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Host-guest selectivity in a series of isoreticular metal-organic frameworks: observation of acetylene-to-alkyne and carbon dioxide-to-amide interactions

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Abstract

In order to develop new porous materials for applications in gas separations such as natural gas upgrading, landfill gas processing and acetylene purification it is vital to gain understanding of host-substrate interactions at a molecular level. Herein we report a series of six isoreticular metal-organic frameworks (MOFs) for selective gas adsorption. These materials do not incorporate open metal sites and thus provide an excellent platform to investigate the effect of the incorporation of ligand functionality via amide and alkyne groups on substrate binding. By reducing the linker length of our previously reported MFM-136, we report much improved CO$_2$/CH$_4$ (50:50) and CO$_2$/N$_2$ (15:85) selectivity values of 20.2 and 65.4, respectively (1 bar and 273 K), in the new amide-decorated MOF, MFM-126. The CO$_2$ separation performance of MFM-126 has been confirmed by dynamic breakthrough experiments. In situ inelastic neutron scattering and synchrotron FTMIR microspectroscopy were employed to elucidate dynamic interactions of adsorbed CO$_2$ molecules within MFM-126. Upon changing the functionality to an alkyne group in MFM-127, the CO$_2$ uptake decreases but the C$_2$H$_2$ uptake increases by 68%, leading to excellent C$_2$H$_2$/CO$_2$ and C$_2$H$_2$/CH$_4$ selectivities of 3.7 and 21.2, respectively. Neutron powder diffraction enabled the direct observation of the preferred binding domains in MFM-126 and MFM-127, and, to the best of our knowledge, we report the first example of acetylene binding to an alkyne moiety in a porous material, with over 50% of the acetylene observed within MFM-127 displaying interactions (<4 Å) with the alkyne functionality of the framework.

Introduction

Porous metal-organic frameworks (MOFs) have attracted considerable attention due to their promise in a wide range of applications, notably in gas adsorption, selectivity and catalysis. Modulation of organic linkers and metal nodes allows fine-tuning of properties to tailor MOFs for the application of interest. In the field of gas adsorption, MOFs have shown advantages for selective uptake of specific guests, such as CO$_2$ and C$_2$H$_2$. Capture and separation of CO$_2$ from flue gas streams via the utilization of selective and regenerable sorbents, such as MOFs, provides a promising alternative pathway to conventional amine-scrubbers. Moreover, MOF adsorbents also have applications in natural gas (containing ~15% CO$_2$) upgrading, and the selective separation of landfill gas (40-60% CO$_2$). Other industrially significant separations include the purification of C$_2$H$_2$, an important feedstock in the petrochemical industry. C$_2$H$_2$ is produced by the partial combustion of CH$_4$ and hence requires separation from CH$_4$ and CO$_2$ to obtain high-purity C$_2$H$_2$. However, the identical kinetic diameters of 3.30 Å and similar boiling points of -84°C and -79°C, for C$_2$H$_2$ and CO$_2$, respectively, make C$_2$H$_2$/CO$_2$ separation under ambient conditions a highly challenging task.

Common strategies for enhancing host-guest interactions in MOFs include incorporation of open metal sites, polar functional groups (e.g., -NH$_2$, -CONH$_2$, -OH, -F) and narrowing pores channels by use of small ligands. For example, polar nitrogen-containing groups remain a favored approach to enhancing CO$_2$ adsorption, as shown in a crystallographic study that visualized CO$_2$ molecules directly interacting with the amine group in a Zn-MOF. However, we have previously reported neutron diffraction and scattering data revealing that the high CO$_2$ uptake in amide-functionalized MFM-136 is not solely due to
guest-host interactions at the amide group, but instead it is a combination of geometry, pore size and functionality that lead to improved gas sorption properties.\textsuperscript{27} Whilst many MOFs have been reported for their gas sorption properties, it is often difficult to fully account for differences in performance owing to many variables such as surface area, porosity and pore geometry, functionality and presence of open metal sites. Thus, to aid design-based approaches for improved materials, thorough investigations of isoreticular series of MOFs such as the IRMOF,\textsuperscript{28} UiO-66\textsuperscript{29} and MOF-74\textsuperscript{30} series are important.

Herein we present a comprehensive investigation into the roles of functional groups, pore geometry and porosity in enhancing selective gas binding through a series of six isostructural MOFs (MFM-126-128 and MFM-136-138; Table 1). MFM-137 and MFM-138 were designed by adapting previously reported MFM-136,\textsuperscript{27} replacing the amide group with an ethynyl bond and phenyl ring, respectively. Further modification of MFM-136-138 was achieved by removal of the central phenyl unit of the linker to produce ‘shortened’ derivatives, MFM-126-128. This systematic approach allows us to isolate either the effect of varying pore size or functionality to rationalize the properties of these materials. Our approach has been to focus on the role of ligand sites for substrate binding and, significantly, we report herein the first example of binding of acetylene to the alkyne groups in a porous material at crystallographic resolution.

**Experimental**

**Neutron Powder Diffraction (NPD) of Gas-loaded MFM-126 and MFM-127**

NPD data were collected at WISH beamline at ISIS Muon and Neutron facility. Acetone exchanged MFM-126 and MFM-127 were loaded into 11 mm diameter Vanadium cans, heated at 393 K and degassed at 1 \times 10^{-7} \text{ mbar} for 2 days to activate the sample. Data for the bare framework were collected after placing the sample can into a liquid Helium cryostat and cooling to 7 K. CO\textsubscript{2}, C\textsubscript{2}D\textsubscript{2} and CD\textsubscript{4} gases were dosed into the system after warming the system to 250 and 150 K, respectively. The gases were dosed volumetrically from a calibrated volume and, to ensure gases were fully adsorbed into the sample without condensation elsewhere, the system was cooled to 7 K slowly over 3 h. Structure solutions of gas-loaded MFM-126 and MFM-127 were solved by sequential difference Fourier analyses followed by Rietveld refinements using TOPAS software (see ESI Section 4).

**Inelastic Neutron Scattering of CO\textsubscript{2}-loaded MFM-126**

INS data were collected on TOSCA beamline at ISIS Muon and Neutron facility. MFM-126 was loaded into an 11 mm diameter vanadium can and outgassed at 10^{-7} \text{ mbar} at 393 K for 2 days. After placing the sample into a He cooled cryostat INS data of the bare framework were collected at 7 K. A loading of 1.0 CO\textsubscript{2}/Cu was dosed volumetrically from a calibrated volume at room temperature and gradually cooled to 7 K to allow the guest species to fully adsorb into MFM-126. INS data of 1.0 CO\textsubscript{2}/Cu of MFM-126 were collected at 7 K. Experimentally obtained INS data were compared with modelled data obtained via density functional theory (DFT) calculations and simulated using OClimax software (see ESI for further details).

**Synchrotron FTIR Microspectroscopy of CO\textsubscript{2}-loaded MFM-126**

Single crystals of MFM-126 were loaded onto a ZnSe slide and placed into a Linkam FTIR600 variable temperature gas-tight cell fitted with ZnSe windows. The MOF sample was activated \textit{in situ} under a
flow of N\textsubscript{2} whilst heating the Linkam stage to 413 K for 6 h. Partial pressures of zeolite dried gases N\textsubscript{2} and CO\textsubscript{2} were controlled by varying the volumetric flow of the two gases \textit{via} separate mass flow controllers. FTIR spectra were collected at B22 MIRIAM beamline at Diamond Light Source using a polarized and highly bright synchrotron IR source connected to a Bruker Hyperion 3000 IR microscope with a 15x objective and MCT detector (liq. N\textsubscript{2} cooled). Spectra (256 scans) were measured at room temperature with a 20 x 20 \textmu m beam, in the spectral range of 4000–650 cm\textsuperscript{-1} (4 cm\textsuperscript{-1} resolution).

**Gas Breakthrough**

Breakthrough experiments were performed using a Hiden Isochema Automated Breakthrough Analyzer with integrated mass spectrometer. MFM-126 (950 mg) was packed into a stainless steel column and the sample was activated by heating to 393 K under a flow of He (100 mL min\textsuperscript{-1}) overnight. Breakthrough experiments were conducted using gas mixtures of CO\textsubscript{2}/N\textsubscript{2} (15:85) and equimolar CO\textsubscript{2}/CH\textsubscript{4} which were flowed over MFM-126 at a total flow rate of 10 mL min\textsuperscript{-1} at 298 K and 1.0 bar (see ESI for further detail).

**Results and Discussion**

**Structures**

Solvothermal reactions of isophthalate–pyrimidyln linkers H\textsubscript{2}L\textsubscript{1}–H\textsubscript{2}L\textsubscript{6} (Table 1) with Cu(NO\textsubscript{3})\textsubscript{2} affords isostructural (3,6)-connected MOFs of \textit{eea} topology. All these frameworks are constructed from Cu(II) cations bridged by four carboxylate groups from four independent linkers and capped by two pyrimidyl nitrogen donors to form elongated octahedral [Cu\textsubscript{2}(RCOO)\textsubscript{4}(NR)\textsubscript{2}] nodes (Table 1, Figure 1). The isophthalate units bridge adjacent \{Cu\textsubscript{2}\} paddlewheels to form a Kagomé lattice net (Figure 1d), and these are connected by coordination of a pyrimidyl nitrogen center to the axial position of the \{Cu\textsubscript{2}\} paddlewheels. The capping of the \{Cu\textsubscript{2}\} paddlewheels at both axial positions results in the absence of any open Cu(II) sites.

Lu \textit{et al} recently reported HHU-2\textsuperscript{31}, a (3,4,6)-connected Cu(II)-based MOF using H\textsubscript{2}L\textsubscript{1}, but its structure has both pyrimidine N atoms (instead of just one as in MFM-126) bound to Cu(II) ions and therefore does not have free N centers pointing into the pore as observed in MFM-126 and all MOFs in this current series. MFM-137 and MFM-138 are formed by replacement of the amide group of MFM-136 with alkyne and phenyl moieties, respectively. The removal of a central phenyl ring from MFM-136-138 affords shortened derivatives MFM-126-128, respectively.

The MOFs in this series all incorporate two types of cages, the larger of which, cage A (Figure 1a) is comprised of six ligands and six [Cu\textsubscript{2}(RCOO)\textsubscript{4}(NR)\textsubscript{2}] paddlewheel units forming a hexagonal bipyramid. The six \{Cu\textsubscript{2}\} units form the six equatorial vertices of this cage and form the hexagonal window of the Kagomé lattice (Figure 1d). Six pyrimidyl units form the apical vertices, whereby ligands form six of the twelve faces of the hexagonal bipyramid. The smaller cage B (Figure 1b) is constructed from six ligands and six \{Cu\textsubscript{2}\} paddlewheels forming a ditrigonal scalenohedral cage, whereby two sets of three \{Cu\textsubscript{2}\} paddlewheels bridged by three linker isophthalate units form triangular windows of neighboring Kagomé lattices. The overall structure of these MOFs is comprised of discrete cages A and B, which are packed in an alternating manner (Figure 1c), giving highly porous and robust 3D frameworks. Views of the structure down
crystallographic axes of MFM-126 are shown in Figure S3. The phase purity of all material samples was confirmed by powder X-ray diffraction (PXRD) data (Figure S4).

Modulation of porosity and CO\textsubscript{2} adsorption properties

All MOFs were solvent-exchanged with acetone or ethanol before heating at 393 K under dynamic vacuum to produce desolvated materials. The N\textsubscript{2} (77 K) isotherms (Figure S6) reveal that the desolvated MOFs have BET surface areas of 1000–1750 m\textsuperscript{2} g\textsuperscript{-1} and pore volumes of 0.47–0.65 cm\textsuperscript{3} g\textsuperscript{-1} (Table 1). As expected, MFM-136–138 have higher BET surface areas compared to their isostructural shorter derivatives MFM-126–128. The higher BET surface area and pore volume of MFM-127 (C(O)-NH linker) compared with MFM-126 (C≡C linker) can be attributed to the presence of the space-efficient alkyne group in the linker, which has been shown previously to increase the hypothetical maximum surface area of MOFs.\textsuperscript{32} The measured pore volumes compare favorably with those calculated directly from single crystal structures, confirming complete desolvation and phase purity of these materials.

CO\textsubscript{2} adsorption isotherms were measured to 20 bar at 273 and 298 K for all MOFs (Figure S5). Throughout the series, it was found that the CO\textsubscript{2} uptake at 20 bar increased with increasing pore volume, indicating that the pore functionality had little effect on high pressure gas adsorption, where porosity is the dominant factor. For example, a 10% increase in CO\textsubscript{2} uptake at 20 bar is observed in MFM-127 compared with MFM-126 (11.3 and 10.2 mmol g\textsuperscript{-1} at 298 K, respectively), corresponding well with the 11% pore volume increase from MFM-126 to MFM-127. However, at 1.0 bar and 298 K, comparing phenyl-functionalized MOFs MFM-138 and MFM-128 (2.89 and 3.19 mmol g\textsuperscript{-1}, respectively), it was found that the CO\textsubscript{2} uptake is greater in MFM-128, indicating a stronger interaction with the MFM-128 framework at ambient pressure. This suggests that pore geometry has an important role in low pressure gas uptake, with MFM-126-128 all having greater uptake at 1.0 bar CO\textsubscript{2} than the comparative extended derivatives, MFM-136-138 (Figure 2a). The influence of functionality on CO\textsubscript{2} uptake can be assessed by comparing MFM-136 and MFM-137 which show similar porosity (Table 1). MFM-136 and MFM-137 show CO\textsubscript{2} uptakes of 7.30 and 5.76 mmol g\textsuperscript{-1} (273 K), respectively, suggesting that amide functionalized MFM-136 possesses stronger affinity for CO\textsubscript{2} compared to the alkyne groups in MFM-137.

Crucially, however, MFM-126, with the smallest pore volume, has the greatest CO\textsubscript{2} uptake at low pressure across the series, reaching 4.63 mmol g\textsuperscript{-1} at 1 bar and 298 K, presumably due to the greater overlap of attractive interactions between gas molecules and the host framework. This is exemplified further at 0.15 bar, the partial pressure of CO\textsubscript{2} in flue gas streams, where MFM-126 has a 52% higher uptake of CO\textsubscript{2} compared with the next best-performing MOF, MFM-136 (2.94 and 1.94 mmol g\textsuperscript{-1}, respectively) in this series.

Selective sorption in MFM-126 and MFM-127

All the MOFs in this series show highly selective uptakes of CO\textsubscript{2} with respect to CH\textsubscript{4} and N\textsubscript{2} (Figure 2, Table 2). The selective uptake of CO\textsubscript{2} over the other substrates studied is also evidenced by the analysis of heats of adsorption (Table 2 and Figure S19). MFM-126 exhibits the highest CO\textsubscript{2} uptake at low pressures (<1
bar) as well as relatively low CH$_4$ uptake in the same pressure region (Figure 2b). The selectivity values were estimated from the single-component isotherms using ideal adsorbed solution theory (IAST) (Table 2). Considering the relative gas concentrations found in natural gas and flue gas streams, MFM-126 exhibits the highest selectivity values across the series for binary mixtures of both CO$_2$/CH$_4$ (equimolar) and CO$_2$/N$_2$ (15:85 composition) with selectivity values of 20.2 and 65.4, respectively at 1 bar and 273 K (Figure 2d). MFM-126 also exhibits the highest adsorption enthalpy for CO$_2$ of 30.7 kJ mol$^{-1}$, which is significantly higher than 17.3 kJ mol$^{-1}$ for CH$_4$ (Table 2). Conversely, MFM-136 has the lowest CO$_2$/CH$_4$ selectivity value of 4.1 and exhibits similar values for the isosteric heat ($Q_{st}$) for CO$_2$ and CH$_4$ adsorption, 20.1 and 18.9 kJ mol$^{-1}$, respectively. When compared with other leading MOFs, MFM-126 has respectable CO$_2$/CH$_4$ and CO$_2$/N$_2$ selectivity values (Tables S18, S19).

To evaluate the dynamic separation performance of MFM-126, breakthrough experiments were performed with CO$_2$/N$_2$ (15:85) and equimolar CO$_2$/CH$_4$ mixtures (Figure 2e and 2f). The gas mixtures were flowed over a fixed-bed packed with MFM-126 with a total flow of 10 mL min$^{-1}$ at 298 K (1 bar). These breakthrough experiments confirmed the separation potential for both gas mixtures that IAST selectivity calculations predicted (Figure 2d).

Although the amide-functionalised MFM-126 exhibits higher CO$_2$ uptake compared with MFM-127, the functional groups were also investigated for their effect on acetylene adsorption. Interestingly, alkyne-functionalised MFM-127 exhibits a 68% higher acetylene uptake than MFM-126 at 273 K and 1 bar (9.28 and 5.54 mmol g$^{-1}$, respectively, Figure 2c). IAST analysis for MFM-127 reveals selectivity values for equimolar mixtures of C$_2$H$_2$/CO$_2$ and C$_2$H$_2$/CH$_4$ to be 3.7 and 21.2, respectively (Figure S20). This result is comparable to that observed for [Cu$_2$(EBTC)] (H$_4$EBTC=1,1’-ethylenbenzene-3,3’,5,5’-tetracarboxylic acid), which shows enhanced acetylene uptake compared with the non-alkyne bridged analogue MOF-505/MFMM100.$^{35,36}$ Whilst the presence of C≡C···C≡C interactions between acetylene gas and an alkyne organic linker may be postulated, this has not yet been confirmed or observed experimentally.

**In situ neutron powder diffraction (NPD) of gas-loaded MFM-126 and MFM-127**

The absence of open metal sites in this series of MOFs affords an excellent platform to study the role of functional group on gas binding. *In situ* neutron powder diffraction (NPD) has been applied to determine the preferred binding sites of CO$_2$ and CD$_4$ in MFM-126 and MFM-127 at loadings of 1.2 CO$_2$/Cu and 1.0 CD$_4$/Cu), and C$_2$D$_2$ in MFM-127 at a loading of 1.0 C$_2$D$_2$/Cu. NPD data for the desolvated samples confirm the complete removal of guest solvents and an absence of structural distortion from the parent solvated material. Relatively low loadings of 1.0-1.2 adsorbate/Cu were used to assess the strongest binding sites within the material without involving notable adsorbate-adsorbate interactions. These loadings represent typically 25-40% of the saturated capacities of each adsorbate. Fourier difference map analysis of the NPD patterns afforded the location of guest CO$_2$, CD$_4$ and C$_2$D$_2$ molecules, which after further development by Rietveld refinement allowed unambiguous determination of gas positions, orientations and crystallographic occupancies within each sample.
MFMM-126 displays four binding sites for CO$_2$, 1-4 (in decreasing order of occupancy; Figure 3). CO$_2$-1 is situated in small cage B and exhibits co-operative binding between crystallographically equivalent CO$_2$ molecules [C$_4$O$_4$] where the linear bodies of the CO$_2$ molecules lie parallel with an interaction to an adjacent isophthalate ring [D$_3$C≡C·H···O$_2$. . .C = 2.32(5) Å, <C–H·O = 143°] and an isophthalate ring [O$_2$. . .centroid$_{isophthal}$ = 3.15(4) Å, <C=O· centroid = 111°]. In addition, there are short contacts between a pyrimidyl ring [C–H$_{pyrimidine}$···O$_2$. . .C = 2.32(5) Å, <C–H·O = 143°] and an equivalent site to that of CO$_2$-3 is situated in a pocket between cages A and B with two short contacts to amido N-H units [O$_2$. . .H·N$_{amide}$ = 3.77(6) Å, <O·H·N = 124° and O$_2$. . .H·N$_{amide}$ = 3.98(8) Å, <O·H·N = 138°]. Further to this, there are two other close contacts with a pyrimidyl ring [O$_2$. . .C$_{pyrimidine}$ = 2.44(5) Å, C=O·C = 115°] and a side-on interaction with an isophthalate ring [C$_2$. . .H···C$_{isophthal}$ = 3.34(12) Å, <C·H·C = 172°]. CO$_2$-4 is positioned at the periphery of larger cage A with a hydrogen bond to an amido N-H [O$_2$. . .H·N = 4.14(9) Å, <O·H·N = 149°] as well as lying in a crevice between two isophthalate units [O$_2$. . .C$_{isophthal}$ = 3.14(11) Å, C=O·C = 81° and O$_2$. . .C$_{isophthal}$ = 3.25(10) Å, C=O·C = 96°].

Analysis of CD$_2$-loaded MFMM-126 reveals seven sites 1–7, the first two of which, have significantly higher crystallographic occupancies of 0.630 and 0.590 than the rest (Figure 3). CD$_2$-1, resides in cage B in an equivalent site to that of CO$_2$-2, also with close interactions to isophthalate and pyrimidyl rings [D$_3$C≡H–C$_{isophthal}$ = 2.96(11) Å, <C·H·C = 122° and D$_4$C·H–C$_{pyrimidine}$ = 3.28(4) Å, <C·H·C = 159°]. CD$_2$-2 is found in an identical site to that of CO$_2$-1 located in the center of cage B with two key interactions to an isophthalate ring and an amido carboxyl of the framework [D$_4$C≡H–C$_{isophthal}$ = 2.81(4) Å, <C·H·C = 146° and D$_4$C·O=C$_{amide}$ = 3.00(5) Å, <C·O=C = 140°].

Refinement of NPD data of C$_2$D$_2$-loaded MFMM-127 unveiled five sites, 1–5 (Figure 3). Interestingly, over 50% of C$_2$D$_2$ were found having short contacts (<4 Å) to the framework alkyne units. C$_2$D$_2$-1 is situated in a narrow window between cages A and B, with closest interactions to pyrimidyl and isophthalate rings [D$_3$N$_{pyrimidine}$ = 2.54(5) Å, <C–D·N$_{pyrimidine}$ = 145° and $\eta_2$-D$_2$C·H–C$_{isophthal}$ = 2.78(2) Å, <C·H·C = 108°]. Cooperative binding is visualized between C$_2$D$_2$-1 and C$_2$D$_2$-2 [1-D$_4$C≡C·D·D$_2$ = 1.81(3) Å, <C·D·C = 127°]. C$_2$D$_2$-2 also binds to the framework alkyne [D$_4$D·$\eta_2$C$_{framework}$ = 3.89(5) Å, <C·D·C = 123°] suggesting the framework alkyne has an integral role in the uptake of acetylene in MFMM-127. C$_2$D$_2$-3 is located in the center of cage B with H-bonds to a framework alkyne moiety [D$_4$N$_{framework}$ = 2.68(5) Å, <C–D·C = 120°] as well as close contacts to pyrimidyl and isophthalate rings [$\eta_2$-D$_2$C≡C·H–C$_{pyrimidine}$ = 3.05(8) Å, <C·H·C = 130° and $\eta_2$-C≡CD$_2$·C$_{isophthal}$ = 3.48(3) Å]. C$_2$D$_2$-4 occupies the hydrophobic triangular window of cage B with strong binding to an oxygen of the {Cu$_2$} paddlewheel [D$_2$O$_{paddlewheel}$ = 2.25(5) Å, <C–D·O = 150°] as well as to adjacent isophthalate rings [D$_3$C·H–C$_{isophthal}$ = 2.45(2) Å, <C·H·C = 120° and $\eta_2$-C≡CD$_2$·H–C$_{isophthal}$ = 2.89(1) Å, <C·H·C = 124°].
Three CO$_2$ binding domains, 1-3, were found in MFM-127 (Figure 3). CO$_2$-1 is situated in an equivalent site to C$_2$D$_2$-4 with a close contact to a carboxylate C$^{5\text{r}}$ [O$_{\text{CO}_2}$ · · C$_{\text{COO}}$ = 3.96(6) Å, <C–O · · C = 100°] as well as side-on interactions with isophthalate rings [O$_{\text{CO}_2}$ · · H-C$_{\text{isophthal}}$ = 2.27(1) Å, <C–H · · O = 135° and C$_{\text{CO}_2}$ · · H-C$_{\text{isophthal}}$ = 2.95(7) Å, <C–H · · C = 114°]. CO$_2$-2 occupies the corresponding site to CO$_2$-1 in MFM-126. Similarly to MFM-126, cooperative binding is exhibited between crystallographically equivalent CO$_2$-2 molecules in cage B of MFM-127 [C$_{\text{CO}_2}$ · · O$_{\text{CO}_2}$ = 3.04(2) Å, <C=O · · C = 128°]. Crucially, these results reveal the key role of the amide groups on selective adsorption of CO$_2$ in MFM-126 as well as that alkyne moieties do not act as effective adsorption sites for CO$_2$ in MFM-127.

NPD data for CD$_4$-loaded MFM-127 exposed only two noteworthy sites of interaction. Both sites correspond directly to CD$_4$ sites 1&2 observed in MFM-126, respectively. In MFM-127, CD$_4$-1 resides in the hydrophobic triangular windows of cage B [D$_4$C · · H-C$_{\text{isophthal}}$ = 2.93(1) Å, <C–H · · C = 120°], further showing that this pocket provides an optimal environment for CD$_4$. CD$_4$-2 is found in the center of cage B and interacts weakly to the framework alkyne [D$_4$C · · N$_2$C= framework = 4.39(1) Å] revealing that the alkyne moiety has little effect on CD$_4$ adsorption.

Thus, significantly, the NPD study reveals that it is a combination of cooperative binding as well as the amide functionality that leads to enhanced interaction of CO$_2$ with MFM-126. On the other hand, NPD data reveals that alkyne-functionalized MFM-127 exhibits much weaker interaction with CO$_2$, but that the alkyne moieties play critical roles in acetylene binding, with over half of adsorbed acetylene exhibiting interactions (<4 Å) to alkyne moieties in the pore of MFM-127. This represents the first example of direct visualization of acetylene binding to an alkyne moiety in porous materials.

**Inelastic neutron scattering (INS) studies of CO$_2$-loaded MFM-126**

To gain further understanding into CO$_2$ binding in MFM-126, inelastic neutron scattering (INS) was measured as a function of CO$_2$-loading (Figure S18). The INS spectrum for the bare MOF exhibits numerous vibrational modes which have been assigned by comparison with a DFT-calculated INS spectrum (Figure S17). Interestingly, unlike previously reported with iso-structural MFM-136,$^{27}$ MFM-126 exhibits significant interactions with guest CO$_2$. Upon CO$_2$ loading, there is a shift in the peak at 82.8 (assigned to the in-plane bending of the amide group) to 84.1 meV signifying an interaction between adsorbed CO$_2$ and the amide group, such as those visualized in the structure model of CO$_2$-loaded MFM-126. This result contrasts with that of MFM-136$^{27}$ and confirms the importance of cooperativity between functional groups (in this case amide) and the pore geometries on guest binding.

**In situ synchrotron FT-IR microspectroscopy of MFM-126**

To investigate further the nature of host-guest interactions, in situ synchrotron FT-IR microspectroscopy was conducted on a single crystal of activated MFM-126. FTIR spectra were collected as a function of CO$_2$-loading by increasing the partial pressure of CO$_2$ in N$_2$ from 0 to 1.0 bar (ppCO$_2$) (Figure 4). The $v_1+v_3$ (3695 cm$^{-1}$) and $2v_2+v_3$ (3590 cm$^{-1}$) combination bands of CO$_2$ (Figure 4a) were used to monitor CO$_2$ sorption as the fundamental antisymmetric stretch at ~2348 cm$^{-1}$ saturates at ppCO$_2$ above 0.2
bar. These combination bands are red-shifted from their free values (3714 and 3612 cm\(^{-1}\), respectively) at all partial pressures of CO\(_2\) loading and increase in intensity as a function of ppCO\(_2\), confirming that CO\(_2\) interacts strongly with the framework (Figure 4a). Activated MFM-126 has a \(\nu\)(N-H) stretch at 3306 cm\(^{-1}\) and upon increasing ppCO\(_2\) from 0 to 1 bar, this band shifts by 36 cm\(^{-1}\) to 3270 cm\(^{-1}\). In addition, the observed shift of the amide \(\nu\)(C=O) stretching band by 10 cm\(^{-1}\) (from 1684 cm\(^{-1}\) in the absence of CO\(_2\) to 1674 cm\(^{-1}\) at 1.0 bar ppCO\(_2\); Figure 4c) further indicates CO\(_2\) adsorption directed by the amide group in MFM-126. Overall, these observations are highly consistent with the NPD and INS results.

Conclusions

A series of iso-retticular (3,6)–connected pyrimidyl isophthalate Cu(II)–based MOFs, of rare eea topology have been synthesized and characterized. Although MFM-136 exhibits the highest CO\(_2\) uptake at 20 bar, it was found that upon shortening the linker unit to form MFM-126, selectivity of CO\(_2\) uptake at 1 bar increases dramatically. The relative ease of synthesis of MFM-126 coupled with its high selectivity for binary mixtures of CO\(_2/\)CH\(_4\) and CO\(_2/N_2\), position this MOF a viable candidate for CO\(_2\) separations. Furthermore, the CO\(_2\) separation performance of MFM-126 has been confirmed by dynamic breakthrough experiments. NPD data of CO\(_2\)-loaded MFM-126 has revealed that cooperative binding of CO\(_2\) (at position CO\(_2\)-1) and binding to amide groups that decorate cage B both have strong effects on the observed selective CO\(_2\) binding. The \textit{in situ} spectroscopic studies using INS and FTIR also establish that adsorbed CO\(_2\) interacts strongly with the amide groups of MFM-126, with significant shifts of amide (C=O and N-H) vibrational bands on CO\(_2\) loading. Replacing the amide-group in MFM-126 with an alkyne-group to give MFM-127 leads to a decrease in both CO\(_2\) and CH\(_4\) uptake capacities relative to MFM-126, but affords a 68% greater C\(_2\)H\(_2\) capacity than MFM-126. NPD experiments reveal for the first time that acetylene interacts directly with alkyne moieties of MFM-127 in the pore. Notably, over 50% of the acetylene observed within MFM-127 displays strong interactions (<4 Å) with the alkyne functionality of the framework. The understanding gained in this study provide further insights into the development of materials showing improved gas binding \textit{via} specific interaction to ligand sites within the MOF.

References:

Acknowledgement

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Additional information

Supplementary information is available in the online version of the paper. Correspondence and requests for materials should be addressed to S.Y. and M.S. CCDC-1857732–1857743 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Competing financial interests

The authors declare no competing financial interests.
Figures and Tables

Table 1. Structures of linkers, coordination environments, cage lengths, BET surface areas and experimentally and calculated pore volumes for MFM-126–128 and MFM-136–138. Colors: C, grey; H, white; O, red; N, blue; Cu, teal.

<table>
<thead>
<tr>
<th></th>
<th>MFM-126</th>
<th>MFM-127</th>
<th>MFM-128</th>
<th>MFM-136*</th>
<th>MFM-137</th>
<th>MFM-138</th>
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<td>Cage sizes</td>
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<tr>
<td>Long Cage (A) Length / Å</td>
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<td>0.57</td>
<td>0.57</td>
<td>0.64</td>
<td>0.67</td>
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*Previously reported.²⁷
Figure 1. Views of crystal structure of MFM-126. (a) cage A; (b) cage B. (c) View of the alternate packing of cages A (void space coloured orange) and B (void space coloured plum). (d) View along the c-axis of the Kagomé lattice in MFM-126. Colours: C, grey; H, white; O, red; N, blue; Cu, teal.

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<th>MOF</th>
<th>CO\textsubscript{2} Uptake / mmol g\textsuperscript{-1} (1 bar)</th>
<th>CH\textsubscript{4} Uptake / mmol g\textsuperscript{-1} (1 bar)</th>
<th>S\textsubscript{CO\textsubscript{2}/CH\textsubscript{4}} (50:50, 1 bar)</th>
<th>S\textsubscript{CO\textsubscript{2}/N\textsubscript{2}} (15:85, 1 bar)</th>
<th>Q\textsubscript{st} / kJ mol\textsuperscript{-1} (virial method 1)</th>
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Figure 2. a) Sorption isotherms for CO\textsubscript{2} and CH\textsubscript{4} in MFM-126–128 and MFM-136–138 at 298 K. b) Sorption isotherms for CO\textsubscript{2}, CH\textsubscript{4} and N\textsubscript{2} in MFM-126 at 273 and 298 K. c) Sorption isotherms for C\textsubscript{2}H\textsubscript{2}, CO\textsubscript{2} and CH\textsubscript{4} in MFM-127 and for C\textsubscript{2}H\textsubscript{2} in MFM-126 at 273 K. d) IAST selectivity for CO\textsubscript{2}/N\textsubscript{2} (15:85) and equimolar CO\textsubscript{2}/CH\textsubscript{4} in MFM-126 at 273 and 298 K. e and f) Experimental breakthrough curves for the adsorption of CO\textsubscript{2}/N\textsubscript{2} (15:85) and equimolar CO\textsubscript{2}/CH\textsubscript{4} mixtures flowing through a 0.9 mL fixed-bed of MFM-126 at 298 K with a total gas flow of 10 mL min\textsuperscript{-1} at atmospheric pressure. After breakthrough of both species a He purge was applied leading to desorption of all components.
Figure 3. Binding sites of guests in MFM-126 and MFM-127 derived from Rietveld refinement of NPD data with quoted in distances in Å. Colors: C, black; H, white; O, red; N, blue; Cu, teal. Refined chemical occupancies of guest-molecules in square brackets.
Figure 4. Micro-FTIR spectra of a single crystal of MFM-126 as a function of CO₂-loading incrementally from 0 to 1 bar ppCO₂ focusing on a) the CO₂ combination bands at 3695 and 3590 cm⁻¹; b) ν(N-H) stretching band shifting from 3306 cm⁻¹ at 0% loading of CO₂ (in N₂) to 3270 cm⁻¹ at 1 bar ppCO₂; c) the ν(N-H) bending mode shifting from 1684 cm⁻¹ at 0 bar ppCO₂ (in N₂) to 1674 cm⁻¹ at 1 bar ppCO₂. All spectra were recorded referenced to the blank cell as a function of CO₂ loading to remove contributions of free gaseous CO₂.