Reversible coordinative binding and separation of sulphur dioxide in a robust metal-organic framework with open copper sites

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Emissions of sulphur dioxide (SO\textsubscript{2}) from flue gas and marine transport have detrimental impacts on the environment and human health, but SO\textsubscript{2} is also an important industry feedstock if it can be recovered, stored and transported efficiently. Here we report the exceptional adsorption and separation of SO\textsubscript{2} in a new porous material, [Cu\textsubscript{2}(L)] (H\textsubscript{4}L = 4',4'''- (pyridine-3,5-diy1)bis([1,1'-biphenyl]-3,5-dicarboxylic acid), MFM-170. MFM-170 exhibits fully reversible SO\textsubscript{2} uptake of 17.5 mmol g\textsuperscript{-1} at 298 K, 1.0 bar, and the SO\textsubscript{2} binding domains for trapped molecules within MFM-170 have been determined. Significantly, we report the first example of reversible co-ordination of SO\textsubscript{2} to open Cu(II) sites in a porous material, contributing to excellent adsorption thermodynamics and selectivities for SO\textsubscript{2} binding, as well as facile regeneration of MFM-170 post adsorption. MFM-170 is stable to water, acid and base and shows significant promise for the dynamic separation of SO\textsubscript{2} from simulated flue gas mixtures, as confirmed by breakthrough experiments.

The use of fossil fuels is a major contributer to many serious environmental issues, but transition to clean energy sources remains challenging as new technologies take time to fully develop. A significant problem is the release of SO\textsubscript{2}, for which antrophogenic sources account for >87\% of global emissions.\textsuperscript{1} SO\textsubscript{2} has detrimental effects on the environment and human health, but is also an important feedstock for the production of sulphuric acid. Furthermore, trace amounts of SO\textsubscript{2} can greatly reduce the activity of amine-based scrubbers for CO\textsubscript{2} from flue gas,\textsuperscript{2} as well as irreversibly poisoning catalysts for selective NO\textsubscript{x} reduction\textsuperscript{3} and CH\textsubscript{4} combustion.\textsuperscript{4}

In recent years, there has been growing interest in the development of dry regenerable sorbents for SO\textsubscript{2} operating under ambient conditions.\textsuperscript{5,7} These materials offer advantages over existing wet flue gas desulphurisation (FDG) technologies by reducing energy and water requirements and minimising the generation of solid and liquid waste. Importantly, regeneration of sorbents allows recovery of saleable SO\textsubscript{2}, which can be utilised further via conversion to elemental sulphur or sulfuric acid. Regenerable SO\textsubscript{2} sorbents are often used for scrubbing of sulphur by absorption of acid plant tail gases, as well as smelter off-gases (containing up to 8\% SO\textsubscript{2}), allowing the recovered SO\textsubscript{2} to be cycled to the front end of the plant.\textsuperscript{8} These processes are typically based on alkaline solutions, which require high temperatures and/or further reaction for regeneration. Desirable properties of solid sorbents operating via pressure swing adsorption (PSA) mechanisms include: (i) high SO\textsubscript{2} capacity, (ii) rapid sorption rate, (iii) low attrition rate (no loss of SO\textsubscript{2} capacity over many cycles), (iv) ease of regeneration, and (v) high selectivity. High capacity sorbents for SO\textsubscript{2} can also be used for safe transportation of recovered gaseous SO\textsubscript{2} under ambient conditions, without the large energy demands required for pressurisation to liquid SO\textsubscript{2} or reduction to solid elemental sulphur.

Porous metal-organic frameworks (MOFs) are emerging sorbents that have been studied extensively for uptake and separation of a wide variety of gases, notably CO\textsubscript{2}, H\textsubscript{2} and hydrocarbons,\textsuperscript{9,14} but their application to SO\textsubscript{2} capture has been hindered by the toxic and highly corrosive nature of this substrate. To date, several MOFs have been tested as SO\textsubscript{2} adsorbents (Table 1, Fig 2),\textsuperscript{15-25} but many exhibit limited stability and/or reversibility under near-ambient conditions. Current top-performing MOFs for SO\textsubscript{2}
adsorption at 298 K and 1.0 bar include MFM-202a (10.2 mmol g\(^{-1}\))\(^{18}\) and SIFSIX-1-Cu (11.0 mmol g\(^{-1}\))\(^{16}\). The former is subject to an irreversible phase change on SO\(_2\) uptake, whilst the steep uptake of the latter may render it unfeasible for practical PSA applications.\(^{26,27}\) Indeed, a trade-off often exists between the uptake at low-pressure and the energy cost of system regeneration. Another consideration is that sorbents for use in FGD processes must be located upstream of CO\(_2\) scrubbing units, and therefore require high selectivity for SO\(_2\) over CO\(_2\) at low partial pressures of SO\(_2\) (~2000 ppm). Although open metal sites in MOFs can improve gas binding selectivity, the resultant MOFs are often subject to severe framework degradation upon contact with water, precluding their practical applications.\(^{28-31}\) Similarly, coordination of strongly complexing SO\(_2\) molecules to open metal centres can disrupt the linker-metal coordination and cause structural collapse.

Herein, we report the first example of reversible coordinative binding of SO\(_2\) to open Cu(II) sites in a remarkably robust material, MFM-170, leading to optimal adsorption and selectivity for SO\(_2\). Coordination of the pyridyl N-donor to one axial site of the Cu\(_2\)(O\(_2\)CR)\(_4\) paddlewheel unit leads to an unusual (3,36)-connected \(\text{txt}\) framework which, on removal of axial water, affords one open Cu(II) site per Cu\(_2\)(O\(_2\)CR)\(_4\) paddlewheel in MFM-170. Significantly, at 298 K and 1.0 bar, MFM-170 exhibits an unprecedented uptake of SO\(_2\) of 17.5 mmol g\(^{-1}\), which can be fully regenerated at ambient temperature. We have unravelled the high selectivity of MFM-170 for SO\(_2\) and have probed the nature of host-guest binding using \textit{in situ} single crystal X-ray diffraction, FTIR micro-spectroscopy and neutron scattering. Importantly, breakthrough experiments of simulated flue gas mixtures demonstrate that MFM-170 has excellent separation properties, even in the presence of water and at elevated temperatures (up to 348 K). The stability of MFM-170 to wet SO\(_2\) has been confirmed by long duration synchrotron X-ray diffraction experiments. Furthermore, we directly investigate the effect of the open copper sites on SO\(_2\) uptake and selectivity by comparing MFM-170 to the coordinatively saturated parent structure MFM-170-H\(_2\)O, in which H\(_2\)O is retained at the axial Cu(II) site within the Cu\(_2\)(O\(_2\)CR)\(_4\) paddlewheel.

\textbf{Results and Discussions}

\textit{Synthesis and structural analysis of MFM-170-solv}. Solvothermal reaction of a pyridine-containing tetracarboxylate linker 4',4''-(pyridine-3,5-diyl)bis[[1,1'-biphenyl]-3,5-dicarboxylic acid] (H\(_2\)L, Fig. 1a) and Cu(NO\(_3\))\(_2\)-2.5H\(_2\)O in a mixture of DMF and H\(_2\)O (v/v = 5:1) under acidic conditions (HNO\(_3\)) yielded blue octahedral crystals of [Cu\(_2\)(L)(H\(_2\)O)]-6DMF, denoted as MFM-170-H\(_2\)O-solv. Single crystal X-ray diffraction reveals that MFM-170-H\(_2\)O-solv crystallises in the cubic space group \(Im-3m\) to form a rarely observed (3,36)-connected net with \(\text{txt}\) topology (Fig. 1b).\(^{32-34}\) The metal cluster consists of a Cu\(_2\)(O\(_2\)CR)\(_4\) paddlewheel with four isophthalate units occupying the equatorial sites and one pyridyl N-donor from the ligand coordinating to the axial site of one Cu atom. The axial position of the other Cu atom of the Cu\(_2\)(O\(_2\)CR)\(_4\) unit is occupied by a water molecule. The framework is constructed from Cu\(_2\)(RC\(_6\)H\(_4\)(CO\(_2\)))\(_2\)]\(_{24}\) cuboctahedron, which acts as a 36-connected node, joined in a cubic array to six adjacent cuboctahedra by four ligands each (Fig. 1c). The overall framework can be visualised as this smaller cubic net which is connected to a secondary identical net via the 12 corners of the cuboctahedra via Cu-N bonds (Fig. 1d).
Thus, each ligand is a 3-connected node, with two isophthalate moieties that each connect an edge of a cuboctahedron, and one pyridyl N atom which joins a corner of a cuboctahedron.

The interconnected void spaces in MFM-170 can be considered as three distinct cages, denoted as A, B and C (Fig. 1c). The metal-organic cuboctahedra (denoted as cage A) have a dimension of 15.9 Å, comprised of alternating triangular and square faces. Each square face of cage A joins it to a cage B, which is formed by four V-shaped linkers bowing outward to create a prolate pore (width of 16.3 Å; length of 22.2 Å). Cage C is the smallest of the three and connects the triangular faces of cage A, measuring 12.8 Å between opposite triangular faces, and 14.2 Å between opposite C atoms.

Thermal and chemical stability of MFM-170. Thermogravimetric analysis (TGA) of MFM-170-H2O-solv shows thermal stability up to ~620 K, confirmed by variable temperature PXRD analysis (Figs. S4, S8). The chemical robustness of MFM-170-H2O-solv was investigated by exposing an as-synthesised sample to a range of harsh environmental conditions, including suspending the sample in boiling water and aqueous solutions of pH between 2-12. No loss in crystallinity was observed by PXRD after exposure to these conditions (Figs. 4b, S2, S3, S6). More importantly, desolvated MFM-170 can be re-hydrated fully and reversibly to give MFM-170-H2O upon contact with water without loss of crystallinity. Reversible water adsorption isotherms at 293 and 303 K are shown in Fig. S10. To assess the long-term stability of MFM-170 to humid SO2 and water, synchrotron PXRD data were collected for wet SO2-loaded MFM-170 samples every week for 10 weeks (Fig. S7; see SI for further details). No loss of crystallinity or change in the structure of this material was observed (Table S3), confirming the excellent chemical resilience of the framework. The remarkable stability of MFM-170 is attributed to the unusual framework connectivity where the axially-coordinated pyridyl N-donors interlock the two cubic nets and block one of the two axial Cu(II) sites.

Analysis of gas adsorption isotherms of MFM-170 and MFM-170-H2O. Desolvated MFM-170 possesses a BET surface area of 2408 m2 g-1 (consistent with the calculated surface area of 2456 m2 g-1 based upon the crystal structure) and a pore volume of 0.88 cm3 g-1 (calculated from the N2 isotherm at 77 K, Fig. S9), consistent with that (0.87 cm3 g-1; solvent-accessible void space of 61%) derived from the single crystal structure. Significantly, MFM-170 shows an unprecedented SO2 uptake of 19.4 mmol g-1 (or 1.24 g g-1) at 273 K and 1.0 bar (Fig. 3). To the best of our knowledge, this represents the highest known SO2 uptake capacity in porous materials, followed by MFM-601 (16.9 mmol g-1)15, MFM-202a (13.0 mmol g-1)18 and mesoporous silicate MCM-41 (11.6 mmol g-1)35 under the same conditions. The performance of state-of-the-art porous materials under ambient conditions is summarised in Table 1 and Fig. 2, where a general linear relationship between SO2 uptake and BET surface area is observed. MFM-170 exhibits the highest reported SO2 adsorption capacity of 17.5 mmol g-1 at 298 K and 1.0 bar, notably exceeding the current leading MOFs, such as MFM-601 (12.3 mmol g-1)15, SIFSIX-1-Cu (11.0 mmol g-1)16, [Zn2(L1)2(bipy)] (10.9 mmol g-1, at 293 K),17 and Ni(bdc)(ted)0.5 (10.0 mmol g-1).19 At 298 K and 1.0 bar, the volumetric storage density of SO2 in MFM-170 is 307 times that of gaseous SO2 under the same conditions, or 75 times of that of compressed SO2 (P0 = 3.9 bar) in a pressure vessel (packing efficiency and system volume are not taken into consideration). Furthermore, MFM-170 shows high SO2 adsorption
at elevated temperatures (11.6 mmol g−1 at 333 K and 1 bar). Uptake of SO2 in MFM-170 shows a reversible type I isotherm with high uptakes at low pressure (Fig. 3); at 273 K the uptake at 0.03 bar is 6.5 mmol g−1. Despite the high uptake at low pressure, the excellent reversibility of the SO2 isotherms at 273-333 K indicates that MFM-170 can be fully regenerated under pressure-swing conditions. More significantly, no loss of adsorption capacity of SO2 was detected in MFM-170 after 50 adsorption-desorption cycles at 298 K, and PXRD analysis of MFM-170 after these 50 cycles confirms the full retention of crystal structure, reflecting the exceptional chemical and thermal stability of this material (Fig. 4).

To probe the effect of the open metal sites on SO2 uptake, isotherms were measured for the coordinatively saturated parent material, MFM-170·H2O, in which the axial water molecule is retained on the Cu(II) site. The SO2 isotherm of MFM-170·H2O at 273 K shows a reduced but still exceptionally high uptake of SO2 (16.2 mmol g−1) (Fig. S15). The difference in adsorption at 1.0 bar between MFM-170·H2O and MFM-170 corresponds to approximately twice the density of open Cu(II) sites (1.46 mmol g−1), suggesting that the presence of open metal sites has a key role in promoting the SO2 uptake.

In comparison to the high SO2 uptake at 298 K and 1 bar, MFM-170 uptakes only 3.04 mmol g−1 of CO2, 1.33 mmol g−1 of CH4, 0.38 mmol g−1 of CO and 0.28 mmol g−1 of N2 under the same conditions (Figs. 3a, S11-14). The selectivity values of MFM-170 for SO2/CO2, SO2/N2, SO2/CO and SO2/CH4 were calculated from single component isotherms at 298 K (Figs. S19, S20). Due to the negligible interaction of N2 with the framework, MFM-170 exhibits a high IAST selectivity of 944 for an equimolar mixture of SO2/N2 at 1.0 bar. Furthermore, MFM-170 also has high selectivity values of 260, 203 and 35 for SO2/CH4, SO2/CO and SO2/CO2, respectively. More importantly and considering the relatively low concentrations of SO2 present in flue gas, decreasing the SO2:X ratio from 50:50 to 1:99 still affords high selectivity values for SO2/N2 (260) and SO2/CO2 (28). These values are lower than those reported for SIFSIX-2-Cu-i,10 which possesses much narrower pores than MFM-170.

**Determination of the binding domains for adsorbed SO2 molecules in MFM-170 and MFM-170·H2O.** The binding domains of SO2 were studied using *in situ* synchrotron X-ray single crystal diffraction. Structural analysis of desolvated MFM-170 confirms the complete removal of free solvents in the pore and bound water molecules on the Cu(II) sites, generating twelve open Cu(II) sites on the internal surface of cage A in desolvated MFM-170. Refinement of the diffraction data for the SO2-loaded sample at 298 K revealed significant residual electron densities which were sequentially assigned as six distinct binding sites (1-6) in order of decreasing occupancy, giving a formula of [Cu2(L)(SO2)0.67](SO2)4.79 (denoted as MFM-170·5.46SO2) (Fig. 5). Interestingly, the smallest cage C accounts for ~45% of all located SO2 molecules, whilst ~25% is found in the cuboctahedral cage A. No ordered SO2 molecules were located in the largest cage B reflecting the large void space and lack of functional groups lining the pore.

The primary binding site, 1, is situated on a three-fold rotational axis in the triangular window of cage A and has full occupancy. The SSO2 atom points towards the Cu2(O2CR)4 paddlewheel, forming close contacts with two carboxylate O centers [SSO2(δ+)⋯(δ)O =3.16(3) Å]. Simultaneously, the OSO2 atom located in the centre of the window forms a three-fold supplementary interaction to the isophthalate C-H
groups lining the window \([\text{O}_2\text{SO}^\cdots \text{C}] = 4.18(3) \, \text{Å}, <\text{O}^\cdots \text{H}^\cdots \text{C} = 140.5(6)^\circ\). \text{SO}_2(2) is coordinated to the open \text{Cu}(II) site in an end-on manner \([\text{O}_2\text{SO}^2\text{Cu} = 2.28(10) \, \text{Å}]\) with an occupancy of 0.67. The \text{O}_2\text{SO}^2\text{Cu} bond distance is shorter than the sum of van der Waals radius of \text{Cu} and \text{O} (2.92 Å), confirming the formation of a covalent bond. The two \text{O}_2\text{SO}^2 atoms are parallel to the \text{Cu}^\cdots \text{Cu} axis, whilst the \text{S}_2\text{SO}^2 is disordered about a \text{C}_2 axis. Significantly, this is the first crystallographic example of \text{SO}^2 coordination at open metal sites within a MOF structure. Remarkably, the \text{Cu}(II) center is not the most occupied site, which is at least in part due to steric hindrance created by site 1; the twelve \text{Cu}(II) sites line the internal surface of cage \text{A} and are therefore accessed through the square faces as the triangular windows are fully occupied by \text{SO}_2 molecules.

\text{SO}_2(3) (occupancy = 0.47) is located in a crevice between cage \text{B} of one net and a perpendicular cage \text{B} of the second net. This small pocket accommodates interactions with the face of the pyridine ring \([\text{S}_2\text{SO}^2\cdots \text{N}] = 3.48(18) \, \text{Å}]\) and phenyl \text{H} atoms \([\text{O}_2\text{SO}^2\cdots \text{C}^4] = 3.20(4) \, \text{Å}, \text{O}_2\text{SO}^2\cdots \text{C}^{11} = 4.80(4) \, \text{Å}], accounting for \sim 30\% of all located \text{SO}_2 molecules. \text{SO}_2(4) (occupancy = 0.32), is found in cage \text{C} and situated with the \text{S} atom facing the carboxylate oxygens of the paddlewheel \([\text{S}_2\text{SO}^2(\delta^\cdots)\cdots(\delta^\cdots)\text{O}^1 = 3.67(3) \, \text{Å}]\) and interacts with neighbouring phenyl rings \([\text{O}_2\text{SO}^2\cdots \text{C}^7] = 3.70(5) \, \text{Å}, \text{O}_2\text{SO}^2\cdots \text{ring centroid} = 3.26(5) \, \text{Å}]\). \text{SO}_2(5) is found in the square face between cages \text{A} and \text{B} with an occupancy of 0.26. Whilst no significant interaction with the framework was identified, dipole interactions between the adsorbed \text{SO}_2 molecules were observed \([\text{S}_2\text{SO}^2(2\cdots)\cdots \text{O}_2\text{SO}^2(5)] = 2.54(6) \, \text{Å}, \text{O}_2\text{SO}^2(2\cdots)\cdots \text{S}_2\text{SO}^2(6) = 2.88(5) \, \text{Å}]. The least populated site (6) (occupancy = 0.23) is sandwiched between two phenyl rings in cage \text{C} and forms interactions between the \text{S}(\delta^+) and the phenyl π-electrons at distances of 3.28(15) and 3.30(15) Å, measured between the ring centroids and \text{S}_2\text{SO}^2.

We sought to examine the most thermodynamically favoured site \textit{via} controlled desorption of MFM-170-5.46SO_2. Crucially, diffraction data collected for the sample under dynamic vacuum at 298 K showed that almost all adsorbed \text{SO}_2 molecules were removed from the structure of MFM-170, leaving just the \text{Cu}(II)-bound \text{SO}_2(2) with an occupancy of 0.09. This confirms that the \text{Cu}(II) site is indeed the thermodynamically strongest binding site but is sufficiently weak to be almost entirely desorbed on reduction of pressure. Interestingly, DFT calculations indicated that for MFM-74(M) (M = Mg, Ni, Co, Zn), the sites with highest binding energies for \text{SO}_2 were located at the open metal sites.\(^{37}\) For MFM-170 the multi-site cooperative binding between \text{SO}_2 molecules results in an optimal balance of high selectivity and excellent reversibility of the \text{SO}_2 adsorption that is observed. Subsequent brief heating to 400 K fully regenerated MFM-170 without any loss of crystallinity.

To investigate the nature of \text{SO}_2 binding in the absence of open metal sites, a single crystal of MFM-170-H_2O-solv was activated under mild conditions to remove free solvent molecules whilst leaving the axial water molecule bound to the \text{Cu} centre. The resultant MFM-170-H_2O was loaded with 1 bar \text{SO}_2 and subsequent refinement of the diffraction data gave a structure with formula of \([\text{Cu}_2(L)(\text{H}_2\text{O})_{0.79}](\text{SO}_2)_{3.27}\) (denoted MFM-170-H_2O-3.27SO_2). Significantly, of the six \text{SO}_2 molecules previously located in MFM-170-5.46SO_2, four are also present in MFM-170-H_2O-3.27SO_2 (Fig. S26). Clearly, the site Cu(II)-bound \text{SO}_2(2) was absent in MFM-170-H_2O-3.27SO_2, and as \text{SO}_2(2) is a primary
site of interaction for SO$_2$(5), the latter was not located either. However, overall the structural analysis shows that saturation of the copper sites in MFM-170 with H$_2$O does not greatly reduce the SO$_2$ binding capacity, consistent with the retention of high uptake capacity in MFM-170·H$_2$O.

**In situ spectroscopic analysis of host-guest binding dynamics.** In situ FTIR spectroscopic studies were conducted for MFM-170 as a function of SO$_2$ loading (Fig. 6). The growth of a new peak at 1143 cm$^{-1}$ was assigned to the v$_1$ symmetric stretch of adsorbed SO$_2$, which increases as a function of SO$_2$ partial pressure (pp). This symmetric band is red-shifted from 1152 cm$^{-1}$ ($\Delta = -9$ cm$^{-1}$) for free SO$_2$, confirming its interaction with the framework. A second new band, assigned to the v$_3$ asymmetric stretch of adsorbed SO$_2$, grows and red-shifts from 1340 cm$^{-1}$ at 0.01 ppSO$_2$ to 1320 cm$^{-1}$ at 0.10 ppSO$_2$. These bands show larger shifts compared to gas phase SO$_2$ ($\Delta = -41$ cm$^{-1}$ at 0.10 ppSO$_2$), but are consistent with physisorption of SO$_2$.\textsuperscript{37,38}

Significant vibrational changes of the framework were also observed on SO$_2$ adsorption. The carboxylate v$_\text{as}$(COO) mode at 1658 cm$^{-1}$ and v$_\text{c}$(COO) mode at 1470 cm$^{-1}$ of MFM-170 decrease in intensity and are red-shifted to 1648 cm$^{-1}$ ($\Delta = -10$ cm$^{-1}$) and 1462 cm$^{-1}$ ($\Delta = -8$ cm$^{-1}$) at 0.50 ppSO$_2$, respectively. Interestingly, this is distinct from the blue-shifts of these bands observed in previously reported MOFs on SO$_2$ loading.\textsuperscript{19} This is likely due to the lack of open metal sites in those reported structures, and therefore is consistent with interactions of SO$_2$ with the Cu site in MFM-170. Furthermore, a red-shift ($\Delta = -16$ cm$^{-1}$) of the band at 1595 cm$^{-1}$ on SO$_2$ binding, assigned to the pyridine ring vibrational band v(CC/CN), suggests a weakening of the pyridine N-Cu coordination on SO$_2$ adsorption.\textsuperscript{39}

**In situ** INS experiments were conducted for dry and wet MFM-170 to gain further insight into the dynamics of SO$_2$ binding (Figs. 6, S24). Comparison of the spectra of bare MFM-170 and MFM-170·H$_2$O allows clear assignment of peaks assigned to water with a translational mode at 30 meV, rocking mode at 48 meV and wagging and twisting modes at 61 and 66 meV. The peak observed at 8.3 meV in the bare MOF can be attributed to a lattice mode which, on SO$_2$ loading, increases in intensity and shifts to 9.2 meV, suggesting a stiffening effect in MFM-170 on SO$_2$ binding. Overall, there is lack of change to the INS features upon SO$_2$ adsorption in MFM-170, indicating a moderate-to-weak host-guest interaction, fully consistent with the reversibility of SO$_2$ adsorption and full retention of the crystal structure of MFM-170 on regeneration. Upon SO$_2$ loading of MFM-170·H$_2$O, notable spectral changes are observed, attributed to interactions between bound water and SO$_2$ molecules. The broad translational band increases in intensity, whilst the water rocking mode increases in intensity with a blue-shift from 48 to 49 meV. The librational mode at 66 meV also blue-shifts to 67 meV with a decrease in intensity. Importantly, subsequent activation of the SO$_2$-adsorbed MFM-170·H$_2$O at 373 K under vacuum removed all peaks assigned to water, and led to a spectrum consistent with the dry bare MOF, further evidencing the stability of the MOF to humid SO$_2$.

**Dynamic breakthrough separation of SO$_2$ in MFM-170.** To test the effect of humidity on SO$_2$ adsorption in MFM-170, dynamic breakthrough experiments were conducted using gas mixtures of either 99.75% He and 2500 ppm SO$_2$ or 98.25 % He, 1.5 % H$_2$O, 2500 ppm SO$_2$ (Fig. 3c). Due to the experimental set-up, He was used instead of N$_2$ as a non-interacting component (see SI for details). Under dry conditions, SO$_2$ begins to breakthrough at dimensionless time $\tau = 420$ and reaches a maximum by $\tau = 1400$. With the
addition of 1.5% water, MFM-170 exhibits a slightly reduced SO2 retention time at $\tau = 370$. Importantly, three cycles of SO2 breakthrough and desorption (1 x dry cycle and 2 x wet cycles; Fig 3c) confirmed no significant deterioration in performance. To investigate further the separation ability for SO2/CO2, breakthrough experiments were also carried out using simulated flue gas mixtures for a fully-activated sample and a water-saturated sample of MFM-170 (81.6-84.8% He, 15-18% CO2 and 2500-4050 ppm SO2; Fig. 3d). For the dry sample, the breakthrough curve at 298 K shows that CO2 is the first component eluted through the fixed-bed packed of MFM-170 and breaks through at dimensionless time $\tau =14$. In comparison, SO2 was selectively retained by MFM-170 and breaks through much later ($\tau \approx 350$) with maximum output observed by $\tau =1450$. After the breakthrough of SO2, the packed bed was regenerated at 298 K by flowing pure helium through it, and this results in rapid desorption of both CO2 and SO2. No more SO2 was detected in the effluent stream when the temperature was subsequently increased to 423 K, indicating the complete desorption of SO2 and regeneration of MFM-170 at 298 K. Crucially, the ability of MFM-170 to separate SO2 from CO2 in the presence of a large quantity of water was confirmed by repeating the breakthrough experiments with a water-saturated fixed-bed. The column was exposed to a stream of 3% H2O in He until breakthrough and saturation of water was observed. The subsequent breakthrough experiment demonstrated excellent SO2/CO2 separation under these conditions (Fig. 3d). Interestingly, whilst the breakthrough times were slightly decreased for both components than in the above experiments, CO2 is affected more severely with a much steeper breakthrough. Unlike the dry sample, a significant roll-up effect is observed for CO2 under humid conditions, indicating a large displacement of weakly bound CO2 by SO2, likely due to the formation of H2SO3 complexes in the pore. This suggests that the SO2/CO2 separation in MFM-170 could be enhanced under humid conditions. It has been suggested that 313-333 K represents a temperature range that is suitable for purifying flue gas streams from coal-fired powerplants. Therefore, breakthrough experiments were also attempted for an activated packed bed of MFM-170 at elevated temperatures of 323 and 348 K (Fig. S25). Importantly, a very clear separation between CO2 and SO2 is evident at both temperatures, though, as expected, with reduced retention time.

Conclusions

The development of efficient strategies to fully mitigate emissions of SO2 from combustion and to achieve efficient SO2 storage and safe transport remains a fundamental challenge for many industries, power-plants and marine transport sectors. Although emerging MOF materials show great promise as sorbents for a wide range of inert gases, relatively little success has been achieved on the adsorptive removal of SO2, primarily due to the generally limited reversibility and/or stability of MOFs upon contact with highly corrosive SO2. The present work describes a high SO2 uptake of 17.5 mmol g$^{-1}$ at ambient conditions in a remarkably stable MOF with open Cu(II) sites with high selectivity for SO2 over CO2 and N2. The binding sites of SO2 in MFM-170 have been elucidated using in situ single crystal diffraction which revealed the reversible coordination of SO2 at open Cu(II) sites and five other binding sites at crystallographic resolution. Crucially, the open Cu(II) site has been identified as the most thermodynamically favoured binding site for SO2. In addition to static crystallography studies, dynamic
vibrational modes were investigated using INS and FT-IR microscopy as a function of SO\textsubscript{2} loading. The industrial promise of MFM-170 has been demonstrated through dynamic breakthrough experiments which showed efficient separation of SO\textsubscript{2} from simulated flue gas mixtures, even in the presence of water and at elevated temperatures.

**References.**

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Synthesis of MFM-170-solv: [Cu₂(C₂H₅NO)(H₂O)] 6(C₂H₅NO): H₂L (192 mg, 0.36 mmol) and Cu(NO₂)₂·2.5H₂O (298 mg, 1.28 mmol) were dissolved in a solution of DMF:H₂O (48 mL, 5:1) and acidified with conc. HNO₃ (0.3 mL). The solution was heated in a Schott bottle at 80°C for 18 h until blue octahedral crystals precipitated. The activated crystals were then cooled to ca. 300 K before being dosed with 1 bar of SO₂. The locations of the SO₂ molecules could be discerned from the Fourier difference maps at 300 K (MFM-170, MFM-170-0.09SO₂, MFM-170-H₂O and MFM-170-H₂O-3.27SO₂).

Methods

SO₂ safety: All systems involved in the supply, delivery and measurement of SO₂ were rigorously leak tested and used only within range of a SO₂ detection system with a sensitivity of 0.1 ppm. All gases exhausted from experimental apparatus were diluted with a flow of N₂ and fed into fume hood extracts.

Crystal Data for MFM-170-H₂O-solv [Cu₂(C₃₃H₁₇NO₃)(H₂O)₆]: blue octahedron (0.1 x 0.1 x 0.1 mm). Cubic, Im-3m, a = 33.5294(17) Å, V = 37963(7) Å, Z = 24, ρ calc = 0.729 g cm⁻³, T -1.144 mm⁻¹, F(000) = 8413. A total of 45304 reflections were collected, of which 1475 were unique giving R int = 0.153. Final R₁ (wR₂) = 0.0465 (0.1226) with GoF = 1.130. The final difference Fourier extreme were 0.427 and -0.568 eÅ⁻³.

Crystal Data for desolvated MFM-170 [Cu₂(C₃₃H₁₇NO₃): purple octahedron (0.1 x 0.1 x 0.1 mm). Cubic, Im-3m, a = 33.609(2) Å, V = 37694(6) Å, Z = 24, ρ calc = 0.722 g cm⁻³, T -0.568 eÅ⁻³. A total of 42452 reflections were collected, of which 1043 were unique giving R int = 0.197. Final R₁ (wR₂) = 0.039 (0.097) with GoF = 1.045. The final difference Fourier extreme were 0.320 and -0.381 eÅ⁻³.

Crystal Data for MFM-170-5.46SO₂ [Cu₂(C₃₃H₁₇NO₃)(SO₂)₈(H₂O)]: blue octahedron (0.1 x 0.1 x 0.1 mm). Cubic, Im-3m, a = 33.5808(17) Å, V = 37868(6) Å, Z = 24, ρ calc = 1.086 g cm⁻³, T -1.144 mm⁻¹, F(000) = 12448.
A total of 105823 reflections were collected, of which 2202 were unique giving R int = 0.186. Final R1 (wR2) = 0.117 (0.331) with GoF = 1.663. The final difference Fourier extreme were 1.577 and -0.474 eÅ⁻³.

**Crystal Data for MFM-170-0.09SO2 [Cu2(C3H17NO3)(SO2)3]0.5;** blue octahedron (0.1 x 0.1 x 0.1 mm). Cubic, Im-3m, a =33.5458(19) Å, V = 37750(6) Å³, Z = 24, µcalcd = 0.727 g cm⁻¹ µcalcd = 0.890 mm⁻¹, F(000) = 8324. A total of 73416 reflections were collected, of which 1471 were unique giving R int = 0.173. Final R1 (wR2) = 0.0411 (0.092) with GoF = 1.083. The final difference Fourier extreme were 0.517 and -0.474 eÅ⁻³.

**Crystal Data for MFM-170-H2O [Cu2(C3H17NO3)(H2O)10]0.5;** blue octahedron (0.1 x 0.1 x 0.1 mm). Cubic, Im-3m, a =33.4562(16) Å, V = 37448(5) Å³, Z = 24, µcalcd = 0.736 g cm⁻¹ µcalcd = 0.895 mm⁻¹, F(000) = 8376. A total of 110623 reflections were collected, of which 2211 were unique giving R int = 0.0699. Final R1 (wR2) = 0.0565 (0.1799) with GoF = 1.124. The final difference Fourier extreme were 0.702 and -0.458 eÅ⁻³.

**Crystal Data for MFM-170-H2O-3.27SO2 [Cu2(C3H17NO3)(H2O)6.78][SO2]3.27;** blue octahedron (0.1 x 0.1 x 0.1 mm). Cubic, Im-3m, a =33.610(4) Å, V = 37968(12) Å³, Z = 24, µcalcd = 0.951 g cm⁻¹ µcalcd = 1.039 mm⁻¹, F(000) = 10957. A total of 84668 reflections were collected, of which 1720 were unique giving R int = 0.078. Final R1 (wR2) = 0.0947 (0.3006) with GoF = 1.529. The final difference Fourier extreme were 0.909 and -0.618 eÅ⁻³.

A more detailed description of single crystal X-ray diffraction data can be found in the supplementary information.

**Gas adsorption isotherms and breakthrough experiment:** Measurements of SO2 adsorption isotherms (0–1 bar) were performed using a Xemis gravimetric adsorption apparatus (Hiden Isochema, Warrington, UK) equipped with a clean ultrahigh vacuum system. The pressure in the system is accurately regulated by mass flow controllers. Research grade SO2 and He were purchased from AIRLIQUIDE or BOC and used as received. In a typical gas adsorption experiment, 70-100 mg of MFM-170·H2O·solv was loaded into the Xemis, and degassed at 423 K and high dynamic vacuum (10⁻¹⁰ bar) for 1 day to give desolvated MFM-170.

Breakthrough experiments were carried out in a 7 mm diameter fixed-bed tube of 120 mm length packed with 1.5 g of MFM-170 powder (particle size < 5 microns). The total volume of the bed was ca. 5 cm³. The sample was heated at 423 K under a flow of He for 2 days for complete activation. The fixed-bed was then cooled to room temperature (298 K) using a temperature programmed water bath and the breakthrough experiment was performed with streams of SO2 (0.5% diluted in He) and CO2 at atmospheric pressure and room temperature. The flow rate of the entering gas mixture was maintained at 47 mL min⁻¹, and the gas concentration, C, of SO2 and CO2 at the outlet determined by mass spectrometry and compared with the corresponding inlet concentration C₀, where C/C₀ = 1 indicates complete breakthrough. A more detailed description is given in SI.

**Supplementary Information** is available in the online version of the paper.

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**Author Information.** The crystal structures are available free of charge from the Cambridge Crystallographic Data Centre under reference number CCDC-1538125-6, 1538129, 1853512-4. Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests. Correspondence and requests for materials should be addressed to S.Y. (Sihai.Yang@manchester.ac.uk) and M.S. (M.Schroder@manchester.ac.uk).

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**Data availability.** All relevant data are available from the authors, and/or are included with the manuscript.
Fig. 1: Structure of MFM-170 solved from single crystal X-ray data. Views of a) structure of $\text{H}_4\text{L}$; b) the unit cell of MFM-170; c) the simplified structure showing the ‘smaller’ net of MFM-170; d) full structure resulting from connection of the two smaller nets; e) metal-ligand Cages $A$, $B$ and $C$, observed in MFM-170.
Table 1: Comparison of data for SO\textsubscript{2} adsorbents.

| Material                   | BET Surface Area (m\textsuperscript{2} g\textsuperscript{-1}) | Open Metal Site | 1 Bar SO\textsubscript{2} Uptake at 298 K (mmol g\textsuperscript{-1}) | Ref        |
|----------------------------|-------------------------------------------------------------|-----------------|--------------------------------------------------------------------------|------------|
| MFM-170                    | 2,408                                                       | Y               | 17.5                                                                     | This work  |
| MFM-170-H\textsubscript{2}O| 2,003                                                       | N               | 13.0                                                                     | This work  |
| MFM-601                    | 3644                                                        | N               | 12.3                                                                     | 15         |
| SIFSIX-1-Cu                | 1,337                                                       | N               | 11.0                                                                     | 16         |
| [Zn(L\textsubscript{1})\textsubscript{2}(bipy)] | 275\textsuperscript{a}                                      | N               | 10.9\textsuperscript{b}                                                 | 17         |
| MFM-202\textsubscript{a}   | 2,220                                                       | N               | 10.2\textsuperscript{c}                                                 | 18         |
| Ni(bdc)(ted)\textsubscript{3.5} | 1,783                                                      | N               | 10.0                                                                     | 19         |
| Mg-MOF-74                  | 1,475                                                       | Y               | 8.6                                                                      | 19         |
| MFM-300(In)                | 1,071                                                       | N               | 8.3                                                                      | 20         |
| MFM-305                    | 799                                                         | N               | 7.0                                                                      | 21         |
| SIFSIX-2-Cu-i              | 735                                                         | N               | 6.9                                                                      | 16         |
| PI-COF-m                   | 1,003                                                       | n/a             | 6.5                                                                      | 22         |
| SIFSIX-2-Cu                | 3,140                                                       | N               | 6.5                                                                      | 16         |
| [Zn\textsubscript{3}(L\textsubscript{1})\textsubscript{2}(bpe)] | 379\textsuperscript{a}                                     | N               | 6.4\textsuperscript{b}                                                 | 17         |
| PI-COF-m10                 | 831                                                         | n/a             | 6.3                                                                      | 22         |
| PI-COF-m20                 | 548                                                         | n/a             | 5.6                                                                      | 22         |
| PI-COF-m40                 | 279                                                         | n/a             | 5.5                                                                      | 22         |
| MFM-305-CH\textsubscript{3} | 256                                                         | N               | 5.2                                                                      | 21         |
| MFM-600                    | 2281                                                        | N               | 5.0                                                                      | 15         |
| PI-COF-m60                 | 93                                                          | n/a             | 4.7                                                                      | 22         |
| Zn(bdc)(ted)\textsubscript{3.5} | 1,888                                                       | N               | 4.4                                                                      | 19         |
| KAUST-8                    | 250                                                         | Y               | -2.9\textsuperscript{a}                                                | 25         |
| SIFSIX-3-Ni                | 223                                                         | N               | 2.7                                                                      | 16         |
| KAUST-7                    | 280                                                         | N               | -2.6\textsuperscript{a}                                                | 25         |
| Prussian Blue (CoCo)       | 712                                                         | N               | 2.5                                                                      | 23         |
| [Zn(μ-\textsubscript{2}O)(L\textsubscript{1})\textsubscript{3}] | 299\textsuperscript{a}                                     | N               | 2.2\textsuperscript{b}                                                 | 17         |
| FMOF-2                     | 378                                                         | Y               | 2.2                                                                      | 24         |
| SIFSIX-3-Zn                | 250                                                         | N               | 2.1                                                                      | 16         |

\textsuperscript{a} DFT-calculated surface area \textsuperscript{b} 293K. \textsuperscript{c} MFM-202\textsubscript{a} exhibits reversible SO\textsubscript{2} adsorption at 273-303K, but undergoes an irreversible phase change at lower temperatures. \textsuperscript{d} estimated from isotherm
Fig. 2: Comparison of $\text{SO}_2$ uptakes of reported MOFs and COFs at 1.0 bar and 298 K. Plot of $\text{SO}_2$ adsorption (1.0 bar, 298 K) against BET surface area. Open symbols denote the presence of open metal sites in the MOF structure.
Fig. 3: Gas sorption properties of MFM-170. a) Adsorption and desorption isotherms for MFM-170 at 298 K up to 1 bar for SO$_2$ (black), CO$_2$ (red), N$_2$ (blue) and CO (purple); b) SO$_2$ adsorption and desorption isotherms for MFM-170 at 273-333 K up to 1 bar. Wt % is in terms of SO$_2$(g)/MOF(g). c) Breakthrough curves for SO$_2$ at 298 K under dry (solid line) and humid (dashed line) conditions. The consistency in the retention time for SO$_2$ under humid conditions confirms the high stability of MFM-170. Dry conditions: 99.75% He, 2500 ppm SO$_2$; Wet Conditions: 98.25% He, 1.5% H$_2$O, 2500 ppm SO$_2$. Flow rate 26 mL min$^{-1}$. d) Comparison of the binary SO$_2$/CO$_2$ dynamic separations at 298 K under dry (solid line) and humid (dashed line) conditions. The dry sample was first activated under a flow of He at 423 K and the subsequent gas mixture composition was 84.75% He, 15% CO$_2$ and 2500 ppm SO$_2$ at a total flow rate of 26 mL min$^{-1}$. For experiments under humid conditions, the bed was first exposed to a flow of 3% H$_2$O in He until breakthrough of water (not shown). The subsequent gas mixture composition was ~81.6% He, 18% CO$_2$ and 4050 ppm SO$_2$ with a total flow rate of 16 mL min$^{-1}$. Dimensionless time, $\tau$, is equal to $\frac{tu}{\varepsilon L}$, where $t$ is the actual breakthrough time, $u$ is the gas velocity, $\varepsilon$ is the fractional porosity and $L$ is the length of the fixed bed. See Supplementary Information for details.
**Fig. 4. Chemical stability tests for MFM-170.** a) 50 adsorption-desorption cycles for SO$_2$ in MFM-170 at 298 K. No loss of uptake capacity is observed. b) PXRD analysis of MFM-170 exposed to various external conditions. Changes of intensities of Bragg peaks correspond to the inclusion of guest species in the pores of MFM-170. Pawley refinements are shown in the Supplementary Information.
Fig. 5: Positions of SO\textsubscript{2} molecules located within the pores of MFM-170\textcdot5.46SO\textsubscript{2} from \textit{in situ} single crystal XRD. a) Packing of SO\textsubscript{2} with in cages A, B and C. No ordered SO\textsubscript{2} was found in cage B. Size of the coloured balls depicting sites 1-6 are proportional to their occupancy. Site 3 is found in a crevice between two perpendicular cage B and are therefore not shown in the cages. b) Site (colour, occupancy): 1 (orange, 1.00); 2 (purple, 0.670); 3 (red, 0.468); 4 (blue 0.316); 5 (green, 0.262); and 6 (yellow, 0.233). c) Intermolecular interactions between adsorbed SO\textsubscript{2} molecules. SO\textsubscript{2} molecules have been magnified slightly for clarity. Distances are in Å.
Fig 6. *In situ* vibrational spectra of MFM-170. a-c) FT-IR spectra of MFM-170 at various SO\(_2\) loadings up to 0.50 ppSO\(_2\): a) Redshift of carboxylate ν\(_{as}\)(COO) stretching mode at 1658 cm\(^{-1}\) and pyridine ring vibrational band ν(CC/CN) at 1595 cm\(^{-1}\); b) Red shift of ν\(_{as}\)(COO) stretching mode at 1470 cm\(^{-1}\) and the ν\(_3\) asymmetric stretch of adsorbed SO\(_2\); c) growth of a new band at 1143 cm\(^{-1}\) assigned to the ν\(_1\) symmetric stretch of adsorbed SO\(_2\). All FT-IR spectra were collected at 1.0 bar, using N\(_2\) as a balancing gas. The fundamental ν\(_3\) antisymmetric stretch of gas phase SO\(_2\) at 1361 cm\(^{-1}\) saturates at low partial pressures in this experiment, and therefore the region of 1400-1300 cm\(^{-1}\) was only monitored up to 0.10 ppSO\(_2\). d-f) INS spectra of MFM-170: d) Activated MFM-170 and MFM-170\(\cdot\)H\(_2\)O. Additional peaks in MFM-170\(\cdot\)H\(_2\)O are attributed to vibrational modes of water molecules; e) Activated MFM-170 and MFM-170\(\cdot\)SO\(_2\). Minimal difference is observed between the two spectra; f) MFM-170\(\cdot\)H\(_2\)O and MFM-170\(\cdot\)H\(_2\)O\(\cdot\)SO\(_2\). Shifts in water modes are observed indicating H\(_2\)O···SO\(_2\) interactions.