Post-synthetic modulation of the charge distribution in a metal–organic framework for optimal binding of carbon dioxide and sulfur dioxide†

Lei Li,ab Ivan da Silva,cd Daniil I. Kolokolov,de Xue Han,ad Jiangnan Li,a Yongqiang Cheng,f Luke L. Daemen,† Christopher G. Morris,ag Harry G. W. Godfrey,a Nicholas M. Jacques,a Xinran Zhang,a Pascal Manuel,c Mark D. Frogley,g Claire A. Murray,g Anibal J. Ramirez-Cuesta,g Gianfelice Cinque,g Chiu C. Tang,g Alexander G. Stepanov,de Sihai Yang ef and Martin Schroder f,a

Modulation of pore environment is an effective strategy to optimize guest binding in porous materials. We report the post-synthetic modification of the charge distribution in a charged metal–organic framework, MFM-305-CH3·[Al(OH)4][LiCl]. [(H3L)Cl = 3,5-dicarboxy-1-methylpyridinium chloride] and its effect on guest binding. MFM-305-CH3 shows a distribution of cationic (methylpyridinium) and anionic (chloride) centers and can be modified to release free pyridyl N-centres by thermal demethylation of the 1-methylpyridinium moiety to give the neutral isostructural MFM-305. This leads simultaneously to enhanced adsorption capacities and selectivities (two parameters that often change in opposite directions) for CO2 and SO2 in MFM-305. The host–guest binding has been comprehensively investigated by in situ synchrotron X-ray and neutron powder diffraction, inelastic neutron scattering, synchrotron infrared and 2H NMR spectroscopy and theoretical modelling to reveal the binding domains of CO2 and SO2 in these materials. CO2 and SO2 binding in MFM-305-CH3 is shown to occur via hydrogen bonding to the methyl and aromatic-CH groups, with a long range interaction to chloride for CO2. In MFM-305 the hydroxyl, pyridyl and aromatic C–H groups bind CO2 and SO2 more effectively via hydrogen bonds and dipole interactions. Post-synthetic modification via dealkylation of the as-synthesised metal–organic framework is a powerful route to the synthesis of materials incorporating active polar groups that cannot be prepared directly.

Introduction

The release of CO2 and SO2 into the atmosphere from combustion of fossil fuels causes significant environmental problems and health risks.1–4 The wholesale replacement of the carbon-based energy supply is highly challenging, not least because of the existing infrastructure.3 It is therefore vital to mitigate the emissions of these acidic gases post combustion. At present, several technologies are used to capture CO2 and SO2, such as amine scrubbing, absorption in organic solvents, ionic liquids and limestone slurry.4–7 However, the considerable costs and the substantial energy input required for system regeneration significantly limit their long-term application. Powerful drivers therefore exist to develop new systems showing high adsorption capacity, selectivity, storage density and excellent reversibility to sequester these gases.

Metal–organic frameworks (MOFs) constructed from metal ions and clusters bridged by organic ligands are an emerging class of porous materials showing highly crystalline structures
and great promise for gas adsorption and storage. MOFs can exhibit very high surface areas and, more importantly, have tunable pore environments with predictable pore size and can incorporate specific functional groups. MOFs have been studied extensively as sorbents for CO₂ under post-combustion conditions. In contrast, adsorption of SO₂ in MOFs has been rarely reported due to the limited stability of coordination compounds to reactive and corrosive SO₂. Development of new stable porous materials with optimal SO₂ and CO₂ adsorption property thus remains significant challenge. Optimising the interactions between hosts and substrate molecules to enhance the storage capacity, density and selectivity is the key to overcoming these barriers. For this reason, visualisation of the host-guest interactions involved in the MOF-gas binding interactions is crucial for the design of new materials. Interpretation of adsorption mechanisms by in situ experiments as a function of gas loading can afford keen insights into the preferred binding sites within pores and the interaction to the pore interior. Open metal sites and pendent functional groups (e.g., amine, hydroxyl group and nitrogen-containing aromatic rings) have been found to act as specific sites for CO₂ and SO₂ binding.

Ionic liquids are composed of cations such as ammonium, pyridinium, phosphonium and imidazolium groups, and the solubility of CO₂ and SO₂ in these systems is often high owing to strong acid–base interactions. The incorporation of functionalized organic ligands within MOFs and post synthetic modification can be used to control the number and types of functional groups within the pores. Cleavage of C–N bonds and hydrolysis of methyl viologen in alkaline solution have been observed. However, the dealkylation of pre-formed MOFs has not been reported previously, although adsorption of CO₂ in two imidazolium–pyridinium cation-containing MOFs has been observed. We report the synthesis of a highly unusual MOF, 

Results and discussion

Structural analysis of MFM-305-CH₃

Solventureaction of AlCl₃·6H₂O, [H₂L]Cl ([H₂L]Cl = 3,5-dicarboxy-1-methylpyridinium chloride) in a mixture of methanol and water (v/v = 12) at 130 °C for 3 days afforded MFM-305-CH₃-solv, [Al(OH)L]Cl-solv, as a white crystalline powder in ca. 45% yield. The structure of MFM-305-CH₃-solv has been determined by high resolution synchrotron X-ray powder diffraction (SPXRD). MFM-305-CH₃-solv crystallizes in the space group I4₁/amd and has an open structure comprising cis-connected, corner-sharing chains of [AlO₄(OH)]⁻ bridged by dicarboxylate ligands. The Al(III) centre shows octahedral coordination defined by four carboxylate oxygen atoms from the ligand [Al–O = 2.048(8) and 1.881(3) Å; each appears twice] and two oxygen atoms from two µ₂-hydroxyl groups [Al–O = 1.776(6) Å]. Adjacent Al(III) centers are linked by a µ₂-hydroxyl group to form an extended chain of [AlO₄(OH)]⁻ along the c axis. The ligands further bridge [AlO₄(OH)]⁻ chains to give a three dimensional network with square-shaped channels filled with disordered guest solvents. The window size of the channel is approximately 4.6 × 4.6 Å taking van der Waals radii into consideration (Fig. 1 and S23†). Overall, the metal–ligand connection in MFM-305-CH₃-solv is comparable to that in MFM-300 (ref. 21) and CAU-
10. The total free solvent volume in MFM-305-CH3-solv was estimated by PLATON/SOLV to be 28.5%. 

Guest solvent molecules in the pores can be removed by heating at 110 °C under vacuum for 10 h to give the desolvated material MFM-305-CH3, which retains the structure of the solvated material as determined by SXRD. As expected, the framework of desolvated MFM-305-CH3 is cationic since it incorporates pyridinium moieties, and these are balanced by chloride ions that hydrogen bond to the hydroxyl groups and aromatic –CH groups on the pyridine ring [Cl···HO = 2.01(1) Å; Cl···HC = 2.47(1) Å]. As a result, the µ2-OH groups in MFM-305-CH3 are hindered by the Cl− ions and are thus not accessible to guest molecules, leaving 1-methylpyridinium and chloride ion as potential sites for guest interaction. The stability and rigidity of the framework in MFM-305-CH3 has been confirmed by variable temperature PXRD (50–550 °C) (Fig. S2†), which confirms framework decomposition above 450 °C.

Structural analysis of MFM-305

TGA-MS measurements of desolvated MFM-305-CH3 shows that the methyl and chloride groups can be removed from the pore at 150–300 °C (Fig. S3†) giving the iso-structural neutral material MFM-305. To prepare a bulk sample of MFM-305, as-synthesized MFM-305-CH3-solv was heated at 180 °C under vacuum for 16 h to completely remove the guest solvents and CH3Cl (Fig. S4†). A change in color from white to pale yellow is observed on going from MFM-305-CH3 to MFM-305. SXRD analysis of MFM-305 confirms that it retains the same space group I41/amd, but shows a slight contraction along the a/b axis (Δ = 0.06%) and c axis (Δ = 4%) with an extended channel size of 5.6 × 5.6 Å. The total free solvent volume in MFM-305 was estimated by PLATON/SOLV to be 39.9%. The most significant change is conversion of the methylpyridinium species in MFM-305-CH3 to a free pyridyl moiety in MFM-305 and formal loss of CH3Cl. The bridging hydroxyl groups in MFM-305 are now exposed because of the removal of chloride (see below). Moreover, the pyridyl groups are now accessible within the pores of MFM-305, and IR spectroscopy confirms the loss of the stretching vibration of the –CH3 group at 2988 cm−1 on going from MFM-305-CH3 to MFM-305 (Fig. S7†). The complete removal of Cl− in MFM-305 has been confirmed by XPS spectroscopy (Fig. S5 and S6†). Interestingly, the post-synthetic modification leads to distinct pore environments for isostructural MFM-305-CH3 and MFM-305, and thus provides an excellent platform to examine their capabilities of guest binding and selectivity. To the best of our knowledge, this is the first example of studying the mechanism of guest adsorption within an isostructural pair of MOFs with charged and neutral pore environments of this kind (Table 1).

Gas adsorption analysis

N2 isotherms at 77 K for desolvated MFM-305-CH3 and desolvated MFM-305 both show type-I profiles confirming retention of microporosity. The BET surface area and total pore volume for MFM-305-CH3 are estimated to be 256 m² g⁻¹ and 0.181 cm³ g⁻¹, respectively, and 779 m² g⁻¹ and 0.372 cm³ g⁻¹, respectively, for MFM-305 confirming a ~2.0 fold increase in porosity upon the modification (Fig. 2a, Table S1†). Horváth–Kawazoe (HK) analysis of the N2 isotherm confirms a pore size distribution centered at 5.2 and 6.2 Å for MFM-305-CH3 and MFM-305, respectively (Fig. 2b). The increase in pore size is consistent with those confirmed by X-ray structural analysis.

CO2 isotherms at 195 K and 1.0 bar show saturated uptake capacities of 4.23 and 5.69 mmol g⁻¹ for MFM-305-CH3 and MFM-305, respectively (Fig. S24†). The increase (ca. 33%) is much smaller than that of N2 isotherm, consistent with the reduced kinetic diameter of CO2 (3.30 Å) compared to N2 (3.89 Å). At 273 K and 298 K, MFM-305-CH3 shows CO2 uptakes of 2.67 and 2.41 mmol g⁻¹, respectively, at 1.0 bar (Fig. 2c and d). In comparison, the values for MFM-305 were recorded as 3.55 and 3.02 mmol g⁻¹, respectively. The CO2 uptake at 0.15 bar, which is relevant to its partial pressure in flue gas, are 0.86 mmol g⁻¹ for MFM-305-CH3 and 1.76 mmol g⁻¹ for MFM-305. This uptake is higher than that of H12[CuCl2(BTTri)3]·2H2O (BTTri = 1,3,5-tris[1H-1,2,3-triazol-5-yl]benzene) (0.682 mmol g⁻¹) and NH2-MIL-101(1Cr) (0.5 mmol g⁻¹), but lower than that of MFM-300[Al] (2.64 mmol g⁻¹),23 MOF-74(M) (M = Mg, Ni, Co) (5.3, 2.7, 2.7 mmol g⁻¹, respectively) and the amine-modified MIL-101 (4.2 mmol g⁻¹) under the same conditions.

The excellent stability of these two MOFs motivated us to measure the adsorption isotherm of SO2. At 298 K and 1.0 bar, MFM-305-CH3 and MFM-305 show SO2 adsorption capacities of 5.16 and 6.99 mmol g⁻¹, respectively (Table S2†), and only lower than that of MFM-300(In) (8.28 mmol g⁻¹), Mg-MOF-74 (8.6 mmol g⁻¹), Ni(bdc)(ted)0.5 (9.97 mmol g⁻¹) and tept (H2bdc = terephthalic acid; ted = triethylendiamine), MFM-202a (10.2 mmol g⁻¹) and SIFSIX-1-Cu (11.01 mmol g⁻¹), which have higher surface areas of 1071, 1525, 1783, 2220 and 3140 m² g⁻¹, respectively. At 303 K, MFM-305 shows an adsorption capacity

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Unit cell parameters of MFM-305-CH3 and MFM-305</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>All(OH)(C6H4NO4)Cl</td>
</tr>
<tr>
<td>M (g/mol)</td>
<td>259.6</td>
</tr>
<tr>
<td>Space group</td>
<td>I41/amd</td>
</tr>
<tr>
<td>a, b (Å)</td>
<td>21.48(6)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>10.90(3)</td>
</tr>
<tr>
<td>Volume (Å³)</td>
<td>5030(30)</td>
</tr>
<tr>
<td>BET surface area/m² g⁻¹</td>
<td>256</td>
</tr>
<tr>
<td>Pore volume</td>
<td>0.181</td>
</tr>
<tr>
<td></td>
<td>(P/P0 = 0.95)/cm³ g⁻¹</td>
</tr>
<tr>
<td>Pore volume (Cal.)/cm³ g⁻¹</td>
<td>0.209</td>
</tr>
<tr>
<td>Pore size (Cal.)/Å</td>
<td>4.6</td>
</tr>
<tr>
<td>CO2 uptake/mmol g⁻¹</td>
<td>2.98/2.39</td>
</tr>
<tr>
<td>(273/298 K)</td>
<td>(273/298 K)</td>
</tr>
<tr>
<td>SO2 uptake/mmol g⁻¹</td>
<td>5.29/5.16</td>
</tr>
</tbody>
</table>
for SO$_2$ of 6.70 mmol g$^{-1}$ at 1.0 bar, and a high uptake of 3.94 mmol g$^{-1}$ at 0.025 bar, comparable to the best-behaving MOFs. Using the total pore volume, the storage density of SO$_2$ in a given MOF system can be estimated; those for MFM-305-CH$_3$, SIFSIX-1-Cu, MFM-305 and MFM-300(In) are calculated to be 1.83, 1.70, 1.20 and 1.27 g cm$^{-3}$, respectively at 298 K and 1.0 bar. Thus, MFM-305-CH$_3$ gives a notably higher storage density that is 70% of liquid density of SO$_2$ at 273 K (2.63 g cm$^{-3}$), indicating the presence of efficient packing of adsorbed gas molecules within the pore.

Both MFM-305-CH$_3$ and MFM-305 show highly selective SO$_2$ uptakes. At 298 K, MFM-305-CH$_3$ and MFM-305 exhibit very steep adsorption profiles for SO$_2$ between 0 and 20 mbar, leading to an uptake of 3.59 and 3.94 mmol g$^{-1}$, respectively, accounting for 70% and 56% of the total uptake at 1.0 bar. In contrast, under the same conditions, MFM-305-CH$_3$ and MFM-305 show a much lower uptake of CO$_2$ (i.e., 0.15 and 0.40 mmol g$^{-1}$, respectively).
Moreover, the uptakes of N₂ under the same conditions are negligible (<0.01 mmol g⁻¹) in these two materials. The isosteric heat of adsorption (Qₐₐ) for CO₂ in MFM-305-CH₃ and MFM-305 both lie in the range of 29-34 kJ mol⁻¹; on average the Qₐₐ of MFM-305 is ca. 3 kJ mol⁻¹ higher than MFM-305-CH₃ (Fig. 2e). The Qₐₐ for adsorption of SO₂ in MFM-305 and MFM-305-CH₃ is estimated to be 39-43 kJ mol⁻¹ and 30-32 kJ mol⁻¹, respectively (Fig. 2g). MFM-305 displays a higher Qₐₐ value for SO₂ uptake than MFM-305-CH₃, indicating the presence of enhanced host-guest binding affinity upon the pore modification. To further evaluate their potential for gas separation, the selectivities for CO₂/N₂(S₃N), SO₂/CO₂ (S₃C) and SO₂/N₂ (S₃N) at 298 K have been calculated using ideal adsorbed solution theory (IAST)⁶⁰ over a wide range of molar compositions (i.e., 1 : 99 to 50 : 50) (Fig. 2f, h, S31 and S33†). Significantly, for a 5 : 95 mixture of SO₂/CO₂ and a 15 : 85 mixture of CO₂/N₂, MFM-305-CH₃ and MFM-305 both show exceptionally high IAST selectivities, and these are enhanced by the presence of water vapor, the breakthrough of SO₂ from MFM-305-CH₃, indicating the presence of enhanced host-guest binding affinity upon the pore modification. The calculations for S₃N are subject to large uncertainties due to the extremely low uptake of N₂. The adsorptive removal of low concentration SO₂ by MFM-305 has been confirmed by breakthrough experiments in which a stream of SO₂ (2500 ppm diluted in He/N₂) was passed through a packed bed of MFM-305 under ambient conditions (Fig. 3a). As expected, He and N₂ were the first to elute through the bed, whereas SO₂ was retained selectively under dry condition (Fig. 3a). On saturation (dimensionless time > 500), SO₂ breaks through from the bed and reaches saturation gradually. The ability of MFM-305 to capture SO₂ in the presence of moisture has also been demonstrated by breakthrough experiments using a wet stream of SO₂ (Fig. 3b). In the presence of water vapor, the breakthrough of SO₂ from MFM-305 slightly reduces to 420 (dimensionless time) as a result of competitive adsorption of water. Thus, the marked differences in adsorption profiles, uptake capacities, Qₐₐ for SO₂, CO₂ and N₂, the corresponding IAST selectivity and the dynamic adsorption experiments indicate the potential of MFM-305-CH₃ and MFM-305 have the potential to act as selective adsorbents for CO₂ and SO₂.

Determination of binding domains for adsorbed CO₂ and SO₂

We sought to determine the binding domains for CO₂ and SO₂ in the pores of MFM-305-CH₃ and MFM-305 since comparison between the binding sites within these two materials affords a direct observation of the effect of pore environment on guest binding. High resolution SXRD data were collected at 198 K for CO₂-loaded samples and at 298 K for SO₂-loaded samples at 1 bar. SXRD data enabled full structural analysis via Rietveld refinement (Fig. S8-S22†) to yield the positions, orientations and occupancies of adsorbed CO₂ and SO₂ molecules (Fig. 4 and S33†). Overall, all gas-loaded samples retain the H₄/amd space group and two crystallographically independent binding sites (I and II) are observed in each case.

In CO₂-loaded MFM-305-CH₃, CO₂ (occupancy = 0.32) interacts with the methyl group with a H-C-OCO distance of 2.54(1) Å, indicating the formation of a weak hydrogen bond. CO₂ also forms supramolecular interactions with aromatic -CH groups on neighboring pyridinium rings [OCO-…HC = 2.87(2) Å]. Additionally, dipole interactions were observed between CO₂ and Cl⁻ [OCO-…Cl⁻ = 3.78(1) Å, ∠O-C-…Cl⁻ = 99.2(8)°].⁶⁰,⁴¹ CO₂ (occupancy = 0.41) binds to the aromatic –CH group [OCO…H-…HC = 3.50(1) Å]. Further dipole interactions were observed between CO₂ and CO₂ [O-C-CO = 3.87(1) Å; O-C-CO = 4.10(1) Å] in a typical T-shape arrangement.⁴²

In CO₂-loaded MFM-305, CO₂ (occupancy = 0.48) interacts with the hydroxyl group in an end-on mode [OH…OCO = 3.45(3) Å]. This distance is longer than that obtained for CO₂-loaded MFM-305(Al) [2.98(4) Å] studied by PXRD at 273 K.⁴⁰ CO₂ also interacts with the exposed pyridine nitrogen atom via a dipole interaction [OCO…N = 2.89(1) Å]. Additionally, a series of weak supramolecular contacts of CO₂ to surrounding –CH groups [OCO…HC = 2.44(1); 2.73(1) Å] are also observed. Further dipole interactions are found between CO₂ and CO₂ with intermolecular C-C-C distances of 3.09(1)/3.14(1) Å, comparable to that observed in dry ice [3.178(1) Å].⁴²

At 298 K SO₂-loaded MFM-305-CH₃ shows the SO₂ molecule (occupancy = 0.30) binding to two adjacent methyl groups simultaneously [OSO…HC = 2.49(3) Å]. SO₂ also forms hydrogen bonds with surrounding –CH groups [OSO…HC = 2.54(2) Å]. SO₂ (occupancy = 0.47) lies perpendicular to SO₂ [S-C-CO = 3.83(2) and 3.97(3) Å] and parallel to the pyridinium ring [OSO…HC = 3.95(1) Å]. The SO₂ intermolecular distances within MFM-305-CH₃ are comparable to that observed in the crystal structure of SO₂ (3.10 Å),⁴⁴ confirming the very efficient packing of adsorbed SO₂ molecules leading to its high observed storage density.

Fig. 3 Dimensionless breakthrough curve of 0.25% SO₂ (2500 ppm) diluted in He/N₂ under (a) dry and (b) wet conditions through a fixed-bed packed with MFM-305 at 298 K and 1 bar.
In MFM-305, SO$_2^-$ (occupancy = 0.39) primarily binds to the pyridyl N-atom via a dipole interaction [O$-$SO$_2^-$/N = 2.78(1) Å] and also forms hydrogen bonds with the exposed hydroxyl group [–OH$-$OSO = 3.42(4) Å] as well as the surrounding –CH groups [–CH$-$OSO = 2.63(3) and 3.14(3) Å]. Further dipole interactions were observed between SO$_2^-$ molecules on sites I and II' with intramolecular distance of 4.29(2) Å. Overall, these observations confirm that the methyl group and –CH groups are the primary binding sites in MFM-305-CH$_3$ for both CO$_2$ and SO$_2$. In contrast, modulation of the pore environment in MFM-305 induces notable shifts of binding sites to the free pyridyl nitrogen center and hydroxyl group. This study offers a comprehensive understanding of the synergistic effect of functional groups on the binding of CO$_2$ and SO$_2$ in these materials.

Analysis of host–guest binding via inelastic neutron scattering (INS)

To directly visualise the multiple supramolecular host–guest binding modes in these systems, INS spectra of bare and CO$_2$-loaded MFM-305-CH$_3$ and MFM-305 (1 gas/Al) were collected at 5 K (Fig. 5). In addition, the structural models obtained from X-ray crystallographic studies were optimized by DFT calculations. The corresponding DFT-calculated INS spectra show good agreement with the experimental data (Fig. S35–S39†). Comparison of the INS spectra of desolvated MFM-305-CH$_3$ and MFM-305 shows (Fig. S35†) three distinct low-energy peaks at 13, 27, 36 and 19, 28, 37 meV, respectively, related to the lattice modes of MFM-305-CH$_3$ and MFM-305. The most significant change is the absence of the –CH$_3$ rotation/torsion mode at 20 meV in MFM-305, confirming full demethylation by the post-synthetic modification procedure. The groups of peaks observed at 40–85 meV and 85–200 meV in MFM-305-CH$_3$ are assigned to wagging/bending modes of the bridging hydroxyl group and of the aromatic C–H bonds, respectively. As crystallographic studies confirm above, the hydroxyl groups within MFM-305-CH$_3$ form hydrogen bonds to the chloride ion in the pores. Upon demethylation, the peaks at 40, 69 and 83 meV in MFM-305-CH$_3$ shifts to higher energies at 53, 83, 115 and 119 meV in MFM-305, consistent with the removal of the chloride ions.

Addition of CO$_2$ in MFM-305-CH$_3$ is accompanied by significant change to peaks at 13 and 27 meV, indicating stiffening of the lattice modes as a result of CO$_2$ inclusion. Large intensity changes were observed for the peaks at 20 meV, indicating the hindrance of rotation motion of –CH$_3$ groups upon CO$_2$ binding, consistent with the formation of hydrogen bonds.
as observed in the structural models. This is further accompanied by small red shifts for the peaks between 85 and 200 meV (bending modes of –CH groups). Thus, the INS result confirms that the methyl and –CH groups are the effective binding sites for CO2 in MFM-305-CH3. Addition of CO2 in MFM-305 leads to similar changes of peaks at 19, 28 and 37 meV. Significant changes to peak at 53, 83, 115 and 119 meV indicate that the bridging hydroxyl is directly involved in binding to CO2. The peaks between 120 and 200 meV also show notable changes in the C–H modes on CO2 binding. This result confirms unambiguously that the –OH group and pyridine ring are the primary binding site for CO2 in MFM-305, in excellent agreement with the crystallographic study. The combination bands of the \( \nu(\mu_2-\text{OH}) \) vibrations within MFM-305-CH3 centered at 1555 cm\(^{-1}\) shifts to 1560 cm\(^{-1}\), and that at 1552 cm\(^{-1}\) in MFM-305 shifts to 1566 cm\(^{-1}\) upon CO2 loading, consistent with the formation of supplementary interactions between CO2 molecules and pyridinium or pyridyl rings (Fig. S40†). Thus, the observed changes in IR experiments gives further evidence and supports the distinct interactions between guest CO2 molecules and these two porous MOFs.

Analysis of CO2 binding via in situ synchrotron infrared micro-spectroscopy

In order to study the interaction between adsorbed CO2 molecules and the MOF hosts at 298 K, an in situ synchrotron IR micro-spectroscopic study\(^2\) was carried out as a function of CO2 loading. Upon desolvation of MFM-305-CH3 under a dry He flow, an absorption band at 3690 cm\(^{-1}\) corresponding to the \( \nu(\mu_2-\text{OH}) \) stretching mode is observed. Upon dosing CO2 up to 1.0 bar, this peak remained at the same position, but the peak intensity increased slightly indicating a through-space effect due to the weak interaction between Cl\(^–\) and CO2 molecules (Fig. 5b). In contrast, upon dosing desolvated MFM-305 with 1.0 bar CO2, the peak at 3690 cm\(^{-1}\) shifts very slightly but the peak intensity decreases notably (Fig. 5d) indicating the presence of a strong interaction between CO2 and hydroxyl groups, entirely consistent with the crystallographic study. The combination bands of the –C==C– vibrations\(^44\) within MFM-305-CH3 centered at 1555 cm\(^{-1}\) shifts to 1560 cm\(^{-1}\), and that at 1552 cm\(^{-1}\) in MFM-305 shifts to 1566 cm\(^{-1}\) upon CO2 loading, consistent with the formation of supplementary interactions between CO2 molecules and pyridinium or pyridyl rings (Fig. S40†). Thus, the observed changes in IR experiments gives further evidence and supports the distinct interactions between guest CO2 molecules and these two porous MOFs.

Analysis of host–CO2 binding via in situ \(^2\)H NMR spectroscopy

The –CH\(_3\) group in the 1-methylpyridinium dicarboxylate linker represents a fast stochastic rotor or natural isolated gyroscope. As such, its rotational parameters can be used to track the possible binding interaction with the guest molecules.\(^5\) We were interested to probe further the dynamic changes of the methyl groups on CO2 binding by synthesising MFM-305-CD3 and studying it by solid state \(^2\)H NMR spectroscopy over a wide temperature range (90–300 K). MFM-305-CD3 was obtained using the same synthetic route described above but using the deuterated ligand, 3,5-dicarboxy-1-methyl-\(d_3\)-pyridinium chloride. Two samples were used in this \(^2\)H NMR study: guest-free MFM-305-CD3 and CO2-loaded MFM-305-CD3.
Typically the –CD₃ group is expected to exhibit very fast uniaxial rotation and hence its dynamics can be probed by ²H NMR spin-lattice (T₁) relaxation, which is sensitive to rapid (rate > 10⁸ s⁻¹) motions.⁴⁵,⁴⁶ The T₁ relaxation curves (Fig. 6) show for both materials that the temperature dependence is characterised by two regions of monotonous decrease separated by a local minimum (marked as a and c in Fig. 6). Such behavior shows that in addition to the usual uniaxial rotations, the methyl groups perform another type of motion – a faster one, as it governs the relaxation curve notably at lower temperatures (marked b and d in Fig. 6). In CO₂-loaded MFM-305-CD₃, both modes are notably slower which is reflected in the behavior of the T₁ curves behavior at ~180 K and ~100 K. A quantitative analysis requires a model of rotation (Fig. 6d and e): considering the close contact of the –CD₃ group with the neighboring linker (d ~ 3 Å), it is reasonable to assume that the slower (a, c) motion (k₁, kₐ₁) reflects the uniaxial rotation of the –CD₃ group about its Cₛ symmetry axis aligned along the N–CD₃ bond, while the faster (b, d) motion (k₂, kₐ₂) represents small angular librations of the rotating axis restricted within borders ±γ₂lib.

Parameters derived within such a model confirm that the rotation along N–CD₃ axis (E₁ = 4.2 kJ mol⁻¹, k₁ = 2.1 × 10¹⁰ s⁻¹) reaches a rate of kₐ₁ ~ 10⁸ s⁻¹ at 100 K (a), while in the presence of the CO₂ it is ~10 times slower with kₐ₂ ~ 10⁷ s⁻¹ (E₂ = 4.2 kJ mol⁻¹, kₐ₂ = 1.8 × 10⁹ s⁻¹), and reaches 10⁶ s⁻¹ at 180 K (c). Hence, by interacting with CO₂, the pre-exponential factor of the –CD₃ rotation is affected. This indicates that although the interaction with CO₂ is not sufficient to increase the activation barrier of the rotation, the dynamic density of guests around the methyl groups is tight enough and sufficient to slow down the rotation rate by 10-fold by random collisions. Similarly, the libration mode is affected as well and the pre-exponential is faster and reaches its characteristic minimum below 90 K (b, d). For MFM-305-CD₃ its rate at 100 K is k₂ ≈ 10¹¹ s⁻¹, while for CO₂-loaded MFM-305-CD₃ it is notably slower and can be resolved unambiguously (E₂ = 5.1 kJ mol⁻¹, k₂ = 0.65 × 10¹⁵ s⁻¹) with kₐ₂ ~ 10¹⁰ s⁻¹ (100 K).

Notably, the amplitude of the restricted librations also sense the presence of CO₂ with γ₂lib ~ 5° decreasing to γ₂lib ~ 2°. This decrease in libration angle coupled with the strong deceleration of both motional modes by ~10 times in the presence of CO₂ evidences the interaction of CO₂ guests with the methyl groups within the MOF pores.

**Structural dynamics of restricted CO₂ molecules in the pore**

To investigate the dynamics of host–guest interaction, we sought to study the structural flexibility of restricted CO₂ molecules (e.g., positions, orientations and occupancies) within the pores of MFM-305-CH₃ and MFM-305 via variable temperature SPXRD. Le Bail analysis reveals changes in lattice parameters of CO₂-loaded samples as a function of temperature (Fig. 7, Table S3†). As the temperature decreases from 273 K to 117 K, the lattice parameters of CO₂-loaded MFM-305-CH₃ contract along all directions (ΔV/V = 0.7%), whereas MFM-305 expands along c axis (Δa/a = 1.3%) and contracts along the a/b axes (Δa/a = 0.02%) as the temperature decreases from 270 K to 100 K (Fig. S41†). Throughout the temperature range studied, two independent binding sites for CO₂ molecules were observed in both samples. In general, the intermolecular distances of

---

**Fig. 6** View of the temperature dependence of ²H NMR spin–lattice relaxation for –CD₃ groups. (a) Experimental results for guest free MFM-305-CH₃ (black circles) and for CO₂@MFM-305-CH₃ (1 mol per cavity) (red squares). (b and c) The simulated curve for MFM-305-CH₃ and CO₂@MFM-305-CH₃ based upon two relaxation mechanisms corresponding to the two dynamic states of the –CD₃ groups. (d and e) Representation of possible –CD₃ motions in MFM-305-CH₃ cavity.
MOF–CO₂ and CO₂–CO₂ decrease continuously as the temperature decreases (Tables S3 and S4†).

The CO₂ supply was maintained at 1.0 bar on going from room temperature to 198 K. In MFM-305-CH₃, the occupancy of CO₂ (I + II) increased from 0.60 to 0.70 from 273 K to 230 K, with COI₂ hydrogen bonding with the methyl group and the –CH groups on the pyridyl ring. The hydrogen bond distances [OC₁I–H₃C] decrease steadily from 3.10(2) to 2.38(2) Å from 273 K to 117 K, indicating that the strength of these hydrogen bonds is highly sensitive to temperature (Fig. 7, Table S4†). Interestingly, as the temperature decreases, we observe significant re-arrangement of restricted CO₂ molecules at site I and II. COI₂ molecules move closer to the pore surface and rotate to drive the oxygen atoms closer to the ligands to form stronger hydrogen bonds. COI₂ and COII₂ retain their T-shape arrangement, but move closer to each other. From 273 K to 117 K, the ratio [i.e. COI₂/(COI₂ + COII₂) × 100%] of the occupancy of site I decreases from 50(2)% to 40(2)%, while the occupancy of site II increases from 50(2)% to 60(1)%.

The activation energy (Eₐ) of the site configuration and occupancy was calculated using the Arrhenius equation as a function of temperature. From 273 K to 117 K, Eₐ for site I is 0.233 kJ mol⁻¹, and for site II it is −0.128 kJ mol⁻¹. The changes of site configuration and occupancy reveal that the host–guest binding is highly sensitive to temperature via intra-pore re-arrangement.

Variable temperature PXRD data were collected for MFM-305 using the same method. COI₂ forms hydrogen bonds with hydroxyl group and the –CH groups of the pyridyl ring, and the free N-center of the pyridyl ring interacts with CO₂ via dipole interactions. The hydrogen bond distance (OC₂₁–HO) and the distance of CO₂ to the N-center (N–O CO₂₁) both reduce from 4.20(3) to 3.34(4) and from 3.16(1) to 2.96(1) Å, respectively, as the temperature is lowered from 270 K to 100 K. The intermolecular distances between COI₂ and COII₂ (OC₂₁–OC₂₂ and OC₂₁–OC₂₁) reduce from 5.03(2) to 3.07(1) Å and 5.04(3) to 2.94(1) Å, respectively, from 270 K to 100 K (Fig. 7, Table S4†). From 270 K to 198 K, the total CO₂ occupancy increases from 0.5 to 0.92, which was retained to 100 K. From 270 K to 198 K, the ratio of COI₂ decreases from 74(1)% to 53(1)%, and that of COII₂ increases from 26(1) to 47(1)%. Below 198 K, the ratio of COI₂ increase slightly to 57(1)% and that of COII₂ decreases to 43(1)%. COI₂ is in a cross-tunnel mode at 270 K. COII₂ molecules are
parallel to the pyridine ring at 270 K, and rotate to be almost parallel to $\text{CO}_2^+$ with reducing temperature. From 270 K to 198 K, the $E_a$ of $\text{CO}_2^+$ and $\text{CO}_2^0$ are 2.068 and $-2.842$ kJ mol$^{-1}$, respectively, and from 198 K to 100 K, the $E_a$ values are $-0.125$ kJ mol$^{-1}$ and 0.154 kJ mol$^{-1}$ for $\text{CO}_2^+$ and $\text{CO}_2^0$, respectively. The $E_a$ for adsorbed $\text{CO}_2$ molecules in MFM-305 is significantly higher than that of MFM-305-CH$_3$ at 270–198 K, indicating the formation of stronger host–guest interactions in MFM-305. This study confirms that the host–guest interaction between functional groups and $\text{CO}_2$ molecules in these two MOFs follows the trend of hydroxyl/pyridyl groups–$\text{CO}_2$ > $\text{CO}_2$–$\text{CO}_2$ > methyl group–$\text{CO}_2$. Thus, the simultaneous enhancements of adsorption capacity and host–guest binding affinity upon pore modification on going from MFM-305-CH$_3$ to MFM-305 can be fully rationalised.

The crystal structure of $\text{CO}_2$-loaded MFM-305-CH$_3$ was also determined at 7 K by neutron powder diffraction which confirms retention of the space group $I4_1/amd$. Interestingly, a completely new structure was resolved where only one binding domain for adsorbed $\text{CO}_2$ was located near the methyl group (Fig. S34†). The adsorbed $\text{CO}_2$ molecules are disordered about a 2-fold rotation axis and in a cross-tunnel mode interacting with the methyl group with a CH$_3$─$\text{OCO}$ distance of 3.58(2) Å. $\text{CO}_2$ also binds to the pyridinium-hydrogen atoms with a CH$^+$─$\text{OCO}$ distance at 3.08(2) Å. This result confirms the significant impact of temperature on the binding sites and orientation of adsorbed $\text{CO}_2$ molecules in MFM-305-CH$_3$.

Conclusions

We have reported here the synthesis and characterisation of porous MFM-305-CH$_3$, and its transformation via post-synthetic demethylation to give the isostructural, neutral MFM-305. The post-synthetic modification has enabled direct modulation of the pore environment, including changes in charge distribution and accessible functional groups. Significantly, MFM-305 shows simultaneously enhanced $\text{CO}_2$ and $\text{SO}_2$ uptake and $\text{CO}_2$/N$_2$ and SO$_2$/CO$_2$ selectivities over MFM-305-CH$_3$; these two factors are widely known to display a trade-off in porous materials. A comprehensive investigation of the host–guest binding using a combination of synchrotron X-ray and neutron powder diffraction, INS, $^3$H NMR and IR spectroscopy and modelling has unambiguously revealed the role of Lewis acid, Lewis base, chloride ions, methyl and hydroxyl groups in the supramolecular binding of guest molecules within the pores of both MOFs. Considering that these two MOFs have similar pore shape and size, the distinct binding mechanisms to guest molecules between these two samples is a direct result of the charge modulation. We have also confirmed that post-synthetic modification via dealkylation of the as-synthesised metal-organic framework is a powerful route to the synthesis of materials incorporating active polar groups, in this case a free pyridyl N-donor. Thus, deprotection of the as-synthesized MOF allows the synthesis of materials that cannot as yet, in our hands, be synthesised directly.

Conflicts of interest

The authors declare no competing financial interests.

Acknowledgements

We thank EPSRC (EP/I011870 to MS), ERC (AdG 742041 to MS) and University of Manchester for funding. We are especially grateful to STFC and the ISIS Neutron Facility for access to the Beamlines TOSCA and WISH, to Diamond Light Source for access to Beamlines I11 and B22 and to ORNL for access to Beamline VISION. LL thanks for the International Postdoctoral Exchange Fellowship Program from China and the Sino-British Fellowship (Royal Society) for support. The computing resources were made available through the VirtuES and ICEMAN projects, funded by Laboratory Directed Research and Development program at ORNL. DIK and AGS acknowledge financial support within the framework of the budget project #AAAA-A17-117041710084-2 of the Boreskov Institute of Catalysis.

Notes and references