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Observation of binding of carbon dioxide to nitro-decorated metal–organic frameworks†‡

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Metal–organic frameworks (MOFs) functionalised with amine, amide and hydroxyl groups show great promise for CO₂ binding due to their ability to form hydrogen bonds to CO₂. Herein we report the adsorption and selectivity of CO₂ in four iso-reticular MOFs adopting the NbO topology. Functionalisation of the parent MOF, MFM-102, with –NO₂, –NH₂ and alkyl groups leads to an enhancement of CO₂ adsorption of up to 36% for the NO₂-decorated MOF and with raised selectivity. MFM-102-NO₂ shows the highest adsorption capacity for CO₂ (184 cm³ g^{−1} at 273 K and 1.0 bar) within this series, comparable to the best-behaving iso-reticular MOFs. At 298 K and 1.0 bar, MFM-102-NO₂ shows a CO₂/CH₄ selectivity of 5.0. *In situ* inelastic neutron scattering and synchrotron FT-IR micro-spectroscopy were employed to elucidate the host–guest interaction dynamics within CO₂-loaded MFM-102-NO₂. Neutron powder diffraction enabled the direct observation of the preferred binding domains in MFM-102-NO₂, and, to the best of our knowledge, we report the first example of CO₂ binding to a –NO₂ group in a porous MOF. Synergistic effects between the –NO₂ group and the open metal sites lead to optimal binding of CO₂ molecules within MFM-102-NO₂ via hydrogen bonding to C–H groups.

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Introduction

Emissions of carbon dioxide (CO₂) are causing significant environmental impacts.¹ However, CO₂ is also an inexpensive, non-toxic and a potentially abundant renewable C₁ source, and, therefore, the development of cost-effective and efficient methods for carbon capture and storage (CCS) is a major target. State-of-the-art CCS is often based upon scrubbing systems that rely heavily upon the use of toxic and corrosive amines, and

require high operational cost. In contrast, reversible physisorption of CO₂ within porous materials is a promising approach with the potential of low running-cost and high efficiency. A wide spectrum of materials, such as zeolites, activated carbons, ionic liquids and silica-based materials have been investigated for CO₂ adsorption.^{2–5}

Metal–organic framework (MOF) materials show potential for gas adsorption and storage owing to their high porosity and designed pore size and structure reflecting their versatility via incorporation of active binding sites by decoration of the pores with functional groups and/or by incorporation of open metal sites.^{6,7} MOFs decorated with –NH₂,⁸ –OH,⁹ –CONH–,¹⁰ piperazine,¹¹ and pyridyl groups¹² have been explored extensively for CO₂ adsorption. The nitro group (–NO₂) is one of the most powerful electron-withdrawing groups, which can polarise –CH groups on phenyl rings. We argued that potentially this might lead to enhanced interactions between –CH groups and adsorbed CO₂ molecules, and moreover, the –NO₂ group might itself serve as a binding site for CO₂ molecules via dipole/quadrupole interactions.^{13,14} However, to date, experimental evidence of CO₂ binding to NO₂-decorated MOFs has not been reported. Herein, we report the adsorption and selectivity of CO₂ in four iso-reticular NbO-type MOFs with different organic functional groups, namely –NO₂, –NH₂ and alkyl groups. The introduction of these functional groups inevitably reduces the pore volume of the parent MOF, but leads to notable enhancement in CO₂

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‡ The crystal data for MFM-102-NO₂, MFM-102-NH₂, and bare MFM-102-NO₂, CCDC 1857304, 1857305 and 1857873, respectively, were previously reported in ref. 16.

adsorption. In particular, the NO₂-functionalised MOF MFM-102-NO₂ shows a 36% increase in CO₂ uptake compared to the parent MFM-102, confirming a positive effect on CO₂ binding. A combination of static and dynamic experiments using *in situ* neutron powder diffraction (NPD), inelastic neutron scattering (INS) and synchrotron-based IR micro-spectroscopy have been applied to study the binding domains of adsorbed CO₂ and the host-guest binding dynamics in MFM-102-NO₂ as a function of CO₂ loading to reveal fundamental insights into the mechanisms for enhanced CO₂ adsorption.¹⁵

Experimental

Material and instrumentation

Chemicals and reagents were purchased from Fisher Scientific, Sigma Aldrich or Fluorochem and used as received without further purification. The detailed synthesis of MFM-102 has been reported previously.¹⁶ ¹H NMR and ¹³C NMR spectra were measured on a Bruker AV400 or AV500 spectrometer. High-resolution electrospray mass spectra were measured on a Bruker MicroTOF spectrometer with samples dissolved in MeOH, and scanning was conducted in both positive and negative modes. Infrared (IR) spectra were recorded in the 400–4000 cm^{−1} range in ATR sampling mode with a Thermo Scientific iD5 diamond ATR on a Nicolet iS5 FT-IR spectrometer, and elemental analysis was carried out on a CE-440 elemental analyser (EAI Company). TGA measurements were performed using a PerkinElmer TGA 7 Gravimetric Analyser under a flow of N₂ (20 ml min^{−1}) at a heating rate of 5 °C min^{−1}. Powder X-ray diffraction (PXRD) patterns were obtained on a PANalytical X'Pert Pro MPD diffractometer in Bragg-Brentano geometry with Cu-K_{α1} radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 30 mA over 2θ range 3–40°. Samples were evenly dispersed on zero-background silicon plates with a cavity depth of 0.3 mm.

Neutron powder diffraction (NPD) of gas-loaded MFM-102-NO₂

NPD data were collected at WISH beamline at ISIS Muon and Neutron facility. Acetone exchanged MFM-102-NO₂ was loaded into vanadium cans of 11 mm diameter, and the sample was activated by heating at 393 K and at 1×10^{-7} mbar for 2 days. Data for the bare framework were collected after placing the sample can into a liquid He cryostat and cooling to 7 K. CO₂ gas was dosed into the system after warming to 290 K. The gases were dosed volumetrically from a calibrated volume, and to ensure gases were fully adsorbed into the sample without condensation elsewhere the system was cooled to 7 K slowly over 3 h. Structure solutions of gas-loaded MFM-102-NO₂ were solved by sequential difference Fourier analyses followed by Rietveld refinements (see ESI† Section 4).

Inelastic neutron scattering (INS) of CO₂-loaded MFM-102-NO₂ and MFM-102-NH₂

INS data were collected on the TOSCA beamline at ISIS Muon and Neutron facility and on the VISION spectrometer at Spallation Neutron Source, Oak Ridge National Laboratory (USA).

MFM-102-NO₂ and MFM-102-NH₂ were loaded into a vanadium can of 11 mm diameter and outgassed at 10^{-7} mbar at 393 K for 2 days. After placing the sample into a He cooled cryostat, INS data of the bare framework were collected at 7 K. CO₂ was dosed volumetrically from a calibrated volume at room temperature and gradually cooled to 7 K to allow the gas to fully adsorb into MFM-102-NO₂ and MFM-102-NH₂. INS data of CO₂-loaded MFM-102-NO₂ and CO₂-loaded MFM-102-NH₂ were collected at 7 K. Experimentally obtained INS data were compared with modelled data obtained *via* density functional theory (DFT) calculations (see ESI† for further details).

Synchrotron FTIR micro-spectroscopy of CO₂-loaded MFM-102-NO₂

Single crystals of MFM-102-NO₂ were loaded onto a ZnSe slide and placed into a Linkam FTIR600 variable temperature gas-tight cell fitted with ZnSe windows. The MOF sample was activated *in situ* under a flow of N₂ whilst heating the Linkam stage to 413 K for 6 h. Partial pressures of zeolite dried gases N₂ and CO₂ were controlled by varying the volumetric flow of the two gases *via* separate mass flow controllers. FTIR spectra were collected at B22 MIRIAM beamline at Diamond Light Source using a highly bright synchrotron IR source connected to a Bruker Hyperion 3000 IR microscope with a 15× objective and MCT detector (liq. N₂ cooled). Spectra (256 scans) were measured at room temperature with a $20 \times 20 \mu\text{m}$ beam, in the spectral range of 4000–650 cm^{−1} (4 cm^{−1} resolution).

Results and discussion

Synthesis, structure and porosity

MFM-102, MFM-102-NH₂, MFM-102-NO₂ and MFM-111 were synthesised according to our previously reported methods,^{16–18} and the phase purity of all bulk materials was confirmed by powder X-ray diffraction (see ESI† Section 1). All four MOFs are iso-structural and crystallise in the trigonal space group *R3m*. The framework is built from Cu₂(O₂CR)₄ paddlewheel units in which two Cu^{II} cations are bridged by four carboxylate groups surrounded the [Cu⋯Cu] axis and two terminal H₂O molecules at axial positions to form a [Cu₂(O₂CR)₄(OH₂)₂] node. These Cu₂(O₂CR)₄ units are bridged by the diisophthalate ligands to afford a 3D extended NbO-type network. Within each framework, there are two different types of metal-ligand cages (denoted as A and B) in a 1 : 1 ratio (Fig. 1). Cage A consists of six Cu₂(O₂CR)₄ paddlewheels and six linkers to give a spherical shape of 15 Å diameter. Cage B is constructed of twelve Cu₂(O₂CR)₄ paddlewheels residing at the vertices and six ligands on the faces to form an ellipsoid shaped cavity of 32 Å along the *c* axis and 18 Å across *ab* plane. Due to the alternative packing of cages A and B, the alkyl, nitro, and amino groups are directly grafted into the pore walls, providing an excellent platform to study their role in guest binding. The Brunauer-Emmett-Teller (BET) surface area and pore volume of MFM-102, MFM-111, MFM-102-NH₂, MFM-102-NO₂ were determined to be 3412, 2930, 2928, 2893 m² g^{−1} and 1.29, 1.19, 1.12, 1.14 cm³ g^{−1}, respectively, from N₂ isotherms at 77 K. As



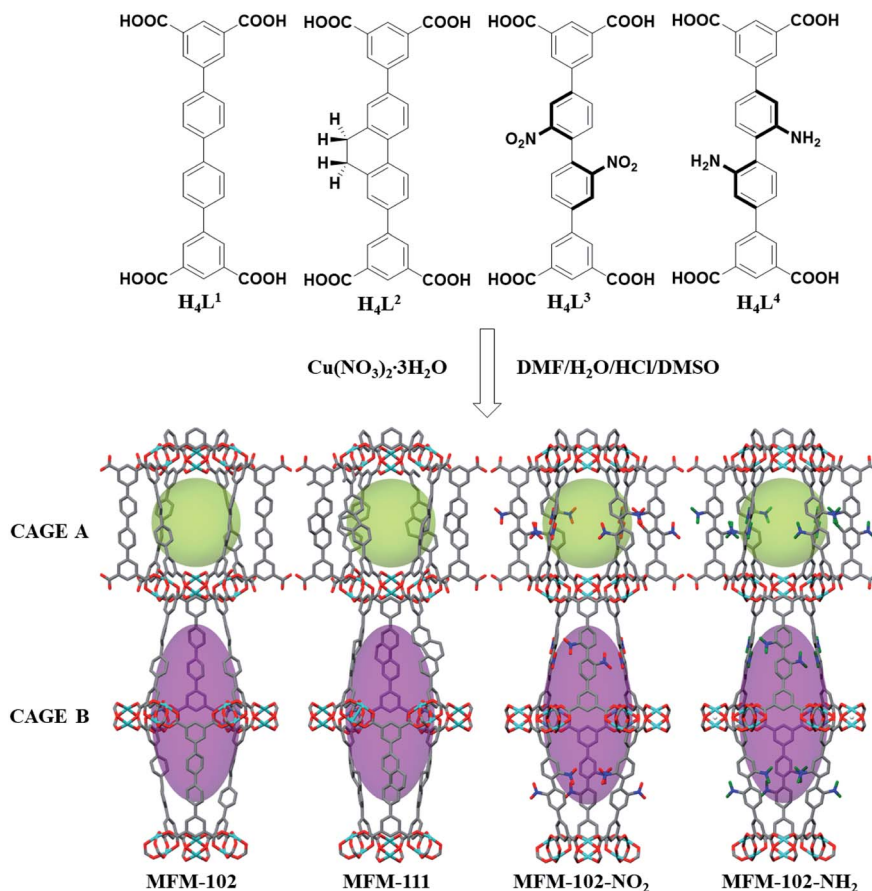


Fig. 1 Views of organic ligands used to construct the MFM-102 series of MOFs and the X-ray crystal structures of MFM-102, MFM-111, MFM-102-NO₂ and MFM-102-NH₂. The functional groups are highlighted in ball-stick mode. (C, dark grey; O, red; N, blue; Cu, turquoise; all coordinated H₂O and hydrogen atoms are omitted for clarity, except for the hydrogen atoms on the –NH₂ group, green).

expected, the porosity of decorated complexes reduces compared to the parent MOF, and so introduction of alkyl, –NH₂ and –NO₂ groups into MFM-102 leads to reduction in BET surface areas of 14%, 14% and 15%, respectively.

Gas adsorption properties

Adsorption isotherms of CO₂ and CH₄ were recorded at 273 and 298 K up to 1 bar. All isotherms are completely reversible, and show fast adsorption–desorption kinetics with equilibrium achieved typically within 3–5 min. Uptake of CO₂ at 273 K and 1.0 bar were recorded as 184, 178, 165, 135 cm³ g^{−1} for MFM-102-NO₂, MFM-102-NH₂, MFM-111 and MFM-102, respectively (Fig. 2a). Interestingly, despite the reduction in porosity, the introduction of alkyl, –NH₂ and –NO₂ groups into MFM-102 leads to enhancement on the CO₂ uptake of resultant MOFs by 22%, 32% and 36%, respectively. Notably, the CO₂ uptake of MFM-102-NO₂ is comparable to the best-performing isoreticular MOF (NJU-Bai-14, 187 cm³ g^{−1}) under the same conditions.¹⁹ Similar enhancement of CO₂ adsorption was also observed at 298 K for the decorated MOFs (Fig. 2b), and these uptakes are comparable to other leading NbO-type MOFs (Table 1). In sharp contrast, these MOFs show similarly low uptakes of CH₄ at 273 and 298 K and 1.0 bar (ranging from 30 cm³ g^{−1} to 20 cm³ g^{−1}). This result indicates the potential of MFM-102-NO₂

as a promising material for selective adsorption of CO₂. The adsorption selectivities for equimolar mixtures of CO₂/CH₄ within these MOFs have been calculated using ideal adsorbed solution theory (IAST) using the experimental single-component isotherm data (Fig. S4 and S5†). At 298 K and 1 bar, the CO₂/CH₄ (50 : 50) selectivity is 5.0, which is comparable to those reported for other Cu-based MOFs with similar porosity, such as NJU-Bai12 (5.0),²⁰ ZJNU-81(5.5),²¹ ZJNU-82 (5.4),²¹ ZJNU-83 (4.9),²¹ ZJU-15 (4.4) (ref. 22) and ZJNU-57 (5.5),²³ but which do not show NbO topologies.

The isosteric heats of adsorption (Q_{st}) of CO₂ were calculated using virial method based on isotherm data at 273 and 298 K (Fig. 2c). The values for Q_{st} at low surface coverage range from 24.0 to 24.6 kJ mol^{−1}, comparable to other MOFs of NbO topology with a high density of open Cu(II) sites (Table 1). With increasing CO₂ loading, the values of Q_{st} steadily reduce in all four cases. Interestingly, the Q_{st} values of MFM-102 drop more rapidly than functionalised materials with increasing loading, indicating the presence of additional binding sites in the decorated MOFs.

In situ neutron powder diffraction (NPD) of CO₂-loaded MFM-102-NO₂

In situ NPD was employed to determine the binding domains for adsorbed CO₂ molecules within desolvated MFM-102-NO₂ at





Fig. 2 Adsorption isotherms for desolvated MFM-102, MFM-111, MFM-102-NO₂ and MFM-102-NH₂ (a) 273 K, (b) 298 K. Solid and open symbols represent adsorption and desorption, respectively. (c) Heat of adsorption as a function of CO₂ uptake derived by the virial method.

a loading of 2.0 CO₂/Cu. NPD data for the desolvated complex confirm the complete removal of guest solvents, including coordinated H₂O molecules on the Cu sites, and no significant structural distortion is observed compared to the parent solvated material. A loading of 2.0 CO₂/Cu was used to assess the strongest binding sites within the material without involving notable adsorbate-adsorbate interactions. Fourier difference map analysis of the NPD patterns afforded the location of guest CO₂ molecules, which after further development by Rietveld refinement, allowed

unambiguous determination of gas positions, orientations and crystallographic occupancies within each sample.

MFM-102-NO₂ displays six binding sites for CO₂ (denoted as I to VI with decreasing occupancies, Fig. 3 and 4). Significantly, site I (occupancy = 0.50) was found not to be at the open Cu(II) sites but is confined to the window between Cages A and B. At site I, CO₂¹ forms supramolecular interactions to aromatic -CH group from two adjacent NO₂-substituted phenyl rings [O_{CO₂}...HC- = 2.13(5), 2.42(8) Å]. It is noteworthy that -NO₂ is a strong electron-withdrawing groups which leads to

Table 1 Comparison of CO₂ uptakes in selected Cu-MOFs of NbO topology

MOFs	CO ₂ uptake, 273 K (cm ³ g ⁻¹)	CO ₂ uptake, 298 K (cm ³ g ⁻¹)	V _p , pore volume (cm ³ g ⁻¹)	BET area (m ² g ⁻¹)	Q _{st} (kJ mol ⁻¹)	Ref.
ZJNU-44	175	116	0.894	2314	—	24
ZJNU-43	180	103	0.894	2243	—	24
ZJNU-45	163	107	0.877	2232	—	24
ZJNU-40	—	86	0.997	2072	24.0	25
ZJNU-41	—	97	0.837	2530	23.5	26
ZJU-8	175	98	1.022	2501	21.9	27
NJU-Bai-14	187	100	0.942	2384	24.5	19
MFM-101	164	86	1.080	2805	—	25
MFM-102	135	74	1.297	3412	24.0	This work
MFM-102-NO ₂	184	96	1.118	2893	24.6	This work
MFM-102-NH ₂	180	97	1.140	2928	24.4	This work
MFM-111	165	88	1.190	2930	24.2	This work
MFM-130	109	59	1.000	2173	26.0	28



Fig. 3 View of the binding sites for adsorbed CO₂ molecules in MFM-102-NO₂ and the relative positions of these positions in the framework cages [C, dark grey; O, red; N, blue; Cu, turquoise and CO₂ molecules at site I (yellow), site II (green), site III (brown), site IV (ruby), site V (blue) and site VI (purple)].



Fig. 4 The positions of the CO₂ in the framework cage A (a) and B (b) of MFM-102-NO₂. CO₂ molecules are at site I (yellow), site II (green), site III (brown), site IV (ruby), site V (blue) and site VI (purple).

polarisation of adjacent –CH moieties. These –CH groups therefore show enhanced acidity and thus act as effective hydrogen bond donors to CO₂ molecules. Site II and III (occupancy = 0.49 and 0.28, respectively) reside at the open Cu(II) centre [$\text{O}_{\text{CO}_2} \cdots \text{Cu} = 2.27(7) \text{ \AA}$ and $3.24(7) \text{ \AA}$ for site II and III, respectively]. Site IV (occupancy = 0.28) is stabilised by the dipole/quadrupole interaction between $\text{O}(\delta^-)$ of the –NO₂ group from 2 neighbouring phenyl rings and the $\text{C}(\delta^+)$ centre of CO₂ with distances of $3.20(6)$ and $2.87(9) \text{ \AA}$. Site V (occupancy = 0.20) was found close to the isophthalate phenyl ring

[$\text{O}_{\text{CO}_2} \cdots \text{HC} = 1.72(9) \text{ \AA}$] and the NO₂-decorated phenyl ring [$\text{O}_{\text{CO}_2} \cdots \text{HC} = 1.91(4) \text{ \AA}$] stabilised by interactions with aromatic hydrogen atoms. At site VI (occupancy = 0.167), the C atom of CO₂ is close to the two oxygen atoms from carboxylate groups of the $[\text{Cu}_2(\text{O}_2\text{CR})_4]$ paddlewheel with distances of $3.30(1)$ – $3.34(5) \text{ \AA}$. Overall, the effects of –NO₂ groups on CO₂ binding are two-fold: (i) polarising neighbouring phenyl C–H bonds *via* the conjugate effect of the aromatic ring bound to electron-withdrawing –NO₂ groups (site I), and (ii) creating additional adsorption sites *via* direct dipole/quadrupole interaction of –NO₂ with CO₂ (site IV).

In situ synchrotron FT-IR micro-spectroscopy of MFM-102-NO₂

To investigate further the nature of host–guest interactions, *in situ* synchrotron FT-IR micro-spectroscopy was conducted on a single crystal of activated MFM-102-NO₂. FTIR spectra were collected as a function of CO₂-loading by increasing the partial pressure of CO₂ in N₂ from 0 to 1.0 bar (ppCO₂) (Fig. 5a). Gaseous CO₂ has three fundamental vibrational modes: the symmetric C=O stretching mode ν_1 (1388 cm^{-1}), a doubly-degenerate bending mode ν_2 (667 cm^{-1}) and an asymmetric stretching vibration ν_3 (2349 cm^{-1}) (Table S1†).²⁹ The $\nu_1 + \nu_3$ (3714 cm^{-1}) and $2\nu_2 + \nu_3$ (3612 cm^{-1}) combination bands of CO₂ (Fig. 5a) were used to monitor CO₂ sorption as the fundamental anti-symmetric stretch at $\sim 2348 \text{ cm}^{-1}$ saturates at ppCO₂ above 0.2 bar. On adsorption, a combination of electrostatic and dispersion forces between CO₂ and the pore surface weakens the C=O bonds in CO₂, leading to the observed redshift of IR bands of adsorbed CO₂ to lower frequencies (3700 and 3600 cm^{-1} , respectively) compared to those observed in gas phase (Table S1†). If CO₂ strongly coordinates to an open metal





Fig. 5 (a) IR spectra showing the adsorption of CO₂ into MFM-102-NO₂ and demonstrating the growth in $\nu_1 + \nu_3$ and $2\nu_2 + \nu_3$ combination bands for CO₂ near 3700 cm^{-1} and 3600 cm^{-1} . (b) Changes in intensity and broadening of the N=O asymmetric stretching vibration with CO₂ loading. (c) INS spectra for activated MFM-102-NO₂ and MFM-102-NO₂ with CO₂ loading. (d) Difference INS plot, derived by subtracting INS spectra for CO₂-loaded MFM-102-NO₂ and bare MFM-102-NO₂ spectra. (e) and (f) are the same as (c) and (d), respectively, but replacing MFM-102-NO₂ with MFM-102-NH₂.

site, the molecular symmetry is lowered and the degeneracy of the ν_2 bending mode is removed, splitting the band into two peaks.³⁰ Three IR spectra of the activated, 10% CO₂- and 100% CO₂-loaded MFM-102-NO₂ reveal the changes in the peak at 660 cm^{-1} . This peak shows a significant increase in intensity at 10% CO₂ loading, and broadens and splits into two peaks at

657 cm^{-1} and 663 cm^{-1} at 100% CO₂ loading (Fig. S7a†). The IR band of the host framework reveals some interesting features. There is a continuous red shift of the band at 1670 cm^{-1} (the C=O stretching mode of -COO groups³¹) with increasing CO₂ loading, consistent with the interactions between CO₂ molecules and [Cu₂(O₂CR)₄] paddlewheel units (site VI, Fig. S7b†). An

apparent change in the peak shape and intensity at 1537 cm^{-1} (N–O asymmetric stretching mode in the $-\text{NO}_2$ group³²) suggests dipole/quadrupole interaction between the $-\text{NO}_2$ groups and adsorbed CO_2 molecules (Fig. 5b). In the low energy regions, the peak at 1025 cm^{-1} (corresponding to C–H out-of-plane wagging³³) gradually decreases in intensity with increasing CO_2 loading, while the peak at 1005 cm^{-1} grows and shifts to lower energy (Fig. S7c†). These changes in FTIR spectra are in excellent agreement with the presence of multiple interactions between the framework and CO_2 molecules as observed by the NPD experiment.

Inelastic neutron scattering (INS) studies of CO_2 -loaded MFM-102- NO_2 and MFM-102- NH_2

To gain further insight into the host–guest dynamics of CO_2 -loaded MFM-102- NO_2 , *in situ* INS has been investigated. The calculated INS spectrum of bare MOF was found to be in good agreement with the experimental INS data (Fig. S8†) leading to assignment of all the vibrational modes. In the INS spectrum of CO_2 -loaded MFM-102- NO_2 , all the INS peaks shift slightly to higher energy, attributed to a stiffening effect of the host–guest lattice on CO_2 adsorption (Fig. 4c). There are changes in the peak intensity at 164 and 193 meV, corresponding to the symmetrical and asymmetrical stretching of $-\text{NO}_2$ groups. The various distortion motions of the phenyl rings (83 meV), out-of-plane C–H bending on the isophthalate rings (116 meV) and in-plane C–H bending on phenyl rings (136 meV) increase in intensity. These results confirm the important role of $-\text{NO}_2$ and $-\text{CH}$ groups on the adsorption of CO_2 . Similarly, the difference INS spectra of CO_2 -adsorbed MFM-102- NH_2 also show changes in intensity of the peaks at 80, 117, 119 meV, originating from various in-plane deformational vibrations of the phenyl rings and the wagging motion of aromatic C–H groups. These changes are attributed to the reduction of the motion of aromatic C–H groups with the introduction of CO_2 into the framework.

Conclusions

We report a comprehensive investigation of the adsorption and binding of CO_2 in four iso-reticular MOFs with varying functional groups. Introduction of $-\text{NO}_2$ group to the parent MOF, MFM-102, leads a 15% reduction on the BET surface area but a 36% enhancement on the CO_2 adsorption capacity at 273 K and 1.0 bar. NPD analysis of CO_2 -loaded MFM-102- NO_2 reveals cooperative binding of CO_2 to $-\text{CH}$ hydrogen bond donors that is enhanced by the electron withdrawing effects of the $-\text{NO}_2$ groups that decorate pore walls. In addition, direct interaction of CO_2 with the open metal sites and the $-\text{NO}_2$ groups is observed, thus enhancing further interaction of the MOF with CO_2 . The *in situ* spectroscopic studies using INS and FTIR spectroscopy establish that adsorbed CO_2 molecules interact strongly with the $-\text{NO}_2$ and $-\text{CH}$ groups of MFM-102- NO_2 , with apparent shifts and changes of intensity of N=O and C–H vibrational bands on CO_2 loading. This work provides a fundamental understanding of the effect of the $-\text{NO}_2$ group on CO_2

adsorption, and the information gained here provides further insights into the development of materials showing improved gas binding *via* specific interaction with ligand sites within the MOF structure.

Conflicts of Interest

The authors declare no competing interests.

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