Computationally-Aided Design of Amine-Grafted MOFs for Direct Air Capture

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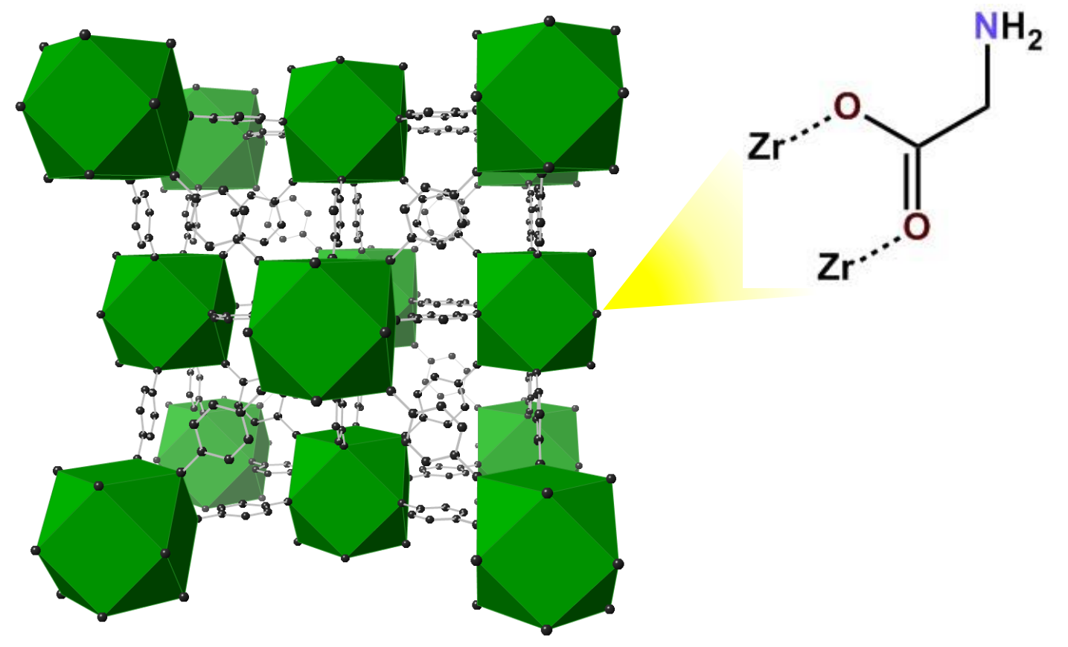
Introduction and Significance

Realization of a low-carbon future, while remaining reliant on fossil fuel-based energy generation, requires the development and optimization of materials that provide low cost and energy-efficient means of separating carbon CO_2 from post-combustion flue gas streams and/or from the atmosphere itself. Many composite materials for carbon capture applications make use of highly CO_2-philic porous particles as additives to a polymer matrix (contactor) to enhance adsorption. These additives consist of high-surface area materials such as porous silica, porous carbon, or metal-organic frameworks (MOFs), and are often chemically modified to enhance their CO_2 binding affinity. To that end, the incorporation of amine groups is one of the most consistent modifications used to increase the CO_2 uptake and selectivity of porous substrates. Therefore, an urgent task for researchers is the development of efficient means by which to incorporate a high density of amine groups, which bind strongly to the scaffolding of the porous substrate in order to maximize CO_2 uptake capacity and to prevent leaching.

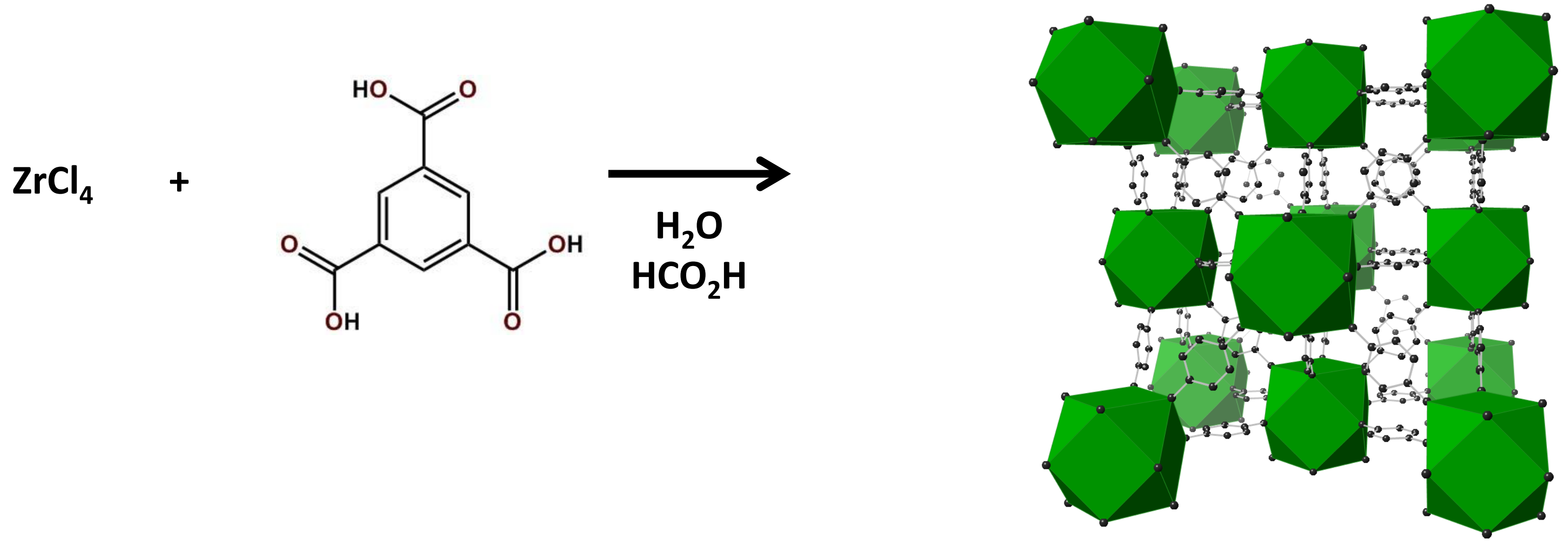


1. Ideal MOF Platform: Robust Structure with High Density of Ligand Exchange Sites

Among the available porous substrates, many MOFs provide a particularly high density of well-defined functional groups and/or coordination sites, which can be targeted for the grafting of molecular amines. Herein, simple ligand exchange reactions are used to incorporate strongly bound amine molecules to a MOF in a single step. MOF-808 was chosen due to it being a relatively inexpensive, highly-stable structure that contains ligand-accessible Zr_6-oxo clusters.

Low-Cost Efficient Synthesis

- Hydrothermal reaction
- Low-cost organic linker
- High yield per volume of solvent



$[Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4](C_9H_3O_6)_2(CHO_2)_6$

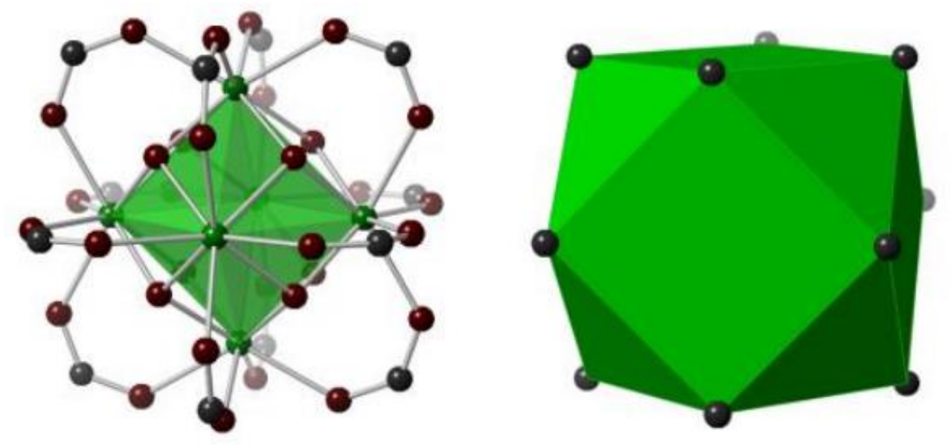
MOF-808
- Robust structure
- Easy to functionalize
- Commercially available components

Robust Structure

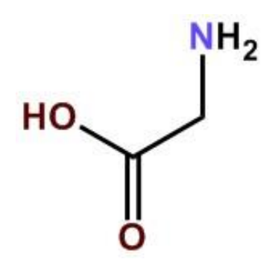
- Orthogonal modification technique
- Ability to attach a variety of groups

Ease of Functionalization

- 12 carboxylate binding sites, but only 6-connected nodes
- Ligand exchange at non-linker sites
- Ligands (carboxylate) strongly bound



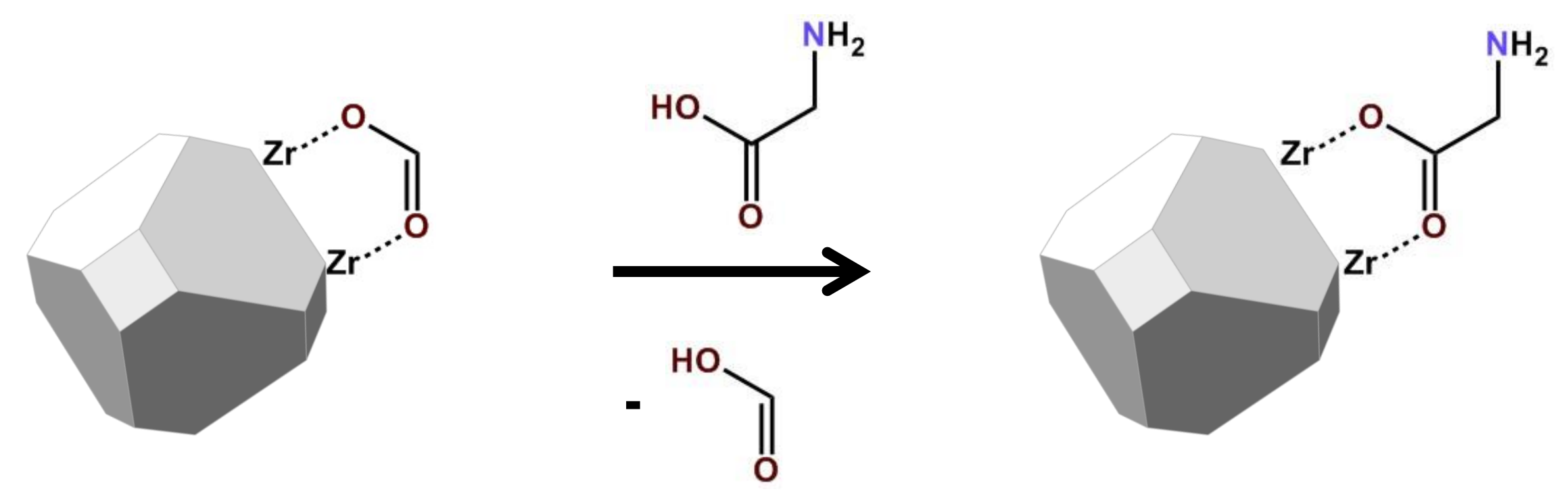
$Zr_6(\mu_3\text{-}OH)_4(\mu_3\text{-}O)_4(CO_2)_{12}$

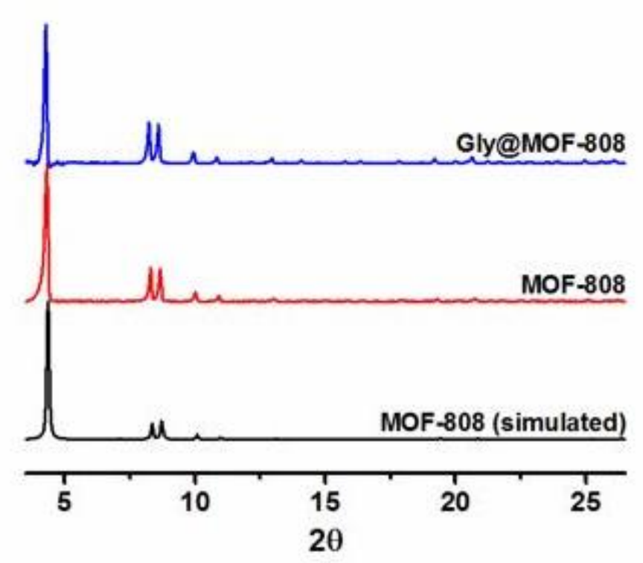


Glycine
- Low-cost amine source
- Has both carboxylate and amine groups
- Small enough to diffuse through MOF pores

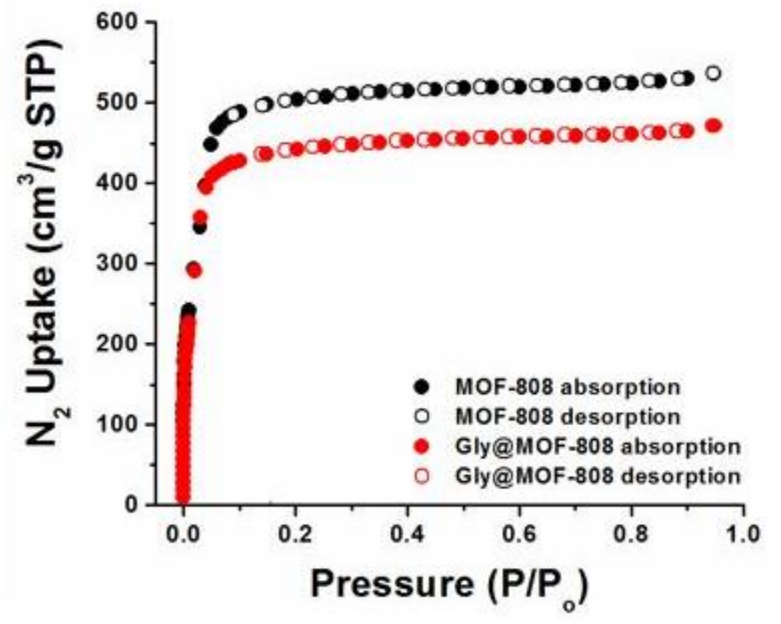
2. Developing MOF Platform: Post Synthetic Modification and Characterization

Before surface functionalization, a baseline of unfunctionalized **UiO-66** crystals of variable sizes must be established so that particle size and surface functionality can be adjusted orthogonally. Particles of **MOF-808** were prepared and characterized with N_2 and CO_2 gas adsorption studies; TEM imaging (particle size); ^{1}H NMR (glycine quantification and composition); and XRD (crystallinity and phase purity).

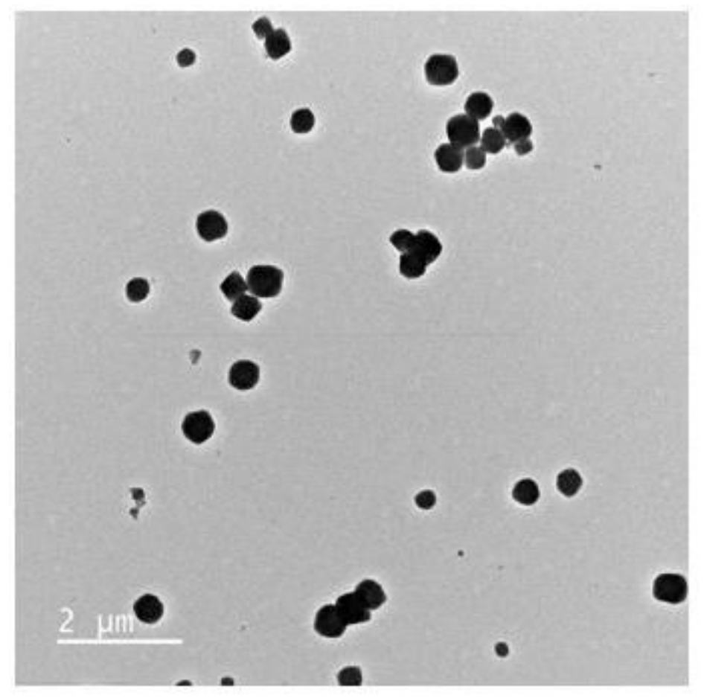




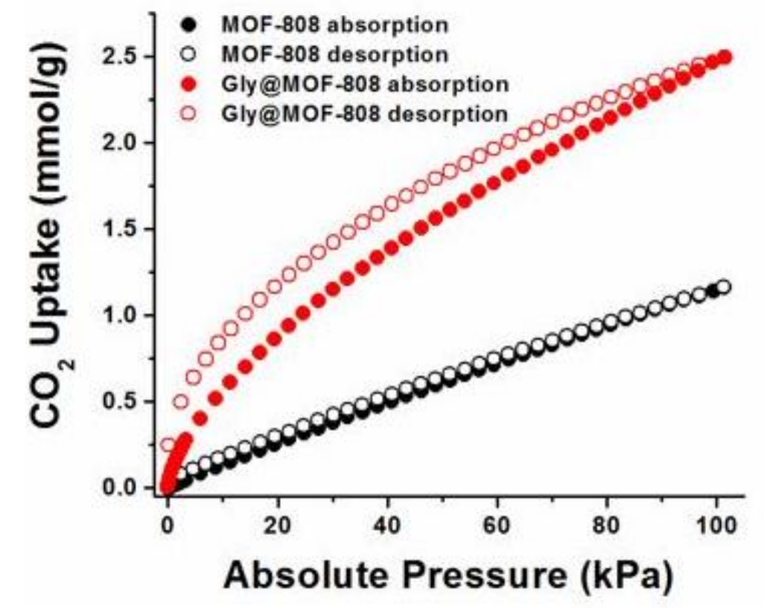
PXRD patterns collected for **MOF-808** samples showing intact crystallinity before and after functionalization.



Selected N_2 isotherms collected at 77 K for **MOF-808** before and after functionalization. BET surface areas calculated to be 1922 and 1675 m^2/g, respectively.



Sample TEM image of as synthesized **MOF-808** with calculated size distribution 370±80 nm (n=100).

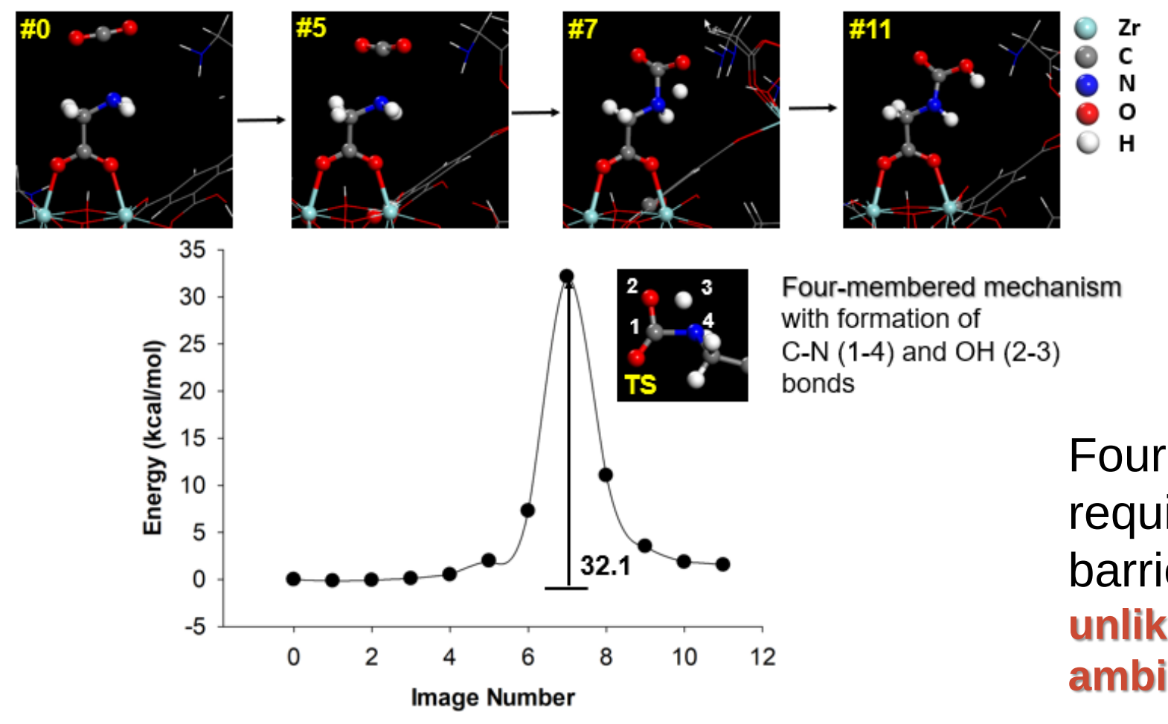


Selected CO_2 isotherms collected at 298 K for **MOF-808** particles before and after functionalization.

3. Computational Investigations

First Principles Calculations. The adsorption mechanisms of CO_2 in MOF-808 under dry and wet conditions were determined using plane-wave density functional theory (DFT) calculations. The models used consider the full 3D periodicity of the MOF material. Calculations were done using Perdew–Burke–Ernzerhof (PBE) exchange correlation functional corrected to include long-range van der Waals interactions using the D3 method of Grimme and Becke-Johnson damping. Mapping of the minimum energy reaction pathways has been done using nudged elastic band calculations.

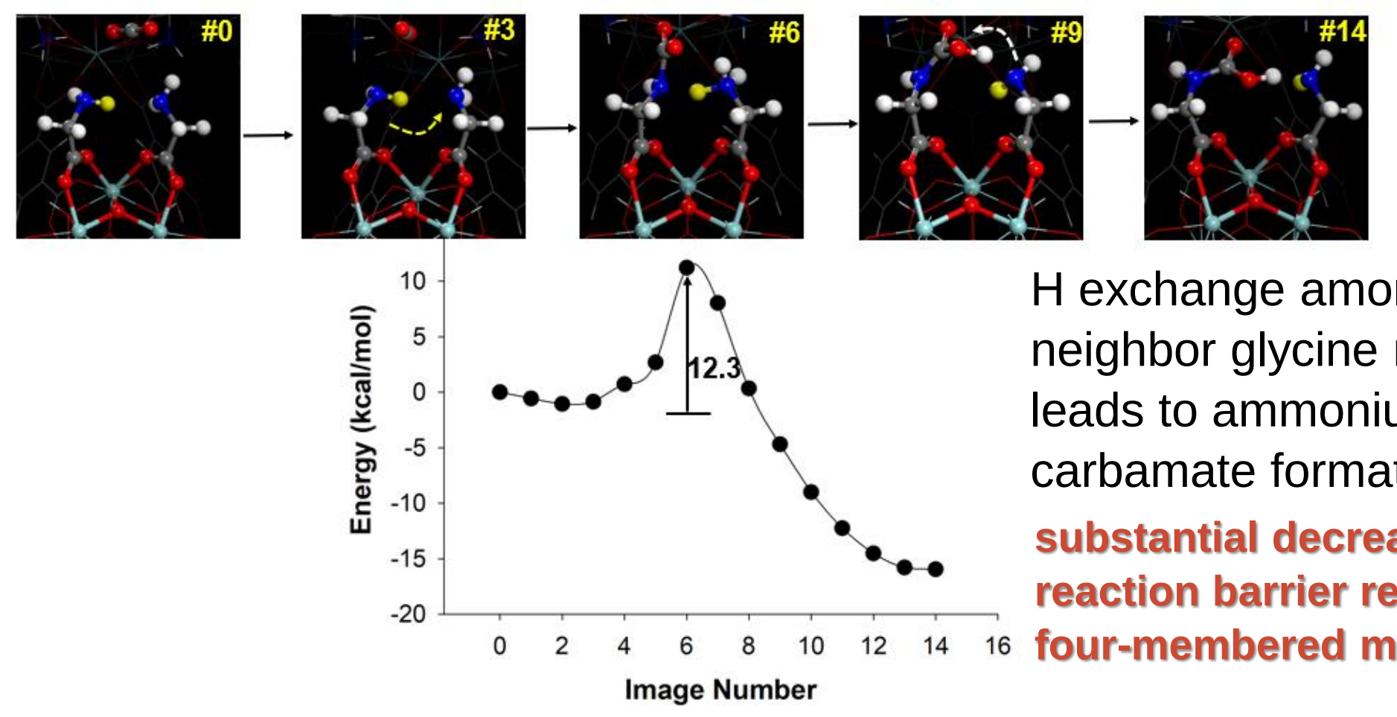
Direct H Transfer Mechanism (Dry Conditions)



Four-membered mechanism with formation of C-N (1-4) and OH (2-3) bonds

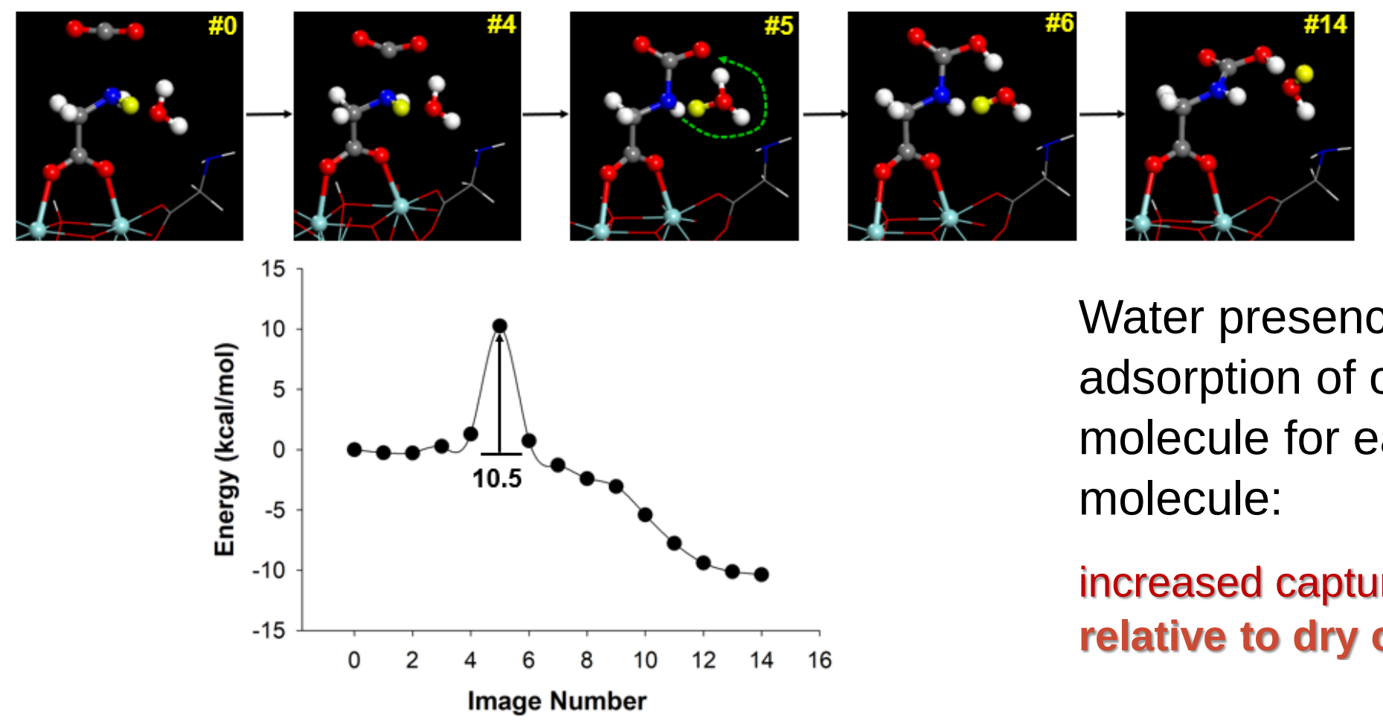
Four-membered mechanism requires overcoming high barriers: **unlikely to take place at ambient conditions**

CO_2 Chemisorption Mediated by Amine Pairs (Dry Conditions)



H exchange among neighbor glycine molecules leads to ammonium carbamate formation: **substantial decrease of reaction barrier relative to four-membered mechanism**

Water-Assisted CO_2 Chemisorption



Water presence allows adsorption of one CO_2 molecule for each glycine molecule: **increased capture efficiency relative to dry conditions**

Acknowledgement and Disclaimer

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