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Tailoring the Pore Environment of Metal-Organic and Molecular Materials Decorated with Inorganic Anions: Platforms for Highly Selective Carbon Capture

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Tailoring the Pore Environment of Metal-Organic and Molecular Materials Decorated with Inorganic Anions: 
Platforms for Highly Selective Carbon Capture

by

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A thesis submitted in partial fulfillment of the requirements of the degree of
Master of Science
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DEDICATION

This work is dedicated to my parents and my aunt Terry for their immeasurable love and support.
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ABSTRACT

Due to their high surface areas and structural tunability, porous metal-organic materials, MOMs, have attracted wide research interest in areas such as carbon capture, as the judicious choice of molecular building block (MBB) and linker facilitates the design of MOMs with myriad topologies and allows for a systematic variation of the pore environment. Families of MOMs with modular components, i.e. MOM platforms, are eminently suitable for targeting the selective adsorption of guest molecules such as CO$_2$ because their pore size and pore functionality can each be tailored independently. MOMs with saturated metal centers (SMCs) that promote strong yet reversible CO$_2$ binding in conjunction with favorable adsorption kinetics are an attractive alternative to MOMs containing unsaturated metal centers (UMCs) or amines. Whereas MOMs with SMCs and exclusively organic linkers typically have poor CO$_2$ selectivity, it has been shown that a versatile, long known platform with SMCs, pillared square grids with inorganic anion pillars and pCu topology, exhibits high and selective CO$_2$ uptake, a moderate CO$_2$ binding affinity, and good stability under practical conditions. As detailed herein, the tuning of pore size and pore functionality in this platform has modulated the CO$_2$ adsorption properties and revealed variants with unprecedented selectivity towards CO$_2$ under industrially relevant conditions, even in the presence of moisture.

With the aim of tuning pore chemistry while preserving pore size, we initially explored the effect of pillar substitution upon the carbon capture properties of a pillared square grid, [Cu(bipy)$_2$(SiF$_6$)] (SIFSIX-1-Cu). Room temperature CO$_2$, CH$_4$, and N$_2$ adsorption isotherms revealed that substitution of the SiF$_6^{2-}$ (“SIFSIX”) inorganic pillar with TiF$_6^{2-}$ (“TIFSIX”) or SnF$_6^{2-}$ (“SNIFSIX”) modulated CO$_2$ uptake, CO$_2$ affinity (heat of adsorption, $Q_{st}$), and selectivity vs. CH$_4$ and N$_2$. TIFSIX-1-Cu and SNIFSIX-1-Cu were calculated to exhibit the highest CO$_2$/N$_2$ and CO$_2$/CH$_4$ adsorption selectivities of the series,
respectively. Modeling studies of TIFSIX-1-Cu and SIFSIX-1-Cu suggested that the enhancements in low pressure CO$_2$ uptake and CO$_2$ selectivity in the former arose from the stronger polarization of CO$_2$ molecules by TIFSIX-1-Cu. The stronger framework-CO$_2$ interaction at the primary binding site in TIFSIX-1-Cu correlates with the greater electronegativity of the pillar fluorine atoms relative to those in SIFSIX-1-Cu, and in turn to the higher polarizability of Ti$^{4+}$ vs. Si$^{4+}$.

The effect of tuning pore size upon the carbon capture performance of pillared square grid nets was next investigated. Linker substitution afforded three variants, SIFSIX-2-Cu, SIFSIX-2-Cu-i, and SIFSIX-3-Zn, with pore sizes ranging from nanoporous (13.05 Å in SIFSIX-2-Cu) to ultramicroporous (3.84 Å in SIFSIX-3-Zn). Single-gas adsorption isotherms showed that SIFSIX-2-Cu-i, a doubly interpenetrated polymorph of SIFSIX-2-Cu with contracted pores (5.15 Å), exhibited far higher CO$_2$ uptake, $Q_{st}$ towards CO$_2$, and selectivity towards CO$_2$ vs. CH$_4$ and N$_2$ than its non-interpenetrated counterpart. Further contraction of the pores afforded SIFSIX-3-Zn, a MOM with enhanced CO$_2$ binding affinity and selectivity vs. SIFSIX-2-Cu-i. Remarkably, the selectivity of SIFSIX-3-Zn towards CO$_2$ was found to be unprecedented among porous materials. Equilibrium and column breakthrough adsorption tests involving gas mixtures meant to mimic post-combustion carbon capture (CO$_2$/N$_2$), natural gas/biogas purification (CO$_2$/CH$_4$), and syngas purification (CO$_2$/H$_2$) confirmed the high selectivities of SIFSIX-2-Cu-i and SIFSIX-3-Zn. Gas mixture experiments also revealed that SIFSIX-3-Zn exhibited optimal CO$_2$ adsorption kinetics. Most importantly, the CO$_2$ selectivity of SIFSIX-2-Cu-i and SIFSIX-3-Zn was minimally affected in the presence of moisture. Modeling studies of CO$_2$ adsorption in SIFSIX-3-Zn (experimental $Q_{st}$ ~ 45 kJ/mol at all loadings) revealed strong yet reversible electrostatic interactions between CO$_2$ molecules and the SIFSIX pillars lining the confined channels of the material.

Porous materials based upon the non-covalent assembly of discrete MBBs can also exhibit high surface areas and systematically tunable pore environments. Molecular porous material (MPM) platforms have begun to emerge despite the greater challenge of designing such materials in comparison to MOMs. Herein we report the tuning of pore functionality in an MPM platform based upon an extensive hydrogen-
bonded network of paddlewheel-shaped [Cu(ade)₄L₂] complexes (ade = adenine; L = axial ligand). The substitution of Cl axial ligands with inorganic TIFSIX moieties has produced [Cu₂(ade)₄(TiF₆)₂], MPM-1-TIFSIX, a variant with enhanced CO₂ separation performance and stability. Single-gas adsorption isotherms reveal that MPM-1-TIFSIX exhibits the highest CO₂ uptake and CO₂ Qₛₜ yet reported for an MPM as well as high selectivity towards CO₂ vs. CH₄ and N₂. Modeling studies indicated strong electrostatic interactions between CO₂ and the TIFSIX ligands lining the pores of MPM-1-TIFSIX. In addition to dramatically surpassing MPM-1-Cl with regard to CO₂ separation performance, MPM-1-TIFSIX exhibits thermal stability up to 568 K and retains its performance even after immersion in water for 24 hrs.

Comprehensively, the results presented herein affirm that porous materials featuring inorganic anions and SMCs can exhibit high and selective CO₂ uptake, sufficient stability, and facile activation conditions without the drawbacks associated with UMCs and amines, i.e. competitive water adsorption and high regeneration energy, respectively.
CHAPTER ONE:

Introduction

Metal-Organic Materials

Research on metal-organic materials, MOMs, has accelerated in recent years due to their unprecedented levels of permanent porosity and structural tunability. This combination of features is unique among porous materials and has motivated the study of MOMs for applications such as gas separation, gas storage, catalysis, drug delivery, and sensing. Formed via the self-assembly of single metal ion or metal cluster nodes (molecular building blocks, MBBs) and multifunctional ligands, these crystalline materials can possess surface areas exceeding 7000 m$^2$/g and are amenable to design. The appropriate choice of MBBs and linkers enables the synthesis of MOMs with predictable topologies, while the modularity of their components allows for systematic variation of pore size and pore chemistry in accordance with the principles of crystal engineering. As embodied by the study of families of MOMs with the same MBB and topology (i.e. MOM platforms), crystal engineering affords valuable insight into structure-property relationships and allows materials to be designed for specific applications.

The “node and linker” approach, whereby a node is 3-connected (3-c) or greater and a linker is 2-connected (2-c), was first outlined by Robson and serves as a blueprint for the rational construction of MOMs with 0D (e.g. nanoballs or metal-organic polyhedra, MOPs), 1D (e.g. chains), 2D (e.g. sheets), or 3D (e.g. porous coordination networks, PCNs; porous coordination polymers, PCPs; or metal-organic frameworks, MOFs) periodicity. This strategy facilitated the development of early MOM
platforms with topologies\textsuperscript{15} including sql,\textsuperscript{16} pcu,\textsuperscript{14,17} dia,\textsuperscript{18} and tbo\textsuperscript{19} (see footnote\textsuperscript{³}). These platforms are versatile from a design perspective because each can be prepared from pyridyl- or carboxylate-based MBBs and because precise control of pore scale and pore chemistry is possible. Early sql and pcu networks belonging to the first generation of MOMs were assembled from linear dipyridyl linkers and 4-c or 6-c MBBs, e.g. [M(pyridyl)]\textsubscript{4}(L)\textsubscript{2} (Figure 1.1).\textsuperscript{16a,17} Second generation MOMs based upon dicarboxylate linkers and robust metal cluster MBBs, e.g. [M\textsubscript{2}(O\textsubscript{2}CR)\textsubscript{4}(L)\textsubscript{2}] square paddlewheels/octahedra,\textsuperscript{20} [Zn\textsubscript{4}(µ\textsubscript{4}-O)(O\textsubscript{2}CR)\textsubscript{6}] octahedra,\textsuperscript{3a} and [M\textsubscript{3}(µ\textsubscript{3}-O)(O\textsubscript{2}CR)\textsubscript{6}] trigonal prisms,\textsuperscript{21} were developed thereafter. Although the initial report of permanent porosity in a MOM involved a first generation material, [M\textsubscript{2}(bipy)\textsubscript{3}(NO\textsubscript{3})\textsubscript{4}]·(xH\textsubscript{2}O) (M = Co\textsuperscript{2+}, Ni\textsuperscript{2+}, Zn\textsuperscript{2+}; bipy = 4,4'-bipyridine),\textsuperscript{22} second generation MOMs such as MOF-5 (IRMOF-1)\textsuperscript{14} and HKUST-1\textsuperscript{19} ushered in the era of ultra-high surface area.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Representative molecular building blocks (MBBs) that function as nodes in first generation (a) and second generation (b-d) metal-organic materials: a) [M(pyridyl)]\textsubscript{4}(L)\textsubscript{2} square/octahedron; b) [M\textsubscript{2}(O\textsubscript{2}CR)\textsubscript{4}(L)\textsubscript{2}] square/octahedron; c) [Zn\textsubscript{4}(µ\textsubscript{4}-O)(O\textsubscript{2}CR)\textsubscript{6}] octahedron; d) [M\textsubscript{3}(µ\textsubscript{3}-O)(O\textsubscript{2}CR)\textsubscript{6}] trigonal prism.}
\end{figure}

\textbf{Square Grid (sql) and Pillared Square Grid (pcu) MOMs}

Each of the above classes of MOM forms from readily accessible, high symmetry MBBs. Platforms with 2D sql topology, i.e. square grids, result from the assembly of 4-c square

\footnote{Unique network topologies are designated herein with 3-letter codes established by the Reticular Chemistry Structure Resource (RCSR) database (ref. 15).}
[M(pyridyl)$_2$(L)$_2$] or [M$_2$(O$_2$CR)$_4$(L)$_2$] MBBs and linear linkers (Figure 1.2). The sheets possess square windows and can adopt a clay-like layered arrangement$^{16a}$ or exhibit interpenetration.$^{23}$ 3D nets based on the pcu topology are constructed from 6-c octahedral MBBs and possess square channels and saturated metal centers (SMCs). In addition to the IRMOF platform that is based on a single linker,$^{3a}$ pcu platforms may be assembled by cross-linking the axial positions of square MBBs with a second moiety (pillar) as demonstrated in SIFSIX-1-M (M = Zn, Cu)$^{17}$ and DMOF-1$^{20b}$ (Figure 1.3), the prototypal pillared square grids based upon dipyridyl and dicarboxylate linkers, respectively. That both the linker and pillar may be varied in pillared square grids increases the tailorability of these materials relative to IRMOFs. Interpenetration of multiple networks$^{24}$ can occur in each of these platforms and strategies have been developed which harness interpenetration as a means of pore size control.$^{25}$

![Figure 1.2. Prototypal non-interpenetrated square grid (sql) nets: a) [Cd(bipy)$_2$(NO$_3$)$_2$]; b) [Zn$_2$(1,4-bdc)(H$_2$O)$_2$], MOF-2 (1,4-bdc = 1,4-benzenedicarboxylate).](image-url)
Figure 1.3. Prototypal pcu MOMs: a) [Zn(bipy)$_2$(SiF$_6$)], SIFSIX-1-Zn, pillared square grid; b) [Zn$_2$(1,4-bdc)(dabco)], DMOF-1, pillared square grid; c) [Zn$_4$(1,4-bdc)$_3$], MOF-5. Hydrogen atoms are not shown on the dabco pillars in b).

2D Interpenetrated Square Grids. Along with dia nets, square grids were prominent at the dawn of MOM chemistry. The prototypal square grid MOM, reported in 1990 and composed of cationic [Zn(bipy)$_2$(H$_2$O)$_2$]$^{2+}$ sheets, exhibited 2D-to-3D inclined interpenetration whereby two infinitely stacked arrays of grids interlocked with one another in an inclined fashion to yield a 3D network with square channels that were occupied by SiF$_6^{2-}$ counterions (Figure 1.4). The modularity of the node metal, linker, and anion in this structure was subsequently demonstrated. Parallel interpenetration can occur in square grid variants that are propagated by angular or flexible linkers due to the undulating nature of the grids. Studies concerning the properties of 2D interpenetrated grids have spanned a variety of topics including porosity, magnetism, post-synthetic modification (PSM), and supramolecular isomerism.
Figure 1.4. The prototypal square grid exhibiting 2D-to-3D inclined interpenetration, \([\text{Zn(bipy)}_2(\text{H}_2\text{O})_2](\text{SiF}_6)\). The green layers represent the second set of interpenetrating nets. Both sets of square grids are viewed edge-on and the \(\text{SiF}_6^{2-}\) counterions are shown in space-filling mode.

2D Non-interpenetrated Square Grids. The first non-interpenetrated square grid with nanoscale cavities, \([\text{Cd(bipy)}_2(\text{NO}_3)_2]\), was reported in 1994 (Figure 1.2a) and crystallized in the presence of o-dibromobenzene guest molecules.\(^\text{16a}\) The lack of interpenetration in this MOM was likely a result of stacking interactions between the linker and the aromatic guest occupying the square cavities. Notably, o-dibromobenzene was selectively clathrated by \([\text{Cd(bipy)}_2(\text{NO}_3)_2]\) over m- and p-dibromobenzene. In perhaps the first application of a MOM as a heterogeneous catalyst, this material promoted the shape-selective cyanosilylation of aldehydes.

Non-interpenetrated dipyridyl grids that crystallized in the presence of aromatic guests have also been explored from the perspective of topology and network design,\(^\text{30}\) while the adoption of longer linkers has expanded the cavity size of these materials to 20 Å.\(^\text{31}\)

The prototypal non-interpenetrated square grid based upon \([\text{M}_2(\text{O}_2\text{CR})_4]\) square paddlewheel MBBs and dicarboxylate linkers, MOF-2 (Langmuir surface area = 310 m\(^2\)/g; Figure 1.2b), was among the first permanently porous MOMs.\(^\text{16b}\) Like dipyridyl square grids, carboxylate square grids are amenable to node metal and linker substitution. However, a salient difference exists between square grids based upon \([\text{M}_2(\text{O}_2\text{CR})_4]\) and \([\text{M(pyridyl)}_4]^{2+}\) MBBs with divalent metals: while the former are likely to
be uncharged, the latter are cationic. This distinction becomes relevant when considering the types of pillars that are suitable for each platform.

Shortly after MOF-2 was communicated and in the ensuing decade, platforms based upon the square paddlewheel and other versatile carboxylate MBBs, e.g. \([\text{Zn}_4(\mu_3-O)(O_2CR)_6]\) octahedra and \([\text{M}_3(\mu_3-O)(O_2CR)_6]\) trigonal prisms, became dominant in MOM chemistry. This paradigm shift was spurred by the design of two prototypal MOMs with unprecedented permanent porosity: MOF-5 and HKUST-1 \{Brunauer-Emmett-Teller (BET) surface areas of ca. 3000 and 1800 m\(^2\)/g, respectively\}.\(^{14,19}\) A relatively small subclass of 3D carboxylate-linked MOMs, pillared paddlewheel square grids (e.g. DMOF-1), was also introduced.\(^{20b,32}\) While this square grid platform is outside the scope of this narrative, it is pertinent to the broader class of pillared square grid MOMs and will be briefly discussed.

**Pillared Square Grids.** The prototypal pillared paddlewheel square grid, DMOF-1 (Figure 1.3b), was reported in 2004 and was based upon 1,4-benzenedicarboxylate (1,4-bdc) linkers and neutral 1,4-diazabicyclo[2.2.2]octane (dabco) pillars.\(^{20b}\) Ensuing studies used linker and pillar substitution to produce analogues with varied pore size and organic functionality. Representative features of this platform include the presence of SMCs and exclusively organic linkers/pillars. Pore size was expanded by using longer linkers and by substituting the dabco pillar with bipy and other dipyridyl analogues, though the use of longer linkers/pillars sometimes facilitated interpenetration. The permanent porosity of many variants (BET surface areas ranging from 200 to >2000 m\(^2\)/g) prompted investigation of their gas adsorption properties. Low pressure \(\text{H}_2\) sorption studies of analogues with surface areas of 1400-2100 m\(^2\)/g found that those with smaller pores and lower surface area exhibited greater affinity for \(\text{H}_2\) at 77 K as measured by relative surface coverage.\(^{32}\) Pillared paddlewheel square grids have also been researched in the context of gas separation\(^{33}\) and catalysis.\(^{34}\) The modularity of this platform makes it optimal for exploring the relationship between pore size and host-guest interactions.

Paddlewheel square grids are almost exclusively uncharged, thus neutral organic molecules (e.g. dabco, bipy, and other dipyridyls) are highly suitable as pillars. However, platforms possessing SMCs and
exclusively organic linkers are at a disadvantage in applications where strong host-guest electrostatic interactions are needed. Selective CO$_2$ adsorption under ambient conditions (≈1 atm and 298 K) is one such application and indeed these MOMs typically exhibit low to moderate CO$_2$ uptake and selectivity.$^{2b}$ The cationic nature of dipyridyl square grids allows for the use of divalent inorganic anions as pillars to crosslink the grids in an axial-to-axial fashion, thereby generating a neutral pcu net. [Zn(bipy)$_2$(SiF$_6$)] (SIFSIX-1-Zn), the prototypal pillared square grid and among the first pcu MOMs (Figure 1.3a),$^{17}$ was an early example of MOM design in that its structure was predictable based upon the geometry of its components. SiF$_6^{2-}$ (SIFSIX) pillars crosslinked the [Zn(bipy)$_2$]$^{2+}$ grids to form a pcu net with 8 x 8 Å$^2$ square channels, the corners of which were lined by the equatorial fluorine atoms of the pillars. A permanently porous, isostructural variant of SIFSIX-1-Zn with Cu$^{2+}$ nodes, SIFSIX-1-Cu, was introduced in 2000 and exhibited a high BET surface area (1337 m$^2$/g) and high CH$_4$ capacity at 298 K and 35 atm (145.6 cm$^3$/g).$^{35}$ SIFSIX-1-Cu far exceeded the CH$_4$ uptake of zeolite 5A (82.9 cm$^3$/g), the best known CH$_4$ adsorbent at the time. The modularity of the inorganic pillar was first demonstrated in this platform by the synthesis of Cu$^{2+}$ analogues with GeF$_6^{2-}$ and NO$_3^-$/PF$_6^-$ pillars.$^{28a}$ Separate studies employed linker variation$^{36}$ and interpenetration$^{37}$ to produce five novel SIFSIX-pillared analogues with Zn$^{2+}$ nodes and varying pore sizes, affirming the modularity of the linker. Three of these variants were non-interpenetrated and the use of longer linkers enlarged the channel dimensions up to 15.6 Å, while the longest linkers led to doubly interpenetrated analogues with open channels (Figure 1.5a). Lastly, a permanently porous variant reported in 2009, [Zn(pyz)$_2$(SiF$_6$)] (SIFSIX-3-Zn), was the first MOM in this platform with contracted pores relative to the prototype (pore size = 3.84 Å).$^{38}$ Figure 1.5b presents a selection of dipyridyl linkers that have been used in the construction of square grids and pillared square grids. While pcu is among the most common MOM topologies, the properties of dipyridyl square grids pillared by inorganic anions have been scarcely explored compared to those of carboxylate-based platforms. As detailed herein, we chose to explore this family of MOMs from the perspective of CO$_2$ capture by systematically tuning pore size and pore functionality.
**Figure 1.5.** a) [Zn(dpn)₂(SiF₆)]₂, a doubly interpenetrated pcu variant. The second, interpenetrating net in [Zn(dpn)₂(SiF₆)]₂ is illustrated in green; b) Dipyridyl linkers used in the assembly of square grid and pillared square grid MOMs (clockwise from top left): pyrazine (pyz); 4,4'-bipyridine (bipy); 1,2-di(4-pyridyl)ethane; trans-1,2-bis(4-pyridyl)ethylene (bpe); trans-4,4'-azodipyridine; N-(4-pyridyl)-isonicotinamide; 1,2-di(4-pyridyl)acetylene (dpa); 1,4-di(4-pyridyl)benzene; 2,6-di(4-pyridyl)naphthalene (dpn); 4,4'-di(4-pyridyl)diphenyl.

**MOMs as selective CO₂ adsorbents**

The challenge of efficiently separating CO₂ from industrial gas streams has important implications related to climate change and energy production, as fossil fuel consumption continues to rise despite the increasing adoption of alternative energy sources. From 1970 to 2004, global CO₂ emissions from the combustion of coal and other carbon-based fuels grew by 80%.

Further, electricity production by coal and natural gas power plants is projected to nearly double from 2007 to 2035. Given that the transition to alternative energy sources will be gradual and that fossil fuel use will increase in the near term due to population growth and economic development, an immediate need for efficient CO₂ capture technologies exists. In addition to being present in post-combustion flue gas (primarily CO₂/N₂), CO₂ is an impurity in several industrial gas mixtures relevant to energy production processes, e.g. natural gas upgrading (CO₂/CH₄), biogas purification (CO₂/CH₄), and shifted syngas purification (CO₂/H₂). These separations are carried out near ambient temperature within various pressure regimes. Post-combustion
capture and biogas purification operate at ambient pressure, while natural gas upgrading and shifted syngas purification are implemented at higher pressures.

Current methods of CO₂ separation typically have a large energy penalty associated with regeneration of the capture material. A standard practice involves the use of highly selective aqueous amines (e.g. monoethanolamine, MEA) that chemically react with CO₂ to form carbamates or bicarbonates, but the high desorption energy and the high heat capacity of water require a large energy input in order to regenerate the amine. Amine recycling can comprise up to 30% of the total energy production of a coal-fired power plant. Porous solids such as zeolites, activated carbons, and MOMs have been widely investigated as alternatives to amines because they can bind CO₂ more reversibly and they possess lower heat capacities than liquids.⁹

In addition to being inexpensive, nontoxic, and thermochemically robust, the optimal adsorbent for CO₂ separation must balance high CO₂ capacity and selectivity with ease of regeneration. CO₂ selectivity may arise from favorable adsorption thermodynamics or kinetics. The difference between the isosteric heat of adsorption (Qₛₐ) towards CO₂ and that towards another mixture component is related to thermodynamic CO₂ selectivity, whereas materials with pore sizes that approach the kinetic diameter of CO₂ can exhibit kinetic selectivity due to size exclusion or differences in diffusion rates (kinetic diameters: CO₂ = 3.3 Å; CH₄ = 3.76 Å; N₂ = 3.64-3.80 Å). The Qₛₐ towards CO₂ is generally proportional to the amount of energy required to regenerate the adsorbent. MOMs with SMCs that promote strong physisorption of CO₂ (i.e. adsorption without the formation of chemical bonds) are expected to offer the desired balance between binding strength and regenerability. Unlike the Qₛₐ of MOMs with unsaturated metal centers (UMCs), the Qₛₐ of MOMs with SMCs generally remains constant as loading increases, minimizing the impact of loading on separation performance. Further, the moisture present in many industrial gas streams (flue gas contains ca. 6% water) competes strongly with CO₂ for binding to UMCs and can dramatically reduce CO₂ capacity and selectivity.
Selectivity is predicted from single-gas isotherms or measured directly *via* gas mixture experiments. Using single-gas isotherms, selectivity is estimated *via*: 1) Ideal adsorbed solution theory (SIAST); 2) the selectivity factor (for post-combustion CO$_2$/N$_2$, $S = \frac{\text{uptake of CO}_2 \text{ at 0.15 atm}}{\text{uptake of N}_2 \text{ at 0.75 atm}}$); 3) the ratio of uptakes at 1 atm, i.e. relative uptake; 4) the ratio of the Henry's constants (slopes) of the isotherms at low pressure. IAST has become the standard tool for assessing selectivity because it has accurately predicted gas mixture adsorption in zeolites and MOMs and because, unlike the other methods, it accounts for competitive adsorption behavior. Breakthrough experiments using gas mixtures are the most common technique for directly measuring selectivity and involve monitoring the time required for each gas to pass through a column packed with adsorbent. Such experiments account for the dynamic (i.e. non-equilibrium) factors involved in mixed gas adsorption and are the most accurate reproduction of real-world separation conditions.

Whereas zeolites and activated carbons feature high surface area and excellent thermochemical stability, both types of material carry significant drawbacks with regard to CO$_2$ separations. Activated carbons exhibit surface areas comparable to MOMs but these amorphous materials lack tailorability and the relatively uniform electric potential of their pore surfaces typically affords a low Q$_s$ towards CO$_2$, resulting in poor uptake and selectivity at low pressures. Zeolites often exist as anionic frameworks that contain UMCs as counterions. Though over 200 zeolite topologies are known,[reference for zeolite database website] these materials are superseded by MOMs in terms of modularity, structural diversity, and surface area. Zeolite 13X, a benchmark material in the context of CO$_2$ separation, exhibits high CO$_2$ uptake (105.3 cm$^3$/g at 298 K and 1 atm), a moderately high Q$_s$ towards CO$_2$ (37.2 kJ/mol at low loading), and among the highest selectivities towards CO$_2$ vs. CH$_4$ and N$_2$ at 298 K and 1 atm (S$_\text{IAST}$ = 103 for a 50:50 CO$_2$/CH$_4$ mixture and 420 for a 10:90 CO$_2$/N$_2$ mixture). This behavior is driven primarily by the chemisorption of CO$_2$ onto UMCs. Whereas UMCs enable strong and selective CO$_2$ binding, Q$_s$ and selectivity typically drop sharply at low loading once the UMCs become saturated. The desorption of
guests from UMCs often requires heating to activate the adsorbent, while the hydrophilicity of UMCs frequently causes a dramatic reduction in CO\textsubscript{2} uptake and selectivity under humid conditions.\textsuperscript{43}

The systematic manipulation of pore size and pore chemistry in MOM platforms has advanced the knowledge of the structural features necessary for high-performance carbon capture,\textsuperscript{2b,44} fostering the development of MOMs with higher CO\textsubscript{2} capacity and selectivity than any other class of porous material. Notably, the literature reveals that MOMs which exhibit the highest CO\textsubscript{2} uptakes and selectivities under ambient conditions generally possess surface areas below 2000 m\textsuperscript{2}/g, suggesting that small to moderate pore size (ca. 1.2 nm or less) is most effective for CO\textsubscript{2} adsorption under these circumstances. In contrast, CO\textsubscript{2} adsorption capacity tends to scale with surface area and pore volume at the higher pressures relevant to gas storage applications. With regard to carbon capture, MOMs can be classified according to whether they have UMCs, Lewis basic sites (LBSs), or SMCs. The incorporation of multiple types of functional sites (e.g. UMCs and LBSs) into a single material has also been employed as a strategy to enhance CO\textsubscript{2} uptake and selectivity.\textsuperscript{45} In order to create a proper context for the results presented in Chapters 2-4 and to highlight important relationships between host structure and CO\textsubscript{2} adsorption, the carbon capture properties of representative MOM platforms that possess each type of structural feature (i.e. UMCs, LBSs, or SMCs) will be detailed in this chapter. A more comprehensive view of carbon capture in MOMs can be found in recent review articles.\textsuperscript{2,44}

**MOMs with Unsaturated Metal Centers.** MOMs with UMCs have been extensively studied for carbon capture because they promote strong binding with CO\textsubscript{2}. For instance, the M-MOF-74/CPO-27-M/M-dobdc platform\textsuperscript{46} (Figure 1.6) exhibits the highest gravimetric CO\textsubscript{2} uptake of any porous material (185.9 cm\textsuperscript{3}/g for Mg-MOF-74) at 298 K and 1 atm and is among the most selective towards CO\textsubscript{2} vs. CH\textsubscript{4} and N\textsubscript{2}. Mg-MOF-74 is also superior among MOMs in terms of volumetric CO\textsubscript{2} uptake (162 cm\textsuperscript{3}/cm\textsuperscript{3}). A neutral 3D platform composed of [Mg\textsubscript{2}O\textsubscript{2}(O\textsubscript{2}CR)\textsubscript{2}] infinite rod-shaped secondary building units (SBUs) and linear 2,5-dioxido-1,4-benzenedicarboxylate (dobdc) linkers, Mg-MOF-74 possesses cylindrical channels of ca. 11 Å in diameter which are lined by UMCs. Metal substitution has shown that the Lewis
acidity of the UMCs can dramatically impact CO$_2$ uptake and Q$_{st}$ under conditions relevant to carbon capture.\textsuperscript{46c} MOF-74 variants based upon Zn, Co, and Ni exhibit similar BET surface areas, while the surface area of Mg-MOF-74 is higher (1495 m$^2$/g) owing to the lighter metal. Low pressure isotherms revealed stark differences in CO$_2$ uptake and binding affinity for this series, with Mg-MOF-74 displaying the highest gravimetric uptake over the full pressure range. The steepness of the Mg-MOF-74 isotherm at low pressure led to a CO$_2$ capacity of more than twice that of the other variants at 0.1 atm. In accordance with its sharper uptake at 0.1 atm, Mg-MOF-74 exhibited a higher CO$_2$ Q$_{st}$ than the transition metal analogues (47 kJ/mol at zero loading), though its CO$_2$ binding affinity falls to ca. 30 kJ/mol at higher loading. The superior uptake and Q$_{st}$ of Mg-MOF-74 were attributed to the stronger ionic character of the Mg-O bond formed between the UMCs and CO$_2$. This MOM exhibits exceptional CO$_2$ selectivity under ambient conditions (298 K, 1 atm) as predicted by IAST \{(15:85 CO$_2$/N$_2$ = 182.1 (296 K); 50:50 CO$_2$/CH$_4$ = 137)\}\textsuperscript{42b,47} and as shown by gas mixture breakthrough experiments.\textsuperscript{48}

Though Mg-MOF-74 has exceptional CO$_2$ capacity and selectivity, the separation performance of MOF-74 variants suffers in the presence of humidity due to competitive water adsorption, as demonstrated \textit{via} breakthrough experiments involving simulated flue gas (20:80 CO$_2$/N$_2$ at 70% relative humidity).\textsuperscript{43b} Exposure to a humid gas mixture reduced the initial CO$_2$ capacity of Mg-MOF-74 by 84% after a single regeneration cycle (150°C under argon), while Ni- and Co-MOF-74 retained 60 and 85% of their initial capacity, respectively. The negative impact of water on CO$_2$ uptake has also been demonstrated in other MOMs with UMCs.\textsuperscript{43a,49}
Another UMC-based platform, the (3,24)-c \textbf{rht} net, illustrates how pore size and surface features may be tailored to enhance CO$_2$ adsorption. This polyhedral MOM is composed of 24-c nanoball supermolecular building blocks (SBBs)\textsuperscript{30} and 3-c organic or metal-organic tri-isophthalate-functionalized MBBs. Each SBB is assembled from 12 paddlewheel MBBs and 24 bridging isophthalates and possesses 24 UMCs upon activation. Among \textbf{rht} variants with organic 3-c MBBs, pore size and pore chemistry have been tuned by changing the scale and decoration, respectively, of the ligand.

\textbf{rht} MOMs based upon tri-isophthalate ligands decorated with Lewis basic sites (LBSs) have been shown to exhibit enhanced CO$_2$ uptake, affinity, and selectivity relative to analogues with alkyne-decorated ligands. The performance of two \textbf{rht} variants, Cu-TPBTM and PCN-61 (BET surface areas = 3160 and 3350 m$^2$/g), decorated with acylamide and alkyne groups, respectively, was assessed in the context of CO$_2$/N$_2$ separation.\textsuperscript{31} Single-gas CO$_2$ and N$_2$ isotherms collected at 298 K up to 20 atm revealed a markedly larger CO$_2$ uptake (23.5 vs. 21.4 mmol/g at 20 atm) and $Q_{st}$ (26.3 vs. 22.0 kJ/mol at zero loading) at all pressures for Cu-TPBTM compared to PCN-61, concurrent with relatively low N$_2$ uptake by each MOM. Accordingly, Cu-TPBTM exhibited higher CO$_2$/N$_2$ selectivity than PCN-61 over the full loading range ($S_{\text{IAST}}$ = 11.5 vs. 8 for a 50:50 mixture at 1 atm). As these variants have comparable
surface areas and pore sizes, the enhancements in Cu-TPBSTM were attributed to dipole-quadrupole interactions and/or NH−OCO hydrogen bonds between the surface acylamide groups and CO₂.

Further enhancements in CO₂ uptake and selectivity were realized in Cu-TDPAT, an rht variant based on an amine- and triazine-functionalized ligand (Figure 1.7). Cu-TDPAT features the smallest pores and BET surface area (1938 m²/g) in the rht family and was found to exhibit the highest CO₂ uptake among all variants at 298 K (31.3 cm³/g 0.1 atm and 132 cm³/g at 1 atm). The Qₘ of Cu-TDPAT towards CO₂ (42.2 kJ/mol at zero loading), unprecedented among rht MOMs and comparable to that of Mg-MOF-74, decreased to ca. 25 kJ/mol at higher loading. IAST calculations for a 10:90 CO₂/N₂ mixture at 1 atm revealed a dramatic improvement in selectivity for Cu-TDPAT (S_{IAST} = 79) over Cu-TPBSTM. The enhanced CO₂ uptake, Qₘ, and selectivity of Cu-TDPAT vs. Cu-TPBSTM and PCN-61 were attributed to the higher density of LBSs in concert with the more confined pores.

![Figure 1.7. a) A portion of the structure of Cu-TDPAT; b) (clockwise from top left) alkyne-, acylamide-, and amine-/triazine-functionalized ligands that serve as 3-c nodes in rht MOMs.](image)

**MOMs with Lewis Basic Sites.** The pre- or post-synthetic coordination of strong Lewis bases, e.g. alkylamines or hydroxide ions, onto UMCs has been employed to create MOMs with high Qₘ (70-110 kJ/mol at zero loading) and high selectivity towards CO₂. For example, the grafting of dimethylethlenediamine (mmen) onto the UMCs of an expanded Mg-dobdc analogue has afforded
mmen-Mg-dobpdc (dobpdc = 4,4’-dioxido-3,3’-biphenyldicarboxylate), a MOM with remarkably sharp CO₂ uptake (70.3 cm³/g at 0.15 atm; 86.5 cm³/g at 1 atm) and high CO₂/N₂ selectivity (S = 198.1) at 298 K. The initial Qₜ towards CO₂ in mmen-Mg-dobpdc (71 kJ/mol) is maintained up to a CO₂ loading of ca. 56 cm³/g and results from chemisorption onto the coordinated amines. At this loading, the amine sites become saturated and the CO₂ binding affinity rapidly decreases to 23 kJ/mol. Whereas mmen-Mg-dobpdc is estimated to afford more facile regeneration than MEA under temperature swing conditions (2.3 vs 3.5 MJ per kg of CO₂ captured), the regeneration of MOMs which chemically bind CO₂ is likely to require more energy than that of MOMs which rely on strong physisorption.

Other MOMs with strong LBSs that exploit chemisorption include PEI-MIL-101-100 and MAF-X27ox. The former was produced via post-synthetic grafting of amines onto UMCs, while the latter features monodentate hydroxide ligands, UMCs, and an initial CO₂ Qₜ of 110 kJ/mol. Both compounds exhibit large CO₂ uptake (112 cm³/g for PEI-MIL-101-100; 150.1 cm³/g for MAF-X27ox) and remarkable CO₂/N₂ selectivity (S = 609.1 and 262, respectively) under ambient conditions.

The incorporation of less basic LBSs onto bridging ligands can afford more reversible CO₂ binding (Qₜ values of 30-55 kJ/mol) as exemplified by NJFU-2a (BET surface area = 1223 m²/g), a ligand-to-axial pillared square grid based upon square paddlewheel MBBs and possessing uncoordinated pyrimidine groups. The confined pores and LBSs in NJFU-2a afford a moderately high Qₜ towards CO₂ of 38.2 kJ/mol along with moderate CO₂ uptake (59 cm³/g) and high CO₂/N₂ IAST selectivity (195.1 for a 15:85 mixture) at 298 K and 1 atm.

**MOMs with Saturated Metal Centers.** Among MOM platforms containing SMCs, zeolitic imidazolate frameworks (ZIFs) are perhaps the most widely studied. Based upon polyhedral cages formed from tetrahedral nodes and angular imidazolate linkers, these neutral frameworks exhibit zeolitic topologies and feature pores that are larger in scale than those of zeolites. Structure has been fine-tuned in ZIFs by variation of the organic functionality on the linker. While ZIFs are structurally diverse and have high thermochemical stability, they generally have low CO₂ uptake and selectivity vs. CH₄ and N₂. ZIF-
78 (BET surface area = 620 m²/g; Figure 1.8), the top-performing ZIF with respect to carbon capture, is decorated with nitro groups and exhibits a CO₂ uptake of ca. 47 cm³/g at 298 K and 1 atm. The CO₂/CH₄ and CO₂/N₂ relative uptakes and the CO₂/N₂ selectivity factor at 298 K for ZIF-78 (3.6, 11.8, and 29, respectively) are average among MOMs. The low selectivities of most ZIFs are indicative of the relatively weak CO₂-framework interactions that occur in MOMs with SMCs and exclusively organic linkers (excluding amine-functionalized MOMs).

**Figure 1.8.** a) The linkers present in [Zn(nbIm)(nIm)], ZIF-78: nIm = 2-nitroimidazole (top); nbIm = 5-nitrobenzimidazole (bottom); b) View of the large channels in the crystal structure of ZIF-78.

UTSA-16 (BET surface area = 628 m²/g) is a notable example of a highly selective MOM with SMCs and confined pores (3.3 x 5.4 Å²) in which single CO₂ molecules can form multiple binding contacts with the pore walls. Neutron powder diffraction measurements conducted upon CO₂-loaded UTSA-16 revealed that coordinated water molecules and uncoordinated carboxylic OH groups in this dia net each form contacts with the same CO₂ molecule. UTSA-16 exhibits one of the highest volumetric CO₂ uptakes among MOMs (160 cm³/cm³ at 296 K and 1 atm) and is remarkably selective towards CO₂/CH₄ (S_{IAST} = 34 for a 50:50 mixture) and CO₂/N₂ (S_{IAST} = 315 for a 15:85 mixture). However, removal of the coordinated water at elevated temperatures affords a nonporous compound.

**MOMs with Inorganic Anions as Pillars.** Motivated by the versatility of pillared dipyridyl square grids and the lack of carbon capture studies involving this platform, our group chose to explore the impact
of pore size upon the CO$_2$ uptake and selectivity of these MOMs. Accordingly, the previously reported SIFSIX-1-Cu and a new expanded variant based on a longer linker, [Cu(bpe)$_2$(SiF$_6$)] {(SIFSIX-4-Cu; bpe = 1,2-bis(4-pyridyl)ethylene)}, were evaluated via low pressure CO$_2$, CH$_4$, N$_2$, and H$_2$O isotherms at 298 K. SIFSIX-1-Cu and SIFSIX-4-Cu (Figure 1.9) exhibited BET surface areas of 1468 and 2718 m$^2$/g and effective window sizes of ca. 8 and 10.6 Å, respectively. Significantly, it was observed that the CO$_2$ uptake of SIFSIX-1-Cu at 1 atm (117.6 cm$^3$/g) surpassed that of zeolite 13X and most MOMs with UMCs. Further, the CH$_4$ uptake of SIFSIX-1-Cu at 1 atm was 10.1 times lower than the CO$_2$ uptake, suggesting that this MOM exhibited high CO$_2$/CH$_4$ selectivity under ambient conditions. The CO$_2$ uptake of SIFSIX-4-Cu at 1 atm (61.6 cm$^3$/g) was approximately half that of SIFSIX-1-Cu; however, the former maintained a high CO$_2$/CH$_4$ relative uptake (6.2) despite having nearly twice the surface area of the latter.

Figure 1.9. Pillared square grid MOMs: a) [Cu(bipy)$_2$(SiF$_6$)], SIFSIX-1-Cu; b) [Cu(bpe)$_2$(SiF$_6$)], SIFSIX-4-Cu.

The Q$_{st}$ of SIFSIX-1-Cu and SIFSIX-4-Cu towards CO$_2$ (27 and 21 kJ/mol, respectively) remained consistent at all loadings, reflecting the physisorption of CO$_2$ onto an energetically homogeneous surface. The Q$_{st}$ of SIFSIX-1-Cu is lower than the initial value of materials with high affinity UMCs such as Mg-dobdc (47 kJ/mol), MIL-100 (63 kJ/mol), and zeolite 13X (37.2 kJ/mol). IAST calculations for a 50:50 CO$_2$/CH$_4$ mixture afforded impressive selectivities for SIFSIX-
1-Cu (10) and SIFSIX-4-Cu (8) that remained steady over the full loading range. The CO$_2$ selectivity was hypothesized to originate from favorable electrostatic interactions between CO$_2$ and the SIFSIX pillars. It is noteworthy that DMOF-1, a MOM with comparable pore size that is based on organic pillars, exhibits a CO$_2$/CH$_4$ selectivity of only ca. 3.4 under similar conditions. Lastly, the water uptakes of SIFSIX-1-Cu (20.5 wt%) and SIFSIX-4-Cu (19 wt%) at 1 atm and 298 K were far lower than those of MOMs with UMCs such as MIL-101 (135 wt%) and HKUST-1 (52.0 wt%), implying that MOMs with SMCs may be less prone to a loss of separation performance under practical conditions.

The SIFSIX platform is representative of MOMs with SMCs that exploit physisorption to generate high CO$_2$ uptake in conjunction with poor uptake of CH$_4$, N$_2$, and H$_2$O. The superior CO$_2$ uptake, $Q_{st}$, and selectivity of SIFSIX-1-Cu vs. SIFSIX-4-Cu is attributable to the smaller pore size in the former, which facilitates a better overlap of the attractive potential fields of opposite pore walls. These MOMs satisfy other important criteria for practical utility in that they are activated at room temperature, are relatively water stable, and are built from low cost MBBs.

The impact of inorganic anion pillars on CO$_2$ affinity and selectivity was further illustrated by our group in a pillared square grid platform with the novel mmo topology. In contrast to the linear pillaring facilitated by SIFSIX, tetrahedral inorganic species such as CrO$_4^{2-}$ (CROFOUR), MoO$_4^{2-}$ (MOOFOUR), and WO$_4^{2-}$ (WOFOUR) may pillar square grids in an angular fashion. The prototypal mmo net consists of [M(bpe)$_2$]$^{2+}$ grids (M = Ni$^{2+}$, Co$^{2+}$) that are crosslinked by CROFOUR or MOOFOUR pillars to form a self-catenated 3D framework with SMCs. Each inorganic pillar in this platform projects two uncoordinated oxygen atoms into small open channels (Figure 1.10). MOOFOUR-1-Ni, CROFOUR-1-Ni, and WOFOUR-1-Ni are each permanently porous (Langmuir surface areas = 505, 456, and 315 m$^2$/g, respectively) and their carbon capture-related sorption properties were assessed via low pressure CO$_2$, CH$_4$, and N$_2$ isotherms at 298 K. All three MOMs exhibited sharp CO$_2$ uptake at low pressures (55, 51, and 43 cm$^3$/g at 1 atm for MOOFOUR-1-Ni, WOFOUR-1-Ni, and CROFOUR-1-Ni, respectively). The steep CO$_2$ uptake by these MOMs suggested a high binding affinity and the relatively poor CH$_4$ and N$_2$
adsorption implied a high selectivity towards CO$_2$. At 1 atm, the CH$_4$ uptakes of WOFOUR-1-Ni, MOOFOUR-1-Ni, and CROFOUR-1-Ni were 11.5, 11.5, and 13 cm$^3$/g, respectively, while the corresponding N$_2$ uptakes were 3.5, 4.5, and 4 cm$^3$/g. WOFOUR-1-Ni and MOOFOUR-1-Ni thus outperformed CROFOUR-1-Ni, suggesting that CO$_2$ was more strongly attracted to the WOFOUR and MOOFOUR pillars.

Figure 1.10. The prototypal mmo net, [M(bpe)$_2$(M’O$_4$)] (M = Ni$^{2+}$, Co$^{2+}$; M’ = Cr$^{6+}$, Mo$^{6+}$). The pillars lining the channels are shown in ball-and-stick mode.

The high binding affinity of WOFOUR-1-Ni, MOOFOUR-1-Ni and CROFOUR-1-Ni towards CO$_2$ was reflected by initial Q$_st$ values of 65.5, 56, and 50 kJ/mol, successively, which fell to 37, 33, and 27 kJ/mol at 1 atm. The Q$_st$ of all three variants at low loading surpasses that of materials with UMCs including Mg-MOF-74, HKUST-1, and zeolite 13X. Despite their modest CO$_2$ uptakes, WOFOUR-1-Ni, MOOFOUR-1-Ni, and CROFOUR-1-Ni possess among the highest IAST selectivities yet seen at low loading. WOFOUR-1-Ni exhibited the highest 10:90 CO$_2$/N$_2$ and 50:50 CO$_2$/CH$_4$ selectivities (2158 and 372, respectively) of the three analogues at zero loading and selectivities of 179 and 26 at 1 atm. The corresponding values for MOOFOUR-1-Ni were 1820 and 182, respectively, and decreased to 86 and 40 at 1 atm. The selectivities of CROFOUR-1-Ni were 1240 and 170 at zero loading and 195 and 25 at 1 atm.
Modeling studies of the mmo analogues identified a primary sorption site at which a single CO\textsubscript{2} molecule simultaneously formed contacts with the oxygen atoms of multiple pillars. The magnitude of the dipole induced in CO\textsubscript{2} at this site was found to be greatest in WOFOUR-1-Ni, followed by MOOFOUR-1-Ni and CROFOUR-1-Ni, suggesting that the strength of the CO\textsubscript{2}-framework interactions in this platform was proportional to the polarizability of the pillar metal (order of polarizability: W > Mo > Cr). Indeed, the order of selectivities towards CO\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4} at zero loading parallels the order of polarizability of the pillar metals in this platform. Finally, all three MOMs were highly robust in that the as-synthesized samples remained crystalline after immersion in water for months, boiling water for a day, or 0.1 M NaOH for a week.

Pillared square grids based upon dipyridyl linkers and inorganic anion pillars are clearly a versatile platform because each framework component (node metal, linker, pillar, and pillar metal) is amenable to substitution. Pore size can be controlled by the choice of linker, numerous node metals and pillars are available, and molecular recognition can be tuned via the choice of pillar in order to target specific adsorbates. As detailed in Chapters 2 and 3, we set about further tuning pore size and pore chemistry in this platform in order to explore the effect upon practically relevant CO\textsubscript{2} separations.

**Molecular Porous Materials**

In the vast majority of permanently porous materials (e.g. zeolites and MOMs), retention of the host structure upon guest removal is a result of strong, directional bonding between framework components. By comparison, porosity is less likely in compounds based upon discrete molecules because weaker intermolecular forces, e.g. hydrogen bonding and aromatic interactions, often do not preclude efficient crystal packing. Further, the guest molecules which may be enclathrated in such compounds can be critical to the structural integrity of the host lattice. While most inclusion compounds lack permanent porosity, molecular porous materials (MPMs) that exhibit reversible gas uptake have been known to exist for some time.\textsuperscript{62} Early examples include β-trans-[M(4-methylpyridine)\textsubscript{4}(SCN)\textsubscript{2}] (M = Co\textsuperscript{2+}, Ni\textsuperscript{2+}, Mn\textsuperscript{2+};
Figure 1.11 and Dianin’s compound (4-p-hydroxyphenyl-2,3,4-trimethylchroman), each of which reversibly adsorbs different gases and hydrocarbon vapors. Although the number of highly porous MPMs has risen significantly in recent years, MPMs that exhibit surface areas comparable to those of MOMs (>1000 m²/g) remain uncommon.

**Figure 1.11.** (a) The trans-[M(4-methylpyridine)₄(SCN)₂] (M = Co²⁺, Ni²⁺, Mn²⁺) complex; b) the crystal packing arrangement in β-trans-[M(4-methylpyridine)₄(SCN)₂]. A single MBB is illustrated in green.

### Intrinsic vs. Extrinsic Porosity

Porosity in MPMs can be classified as either intrinsic (within the molecules) or extrinsic (outside the molecules). Molecules with inherent cavities, including organic cage compounds, tert-butylcalix[4]arene, cucurbit[n]urils, metal-organic macrocycles, metal-organic squares (MOSs), metal-organic cubes (MOCs), and metal-organic polyhedra (MOPs), are intrinsically porous and may also pack in a manner which generates extrinsic porosity. In contrast, MPMs which possess only extrinsic porosity are composed of molecules which lack cavities. Porosity in these materials arises only as a result of inefficient crystal packing. MPMs with just extrinsic porosity are exemplified by triptycene-tris(benzimidazolone) (TTBI), phthalocyanine unsolvated nanoporous crystals (PUNCs), hydrogen-bonded organic frameworks (HOFs), supramolecular organic frameworks (SOFs), and certain linear dipeptides. Though robust MPMs with predictable structures are known, there are currently few studies
which focus on fine-tunable MPM platforms. However, recent examples of rationally constructed MPMs suggest that platforms based upon the judicious choice of MBB and supramolecular synthon are attainable. Among available synthons, hydrogen bonds are perhaps the most likely to sustain robust MPMs due to their relatively high strength and directionality. TTBI, MOSs, MOCs, and certain organic cage compounds are important from a design perspective and will be discussed below.

**Designable MPMs**

A key feature of a porous material platform is the modularity of its components. The modular and predictable assembly of a series of intrinsically porous organic [4+6] imine cages into binary cocrystals has been shown to be driven by chiral recognition. Three cage modules having various sizes and opposite chiralities were found to selectively cocrystallize with one another instead of with cages of the same chirality, affording a series of MPMs with BET surface areas ranging from 437 to 980 m$^2$/g. By contrast, the largest of the four cage modules preferred a homochiral packing arrangement and exhibited a surface area of 1333 m$^2$/g. Remarkably, *ab initio* density functional theory and lattice energy calculations correctly predicted the preferred chiral pairing and crystal structure, respectively, of each of the four MPMs. The so-called “lock-and-key” pairing of heterochiral cages can be viewed as a directional synthon with comparability to other interactions such as hydrogen bonding and the sextuplet aryl embrace.

TTBI is representative of organic, hydrogen-bonded MPMs which exhibit only extrinsic porosity. Upon noticing that most crystalline 4,5-disubstituted benzimidazolones form an infinite ribbon-like motif based on complementary hydrogen bonding, Mastalerz and colleagues reasoned that this synthon might be well suited to sustain a robust and porous net. TTBI was thus designed as a rigid, D$_{3h}$-symmetric, trifunctional MBB. Crystallization of TTBI revealed that two of the imidazolone groups in each MBB formed the expected infinite ribbon-like hydrogen-bonded motif, while the third formed a similar infinite synthon. The resultant net (Figure 1.12) contained large cylindrical channels (14.5 Å in width) and exhibited the highest BET surface area by far among MPMs with only extrinsic porosity (2796 m$^2$/g). The porosity of TTBI was maximized in part due to the absence of aromatic stacking interactions,
which would otherwise reduce the available surface area by promoting the close overlap of MBBs. An infinite ribbon-like hydrogen-bond synthon similar to that in TTBI has also been observed in HOF-1.\textsuperscript{74a,78}

![Figure 1.12](image.png)

**Figure 1.12.** a) Triptycene-tris(benzimidazolone), TTBI; b) An infinite ribbon-like hydrogen bond motif present in the crystal structure of TTBI; c) View of the large cylindrical channels in the structure of TTBI. One MBB is shown in space-filling mode.

TTBI exhibited the highest CO\textsubscript{2} uptake among all MPMs at 273 K (80.7 cm\textsuperscript{3}/g at 1 atm) at the time of publication, though this value is presumed to be significantly lower at 298 K. It is noteworthy that the CO\textsubscript{2} uptake of TTBI is considered to be modest with respect to that of top-performing MOMs, e.g. Mg-dobdc. The moderate CO\textsubscript{2} uptake and low CO\textsubscript{2}/CH\textsubscript{4} relative uptake (relative uptake = 4 at 273 K and 1 atm) of TTBI are attributable to its large pores and exclusively organic composition.

MOC-2 [In\textsubscript{8}(HImDC)\textsubscript{12}] (MOC-2; ImDC = 4,5-imidazoledicarboxylate) represents another example of an MPM that is based on a predictable and extensive network of complementary hydrogen bonds.\textsuperscript{70} The intrinsically porous cubes in MOC-2 contain In\textsuperscript{3+} SMCs as vertices which are bridged by linear, bis-chelating ImDC linkers. Each MOC serves as a node and is decorated with 24 uncoordinated oxygen atoms (3 at each vertex). A total of 24 hydrogen bonds exist between each cube and 8 neighboring cubes to yield a network with the zeolitic aeo topology (Figure 1.13). The topology of MOC-2 is rationalizable given that cubes, i.e. double 4-membered rings, have long been known as composite
building units in zeolites. Two types of channels exist in MOC-2 and the material exhibits one of the highest Langmuir surface areas among MPMs (1420 m$^2$/g). The water stability of MOC-2 reflects the robustness of the hydrogen-bonded network. MOCs and metal-organic squares (MOSs) are also known to form porous hydrogen-bonded nets based upon other zeolitic topologies, e.g. ast, gis, and rho. The cases of TTBI and MOCs/MOSs demonstrate that the use of established design principles (i.e. the reasoned choice of MBB geometry and decoration) can yield robust, predictable, and highly porous hydrogen-bonded networks.

![Image](image1)

**Figure 1.13.** a) Complementary hydrogen bonding between the corners of neighboring [In$_8$(HImDC)$_{12}$] cubes in MOC-2. Carboxylic hydrogen atoms are not shown; b) The packing arrangement of cubes in MOC-2. The central MBB is shown in space-filling mode.

**Selective CO$_2$ Adsorption in MPMs**

Thus far there have been few studies of selective CO$_2$ adsorption in MPMs compared to the number of such studies involving MOMs. Reports have shown that MPMs are capable of exhibiting the necessary traits of a carbon capture material: generous CO$_2$ uptake; a $Q_{st}$ towards CO$_2$ of $>40$ kJ/mol; selectivity towards CO$_2$ vs. CH$_4$ and N$_2$ under ambient conditions; thermal and water stability. However, the task of identifying a single MPM with all of these attributes persists. It should be noted that the carbon
capture suitability of MPMs can be ambiguous when: 1) gas adsorption isotherms are collected at temperatures below 298 K; 2) adsorption selectivity is estimated using disparate methods (e.g. relative uptake, Henry slope ratio, IAST); 3) surface area is unreported; 4) phase transformation upon desolvation in MPMs with weak intermolecular forces complicates the elucidation of structure-property relationships. The selective CO$_2$ adsorption properties of a range of representative MPMs are discussed herein.

P5-SOF, an MPM composed of intrinsically porous perhydroxyl-pillar[5]arenes, exhibits moderate CO$_2$ uptake (45 cm$^3$/g at 298 K and 1 atm) and is predicted to be highly selective towards CO$_2$ vs. CH$_4$ and N$_2$. Each macrocycle contains 5 hydroquinone units and is decorated with 10 hydroxyl groups. While the CO$_2$/CH$_4$ and CO$_2$/N$_2$ relative uptakes (3.7 and 5.7, respectively) and the CO$_2$/N$_2$ selectivity factor (S = 23) of P5-SOF are rather low, a sharp uptake of CO$_2$ (ca. 30 cm$^3$/g at 0.15 atm) and a low uptake of CH$_4$ and N$_2$ at low pressures suggest that this MPM is highly selective towards CO$_2$ (Henry slope ratios: CO$_2$/CH$_4$ = 375; CO$_2$/N$_2$ = 339). The CO$_2$ Q$_a$ of P5-SOF (as high as 44 kJ/mol) is among the highest observed in MPMs and likely arises from CO$_2$-hydroxyl interactions. Due to the lack of single crystal X-ray data, the factors which contribute to the selectivity of P5-SOF (e.g. pore size) are uncertain.

Cucurbit[n]urils, macrocycles decorated with carbonyl groups, are well known among MPMs for their favorable CO$_2$ adsorption profiles. A crystalline form of cucurbit[6]uril (Form II; BET surface area = 276 m$^2$/g) exhibits the highest known CO$_2$ uptake at 298 K among MPMs (76 cm$^3$/g at 1 atm) and one of the highest CO$_2$/N$_2$ selectivities (relative uptake = 30.4; S = 92). The high Q$_a$ towards CO$_2$ (ca. 32.5 kJ/mol at all loadings) of another crystal form of cucurbit[6]uril (Form I; Figure 1.14) with extrinsic channels was attributed to multiple binding contacts that were observed in the X-ray structure of the CO$_2$-loaded material at 90 K, including C-H…OCO (average distance = 2.575 Å) and carbonyl-CO$_2$ interactions. An amorphous form of cucurbit[7]uril with a BET surface area of 293 m$^2$/g exhibits one of the highest binding affinities towards CO$_2$ among MPMs (Q$_a$ = 40 kJ/mol at zero loading) as well as moderate CO$_2$ uptake (50 cm$^3$/g) and a high CO$_2$/CH$_4$ relative uptake (8.3).
HOF-8d, an extensively porous hydrogen-bonded organic framework based on N1,N3,N5-tris(4-pyridyl)benzene-1,3,5-tricarboxamide (TPBTC), also features significant CO$_2$ uptake (57.3 cm$^3$/g at 298 K and 1 atm) and highly selective adsorption of CO$_2$ vs. N$_2$ (relative uptake $>$57.3; S $>$112.5) under ambient conditions.$^{74b}$ The as-synthesized form of HOF-8d, HOF-8, consists of hydrogen-bonded sheets of TPBTC (6 hydrogen bonds per molecule; Figure 1.15) which stack in the third dimension to form channels with dimensions of 6.8 × 4.5 Å$^2$. A minor phase change may occur upon desolvation of HOF-8 and thus the origins of the sharp CO$_2$ uptake and high CO$_2$ selectivity of HOF-8d are uncertain. Though the size-selective adsorption of CO$_2$ vs. N$_2$ cannot be ruled out, the acylamide groups present in HOF-8d are likely to contribute to the favorable CO$_2$ uptake and selectivity. Notably, HOF-8 is insoluble in water and stable at temperatures up to 240°C.
Figure 1.15. a) N1,N3,N5-tris(4-pyridyl)benzene-1,3,5-tricarboxamide, TPBTC, the MBB comprising HOF-8; b) A hydrogen-bonded layer in the crystal structure of HOF-8. One MBB is shown in green.

Among organic cage compounds, the highest CO$_2$ uptake under ambient conditions (74 cm$^3$/g at 298 K and 1 atm) was observed in a hydroxyl-decorated cage formed via a [2+3] imine condensation (compound 3b in reference). This MPM adsorbs a negligible amount of N$_2$ at 77 K (BET surface area = 30 m$^2$/g) but exhibits a high relative CO$_2$/CH$_4$ relative uptake (9.7) and the linear shape of the CO$_2$ adsorption isotherm suggests a moderate Q$_d$ towards CO$_2$. The crystal structure of solvated 3b revealed that the cages interact via CH⋯O, CH⋯π, and π⋯π contacts, whereas the hydroxyl groups engage in intramolecular OH⋯N hydrogen bonds. As has been observed in similar organic cages, the structure of the desolvated compound was unknown due to a phase change that occurred upon activation. Several other organic imine cages with surface areas ranging from 437 to 1377 m$^2$/g exhibit low to moderate CO$_2$ capacities at 1 atm (47-75.5 cm$^3$/g) as well as low CO$_2$/CH$_4$ relative uptakes (1.8-5.1).

The assembly of rigid MBBs decorated with groups capable of directional and complementary hydrogen bonding has been established as a viable path towards robust MPMs. The coordination of appropriately decorated ligands to metal ions can be employed to create MBBs with a well-defined geometry and numerous hydrogen bonding synthons are available for linking the MBBs into
a network.\textsuperscript{85} In this context, metal-adenine complexes are known to form stable hydrogen-bonded MPMs. For instance, paddlewheel-shaped \([\text{Cu}_2(\text{ade})_4\text{Cl}_2]^2+\) (ade = adenine) complexes were shown to crystallize with Cl\(^-\) counterions into an MPM sustained by ade-ade hydrogen bonds and ade-Cl\(^-\) interactions, \([\text{Cu}_2(\text{ade})_4\text{Cl}_2]\text{Cl}_2\) (Figure 1.16).\textsuperscript{86}

![Figure 1.16](image)

**Figure 1.16.** a) The paddlewheel complex present in \([\text{Cu}_2(\text{ade})_4\text{Cl}_2]\text{Cl}_2\), MPM-1-Cl; b) View of the channels in the crystal structure of MPM-1-Cl. Chloride ligands are illustrated in green.

Each paddlewheel MBB in \([\text{Cu}_2(\text{ade})_4\text{Cl}_2]\text{Cl}_2\) participates in 12 contacts with neighboring network components and contains two axial Cl ligands that point into hourglass-shaped channels (channel width ~ 6.2 Å). Hereafter referred to as MPM-1-Cl, this network maintains its structural integrity at temperatures up to 240°C. MPM-1-Cl offers the potential for fine-tuning of pore functionality via substitution of the axial ligands which line the channels. Our observation that inorganic anions can promote high CO\(_2\) selectivity motivated us to explore them as substitutes for the axial Cl ligands in MPM-1-Cl. Accordingly, replacing Cl with TIFSIX produced a novel variant, MPM-1-TIFSIX, based upon a closely related hydrogen-bonding network. The large enhancements in CO\(_2\) capacity, CO\(_2\) selectivity, and stability resulting from axial ligand substitution in this platform are detailed in Chapter 4.
References

4. a) Batten, S. R.; Nev...

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CHAPTER TWO:
Enhancement of CO$_2$ Selectivity in a Pillared pcu MOM Platform through Pillar Substitution

Note to Reader
Portions of this chapter were previously published in *Chem. Commun.* 2013, 49, 1606-1608 and have been reproduced with the permission of The Royal Society of Chemistry. Computer modeling and IAST calculations were performed by the group of Dr. Brian Space.

Introduction
Our increasing dependence on carbon based fuels and the impact of such fuels on climate change have spurred interest in developing efficient carbon capture technologies. CO$_2$/CH$_4$ and CO$_2$/N$_2$ separations, aimed at natural gas purification and post-combustion carbon capture, respectively, have therefore become a primary research objective in the field of porous metal-organic materials, MOMs.$^1$ The potential for high permanent porosity coupled with structural tunability means that MOMs$^2$ are particularly suited to elucidate the structural features that promote selective CO$_2$ adsorption. MOM platforms, families of related MOMs with modular components, are applicable in this context as they facilitate tailoring of pore size and functionality to selectively target a chosen adsorbate.

Structural tuning in MOM platforms can be accomplished through variation of framework composition, e.g. metal nodes, linkers or, if appropriate, extra-framework ions. In the context of adsorption, platforms can be conveniently divided into those with unsaturated metal centers (UMCs) and those with saturated metal centers (SMCs). Versatile platforms containing UMCs include those sustained by [M$_2$(O$_2$CR)$_4$] square paddlewheels (e.g. *rht*$_3$ and *tbo*$_4$ nets), [M$_3$(µ$_3$-O)(O$_2$CR)$_6$] trigonal prisms (e.g.
MIL-100/101),\textsuperscript{5} and infinite $[\text{M}_2\text{O}_5(\text{O}_2\text{CR})_2]$ rods (e.g. M-dobdc).\textsuperscript{6} Platforms with SMCs include zeolitic imidazolate frameworks (ZIFs)\textsuperscript{7} and pillared sheets,\textsuperscript{8} of which pillared dipyridyl and pillared dicarboxylate square grids are subclasses. Pillared square grids based upon octahedral nodes and two different linkers are readily fine-tunable; one linker generates the grids, while the other (the pillar) crosslinks the grids through axial metal sites to form a pecu net with square channels. Early reports of pillared square grid MOMs include those based upon SiF$_6^{2-}$ pillars, 4,4’-bipyridine (bipy) linkers, and either Zn(II)$^{8a}$ or Cu(II)$^{8b}$ nodes.

MOMs with UMCs such as Mg-dobdc can bind CO$_2$ with high selectivity via chemisorption, but the isosteric heat of adsorption ($Q_{st}$) often drops sharply after the UMCs become saturated. In addition, water, which composes ca. 6% of flue gas, strongly competes with CO$_2$ for UMCs and may thereby diminish separation performance in a humid environment.\textsuperscript{9} MOMs with SMCs that can achieve selective adsorption without reliance on metal-sorbate coordination bonding are an appealing alternative which can afford the benefit of lower activation and regeneration temperatures.

Recently we reported that a previously known MOM$^{8b}$ containing SiF$_6^{2-}$ pillars, $[\text{Cu(bipy)}_2(\text{SiF}_6)_n]$, SIFSIX-1-Cu, displays high CO$_2$ uptake and selectivity at all loadings.\textsuperscript{10} An expanded variant, $[\text{Cu(bpe)}_2\text{SiF}_6]_n$ (bpe = 1,2-bis(4-pyridyl)ethylene), also exhibits high CO$_2$ selectivity despite having significantly larger pores and surface area. Importantly, both compounds exhibit considerably lower H$_2$O uptake compared to MOMs with UMCs. These observations prompted us to examine the effect of other hexafluorometalate ($\text{MF}_6^{2-}$) pillars on CO$_2$ adsorption, as we reasoned that variation of the pillar metal would impact the electrostatics that drive molecular recognition towards CO$_2$.

**Structures**

Herein we report the synthesis, structure, and gas adsorption properties of two variants of SIFSIX-1-Cu, $[\text{Cu(bipy)}_2\text{TiF}_6]_n$ (TIFSIX-1-Cu)$^{11}$ and $[\text{Cu(bipy)}_2\text{SnF}_6]_n$ (SNIFSIX-1-Cu), the first examples of crystallographically characterized 3D nets based upon the respective pillars. Room
temperature diffusion of a methanol solution of bipy into an ethylene glycol solution of Cu(NO$_3$)$_2$·2.5H$_2$O and (NH$_4$)$_2$MF$_6$ (M = Ti$^{4+}$, Sn$^{4+}$) afforded purple plates of TIFSIX-1-Cu and SNIFSIX-1-Cu in 90.2 and 93.8% yield, respectively (see Appendix A). Single crystal X-ray diffraction (Appendix A, Table A1) revealed that TIFSIX-1-Cu and SNIFSIX-1-Cu are isostructural to SIFSIX-1-Cu, all crystallizing in $P4/mmm$ as a pce net with Cu$^{2+}$ cations bonded to 4 equatorial bipy linkers and pillared in the axial direction by TiF$_6^{2-}$ or SnF$_6^{2-}$ moieties. PXRD patterns of as-synthesized TIFSIX-1-Cu and SNIFSIX-1-Cu match those calculated from single crystal data (Appendix A, Figs. A1 and A2).

The bipy linkers and nodes in TIFSIX-1-Cu and SNIFSIX-1-Cu form 2D square grids$^{11-12}$ parallel to the $a$ and $b$ axes which are pillared in the third dimension along the $c$ axis (Fig. 2.1) to form a neutral framework with ca. 8 Å x 8 Å square channels (accounting for van der Waals radii). The Cu-bipy-Cu distance in TIFSIX-1-Cu and SNIFSIX-1-Cu is nearly equal to that in SIFSIX-1-Cu (11.10, 11.12, and 11.11 Å, respectively) whereas the Cu-pillar-Cu distances increase slightly with the size of the pillar metal (8.41, 8.63, and 8.11 Å, respectively).

![Figure 2.1](image)

**Figure 2.1.** The crystal structure of TIFSIX-1-Cu viewed along the $c$ axis (left) and $a$ axis (right).

Thus, the large channels of SIFSIX-1-Cu, TIFSIX-1-Cu and SNIFSIX-1-Cu have nearly equal dimensions while the intersheet distance increases only marginally as the pillar metal increases in size. The isostructural nature of SIFSIX-1-Cu, TIFSIX-1-Cu, and SNIFSIX-1-Cu enabled us to investigate the
effects of the pillar on CO₂ capacity/selectivity and trace any variation in these properties to the electrostatic nature of the pillars.

**Gas Adsorption Properties**

Solvent-exchanged samples of TIFSIX-1-Cu and SNIFSIX-1-Cu were evacuated at room temperature and N₂ isotherms were recorded at 77 K, revealing reversible type-I adsorption corresponding to BET surface areas of 1690 and 1523 m²/g, respectively (Appendix A, Figs. A3 and A4). Interestingly, the gravimetric surface areas of TIFSIX-1-Cu and SNIFSIX-1-Cu surpass that of SIFSIX-1-Cu although they contain heavier pillar metals.

To evaluate the CO₂ separation performance of TIFSIX-1-Cu and SNIFSIX-1-Cu, single-component CO₂, CH₄, and N₂ isotherms were collected at 298 K up to 1 atm (Fig. 2.2). A summary of sorption data along with a comparison to SIFSIX-1-Cu is presented in Table A2 (Appendix A). At 1 atm, the CO₂ uptakes of TIFSIX-1-Cu and SNIFSIX-1-Cu were measured to be 106.3 and 93.9 cm³/g, respectively.

![Figure 2.2](image_url)  
*Figure 2.2. CO₂, CH₄, and N₂ isotherms at 298 K for TIFSIX-1-Cu (a) and SNIFSIX-1-Cu (b).*
A literature survey reveals few MOMs with higher gravimetric CO$_2$ uptake than that of TIFSIX-1-Cu under these conditions (Appendix A, Table A3). Of these MOMs, SIFSIX-1-Cu is the only one based upon SMCs. At 0.15 atm, the CO$_2$ uptakes of TIFSIX-1-Cu and SNIFSIX-1-Cu were 20.4 and 18.0 cm$^3$/g, respectively. The uptake exhibited by TIFSIX-1-Cu at this pressure is superior to that exhibited by SIFSIX-1-Cu (18.1 cm$^3$/g), reflecting stronger sorbent-CO$_2$ interaction at low loading upon substitution of Si$^{4+}$ with Ti$^{4+}$. The $Q_{st}$ towards CO$_2$ for each compound was determined by applying the virial method to the isotherms at 273 and 298 K (Appendix A, Fig. A5). Both MOMs exhibit a $Q_{st}$ of ca. 26.5 kJ/mol at zero loading, which is nearly the same as SIFSIX-1-Cu and is high with respect to MOMs without UMCs or amine functionality. As loading increases, the $Q_{st}$ of TIFSIX-1-Cu surpasses that of SIFSIX-1-Cu, which presumably reflects stronger interaction between CO$_2$ and the TiF$_6^{2-}$ pillars.

Similarly to SIFSIX-1-Cu, the uptakes of CH$_4$ and N$_2$ in TIFSIX-1-Cu and SNIFSIX-1-Cu are substantially lower than the respective CO$_2$ uptakes (CH$_4$: 12.4 and 10.8 cm$^3$/g; N$_2$: 4.5 and 5.0 cm$^3$/g), which prompted us to compare their predicted separation performance in terms of CO$_2$/CH$_4$ relative uptake at 1 atm. The CO$_2$/CH$_4$ relative uptakes of TIFSIX-1-Cu and SNIFSIX-1-Cu, defined by the CO$_2$/CH$_4$ uptake ratio at 1 atm and 298 K, are 8.6 and 8.7, respectively.

These values are slightly below that of SIFSIX-1-Cu (9.9) but greater than the vast majority of MOMs. Upon plotting CO$_2$/CH$_4$ relative uptake against CO$_2$ capacity we found that SIFSIX-1-Cu, TIFSIX-1-Cu and SNIFSIX-1-Cu lie at the top of both categories among reported MOMs (Fig. 2.3 and Appendix A, Table A4). In other words, high CO$_2$/CH$_4$ relative uptake does not compromise CO$_2$ capacity in this platform. We have also modeled interactions between CO$_2$ and the pillars (Appendix A, Figs. A6-A9) and conducted a series of IAST$^{13}$ calculations (Appendix A, Figs. A10 and A11). Grand Canonical Monte Carlo simulations of equilibrium CO$_2$ adsorption in each of the three compounds reveal that the primary adsorption site, based upon the distance and the dipole induced in CO$_2$, is located at the pillar equatorial fluorine atoms. Simulations also confirm that this interaction is stronger in TIFSIX-1-Cu than in SIFSIX-1-Cu owing to the higher polarizability of Ti$^{4+}$ relative to Si$^{4+}$. The IAST calculations
predict the 50:50 CO$_2$/CH$_4$ and 10:90 CO$_2$/N$_2$ mixture selectivities of SIFSIX-1-Cu, TIFSIX-1-Cu and SNIIFSIX-1-Cu at 298 K from the pure component isotherms. The trend in CO$_2$/CH$_4$ IAST selectivities (Appendix A, Fig. A10) differs from the trend in relative uptakes, with TIFSIX-1-Cu and SNIIFSIX-1-Cu exhibiting greater selectivity than SIFSIX-1-Cu over the full pressure range. At 1 atm, SNIIFSIX-1-Cu was calculated as having the highest selectivity (12.1), followed by TIFSIX-1-Cu (11.2) and SIFSIX-1-Cu (10.6). The selectivity of SNIIFSIX-1-Cu under these conditions supersedes that of most MOMs with SMCs including all ZIFs, MOF-5, UMCM-1, MIL-53(Al), and MOF-177 as well as MOMs with UMCs such as HKUST-1 and MIL-101(Cr) (Appendix A, Table A5). [Zn(bdc)(dabco)$_{0.5}$] (DMOF-1), a structurally related MOM with similar pore size and organic pillars, has a selectivity of ca. 3.4. MOMs with SMCs which have higher selectivity than SNIIFSIX-1-Cu include UTSA-49a (ca. 96), NH$_2$-MIL-53(Al)-vnp (ca. 45), MOOFOUR-1-Ni (ca. 40), and UTSA-16 (ca. 36). The pores of these MOMs are lined with tetrazole, amine, MoO$_4^{2-}$, and H$_2$O moieties, respectively, and each material has pore dimensions which may promote the size-selective adsorption of CH$_4$ (3.6 Å x 4.0 Å for UTSA-49a and 3.3 Å x 5.4 Å for UTSA-16).

Figure 2.3. Comparison of CO$_2$/CH$_4$ relative uptake and gravimetric CO$_2$ uptake of MOMs in the literature (green) to those reported herein (pink).
The CO₂/N₂ IAST selectivity calculations (Appendix A, Fig. A11) predict that TIFSIX-1-Cu has significantly higher CO₂/N₂ separation capability than SIFSIX-1-Cu up to 1 atm. At 1 atm, the sequence of selectivities is TIFSIX-1-Cu > SIFSIX-1-Cu > SNIFSIX-1-Cu (29.5, 26.5, and 21.9, respectively). As with the enhancements in 0.15 atm CO₂ uptake and Qₘ, the increase in CO₂/N₂ selectivity in TIFSIX-1-Cu relative to SIFSIX-1-Cu is attributable to replacement of SiF₆²⁻ by TiF₆²⁻.

Conclusions

In summary, we have detailed herein the modification of a long-known MOM platform to generate two variants, TIFSIX-1-Cu and SNIFSIX-1-Cu, representing the first crystallographically characterized 3D nets containing TiF₆²⁻ and SnF₆²⁻ moieties, respectively. Like SIFSIX-1-Cu, these MOMs are synthesized in a single step from commercially available starting materials, are activated at room temperature, and exhibit high CO₂ capacity and selectivity under ambient conditions relative to MOMs with SMCs. All three variants have remarkable CO₂/CH₄ relative uptake and CO₂ uptake at 298 K and 1 atm. Furthermore, although TIFSIX-1-Cu and SNIFSIX-1-Cu exceed SIFSIX-1-Cu in surface area, tuning of the pillaring functionality has led to the enhancement of CO₂/CH₄ and/or CO₂/N₂ selectivity. Modeling studies support the experimental finding that substitution of Si⁴⁺ with Ti⁴⁺ in the pillar enhances the sorbent-CO₂ interaction. This study implies that certain inorganic anions can be comparable to UMCs in terms of their affinity for CO₂ but without some of the drawbacks associated with UMCs (i.e. the formation of coordination bonds, which often entails heating for adsorbent regeneration). Indeed, coupling high CO₂ capacity and selectivity with a more reversible adsorption mechanism represents a promising alternative to MOMs that rely on adsorption onto UMCs.

References


CHAPTER THREE:

Porous Materials with Optimal Adsorption Thermodynamics and Kinetics for CO₂ Separation

Note to Reader

Portions of this chapter have been previously published in Nugent, P.; Belmabkhout, Y.; Burd, S. D.; Cairns, A. J.; Luebke, R.; Forrest, K.; Pham, T.; Ma, S.; Space, B.; Wojtas, L.; Eddaoudi, M.; Zaworotko, M. J. Nature 2013, 495, 80-84 and are reproduced with the permission of Nature Publishing Group. Materials synthesis was conducted by P.N. and S.D.B.; X-ray crystallography conducted by L.W., R.L., and P.N.; Low pressure single-gas adsorption conducted by P.N., S.D.B., Y.B., and A.J.C.; High pressure single-gas adsorption, low pressure gas mixture adsorption, adsorption kinetics, column breakthrough, and IAST calculations conducted by Y.B.; Computer modeling conducted by K.F. and T.P.

Introduction

The energy costs associated with the separation and purification of industrial commodities such as gases, fine chemicals, and fresh water currently represent ca. 15% of global energy production, and the demand for such commodities is projected to triple by 2050 (ref. 1). The challenge of developing effective separation and purification technologies that have much smaller energy footprints is greater for CO₂ than for other gases; in addition to its involvement in climate change, CO₂ is an impurity in natural gas, biogas (natural gas produced from biomass), syngas (CO/H₂, the main source of hydrogen in refineries) and many other gas streams. In the context of porous crystalline materials that can exploit both equilibrium and kinetic selectivity, size selectivity and targeted molecular recognition are attractive characteristics for CO₂ separation and capture, as exemplified by zeolites 5A and 13X (ref. 2), as well as metal–organic
Here we report that a crystal engineering\textsuperscript{3b} or reticular chemistry\textsuperscript{3c,3d} strategy that controls pore functionality and size in a series of MOMs with SMCs and periodically arrayed hexafluorosilicate (SiF\textsubscript{6}\textsuperscript{2-}) anions enables a ‘sweet spot’ of kinetics and thermodynamics that offers a high volumetric uptake of CO\textsubscript{2} at low partial pressure (<0.15 bar). Most importantly, such MOMs offer an unprecedented CO\textsubscript{2} sorption selectivity vs. N\textsubscript{2}, H\textsubscript{2}, and CH\textsubscript{4}, even in the presence of moisture. These MOMs are therefore relevant to CO\textsubscript{2} separation in the context of post-combustion (flue gas, CO\textsubscript{2}/N\textsubscript{2}), pre-combustion (shifted synthesis gas stream, CO\textsubscript{2}/H\textsubscript{2}) and natural gas upgrading (natural gas clean-up, CO\textsubscript{2}/CH\textsubscript{4}).

Porous materials with UMCs\textsuperscript{4} or organic amines that chemically interact with CO\textsubscript{2} enhance selectivity for CO\textsubscript{2} in the presence of other gases. However, there are drawbacks: high energy costs associated with activation, regeneration and recycling of the sorbent material, especially for amines;\textsuperscript{5} competition with water vapor, especially for UMCs;\textsuperscript{6} and selectivity tends to monotonically decrease with increased loading of sorbate. Consequently, there remains a need for sorbents with favorable CO\textsubscript{2} sorption kinetics and thermodynamics over a wide range of CO\textsubscript{2} loading that would permit efficient CO\textsubscript{2} capture with low regeneration costs. MOMs are attractive in this context because they are inherently modular—that is, they consist of metals or metal clusters (‘nodes’ or ‘molecular building blocks’) coordinated to multifunctional organic ligands (‘linkers’) — and they offer extra-large surface areas, up to 7000 m\textsuperscript{2}/g (ref. 3g). However, although extra-large surface area facilitates high gravimetric uptake of gases at low temperature and/or high pressure, it is not necessarily conducive to efficient separations under practical conditions. In this chapter we address how to optimize the thermodynamics and kinetics of gas adsorption through a class of MOMs that is amenable to crystal engineering or isoreticular chemistry in a manner that facilitates precise control over pore size and functionality: namely, pillared square grids, 2D nets based on linked metal nodes that are pillared via SiF\textsubscript{6}\textsuperscript{2-} anions (‘SIFSIX’) in the third dimension to form 3D nets with primitive-cubic (\textbf{pccu}) topology.\textsuperscript{7}
[Cu(bipy)$_2$(SiF$_6$)$_n$, a prototypal pcu net that remains one of the best sorbents for CH$_4$ as measured by volumetric uptake,$^8$ exhibits highly selective CO$_2$ uptake vs. both CH$_4$ and N$_2$ at 1 bar and 298 K (ref. 9). In the absence of UMCs or amine groups, we attributed this behavior to favorable interactions between CO$_2$ and SIFSIX. This compound, SIFSIX-1-Cu, exhibits 1D square channels (pore size 9.54 Å; here and throughout this chapter, pore sizes are given as diagonal dimensions) aligned by a periodic array of SIFSIX pillars, and is prototypical for a class of compounds that is amenable to pore-size tuning. In this chapter we report the synthesis, structure, and sorption properties of three variants of SIFSIX-1-Cu with expanded and contracted pore sizes.

**Structures**

Reaction of 4,4’-dipyridylacetylene, dpa (ref. 10), with CuSiF$_6$ afforded purple rod-shaped crystals of [Cu(dpa)$_2$(SiF$_6$)$_n$, which we refer to as SIFSIX-2-Cu (see Appendix B for synthetic and crystallographic details for this and other compounds reported in this chapter). SIFSIX-2-Cu forms the expected pcu net with square channels of pore dimensions 13.05 Å (Fig. 3.1a). The interpenetrated polymorph, SIFSIX-2-Cu-i (Fig. 3.1b), is composed of doubly interpenetrated nets that are isostructural to the nets in SIFSIX-2-Cu. The independent nets are staggered with respect to one another, affording 5.15 Å pores (Fig. 3.1b). The isoreticular MOM based on pyrazine (pyr), SIFSIX-3-Zn, [Zn(pyr)$_2$(SiF$_6$)$_n$, was prepared according to published procedures$^{11}$ and is also a pcu net which encloses 3.84 Å channels (Fig. 3.1c). Pore sizes in this series therefore range from ultramicroporous to nanoporous. Bulk purity was confirmed using powder X-ray diffraction (PXRD) patterns (Appendix B, Figs. B1–B3).

**Gas Adsorption and Separation Properties, Recyclability, and Separation Performance under Humid Conditions**

Activation of SIFSIX-2-Cu and SIFSIX-2-Cu-i (evacuation at 298 K for 12 h) afforded BET apparent surface areas of 3140 and 735 m$^2$/g, respectively (corresponding Langmuir values, 3370 and 821
m²/g), from N₂ adsorption isotherms at 77 K. Micropore volumes are in good agreement with corresponding theoretical values (Appendix B, Fig. B4 and Table B3). SIFSIX-3-Zn adsorbs minimal amounts of N₂ at 77 K and thus its surface area (250 m²/g) was determined from the CO₂ isotherm collected at 298 K (ref. 12).

Figure 3.1. The variable pore size channel structures of SIFSIX-2-Cu, SIFSIX-2-Cu-i and SIFSIX-3-Zn. a) SIFSIX-2-Cu; pore size 13.05 Å, BET surface area (N₂) 3,140 m²/g; b) SIFSIX-2-Cu-i; pore size 5.15 Å, BET surface area (N₂) 735 m²/g; c) SIFSIX-3-Zn; pore size 3.84 Å, surface area (determined from CO₂ isotherm) 250 m²/g. Color code: C (grey), N (blue), Si (yellow), F (light blue), H (white). Guest molecules are omitted for clarity. The green net represents the interpenetrated net in SIFSIX-2-Cu-i. The linker present in SIFSIX-2-Cu and SIFSIX-2-Cu-i is 4,4’-dipyridylacetylene (dpa) whereas that in SIFSIX-3-Zn is pyrazine (pyr).

Low pressure CO₂, CH₄ and N₂ sorption data were collected at 298 K (Table 3.1 and Appendix B, Fig. B5a). SIFSIX-2-Cu exhibited CO₂ uptake of 41.4 cm³/g (equivalent to 1.84 mmol/g or 81.3 mg/g) at 298 K and 1 bar, but its denser polymorph, SIFSIX-2-Cu-i, exhibited substantially higher values of 121.2 cm³/g (5.41 mmol/g, 238 mg/g). Such behavior has also been observed in the context of hydrogen adsorption.¹³ A review of the literature reveals that the gravimetric CO₂ uptake of SIFSIX-2-Cu-i at 298 K and 1 bar is among the highest yet reported in the context of MOMs {e.g. Mg-dobdc (ref. 4), Co-dobdc (ref. 4), MIL-101 (ref. 14), [Cu(Me-4py-trz-ia)] (ref. 15), partially hydrated HKUST-1 (ref. 16), and Cu-TDPAT (ref. 17)}. Notably, the above-mentioned benchmark MOMs possess higher surface area, are less dense than SIFSIX-2-Cu-i, and contain UMCs. Volumetric CO₂ uptake of SIFSIX-2-Cu-i at atmospheric pressure approaches that of Mg-dobdc (151 vs. 162 v/v). Ideal adsorbed solution theory (IAST)¹⁸
calculations indicate binary gas adsorption selectivity (Appendix B, Fig. B5b) under practically relevant conditions (298 K; CH₄ and N₂ mole fractions equal to 0.5 and 0.9, respectively) to be dramatically higher for SIFSIX-2-Cu-i than SIFSIX-2-Cu for both CO₂/CH₄ (33 vs. 5.3) and CO₂/N₂ (140 vs. 13.7). These findings agree with the CO₂/CH₄ (51) and CO₂/N₂ (72) selectivities determined experimentally for SIFSIX-2-Cu-i using column breakthrough tests, a technique that determines the necessary time for a given volume of a gas to pass through a given sorbent bed column (Appendix B, Fig. B6). To the best of our knowledge, the CO₂/CH₄ and CO₂/N₂ IAST selectivities exhibited by SIFSIX-2-Cu-i are among the highest yet reported for a MOM without UMCs or amino groups. We attribute these observations to the enhanced Qₘ of SIFSIX-2-Cu-i vs. SIFSIX-2-Cu (45% higher at minimum loading, 71.5% greater at 2.8 mmol/g; Appendix B, Fig. B5c). This increase is presumably attributable to better overlap of attractive potential fields of opposite walls in the relatively narrower pores of SIFSIX-2-Cu-i. SIFSIX-2-Cu-i is particularly suitable for CO₂ separation from syngas, as shown by its selectivity (240) for CO₂ vs. H₂ in a 30:70 CO₂/H₂ mixture, and as determined from breakthrough experiments (Appendix B, Fig. B6c).

The heart of pressure- and temperature-swing adsorption (PSA and TSA) processes for CO₂ removal is the adsorbent bed: a recent study projected that a CO₂/N₂ selectivity of 500 combined with a capacity of 2-4 mmol/g for a 10:90 CO₂/N₂ mixture would be required for practical utility (Appendix B, Fig. B7). Figure 3.2a and 3.2b presents the CO₂ adsorption isotherms of SIFSIX-2-Cu-i and SIFSIX-3-Zn, respectively, collected at sub-atmospheric pressures after activation at 298 K. Contraction of the pores led to a sharp increase in CO₂ uptake at low CO₂ loading, with nearly 11 wt% at 0.1 bar for SIFSIX-3-Zn vs. 4.4 wt% at 0.1 bar for SIFSIX-2-Cu-i. Notably, the CO₂ uptake for SIFSIX-3-Zn reached saturation at relatively low pressures (ca. 0.3 bar; Appendix B, Fig. B8), whereas the isotherm for CO₂ adsorption on SIFSIX-2-Cu-i reached a plateau at relatively higher pressures (5-7 bar) (Appendix B, Fig. B9b). As a result, SIFSIX-3-Zn exhibits high volumetric CO₂ uptake that is comparable to those of Mg-dobdc (ref. 4) and UTSA-16 (ref. 20) at a CO₂ partial pressure typical for post-combustion CO₂ capture (Appendix B, Fig. B25).
**Table 3.1. Gas Adsorption/CO\textsubscript{2} Selectivity Results and Comparisons**

<table>
<thead>
<tr>
<th>Property</th>
<th>SIFSIX-2-Cu</th>
<th>SIFSIX-2-Cu-(i)</th>
<th>SIFSIX-3-(Zn)</th>
<th>Mg-dobdc*</th>
<th>13X†</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore size (Å)</td>
<td>13.05</td>
<td>5.15</td>
<td>3.84</td>
<td>10.8</td>
<td>10</td>
</tr>
<tr>
<td><strong>Single-Gas Data (298 K)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{CO}_2) Q\text{stat} \text{ at low CO}_2 \text{ loading} (kJ/mol)</td>
<td>22</td>
<td>31.9</td>
<td>45</td>
<td>47-52</td>
<td>44-54</td>
</tr>
<tr>
<td>(\text{CO}_2) uptake at 0.1 bar/1 bar (mg/g)</td>
<td>10/81.3</td>
<td>76/238</td>
<td>105/112</td>
<td>220/352</td>
<td>106/220</td>
</tr>
<tr>
<td>(\text{CO}_2) uptake at 0.1 bar/1 bar (cm\textsuperscript{3}/cm\textsuperscript{3})</td>
<td>3/26</td>
<td>48/151</td>
<td>84/90</td>
<td>101/162</td>
<td>61/126</td>
</tr>
<tr>
<td>CH\textsubscript{4} uptake at 1 bar (mg/g)</td>
<td>6.2</td>
<td>7.5</td>
<td>12.6</td>
<td>17.8</td>
<td>4.2</td>
</tr>
<tr>
<td>(\text{N}_2) uptake at 1 bar (mg/g)</td>
<td>4.9</td>
<td>4.2</td>
<td>6.4</td>
<td>NA</td>
<td>6.4</td>
</tr>
<tr>
<td>H\textsubscript{2} uptake at 1 bar (mg/g)</td>
<td>NM</td>
<td>0.2</td>
<td>1.37</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Mixed-Gas Data (298 K)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>(\text{CO}_2) uptake in (\text{CO}_2)/(\text{N}_2) 10:90 mixture at 1 bar (mg/g)</td>
<td>8.4‡</td>
<td>70‡/55§</td>
<td>99.9‡/104.4¶</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>(\text{CO}_2) uptake in (\text{CO}_2)/(\text{CH}_4) 50:50 mixture at 1 bar (mg/g)</td>
<td>42.8‡</td>
<td>183‡/138§</td>
<td>108‡/110¶</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>(\text{CO}_2) uptake in (\text{CO}_2)/(\text{H}_2) 30:70 mixture at 1 bar (mg/g)</td>
<td>NM</td>
<td>85§</td>
<td>112•</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Selectivity at 1 bar</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{CO}_2)/(\text{N}_2)</td>
<td>13.7‡</td>
<td>140‡/72§</td>
<td>1818‡/1700¶</td>
<td>NA</td>
<td>420‡</td>
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<tr>
<td>(\text{CO}_2)/(\text{CH}_4)</td>
<td>5.3‡</td>
<td>33‡/51§</td>
<td>231‡/350¶</td>
<td>137‡</td>
<td>103‡</td>
</tr>
<tr>
<td>(\text{CO}_2)/(\text{H}_2)</td>
<td>NM</td>
<td>240§</td>
<td>&gt; 1800</td>
<td>800*</td>
<td>NA</td>
</tr>
</tbody>
</table>

NA: not available; NM: not measured; ‡ IAST; § breakthrough experiments; • mixture gravimetric (G) experiment; ¶ mixture gravimetric-densimetric gas analysis (GDGA) experiment; * Ref. 25 (313 K data); † Ref. 21 (298 K data).

Figure 3.2c presents the \(Q_\text{stat}\) of \(\text{CO}_2\) adsorption for SIFSIX-2-Cu-i and SIFSIX-3-\(Zn\) from variable temperature isotherms (Figs. 3.2a and 3.2b), and the \(Q_\text{stat}\) of up to 45 kJ/mol is consistent with the steepness of the \(\text{CO}_2\) isotherms. The relatively constant \(Q_\text{stat}\) indicates homogeneous binding sites over the full range of \(\text{CO}_2\) loading (Fig. 3.2c). These \(Q_\text{stat}\) values are in the ‘sweet spot’ favorable for efficient, reversible adsorption-desorption—that is, strong but still reversible—and are supported by modeling studies (Fig. 3.2d; Appendix B, Figs. B27-B29).
The CO₂ selectivity of SIFSIX-3-Zn was investigated via column breakthrough tests using binary 10:90 CO₂/N₂ (Fig. 3.2e) and 50:50 CO₂/CH₄ gas mixtures (Fig. 3.2f) at 298 K and atmospheric pressure, and compared to the corresponding breakthrough tests on SIFSIX-2-Cu-i. Remarkably, SIFSIX-3-Zn showed much higher selectivity (495 and 109 for 10:90 CO₂/N₂ and 50:50 CO₂/CH₄, respectively) than SIFSIX-2-Cu-i, as CO₂ was retained for longer times (e.g. 2000 s vs. 300 s for CO₂/N₂). Notably, N₂ and CH₄ breakthrough occurred within seconds, indicative of high selectivity toward CO₂. To support and confirm the high selectivity derived from the breakthrough experiments, single-gas (CO₂, N₂, CH₄ and H₂) sorption isotherms were measured at low and high pressures and IAST calculations were used to predict adsorption equilibria for the following binary mixtures: 5:95 CO₂/CH₄, 50:50 CO₂/CH₄, 10:90 CO₂/N₂, and 30:70 CO₂/H₂. These mixtures mimic natural gas upgrading, biogas treatment, and post- and pre-combustion capture applications, respectively.

The CO₂ adsorption selectivity of SIFSIX-3-Zn calculated for binary gas separation vs. CH₄ and N₂ was unprecedented at publication (Figs. 3.3a and 3.3b), outperforming Mg-dobdc (ref. 4), UTSA-16 (ref. 20) and zeolite 13X (ref. 21). Indeed, the selectivity of SIFSIX-3-Zn is comparable to that of amine-functionalized MOMs (e.g. PEI-MIL-101-100, mmen-Mg-dobpdc, and [Zn₂(atz)₂(ox)])²² and amine-bearing mesoporous silica,²³ particularly at low CO₂ partial pressure. To our knowledge, the only porous material with higher selectivity towards 10:90 CO₂/N₂ under ambient conditions is SIFSIX-3-Cu, a recently reported isostructural variant of SIFSIX-3-Zn with Cu²⁺ nodes (see Chapter 5).²⁴ The calculated selectivity of SIFSIX-3-Zn for CO₂/N₂ (that is, 1539 ± 307 at 1 bar and 298 K) was validated by gas mixture gravimetric adsorption experiments at various pressures (Figs. 3.3c and 3.3d).
Figure 3.2. a) and b) Variable temperature CO$_2$ sorption isotherms for SIFSIX-2-Cu-i (a) and SIFSIX-3-Zn (b); c) $Q_{st}$ of CO$_2$ adsorption on SIFSIX-2-Cu-i and SIFSIX-3-Zn in the low pressure region; d) The modeled structure of a 3 x 3 x 3 box of unit cells of SIFSIX-3-Zn reveals close interactions between the electropositive carbon atoms of CO$_2$ molecules and fluorine atoms of SIFSIX anions. Color code: C (grey), H (white), N (blue), O (red), Si (yellow), F (green), Zn (purple); e) Column breakthrough experiment for a CO$_2$/N$_2$ 10:90 gas mixture (298 K, 1 bar) carried out on SIFSIX-2-Cu-i and SIFSIX-3-Zn; f) As e) but for a CO$_2$/CH$_4$ 50:50 gas mixture (298 K, 1 bar).
With regards to CO₂/H₂ mixtures, adsorption isotherms of 30:70 CO₂/H₂ were collected and showed similar shapes and uptakes to that obtained using pure CO₂ (Appendix B, Fig. B10). This indicates that SIFSIX-3-Zn adsorbs CO₂ with very large selectivity vs. H₂ (higher than 1800), making it potentially suitable for pre-combustion capture or H₂ purification. Because of the large error associated with H₂ adsorption measurement (due to the relatively low uptake), quantitative measurements of CO₂/H₂ selectivity were not possible. We note that calculated and measured selectivities exceeding 1000 are often subject to uncertainties associated with measurement of the uptake of weakly adsorbed gases. Therefore, it would be inappropriate in this case to make quantitative comparisons between different adsorbents such as SIFSIX-3-Zn and Mg-dobdc (800 at 1 bar and 313 K).²⁵

To confirm the synergistic nature of the thermodynamics and kinetics for CO₂ capture, competitive adsorption kinetic studies of the above gas mixtures were conducted and are presented in Fig. 3.3e. We note that the CO₂ non-equilibrium uptake at equal times for CO₂/N₂, CO₂/CH₄ and CO₂/H₂ mixtures follows the behavior of pure CO₂. In addition, at equilibrium the total CO₂ uptake from the CO₂-containing gas mixtures agrees perfectly with the equilibrium uptake for pure CO₂. These distinctive findings show that when CO₂-containing mixtures are in contact with SIFSIX-3-Zn, CO₂ adsorbs more strongly and faster than N₂, O₂, CH₄ and H₂, thus occupying all the available space and sorption sites and consequently excluding other gases. Most importantly, SIFSIX-3-Zn fulfills the demanding attributes (Appendix B, Fig. B7) required for economical and efficient CO₂ post-combustion separation. Further, increasing the adsorption temperature did not significantly reduce the steepness of the CO₂ adsorption isotherm for SIFSIX-3-Zn (Fig. 3.2b; Appendix B, Fig. B8); this is a desirable feature in many CO₂ separation and purification applications.
Figure 3.3. a) IAST CO$_2$ selectivity for two different CO$_2$/CH$_4$ mixtures on SIFSIX-2-Cu-i and SIFSIX-3-Zn compared to Mg-dobdc and 13X zeolite at 298 K. Experimental data using gravimetric-densimetric gas analysis (GDGA) are provided for comparison; b) IAST CO$_2$/CH$_4$ 50:50 adsorption isotherm prediction compared to experimental pure CO$_2$, CH$_4$, and CO$_2$/CH$_4$ 50:50 gas mixture adsorption isotherms collected using gravimetric (G) adsorption experiments for SIFSIX-3-Zn at 298 K; c) IAST CO$_2$ adsorption selectivity of SIFSIX-2-Cu-i, SIFSIX-3-Zn and 13X zeolite for CO$_2$/N$_2$ 10:90 at 298 K; d) IAST CO$_2$/N$_2$ 10:90 adsorption isotherm predictions compared to experimental pure CO$_2$, N$_2$, and CO$_2$/N$_2$ 10:90 gas mixture adsorption isotherms collected using gravimetric (G) adsorption experiments for SIFSIX-3-Zn at 298 K; e) Kinetics of adsorption of SIFSIX-3-Zn for pure gases and gas mixtures containing various compositions of CO$_2$; f) PXRD patterns of SIFSIX-2-Cu-i after multiple cycles of breakthrough tests, high-pressure sorption, and water sorption experiments (compared to the calculated pattern).
Whereas the sorbents reported here exhibit very good performance with respect to CO$_2$ selectivity, their amenability to recycling and efficacy in the presence of moisture must also be addressed. The former was validated via adsorption–desorption cycle experiments conducted at 323 K and 0.15 bar (Appendix B, Fig. B14). The latter—specifically, the effect of water vapor on the CO$_2$ capacity and selectivity of SIFSIX-2-Cu-i and SIFSIX-3-Zn—was evaluated via a series of adsorption measurements. The water vapor adsorption isotherms were found to be of type I, with uptakes of 20 wt% and 11 wt%, respectively, at 74% relative humidity (Appendix B, Fig. B26). Water adsorption affinity/capacity is reduced in the presence of CO$_2$ gas mixtures, as shown by breakthrough experiments, especially for SIFSIX-3-Zn (Appendix B, Figs. B16 and B18). Importantly, the presence of water in the given gas mixture had a negligible effect at elevated CO$_2$ concentrations (Appendix B, Figs. B15 and B16) in the case of SIFSIX-2-Cu-i. Regarding the 30:70 CO$_2$/H$_2$ mixture, CO$_2$ uptake and selectivity were only slightly reduced in the presence of moisture (1.61 mmol/g and 191 at 74% relative humidity vs. 1.99 mmol/g and 237 at 0% relative humidity for SIFSIX-2-Cu-i; Appendix B, Fig. B16). Whereas SIFSIX-2-Cu-i was structurally unchanged by exposure to moisture (Fig. 3.3f), SIFSIX-3-Zn undergoes a reversible phase change at relatively high humidity (Appendix B, Figs. B21–B24).

Conclusions

We have demonstrated how a crystal engineering or reticular chemistry approach to pore size control, coupled with favorable electrostatic interactions provided by an array of inorganic anions, affords porous materials with exceptional selectivity, recyclability, and moisture stability in the context of several industrially relevant CO$_2$ separation applications. The structural features and exceptional mixed-gas sorption properties of the SIFSIX compounds reported here show that it is now possible to combine equilibrium$^{4,5,21}$ and kinetic$^{26}$ adsorption selectivity in the same porous material to facilitate effective CO$_2$ separation and capture.
References

CHAPTER FOUR:
A Robust Molecular Porous Material with High CO₂ Uptake and Selectivity

Note to Reader
Portions of this chapter have been previously published in J. Am. Chem. Soc. 2013, 135, 10950-10953 and are reproduced with the permission of the American Chemical Society. Computer modeling and IAST calculations were performed by the group of Dr. Brian Space.

Introduction
Because of their extra-large surface areas and structural tunability, porous coordination polymers (PCPs)¹ and metal–organic frameworks (MOFs)² are promising candidates for gas separations,³ gas storage,⁴ heterogeneous catalysis,⁵ and sensing.⁶ Comparatively, although many molecular inclusion compounds are known,⁷ molecular solids that exhibit permanent porosity to the degree observed in PCPs are rare, presumably because molecular building blocks exhibit a tendency to pack more densely than PCPs. Therefore, the design of robust molecular porous materials (MPMs)⁸ with fine-tunable components is more challenging than in the case of PCPs. Porosity in MPMs, as defined by reversible gas adsorption, is classified as either intrinsic (inside the molecules) or extrinsic (between the molecules). Intrinsically porous MPMs are exemplified by cucurbit[n]urils,⁹ tert-butylcalix[4]arene,¹⁰ organic cage compounds,¹¹ metal–organic cubes (MOCs) and squares (MOSs),¹² metal–organic macrocycles,¹³ and metal–organic polyhedra (MOPs).¹⁴ Cucurbit[n]urils, organic cage compounds, MOCs, MOSs, and MOPs possess both extrinsic and intrinsic porosity, while triptycene tris-(benzimidazolone) (TTBI),¹⁵ PUNCs,¹⁶ certain linear dipeptides,¹⁷ SOF-1a,¹⁸ and HOF-1¹⁹ exhibit just extrinsic porosity. TTBI presently exhibits one of the
highest BET surface areas among MPMs (2796 m²/g), but its CO₂ uptake at 273 K and 1 atm is only 81 cm³/g. While very few MPMs exhibiting surface areas above 1000 m²/g have been reported, recent reports suggest that non-covalent forces, including hydrogen bonding, can be utilized to rationally construct families of porous materials that are fine-tunable (i.e. platforms). Robust hydrogen-bonded MPMs which assemble in a predictable manner (e.g. MOCs, MOSs, TTBI, and certain dia nets) are particularly attractive from a design perspective.

The search for porous materials is driven by the advantages that physisorption might offer over costly and energy-intensive technologies such as amine scrubbing and cryogenic distillation. A viable CO₂ capture material should exhibit high selectivity vs. CH₄ and N₂ as well as thermal and water stability. We herein report a new class of MPMs in the context of physisorptive CO₂ capture through the study of an MPM platform that exhibits such features. A number of existing MPMs are known to exhibit selective CO₂ adsorption, but their performance does not yet approach that of PCPs. Specifically, the fact that inorganic anions can enhance CO₂ uptake and selectivity prompted us to study the effect of axial ligand substitution in an extrinsically porous hydrogen-bonding network based upon a discrete dinuclear paddlewheel (PW) complex. [Cu₂(adec)₂Cl₂]Cl₂ (ade = adenine), designated MPM-1-Cl, was thereby modified to afford [Cu₂(adec)₄(TiF₆)₂] (MPM-1-TIFSIX), a robust MPM with high CO₂ uptake and selectivity under conditions relevant to carbon capture.

**Structures**

We reasoned that pore functionality could be systematically varied by substituting the Cl⁻ ligands lining the channels of MPM-1-Cl. We chose TiF₆²⁻ (“TIFSIX”) for this purpose, as a porous net containing TIFSIX exhibited higher CO₂/N₂ selectivity and higher CO₂ uptake at low loading relative to variants containing SiF₆²⁻ (SIFSIX) and SnF₆²⁻ (SNIFSIX). Accordingly, solvent diffusion of a 1:1 acetonitrile/H₂O solution of ade into an aqueous solution of Cu(NO₃)₂·2.5H₂O and (NH₄)₂TiF₆ afforded purple, rectangular prismatic single crystals of [Cu₂(adec)₄(TiF₆)₂]·2CH₃CN (MPM-1-TIFSIX) in 51%
yield after 4 days (see Appendix C). Single-crystal X-ray diffraction (XRD) revealed that MPM-1-TIFSIX consists of neutral PWs that crystallize in space group $R\overline{3}m$ with a motif very similar to that of MPM-1-Cl (Figure 4.1; Appendix C, Table C1).

The PW complexes in MPM-1-TIFSIX feature four bridging equatorial ade ligands and two monodentate axial TIFSIX ligands, and they self-assemble into an extrinsically porous hydrogen-bonding network. The net is reminiscent of a kagomé lattice, and like that in MPM-1-Cl, it contains hourglass-shaped channels (~7.0 and 6.2 Å diameter in MPM-1-TIFSIX and MPM-1-Cl, respectively) and small trigonal channels that lie parallel to the c axis. The larger channels, which are lined with TIFSIX anions, and the small channels, which are occupied by acetonitrile molecules, are wider than those in MPM-1-Cl.

![Figure 4.1](image_url)

Figure 4.1. Views of (left) the PW complexes and (right) the networks along the c axis in (a) MPM-1-Cl and (b) MPM-1-TIFSIX. Solvent is omitted for clarity. Atom colors: Cu, peach; Cl, green; Ti, silver; F, cyan; C, gray; N, blue; H, white.

The hydrogen bonding network in MPM-1-TIFSIX is more extensive than that in MPM-1-Cl. While each PW in MPM-1-Cl forms a total of 12 contacts (eight with its nearest neighbors and four to Cl\(^-\) counterions), each PW in MPM-1-TIFSIX interacts with its eight nearest neighbors \textit{via} a total of 24
contacts. While the ade–ade contacts in MPM-1-TIFSIX share the same complementary motif as those in MPM-1-Cl, differences in the hydrogen bonding in the two networks result from the nature of the axial ligand (Figure 4.2). In MPM-1-Cl, the counterions are directly engaged in the hydrogen bonding network and link the ade moieties of adjacent PWs. The axial Cl⁻ ligands form no contacts with other network components. In contrast, the bulkier TIFSIX ligands in MPM-1-TIFSIX assume a role in the network analogous to that played by the counterions in MPM-1-Cl (Figure 4.2). The F···HN contacts (2.73, 2.82, and 2.94 Å) in the former are shorter and more numerous than the Cl···HN contacts (3.03 Å) in the latter. The hydrogen-bond motif adopted by the TIFSIX ligands causes the PWs to tilt 7.7° (relative to those in MPM-1-Cl) towards an orientation that is closer to perpendicular with the ab plane. This subtle change in orientation is responsible for the wider channels in MPM-1-TIFSIX relative to MPM-1-Cl.

Figure 4.2. Hydrogen-bonding motifs in (a) MPM-1-Cl and (b) MPM-1-TIFSIX. Hydrogen bonds are shown as red dashed lines. Portions of the enlarged structures on the right are omitted for clarity.
Gas Adsorption Properties

MPM-1-Cl was synthesized according to the reported procedure\textsuperscript{26} to further study its gas sorption behavior and compare it to MPM-1-TIFSIX. Powder X-ray diffraction (PXRD) patterns of as-synthesized MPM-1-TIFSIX and MPM-1-Cl were observed to match those calculated from single-crystal data (Appendix C, Figures C1 and C2). We validated that the reported surface area of MPM-1-Cl measured by N\textsubscript{2} adsorption at 77 K is much lower than expected (68 m\textsuperscript{2}/g). However, the CO\textsubscript{2} isotherm measured at 195 K displays reversible type-I character and reveals an experimental (calculated)\textsuperscript{28} Langmuir surface area of 637 (786) m\textsuperscript{2}/g (Appendix C, Figures C3 and C4). The authors of the initial study concluded that strong interactions between N\textsubscript{2} and the channel windows at 77 K hinder diffusion into the material. Restricted N\textsubscript{2} uptake at 77 K but type-I CO\textsubscript{2} uptake at 195 K has been observed previously in materials with pore sizes larger than the kinetic diameter of N\textsubscript{2} (see Appendix C).\textsuperscript{29} Single-gas CO\textsubscript{2}, CH\textsubscript{4}, and N\textsubscript{2} isotherms were collected for MPM-1-Cl at 298 K up to 1 atm (Figure 4.3). Uptakes of 44.2, 13.8, and 4.7 cm\textsuperscript{3}/g, respectively, at 1 atm were measured.

![Graph](image)

**Figure 4.3.** Low-pressure CO\textsubscript{2}, CH\textsubscript{4}, and N\textsubscript{2} isotherms collected at 298 K and (inset) CO\textsubscript{2} Q\textsubscript{st} for MPM-1-Cl.

Activation of MPM-1-TIFSIX at room temperature resulted in reversible type-I adsorption of CO\textsubscript{2} at 195 K and an experimental (calculated) BET surface area of 840 (809) m\textsuperscript{2}/g. The higher surface
area can be attributed to the greater channel width and solvent-accessible volume of MPM-1-TIFSIX (49.4% vs. 36.5% for MPM-1-Cl). Void analysis of the desolvated form of MPM-1-TIFSIX using Mercury\textsuperscript{31} (probe radius = 1.65 Å) revealed the existence of an accessible passage connecting the large channels that is not present in MPM-1-Cl. The analysis also suggested that the small channels in MPM-1-TIFSIX are accessible, unlike those in MPM-1-Cl (Appendix C, Figures C5-C7). The CO\textsubscript{2} isotherm of MPM-1-TIFSIX at 298 K (Figure 4.4) revealed much steeper adsorption at low partial pressures and 103% greater uptake at 1 atm (89.6 cm\textsuperscript{3}/g) than observed for MPM-1-Cl. Indeed, the CO\textsubscript{2} uptake by MPM-1-TIFSIX under ambient conditions is superior to that of most PCPs and is to our knowledge the highest yet exhibited by an MPM. For comparison, cucurbit[6]uril (Form II), HOF-8d, and P5-SOF have CO\textsubscript{2} capacities of 76, 57.3, and 45 cm\textsuperscript{3}/g, respectively.\textsuperscript{24b,32} The CH\textsubscript{4} and N\textsubscript{2} uptakes for MPM-1-TIFSIX at 1 atm were found to be 18.5 and 8.0 cm\textsuperscript{3}/g, respectively.

![Figure 4.4](image)

**Figure 4.4.** Low-pressure CO\textsubscript{2}, CH\textsubscript{4}, and N\textsubscript{2} isotherms collected at 298 K and (inset) CO\textsubscript{2} Q\textsubscript{st} for MPM-1-TIFSIX.

The shape of the CO\textsubscript{2} isotherm in MPM-1-TIFSIX relative to that of MPM-1-Cl suggests that the former exhibits a significantly higher isosteric heat of adsorption (Q\textsubscript{st}) and selectivity toward CO\textsubscript{2} over CH\textsubscript{4} and N\textsubscript{2}. The CO\textsubscript{2} Q\textsubscript{st} values (Figures 4.3 and 4.4), which were calculated by fitting the 273 and 298 K
isotherms to the virial equation (Appendix C, Figures C8 and C9), reveal that MPM-1-TIFSIX has a far higher affinity toward CO$_2$ at low loading (44.4 vs. 23.8 kJ/mol). To our knowledge, the CO$_2$ Q$_{st}$ of MPM-1-TIFSIX at zero loading is the highest yet observed among MPMs$^{9b,24d,33}$ and is comparable to that of top-performing PCPs with saturated metal centers (SMCs) such as MOOFOUR-1-Ni,$^{25b}$ SIFSIX-3-Zn,$^{25c}$ and UTSA-16$^{34}$ ($Q_{st}$ = 56, 45, and 35 kJ/mol, respectively). Mg-dobdc, a PCP with unsaturated metal centers (UMCs), exhibits an initial $Q_{st}$ of 47 kJ/mol.$^{35}$

The shapes of the $Q_{st}$ curves further suggest that MPM-1-TIFSIX possesses two or more CO$_2$ binding sites with different affinities whereas MPM-1-Cl is much more homogeneous in terms of binding sites. The results of grand canonical Monte Carlo (GCMC) simulations of CO$_2$ sorption in MPM-1-TIFSIX are in good agreement with the experimental data and further suggest the presence of multiple binding sites (Appendix C, Figures C10–C13 and Table C2). The primary binding site involves coordination of CO$_2$ to two TIFSIX anions in a confined passage connecting the large channels. Secondary binding to the TIFSIX anions lining the large channels also occurs. Charge–quadrupole interactions govern the binding at the first two sites. Lastly, sorption was observed in the small channels. Consistent with recent findings involving pcu and mmo nets,$^{25,36}$ these results affirm that inorganic anions can drive CO$_2$ selectivity. Because of the confined space at the primary and tertiary adsorption sites, size exclusion may also contribute to the selectivity towards CO$_2$ vs. CH$_4$ and N$_2$.

To predict the CO$_2$ separation performance of MPM-1-TIFSIX and MPM-1-Cl at 298 K, selectivities for 10:90 CO$_2$/N$_2$ and 50:50 CO$_2$/CH$_4$ binary mixtures were calculated up to 1 atm from the pure-component isotherms via ideal adsorbed solution theory (IAST) (Appendix C, Table C3).$^{37}$ These mixture compositions mimic those found in post-combustion capture and biogas purification, respectively. Strikingly, substitution of TIFSIX in place of Cl$^-$ affords 6-fold and 5-fold enhancements in the CO$_2$ selectivity at 1 atm (Figure 4.5) for the CO$_2$/N$_2$ and CO$_2$/CH$_4$ mixtures, respectively (CO$_2$/N$_2$: 74.1 vs. 12.5; CO$_2$/CH$_4$: 20.3 vs. 4.0). The selectivity of MPM-1-TIFSIX towards CO$_2$ vs. CH$_4$ and N$_2$ under these conditions is among the highest reported for MPMs and greater than those of the majority of
PCPs.\textsuperscript{3b,3c} Although IAST is considered to be the most accurate method for predicting gas mixture adsorption, selectivity data based upon IAST is scarce in the MPM literature. However, top-performing MPMs as measured by the CO\textsubscript{2}/N\textsubscript{2} selectivity factor include cucurbit[6]uril (Form II; S = 92)\textsuperscript{24c} and HOF-8d (S > 112.5).\textsuperscript{24b} It should be noted that most MPMs with high selectivity have significantly lower CO\textsubscript{2} uptake than MPM-1-TIFSIX.\textsuperscript{11c,13,24b,38} For instance, the most selective organic cage compound (S = 78 for CO\textsubscript{2}/N\textsubscript{2}) adsorbs only 2.27 cm\textsuperscript{3}/g of CO\textsubscript{2} at 293 K and 1 atm.\textsuperscript{11c}

**Stability**

In addition to selectivity, practical CO\textsubscript{2} separations require materials that possess thermal and water stability (flue gas is composed of \textit{ca.} 6\% water). MPM-1-TIFSIX was evaluated for these criteria \textit{via} variable-temperature PXRD and sorption measurements (Appendix C, Figures C14–C16). PXRD revealed that MPM-1-TIFSIX retains its crystal structure at 568 K and after immersion in water at room temperature for 24 h (Appendix C, Figure C1). Sorption isotherms of activated MPM-1-TIFSIX after water exposure confirmed that the surface area and CO\textsubscript{2} uptake are minimally affected. By comparison, MPM-1-Cl exhibits thermal stability up to 513 K but loses its crystallinity after exposure to water for 24 h.\textsuperscript{26}
Figure 4.5. IAST selectivities for 50:50 CO₂/CH₄ (green; left ordinate) and 10:90 CO₂/N₂ (blue; right ordinate) binary mixtures predicted at 298 K for MPM-1-TIFSIX (★) and MPM-1-Cl (●).

Conclusions

In summary, through axial ligand substitution we have diversified an extrinsically porous MPM platform to include a TIFSIX-functionalized variant with SMCs that is sustained by an extensive hydrogen-bonding network. MPM-1-TIFSIX can be synthesized in a single step from commercially available starting materials and activated at room temperature. In addition to dramatically surpassing MPM-1-Cl with regard to CO₂ separation performance, MPM-1-TIFSIX exhibits the highest CO₂ uptake and Qₘₐₜ observed in an MPM and among the highest CO₂/N₂ and CO₂/CH₄ selectivities. MPM-1-TIFSIX also exhibits excellent thermal and water stability, which are as important as selectivity for practical applications. Further studies will be conducted on gas mixtures, and the effect of decoration with other inorganic anions (e.g., SiF₆²⁻, SnF₆²⁻, and ZrF₆²⁻) on the selectivity will be addressed.

References

CHAPTER FIVE:
Recent Progress, Conclusions, and Future Directions

Recent Progress

A recently reported variant of SIFSIX-3-Zn with Cu$^{2+}$ nodes and marginally smaller pores, [Cu(pyr)$_2$(SiF$_6$)] (SIFSIX-3-Cu), was found to exhibit enhanced CO$_2$ uptake at very low pressures as well as improved adsorption enthalpy towards CO$_2$ ($Q_a \sim 54$ kJ/mol) at all loadings.$^1$ The contracted pore size in SIFSIX-3-Cu (3.5 Å) relative to that in SIFSIX-3-Zn (3.84 Å) arises from Jahn-Teller distortion of the Cu$^{2+}$ coordination environment that presumably affords closer binding contacts between each adsorbed CO$_2$ molecule and four neighboring SIFSIX pillars. The pore size of SIFSIX-3-Cu is also likely to promote the size exclusion of larger gases, e.g. CH$_4$ and N$_2$. Whereas the single-gas CO$_2$ uptake of SIFSIX-3-Cu at 298 K and 1 bar is foreseeably similar to that of SIFSIX-3-Zn, the uptake at pressures up to ca. 0.015 bar is significantly enhanced (82.6 vs. 55 cm$^3$/cm$^3$ at 0.01 bar). Column breakthrough experiments revealed that the selectivity of SIFSIX-3-Cu towards CO$_2$ in a 0.1:99.9 CO$_2$/N$_2$ mixture (~2.5 times the CO$_2$ concentration in air) at 298 K was ca. 50% higher than that of SIFSIX-3-Zn (10500 vs. 7259) and, as observed in the latter MOM, selectivity was retained under humid conditions (74% RH).

The estimated CO$_2$/N$_2$ selectivity of SIFSIX-3-Cu is also markedly higher under post-combustion capture conditions ($S_{IAST}$ for a 10:90 mixture: 15000 vs. ~ 1800 for SIFSIX-3-Zn). Like the Zn$^{2+}$ analogue, SIFSIX-3-Cu exhibits rapid adsorption kinetics that follow the adsorption behavior of pure CO$_2$, as determined from gas mixture gravimetric experiments (10:90 CO$_2$/N$_2$, 50:50 CO$_2$/CH$_4$, and 30:70 CO$_2$/H$_2$). PXRD measurements recorded after multiple adsorption cycles in a humid environment affirmed the recyclability and water stability of SIFSIX-3-Cu. The unprecedented CO$_2$ uptake at low
pressures, exceptional CO\textsubscript{2} selectivity, favorable adsorption kinetics, and stability of SIFSIX-3-Cu place it among the top candidates for post-combustion CO\textsubscript{2} capture and make it especially promising for direct-air and trace CO\textsubscript{2} capture.

**Conclusions**

Due to their high surface areas, tunable pore environments, and relative stability, MOMs are likely to have a lasting impact on materials science and their large-scale technological application may soon be realized. The effects of tuning pore size and/or pore functionality upon the carbon capture properties of two porous material platforms with SMCs—pillared square grid MOMs with \textbf{pcu} topology and hydrogen-bonded MPMs—have been detailed herein. Both platforms are decorated with inorganic anions that possess a strong yet reversible affinity towards CO\textsubscript{2} as a result of favorable electrostatic interactions.

Substitution of the inorganic pillar in a long known \textbf{pcu} MOM, SIFSIX-1-Cu, with TiF\textsubscript{6}\textsuperscript{2-} and SnF\textsubscript{6}\textsuperscript{2-} afforded two variants with high room temperature CO\textsubscript{2} uptake, pore sizes comparable to the parent material, and modulated CO\textsubscript{2} selectivity depending upon the pillar. The MFSIX-1-Cu series exhibits high CO\textsubscript{2}/CH\textsubscript{4} and CO\textsubscript{2}/N\textsubscript{2} selectivity among MOMs with relatively large pores and SMCs. The enhanced CO\textsubscript{2} selectivity of TIFSIX-1-Cu vs. SIFSIX-1-Cu correlates with the higher charge density residing on the pillar fluorine atoms, which in turn results from the greater polarizability of Ti\textsuperscript{4+} vs. Si\textsuperscript{4+}.

Pore size was then tuned in this platform \textit{via} linker substitution and interpenetration to yield three variants with dramatically different CO\textsubscript{2} uptakes and selectivities. A doubly interpenetrated variant with dpa linkers, SIFSIX-2-Cu-i, adsorbed far more CO\textsubscript{2} than a non-interpenetrated variant, SIFSIX-2-Cu, despite having a fraction of the surface area. Indeed, SIFSIX-2-Cu-i exhibits one of the highest gravimetric CO\textsubscript{2} uptakes among MOMs at 298 K and 1 atm. Further contraction of the pores yielded SIFSIX-3-Zn, a material with enhanced Q\textsubscript{a} vs. SIFSIX-2-Cu-i and unprecedented selectivity towards CO\textsubscript{2} vs. CH\textsubscript{4}, N\textsubscript{2}, and H\textsubscript{2} under industrially relevant conditions. Remarkably, the CO\textsubscript{2} selectivity of SIFSIX-3-
Zn is maintained in a humid environment and results from an optimal interplay of adsorption energetics and kinetics.

Finally, the substitution of Cl⁻ axial ligands lining the pores of an extrinsically porous hydrogen-bonded network with TiF₆²⁻ afforded MPM-1-TIFSIX, a variant with markedly enhanced stability, CO₂ uptake, CO₂ affinity, and selectivity towards CO₂ vs. CH₄ and N₂ at 298 K. Notably, the CO₂ uptake and CO₂ Qₑ of MPM-1-TIFSIX are unmatched among MPMs. The TIFSIX ligands in MPM-1-TIFSIX increase the stability of the hydrogen-bonded network, as observed by the improved thermal and water stability of MPM-1-TIFSIX vs. MPM-1-Cl. The former maintains crystallinity up to 568 K and its porosity is preserved even after immersion in water for 24 hrs.

In summary, the results presented herein demonstrate that porous materials featuring inorganic anions and SMCs can exhibit high and selective CO₂ uptake, sufficient stability, and facile activation conditions without the drawbacks associated with UMCs and amines, i.e. competitive water adsorption and high regeneration energy, respectively.

**Future Directions**

As the use of porous material platforms featuring SMCs and certain inorganic anions has only recently been revealed as an effective strategy for CO₂ capture, it is likely that such materials will contribute meaningfully to the future of materials science. These compounds are attractive candidates for further study because:

- They exhibit an affinity towards CO₂ that is comparable to that of materials with UMCs, coupled with a low affinity toward other industrially relevant gases (CH₄, N₂, and H₂).
- The physical adsorption of CO₂ *via* favorable electrostatics is more reversible than adsorption *via* chemical bonding.
- They can exhibit a greater selectivity towards CO₂ than MOMs with UMCs without the loss in separation performance that is often observed in MOMs with UMCs upon exposure to water vapor.
• Few inorganic anions have been explored to date in the context of porous materials.

• Inorganic anions can function in multiple roles (i.e. as linkers, counterions, or nodes), therefore a wide variety of platforms are potentially accessible.

• Inorganic anions can be fine-tuned to modulate adsorption affinity, e.g. by variation of the central metal ion as in SiF$_6^{2-}$/TiF$_6^{2-}$/SnF$_6^{2-}$/ZrF$_6^{2-}$ and CrO$_4^{2-}$/MoO$_4^{2-}$/WO$_4^{2-}$.

References

Appendix A:
Enhancement of CO₂ Selectivity in a Pillared *pcu* MOM Platform through Pillar Substitution

**Materials and Methods**

All reagents and solvents are commercially available and were used without further purification.

Preparation of $[\text{Cu(bipy)}_2(\text{TiF}_6)]$, TIFSIX-1-Cu: In a small test tube, 0.15 mmol (23.4 mg) of 4,4’-bipyridine in 3 mL of methanol was layered onto 3 mL of an ethylene glycol solution containing 0.076 mmol (17.7 mg) of Cu(NO₃)₂·2.5H₂O and 0.076 mmol (15.0 mg) of (NH₄)₂TiF₆. Purple plate-shaped crystals formed in 90.2% yield after 2 weeks.

Preparation of $[\text{Cu(bipy)}_2(\text{SnF}_6)]$, SNIFSIX-1-Cu: In a small test tube, 0.11 mmol (17.2 mg) of 4,4’-bipyridine in 3 mL of methanol was layered onto 3 mL of an ethylene glycol solution containing 0.056 mmol (13.0 mg) of Cu(NO₃)₂·2.5H₂O and 0.056 mmol (15.1 mg) of (NH₄)₂SnF₆. Purple plate-shaped crystals formed in 93.8% yield after 2 weeks.

Powder X-ray diffraction (PXRD) was carried out at room temperature on a Bruker D8 Advance 0/20 diffractometer using Cu-Kα radiation ($\lambda = 1.5418$ Å). 20 scans between 3° and 40° with a step size of 0.02° were performed for a duration of 30 minutes. Gas adsorption measurements were conducted on a Micromeritics ASAP 2020 surface area and porosity analyzer. Prior to data collection, TIFSIX-1-Cu and SNIFSIX-1-Cu were exchanged with methanol 3 times daily for 2 days and degassed under high vacuum at room temperature for 16 hours.

Single crystal X-ray diffraction data for TIFSIX-1-Cu and SNIFSIX-1-Cu were collected on a Bruker-AXS SMART APEX/CCD diffractometer using CuKα radiation ($\lambda = 1.5418$ Å, $T = 228(2)$ K). Indexing was performed using APEX2.¹ Data integration and reduction were completed using SaintPlus 6.01.² Absorption correction was performed by the multi-scan method implemented in SADABS.³ Space
groups were determined using XPREP implemented in APEX2. Structures were solved with SHELXS-97 (direct methods) and refined on F^2 using nonlinear least-squares techniques with SHELXL-97 contained in APEX2, WinGX v1.70.01, and OLEX2 v1.1.5 program packages. All non-hydrogen atoms were refined anisotropically. The Ti-F bond distances for disordered F atoms in TIFSIX-1-Cu were refined using restraints. The pyridyl rings in both structures were disordered over two positions. In both structures the contribution of disordered solvent molecules was treated as diffuse using the Squeeze routine implemented in Platon. Table A1 summarizes the crystallographic data for TIFSIX-1-Cu and SNIFSIX-1-Cu.

### Supplementary Tables

**Table A1.** Crystal Data and Structure Refinement for TIFSIX-1-Cu and SNIFSIX-1-Cu.

<table>
<thead>
<tr>
<th>Compound</th>
<th>TIFSIX-1-Cu</th>
<th>SNIFSIX-1-Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{20}H_{16}CuF_{6}N_{4}Ti</td>
<td>C_{20}H_{16}CuF_{6}N_{4}Sn</td>
</tr>
<tr>
<td>Formula weight</td>
<td>537.81</td>
<td>608.60</td>
</tr>
<tr>
<td>Temperature / K</td>
<td>228(2)</td>
<td>228(2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>tetragonal</td>
<td>tetragonal</td>
</tr>
<tr>
<td>Space group</td>
<td>P4/mmm</td>
<td>P4/mmm</td>
</tr>
<tr>
<td>a / Å</td>
<td>11.1001(6)</td>
<td>11.116(5)</td>
</tr>
<tr>
<td>b / Å</td>
<td>11.1001(6)</td>
<td>11.116(5)</td>
</tr>
<tr>
<td>c / Å</td>
<td>8.4055(7)</td>
<td>8.627(5)</td>
</tr>
<tr>
<td>α / °</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>β / °</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>γ / °</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>Volume / Å³</td>
<td>1035.66(12)</td>
<td>1066.0(9)</td>
</tr>
<tr>
<td>Z</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( \rho_{\text{calc}} / \text{mg/mm}^3 )</td>
<td>0.862</td>
<td>0.948</td>
</tr>
<tr>
<td>m / mm^3</td>
<td>2.593</td>
<td>5.587</td>
</tr>
<tr>
<td>F(000)</td>
<td>269.0</td>
<td>297.0</td>
</tr>
<tr>
<td>Crystal size / mm^3</td>
<td>0.02 \times 0.02 \times 0.01</td>
<td>0.02 \times 0.02 \times 0.01</td>
</tr>
<tr>
<td>20 range for data collection</td>
<td>10.52 to 132.64°</td>
<td>7.96 to 133.06°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-13 ≤ h ≤ 13, -9 ≤ k ≤ 12, -9 ≤ l ≤ 8</td>
<td>-13 ≤ h ≤ 12, -12 ≤ k ≤ 12, -9 ≤ l ≤ 10</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>5175</td>
<td>5235</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>573[R(int) = 0.0698]</td>
<td>603[R(int) = 0.0557]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>573/3/48</td>
<td>603/0/40</td>
</tr>
<tr>
<td>Goodness-of-fit on F^2</td>
<td>1.054</td>
<td>1.188</td>
</tr>
<tr>
<td>Final R indices [I&gt;2σ(I)]</td>
<td>( R_1 = 0.0362, wR_2 = 0.1083 )</td>
<td>( R_1 = 0.0317, wR_2 = 0.0732 )</td>
</tr>
<tr>
<td>Final R indices [all data]</td>
<td>( R_1 = 0.0385, wR_2 = 0.1095 )</td>
<td>( R_1 = 0.0328, wR_2 = 0.0748 )</td>
</tr>
<tr>
<td>Largest diff. peak/hole / eÅ^{-3}</td>
<td>0.36/-0.39</td>
<td>0.69/0.81</td>
</tr>
<tr>
<td>MOM</td>
<td>SIFSIX-1-Cu</td>
<td>TIFSIX-1-Cu</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
<td>-------------</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>[Cu(bipy)$_2$(SiF$_6$)$_2$]</td>
<td>[Cu(bipy)$_2$(TiF$_6$)$_2$]</td>
</tr>
<tr>
<td>Theoretical pore volume (cm$^3$/g)</td>
<td>0.683</td>
<td>0.696</td>
</tr>
<tr>
<td>BET surface area (m$^2$/g)</td>
<td>1468</td>
<td>1690</td>
</tr>
<tr>
<td>BET surface area (m$^2$/cm$^3$)</td>
<td>1261</td>
<td>1457</td>
</tr>
<tr>
<td>CO$_2$ uptake at 298 K, 1 atm (cm$^3$/g)</td>
<td>115.2</td>
<td>106.3</td>
</tr>
<tr>
<td>CO$_2$ uptake at 298 K, 1 atm (cm$^3$/cm$^3$)</td>
<td>99.0</td>
<td>91.6</td>
</tr>
<tr>
<td>CO$_2$ uptake at 298 K, 0.15 atm (cm$^3$/g)</td>
<td>18.1</td>
<td>20.4</td>
</tr>
<tr>
<td>CO$_2$ uptake at 298 K, 0.15 atm (cm$^3$/cm$^3$)</td>
<td>15.5</td>
<td>17.6</td>
</tr>
<tr>
<td>CO$_2$ Q$_a$ at zero loading (kJ/mol)</td>
<td>26.5</td>
<td>26.6</td>
</tr>
<tr>
<td>CO$_2$/CH$_4$ relative uptake at 298 K, 1 atm</td>
<td>9.9</td>
<td>8.6</td>
</tr>
<tr>
<td>CO$_2$/N$_2$ relative uptake at 298 K, 1 atm</td>
<td>28.1</td>
<td>23.6</td>
</tr>
<tr>
<td>50:50 CO$_2$/CH$_4$ selectivity at 298 K, 1 atm</td>
<td>10.6</td>
<td>11.2</td>
</tr>
<tr>
<td>10:90 CO$_2$/N$_2$ selectivity at 298 K, 1 atm</td>
<td>26.5</td>
<td>29.5</td>
</tr>
</tbody>
</table>
**Table A3.** Gravimetric CO$_2$ Uptake of Selected MOMs at 298 K and 1 atm.

<table>
<thead>
<tr>
<th>MOM</th>
<th>CO$_2$ Uptake at 298 K, 1 atm (cm$^3$/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-dobdc</td>
<td>193.0</td>
<td>8</td>
</tr>
<tr>
<td>Co-dobdc</td>
<td>169.0</td>
<td>9</td>
</tr>
<tr>
<td>Ni-dobdc</td>
<td>160.0</td>
<td>9</td>
</tr>
<tr>
<td>Fe-dobdc</td>
<td>159.0</td>
<td>10</td>
</tr>
<tr>
<td>[Cu(Me-4py-trz-ia)]</td>
<td>136.6</td>
<td>11</td>
</tr>
<tr>
<td>Cu-TDPAT</td>
<td>132.2</td>
<td>12</td>
</tr>
<tr>
<td>HKUST-1</td>
<td>126.0 (a)</td>
<td>13</td>
</tr>
<tr>
<td>Cu-TPBTM</td>
<td>118.5</td>
<td>14</td>
</tr>
<tr>
<td>SIFSIX-1-Cu</td>
<td>115.2</td>
<td>15</td>
</tr>
<tr>
<td>UTSA-20</td>
<td>112.0 (b)</td>
<td>16</td>
</tr>
<tr>
<td>Zn-dobdc</td>
<td>109.8</td>
<td>17</td>
</tr>
<tr>
<td>PCN-26</td>
<td>109.1</td>
<td>18</td>
</tr>
<tr>
<td>Mg-dobpdc</td>
<td>108.6</td>
<td>19</td>
</tr>
<tr>
<td>TIFSIX-1-Cu</td>
<td>106.3</td>
<td>This work</td>
</tr>
</tbody>
</table>

(a) 293 K, 1.1 atm; (b) 300 K.
Table A4. CO$_2$/CH$_4$ Relative Uptakes and CO$_2$ Uptakes of MOMs at 298 K and 1 atm (see Chapter 2, Fig. 2.3).

<table>
<thead>
<tr>
<th>MOM</th>
<th>CO$_2$/CH$_4$ Relative Uptake</th>
<th>CO$_2$ Uptake (cm$^3$/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CUK-1</td>
<td>10.88</td>
<td>87.0</td>
<td>20</td>
</tr>
<tr>
<td>SIFSIX-1-Cu</td>
<td>9.90</td>
<td>115.2</td>
<td>15</td>
</tr>
<tr>
<td>SNIFSIX-1-Cu</td>
<td>8.70</td>
<td>93.9</td>
<td>This work</td>
</tr>
<tr>
<td>TIFSIX-1-Cu</td>
<td>8.60</td>
<td>106.3</td>
<td>This work</td>
</tr>
<tr>
<td>Mg-dobdc</td>
<td>8.21</td>
<td>193.0</td>
<td>8</td>
</tr>
<tr>
<td>CD-MOF-2</td>
<td>7.73</td>
<td>58.0</td>
<td>21</td>
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<td>UTSA-16</td>
<td>7.62 (a)</td>
<td>102.5</td>
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<td>SIFSIX-4-Cu</td>
<td>6.26</td>
<td>62.1</td>
<td>15</td>
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<tr>
<td>iso1</td>
<td>6.25</td>
<td>28.0</td>
<td>23</td>
</tr>
<tr>
<td>MgH$_2$ODTMP</td>
<td>5.40 (b)</td>
<td>12.1</td>
<td>24</td>
</tr>
<tr>
<td>Cu-TDPAT</td>
<td>5.36</td>
<td>132.2</td>
<td>12</td>
</tr>
<tr>
<td>UTSA-20</td>
<td>5.31 (c)</td>
<td>112.0</td>
<td>16</td>
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<tr>
<td>CAU-1</td>
<td>4.83</td>
<td>87.0</td>
<td>25</td>
</tr>
<tr>
<td>NOTT-202</td>
<td>4.79 (d)</td>
<td>31.6</td>
<td>26</td>
</tr>
<tr>
<td>SNU-50</td>
<td>4.71</td>
<td>80.0</td>
<td>27</td>
</tr>
<tr>
<td>ZIF-82</td>
<td>4.64</td>
<td>51.0</td>
<td>28</td>
</tr>
<tr>
<td>PCN-26</td>
<td>4.53</td>
<td>109.1</td>
<td>18</td>
</tr>
<tr>
<td>Cu$_2$(TCMBT)(bpp)(μ$_3$-OH)</td>
<td>4.48</td>
<td>44.8</td>
<td>29</td>
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<tr>
<td>UiO-66-NH$_2$</td>
<td>4.42</td>
<td>67.2</td>
<td>30</td>
</tr>
<tr>
<td>UiO-66-2,5-(OMe)$_2$</td>
<td>4.34</td>
<td>58.2</td>
<td>30</td>
</tr>
<tr>
<td>Zn$_3$(OH)$_2$(1,2,4-btc)$_2$</td>
<td>4.20 (e)</td>
<td>42.0</td>
<td>31</td>
</tr>
<tr>
<td>Cu(bdc-OH)</td>
<td>4.00 (a)</td>
<td>52.0</td>
<td>32</td>
</tr>
<tr>
<td>MIL-120</td>
<td>4.00 (b)</td>
<td>72.0</td>
<td>33</td>
</tr>
<tr>
<td>NOTT-140</td>
<td>3.96 (d)</td>
<td>93.0</td>
<td>34</td>
</tr>
<tr>
<td>PCN-80</td>
<td>3.90 (e)</td>
<td>61.1</td>
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<td>ZIF-78</td>
<td>3.85</td>
<td>50.0</td>
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<td>ZIF-81</td>
<td>3.80</td>
<td>38.0</td>
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<tr>
<td>UiO-66-NO$_2$</td>
<td>3.76</td>
<td>57.1</td>
<td>30</td>
</tr>
<tr>
<td>Zn$_2$(bta)$_2$(tda)$_2$</td>
<td>3.70 (e)</td>
<td>37.0</td>
<td>36</td>
</tr>
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<td>ZIF-68</td>
<td>3.60</td>
<td>36.0</td>
<td>28</td>
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<tr>
<td>ZIF-95</td>
<td>3.58</td>
<td>18.6</td>
<td>37</td>
</tr>
<tr>
<td>UiO-66</td>
<td>3.56</td>
<td>39.2</td>
<td>30</td>
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<tr>
<td>Cu$_2$(TerTri)$_2$(dabco)</td>
<td>3.56</td>
<td>32.0</td>
<td>38</td>
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<tr>
<td>ZIF-69</td>
<td>3.55</td>
<td>39.0</td>
<td>28</td>
</tr>
<tr>
<td>UiO-66-1,4-Naphthyl</td>
<td>3.51</td>
<td>34.7</td>
<td>30</td>
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<tr>
<td>SNU-21S</td>
<td>3.46</td>
<td>56.5</td>
<td>39</td>
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<tr>
<td>ZIF-79</td>
<td>3.30</td>
<td>33.0</td>
<td>28</td>
</tr>
<tr>
<td>SNU-21H</td>
<td>3.29</td>
<td>49.1</td>
<td>39</td>
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<td>SNU-25</td>
<td>3.27</td>
<td>33.4</td>
<td>40</td>
</tr>
<tr>
<td>ZIF-100</td>
<td>3.19</td>
<td>20.0</td>
<td>37</td>
</tr>
<tr>
<td>Zn$_2$(4,4′-bipy)$_2$ (FIR-2)</td>
<td>3.18</td>
<td>35.0</td>
<td>41</td>
</tr>
<tr>
<td>MIL-101(Cr)</td>
<td>3.14 (f)</td>
<td>24.6</td>
<td>42</td>
</tr>
<tr>
<td>ZIF-70</td>
<td>3.11</td>
<td>28.0</td>
<td>28</td>
</tr>
<tr>
<td>Zn$_3$(ndc)$_3$(DPNI)</td>
<td>2.70</td>
<td>29.7</td>
<td>43</td>
</tr>
<tr>
<td>MOF-508b</td>
<td>2.57 (b)</td>
<td>40.3</td>
<td>44</td>
</tr>
<tr>
<td>SNU-77H</td>
<td>2.32</td>
<td>20.1</td>
<td>45</td>
</tr>
<tr>
<td>Eu$_2$(TPO)$_2$(HCOO)</td>
<td>1.52</td>
<td>31.8</td>
<td>46</td>
</tr>
<tr>
<td>Y$_2$(TPO)$_2$(HCOO)</td>
<td>1.41</td>
<td>43.4</td>
<td>46</td>
</tr>
</tbody>
</table>

(a) 296 K; (b) 303 K; (c) 300 K; (d) 293 K; (e) 295 K; (f) 313 K.
Table A5. 50:50 CO$_2$/CH$_4$ IAST Selectivities of Selected MOMs at 298 K and 1 atm.

<table>
<thead>
<tr>
<th>MOM</th>
<th>Selectivity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZIF-78</td>
<td>10</td>
<td>22,28</td>
</tr>
<tr>
<td>ZIF-8</td>
<td>1.32</td>
<td>47</td>
</tr>
<tr>
<td>ZIF-82</td>
<td>9.8 (a)</td>
<td>28</td>
</tr>
<tr>
<td>ZIF-95</td>
<td>4.3 (a)</td>
<td>37</td>
</tr>
<tr>
<td>MOF-5</td>
<td>2.3</td>
<td>48</td>
</tr>
<tr>
<td>UMCM-1</td>
<td>1.82</td>
<td>47</td>
</tr>
<tr>
<td>MIL-53(Al)</td>
<td>2.30</td>
<td>47</td>
</tr>
<tr>
<td>MOF-177</td>
<td>0.89</td>
<td>47</td>
</tr>
<tr>
<td>[Zn(bdc)(dabco)$_{0.5}$]</td>
<td>3.4 (b)</td>
<td>49</td>
</tr>
<tr>
<td>HKUST-1</td>
<td>~ 8</td>
<td>22,50</td>
</tr>
<tr>
<td>MIL-101(Cr)</td>
<td>~ 12</td>
<td>22,50</td>
</tr>
</tbody>
</table>

(a) ratio of Henry’s constants; (b) 294 K.

Powder X-ray Diffraction

Figure A1. Experimental and calculated PXRD patterns for TIFSIX-1-Cu.
Figure A2. Experimental and calculated PXRD patterns for SNIFSIX-1-Cu.

Gas Adsorption

Figure A3. N\textsubscript{2} isotherm at 77 K for TIFSIX-1-Cu.
Computational Methods and Results

Modeling studies were performed to investigate the gas adsorption behavior in SIFSIX-1-Cu, TIFSIX-1-Cu, and SNIFSIX-1-Cu. Highly accurate and transferable CO₂, CH₄, and N₂ potentials were
developed using a previously described fitting procedure. Simulation parameters including atomic point partial charges, repulsion/dispersion parameters, and atomic point polarizabilities were also developed according to previous considerations. Grand canonical Monte Carlo (GCMC) simulations were able to predict the primary and secondary CO₂ adsorption sites based upon both binding energy and the magnitude of the dipole induced in CO₂. In all three MOMs, this interaction occurs between the carbon atom of CO₂ and the equatorial fluorines of the MF₆²⁻ (M = Si⁴⁺, Ti⁴⁺, Sn⁴⁺) moieties (Fig. A6). Further, comparison of the radial distribution functions, dipole distributions, and polarizability data of TIFSIX-1-Cu and SIFSIX-1-Cu (described below) are consistent with an enhanced framework-CO₂ interaction in the former due to the substitution of Si⁴⁺ with Ti⁴⁺. Full details concerning modeling of the gas adsorption and separation mechanisms in these compounds will be described in a future manuscript.

![Figure A6](image)

**Figure A6.** Snapshot of the primary CO₂ binding site in TIFSIX-1-Cu as determined from modeling studies. Atom colors: C = gray, H = white, O = red, N = blue, F = green, Cu = tan, Ti = violet.

**Radial Distribution Function and Dipole Distribution**

Examination of the radial distribution functions, g(r), of CO₂ molecules <11 Å from the pillaring metal in SIFSIX-1-Cu and TIFSIX-1-Cu reveals maxima at ca. 4.55 Å and 3.95 Å, respectively (Fig. A7). These peaks correspond to the closest interaction between the carbon atom of CO₂ and the equatorial fluorines of the MF₆²⁻ pillars (Fig. A6). The smaller CO₂-M distance observed for TIFSIX-1-Cu signifies a
stronger electrostatic attraction between the pillar and CO$_2$ in this variant compared to SIFSIX-1-Cu. The area under the 3.95 Å radial distribution peak in TIFSIX-1-Cu relative to that of the 4.55 Å peak in SIFSIX-1-Cu indicates that there is a larger population of CO$_2$ molecules interacting with the equatorial fluorines in the former. The distances between the equatorial fluorine atom and the carbon atom of the closest sorbed CO$_2$ were found to be 2.103 Å in TIFSIX-1-Cu and 2.850 Å in SIFSIX-1-Cu.

**Figure A7.** The radial distribution functions of CO$_2$ molecules about the Si/Ti atoms in SIFSIX-1-Cu (blue) and TIFSIX-1-Cu (green) as observed from CO$_2$ adsorption simulations at 298 K and 1.0 atm.

Further insight into the favored CO$_2$ adsorption sites for SIFSIX-1-Cu and TIFSIX-1-Cu was obtained through molecular simulation studies involving explicit polarization. Similar methods were employed previously for H2 adsorption in highly polar MOFs such as In-soc-MOF and PCN-61. The normalized distribution of induced dipoles for CO$_2$ molecules adsorbed in the pores of SIFSIX-1-Cu and TIFSIX-1-Cu reveals two distinct peaks corresponding to different regions of sorbate occupancy (Fig. A8). For TIFSIX-1-Cu, the high dipole peak from 0.40 to 0.60 D correlates to the interaction between CO$_2$ and the equatorial fluorine atoms of the TiF$_6^{6-}$ groups (i.e. the primary adsorption site; Fig. A9, red shaded areas). The primary adsorption site is similar in the case of SIFSIX-1-Cu, though the dipole magnitudes are slightly lower (0.30 to 0.50 D). This data indicates that TIFSIX-1-Cu induces higher
dipoles on CO$_2$ molecules upon adsorption due to the greater polarizability of Ti$^{4+}$ relative to Si$^{4+}$. A peak from 0.05 to 0.15 D was also observed for both compounds which corresponds to a secondary adsorption site (Fig. A9, cyan shaded areas) whereby CO$_2$ coordinates to the CO$_2$ molecules that are already occupying the primary adsorption site.

**Figure A8.** The normalized CO$_2$ dipole distribution from simulations of CO$_2$ adsorption in SIFSIX-1-Cu (blue) and TIFSIX-1-Cu (green) at 298 K and 1.0 atm.

**Figure A9.** Three-dimensional histograms showing the CO$_2$ adsorption sites in SIFSIX-1-Cu/TIFSIX-1-Cu: (a) c axis view; (b) a/b axis view. Red and cyan regions correspond to CO$_2$ molecules adsorbed at the primary and secondary dipole sites, respectively.
Polarizability Calculations

To determine the atomic point polarizabilities of Si$^{4+}$ and Ti$^{4+}$, polarizability tensors of gas phase SiF$_6^{2-}$ and TiF$_6^{2-}$ were calculated by restricted Hartree-Fock methods with the aug-cc-pVDZ basis set using QChem code. The polarizability for Si$^{4+}$/Ti$^{4+}$ was then determined by fitting the molecular polarizability tensor for SiF$_6^{2-}$/TiF$_6^{2-}$, calculated using the Thole-Applequist model, to the Hartree-Fock polarizability tensor form. For this calculation, all F atoms were assigned the fluorine polarizability value as parameterized by van Duijnen et al. Following this procedure, the polarizabilities of Si$^{4+}$ and Ti$^{4+}$ were calculated to be 2.1330 Å$^3$ and 3.2428 Å$^3$, respectively. These polarizabilities reinforce the assertion that the equatorial fluorines possess greater electron density when bound to Ti$^{4+}$ than to Si$^{4+}$, leading in turn to enhanced interaction with CO$_2$.

IAST Calculations

In order to predict binary mixture adsorption in SIFSIX-1-Cu, TIFSIX-1-Cu, and SNIFSIX-1-Cu, the respective single-component CO$_2$, CH$_4$, and N$_2$ adsorption isotherms were first fit to the dual-site Langmuir-Freundlich equation:

\[
\begin{align*}
    n &= n_{m1}b_1 P^{(1/t_1)} + n_{m2}b_2 P^{(1/t_2)} \\
    &= \frac{n_{m1}b_1 P^{(1/t_1)}}{1 + b_1 P^{(1/t_1)}} + \frac{n_{m2}b_2 P^{(1/t_2)}}{1 + b_2 P^{(1/t_2)}}
\end{align*}
\]

In this equation, $n$ is the amount adsorbed per mass of adsorbent (in mol/kg), $P$ is the total pressure (in kPa) of the bulk gas at equilibrium with the adsorbed phase, $n_{m1}$ and $n_{m2}$ are the saturation uptakes (in mol/kg) for sites 1 and 2, $b_1$ and $b_2$ are the affinity coefficients (in kPa$^{-1}$) for sites 1 and 2, and $t_1$ and $t_2$ are the heterogeneity factors for sites 1 and 2. All isotherms were fitted with $R^2 \geq 0.9999$. This equation has been used to fit isotherm data for a variety of MOMs. The fitted isotherm parameters were applied to perform the necessary integrations according to ideal adsorbed solution theory (IAST).
Afterwards, the selectivity for component $i$ relative to component $j$ was calculated by the following equation:

$$S_{i/j} = \frac{x_i y_j}{x_j y_i}$$

where $x_i$ and $y_i$ are the mole fractions of component $i$ in the adsorbed and bulk phases, respectively.

**Figure A10.** 50:50 CO$_2$/CH$_4$ IAST selectivities for TIFSIX-1-Cu, SIFSIX-1-Cu, and SNIFSIX-1-Cu at 298 K.
Figure A11. 10:90 CO$_2$/N$_2$ IAST selectivities for TIFSIX-1-Cu, SIFSIX-1-Cu, and SNIFSIX-1-Cu at 298 K.

Additional References

2. Bruker SAINT Data Reduction Software; Bruker AXS Inc., Madison, WI, USA 2009.


APPENDIX B:

Porous Materials with Optimal Adsorption Thermodynamics and Kinetics for CO₂ Separation

Synthesis

All chemicals with the exception of 1,2-di-(4-pyridyl)acetylene (dpa) were obtained commercially and used as received without further purification. Synthesis of dpa was accomplished by a minor modification of a previously reported procedure.¹

1,2-di-(4-pyridyl)acetylene, dpa

Br₂ (3.5 mL, 10.8 g, 68 mmol) was added dropwise to a stirred solution of trans-1,2-bis(4-pyridyl)ethylene (3.52 g, 19.3 mmol) in HBr (48%, 46.5 mL) at 0°C. The mixture was stirred at 120°C for 2 hrs and subsequently cooled to room temperature yielding an orange precipitate. After chilling in ice for 30 min. the solid was filtered, washed with water, and then stirred in aqueous NaOH (2 M, 120 mL) for 30 min. The resulting white solid, 1,2-dibromo-1,2-bis(4-pyridyl)ethane, was filtered, washed with 250 mL of water, and dried under vacuum for 24 hrs (yield 5.1 g, 77%). Finely cut Na (2.2 g, 96 mmol) was stirred in t-BuOH (120 mL, dried over 4 Å molecular sieves) at 80°C under nitrogen until dissolution (20 hrs). 1,2-dibromo-1,2-bis(4-pyridyl)ethane (4.0 g, 11.7 mmol) was added in portions and the mixture was stirred under nitrogen at 80°C for 4 hrs. The mixture was next cooled to room temperature and EtOH was added (20 mL), followed by water (20 mL, CAUTION!). The brown solution was extracted with CHCl₃ until the extracts became colorless (ca. 4 × 70 mL) and then the CHCl₃ was evaporated to give a brown solid, which was recrystallized from toluene (overall yield 43%).

85
SIFSIX-2-Cu, [Cu(dpa)$_2$(SiF$_6$)]$_n$

Room temperature diffusion of an ethanol solution of dpa (2 mL, 0.115 mmol) into an ethylene glycol solution of CuSiF$_6$ (2 mL, 0.149 mmol) produced purple rod-shaped crystals of SIFSIX-2-Cu after 2 weeks in 87.4% yield (based on dpa).

SIFSIX-2-Cu-i, [Cu(dpa)$_2$(SiF$_6$)$_n$•2.5CH$_3$OH

Blue plate single crystals of SIFSIX-2-Cu-i were synthesized in 99.8% yield (based on dpa) by room temperature diffusion of a methanol solution of CuSiF$_6$ (2 mL, 0.149 mmol) into a DMSO solution of dpa (2 mL, 0.115 mmol) for 1 week. An alternative direct mixing method was used to produce powdered samples of SIFSIX-2-Cu-i. A methanol solution of dpa (4 mL, 0.270 mmol) was stirred with an aqueous solution of CuSiF$_6$ (4 mL, 0.258 mmol) resulting in a purple precipitate, which was then heated at 85°C for 12 hrs (83.3% yield based on dpa).

SIFSIX-3-Zn, [Zn(pyr)$_n$(SiF$_6$)]$_n$

SIFSIX-3-Zn was synthesized using a previously known procedure by room temperature diffusion of a methanol solution of pyrazine (2 mL, 1.3 mmol) into a methanol solution of ZnSiF$_6$ (2 mL, 0.6 mmol). Crystals were harvested after 3 days.
Low Pressure Gas Adsorption

Crystalline samples of SIFSIX-2-Cu-i and SIFSIX-3-Zn were activated for low pressure gas sorption analysis by washing the as-synthesized material with DMF followed by solvent exchange in methanol (MeOH) for 3 days. The activated samples (80 – 160 mg) were transferred to a pre-weighed 6-mm large bulb glass sample cell and evacuated at room temperature for 92 hrs (SIFSIX-2-Cu-i) or 25 hrs (SIFSIX-3-Zn) on an Autosorb-1C (Quantachrome Instruments) low pressure adsorption instrument equipped with a turbo molecular vacuum pump. The low pressure gas sorption isotherms in Figure B5 were collected on an ASAP 2020 Surface Area and Porosity Analyzer (Micromeritics) after activation of SIFSIX-2-Cu and SIFSIX-2-Cu-i as follows. As-synthesized SIFSIX-2-Cu was exchanged with 1:1 ethylene glycol/ethanol for 3 days and then ethanol for 5 days. The sample was degassed at room temperature under high vacuum (<5µm Hg) for 16 hrs prior to sorption analysis. During evacuation a color change from dark purple to aqua blue was observed. SIFSIX-2-Cu-i (synthesized by direct mixing) was activated by solvent exchange in MeOH for 3 days followed by evacuation at room temperature for 16 hrs, during which time a color change from light purple to light blue occurred.

The apparent surface areas of SIFSIX-2-Cu-i and SIFSIX-3-Zn were determined from the nitrogen adsorption isotherm collected at 77 K and the CO₂ adsorption isotherm collected at 298 K, respectively by applying the Brunauer-Emmett-Teller (BET) and Langmuir models. The determination of the isosteric heat of adsorption (Qₛ) for CO₂ in Figure 2c (main article) was estimated by applying the Clausius-Clapeyron expression using the CO₂ sorption isotherms measured at 258, 273, 288 and 298 K for SIFSIX-2-Cu-i and 298, 308, 318, 328 and 338 K for SIFSIX-3-Zn. The bath temperature was precisely controlled using a Julabo recirculating control system containing a mixture of ethylene glycol and water. Data points below 0.76 Torr were not used for this calculation, in order to avoid possible artifacts at very low coverage. The Qₛ curves in Figure B5c were estimated by applying the virial equation to the CO₂ isotherms at 273 and 298 K (Figures B12 and B13).
High Pressure Single-Gas Adsorption (Gravimetric Technique)

Adsorption equilibrium measurements of pure gases were performed using a Rubotherm gravimetric-densimetric apparatus (Bochum, Germany) (Scheme B1), composed mainly of a magnetic suspension balance (MSB) and a network of valves, mass flowmeters and temperature and pressure sensors. The MSB overcomes the disadvantages of other commercially available gravimetric instruments by separating the sensitive microbalance from the sample and the measuring atmosphere and is able to perform adsorption measurements across a wide pressure range, i.e. from 0 to 20 MPa. The adsorption temperature may also be controlled within the range of 77 K to 423 K. In a typical adsorption experiment, the adsorbent is precisely weighed and placed in a basket suspended by a permanent magnet through an electromagnet. The cell in which the basket is housed is then closed and vacuum or high pressure is applied.

Scheme B1. Representation of the Rubotherm gravimetric-densimetric apparatus.
The evacuated adsorbent is then exposed to a continuous gas flow (typically 50 mL/min) or static mode at a constant temperature. The gravimetric method allows the direct measurement of the reduced gas adsorbed amount $\Omega$. Correction for the buoyancy effect is required to determine the excess adsorbed amount using equation 1, where $V_{\text{adsorbent}}$ and $V_{\text{ss}}$ refer to the volume of the adsorbent and the volume of the suspension system, respectively. These volumes are determined using the helium isotherm method by assuming that helium penetrates all open pores of the materials without being adsorbed. The density of the gas is determined experimentally using a volume-calibrated titanium cylinder. By weighing this calibrated volume in the gas atmosphere, the local density of the gas is also determined. The simultaneous measurement of adsorption capacity and gas phase density as a function of pressure and temperature is therefore possible. The excess uptake is the only experimentally accessible quantity and there is no reliable experimental method to determine the absolute uptake. For this reason, only the excess amounts are considered in this work.

$$\Omega = m_{\text{excess}} - \rho_{\text{gas}}(V_{\text{adsorbent}} + V_{\text{ss}})$$ (1)

The pressure is measured using two Drucks high pressure transmitters ranging from 0.5 to 34 bar and 1 to 200 bar, respectively, and one low pressure transmitter ranging from 0 to 1 bar. Prior to each adsorption experiment, about 100 mg to 300 mg of sample is outgassed at 433 K under a residual pressure of $10^{-4}$ mbar. The temperature during adsorption measurements is held constant by using a thermostated circulating fluid.

**High Pressure Gas Mixture Adsorption (Gravimetric-Densimetric Gas Analysis Technique)**

Adsorption measurements of binary gas mixtures were carried out using a Rubotherm gravimetric-densimetric technique coupled to a gas analyzer, i.e. a gas chromatograph (GC) or a mass spectrometer (MS) (Scheme B2), enabling accurate measurements of mixture gas adsorption in the pressure range of 0-10 bar. The gas dosing system contains mass flow controllers (MFC) for gas premixing. Premixed gases can be also supplied. The sample (up to 2 g) is placed in a closed sample
holder to prevent disturbance of the fine powder samples during gas expansion from the dosing cell to adsorption cell, and outgassed at a maximum temperature of 298 K before the adsorbent mass is measured.

Scheme B2. Representation of the Rubotherm gravimetric-densimetric gas analysis (GDGA) apparatus for mixture gas adsorption at low and high pressure.

At the beginning of an experiment, the whole installation is under vacuum, and then the premixed gas is supplied to the first dosing volume ($V_1$) while the adsorption cell is kept isolated ($V_4$ and $V_6$ closed). Knowing the dosing volume, the pressure and the temperature and using an appropriate ($p - v - T$) equation of state (EOS) the amount of gas introduced can be determined and controlled to match the amount of adsorbent available for analysis which is a critical factor influencing the accuracy of the set-up. The circulation pump is switched on to homogenize the gas mixture. The system allows checking the initial gas composition by sampling the premixed gas to the gas analysers. Once the mixture is completely homogeneous it is directed in the adsorption cell by opening valves $V_4$ and $V_6$ then the circulation pump is switched on. Once the adsorption equilibrium is reached, the circulation pump is switched off and the mass is monitored with the magnetic balance, the mass being recorded every 10 min. If the standard
deviation is under 50 μg, the value is recorded; otherwise, the circulation pump is switched on for additional time and the control of equilibrium state is repeated. When the mass is stable, the mass, temperature and pressure are then recorded. Valve V₁₁ is then opened and the gas phase after adsorption analyzed by GC or MS. Using an appropriate \((p − ν − T)\) EOS for the studied mixture, in addition to the pressure, temperature and gas mixture composition after adsorption, the number of moles adsorbed of compound 1 can be calculated using equation (2):

\[
n_{1\text{ads}} = \frac{P \cdot V_1 \cdot y'_1}{R \cdot T} + y_1 \cdot \left( \frac{m_{\text{ads}}}{M_2} \cdot \frac{P \cdot V_1 \cdot y'_1}{R \cdot T} - \frac{P \cdot V_1 \cdot y'_2}{R \cdot T} \right) \cdot \frac{1}{1 + y_1 \cdot \left( \frac{M_1}{M_2} - 1 \right) \cdot \frac{m_{\text{sample}}}{m_{\text{ads}}}}
\]  

(2)

where:

\(n_{1\text{ads}}\): adsorbed amount of compound 1,

\(P\): pressure in the dosing cell

\(V_1\): volume of the dosing cell

\(y'_1\): gas phase composition before adsorption

\(y_1\): gas phase composition after adsorption of compound 1

\(T\): temperature

\(R\): ideal gas constant

\(m_{\text{ads}}\): total adsorbed amount in mg

\(M_1\): Molecular weight of compound 1

\(M_2\): Molecular weight of compound 2

\(m_{\text{sample}}\): mass the the evacuated sample

The number of moles adsorbed of compound 2, \(n_{2\text{ads}}\), is calculated using equation 3:

\[
n_{2\text{ads}} = \frac{m_{\text{ads\,total}}}{M_1 \cdot y_1 + M_2 \cdot y_2} - n_{1\text{ads}}
\]  

(3)

The adsorbed phase composition of compounds 1 and 2 are calculated using equations 4 and 5:
\[ x_1 = \frac{n_{1ads}}{n_{adstot}} \quad (4); \quad x_2 = \frac{n_{2ads}}{n_{adstot}} \quad (5) \]

The selectivity of compound 2 over 1 is calculated using equation 6:

\[
S_{2/1} = \frac{x_2}{x_1} \frac{y_2}{y_1} \quad (6)
\]

**Column Breakthrough Experiments**

The experimental set-up used for dynamic breakthrough measurements is shown in Scheme B3. The gas manifold consisted of three lines fitted with mass flow controllers. Line “A” is used to feed an inert gas, most commonly helium, to activate the sample before each experiment. The other two lines, “B” and “C” feed a mixture of CO₂ and other gases like N₂, CH₄, H₂. Hence, gas mixtures with concentrations representative of different industrial gases may be prepared. Whenever required, gases flowing through lines “B” and “C” may be mixed before entering a column packed with SIFSIX-2-Cu-i and SIFSIX-3-Zn using a four-way valve. The stainless steel column was 27 mm in length with 4 mm of inner (6.4 mm outer) diameter. The column downstream was monitored using a Hiden mass spectrometer. In a typical experiment, 0.1-0.4 g of adsorbent was treated at 298 K overnight under helium flow of 5 mL/min, then the gas flow was switched to the desired gas mixture at the same flow rate. The complete breakthrough of CO₂ and other species was indicated by the downstream gas composition reaching that of the feed gas. Experiments in the presence of 74% relative humidity (RH) were performed by passing the gas mixture through water vapor saturator at 20°C.
Scheme B3. Representation of the column breakthrough experiment.

The adsorption capacity for each compound was estimated from the breakthrough curves using the following equation:

\[ n_{adsi} = FC_i t_i \]  
(7)

where \( n_{adsi} \) is the adsorption capacity of the compound \( i \), \( F \) is the total molar flow, \( C_i \) is the concentration of compound \( i \) entering the column and \( t_i \) is the time corresponding to compound \( i \), which is estimated from the breakthrough profile.

The selectivity of \( \text{CO}_2 \) over species \( i \) in the binary mixture of \( \text{CO}_2 \) and species \( i \) is determined using the following equation:

\[ S_{\text{CO}_2/i} = \frac{x_{\text{CO}_2}}{y_{\text{CO}_2}} \frac{x_i}{y_i} \]  
(8)
where \( x \) and \( y \) are the molar compositions of the adsorbed phase and the gas phase, respectively.

**Kinetics of Gas Adsorption**

Kinetic studies of \( \text{CO}_2, \text{N}_2, \text{O}_2, \text{H}_2 \) and \( \text{CH}_4 \) adsorption on SIFSIX-3-Zn were carried out using the Rubotherm gravimetric apparatus operating in dynamic regime (Scheme B1). Initially, SIFSIX-3-Zn was properly evacuated at 298 K. In order to achieve an immediate constancy of pressure (0.5 bar) during kinetics tests and avoid the often noisy uptake during the rapid introduction of the studied gas, an initial baseline was set-up using helium gas at 0.5 bar for single gases and 1 bar for mixture, then the studied single gas or mixture is flushed with a flow of 300 mL/min to avoid any dependence of the kinetics on the mass flow controller. The fractional uptake was calculated by dividing the non-equilibrium uptake at time \( t_i \) by the equilibrium uptake at equilibrium. Adsorption kinetics analysis involving \( \text{CO}_2/\text{N}_2 \) 10:90 was carried out at 5 bar to compensate for the combination of the low \( \text{CO}_2 \) partial pressure and the large sample mass (1 g).
X-Ray Diffraction

PXRD patterns were recorded at room temperature on a Bruker D8 ADVANCE diffractometer at 20 kV, 5 mA for Cu-Kα (λ = 1.54056 Å), with a scan speed of 1 s/step and a step size of 0.02° in 2θ (total scan duration = 30 min.).

Single crystal X-ray diffraction data for SIFSIX-2-Cu were collected using a Bruker-AXS SMART-APEXII CCD diffractometer equipped with CuKα radiation (λ = 1.54178 Å). Diffraction data for SIFSIX-2-Cu-i were collected using synchrotron radiation (λ = 0.49594 Å) at the Advanced Photon Source, Chicago, IL.

Indexing was performed using APEX2 (difference vectors method). Data integration and reduction were performed using SaintPlus 6.01. Absorption correction was performed by the multi-scan method implemented in SADABS. Space groups were determined using XPREP implemented in APEX2. The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL-97 (full-matrix least-squares on F²) contained in APEX2 and WinGX v1.70.01 programs packages. Hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using a riding model with isotropic thermal parameters: U_{iso(H)} = 1.2U_{eq(CF)}.

For SIFSIX-2-Cu the contribution of heavily disordered solvent molecules was treated as diffuse using the Squeeze procedure implemented in Platon. A methanol molecule in the structure of SIFSIX-2-Cu-i is disordered over two positions. The amount of methanol in the crystal was established through occupancy refinement of the oxygen atom. The hydrogen atom of the hydroxyl group was placed in a geometrically calculated position and refined using an H···F distance restraint. This distance was chosen based on a search of the Cambridge Structural Database. For both structures the disordered SiF₆ was refined using the SADI geometry restraint. Crystal data and refinement conditions are shown in Tables B1 and B2.
Effect of Moisture upon Gas Adsorption

The impact of water vapor on CO$_2$ capacity and selectivity was evaluated in both SIFSIX-2-Cu-i and SIFSIX-3-Zn. CO$_2$ cyclic adsorption studies were performed at relative humidity levels similar to those in real applications, i.e. 74% RH. Results are summarized below:

- Water vapor adsorption isotherms for SIFSIX-2-Cu-i and SIFSIX-3-Zn collected under pure N$_2$ atmosphere reveal type-I behavior with water uptakes of 20 wt% and 11 wt%, respectively at 74% RH.

- Water sorption affinity/capacity was reduced in the presence of CO$_2$ gas mixtures as revealed by breakthrough experiments at 74% RH for both CO$_2$/H$_2$ 30:70 and CO$_2$/N$_2$ 10:90 mixtures (1.2-1.5 wt% for SIFSIX-2-Cu-i and SIFSIX-3-Zn). Each material, particularly SIFSIX-3-Zn, exhibits remarkably selective CO$_2$ adsorption in the presence of water. (Figures B15a, B15b, B16a and B16b).

- Interestingly, the presence of water in the mixture (e.g. CO$_2$/H$_2$ 30:70) has a negligible effect at elevated CO$_2$ concentrations. Breakthrough time for CO$_2$ in the presence of 74% RH is only marginally shorter than under dry conditions, thus CO$_2$ uptake and selectivity in the humid mixture are only slightly reduced (1.61 mmol/g and 191 at 74% RH vs. 1.99 mmol/g and 237 at 0% RH for SIFSIX-2-Cu-i; Figure B15b).

Analysis of the effect of adsorption/breakthrough cycling on SIFSIX-3-Zn shows very little alteration of CO$_2$ uptake and selectivity in CO$_2$/H$_2$ 30:70 and CO$_2$/N$_2$ 10:90 mixtures after multiple adsorption cycles. Additionally, the CO$_2$ breakthrough time was not reduced at 74% RH as compared to the breakthrough time at 0% RH (Figures B16a and B16b). This finding is extremely significant; H$_2$O vapor has a negligible effect on the CO$_2$ capture properties, in contrast to the benchmark zeolite 13X, where extensive drying of the gas stream is required to achieve optimal separations.\textsuperscript{8}

In addition, the PXRD pattern of SIFSIX-2-Cu-i at variable degrees of RH (5-95%; Figure B17) showed that crystallinity was retained when the compound was in contact with H$_2$O in the presence of
relevant gas mixtures. Variable temperature powder X-ray diffraction (VT-PXRD) experiments reveal thermal stability up to at least 573 K (Figure B18).

Notably, SIFSIX-3-Zn exhibits a phase change when exposed to RH higher than 35%, as indicated by PXRD peak shifts and the appearance of additional peaks (Figure B19). Regeneration of the original material, as verified by the reappearance of the major diffraction peaks, is accomplished by heating SIFSIX-3-Zn under vacuum for several hrs at 323-373 K. Reducing the RH alone did not reverse the phase change (Figure B20). PXRD analyses of regenerated SIFSIX-3-Zn after cyclic breakthrough tests at 74% RH and after high pressure sorption experiments confirm the presence of the original material (Figure B21). VT-PXRD experiments demonstrate that SIFSIX-3-Zn maintains crystallinity up to 523 K (Figure B22).

**Computational Studies**

Force field parameters required for modeling sorbate-MOF interactions were established, including repulsion and dispersion parameters, atomic partial point charges, and interacting atomic point polarizabilities according to considerations presented previously. Grand Canonical Monte Carlo (GCMC) simulations were performed to model CO$_2$ sorption in SIFSIX-3-Zn at experimentally-considered state points.

GCMC-generated CO$_2$ adsorption isotherms for SIFSIX-3-Zn (Figure B25) are in good agreement with experimental data. The associated molecular configurations reveal that maximum loading at the temperatures considered occurs at one CO$_2$ molecule per unit cell. Figure B26 shows the electropositive carbon atoms of CO$_2$ interacting strongly with four negatively charged framework fluorine atoms, directing the carbon atoms along the channels parallel to the SIFSIX-3-Zn pillars, consistent with steric constraints.
The simulated Q\(_a\) values are in excellent agreement with experiment, showing a relatively constant Q\(_a\) of ca. 45 kJ/mol for loadings of up to one CO\(_2\) molecule per unit cell (Figure B27). This is consistent with saturation of the favored sorption sites.

The polarizable CO\(_2\) model used in this work was developed using a previously described procedure.\(^{10}\) To verify the accuracy of the model in the bulk environment, an isothermal pressure-density plot was produced at 298.15 K using Grand canonical Monte Carlo (GCMC) methods and the results were compared to the corresponding experimental data.\(^{11}\) The isotherm for the model was found to be in excellent agreement with experimental data for the considered pressure range to within joint uncertainties (Figure B28).
Supplementary Tables

Table B1. Crystal data and structure refinement for SIFSIX-2-Cu.

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</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.0515, wR₂ = 0.1046</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.654 and -0.366 e/Å⁻³</td>
</tr>
</tbody>
</table>
Table B2. Crystal data and structure refinement for SIFSIX-2-Cu-i.

<table>
<thead>
<tr>
<th>Identification code</th>
<th>SIFSIX-2-Cu-i, [Cu(dpa)$_2$(SiF$_6$)$_6$]$_n$ • 2.5CH$_3$OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{26.50}$H$</em>{26}$CuF$_{6}$N$_4$O$_2$.5Si</td>
</tr>
<tr>
<td>Formula weight</td>
<td>646.14</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.49594 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Tetragonal, I4/mmm</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 13.6490(11) Å     α = 90°</td>
</tr>
<tr>
<td></td>
<td>b = 13.6490(11) Å     β = 90°</td>
</tr>
<tr>
<td></td>
<td>c = 8.0920(6) Å      γ = 90°</td>
</tr>
<tr>
<td>Volume</td>
<td>1507.5(2) Å$^3$</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>2, 1.423 g/cm$^3$</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.282 mm$^{-1}$</td>
</tr>
<tr>
<td>F(000)</td>
<td>660</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.02 x 0.01 x 0.01 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.04 to 19.68°</td>
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<tr>
<td>Limiting indices (h, k, l)</td>
<td>(-18/18, -16/18, -8/9)</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>11521 / 535 (R$_{int}$ = 0.0444)</td>
</tr>
<tr>
<td>Completeness to theta =</td>
<td>17.39°</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9972 and 0.9944</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F$^2$</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>535 / 2 / 58</td>
</tr>
<tr>
<td>Goodness-of-fit on F$^2$</td>
<td>1.012</td>
</tr>
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<td>Final R indices [I&gt;2σ(I)]</td>
<td>R$_1$ = 0.0455, wR$_2$ = 0.1432</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R$_1$ = 0.0488, wR$_2$ = 0.1456</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.379 and -0.517 e/Å$^3$</td>
</tr>
</tbody>
</table>
Table B3. Comparison of experimental and theoretical micropore volumes (cm$^3$/g) of SIFSIX-2-Cu and SIFSIX-2-Cu-i.

<table>
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<tr>
<th>MOM</th>
<th>$V_{\text{calc}}^a$</th>
<th>$V_{\text{exp}}^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIFSIX-2-Cu</td>
<td>1.10</td>
<td>1.15</td>
</tr>
<tr>
<td>SIFSIX-2-Cu-i</td>
<td>0.25</td>
<td>0.26</td>
</tr>
</tbody>
</table>

$^a$ calculated by Platon$^9,10$

$^b$ experimental value determined by t-plot method

Table B4. Force field parameters for the polarizable CO$_2$ model used in the molecular simulations in this work.

<table>
<thead>
<tr>
<th>Atomic Site</th>
<th>Distance (Å)$^a$</th>
<th>$\sigma$ (Å)</th>
<th>$\varepsilon$ (K)</th>
<th>$q$ (e$^-$)</th>
<th>$\alpha^\circ$ (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.000</td>
<td>3.30366</td>
<td>19.61757</td>
<td>0.77134</td>
<td>1.2281</td>
</tr>
<tr>
<td>O</td>
<td>1.162</td>
<td>0.00000</td>
<td>0.00000</td>
<td>-0.38567</td>
<td>0.7395</td>
</tr>
<tr>
<td>OA$^b$</td>
<td>1.208</td>
<td>2.99429</td>
<td>46.47457</td>
<td>0.00000</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

$^a$ refers to the distance from the molecular center-of-mass.

$^b$ refers to the off-atom positions.
Supplementary Figures

Figure B1. Room temperature PXRD patterns of SIFSIX-2-Cu.
Figure B2. Room temperature PXRD patterns of SIFSIX-2-Cu-i.
Figure B3. Room temperature PXRD patterns of SIFSIX-3-Zn.
Figure B4. N$_2$ adsorption isotherms of SIFIX-2-Cu (red) and SIFIX-2-Cu-i (blue) at 77 K. Adsorption and desorption are represented by closed and open symbols, respectively.
Figure B5. a) Low pressure isotherms at 298 K for SIFSIX-2-Cu (red) and SIFSIX-2-Cu-i (purple); b) CO\textsubscript{2}/N\textsubscript{2} 10:90 and CO\textsubscript{2}/CH\textsubscript{4} 50:50 IAST selectivities of SIFSIX-2-Cu and SIFSIX-2-Cu-i, calculated from the low pressure isotherms at 298 K; c) CO\textsubscript{2} Q\textsubscript{s} of SIFSIX-2-Cu and SIFSIX-2-Cu-i, estimated from low pressure isotherms at 273 and 298 K by the virial method.
Figure B6. Column breakthrough experiments for a) CO$_2$/N$_2$ 10:90; b) CO$_2$/CH$_4$ 50:50; and c) CO$_2$/H$_2$ 30:70 binary gas mixtures at 298 K and 1 bar on SIFSIX-2-Cu-i.
Figure B7. Relationship between cost of CO$_2$ capture, CO$_2$ selectivity, and working CO$_2$ capacity for solid sorbents.$^{12}$
Figure B8. Low pressure, variable temperature CO$_2$ isotherms for SIFSIX-3-Zn.
Figure B9. High pressure single-gas CO$_2$, N$_2$, CH$_4$, O$_2$, and H$_2$ adsorption isotherms for (a) SIFSiX-3-Zn and (b) SIFSiX-2-Cu-i.
Figure B10. Experimental CO$_2$/H$_2$ 30:70 adsorption isotherms as compared to experimental pure CO$_2$ and H$_2$ isotherms at 298 K for SIFSIX-3-Zn.
Figure B11. Fractional uptake of CO$_2$, N$_2$, CH$_4$ and H$_2$ on SIFSix-3-Zn at 0.5 bar and 298 K.
Figure B12. Virial fit of the CO$_2$ isotherms of SIFSIX-2-Cu at 273 and 298 K (see Figures B5a and B5c).

\begin{align*}
\text{a}_0 &= -2650.71 \\
\text{a}_1 &= 209154.4 \\
\text{a}_2 &= -9.385E7 \\
\text{a}_3 &= 2.553E10 \\
\text{a}_4 &= -5.958E12 \\
\text{a}_5 &= 5.320E14 \\
\text{adj } R^2 &= .99999
\end{align*}
Figure B13. Virial fit of the CO$_2$ isotherms of SIFSIX-2-Cu-i at 273 and 298 K (see Figures B5a and B5c).
Figure B14. Cyclic CO$_2$ adsorption on SIFSiX-3-Zn using vacuum swing regeneration mode at 323 K and 0.15 bar.

Figure B15. Example of one cycle column breakthrough experiment for a CO$_2$/N$_2$ 10:90 binary gas system at 298 K and 1 bar under dry conditions and in the presence of 74% RH carried out on SIFSiX-2-Cu-i.
Figure B16. Example of one cycle column breakthrough experiment for a CO$_2$/H$_2$ 30:70 binary gas system at 298 K and 1 bar under dry conditions and in the presence of 74% RH carried out on SIFSIX-2-Cu-i.

Figure B17. Example of one cycle column breakthrough experiment for a CO$_2$/N$_2$ 10:90 binary gas system at 298 K and 1 bar under dry conditions and in the presence of 74% RH carried out on SIFSIX-3-Zn.
Figure B18. Example of one cycle column breakthrough experiment for a CO$_2$/H$_2$ 30:70 binary gas system at 298 K and 1 bar under dry conditions and in the presence of 74% RH carried out on SIFSIX-3-Zn.
Figure B19. PXRD patterns of SIFSIX-2-Cu-i when exposed to varying relative humidity under N\textsubscript{2} atmosphere.

Figure B20. VT-PXRD patterns of SIFSIX-2-Cu-i under vacuum at non-ambient temperatures (173 K- 573 K).
Figure B21. PXRD patterns of SIFSIX-3-Zn when exposed to varying relative humidity under N₂ atmosphere.

Figure B22. PXRD of SIFSIX-3-Zn after humidity PXRD experiment and regeneration by heating under vacuum.
Figure B23. PXRD of SIFSIX-3-Zn after multiple cycles of humid breakthrough experiments and high pressure sorption experiments compared to the calculated powder pattern.

Figure B24. VT-PXRD patterns of SIFSIX-3-Zn under vacuum and at non-ambient temperatures (173 K- 573 K).
Figure B25. CO$_2$ volumetric adsorption capacity at low pressure (0-0.25 bar) and 298 K for SIFSIX-3-Zn, Mg-dobdc (313 K), UTSA-16 and SIFSIX-2-Cu-i.

Figure B26. Water adsorption isotherm on SIFSIX-2-Cu-i and SIFSIX-3-Zn at 298 K after activation at 323 K.
Figure B27. GCMC-generated CO$_2$ sorption isotherms for SIFSIX-3-Zn.
Figure B28. Simulations show CO$_2$ molecules adsorbed in the pores of SIFSIX-3-Zn with the electropositive carbon atoms attracted to the SiF$_6^{2-}$ pillaring anions.
Figure B29. Simulated and experimental CO$_2$ $Q_{st}$ plots for SIFSIX-3-Zn.

Figure B30. Pressure-density isotherm for CO$_2$ at 298.15 K for the CO$_2$ model used in this work (red) compared to experimental data (black).
Additional References

APPENDIX C:

A Robust Molecular Porous Material with High CO$_2$ Uptake and Selectivity

Materials and Methods

Reagents and solvents were purchased from Sigma Aldrich or Fisher Scientific and used as received without further purification.

Preparation of [Cu$_2$(ade)$_4$(TiF$_6$)$_2$], MPM-1-TIFSIX: At room temperature, 0.152 mmol (20.5 mg) of adenine dissolved in 3 mL of 1:1 acetonitrile/H$_2$O was layered above 3 mL of an aqueous solution containing 0.076 mmol (17.6 mg) of Cu(NO$_3$)$_2$·2.5H$_2$O and 0.076 mmol (15.0 mg) of (NH$_4$)$_2$TiF$_6$. 1 mL of 1:1 acetonitrile/H$_2$O was layered between the top and bottom solutions to slow the rate of reaction. Purple, rectangular prismatic crystals formed in 51% yield after 4 days.

Room temperature powder X-ray diffraction (PXRD) was carried out on a Bruker D8 Advance $\theta/\theta$ diffractometer (generator at 40kV, 40 mA; Cu-Kα,λ = 1.5418 Å) equipped with a 1D LynxEye Super Speed detector and 0.02 mm Ni filter. 2θ scans from 4-50° (step size = 0.02°) were performed for a duration of 19 minutes. For variable temperature PXRD measurements, the instrument was outfitted with an Anton Paar TTK450 variable temperature chamber and 2θ scans from 3-40° (step size = 0.02°) were performed for a duration of 9 min, 15 s.

Degassing and gas adsorption measurements and were conducted on a Micromeritics ASAP 2020 surface area and porosity analyzer equipped with two turbo molecular pumps (one for degassing and one for analysis). Prior to data collection, MPM-1-TIFSIX and MPM-1-Cl were exchanged with methanol 3 times daily for 2 days and degassed under dynamic high vacuum (<10μm Hg) at room temperature for 12 hours. High vacuum was maintained at a pressure <3 μm Hg for the final 9.5 hours of activation.
Activation was verified by ensuring that the outgassing rate of each sample was below the limit of detection (<1 μm Hg/min) during the final 8 hours of evacuation.

Single crystal X-ray diffraction data for MPM-1-TIFSIX were collected at 100(2) K on a Bruker-AXS D8 VENTURE diffractometer equipped with a PHOTON-100/CMOS detector (CuKα, λ = 1.5418 Å). Indexing was performed using APEX2.¹ Data integration and reduction were completed using SaintPlus 6.01.² Absorption correction was performed by the multi-scan method implemented in SADABS.³ The space group was determined using XPREP implemented in APEX2.¹ The structure was solved with SHELXS-97 (direct methods)⁴ and refined on F² (nonlinear least-squares method) with SHELXL-97 contained in APEX2,WinGX v1.70.01,⁴⁵ and OLEX2 v1.1.5⁶ program packages. All non-hydrogen atoms were refined anisotropically. The contribution of disordered solvent molecules was treated as diffuse using the Squeeze routine implemented in Platon.⁷
Table C1. Crystal data and structure refinement for MPM-1-TIFSIX.

<table>
<thead>
<tr>
<th>Compound</th>
<th>MPM-1-TIFSIX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{24}H_{26}Cu_{2}F_{12}N_{22}Ti_{2}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1073.55</td>
</tr>
<tr>
<td>Temperature / K</td>
<td>100(2)</td>
</tr>
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<td>Crystal system</td>
<td>trigonal</td>
</tr>
<tr>
<td>Space group</td>
<td>$\overline{R}3m$</td>
</tr>
<tr>
<td>a / Å</td>
<td>32.3397(7)</td>
</tr>
<tr>
<td>b / Å</td>
<td>32.3397(7)</td>
</tr>
<tr>
<td>c / Å</td>
<td>13.7255(3)</td>
</tr>
<tr>
<td>α / °</td>
<td>90.00</td>
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<tr>
<td>β / °</td>
<td>90.00</td>
</tr>
<tr>
<td>γ / °</td>
<td>120.00</td>
</tr>
<tr>
<td>Volume / Å³</td>
<td>12431.7(7)</td>
</tr>
<tr>
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<td>9</td>
</tr>
<tr>
<td>$\rho_{\text{calc}}$ / mg/mm³</td>
<td>1.291</td>
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<tr>
<td>m / mm⁻¹</td>
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</tr>
<tr>
<td>F(000)</td>
<td>4806</td>
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<tr>
<td>Crystal size / mm³</td>
<td>0.22 × 0.12 × 0.12</td>
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<td>2θ range for data collection</td>
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<td>Index ranges</td>
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<td>Reflections collected</td>
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</tr>
<tr>
<td>Independent reflections</td>
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</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>2717 / 0 /161</td>
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<td>1.052</td>
</tr>
<tr>
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<tr>
<td>Final R indices [all data]</td>
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</tr>
<tr>
<td>Largest diff. peak/hole / eÅ⁻³</td>
<td>0.735 / -0.959</td>
</tr>
</tbody>
</table>

Previously Reported [Cu₅(ade)₄X₂] Paddlewheel Compounds

[Cu₅(ade)₄Cl₂]Cl₂·6H₂O: The parent compound based upon [Cu₅(ade)₄X₂] paddlewheels (X = axial ligand), [Cu₅(ade)₄Cl₂]Cl₂·6H₂O, crystallized from aqueous solution in space group Cmca as a close-packed structure in which no ade-ade or ade-Cl hydrogen bonds are present.⁸ The bridging
equatorial ade ligands of each paddlewheel, PW, assume an up-up-down-down arrangement. Water molecules of hydration form hydrogen bonds to all available ade sites and to the Cl' counterions.

\[
\text{[Cu}_2(\text{ade})_4\text{Cl}_2] \text{Cl}_2 \text{ (MPM-1-Cl): MPM-1-Cl, a solvate of the parent compound,}^9 \text{ crystallized from methanol in space group } R\bar{3}m. \text{ MPM-1-Cl contains the same cationic PW dimers as the parent but adopts an open structure which encloses hourglass-shaped (diameter 6.2 Å) and small trigonal channels that lie parallel to the } c \text{ axis. Axial Cl' ligands line the larger channels. Each PW in MPM-1-Cl engages in 12 hydrogen bonds: 8 to its four nearest neighbors and 4 to Cl' counterions which link ade ligands of adjacent PWs through Cl'--HN contacts (3.03 Å).}
\]

**Surface Area Determination for MPM-1-Cl**

Crystal structures of MPM-1-Cl collected at 100 and 298 K by Thomas-Gipson et al. indicated no significant change in pore size with temperature. However, \( N_2 \) isotherms collected at 77 K revealed negligible uptake and a Langmuir surface area of only 30 m\(^2\)/g.\(^9\) The authors concluded that strong interactions between \( N_2 \) and the channel windows of MPM-1-Cl hinder diffusion into the material. The coexistence of restricted \( N_2 \) uptake at 77 K and type-I CO\(_2\) uptake at 195 K has been observed previously in materials with pore sizes larger than the kinetic diameter of \( N_2 \).\(^{10}\) It has been proposed that the greater thermal energy of CO\(_2\) and the more favorable adsorption enthalpy of CO\(_2\) onto polar surfaces permit the CO\(_2\) molecules to overcome the diffusional barrier experienced by \( N_2 \) at 77 K.\(^{10a}\)
Powder X-ray Diffraction

Figure C1. Calculated and experimental (298 K) PXRD patterns for MPM-1-TIFSIX.

Figure C2. Calculated and experimental (298 K) PXRD patterns for MPM-1-C1.
Gas Adsorption in MPM-1-Cl

Figure C3. $N_2$ isotherm collected at 77 K for MPM-1-Cl.

Figure C4. $CO_2$ isotherm collected at 195 K for MPM-1-Cl.
Void Analysis

Figure C5. The contact surface (gold) generated by a spherical probe (radius = 1.65 Å) in MPM-1-TIFSIX suggests that the small channels and the passages connecting the large channels are accessible (Mercury CSD 3.1).

Figure C6. View of the passage connecting the large channels in MPM-1-TIFSIX.
Figure C7. The contact surface (gold) generated by a spherical probe (radius = 1.65 Å) in MPM-1-Cl suggests that the small channels are not accessible.

Isotherm Fitting

Figure C8. Coefficients and adjusted $R^2$ value obtained from fitting the CO$_2$ isotherms of MPM-1-TIFSIX at 273 and 298 K to the virial equation.
Figure C9. Coefficients and adjusted $R^2$ value obtained from fitting the CO$_2$ isotherms of MPM-1-Cl at 273 and 298 K to the virial equation.

Computational Methods and Results

Molecular simulation parameters used in the computational studies of MPM-1-TIFSIX were derived according to methods described previously. These include repulsion/dispersion, permanent electrostatics, and induced dipole parameters that were modeled using the Lennard-Jones 12-6 potential, partial charges with Ewald summation, and Thole-Applequist many-body polarization, respectively.

For repulsion/dispersion, the Lennard-Jones parameters from the OPLS-AA force field were used for all atoms where appropriate; otherwise, the parameters were taken from the Universal Force Field (UFF).

Partial charges for the atoms in MPM-1-TIFSIX were determined from electronic structure calculations on several fragments that mimic the chemical environment of the compound. Examination of the unit cell revealed 21 atoms in chemically distinct atomic environments (Figure C10); this served as the basis for selecting viable fragments for charge fitting calculations. The addition of hydrogen atoms, where appropriate, was required for the chemical termination of fragment boundaries. Representational
fragments for MPM-1-TIFSIX can be found as .xyz files online in the Supporting Information for this manuscript.

Calculations on each fragment were performed using the NWChem *ab initio* simulation software. All light atoms were treated with the 6-31G* basis set. For the Cu$^{2+}$ and Ti$^{4+}$ ions, the LANL2DZ effective core potential basis set was used to treat the inner electrons of these many-electron species. The partial charges were determined through a least-squares fit approach to the electrostatic potential surface of each fragment. For each chemically distinct atom, the partial charges were averaged between the fragments. Atoms that are buried or located on the edges of the fragments were not included in the averaging. The averaged partial charges for each chemically distinct atom in MPM-1-TIFSIX are presented in Table C2.

Many-body polarization effects were parameterized using atomic point polarizabilities. The polarizabilities used for all light atoms were taken from van Duijnen et al., while the polarizabilities for Cu$^{2+}$ and Ti$^{4+}$ were taken from previous work. Simulations of CO$_2$ sorption in MPM-1-TIFSIX were performed using grand canonical Monte Carlo (GCMC) methods in a $1 \times 1 \times 2$ system cell of the MPM. Two five-site CO$_2$ models that were developed previously were used: a model including only van der Waals and electrostatic parameters (referred to as ‘Elec’) and a model including van der Waals, electrostatics, and induced dipole parameters (referred to as ‘Pol’).

All simulations were performed using the Massively Parallel Monte Carlo (MPMC) code. For all state points considered, the simulations consisted of $1 \times 10^6$ Monte Carlo steps to guarantee equilibration, followed by an additional $1 \times 10^6$ steps to sample the desired thermodynamic properties.
Table C2. Partial charges (in $e^-$) for the chemically distinct atoms as defined in MPM-1-TIFSIX. Numerical labels correspond to Figure C10.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Label</th>
<th>$q$ ($e^-$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>1</td>
<td>0.6497</td>
</tr>
<tr>
<td>Ti</td>
<td>2</td>
<td>1.7495</td>
</tr>
<tr>
<td>F</td>
<td>3</td>
<td>$-0.5410$</td>
</tr>
<tr>
<td>F</td>
<td>4</td>
<td>$-0.5997$</td>
</tr>
<tr>
<td>F</td>
<td>5</td>
<td>$-0.6020$</td>
</tr>
<tr>
<td>F</td>
<td>6</td>
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</tr>
<tr>
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</tr>
<tr>
<td>N</td>
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</tr>
<tr>
<td>N</td>
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</tr>
<tr>
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<tr>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
<td>C</td>
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</tr>
<tr>
<td>C</td>
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</tr>
<tr>
<td>C</td>
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<td>0.9228</td>
</tr>
<tr>
<td>H</td>
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<tr>
<td>H</td>
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<tr>
<td>H</td>
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<tr>
<td>H</td>
<td>21</td>
<td>0.4667</td>
</tr>
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</table>
**Figure C10.** Numbering scheme for the chemically distinct atoms in MPM-1-TIFSIX (see Table C2). Atom colors: C, grey; H, white; N, blue; F, cyan; Ti, silver; Cu, orange.

**Figure C11.** Comparison of the experimental CO$_2$ isotherm at 298 K for MPM-1-TIFSIX to GCMC-simulated isotherms obtained via the ‘Elec’ and ‘Pol’ models. Error bars are shown in black.
Figure C12. Comparison of experimental CO$_2$ $Q_{st}$ values to those obtained from simulated isotherms using the ‘Elec’ and ‘Pol’ models.

Figure C13. Views of the CO$_2$ binding sites in MPM-1-TIFSIX as observed from simulation. The primary binding site (left) corresponds to sorption in a small passage joining the large channels, whereby CO$_2$ coordinates simultaneously to the equatorial fluorine atoms of two proximal TIFSIX groups. The secondary binding site (middle) involves sorption onto the TIFSIX groups lining the large channels. Orientational constraints are not imposed upon CO$_2$ molecules at this site. The tertiary binding site (right) is located in the small channels. Atom colors: C, cyan; H, white; N, blue; O, red; F, green; Ti, silver; Cu, gold.
IAST Calculations

To predict binary mixture adsorption in MPM-1-TIFSIX and MPM-1-Cl, the single-component CO₂, CH₄, and N₂ adsorption isotherms were first fit to the dual-site Langmuir-Freundlich equation:\textsuperscript{23}

\[
n = \frac{n_{m1}b_1P(\frac{1}{t_1})}{1 + b_1P(\frac{1}{t_1})} + \frac{n_{m2}b_2P(\frac{1}{t_2})}{1 + b_2P(\frac{1}{t_2})}
\]

In this equation, \(n\) is the amount adsorbed per mass of adsorbent (mol/kg), \(P\) is the total pressure (kPa) of the bulk gas at equilibrium with the adsorbed phase, \(n_{m1}\) and \(n_{m2}\) are the saturation uptakes (mol/kg) for sites 1 and 2, \(b_1\) and \(b_2\) are the affinity coefficients (kPa\(^{-1}\)) for sites 1 and 2, and \(t_1\) and \(t_2\) are the heterogeneity factors for sites 1 and 2. All isotherms were fitted with \(R^2 \geq 0.9999\). This equation has been used to fit isotherm data for a variety of PCPs.\textsuperscript{24} The fitted isotherm parameters were applied to perform the necessary integrations according to IAST.\textsuperscript{25} The selectivity, \(S\), for component \(i\) vs. component \(j\) was calculated by the following equation:

\[
S_{ij} = \frac{x_i y_j}{x_j y_i}
\]

where \(x_i\) and \(y_i\) are the mole fractions of component \(i\) in the adsorbed and bulk phases, respectively.

Table C3. Parameters obtained from dual-site Langmuir-Freundlich fitting of the experimental 298 K CO₂, CH₄, and N₂ isotherms for MPM-1-TIFSIX and MPM-1-Cl.

<table>
<thead>
<tr>
<th></th>
<th>MPM-1-TIFSIX</th>
<th></th>
<th>MPM-1-Cl</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO₂</td>
<td>CH₄</td>
<td>N₂</td>
<td>CO₂</td>
</tr>
<tr>
<td>(n_{m1}) (mol/kg)</td>
<td>7.6054936</td>
<td>2.30172905</td>
<td>2.05785247</td>
<td>5.88888353</td>
</tr>
<tr>
<td>(n_{m2}) (mol/kg)</td>
<td>1.71337922</td>
<td>1.5556105</td>
<td>0.35067924</td>
<td>6.33510078</td>
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<tr>
<td>(b_1) (kPa(^{-1}))</td>
<td>0.00434629</td>
<td>1.5858E-05</td>
<td>1.38E-05</td>
<td>0.00186894</td>
</tr>
<tr>
<td>(b_2) (kPa(^{-1}))</td>
<td>0.28996804</td>
<td>0.00612447</td>
<td>0.01006389</td>
<td>0.00372652</td>
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<tr>
<td>(t_1)</td>
<td>0.98253203</td>
<td>0.52935845</td>
<td>0.53025146</td>
<td>0.8374132</td>
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<tr>
<td>(t_2)</td>
<td>1.33977633</td>
<td>0.98567384</td>
<td>0.95222032</td>
<td>3.04316904</td>
</tr>
</tbody>
</table>
Variable Temperature PXRD and Water Stability

**Figure C14.** Comparison of the calculated PXRD pattern to experimental patterns collected at 298, 358, 418, 478, and 568 K for MPM-1-TIFSIX.

**Figure C15.** Comparison of the 77 K N\textsubscript{2} isotherms collected on activated MPM-1-TIFSIX before and after immersion in H\textsubscript{2}O for 24 hrs.
Figure C16. Comparison of the 298 K CO$_2$ isotherms collected on activated MPM-1-TIFSIX before and after immersion in H$_2$O for 24 hrs.

Additional References

2. Bruker SAINT Data Reduction Software; Bruker AXS Inc., Madison, WI, USA 2009.
APPENDIX D:
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Enhancement of CO\textsubscript{2} selectivity in a pillared pcu MOM platform through pillar substitution


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Porous materials with optimal adsorption thermodynamics and kinetics for CO2 separation

Author: Patrick Nugent, Youssif Belmabkhout, Stephen D. Burd, Amy J. Cairns, Ryan Luebke, Katherine Forrest

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Patrick Nugent was born in Hollywood, FL. He obtained a B.S. in Chemistry from the University of South Florida (USF) in 2008 and joined the Zaworotko research group at USF as a graduate student in 2009.

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He has presented his work at various colloquia including the 2012 Gordon Research Conference on Crystal Engineering in Waterville Valley, NH and the Spring 2013 National Meeting of the American Chemical Society in New Orleans, LA. In 2013 he attended the American Crystallographic Association Summer Course for Chemical Crystallography at Northwestern University in Evanston, IL.

Patrick has authored several papers in established scientific journals, e.g. Nature, the Journal of the American Chemical Society, and Chemical Communications.