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Selective capture of carbon dioxide from hydrocarbons using a metal-organic framework

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Efficient and sustainable methods for carbon dioxide capture are highly sought after. Mature technologies involve chemical reactions that absorb CO₂, but they have many drawbacks. Energy-efficient alternatives may be realised by porous physisorbents with void spaces that are complementary in size and electrostatic potential to molecular CO₂. Here, we present a robust, recyclable and inexpensive adsorbent termed MUF-16. This metal-organic framework captures CO₂ with a high affinity in its one-dimensional channels, as determined by adsorption isotherms, X-ray crystallography and density-functional theory calculations. Its low affinity for other competing gases delivers high selectivity for the adsorption of CO₂ over methane, acetylene, ethylene, ethane, propylene and propane. For equimolar mixtures of CO₂/CH₄ and CO₂/C₂H₂, the selectivity is 6690 and 510, respectively. 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, including pure methane and acetylene.

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Chemical separation processes consume vast quantities of energy¹. Economical and practical pathways to alleviating this burden are required. This is especially relevant to the capture of CO₂, which is a common impurity in crude gas streams. CO₂ removal is integral to upgrading natural gas and biogas, for example, and to the purification of valuable hydrocarbons prior to polymerisation or chemical derivatization². These processes are separations that rely on discrimination between CO₂ and other gases. One established technology is to trap the CO₂ by a chemical reaction with an absorbent. This typically involves chemisorption to an amine in aqueous solution^{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 pipelines⁵. 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 CO₂ in nanoporous materials is an attractive alternative^{6,7}. Physisorption is governed by weak, non-covalent bonding interactions in pores that are structured on the molecular scale⁸. Ideally, they lower the energy requirements for regeneration since driving off the trapped CO₂ simply involves breaking interactions that are inherently weak. Effective physisorbents combine rapid guest diffusion, recyclability and long-term stability with selectivity for CO₂ over competing gases at relevant concentrations⁹. Thus, they may offer a sustainable solution to CO₂ capture. In this context, metal-organic frameworks (MOFs) have risen to prominence^{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^{15,16}. In turn, this allows interactions between framework hosts and molecular guests to be tailored. In the search of effective MOF physisorbents, simply searching for materials with ever-higher levels of CO₂ uptake per se may not deliver adsorbents that are adept at gas separations since the adsorption of non-CO₂ components may also increase. Instead, significant advances will emerge by suppressing the uptake of these competing gases^{17,18}, 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 CO₂ from hydrocarbons is an important process². While natural gas and biogas are primarily composed of methane (at high pressure and low pressure, respectively), contamination by CO₂ can prevent optimal heat release from gas combustion, and cause pipeline corrosion and dry ice formation¹⁹. MOFs, however, offer a means of reducing the CO₂ concentration in the presence of dominant quantities of methane^{10,20,21}. Acetylene (C₂H₂) is an essential feedstock for the industrial production of commodity materials^{22,23}. When acetylene is generated, however, it typically coexists with CO₂ impurities²⁴. The separation of C₂H₂ and CO₂ is challenging due to their similar physical properties (Supplementary Table 4). MOF physisorbents offer a potential solution but most show an affinity toward C₂H₂ rather than CO₂¹¹. The selective adsorption of the CO₂ 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 CO₂ during the desorption step²⁵. 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 other hydrocarbons are in particular demand.

In this work, we present a MOF, termed MUF-16 (MUF = Massey University Framework) that exhibits inverse selectivity: the adsorption of carbon dioxide in preference to hydrocarbon guests. The carbon dioxide is efficiently sequestered by hydrogen bonding and a range of other favourable noncovalent interactions. This underpins high selectivities for the separation a range of gas mixtures that are relevant to natural gas and industrial feedstocks. Being economical to produce on scale, stable and recyclable, MUF-16 has many of the qualities of an attractive adsorbent.

Results

Synthesis and characterisation. Inspired by the superb properties of MOFs derived from straightforward and readily-available linkers^{26,27}, our interest was captured by the MUF-16 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 (Fig. 1a). This delivers compounds with the general formula [M(Haip)₂]^{28,29}, 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 (Supplementary Table 1). The three frameworks are isostructural, belonging to the *I2/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 μ_2 -bridging carboxylate groups (Fig. 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 (Fig. 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 (Fig. 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, Fig. 1d). In their as-synthesised 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 (Supplementary Fig. S2). Their purity was established by both elemental analysis and powder X-ray diffraction (Supplementary Fig. 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 Supplementary Figs. S6–S8, S13a).

As suggested by pore evident in their SCXRD structures, the MUF-16 frameworks are accessible to a range of incoming gases. 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 (Supplementary Figs. S19–S21). Total pore volumes of 0.11 cm³/g were established for all three frameworks (Supplementary Table 3). 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 (Supplementary Fig. S12).

Gas adsorption measurements. CO₂ isotherms were collected at 293 K and up to 1 bar (Fig. 2a and see Supplementary Fig. S11 for

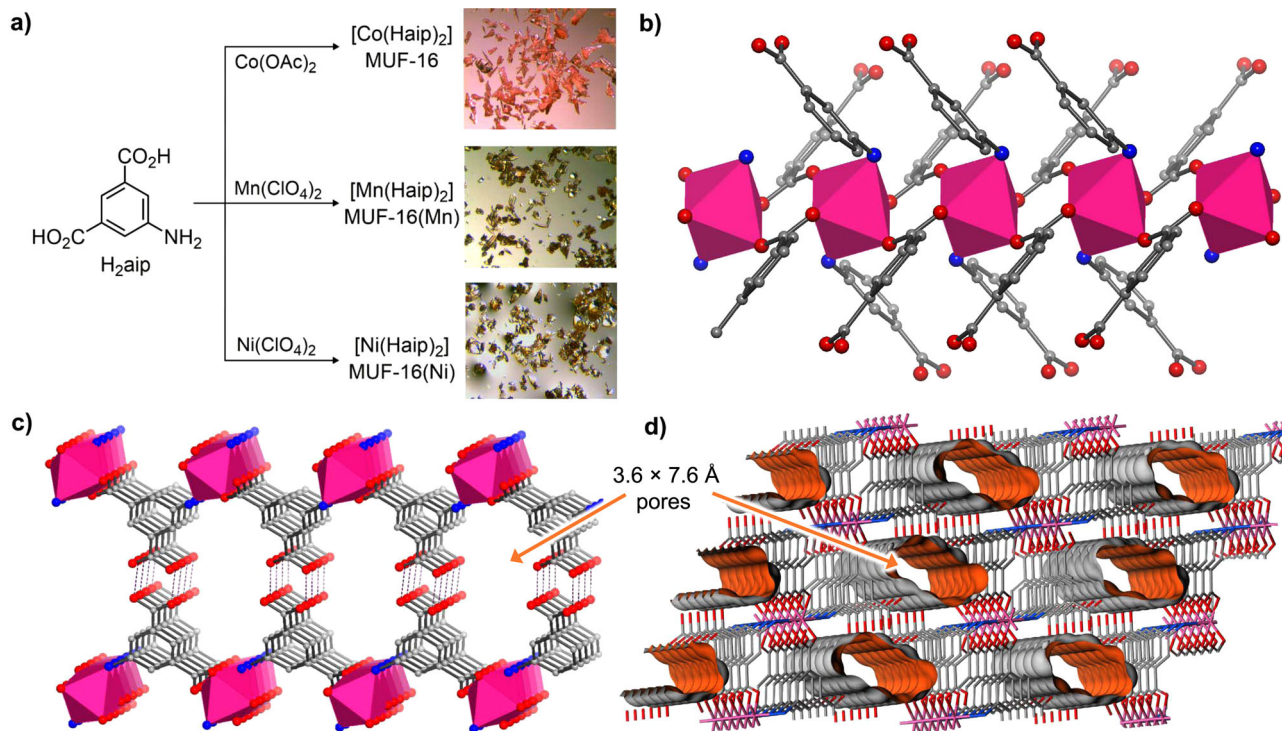


Fig. 1 Synthesis and structure of MUF-16 materials. **a** Synthetic routes to the MUF-16 family and optical micrographs of the reaction products. **b** Infinite secondary building units (iSBUs) in MUF-16 comprise one-dimensional cobalt(II) chains connected by μ_2 -bridging carboxylate groups of the Haip ligands (H_2aip = 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.

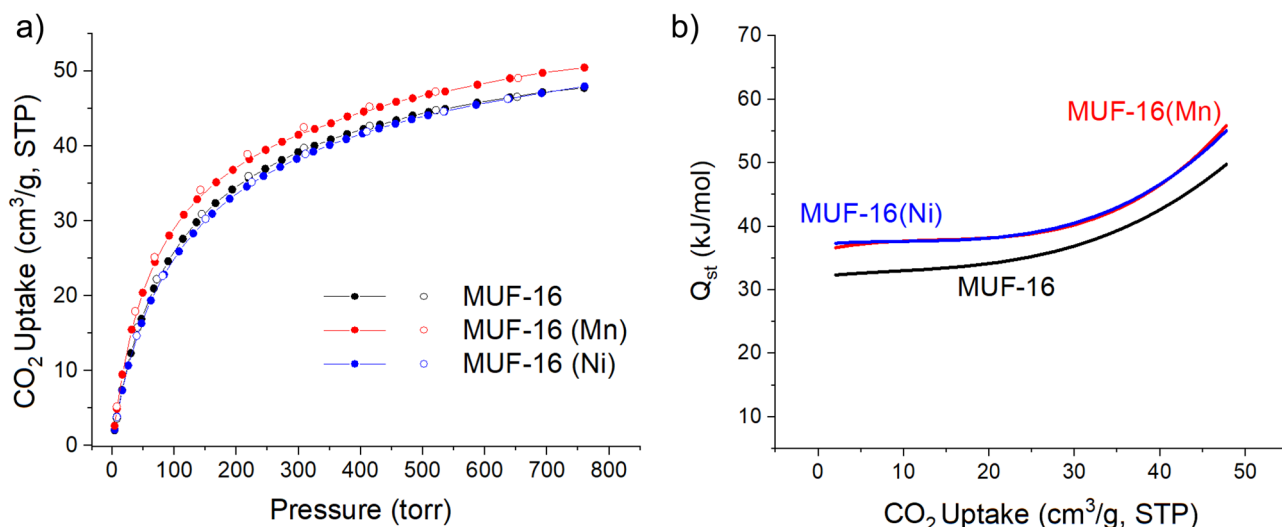


Fig. 2 CO₂ adsorption on MUF-16 materials. **a** Volumetric adsorption (filled circles) and desorption (open circles) isotherms of CO₂ at 293 K and for MUF-16 (black), MUF-16(Mn) (red), and MUF-16(Ni) (blue). **b** Heats of adsorption (Q_{st}) calculated for CO₂ binding to MUF-16 (black), MUF-16(Mn) (red), and MUF-16(Ni) (blue) as a function of CO₂ uptake. A high affinity for CO₂ coupled to a moderate heat of adsorption promise an adsorbent that takes up significant quantities of gas yet is easily recycled. Source data are provided as a Source Data file.

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 (Supplementary Table 5). CO₂ uptake is only marginally higher at 273 K (Supplementary Fig. 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 (Fig. 2b). The Q_{st} increases at higher loadings, which can be attributed to attractive intermolecular interactions when the CO₂ loading levels are high, which enhance the framework-CO₂ affinity. These interactions were experimentally verified by SCXRD (vide infra). The moderate Q_{st} values, even at high CO₂ loading³⁰, are well below values observed for MOFs with open metal sites³¹. 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^{32,33}. 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 structures and CO₂ adsorption profiles (Fig. 2a and Supplementary Fig. 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 (Supplementary Table 2). 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 (Fig. 3a). Second, these contacts are favourable since the electric quadrupole of the CO₂ is complementary to the polarisation 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 hydrogen bonds with framework 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 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 and refinement of the CO₂ occupancies gave 0.77 CO₂ molecules per Mn centre, which agrees with the adsorption isotherm (Supplementary Table 5) allowing for uncertainties in the exact CO₂ pressure in the X-ray capillaries. The CO₂ guest molecules are aligned along the channels and tilted with respect to the pore axis (Fig. 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 Q_{st} as a function of gas loading observed in

the adsorption isotherms. A computational DFT model agrees with the SCXRD structure (Supplementary Fig. S60).

The strong adsorption of nitrous oxide, N₂O, by MUF-16 corroborates this model of CO₂ binding. The size and electrostatic distribution of N₂O closely match those of CO₂ (Supplementary Fig. 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, which 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 (Fig. 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. Since only modest quantities of these gases are adsorbed, care was taken to ensure the accuracy of these measurements by using large sample quantities. The Q_{st} values for the hydrocarbon gases are much lower than for CO₂ (Supplementary Table 6). The water vapour adsorption isotherm of MUF-16 was measured at 298 K, showing the steady uptake of water until saturation is reached at around two molecules per Co centre (Supplementary Fig. S13b). The isotherm is fully reversible indicating that the adsorbed water is easily removed without perturbation of the framework.

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)³⁴ and exceeded by only one other reported material (SIFSIX-14-Cu-i, 85) (Supplementary Table 10)³⁵. 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^{25,36–50}. 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 CO₂ over small hydrocarbons, is a sought after yet seldom

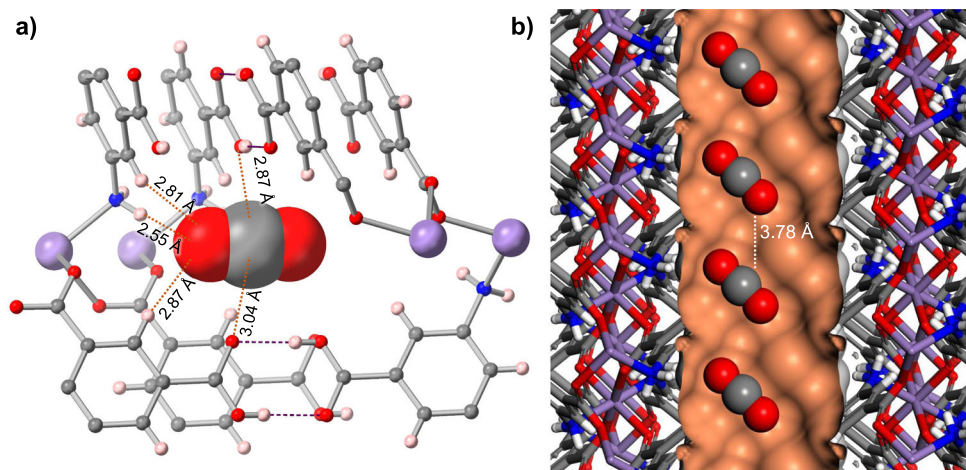


Fig. 3 CO₂ capture by MUF-16. **a** The adsorption sites of CO₂ molecules in the pores of MUF-16(Mn), as determined by single-crystal X-ray diffraction. The CO₂ is depicted in space-filling mode. Key intermolecular distances between MUF-16(Mn) and the adsorbed CO₂ are shown with dashed orange lines. 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.

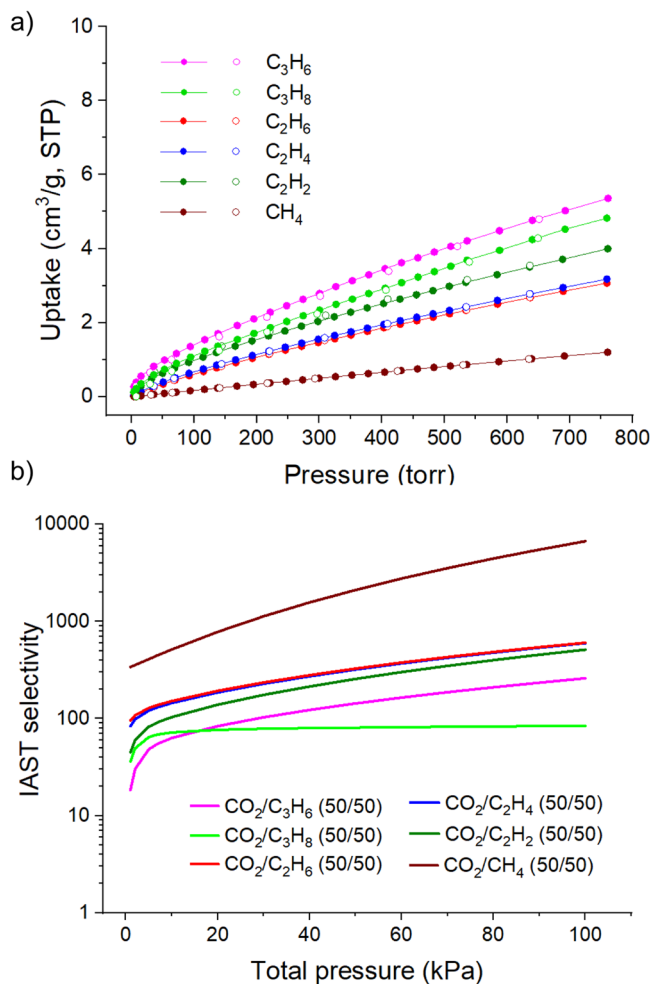


Fig. 4 Gas uptake and calculated separation by MUF-16. **a** Experimental CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₆ and C₃H₈ adsorption (solid spheres) and desorption (open spheres) isotherms of MUF-16 measured at 293 K. **b** Predicted IAST selectivities, displayed with a log scale, of MUF-16 for various gas mixtures at 293 K. Source data are provided as a Source Data file.

reported phenomenon^{25,51–57}. With an uptake ratio of 12, MUF-16 surpasses previously reported materials that preferentially adsorb CO₂ over C₂H₂, including SIFSIX-3-Ni (1.2 at 298 K and 0.1 bar)²⁵, CD-MOF-2 (1.3 at 298 K and 1 bar)⁵¹, K₂[Cr₃O(OOCH)₆(4-ethylpyridine)₃]₂[α-SiW₁₂O₄₀] (4.5 at 278 K and 1 bar)⁵⁵, [Mn(bdc)(dpe)] (6.4 at 273 K and 1 bar)⁵² and [Tm₂(OH-bdc)₂(μ₃-OH)₂(H₂O)₂]⁵⁸ (2.8 at 298 K and 1 bar) (Supplementary Table 11). The diminished affinity of MUF-16 for C₂H₂ results from the reversed quadrupole moment of this guest vis-à-vis CO₂ (Supplementary Fig. S10). Since C₂H₂ is polarised oppositely to CO₂ it is electrostatically repelled by the functional groups that line binding pockets in MUF-16. The upshot is inverse selectivity for CO₂ over acetylene.

Separations using MUF-16. Building on the preferential affinity indicated by the uptake ratios, we quantified the selectivity of MUF-16 by Ideal Adsorbed Solution Theory (IAST) calculations⁵⁹. At 293 K and 1 bar, the IAST selectivity of MUF-16 for CO₂ over CH₄ (50/50 mixture) is 6690 (Fig. 4b). MUF-16 is thus the best physisorbent known for this separation that does not operate by molecular sieving (Fig. 5 and Supplementary Table 10). For equimolar mixtures of CO₂ and C₂H₂, C₂H₄, C₂H₆, C₃H₆ or C₃H₈ the selectivity of MUF-16 is also high (Table 1).

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 _{st}			
CO ₂ ^a	32.3	36.6	37.3
Uptake ^b			
CO ₂	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 ^c	6690	470	1220
CO ₂ /C ₂ H ₂ ^c	510	31	46
CO ₂ /C ₂ H ₄ ^c	600	150	130
CO ₂ /C ₂ H ₆ ^c	600	55	110
CO ₂ /C ₃ H ₆ ^c	260	—	—
CO ₂ /C ₃ H ₈ ^c	84	—	—

^aIn kJ/mol at zero loading.

^bIn cm³/g.

^c50/50 ratio at 1 bar and 293 K as calculated by IAST.

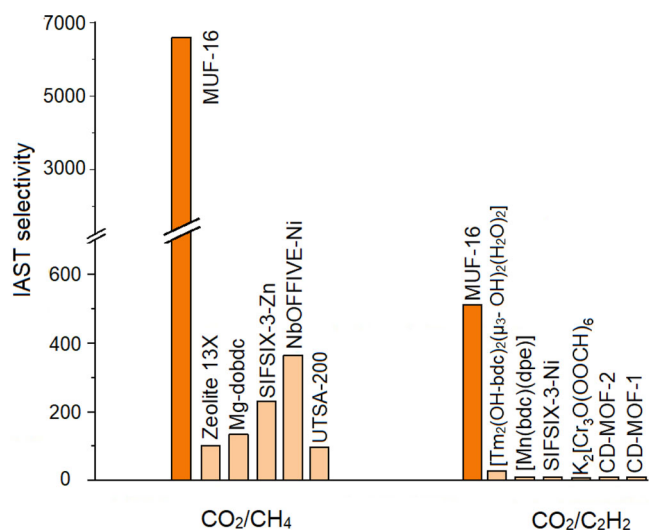


Fig. 5 Separation performance of MUF-16 compared to top-performing materials. IAST selectivity of MUF-16 in comparison to a selection of physisorbents for CO₂/CH₄ (50/50) and CO₂/C₂H₂ (50/50) mixtures at ambient temperature and 1 bar (see Supplementary Table 11 for details). For clarity, the y axis is broken in two parts with different scales.

With a selectivity of 510, MUF-16 is elevated well beyond other materials for the capture of CO₂ from CO₂/C₂H₂ (50/50) mixtures (Fig. 5 and Supplementary Table 11). As recognised in the literature for related systems^{17,18,60}, these high selectivities emerge by suppressing the uptake of the hydrocarbon gases while maintaining proficient CO₂ capture.

While the pore characteristics of MUF-16 clearly favour the uptake of CO₂ 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 can adsorb CH₄, C₂H₂ and C₂H₆ (Supplementary Fig. S15). Guest molecules of this size can freely

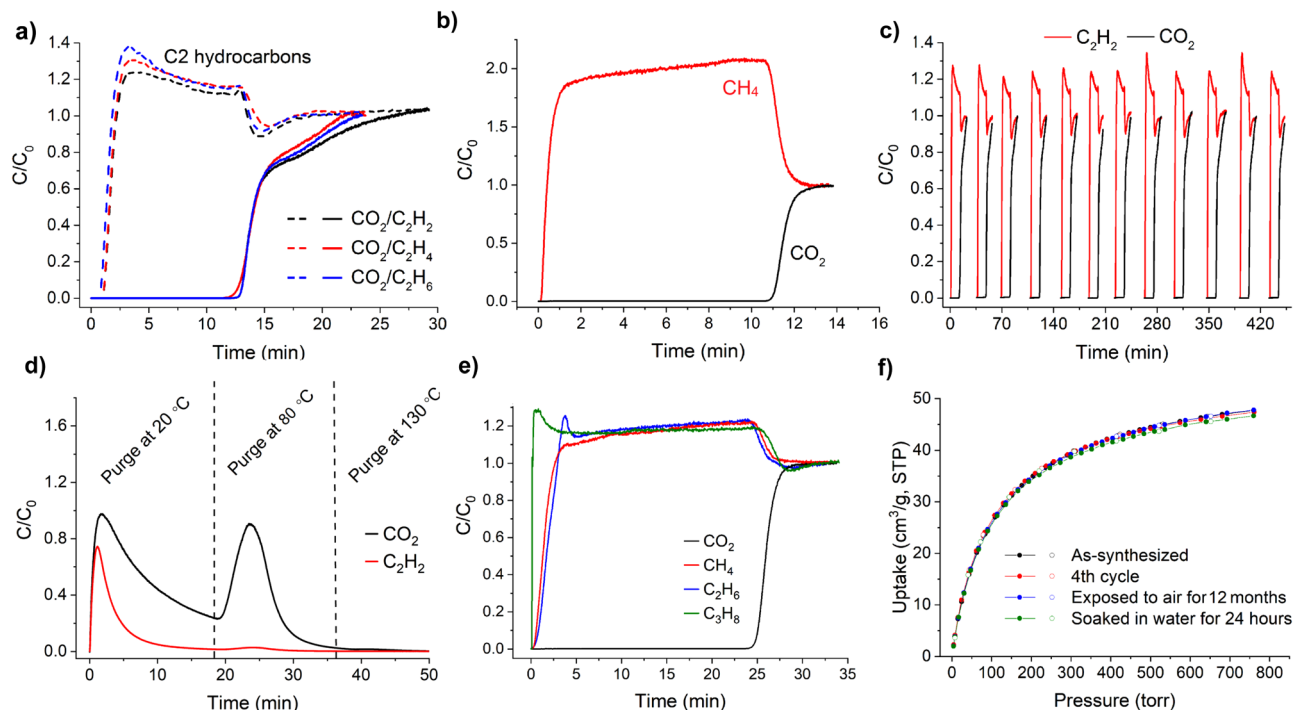


Fig. 6 Gas separation by MUF-16. **a** Experimental breakthrough curves for 50/50 mixtures of CO_2 and the three C2 hydrocarbons (measured independently) at 293 K and 1.1 bar in an adsorption column packed with MUF-16. **b** Experimental breakthrough curves for 50/50 mixtures of CO_2 and CH_4 at 293 K and 1.1 bar in an adsorption column packed with MUF-16. **c** Twelve separation cycles for a $\text{CO}_2/\text{C}_2\text{H}_2$ 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_2H_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 $\text{CO}_2/\text{CH}_4/\text{C}_2\text{H}_6/\text{C}_3\text{H}_8$ 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. Source data are provided as a Source Data file.

enter the pore network of MUF-16 at this low temperature. However, since uptake is low at ambient temperatures interactions of these gases with the framework must be weak. Further, the kinetics of adsorption of several guest molecules were measured (Supplementary Fig. 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. We also considered whether a structural change of the framework might underly the gas selectivity, as observed for related systems⁵². However, XRD measurements show that the framework structure is largely conserved around room temperature in vacuo, in air and under CO_2 (Supplementary Fig. S6). The CO_2 adsorption isotherms at elevated temperatures show no sign of flexibility or gate opening (Supplementary Fig. S11), nor does the CH_4 isotherm at high pressure (Figure S15). In the specific case of C_2H_4 at 195 K, there is evidence of modest gate opening, which will be fully evaluated in future work (Figure S15).

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: $\text{CO}_2/\text{C}_2\text{H}_6$ (50/50), $\text{CO}_2/\text{C}_2\text{H}_4$ (50/50), $\text{CO}_2/\text{C}_2\text{H}_2$ (50/50 and 5/95) and CO_2/CH_4 (50/50 and 15/85) (Fig. 6a, b; Supplementary Figs. 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.

Complete separation was realised 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 (Supplementary Table 7). 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 stage. In literature reports to date, the capture of CO_2 over C2 hydrocarbons has so far largely been restricted to cryogenic temperatures and/or static conditions^{52–55,57,61}. With respect to $\text{CO}_2/\text{C}_2\text{H}_2$ mixtures at ambient temperatures, we are aware of only a few reported materials, CD-MOF-1⁵¹, CD-MOF-2⁵¹ SIFSIX-3-Ni²⁵, and $[\text{TM}_2(\text{OH}-\text{bdc})_2(\mu_3-\text{OH})_2(\text{H}_2\text{O})_2]$ ⁵⁸ for which this inverse trapping of CO_2 has been verified by experimental breakthrough measurements. Since these MOFs adsorb C_2H_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 tests revealed that MUF-16 maintains its CO_2 uptake and the complete removal of CO_2 over at least 12 separation cycles (Fig. 6c). MUF-16 was regenerated between cycles by placing it under vacuum or by purging with an inert gas

(Fig. 6d). Virtually all of the adsorbed acetylene and around half of the CO₂ 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 CO₂, we simulated breakthrough curves of feed gases with low CO₂ partial pressures. First, a mass transfer coefficient was empirically determined based on measured breakthrough results to produce a match between simulated and experimental breakthrough curves^{26,62}. With this realistic mass transfer coefficient in hand, we predicted breakthrough curves using feeds containing 0.1% CO₂ in C₂H₂ (Supplementary Fig. S57). These calculations revealed that MUF-16 can eliminate trace quantities of CO₂, as often required in industrial processes.

We then turned our attention to the separation of more complex gas mixtures. MUF-16 captures the CO₂ from CO₂/CH₄/C₂H₆/C₃H₈ (15/80/4/1) feed mixtures at 1.1 bar. Here, we observed CH₄, C₂H₆ and C₃H₈ to break through quickly with steep elution profiles (Fig. 6e). Crucially, the larger C₂H₆ and C₃H₈ components do not diminish the CO₂ capture capabilities of MUF-16. This is an important observation for the removal of CO₂ from natural gas, where mixed-gas separations involving these hydrocarbons are often required yet the pool of competent materials is limited^{19,63}. To further probe the applicability of MUF-16 to natural gas sweetening, we conducted breakthrough measurements at a higher pressure of 9 bar. CO₂ was cleanly removed from the gas stream (Supplementary Figs. S45 and S46). Breakthrough simulations at pressures relevant to natural gas processing (50 bar) lead to the prediction that MUF-16 can capture CO₂ from natural gas (Supplementary Fig. S50). Water vapour is a component of crude natural gas streams and it can affect gas adsorption by physisorbents^{64,65}. To test the moisture resistance of MUF-16, we measured its CO₂ adsorption properties after exposure to air and immersion in water (Fig. 6f). The framework retains its CO₂ adsorption capacity following these mistreatments. More detailed analysis, including the impact of water vapour on gas separation and the resistance of MUF-16 to other common natural gas impurities such as H₂S, is an important next step.

In summary, the pores in MUF-16 are complementary to CO₂ in size and electrostatic potential. This allows H-bonding and other noncovalent interactions to trap the guest CO₂. Other guests, specifically methane and the C₂ hydrocarbons, do not bind efficiently. This arises from the reversed polarity of these guests with respect to CO₂ and results in a strong preference for CO₂ over methane and inverted selectivity for CO₂ over C₂ and C₃ hydrocarbon guests. MUF-16 shows exceptional performance for CO₂/CH₄ and CO₂/C₂H₂ separations across a range of CO₂/hydrocarbon compositions and pressures. These observations are relevant to the practical challenges of purifying natural gas and industrial feedstocks. MUF-16 has the potential to be produced economically on large scales and its chemical stability and recyclability meet the demands of a long-lived physisorbent. Given these characteristics, MUF-16 is a promising physisorbent for the capture of CO₂.

Data availability

Source data are provided with this paper. Crystallographic data and files of MUF-16 as synthesized, under vacuum and loaded with CO₂ have been deposited (CCDC 1948901 - 1948905). Additional graphics, TG curves, PXRD diffractograms, multiple cycle adsorption isotherms, dual site Langmuir isotherm model fitting, isosteric heat of adsorption calculations, BET surface area calculations, IAST calculations of adsorption selectivities, breakthrough curves simulations and models used and column breakthrough test setup with procedures and measurements, and the DFT results are available as Supplementary Information.

Further data that support the findings of this study are available from the corresponding author upon reasonable request. Source data are provided with this paper.

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Author contributions

The manuscript was written through the contributions of O.T.Q. and S.G.T. who designed and performed the experiments, analysed the results and jointly wrote the paper. R.B. performed the DFT calculations. A patent on MUF-16 has been lodged (WO 2020/130856 A1).

Competing interests

The authors declare no competing interests.

Additional information

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