Selective Capture of Carbon Dioxide from Hydrocarbons Using a Metal-Organic Framework: Relevance to the Purification of Natural Gas and Acetylene

Omid T. Qazvini\textsuperscript{1,2} and Shane G. Telfer*\textsuperscript{1}

\textsuperscript{1}MacDiarmid Institute for Advanced Materials and Nanotechnology, School of Fundamental Sciences, Massey University, Palmerston North, New Zealand
\textsuperscript{2}Department of Chemical Engineering and Analytical Science, The University of Manchester, Oxford Road, Manchester M13 9PL, UK.

Abstract: Efficient and sustainable methods for carbon dioxide (CO\textsubscript{2}) capture are highly sought after. Mature technologies involve chemical reactions that absorb CO\textsubscript{2} but they have many drawbacks. Energy-efficient alternatives may be realized by porous physisorbers with void spaces that are complementary in size and electrostatic potential to molecular CO\textsubscript{2}. Here, we present a robust, recyclable and inexpensive adsorbent termed MUF-16 (MUF = Massey University Framework). This metal-organic framework captures CO\textsubscript{2} with a high affinity in its one-dimensional channels. The position of the CO\textsubscript{2} molecules sequestered in the framework pores, as determined by X-ray crystallography, illustrate how complementary noncovalent interactions envelop the CO\textsubscript{2} while repelling other guest molecules. The low affinity of the MUF-16 pores for these competing gases underpins new benchmarks for the adsorption of CO\textsubscript{2} over methane, acetylene, ethylene, ethane, propylene and propane. IAST calculations show that for 50/50 mixtures at 293 K and 1 bar, the CO\textsubscript{2}/CH\textsubscript{4} selectivity is 6690 and the CO\textsubscript{2}/C\textsubscript{2}H\textsubscript{4} selectivity is 510, for example. Breakthrough gas separations under dynamic conditions benefit from short time lags in the elution of the weakly-adsorbed component to deliver high-purity hydrocarbon products. Ultimately, MUF-16 may be applicable to the removal of CO\textsubscript{2} from sources such as natural gas and chemical feedstocks.

Introduction

Chemical separation processes consume vast quantities of energy.\textsuperscript{1} Economical and practical pathways to alleviating this burden are required. This is especially relevant to the capture of CO\textsubscript{2}, which is a common impurity in crude gas streams. CO\textsubscript{2} removal is integral to upgrader natural gas and biogas, for example, and to the purification of valuable hydrocarbons prior to polymerization or chemical derivatization.\textsuperscript{2} These processes are separations that rely on discrimination between CO\textsubscript{2} and other gases. One established technology to trap the CO\textsubscript{2} by a chemical reaction with an absorbent. This typically involves chemisorption to an amine in aqueous solution.\textsuperscript{3, 4} Chemisorption incurs multiple drawbacks, however, including a high energy penalty during regeneration, amine losses due to degradation and evaporation, and the corrosion of hardware and pipelines.\textsuperscript{5} Other conventional separation methods involve solvent extraction or cryogenic distillation, which are burdened with a high energy penalty and large amount of solvent waste.

The physisorption of CO\textsubscript{2} in nanoporous materials is an attractive alternative.\textsuperscript{6, 7} Physisorption is governed by weak, noncovalent bonding interactions in pores that are structured on the molecular scale.\textsuperscript{8} Ideally, they lower the energy requirements for regeneration since driving off the trapped CO\textsubscript{2} simply involves breaking interactions that are inherently weak. Effective physisorbers combine rapid guest diffusion, recyclability and long-term stability with selectivity for CO\textsubscript{2} over competing gases at relevant concentrations.\textsuperscript{9} Thus, they may offer a sustainable solution to CO\textsubscript{2} capture. In this context, metal-organic frameworks (MOFs) have risen to prominence.\textsuperscript{10-14} MOF materials are built up from metal ions and organic ligands, and their pore shape, size and chemical environment can be systematically designed. In turn, this allows interactions between framework hosts and molecular guests to be tailored. In the search of effective MOF physisorbers, it is clear that simply searching for materials with ever-higher levels of CO\textsubscript{2} uptake \textit{per se} is unlikely to produce an adsorbent that is adept at gas separations. Instead, significant advances will emerge by suppressing the uptake of competing gases,\textsuperscript{15, 16} developing scalable synthetic protocols, mitigating the impact of common impurities such as water vapour and oxygen, and developing low energy pathways to adsorbent recycling.

The removal of CO\textsubscript{2} from hydrocarbons is an important process.\textsuperscript{2} While natural gas and biogas are primarily composed of methane (at high pressure and low pressure, respectively), contamination by CO\textsubscript{2} can prevent optimal heat release from gas combustion, and cause pipeline corrosion and dry ice formation.\textsuperscript{17} MOFs, however, offer a means of reducing the CO\textsubscript{2} concentration in the presence of dominant quantities of methane.\textsuperscript{10, 18, 19} Acetylene (C\textsubscript{2}H\textsubscript{2}) is an essential feedstock for the industrial production of commodity materials.\textsuperscript{20, 21} When acetylene is generated, however, it typically coexists with CO\textsubscript{2} impurities.\textsuperscript{22} The separation of C\textsubscript{2}H\textsubscript{2} and CO\textsubscript{2} is challenging due to their similar physical properties (Table S4). MOF physisorbers offer a potential solution but most show an affinity toward C\textsubscript{2}H\textsubscript{2} rather than CO\textsubscript{2}.\textsuperscript{11} The selective adsorption of the CO\textsubscript{2} component has seldom been reported despite its operational simplicity in process design and the promise of energy efficiency. Conversely, gas purification using hydrocarbon-selective MOFs requires additional stages if the eluent is contaminated by adsorbed CO\textsubscript{2} during the desorption step.\textsuperscript{23} Despite recent advances in MOF chemistry, challenges remain in producing framework adsorbents that combine good separation capabilities with wider performance characteristics such as...
scalability, recyclability and easy low-energy regeneration. MOF adsorbents that may be applied to methane purification and that preferentially adsorb CO₂ from C₂H₂ are in particular demand.

Figure 1. (a) Synthetic routes to the MUF-16 family and optical micrographs of the reaction products. (b) Infinite secondary building units (iSBUs) in MUF-16 comprise one-dimensional cobalt(II) chains connected by μ₂-bridging carboxylate groups of the Haip ligands (H₂aip = 5-aminoisophthalic acid). The cobalt(II) ions are depicted as filled octahedra. (c) The iSBUs are linked into planar two-dimensional sheets by the Haip ligands and further connected into a three-dimensional framework by hydrogen bonding (depicted as dashed lines) between adjacent sheets. (d) MUF-16 features one-dimensional channels with approximate dimensions of 3.6 × 7.6 Å that propagate through the framework. The Connolly surface of the framework is shown in orange and defined with a probe of diameter 1.0 Å. Colour code: Co = magenta; O = red; C = grey, N = blue.

Results and Discussion

Inspired by the superb properties of MOFs derived from straightforward and readily-available linkers,²⁴ ²⁵ our interest was captured by the MUF-16 (MUF = Massey University Framework) series of materials. These frameworks are prepared by combining 5-aminoisophthalic acid (H₂aip), an inexpensive, commercially-available linker, with cobalt(II), nickel(II), or manganese(II) salts in methanol (Figure 1a). This delivers a family of compounds with the general formula [M(Haip)₂]²⁶ ²⁷ referred to as MUF-16 (M = Co), MUF-16(Ni) and MUF-16(Mn), respectively. These easily-handled crystalline materials are high yielding on gram scales and tolerant to oxygen and water vapour. Their crystal structures were determined by single crystal X-ray diffraction (Table S1). The three frameworks are isostructural, belonging to the P2/a space group. Individually, the metal ions adopt an octahedral geometry with four carboxylate and two amino donors arranged trans to one another. These ions are aligned into one-dimensional chains along a crystallographic axis supported on each side by μ₂-bridging carboxylate groups (Figure 1b). Adjacent chains are connected into two-dimensional sheets by Haip ligands that extend across the plane by coordinating to adjacent one-dimensional chains with both their amino and carboxylate donors (Figure 1b). Only one of the two carboxyl groups of each Haip ligand coordinates to the metal. The other remains protonated and engages in hydrogen-bonding with a partner from an adjacent layer (Figure 1c). These interactions link the layers into three-dimensional frameworks. The frameworks support one-dimensional channels of approximately 3.6 × 7.6 Å (accounting for the van der Waals surfaces of the atoms, Figure 1d). In their as-synthesized form the pores contain occluded water, which can be easily removed by heating at 130 °C in vacuo.

Thermogravimetric analysis demonstrated the thermal stability of the MUF-16 materials beyond 330 °C (Figure S2). Their purity was established by both elemental analysis and powder X-ray diffraction (Figure S5). The frameworks are chemically
robust, being unaffected by soaking in water or exposure to humid air for prolonged periods, as confirmed by powder X-ray diffraction and gas adsorption analysis (vide infra and Figures S6-S8 and S13).

As suggested by SCXRD, the MUF-16 frameworks are accessible to a range of incoming gases. Activation to give permanently porous materials is straightforward. Nitrogen adsorption isotherms measured at 77 K gave BET surface areas of 214, 205 and 204 m²/g for MUF-16, MUF-16(Mn), and MUF-16(Ni), respectively (Figures S19-S21). Total pore volumes of 0.11 cm³/g were established for all three frameworks (Table S3). These values are comparable with the geometric surface areas and pore volumes calculated from the crystallographic coordinates. The pore size distribution of MUF-16 also was calculated, which is consistent with the pore dimensions observed by SCXRD (Figure S12).

CO₂ isotherms were collected at 293 K and up to 1 bar (Figure 2a and see Figure S11 for other temperatures). Both MUF-16 and MUF-16(Ni) take up 2.13 mmol/g (48 cm³/g) at 1 bar, and MUF-16(Mn) adsorbs 2.25 mmol/g (50.5 cm³/g). This equates to approximately 0.9 molecules of CO₂ per metal site (Table S5). CO₂ saturation is only marginally higher at 273 K (Figure S11). The isosteric heat of adsorption (Q_st) at zero-coverage was calculated to be 32 kJ/mol for MUF-16 and 37 kJ/mol for its Ni and Mn analogues (Figure 2b). The Q_st increases at higher loadings, which can be attributed to intermolecular interactions between the adsorbates when the CO₂ loading levels are high. These interactions were experimentally verified by SCXRD (vide infra). The moderate Q_st values, even at high CO₂ loading, are well below values observed for MOFs with open metal sites. It follows that the energy required to regenerate the frameworks by CO₂ desorption is likely to be low.

Single-crystal X-ray diffraction was used to identify the CO₂ binding sites in these frameworks. MUF-16(Mn) was selected for this study since its darker colour streamlined crystal handling (the pale colour of the Co(II) and Ni(II) analogues make them difficult to see when loaded in a glass capillary). The results obtained for MUF-16(Mn) are directly applicable to MUF-16 and MUF-16(Ni) due to their identical structure and CO₂ adsorption behavior (Figures 2a and S5). After transferring a MUF-16(Mn) single crystal into a capillary, it was activated in vacuo and the capillary flame-sealed. This allowed the guest-free structure of MUF-16(Mn) to be determined crystallographically (Table S2). We then filled CO₂ into the capillary to a pressure of 1.1 bar to determine the structure of the CO₂-loaded framework. We noted only minor changes to the framework itself upon evacuation and filling with CO₂. A clear picture of the affinity of MUF-16 for CO₂ arises from the CO₂-loaded SCXRD structure. First, the dimensions of the framework pores are well matched to the size of the CO₂ molecules. This allows the guests to be enveloped by multiple non-covalent contacts (Figure 3a). Second, these contacts are favourable since the electric quadrupole of the CO₂ is complementary to the polarization of the MUF-16 pore surface. For example, one of the electronegative oxygen atoms of each CO₂ molecule engages in N–H···O and C–H···O interactions with hydrogen atoms of amino and phenyl groups at distances of 2.55, 2.81, and 2.87 Å. The electropositive carbon atom of each CO₂ molecule engages in similar close-range contacts with the oxygen atoms of two non-coordinated carboxyl groups (2.87 and 3.04 Å). Two sites, which are related by crystallographic symmetry and share a common location for one of the oxygen atoms, are available to the CO₂ guests. They are occupied with a 50/50 ratio to give one CO₂ molecule per Mn centre overall, in accord with the adsorption isotherm. The CO₂ guest molecules are aligned along the channels and tilted with respect to the pore axis (Figure 3b). Attractive C···O intermolecular interactions
between adjacent molecules are evident at a distance of 3.78 Å. This array of CO₂ guests probably underlies the observed increase in Qₜ as a function of gas loading observed in the adsorption isotherms.

The adsorption of nitrous oxide, N₂O, by MUF-16 corroborates this model of CO₂ affinity. The molecular size and electrostatic distribution of N₂O closely matches that of CO₂ (Figure S9). In parallel with CO₂, N₂O possesses atoms with partial negative charges at its termini that can bind to positively-charged regions of the pore surface, and vice-versa for its central nitrogen atom. MUF-16 adsorbs 1.91 mmol/g (43 cm³/g) of N₂O at 1 bar and 293 K. This is only slightly less than the uptake of CO₂.

The high uptake of CO₂ by MUF-16 contrasts with its low affinity for hydrocarbons. Adsorption isotherms of CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₆ and C₃H₈ were measured on MUF-16 at 293 K (Figure 4a and Table 1). MUF-16 takes up just 1.20 cm³/g of CH₄ at 1 bar and 293 K and 3.99 cm³/g of C₂H₂. The highest adsorption amount was 5.35 cm³/g observed for C₃H₆. The Qₜ values for these gases are much lower than for CO₂ (Table S6). Since only modest quantities of these gases are adsorbed, care was taken to ensure the accuracy of these measurements by using large sample quantities.

Figure 3. (a) The adsorption sites of CO₂ molecules in the pores of MUF-16(Mn), as determined by single-crystal X-ray diffraction. The CO₂ is depicted in space-filling mode. Key intermolecular distances between MUF-16(Mn) and the adsorbed CO₂ are shown with dashed orange lines. A second, symmetry-equivalent CO₂ adsorption site exists. (b) Adsorbed CO₂ molecules in MUF-16(Mn) highlighting the arrangement of adsorbed CO₂ in the framework channels and potential attractive noncovalent interactions between adjacent guests. The CO₂ molecules are shown in representative orientations in one of two symmetry-related crystallographic orientations. Colour code: manganese = lilac; nitrogen = blue; oxygen = red; carbon = grey; hydrogen = pale pink or white; pore Connolly surface = orange.

Uptake ratios provide a useful indication of the preference of an adsorbent for certain gases over others. For MUF-16, the CO₂/CH₄ uptake ratio is 39.8 (293 K and 1 bar). This is comparable to [Cd₂L(H₂O)] (42.9) and exceeded by only one other reported material (SIFSIX-14-Cu-i, 85) (Table S10). Typical physisorbents show a preference for unsaturated hydrocarbons over CO₂, especially when bonding between the guest’s π electrons and open metal sites can occur. However, MUF-16 exhibits a uniform preference for CO₂ over all C2 and C3 hydrocarbons at 293 K and 1 bar (Table 1). Here, the uptake ratios fall between 12 (acetylene), 15.6 (ethane) and 8.9 (propene). While the limited uptake of CH₄ is a well-established function of
its small size and low polarizability, the low affinity of MUF-16 for larger and more polar/polarizable hydrocarbon guests is notable. Inverted selectivity of this kind, that is, a preference for CO$_2$ over small hydrocarbons, is a sought after yet seldom reported phenomenon.\textsuperscript{23, 46-52} With an uptake ratio of 12, MUF-16 surpasses all reported materials that preferentially adsorb CO$_2$ over C$_2$H$_2$, including SIFSIX-3-Ni (1.2 at 298 K and 0.1 bar)\textsuperscript{23}, CD-MOF-2 (1.3 at 298 K and 1 bar)\textsuperscript{46}, K$_2$[C$_6$O(OOCH)$_6$(4-ethylpyridine)]$_2$[α-SiW$_{12}$O$_{40}$] (4.5 at 270 K and 1 bar)\textsuperscript{46} and [Mn(bdc)(dpe)] (6.4 at 273 K and 1 bar)\textsuperscript{47} (Table S11). The diminished affinity of MUF-16 for C$_2$H$_2$ may result from the reversed quadrupole moment of this guest vis-à-vis CO$_2$. Specifically, electropositive regions around the C$_2$H$_2$ termini may induce repulsive interactions with the framework pore surface, as illustrated by a hypothetical loading model (Figure S10).

Building on the preferential affinity indicated by the uptake ratios, we quantified the selectivity of MUF-16 by Ideal Adsorbed Solution Theory (IAST) calculations.\textsuperscript{53} At 293 K and 1 bar, the IAST selectivity of MUF-16 for CO$_2$ over CH$_4$ (50/50 mixture) is 6690 (Figure 4b). MUF-16 is thus the best physisorbents known for this separation (Figure 5 and Table S10). For equimolar mixtures of CO$_2$ and C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$, C$_3$H$_6$ and C$_3$H$_8$ the selectivity of MUF-16 is also high (Table 1). Here, MUF-16 sets a new benchmark for the separation of CO$_2$/C$_2$H$_2$ (50/50) with a selectivity of 510. As recognised in the literature for related systems,\textsuperscript{15, 16, 54} high selectivities emerge by suppressing the uptake of the hydrocarbon gases while maintaining proficient CO$_2$ capture.

While the pore characteristics of MUF-16 clearly favour the uptake of CO$_2$ over other gases, its affinity could potentially rely on molecular sieving if the larger adsorbates are excluded from the framework on the basis of their size. This was ruled out by measuring hydrocarbon adsorption isotherms at 195 K, which showed that MUF-16 is able to take up significant amounts of CH$_4$, C$_2$H$_2$ and C$_2$H$_6$ (Figure S15). Guest molecules of this size can freely enter the pore network of MUF-16. However, since

| Table 1. Summary of gas adsorption data and IAST-calculated selectivities for the MUF-16 family at 1 bar and 293 K. |
|-----------------|-----------------|-----------------|
|                | MUF-16 | MUF-16(Mn) | MUF-16(Ni) |
| Q$_s$CO$_2$ | 32.3   | 36.6   | 37.3   |
| CO$_2$ uptake | 47.78  | 50.5   | 47.97  |
| CH$_4$       | 1.20   | 3.10   | 2.77   |
| C$_2$H$_2$   | 3.99   | 9.69   | 7.53   |
| C$_2$H$_4$   | 3.17   | 8.31   | 5.42   |
| C$_2$H$_6$   | 3.06   | 8.81   | 5.67   |
| C$_3$H$_6$   | 5.35   | -      | -      |
| C$_3$H$_8$   | 4.82   | -      | -      |
| IAST selectivity CO$_2$/CH$_4$ | 6690 | 470 | 1220 |
| CO$_2$/C$_2$H$_2$ | 510 | 31 | 46 |
| CO$_2$/C$_2$H$_4$ | 600 | 150 | 130 |
| CO$_2$/C$_2$H$_6$ | 600 | 55 | 110 |
| CO$_2$/C$_3$H$_6$ | 260 | - | - |
| CO$_2$/C$_3$H$_8$ | 84 | - | - |

\textsuperscript{a} In kJ/mol at zero loading. \textsuperscript{b} In cm$^3$/g. \textsuperscript{c} 50/50 ratio at 1 bar and 293 K as calculated by IAST.
their uptake is low at ambient temperatures their interactions with the framework must be weak. Further, the kinetics of adsorption of several guest molecules were measured (Figure S16). All gases display a similar kinetic profile and reach their equilibrium uptake in well under one minute. Therefore, thermodynamic — rather than kinetic — effects have the most decisive impact on the differential affinity of these gases for MUF-16.

**Figure 4.** (a) Experimental CH₄, C₂H₂, C₂H₄, C₃H₆, C₃H₈ and C₃H₆ adsorption (solid spheres) and desorption (open spheres) isotherms of MUF-16 measured at 293 K. (b) Predicted IAST selectivities, displayed with a log scale, of MUF-16 for various gas mixtures at 293 K.

**Figure 5.** IAST selectivity of MUF-16 in comparison to a selection of top-performing physisorbents for CO₂/CH₄ (50/50) and CO₂/C₂H₆ (50/50) mixtures at ambient temperature and 1 bar. For clarity, the y axis is broken in two parts with different scales.
Invigorated by these results, we then investigated the feasibility of CO$_2$/hydrocarbon separations under dynamic conditions. Experimental breakthrough curves were measured for various gas mixtures at 293 K and 1.1 bar: CO$_2$/C$_2$H$_6$ (50/50), CO$_2$/C$_2$H$_4$ (50/50) and CO$_2$/C$_2$H$_2$ (50/50 and 5/95) (Figures 6a,b S44 and S51). Figure 6a,b shows the dimensionless concentration of CO$_2$ and the hydrocarbons (measured independently) exiting an adsorbent bed packed with MUF-16 (0.9 gram) as a function of time.

Figure 6. (a) Experimental breakthrough curves for 50/50 mixtures of CO$_2$ and the three C2 hydrocarbons (measured independently) at 293 K and 1.1 bar in an adsorption column packed with MUF-16. (b) Experimental breakthrough curves for 50/50 mixtures of CO$_2$ and C$_2$H$_4$ at 293 K and 1.1 bar in an adsorption column packed with MUF-16. (c) Twelve separation cycles for a CO$_2$/C$_2$H$_2$ mixture (50/50 mixture). Each separation process was carried out at 293 K and 1.1 bar. MUF-16 was regenerated between cycles by placing it under vacuum at ambient temperature for 20-25 min. (d) Experimental desorption profile of MUF-16 following the separation of CO$_2$ and C$_2$H$_2$ upon heating under a helium flow of 5 ml/min at 1.1 bar. No adsorbates were removed upon further heating at 130 °C indicating that they had been fully expelled at lower temperatures. (e) Experimental breakthrough curves for a 15/80/4/1 CO$_2$/CH$_4$/C$_2$H$_6$/C$_3$H$_8$ mixture at 1.1 bar and 293 K in an adsorption column packed with MUF-16. (f) CO$_2$ adsorption isotherms (293 K) of as-synthesized MUF-16 after four consecutive adsorption-desorption cycles, after exposing it to air with ~80% humidity for 12 months, and after immersion in water for 48 hours.

Complete separation was realized by MUF-16, whereby the hydrocarbons broke through from the column at an early stage because of their low affinity for the framework. Conversely, the signal of CO$_2$ was not detected for at least 10 minutes due to its adsorption by MUF-16. The dynamic adsorption capacity for CO$_2$ fell in the range 1.2 – 1.5 mmol/g which is nearly identical to the equilibrium capacity at the relevant partial pressures of CO$_2$ (Table S7). Significant volumes of pure hydrocarbons can be obtained in this way. Productivity calculations showed 1 kg of MUF-16 produces 27 L of the hydrocarbons from an equimolar mixture with CO$_2$ at 293 K and 1 bar. The ability of MUF-16 to selectively adsorb CO$_2$ is an important advantage of this MOF as pure hydrocarbons can be produced directly in a single adsorption. In literature reports to date, the capture of CO$_2$ over C$_2$ hydrocarbons has so far largely been restricted to cryogenic temperatures and/or static conditions. With respect to CO$_2$/C$_2$H$_2$ mixtures at ambient temperatures, we are aware of only three reported materials, CD-MOF-1$_{46}$, CD-MOF-2$_{46}$ and SIFSIX-3-Ni, for which CO$_2$ trapping has been verified by experimental breakthrough measurements. Since these MOFs adsorb C$_2$H$_2$ (in addition to CO$_2$) strongly at moderate pressures, their uptake ratios are modest. They are limited to very low partial pressures of CO$_2$ and suffer from low productivity.

Subsequent multiple breakthrough tests revealed that MUF-16 maintains its CO$_2$ uptake and the complete removal of CO$_2$ over at least 12 separation cycles (Figure 6c). MUF-16 was regenerated between cycles by placing it under vacuum or by purging with an inert gas (Figure 6d). Virtually all of the adsorbed acetylene and around half of the CO$_2$ can be removed from the bed by purging at room temperature. The remainder can be fully desorbed at 80 °C.

To investigate separations involving trace CO$_2$, we simulated breakthrough curves of feed gases with low CO$_2$ partial pressures. First, a mass transfer coefficient was empirically determined based on measured breakthrough results. This
produces an excellent match between simulated and experimental breakthrough curves. With this realistic mass transfer coefficient in hand, we predicted breakthrough curves using feeds containing 0.1% CO$_2$ in C$_2$H$_2$ (Figure S57). These calculations revealed that MUF-16 is capable of eliminating trace quantities of CO$_2$, as often required in industrial processes.

We then turned our attention to the separation of more complex gas mixtures. Using CO$_2$/CH$_4$/C$_2$H$_6$/C$_3$H$_8$ (15/80/4/1) as a feed mixture, we observed complete CO$_2$ capture by MUF-16. CH$_4$, C$_2$H$_6$ and C$_3$H$_8$ broke through quickly with steep elution profiles (Figure 6e). Crucially, the relatively large adsorbates C$_2$H$_6$ and C$_3$H$_8$ do not diminish the CO$_2$ capture capabilities of MUF-16. This is an important observation for the removal of CO$_2$ from both biogas and natural gas, which often contain these hydrocarbons. To further probe its applicability to natural gas sweeting, we conducted breakthrough measurements at higher pressure (9 bar). CO$_2$ was cleanly removed from the gas stream (Figures S45 and S46). Breakthrough simulations at pressures relevant to natural gas processing (50 bar) led to the prediction that MUF-16 can competeably capture CO$_2$ from natural gas (Figure S50). Water vapour is a component of crude natural gas streams and it can affect gas adsorption by physiosorbtents.

To test the moisture resistance of MUF-16, we measured its CO$_2$ adsorption properties after exposure to air and immersion in water (Figure 6f). The framework retains its CO$_2$ adsorption capacity following these mistreatments. More detailed analysis, including the resistance of MUF-16 to other common natural gas impurities such as H$_2$S, is an important next step.

**Conclusion**

The pores in MUF-16 are complementary to CO$_2$ in size and electrostatic potential. This underlies its high affinity for molecular CO$_2$ guests. Fortuitously, its pores have a low affinity for methane and C2 and C3 hydrocarbons. The intersection of these characteristics imbues the material with a high selectivity for CO$_2$ over hydrocarbon guests. Benchmark selectivities were determined for CO$_2$/CH$_4$ and CO$_2$/C$_2$H$_6$ separations. MUF-16 operates efficiently across a range of CO$_2$/hydrocarbon mixtures and pressures. These data highlight the performance improvements that are embodied in MUF-16. These findings are relevant to the practical challenges of purifying both natural gas and industrial feedstocks. MUF-16 has the potential to be produced economically on large scales and its chemical stability meets the demands of a long-lived physiosorbtent. Given these characteristics, MUF-16 has promise for applications involving the capture of CO$_2$ from hydrocarbon streams.

**Supporting Information**

Crystallographic data and files of MUF-16 as synthesized, under vacuum and loaded with CO$_2$ (CCDC 1948901, 1948905 and 1948904), additional structural plot, TG curves, PXRD, multiple cycle sorption isotherm, dual site Langmuir isotherm model fitting, isosteric heat of adsorption calculation, BET surface area calculations, IAST calculations of adsorption selectivities, breakthrough curves simulations and models used and column breakthrough test setup with procedures and measurements (PDF). This material is available free of charge via the Internet at...

**Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

A patent on MUF-16 has been lodged (WO 2020/130856 A1).

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Entry for the Table of Contents
Supplementary Materials for

Selective Capture of Carbon Dioxide from Hydrocarbons Using a Metal-Organic Framework: Relevance to the Purification of Natural Gas and Acetylene

Omid T. Qazvini\textsuperscript{1,2} and Shane G. Telfer\textsuperscript{*}\textsuperscript{1}

\textsuperscript{1}MacDiarmid Institute for Advanced Materials and Nanotechnology, School of Fundamental Sciences, Massey University, Palmerston North, New Zealand.

\textsuperscript{2}Department of Chemical Engineering and Analytical Science, The University of Manchester, Oxford Road, Manchester M13 9PL, UK.

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1. General procedures and information

All starting compounds and solvents were used as received from commercial sources without further purification unless otherwise noted. Elemental analyses were performed by the Campbell Microanalytical Laboratory at the University of Otago, New Zealand.

2. Synthesis

2.1 MUF-16 ([Co(Haip)]2)

*Small-scale synthesis:*

A mixture of Co(OAc)2·4H2O (0.625 g, 2.5 mmol), 5-aminoisophthalic acid (1.8 g, 10 mmol), methanol (80 mL) and water (5 ml) were sonicated for 20 min in a sealed 1000 mL Schott bottle, which was then heated in a pre-heated oven at 85 °C for 2 hours under autogenous pressure. After cooling the oven to room temperature, the resulting pink crystals were isolated by decanting off the mother liquor, washed with methanol several times and dried under vacuum at 130 °C for 20 h. Yield: 0.98 g (94% based on cobalt) of guest-free MUF-16.

![Fig. S1. Crystal of MUF-16.](image)

2.2 MUF-16(Mn) and MUF-16(Ni) ([Mn(Haip)]2 and [Ni(Haip)]2)

A mixture of M(ClO4)2·6H2O (where M = Mn or Ni) (1.25 mmol), 5-aminoisophthalic acid (2.50 mmol, 0.45 g), and NH4NO3 (2.50 mmol, 0.20 g) with a mixed-solvent of CH3CN (20 mL) and CH3OH (15 mL) were sonicated for 20 min and sealed in a 100 mL Teflon-lined stainless-steel reaction vessel and heated at 160 °C for two days under autogenous pressure. After cooling the oven to room temperature, the resulting brownish-coloured crystals were isolated by decanting off the mother liquor, then washed
with methanol several times and dried under vacuum at 130 °C for 20 h. Yields: 0.21 g (40% based on Mn) of guest free MUF-16(Mn), and 0.28 g (53% based on Ni) of guest-free MUF-16(Ni).

2.3 Elemental analyses of the MUF-16 frameworks.

|                      | C: calcd./found | H: calcd./found | N: calcd./found |
|----------------------|-----------------|-----------------|-----------------|
| MUF-16·H₂O          | 43.95/43.49     | 3.23/3.23       | 6.41/6.40       |
| MUF-16(Mn)·H₂O      | 44.36/44.05     | 3.26/3.42       | 6.47/6.64       |
| MUF-16(Ni)·H₂O      | 43.98/44.18     | 3.23/3.57       | 6.41/6.90       |
3. Thermogravimetric Analysis (TGA)

Freshly prepared MOF samples were washed with MeOH, and then activated at 130 °C under vacuum for 10 hours. Samples were exposed to air for one hour and then transferred to an aluminium sample pan. Measurements were then commenced under an N₂ flow with a heating rate of 5 °C /min.

![TGA curves](attachment:image.jpg)

**Fig. S2.** TGA curves of MUF-16, MUF-16(Mn), and MUF-16(Ni) under N₂.
4. Single crystal X-ray diffraction

A Rigaku Spider diffractometer equipped with a MicroMax MM007 rotating anode generator (Cu\textsubscript{K\alpha} radiation, 1.54180 Å), high-flux Osmic multilayer mirror optics, and a curved image plate detector was used to collect SCXRD data.

4.1 As-synthesized MUF-16, MUF-16(Ni) and MUF-16(Mn)

General

MOF crystals were analysed after removing them from methanol. Room temperature data collections produced better refinement statistics than low temperature data collections. All atoms were found in the electron density difference map. All atoms were refined anisotropically, except hydrogen atoms and certain of the water molecules in the pores (as specified below). The structures of solvated MUF-16\textsuperscript{1} and MUF-16(Mn)\textsuperscript{2} have been reported previously.

MUF-16

O15 of an occluded H\textsubscript{2}O molecule was refined isotropically. Despite numerous data collections, the wR\textsubscript{2} value remained high due to an inherent lack of precise ordering in the material. A small (1.95 eÅ\textsuperscript{3}) electron density peak remained near the Co site.

MUF-16(Ni)

The crystals diffracted to a resolution of just 1.0 Å thus the calculated \(\sin(\theta_{\text{max}})/\text{wavelength}\) is 0.4999. This limited the number of data and produced a relatively low data: parameter ratio (7.3) and low precision on the C-C bonds. Despite numerous data collections, the wR\textsubscript{2} value remained high due to an inherent lack of precise ordering in the material. And a small (1.55 eÅ\textsuperscript{3}) electron density peak remained near the Ni site.

A solvent mask was calculated and 124 electrons were found in a volume of 308 Å\textsuperscript{3} in one void per unit cell. This is consistent with the presence of three disordered water molecules per asymmetric unit, which account for 120 electrons per unit cell.
Table S1. Crystal data and structure refinement details for MUF-16, MUF-16(Mn) and MUF-16(Ni).

|                  | MUF-16          | MUF-16(Mn)       | MUF-16(Ni)       |
|------------------|-----------------|-----------------|-----------------|
| Formula          | Co(Haip)₂·2H₂O  | Mn(Haip)₂·3H₂O  | Ni(Haip)₂·3H₂O  |
| CCDC deposition  | 1948901         | 1948902         | 1948903         |
| Empirical formula| C₁₆H₁₆CoN₂O₁₀   | C₁₆H₁₈MnN₂O₁₁  | C₁₆H₁₈N₂NiO₁₁  |
| Formula weight   | 455.24          | 471.28          | 473.3           |
| Temperature / K  | 292             | 292             | 293.0           |
| Crystal system   | monoclinic      | monoclinic      | monoclinic      |
| Space group      | I2/a            | I2/a            | I2/a            |
| a / Å            | 15.3514(15)     | 25.2367(14)     | 15.4963(11)     |
| b / Å            | 4.4232(4)       | 4.57990(10)     | 4.5780(2)       |
| c / Å            | 25.614(4)       | 15.4895(11)     | 25.230(2)       |
| α / °            | 90              | 90              | 90              |
| β / °            | 94.294(10)      | 96.046(8)       | 96.177(8)       |
| γ / °            | 90              | 90              | 90              |
| Volume / Å³      | 1734.4(4)       | 1780.34(17)     | 1779.5(2)       |
| Z                | 4               | 4               | 4               |
| ρ calc / g cm⁻³  | 1.743           | 1.758           | 1.564           |
| μ / mm⁻¹         | 8.357           | 6.682           | 2.020           |
| F(000)           | 932.0           | 972.0           | 856.0           |
| Resolution range for data / Å | 0.81 | 0.81 | 1.0 |
| Reflections collected | 7472 | 14132 | 6610 |
| Independent reflections | 1594 [R int = 0.0918, R sigma = 0.0917] | 1668 [R int = 0.1054, R sigma = 0.1158] | 925 [R int = 0.0917, R sigma = 0.0852] |
| Data/restraints/parameters | 1594/2/136 | 1668/1/149 | 925/0/126 |
| Goodness-of-fit on F² | 1.301 | 1.152 | 1.649 |
| Final R indices [I>2σ(I)] | R₁ = 0.1185, wR₂ = 0.3035 | R₁ = 0.0740, wR₂ = 0.1821 | R₁ = 0.1517, wR₂ = 0.3672 |
| Final R indices [all data] | R₁ = 0.1576, wR₂ = 0.3785 | R₁ = 0.1350, wR₂ = 0.2421 | R₁ = 0.2061, wR₂ = 0.4467 |
| Largest diff. peak/hole / e Å⁻³ | 0.93/-1.26 | 0.57/-0.51 | 0.77/-0.83 |
4.2 Single crystal X-ray crystallography under vacuum and loaded with CO₂

Capillary SCXRD was performed for a single crystal of MUF-16(Mn) both under vacuum and loaded with CO₂ at around 1.1 bar and 20 °C based on the following steps:

First a single crystal was chosen with an appropriate size (~ 0.1 × 0.1 × 0.1 mm) and soaked in ethanol. A small capillary tube with around 0.2 mm in diameter and 50 mm in length (which is open at both ends) was made by burning and shaping the neck of a glass pipette (referred to as the ‘home-made capillary’). The home-made capillary was then used to trap the crystal inside it. Normally, the crystal flowed through the capillary carried by the ethanol stream.

The home-made capillary was then transferred into a standard 0.3 mm capillary. A long capillary (0.2 mm in diameter) was used to push the home-made capillary to the very bottom of the 0.3 mm capillary.

Around 6 or 7 crystals of cobalt chloride hydrate were then transferred to the 0.3 mm capillary and placed on the top of the home-made capillary. The cobalt chloride was used as a visual indicator of the level of water vapour in the capillary based on its pink → blue colour change upon dehydration.

The top of the 0.3 mm capillary was then covered by glass wool to avoid the elutriation of cobalt chloride crystals during activation.

The capillary assembly was then connected to an adsorption apparatus (Quantachrome-Autosorb-iQ2) using appropriate Swagelok fittings (Fig. S3) and was kept under vacuum and a temperature of 140 °C for around 5 hours so that the vacuum level reached 0.0008 torr. At this point the cobalt chloride crystals were blue in colour (anhydrous).

The capillary was flame sealed to trap the crystal under vacuum. Alternatively, the capillary was filled with CO₂ to a pressure of 1.2 bar and then flame sealed.

Fig. S3. Swagelok fittings for connecting capillary to Quantachrome-Autosorb-iQ2.
4.3 Refinement details for guest-free and CO$_2$-loaded MUF-16(Mn)

**General**

Certain reflections were omitted from the refinement process since they were mismeasured due to the presence of the glass capillary. All non-hydrogen atoms were found in the Fourier difference map.

**MUF-16(Mn) in vacuo**

The crystals diffracted to a resolution of just 0.90 Å thus the calculated $\sin(\theta_{\text{max}})/\text{wavelength}$ is 0.555.

**MUF-16(Mn) under CO$_2$**

The crystals diffracted to a resolution of just 1.08 Å thus the calculated $\sin(\theta_{\text{max}})/\text{wavelength}$ is 0.463. This limited the number of data and produced a relatively low data: parameter ratio (5.3) and low precision on the C-C bonds.

A strong electron density peak was observed in the middle of the pore and two weaker areas of electron density towards the pore surface. The central dense area was assigned to be an oxygen (O15) with a fixed occupancy of 1 (lowing for its location on a special position), while the other two areas were ascribed to oxygen (O16) and carbon (C17) atoms with fixed occupancies of 0.5. This describes two disordered CO$_2$ molecules that occupy one of two sites. The two molecules share an O atom. Overall, this equates to one CO$_2$ molecule per Mn centre which is in agreement with the adsorption isotherm. The C=O bond lengths were restrained to 1.16 Å and the O=C=O angle to 180°. The C and O atoms of the CO$_2$ were refined isotropically.
Table S2. SCXRD data and refinement details of guest-free and CO2-loaded MUF-16(Mn).

|                      | MUF-16(Mn) in vacuo | MUF-16(Mn) under CO2 (1.1 bar) |
|----------------------|----------------------|-------------------------------|
| Formula              | Mn(Haip)₂            | Mn(Haip)₂·CO₂                 |
| CCDC deposition no.  | 1948905              | 1948904                       |
| Empirical formula    | C₁₆H₁₂MnN₂O₈        | C₁₇H₁₂MnN₂O₁₀                 |
| Formula weight       | 415.22               | 459.23                        |
| Temperature/K        | 292                  | 292                           |
| Crystal system       | monoclinic           | monoclinic                    |
| Space group          | I 2/a                | I 2/a                         |
| a/Å                  | 15.4872(11)          | 15.5719(10)                   |
| b/Å                  | 4.51930(10)          | 4.52010(10)                   |
| c/Å                  | 25.4913(13)          | 25.438(2)                     |
| α/°                  | 90                   | 90                            |
| β/°                  | 97.080(16)           | 97.108(8)                     |
| γ/°                  | 90                   | 90                            |
| Volume/Å³            | 1770.56(17)          | 1776.7(2)                     |
| Z                    | 4                    | 4                             |
| ρcalc/g cm⁻³         | 1.558                | 1.717                         |
| μ/mm¹                | 6.512                | 6.646                         |
| F(000)               | 844.0                | 932.0                         |
| Data range for refinement/Å | 0.90 | 1.08 |
| Reflections collected/ind. | 7515/1214 [R_int = 0.1632, R_σ = 0.1964] | 8177/713 [R_int = 0.1104, R_σ = 0.0804] |
| Data/restraints/parameters | 1214/0/129 | 713/90/136 |
| Goodness-of-fit on F² | 0.862                | 1.216                         |
| Final R indexes [I>2σ (I)] | R₁ = 0.0510, wR₂ = 0.0954 | R₁ = 0.0868, wR₂ = 0.2280 |
| Final R indexes [all data] | R₁ = 0.1341, wR₂ = 0.1112 | R₁ = 0.1278, wR₂ = 0.2915 |
| Largest diff. peak/hole / e Å⁻³ | 0.35/0.48 | 0.56/0.58 |
5. Powder X-ray diffraction patterns

The data were obtained from freshly prepared MOF samples that had been washed several times with MeOH. MOF crystals were analysed right after removing them from MeOH. The two-dimensional images of the Debye rings were integrated with 2DP to give 20 vs I diffractograms. Predicted powder patterns were generated from single crystal structures using Mercury.

For aging experiments on the frameworks, after washing as-synthesized samples several times with MeOH, they were activated and were aged in air at 70-85% relative humidity or water at 20 °C.

![Graph showing PXRD patterns of MUF-16, MUF-16(Mn) and MUF-(Ni) with comparisons between measurements on as-synthesized bulk samples and diffractograms predicted from SCXRD structures.]

**Fig. S5.** PXRD patterns of MUF-16, MUF-16(Mn) and MUF-(Ni) with comparisons between measurements on as-synthesized bulk samples and diffractograms predicted from SCXRD structures.
Fig. S6. PXRD patterns of MUF-16 showing that its structure remains unchanged after activation at 130 °C under vacuum, after isotherm measurements, after breakthrough experiments, after exposure to an air with relative humidity of >80% for at least 12 months and after immersion in water for two weeks.

Fig. S7. PXRD patterns of MUF-16(Mn) showing that its structure remains unchanged after activation at 130 °C under vacuum, after isotherm measurements, after exposure to an air with relative humidity of >80% for at least 12 months and after immersion in water for 2 weeks.
Fig. S8. PXRD patterns of MUF-16(Ni) showing that its structure remains unchanged after activation at 130 °C under vacuum, after isotherm measurements, after exposure to an air with relative humidity of >80% for at least 12 months and after immersion in water for 2 weeks.

6. Textural properties and low-pressure gas adsorption measurements

Single crystal structures of MUF-16, MUF-16(Mn) and MUF-16(Ni) were used directly for all the calculations and simulations without modification except removal of occluded solvent, where relevant. The Zeo++\(^3\) code and RASPA\(^4\) were used to calculate their pore volumes and surface areas with the use of H\(_2\) and He probes, respectively.
**Table S3.** Some calculated and experimentally determined properties of the MUF-16 family.

|                                  | MUF-16 | MUF-16(Mn) | MUF-16(Ni) |
|----------------------------------|--------|------------|------------|
| Geometric surface area (m²/g, Zeo++) | 313    | 315        | 313        |
| BET surface area (m²/g, from experimental N₂ isotherm/77 K) | 214    | 205        | 204        |
| Calculated void fraction (%) RASPA2 | 17.3   | 17.0       | 16.7       |
| Calculated pore volume (cm³/g, RASPA2) | 0.10   | 0.11       | 0.11       |
| Pore volume (cm³/g, from experimental N₂ isotherm/77 K) | 0.11   | 0.12       | 0.11       |

**Fig. S9.** Left: Electrostatic potential maps of (a) CO₂, (b) (N₂O) (c) C₂H₂, (d) C₂H₄, (e) C₂H₆ and (f) C₃H₈ Blue/green = positive; red/orange = negative; Right: Volumetric adsorption isotherms of N₂O measured at different temperatures for MUF-16.

**Table S4.** Physicochemical characteristics of different gasses relevant to their separation.⁵⁻⁸

|        | Boiling point (K) | Molecular dimensions (Å) | Polarizability (Å³) | Dipole moment ×1⁰⁻¹⁹/esu cm² | Quadrupole moment ×1⁰⁻²⁶/esu cm² |
|--------|-------------------|--------------------------|---------------------|-------------------------------|---------------------------------|
| CO₂    | 216.5             | 3.18×3.33×5.36           | 2.91                | 0                            | -4.3                            |
| CH₄    | 111.66            | 3.82×3.94×4.10           | 2.59                | 0                            | 0                               |
| C₂H₂   | 188.4             | 3.32×3.34×5.7            | 3.33-3.93           | 0                            | +7.5                            |
| C₂H₄   | 169.4             | 3.28×4.18×4.84           | 4.25                | 0                            | +1.5                            |
| C₂H₆   | 184.5             | 3.81×4.82×4.08           | 4.43-4.47           | 0                            | +0.65                           |
| C₃H₈   | 231.0             | 6.80×4.20×3.80           | 6.29-6.37           | 0.084                         | -                               |
| C₃H₆   | 225.4             | -                        | 6.26                | 0.366                         | -                               |
**Fig. S10.** Schematic of electrostatic potential distribution on the pore surface of MUF-16 leads to repulsive interactions with guest C$_2$H$_2$ molecules if they occupy the sites crystallographically observed for the binding of CO$_2$.

For adsorption measurements, as-synthesized samples were washed with anhydrous methanol several times and 50-1000 mg was transferred into a pre-dried and weighed sample tube. Large sample quantities (~1 g) were used to measure isotherms of the weakly-adsorbing gases to ensure that the recorded uptake measurements were reliable. To activate the sample, it was heated at rate of 10°C/min to a temperature of 130 °C under a dynamic vacuum with a turbomolecular pump for 20 hours.

**Table S5.** Uptake capacity of MUF-16 for CO$_2$ at 293 K and 1 bar.

|       | Uptake (wt%) | Molecules of CO$_2$ per unit cell | Molecules of CO$_2$ per metal | Fraction of void volume occupied by CO$_2^*$ |
|-------|--------------|-----------------------------------|-----------------------------|---------------------------------------------|
| MUF-16          | 9.38         | 3.57                              | 0.89                        | 0.67                                        |
| MUF-16(Ni)     | 9.41         | 3.58                              | 0.89                        | 0.68                                        |
| MUF-16(Mn)     | 9.90         | 3.74                              | 0.93                        | 0.70                                        |

$^*$The fraction of the total free volume of MUF-16 that is occupied by adsorbate molecules. This was calculated from the accessible void fraction given by RASPA2 software (Table S3), the molecular volume of the CO$_2$ adsorbates (56.75 Å$^3$/molecule) and the total number of adsorbate molecules.
**Fig. S11.** Volumetric adsorption (filled circles) and desorption (open circles) isotherms of CO$_2$ at different temperatures for MUF-16.

**Fig. S12.** Pore size distribution of MUF-16 calculated from its CO$_2$ adsorption isotherm at 273 K using a NLDFT method.
Fig. S13. CO$_2$ adsorption isotherms (293 K) of as-synthesized MUF-16 after four consecutive adsorption-desorption cycles, after exposing it to air with ~80% humidity for 6 months, and after immersion in water for 48 hours.

Fig. S14. Volumetric adsorption (filled circles) and desorption (open circles) isotherms of N$_2$ for MUF-16 (black), MUF-16(Mn) (red) and MUF-16(Ni) (blue) measured at 77 K.
**Fig. S15.** Volumetric adsorption (filled circles) and desorption (open circles) isotherms \( \text{C}_2\text{H}_2 \) (red), \( \text{C}_2\text{H}_6 \) (blue) and \( \text{CH}_4 \) (purple) measured at 195 K for MUF-16.

![Graph showing volumetric adsorption and desorption isotherms](image)

**Fig. S16.** Kinetic profiles of different gas uptake by MUF-16 at 293 K upon exposing an evacuated sample to a dose of gas equal to its measured total adsorption of that gas at 1 bar. \( q \) is the amount of uptake at time \( t \) and \( q_0 \) is the final uptake amount.

![Graph showing kinetic profiles of different gas uptake](image)
Fig. S17. Volumetric adsorption (filled circles) and desorption (open circles) isotherms of different gases by MUF-16(Mn) at 293 K.

Fig. S18. Volumetric adsorption (filled circles) and desorption (open circles) isotherms of different gases by MUF-16(Ni) at 293 K.

7. Calculation of BET surface areas

BET surface areas were calculated from N₂ adsorption isotherms at 77 K according to the following procedures⁹:
1) The isotherm region where $v(1 - P/P_0)$ increases versus $P/P_0$, where $v$ is the amount of N\textsubscript{2} adsorbed, was identified.

2) Within this isotherm region, sequential data points that led to a positive intercept in the plot of $P/P_0$ against $v(1 - P/P_0)$, were found. This plot yields a slope $a$, and a positive intercept $b$. The amount of gas molecules adsorbed in the initial monolayer is $v_m = \frac{1}{a+b}$.

3) The BET surface area was calculated according to the following equation:

$$A_{BET} = v_m (cm^3 g^{-1}) \times \frac{1}{22400 (cm^3)} \times \sigma_0 (\text{Å}^2) \times N_A (mol^{-1}) \times 10^{-20} \left(\frac{m^2}{\text{Å}^2}\right)$$

Where $N_A$ is Avogadro’s constant, and $\sigma_0$ is the cross-sectional area of a N\textsubscript{2} molecule, which is 16.2 Å\textsuperscript{2}.

Fig. S19. N\textsubscript{2} adsorption isotherm at 77 K and BET surface area plots for MUF-16.
Fig. S20. $N_2$ adsorption isotherm at 77 K and BET surface area plots for MUF-16(Mn).

Fig. S21. $N_2$ adsorption isotherm at 77 K and BET surface area plots for MUF-16(Ni).
8. Heat of adsorption

Isosteric heat of adsorption ($Q_{st}$) values were calculated from isotherms measured at 293K, 298K and 303 K for CO₂. The isotherms were first fit to a virial equation:

$$\ln P = \ln N + \frac{1}{T} \sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i$$

Where $N$ is the amount of gas adsorbed at the pressure $P$, $a$ and $b$ are virial coefficients, $m$ and $n$ are the number of coefficients required to adequately describe the isotherm. To calculate $Q_{st}$, the fitting parameters from the above equation were input into the following equation:

$$Q_{st} = -R \sum_{i=0}^{m} a_i N^i$$

![Graph showing virial fittings for CO₂ adsorption isotherms of MUF-16.](image)

**Fig. S22.** Virial equation fits for CO₂ adsorption isotherms of MUF-16.
Fig. S23. Virial equation fits for CO$_2$ adsorption isotherms of MUF-16(Mn).

Fig. S24. Virial equation fits for CO$_2$ adsorption isotherms of MUF-16(Ni).

Table S6. $Q_{st}$ values at low coverage for MUF-16 with various gases.

| gas     | CO$_2$ | C$_2$H$_6$ | C$_2$H$_4$ | C$_2$H$_2$ | CH$_4$ |
|---------|--------|------------|------------|------------|--------|
| $Q_{st}$ (kJ/mol) | 32.3   | 24.8       | 24.9       | 25.8       | 18.6   |
9. IAST calculations

Mixed gas adsorption isotherms and gas selectivities for different mixtures of CO₂/C₂H₆, CO₂/C₂H₄, CO₂/C₂H₆, CO₂/N₂, CO₂/CH₄ and CO₂/H₂ at 293 K were calculated based on the ideal adsorbed solution theory (IAST) proposed by Myers and Prausnitz. In order to predict the sorption performance of MUF-16 toward the separation of binary mixed gases, the single-component adsorption isotherms were first fit to a Dual Site Langmuir or a Dual Site Langmuir Freundlich model, as below:

\[
q = \frac{q_1b_1P}{1 + b_1P} + \frac{q_2b_2P}{1 + b_2P}
\]

\[
q = \frac{q_1b_1P^{1/t_1}}{1 + b_1P^{1/t_1}} + \frac{q_2b_2P^{1/t_2}}{1 + b_2P^{1/t_2}}
\]

Where \(q\) is the uptake of a gas; \(P\) is the equilibrium pressure and \(q_1, b_1, t_1, q_2, b_2\) and \(t_2\) are constants. These parameters were subsequently used for the IAST calculations.

![Dual-site Langmuir fits of various adsorption isotherms for MUF-16 at 293 K.](image)

**Fig. S25** Dual-site Langmuir fits of various adsorption isotherms for MUF-16 at 293 K.
Fig. S26. Dual-site Langmuir fits of various adsorption isotherms for MUF-16(Mn) at 293 K.
**Fig. S27.** Dual-site Langmuir fits of various adsorption isotherms for MUF-16(Ni) at 293 K.
**Fig. S28.** Dual-site Langmuir Freundlich fits for $K_2[Cr_3O(OOCH)_6(4$-ethylpyridine)$_3]_{2}[\alpha$-$SiW_{12}O_{40}]$ at 278 K. Isotherm data were extracted from $^6$ using a digitizer software.

**Fig. S29.** Mixed-gas isotherms and selectivity of MUF-16 predicted by IAST for a mixture of 50/50 CO$_2$/C$_2$H$_2$ at 293 K.
Fig. S30. Mixed-gas isotherms and selectivity of MUF-16 predicted by IAST for a mixture of 5/95 CO$_2$/C$_2$H$_2$ at 293 K.

Fig. S31. Mixed-gas isotherms and selectivity of MUF-16 predicted by IAST for a mixture of 0.1/99.9 CO$_2$/C$_2$H$_2$ at 293 K.
Fig. S32. Mixed-gas isotherms and selectivity of MUF-16 predicted by IAST for a mixture of 50/50 CO₂/C₂H₄ at 293 K.

Fig. S33. Mixed-gas isotherms and selectivity of MUF-16 predicted by IAST for a mixture of 50/50 CO₂/C₂H₆ at 293 K.
**Fig. S34.** Mixed-gas isotherms and selectivity of MUF-16 predicted by IAST for a mixture of 50/50 CO₂/CH₄ at 293 K.

**Fig. S35.** Mixed-gas isotherms and selectivity of MUF-16 predicted by IAST for a mixture of 15/85 CO₂/CH₄ at 293 K.
**Fig. S36.** Mixed-gas isotherms and selectivity of MUF-16 predicted by IAST for a mixture of 15/85 CO$_2$/CH$_4$ at 293 K up to 50 bar.

**Fig. S37.** Mixed-gas isotherms and selectivity of MUF-16 predicted by IAST for a mixture of 50/50 CO$_2$/C$_3$H$_6$ at 293 K.
**Fig. S38.** Mixed-gas isotherms and selectivity of MUF-16 predicted by IAST for a mixture of 50/50 CO$_2$/C$_3$H$_8$ at 293 K.

**Fig. S39.** IAST selectivity for a 50/50 mixture of CO$_2$/CH$_4$ at 293 K for the MUF-16 family.
**Fig. S40.** IAST selectivity for a 50/50 mixture of CO₂/C₂H₂ at 293 K for the MUF-16 family.

**Fig. S41.** IAST selectivity for a 50/50 mixture of CO₂/C₂H₄ at 293 K for the MUF-16 family.
Fig. S42. IAST selectivity for a 50/50 mixture of CO₂/C₂H₆ at 293 K for the MUF-16 family.

10. Breakthrough separation experiments and simulations

Fig. S43. A schematic of the experimental column breakthrough setup.
Table S7. Summary of inlet gas feed streams, outlet compositions and associated data for experimental breakthrough tests using a MUF-16 adsorbent bed.

| Gas mixture | Total pressure (bar) | Inlet CO₂ partial pressure (bar) | Flowrate (mL_N/min) | Upper limit for CO₂ concentration in effluent (ppmv) | Breakthrough point of CO₂ (min) | CO₂ concentration in effluent at breakthrough point (ppmv) | Dynamic adsorption capacity (mmol/g) | Equilibrium adsorption capacity (mmol/g) |
|-------------|----------------------|----------------------------------|---------------------|-----------------------------------------------------|-------------------------------|--------------------------------------------------------|-------------------------------------|---------------------------------------|
| CO₂/CH₄ (50/50) | 1                    | 0.5                              | 6                   | 500                                                 | 10.6                          | 600                                                   | 1.53                                | 1.85                                  |
| CO₂/CH₄ (15/85) | 1                    | 0.15                             | 6                   | 520                                                 | 25.6                          | 600                                                   | 1.13                                | 1.23                                  |
| CO₂/CH₄ (15/85) | 1                    | 0.15                             | 6                   | 360                                                 | 44.8                          | 600                                                   | 2.01                                | -                                     |
| CO₂/CH₄+C₂H₆+C₃H₈ (15/80/4/1) | 1                    | 0.15                             | 6                   | 520                                                 | 24.6                          | 600                                                   | 1.09                                | 1.23                                  |
| CO₂/CH₄+C₂H₆+C₃H₈ (15/80/4/1) | 9                    | 0.15                             | 6                   | 390                                                 | 42.5                          | 600                                                   | 1.93                                | -                                     |
| CO₂/C₂H₂ (50/50)* | 1                    | 0.33                             | 6                   | 500                                                 | 12.3                          | 600                                                   | 1.23                                | 1.64                                  |
| CO₂/C₂H₂ (5/95) | 1                    | 0.035                            | 6.85                | 540                                                 | 15.1                          | 600                                                   | 0.18                                | 0.46                                  |
| CO₂/C₂H₄ (50/50)* | 1                    | 0.33                             | 6                   | 500                                                 | 11.9                          | 600                                                   | 1.19                                | 1.64                                  |
| CO₂/C₃H₆ (50/50)* | 1                    | 0.33                             | 6                   | 500                                                 | 12.2                          | 600                                                   | 1.22                                | 1.64                                  |

* 2 mL_N/min of helium was used as carrier gas in this experiment.
10.1. CO\textsubscript{2}/CH\textsubscript{4} and CO\textsubscript{2}/CH\textsubscript{4}+C\textsubscript{2}H\textsubscript{6}+C\textsubscript{3}H\textsubscript{8} breakthrough separations

Activated MUF-16 (0.9 g) was placed in an adsorption column (6.4 mm in diameter × 11 cm in length) to form a fixed bed. The adsorbent was activated at 130 °C under high vacuum for 7 hours and then the column was left under vacuum for another 3 hours while being cooled to 20 °C. The column was then purged under a 20 mL/min flow of He gas for 1 hr at 1.1 bar prior to the breakthrough experiment. A gas mixture containing CO\textsubscript{2}/CH\textsubscript{4} or CO\textsubscript{2}/CH\textsubscript{4}+C\textsubscript{2}H\textsubscript{6}+C\textsubscript{3}H\textsubscript{8} was introduced to the column at 1.1 bar and 9 bar for CO\textsubscript{2}/CH\textsubscript{4} and CO\textsubscript{2}/CH\textsubscript{4}+C\textsubscript{2}H\textsubscript{6}+C\textsubscript{3}H\textsubscript{8}) and 20 °C.

A feed flowrate of 6 mL/min was set. The operating pressure was controlled at 1.1 or 9 bar with a back-pressure regulator. The outlet composition was continuously monitored by a SRS UGA200 mass spectrometer. The CO\textsubscript{2} was deemed to have broken through from the column when its concentration reached 600 ppmv.

![Experimental breakthrough curves for a mixture of 15/85 CO\textsubscript{2}/CH\textsubscript{4} at 1.1 bar and 293 K in an adsorption column packed with MUF-16.](image)

**Fig. S44.** Experimental breakthrough curves for a mixture of 15/85 CO\textsubscript{2}/CH\textsubscript{4} at 1.1 bar and 293 K in an adsorption column packed with MUF-16.
Fig. S45. Experimental breakthrough curves for a mixture of 15/85 CO$_2$/CH$_4$ at 9 bar and 293 K in an adsorption column packed with MUF-16.

Fig. S46. Experimental breakthrough curves for a mixture of 15/80/4/1 CO$_2$/CH$_4$/C$_2$H$_6$/C$_3$H$_8$ at 9 bar and 293 K in an adsorption column packed with MUF-16.
10.1.4. Simulations of CO$_2$/CH$_4$ breakthrough curves

The simulation of breakthrough curves was carried out using a previously reported method.$^{12,13}$ A value for the mass transfer coefficient (k) was obtained by empirical tuning the steepness of the predicted breakthrough curves to match the experimental curve. The mass transfer coefficient tuned in this way was later used to predict breakthrough curves for other feed mixtures and operating pressures. A summary of adsorption column parameters and feed characterizations are presented in Table S8.

**Table S8.** Adsorption column parameters and feed characterizations used for the simulations for MUF-16.

| Adsorption bed | Feed |
|----------------|------|
| Length: 110 mm | Flow rate: 6 mL/min |
| Diameter: 6.4 mm | Temperature: 293 K |
| Amount of adsorbent in the bed: 0.9 g | Pressure: 1.1 bar |
| Adsorbent density: 1.674 g/cm$^3$ | Carrier gas flow rate: No carrier gas was used |
| Adsorbent average radius: 0.2 mm | k$_{CO_2}$: 0.029 s$^{-1}$ |
| k$_{CO_2}$: 0.029 s$^{-1}$ | k$_{CH_4}$: 0.00021 s$^{-1}$ |

**Fig. S47.** Experimental breakthrough curves in comparison to simulated one for a mixture of 50/50 CO$_2$/CH$_4$ at 1.1 bar and 293 K in an adsorption column packed with MUF-16.
**Fig. S48.** Experimental breakthrough curves in comparison to simulated one for a mixture of 15/85 CO₂/CH₄ at 1.1 bar and 293 K in an adsorption column packed with MUF-16.

**Fig. S49.** Experimental breakthrough curves in comparison to simulated one for a mixture of 15/85 CO₂/CH₄ at 9 bar and 293 K in an adsorption column packed with MUF-16.
Fig. S50. Simulated breakthrough curves for a mixture of 15/85 CO$_2$/CH$_4$ at 50 bar and 293 K in an adsorption column packed with MUF-16.

10.2 CO$_2$/C$_2$ hydrocarbon separations

In a typical breakthrough experiment, 0.9 g of activated MUF-16 was placed in an adsorption column (6.4 mm in diameter × 11 cm in length) to form a fixed bed. The adsorbent was activated at 130 °C under high vacuum for 7 hours and then the column was left under vacuum for another 3 hours while being cooled to 20 °C. The column was then purged under a 20 mL$_N$/min flow of He gas for 1 hr at 1.1 bar prior to the breakthrough experiment. A gas mixture containing different gas pairs of CO$_2$ and C$_2$H$_2$, C$_2$H$_6$ or C$_2$H$_4$ along with He as a carrier gas was introduced to the column at 1.1 bar and 20 °C. A feed flowrate of 6.0 or 6.85 mL$_N$/min (including helium) was set for the experiments with 50/50 and 5/95 mixture of gases, respectively, and the flowrate of He in the feed was kept constant at 2 mL$_N$/min for all the experiments. The operating pressure was controlled at 1.1 bar with a back-pressure regulator. The outlet composition was continuously monitored by a SRS UGA200 mass spectrometer. The CO$_2$ was deemed to have broken through from the column when its concentration reached 600 ppmv.
**Fig. S51.** Experimental breakthrough curves for a mixture of 5/95 CO$_2$/C$_2$H$_2$ at 1.1 bar and 293 K in an adsorption column packed with MUF-16.

**Fig. S52.** Experimental breakthrough curves for a mixture of 50/50 CO$_2$/C$_2$H$_4$ at 1.1 bar and 293 K in an adsorption column packed with MUF-16.
**Fig. S53.** Experimental breakthrough curves for a mixture of 50/50 CO\textsubscript{2}/C\textsubscript{2}H\textsubscript{6} at 1.1 bar and 293 K in an adsorption column packed with MUF-16.

**Adsorbent regeneration**

The desorption behaviour of CO\textsubscript{2} and C\textsubscript{2}H\textsubscript{2} from the adsorption column was also investigated. Once the adsorbent was saturated with an equimolar mixture of CO\textsubscript{2} and C\textsubscript{2}H\textsubscript{2}, the column was purged with a helium flow of 5 mL/min for 18 mins at 20 °C at 1 bar while monitoring the effluent gas. Then the column was then heated to 80 °C with a ramp of 10 °C/min for 20 mins. Finally, the column was heated to 130 °C with the same ramping for 15 min before cooling to 20 °C. A breakthrough measurement was then performed, which showed that the absorbent had been fully regenerated.
Figure S54. Desorption behaviour of the adsorbates through heating the column at 1 bar under a helium flow of 5 mL\textsubscript{N}/min. C\textsubscript{2}H\textsubscript{2} is fully removed from the bed by purging with helium at room temperature. CO\textsubscript{2} is completely desorbed from the column upon heating to 80 °C with a flow of helium. No adsorbates remained to be removed upon further heating to 130 °C.

10.2.1. Simulations of CO\textsubscript{2}/C\textsubscript{2}H\textsubscript{2} breakthrough curves

The simulation of breakthrough curves for CO\textsubscript{2}/C2 hydrocarbons was carried out using the method reported above. A summary of adsorption column parameters and feed characterizations are presented in Table S9.

Table S9. Adsorption column parameters and feed characterizations used for the simulations for MUF-16.

| Adsorption bed | Feed |
|----------------|------|
| Length: 110 mm | Flow rates: |
| Diameter: 6.4 mm | 6 mL\textsubscript{N}/min for equimolar and 0.1/99.9 mixtures, and 6.85 mL\textsubscript{N}/min for the 5/95 mixture. |
| Amount of adsorbent in the bed: 0.9 g | Temperature: 293 K |
| Bed voidage: 0.84 | Pressure: 1.1 bar |
| Adsorbent average radius: 0.2 mm | Carrier gas (He) flow rate: 2 mL\textsubscript{N}/min. |
| k\textsubscript{CO2}: 0.021 s\textsuperscript{-1} | |
| k\textsubscript{C2H2}: 0.024 s\textsuperscript{-1} | |
Fig. S55. Experimental breakthrough curves in comparison to simulated one for a mixture of 50/50 CO₂/C₂H₂ at 1.1 bar and 293 K in an adsorption column packed with MUF-16.

Fig. S56. Experimental breakthrough curves in comparison to simulated one for a mixture of 5/95 CO₂/C₂H₂ at 1.1 bar and 293 K in an adsorption column packed with MUF-16.
Fig. S57. Simulated breakthrough curves for a mixture of 0.1/99.9 CO$_2$/C$_2$H$_2$ at 1.1 bar and 293 K in an adsorption column packed with MUF-16.

11. Tabulated separation metrics

The CO$_2$/CH$_4$ and CO$_2$/C$_2$H$_2$ separation parameters of MUF-16 in comparison to top-performing MOFs and related materials are presented in Tables S9 and S10. Materials with molecular sieving mechanisms are excluded from this analysis. IAST selectivities are presented for a 50/50 CO$_2$/CH$_4$ and CO$_2$/C$_2$H$_2$ at 1 bar, unless otherwise stated. $Q_{st}$ values are reported at low loading, unless otherwise stated. Uptake ratios are calculated by dividing the uptake of CO$_2$ by that of CH$_4$ or C$_2$H$_2$ (all at 1 bar and the specified temperature in the Table S9 and S10). These were taken from either a direct statement of relevant details in the manuscript or were extracted from Figs. by a digitizer software.
Table S10. Metrics relevant to \( \text{CO}_2/\text{N}_2/\text{CH}_4 \) separations for MUF-16 in comparison to a selection of materials reported in the literature.

| Material                          | T (°C) | P (bar) | \( \text{CO}_2 \) uptake (cc/g) | \( Q_{st}(\text{CO}_2) \) (kJ/mol) | Uptake ratio | IAST selectivity (50/50) |
|-----------------------------------|--------|---------|---------------------------------|--------------------------------------|--------------|--------------------------|
| This work                         |        |         |                                 |                                      |              |                          |
| MUF-16                            | 20     | 1       | 47.8 | 1.2 | 32 | 39.8 | 6686 |
| MUF-16(Mn)                        | 20     | 1       | 50.5 | 3.1 | 37 | 16.3 | 470  |
| MUF-16(Ni)                        | 20     | 1       | 48.0 | 2.8 | 37 | 17.3 | 1215 |
| Zeolite 13X14,15                   | 25     | 1       | 112  | 13  | 44.54 | 8.6 | 103  |
| Zeolite 5A16,17                    | 30     | 1       | 75.5 | 11.8 | 23 | 6.4 | n/a  |
| Zeolite 4A18,19                    | 30-32  | 1       | 105.3 | 15 | 39 | 7 | n/a  |
| BPL Activated carbon20.           | 25     | 1       | 46.2 | 20.2 | 21 | 2.3 | 4   |
| SIFSIX-3-Zn15                     | 25     | 1       | 57.1 | 17.6 | 45 | 3.2 | 230  |
| [Cd\(_2\)](\text{H}_2\text{O})\text{H}_2\text{O}22 | 20     | 1       | 47.2 | 1.1 | 37 | 42.9 | n/a  |
| UTSA-12023                        | 23     | 1       | 112  | 20.8 | 27 | 5.4 | 96   |
| UTSA-1624,25                      | 23     | 1       | 96   | 13.2 | 33 | 7.3 | 38   |
| HKUST-125-27                      | 25     | 1       | 103  | 18.7 | 35 | 7.4 | 5.5  |
| Mg-dobdc15,25,28,29               | 23     | 1       | 190  | 25  | 47-52 | 7.6 | 130  |
| IITKGP-5a10                       | 22     | 1       | 49   | 13.6 | 23 | 3.6 | 24   |
| WOFOUR-1-Ni31                     | 25     | 1       | 52   | 11.5 | 66 | 4.5 | 26\textsuperscript{a} |
| SIFSIX-2-Cu-i15                   | 25     | 1       | 121  | 10.5 | 32 | 11.5 | 33   |
| CAU-132                           | 0      | 1       | 165  | 27  | 48 | 6.1 | 28\textsuperscript{b} |
| NbOFFIVE-Ni33,34                  | 25     | 1       | 51.7 | 2.2 | 54 | 23.1 | 366  |
| TIFSIX-3-Ni33,34                  | 25     | 1       | 48.6 | 4.8 | 50 | 10.2 | 158  |
| SIFSIX-14-Cu-i35                  | 20     | 1       | 110.5 | 1.3 | 38 | 85 | n/a  |
| SIFSIX-3-Ni33,34                  | 25     | 1       | 64.5 | 6.6 | 51 | 8.9 | 130  |

Values were generally taken from either a direct statement in the manuscript or were extracted from relevant Figs. by a digitizer software. Materials with molecular sieving mechanisms are excluded from this analysis. \textsuperscript{a}IAST is calculated for a 10/90 mixture. \textsuperscript{b}Selectivity was calculated from the slope of isotherms at low pressures (Henry constants). \textsuperscript{c}Heat of adsorption averaged over \( \text{CO}_2 \) uptakes.
Table S11. Separation metrics relevant to C$_2$H$_2$/CO$_2$ separations for MUF-16 in comparison to other top-performing materials reported in the literature.

| MOF                        | T (°C) | P (bar) | CO$_2$ uptake (mmol/g) | C$_2$H$_2$ uptake (mmol/g) | $Q_{st}$ of CO$_2$ (kJ/mol) | $Q_{st}$ of C$_2$H$_2$ (kJ/mol) | Uptake ratio* | IAST selectivity (50/50)* |
|----------------------------|--------|---------|------------------------|----------------------------|-----------------------------|--------------------------------|----------------|-----------------------------|
| CO$_2$-selective MOFs      |        |         |                        |                            |                             |                                |                |                             |
| MUF-16                     | 20     | 1       | 2.14                   | 0.18                       | 32                          | 25.8                           | 12.0           | 510                         |
| [Mn(bdc)(dpe)]$_3^{36}$    | 0      | 1       | 2.08                   | 0.32                       | 29.5                        | 27.8                           | 6.4            | 9.0                         |
| SIFSIX-3-Ni$_3^{37}$       | 25     | 1       | 2.80                   | 3.30                       | 51                          | 36.5                           | 0.8            | 7.5*                        |
| K$_2$[Cr$_3$(OOCH)$_6$]$_6$| 5      | 1       | 0.50                   | 0.10                       | 38                          | 30                             | 4.5            | 5.6*                        |
| CD-MOF-1$_{38}$            | 25     | 1       | 2.87                   | 2.23                       | 41                          | 17                             | 1.3            | 3.4*                        |
| CD-MOF-2$_{38}$            | 25     | 1       | 2.67                   | 2.03                       | 67.5                        | 25                             | 1.3            | 6.1*                        |
| **C$_2$H$_2$-selective MOFs** |       |         |                        |                            |                             |                                |                |                             |
| UTSA-300a$_{39}$           | 25     | 1       | 0.15                   | 3.10                       | -                           | 57                             | 20.6           | 700                         |
| NKMOF-1-Ni$_{40}$          | 25     | 1       | 2.27                   | 2.67                       | 41                          | 60                             | 1.2            | 22                          |
| HOF-3a$_{41}$              | 23     | 1       | 0.93                   | 2.14                       | 42                          | 19.5                           | 2.3            | 21                          |
| [Ni$_3$(HCOO)$_6$]$_3^{12}$| 25     | 1       | 3.00                   | 4.20                       | 24.5                        | 41                             | 1.4            | 21                          |
| SNNU-45$_{43}$             | 25     | 1       | 4.34                   | 5.98                       | 27.1                        | 40                             | 1.37           | 4.5                         |
| ZJU-196a$_{44}$            | 25     | 1       | 0.35                   | 3.70                       | -                           | 39                             | 10.6           | 18                          |
| JCM-1$_{45}$               | 25     | 1       | 1.69                   | 3.34                       | 33                          | 36.5                           | 2.0            | 14                          |
| DICRO-4-Ni-i$_{36}$        | 25     | 1       | 1.02                   | 1.91                       | 34                          | 38                             | 1.9            | 13.5                        |
| UTSA-74a$_{47}$            | 25     | 1       | 3.00                   | 4.80                       | 25.5                        | 31.5                           | 1.6            | 8                           |
| TIFSIX-2-Cu-i$_{37}$       | 25     | 1       | 4.20                   | 4.10                       | 36                          | 46                             | 0.97           | 6                           |
| Cu-BTC$_{25, 41, 48}$      | 25     | 1       | 5.10                   | 8.90                       | 26.9                        | 30                             | 1.7            | 5.5                         |
| MAF-2$_{49}$               | 25     | 1       | 0.82                   | 3.90                       | 27                          | 33                             | 4.7            | 5                           |
| UTSA-50a$_{41}$            | 23     | 1       | 3.10                   | 4.10                       | 27.8                        | 32                             | 1.3            | 5                           |
| FJU-90a$_{41}$             | 25     | 1       | 4.92                   | 8.03                       | 21                          | 25                             | 1.6            | 4.3                         |
| ZJU-60a$_{41}$             | 23     | 1       | 3.12                   | 6.69                       | 15.5                        | 17.5                           | 2.1            | 4                           |
| ZJU-10a$_{32}$             | 25     | 1       | 3.66                   | 7.58                       | 26                          | 39                             | 2.1            | 4                           |
| MFM-188$_{53}$             | 25     | 1       | 5.35                   | 10.20                      | 20.8                        | 32.5                           | 1.9            | 3.7                         |
| FeNi-M’MOF$_{54}$          | 25     | 1       | 2.72                   | 4.29                       | 24.5                        | 32.8                           | 1.6            | 22.5                        |

Values were taken from either a direct statement in the manuscript or were extracted from relevant Figs. by a digitizer software, * $Q_{st}$ at low coverage. ** Uptake ratios and IAST selectivities are given with respect to the ratio of the highly adsorbed component to the weakly adsorbed component from an equimolar mixture. * * Isotherm data were extracted from literature for 3-Ni$_{37}$ and for CD-MOFs* and to calculate IAST selectivity for an equimolar mixture.
**Fig. S58.** IAST selectivity of MUF-16 family for an equimolar mixture of CO$_2$/CH$_4$ in comparison to top top-performing MOFs at 1 bar and ambient temperature versus their uptake ratio at 1 bar.

**Fig. S59.** Predicted IAST selectivity (log scale) from an equimolar mixture of CO$_2$/C$_2$H$_2$ plotted against uptake ratio at 1 bar and 293-298 K (except for IC (278 K) and [Mn(bdc)(dpe)] (273 K)) for MUF-16 in comparison to the best materials reported to date. Selectivity and uptake ratios are defined as CO$_2$/C$_2$H$_2$ and C$_2$H$_2$/CO$_2$ for CO$_2$-selective and C$_2$H$_2$-selective materials, respectively.
12. References

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