

Cite this: *Chem. Sci.*, 2019, **10**, 1472 All publication charges for this article have been paid for by the Royal Society of Chemistry

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

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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-CH<sub>3</sub>,  $[\text{Al}(\text{OH})(\text{L})\text{Cl}] \cdot [(\text{H}_2\text{L})\text{Cl}]$  = 3,5-dicarboxy-1-methylpyridinium chloride] and its effect on guest binding. MFM-305-CH<sub>3</sub> 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 CO<sub>2</sub> and SO<sub>2</sub> 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 <sup>2</sup>H NMR spectroscopy and theoretical modelling to reveal the binding domains of CO<sub>2</sub> and SO<sub>2</sub> in these materials. CO<sub>2</sub> and SO<sub>2</sub> binding in MFM-305-CH<sub>3</sub> is shown to occur via hydrogen bonding to the methyl and aromatic-CH groups, with a long range interaction to chloride for CO<sub>2</sub>. In MFM-305 the hydroxyl, pyridyl and aromatic C–H groups bind CO<sub>2</sub> and SO<sub>2</sub> 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.

Received 30th April 2018  
Accepted 30th October 2018

DOI: 10.1039/c8sc01959b

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## Introduction

The release of CO<sub>2</sub> and SO<sub>2</sub> into the atmosphere from combustion of fossil fuels causes significant environmental problems and health risks.<sup>1,2</sup> The wholesale replacement of the carbon-based energy supply is highly challenging, not least because of the existing infrastructure.<sup>3</sup> It is therefore vital to mitigate the emissions of these acidic gases post combustion. At present, several technologies are used to capture CO<sub>2</sub> and SO<sub>2</sub>, such as amine scrubbing, absorption in organic solvents, ionic liquids and limestone slurry.<sup>4–7</sup> 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

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<sup>†</sup> Electronic supplementary information (ESI) available: Synthetic details, structural data, figures, PXRD patterns, TGA, IR spectroscopic and sorption analyses. This material is available in the online version of paper. Correspondence of requests for materials should be addressed to S. Y. and M. S. CCDC 1580818–1580823, 1580825–1580829, 1580831, 1580832, 1580833, 1580834. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8sc01959b

and great promise for gas adsorption and storage.<sup>8</sup> MOFs can exhibit very high surface areas and, more importantly, have tunable pore environments with predictable pore size<sup>9</sup> and can incorporate specific functional groups.<sup>10–14</sup> MOFs have been studied extensively as sorbents for CO<sub>2</sub> under post-combustion conditions.<sup>11,13–22</sup> In contrast, adsorption of SO<sub>2</sub> in MOFs has been rarely reported due to the limited stability of coordination compounds to highly reactive and corrosive SO<sub>2</sub>.<sup>21–27</sup> Development of new stable porous materials with optimal SO<sub>2</sub> and CO<sub>2</sub> 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. Interrogation of adsorption mechanisms by *in situ* experiments as a function of gas loading can afford key insights into the preferred binding sites within pores and the interaction to the pore interior.<sup>13,14,21,22</sup> Open metal sites<sup>11,28</sup> and pendent functional groups (*e.g.*, amine, hydroxyl group and nitrogen-containing aromatic rings)<sup>13,14,21,22,29</sup> have been found to act as specific sites for CO<sub>2</sub> and SO<sub>2</sub> binding.

Ionic liquids are composed of cations such as ammonium, pyridinium, phosphonium and imidazolium groups, and the solubility of CO<sub>2</sub> and SO<sub>2</sub> in these systems is often high owing to strong acid–base interaction.<sup>6,30–32</sup> The incorporation of functionalized organic ligands within MOFs,<sup>23–25</sup> and post synthetic modification can be used to control the number and types of functional groups within the pores.<sup>15–17</sup> Cleavage of C–N bonds and hydrolysis of methyl viologen in alkaline solution have been observed.<sup>18,19</sup> However, the dealkylation of pre-formed MOFs has not been reported previously, although adsorption of CO<sub>2</sub> in two imidazolium–pyridinium cation-containing MOFs has been observed.<sup>10,33</sup> We report the synthesis of a highly unusual charged material MFM-305-CH<sub>3</sub>, [Al(OH)(L)]Cl, [(H<sub>2</sub>L)Cl = 3,5-dicarboxy-1-methylpyridinium chloride] incorporating cationic (methylpyridinium) and anionic (chloride) components giving the material zwitterionic features. By heating MFM-305-CH<sub>3</sub> at 180 °C, the 1-methylpyridiniumdicarboxylate ligand undergoes *in situ* demethylation to give the pyridine-based neutral complex MFM-305 showing the same overall framework topology. Demethylation coupled to loss of chloride anion exposes the bridging hydroxyl group in the MOF pore for hydrogen bonding to substrates, with MFM-305-CH<sub>3</sub> and MFM-305 showing distinct charge distributions and pore environments decorated with different functional groups. This provides a unique platform to investigate the precise roles of Lewis acid, Lewis base, chloride, methyl, pyridine and hydroxyl groups in the binding of guest molecules. Through *in situ* synchrotron X-ray diffraction, neutron diffraction, IR, <sup>2</sup>H NMR and neutron spectroscopic experiments, the binding of CO<sub>2</sub> and SO<sub>2</sub> has been comprehensively investigated in these two porous materials. All experiments show that the binding domains for CO<sub>2</sub> and SO<sub>2</sub> molecules are directly affected by the tuning of surface charge distribution and functional groups. Significantly, simultaneously enhanced adsorption capacity and selectivity have been observed on going to MFM-305. We also report a unique study

of structural dynamics of restricted guest molecules in MOFs as a function of temperature, showing the unprecedented mobility of CO<sub>2</sub> molecule within the pores.

## Results and discussion

### Structural analysis of MFM-305-CH<sub>3</sub>

Solvothermal reaction of AlCl<sub>3</sub>·6H<sub>2</sub>O, [H<sub>2</sub>L]Cl ([H<sub>2</sub>L]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-CH<sub>3</sub>-solv, [Al(OH)(L)]Cl·solv, as a white crystalline powder in *ca.* 45% yield. The structure of MFM-305-CH<sub>3</sub>-solv has been determined by high resolution synchrotron X-ray powder diffraction (SPXRD). MFM-305-CH<sub>3</sub>-solv crystallizes in the space group *I*4<sub>1</sub>/*amd* and has an open structure comprising *cis*-connected, corner-sharing chains of [AlO<sub>4</sub>(OH)<sub>2</sub>]<sub>∞</sub> bridged by dicarboxylate ligands. The Al<sup>III</sup> 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 μ<sub>2</sub>-hydroxyl groups [Al–O = 1.776(6) Å]. Adjacent Al<sup>III</sup> centers are linked by a μ<sub>2</sub>-hydroxyl group to form an extended chain of [AlO<sub>4</sub>(OH)<sub>2</sub>]<sub>∞</sub> along the *c* axis. The ligands further bridge [AlO<sub>4</sub>(OH)<sub>2</sub>]<sub>∞</sub> 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-CH<sub>3</sub>-solv is comparable to that in MFM-300 (ref. 21) and CAU-

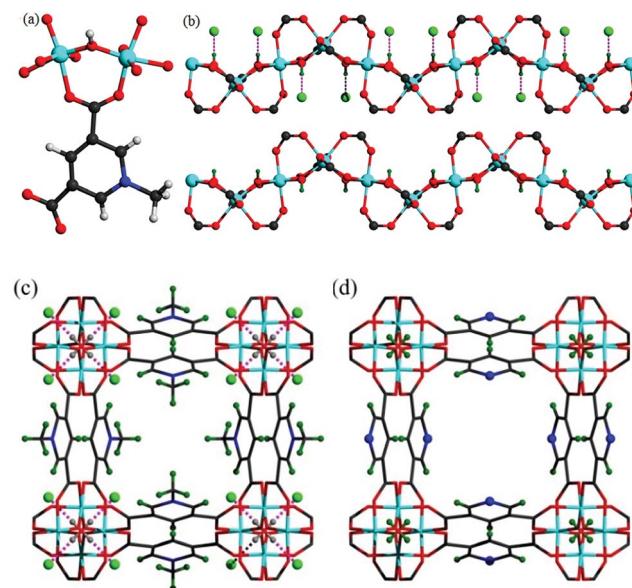


Fig. 1 (a) View of the coordination environment for ligand L<sup>–</sup> and the Al<sup>(III)</sup> centre. (b) View of the corner-sharing octahedral chain of [AlO<sub>4</sub>(OH)<sub>2</sub>]<sub>2</sub>...Cl. The μ<sub>2</sub>-(OH) groups form hydrogen bond to Cl<sup>–</sup>. Views of (c) MFM-305-CH<sub>3</sub> and of (d) MFM-305. The pore size is ~4.6 × 4.6 Å for MFM-305-CH<sub>3</sub> and ~5.6 × 5.6 Å for MFM-305 taking into consideration van der Waals radii. The methyl groups (olive) and chloride ions (green) in MFM-305-CH<sub>3</sub>; N atoms (blue) and hydroxyl group (olive) in MFM-305.



10.<sup>34</sup> The total free solvent volume in MFM-305-CH<sub>3</sub>-solv was estimated by PLATON/SOLV to be 28.5%.<sup>35</sup>

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-CH<sub>3</sub>, which retains the structure of the solvated material as determined by SPXRD. As expected, the framework of desolvated MFM-305-CH<sub>3</sub> 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 pyridinium ring [ $\text{Cl} \cdots \text{H}_2\text{O} = 2.01(1) \text{ \AA}$ ;  $\text{Cl} \cdots \text{H}_2\text{C} = 2.47(1) \text{ \AA}$ .<sup>36,37</sup> As a result, the  $\mu_2$ -OH groups in MFM-305-CH<sub>3</sub> are hindered by the Cl<sup>-</sup> 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-CH<sub>3</sub> 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-CH<sub>3</sub> 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-CH<sub>3</sub>-solv was heated at 180 °C under vacuum for 16 h to completely remove the guest solvents and CH<sub>3</sub><sup>+</sup>/Cl<sup>-</sup> (Fig. S4†). A change in color from white to pale yellow is observed on going from MFM-305-CH<sub>3</sub> to MFM-305. SPXRD analysis of MFM-305 confirms that it retains the same space group *I4<sub>1</sub>/amd*, but shows a slight contraction along the *a/b* axis ( $\Delta = 0.06\%$ ) and *c* axis ( $\Delta = 4\%$ ) 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%.<sup>35</sup> The most significant change is conversion of the methylpyridinium species in MFM-305-CH<sub>3</sub> to a free pyridyl moiety in MFM-305 and formal loss of CH<sub>3</sub>Cl. 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 -CH<sub>3</sub> group at 2988 cm<sup>-1</sup> on going from MFM-305-CH<sub>3</sub> to MFM-305 (Fig. S7†). The complete removal of Cl<sup>-</sup> in MFM-305 has been confirmed by XPS spectroscopy (Fig. S5 and S6†). Interestingly, the post-synthetic modification leads to distinct pore environments for iso-structural MFM-305-CH<sub>3</sub> 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

N<sub>2</sub> isotherms at 77 K for desolvated MFM-305-CH<sub>3</sub> and desolvated MFM-305 both show type-I profiles confirming retention of microporosity. The BET surface area and total pore volume for MFM-305-CH<sub>3</sub> are estimated to be 256 m<sup>2</sup> g<sup>-1</sup> and 0.181 cm<sup>3</sup> g<sup>-1</sup>, respectively, and 779 m<sup>2</sup> g<sup>-1</sup> and 0.372 cm<sup>3</sup> g<sup>-1</sup>,

Table 1 Unit cell parameters of MFM-305-CH<sub>3</sub> and MFM-305

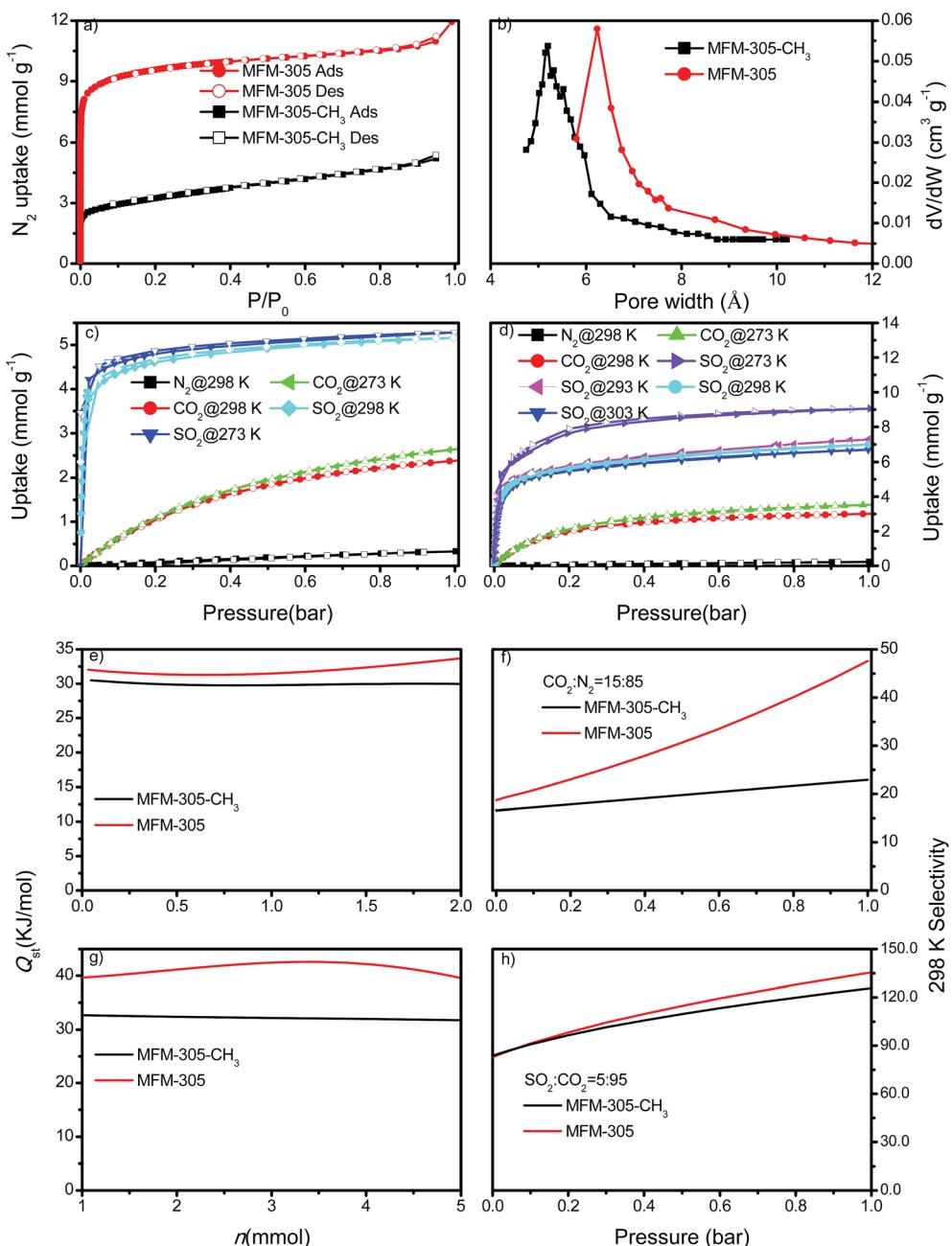
	MFM-305-CH <sub>3</sub>	MFM-305
Formula	Al(OH)(C <sub>8</sub> H <sub>6</sub> NO <sub>4</sub> )Cl	Al(OH)(C <sub>7</sub> H <sub>3</sub> NO <sub>4</sub> )
<i>M</i> <sub>r</sub>	259.6	209.1
Space group	<i>I4<sub>1</sub>/amd</i>	<i>I4<sub>1</sub>/amd</i>
<i>a</i> , <i>b</i> (Å)	21.48(6)	21.495(3)
<i>c</i> (Å)	10.90(3)	10.457(2)
Volume (Å <sup>3</sup> )	5030(30)	4831.6(1)
BET surface area/m <sup>2</sup> g <sup>-1</sup>	256	779
Pore volume	0.181	0.372
( <i>P/P</i> <sub>0</sub> = 0.95)/cm <sup>3</sup> g <sup>-1</sup>		
Pore size (HK)/Å	5.2	6.2
Pore volume (Cal.)/cm <sup>3</sup> g <sup>-1</sup>	0.209	0.347
Pore size (Cal.)/Å	4.6	5.6
CO <sub>2</sub> uptake/mmol g <sup>-1</sup> (273/298 K)	2.98/2.39	3.55/2.65
SO <sub>2</sub> uptake/mmol g <sup>-1</sup> (273/298 K)	5.29/5.16	9.05/6.99

respectively, for MFM-305 confirming a ~2.0 fold increase in porosity upon the modification (Fig. 2a, Table S1†). Horváth-Kawazoe (HK) analysis<sup>38</sup> of the N<sub>2</sub> isotherm confirms a pore size distribution centered at 5.2 and 6.2 Å for MFM-305-CH<sub>3</sub> and MFM-305, respectively (Fig. 2b). The increase in pore size is consistent with those confirmed by X-ray structural analysis.

CO<sub>2</sub> isotherms at 195 K and 1.0 bar show saturated uptake capacities of 4.23 and 5.69 mmol g<sup>-1</sup> for MFM-305-CH<sub>3</sub> and MFM-305, respectively (Fig. S24†). The increase (*ca.* 33%) is much smaller than that of N<sub>2</sub> isotherm, consistent with the reduced kinetic diameter of CO<sub>2</sub> (3.30 Å) comparing to N<sub>2</sub> (3.89 Å). At 273 K and 298 K, MFM-305-CH<sub>3</sub> shows CO<sub>2</sub> uptakes of 2.67 and 2.41 mmol g<sup>-1</sup>, 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<sup>-1</sup>, respectively. The CO<sub>2</sub> uptake at 0.15 bar, which is relevant to its partial pressure in flue gas, are 0.86 mmol g<sup>-1</sup> for MFM-305-CH<sub>3</sub> and 1.76 mmol g<sup>-1</sup> for MFM-305. This uptake is higher than that of H<sub>3</sub>[(Cu<sub>4</sub>Cl)<sub>3</sub>(BTTri)<sub>8</sub>]-en (BTTri = 1,3,5-tris(1H-1,2,3-triazol-5-yl)benzene) (0.682 mmol g<sup>-1</sup>)<sup>39</sup> and NH<sub>2</sub>-MIL-101(Cr) (0.5 mmol g<sup>-1</sup>),<sup>47</sup> but lower than that of MFM-300(Al) (2.64 mmol g<sup>-1</sup>),<sup>21</sup> MOF-74(M) (M = Mg, Ni, Co) (5.3, 2.7, 2.7 mmol g<sup>-1</sup>, respectively)<sup>48</sup> and the amine-modified MIL-101 (4.2 mmol g<sup>-1</sup>)<sup>49</sup> under the same conditions.

The excellent stability of these two MOFs motivated us to measure the adsorption isotherm of SO<sub>2</sub>. At 298 K and 1.0 bar, MFM-305-CH<sub>3</sub> and MFM-305 show SO<sub>2</sub> adsorption capacities of 5.16 and 6.99 mmol g<sup>-1</sup>, respectively (Fig. 2c and d). Importantly, the SO<sub>2</sub> uptake is fully reversible in both materials, and no loss of crystallinity or porosity was observed for the regenerated samples. At 298 K and 1.0 bar, the SO<sub>2</sub> uptake of MFM-305 is notably higher than that of most solid sorbents in the literature (Fig. S29,† Table S2†), and only lower than that of MFM-300(Al) (8.28 mmol g<sup>-1</sup>), Mg-MOF-74 (8.6 mmol g<sup>-1</sup>), Ni(bdc)(ted)<sub>0.5</sub> (9.97 mmol g<sup>-1</sup>) (H<sub>2</sub>bdc = terephthalic acid; ted = triethylenediamine), MFM-202a (10.2 mmol g<sup>-1</sup>) and SIFSIX-1-Cu (11.01 mmol g<sup>-1</sup>), which have higher surface areas of 1071, 1525, 1783, 2220 and 3140 m<sup>2</sup> g<sup>-1</sup>, respectively.<sup>21–27</sup> At 303 K, MFM-305 shows an adsorption capacity





**Fig. 2** Gas adsorption data. (a) Adsorption isotherms for  $\text{N}_2$  in MFM-305-CH<sub>3</sub> and MFM-305 at 77 K and 1.0 bar. (b) Comparison of the pore size of MFM-305-CH<sub>3</sub> and MFM-305. (c) Adsorption isotherms for  $\text{CO}_2$ ,  $\text{SO}_2$  and  $\text{N}_2$  in MFM-305-CH<sub>3</sub> at 273 and 298 K and 1.0 bar. (d) Adsorption isotherms for  $\text{CO}_2$ ,  $\text{SO}_2$  and  $\text{N}_2$  in MFM-305 at 273, 293, 298 and 303 K and 1.0 bar. Variation of isosteric heat of adsorption  $Q_{\text{st}}$  as a function of (e)  $\text{CO}_2$  and (g)  $\text{SO}_2$  uptake for MFM-305-CH<sub>3</sub> and MFM-305 calculated from adsorption isotherms measured at 273 and 298 K. Comparison of the IAST selectivity of (f)  $\text{CO}_2/\text{N}_2$  (15 : 85) and (h)  $\text{SO}_2/\text{CO}_2$  (5 : 95) in MFM-305-CH<sub>3</sub> and MFM-305 at 298 K.

for  $\text{SO}_2$  of 6.70 mmol g<sup>-1</sup> at 1.0 bar, and a high uptake of 3.94 mmol g<sup>-1</sup> at 0.025 bar, comparable to the best-behaving MOFs.<sup>50</sup> Using the total pore volume, the storage density of  $\text{SO}_2$  in a given MOF system can be estimated; those for MFM-305-CH<sub>3</sub>, SIFSIX-1-Cu-i, MFM-305 and MFM-300(In) are calculated to be 1.83, 1.70, 1.20 and 1.27 g cm<sup>-3</sup>, respectively at 298 K and 1.0 bar. Thus, MFM-305-CH<sub>3</sub> gives a notably higher storage density that is 70% of liquid density of  $\text{SO}_2$  at 263 K (2.63 g cm<sup>-3</sup>), indicating the

presence of efficient packing of adsorbed gas molecules within the pore.

Both MFM-305-CH<sub>3</sub> and MFM-305 show highly selective  $\text{SO}_2$  uptakes. At 298 K, MFM-305-CH<sub>3</sub> and MFM-305 exhibit very steep adsorption profiles for  $\text{SO}_2$  between 0 and 20 mbar, leading to an uptake of 3.59 and 3.94 mmol g<sup>-1</sup>, respectively, accounting for 70% and 56% of the total uptake at 1.0 bar. In contrast, under the same conditions, MFM-305-CH<sub>3</sub> and MFM-305 show a much lower uptake of  $\text{CO}_2$  (*i.e.*, 0.15 and 0.40 mmol g<sup>-1</sup>, respectively).

Moreover, the uptakes of  $\text{N}_2$  under the same conditions are negligible ( $<0.01 \text{ mmol g}^{-1}$ ) in these two materials. The isosteric heat of adsorption ( $Q_{\text{st}}$ ) for  $\text{CO}_2$  in MFM-305- $\text{CH}_3$  and MFM-305 both lie in the range of 29–34  $\text{kJ mol}^{-1}$ ; on average the  $Q_{\text{st}}$  of MFM-305 is *ca.* 3  $\text{kJ mol}^{-1}$  higher than MFM-305- $\text{CH}_3$  (Fig. 2e). The  $Q_{\text{st}}$  for adsorption of  $\text{SO}_2$  in MFM-305 and MFM-305- $\text{CH}_3$  is estimated to be 39–43  $\text{kJ mol}^{-1}$  and 30–32  $\text{kJ mol}^{-1}$ , respectively (Fig. 2g). MFM-305 displays a higher  $Q_{\text{st}}$  value for  $\text{SO}_2$  uptake than MFM-305- $\text{CH}_3$ , indicating the presence of enhanced host–guest binding affinity upon the pore modification. To further evaluate their potential for gas separation, the selectivities for  $\text{CO}_2/\text{N}_2(S_{\text{CN}})$ ,  $\text{SO}_2/\text{CO}_2(S_{\text{SC}})$  and  $\text{SO}_2/\text{N}_2(S_{\text{SN}})$  at 298 K have been calculated using ideal adsorbed solution theory (IAST)<sup>40</sup> over a wide range of molar compositions (*i.e.*, 1 : 99 to 50 : 50) (Fig. 2f, h, S31 and S32†). Significantly, for a 5 : 95 mixture of  $\text{SO}_2/\text{CO}_2$  and a 15 : 85 mixture of  $\text{CO}_2/\text{N}_2$ , MFM-305- $\text{CH}_3$  and MFM-305 both show exceptionally high IAST selectivities, and these are enhanced by the pore modification. The calculations for  $S_{\text{SN}}$  are subject to large uncertainties due to the extremely low uptake of  $\text{N}_2$ . The adsorptive removal of low concentration  $\text{SO}_2$  by MFM-305 has been confirmed by breakthrough experiments in which a stream of  $\text{SO}_2$  (2500 ppm diluted in  $\text{He}/\text{N}_2$ ) was passed through a packed bed of MFM-305 under ambient conditions (Fig. 3a). As expected,  $\text{He}$  and  $\text{N}_2$  were the first to elute through the bed, whereas  $\text{SO}_2$  was retained selectively under dry condition (Fig. 3a). On saturation (dimensionless time  $> 500$ ),  $\text{SO}_2$  breaks through from the bed and reaches saturation gradually. The ability of MFM-305 to capture  $\text{SO}_2$  in the presence of moisture has also been demonstrated by breakthrough experiments using a wet stream of  $\text{SO}_2$  (Fig. 3b). In the presence of water vapor, the breakthrough of  $\text{SO}_2$  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,  $Q_{\text{st}}$  between  $\text{SO}_2$ ,  $\text{CO}_2$  and  $\text{N}_2$ , the corresponding IAST selectivity and the dynamic adsorption experiments indicate the potential of MFM-305- $\text{CH}_3$  and MFM-305 have the potential to act as selective adsorbents for  $\text{CO}_2$  and  $\text{SO}_2$ .

### Determination of binding domains for adsorbed $\text{CO}_2$ and $\text{SO}_2$

We sought to determine the binding domains for  $\text{CO}_2$  and  $\text{SO}_2$  in the pores of MFM-305- $\text{CH}_3$  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 SPXRD data were collected at 198 K for  $\text{CO}_2$ -loaded samples and at 298 K for  $\text{SO}_2$ -loaded samples at 1 bar. SPXRD data enabled full structural analysis *via* Rietveld refinement (Fig. S8–S22†) to yield the positions, orientations and occupancies of adsorbed  $\text{CO}_2$  and  $\text{SO}_2$  molecules (Fig. 4 and S33†). Overall, all gas-loaded samples retain the  $I4_1/\text{amd}$  space group and two crystallographically independent binding sites (I and II) are observed in each case.

In  $\text{CO}_2$ -loaded MFM-305- $\text{CH}_3$ ,  $\text{CO}_2^{\text{I}}$  (occupancy = 0.32) interacts with the methyl group with a  $\text{H}_3\text{C}\cdots\text{OCO}$  distance of 2.54(1)  $\text{\AA}$ , indicating the formation of a weak hydrogen bond.  $\text{CO}_2^{\text{I}}$  also forms supramolecular interactions with aromatic  $-\text{CH}$  groups on neighboring pyridinium rings [ $\text{OCO}\cdots\text{HC} = 2.87(2)$   $\text{\AA}$ ]. Additionally, dipole interactions were observed between  $\text{CO}_2^{\text{I}}$  and  $\text{Cl}^-$  [ $\text{OCO}\cdots\text{Cl}^- = 3.78(1)$   $\text{\AA}$ ,  $\angle \text{O}-\text{C}\cdots\text{Cl}^- = 99.2(8)^\circ$ ]<sup>30,41</sup>.  $\text{CO}_2^{\text{II}}$  (occupancy = 0.41) binds to the aromatic  $-\text{CH}$  group [ $\text{OCO}^{\text{II}}\cdots\text{HC} = 3.50(1)$   $\text{\AA}$ ]. Further dipole interactions were observed between  $\text{CO}_2^{\text{I}}$  and  $\text{CO}_2^{\text{II}}$  [ $\text{O}^{\text{I}}\cdots\text{C}^{\text{II}} = 3.87(1)$   $\text{\AA}$ ;  $\text{O}^{\text{II}}\cdots\text{C}^{\text{I}} = 4.10(1)$   $\text{\AA}$ ] in a typical T-shape arrangement.<sup>42</sup>

In  $\text{CO}_2$ -loaded MFM-305,  $\text{CO}_2^{\text{I}}$  (occupancy = 0.48) interacts with the hydroxyl group in an end-on mode [ $\text{OH}\cdots\text{OCO} = 3.45(3)$   $\text{\AA}$ ]. This distance is longer than that obtained for  $\text{CO}_2$ -loaded MFM-300(Al) [2.298(4)  $\text{\AA}$ ] studied by PXRD at 273 K.<sup>20</sup>  $\text{CO}_2^{\text{I}}$  also interacts with the exposed pyridine nitrogen atom *via* a dipole interaction [ $\text{OCO}\cdots\text{N} = 2.89(1)$   $\text{\AA}$ ]. Additionally, a series of weak supramolecular contacts of  $\text{CO}_2^{\text{I}}$  to surrounding  $-\text{CH}$  groups [ $\text{OCO}\cdots\text{HC} = 2.44(1)$ ; 2.73(1)  $\text{\AA}$ ] are also observed. Further dipole interactions are found between  $\text{CO}_2^{\text{I}}$  and  $\text{CO}_2^{\text{II}}$  with intermolecular  $\text{C}^{\text{I}}\cdots\text{O}^{\text{II}}/\text{C}^{\text{II}}\cdots\text{O}^{\text{I}}$  distances of 3.09(1)/3.14(1)  $\text{\AA}$ , comparable to that observed in dry ice [3.178(1)  $\text{\AA}$ ].<sup>42</sup>

At 298 K  $\text{SO}_2$ -loaded MFM-305- $\text{CH}_3$  shows the  $\text{SO}_2^{\text{I}}$  molecule (occupancy = 0.30) binding to two adjacent methyl groups simultaneously [ $\text{OSO}\cdots\text{H}_3\text{C} = 2.49(3)$   $\text{\AA}$ ].  $\text{SO}_2^{\text{I}}$  also forms hydrogen bonds with surrounding  $-\text{CH}$  groups [ $\text{OSO}\cdots\text{HC} = 2.54(2)$   $\text{\AA}$ ].  $\text{SO}_2^{\text{II}}$  (occupancy = 0.47) lies perpendicular to  $\text{SO}_2^{\text{I}}$  [ $\text{S}^{\text{I}}\cdots\text{O}^{\text{II}}/\text{S}^{\text{II}}\cdots\text{O}^{\text{I}} = 3.38(2)$  and 3.97(3)  $\text{\AA}$ ] and parallel to the pyridinium ring [ $\text{OSO}\cdots\text{HC} = 3.95(1)$   $\text{\AA}$ ]. The  $\text{SO}_2$  intermolecular distances within MFM-305- $\text{CH}_3$  are comparable to that observed in the crystal structure of  $\text{SO}_2$  (3.10  $\text{\AA}$ ),<sup>43</sup> confirming the very efficient packing of adsorbed  $\text{SO}_2$  molecules leading to its high observed storage density.

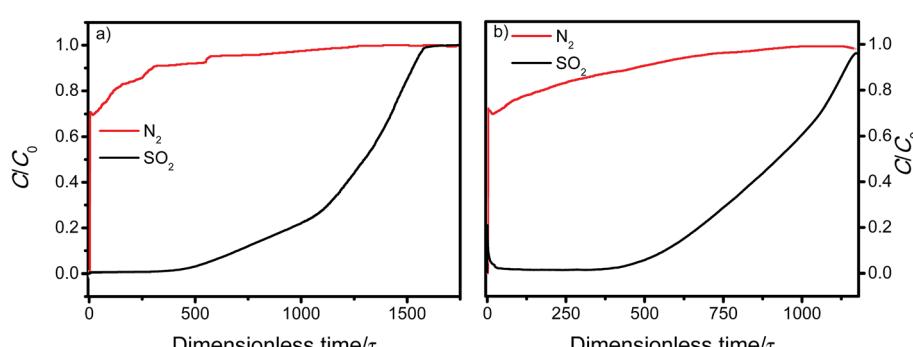
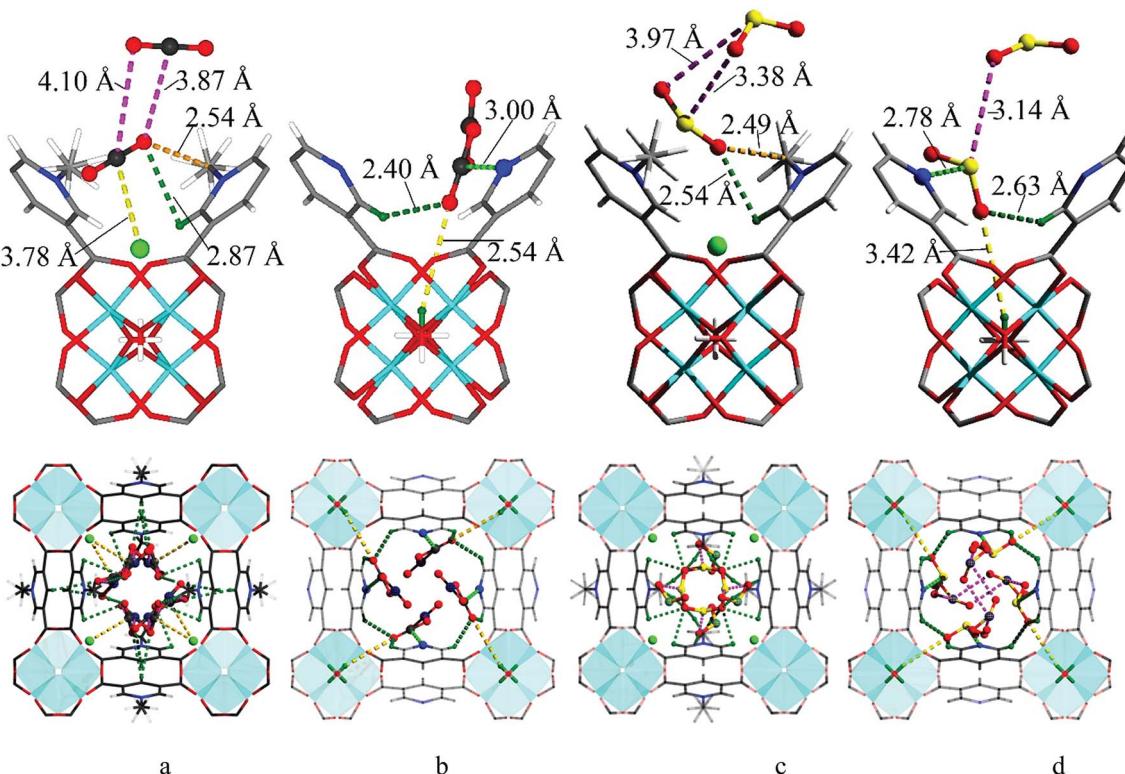


Fig. 3 Dimensionless breakthrough curve of 0.25%  $\text{SO}_2$  (2500 ppm) diluted in  $\text{He}/\text{N}_2$  under (a) dry and (b) wet conditions through a fixed-bed packed with MFM-305 at 298 K and 1 bar.





**Fig. 4** The crystal structures of  $\text{CO}_2$  and  $\text{SO}_2$ -loaded MFM-305- $\text{CH}_3$  and MFM-305 studied by powder diffraction at 298 K. (a) Interactions of  $\text{CO}_2$  molecule with the methyl, chloride ions and the  $-\text{CH}$  on pyridyl groups in MFM-305- $\text{CH}_3$ . (b) Interactions of  $\text{CO}_2$  molecule with the N- and C-H groups of pyridyl centre and the hydroxyl group in MFM-305. (c) Interactions of  $\text{SO}_2$  molecule with the methyl, chloride ions and the  $-\text{CH}$  on pyridyl groups in MFM-305- $\text{CH}_3$ . (d) Interactions of  $\text{SO}_2$  molecule with the N- and  $-\text{CH}$  centres of pyridyl and the hydroxyl group in MFM-305. Carbon, black; hydrogen, olive; oxygen, red; interactions between  $\text{CO}_2$  and frameworks C-H are shown in olive dashed line; interactions between adsorbed  $\text{CO}_2$  molecules and hydroxyl are shown in orange dashed line; interactions between adsorbed  $\text{CO}_2$  molecules and chloride ions are shown in yellow dashed line; interactions between adsorbed  $\text{CO}_2$  molecules and N atoms are shown in light green dashed line.

In MFM-305,  $\text{SO}_2^{\text{I}^{\prime}}$  (occupancy = 0.39) primarily binds to the pyridyl N-atom *via* a dipole interaction [ $\text{OSO}\cdots\text{N} = 2.78(1)$  Å] and also forms hydrogen bonds with the exposed hydroxyl group [ $-\text{OH}\cdots\text{OSO} = 3.42(4)$  Å] as well as the surrounding  $-\text{CH}$  groups [ $-\text{CH}\cdots\text{OSO} = 2.63(3)$  and  $3.14(3)$  Å]. Further dipole interactions were observed between  $\text{SO}_2$  molecules on sites I' and II' with intramolecular distance of  $4.29(2)$  Å. Overall, these observations confirm that the methyl group and  $-\text{CH}$  groups are the primary binding sites in MFM-305- $\text{CH}_3$  for both  $\text{CO}_2$  and  $\text{SO}_2$ . 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  $\text{CO}_2$  and  $\text{SO}_2$  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  $\text{CO}_2$ -loaded MFM-305- $\text{CH}_3$  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- $\text{CH}_3$  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- $\text{CH}_3$  and MFM-305. The most significant change is the absence of the  $-\text{CH}_3$  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- $\text{CH}_3$  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- $\text{CH}_3$  form hydrogen bonds to the chloride ion in the pores. Upon demethylation, the peaks at 40, 69 and 83 meV in MFM-305- $\text{CH}_3$  shifts to higher energies at 53, 83, 115 and 119 meV in MFM-305, consistent with the removal of the chloride ions.

Addition of  $\text{CO}_2$  in MFM-305- $\text{CH}_3$  is accompanied by significant change to peaks at 13 and 27 meV, indicating stiffening of the lattice modes as a result of  $\text{CO}_2$  inclusion. Large intensity changes were observed for the peaks at 20 meV, indicating the hindrance of rotation motion of  $-\text{CH}_3$  groups upon  $\text{CO}_2$  binding, consistent with the formation of hydrogen bonds



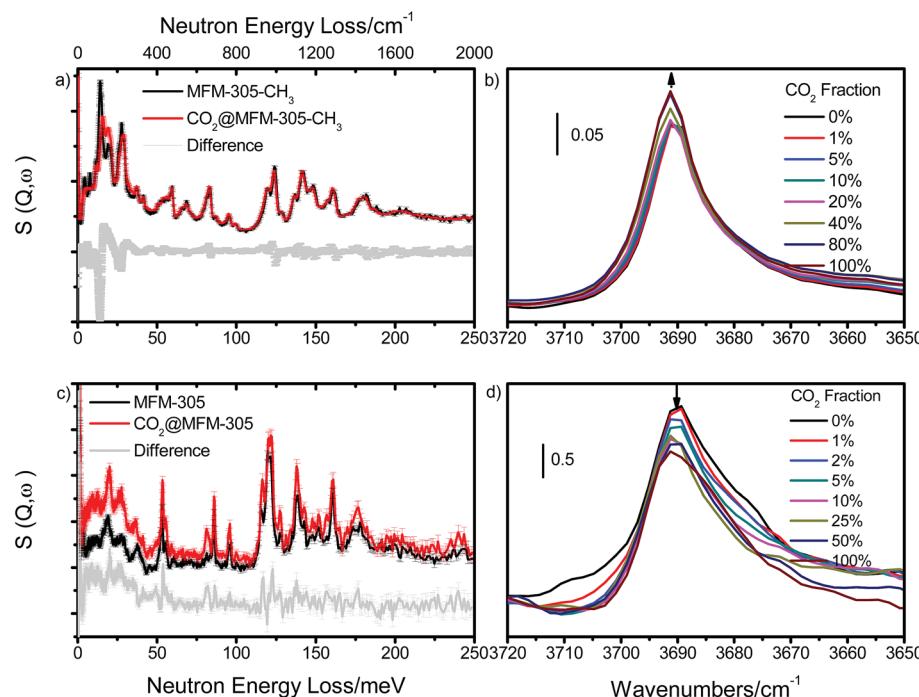


Fig. 5 Comparison of (a and c) the INS spectra and (b and d) IR spectra for bare MFM-305-CH<sub>3</sub> and MFM-305. INS and IR spectra offer vibrational information on the –CH<sub>3</sub>–CH–OH stretching and deformation region. (a) Comparison of the INS spectra for bare and CO<sub>2</sub>-loaded MFM-305-CH<sub>3</sub>. (b) IR spectra in the  $\nu(\mu_2\text{-OH})$  stretch region of CO<sub>2</sub>-loaded MFM-305-CH<sub>3</sub>. (c) Comparison of the INS spectra for bare and CO<sub>2</sub>-loaded MFM-305. (d) IR spectra of the  $\nu(\mu_2\text{-OH})$  stretch region of MFM-305 for CO<sub>2</sub>-loading. IR and INS data were collected at 298 K and 5 K, respectively.

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 CO<sub>2</sub> in MFM-305-CH<sub>3</sub>. Addition of CO<sub>2</sub> 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 CO<sub>2</sub>. The peaks between 120 and 200 meV also show notable changes in the C–H modes on CO<sub>2</sub> binding. This result confirms unambiguously that the –OH group and pyridine ring are the primary binding site for CO<sub>2</sub> in MFM-305, in excellent agreement with the crystallographic results. Thus, the INS results have confirmed the shifts of primary binding sites upon the modification of pore charge distribution.

#### Analysis of CO<sub>2</sub> binding via *in situ* synchrotron infrared micro-spectroscopy

In order to study the interaction between adsorbed CO<sub>2</sub> molecules and the MOF hosts at 298 K, an *in situ* synchrotron IR micro-spectroscopic study<sup>22</sup> was carried out as a function of CO<sub>2</sub> loading. Upon desolvation of MFM-305-CH<sub>3</sub> under a dry He flow, an absorption band at 3690 cm<sup>–1</sup> corresponding to the  $\nu(\mu_2\text{-OH})$  stretching mode is observed. Upon dosing CO<sub>2</sub> 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<sup>–</sup> and CO<sub>2</sub> molecules

(Fig. 5b). In contrast, upon dosing desolvated MFM-305 with 1.0 bar CO<sub>2</sub>, the peak at 3690 cm<sup>–1</sup> shifts very slightly but the peak intensity decreases notably (Fig. 5d) indicating the presence of an strong interaction between CO<sub>2</sub> and hydroxyl groups, entirely consistent with the crystallographic study. The combination bands of the –C=C– vibrations<sup>44</sup> within MFM-305-CH<sub>3</sub> centered at 1555 cm<sup>–1</sup> shift to 1560 cm<sup>–1</sup>, and that at 1552 cm<sup>–1</sup> in MFM-305 shifts to 1566 cm<sup>–1</sup> upon CO<sub>2</sub> loading, consistent with the formation of supplementary interactions between CO<sub>2</sub> 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 CO<sub>2</sub> molecules and these two porous MOFs.

#### Analysis of host–CO<sub>2</sub> binding via *in situ* <sup>2</sup>H NMR spectroscopy

The –CH<sub>3</sub> 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.<sup>45</sup> We were interested to probe further the dynamic changes of the methyl groups on CO<sub>2</sub> binding by synthesising MFM-305-CD<sub>3</sub> and studying it by solid state <sup>2</sup>H NMR spectroscopy over a wide temperature range (90–300 K). MFM-305-CD<sub>3</sub> was obtained using the same synthetic route described above but using the deuterated ligand, 3,5-dicarboxy-1-methyl-*d*<sub>3</sub>-pyridinium chloride. Two samples were used in this <sup>2</sup>H NMR study: guest-free MFM-305-CD<sub>3</sub> and CO<sub>2</sub>-loaded MFM-305-CD<sub>3</sub>.

Typically the  $-\text{CD}_3$  group is expected to exhibit very fast uniaxial rotation and hence its dynamics can be probed by  $^2\text{H}$  NMR spin-lattice ( $T_1$ ) relaxation, which is sensitive to rapid (rate  $> 10^6 \text{ s}^{-1}$ ) motions.<sup>45,46</sup> The  $T_1$  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  $\text{CO}_2$ -loaded MFM-305- $\text{CD}_3$ , both modes are notably slower which is reflected in the behavior of the  $T_1$  curves behavior at  $\sim 180 \text{ K}$  and  $\sim 100 \text{ K}$ . A quantitative analysis requires a model of rotation (Fig. 6d and e): considering the close contact of the  $-\text{CD}_3$  group with the neighboring linker ( $d \sim 3 \text{ \AA}$ ), it is reasonable to assume that the slower (a, c) motion ( $k_1, k_1'$ ) reflects the uniaxial rotation of the  $-\text{CD}_3$  group about its  $C_3$  symmetry axis aligned along the  $\text{N}-\text{CD}_3$  bond, while the faster (b, d) motion ( $k_2, k_2'$ ) represents small angular librations of the rotating axis restricted within borders  $\pm \gamma_{\text{lib}}$ .

Parameters derived within such a model confirm that the rotation along  $\text{N}-\text{CD}_3$  axis ( $E_1 = 4.2 \text{ kJ mol}^{-1}, k_{10} = 2.1 \times 10^{10} \text{ s}^{-1}$ ) reaches a rate of  $k_1 \sim 10^8 \text{ s}^{-1}$  at  $100 \text{ K}$  (a), while in the presence of the  $\text{CO}_2$  it is  $\sim 10$  times slower with  $k_1' \sim 10^7 \text{ s}^{-1}$  ( $E_1' = 4.2 \text{ kJ mol}^{-1}, k_{10}' = 1.8 \times 10^9 \text{ s}^{-1}$ ), and reaches  $10^8 \text{ s}^{-1}$  at  $180 \text{ K}$  (c). Hence, by interacting with  $\text{CO}_2$ , the pre-exponential factor of the  $-\text{CD}_3$  rotation is affected. This indicates that although the interaction with  $\text{CO}_2$  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<sup>45</sup> below  $90 \text{ K}$  (b, d). For MFM-305- $\text{CD}_3$  its rate at  $100 \text{ K}$  is  $k_2 \sim 10^{11} \text{ s}^{-1}$ , while for  $\text{CO}_2$ -loaded MFM-305- $\text{CD}_3$  it is notably slower and can be resolved unambiguously ( $E_2' = 5.1 \text{ kJ mol}^{-1}, k_{20}' = 0.65 \times 10^{13} \text{ s}^{-1}$ ) with  $k_2' \sim 10^{10} \text{ s}^{-1}$  ( $100 \text{ K}$ ). Notably, the amplitude of the restricted librations also sense the presence of  $\text{CO}_2$  with  $\gamma_{\text{lib}} \sim 5^\circ$  decreasing to  $\gamma_{\text{lib}}' \sim 2^\circ$ . This decrease in libration angle coupled with the strong deceleration of both motional modes by  $\sim 10$  times in the presence of  $\text{CO}_2$  evidences the interaction of  $\text{CO}_2$  guests with the methyl groups within the MOF pores.

### Structural dynamics of restricted $\text{CO}_2$ molecules in the pore

To investigate the dynamics of host–guest interaction, we sought to study the structural flexibility of restricted  $\text{CO}_2$  molecules (e.g., positions, orientations and occupancies) within the pores of MFM-305- $\text{CH}_3$  and MFM-305 *via* variable temperature SPXRD. *Le Bail* analysis reveals changes in lattice parameters of  $\text{CO}_2$ -loaded samples as a function of temperature (Fig. 7, Table S3†). As the temperature decreases from  $273 \text{ K}$  to  $117 \text{ K}$ , the lattice parameters of  $\text{CO}_2$ -loaded MFM-305- $\text{CH}_3$  contract along all directions ( $\Delta V/V = 0.7\%$ ), whereas MFM-305 expands along  $c$  axis ( $\Delta c/c = 1.3\%$ ) and contracts along the  $a/b$  axes ( $\Delta a/a = 0.02\%$ ) as the temperature decreases from  $270 \text{ K}$  to  $100 \text{ K}$  (Fig. S41†). Throughout the temperature range studied, two independent binding sites for  $\text{CO}_2$  molecules were observed in both samples. In general, the intermolecular distances of

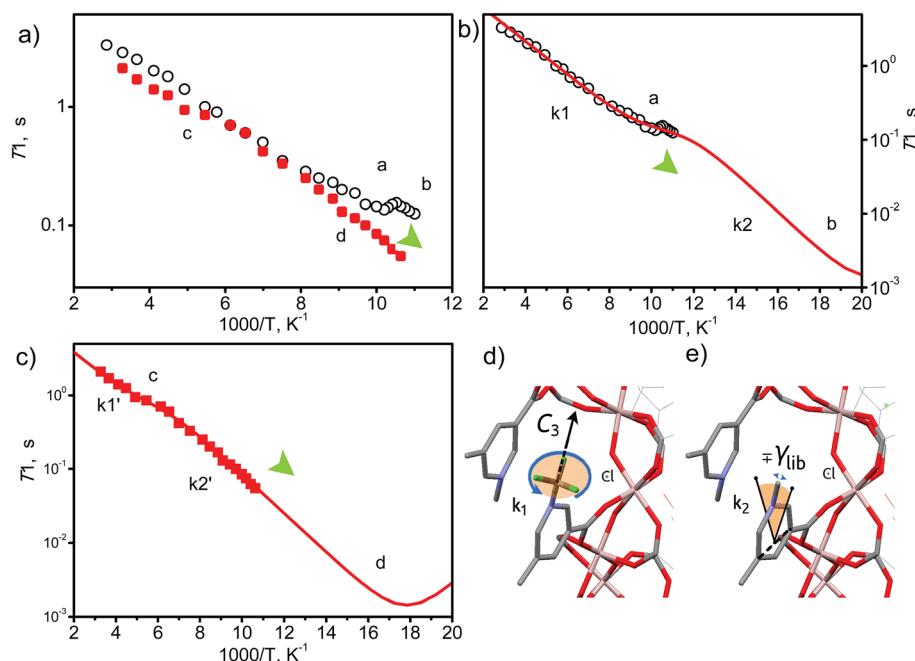


Fig. 6 View of the temperature dependence of  $^2\text{H}$  NMR spin-lattice relaxation for  $-\text{CD}_3$  groups. (a) Experimental results for guest free MFM-305- $\text{CH}_3$  (black circles) and for  $\text{CO}_2$ @MFM-305- $\text{CH}_3$  (1 mol per cavity) (red squares). (b and c) The simulated curve for MFM-305- $\text{CH}_3$  and  $\text{CO}_2$ @MFM-305- $\text{CH}_3$  based upon two relaxation mechanisms corresponding to the two dynamic states of the  $-\text{CD}_3$  groups. (d and e) Representation of possible  $-\text{CD}_3$  motions in MFM-305- $\text{CH}_3$  cavity.



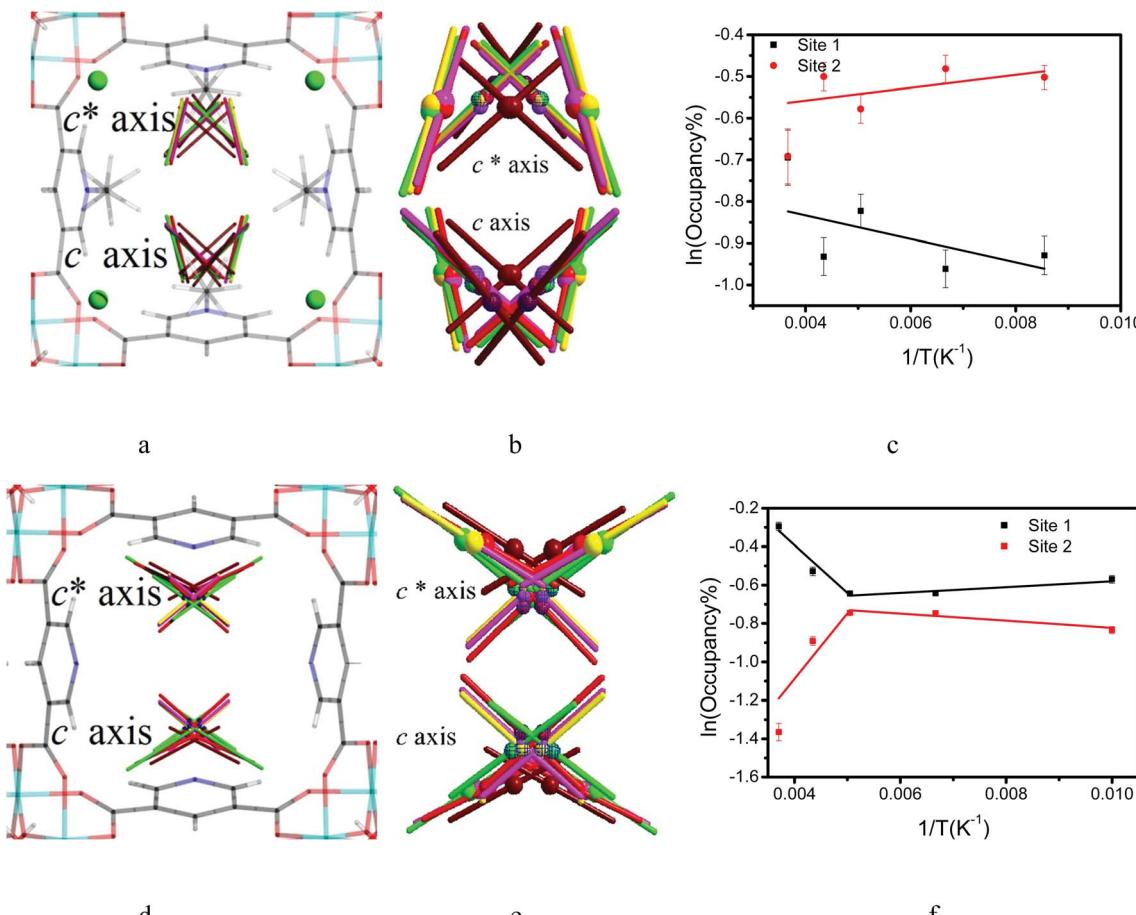


Fig. 7 Comparison of the crystal structures of  $\text{CO}_2$ -loaded MFM-305- $\text{CH}_3$  and MFM-305 studied by synchrotron X-ray powder diffraction at variable temperatures. Dynamic structures of  $\text{CO}_2$  under different temperature (270 K, dark red; 230 K, red; 198 K, pink; 150 K, yellow; 117/100 K, bright green) in (a) MFM-305- $\text{CH}_3$  and (d) MFM-305. (b and e) Enlarged views of the multiple  $\text{CO}_2$  regions in (a) and (d) at site I (solid symbol) and site II (patterned symbol). Occupancies of  $\text{CO}_2$  at site I and II in (c) MFM-305- $\text{CH}_3$  and (f) MFM-305.

MOF- $\text{CO}_2$  and  $\text{CO}_2$ - $\text{CO}_2$  decrease continuously as the temperature decreases (Tables S3 and S4†).

The  $\text{CO}_2$  supply was maintained at 1.0 bar on going from room temperature to 198 K. In MFM-305- $\text{CH}_3$  the occupancy of  $\text{CO}_2$  (I + II) increased from 0.60 to 0.70 from 273 K to 230 K, with  $\text{CO}_2^{\text{I}}$  hydrogen bonding with the methyl group and the  $-\text{CH}$  groups on the pyridyl ring. The hydrogen bond distances [ $\text{OCO}^{\text{I}}-\text{H}_3\text{C}$ ] 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 rearrangement of restricted  $\text{CO}_2$  molecules at site I and II.  $\text{CO}_2^{\text{I}}$  molecules move closer to the pore surface and rotate to drive the oxygen atoms closer to the ligands to form stronger hydrogen bonds.  $\text{CO}_2^{\text{I}}$  and  $\text{CO}_2^{\text{II}}$  retain their T-shape arrangement, but move closer to each other. From 273 K to 117 K, the ratio [*i.e.*  $\text{CO}_2^{\text{I}}/(\text{CO}_2^{\text{I}} + \text{CO}_2^{\text{II}}) \times 100\%$ ] 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 ( $E_a$ ) of the site configuration and occupancy was calculated using the Arrhenius equation as a function of temperature. From 273 K to

117 K,  $E_a$  for site I is 0.233 kJ mol<sup>-1</sup>, and for site II it is -0.128 kJ mol<sup>-1</sup>. 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.  $\text{CO}_2^{\text{I}}$  forms hydrogen bonds with hydroxyl group and the  $-\text{CH}$  groups of the pyridyl ring, and the free N-center of the pyridyl ring interacts with  $\text{CO}_2$  *via* dipole interactions. The hydrogen bond distance ( $\text{OCO}^{\text{I}}-\text{HO}$ ) and the distance of  $\text{CO}_2$  to the N-center ( $\text{N}-\text{OCO}^{\text{I}}$ ) 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  $\text{CO}_2^{\text{I}}$  and  $\text{CO}_2^{\text{II}}$  ( $\text{OCO}^{\text{I}}-\text{OCO}^{\text{II}}$  and  $\text{OCO}^{\text{I}}-\text{OCO}^{\text{II}''}$ ) reduce from 5.03(2) to 3.07(1) Å and 5.04(3) to 2.94(1) Å, respectively, from 270 to 100 K (Fig. 7, Table S4†). From 270 K to 198 K, the total  $\text{CO}_2$  occupancy increases from 0.5 to 0.92, which was retained to 100 K. From 270 K to 198 K, the ratio of  $\text{CO}_2^{\text{I}}$  decreases from 74(1)% to 53(1)%, and that of  $\text{CO}_2^{\text{II}}$  increases from 26(1) to 47(1)%. Below 198 K, the ratio of  $\text{CO}_2^{\text{I}}$  increase slightly to 57(1)% and that of  $\text{CO}_2^{\text{II}}$  decreases to 43(1)%.  $\text{CO}_2^{\text{I}}$  is in a cross-tunnel mode at 270 K.  $\text{CO}_2^{\text{II}}$  molecules are

parallel to the pyridine ring at 270 K, and rotate to be almost parallel to  $\text{CO}_2^{\text{I}^{\prime}}$  with reducing temperature. From 270 K to 198 K, the  $E_a$  of  $\text{CO}_2^{\text{I}^{\prime}}$  and  $\text{CO}_2^{\text{II}^{\prime}}$  are 2.068 and  $-2.842 \text{ kJ mol}^{-1}$ , respectively, and from 198 K to 100 K, the  $E_a$  values are  $-0.125 \text{ kJ mol}^{-1}$  and  $0.154 \text{ kJ mol}^{-1}$  for  $\text{CO}_2^{\text{I}^{\prime}}$  and  $\text{CO}_2^{\text{II}^{\prime}}$ , respectively. The  $E_a$  for adsorbed  $\text{CO}_2$  molecules in MFM-305 is significantly higher than that of MFM-305- $\text{CH}_3$  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- $\text{CH}_3$  to MFM-305 can be fully rationalised.

The crystal structure of  $\text{CO}_2$ -loaded MFM-305- $\text{CH}_3$  was also determined at 7 K by neutron powder diffraction which confirms retention of the space group  $I4_1/\text{amd}$ . 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  $\text{CH}_3\cdots\text{QCO}$  distance of  $3.58(2) \text{ \AA}$ .  $\text{CO}_2$  also binds to the pyridinium–hydrogen atoms with a  $\text{CH}\cdots\text{QCO}$  distance at  $3.08(2) \text{ \AA}$ . This result confirms the significant impact of temperature on the binding sites and orientation of adsorbed  $\text{CO}_2$  molecules in MFM-305- $\text{CH}_3$ .

## Conclusions

We have reported here the synthesis and characterisation of porous MFM-305- $\text{CH}_3$ , 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  $\text{CO}_2/\text{N}_2$  and  $\text{SO}_2/\text{CO}_2$  selectivities over MFM-305- $\text{CH}_3$ ; these two factors are widely known to display a trade-off in porous materials. A comprehensive investigation of the host–guest binding using a combinations of synchrotron X-ray and neutron powder diffraction, INS,  $^2\text{H}$  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 synthesized 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 #AAAAA-A17-117041710084-2 of the Boreskov Institute of Catalysis.

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