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.

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 adsorption.
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-Kα radiation (λ = 1.5406 Å) 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 at 373 K over 3 h. 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. 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 × 20 μm 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 crystalline in the trigonal space group R3m. The framework is built from Cu3(O2CR)4 paddlewheel units in which two Cu⁺ cations are bridged by four carboxylate groups surrounding the [Cu–…Cu] axis and two terminal H2O molecules at axial positions to form a [Cu3(O2CR)4(OH)2] node. These Cu3(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 Cu3(O2CR)4 paddlewheels and six linkers to give a spherical shape of 15 Å diameter. Cage B is constructed of twelve Cu3(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
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
Adsortion 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-Bai12 [5.0], ZJNU-81(5.5), ZJNU-82 (5.4), ZJNU-83 (4.9), ZJU-15 (4.4) (ref. 22) and ZJNU-57 (5.5), but which do not show NBO topologies.

The isosteric heats of adsorption (Qₑst) of CO₂ were calculated using virial method based on isotherm data at 273 and 298 K (Fig. 2c). The values for Qₑst 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 Qₑst steadily reduce in all four cases. Interestingly, the Qₑst 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 298 K and 1 bar (Fig. 2b). The in situ NPD data indicates the presence of additional binding sites in the decorated MOFs.
a loading of 2.0 CO$_2$/Cu. NPD data for the desolvated complex confirm the complete removal of guest solvents, including coordinated H$_2$O molecules on the Cu sites, and no significant structural distortion is observed compared to the parent solvated material. A loading of 2.0 CO$_2$/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 CO$_2$ molecules, which after further development by Rietveld refinement, allowed unambiguous determination of gas positions, orientations and crystallographic occupancies within each sample.

MFM-102-NO$_2$ displays six binding sites for CO$_2$ (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, CO$_2$ forms supramolecular interactions to aromatic –CH group from two adjacent NO$_2$-substituted phenyl rings [O$_{CO_2}$–H–C= 2.13(5), 2.42(8) Å]. It is noteworthy that –NO$_2$ is a strong electron-withdrawing groups which leads to

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**Table 1** Comparison of CO$_2$ uptakes in selected Cu-MOFs of NbO topology

<table>
<thead>
<tr>
<th>MOFs</th>
<th>CO$_2$ uptake, 273 K (cm$^3$ g$^{-1}$)</th>
<th>CO$_2$ uptake, 298 K (cm$^3$ g$^{-1}$)</th>
<th>$V_p$ pore volume (cm$^3$ g$^{-1}$)</th>
<th>BET area (m$^2$ g$^{-1}$)</th>
<th>$Q_m$ (kJ mol$^{-1}$)</th>
<th>Ref.</th>
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<tr>
<td>ZJNU-44</td>
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<tr>
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<td>0.894</td>
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<td>—</td>
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<td>1.000</td>
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polarisation of adjacent –CH moieties. These –CH groups therefore show enhanced acidity and thus act as effective hydrogen bond donors to CO$_2$ molecules. Site II and III (occupancy = 0.49 and 0.28, respectively) reside at the open Cu(II) centre [O$_{\text{CO2}}$⋯Cu = 2.27(7) Å and 3.24(7) Å for site II and III, respectively]. Site IV (occupancy = 0.28) is stabilised by the dipole/quadrupole interaction between O(6$^-$) of the –NO$_2$ group from 2 neighbouring phenyl rings and the C(6$^-$) centre of CO$_2$ with distances of 3.20(6) and 2.87(9) Å. Site V (occupancy = 0.20) was found close to the isophthalate phenyl ring [O$_{\text{CO2}}$⋯–HC$^-$ = 1.72(9) Å] and the NO$_2$-decorated phenyl ring [O$_{\text{CO2}}$⋯–HC$^-$ = 1.91(4) Å] stabilised by interactions with aromatic hydrogen atoms. At site VI (occupancy = 0.167), the C atom of CO$_2$ is close to the two oxygen atoms from carboxylate groups of the [Cu$_2$(O$_2$CR)$_4$] paddlewheel with distances of 3.30(1)–3.34(5) Å. Overall, the effects of –NO$_2$ groups on CO$_2$ binding are two-fold: (i) polarising neighbouring phenyl C–H bonds via the conjugate effect of the aromatic ring bound to electron-withdrawing –NO$_2$ groups (site I), and (ii) creating additional adsorption sites via direct dipole/quadrupole interaction of –NO$_2$ with CO$_2$ (site IV).

In situ synchrotron FT-IR micro-spectroscopy of MFM-102-NO$_2$

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-NO$_2$. FTIR spectra were collected as a function of CO$_2$-loading by increasing the partial pressure of CO$_2$ in N$_2$ from 0 to 1.0 bar (ppCO$_2$) (Fig. 5a). Gaseous CO$_2$ has three fundamental vibrational modes: the symmetric C=O stretching mode $n_1$ (1388 cm$^{-1}$), a doubly-generate bending mode $v_2$ (667 cm$^{-1}$) and an asymmetric stretching vibration $v_3$ (2349 cm$^{-1}$) (Table S1†). The $v_1 + v_3$ (3714 cm$^{-1}$) and $2v_2 + v_3$ (3612 cm$^{-1}$) combination bands of CO$_2$ (Fig. 5a) were used to monitor CO$_2$ sorption as the fundamental anti-symmetric stretch at ~2348 cm$^{-1}$ saturates at ppCO$_2$ above 0.2 bar. On adsorption, a combination of electrostatic and dispersion forces between CO$_2$ and the pore surface weakens the C=O bonds in CO$_2$, leading to the observed redshift of IR bands of adsorbed CO$_2$ to lower frequencies [3700 and 3600 cm$^{-1}$, respectively] compared to those observed in gas phase (Table S1†). If CO$_2$ strongly coordinates to an open metal
site, the molecular symmetry is lowered and the degeneracy of the $v_2$ bending mode is removed, splitting the band into two peaks. Three IR spectra of the activated, 10% CO$_2$ and 100% CO$_2$-loaded MFM-102-NO$_2$ reveal the changes in the peak at 660 cm$^{-1}$. This peak shows a significant increase in intensity at 10% CO$_2$ loading, and broadens and splits into two peaks at 657 cm$^{-1}$ and 663 cm$^{-1}$ at 100% CO$_2$ 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 groups$^{33}$) with increasing CO$_2$ loading, consistent with the interactions between CO$_2$ molecules and [Cu$_3$(O$_2$CR)$_4$]$_x$ 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 –NO\(_2\) group\(^{32}\)) suggests dipole/quadrupole interaction between the –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 wagging\(^{33}\)) 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 –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 –NO\(_2\) and –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 –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 –CH hydrogen bond donors that is enhanced by the electron withdrawing effects of the –NO\(_2\) groups that decorate pore walls. In addition, direct interaction of CO\(_2\) with the open metal sites and the –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 –NO\(_2\) and –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 –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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Notes and references