 uptake and selectivity upon interpenetration underscores the importance of ultra-micropore confinement. Indeed,

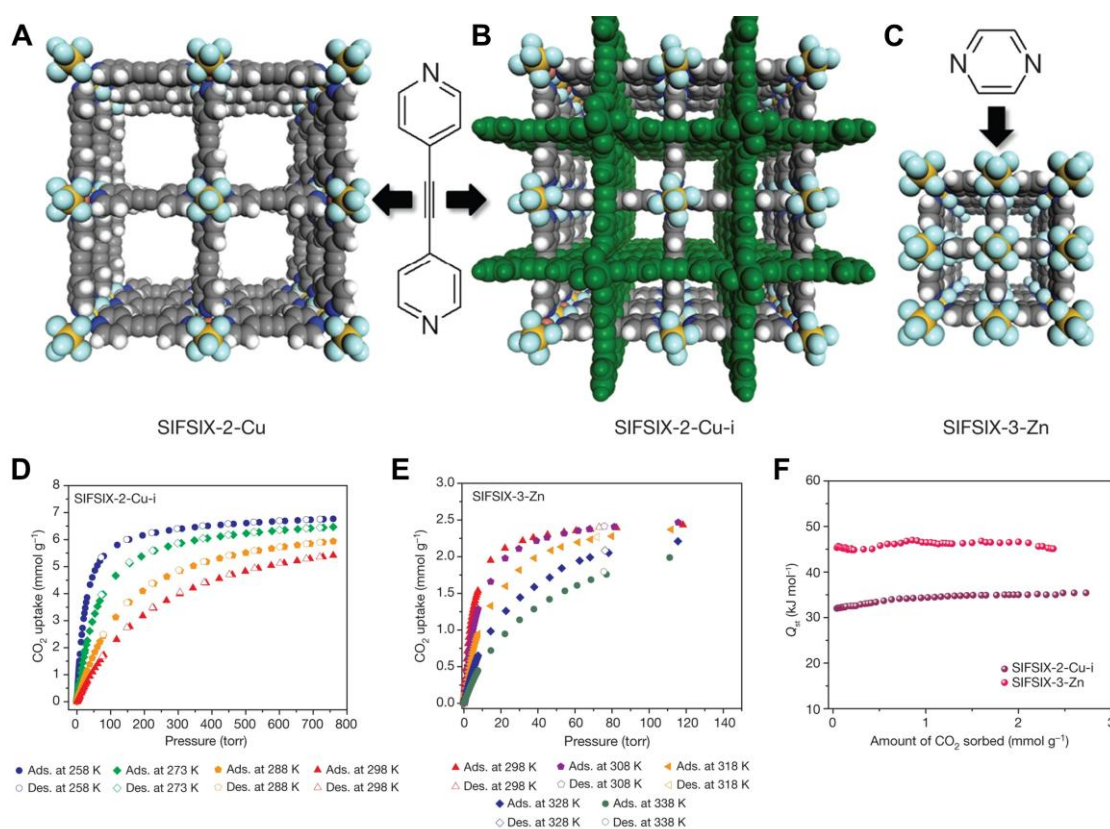


Figure 1.11: (A–C) Crystal structures of SIFSIX materials showing tunable pore sizes: (A) SIFSIX-2-Cu (13.05 Å), (B) SIFSIX-2-Cu-i (5.15 Å), and (C) SIFSIX-3-Zn (3.84 Å). Color code: C–grey, N–blue, Si–yellow, F–light blue, H–white. (D–E) CO_2 adsorption isotherms of SIFSIX-2-Cu-i and SIFSIX-3-Zn at variable temperatures. (F) Isothermic heat of CO_2 adsorption (Q_{st}) for SIFSIX-2-Cu-i and SIFSIX-3-Zn. (Adapted from ref. 85 with permission from © 2013, Springer Nature Limited).

IAST calculations show that CO_2/N_2 selectivity jumps from 13.7 to 140 upon moving from SIFSIX-2-Cu to SIFSIX-2-Cu-i, while CO_2/CH_4 selectivity increases from 5.3 to 33. SIFSIX-3-Zn exhibited the highest selectivity among the series, with a CO_2/N_2 ratio of 495 and CO_2/CH_4 of 109, as calculated from breakthrough experiments. Despite high heats of adsorption (33 kJ/mol for SIFSIX-2-Cu-i and 45 kJ/mol for SIFSIX-3-Zn), adsorption/desorption remains reversible due to favourable diffusion dynamics (Figure 1.11F). Importantly, SIFSIX-3-Zn shows significant CO_2 uptake ($\sim 11 \text{ wt}\%$) at 0.1 bar and 298 K, an attribute that is crucial for post-combustion capture applications.

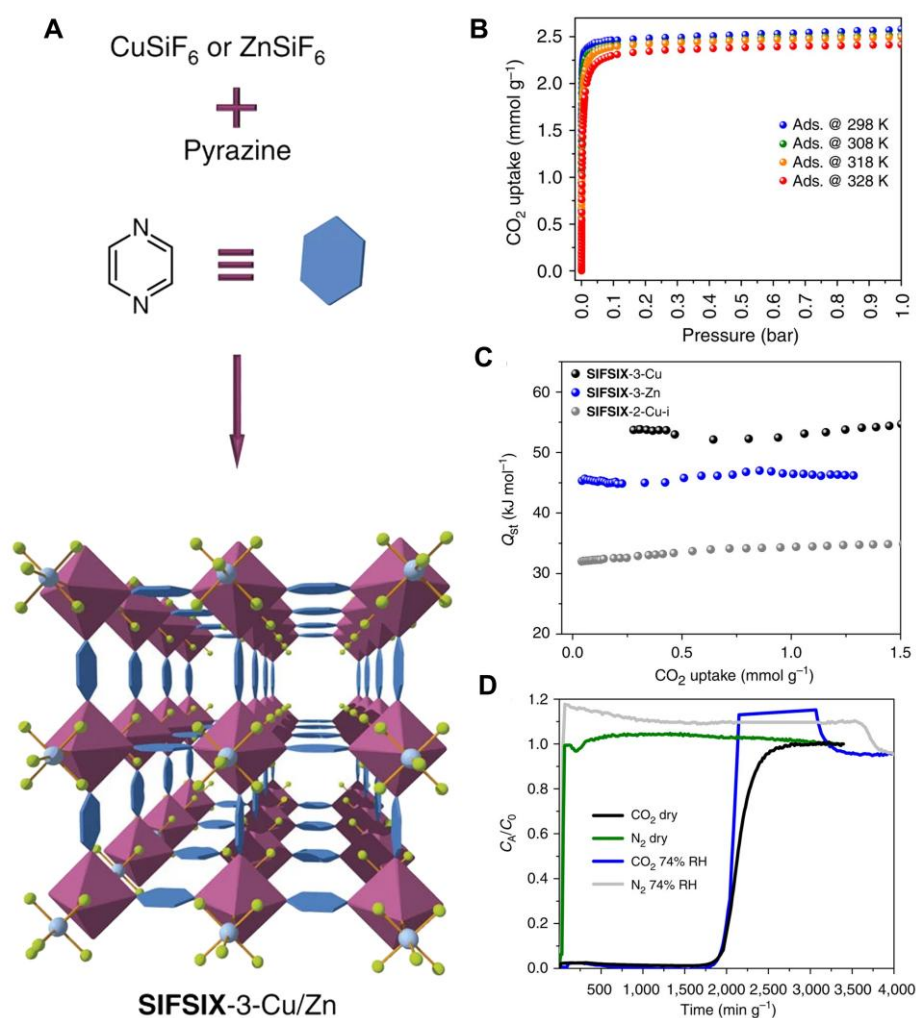


Figure 1.12: (A) Three-dimensional crystal structures of SIFSIX-3-Zn and SIFSIX-3-Cu illustrating pore size tuning ($\sim 3.84 \text{ \AA}$ for Zn and $\sim 3.5 \text{ \AA}$ for Cu) achieved via metal substitution. Color code: pyrazine ligands = blue polygons; Zn/Cu nodes = purple

polyhedra; Si = light blue spheres; F = light green spheres. (B) CO₂ isotherms for SIFSIX-3-Cu at different temperatures showing steep uptake at low pressures. (C) Isothermic heat of CO₂ adsorption at low coverage for SIFSIX-3-Cu, SIFSIX-3-Zn, and SIFSIX-2-Cu-i. (D) Breakthrough tests showed longer CO₂ retention for SIFSIX-3-Cu (~1922 min g⁻¹) vs. SIFSIX-3-Zn (~798 min g⁻¹), confirming higher selectivity.

Following the promising results obtained from SIFSIX-2-Cu, SIFSIX-2-Cu-i, and SIFSIX-3-Zn (Figure 1.11A-C), which demonstrated the effectiveness of ultra-microporous MOFs for CO₂ separation through pore size tuning and electrostatic interactions, Eddaoudi and co-workers¹³⁵ further advanced this design strategy by developing SIFSIX-3-Cu (Figure 1.12A). This Cu-based analogue of SIFSIX-3-Zn features a slightly contracted pore size (~3.5 Å), resulting in enhanced CO₂ binding affinity and uptake at very low partial pressure conditions relevant to direct air capture (DAC). The substitution of Zn²⁺ with Cu²⁺ led to ~20% higher heat of adsorption (~54 kJ mol⁻¹), steeper CO₂ adsorption isotherms, and improved CO₂/N₂ selectivity (~50% increase at 1000 ppm CO₂) (Figure 1.12B-C). Breakthrough experiments confirmed that CO₂ adsorbs preferentially over N₂, CH₄, and H₂, even under humid conditions. Moreover, the framework retained its crystallinity after multiple sorption cycles, underscoring its moisture stability and recyclability. This work underscores how fine-tuning pore size and adsorption energetics enables the rational design of MOFs tailored for low-concentration CO₂ capture.

Driven by earlier success of SIFSIX-3-Zn and SIFSIX-3-Cu, Eddaoudi and co-workers⁹⁵ (2016) developed a hydrolytically stable MOF, NbOFFIVE-1-Ni, designed for efficient CO₂ capture at trace concentrations. Synthesized via a hydrothermal reaction involving Nb₂O₅, Ni(NO₃)₂·6H₂O, and pyrazine in aqueous HF, this framework replaces the SiF₆²⁻ pillars with (NbOF₅)²⁻ and employs Ni²⁺ as the metal center (Figure 1.12 A). These modifications produce contracted square-shaped channels (~3.21 Å) lined with periodically aligned fluorine atoms, which significantly enhance CO₂-framework electrostatic interactions while improving water tolerance. NbOFFIVE-1-Ni exhibited exceptional CO₂ uptake (~1.3 mmol/g at 400 ppm, 298 K) and complete desorption at 328 K with moderate energy input (~54 kJ/mol), a performance superior to most physical adsorbents (Figure 1.12B-C). SCXRD studies confirmed that CO₂

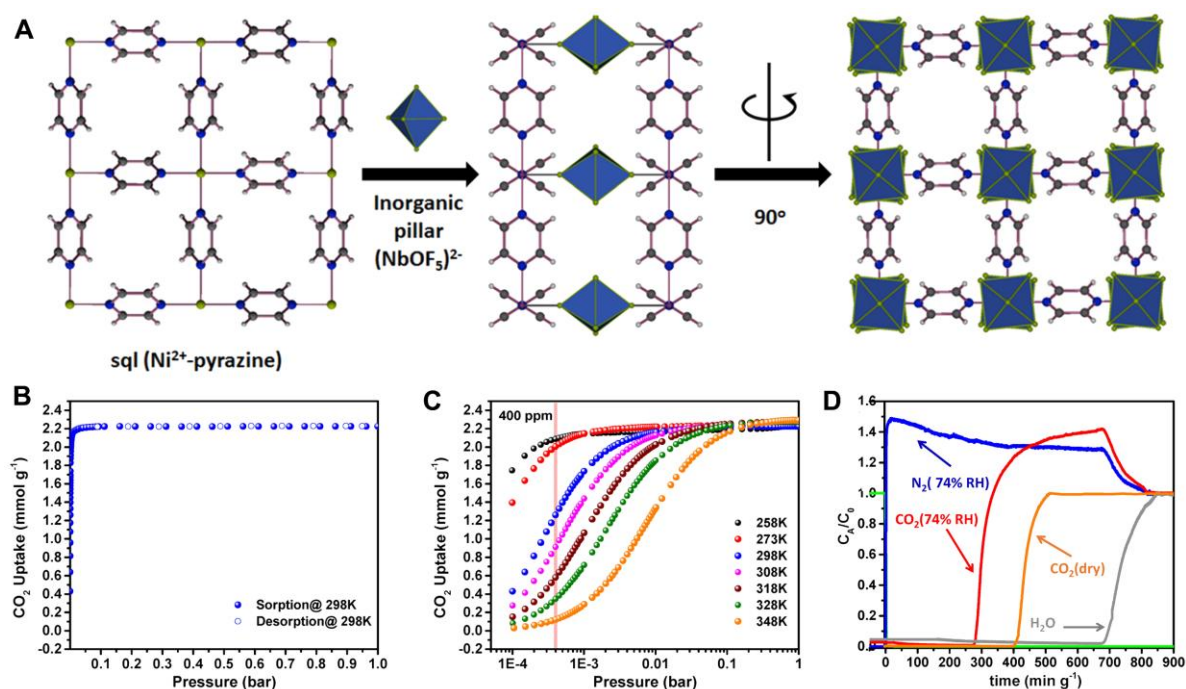


Figure 1.12: (A) Design strategy for synthesizing a 3D ultramicroporous framework with square channels using NbOF_5^{2-} pillars. (B) CO_2 adsorption isotherm of NbOFFIVE-1-Ni measured at 298 K up to 1 bar. (C) CO_2 adsorption isotherms of NbOFFIVE-1-Ni collected at various temperatures. (D) CO_2/N_2 breakthrough for NbOFFIVE-1-Ni at 298 K under dry and humid conditions. (Adapted from ref. 95 with permission from © 2016, American Chemical Society).

molecules localize near the fluorine-rich channel walls, supporting a strong but reversible physisorption mechanism ideal for low-pressure CO_2 capture.

1.6.5 Aluminum Formate ($\text{Al}(\text{HCOO})_3$) as a cost-effective and scalable CO_2 adsorbent

Cheetham and co-workers¹⁴⁸ reported a cost-effective and scalable aluminum-based metal–organic framework (MOF), $\text{Al}(\text{HCOO})_3$ referred to as ALF as a promising candidate for post-combustion CO_2 capture. ALF can be synthesized from inexpensive commodity chemicals, aluminum hydroxide and formic acid, without the need for additional solvents. Structural analysis using Rietveld refinement of neutron powder diffraction (NPD) data confirmed a ReO_3 -type framework comprising two distinct types

of pores: small cavities (SCs, ~ 4.1 Å) and large cavities (LCs, ~ 4.5 Å), with SCs occurring three times more frequently than LCs (Figure 1.13A-B). The orientation of formate ligands in these cavities provides a unique pore environment that selectively favors CO₂ adsorption. While ALF does not adsorb N₂ under ambient conditions, it shows high CO₂ uptake at low pressures and elevated temperatures (up to 323 K), attributed to size-selective diffusion and confinement effects in the SC channels (Figure 1.13C). The presence of hysteresis in desorption profiles further suggests diffusion limitations and potential entrapment of CO₂ within the narrow pores.

Breakthrough experiments performed with a 15:85 CO₂:N₂ gas mixture at 323 K demonstrated ALF's capability to separate CO₂ under flue gas-relevant conditions, although performance declined under humid environments (Figure 1.13D-E). Nonetheless, ALF exhibited exceptional tolerance to acidic and basic conditions and maintained its structural integrity after immersion in boiling water and corrosive media.

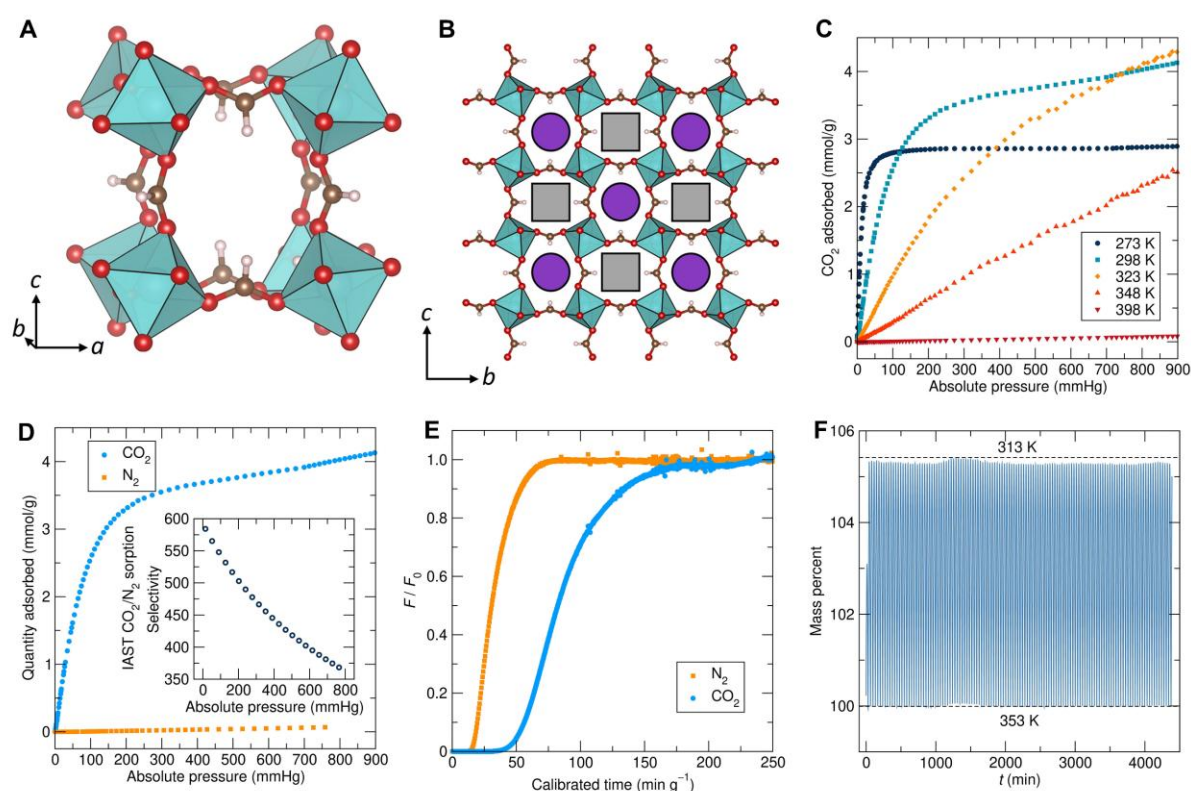


Figure 1.13: (A) Crystal structure of ALF at 300 K from neutron diffraction. (B) Illustration of two interpenetrating channels in ALF: LC-SC-LC (purple circles) and SC-

SC-SC (gray squares). (C) CO₂ adsorption isotherms at multiple temperatures. (D) CO₂ and N₂ isotherms at 298 K, with IAST-derived CO₂/N₂ selectivity for a 15/85 mixture shown in the inset. (E) Breakthrough curves for 15/85 CO₂/N₂ gas mixture at 323 K. (F) TGA cycling under dry CO₂ for 130 cycles, with adsorption at 313 K and desorption at 353 K.

Thermogravimetric cycling up to 130 cycles confirmed its excellent thermal and operational stability (Figure 1.13F). Humidity tolerance was evaluated by exposing ALF to 85% relative humidity at 85 °C for durations ranging from 1 to 24 hours, after which PXRD, TGA, and CO₂ adsorption analyses consistently showed retention of crystallinity and performance, confirming outstanding hydrolytic stability. Additionally, the material's high density, good pelletizability, and compatibility with industrial process modelling (meeting U.S. DOE recovery and purity targets) make ALF an attractive low-cost alternative to other benchmark MOFs such as CALF-20. These features collectively position ALF as a strong candidate for scalable CO₂ capture in post-combustion applications.

1.6.6 CO₂ Adsorption in a Nickel-Isonicotinate MOF (Ni-4PyC, IISERP-MOF2)

Vaidhyathan and co-workers⁹⁴ recently reported an ultra-microporous metal–organic framework, Ni-4PyC, synthesized from a single, commercially available ligand 4-pyridylcarboxylate (4PyC) and nickel(II). The material adopts a three-dimensional cubic framework comprising Ni dimers and isolated Ni centers connected via 4PyC linkers, forming dual ultra-microporous channels (~3.5 and 4.8 Å) (Figure 1.14A). Despite having a modest surface area of 945 m²/g, Ni-4PyC demonstrates a high CO₂ working capacity of 3.95 mmol/g and an impressive CO₂ uptake of 8.2 mmol/g at 298 K and 10 bar (3.6 mmol/g at 303 K and 1 bar) (Figure 1.14B). It also shows exceptional CO₂/H₂ selectivities of 285 and 230 for 20:80 and 40:60 gas mixtures, respectively, under conditions relevant to precombustion CO₂ capture (Figure 1.14C).

The framework demonstrates robust cycling performance with a heat of adsorption of 34 kJ/mol at zero coverage, dropping to 28 kJ/mol at higher loadings, allowing for low-energy regeneration under PSA conditions. Notably, positron annihilation lifetime

spectroscopy (PALS) and CO₂ adsorption simulations confirmed the pore size distribution and cooperative guest–guest interactions that contribute to the high adsorption enthalpy. Ni-4PyC also shows excellent hydrothermal and hydrostatic stability, remaining intact after prolonged exposure to steam and high-pressure humid gas streams. This study highlights the potential of small-ligand-based MOFs in industrial CO₂ separation, especially for H₂ purification, where high working capacity, strong selectivity, and operational durability are critical. The one-pot, scalable synthesis and structural resilience make Ni-4PyC a valuable platform for further exploration of ultra-microporous MOFs in gas separation applications.

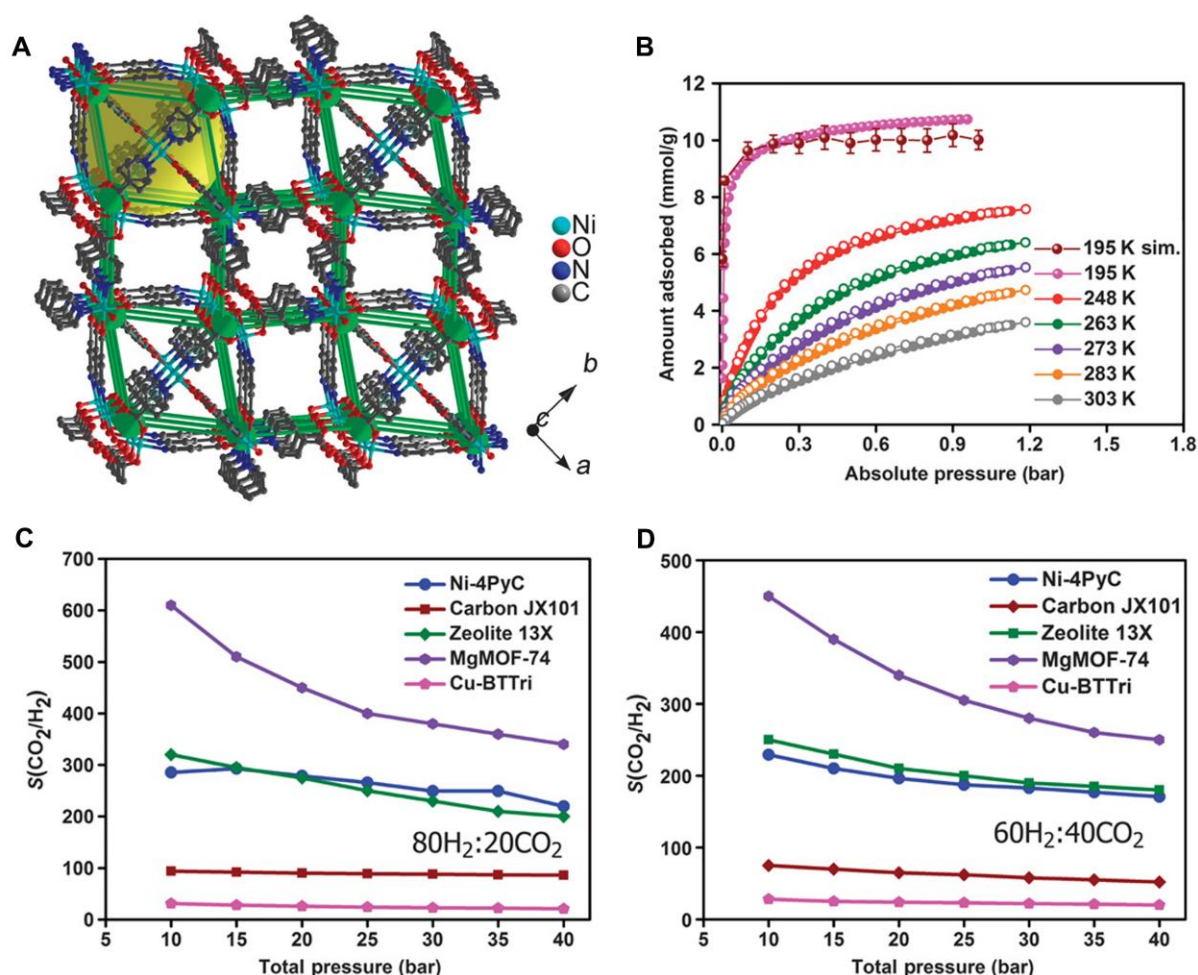


Figure 1.14: (A) Single-crystal structure of Ni-4PyC MOF showing distorted cubic network (green) formed by Ni dimers and PyC linkers. (B) CO₂ adsorption isotherms measured at various temperatures. (C and D) H₂/CO₂ selectivity of Ni-4PyC compared

to other MOFs and industrial adsorbents for 80:20 and 60:40 H_2/CO_2 mixtures at 313 K.

1.6.7 Hydrolytically Stable PCN-200 Framework for Efficient CO_2 Separation

Zhou and coworkers¹⁴⁹ developed a copper-based metal–organic framework, PCN-200, synthesized from tetrazolate-5-carboxylic acid (tzc) and 1,3-di(4-pyridyl)propane (dpp) as organic linkers. The framework comprises two-dimensional layers formed by μ_3 -bridging tzc ligands aligned in the bc plane, which are further connected via flexible dpp linkers to construct a three-dimensional porous architecture with one-dimensional channels oriented along the c axis (Figure 1.15A-B). The flexible propylene unit in the dpp ligand enable a stimulus-responsive framework contraction upon activation, decreasing the unit cell volume from 2489 to 2226 $\text{\AA}^3$ and yielding narrow pore channels (~ 4.4 $\text{\AA}$) suitable for size-selective gas adsorption (Figure 1.15C).

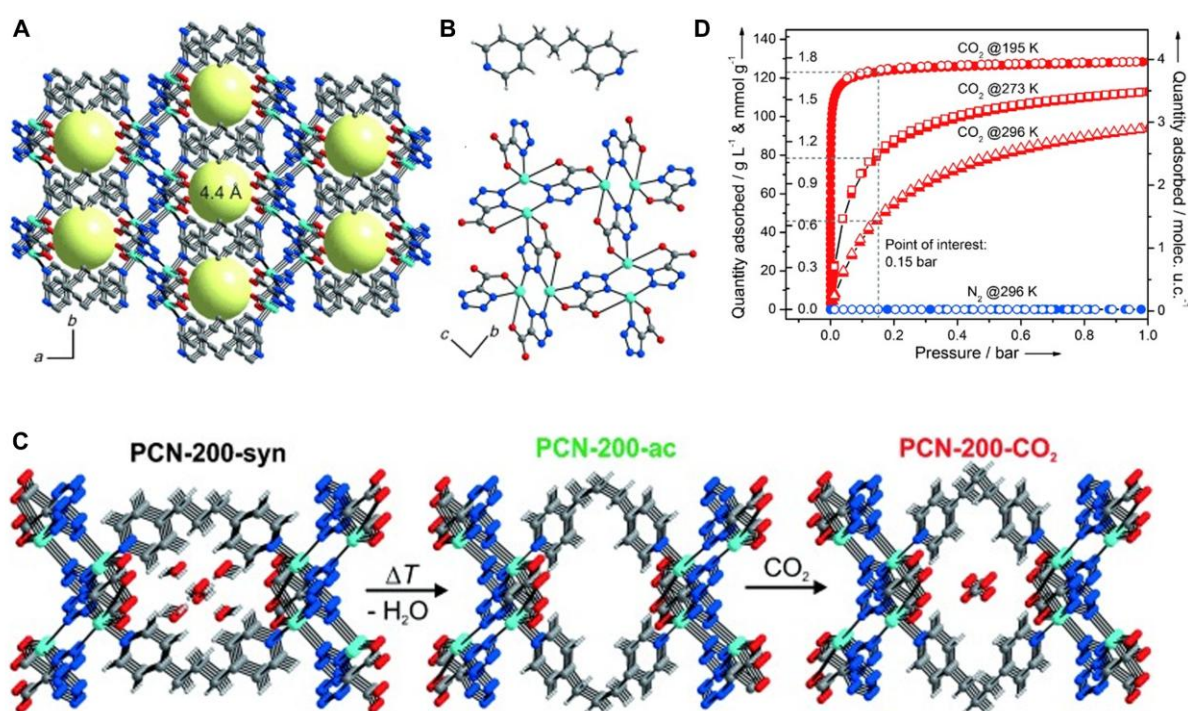


Figure 1.15: (A-B) Crystal structure of PCN-200: (A) View along c axis; (B) structure of dpp linker and $[Cu(tzc)]_n$ layer along a axis (C) Structural transformation of PCN-200 upon activation and CO_2 adsorption. (D) CO_2 and N_2 adsorption isotherms

measured across various temperatures. (Adapted from ref. 149 with permission from © 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

PCN-200 exhibits excellent thermal stability (up to 218 °C) and maintains its structural integrity and porosity in harsh chemical environments, including boiling water and acidic/basic conditions ranging from pH 2 to 12. Although its CO₂ uptake at 296 K and 1 bar is moderate (~1.25 mmol/g) (Figure 1.15D), the high heats of adsorption (38 and 49 kJ/mol, derived from virial and Langmuir models, respectively) reflect strong CO₂-framework interactions. In situ diffraction studies and simulation analyses revealed multiple CO₂ binding sites within the pore channels, contributing to high CO₂/N₂ selectivity values of 260 (50:50) and 205 (15:85) under simulated flue gas conditions. Despite its very high selectivity and stability, the relatively low CO₂ adsorption capacity limits the practical utility of PCN-200 in large-scale carbon capture applications.

1.6.8 Cobalt-Based Bio-MOF Series Functionalized with Adenine for Selective CO₂ Uptake

A notable class of ultra-microporous metal–organic frameworks based on cobalt and adeninate ligands, known as bio-MOFs-11 to 14, was developed by Rosi and co-workers¹⁵⁰ to explore structure property relationships for CO₂ capture and stability in humid environments. These MOFs are constructed from Co(II) paddle-wheel units coordinated to adenine and monocarboxylate ligands such as acetate (bio-MOF-11), propionate (bio-MOF-12), butyrate (bio-MOF-13), and valerate (bio-MOF-14) (Figure 1.16 A-D). All members of this series crystallize in the same tetragonal $I4_1/a$ space group and exhibit the lvt topology, forming 3D frameworks with unidirectional channels.

Despite a systematic decrease in BET surface area with increasing alkyl chain length from 1148 m²/g in bio-MOF-11 to just 17 m²/g in bio-MOF-14 the selectivity for CO₂ over N₂ increased (Figure 1.16E-F). This enhancement is attributed to both the narrowing of pore apertures and the increased hydrophobicity induced by the longer chains, leading to size-exclusion effects and stronger CO₂-framework interactions, especially in bio-MOF-14. Interestingly, bio-MOF-14 displayed stepwise CO₂

adsorption behaviour, indicative of a gating mechanism enabled by the flexible valerate side chains, a property uncommon in rigid MOFs at ambient conditions (Figure 1.16F).

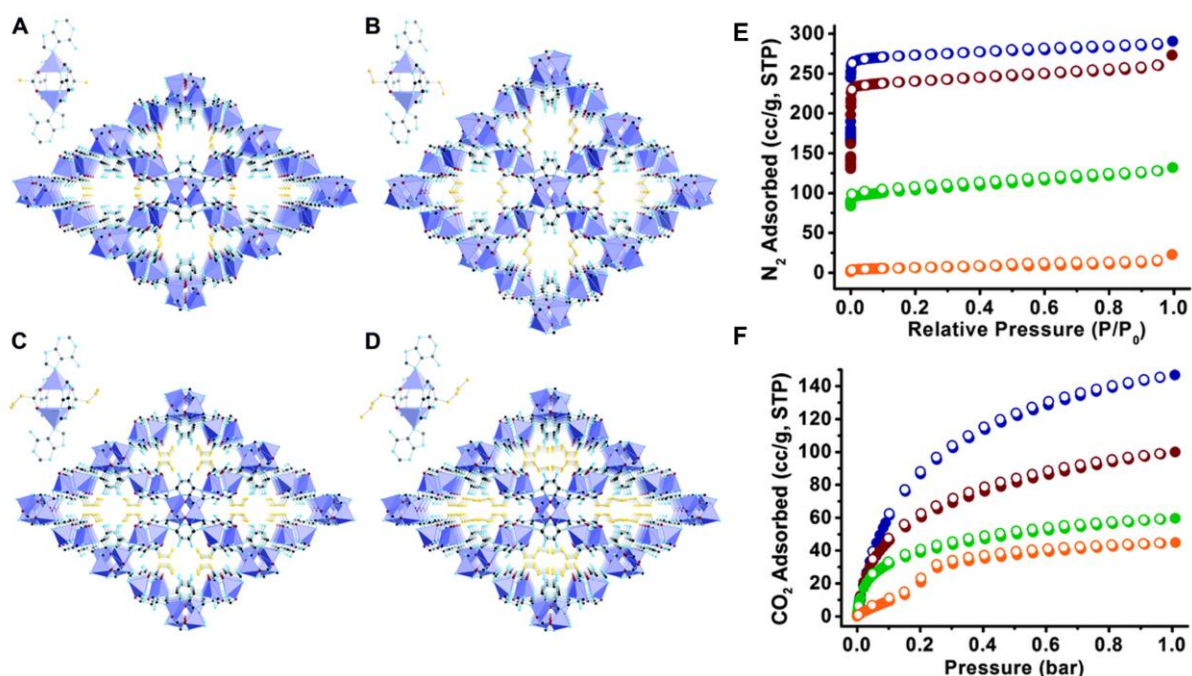


Figure 1.16: X-ray structures of bio-MOF-11 to bio-MOF-14 (A-D). Insets highlight the Co(II)-adeninate-carboxylate paddle-wheel clusters as secondary building units. E-F) CO₂ adsorption isotherms of bio-MOF-11 (navy), bio-MOF-12 (dark red), bio-MOF-13 (green), and bio-MOF-14 (orange) at 273 K, along with corresponding N₂ adsorption isotherms measured at 77 K. (Adapted from ref. 150 with permission from © 2013 from Royal Society of Chemistry).

Lewis-basic amino and pyrimidine sites in cobalt–adeninate MOFs enhance CO₂ selectivity over N₂, with selectivity ratios reaching over 100:1 depending on ligand chain length. IAST simulations confirmed improved performance in more hydrophobic variants, especially bio-MOF-13 and bio-MOF-14. Notably, bio-MOF-14 retained its structure and porosity after prolonged water exposure, unlike bio-MOF-11. These results highlight the role of ligand tuning in achieving both selective CO₂ capture and water stability under realistic conditions.

1.6.9 Cobalt-Citrate-Based Ultramicroporous MOF

Chen and co-workers developed UTSA-16⁹², a citrate-based ultra-microporous metal–organic framework with the formula $[K(H_2O)_2Co_3(cit)(Hcit)] \cdot nH_2O$, which shows excellent CO_2 capture under ambient conditions. The structure features Co_4O_4 cubane-type clusters as secondary building units, interconnected by citric acid ligands that bridge two tetrahedrally coordinated $Co(II)$ centers and two K^+ ions. These potassium ions are further stabilized by coordinated water molecules, resulting in a three-dimensional open framework with diamondoid connectivity. The framework forms narrow pore windows ($\sim 3.3 \times 5.4 \text{ \AA}$), which are well-suited for size-selective CO_2 adsorption (Figure 1.17A-B). Gas sorption studies show that UTSA-16 achieves a high CO_2 uptake of approximately $160 \text{ cm}^3/\text{cm}^3$ at 296 K and 1 bar, placing it among the most effective MOFs for low-pressure CO_2 capture. Its adsorption performance is com

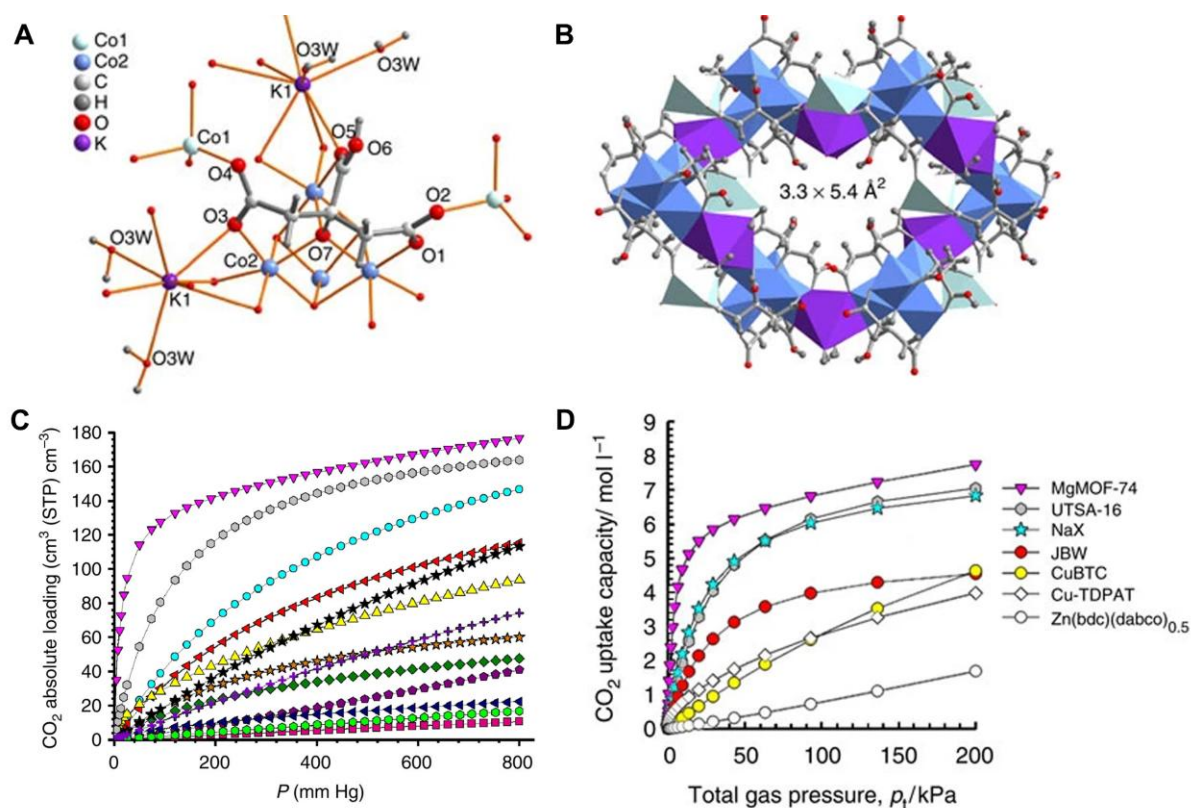


Figure 1.17: A) Citrate-metal coordination environment in the UTSA-16 MOF B) Diamondoid cage in UTSA-16 with a narrow window ($3.3 \times 5.4 \text{ \AA}^2$). (C-D) CO_2 adsorption isotherms at 296 K and 1 bar for various MOFs: Mg-MOF-74 (magenta $\blacktriangledown$),

UTSA-16 (grey hexagon), Zn-MOF-74 (cyan ●), bio-MOF-11 (red ◁), CuBTC (black ★), Cu-TDPAT (yellow ▲), UTSA-20a (violet ×), ZIF-78 (orange ★), $\text{Zn}_5(\text{BTA})_6(\text{TDA})_2$ (olive ◆), $\text{Zn}(\text{bdc})(\text{dabco})$ (purple ◆), MIL-101 (navy ◁), Yb(BPT) (green hexagon), and MOF-177 (pink ■).

-parable to that of Mg-MOF-74, but with enhanced stability in humid environments (Figure 1.17C-D). Simulated pressure swing adsorption (PSA) experiments confirm its capability to efficiently separate CO_2 from both CO_2/N_2 and CO_2/CH_4 mixtures. Neutron diffraction analyses attribute this performance to strong interactions between CO_2 molecules and the framework's terminal water sites, along with confinement effects within the pore cages. Unlike many open-metal-site MOFs, UTSA-16 maintains its structural integrity and adsorption capacity upon exposure to ambient moisture.⁹²

1.6.10 Scalable Ambient-Pressure Synthesis of Robust MIL-120(Al)-AP for Efficient Post-Combustion CO_2 Capture

Serre and co-workers¹⁵¹ recently reported the synthesis of a highly robust and cost-effective aluminum-based metal-organic framework, MIL-120(Al), designed for post-combustion CO_2 capture. Constructed from aluminum ions and 1,2,4,5-benzenetetracarboxylate (BTeC) ligands, the framework features infinite Al-OH chains connected via tetracarboxylate linkers, forming a three-dimensional microporous network with narrow one-dimensional channels (Figure 1.18 A). A green and scalable ambient-pressure synthesis route was developed using only water and inexpensive commercial precursors, replacing the previously used high-temperature hydrothermal method. The resulting material, MIL-120(Al)-AP, demonstrated excellent crystallinity, thermal stability up to 400 °C, and remarkable hydrolytic stability retaining structure and CO_2 uptake capacity even after prolonged exposure to boiling water. Gas sorption measurements revealed a high CO_2 uptake of 1.9 mmol g⁻¹ at 0.1 bar and 3.87 mmol g⁻¹ at 1 bar (298 K), along with significantly lower N_2 adsorption (0.32 mmol g⁻¹ at 0.9 bar), resulting in very good CO_2/N_2 selectivity (~90). A moderate isosteric heat of CO_2 adsorption (-41 kJ mol⁻¹) indicates low regeneration energy requirements (Figure 1.18 B-E). In situ synchrotron PXRD and DFT calculations

confirmed that the high CO₂ affinity arises from interactions with densely packed μ_2 -OH groups and aromatic ring surfaces lining the channels.

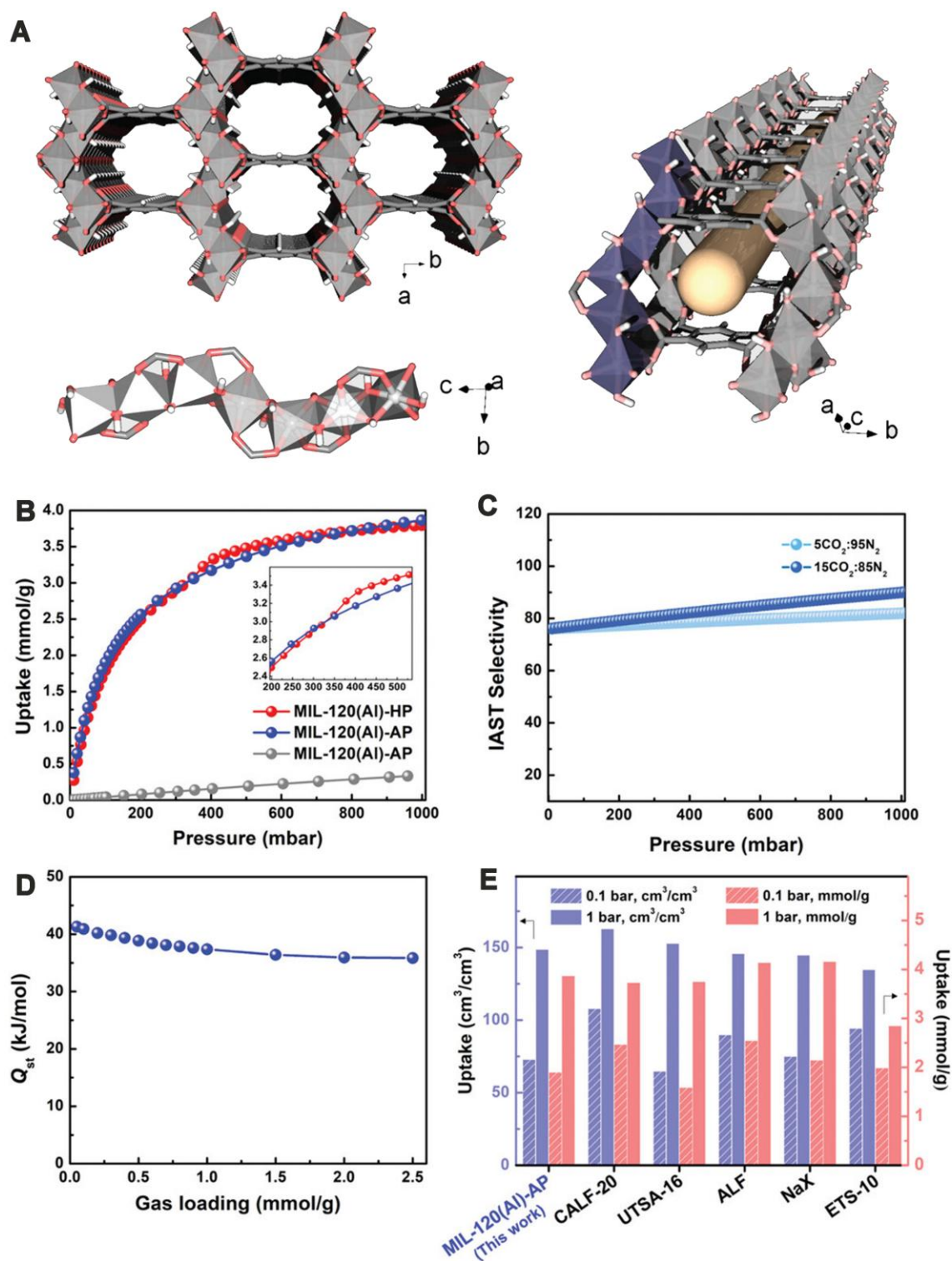


Figure 1.18: (A) Crystal structure of MIL-120(Al) viewed along the [001] direction, highlighting the narrow 1D channels. The framework consists of Al hydroxo-chains constructed from trans–cis edge-sharing $\text{Al}(\text{OH})_4\text{O}_2$ octahedra (Color code: $\text{Al}(\text{OH})_4\text{O}_2$, gray polyhedra; C, gray; O, light red; H, white). CO_2 adsorption behaviour of MIL-120(Al)-HP and MIL-120(Al)-AP at 298 K. (B) CO_2 and N_2 adsorption isotherms; inset shows step region. (C) IAST-predicted CO_2/N_2 selectivity for MIL-120(Al)-AP. (D) Isosteric heat of CO_2 adsorption vs uptake. (E) Gravimetric and volumetric CO_2 uptake comparison with leading MOFs and zeolites at 0.1 and 1 bar.

Additionally, kilogram-scale synthesis was demonstrated with space-time yields comparable to benchmark industrial sorbents, and techno-economic assessment estimated a production cost of approximately \$13 per kg, among the lowest ever reported for MOFs. These characteristics position MIL-120(Al)-AP as a highly viable material for practical CO_2 capture from flue gas, “especially under TSA-based processes using low-grade waste heat.

1.6.11 Zinc-Imidazolate and Triazolate Frameworks for Enhanced CO_2 Capture: From MAF-4 to MAF-66

Zeolite-like metal–imidazolate frameworks (ZIFs) have garnered significant attention for gas storage and separation, particularly CO_2 capture, due to their structural robustness, tunable porosity, and high thermal and chemical stability. Among these, the sodalite (SOD)-type framework $[\text{Zn}(\text{mim})_2]$ (MAF-4, where $\text{mim}^- = 2$ -methylimidazolate) is a prototypical ZIF exhibiting high porosity and exceptional stability.^{142,152} However, its CO_2 adsorption performance is relatively weak.

This limitation arises from the fully coordinated nature of the imidazolate linkers; all nitrogen atoms are bound to $\text{Zn}(\text{II})$ centers, leaving no accessible lone pairs to interact with guest CO_2 molecules. Consequently, MAF-4 shows limited uptake of small gas molecules like H_2 , CO_2 , and C_2H_2 due to the absence of strong adsorption sites on its internal surface. To overcome this limitation, Xiao-Ming Chen and co-workers¹⁵³ synthesized MAF-7, an analogue incorporating 3-methyl-1,2,4-triazolate (mtz^-) linkers instead of mim^- (Figure 1.19A). This substitution introduces uncoordinated nitrogen

atoms into the pore surface, enhancing the framework's polarity and lewis basicity, and resulting in a significant improvement in CO₂ uptake (62.5 cm³ g⁻¹ for MAF-7 vs. 29.3 cm³ g⁻¹ for MAF-4 at 273 K and 1 atm) (Figure 1.19B). Additionally, MAF-7 exhibits good hydrolytic stability and water uptake, making it a viable candidate for humid CO₂ capture applications.

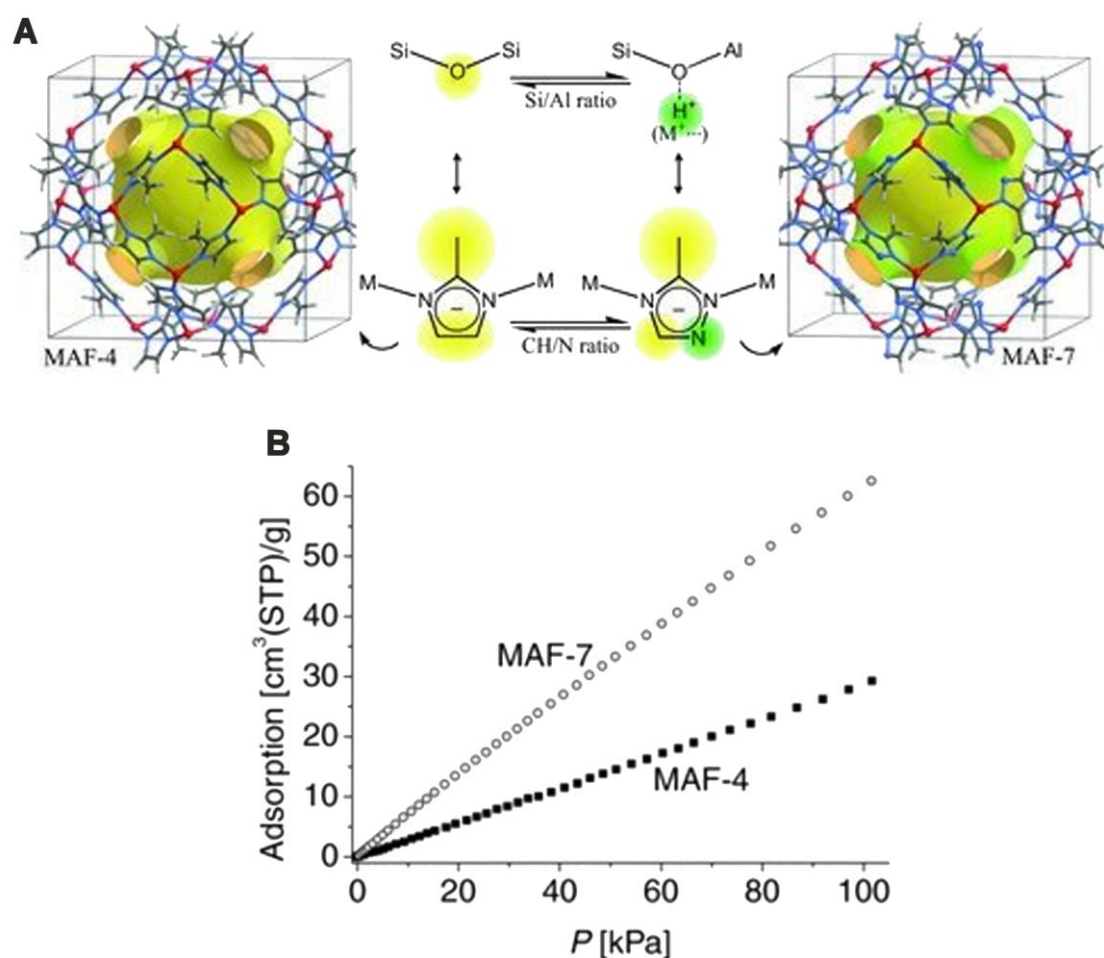


Figure 1.19: (A) Framework design and pore surface tuning in inorganic and MOF zeolites; hydrophobic (yellow) and hydrophilic (green) regions highlighted. (B) CO₂ isotherms of MAF-4 and MAF-7 at 273 K showing enhanced uptake in MAF-7.

To further enhance CO₂ adsorption performance, the same group introduced 3-amino-1,2,4-triazolate (atz⁻) ligands to increase the density of Lewis basic sites within the framework¹⁴¹. This modification led to the synthesis of [Zn(atz)₂] (MAF-66), prepared via a room-temperature reaction between Zn(OH)₂ and Hatz in aqueous media. Unlike the SOD topology of MAF-4 and MAF-7, MAF-66 crystallizes in a non-interpenetrated diamondoid (dia) topology, yielding a 3D network with a high void volume (~49.8%) (Figure 1.20A). The atz⁻ ligands tetrahedrally coordinate Zn(II) ions similar to imidazolate linkers, but the presence of uncoordinated nitrogen atoms and terminal –NH₂ groups enriches the pore surface, significantly enhancing CO₂ binding affinity. MAF-66 displays permanent porosity with a BET surface area of 1014 m²/g and achieves a high CO₂ uptake of 6.26 mmol/g at 273 K and 1 atm (Figure 1.20B). Moreover, it exhibits excellent CO₂/N₂ selectivity, with a Henry's law ratio of 403 and IAST selectivity of 282 at 273 K, attributed to the nitrogen-rich pore environment. In situ IR and PXRD studies further confirm strong CO₂-framework interactions.

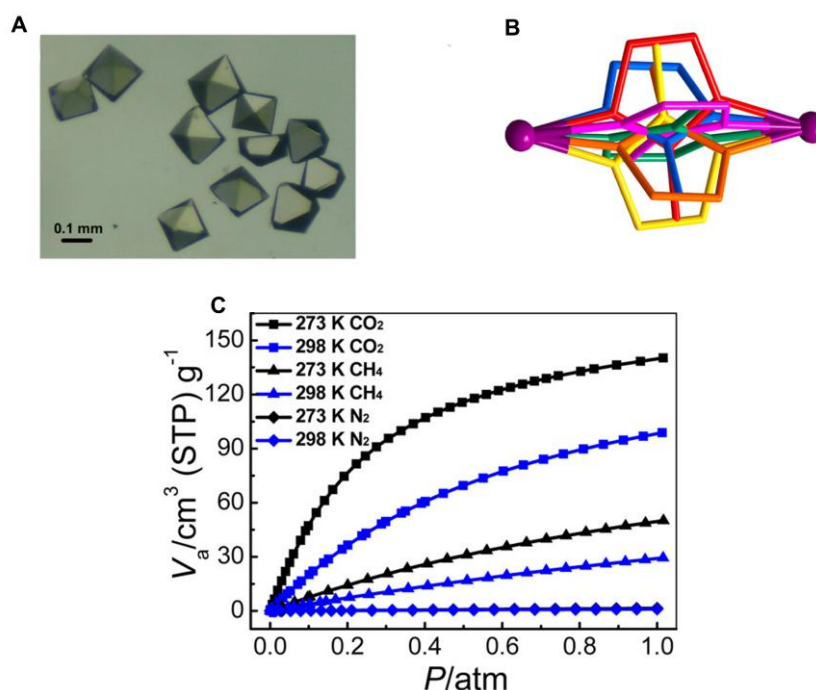


Figure 1.20: (A-B) Photograph of single crystals of MAF-66 and structural fragment showing two Zn atoms bridged by 6-fold disordered atz⁻ ligands. C) Ambient-temperature adsorption isotherms of CO₂, CH₄, and N₂. (Adapted from ref. 141 with permission from © 2012, American Chemical Society).

Although its moderate heat of adsorption (~ 26.0 kJ/mol) indicates a physisorption-dominated mechanism, the structural stability and high selectivity make MAF-66 a promising candidate for CO₂ capture under flue gas conditions. Nevertheless, the use of costly or corrosive solvents during synthesis may pose scalability challenges, highlighting the need for greener synthetic strategies.

1.7. Scope and Objectives of the Thesis

The mounting threat of climate change and industrial emissions has spurred the hunt for materials capable of efficiently and selectively capturing CO₂ under realistic conditions. Among the promising candidates, metal–organic frameworks (MOFs) have emerged as a leading class of materials due to their high surface areas, excellent selectivity, and tunable pore chemistry. However, a critical challenge remains: developing MOFs that not only demonstrate high CO₂ uptake at low concentrations and in the presence of moisture, but also preserve their effectiveness under difficult circumstances such as high humidity and the addition of SO_x/NO_x gasses. While MOFs like MOF-74 display strong CO₂ adsorption, they suffer from poor water stability. Others may offer good selectivity and moisture tolerance but lack scalability or are too expensive for practical use. An ideal MOF for industrial application must combine high capacity, selectivity, water/acid resistance, recyclability, scalability, and cost-effectiveness in a balanced manner.

In this context, CALF-20 has emerged as a strong candidate, meeting many of these requirements. It is a zinc-triazolate-based layered-pillared MOF constructed using oxalate as a bridging linker. CALF-20 is known for its excellent water stability, High capacity, capturing CO₂ in presence of water (<40%) and scalability. However, it faces two key limitations: (i) performance drops at higher humidity (>40% RH), and (ii) CO₂ uptake is limited at low concentrations. Moreover, its structurally simple framework offers limited scope for further functional tuning. Despite its success, the reasons behind CALF-20's humidity tolerance and steam stability are not fully understood. This highlights the need for deeper exploration of zinc-triazolato-oxalate frameworks both to understand their structural behavior and to develop improved analogues with better gas sorption performance.

This thesis focuses on the design and synthesis of new zinc–triazolate-based ultramicroporous MOFs incorporating short linkers such as oxalate, formate, and acetate, and on studying their structural properties and gas adsorption behavior, with particular emphasis on CO₂ capture under humid and low-concentration conditions. Two main strategies were adopted to achieve this goal. In the first approach, we aimed to retain the layered-pillared architecture of CALF-20 but modified its components by replacing oxalate with smaller bridging ligands such as formate and acetate. The incorporation of formate aimed to create narrower pores for enhanced CO₂ uptake at low pressure, while acetate was introduced to impart hydrophobicity to the pore environment, maintaining high CO₂ capacity. This led to the development of **IISERP-MOF16** (formate-based) and **IISERP-MOF28** (acetate-based), both structurally close to CALF-20. These investigations are described in Chapters 2 and 3 (Figure 1.21).

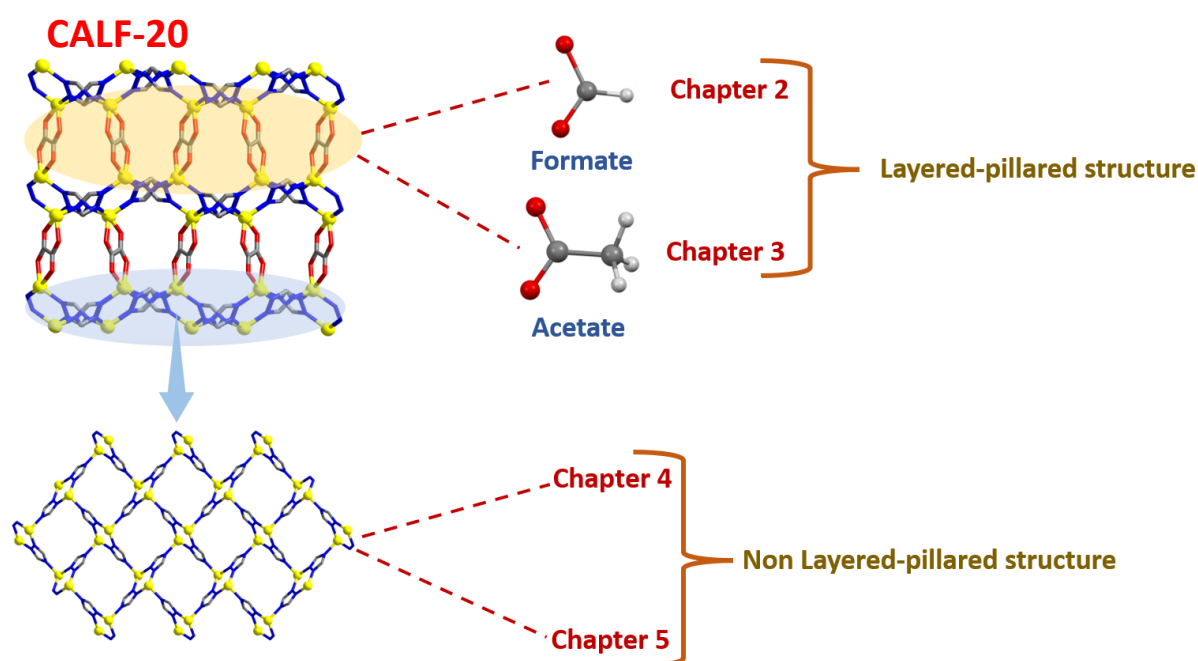


Figure 1.21: Schematic representation of the synthetic strategies employed to develop new ultramicroporous zinc-triazolate-based MOFs

In a parallel and more radical approach, we aimed to disrupt the natural tendency of zinc-triazolate systems to form layer structures by adjusting the oxalate-to-triazolate

ratio and synthetic conditions. This strategy enabled the formation of structurally distinct, non-layered MOFs, such as **IISERP-MOF35** and **IISERP-MOF36**, which are discussed in Chapters 4 and 5 (Figure 1.21). These frameworks exhibit new topologies and unique pore environments for improved gas adsorption. Among these, IISERP-MOF36 is particularly interesting, it was synthesized under ambient conditions using only water as the solvent, making it a highly cost-effective material compared to other zinc-triazolate-oxalate systems. One major challenge throughout these efforts was ensuring phase purity and reproducibility, as even slight variations in pH, solvent, or temperature could lead to entirely different phases.

Despite these challenges, all MOFs were successfully synthesized in pure phase, scaled up to the gram scale, and exhibited good CO₂ uptake, high CO₂/N₂ selectivity, excellent reusability, and strong water stability.

Overall, by addressing the limitations of CALF-20 through thoughtful structural modifications and topological control, this thesis aims to bridge the gap between high-performance and scalable CO₂ adsorbents. The findings contribute to a deeper understanding of structure–property relationships in zinc–azolate frameworks and open new directions for developing robust, selective, and humidity-tolerant materials for practical CO₂ capture applications.

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Chapter 2

**Structure-Property Discernments
from a Hydrophobic Zinc-
Diaminotriazole-Formate Metal
Organic Framework (MOF)
Exhibiting Superior CO₂/H₂O Binary**

2.1 Introduction

Global warming presents a serious threat to Earth's biodiversity and ecological balance mainly because of the relentless emission of greenhouse gases that trap infrared radiation and increase the planet's average temperature. Among these gases, carbon dioxide (CO₂) is the most prevalent, and its atmospheric levels keep rising at an alarming rate.^{1,2} A key source of this increase is the burning of fossil fuels, especially coal, in industrial and power generation sectors.^{3,4} To lessen the environmental impact of these emissions, developing efficient CO₂ capture technologies is essential. Various materials such as zeolites, polymers, ionic liquids, amine-based solvents, and Metal-Organic Frameworks (MOFs) have been studied for this purpose.⁵⁻⁶ Among them, MOFs stand out because of their exceptionally high surface areas, chemical tunability, and precisely defined pore structures, which allow for selective and reversible CO₂ adsorption.⁷⁻¹⁰ In particular, ultramicroporous MOFs (UM-MOFs), defined by pore apertures smaller than 7 Å, have demonstrated exceptional performance in capturing CO₂.¹¹⁻²⁰ Recent studies suggest that metal-azolate-based ultramicroporous MOFs have garnered significant attention due to the tridentate coordination nature of azole rings, which form robust and stable structural motifs upon binding with metal ions.²¹⁻³² These frameworks not only exhibit excellent scalability but also demonstrate remarkable performance under humid conditions.^{27,32} A notable example is CALF-20, a layered pillared structure composed of zinc centers, triazole linkers, and oxalate pillars. CALF-20 exhibits high CO₂ uptake, excellent CO₂/N₂ selectivity, and outstanding structural and functional stability under humid conditions.²⁷ Remarkably, it retains its performance even at 40% relative humidity an uncommon trait among MOFs. These properties make CALF-20 a strong candidate for cost-effective, steam-based selective CO₂ capture. Recent studies have also highlighted structural transformations during humid CO₂ adsorption, which influence the diffusion of CO₂ and water within the framework.³³⁻³⁷ Despite these advantages, the material's hydrophobic nature and its interaction with water are not yet fully understood, limiting the fundamental insights needed to guide further improvements and optimize performance.

To address these challenges, we designed a new UM-MOF inspired by CALF-20, incorporating strategic structural modifications to enhance performance and probe structure-function relationships. Specifically, the oxalate linker was replaced with a shorter formate unit to further restrict pore dimensions and potentially improve CO₂ uptake under both dry and humid environments. Simultaneously, 3,5-diamino-1,2,4-triazole was employed in place of triazole to introduce basic nitrogen sites into the framework, aiming to strengthen interactions with CO₂ molecules through acid–base affinity. After systematic optimization of the reaction conditions, a robust three-dimensional Zn_DamTz_Formate MOF (**IISERP-MOF16**) was synthesized via a solvothermal route. The structural features and gas sorption properties of this material were thoroughly characterized. In particular, its CO₂ adsorption capacity and performance under humid conditions, including competitive CO₂/H₂O adsorption, are studied in detail.

2.2 Experimental section

2.2.1 Synthesis of IISERP-MOF16

Zinc acetate dihydrate (0.5 mmol) and 3,5-diamino-1,2,4-triazole (0.5 mmol) were mixed in a solution of 3 mL DMF and 3 mL water and heated at 150 °C for 48 hours under solvothermal conditions. After the reaction, square-shaped, colourless crystals were collected by filtration and washed well with methanol. Once air-dried, the product showed a yield of around 78% based on the amount of zinc. Powder X-ray diffraction confirmed that the crystals matched the pure phase of **IISERP-MOF16**. By increasing the quantities proportionally, up to 3 grams of the MOF could be produced in a single synthesis.

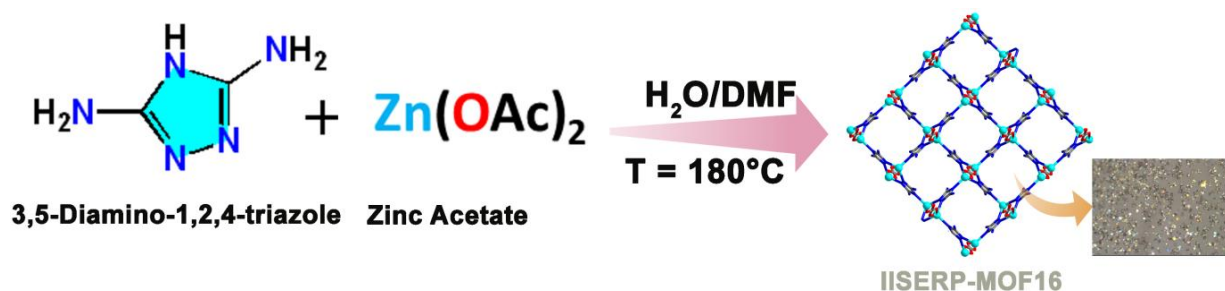


Figure. 2.1 Schematic illustration of the synthetic route used for the preparation of **IISERP-MOF16**.

2.2.1 Single crystal structure determination

Single-crystal X-ray diffraction data for **IISERP-MOF16** were collected using a Bruker SMART APEX diffractometer equipped with a Photon 100 CMOS detector and a microfocus Mo-K α radiation source. The crystal was mounted on a nylon cryo-loop using Paratone-N oil, and data were recorded at 150(2) K. The data were processed using the Bruker SAINT software, and absorption corrections were applied using the SADABS program. The crystal structure was solved by the intrinsic phasing method and refined using the SHELXTL 6.3.1 software package. Non-hydrogen atoms were located through successive difference Fourier maps and refined using least-squares methods, while hydrogen atoms were placed in idealized positions and refined using the riding model.

2.2.3 Powder X-ray diffraction

Powder X-ray diffraction (PXRD) measurements were carried out using a Rigaku Miniflex-600 diffractometer, and the data were analyzed using PDXL software. Variable-temperature PXRD (VT-PXRD) experiments were performed in air on a Bruker system equipped with a built-in furnace, allowing in situ heating during data collection.

2.2.4 Infra-red spectroscopy

Infrared (IR) spectra were collected in the 400–4000 cm⁻¹ range using a Nicolet FT-170SX spectrometer with samples prepared as KBr pellets

2.2.5 Thermogravimetric analysis

Thermogravimetric analysis (TGA) of the as-synthesized MOF was carried out using a NETZSCH TGA-DSC instrument. Measurements were conducted under a nitrogen atmosphere (total flow rate: 20 mL/min), with samples heated from 25 °C to 550 °C at a rate of 5 K/min.

2.2.6 Gas adsorption

All low-pressure gas adsorption isotherms were collected using a Micromeritics ASAP 2020HD analyzer with ultra-high purity gases (grade ≥ 4.8). Before measurement, the MOF sample was soaked in methanol for 48 hours, with the solvent refreshed every 12 hours to ensure complete exchange. Approximately 120 mg of the solvent-exchanged material was placed in a glass sample tube and activated by evacuating at 140 °C for 24 hours under vacuum (10^{-3} mbar) until the outgassing rate dropped below 2 μ bar/min.

High-pressure adsorption isotherms for CO₂, CH₄, and N₂ were obtained using a high-pressure volumetric system (iSorb HP1), capable of recording adsorption data from 10 mbar up to 100 bar. Prior to measurement, around 1 g of the adsorbent was degassed at 140 °C under vacuum for 12 hours. Helium was used to determine the free space in the adsorption cell by dosing a known volume into the pre-evacuated system containing the sample. Isotherms were collected at three different temperatures up to a maximum pressure of 20 bar.

In most cases, the adsorption data were fitted using the Single-Site Langmuir (SSL) model.^{S2.1} When significant deviations were observed, modified Langmuir equations were applied to improve fitting accuracy.^{S2.2} It is well established that even minor errors in model fitting can lead to substantial inaccuracies in selectivity predictions. To address this, the Langmuir fitting was performed using the Solver function in Microsoft Excel, which offers a non-linear fitting approach that avoids bias toward either the low- or high-pressure regions, providing a more balanced fit across the entire isotherm.

Single-Site Langmuir (SSL):

$$q_i = q_m \frac{k_i}{1 + k_i P} P$$

Dual-Site Langmuir (DSL):

$$q_i = q_{m,1} \frac{K_1}{1 + K_1 P} P + q_{m,2} \frac{K_2}{1 + K_2 P} P$$

Ideal Adsorbed Solution Theory (IAST):

IAST calculations were carried out using the method reported by Prausnitz et al.^{S2.3} The selectivity equation used for the calculations is given below. Selectivity:

$$S_{1,2} = \frac{\frac{q_1}{p_1}}{\frac{q_2}{p_2}}$$

S2.1. Kemmer, G.; Keller, S. Nat. Protoc., 2010, 5, 267-281.

S2.2 Richter, E.; Schuetz, W.; Myers, A. L. Chem. Eng. Sci., 1989, 44, 1609-1616.

S2.3 Myers, A. L.; Prausnitz, J. M. AIChE J., 1965, 11, 121-127.

2.2.7 Dynamic vapour sorption studies:

Water Isotherms in the presence of nitrogen and carbon dioxide were measured on a gravimetric apparatus i.e., a Dynamic vapor sorption (DVS) analyzer (Surface measurement system, SMS). The DVS can measure water isotherms at an ambient pressure of 1 bar. It records the amount of water vapor adsorbed on the adsorbent by measuring the change in the weight of the sample. Before running the water adsorption experiment, the adsorbent was preheated for 720 minutes in the presence of nitrogen at 150°C. Initially, the water adsorption and desorption experiments in the presence of nitrogen are performed at 30 °C at 10 % Relative Humidity (RH) intervals. An adsorbent weight of 30-100 mg was used for the experiments. At each RH interval, the sample is equilibrated until it reaches the rate of mass change of 0.002 or 720 minutes.

2.3 Results and Discussion

2.3.1 Characterization

The single crystals of Zn_DamTz_Formate (**IISERP-MOF16**) were obtained by solvothermal reaction of Zinc acetate and 3,5 Diaminotriazole, in H₂O and DMF mixture of at 180 °C for two days. The adopted reaction conditions do not utilize formic acid or other direct source of formate in the reaction mixture. However, the single crystal X-ray diffraction (SCXRD) analysis of **IISERP-MOF16** indicated the presence of formate in **IISERP-MOF16** as a linker between two layers. Furthermore, to get clarity of the formate source, we tried to vary the reaction conditions and

starting materials. The utilization of different Zn salts like ZnNO_3 , ZnSO_4 , ZnCO_3 , ZnAc , etc. resulted in the same **IISERP-MOF16** MOF as a pure phase. These experiments suggest that the linking formate in **IISERP-MOF16** is generated in the reaction medium by the hydrolysis of DMF solvent. Importantly, the phase cannot be formed if DMF was not present in the medium. Such transformation of DMF to formate under solvothermal conditions is reported.^{21,38,39} The SCXRD analysis performed on the square-shaped crystals (Fig. 2A.1) of **IISERP-MOF16** revealed that the MOF $[\text{Zn}(\text{Damtz})(\text{Formate})]$, crystallizes in the monoclinic $P2_1/c$ space group ($a = 8.831(4) \text{ \AA}$; $b = 9.192(5) \text{ \AA}$; $c = 9.838(5) \text{ \AA}$) (Table S1). The asymmetric unit of **IISERP-MOF16** was found to be neutral containing one 3,5-Damtz moiety, one formate and one Zn atom (Fig. 2A.2). The Zn atom in **IISERP-MOF16** is in a tetrahedral geometry and is linked to three distinct triazolate groups as well as an oxygen atom from a formate. A closer look at the crystal structure of **IISERP-MOF16** reveals its 3D layered-pillared framework with classical Zn-triazolate layer running along the ac plane pillared by formate units (Fig. 2.2A). The layered pillared structure of **IISERP-MOF16** is similar to the structure of known layered pillared ultramicroporous MOFs like CALF-20 ($[\text{Zn}_2(\text{Tz})_2(\text{Ox})] \cdot 0.5\text{H}_2\text{O}$) and IISERP-MOF32 ($[\text{Zn}_2(\text{Atz})_2(\text{Ox})] \cdot 0.5\text{H}_2\text{O}$). The pillaring formate in **IISERP-MOF16** differentiates it from CALF-20 and IISERP-MOF32 which are pillared by oxalate moiety. The structural similarity of **IISERP-MOF16** to CALF-20 and IISERP-MOF32 prompted a detailed investigation into its characteristics. A comparative analysis of the zinc-triazolate layers in these materials reveals that the $\text{Zn}_4(\text{trz})_4$ tetrameric unit in **IISERP-MOF16** exhibits a higher degree of symmetry; it is a near-perfect square (Fig. 2.2B). Furthermore, the simulated PXRD patterns for **IISERP-MOF16**, CALF-20, and IISERP-MOF32 show close resemblance, suggesting similar structural properties (Fig. 2.2C). Notably, the calculated mean plane distance for **IISERP-MOF16** is $8.32 \text{ \AA}$, which lies between the values observed for CALF-20 and IISERP-MOF32 (Fig. 2A.3). This intermediate distance highlights the unique structural attributes of **IISERP-MOF16** within this series of layered pillared ultramicroporous zinc-triazolate-dicarboxylate MOFs.

The powder X-ray diffraction (PXRD) analysis of **IISERP-MOF16** demonstrated that the as-synthesized sample has a pattern consistent with the one calculated from its single-crystal structure. This confirms the bulk purity of **IISERP-MOF16** (Fig. 2A.4). Thermogravimetric analysis (TGA) showed that **IISERP-MOF16** has a good thermal stability stable up to around 250 °C which was further validate by variable temperature PXRD (Fig. 2A.5 and 2A.6). The initial step like weight loss of 18 % can be attributed to the loss of formate unit present in the framework.

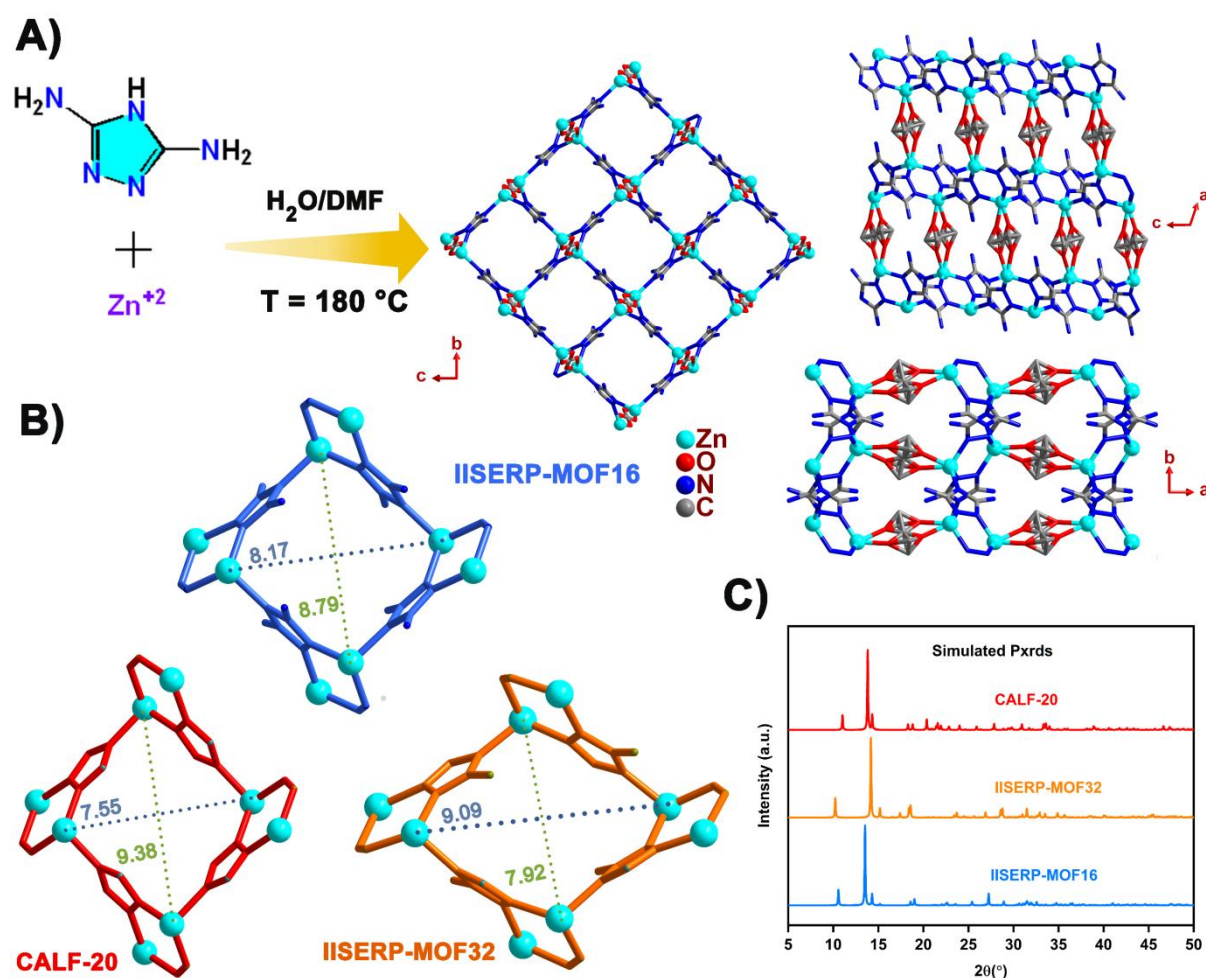


Figure 2.2: (A) Schematic scheme for synthesis (The view of pore also visualizes in **IISERP-MOF16** along c-axis) and packing diagram of **IISERP-MOF16**. (B) A comparison of Zinc triazole dimer grid for **IISERP-MOF16**, **IISERP-MOF32** and **CALF-20**.

20. (C) A comparison simulated PXRDs profile for **IISERP-MOF16**, **IISERP-MOF32** and **CALF-20**.

Furthermore, the Fourier Transform Infrared Spectroscopy (FTIR) spectrum of **IISERP-MOF16** confirms the presence of formate as a pillaring unit in the framework with a characteristic peak at 2923 cm^{-1} corresponding to C-H (HCOO^-) (Fig. 2A.7).

2.3.2 Gas Adsorption Studies

To further evaluate the porous nature of **IISERP-MOF16**, CO_2 adsorption studies were performed at different temperatures (273 K, 283K, 298 K and 313 K). At 298 K and 1 bar pressure, **IISERP-MOF16** resulted in CO_2 and N_2 uptakes of 40.2 and 1.8 cc/g, respectively (Fig. 2.3A and 2A.9). To further understand the underlying mechanism of lower CO_2 uptake capacity of **IISERP-MOF16**, its BET and Langmuir surface areas were calculated by using the 273 K adsorption isotherm. The resulting BET and Langmuir surface areas of $238\text{ m}^2/\text{g}$ and $264\text{ m}^2/\text{g}$ respectively (Fig. 2A.8) for **IISERP-MOF16** are relatively less than those reported of **CALF-20** and **IISERP-MOF32**, warranting its moderate CO_2 uptake capacity. The lesser BET surface area obtained for **IISERP-MOF16** could be due to the presence of two free $-\text{NH}_2$ groups in this MOF, those are occupying the pore space making it less efficient for upcoming CO_2 molecules. The non-local density functional theory (NLDFT) fit for **IISERP-MOF16** indicated a pore size of approximately $5.2\text{ \AA}$, in line with the ultra-microporous region (Fig. 2A.8). Also, the Ideal Adsorbed Solution Theory (IAST) calculations performed using the 298 K CO_2 and N_2 isotherms, employing a nominal composition of $15\text{CO}_2:85\text{N}_2$, yielded a CO_2/N_2 selectivity of 67 at 1 bar (inset: Fig. 2.3B and 2A.9). The selectivity value obtained for **IISERP-MOF16** is sufficient to achieve the benchmarked 99% purity during separation. Furthermore, to check the binding strength of CO_2 with the framework, the heat of adsorption (HOA) value was calculated using density functional theory (DFT) model at 313, 298, and 273 K CO_2 isotherms. This resulted in a HOA value of 32 kJ/mol for **IISERP-MOF16** at zero loading and it reaches 42 kJ/mol for higher loadings (Fig. 2.3B). The moderate HOA value of **IISERP-MOF16** suggests its active regeneration after use.

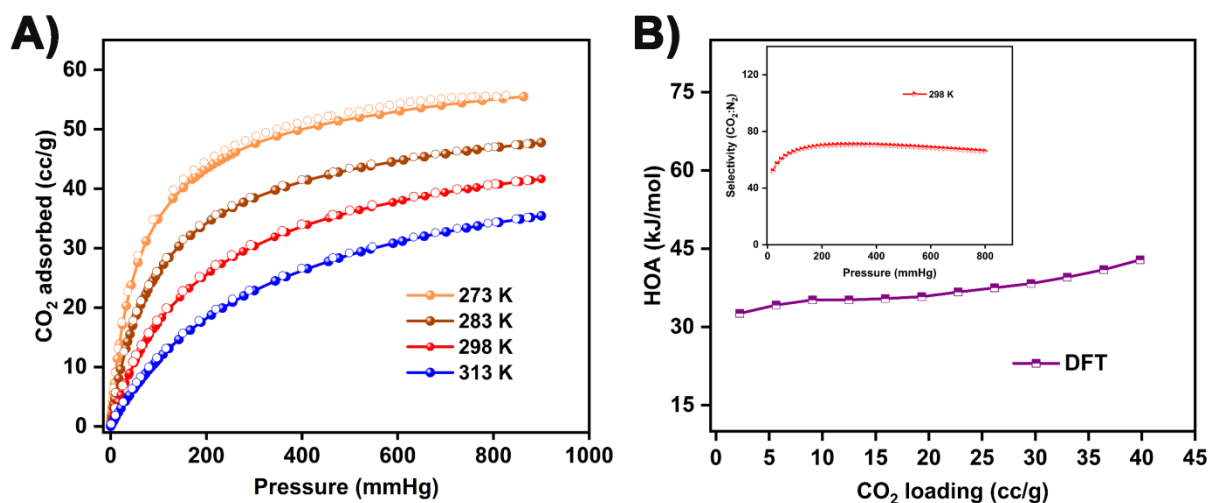


Figure 2.3: (A) The CO₂ adsorption isotherms obtained for **IISERP-MOF16** at different temperatures. (B) The HOA plots from the DFT modelling done using the CO₂ isotherms at 273, 283, and 298 K. Inset: CO₂/N₂ selectivity calculated using the IAST model employing a nominal composition of 15CO₂:85N₂ at different temperatures and 1 bar pressure.

2.3.3 Stability and Competitive H₂O-CO₂ adsorption Studies of MOF

The **IISERP-MOF16** demonstrates significant scalability and cost-effectiveness in capturing CO₂ from flue gas. An ideal metal-organic framework (MOF) for this application should exhibit key characteristics such as selectivity for CO₂ over N₂, functionality in humid conditions, and stability—chemical, mechanical, and thermal after multiple adsorption-desorption cycles. Given that flue gas contains water vapor, nitrogen oxides (NO_x), sulfur oxides (SO_x), and other components, a suitable MOF must maintain low water uptake while remaining stable in aqueous environments. Water adsorption isotherm studies of **IISERP-MOF16** conducted at three temperatures (293 K, 303 K, and 313 K) indicated a lower water uptake compared to CALF-20 (Fig. 2A.10). To accurately assess the MOF's performance under humid conditions, competitive adsorption experiments involving H₂O and CO₂ were

performed using dynamic vapor sorption (DVS) measurements. For comparative analysis, identical experiments were conducted with CALF-20. The DVS results revealed that **IISERP-MOF16** exhibited a CO₂ capacity of 10 cc/g, significantly lower than CALF-20's 43 cc/g under pure CO₂ conditions at 0.15 bar and 50 °C (Fig. 2.4A).

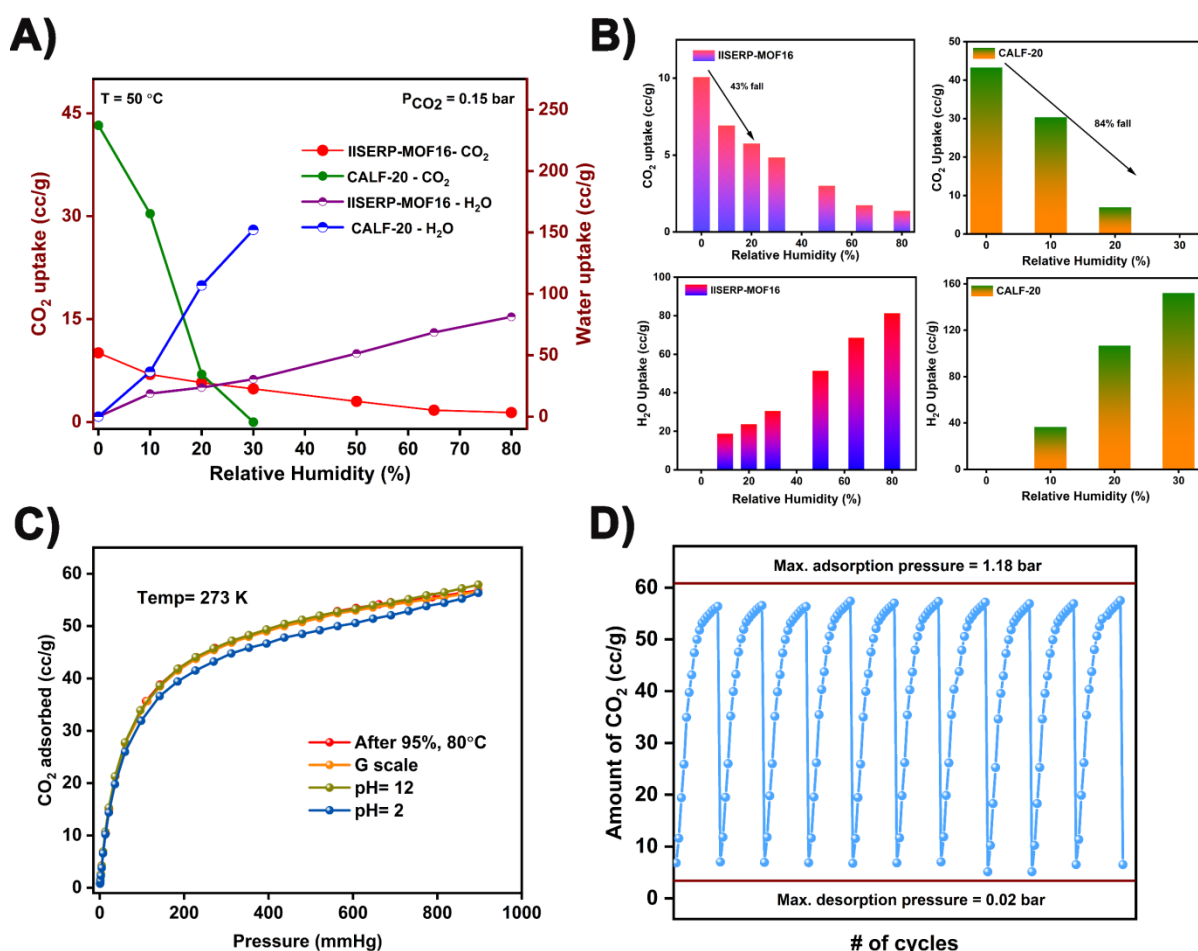


Figure 2.4: (A) CO₂ and H₂O loadings measured via dynamic vapor sorption (DVS) experiments. (B) Retention of CO₂ capacity in **IISERP-MOF16** compared to CALF-20. (C) CO₂ adsorption isotherms for **IISERP-MOF16** subjected to various treatment conditions. (D) CO₂ iso-cycling experiment showing consecutive adsorption-desorption cycles performed on **IISERP-MOF16**.

The higher CO₂ adsorption in CALF-20 most likely due to the more number of oxygens provided by the oxalate units in comparison to the formate in **IISERP-**

MOF16. The CO₂ uptakes measured under DVS aligns with volumetrically measured equilibrium CO₂ loadings. As relative humidity (RH) increased to 20%, CALF-20's CO₂ capacity plummeted to 7 cc/g (an 84% decrease), ultimately reaching zero at 30% RH. In contrast, **IISERP-MOF16** exhibits a 43% decrease in CO₂ capacity at 20% RH; however, it does not reach zero and retains some CO₂ capacity even at 80% RH indicate the possible adsorption of selective CO₂ molecules in the presence of water molecule (Fig. 2.4B). Moreover, the chemical stability of **IISERP-MOF16** is validated by soaking it in different pH graded solutions. No obvious structural changes were noticed for **IISERP-MOF16** even after 5 days of exposure to such harsh conditions, as validated it's their powder patterns (Fig. 2A.11). Also, **IISERP-MOF16** demonstrates a strong stability after 10 days of soaking in different solvents like H₂O, DMF, THF, ACN and MeOH (Fig. 2A.12).

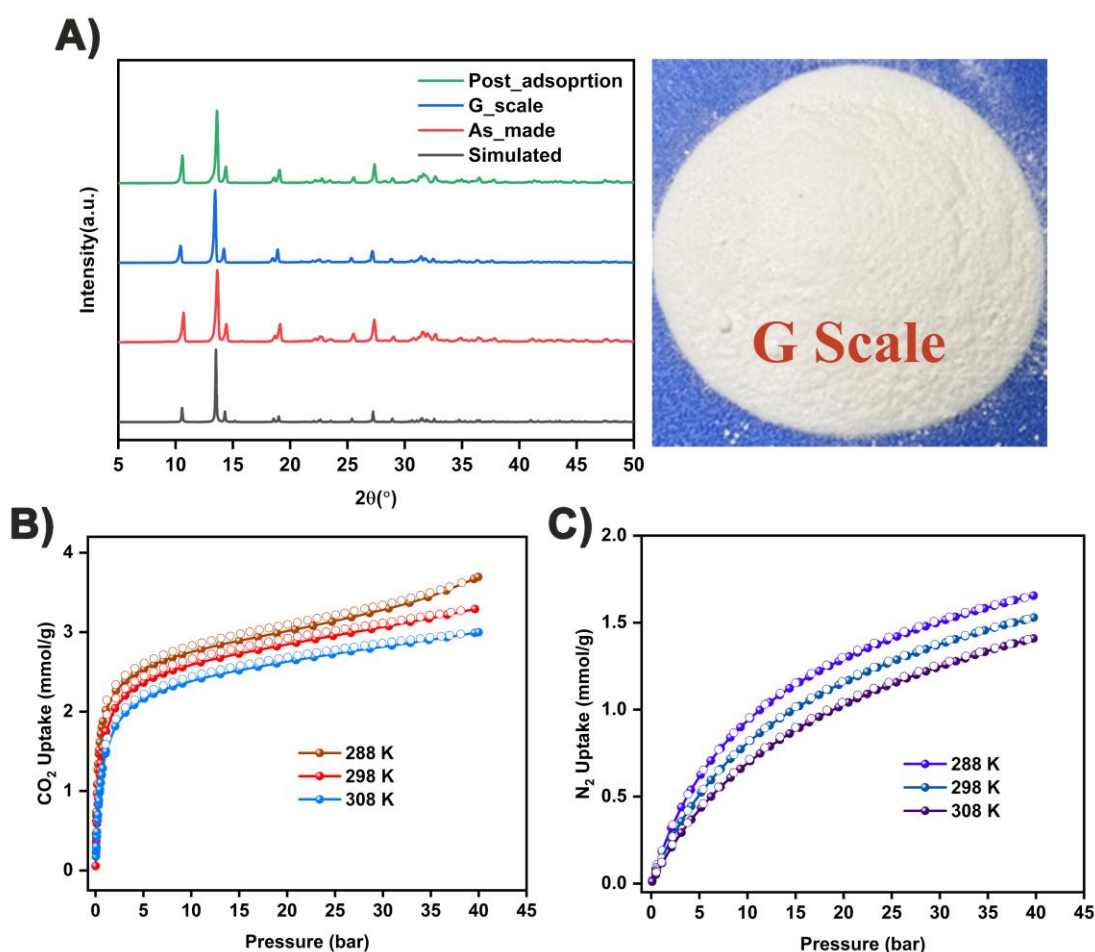


Figure 2.5: (A) PXRD comparison illustrating the bulk purity achieved through gram-scale synthesis, as well as the material's stability during several adsorption-desorption and evacuation cycles. This material can be produced in quantities of up to 5 grams in a single synthesis. (B) High-pressure CO₂ isotherm of **IISERP-MOF16** measured at different temperatures. (C) High-pressure N₂ isotherm of **IISERP-MOF16** measured at different temperatures.

Furthermore, the **IISERP-MOF16** was exposed to a controlled relative humidity (RH) condition of 95 % at a constant temperature of 353 K for 5 hours and was checked for its intact crystallinity via post-PXRD experiments (Fig. 2A.11). The 298 K CO₂ uptakes obtained for the post-chemically treated **IISERP-MOF16** samples authorize its permanent porosity retention characteristics (Fig. 2.4C). To assess recyclability, we conducted ten consecutive CO₂ adsorption and desorption cycles. No significant decrease in volumetric capacity was observed, demonstrating the material's stability during repeated use (Fig. 2.4D). Additionally, **IISERP-MOF16** can be scaled to multi-gram quantities in a single-step synthesis using the solvothermal method (Fig. 2.5A). The results indicate that **IISERP-MOF16** is scalable, exhibits humidity stability, and is both robust and cost-effective. Additionally, it demonstrates recyclability and meets all criteria for CO₂ capture in post-combustion processes, despite its relatively low CO₂ uptake.

Furthermore, we investigated the high-pressure gas adsorption isotherms for CO₂ and N₂ up to 40 bars on **IISERP-MOF16** (Fig. 2.5B-C). These studies revealed that the framework exhibits exceptional structural rigidity, maintaining its integrity and porosity even under elevated pressures. Notably, a significant portion of CO₂ occurs at low pressure, with only a modest increase in uptake observed as the pressure rises to higher levels. This behaviour highlights the strong affinity of the framework for CO₂ at low pressures and underscores its potential for energy-efficient CO₂ capture applications.

2.4 Conclusion

In summary, we have successfully synthesized and characterized a 3D MOF, Zn_DamTz_Formate (**IISERP-MOF16**), featuring a layered pillared architecture closely resembling that of CALF-20 and IISERP-MOF32. A comparative analysis of their structural properties was conducted to understand the influence of framework design on gas adsorption behavior. **IISERP-MOF16** exhibits a relatively lower CO₂ adsorption capacity due to its reduced surface area; however, it demonstrates a moderate heat of adsorption, which facilitates energy-efficient regeneration after use. The material also shows moderate CO₂/N₂ selectivity based on Ideal Adsorbed Solution Theory (IAST) under flue gas conditions. Notably, dynamic vapor sorption measurements reveal that **IISERP-MOF16** maintains CO₂ uptake even at elevated relative humidity levels an improvement over CALF-20, attributed to the presence of free -NH₂ groups within the framework. Despite its moderate CO₂ capacity, the excellent structural stability under various conditions and scalability make this MOF a robust candidate for CO₂ capture from different sources.

2.5 References

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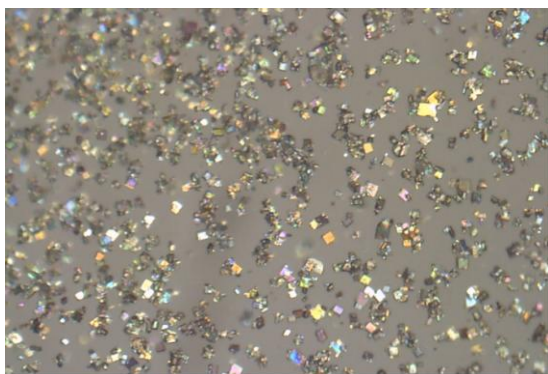


Figure 2A.1. Optical microscopy reveals the formation of square-shaped crystals during the growth process.

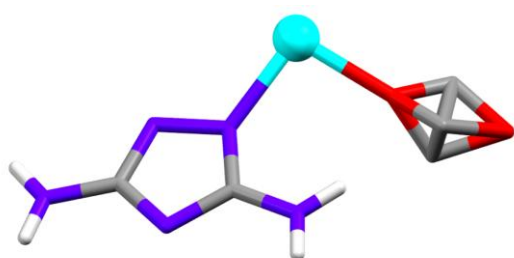


Figure 2A.2. The asymmetric unit of **IISERP-MOF16**. Note: The formate group within the asymmetric unit exhibits disorder.

Table 2A.1: Crystallographic Information for **IISERP-MOF16**.

Lattice Parameters:	
$a/\text{\AA}$	8.831(4)
$b/\text{\AA}$	9.192(5)
$c/\text{\AA}$	9.838(5)
$\alpha/^\circ$	90
$\beta/^\circ$	108.760(15)

$\gamma/^\circ$	90
$V/\text{\AA}^3$	756.2(7)
Crystal System	Monoclinic
Space Group	$P2_1/c$
Color	Colourless
Expt. Crystal description	Square shape
Z	4
T/ K	150 K
Diffraction Source	MoK α
Diffraction radiation wavelength/ $\text{\AA}$	0.71073
Diffraction reflection theta min	2.436
Diffraction reflection theta max	28.211
Reflection number total	1837
Reflection number gt	1430
R1, wR2 [$I > 2\sigma(I)$]	0.063, 0.176
R1, wR2 (all data)	0.080, 0.191
GoF	1.007

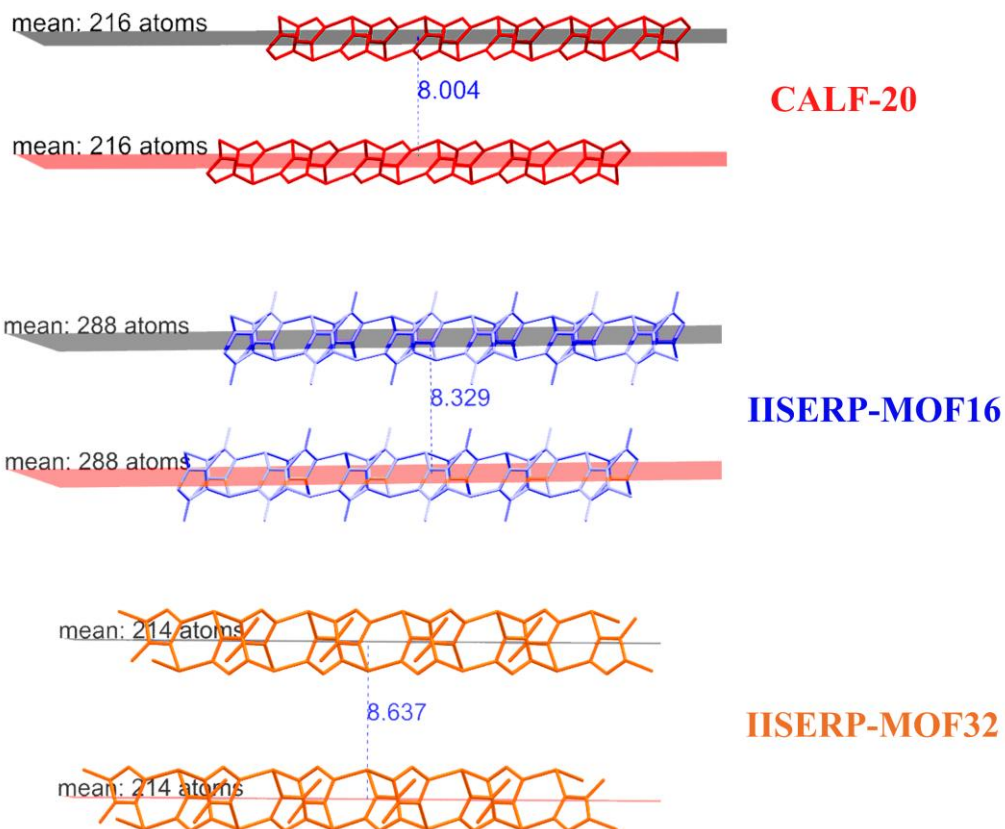


Figure 2A.3. Calculate Mean Plane distance for **IISERP-MOF16**, IISERP-MOF32 and CALF-20.

Powder X-ray diffraction:

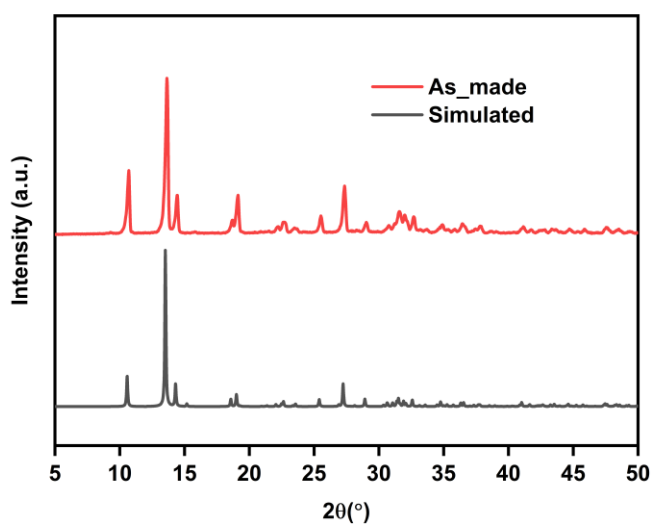


Figure 2A.4. The PXRD profile of **IISERP-MOF16** indicates the bulk purity of the material.

PLATON analysis:

Total estimated solvent-accessible void volume (as determined by the SOLV-Map value) = $191 \text{ \AA}^3$

Unit cell volume, $V = 756.17 \text{ \AA}^3$

Now, Void volume = $(191/756.17) \times 100 = \sim 25.25 \%$ of the **IISERP-MOF16**.

IISERP-MOF16 features a neutral framework, and the formula unit present in its crystal structure is $[\text{Zn}(\text{C}_2\text{N}_5\text{H}_4)(\text{HCOO})] \cdot (\text{H}_2\text{O})_x$, where x denotes the number of water molecules associated with the structure.

Z for **IISERP-MOF16** is 4.

Based on the SQUEEZE results, the solvent-accessible void per unit cell contains 46 electrons. For the asymmetric unit, this corresponds to $46/4 = 11.5$ electrons, which approximately accounts for the presence of one water molecule. Therefore, the formula of formula unit in **IISERP-MOF16** is $[\text{Zn}(\text{C}_2\text{N}_5\text{H}_4)(\text{HCOO})] \cdot \text{H}_2\text{O}$.

The molecular mass of formula unit is = **208 g/mol**

The mass loss attributed to the formate group is approximately 45 g/mol. Therefore, based on PLATON analysis, the expected mass loss is around $(45/208) \times 100 \sim 21.6\%$.

Now, expected mass loss due to 3,5 Diamino-triazole = $(98/208) \times 100 = 47.11 \%$.

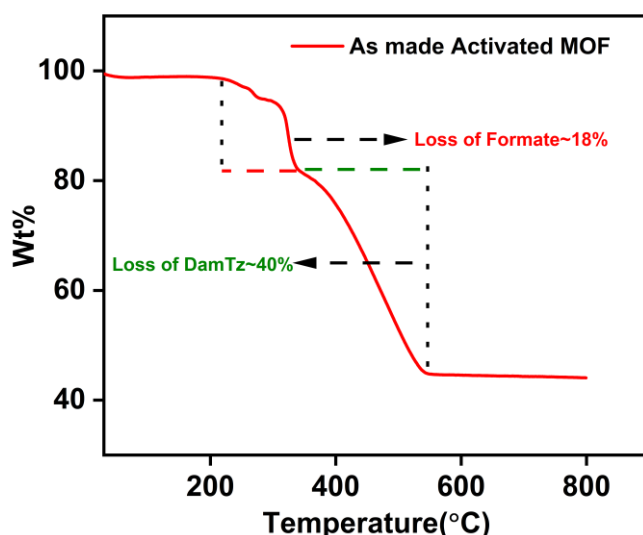


Figure 2A.5. The TGA profile of **IISERP-MOF16** demonstrates its thermal stability up to 300 °C.

This results from the PLATON analysis closely match the experimental TGA data of **IISERP-MOF16**. Both the observed weight loss from TGA and the expected weight loss from PLATON analysis align well, supporting the formula unit of **IISERP-MOF16** as $[\text{Zn}(\text{C}_2\text{N}_5\text{H}_4)(\text{HCOO})]\cdot\text{H}_2\text{O}$.

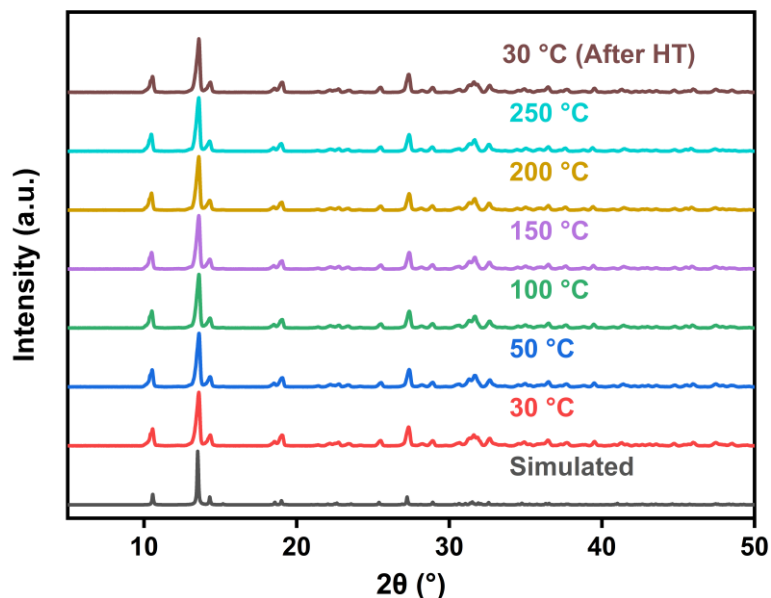


Figure 2A.6. Variable temperature PXRD of **IISERP-MOF16** illustrating the framework's stability and rigidity over a wide range of temperatures.

IR analysis:

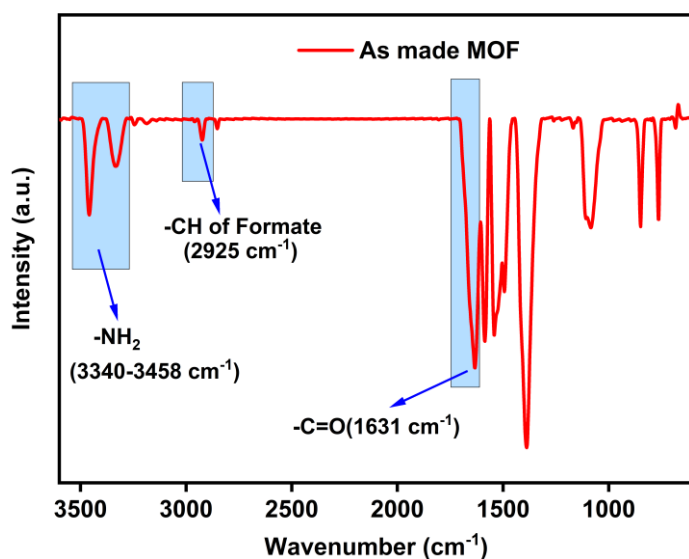


Figure 2A.7. Infra-red spectra of **IISERP-MOF16**, highlighting the characteristic stretching and bending vibrations. Key peaks observed include: IR (cm^{-1}): $\nu(\text{N-H})$: 3340 and 3458; $\nu(\text{C-H})$: 2925s; $\nu(\text{C=O})$: 1631s.

Adsorption Analysis

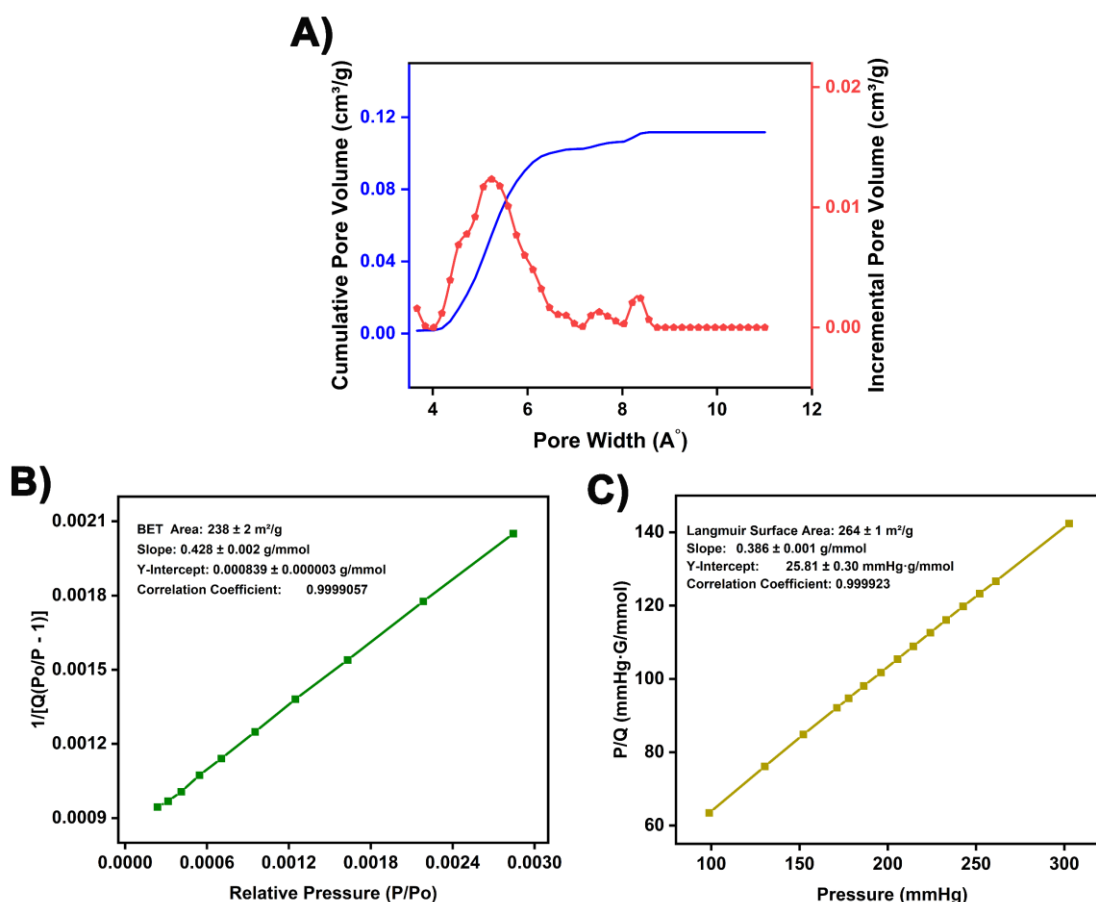


Figure 2A.8. A) The pore size distribution of **IISERP-MOF16** was calculated using the Non-Local Density Functional Theory (NLDFT) method, applying a slit pore model to the CO_2 adsorption isotherm measured at 273 K. B) BET and Langmuir fitting for **IISERP-MOF16** derived from the CO_2 adsorption isotherm at 273 K.

The CO_2/N_2 selectivity for **IISERP-MOF16** was estimated using experimental single-component adsorption isotherms and calculated through Ideal Adsorbed Solution Theory (IAST), assuming a gas mixture composition of 15% CO_2 and 85% N_2 . The calculations were performed at 1 bar total pressure and 313 K, which are representative conditions for post-combustion CO_2 capture.

IAST fitting parameters for IISERP-MOF16 (CO_2/N_2):

Appendix for Chapter 2

At 298 K

Gas A = CO₂

Gas B = N₂

Table S2: Fitted IAST parameters for CO₂/N₂ (15CO₂:85N₂ composition) selectivity at 298 K for **IISERP-MOF16**.

Gas A Constants		Gas B Constants	
q_{s1} (mmol g ⁻¹) =	2.345055599	q_{s1} (mmol g ⁻¹) =	2.33393912
q_{s2} (mmol g ⁻¹) =	0	q_{s2} (mmol g ⁻¹) =	0
K_1 (mbar ⁻¹) =	0.004953641	K_1 (mbar ⁻¹) =	0.00017684
K_2 (mbar ⁻¹) =	0	K_2 (mbar ⁻¹) =	0
n_1 =	0.947000121	n_1 =	0.77042692
n_2 =	0	n_2 =	0
H_1 (mmol mbar ⁻¹ g ⁻¹) =	0.011616564	H_1 (mmol mbar ⁻¹ g ⁻¹) =	0.00082974
H_2 (mmol mbar ⁻¹ g ⁻¹) =	0	H_2 (mmol mbar ⁻¹ g ⁻¹) =	0

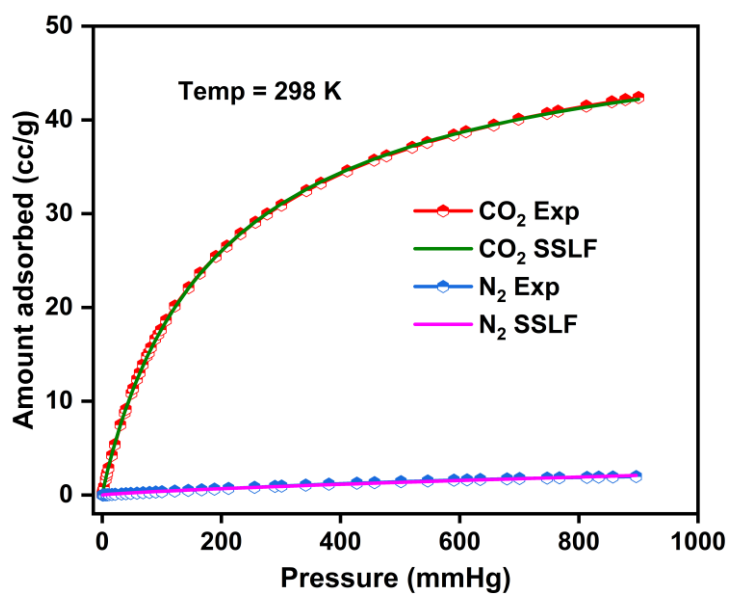


Figure 2A.9. IAST fitting of CO₂ and N₂ isotherms for **IISERP-MOF16** obtained at 298 K.

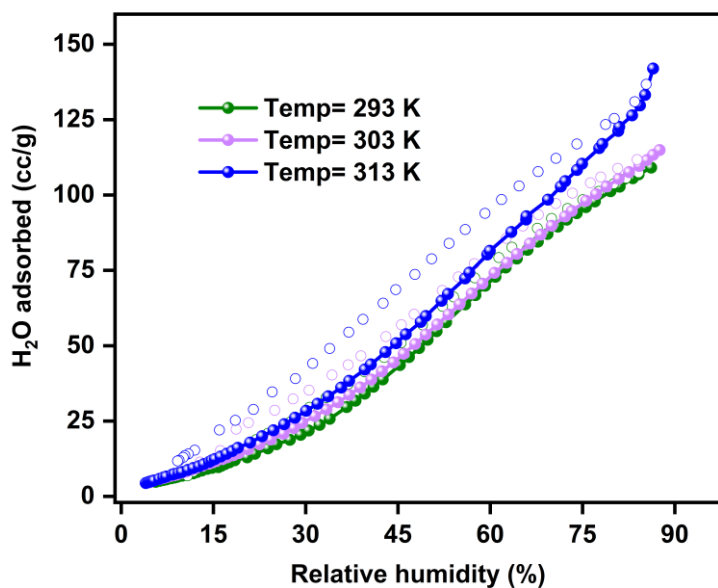


Figure 2A.10. The water adsorption isotherm of **IISERP-MOF16** obtained at 293, 303, and 313 K.

Stability Studies

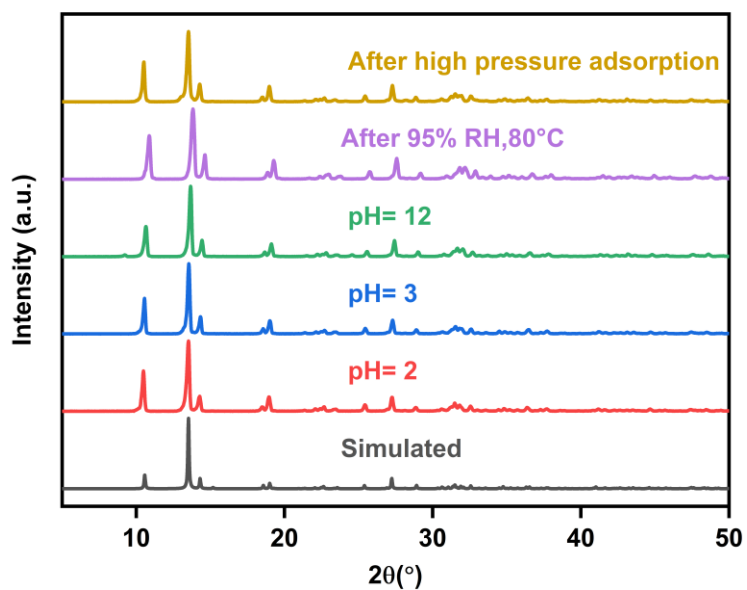


Figure 2A.11. The PXRD patterns of **IISERP-MOF16** were studied under a range of harsh conditions, such as exposure to different pH environments, varying humidity levels, and following high-pressure adsorption processes.

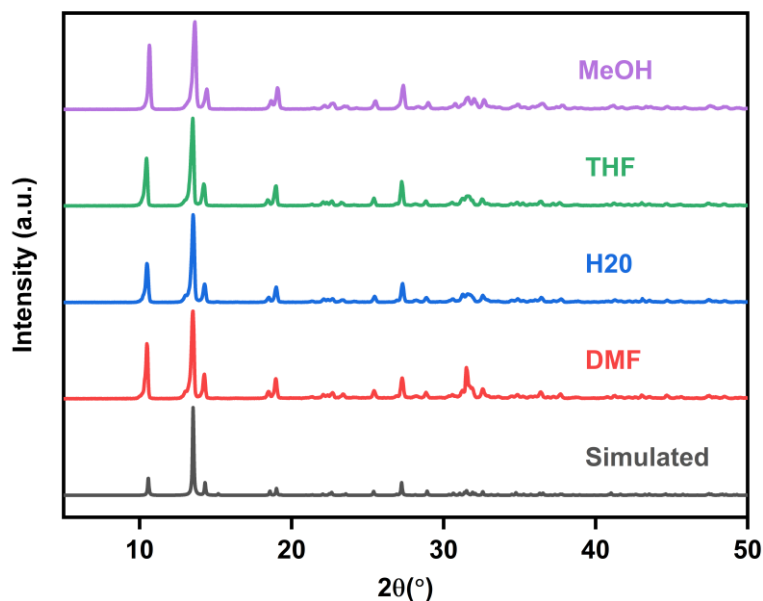


Figure 2A.12. After 10 days of soaking, PXRD profiles show the stability of **IISERP-MOF16** in different solvents.

Chapter 3

**Preferential CO₂ adsorption by an
ultra-microporous 3D zinc-
aminotriazolato-acetate MOF**

3.1 Introduction

Capturing CO₂ present in different concentrations along with other gases is vital to managing global CO₂ concentrations.^{1, 2} Sorbents play a key role here, and metal-organic frameworks (MOFs) form an important class of designable sorbents.³⁻⁸ MOF functionalized with basic groups aids selective adsorption of CO₂ from gas mixtures. In this context, azolate MOFs have gained a special position due to their tridentately linking azole rings, which form stable structural motifs when combined with ions of Zn, Co, Ni, Mn, Fe etc.⁹⁻¹⁸ They can have zeolitic structures or a layered-pillared structure, and some show excellent scalability and ability to do humid CO₂ capture.¹⁹⁻²⁸ Short pillars result in ultra-microporous MOFs, which can converge the basicity of the azolate with the molecular sieving to gain a high CO₂ selectivity.^{21,22,26} While many such layered-pillared MOFs with azolates are reported,²¹⁻³¹ some of the readily accessible pillaring agents have been elusive in generating the sort-out 3D ultra-microporous structures. Achieving this robust 3D framework from simple ligand combinations depends on identifying optimized reaction conditions and its selective CO₂ sorption relies on the binding group's orientations within the pore. All things considered, we particularly want to form a Zn-Atz (Atz = 3-amino-1,2,4-triazolate) layer pillared by acetate ligands. The idea being two short linkers will give rise to ultra-micropores lined by basic triazolate rings and polarizing acetate oxygens, and the CO₂-philic amine groups can decorate their walls. The methyl groups of the acetate should provide the required hydrophobic lining to keep water away, thus making the MOF suited for humid CO₂ capture. We successfully optimized the condition for isolating this Zn-Atz-Acetate MOF with a 3D structure. However, completing the 3D framework from only these ligands (Atz and acetate) required the charge-balancing from a free hydroxide anion that resides in the pore.^{32,33} The sway of this simple structure with diverse chemical sites on CO₂ adsorption is discussed here.

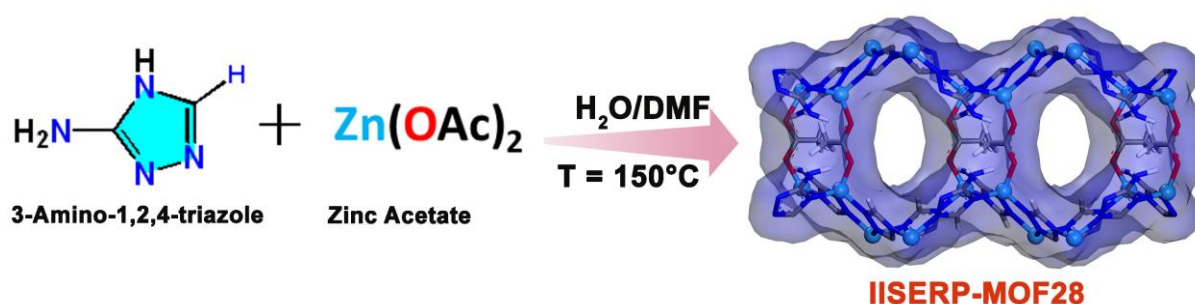
IISERP-MOF28, Zinc aminotriazolato acetato hydroxide, Zn₂(CH₃COO)(C₂N₄H₄)₂.(OH⁻)(H₂O)_x, **1**, was synthesized solvothermally in a DMF+Water system. The role of the solvent is crucial, as using the more commonly used solvent system, water + methanol or ethanol,²¹ leads to the formation of a 2D

layered solid with acetate groups hanging into the interlayer spaces.¹⁰ Using only neat DMF or water does not work. The solvent mixture employed here provides the right basic condition for the generation of hydroxide species.

3.2 Experimental section

3.2.1 Synthesis

A solvothermal reaction between Zinc acetate dihydrate (0.5 mmol) and 3-Amino-1,2,4-Triazole (0.5 mmol) in a solution containing 3 ml DMF +3 ml water was carried out at 150°C for 48hrs. Block shaped colourless crystals were isolated by filtration and were washed with plenty of methanol. The air-dried sample gave a yield of ~70% based on Zn. The PXRD pattern indicated this to be a pure phase of **IISERP-MOF28**. In a single synthesis up to 2g of the MOF was synthesized just by scaling up of the above synthesis.



Scheme 3.1. Synthesis of **IISERP-MOF28**.

3.2.2 Crystallography

Single-crystal X-ray diffraction was done on a Bruker SMART APEX four-circle diffractometer equipped with a CMOS photon 100 detector and Micro focus($1\mu\text{S}$) using a Cu-K α radiation. The crystal of **IISERP-MOF28** was mounted on nylon Cryo loops using Paratone-N oil. Data was collected at 150 (2) K. Total data was integrated using Bruker SAINT Software and using SADABS it was corrected for absorption. Structure was solved using Intrinsic Phasing routine and was refined using the SHELXTL 6.3.1 (2004) software suite. All the non-hydrogen atoms were located from iterative

examination of difference F-maps following which the structure was refined using least-squares method. Hydrogen atoms were fixed geometrically in a riding model.

Table 3.1: Details of crystallographic data collection and structure refinements for IISERP-MOF28.

a/Å	9.7110(9)
b/Å	16.1290(15)
c/Å	9.7091(9)
α /deg	90
β /deg	90
γ /deg	90
V/Å ³	1520.72(2)
Crystal System	Orthorhombic
Space Group	Pnma
Color	colourless
Expt. Crystal description	Block shape
Z	4
T/ K	150 K
Diffraction Source	CuK α
Diffraction radiation wavelength/ Å	1.54178
Diffraction reflection theta min	5.3
Diffraction reflection theta max	69.1
Diffraction reflection theta full	67.79
Reflection number total	1463

Reflection number gt	1341
R1,wR2 [$>2\sigma(I)$]	0.058, 0.174
R1,wR2(all data)	0.062, 0.178
GoF	1.115

3.2.3 Powder X-Ray Diffraction

Powder XRDs were done using a Rigaku Miniflex-600 instrument and processed using PDXL software. The Variable temperature powder X-ray diffraction (VT-PXRD) were carried out on a full fledge Bruker instrument using the in-built furnace and in air.

3.2.4 Infra-red Spectroscopy

The infrared (IR) spectrum was recorded on a Nicolet FT-170SX instrument using KBr discs in the 400–4000 cm^{-1} region.

3.2.5 Thermogravimetric analysis:

Thermogravimetry analysis of as made MOF was performed on NETSZCH TGA-DSC instrument. The routine TGAs were done under N_2 gas flow (20 ml/min) (purge + protective) and samples were heated in the temperature range of 25 to 550 $^{\circ}\text{C}$ with a heating rate of 5 $^{\circ}\text{K min}^{-1}$.

3.2.6 Gas Adsorption

All the gas adsorption analysis were carried out using ~100 mg of **IISERP-MOF28**. Sample was directly activated by evacuation at 150 $^{\circ}\text{C}$ for 24 hrs (10^{-6} mbar) till an outgas rate was ≤ 2 $\mu\text{bar/min}$ was achieved. Then the activated MOF was transferred to the analysis port of Micromeritics ASAP 2020HD or 3-FLEX instrument for the gas sorption analysis. Gas analyses were carried out with ultrahigh purity gases (≥ 4.8 grade).

Langmuir Fits:

In all cases the isotherms were fit to the Single-Site Langmuir (SSL) equation. The isotherms were fit by solving the Langmuir isotherm equation using the solver function in Microsoft Excel. Utilizing this routine circumvents some of the problems associated with favouring either high- or low-pressure regions when linearizing the Langmuir equation and offers a balanced approach.

Single-Site Langmuir (SSL):

$$q_i = q_m \frac{k_i}{1 + k_i P}$$

Dual-Site Langmuir (DSL):

$$q_i = q_{m,1} \frac{K_1}{1 + K_1 P} P + q_{m,2} \frac{K_2}{1 + K_2 P} P$$

Ideal Adsorbed Solution Theory (IAST):

The selectivity equation involved in calculation is provided below.

Selectivity:

$$S_{1,2} = \frac{q_1/q_2}{p_1/p_2}$$

Virial analysis:

The CO₂ adsorption data were collected from 0-1 bar at 313, 298, 283, 273 and 195 K. For virial fitting the 273, 298 and 313 K isotherms were taken and fitted by the virial equation.

$\ln(P) = \ln(V_a) + (A_0 + A_1 V_a + A_2 V_a^2 \dots + A_6 V_a^6)/T + (B_0 + B_1 V_a)$, Where, P is the pressure during experiment, V_a is amount of gas adsorbed, T is temperature, and A₀, A₁, A₂..., A₆ and B₀, B₁ are temperature independent empirical parameters.

3.2.7 Computational Modelling:

All computational calculations and simulations were performed using the Accelrys (Materials Studio V 8.0) software. An adsorption isotherm was simulated using the GCMC routine embedded in the sorption algorithm of the Materials Studio software. For these 1000000, equilibration steps were calculated and the Metropolis algorithm with Drieding forcefield was used. The Lennard–Jones equation, with a cut-off radius of 18.5 Å, was used to calculate the van der Waals interactions. The long-range electrostatic interactions and Coulomb interactions were both obtained by three dimensional Ewald & Group methods, with the accuracy of 1.0 e-5 kcal/mol. The calculations were repeated three times to establish the error-bar (see Fig. 4B of the main text). Following this, the favourable positions for the CO₂ within the MOF were identified using the Simulated Annealing routines embedded in the Materials Studio. A Smart algorithm was employed. A total of 10 cycles with 100000 steps/cycle were used to achieve the low-energy configurations. Charges were calculated using the Qeq charge equilibration method. The above simulations all conducted by the Sorption of the Materials Studio package.

To analyse the adsorption sites of CO₂ on the MOF, we used radial distribution functions (RDFs) extracted from detailed MD simulations carried out using the Forcite Dynamics. The lowest energy configuration from the simulated annealing routine was applied as the input for the MD. A 10 ns NPT MD simulation (1.0 fs time step; T = 298K; P = 1bar for CO₂) was used to reach the equilibrium state; the framework was allowed to relax. Then a 10 ns NVE MD simulation (1.0 fs time step) was used to obtain the final configuration at the lowest energy state.

3.3 Results and discussion

3.3.1 Characterization and crystal structures

The building unit of 1 consists of one tetrahedrally coordinated Zn-atom connected to three different triazolate units and an acetate oxygen (Fig. 3A.1). Every triazolate unit links three Zinc centers and propagates into a Zn-Atz layer (Fig. 3A.1). The adjacent Zn₂Atz₂ dimeric units in this layer are rotated by ~ 90° with respect to each

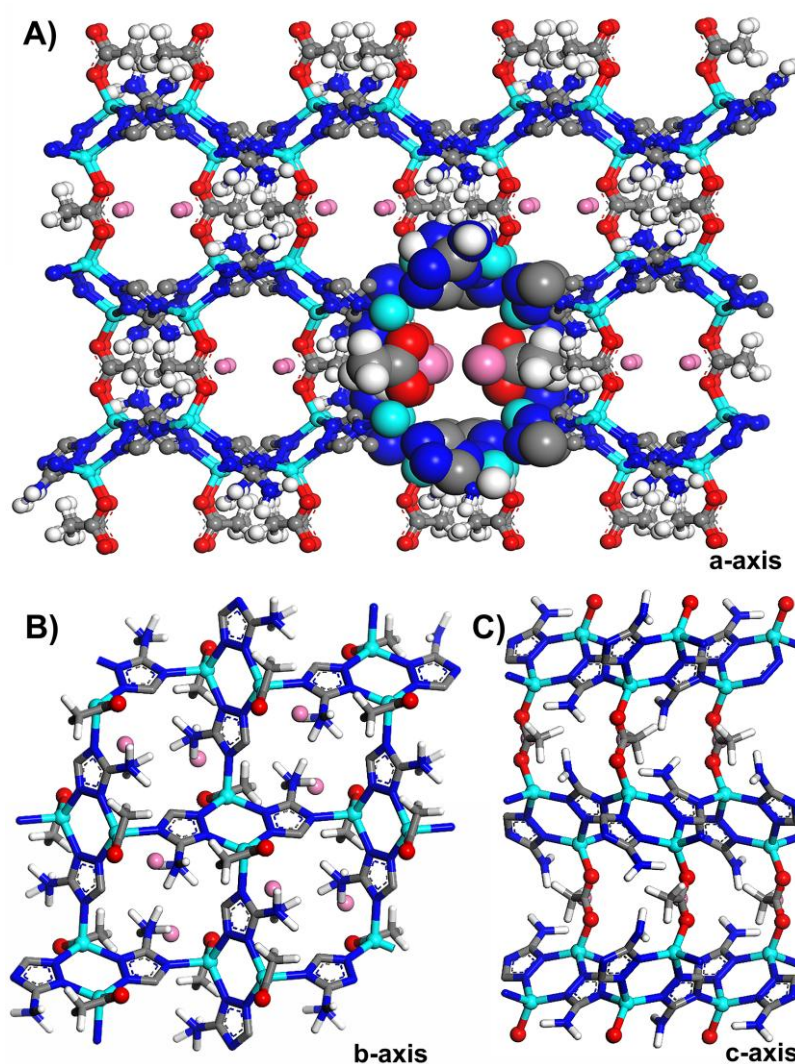


Figure 3.1. A) Three-dimensional structure of **IISERP-MOF28** showing the channels along the a-axis lined by acetate oxygens and occupied by hydroxide ions shown in pink. B) and C) represent the view along the b- and c-axes having spaces decorated by amine and the methyl groups, unfortunately too narrow for guest access.

other, hence lie on two perpendicular planes (Fig. 3A.1). This generates a buckled ZnAtz layer, which enables the adjacent layers stacked along the b-axis to come closer enough to be pillared by the acetate oxygen (μ -2 bridging acetates) into a 3D framework (Fig. 3.1). Note that the acetates are half-occupied for a fully occupied Zn and aminotriazolate unit, necessitating the hydroxide to participate as a charge-balancing counter anion.

The hydroxides reside between the carboxylate units of the acetate; thus, they form a row of anionic charges along the pore walls. Acetate oxygens, hydroxide ions and the triazole rings line the channels running along the *a*-axis (7.9 x 6.6 Å, not factoring the van der Waal radii, Fig. 2.1). Unfortunately, the spaces decorated by the free-amine and the methyl groups do not form solvent-accessible channels (Fig. 3.1(A) and 3.1(C)).

The powder XRD confirmed the bulk purity of the MOF (Fig. 3A.2). The MOF is stable till 260 °C, and the triazolate and carboxylate functionalities are amply incorporated (Fig. 3A.3 and 3A.4).

3.3.2 Gas Adsorption studies

A smooth type 1 adsorption isotherm marks its permanent porosity for N₂ at 77 K (Fig. 3.2 and 3A.5). We applied the Rouquerol consistency criteria to determine the sample's Brunauer-Emmett-Teller (BET) area³⁴. A fit to the adsorption branch yielded a BET area of 497 m²/g (Fig. 3A.5). Nonlocalized Density Functional Theory (NLDFT) fit amounts the pore diameter to be ~5 Å (Fig. 3.2A), which agrees well with the single crystal structure. **1** demonstrated good adsorption properties, with a maximum CO₂ absorption of 3.1 mmol/g at 1 bar and 298 K (Fig. 3.2B) and a saturation CO₂ capacity of 4.0 mmol/g (195 K CO₂ isotherm). At 0.15 bar and 25 °C, **1** adsorbs 2.2 mmol/g CO₂, representing the CO₂'s partial pressure of a typical post-combustion flue gas. Notably, **1** exhibited less N₂ uptake at room temperature (Fig. 3A.6). This high performance from such a simple structured and formulated MOF is noteworthy. The Ideal Adsorbed Solution Theory (IAST) calculation performed using the isotherms collected at 298 and 313 K, employing a nominal composition of 15CO₂:85N₂, yields a CO₂/N₂ selectivity of 75 and 150, respectively (Fig. 3.2C and 3A.8). Although the selectivity values are not as high as those of the recently reported UMMOFs,³⁵⁻³⁹ these are sufficient to achieve the benchmarked 99% purity during separation.⁴⁰ The calculated HOA using both virial and DFT models at 313, 298, and 273 K CO₂ isotherms was 34 kJ/mol at zero loading (Fig. 3.2D and 3A.7) and reaches 27–28 kJ/mol at higher loadings. The moderate heat suggests facile regeneration of **1** after use.

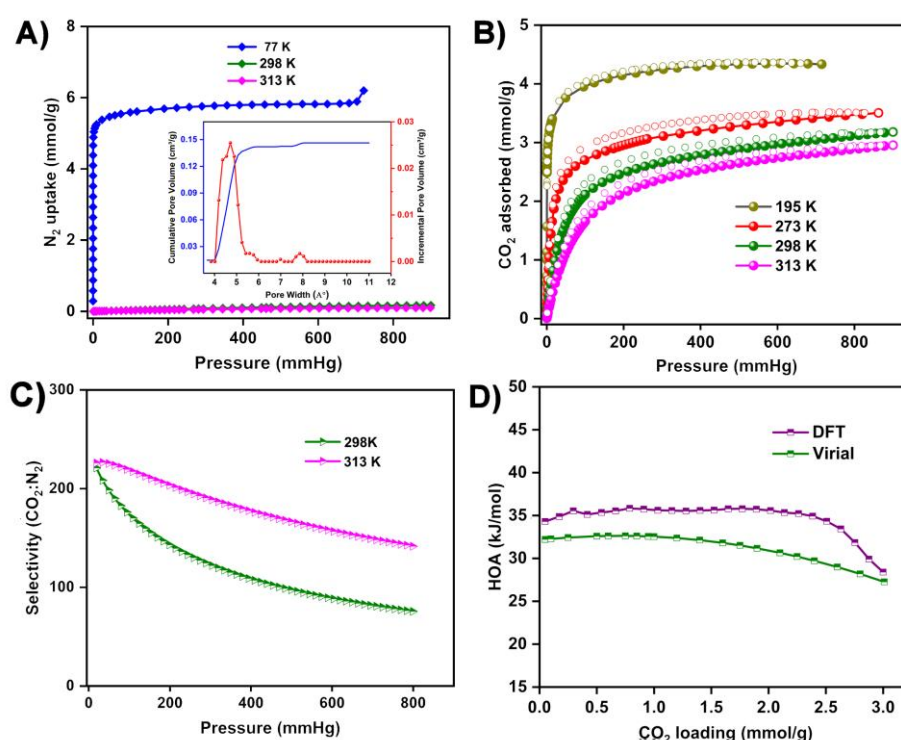


Figure 3.2: (A) N_2 sorption isotherm and (B) CO_2 sorption isotherms of **1** at different temperatures. Inset: the pore size distribution. (C) CO_2/N_2 selectivity calculated using IAST model employing a nominal composition of 15 CO_2 : 85 N_2 . (D) The HOA plots from the virial and DFT modelling done using the CO_2 isotherms at 273, 283, and 298 K.

3.3.3 Stability Studies

Any MOF's critical requirements in its possible industrial applications are crystallinity and porosity retention, and cost-effective scalability. Some MOFs have better-reported properties in one or more of the abovementioned criteria, but only a few meet all the requirements.^{21,41} We checked the chemical stability of **1**; maintained it at different pH conditions by soaking in HCl (acidic) and KOH (basic). The MOF showed no structural changes even after 15 days, as validated by their powder XRDs (Fig. 3.3A) The MOF was stable to soaking in water for 20 days (Fig. 3A.9) and exhibited no structural changes. Some recent physisorptive CO_2 capture processes follow a steam-assisted regeneration²¹ which mandates steam stability on the candidate MOFs. We

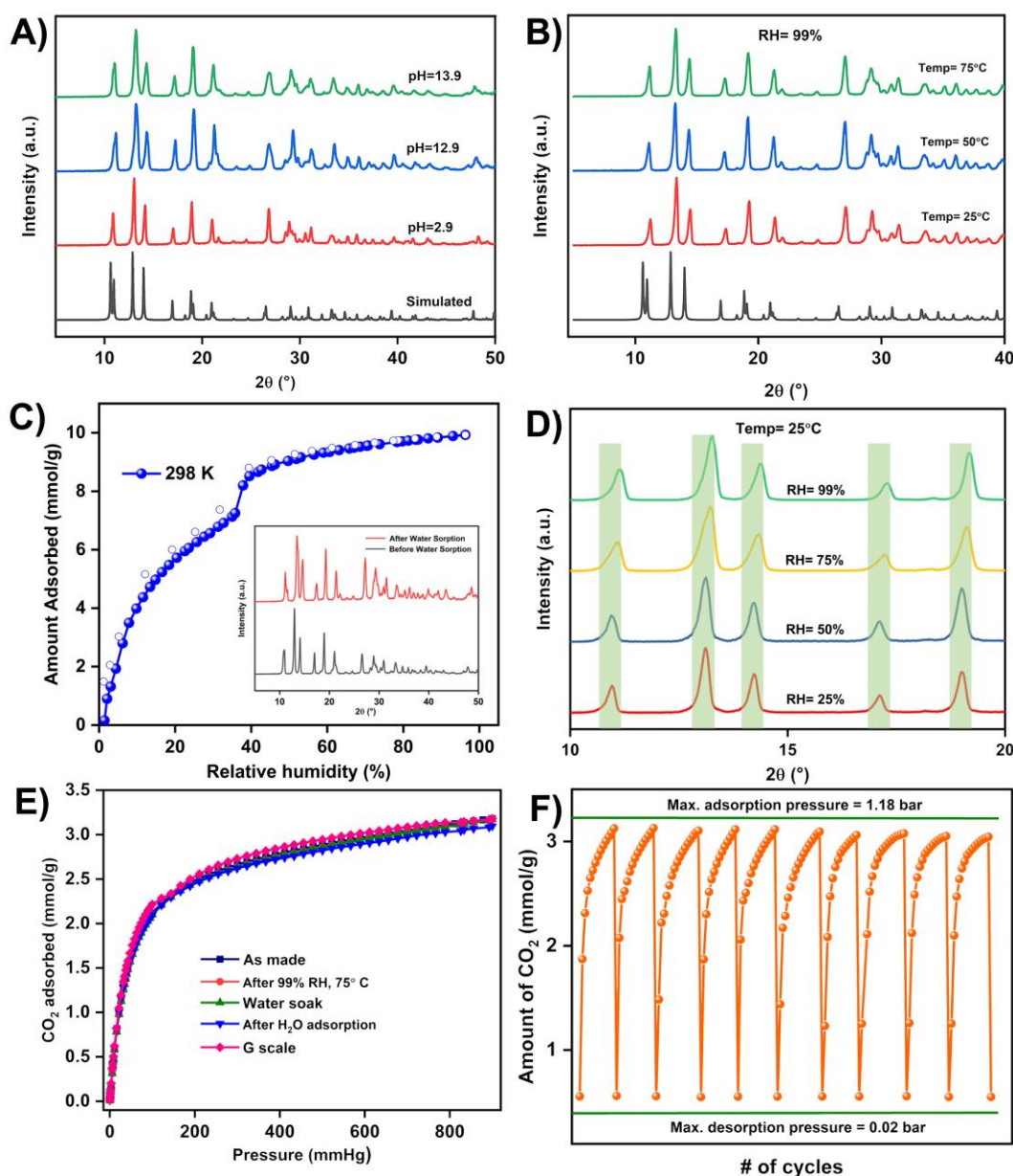


Figure 3.3: PXRDs of **1** kept at (A) different pH condition. (B) different temperatures and constant relative humidity. (C) The water adsorption isotherm of **1** at 298K. Inset: the PXRD of the post adsorption phase. (D) PXRDs of **1** kept at different relative humidity and constant temperature (E) Comparative CO_2 adsorption isotherms of **1**: after soaking in water for one month (blue); after water adsorption (sky blue); gram scale synthesis (pink). (F) iso-cycling for **1**: 10 cycles of a pressure swing of 1.2–0.02 bar.

exposed **1** to controlled humidity conditions (RH=25% to RH=99%) at a constant temperature (25 °C), and the PXRD patterns indicated a negligible loss of crystallinity (Fig. 3.3 and 3A.10). Also, its crystallinity survived when we heated it from 25° to 75°C at 99% RH (Fig. 3.3B). In addition, contact angle measurements showed a water contact angle of 104° (Fig. 3A.10), confirming the hydrophobic nature of the external surface of the **1**, which contributes to its enhanced stability in aqueous environments. The intrinsic hydrolytic stability of the MOF is further supported by a water vapor isotherm and a post-adsorption PXRD (Fig. 3.3C). Further, the 298K CO₂ uptakes of the post-chemically treated samples confirmed the retention of its permanent porosity (Fig. 3.3E). Additionally, the cyclic studies demonstrate that even after 10 cycles, the CO₂ uptake essentially remains the same (Fig. 3.3F). These tests are meaningful in establishing that even monodentate pillaring acetate units combined with the triazolate can afford one of the simplest compositions carrying more than sufficient stability for humid CO₂ capture. Also, **1** could be scaled to multi grams using the solvothermal methods (Fig. 3A.11).

3.3.4 Computational Studies

Different CO₂ interaction sites in **IISERP-MOF28** (triazolate ring, amine groups, hydroxide ions and acetate oxygens), compelled us to investigate the CO₂ locations within the pore (Fig. 3.4A). For this purpose, we simulated the 273K CO₂ adsorption isotherms using GCMC methods embedded in the Accelrys program. The simulated isotherm matched well with the experimental one (Fig. 3.4B). We obtained the optimized CO₂ positions from the lowest energy configuration established using a simulated annealing routine (See SI for details). The final structure optimized to an average energy of -65 kcal/mole/UC (Fig. 3.4C), wherein the CO₂'s were located proximal to the hydroxide ions and the acetate oxygens at acceptable distances.^{42,43} The oxygens of the CO₂ and the framework's functional groups were oriented for hydrogen-bond type interactions (Fig. 3.4C). The simulations yield an average HOA of 32 kJ/mol, which agrees well with the experimental value. Meanwhile, an RDF analysis confirmed the presence of CO₂...OH⁻ (O...O separation = ~2.7 Å) and CO₂...acetate (O...O separation = ~2.9 Å) interactions (Fig. 3.4C). Notably, no CO₂ was found proximal to the amine moiety owing to the lack of space (Fig. 3.4B). Several

zinc-triazolate frameworks have been reported in the literature over the last twenty years.^{10-12,16,17,20,28-31,44} One of the main attractions of these systems has been their readily available ligand and zinc being a benign and relatively cheaper metal. Also, the amphoteric and borderline hard-soft acid-base nature of the Zn^{2+} allows it to bind strongly with N-rich triazole and carboxylate ligands. This accounts for the high chemical stability in this family of azolate MOFs. Among the 3D layered-pillared azolate-carboxylate MOFs, those with short pillars are ultra-microporous and exhibit preferential CO_2 uptake characteristics.^{21-24,26} Few others have Zinc azolate layers decorated with dangling carboxylate moieties (formate, acetate)^{10,29,30,31} or 3D pillaring carbonate or formate.¹² The ZnAtzCO_3 is closely related to the present MOF with an identical structure, except that **1** includes the free charge-balancing hydroxide ions in the channels. This makes this acetate MOF chemically more robust than the carbonate analogue.

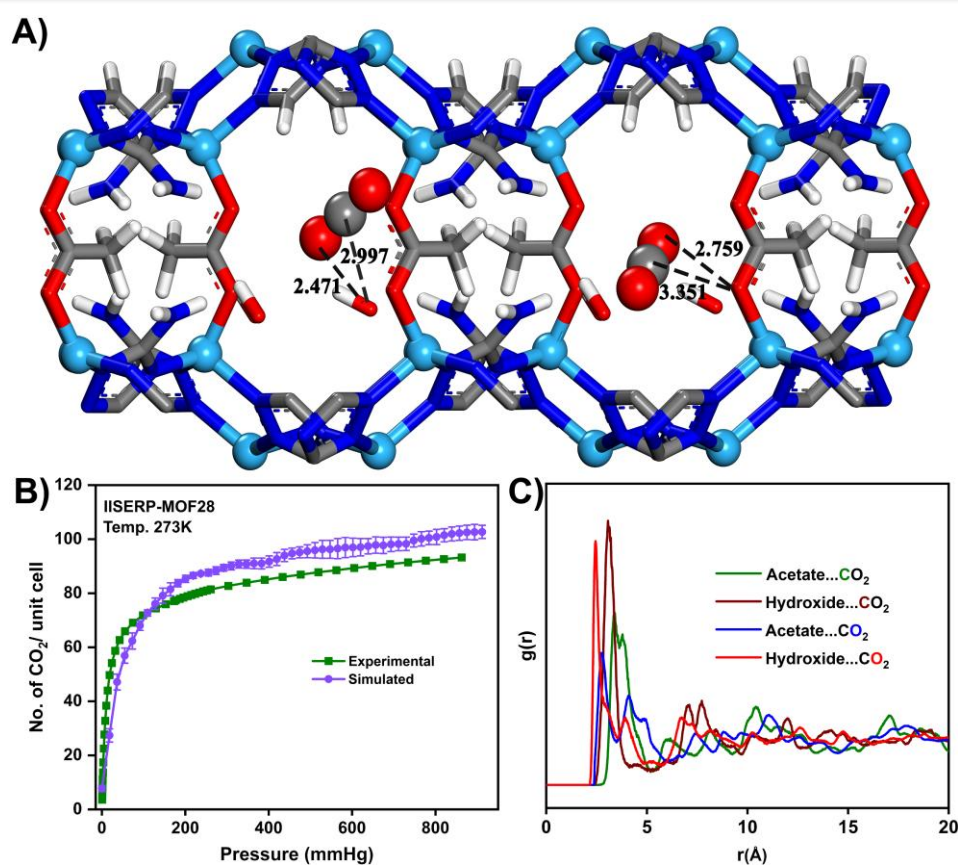


Figure 3.4: (A) and (B) Structure of $\text{CO}_2@1$ obtained from the GCMC modelling and the associated simulated isotherm are shown. The most favourable interaction

distances are mentioned. (C) RDF plots from the MD simulations showing the averaged interaction distances for CO₂ with various sites of the framework.

Encouraged by the promise of triazolate MOFs in humid CO₂ capture^{21-23,28} we investigated the metal-ligand binding strength of these structures using computational methods. Binding energy gives an idea about stability. For this, we simulated 3 x 3 x 3 cells of different Zinc azolate MOFs and calculated their binding energy using the DMOL³. In all cases, we employed solvent-free frameworks to ensure the estimates were entirely metal-ligand related. For **1**, the hydroxide was retained in the pores. The comparison is presented in (Fig. 3.5). The 3D layered-pillared ZnAtzOx^{22,23} and the 3D zeolitic framework, MAF-7,⁴⁴ had the highest binding energy. Surprisingly, the relative binding energy of CALF-20 (3D ZnTzOx)²¹ was low. One major difference in CALF-20 compared to all other frameworks is the lack of pendent amino or methyl groups, which takes away a substantial amount of electrostatic and van der Waal interactions. Also, another 3D ZnAtzOxalate, reported by Aparna et al., with dynamic swiveling oxalate pillars (monodentate),²⁴ had only half the binding energy of the other 3D ZnAtzOx (bidentate oxalates).²² While framework stability is one aspect, it is worth realizing that the 3D network of the CALF20 (P2₁/c) though topologically comparable to the ZnAtzOx (Pbca),²² has more ordered triazoles and less ordered oxalate, while the latter has it reversed. This gives more openness to the CALF-20. Thus, the

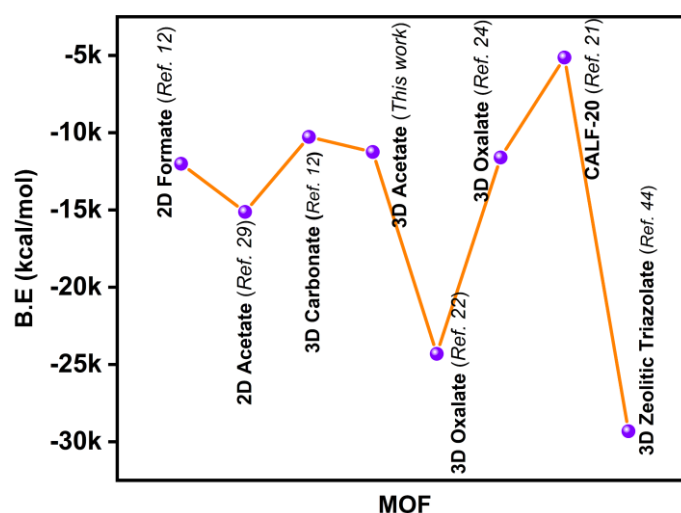


Figure 3.5: Calculated binding energies for different zinc-triazolate MOFs.

presence of pendant/templating amino or methyl group though it helps improve the overall binding strength, leaves the structure less open. Hence improving the binding energy of the CALF-20 lattice or increasing the openness of the other amino-triazolate MOFs could yield superior sorbents for humid CO₂ capture.

3.4 Conclusion

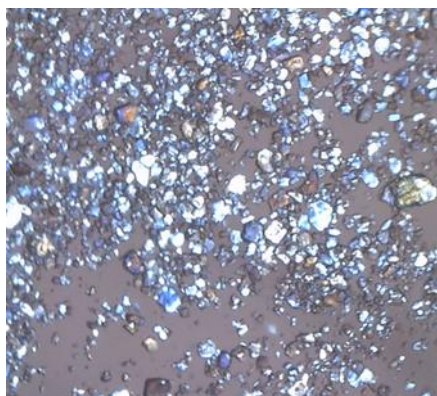
In summary, a 3D cationic framework zinc-aminotriazolato-acetate with guest hydroxide ions in their ultra-micropores is formed. It has most of the attributes required for a humid CO₂ capture and shows good selective uptake of CO₂ with excellent cyclic stability. Disappointingly, the amine groups (CO₂-philic) and the methyl groups (water-repelling) do not line the gas-accessible pores even in this uncomplicated layered (ZnAtz)-pillared(acetate) structure. Consequently, this 3D framework with the simplest composition is yet to bring out these ligands' full potential for humid CO₂ capture. A structural comparison of zinc-azolate MOFs reveals that azolates have the potential to provide high binding energies and open-framework structure. The optimal condition to access both these features in the same structure could hold the key; the pursuit is on.

3.5 References

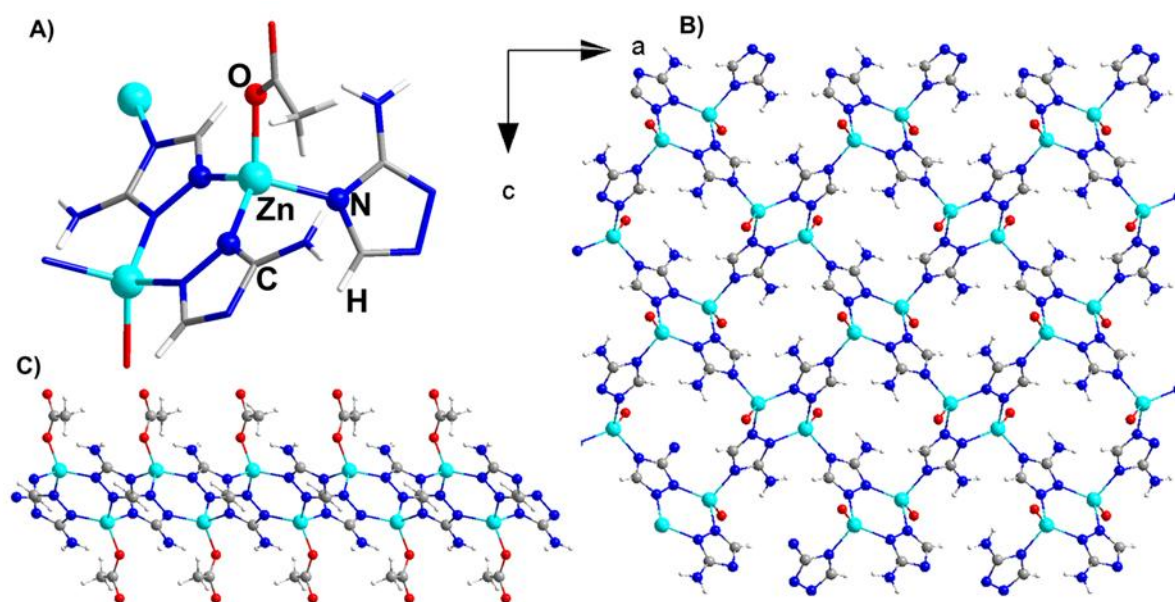
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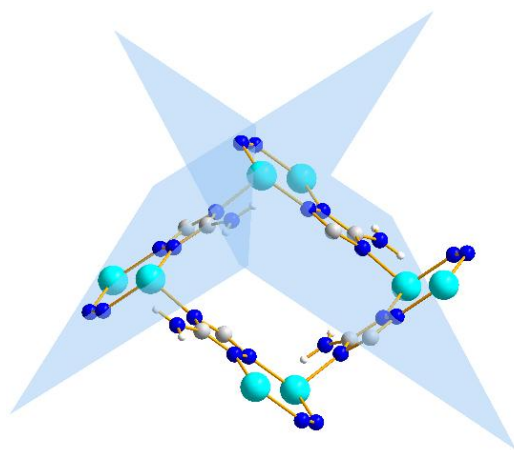
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Photograph S1. Images of the crystals taken under an optical microscope. The crystals adopt block shapes upon growing.



Angle Between adjacent zinc-triazolate planes



Zinc-triazolate MOFs	θ	References
Porous 3D ZnAtzOx	87.385	1
3D ZnAtzCO ₃	81.401	2
IISERP_MOF28 , 3D ZnAtzAcetate	77.836	This work
2D ZnAtzAcetate	75.501	3
Porous 3D ZnAtzOx (dynamic fwk)	70.849	4
CALF-20, Porous 3D ZntzOx	65.525	5
2D ZnAtzFormate	59.097	2

Note: Atz = 3-amino-1,2,4-triazole; tz = 1,2,4-triazole; CO₃ = carbonate; Ox = oxalate.

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Figure 3A.1: A) Basic building unit of **IISERP-MOF28**. Showing the coordination sphere of Zinc, that adopts a tetrahedral geometry. B) Zinc-aminotriazolate layer lying on the ac-plane. Note the oxygens running up-down the layer. C) The layer viewed down the b-axis showing the acetate units running up-down the layer. Color code: Zn- cyan; O- red; C- grey; N- blue and H- white. Bottom: The angle between

the planes defined by the Zn₂ tz₂ dimers within the Zn-triazolate layers. This signifies the extent of buckling within the layer. Highly buckled layers enable short pillars to participate in creating a 3D structure.

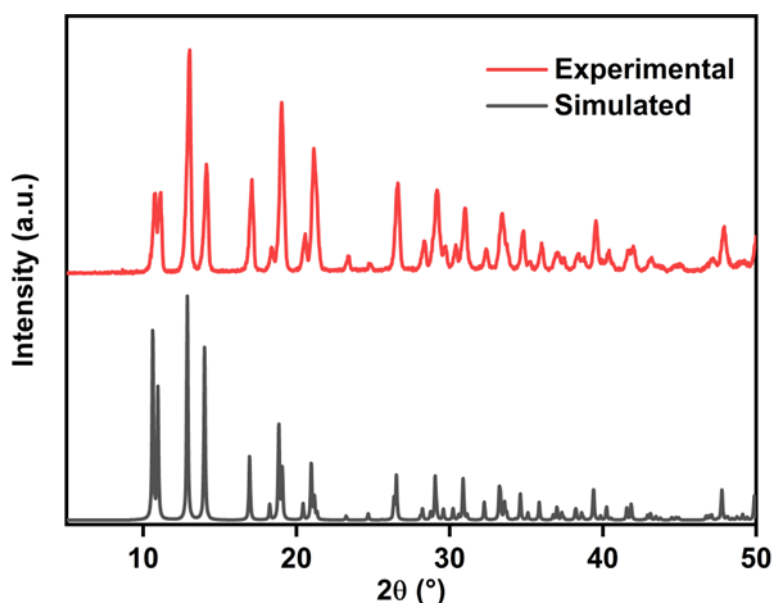


Figure 3A.2: The PXRD profile of **IISERP-MOF28** indicating the bulk purity of the MOF.

PLATON analysis:

Total Potential Solvent Accessible Void Vol (SOLV-Map Value) = 302 Å³

Unit cell volume, V = 1520.72 Å³

Now, Void volume = $(302/1520.72) \times 100 = \sim 19.85\%$ of the **IISERP-MOF28**.

Now, **IISERP-MOF28** (1) has a cationic framework with one hydroxide ions per formula unit. So, formula unit present in the crystal structure of the **IISERP-MOF28** is Zn₂(Atz)₂(Ac)(OH⁻)(H₂O)_x(DMF)_y, where, x,y = any integer represents no of water and dmf molecules.

Z for **IISERP-MOF28** is 4.

Hence the unit cell formula is Zn₈(Atz)₈(Ac)₄(OH⁻)₄(H₂O)_{4x}(DMF)_{4y}

From the squeeze result, electrons found in solvent Accessible Void = 42.
Considering 40 electrons for one DMF molecule.

The final Unit Cell formula $\text{Zn}_8(\text{Atz})_8(\text{Ac})_4(\text{OH}^-)_4(\text{DMF})_4$

and formula of formula unit is $\text{Zn}_2(\text{Atz})_2(\text{Ac})(\text{OH}^-)(\text{DMF})$

DMF weight percentage is 15.7% and from TGA we have approximately 16% weight loss corresponding to DMF.

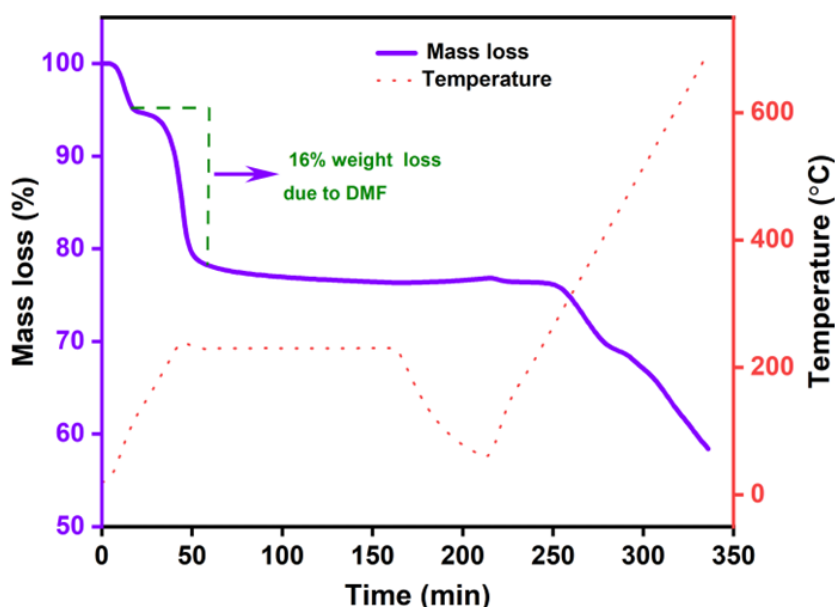


Figure 3A.3: TGA of as made **IISERP-MOF28** showing the thermal stability upto 260°C. The continuous mass loss upto 230 °C is due to the DMF and water molecules present in the pores of the MOF.

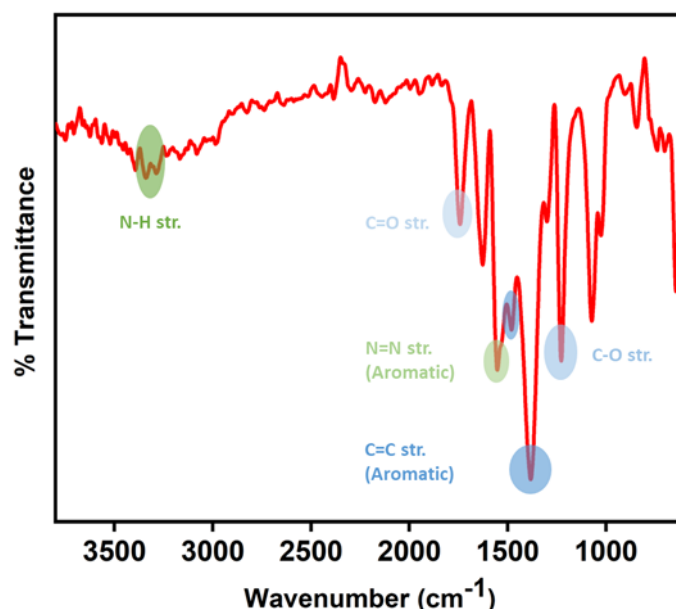


Figure 3A.4: Infra-red spectra of **IISERP-MOF28**, showing the various stretching and bending modes present. Selected peaks: IR (cm⁻¹): $\nu(\text{N-H})$: 3230-3395; $\nu(\text{CO})$: 1740s; $\nu(\text{N=N})$: 1556s; $\nu(\text{C=C})$: 1475 and 1380; $\nu(\text{C-O})$: 1225.

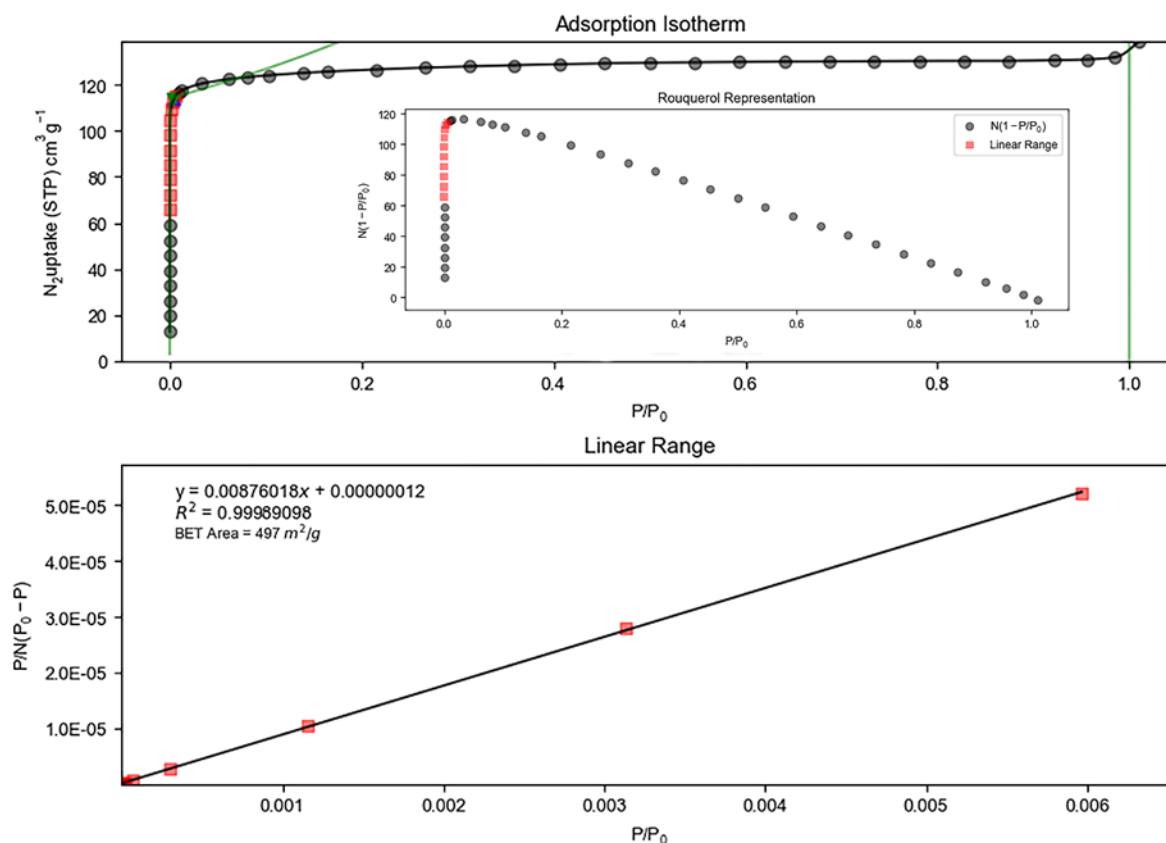


Figure 3A.5: BET fit for the IISERP-MOF28 calculated from the 77K N₂ isotherm.

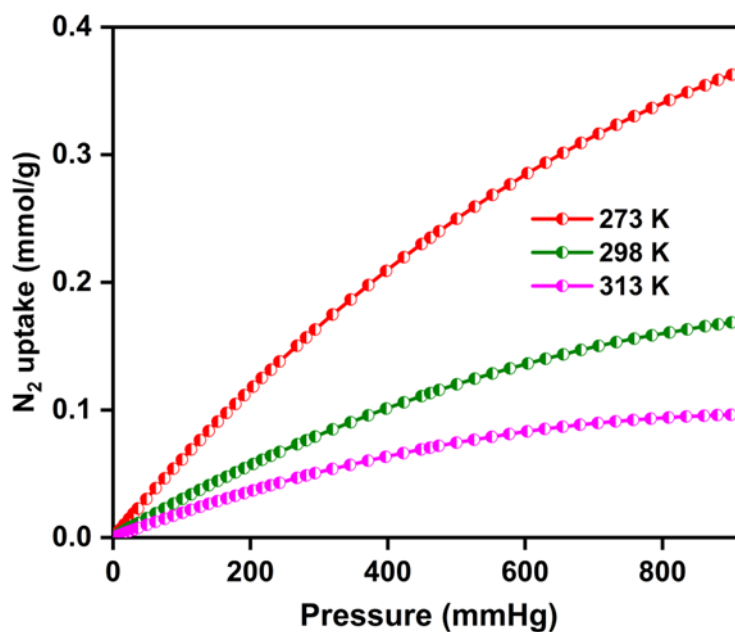


Figure 3A.6: N₂ sorption isotherm of IISERP-MOF28 at different temperatures.

Table 3A.1: Summary of the fitted Virial parameters for **IISERP-MOF28**.

Ao	-3866.518441	Bo	16.25885602
A1	-167.0322344	B1	0.129610206
A2	120.203798	B2	0
A3	-0.006573956	B3	0
A4	0.017728823	B4	0

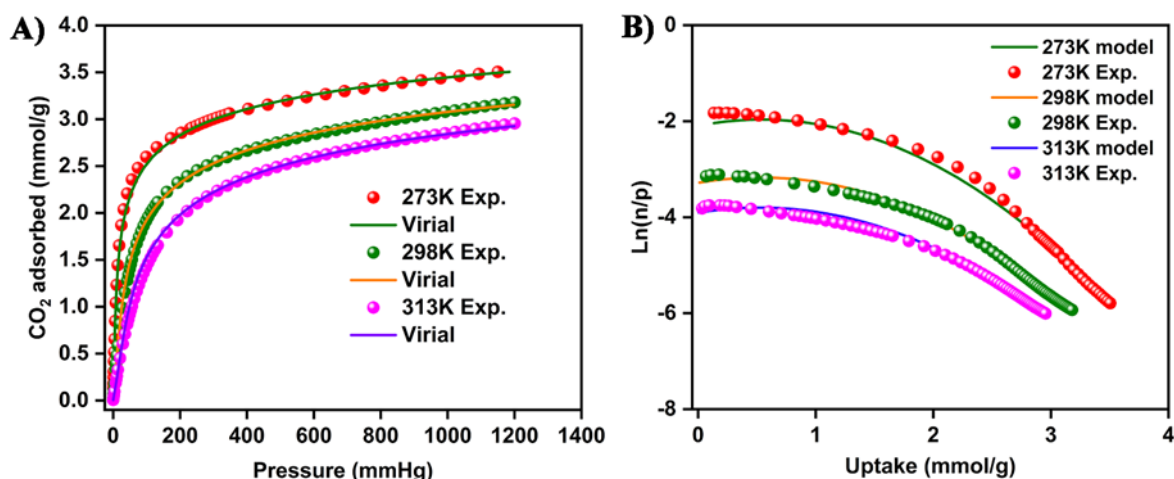


Figure 3A.7: (A) Comparison of experimental isotherms of **IISERP-MOF28** to the ones obtained from virial modelling carried out using CO₂ isotherms collected at 273, 298 and 313K. (B) Virial plots of **IISERP-MOF28** carried out using CO₂ isotherms collected at 273, 298 and 313K.

IAST selectivities:

CO₂/N₂ selectivity was calculated for **IISERP-MOF28** using the experimental single component CO₂ and N₂ isotherms and ideal adsorbed solution theory (IAST) with a nominal composition of 15CO₂:85N₂. At 1 bar total pressure, and 298K & 313K, conditions of relevance to post combustion CO₂ capture.

IAST fitting parameters for IISERP-MOFXX (CO₂/ N₂):

At 298 K

Gas A = CO₂

Gas B = N₂

Table 3A.2: Fitted IAST parameters for CO₂/N₂ (15CO₂:85 N₂ composition) selectivity at 298 K for **IISERP-MOF28**

Gas A Constants		Gas B Constants	
q _{s1} (mmol g ⁻¹) =	3.413531176	q _{s1} (mmol g ⁻¹) =	4.924949522
q _{s2} (mmol g ⁻¹) =	0	q _{s2} (mmol g ⁻¹) =	0
K ₁ (mbar ⁻¹) =	0.022334194	K ₁ (mbar ⁻¹) =	7.44E-05
K ₂ (mbar ⁻¹) =	0	K ₂ (mbar ⁻¹) =	0
n ₁ =	0.880228916	n ₁ =	0.906103856
n ₂ =	0	n ₂ =	0
H ₁ (mmol mbar ⁻¹ g ⁻¹) =	0.076238467	H ₁ (mmol mbar ⁻¹ g ⁻¹) =	0.000366619
H ₂ (mmol mbar ⁻¹ g ⁻¹) =	0	H ₂ (mmol mbar ⁻¹ g ⁻¹) =	0

At 313 K

Gas A = CO₂

Gas B = N₂

Table S6: Fitted IAST parameters for CO₂/ N₂ (15CO₂:85 N₂ 2 composition) selectivity at 313K for **IISERP-MOF28**.

Table 3A.3: Fitted IAST parameters for CO₂/ N₂ (15CO₂:85 N₂ 2 composition) selectivity at 313K for **IISERP-MOF28** .

Gas A Constants		Gas B Constants	
q _{s1} (mmol g ⁻¹) =	3.240186165	q _{s1} (mmol g ⁻¹) =	2.000428068
q _{s2} (mmol g ⁻¹) =	0	q _{s2} (mmol g ⁻¹) =	0
K ₁ (mbar ⁻¹) =	0.007958866	K ₁ (mbar ⁻¹) =	6.89E-05
K ₂ (mbar ⁻¹) =	0	K ₂ (mbar ⁻¹) =	0
n ₁ =	0.939317452	n ₁ =	0.903488549
n ₂ =	0	n ₂ =	0
H ₁ (mmol mbar ⁻¹ g ⁻¹) =	0.025788208	H ₁ (mmol mbar ⁻¹ g ⁻¹) =	0.000137783
H ₂ (mmol mbar ⁻¹ g ⁻¹) =	0	H ₂ (mmol mbar ⁻¹ g ⁻¹) =	0

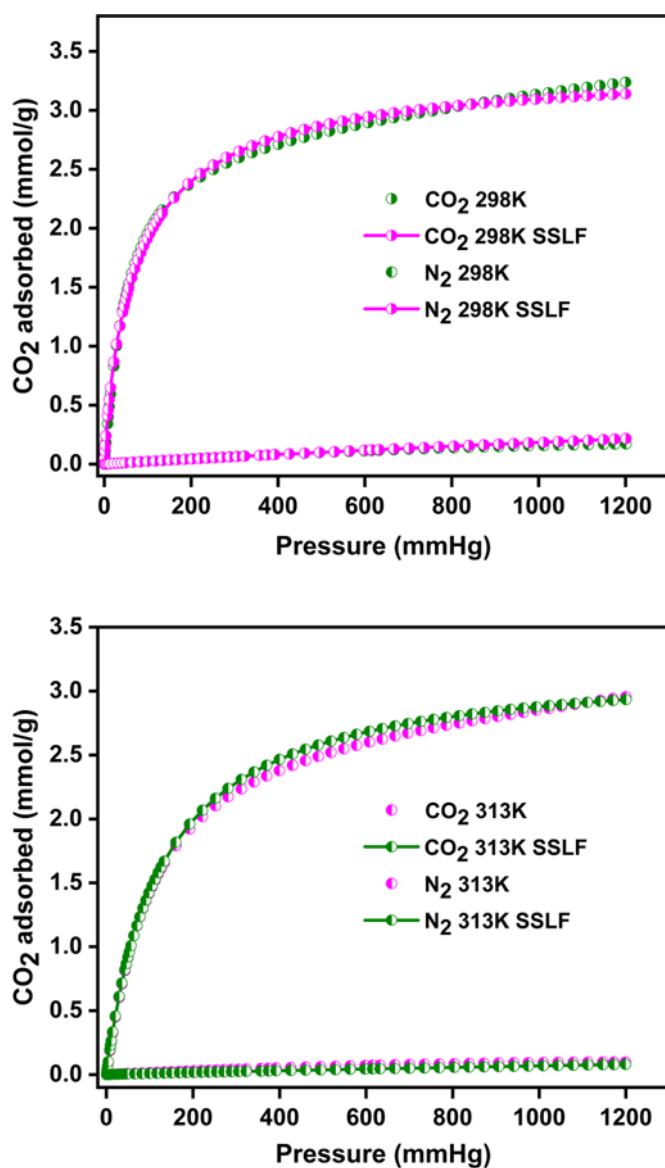


Figure 3A.8: IAST fitting of CO₂ and N₂ isotherms for **IISERP-MOF28** collected at 298 and 313 K.

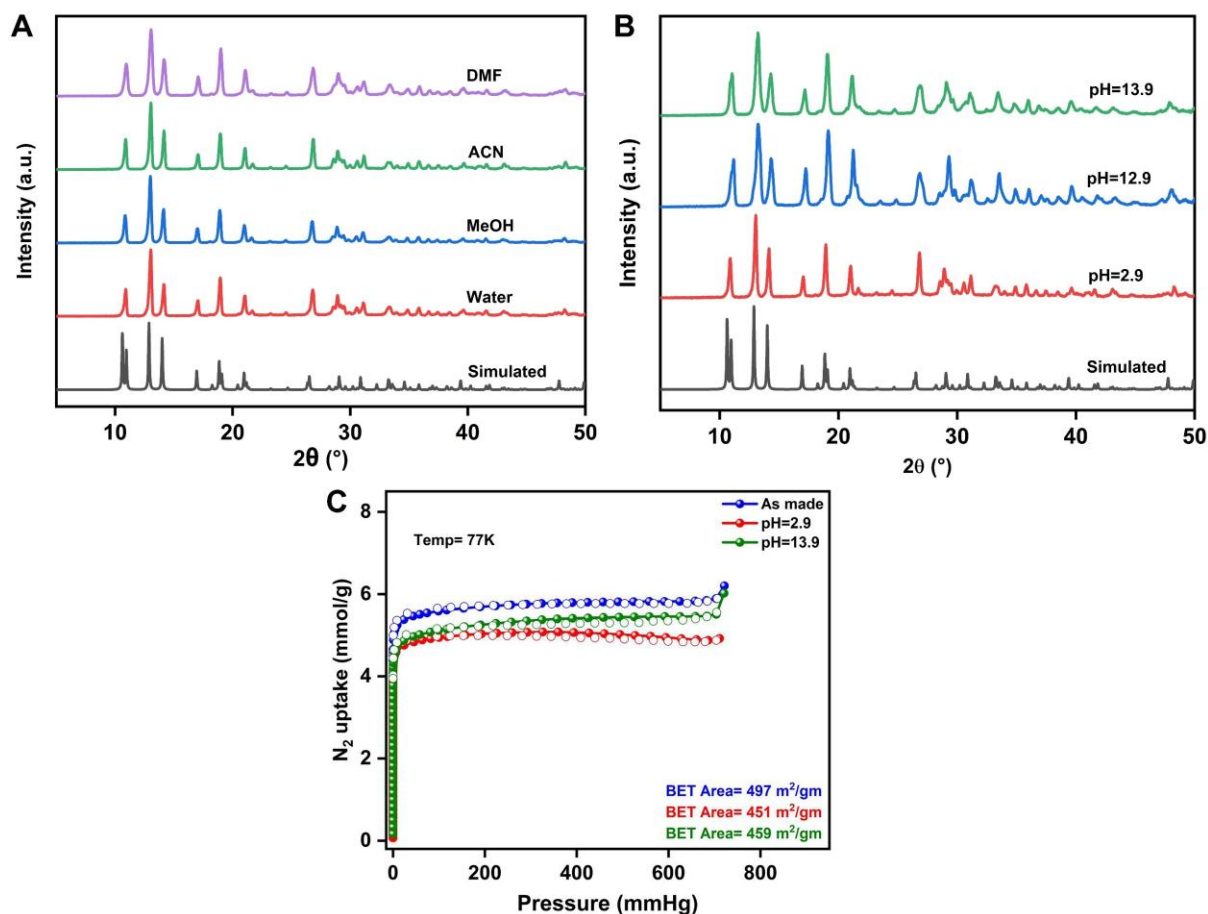
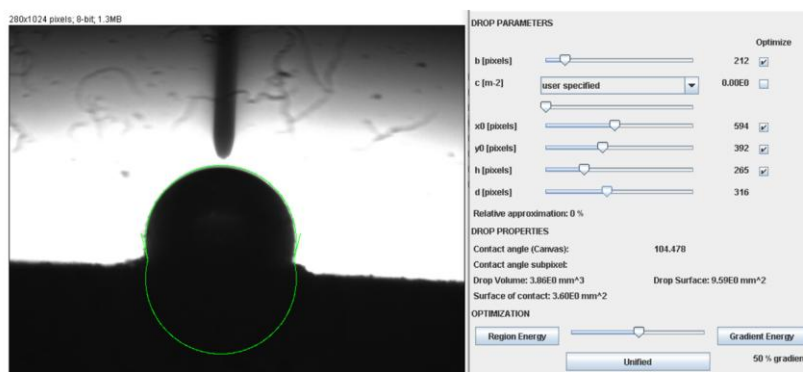


Figure 3A.9: (A) After soaking for 20 days, PXRD profiles demonstrate the stability of **IISERP-MOF28** in various solvents. (B) PXRD patterns of post acid-base treatment of the MOF. (C) 77K liquid N_2 adsorption isotherms of the MOF after treating with acid and base for 15 days.



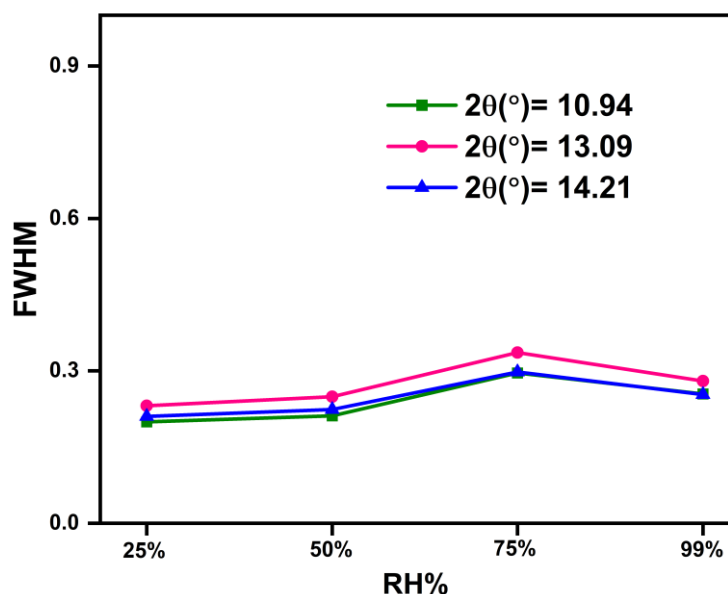


Figure 3A.10: Top: Contact angle measurement for water on IISERP-MOF28. Below: FWHM plot of IISERP-MOF28 at different relative humidity condition at constant temperature.

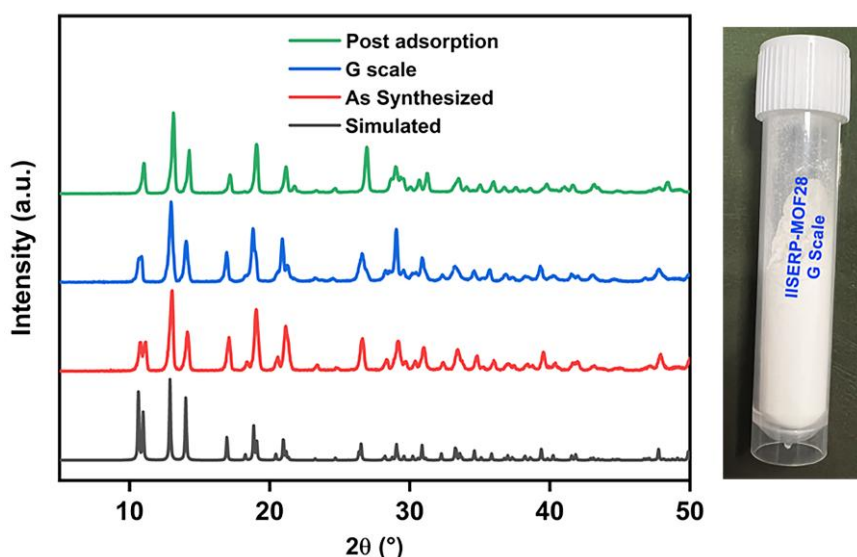


Figure 3A.11: A comparative PXRD plot showing the bulk purity of the gram scale synthesis and the stability of the MOF to the repeated adsorption-desorption and evacuation cycles. Note: This material can be scaled up to 4 gram in a single synthesis.

Table 3A.4 Comparison of the adsorption characteristics of 1 with some of the leading CO₂ capturing MOFs.

MOF	CO ₂ capacity at 298 K (mmol/g)		HOA (kJ/mol)	ref
	0.15 bar	1.0 bar		
IISERP-MOF28	2.2	3.1	32	<i>This work</i>
Calf-20 (303 K)	2.5	3.54	39	<i>Science</i> 2021, 374, 1464–1469
ALF	2.7	3.98	47.9	<i>Sci. Adv.</i> , 2022, 1473
Zn-Atz_Ox (293 K)	2.1	3.65	40	<i>Science</i> 2010, 330, 650.
IISERP-MOF2 (303 K)	1.6	4.1	33	<i>J. Am. Chem. Soc.</i> 2017, 139, 1734–1737
ZnF(daTZ)	0.96	3.3	33	<i>J. Am. Chem. Soc.</i> 2020, 142, 2750–2754
mmen-Mg ₂ (dobpdc)	3.2	3.9	75	<i>J. Am. Chem. Soc.</i> 2012, 134, 7056.
Zn ₃ (Atz) ₃ (PO ₄) (273K)	1.76	3.16	30	<i>Angew. Chem.</i> 2012, 124, 1862.
UTSA-16	2.54	4.4	37	<i>ACS-AMI</i> 2017, 9, 455.
MAF66	1.29	4.41	26	<i>Inorg. Chem.</i> 2012, 51, 9950–9955
Zn ₂ (TRZ) ₂ (Fuma)	1.32	3.92	27	<i>Fuel</i> , 2022
SIFSIX-3-Zn	2.38	2.55	46	<i>Nat. Commun.</i> 2014, 5, 4228.
SIFSIX-3-Cu	2.45	2.6	53	<i>Nat. Commun.</i> 2014, 5, 4228.
MIL-101(Cr)	0.6	2.25	32	<i>Chem. Eng. Sci.</i> 2016, 147, 109.

NH ₂ -MIL-53(Al)	0.9	1.5	38.4	<i>J. Am. Chem. Soc.</i> 2009, 131, 6326.
MIL-91(Ti)	1.5	3.5	44	<i>J. Mater. Chem. A</i> 2016, 4, 1383
CAU-1	1.1	4.0	48	<i>Energy Environ. Sci.</i> 2011, 4, 4522.
bio-MOF-13	1.0	2.0	41	<i>Chem. Sci.</i> 2013, 4, 1746.
bio-MOF-12	1.34	3.15	39	<i>Chem. Sci.</i> 2013, 4, 1746.
JUC-132-Cd	0.65	1.71	30.3	<i>Chem. Commun.</i> 2015, 51, 9463.

Chapter 4

**CO₂-specific gate opening transforms
a dense cation-filled zinc-
aminotriazolato-oxalate framework
into an ultra-microporous MOF**

4.1 Introduction

There has been a lot of interest in creating ultramicroporous metal–organic frameworks (pore size ≤ 6 Å) using small ligands.¹⁻²¹ These frameworks generally exhibit optimal surface area (300–600 m²/g), and their small pores enable intrinsic molecular sieving and chemical influences on the guest molecules.²²⁻²⁹ This makes them suitable for gas separations.^{2, 6-7, 14-20, 24-25, 27, 30-33} In some of the special cases, the guest molecules' interaction with the frameworks become so specific such that selectively the guest opens up the framework at a specific concentration leading to the phenomenon of “gate opening.”³²⁻⁵² There are several MOFs wherein CO₂-assisted gate opening has been observed.^{32, 38-39, 42, 45, 47-49, 51-53} However, a gate opening in a dense framework transforming it into a porous framework is not common.^{32, 51-54} The structural feature responsible for a gate opening can be unique for every MOF.³¹⁻⁵³ Of this, the bond distance has been used as a parameter to define gate opening.^{32, 38}

Currently, there is a lot of attention on CALF-20, a zinc-triazolato-oxalate MOF, [Zn₂(tz)₂(Ox)].solvent], as a CO₂-selective sorbent.¹⁵ It is an ultramicroporous framework that simultaneously meets the three important requirements for an MOF to qualify as an industrial CO₂ sorbent; it displays optimal CO₂ adsorption capacity, has sufficient hydrophobicity, and, due to chelating triazolates and oxalate units, exhibits exceptional steam/hydrolytic stability. This makes it suitable for a cost-effective steam-based selective CO₂ capture.^{15, 55-56} Some interesting structural transformations occur during their humid CO₂ capture and are explained to impact the diffusion of CO₂ vs water within the framework.⁵⁵⁻⁵⁷ Yet, the design of superior sorbents based on CALF-20 is not straightforward. A look into the CALF-20 structure reveals that it has the classic layered-pillared topology (layer = Zn-triazolate; pillar = oxalate), which is ubiquitous in the system of triazolato-oxalates.^{14, 38, 58} However, alternate 3D structures are reported with a different framework and composition.⁵⁹⁻⁶⁴ Anionic frameworks in this family are also known, and they have counter-charge-balancing cations within them, yielding a very dense framework that shows no porosity.⁶² This is anticipated as the charged frameworks possess strong packing achieved via the electrostatic interaction with cationic guests,^{62, 65-67} and hence, concepts of flexibility

or gate opening in such frameworks are counterintuitive, especially because the triazoles and the oxalates bond quite strongly to the metal centers. In contrast to this discussion, earlier, we reported a similar gate opening in another Zn-aminotriazolato-oxalate MOF (IISERP-MOF32, $[\text{Zn}_2(\text{Atz})_2(\text{Ox})]\cdot\text{solvent}$, which had a CALF-20-like layered-pillared topology. In IISERP-MOF32, the framework is quite open (takes up ~ 2.5 mmol/g of CO_2 at 0.15 bar), and this is opened up further by CO_2 to reach an uptake of ~ 5 mmol/g at 1 bar. This is the only framework in this family wherein such gate opening is reported. Of course, CO_2 and water-assisted phase transformation and framework flexibility of CALF-20 is demonstrated, and its importance to diffusion of guests within its ultramicropores is also described.^{21, 56-57, 68-70} Despite the success of CALF-20, the reason behind its unique capabilities as a humid CO_2 -capturing framework with exceptional steam stability and flexibility is still not clear. Hence, a deeper investigation of these Zn-triazolato-oxalate frameworks with a new outlook is necessary.

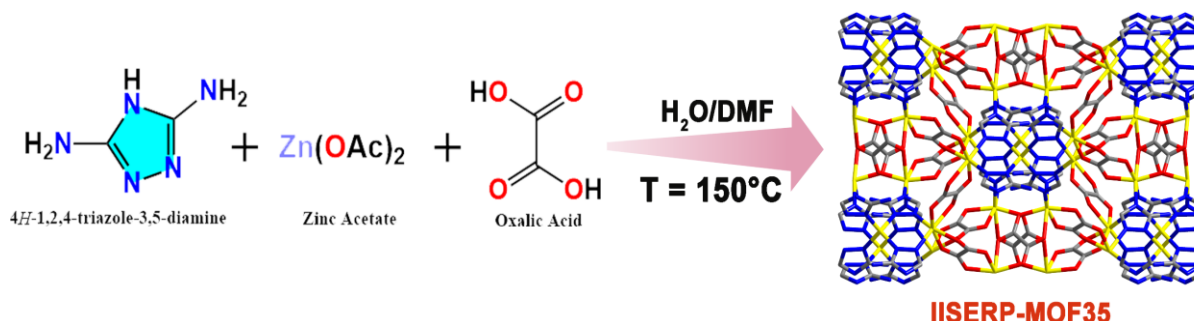
Herein, we report a Zn-aminotriazolato-oxalate MOF (**IISERP-MOF35**, $[(\text{CH}_3)_2\text{NH}_2]_2[\text{Zn}_5(\text{Atz})_4(\text{Ox})_4]\cdot 2\text{H}_2\text{O}$), which has a unique framework that does not resemble the ubiquitous layered-pillared topology prevalent among the CALF-20 and related zinc-triazolato-oxalate systems.^{14-15, 21, 38, 58} The CO_2 -specific gate opening at lower partial pressures makes **IISERP-MOF35** more interesting. Here, not only have we demonstrated CO_2 gate opening in this new dense 3D framework but additionally; by using the single-crystal X-ray diffraction structure, we have identified the structural component that is most likely enabling this gate opening. We have compared it with the existing frameworks in this system, which reveals that the structural motif identified here could help in the futuristic design of creating ultramicroporous frameworks predesigned for guest-assisted flexibility.

4.2 Experimental section

4.2.1 Synthesis

Synthesis of IISERP-MOF35: A solvothermal reaction between Zinc (II) acetate dihydrate (0.5 mmol), 3-AminoTriazole (0.5 mmol) and Oxalic acid dihydrate (0.5 mmol) in a solution containing mixture of 3 ml DMF and 3ml water was carried out at 150 °C for 48 hours. After cooling to room temperature, block shaped crystals of

IISERP-MOF35 were obtained by filtration. The product was washed with plenty of H₂O and methanol. The air-dried product gave a yield of 71%.



Scheme 4.1. Synthesis of **IISERP-MOF35**.

4.2.2 Single crystal structure determination. Single-crystal data were collected on a Bruker SMART APEX four-circle diffractometer equipped with a CMOS photon 100 detector (Bruker Systems Inc.) and with a Mo K α radiation (0.71073 Å). The incident X-ray beam was focused and monochromated using Micro focus (I μ S). Crystal of **IISERP-MOF35** was mounted on nylon Cryo loops with Paratone-N oil. Data was collected at 100 K. Data was integrated using Bruker SAINT Software and was corrected for absorption using SADABS. Structure was solved by Intrinsic Phasing module of the direct methods and refined using the SHELXTL 2014 software suite. All non-hydrogen atoms were located from iterative examination of difference F-maps following which the structure was refined using least-squares method. Hydrogen atoms were placed geometrically in a riding model. The disordered electron density in the pores was assigned using the Platon analysis.

4.2.3 Powder X-ray diffraction. Routine powder X-ray diffraction were carried out using a Rigaku Miniflex-600 instrument and processed using PDXL software. The Variable temperature powder X-ray diffraction (VT-PXRD) were carried out on a full fledged Bruker instrument using the in-built furnace and in air.

4.2.4 Thermogravimetric Analysis. Thermogravimetric analysis was carried out on NETSZCH TGA-DSC system. The TGAs were done under N₂ gas flow (20 ml/min) (purge + protective) and samples were heated from 25 °C to 600 °C at 5 K/min.

4.2.5 IR Spectroscopy. The IR spectra were acquired by using a Bruker Optics ALPHA-E spectrometer with a universal Zn-Se ATR (attenuated total reflection) accessory.

4.2.6 Adsorption Analysis. All low-pressure gas sorption isotherms were measured on a Micromeritics ASAP 2020HD instrument using ultra-high purity gases (≥ 4.8 grade). Sample was first soaked in methanol for 48 hrs with replenishing the solvent in every 12 hrs. Then the solvent exchanged and dried sample (about 120 mg) was transferred to a glass tube for analysis, with one step activation: evacuation at 140 °C on the degas port for 24 hrs (10-3 mbar), at which point the outgas rate was ≤ 2 μ bar/min.

Langmuir Fits:

In most cases, the isotherms were fit to the Single-Site Langmuir (SSL) equation. Also, modified Langmuir equations were utilized to account for significant errors in the Langmuir model. It is widely known that even small fitting errors will have a devastating impact on selectivity calculations.

The isotherms were fit by solving the Langmuir equation using the solver function in Microsoft Excel following a similar protocol to Keller et al.^{S1} Utilizing this routine circumvents some of the problems associated with favouring either high or low-pressure regions when linearizing the Langmuir equation^{S2} and offers a balanced approach.

Single-Site Langmuir (SSL):

$$q_i = q_m \frac{k_i}{1 + k_i P} P$$

Dual-Site Langmuir (DSL):

$$q_i = q_{m,1} \frac{K_1}{1 + K_1 P} P + q_{m,2} \frac{K_2}{1 + K_2 P} P$$

Ideal Adsorbed Solution Theory (IAST):

IAST calculations were undertaken as described by Prausnitz et al.^{S3} The selectivity equation involved in the calculation is provided below.

Selectivity:

$$S_{1,2} = \frac{\frac{q_1}{p_1}}{\frac{q_2}{p_2}}$$

CO₂/N₂ selectivity was calculated for **IISERP-MOF35** using the experimental single component CO₂ and N₂ isotherms and ideal adsorbed solution theory (IAST) with a nominal composition of 15CO₂:85N₂. At 1 bar total pressure, and 313K, conditions relevant to post-combustion CO₂ capture.

High pressure adsorption isotherms for CO₂, CH₄ and N₂ were measured with a high-pressure volumetric analyzer, (iSorb HP1). It is capable of measuring pure component adsorption equilibrium between 10 mbar to 100 bar. The free space in the column is measured by dosing an initially evacuated chamber, filled with adsorbent, with known volume of the Helium gas. Prior to running the high-pressure volumetric isotherm experiment, the adsorbent was activated for 12 hrs under vacuum at 140 °C. The adsorption experiments are performed at three different temperatures up to 20 bar. An adsorbent sample mass of 1 g is used for all the experiments.

4.3 Results and Discussion

4.3.1 Synthesis and Structural Analysis:

The single crystal X-ray diffraction structure analysis reveals that **IISERP-MOF35**, [(CH₃)₂NH₂]₂[Zn₅(3-AmTz)₄(Ox)₄]·2H₂O, crystallizes in a monoclinic system (*a* = 24.012(2) Å; *b* = 11.6086(12) Å; *c* = 17.4800(19) Å; Sp. Gr. C2/c) (Table 4A.1). The molecular structure of **IISERP-MOF35** consists of one C₂O₄²⁻ (oxalate), one Atz- (3-amino triazolate) ligand, and Zn metal. The asymmetric unit of **IISERP-MOF35** constitutes three crystallographically unique Zn⁺² centers (Zn1, Zn2, and Zn3) (Fig. 4A.2A). Notably, the framework [Zn₅(Atz)₄(Ox)₄]²⁻ is anionic and the overall charge neutrality in the framework is governed by two dimethyl ammonium cations. The synthesis of **IISERP-MOF35** involves the utilization of a DMF + H₂O solvent mixture at 150 °C. It is known that DMF undergoes hydrolysis at higher temperatures, leading

to the formation of dimethyl ammonium cation. In the present framework, the stabilization of the 3D framework is supported by the presence of dimethyl ammonium cations located in the pores of the **IISERP-MOF35**; they could be located crystallographically. Generally, the mixture of other solvents (ethanol, methanol, water) leads to the formation of well-explored layered pillared structures.^{14-15, 19, 38} However, in this particular scenario, the reaction temperature plays a vital role in resulting in this unique phase of the material.

To get further insights into the structural properties of **IISERP-MOF35**, its packing diagrams along different crystallographic axes were visualized (Fig. 4A.2B-2D). Importantly, the structure is built-up of very different Zn-Atz secondary building units (SBU) compared to the CALF-15²¹ or CALF-20 or any of the related layered-pillared structures in the Zn-triazolate-oxalate system.^{14-15, 38, 58} Here the SBU is related to the classic Zn-Atz dimers found in CALF-15. In CALF-15 the adjacent dimers are rotated with respect to each other by a $< 90^\circ$ dihedral angle, and are connected to each other through the triazolate ring in a plane leading to a Zn-Atz layer. In contrast, here the adjacent dimers are rotated by 90° with respect to each other which is rare in Zn-triazolate-oxalate layered pillared structures. To make it even more unique, two adjacent dimer-resembling units in **IISERP-MOF35** share a Zinc center (Zn2) making them more of a trimer. Now these trimeric $\text{Zn}_3(\text{Atz})_4$ units are connected by an octahedral zinc center (Zn1), which extends the entire Zn-Atz assembly into an N-rich chain running along the *c*-axis (Fig. 4.1A-D). In this 1D chain, the octahedral Zn3 centers sit on the periphery of the chain and take an effective tetrahedral connection by two oxalate units as shown in (Fig. 4.1E-F); meanwhile, the Zn2 sitting at the center of the zinc trimer are truly tetrahedrally coordinated by four triazolate nitrogens. Similarly, the octahedral Zn1 centers connecting the zinc-trimers into a chain are effectively tetrahedrally connected by two triazolate and two different oxalate units in a tetrahedral fashion. These oxalate units coordinated to the Zn1 and Zn3 centers propagate the structure into a 3D framework. This 3D framework is quite dense with no obvious pores along the crystallographic *a*, *b*, and *c*-directions. However, 1-D channels can be seen along the $[110]$ direction and are filled by the charge-balancing dimethyl ammonium cations (Fig. 4.1H). Thus, the structure is substantially dense

compared to the typical layered-pillared structures built from a $\text{Zn}_2(\text{Atz})_2(\text{Ox})$ composition.^{14, 38, 21, 58} A series of structural figures are presented in the supporting information to provide alternate viewing for clarity (Fig. 4A.2A-2D).

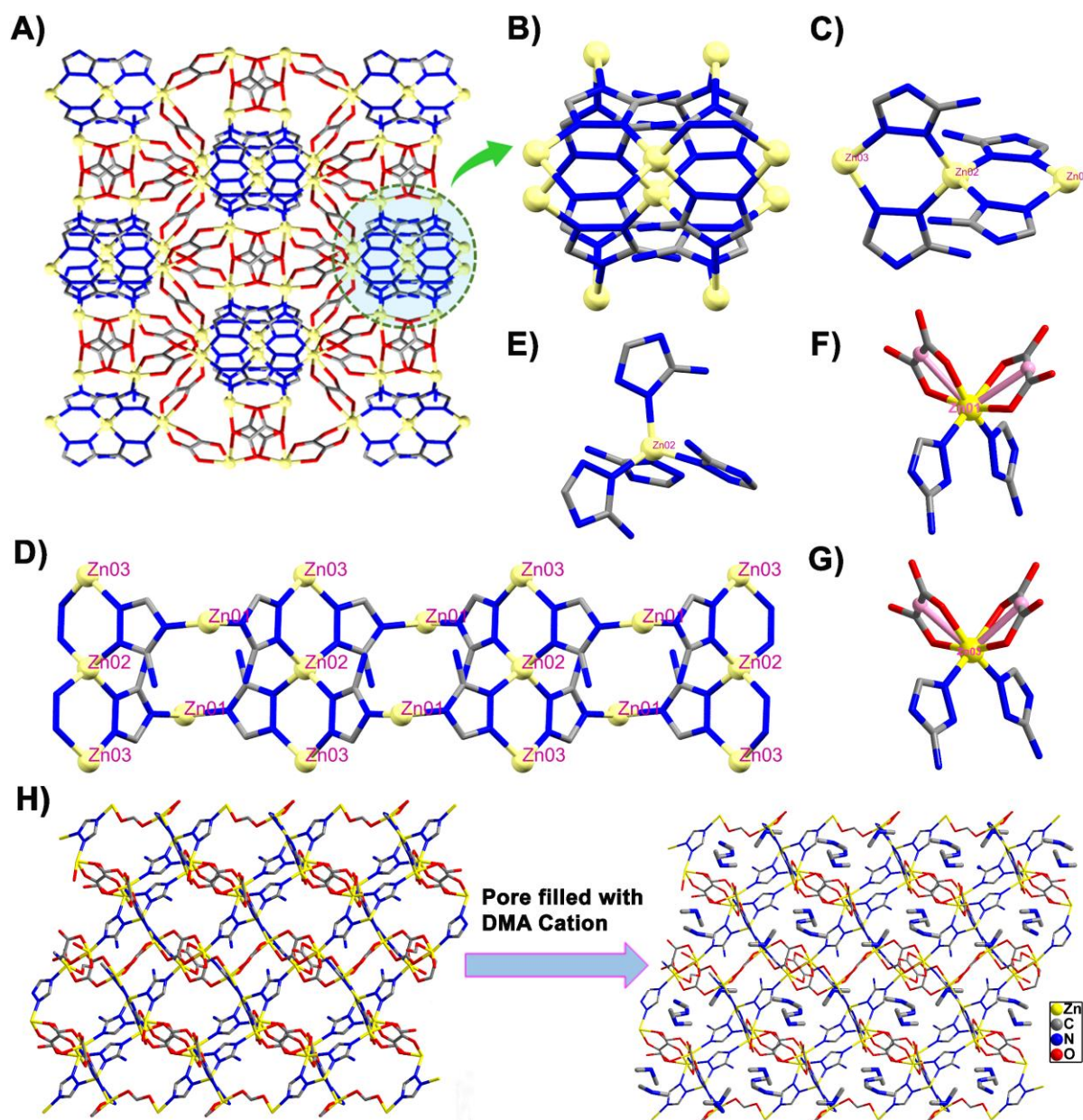


Figure 4.1: (A) The packing diagram of *IISERP-MOF35* along the *c*-axis. (B) Viewing of 1D chain which is running along the crystallographic direction *c*-axis. (C) The $\text{Zn}_3(\text{Atz})_4$ trimeric unit is present in the 1D chain (Zn-triazole cluster). (D) Viewing of 1D-chain Zn-triazole cluster along the *a*-axis. (E-G) Coordination mode of different Zn

centers present in the crystal structure of **IISERP-MOF35**. (H) Packing diagram of **IISERP-MOF35** along the $[110]$ direction, illustrating the pore structure with DMA cations located within the pores. Note: Hydrogens are omitted for clarity.

4.3.2 Bulk characterizations

The bulk phase purity of the as-synthesized **IISERP-MOF35** was confirmed through powder X-ray diffraction (PXRD) analysis. A good match of the simulated PXRD profile with the as-synthesized PXRD profile was observed (Fig. 4A.3). Furthermore, the thermal stability of **IISERP-MOF35** was verified through thermogravimetric analysis (TGA). A close analysis of the TGA profile reveals an initial weight loss (at 80-150 °C) of 4 %, corresponding to the loss of water molecules. A further weight loss of 10 % in a temperature range of 180-290 °C corresponds to the loss of dimethyl ammonium cation. Upon further increasing the temperature, the gradual degradation of the framework could be observed. These studies confirm the stability of **IISERP-MOF35** up to 290 °C (Fig. 4A.4). The infrared spectrum of an activated sample, after removing DMF using methanol exchange and vacuum treatment at 140 °C, reveals distinct peaks indicating the presence of amine (3372 and 3476 cm^{-1}) and carbonyl (1685 cm^{-1}) functional groups, as shown in (Fig. 4A.5).

4.3.3 Gas Adsorption Studies:

The SCXRD packing diagrams of **IISERP-MOF35** confirm its dense amine-rich structure with narrow pores filled with dimethyl cations. By looking at this packing diagram, we expected this material to be non-porous or to have negligible porosity. Literature has many reports on similar kinds of MOFs where these materials are proven to be extremely good sorbents for CO_2 . Contrastingly, there are metal-isonicotinate MOFs with dense framework that get opened-up by CO_2 ^{32, 51} via gating phenomenon. The earlier reported CO_2 -assisted gate opening in ZnAtzOx (**IISERP-MOF32**) system, opens an ultra-microporous framework into a more porous one. Encouraged by these reports, we measured the 77 K N_2 adsorption isotherm of **IISERP-MOF35**. No porosity was observed as would be expected given the dense nature of the **IISERP-MOF35**'s framework. However, the framework showed minimal

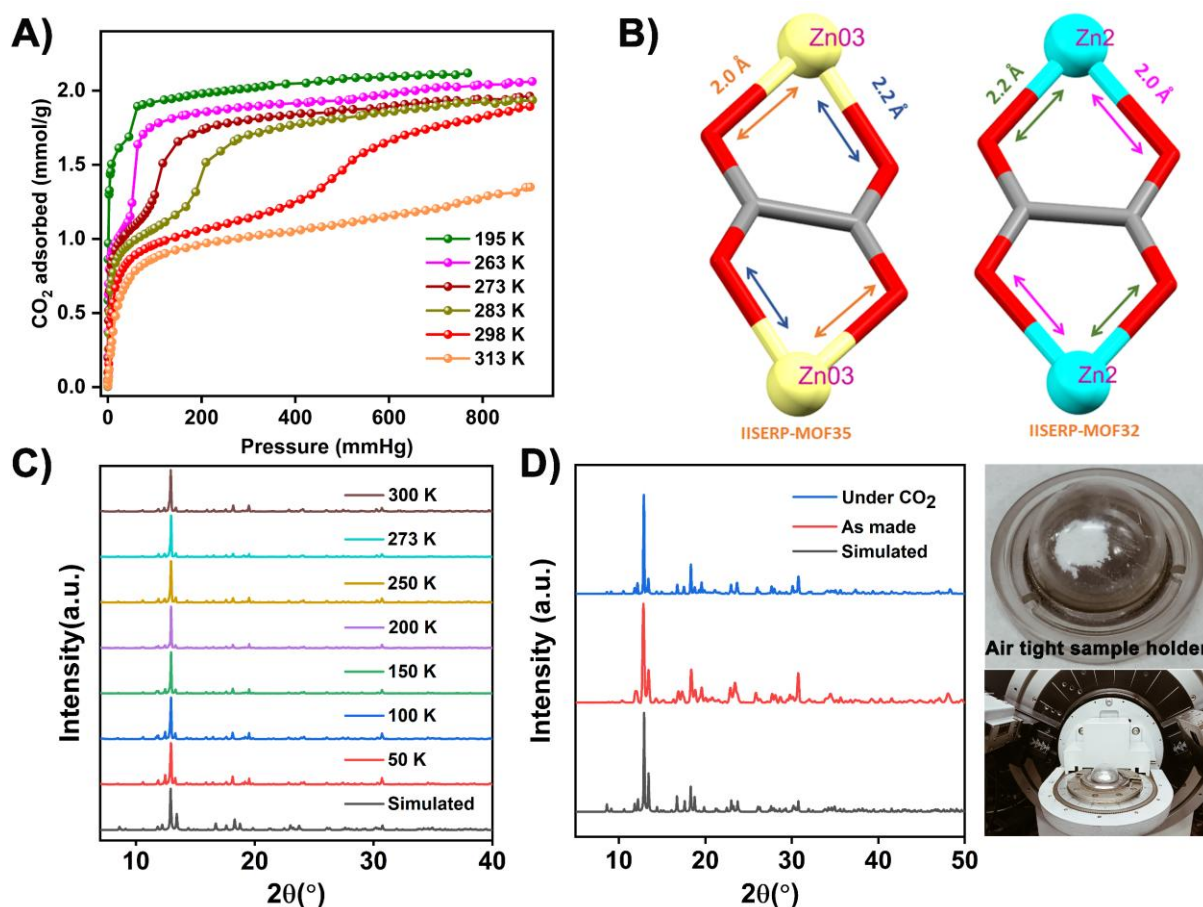


Figure 4.2: (A) The CO₂ isotherm at different temperatures. (B) The diagonal symmetrical Zn-O bond distances in the crystal structure of **IISERP-MOF35** and **IISERP-MOF32**. (C) Low temperature PXRD profiles for **IISERP-MOF35**. (D) A comparative PXRD profile of **IISERP-MOF35** under CO₂ atmosphere to its as-made and simulated profiles.

N₂ uptake even in the 273-313 K temperature range. Following this, we performed CO₂ adsorption at different temperatures (195 K, 263 K -313 K). From the CO₂ isotherm at 273 K, the BET and Langmuir surface area of **IISERP-MOF35** were calculated to be $106 \pm 1 \text{ m}^2\text{g}^{-1}$ and $209 \pm 1 \text{ m}^2\text{g}^{-1}$, respectively (Fig. 4A.6). The pore size distribution calculated by nonlinear density functional theory (NLDFT) resulted in a pore size of 6.5 Å (Fig. 4A.7) for **IISERP-MOF35**, confirming its ultra-microporous

nature suitable for small molecules such as CO₂, N₂, and CH₄ separations (discussed later in the text). To our surprise, this guest-occupied dense framework exhibited stepped CO₂ adsorption isotherms indicating a CO₂-driven structural flexibility. The CO₂ adsorption saturation uptakes were 2.1 mmol/g and 1.8 mmol/g at temperatures of 195 K and 298 K, respectively (Fig. 4.2A). This gate-opening phenomenon persists across different temperatures (298 K, 283 K, 273 K, and 263 K), with the inflexion point shifting towards higher pressures with increasing temperature.

4.3.4 Structural insights into the CO₂-assisted gate opening observed in ZnAtzOx systems

Though the saturation CO₂ uptake even at 195K is only 2 mmol/g, there are some interesting insights provided by these CO₂ isotherms. Notably, the CO₂ opens the framework even at temperature as low as 195 K, which is quite unusual.³⁸ We have observed similar CO₂ assisted gate opening in a neutral ZnAtzOx framework earlier.³⁸ In that case the sample was significantly porous with a CO₂ uptake of ~ 5 mmol/g at 195K and did not show the gating at this low temperature, but had an abrupt gate opening at 273 K (Fig. 4A.8). Thus, by comparison, it is quite unusual that this dense anionic framework of **IISERP-MOF35** is able to achieve nearly a ~ 50% increase in CO₂ uptake by decreasing the temperature from 313 K to 298 K and also, the gate opening persists even at temperature as low as 195 K.

In case of IISERP-MOF32, wherein the ZnAtz layers were pillared by oxalate units, the gate opening could be explained by the relatively longer Zn-O distances adopted by the oxalate units, which enabled them to act like rotating spindles that rotated when the CO₂ pressure was applied. In contrast the structural topology of the **IISERP-MOF35** is completely different and dense. But the CO₂ assisted gate-opening is not too different. The answer lies once again in the Zn-O bond distances. We noticed that one of the Zn-O distances in both IISERP-MOF32 and **IISERP-MOF35** were longer (2.2 Å) (Fig. 4.2B). A comparison across other Zn-triazolate-oxalate systems revealed that there are many other structures with longer Zn-O distances but none showed a CO₂-assisted gate opening (Table 4A.2). This made us look deeper. We realize that only in **IISERP-MOF35** and IISERP-MOF32 this phenomenon is observed and not in

other ZnAtzOx frameworks^{14, 60}. The similarity lies in the fact that both have the longer Zn-O bonds (2.2 Å) symmetrically positioned. However, when we check the distances between zinc and oxygen atoms, we notice that some are shorter (2.0 Å) while others are longer (2.2 Å). These longer bonds, connected to the oxalate, are positioned diagonally, while the relatively shorter Zn-O bonds (< 2.2 Å). This setup might allow the oxalate parts to rotate like a spindle. Interestingly, this symmetrically placed longer Zn-O bonds are found only for the Zn(3) centers and not the Zn(1) centers. This makes only a few percentages of the oxalates work like spindle in case of **IISERP-MOF35** compared to the IISERP-MOF32. This could be the reason for the gate-opening in the former not being as effective as in the latter in enhancing the CO₂ uptake. Of course, there are extra-framework ions in the **IISERP-MOF35** also contribute to the lowered CO₂ porosity. To the best of our knowledge, this is the first time such CO₂-assisted gate opening is observed in a Zn-aminotriazolate-oxalate system which does not have a layered-pillared topology. It is very interesting to note that the presence of same structural feature, symmetrically positioned longer Zn-O bonds, in two different MOF frameworks with significantly different framework structure and composition exhibits similar CO₂-assisted gate opening. Especially in this dense anionic **IISERP-MOF35** with guest-filled pores.

To assess if these gate openings are influenced by temperature effects, we conducted low-temperature PXRD (LT-PXRD) (50 K to 300 K) (Fig 4.2C) and high-temperature PXRD (HT-PXRD) (300 K to 523 K) (Fig 4A.9) experiments, which showed no major structural changes. Analysis of the HT-PXRD data shows a shift in peak positions towards the lower angles, indicating the lattice expansion. The gate-opening behavior was further characterized via in situ PXRD measurements under a CO₂ environment using an air tight sample holder (Fig. 4.2D). Comparative PXRD plots of simulated and as-made samples versus samples in CO₂ atmosphere suggest an increase in crystallinity of the sample in CO₂ atmosphere (Fig. 4A.10). This enhanced crystallinity of **IISERP-MOF35** in the presence of CO₂ can be attributed to the strong interaction between CO₂ molecules and the framework, potentially stabilizing the crystal lattice structure and leading to more pronounced ordering. The strong CO₂-framework

interactions are further supported by the high zero-loading heat of adsorption for CO₂ in **IISERP-MOF35** (54 kJ/mol) (Fig. 4.3A (inset)).

4.3.5 Gas-separation potential of **IISERP-MOF35**

Considering the ultra-microporous nature (6.5 Å) and the sharp CO₂ uptake at low pressure (0.15 bar), observed in the case of this MOF, we investigated its suitability for CO₂ adsorption for the post-combustion process. The negligible adsorption uptake of **IISERP-MOF35** for N₂ at different temperatures 273-313 K (Fig. 4A.11) suggest its potential for CO₂/N₂ separation applications. To further assess the capacity of **IISERP-MOF35** for capturing CO₂ from flue gas (with low CO₂ partial pressures) compositions selectively, a through Ideal Adsorbed Solution Theory (IAST) calculations were carried out. These calculations show that **IISERP-MOF35** has a CO₂ selectivity of 154 (Fig. 4.3A) for an 85% N₂:15% CO₂ gas mixture at 313 K and 1 bar pressure (Fig. 4A.12). This CO₂/N₂ selectivity observed for **IISERP-MOF35** is comparable with some of the well-known materials in the field and indicate the potential of this MOF for efficient CO₂ capture from gas mixtures with low CO₂ concentrations. The preferential uptake of CO₂ over N₂ can be attributed to the ultra-micropore present in the MOF and the presence of asymmetric Zn-O bonds, which imparts flexibility to the framework and enhances the CO₂ adsorption.

A strong affinity of **IISERP-MOF35** towards CO₂ over N₂ at different temperatures, was observed even with its dense structure (as confirmed from SCXRD analysis). The flexibility of **IISERP-MOF35** towards CO₂ motivated us to further explore its high-pressure gas adsorption isotherms for CO₂, N₂ and CH₄ gas molecules. From this analysis, the gating phenomenon in **IISERP-MOF35** for CO₂ gas at low pressure was again confirmed and was found to be consistent with that of the low-pressure measurements (up to 1 bar). In the high-pressure CO₂ isotherm, it is evident that no further gating phenomenon occurs in **IISERP-MOF35** beyond 1 bar, extending up to 20 bars. Additionally, high-pressure measurements (Fig. 4A.13-15) show no gating phenomena for CH₄ and N₂ molecules in **IISERP-MOF35**. Notably, the gate opening in **IISERP-MOF35** is specific only for CO₂ gas and no such effect has been observed for N₂ or CH₄ (Fig. 4.3B).

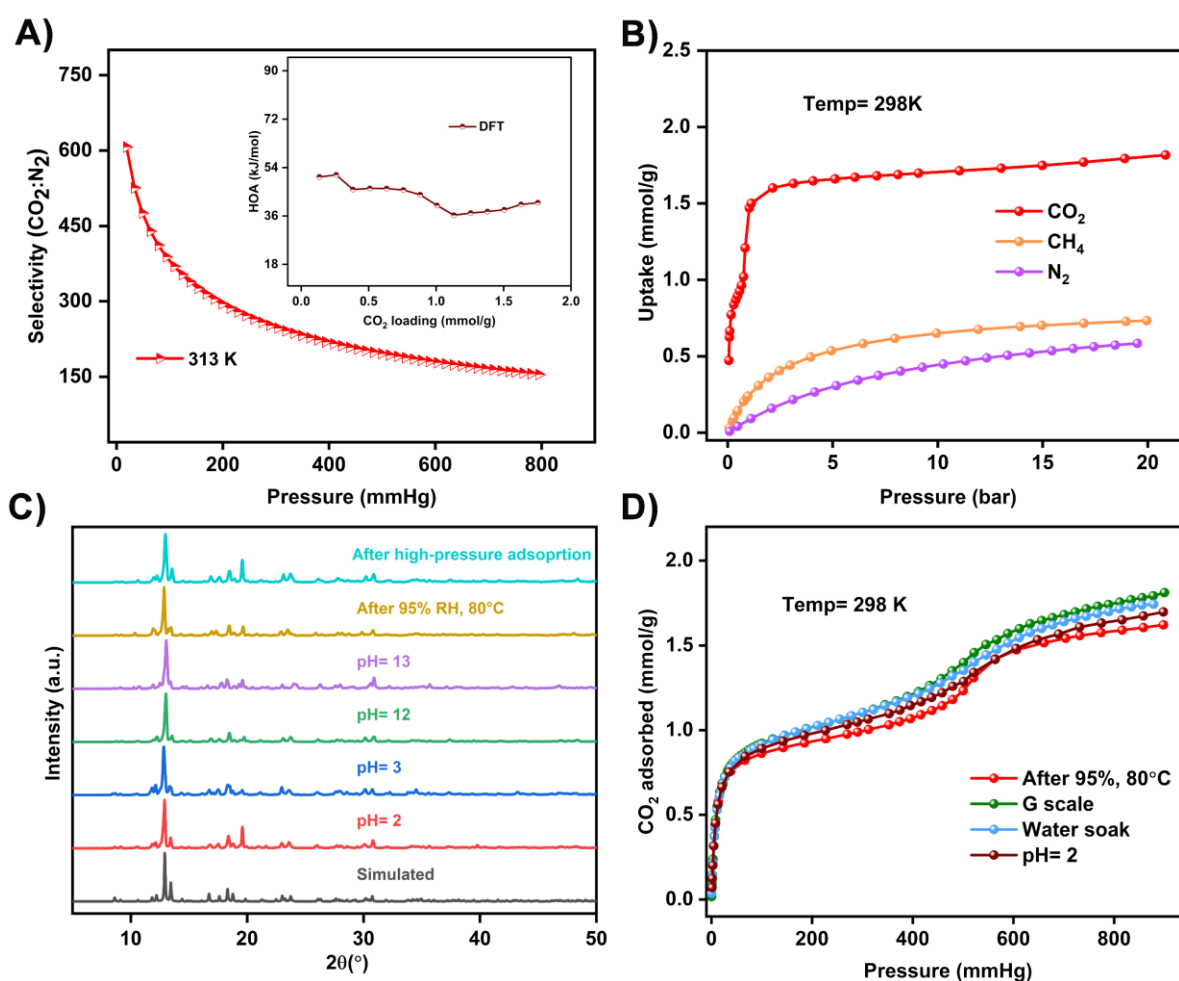


Figure 4.3: (A) CO_2/N_2 selectivity calculated using the IAST model employing a nominal composition of 85% N_2 :15% CO_2 at 313 K and the inset shows the HOA plots from DFT modelling done using the CO_2 isotherms at 273, 283, and 298 K. (B) High-pressure gas adsorption studies for CO_2 , N_2 and CH_4 up to 20 bars at 298 K. (C) The PXRD patterns of **IISERP-MOF35** kept under different harsh conditions (different pH, humidity and post high-pressure adsorption). (D) Comparative CO_2 adsorption isotherms of **IISERP-MOF35** after harsh treatments.

4.3.6 Stability studies

For any MOF to be useful for practical applications, it should possess a good chemical, and hydrolytic stability. We checked the chemical stability of **IISERP-MOF35** by

exposing it to different pH conditions and soaking it in HCl (acidic) and KOH (basic). The MOF showed no structural changes even after 5 days, as validated by its powder XRD patterns (Fig. 4.3C). The MOF was stable after soaking in different solvent for 20 days (Fig. 4A.16) and exhibited no structural changes. Some recent physisorptive CO₂ capture processes follow a steam-assisted regeneration which mandates steam stability on the candidate MOFs.¹⁵ We exposed **IISERP-MOF35** to 95% RH at 80 °C for 12 hours and checked its PXRD pattern. The PXRD analysis indicated a negligible loss of crystallinity in **IISERP-MOF35**, revealing its steam stability (Fig. 4.3C). Subsequently, the 298 K CO₂ uptake values of the post-chemically treated samples confirmed the retention of its permanent porosity (Fig. 4.3D). These tests shed light on the fact that the **IISERP-MOF35** with a dense parent structure shows strong affinity towards CO₂ leading to a transformation to a more open framework; and it bears excellent chemical and steam stability. It has also been demonstrated that **IISERP-MOF35** could be scaled to multi-grams using solvothermal methods (Fig. 4A.17).

4.4 Conclusion

We described a Zn-aminotriazolato-oxalate MOF (**IISERP-MOF35**, $[(CH_3)_2NH_2]_2[Zn_5(Atz)_4(Ox)_4] \cdot 2H_2O$), which has a framework that does not resemble the ubiquitous layered-pillared topology prevalent among the CALF-20 and related zinc-triazolato-oxalate systems. Interestingly, this dense anionic framework with spaces filled by dimethylammonium cations unexpectedly shows a CO₂-specific gate opening. Comparing its structure with an earlier reported Zn-aminotriazolato-oxalate MOF (**IISERP-MOF32**, $[Zn_2(Atz)_2(Ox)] \cdot \text{solvent}$), which had a layered-pillared topology and exhibited CO₂-assisted gate opening, reveals specific structural commonality. The important feature is the symmetrically positioned relatively longer Zn-O bonds formed between the Zn and the oxalate oxygens. Importantly, the gate opening opens a dense, tightly-packed framework to take CO₂. The study captures the unique structural feature of two ultra-microporous MOFs, which are compositionally related but have markedly different frameworks. This structural motif brings framework flexibility from gas-specific interactions. The structural insights could help create open frameworks pre-designed for guest-assisted flexibility.

4.5 References

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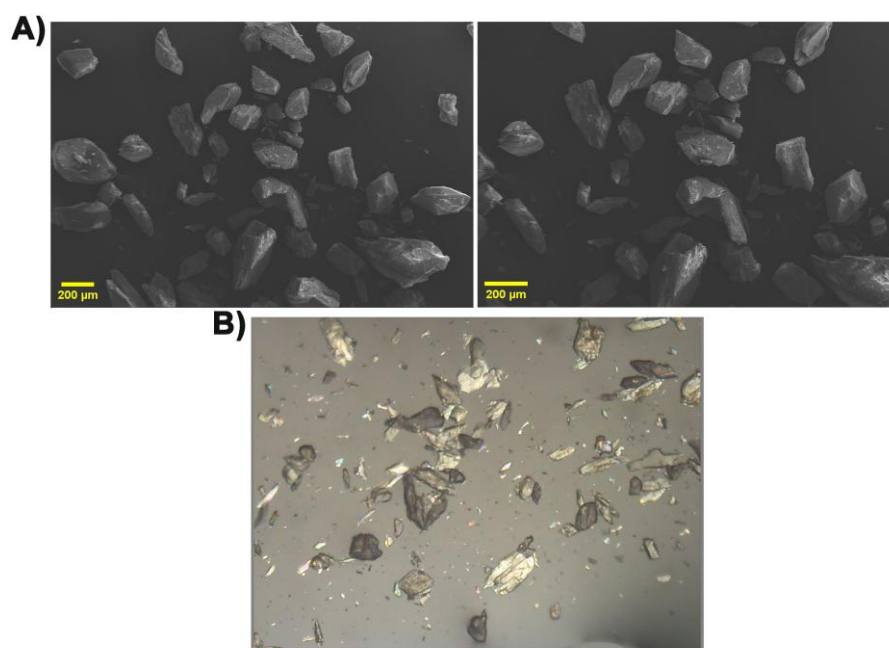


Figure 4A.1: (A) FESEM images of **IISERP-MOF35** at different magnifications show a block-like structure. (B) Optical microscope images of the crystals reveal that they grow into block shapes.

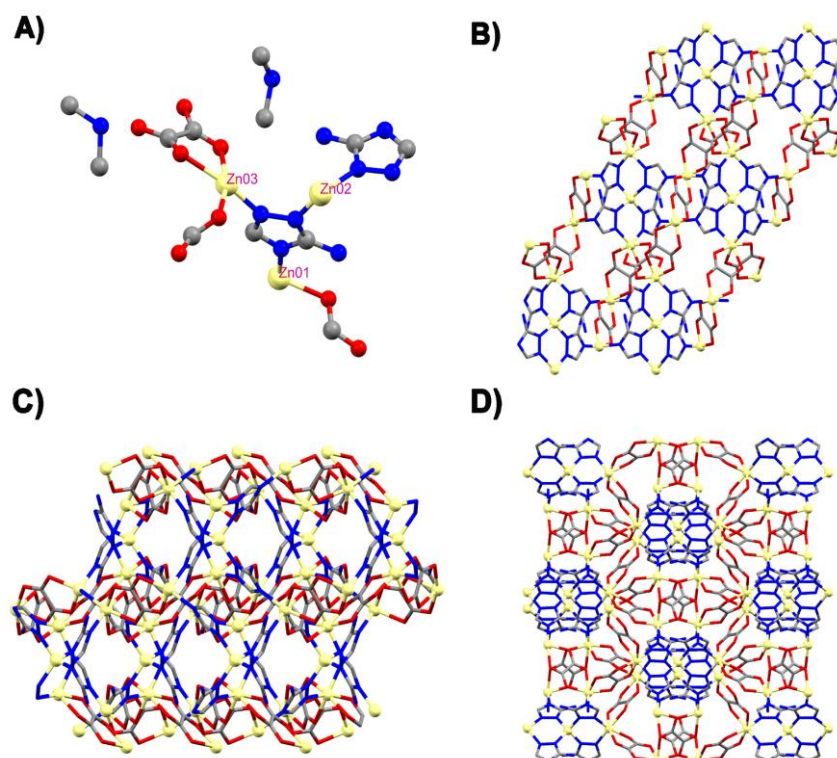


Figure 4A.2: A) The Asymmetric unit for **IISERP-MOF35**. The three-dimensional view of **IISERP-MOF35** (B) along the *a*-axis, (C) along the *b*-axis, and (D) along the *c*-axis.

Table 4A.1: Crystallographic Information for **IISERP-MOF35**.

a/Å	24.012(2)
b/Å	11.6086(12)
c/Å	17.4800(19)
$\alpha/^\circ$	90
$\beta/^\circ$	123.218(2)
$\gamma/^\circ$	90
V/Å ³	4076.3(7)
Crystal System	Monoclinic
Space Group	C2/c
Color	Colourless
Expt. Crystal description	Block shape
Z	4
T/ K	100 K
Diffraction Source	MoK α
Diffraction radiation wavelength/ Å	0.71073
Diffraction reflection theta min	2.026
Diffraction reflection theta max	22.338

Reflection number total	2610
Reflection number gt	2268
R1, wR2 [$I > 2\sigma(I)$]	0.059, 0.160
R1, wR2 (all data)	0.069, 0.170
GoF	1.055

PLATON analysis:

Total Potential Solvent Accessible Void Vol (SOLV-Map Value) = 167.00 Å³

Unit cell volume, V = 4076.3 Å³

Formula unit present in **IISERP-MOF35** is [(CH₃)₂NH₂] [Zn_{2.5}(Ox)₂(3-AmTz)₂]

Again, Z = 4. Hence the unit cell formula is [(CH₃)₂NH₂]₄ [Zn₁₀(Ox)₈(3-AmTz)₈]

The squeeze results suggest that 34 electrons are present from solvent molecules in the unit cell. Hence, per formula unit 34/4 ~ 9 electrons are present. This electron density can be assigned as ~ 1 H₂O molecule. Hence the formula of **IISERP-MOF35** is [(CH₃)₂NH₂] [Zn_{2.5}(Ox)₂(3-AmTz)₂].H₂O

Powder X-ray diffraction:

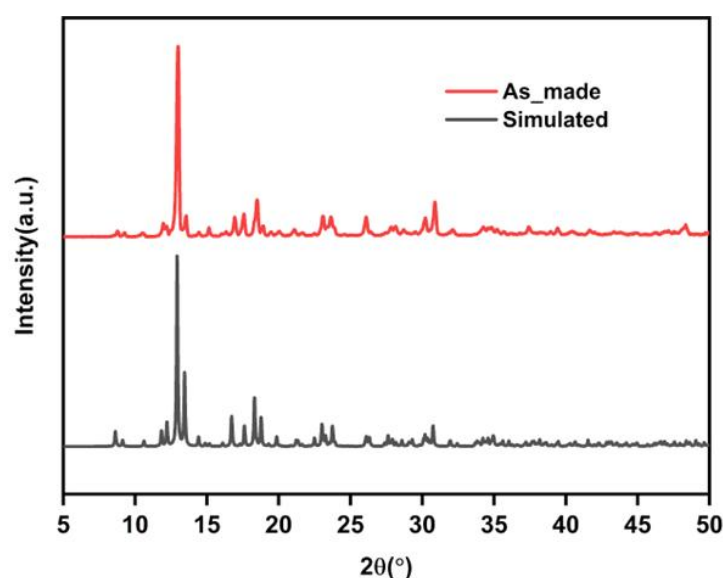


Figure 4A.3: The PXRD profile of **IISERP-MOF35** indicates the bulk purity of the MOF.

TGA analysis:

From SCXRD data and Platon analysis, the formula of **IISERP-MOF35** is confirmed to be $[(\text{CH}_3)_2\text{NH}_2][\text{Zn}_{2.5}(\text{Ox})_2(3\text{-AmTz})_2]\cdot\text{H}_2\text{O}$.

The molecular weight of $[(\text{CH}_3)_2\text{NH}_2][\text{Zn}_{2.5}(\text{Ox})_2(3\text{-AmTz})_2]\cdot\text{H}_2\text{O} = 566.77$ g/mol.

From PLATON analysis, the expected mass loss due to water = $(18/566.77) \times 100 = 3.2\%$

Expected mass loss due to DMA^+ cation = $(46.1/566.77) \times 100 = 8.1\%$

From TGA analysis, the weight loss corresponding to 1 water molecule and DMA^+ cation was found to be $\sim 4\%$ and $\sim 10\%$ respectively supporting the formula unit obtained from Platon analysis.

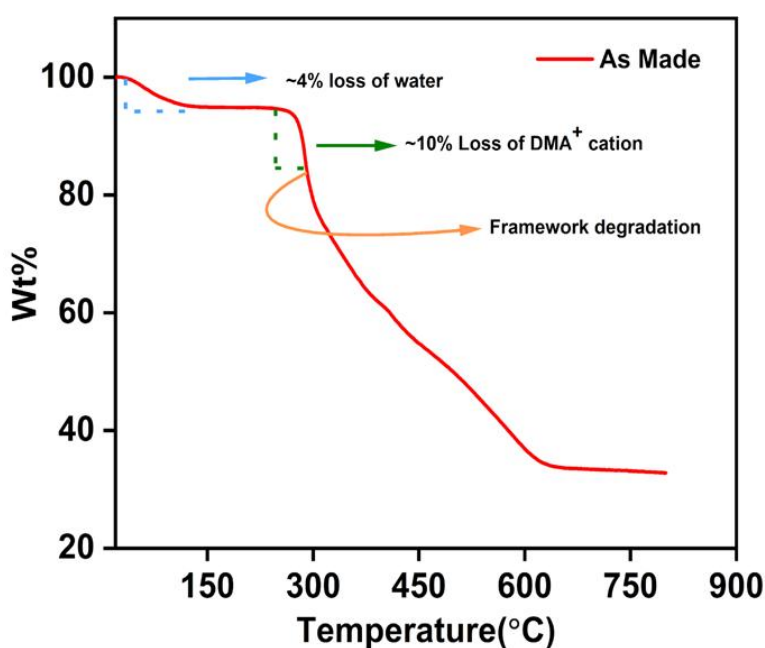


Figure 4A.4: The TGA profile of the **IISERP-MOF35** shows its thermal stability up to 290 °C.

IR analysis:

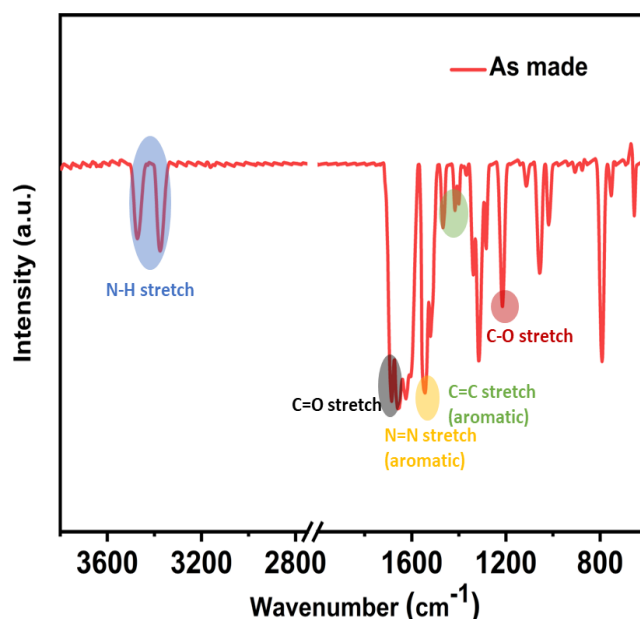


Figure 4A.5: Infra-red spectra of **IISERP-MOF35**, showing the various stretching and bending modes present in it. Selected peaks: IR (cm^{-1}): $\nu(\text{N-H})$: 3372 and 3476; $\nu(\text{C=O})$: 1685s; $\nu(\text{N=N})$: 1546s; $\nu(\text{C=C})$: 1465 and 1414; $\nu(\text{C-O})$: 1214.

Adsorption Analysis

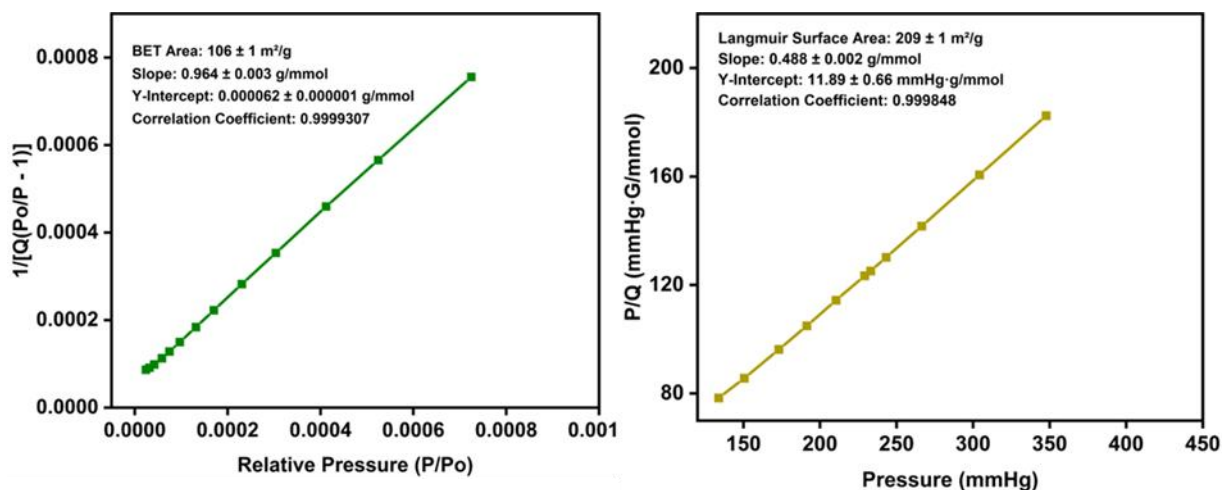


Figure 4A.6: (A) BET fits the activated **IISERP-MOF35** from the 273K CO_2 isotherm. (B) Langmuir fits for the activated **IISERP-MOF35** from the 273K CO_2 adsorption isotherm.

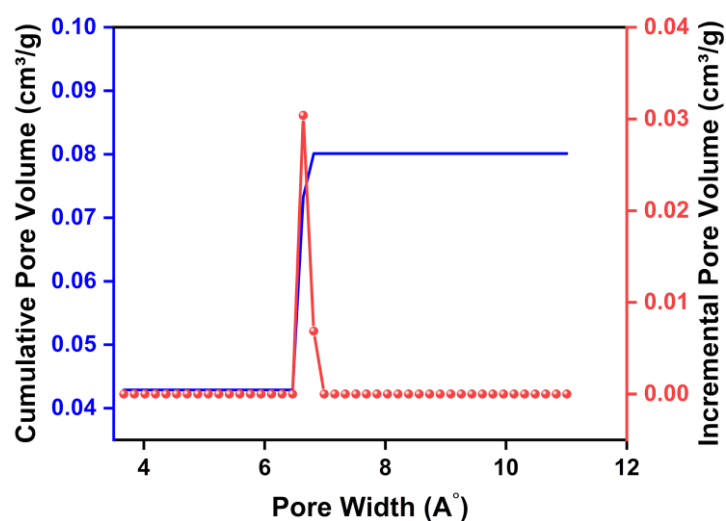


Figure 4A.7: The pore size distribution for the **IISERP-MOF35** was obtained by fitting the NLDFT model to the 273K CO₂ adsorption branch.

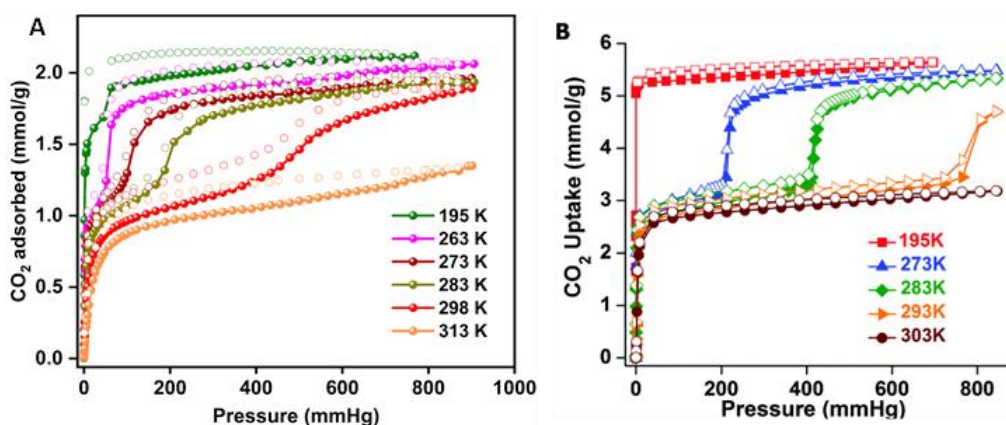


Figure 4A.8: CO₂ adsorption-desorption isotherms of (A) **IISERP-MOF35** and (B) **IISERP-MOF32** at different temperatures showing the gating at different pressures of CO₂.

Table 4A.2: Comparison of Zn-O bond distance in Zn-triazolato-oxalate systems.

MOF	Zn-O (bond distance Å)	Flexible (Yes or No)	Gas Adsorption studies (Yes or No)	Reference
1. $\text{Zn}_2(\text{C}_2\text{O}_4)(\text{C}_2\text{N}_4\text{H}_3)_2(\text{H}_2\text{O})_{0.5}$	2.0 to 2.4	No	Yes	Chem. Commun., 2009, 5230–5232
2. ZnAtzOx (2)	2.0, 2.2 (Diagonally symmetrical)	Yes	Yes	Chem. Commun., 2016, 52, 1851–1854

Appendix for Chapter 4

2. ZnAtzOx (3)	2.02, 2.08, 2.16, 2.33	No	Yes	Chem. Commun., 2016, 52, 1851–1854
2. ZnAtzOx (4)	2.03, 2.10, 2.14, 2.32	No	Yes	Chem. Commun., 2016, 52, 1851–1854
3. Calf-20, [Zn ₂ (tz) ₂ (Ox)].solvent	2.02, 2.2 (Diagonally symmetrical)	Yes	Yes	<i>Science</i> 374, 1464–1469 (2021)
4. Zn-ox-mtz	2.05 to 2.18	No	Yes	<i>J. Am. Chem. Soc.</i> 2023, 145, 25, 13901–13911
5. NU-220	2.03 to 2.18 (Diagonally not symmetrical)	No	Yes	<i>J. Am. Chem. Soc.</i> 2024, 146, 6, 3943–3954
5. CALF-20M-w	2.02, 2.17 (Diagonally symmetrical)	No	Yes	<i>J. Am. Chem. Soc.</i> 2024, 146, 6, 3943–3954
5. CALF-20M-e	2.00, 2.12 (Diagonally symmetrical)	No	Yes	<i>J. Am. Chem. Soc.</i> 2024, 146, 6, 3943–3954
6. {[NH ₂ (CH ₃) ₂][Zn(atz)(ox)]H ₂ O}	2.09, 2.20 and 2.107, 2.188 (Diagonally symmetrical)	No	Yes	<i>RSC Adv.</i> , 2015, 5, 24655
7. {[Zn(ox) _{0.5} (trz)]0.25H ₂ O} _n	2.0, 2.2 (Diagonally symmetrical)	No	No	Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry (2016) 46, 365–369
8. [(CH ₃) ₂ NH ₂] ₃ [Zn ₆ (ox) _{4.5} (trz) ₆]·4H ₂ O	2.10, 2.13, 2.18, 2.25	No	No	Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 161 (2016) 138–143
9. Zn ₂ (trz) ₂ (ox)	2.08, 2.11, 2.17, 2.18	No	No	<i>Cryst. Growth Des.</i> 2007, 7, 11, 2332–2342
10. Zn ₂ (H ₂ O)(C ₂ H ₂ N ₃) ₂ (C ₂ O ₄)·2H ₂ O	2.15	No	No	<i>Inorg. Chem.</i> 2015, 54, 10, 4678–4687
11. {[Zn(atz)(C ₂ O ₄) _{0.5}]·H ₂ O} _n	2.0, 2.2 (Diagonally symmetrical)	No	No	J Inorg Organomet Polym (2014) 24:1027–1031

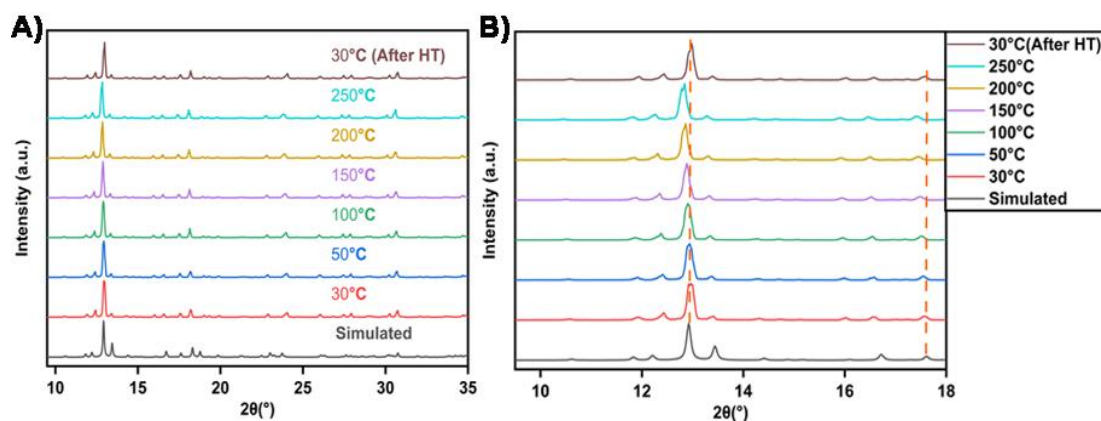


Figure 4A.9: The temperature-dependent PXRD patterns are from 30 °C (300 K) to 250 °C (523 K).

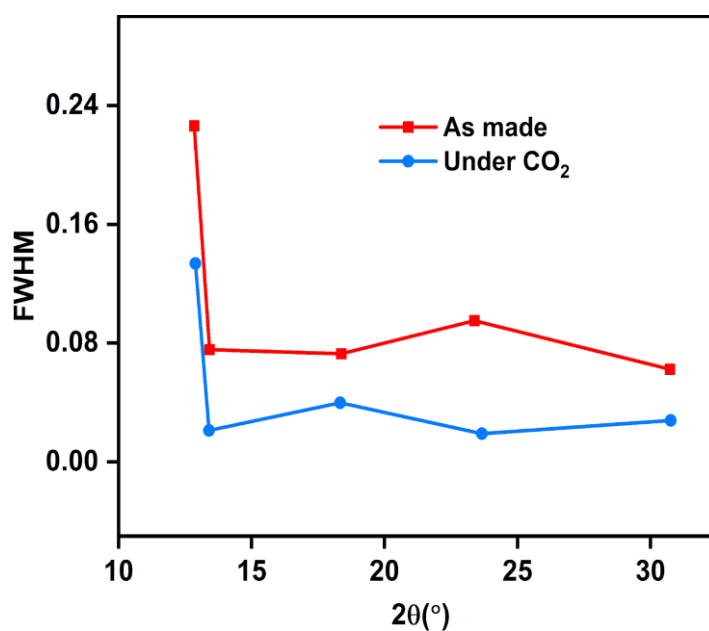


Figure 4A.10: FWHM plot of IISERP-MOF35 as made vs under CO₂.

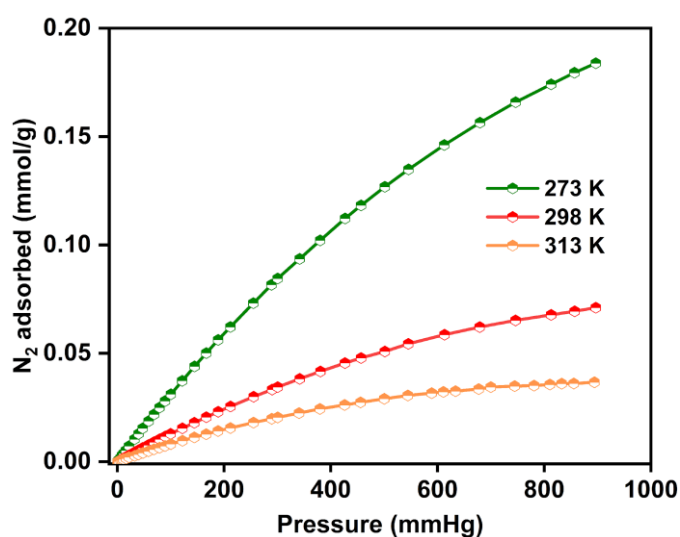


Figure 4A.11: N₂ adsorption isotherm of **IISERP-MOF35** at different temperatures.

IAST fitting parameters for IISERP-MOF35 (CO₂/N₂):

At 313 K

Gas A = CO₂

Gas B = N₂

Table 4A.3: Fitted IAST parameters for CO₂/N₂ (15CO₂:85N₂ composition) selectivity at 313 K for **IISERP-MOF35**.

Gas A Constants		Gas B Constants	
q_{s1} (mmol g ⁻¹) =	1.455300668	q_{s1} (mmol g ⁻¹) =	1.4552917
q_{s2} (mmol g ⁻¹) =	0	q_{s2} (mmol g ⁻¹) =	0
K_1 (mbar ⁻¹) =	0.063703653	K_1 (mbar ⁻¹) =	0.00010818
K_2 (mbar ⁻¹) =	0	K_2 (mbar ⁻¹) =	0
n_1 =	0.642511216	n_1 =	0.79036474
n_2 =	0	n_2 =	0
H_1 (mmol mbar ⁻¹ g ⁻¹) =	0.061090933	H_1 (mmol mbar ⁻¹ g ⁻¹) =	3.8372E-05
H_2 (mmol mbar ⁻¹ g ⁻¹) =	0	H_2 (mmol mbar ⁻¹ g ⁻¹) =	0

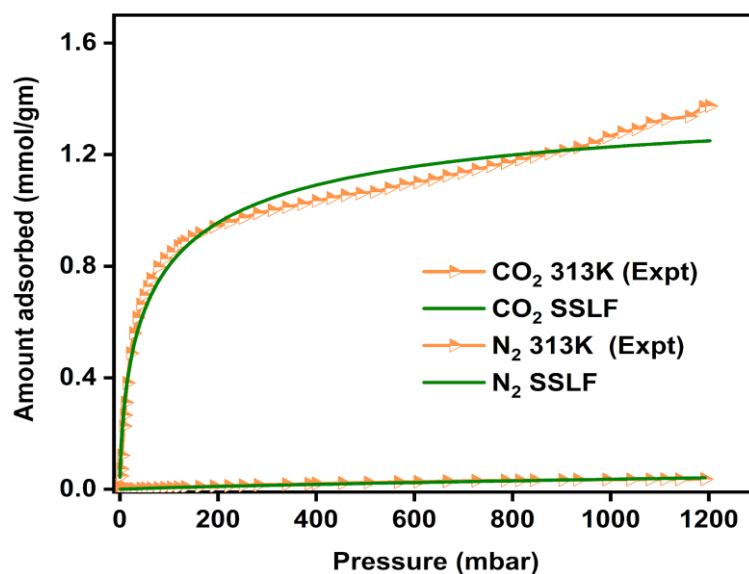


Figure 4A.12: IAST fitting of CO₂ and N₂ isotherms for **IISERP-MOF35** collected at 313 K. *Note:* The best fit achieved for CO₂ isotherm is shown here ($R^2 = 0.98$). Owing to the step wise adsorption of CO₂, a better fit could not be achieved.

High-Pressure Gas adsorption studies

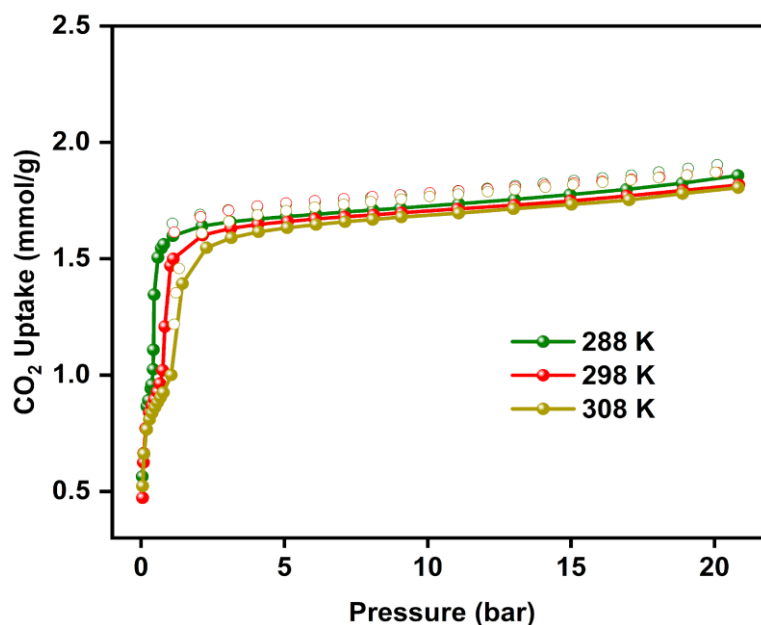


Figure 4A.13: High-pressure CO₂ isotherm of **IISERP-MOF35** measured at different temperatures.

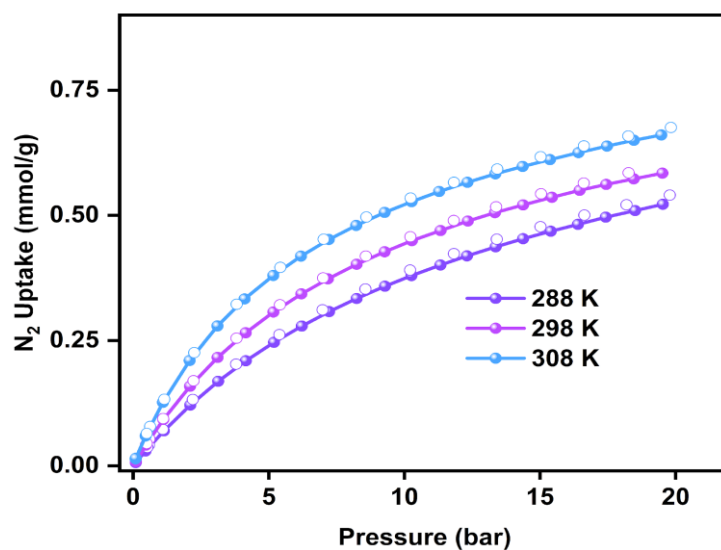


Figure 4A.14: High-pressure N₂ isotherm of **IISERP-MOF35** measured at different temperatures.

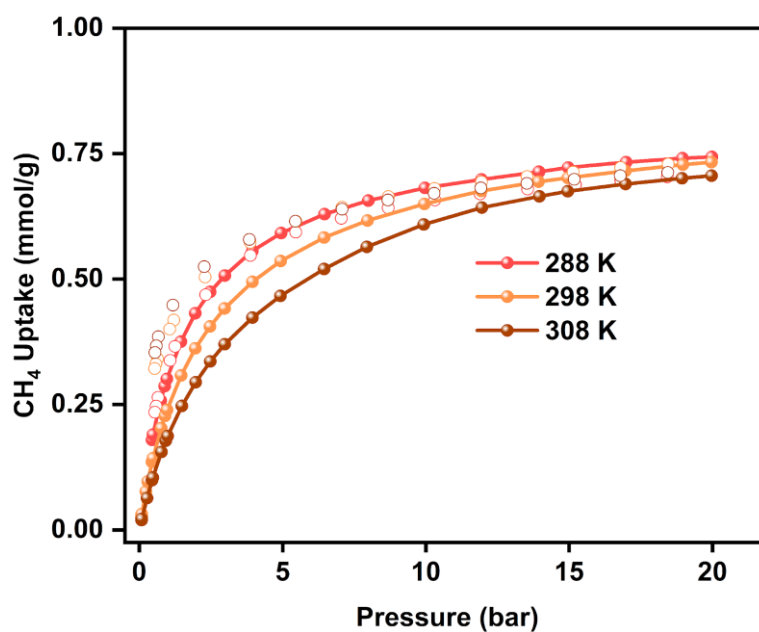


Figure 4A.15: High pressure CH₄ isotherm of **IISERP-MOF35** measured at different temperatures.

Stability Studies

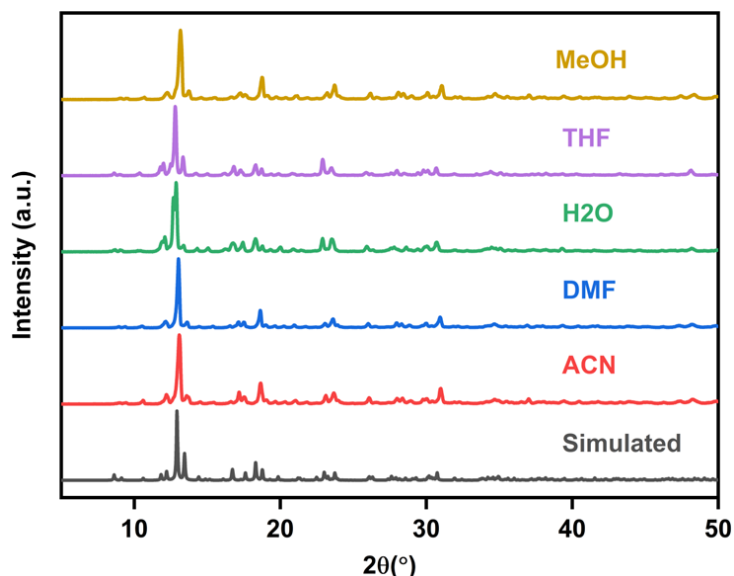


Figure 4A.16: After soaking for 10 days, PXRD profiles demonstrate the stability of IISERP-MOF35 in various solvents.

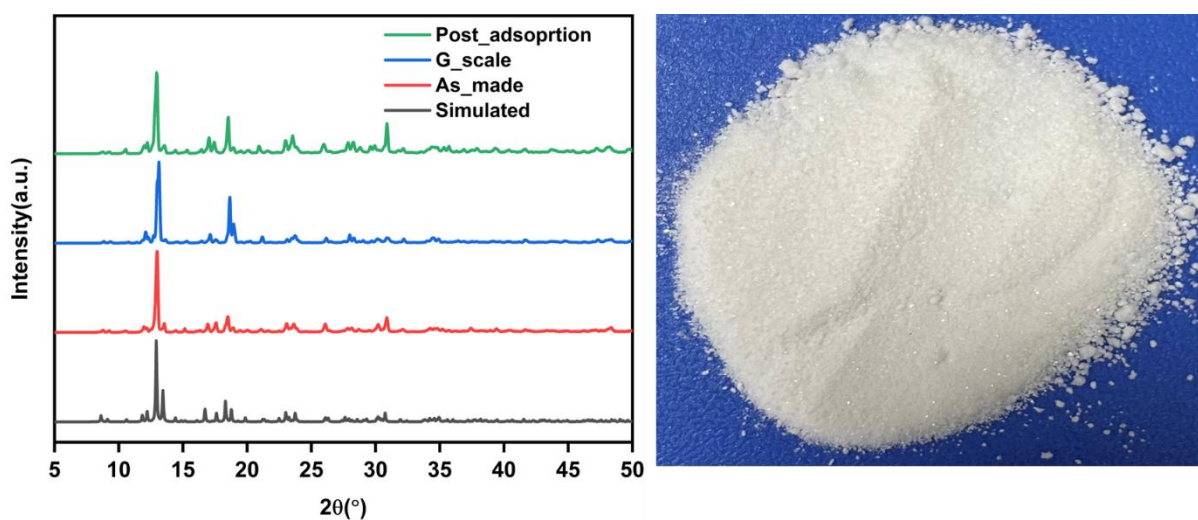


Figure 4A.17: A comparative PXRD plot showing the bulk purity of the gram scale synthesis and the stability of the MOF to the repeated adsorption-desorption and evacuation cycles. Note: This material can be scaled up to 2 gram in a single synthesis.

Chapter 5

**Ultra-Microporous zinc-
diaminotriazolate-oxalate MOF with
nonlayered-pillared structure
showing high carbon dioxide uptakes
at low partial pressures**

5.1 Introduction

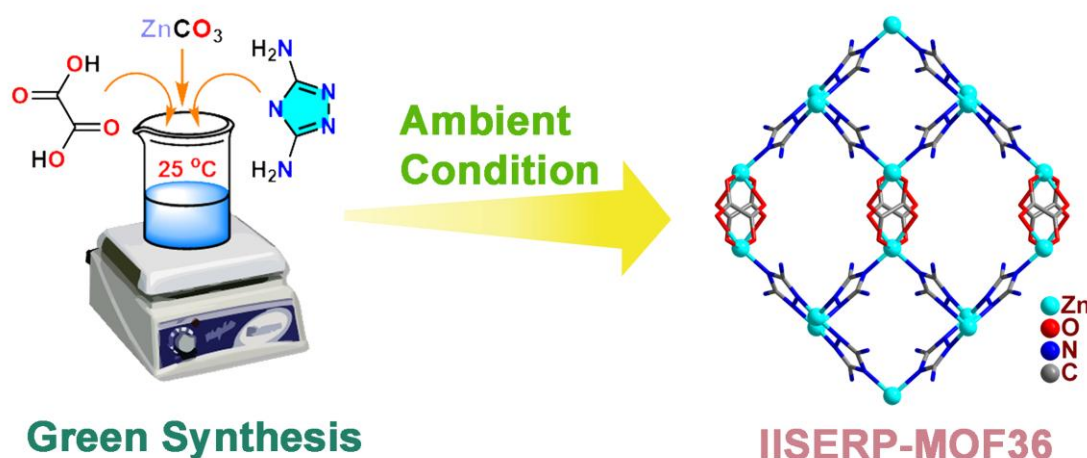
Developing small pore MOFs that can exploit site-specific CO₂ binding in conjunction with molecular sieving is an area of large interest.¹⁻¹⁴ Intense efforts are focussed on advancing these MOF sorbents towards humid CO₂ capture with some promising findings.¹⁵⁻²³ In general, ultra-microporous MOFs have shown unique capabilities in selective capture of CO₂ and exhibit superior hydrolytic stability.²⁴⁻³⁷ The recent success of CALF-15 and CALF-20³⁸⁻⁴² as stable and selective sorbents for low pressure capture of CO₂ has sparked high interest in azolate-oxalate frameworks and in industrially relevant humid CO₂ capture MOF development.⁴⁰⁻⁴⁴ Dicarboxylate-triazolate frameworks have been known for a long time.⁴⁵⁻⁴⁸ Many of them have been investigated for their porous structures and selective CO₂ capture.⁴⁹⁻⁶¹ The elegance of CALF-20 system arises from the simplicity of composition, synthesis, strong metal-ligand bonds and the high guest selectivity arising from ultra-micropores.^{62,63} With these advantages, alternate MOF structures of CALF-20 family with improved CO₂ capacities are a desirable target. The recent research on this class of MOF aims at superior CO₂ capture performance at higher relative humidities, attempts are focused towards understanding the binding site and diffusion properties of this unique MOF, CALF-20, which exhibits superior humid CO₂ capture up to RH of ~30%. CALF-20 itself has been shown to exhibit reversible phase transformation during its activation.⁴³ Studies explaining the molecular level reasons behind the hydrophobicity of CALF-20 and the resulting CO₂ selectivity from binary mixtures have appeared.⁶⁴ Insilico pore engineering studies reveal few alternate ligand choices to improve the CO₂ capacity, and squarate and cubane dicarboxylate score higher.⁶⁵ Independently, the competitive advantage of CALF-20 for CO₂ over water arising from thermodynamic and kinetic reasons have been deliberated.^{66,67} Recently, it has also been demonstrated that functionalizing the triazolates with hydrophobic methyl groups can result in frameworks with superior CO₂ capture than CALF-20 at higher humidities.⁶⁸ With all these sorbent advantages and dynamic features of CALF-20, further development of Zinc-azolate-oxalate MOF is highly rewarding.

In general CALF-15³⁸, CALF-20⁴⁰, IISERP-MOF32⁵³ and most other reported azolate oxalates have a layered-pillared topology, if higher low-pressure CO₂ capacities are to

be envisaged, one needs to go beyond this structure. In this regard, a huge inspiration comes from the series of zeolitic azolates reported by Chen and co-workers and others.⁶⁹⁻⁷² Thus a deep-dive into these 3D non-layered-pillared azolate framework could be an effective strategy. Meanwhile, alternate methods such as covalent linking of amino acids or amines,⁷³⁻⁷⁶ newer hydroxide-based adsorbents are being explored to achieve this^{77,78}. Also, anion-pillared MOFs with highly polarizing ultra-micropores hold promise for low-pressure CO₂ capture.⁷⁹⁻⁸⁶ Enthused by the ability of azolates to form 3D architectures and the success of CALF-20 series, here we have adopted a much simpler approach that is to play with the oxalate/triazolate ratio to synthesize non-layered-pillared compositional analogue. We present a zinc-diaminotriazolato-oxalate MOF with a similar composition but a different structure compared to the CALF-20, but with even steeper uptake of CO₂ at low partial pressures, which is not easy to achieve. Though related structures could exist, here we present a new viewpoint towards this new non-layered-pillared zinc-diaminotriazolato-oxalate structure. Importantly, the CO₂ adsorption is still a completely reversible physisorptive process with apt heat of adsorption. This could be of relevance to the natural gas combined cycle (NGCC) type of processes.

5.2 Experimental section

5.2.1 Synthesis



Synthesis scheme for **IISERP-MOF36** at ambient condition

At room temperature, a 500 ml round bottom glass was taken, Zinc carbonate basic $[\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6]$ (6 mmol, 3.2 g), 3,5-Diamino-1,2,4-Triazole (25 mmol, 3 g) and Oxalic acid (15 mmol, 1.8 g) were added to it. 400 mL of water was added subsequently into the mixture. The mixture was sonicated for at least 2 minutes and then stirred at room temperature for 72 hours, leading to the formation of a white crystalline product. This product was collected by filtration, thoroughly washed with water and methanol, and subsequently air-dried, resulting in a 72% yield.

5.2.2 Single crystal structure determination. Single-crystal X-ray diffraction was done on a Bruker SMART APEX four-circle diffractometer equipped with a CMOS photon 100 detector and Micro focus(I μ S) using a Mo-K α radiation. The crystal of **IISERP-MOF36** was mounted on nylon Cryo loops using Paratone-N oil. Data was collected at 150(2) K. Total data was integrated using Bruker SAINT Software and using SADABS it was corrected for absorption. Structure was solved using Intrinsic Phasing routine and was refined using the SHELXTL 6.3.1 (2004) software suite. All the non-hydrogen atoms were located from iterative examination of difference F-maps following which the structure was refined using least-squares method. Hydrogen atoms were fixed geometrically in a riding model.

5.2.3 Powder X-ray diffraction. Powder XRDs were done using a Rigaku Miniflex-600 instrument and processed using PDXL software. The Variable temperature powder X-ray diffraction (VT-PXRD) were carried out on a full fledged Bruker instrument using the in-built furnace and in air.

5.2.4 Thermogravimetric Analysis. Thermogravimetry analysis of as made MOF was performed on NETSZCH TGA-DSC instrument. The routine TGAs were done under N₂ gas flow (20 ml/min) (purge + protective) and samples were heated in the temperature range of 25 to 800 °C with a heating rate of 5 °K min⁻¹.

5.2.5 IR Spectroscopy. The infrared (IR) spectrum was recorded on a Nicolet FT-170SX instrument using KBr discs in the 400–4000 cm⁻¹ region.

5.2.6 Adsorption Analysis. All low-pressure gas sorption isotherms were measured on a Micromeritics ASAP 2020HD instrument using ultra-high purity gases (≥ 4.8 grade). Sample was first soaked in methanol for 48 hrs with replenishing the solvent in every 12 hrs. Then the solvent exchanged and dried sample (about 120 mg) was

transferred to a glass tube for analysis, with one step activation: evacuation at 140 °C on the degas port for 24 hrs (10^{-3} mbar), at which point the outgas rate was ≤ 2 μ bar/min.

Langmuir Fits:

In most cases, the isotherms were fit to the Single-Site Langmuir (SSL) equation. Also, modified Langmuir equations were utilized to account for significant errors in the Langmuir model. It is widely known that even small fitting errors will have a devastating impact on selectivity calculations.

The isotherms were fit by solving the Langmuir equation using the solver function in Microsoft Excel following a similar protocol to Keller et al.^{S1} Utilizing this routine circumvents some of the problems associated with favouring either high or low-pressure regions when linearizing the Langmuir equation^{S2} and offers a balanced approach.

Single-Site Langmuir (SSL):

$$q_i = q_m \frac{k_i}{1 + k_i P} P$$

Dual-Site Langmuir (DSL):

$$q_i = q_{m,1} \frac{K_1}{1 + K_1 P} P + q_{m,2} \frac{K_2}{1 + K_2 P} P$$

Ideal Adsorbed Solution Theory (IAST):

IAST calculations were undertaken as described by Prausnitz et al.^{S3} The selectivity equation involved in the calculation is provided below.

Selectivity:

$$S_{1,2} = \frac{\frac{q_1}{p_1}}{\frac{q_2}{p_2}}$$

CO₂/N₂ selectivity was calculated for **IISERP-MOF36** using the experimental single component CO₂ and N₂ isotherms and ideal adsorbed solution theory (IAST) with

nominal composition of 15CO₂:85N₂. At 1 bar total pressure, and different temperature, conditions relevant to post-combustion CO₂ capture.

High Pressure gas adsorption: High-pressure adsorption isotherms for CO₂, CH₄, and N₂ were measured with a high-pressure volumetric analyzer (iSorb HP1). It is capable of measuring pure component adsorption equilibrium between 1 and 100 bar. The free space in the column is measured by dosing an initially evacuated chamber, filled with adsorbent, with known volume of the helium gas. Prior to running the high-pressure volumetric isotherm experiment, the adsorbent was activated for 12 h under vacuum at 150 °C. The adsorption experiments are performed at three different temperatures up to 20 bars. An adsorbent sample mass of 1 g is used for all the experiments.

5.2.7. Breakthrough dynamic studies

Pelletized **IISERP-MOF36** (2.144 g, 97.71 wt%, 2.29 wt% binder), was loaded into a cylindrical stainless-steel column (diameter: 10.4 mm, length: 50 mm). The adsorbent was regenerated by flowing pure, dry N₂ (50 mL/min) through the packed column at 120°C for a minimum of 5 hours. The dry adsorbent mass (1.93 g) was determined through TGA analysis of the pelletized **IISERP-MOF36**. Gas mixture humidity was controlled and measured with PID-controlled bubbler systems using Vaisala HMP7 probes. The utilization of multiple mass flow controllers and two bubblers allows for independent control of two gas mixtures, which can be selectively diverted to the bed through the usage of a 4-way valve. In the dry adsorption experiment the column was cooled to 35°C and, at $t = 0$ minutes, the adsorbate gas mixture (15% CO₂, 85% N₂, 50 mL/min) was fed into the column until adsorbent saturation. In the humidified adsorption experiment the column was cooled to 35°C then saturated, at $t = 0$ minutes, by flowing wet gas (10%RH [0.5 mol% H₂O], balance N₂, 50 mL/min) until measured H₂O concentration reached a stable condition. Once H₂O concentration stabilized, the adsorbate gas mixture (15% CO₂, 10% RH [0.5 mol% H₂O], 84% N₂, 50 mL/min) was flowed through the column until complete saturation of both CO₂ and H₂O. In both experiments, once saturated, a desorption process was performed by flowing dry nitrogen through the column (N₂, 35°C, 50 mL/min) until complete CO₂ desorption. The column effluent gas stream was sampled by an MKS Cirrus 3 gas analyzer, then

directed to an Alicat mass flow meter. Following complete desorption, a valve was switched to bypass the column, allowing measurement of the inlet gas composition.

5.2.8 Computational Details

All computational calculations and simulations were performed using Accelrys Materials Studio Version 8.0. An adsorption isotherm was simulated using the Grand Canonical Monte Carlo (GCMC) routine integrated into the sorption algorithm of the Materials Studio software. For these simulations, equilibration steps were calculated using the Metropolis algorithm and by employing the Drieding forcefield. The Lennard-Jones equation, with a cut-off radius of 18.5 Å, was utilized to calculate van der Waals interactions. Long-range electrostatic and Coulomb interactions were both determined using three-dimensional Ewald and Group methods, achieving an accuracy of 1.0×10^{-5} kcal/mol. The calculations were repeated three times to establish an error bar. Following this, the favorable positions for CO₂ within the metal-organic framework (MOF) were identified using the Simulated Annealing routines in the Materials Studio software, utilizing a Smart algorithm. A total of 10 cycles with 100000 steps per cycle were executed to achieve low-energy configurations. Charges were calculated using the Qeq charge equilibration method. All simulations were conducted within the Sorption package of Materials Studio. For the supercell, 10 water molecules were included, representing 2 water molecules per pore.

For the binding energy calculations, a 2 x 2 x 2 supercell was constructed and subjected to a dispersion-corrected density functional theory (DFT) optimization using the CASTEP routine within Materials Studio. A Generalized Gradient Approximation with the Perdew–Burke–Ernzerhof (GGAPBE) functional was used to calculate the exchange and correlation energy of electrons. The SMART finite basis set correction was applied, along with a plane wave basis set cut-off 370 eV. Electronic minimization was performed using the Density Mixing Scheme, and the valence electrons were treated with the OTFG pseudopotentials. The SCF tolerance was set to 1×10^{-6} eV/atom. The calculations were repeated twice to eliminate any bias from the initial configuration. Excellent convergence was achieved each time, with total energies showing negligible differences in the third decimal of the kcal/mol units. The binding

energies were calculated as a difference between the energy of the guest loaded framework vs. the desolvated empty framework.

Molecular Dynamics (MD) Simulations

The lowest energy configuration of the 2 x 2 x 2 supercell containing guest molecules of CO₂ or water was used as the input for the molecular dynamics (MD) simulations. These low energy configurations were from the simulated annealing routine. The MD simulations were performed using the Forcite Dynamics module integrated within the Accelrys Package. For the MD simulations, the initial velocities were generated randomly. We conducted a 10 ns NPT MD simulation (with a time step of 1.0 fs at 300 K) to reach and stabilize an equilibrium state. The Dreiding force field was employed, and Coulombic interactions were handled using group-based summation methods with a cut-off distance of 18.5 Å. We did not modify the size of the charge groups. To control the temperature, we utilized the Nose-Hoover thermostat, while the Berendsen barostat was used for pressure control. We applied an energy tolerance of 5×10^{-5} kcal/mol. Subsequently, we conducted a 10 ns NVE simulation (with a 1.0 fs time step) to generate a low-energy trajectory, from which we analyzed the radial distribution function (RDF) and the mean square displacement (MSD) plots were used to calculate the self-diffusion coefficients of the guest molecules. The same Dreiding force field (version 2.8) was used for these simulations along with the NVE ensemble. Electrostatic and van der Waals interactions were calculated up to a cut-off distance of 18.5 Å. Note: The NPT MD simulations suggest no appreciable change in the lattice parameters during this equilibration step

5.3 Results and discussion

5.3.1 Synthesis and Characterization

The white crystalline **IISERP-MOF36 (1)** (*IISER stands for Indian Institute of Science Education and Research, Pune*) has been synthesised at room temperature. The single crystal X-ray diffraction (SCXRD) analysis of **1** revealed that the MOF crystallizes in the monoclinic crystal system ($a = 8.464(2)$ Å; $b = 12.025(3)$ Å; $c = 7.252(2)$ Å; Sp. Gr. $P2_1/c$) (Table 5A.1), with a composition $[\text{Zn}_2(\text{Damtz})_2(\text{Ox})] \cdot \text{H}_2\text{O}$. The asymmetric unit of **1** contains one diaminotriazolate moiety, one oxalate with half

occupancy, and two Zn centers, each with half occupancy. A closer look at the packing diagram of **1** reveals that the framework adopts a 3D structure and has a pore along the crystallographic c-axis (Fig. 5.1A and 5A.2).

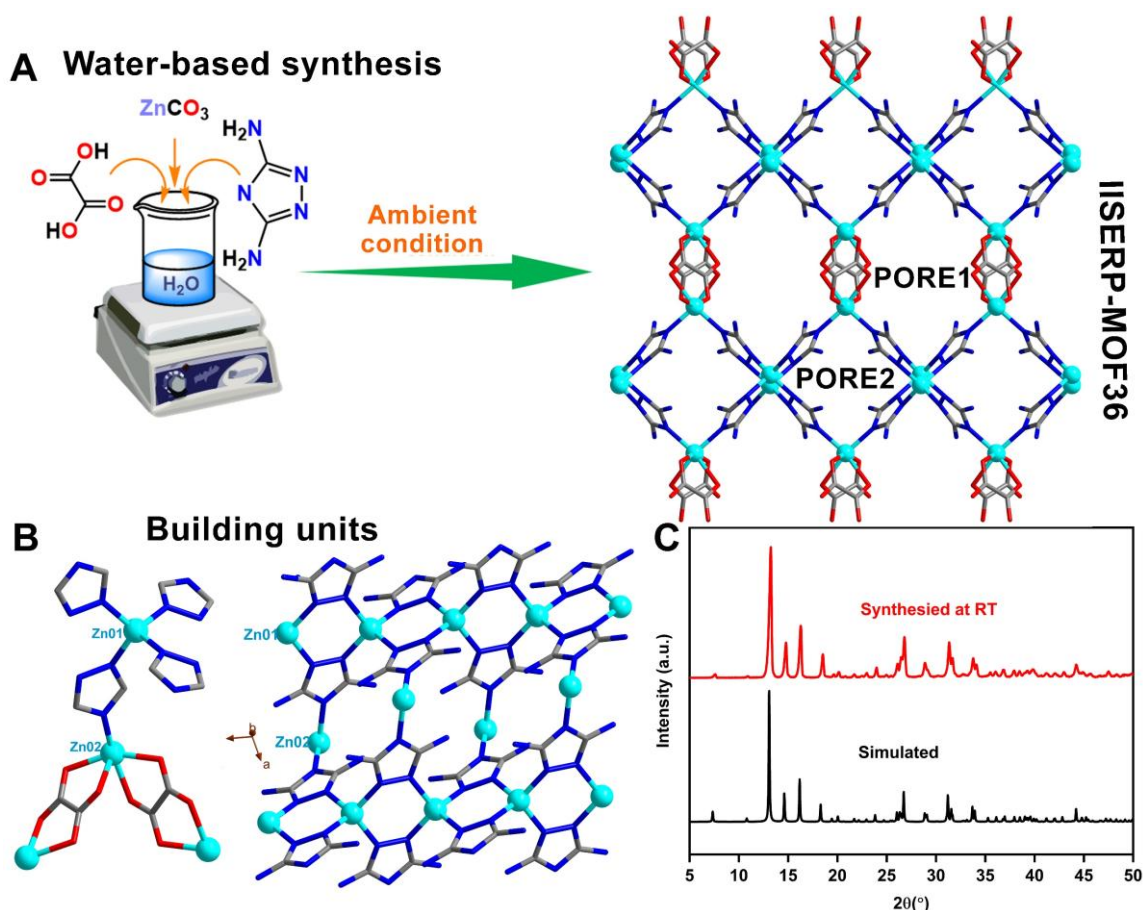


Figure 5.1: (A) Schematic illustration of the greener water-based synthesis of **1**. The 3D framework of **1** has two different pores along the c-axis. (B) Building units of the MOF. The tetrahedral triazolate coordinated and six-coordinated oxalate-triazolate coordinated zinc centers are seen. Zn-Damtz dimer are interlinked by Zn(02) center to form a zinc-azolate layer. The oxalates coordinated to the Zn(02) center make it a 3D framework. (C) The benign water-based room temperature synthesis yields a pure phase of **1** as evidenced by PXRD.

IISERP-MOF36 consists of two types of Zn centers named Zn(1) (tetrahedral) and Zn(2) (octahedral), respectively. The Zn-O distances in the octahedral Zn(2) center

are 2.02 and 2.25 Å, respectively. It is to be noted that the tetrahedral Zn(1) is connected to four different 3,5-Damtz units making a Zn(2) dimeric center. Two adjacent Zn(2) dimeric centers are inter-linked at a 107.11° angle to each other forming a 1D chain structure growing along c-axis. Furthermore, these 1D chains consisting of tetrahedral Zn(2) dimeric centers are connected via octahedral Zn(2) atoms, forming a 2D layer. The octahedral Zn(2) is again connected to two oxalate subunits, which act as pillars to connect these unique layers (Fig 5.1A and B).

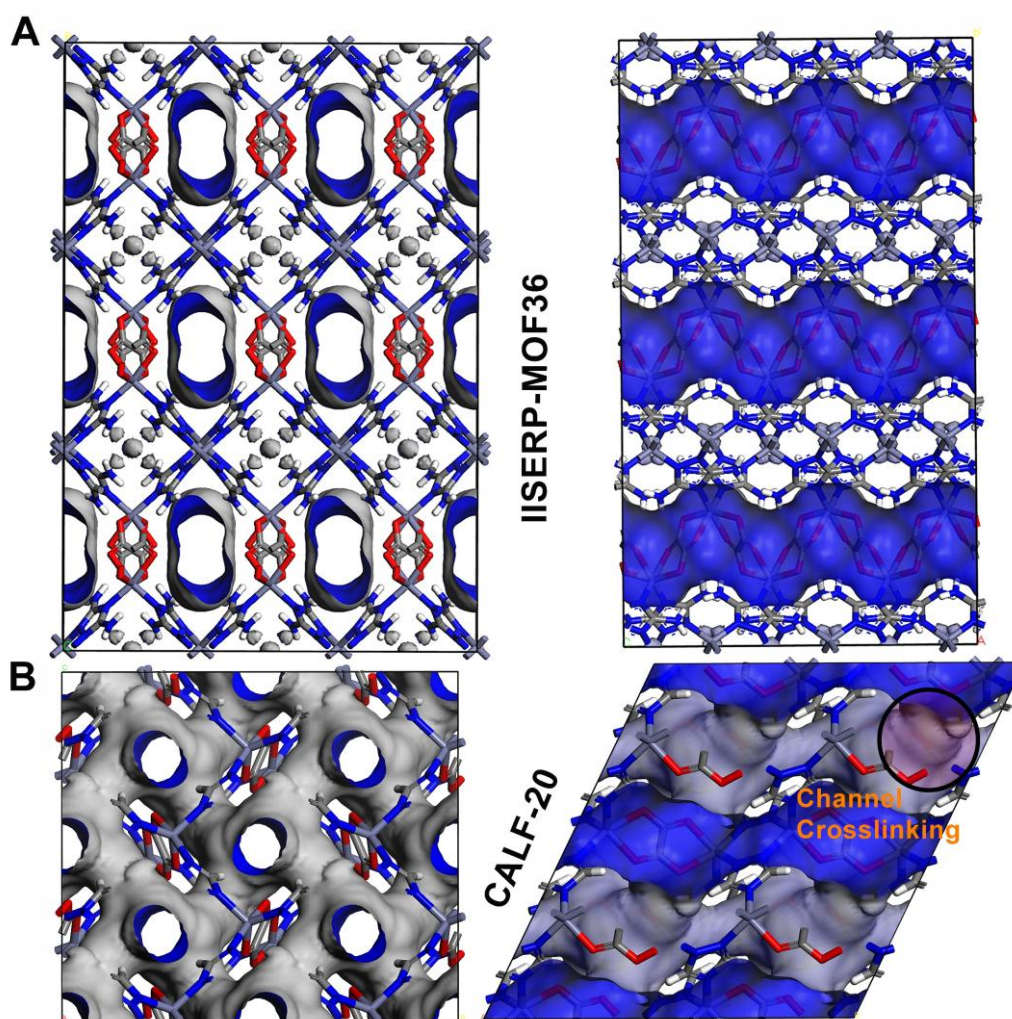


Figure 5.2: A Connolly representation of **1**. A comparison of the pore system of this MOF with the related layered-pillared MOF, CALF-20 is presented. (A) **1** has an elliptical pore which are connected into a truly 1D channel. (B) CALF-20 has a small

pore that opens into a slightly wider space, this results in an undulating cross-linked channels running as a 2D pore system.

The 3D structure of **1** is different from the common layered pillared structures of CALF-20 ($[\text{Zn}_2(\text{Tz})_2(\text{Ox})]\cdot 0.5\text{H}_2\text{O}$),⁴⁰ IISERP-MOF32 ($[\text{Zn}_2(\text{Atz})_2(\text{Ox})]\cdot 0.5\text{H}_2\text{O}$),⁵³ etc. Though the chemical formula of all these MOFs is similar, the topology of **1** distinguishes its structural properties from the above-mentioned MOFs. The major structural difference arises from the fact that in **1** there is a ligand aggregation, leading to two types of spaces. A larger one lined by both diaminotriazolate units and the oxalate (PORE-1, Fig. 5.1A), while the smaller one lined exclusively by diaminotriazolate ligands (PORE-2). In comparison, in CALF-20 all the pores are identical and resemble the PORE-1 of **1**. The Connolly surface representations of **1** vs. CALF-20 further clarifies the 3D-pore structural differences (Fig 5.2A and B). The former is more of 1D channel system with narrow slit pores (Fig 5.2A), while the latter has a more cross-connected 3D pore system with somewhat undulating channels with more space at the widest part (Fig 5.2B). To explore the sway of these structural attributes of **1** in CO_2 adsorption, we set out to study its gas adsorption properties.

The simulated powder X-ray diffraction (PXRD) pattern matches well with the experimental PXRD pattern of the synthesised MOF at room temperature confirming the bulk purity of the material (Fig. 5A.3). To confirm the thermal stability of **1**, we performed thermogravimetric analysis (TGA) which suggests its stability up to 330°C , which was further confirmed by variable temperature PXRD (VTPXRD) patterns (Fig. 5A.4 and 5A.5). The Fourier Transform Infrared Spectroscopy (FTIR) spectral data shows the distinguished peaks for the respective functional groups present in the as made MOF ($\nu(\text{N-H})$: 3356 cm^{-1} and 3452 cm^{-1} ; $\nu(\text{C=O}$, stretching): 1693 cm^{-1}) (Fig. 5A.6).

5.3.2 Gas Adsorption Studies

To assess the porosity of **1**, CO_2 adsorption was studied at different temperatures (195 K, 273 K, 298 K, 313 K and 323 K), wherein the isotherms showed the type 1 behaviour (Fig 5.3A). The BET and Langmuir surface areas were calculated using the adsorption

branch of the 273 K isotherm, yielded BET and Langmuir surface areas of 206 and 231 m²/g, respectively, with a pore volume of 0.12 cm³/g. The non-local density functional theory (NLDFT) fit indicated a pore size of approximately 3.5 Å (Fig. 5.3B and 5A.7-5A.9). At 298 K and 1 bar pressure, the CO₂ and N₂ uptakes were 2.2 mmol/g and 0.44 mmol/g, respectively (Fig 5A.10). At 0.15 bar and 298 K, **1** adsorbs 2.1 mmol/g of CO₂, suggesting its promising capability for CO₂ capture from flue gas. At low pressure the abrupt CO₂ uptake observed for **1** is due to its pore size (3.5 Å) which is very close to the kinetic diameter for CO₂ molecule (3.30 Å).

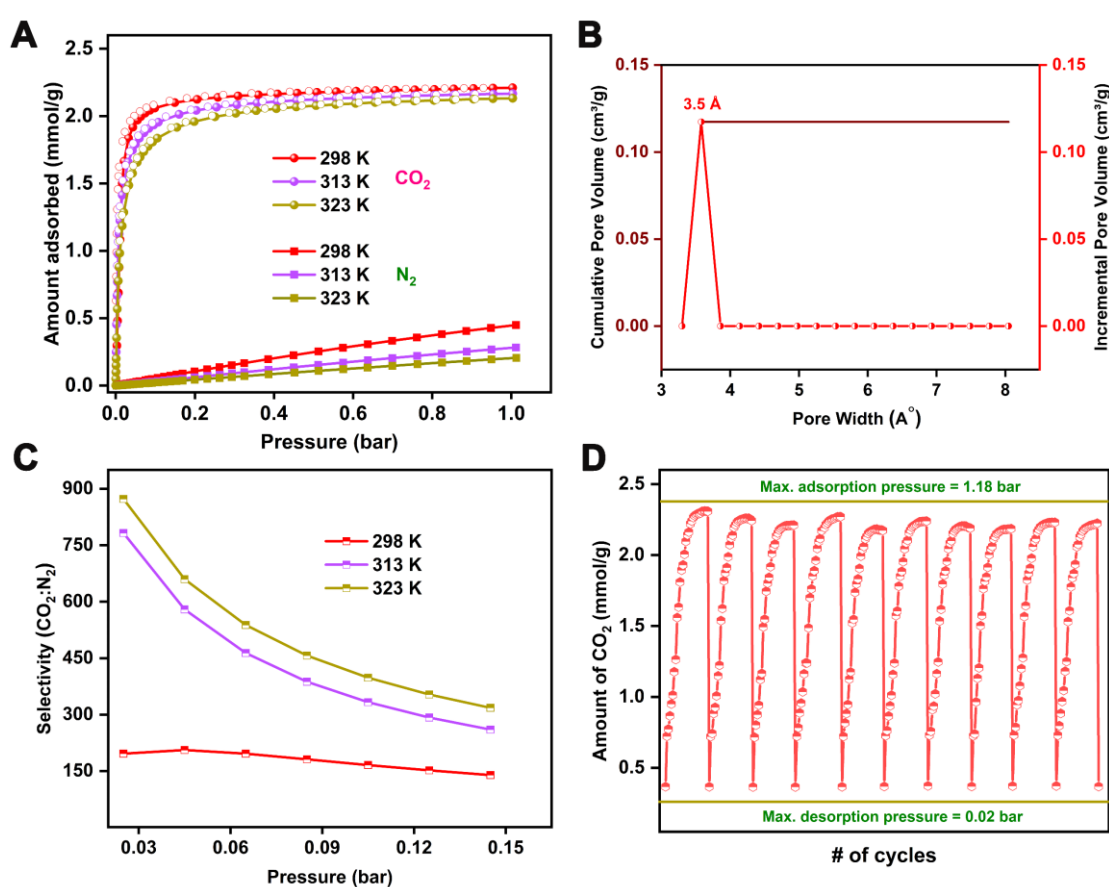


Figure 5.3: (A) The CO₂ and N₂ adsorption isotherms obtained for **1** at different temperatures. (B) The pore size distribution for the **1** obtained using NLDFT fitting to the 273 K CO₂ adsorption branch. (C) CO₂/N₂ selectivity calculated using the IAST model employing a nominal composition of 15CO₂:85N₂ at different temperatures. (D) CO₂ adsorption–desorption cycles at room temperature, with a pressure swing of 1.2 to 0.02 bar, performed for 10 cycles.

The Ideal Adsorbed Solution Theory (IAST) calculations performed using the CO₂ and N₂ isotherms collected at 298, 313 and 323 K, employing a nominal composition of 15CO₂:85N₂, yield a CO₂/N₂ selectivity of 140, 260 and 317, respectively, at 0.15 bar (Fig. 5.3C and Fig 5A.11-14). These selectivity values (at 0.15 bar) are considerably high and are sufficient to achieve the benchmarked greater than 95 % purity during separation. The calculated heat of adsorption (HOA) value using density functional theory (DFT) model at 313, 298, and 273 K CO₂ isotherms is 41 kJ/mol at zero loading (Fig. 5A.15) and it reaches 30 kJ/mol at higher loadings, indicating easy desorption favoring physisorption. To further investigate this, we conducted a CO₂ adsorption isocycling experiment, utilizing vacuum conditions for regeneration between cycles. The results showed consistent CO₂ volumetric capacity over 10 adsorption-desorption cycles without any loss, as illustrated in (Fig 5.3D).

Nevertheless, for capturing CO₂ from the real flue gas where water vapours, NO_x, SO_x, etc. are present, a potential MOF should possess certain key characteristics such as selectivity of CO₂ over N₂, functional ability under wet conditions, chemical/mechanical/thermal stability post adsorption-desorption cycling, low HOA, convenient scalability in a cost-effective manner, etc. To check the stability of **1** under such conditions, its water adsorption isotherm was collected. **1** adsorbs a uptake of ~ 4.7 mmol/g water at 95% RH at 25°C (Fig. 5A.16), lesser than the water uptake of CALF-20. The PXRD pattern of the **1** post water adsorption confirmed its intact crystalline nature (Fig. 5A.16, inset). The chemical stability of **1** was further elucidated by soaking it in solutions of different pH for over 2 days. The MOF showed no structural changes as validated by their powder patterns (Fig. 5.4A). Also, **1** retains its crystallinity after soaking in different solvents (H₂O, DMF, THF, ACN, MeOH, hexane) for 7 days (Fig. 5A.17). Recently demonstrated CALF-20 based Svante's CO₂ capture processes involves a steam-assisted regeneration. This mandates steam stability on the candidate MOFs. We exposed **1** to a controlled relative humidity (RH) condition of 95 % at a constant temperature of 353 K. The post process PXRD patterns indicated no loss of crystallinity in **1** (Fig. 5.4A). The material was further tested for its stability in boiling water (Fig. 5.4A). Thus **1** with similar metal-ligand connectivity as CALF-20

but with a different structure retains all the stabilities exhibited by the former. The CO₂ uptakes obtained at 298 K for the post-chemically treated **1** sample confirm its permanent porosity retention (Fig. 5.4B). We also compared the PXRD patterns of **IISERP-MOF36 (1)**, CALF-20 and IISERP-MOF32 after soaking them in pH 1 solution.

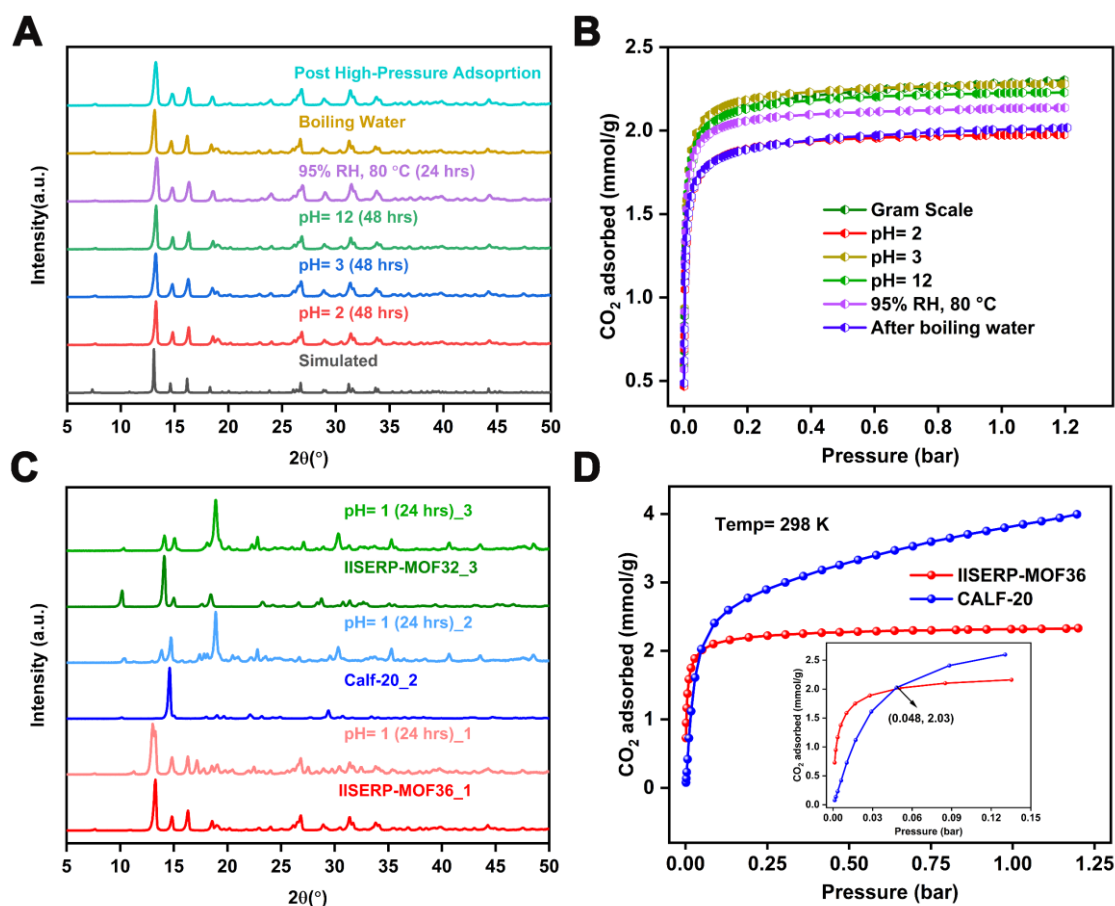


Figure 5.4: PXRD patterns of **1** kept under (A) Different pH conditions (2 to 12), steam (95 % RH, 353 K), boiling water and post high-pressure adsorption. (B) Comparative CO₂ adsorption isotherms of the MOF subjected to different harsh conditions at 298 K. (C) The comparative PXRD patterns obtained for **1**, CALF-20 and IISERP-MOF32 after soaking in solution of pH = 1. (D) Comparative 298 K isotherms of CALF-20 vs. **1** displaying the superiority of the latter in the low-pressure region.

From the obtained PXRD patterns it is evident that **1** shows a better retention in crystallinity as compared to CALF-20 and IISERP-MOF32 (Fig. 5.4C). We compared

the CO₂ adsorption isotherms of CALF-20 and **1**. The former demonstrates higher uptake in the low-pressure region compared to CALF-20 (Fig. 5.4D and 5A.18A-B). These experimental results obtained for the scalable, cost-effective, room temperature synthesized robust **1** verify its suitability for CO₂ capture from flue gas.

5.3.3 Structural aspects from SCXRD IISERP-MOF36 (**1**) vs. IISERP-MOF32 and IISERP-MOF35

Very recently, we demonstrated in another closely related Zinc-aminotriazolate-oxalate framework that the presence of longer Zn-Oxalate bonds can generate coordination flexibility aided rotation of oxalate pillars leading to interesting CO₂ assisted gate opening phenomenon. The SCXRD structure of **1** showed the presence of long symmetrical diagonal Zn-O bonds (2.02 and 2.25 Å) in it, similar to IISERP-MOF32⁵³ and IISERP-MOF35⁸⁶ suggesting the probability of gating phenomenon as observed in the case of IISERP-MOF32.⁵³ However, no such gating phenomena was observed for **IISERP-MOF36** up to 1 bar. We probed for this even at higher pressures. The high-pressure CO₂ and N₂ gas adsorption isotherms of **1** up to 20 bars did not reflect any gating phenomenon (Fig. S19-20). To gain understanding about the absence of gating phenomena in the present MOF **1**, its crystal structure was reconsidered. This confirmed that the same Zn atom is attached to two oxalic acid units, and this restricts the gating phenomenon in **1** even though it possesses long symmetrical diagonally positioned Zn-O bonds, whereas in IISERP-MOF32 Zn atom was attached to only one oxalic acid giving it enough space to rotate like spindle. These subtle structural insights could be valuable to the design of robust as well as flexible ultra-microporous MOFs.

5.3.4 Computational Studies

To understand the strong binding of CO₂ at low partial pressures in **1**, we used both GCMC and DFT. We simulated specifically the low-pressure region of the CO₂ isotherm using the GCMC methods embedded in Materials Studio. The 298 K simulated isotherms displayed significant CO₂ uptakes for both MOFs and the adsorption energies agreed with the experiments (Fig 5.5A). Importantly, a comparison of the simulated isotherms of the **1** vs. CALF-20 performed using same

methods, showed that the former adsorbs CO₂ 2.5 times better and the CO₂ adsorption energy is notably higher and, for the **1** it shows more spread indicating closely related multiple sites. Examining the CO₂-loaded structures of both MOFs reveal that the CO₂'s preferred positions were slight-off from the pore centre, no specific, binding sites on the framework were observed. The average heat of adsorption of the **1** is higher by 5.99 kJ/mol than the CALF-20 (39.676 vs. 33.664 kJ/mol). The CO₂ binding energy calculated using the CASTEP ab-initio DFT method revealed the binding energy of the **1** being very comparable to the binding energy of CALF-20 (68 kJ/mol) (Fig 5.5B-C). When the most probable positions enunciated by the CO₂ densities within the channels are considered, it can be seen that in both MOFs, the CO₂ remain closer to the oxalate units, but in **1** their arrangement favors inter-CO₂ interactions (CO₂⋯CO₂ = 3.30-3.45 Å) not seen in CALF-20 (CO₂⋯CO₂ ~6.78 Å) (Fig 5.5D-E).

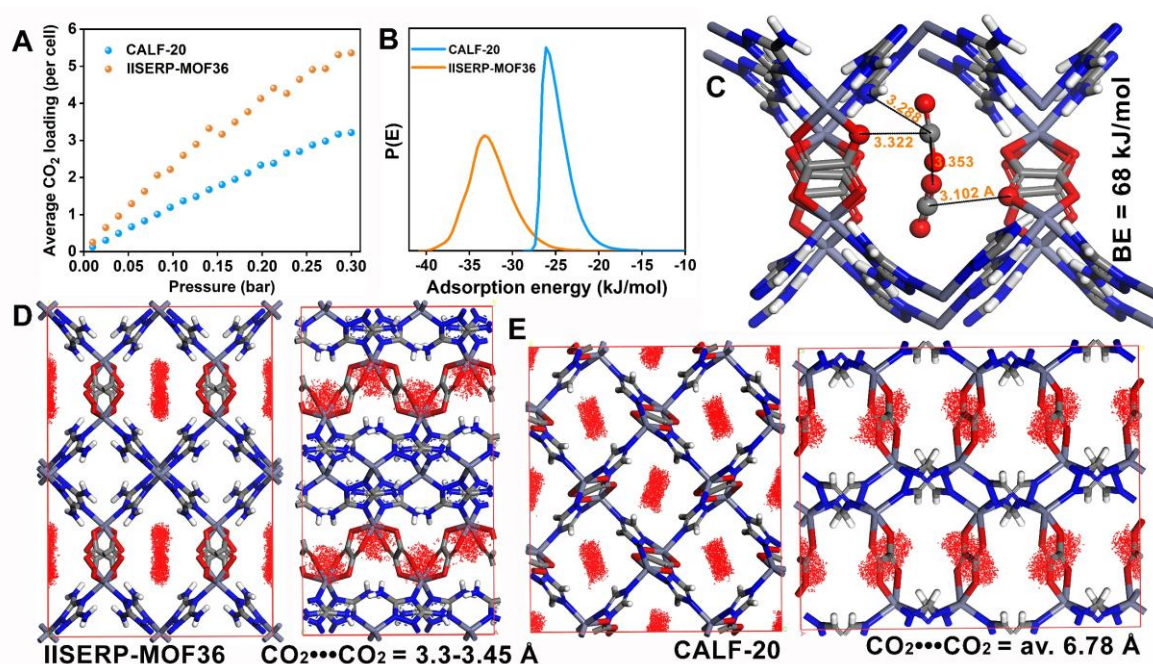


Figure 5.5: Simulation results: (A) Simulated CO₂ adsorption isotherms from GCMC methods displaying the low-pressure region. Comparison reveals the more abrupt uptake displayed by **IISERP-MOF36** over CALF-20. (B) The associated CO₂ adsorption energies agree well with the experimentally observed trend. (C) DFT-optimized structure showing CO₂⋯framework interactions. (D-E) Most probable CO₂ positions within these ultra-micropores shown as electron densities. In both cases, the

CO_2 molecules reside close to the pore centre. However, a comparative view along the orthogonal direction shows the superior CO_2 - CO_2 proximity for the ones assembled in PORE-1 of the **1** could be partly responsible for its exceptional low-pressure uptake.

This could explain the higher low-pressure CO_2 uptakes of the **1**. Also, in CALF-20 the structure is more ordered with all pores being the same, compared to **1**, wherein the smaller pores (PORE-2) are not accessible. This explains the cross-over point in the isotherms at a pressure close to 0.05 bar (Fig. 5A.18A-B), beyond which CALF-20 performs better and has a higher saturation uptake. This comparative analysis signifies the importance of CO_2 ··· CO_2 cooperative interaction within extremely confined ultra-micropores.

5.3.5 Breakthrough Studies

Intrigued by the superior CO_2 capacity of **1** over CALF-20, we decided to investigate if the former can retain its superior CO_2 capture capability under humid conditions. The adsorption performance of **1** in the presence of moisture was evaluated through dynamic column breakthrough analysis, as illustrated in the (Fig 5.6A and 5A.21-22). The breakthrough analysis under Dry/Dry and Wet/Wet conditions revealed a significant impact of moisture on CO_2 adsorption performance (Fig. 5.6B).

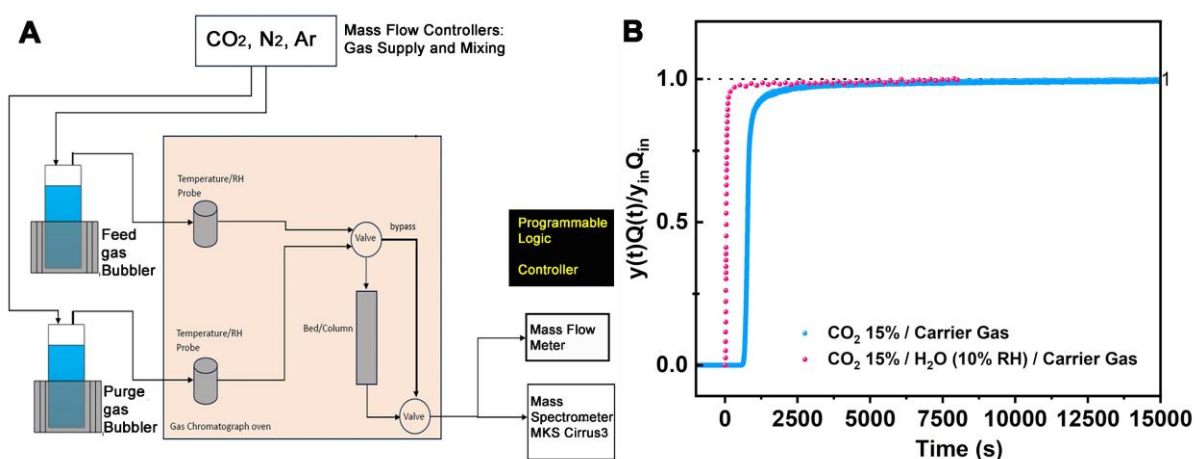


Figure 5.6: (A) General arrangement of components and instrumentation for the dynamic column breakthrough apparatus. (B) Comparison of unary (pure CO₂) vs. binary (CO₂/ water) breakthrough curves at 35°C measured using pellets of **1**.

In the Dry/Dry condition, where both the adsorbent pellets and the gas stream are free from moisture, **1** exhibited a 2.09 mmol/g capacity for CO₂, which is in good agreement with the isotherm value of 2.03 mmol/g at 35°C. However, when subjected to Wet/Wet conditions, where both the adsorbent and the gas stream are in equilibrium with 10 % RH (0.5 mol % H₂O), the CO₂ capacity dropped to 0.04 mmol/g, showing that the competitive CO₂ equilibrium loading was greatly affected by H₂O compared to unary equilibrium. **1** cannot perform like CALF-20 under humid conditions, making it unsuitable for Svante-type steam-based processes. However, it could be a good low-pressure CO₂ capture sorbent for pressure vacuum swing adsorption (PVSA)-type processes.

5.4 Conclusion

The zinc-triazolate-oxalate MOF, CALF-20, has the properties needed to selectively remove CO₂ using an energy-efficient steam-based process. However, there is a desire to enhance its capacity at low partial pressures for use in natural gas combined cycle (NGCC) or direct air capture (DAC). To achieve this, we have developed a zinc-diaminotriazolato-oxalate MOF with a different composition and structure than CALF-20. This new MOF, **1**, demonstrates a steeper uptake of CO₂ at low partial pressures, which is not easy to achieve. Computational modeling investigations reveal that in **1**, the CO₂ colonizes densely and orients to favor CO₂⋯CO₂ interactions, unlike in CALF-20. These findings direct new possibilities for creating superior CO₂ sorbents within this family of physisorbents. However, the hydrophobicity observed in CALF-20 is lost in **1**, so an innovative design with superior CO₂ binding sites needs to be explored.

5.5 References

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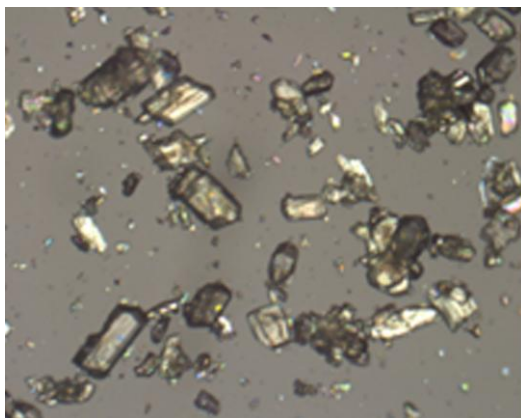


Figure 5A.1: Image of the **IISERP-MOF36** crystals captured using an optical microscope. The crystals habit a rectangular shape upon growing.

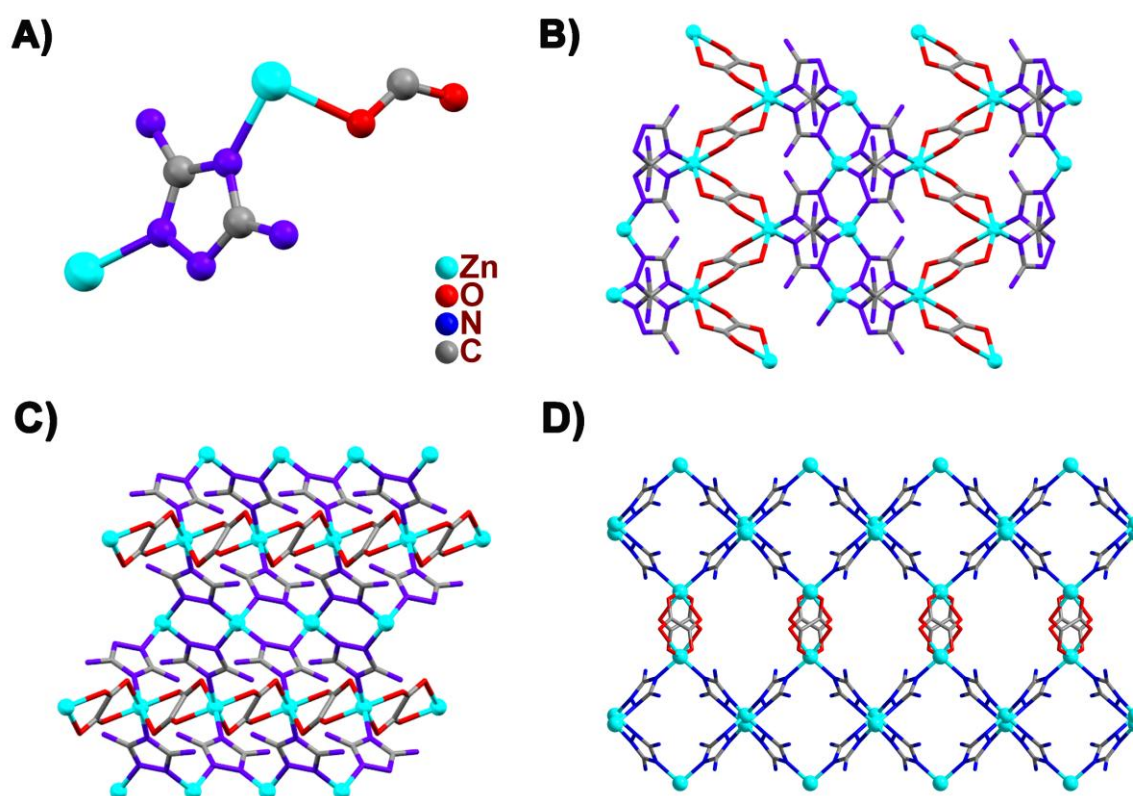


Figure 5A.2: (A) The Asymmetric unit for **IISERP-MOF36**. The three-dimensional view of the MOF (B) along the *a*-axis, (C) along the *b*-axis, and (D) along the *c*-axis.

Table 5A.1: Crystallographic Information for **IISERP-MOF36**.

a/Å	8.464(2)
b/Å	12.025(3)
c/Å	7.252(2)
$\alpha/^\circ$	90
$\beta/^\circ$	104.717 (10)
$\gamma/^\circ$	90
V/Å ³	713.9(3)
Crystal System	Monoclinic
Space Group	<i>P2/c</i>
Color	Colourless
Expt. Crystal description	Rectangle shape
Z	4
T/ K	150 K
Diffraction Source	MoK α
Diffraction radiation wavelength/ Å	0.71073
Diffraction reflection theta min	2.488
Diffraction reflection theta max	28.415

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Reflection number total	1787
Reflection number gt	1474
R1, wR2 [$I > 2\sigma(I)$]	0.049, 0.123
R1, wR2 (all data)	0.062, 0.131
GoF	1.055

Powder X-ray diffraction:

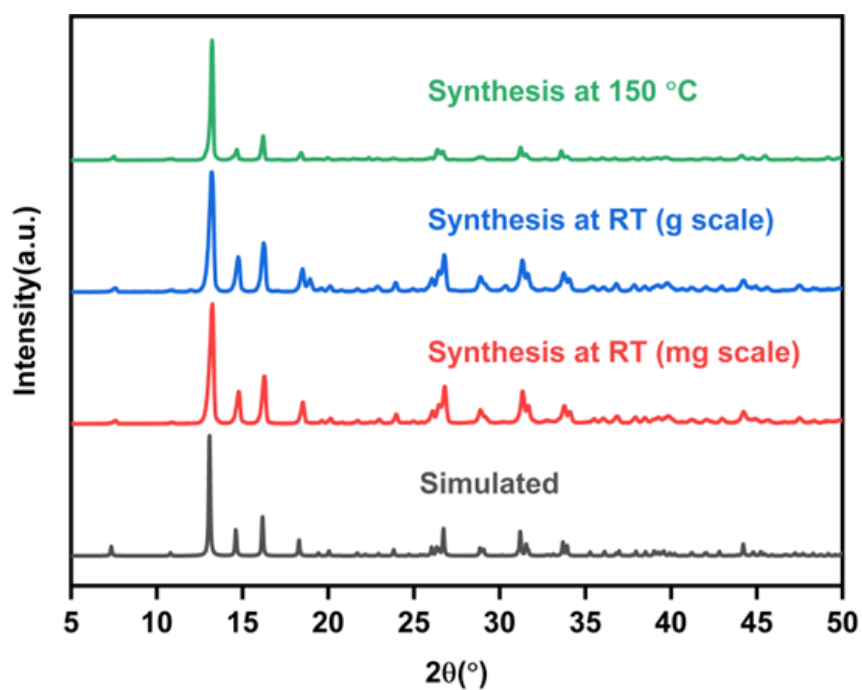


Figure 5A.3: The PXRD patterns of **IISERP-MOF36** prepared at different scales.

TGA analysis:

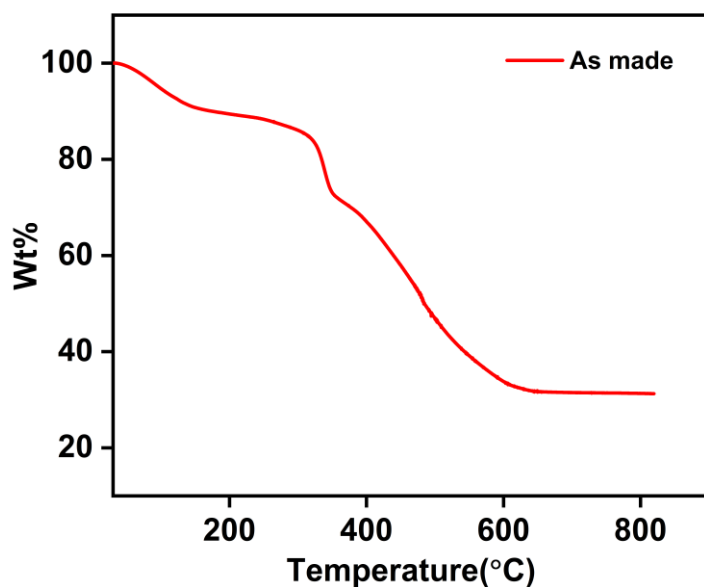


Figure 5A.4: The TGA curve of the **IISERP-MOF36** shows its thermal stability up to 330 °C.

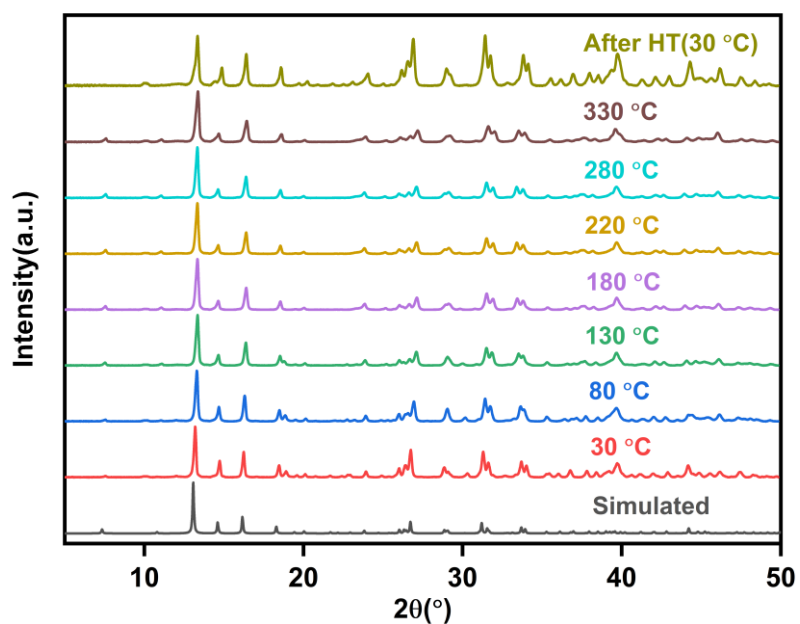


Figure 5A.5: VT-PXRD patterns of the **IISERP-MOF36** showing the retention of crystallinity when heated from 30 to 330 °C.

IR analysis:

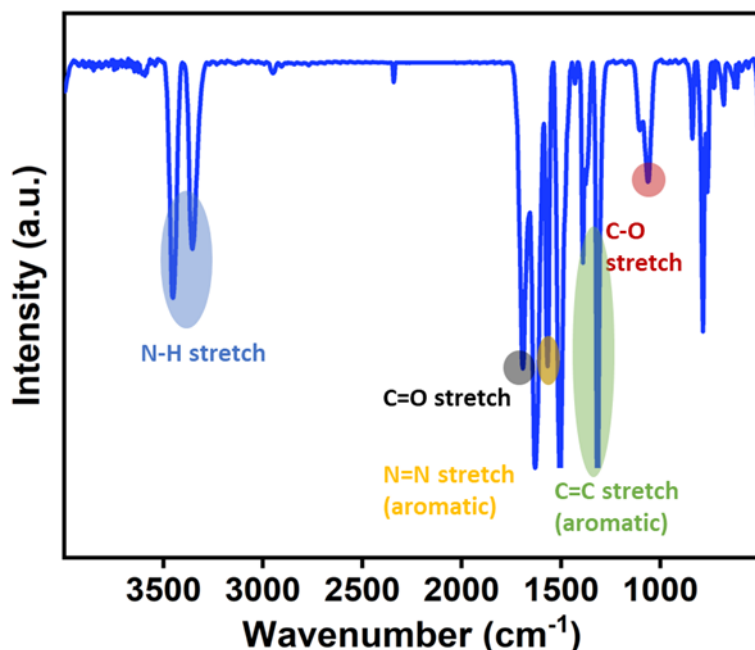


Figure 5A.6: Infra-red spectra of **IISERP-MOF36** showing the various stretching and bending modes present in it. Selected peaks: IR (cm^{-1}): $\nu(\text{N-H})$: 3356 and 3452; $\nu(\text{C=O})$: 1693s; $\nu(\text{N=N})$: 1568s; $\nu(\text{C=C})$: 1390 and 1320; $\nu(\text{C-O})$: 1109.

Adsorption Analysis

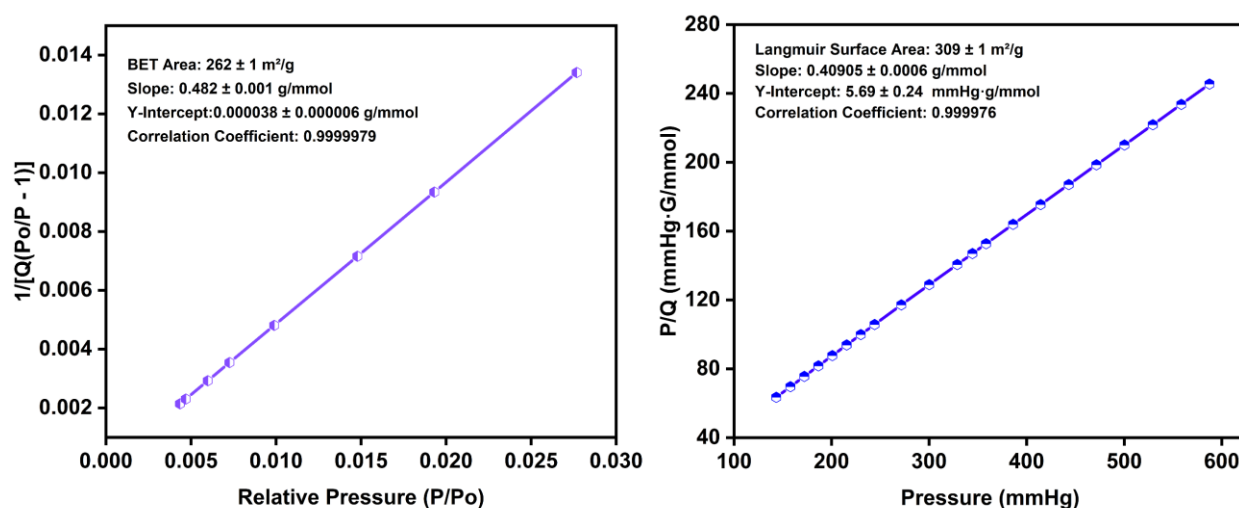


Figure 5A.7: BET and Langmuir fits for the activated **IISERP-MOF36** calculated from the 195 K CO_2 isotherm data.

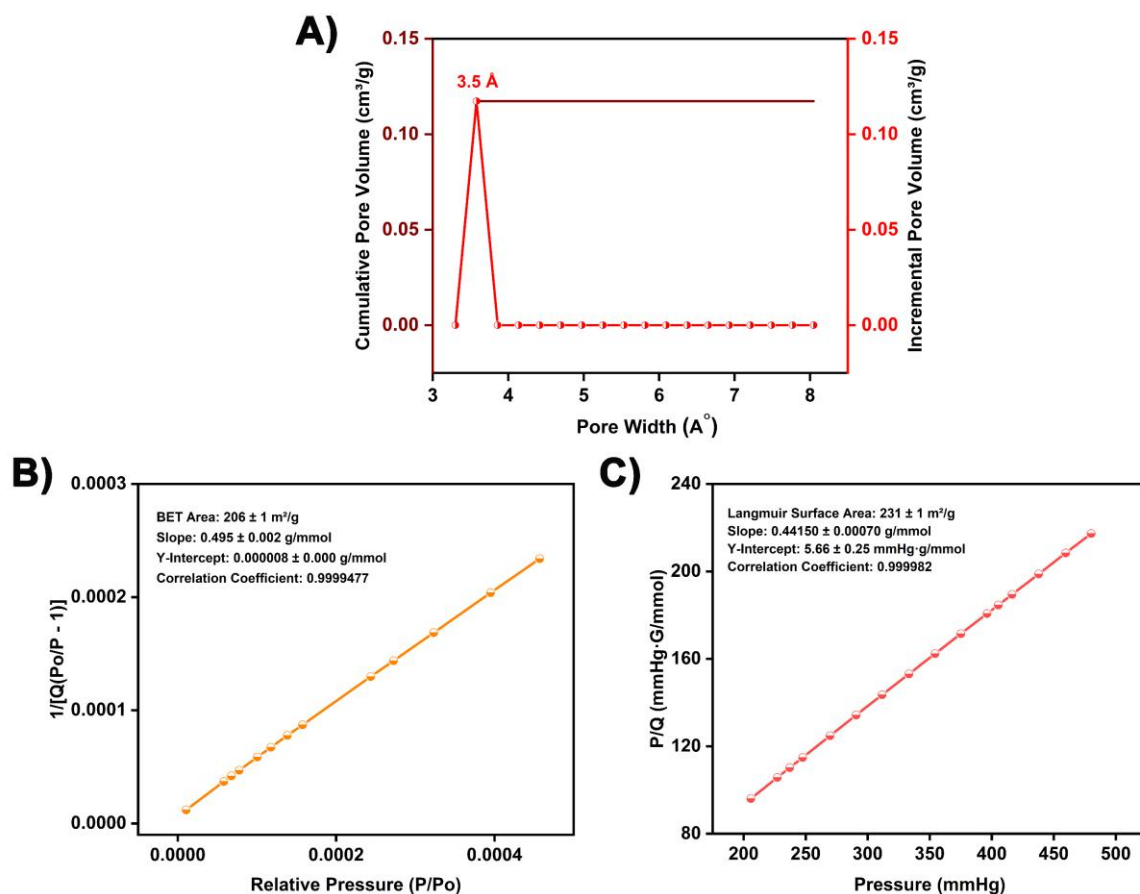


Figure 5A.8: (A) The pore size distribution for the **IISERP-MOF36** obtained by the NLDFT fit (Slit pore model) to the 273 K CO_2 adsorption branch. (B) BET and Langmuir fit calculated using the 273 K CO_2 adsorption isotherm.

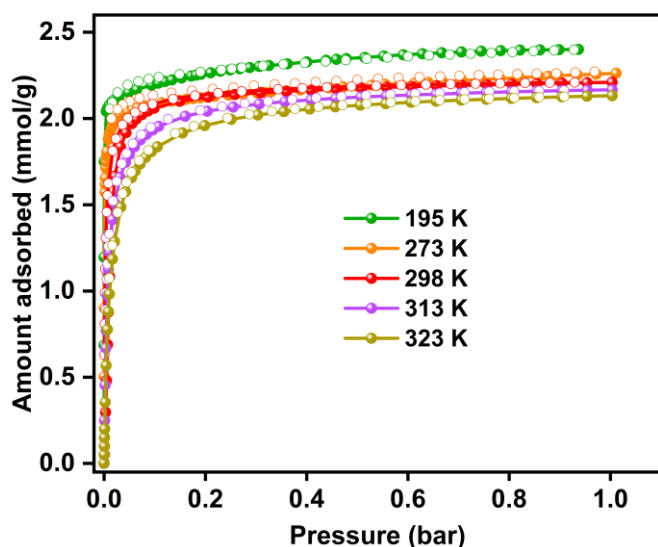


Figure 5A.9: CO_2 adsorption/desorption isotherms of the MOF at different temperatures.

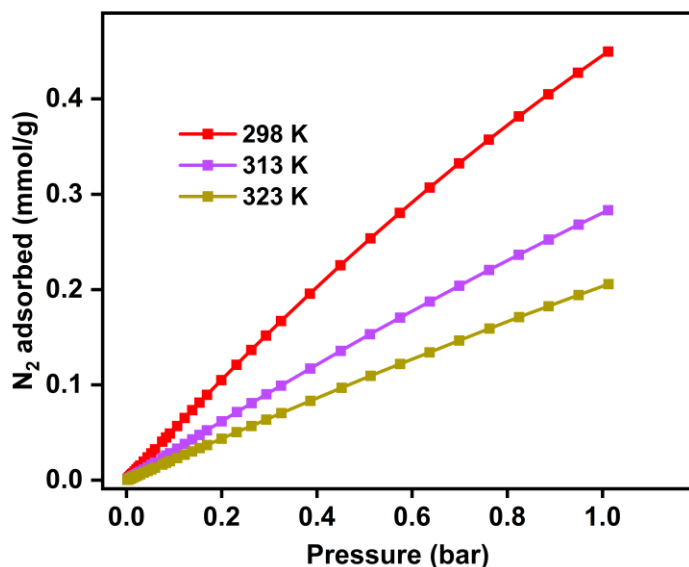


Figure 5A.10: N₂ adsorption isotherm of the MOF at different temperatures.

IAST fitting parameters for IISERP-MOF36 (CO₂/N₂):

At 323 K

Gas A = CO₂

Gas B = N₂

Table 5A.2: Fitted IAST parameters for CO₂/N₂ (15CO₂:85N₂ composition) selectivity at 323 K for **IISERP-MOF36**.

Gas A Constants		Gas B Constants	
q _{s1} (mmol g ⁻¹) =	2.209151862	q _{s1} (mmol g ⁻¹) =	2.31883996
q _{s2} (mmol g ⁻¹) =	0	q _{s2} (mmol g ⁻¹) =	0
K ₁ (mbar ⁻¹) =	0.105294763	K ₁ (mbar ⁻¹) =	5.5984E-05
K ₂ (mbar ⁻¹) =	0	K ₂ (mbar ⁻¹) =	0
n ₁ =	0.861395423	n ₁ =	1.08288777
n ₂ =	0	n ₂ =	0
H ₁ (mmol mbar ⁻¹ g ⁻¹) =	0.061090933	H ₁ (mmol mbar ⁻¹ g ⁻¹) =	3.8372E-05
H ₂ (mmol mbar ⁻¹ g ⁻¹) =	0	H ₂ (mmol mbar ⁻¹ g ⁻¹) =	0

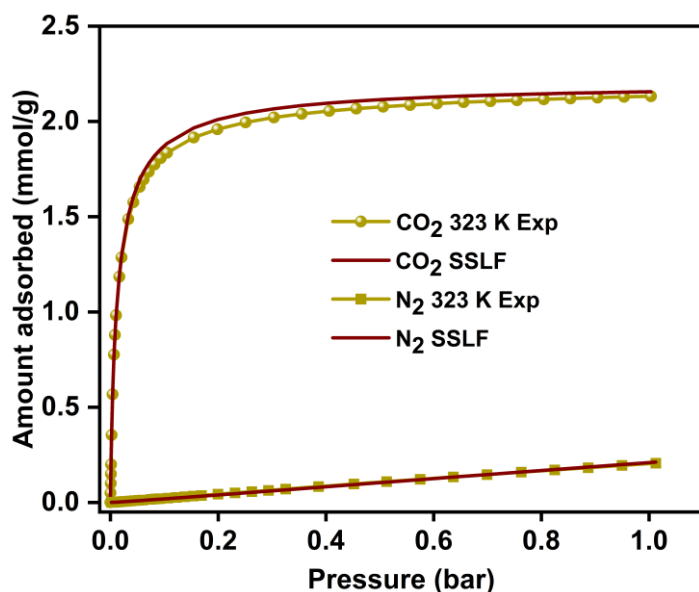


Figure 5A.11: IAST fitting of CO₂ and N₂ isotherms of **IISERP-MOF36** collected at 323 K.

IAST fitting parameters for IISERP-MOF36 (CO₂/N₂):

At 313 K

Gas A = CO₂

Gas B = N₂

Table 5A.3: Fitted IAST parameters for CO₂/N₂ (15CO₂:85N₂ composition) selectivity at 313 K for **IISERP-MOF36**.

Gas A Constants		Gas B Constants	
q _{s1} (mmol g ⁻¹) =	2.20995154	q _{s1} (mmol g ⁻¹) =	2.31854964
q _{s2} (mmol g ⁻¹) =	0	q _{s2} (mmol g ⁻¹) =	0
K ₁ (mbar ⁻¹) =	0.140997508	K ₁ (mbar ⁻¹) =	8.2063E-05
K ₂ (mbar ⁻¹) =	0	K ₂ (mbar ⁻¹) =	0
n ₁ =	0.916172947	n ₁ =	1.07931691
n ₂ =	0	n ₂ =	0
H ₁ (mmol mbar ⁻¹ g ⁻¹) =	0.061090933	H ₁ (mmol mbar ⁻¹ g ⁻¹) =	3.8372E-05

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H ₂ (mmol mbar ⁻¹ g ⁻¹) =	0	H ₂ (mmol mbar ⁻¹ g ⁻¹) =	0
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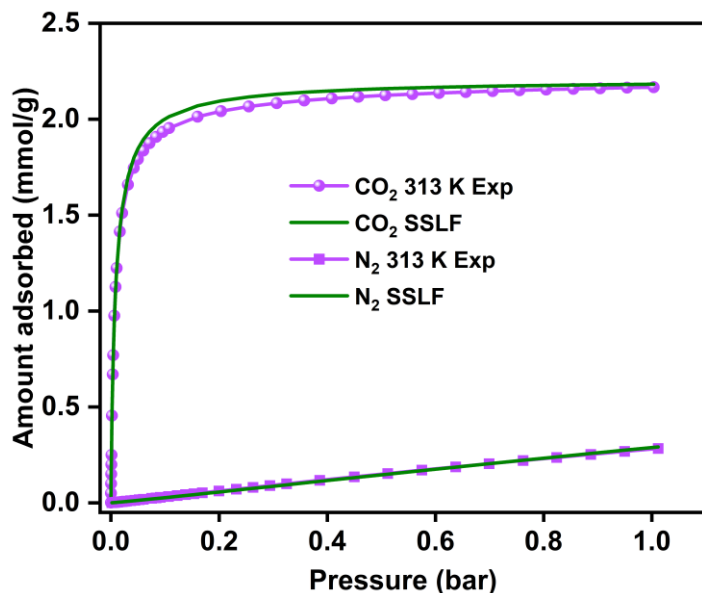


Figure 5A.12: IAST fitting of CO₂ and N₂ isotherms of **IISERP-MOF36** collected at 313 K.

IAST fitting parameters for IISERP-MOF36 (CO₂/N₂):

At 298 K

Gas A = CO₂

Gas B = N₂

Table 5A.4: Fitted IAST parameters for CO₂/N₂ (15CO₂:85N₂ composition) selectivity at 298 K for **IISERP-MOF36**.

Gas A Constants		Gas B Constants	
q _{s1} (mmol g ⁻¹) =	2.219131351	q _{s1} (mmol g ⁻¹) =	1.91146642
q _{s2} (mmol g ⁻¹) =	0	q _{s2} (mmol g ⁻¹) =	0
K ₁ (mbar ⁻¹) =	0.030581626	K ₁ (mbar ⁻¹) =	0.00025628
K ₂ (mbar ⁻¹) =	0	K ₂ (mbar ⁻¹) =	0
n ₁ =	1.470056278	n ₁ =	1.02806498
n ₂ =	0	n ₂ =	0

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H_1 (mmol mbar ⁻¹ g ⁻¹) =	0.067864644	H_1 (mmol mbar ⁻¹ g ⁻¹) =	0.00082974
H_2 (mmol mbar ⁻¹ g ⁻¹) =	0	H_2 (mmol mbar ⁻¹ g ⁻¹) =	0

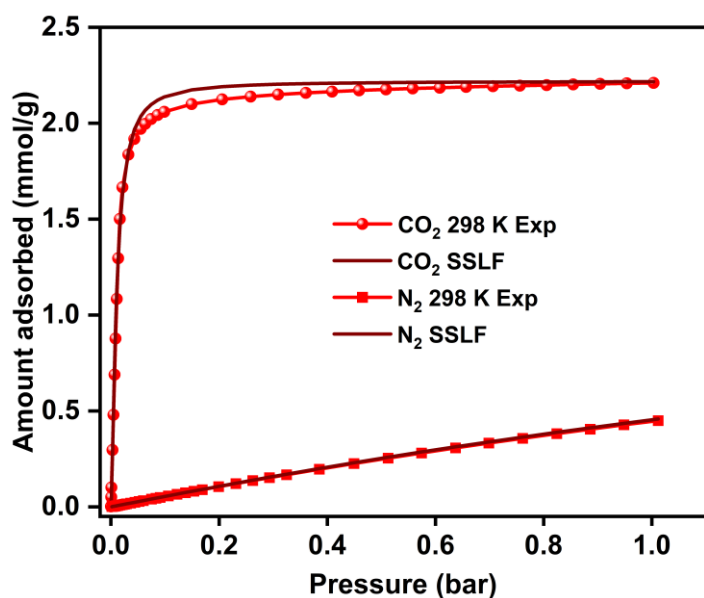


Figure 5A.13: IAST fitting of CO₂ and N₂ isotherms of **IISERP-MOF36** collected at 298 K.

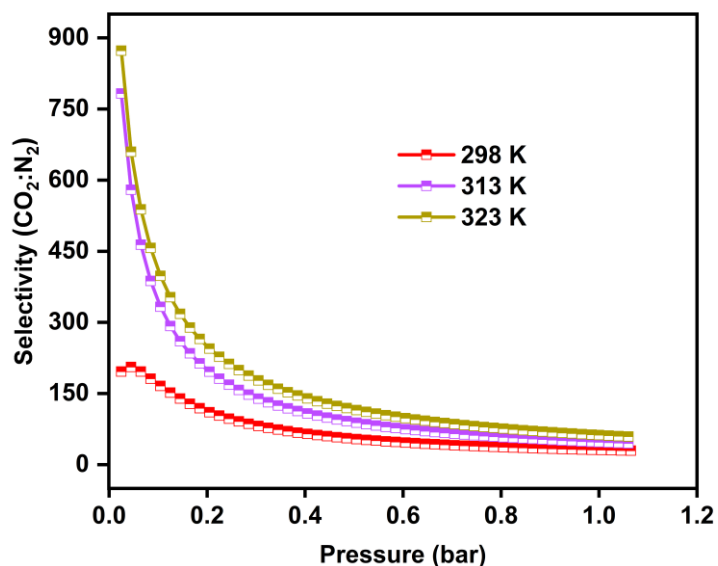


Figure 5A.14: CO₂/N₂ selectivity of the MOF calculated at different temperature using the IAST model employing a nominal composition of 15 CO₂: 85 N₂.

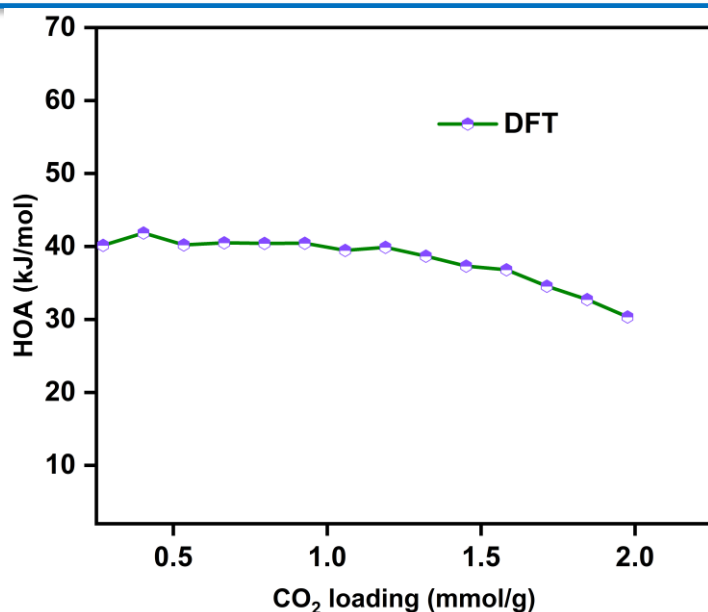


Figure 5A.15: The HOA plots of **IISERP-MOF36** from the DFT fit obtained using the CO₂ isotherms at 273, 298, and 313 K.

Table 5A.5:

MOF	T = 298 K (0.15 bar) CO ₂ uptake (mmol/g)	T = 323 K (0.15 bar) CO ₂ uptake (mmol/g)	Decline in CO ₂ capacity (298 – 323 K)	Refs.
CALF-20	2.6	1.9	27 %	<i>Nat. Commun.</i> , 2024 , 15, 3898.
IISERP-MOF36	2.1	1.9	10 %	This work

A comparison of the CO₂ capacities of CALF20 vs. **IISERP-MOF36**: CALF-20, the first commercialized MOF sorbent utilized for capturing a ton of CO₂ per day from flue gas exhibits a 27 % decrease in the CO₂ capacity on increasing the temperature from 298 to 323 K. However, under identical pressure and temperatures, **IISERP-MOF36** shows only 10 % decrease in CO₂ capacity, highlighting its promising utility for CO₂ capture from the hot flue gas (Table S5).

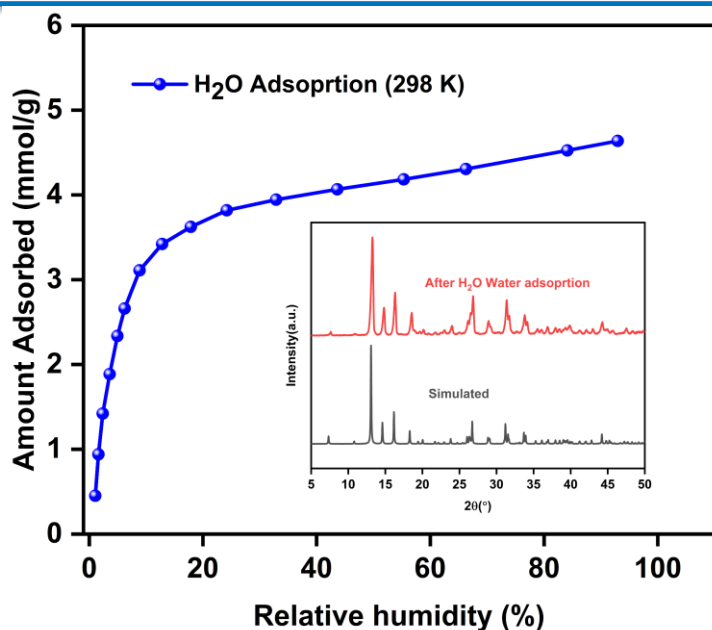


Figure 5A.16: The water adsorption isotherm of **IISERP-MOF36** at 298 K. Inset: The PXRD pattern after water adsorption. A Type 1 isotherm reflects hydrophilicity, unlike CALF-20.

Stability Studies

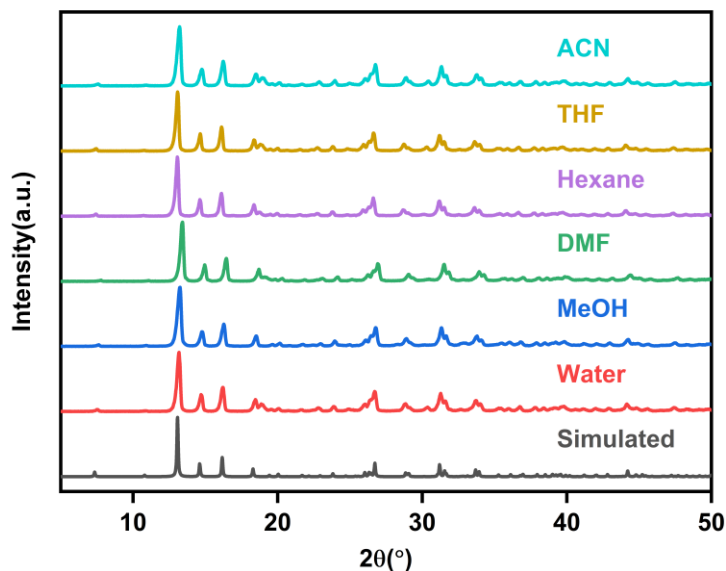


Figure 5A.17: After soaking the **IISERP-MOF36** for at least 10 days, the PXRD profiles demonstrate its stability in various solvents.

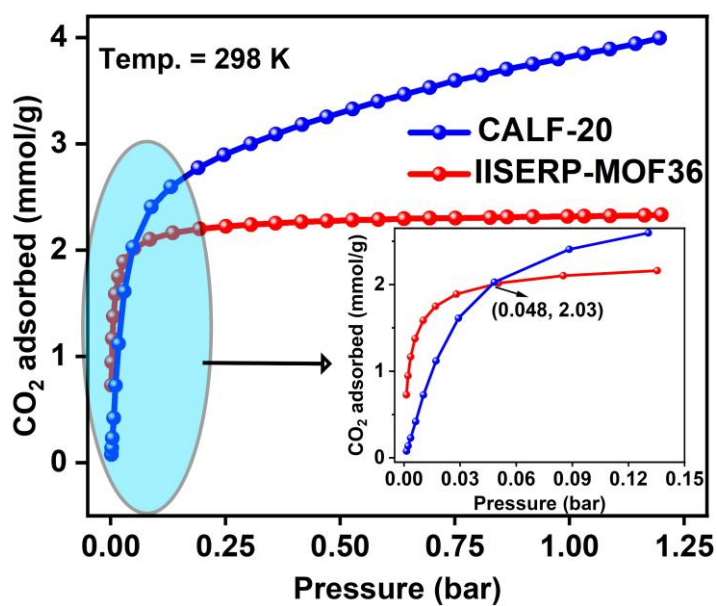


Figure 5A.18A: A comparative plot of 298K CO₂ isotherms of **IISERP-MOF36** and CALF-20.

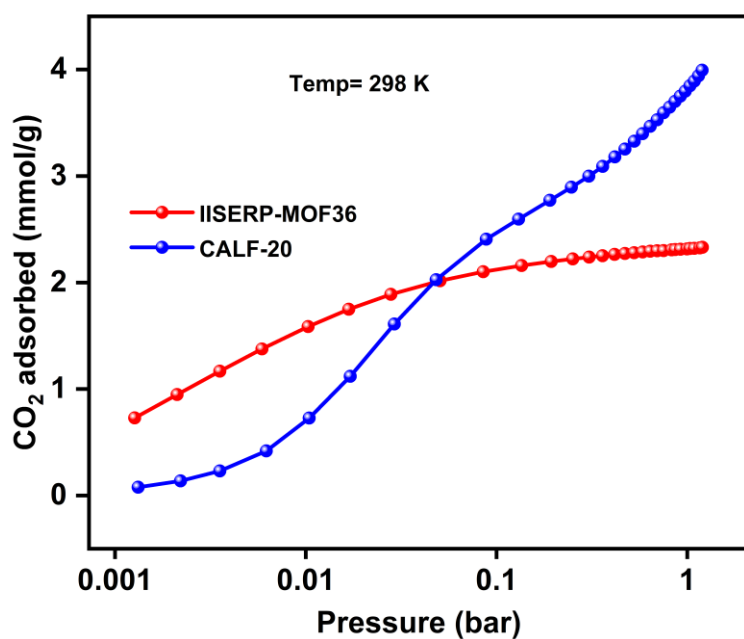


Figure 5A.18B: The single-component adsorption isotherms for CALF-20 and **IISERP-MOF36** at 298 K were plotted using logarithmic coordinates.

High-Pressure Gas adsorption studies

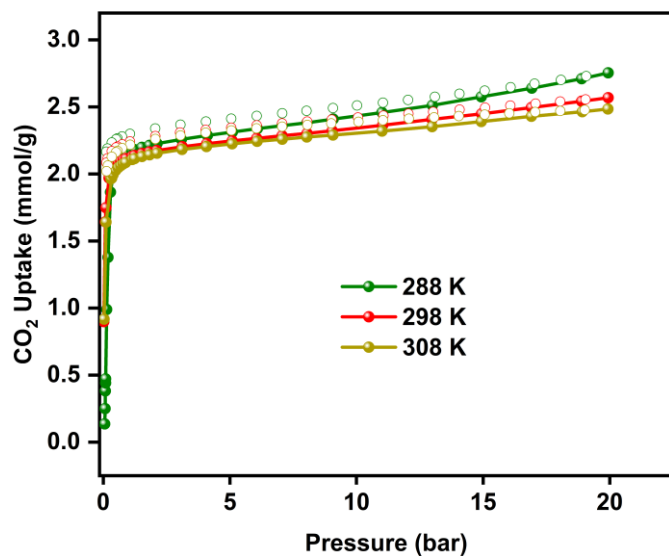


Figure 5A.19: High-pressure CO₂ isotherm of **IISERP-MOF36** measured at different temperatures.

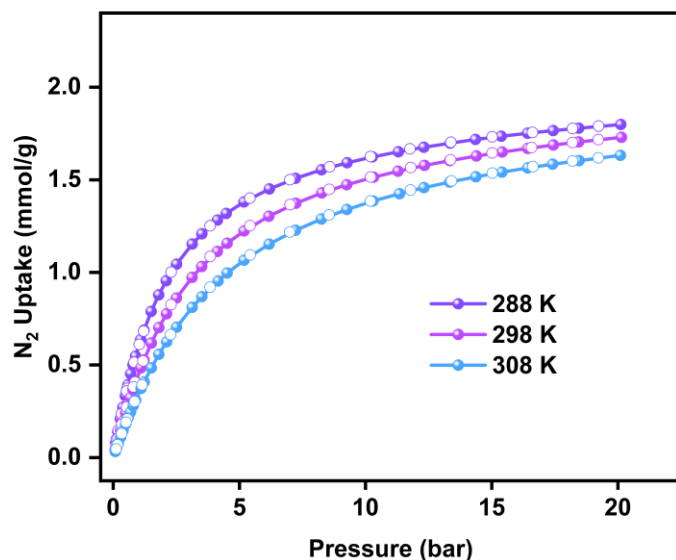


Figure 5A.20: High-pressure N₂ isotherm of **IISERP-MOF36** measured at different temperatures.

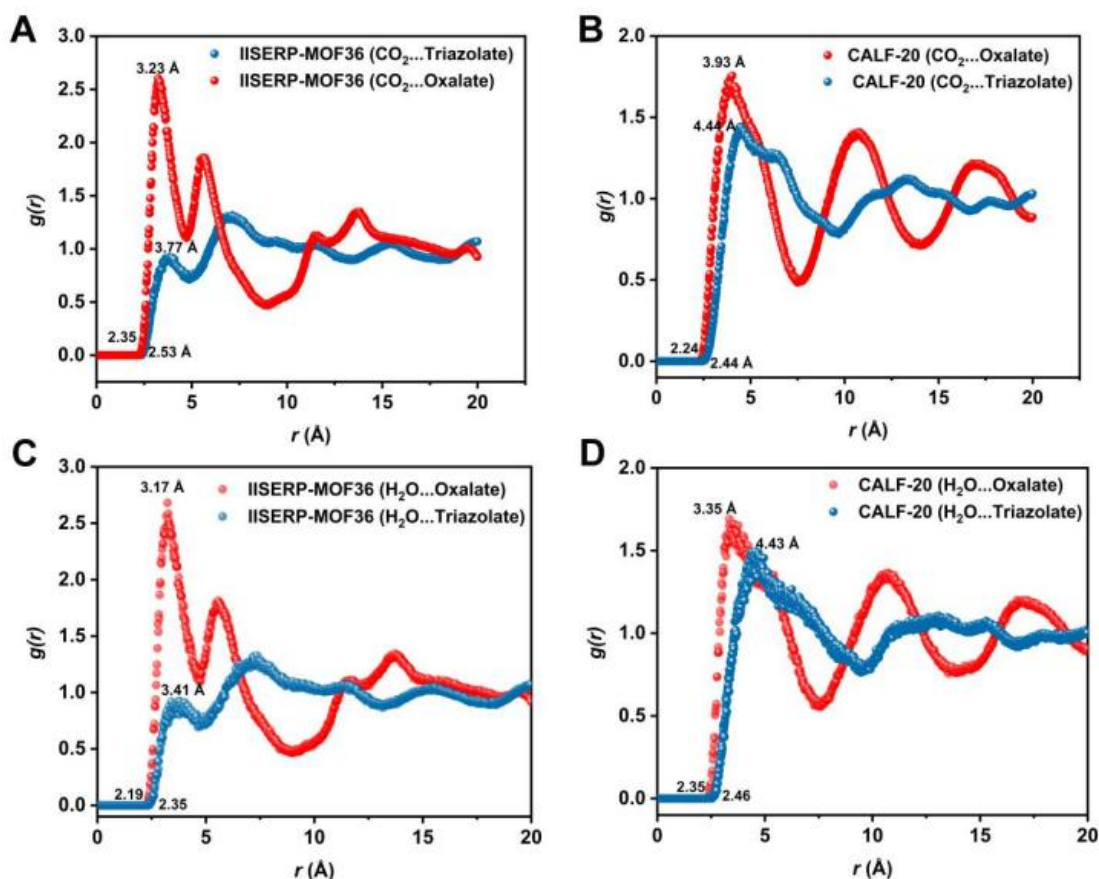


Figure 5A.21: Figure displays the RDF plots from MD simulations. Note that both CO₂ and H₂O exhibit shorter interaction distances with the framework of IISERP-MOF36 compared to CALF-20.

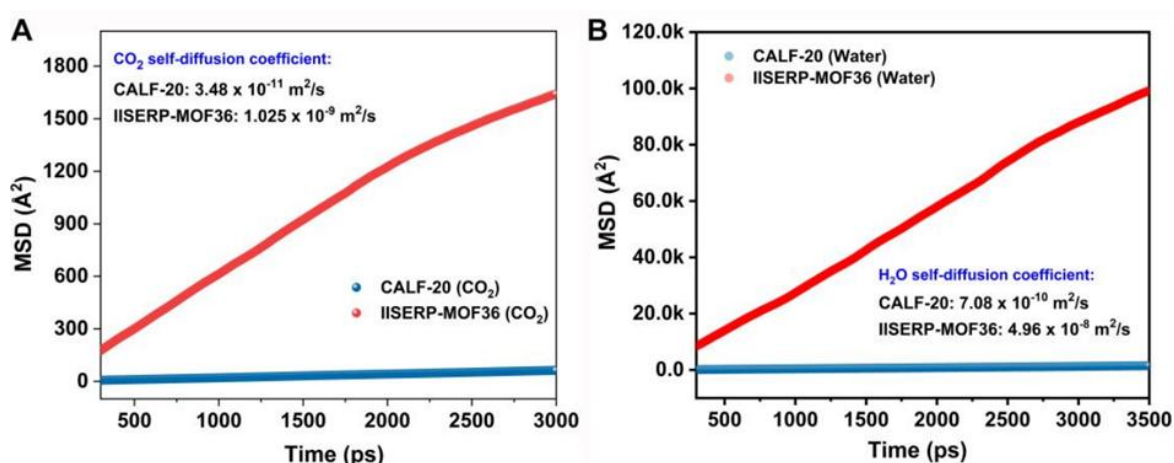


Figure 5A.22: MSD plots from MD simulations (298K) suggest faster diffusion of CO₂ and H₂O in IISERP-MOF36 compared to CALF-20. These are calculated self-diffusion coefficients from idealized models and can be exaggerated, however, given that in

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IISERP-MOF36, both guests show orders of magnitude higher diffusion compared to CALF-20 suggests that they are more favored by the pores of **IISERP-MOF36**, which supports the relatively rapid uptake of CO₂ and water in this MOF.

Breakthrough dynamic studies

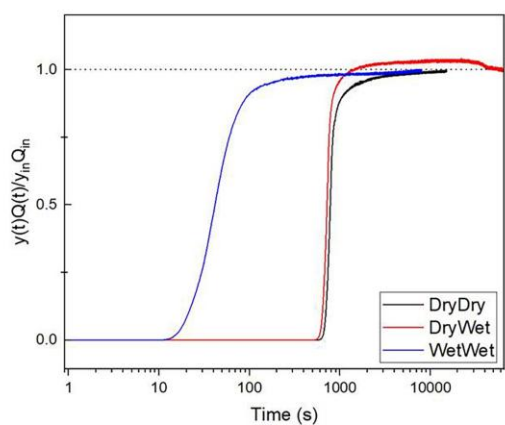
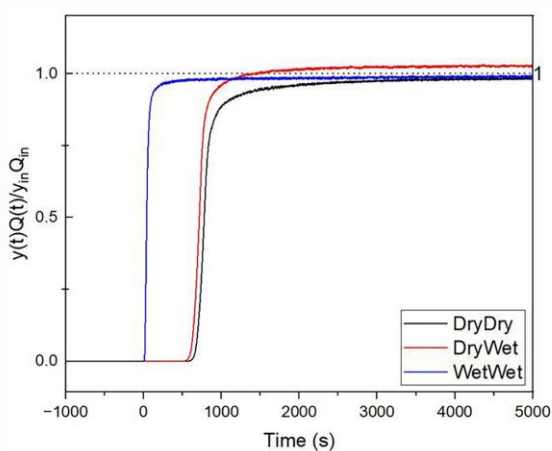
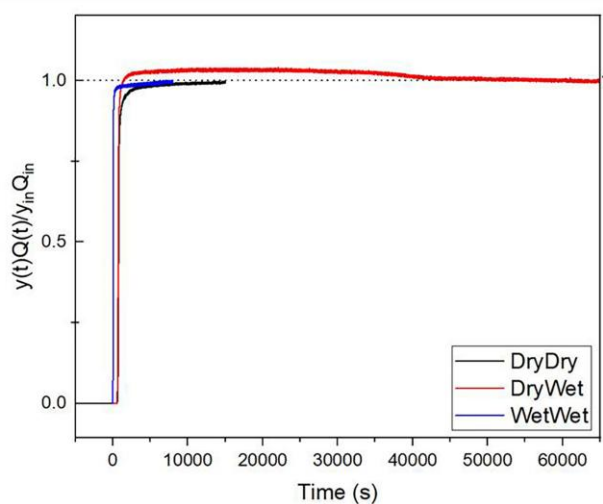
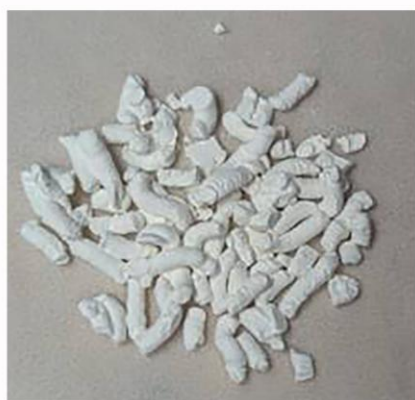


Figure 5A.23: The extrudates of **IISERP-MOF36**. Breakthrough curves under different experimental configurations.

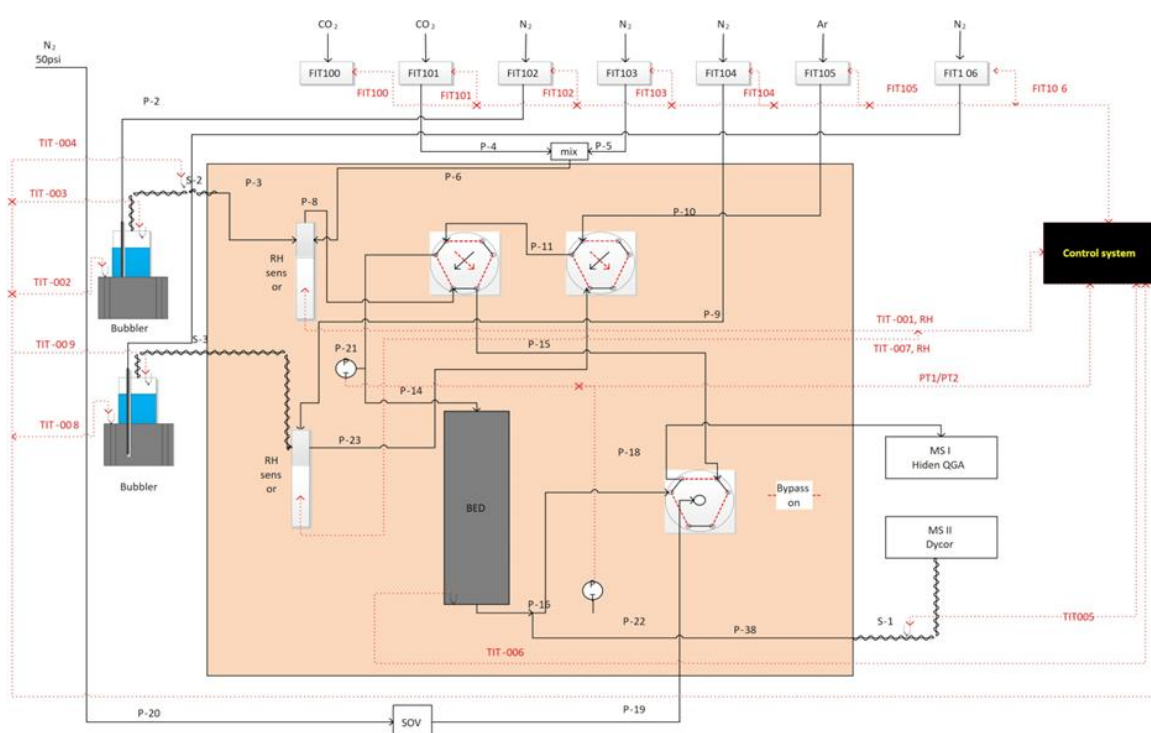


Figure 5A.24: General arrangement of components and instrumentation for the dynamic column breakthrough apparatus.
