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# Adsorption and molecular siting of CO<sub>2</sub>, water, and other gases in the superhydrophobic, flexible pores of FMOF-1 from experiment and simulation†

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FMOF-1 is a flexible, superhydrophobic metal–organic framework with a network of channels and side pockets decorated with –CF<sub>3</sub> groups. CO<sub>2</sub> adsorption isotherms measured between 278 and 313 K and up to 55 bar reveal a maximum uptake of ca. 6.16 mol kg<sup>−1</sup> (11.0 mol L<sup>−1</sup>) and unusual isotherm shapes at the higher temperatures, suggesting framework expansion. We used neutron diffraction and molecular simulations to investigate the framework expansion behaviour and the accessibility of the small pockets to N<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub>. Neutron diffraction *in situ* experiments on the crystalline powder show that CO<sub>2</sub> molecules are favourably adsorbed at three distinct adsorption sites in the large channels of FMOF-1 and cannot access the small pockets in FMOF-1 at 290 K and oversaturated pressure at 61 bar. Stepped adsorption isotherms for N<sub>2</sub> and O<sub>2</sub> at 77 K can be explained by combining Monte Carlo simulations in several different crystal structures of FMOF-1 obtained from neutron and X-ray diffraction under different conditions. A similar analysis is successful for CO<sub>2</sub> adsorption at 278 and 283 K up to ca. 30 bar; however, at 298 K and pressures above 30 bar, the results suggest even more substantial expansion of the FMOF-1 framework. The measured contact angle for water on an FMOF-1 pellet is 158°, demonstrating superhydrophobicity. Simulations and adsorption measurements also show that FMOF-1 is hydrophobic and water is not adsorbed in FMOF-1 at room temperature. Simulated mixture isotherms of CO<sub>2</sub> in the presence of 80% relative humidity predict that water does not influence the CO<sub>2</sub> adsorption in FMOF-1, suggesting that hydrophobic MOFs could hold promise for CO<sub>2</sub> capture from humid gas streams.

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## Introduction

Capturing carbon from flue gas is an important challenge, as fossil fuel combustion continues to be a primary source of energy.<sup>1,2</sup> The search for adsorbents capable of capturing large amounts of CO<sub>2</sub> has led to many studies of adsorption in

nanoporous materials known as metal–organic frameworks (MOFs).<sup>3–5</sup> MOFs have been shown to be promising for a number of separation applications including CO<sub>2</sub> capture at the low partial pressures relevant to flue gas.<sup>6–11</sup> In an early example, Yazaydin *et al.* screened 14 MOFs and concluded that the M/DOBDC series shows exceptionally high CO<sub>2</sub> capacity at room temperature.<sup>12</sup> This can be attributed to the high density of open metal sites, and other studies on CO<sub>2</sub> capture in MOFs have shown similar results.<sup>13</sup> After the CO<sub>2</sub> is captured, it must be stored or used afterward. One option is permanent subterranean storage as a pressurized liquid. Alternatively, it could be converted and used as other chemical products. Darensbourg *et al.* recently reported CO<sub>2</sub> capture in a MOF, HKUST-1, to perform a copolymerization with propylene oxide with a 49.9% conversion rate.<sup>2</sup>

When assessing adsorbents for use with flue gas, the presence of water vapor cannot be ignored.<sup>9</sup> For example, it has been shown that M/DOBDC MOFs show a significant decrease in CO<sub>2</sub> capture capacity under humid conditions.<sup>14,15</sup> Hydrophobic MOFs could be an attractive alternative, due to their ability to

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withstand humid conditions and suppress competitive adsorption of water. A number of studies in the literature have investigated the effects of fluorination and hydrophobicity in MOFs.<sup>16–22</sup> FMOF-1 is a fluorinated metal–organic framework first synthesized by Yang *et al.*<sup>20</sup> It is formed by the reaction of a perfluorinated ligand (3,5-bis(trifluoromethyl)-1,2,4-triazolate ( $Tz^-$ )) with a  $Ag^+$  precursor, leading to  $\{Ag_2[Ag_4Tz_6]\}$ . FMOF-1 exhibits a perfluorinated structure, and the many  $CF_3$  groups lining its channels and small pockets imbue it with hydrophobicity.<sup>20</sup> In principle, the  $CO_2$  quadrupole should be able to interact with the polar C–F groups in FMOF-1, but  $CO_2$  adsorption measurements have not been reported for FMOF-1. In addition, while FMOF-1 has been shown to experience enormous breathing behaviour as a function of temperature either under vacuum or in the presence of  $N_2$ ,<sup>23</sup> the evolution of the FMOF-1 structure has not been studied previously in the presence of other guest molecules or at elevated pressures. Given that changes in framework structure can have a significant effect on the adsorption properties of a porous material, we investigate in this work whether framework flexibility is a general feature of FMOF-1 and the effect of flexibility on adsorption uptake by investigating a wide variety of guest molecules, with a particular focus on  $CO_2$ .

In this paper, experimental  $CO_2$  adsorption isotherms, contact angle measurement of water drops, and *in situ* neutron diffraction results during  $CO_2$  adsorption are reported. Also reported are grand canonical Monte Carlo and quantum mechanical simulations in FMOF-1 to model the adsorption of  $CO_2$  and other guest molecules, including adsorption of  $CO_2$  under humid conditions. The work illustrates the power of a strong feedback loop between experiment and modeling. For example, neutron diffraction studies provided possible crystal structures for simulations of  $CO_2$  adsorption, and measured isotherms and heats of adsorption provided validation of predictions from modeling. In turn, modeling provided insight about molecular siting in FMOF-1 and predictions about the  $CO_2$  capture performance under humid conditions. The flexible nature of FMOF-1 was investigated *via* simulation using four different FMOF-1 structures obtained under different experimental conditions. Correlations between the framework structure and guest uptake were established for three classes of guest molecules, including diatomics at one extreme and bulky hydrocarbons at the other, with  $CO_2$  representing an intermediate category.

## Methods

### FMOF-1 synthesis and adsorption measurements

FMOF-1 was prepared using previously published methods.<sup>20,23</sup> Nitrogen adsorption isotherms at 77 K were measured with a Micromeritics ASAP 2020.  $CO_2$  adsorption measurements were carried out by a VTI/TA Gravimetric High Pressure Sorption Analyzer. This VTI/TA system is equipped with ultra-high vacuum and is capable of variable temperature measurements from  $-196$  °C to  $1000$  °C. It has a flow dosing manifold for high pressure studies and achieves  $0.1$   $\mu g$  resolution with a CI Electronics microbalance. Typically, 100 mg of sample was used for

adsorption measurements. Before each measurement, the sample was purged with helium then evacuated for 60 minutes at  $60$  °C. Measurements were performed at 5 degree intervals from  $5$  ° to  $40$  °C and pressures up to 53 bar or the critical pressure of  $CO_2$  at the set temperature. Isothermic heats of adsorption were derived using a set of isotherms at different temperatures and the Clausius–Clapeyron equation.<sup>24</sup> High purity  $CO_2$  gas was used for the adsorption studies.

### Contact angle measurements

Contact angle measurements were done using a Ramehart manual goniometer (Model # 50-00-1150). Static contact angle was measured. A single drop of water was added using the syringe attached to the goniometer and then the contact angle was measured on the static sessile drop with the gauge provided.

### Neutron powder diffraction measurements

*In situ* neutron powder diffraction measurements were performed at the SNAP beamline of the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL). SNAP is a high flux and medium resolution time-of-flight diffractometer, with tunable detector placement and incident energy range. For this experiment, measurements were made with the two detector banks placed at  $90$  and  $48$  degrees, and the wavelength band used was  $3.5$  Å wide and centered at  $6.4$  Å. This configuration enabled sampling of Bragg reflections in the range  $3$ – $17$  Å, enough to sample the longest (in *d*-spacing) reflections of the sample. Fully activated FMOF-1 powder sample was loaded into a gas cell fabricated with a null scattering TiZr alloy (1 : 2.08 Zr : Ti molar ratio) and warmed to 320 K in a dynamic vacuum. The gas cell was then cooled *via* 200 mbar of He exchange gas on a top loading cold cycle refrigerator cryostat to 290 K for data collection on the bare FMOF-1.  $CO_2$  was then loaded slowly into the FMOF-1 sample at 290 K using a computer-controlled automated gas handling system and held for an hour at 61 bar to ensure the sample cell maintained over the  $CO_2$  saturation pressure (53.2 bar) before and during data collection. High purity  $CO_2$  gas stored at room temperature (296 K) was used directly from the cylinder with no further purification.

Neutron diffraction data were analyzed using the GSAS II package.<sup>25</sup> The locations of  $CO_2$  molecules in FMOF-1 after  $CO_2$  loading were obtained from difference Fourier map and refined accordingly with distance constraints.

### Simulation details

Grand canonical Monte Carlo (GCMC) simulations were employed to investigate the adsorption of  $N_2$ ,  $O_2$ ,  $CO_2$ ,  $H_2O$ , *n*-hexane, and benzene. For each pressure point of the isotherm,  $1 \times 10^5$  GCMC cycles were used for equilibration, after which another  $1 \times 10^5$  cycles were used to calculate the average properties. For water simulations, we used  $5 \times 10^5$  cycles each for equilibration and production runs. Each GCMC cycle is made up of *N* steps, where *N* is the number of adsorbates in the simulation box. (The number of steps per cycle is not allowed to be lower than 20; so if there are fewer than 20 adsorbates in the



simulation box, a cycle consists of 20 steps.) The TraPPE force field was used to model all adsorbates ( $\text{N}_2$ ,<sup>26</sup>  $\text{O}_2$ ,<sup>27</sup>  $\text{CO}_2$ ,<sup>26</sup> *n*-hexane,<sup>28</sup> and benzene<sup>29</sup>) except for water, which was described with the TIP4P model.<sup>30</sup> Lennard-Jones parameters for the framework atoms were taken from the Universal Force Field.<sup>31</sup> Cross Lennard-Jones parameters were determined by Lorentz–Berthelot mixing rules. The partial charges for  $\text{CF}_3$  groups were adopted from the work of Dalvi *et al.*,<sup>32</sup> while partial charges for the rest of the framework were obtained from density functional theory calculations at the B3LYP level of theory using the ChelpG method.<sup>33</sup> Lennard-Jones parameters and partial atomic charges for the adsorbates and FMOF-1 are all listed in the ESI (Tables S3 and S4†). A cutoff distance of 12.8 Å was used for all Lennard-Jones interactions, and tail corrections were neglected. Long-range electrostatic interactions were accounted for using the Ewald summation method. The simulation box was constructed of 4 ( $2 \times 2 \times 1$ ) unit cells with periodic boundary conditions applied in all directions.

Framework atoms were held fixed during the GCMC simulations. To explore the effect of framework flexibility on the adsorption properties, we performed simulations on three different FMOF-1 crystal structures along with the related FMOF-2 polymorph (see Fig. S12 in the ESI†) for  $\text{CO}_2$  adsorption at room temperature. The first published crystal structure of FMOF-1 was obtained under vacuum at 100 K,<sup>23</sup> and this structure shall be referred to as FMOF-1a in this work. A structure obtained under a nitrogen stream at 90 K (ref. 23) shall be referred to here as FMOF-1b. The third FMOF-1 structure is a heretofore-unpublished structure obtained under a carbon dioxide stream at 61 bar and 290 K and will be referred to as FMOF-1c.

### Quantum chemical methods

Density functional theory (DFT) was used to determine the binding free energy of molecules at their most likely adsorption sites. The binding sites in the cylindrical channel and small cavity were simulated individually. The cylindrical channel was truncated from the FMOF-1a structure and was composed of 11 Tz ligands and 9 Ag atoms. The small pocket was truncated from the FMOF-1b structure containing 14 Tz ligands and 10 Ag atoms. Both sites fully accounted for the correct coordination geometry of all metal centers using the neutral singlet state. Equilibrium geometries for guest molecules were found, holding the framework static. The NWChem software package was used for all quantum chemical calculations.<sup>34</sup> We chose to use the BPE0 functional with 6-311G\* Pople basis sets for non-metal atoms and the Stuttgart-97 Effective Core Potential and respective basis sets for silver.<sup>35–38</sup> The empirical dispersion correction DFT-D3 was added to address the long-range effects.<sup>39</sup> The inclusion of dispersion corrections with DFT has been shown to be necessary for the prediction of MOF structures, creating force field parameters, predicting changes in structure, and determining water adsorption sites.<sup>40–44</sup> Orbital comparisons were made using the Mulliken population analysis. The total population density of the empty *versus* the occupied site used the same basis set and framework coordinates.

## Results and discussion

### $\text{CO}_2$ adsorption and contact angle studies

Fig. 1 shows the  $\text{CO}_2$  adsorption isotherms for FMOF-1 at near-ambient temperatures up to 55 bar. The maximum uptake experimentally measured is *ca.* 6.16 mol  $\text{kg}^{-1}$  (11.0 mol  $\text{L}^{-1}$ ; 27.1 wt%; 483  $\text{kg m}^{-3}$ ; 248 V STP  $\text{V}^{-1}$ ) at 298 K and 55 bar. This uptake is more than 2 times higher than that predicted<sup>45</sup> in 2008 based on the rigid structure of FMOF-1 reported in 2007,<sup>20</sup> necessitating further modeling that takes into account the framework flexibility (*vide infra*). The isotherms do not reach a plateau and are inconsistent with a type I adsorption behaviour over this temperature and pressure range, again suggesting flexibility of the framework. This behaviour was determined not to be due to a systematic error in the experimental data, as it has been reproduced multiple times; see Fig. S2 (ESI†). Up to 30 bar, the isotherms can be fit very well with a Toth isotherm (Fig. S1†), and above this pressure the isotherms continue to rise, with a visible inflection at some temperatures.

Upon removing the sample from the instrument after the  $\text{CO}_2$  adsorption studies, we noticed that the powder sample had transformed into a flat, yellow-coloured pellet. TGA and IR studies for pieces of such a pellet revealed essentially identical profiles to the powder sample of FMOF-1. We performed a contact angle experiment for a water droplet upon this pellet. This process proved difficult, as the water droplets tended to bounce and deflect off of the surface of the pellet rather quickly and as complete spheres, suggesting a rather extreme superhydrophobic behaviour of the material. Processing of the resulting image yielded a contact angle of  $\sim 158$ , as shown in Fig. 2, clearly indicating a superhydrophobic behaviour and consistent with the insignificant water adsorption reported earlier for FMOF-1.<sup>46–48</sup> The work herein, therefore, ascertains that FMOF-1 belongs to the “superhydrophobic” category of MOFs, similar to very few other frameworks verified as such from contact angle measurements.<sup>22,49,50</sup>

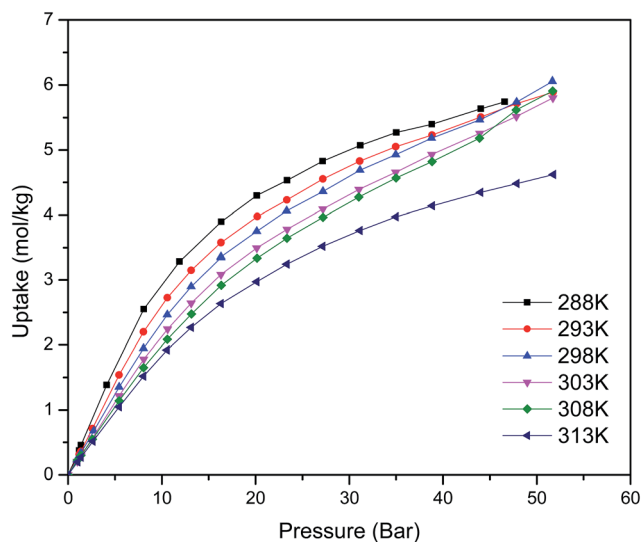


Fig. 1  $\text{CO}_2$  excess adsorption isotherms of FMOF-1 at various near-ambient temperatures.



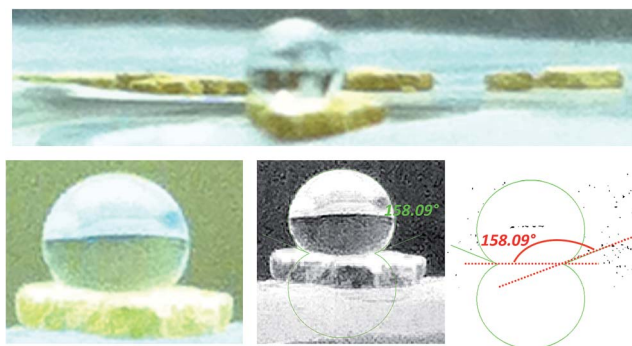


Fig. 2 Images of a water drop on a pellet of FMOF-1 that formed after the high-pressure CO<sub>2</sub> adsorption isotherm experiment shown in Fig. 1; most water droplets in the attempted contact angle experiments deflected off the surface of the pellet quickly as complete spheres. The bottom-right and bottom-middle images show the processing of the bottom-left raw image using the LBADSA plugin for the ImageJ software.<sup>51</sup>

### Neutron diffraction studies

Neutron powder diffraction measurements were performed at the ORNL Spallation Neutrons and Pressure Diffractometer (SNAP) (Table S1<sup>†</sup>). Fig. 3a compares the neutron powder diffraction patterns for the evacuated FMOF-1 and the structure under 61 bar of CO<sub>2</sub> at 290 K. Under this oversaturated pressure condition, the free CO<sub>2</sub> molecules stay in the liquid state. The increase in intensity for the 011 peak at  $\sim 13 \text{ \AA}$  after *in situ* CO<sub>2</sub> loading is clearly discernible. The FMOF-1 sample with adsorbed CO<sub>2</sub> was cooled to 230 K and the pressure was reduced to 4.8 bar for low-temperature measurements. The pressure in the TiZr cell was controlled *via* a computer-controlled gas handling system. Fig. S4 (ESI<sup>†</sup>) shows the evolution of the neutron powder diffraction patterns of the FMOF-1 sample with adsorbed CO<sub>2</sub>. No evidence of solid CO<sub>2</sub> was observed in the structural refinement of the CO<sub>2</sub> loaded samples, indicating that all CO<sub>2</sub> was adsorbed into FMOF-1.

Fig. 3b shows the temperature dependence of the unit cell volume of FMOF-1 at a static pressure of 4.8 bar of CO<sub>2</sub> loading

and compares it with the results obtained under N<sub>2</sub> stream<sup>23</sup> and vacuum.<sup>23</sup> The smooth change in the unit cell volume in CO<sub>2</sub> (open squares) is in contrast to that of FMOF-1 with adsorbed N<sub>2</sub> (red circles in Fig. 3b), in which the loading of N<sub>2</sub> molecules into small cavities of FMOF-1 at temperatures below 119 K causes a huge negative thermal expansion in the crystal structure.<sup>23</sup>

FMOF-1 has two types of pores. The first type are large cylindrical channels extending along both the *x*- and *y*-directions (Fig. 4a and b), with CF<sub>3</sub> groups protruding into the channels. The second pore type is a small cavity, and two pairs of CF<sub>3</sub> groups function as a gate between the small cavity and the large cylindrical channel (see the red circle in Fig. 4c). The pore size distribution and full geometric characterization of FMOF-1 can be found in Fig. S5 and Table S2.<sup>†</sup>

The favourable adsorption sites for CO<sub>2</sub> molecules in FMOF-1 were obtained from difference Fourier map and with the CO<sub>2</sub> molecules refined with distance constraints. Difference Fourier map from initial Rietveld refinements indicate that the CO<sub>2</sub> molecules are located only in the large channels of FMOF-1 at three unique sites. The FMOF-1 structure loaded with CO<sub>2</sub> molecules at 61 bar and 290 K is shown in Fig. 5. The oxygen atoms in the three primary CO<sub>2</sub> adsorption sites are shown as cyan spheres at site I near the framework -CF<sub>3</sub> groups at corners; as red spheres at site II near -CF<sub>3</sub> groups along the crystallographic *c* direction; and as orange spheres at site III in the direction of the large channels. Since there is no CO<sub>2</sub> in the small cavities, when all three CO<sub>2</sub> adsorption sites are fully occupied, there are 24 CO<sub>2</sub> molecules in the unit cell (3.3 mol kg<sup>-1</sup>). This limits the CO<sub>2</sub> uptake capacity in the large cavity to 6 CO<sub>2</sub> molecules per {Ag<sub>2</sub>[Ag<sub>4</sub>Tz<sub>6</sub>] repeat unit.

### Molecular simulation studies and connection to experimental data

In order to verify our simulation parameters, we began by reproducing previously published experimental isotherms for benzene, *n*-hexane, and water in FMOF-1. Fig. 6 compares simulated results in FMOF-1a to the experimental isotherms.

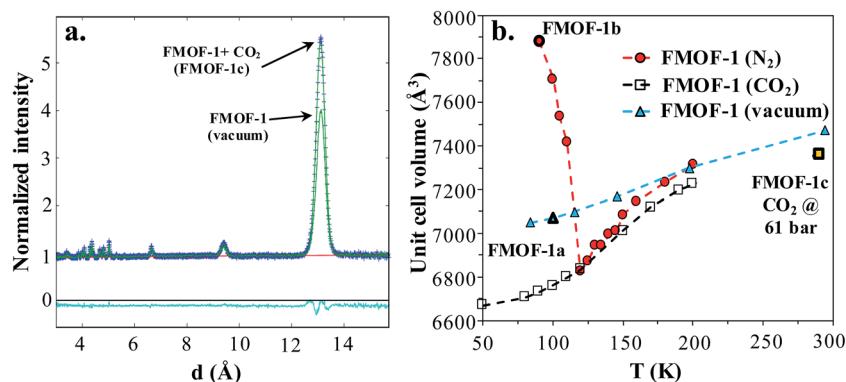


Fig. 3 (a) FMOF-1 neutron powder diffraction patterns measured at 290 K in vacuum (solid green line) and under 61 bar of CO<sub>2</sub> (blue crosses). The residuals (cyan) underneath the zero line are the difference of the observed and refined neutron diffraction profiles of the FMOF-1 sample with adsorbed CO<sub>2</sub>.  $wR = 1.606\%$ ,  $GOF = 1.87$ ,  $N_{\text{obs}} = 1658$ ,  $N_{\text{vals}} = 14$ . Space group  $I42d$ ,  $a = 13.9713(7) \text{ \AA}$ ,  $c = 37.713(4) \text{ \AA}$ ,  $V = 7361.4(7) \text{ \AA}^3$ . (b) Temperature dependence of unit cell volume of FMOF-1 under vacuum,<sup>23</sup> constant stream of N<sub>2</sub> at atmospheric pressure<sup>23</sup> and CO<sub>2</sub> at 4.8 bar. The unit cell volume of FMOF-1 under 61 bar and 290 K (FMOF-1c) is also shown for comparison.



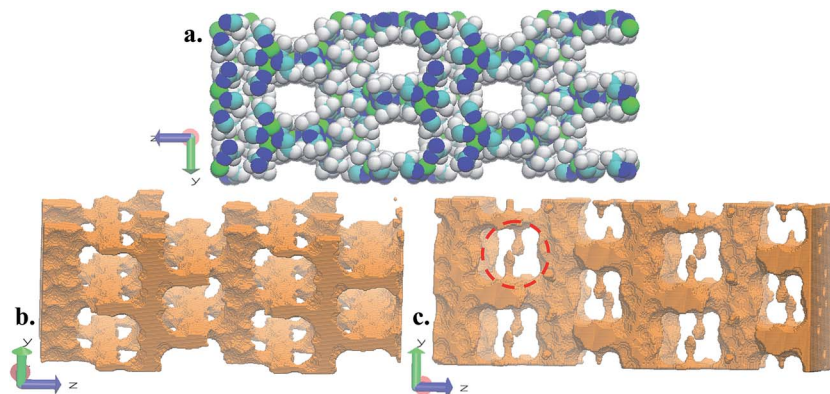


Fig. 4 Schematic views of FMOF-1 channels. (a) Front view of FMOF-1 framework. C, cyan; F, white; N, blue and Ag, green. (b) Illustration of cylindrical channel voids using a 4 Å probe. The cylindrical channels extend along the *x*- and *y*-directions. (c) Representation of channel voids and small pockets protruding alongside the channels highlighted in red circles using a 1 Å probe. Views in (b) and (c) are calculated using the method described by Sarkisov and Harrison.<sup>52</sup>

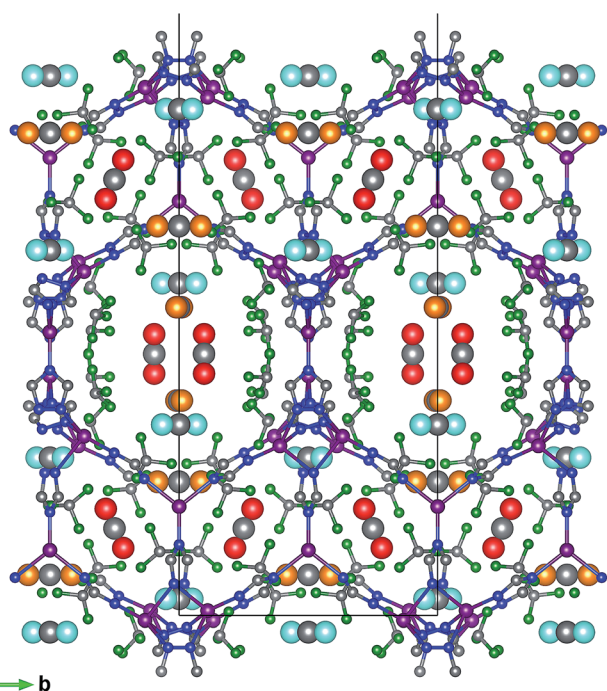


Fig. 5 Crystal structure of adsorbed CO<sub>2</sub> from neutron powder diffraction at 290 K and 61 bar, viewed along the crystallographic *a*-axis. The three CO<sub>2</sub> adsorption sites in FMOF-1 are shown as site I near CF<sub>3</sub> groups at corners with O atoms depicted as cyan spheres; site II near CF<sub>3</sub> groups along *c* direction with O atoms depicted as red spheres; and site III in the direction of the large channels with O atoms depicted as orange spheres.

We see a very good agreement between simulation and experiment for benzene and hexane through the entire pressure range, with saturation loadings around 2 mol kg<sup>-1</sup> and 1.2 mol kg<sup>-1</sup>, respectively. Additionally, both experiment and simulation show no appreciable adsorption of water, thereby confirming the hydrophobic nature of FMOF-1.

However, as shown in Fig. 7a and b, simulated isotherms of N<sub>2</sub> and O<sub>2</sub> adsorption in FMOF-1a drastically underpredict the

saturation loading from experiment by almost 3 mol kg<sup>-1</sup> in both cases. The N<sub>2</sub> and O<sub>2</sub> experimental isotherms show two steps, but the FMOF-1a simulated isotherms do not exhibit this behaviour. This pronounced step can be ascribed to the flexibility of the framework upon adsorption, meaning that N<sub>2</sub> or O<sub>2</sub> adsorption leads to structural changes of the framework, allowing for more molecules to be adsorbed in the framework. Similar adsorption isotherms have been observed in some ZIFs and the MIL series of MOFs due to framework flexibility.<sup>53–59</sup> Since the framework is held rigid in our simulations, we approximated the effect of framework flexibility by simulating isotherms with three different FMOF-1 structures, FMOF-1a, FMOF-1b, and FMOF-1c. FMOF-1b has a larger unit cell volume and channel size than FMOF-1a; the largest cavity diameter in FMOF-1a is 6.1 Å, while in FMOF-1b it is 6.8 Å (see Table S2†). The channel size in FMOF-1c lies between FMOF-1a and FMOF-1b, with a 6.3 Å diameter. Recall from Fig. 3 that the unit cell volume of FMOF-1 varies with temperature and CO<sub>2</sub> loading. Fig. 7 also shows adsorption isotherms of N<sub>2</sub> and O<sub>2</sub> in

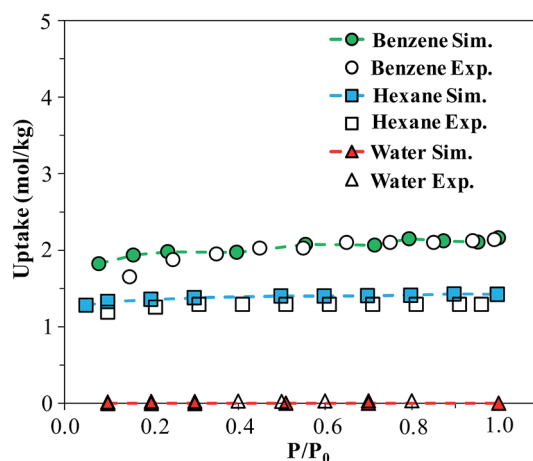


Fig. 6 Simulated and experimental adsorption isotherms for benzene, *n*-hexane, and water in FMOF-1a at 298 K. *P*<sub>0</sub> is the experimental saturation pressure of each adsorbate.



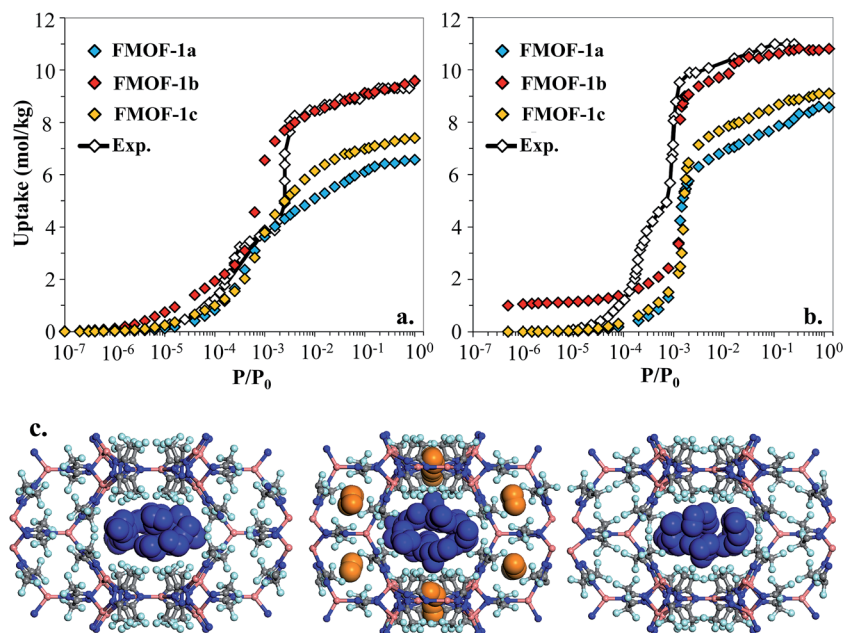


Fig. 7 Experimental adsorption isotherms for (a) N<sub>2</sub> and (b) O<sub>2</sub> at 77 K compared to simulated isotherms in three FMOF-1 structures. In (c) GCMC simulation snapshots for N<sub>2</sub> at saturation loading are shown for FMOF-1a (left), FMOF-1b (middle) and FMOF-1c (right) at 77 K. Nitrogen molecules adsorbed in FMOF-1 large channels and small pockets are illustrated with blue and orange vdW representation, respectively. P<sub>0</sub> is the experimental saturation pressure of each adsorbate.

FMOF-1b and FMOF-1c. The two-step adsorption behaviour observed experimentally can be better described when the simulated isotherms of these different structures are considered. At low loadings, the FMOF-1a and FMOF-1c results agree better with experiment, while at high loadings the saturation loading in the expanded structure (*i.e.* FMOF-1b) is closer to experiment. The maximum amounts adsorbed in FMOF-1b for N<sub>2</sub> and O<sub>2</sub> are 9.6 and 10.7 mol kg<sup>-1</sup>, respectively, which are in excellent agreement with the experimental values.

The results shown in Fig. 7 corroborate that the framework of FMOF-1 goes through structural expansion upon adsorption of guest molecules. The small cavity in FMOF-1b has a diameter of *ca.* 3.4 Å, which is much larger than the small cavity in FMOF-1a or FMOF-1c (*ca.* 2.5 Å) (Table S2†). The kinetic diameters of N<sub>2</sub> and O<sub>2</sub> are 3.64 Å and 3.46 Å,<sup>3</sup> respectively, which suggests that at most one N<sub>2</sub> or O<sub>2</sub> molecule can fit in each small pocket. Interestingly, the window sizes connecting the small pockets to the larger channels are smaller than the kinetic diameters of N<sub>2</sub> and O<sub>2</sub>. However, kinetic diameters do not account for the orientation of the molecule – the cross section of a N<sub>2</sub> or O<sub>2</sub> molecule is *ca.* 2.9 Å,<sup>60</sup> indicating that only FMOF-1b has a window size large enough to admit an N<sub>2</sub> or O<sub>2</sub> molecule. Additionally, since the FMOF-1b structure was obtained at 90 K and the isotherms are measured at 77 K, it is possible that the window size could also be larger at the lower temperature.

To investigate the placement of N<sub>2</sub> within FMOF-1, we compared the position of N<sub>2</sub> molecules adsorbed in the FMOF-1 structures at the saturation loading in the GCMC simulations at 77 K (Fig. 7c). In FMOF-1a and FMOF-1c, N<sub>2</sub> molecules adsorb only in the large cylindrical channels. On the other hand, in FMOF-1b, the N<sub>2</sub> molecules are adsorbed first in the small

pockets at low pressures (Fig. S6†), and it is at the higher pressure that N<sub>2</sub> molecules adsorb in the larger cylindrical channels. In FMOF-1b, molecules prefer to adsorb in the small pores due to the strong interactions between the adsorbed molecules and the Tz ring pairs, and only as the pressure increases do the large channels fill up. Given that only one N<sub>2</sub> molecule can occupy each small pocket, the contribution of small pockets to the total amount adsorbed is 1.1 mol kg<sup>-1</sup> (*i.e.*, 8 molecules per unit cell of FMOF-1b). This uptake accounts for 11% of the total amount adsorbed. The remainder of the adsorption difference between FMOF-1b and FMOF-1c or FMOF-1a is due to additional adsorption in the large channels. As shown in Fig. S6,† a similar adsorption mechanism and placement was observed for O<sub>2</sub> at 77 K. This finding further confirms that the structural expansion of FMOF-1 occurs not only in the small pockets but also increases the capacity of the larger channels for small adsorbates. It is worth mentioning that the simulated adsorption isotherms of larger adsorbates such as *n*-hexane and benzene in FMOF-1b and FMOF-1c show no significant differences when compared to the isotherm calculated for FMOF-1a (Fig. S7†). Both fits for the *n*-hexane and benzene adsorption isotherms obtained for FMOF-1 agree very well with both the experimental data and the simulation thereof (Fig. S8a and S8b,† respectively). The kinetic diameters of *n*-hexane and benzene are 4.3 Å and 5.9 Å, respectively, both of which are much larger than the window and pore size of the small pockets. Therefore, the saturation loading of these large molecules is mainly determined by the volume of the cylindrical channels, resulting in a simple type-1 adsorption isotherm profile, with no adsorption in the smaller pores and no consequent steps in the adsorption isotherms. This finding further



demonstrates that, while the accessibility of the smaller pockets and larger main channels for different expansion levels of FMOF-1 have significant effects on the adsorption properties of small adsorbates (*e.g.*, N<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>), these structural changes have little effect on the uptake of larger adsorbates (*e.g.*, benzene, *n*-hexane, and toluene).

Fig. 8 shows the experimental CO<sub>2</sub> adsorption isotherms in FMOF-1 structures at 278 K and 283 K, along with simulated data for comparison. This initial comparison is restricted to 30 bar, where the experimental isotherms can be fit with a Toth isotherm and FMOF-1 shows less pronounced flexibility and expansion. The simulated isotherms in all three structures agree reasonably well with the experimental data at low pressure. The difference between experiment and simulation increases for FMOF-1b as the pressure increases. At saturation loadings, better agreement between experiment and simulation results is observed for FMOF-1c, the structure that was obtained under the stream of CO<sub>2</sub> (see Fig. 3). The simulation snapshots at high loading show that CO<sub>2</sub> molecules occupy only the large channels in FMOF-1a and FMOF-1c, since the pockets are too small for CO<sub>2</sub> (kinetic diameter: 3.4 Å). Interestingly, even in the expanded structure of FMOF-1b, the CO<sub>2</sub> molecules cannot be fully accommodated inside the small pockets and stay at the windows connecting the large channels to the small pockets as highlighted in the simulation snapshots in Fig. 8c and the CO<sub>2</sub> density profiles shown at high pressure in Fig. S9.†

In order to better understand the CO<sub>2</sub> adsorption behaviour in FMOF-1 at higher pressure (see Fig. 1), we also simulated CO<sub>2</sub> adsorption isotherms at 298 K up to 50 bar for different FMOF-1a–c structures and compared the results to the simulated uptakes obtained for FMOF-2 and the experimental isotherm (Fig. 9a). The FMOF-2 structure is obtained from annealing

FMOF-1 and recrystallizing from a toluene/acetonitrile solution and consists of two enlarged types of pores: hexagonal channels that are *ca.* 18 Å in width and triangular cages that are *ca.* 10 Å in diameter.<sup>46</sup> The maximum amount adsorbed for CO<sub>2</sub> at 298 K is 3.2 mol kg<sup>-1</sup> or 23.4 molecules per unit cell in FMOF-1c. This value is in excellent agreement with the result from neutron powder diffraction experiments at 290 K, where CO<sub>2</sub> uptake capacity of 3.3 mol kg<sup>-1</sup> (24 molecules per unit cell) can be obtained when all three CO<sub>2</sub> adsorption sites in the large cavity are fully occupied under 61 bar of CO<sub>2</sub> loading (see Fig. 5). However, with a small increase in temperature, at 298 K, the simulated CO<sub>2</sub> uptake is significantly lower than the experimental uptake even in the expanded FMOF-1b structure, suggesting further enlargement of the structure at this temperature. It is very clear from Fig. S2† that the CO<sub>2</sub> adsorption of FMOF-1 at room temperature represents a marked deviation from the typical type 1 isotherm. Generally, Toth fit modeling is carried out on type 1 isotherms. In order to obtain a good Toth fit for the CO<sub>2</sub> adsorption at room temperature, the pressure range is scaled down so as to compare experimental data with the simulation data. Fig. S10† shows that the Toth fit agrees well with the FMOF-1b structure. Indeed, the simulated saturation loading of CO<sub>2</sub> in FMOF-2 shows better agreement with the experimental data at elevated pressures around 40 bar, suggesting expansion of FMOF-1 to a more expanded polymorph at higher pressures up to 60 bar. The collective experience of the Omary group with such M-Tz(R<sub>F</sub>)<sub>2</sub> compositions suggests the prevalence of polymorphism and crystallographic isomerism; this is so both with and without gas adsorption assistance. As such, the presumed significant expansions (or compressions) suggested by the closer proximity of the experimental high-pressure CO<sub>2</sub> uptake in FMOF-1 at

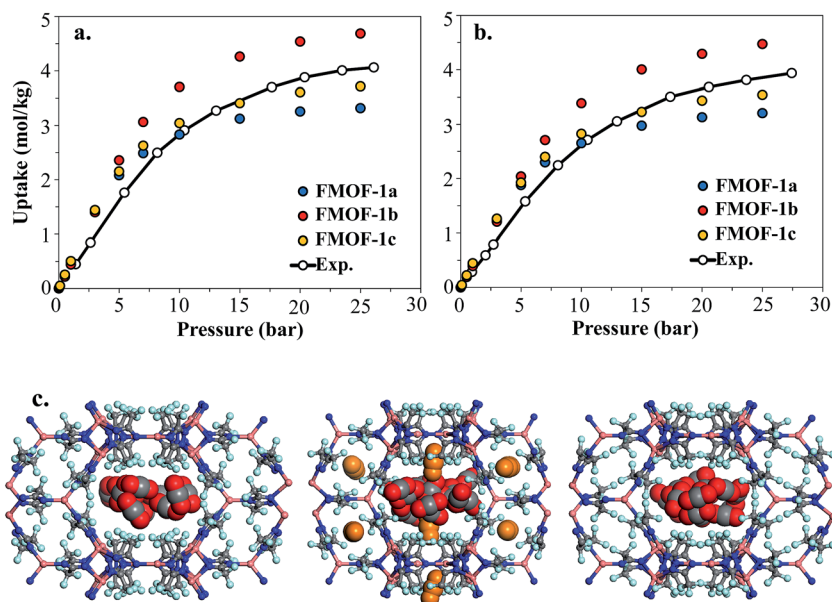


Fig. 8 Experimental adsorption isotherms for CO<sub>2</sub> and simulated isotherms in three FMOF-1 structures at (a) 278 K and (b) 283 K. In (c) GCMC simulation snapshots at saturation loading are shown for FMOF-1a (left), FMOF-1b (middle) and FMOF-1c (right) for CO<sub>2</sub> at 278 K. CO<sub>2</sub> molecules are illustrated in vdW representation, with those adsorbed in the large channels in red and grey and those at the entrance to the small pockets in orange. The experimental and simulated results are excess adsorption isotherms.



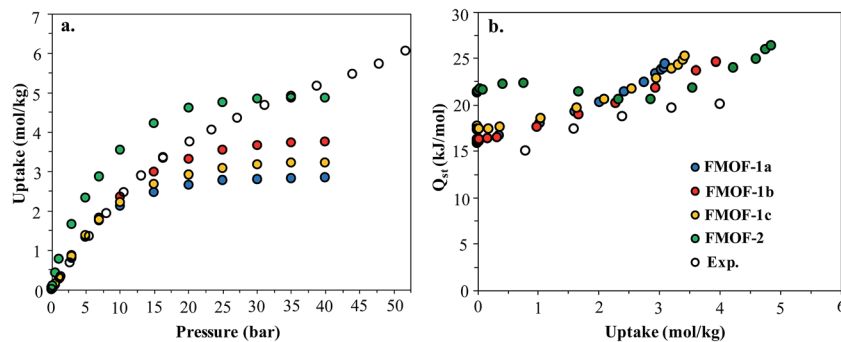


Fig. 9 (a) Experimental excess adsorption isotherms for CO<sub>2</sub> at 298 K in FMOF-1 and simulated excess isotherms in three FMOF-1 structures and FMOF-2. (b) Experimental and simulated heats of adsorption for CO<sub>2</sub> at 298 K.

ambient temperature to the simulated data for the porous-most “emptied” N<sub>2</sub>@FMOF-1 adsorption adduct at 90 K or – better yet – the FMOF-2 structure at 100 K should not be surprising for this highly flexible material.

Fig. 9b compares the isosteric heats of adsorption ( $Q_{st}$ ) obtained from GCMC simulations to the values obtained from variable-temperature experiments. The predicted  $Q_{st}$  values were obtained from the fluctuations of the potential energy over the production cycles in the GCMC simulations for each pressure point. The experimental heats of adsorption were obtained using the Clausius–Clapeyron equation on isotherms from several temperatures (see ESI† for details). In reasonably good agreement with the experimental data, the simulated  $Q_{st}$  values for the three FMOF-1 structures rise smoothly from ~16 to 25 kJ mol<sup>-1</sup> as the loading increases due to an increasing contribution from attractive CO<sub>2</sub>–CO<sub>2</sub> interactions (Fig. S11†). The adsorption heats for FMOF-2 are higher (~22 kJ mol<sup>-1</sup>) at low loadings due to strong adsorption of CO<sub>2</sub> in the small triangular pores. In general, these moderate adsorption heats lie in the typical range for CO<sub>2</sub> adsorption in MOFs.<sup>61,62</sup> In Fig. S11,† the average adsorbate–adsorbent and adsorbate–adsorbate energies from GCMC simulations are shown for CO<sub>2</sub> adsorption in FMOF-1c at 298 K as a function of pressure. The van der Waals interactions between CO<sub>2</sub> and FMOF-1 are clearly dominant with ~–12 kJ mol<sup>-1</sup> contribution, and the coulombic components of the total interaction energy are very small, ~–2 kJ mol<sup>-1</sup>. These results suggest that the fluorine-lined cylindrical pore creates an electrostatic potential that is not very favourable for CO<sub>2</sub> adsorption.

To provide another perspective on guest molecule interactions with FMOF-1, QM methods (UDFT with dispersion) employing cluster models were used to determine the free energy of binding for several guest molecules. The binding sites used in these calculations are located in the cylindrical channel and the small cavity. These sites are represented in Fig. 10 in the extended MOF structure with an overlay of the guest geometry from the cluster calculations.

The 184-atom extended model for the cylindrical channel binding site is taken from the FMOF-1a structure and shown in Fig. 11a. The extended model of the cylindrical channel with coordinated Ag and Tz was truncated with complete metal coordination spheres and ligands. By preserving the metal to

ligand ratio, no atom substitutions were needed. The calculated binding free energies of CO<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub> in the cylindrical channel are given in Table 1. The binding free energies follow the order CO<sub>2</sub> > N<sub>2</sub> > H<sub>2</sub> in the cylindrical channel, indicating selective adsorption of CO<sub>2</sub>. The dispersion contribution increases the magnitude of the binding free energy by ~59–66% in these calculations. Similar results with respect to the relative contribution of dispersion were found by Neaton for carbon dioxide binding in Mg–MOF-74.<sup>44</sup>

The binding free energies in the small cavity of FMOF-1b were also determined for CO<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub> using the truncated model shown in Fig. 11b. The small cavity shows stronger binding for N<sub>2</sub> and H<sub>2</sub> than in the cylindrical channel, with a similar dispersion correction making up 62–79% of the total

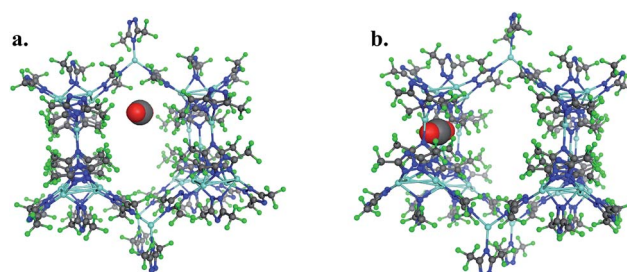


Fig. 10 (a) CO<sub>2</sub> in the cylindrical channel within the extended FMOF-1a structure and (b) CO<sub>2</sub> in the small cavity within the extended FMOF-1b structure.

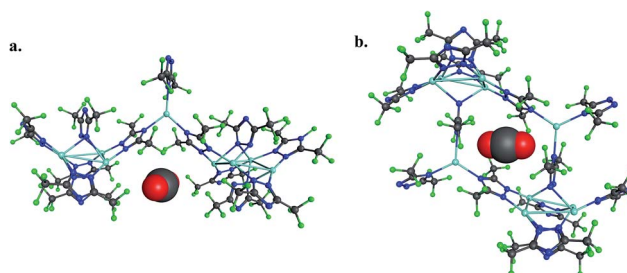
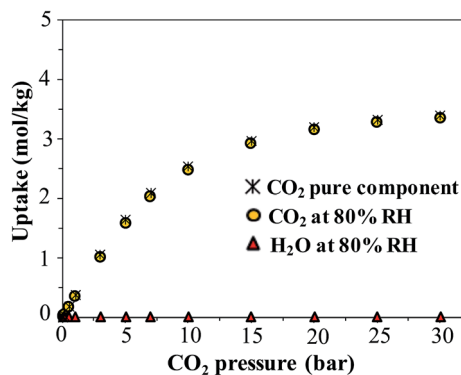


Fig. 11 (a) CO<sub>2</sub> interaction with the 184-atom cluster model for the cylindrical channel taken from the FMOF-1a structure. (b) CO<sub>2</sub> interaction with the 194-atom cluster model for the small cavity taken from the FMOF-1b structure.



**Table 1** DFT binding free energies of various guest molecules with FMOF-1a cylindrical channel and FMOF-1b small cavity

Guest	Cylindrical channel		Small cavity	
	PBE0 (kJ mol <sup>-1</sup> )	PBE0-D3 (kJ mol <sup>-1</sup> )	PBE0 (kJ mol <sup>-1</sup> )	PBE0-D3 (kJ mol <sup>-1</sup> )
CO <sub>2</sub>	-9.2	-23.2	138.6	94.5
N <sub>2</sub>	-7.9	-19.3	-9.0	-39.6
H <sub>2</sub>	-2.1	-6.6	-3.5	-16.8



**Fig. 12** Simulated excess adsorption isotherms at 298 K for pure component CO<sub>2</sub> and a mixture of CO<sub>2</sub> at different pressures with water at 80% relative humidity in FMOF-1c.

binding free energy. The binding of CO<sub>2</sub> in the truncated model of the small cavity is not energetically favourable, in agreement with GCMC simulations and neutron diffraction experimental results.

### Effect of humidity on CO<sub>2</sub> uptake

Finally, we consider the effect of humidity on the CO<sub>2</sub> uptake of FMOF-1. Water is an ever-present component of flue gas, and we hypothesized that hydrophobic MOFs like FMOF-1 should show negligible loss of CO<sub>2</sub> capacity in the presence of water vapor. To test this, we carried out GCMC simulations of CO<sub>2</sub> adsorption in humid conditions. Fig. 12 depicts the excess amount adsorbed for a mixture of CO<sub>2</sub> and H<sub>2</sub>O in FMOF-1c at 80% relative humidity and at different CO<sub>2</sub> pressures. Although the CO<sub>2</sub> uptake at 0.15 bar (the relevant condition in flue gas)<sup>63</sup> is only *ca.* 0.05 mol kg<sup>-1</sup> (0.3 molecules per unit cell), it is shown that for such a superhydrophobic MOF, the uptake of CO<sub>2</sub> is not influenced by the presence of water vapor at all. There is essentially no co-adsorption of water in the presence of CO<sub>2</sub>, thereby explaining why the CO<sub>2</sub> adsorption amount is similar under dry or humid conditions. This result supports the hypothesis that FMOFs can be promising to diminish the effect of humidity on CO<sub>2</sub> adsorption performance.

## Conclusions

We combined atomically detailed calculations and experiments to provide insight into the adsorption of CO<sub>2</sub> and other molecules

in FMOF-1. First, the force field model for FMOF-1 was verified by comparing simulated adsorption isotherms for a variety of adsorbates in FMOF-1 with existing experimental data. Adsorption isotherms of N<sub>2</sub> and O<sub>2</sub> support previous suggestions that FMOF-1 undergoes major structural changes in the presence of guest molecules. This flexibility, however, has little effect on the loading of larger adsorbates such as *n*-hexane and benzene. The two-step isotherms observed for both N<sub>2</sub> and O<sub>2</sub> can be explained by analyzing simulated adsorption isotherms in both contracted and expanded FMOF-1 structures and the accessibility of the small pockets to these smaller adsorbates. We measured CO<sub>2</sub> adsorption isotherms in FMOF-1 and found good agreement between experiment and simulations using the FMOF-1c structure at sub-ambient temperatures. Simulations of CO<sub>2</sub> adsorption in FMOF-1 along with neutron powder diffraction measurements show that CO<sub>2</sub> molecules cannot fit in the small pores of FMOF-1 and reside in the large channels at three distinct adsorption sites. The experimentally measured CO<sub>2</sub> isotherms near and above room temperature suggest significant framework expansion at high CO<sub>2</sub> pressures. Contact angle measurements confirm FMOF-1's previously reported hydrophobic nature, and Monte Carlo simulations predict no uptake of water even up to the vapor pressure of water. Simulations of CO<sub>2</sub> adsorption in the presence of 80% relative humidity show that the amount of CO<sub>2</sub> adsorbed is essentially the same as in the absence of humidity, validating our hypothesis that hydrophobic MOFs could hold promise for CO<sub>2</sub> capture from flue gas.

## Conflict of interest

R. Q. S. has a financial interest in the start-up company NuMat Technologies, which is seeking to commercialize metal-organic frameworks.

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