

Exceptional Adsorption and Binding of Sulfur Dioxide in a Robust Zirconium-Based Metal–Organic Framework

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Supporting Information

ABSTRACT: We report a record-high SO₂ adsorption capacity of 12.3 mmol g^{−1} in a robust porous material, MFM-601, at 298 K and 1.0 bar. SO₂ adsorption in MFM-601 is fully reversible and highly selective over CO₂ and N₂. The binding domains for adsorbed SO₂ and CO₂ molecules in MFM-601 have been determined by *in situ* synchrotron X-ray diffraction experiments, giving insights at the molecular level to the basis of the observed high selectivity.

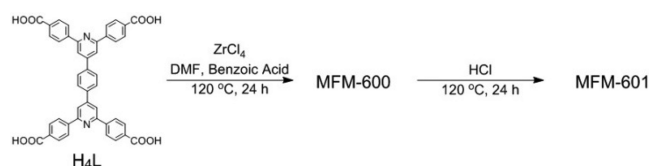
The International Energy Outlook 2017 report produced by the U.S. Energy Information Administration predicts that fossil fuels will account for ~77% of global energy production in 2050, with coal comprising a major component of the overall energy supply.¹ The burning of bituminous, sub-bituminous and lignite coals produces SO₂ at a concentration of between 500 and 3000 ppm, around 95% of which is removed via limestone-scrubbing or the wet-sulfuric-acid processes.² Although these processes are effective, as much as 400 ppm of SO₂ can remain in the exhaust gas, which, when vented to the atmosphere, poses significant health risks and environmental impact.³ Small amounts of SO₂ in flue gas can also react with organo-amines used for CO₂-scrubbing causing permanent loss of activity.⁴ Physisorption of SO₂ by porous materials such as zeolites,⁵ mesoporous silica,⁶ ionic microgels⁷ and activated carbons⁸ using supramolecular host–guest interactions is a promising approach that can give high selectivity, reversibility and low energy penalty for system regeneration. However, these materials generally suffer from low adsorption capacities and exposure to SO₂ often leads to irreversible structural degradation.

Metal–organic frameworks (MOFs) are emerging porous materials constructed from metal clusters with organic linkers,⁹ and their tuneability makes them interesting candidates for many applications.¹⁰ Although much work has focused on the study of gas separations in MOFs, very little effort has been devoted to the sequestration of SO₂,¹¹ since it often leads to severe structural degradation of the material and/or irreversible uptake. Here, we report the exceptional adsorption and reversible binding of SO₂ in two Zr-based MOFs, MFM-600 and MFM-601. MFM-601 is obtained by postsynthetic removal of a linker in an ordered, predictable pattern from

MFM-600. This is accompanied by significant enhancement of gas adsorption in MFM-601, notably simultaneous increases in SO₂ uptake (146%) and selectivity over CO₂ and N₂. Significantly, MFM-601 shows a SO₂ adsorption capacity of 12.3 mmol g^{−1} at 298 K and 1.0 bar, representing the highest value observed to date in porous materials under the same conditions. In addition, the binding domains for adsorbed CO₂ and SO₂ in MFM-610 have been determined by *in situ* synchrotron X-ray diffraction.

4,4',4'',4'''-(1,4-Phenylenebis(pyridine-4,2,6-triyl))tetra benzoic acid (H₄L, Scheme 1) was prepared via a three-step

Scheme 1. Synthesis of MFM-601 from 4,4',4'',4'''-(1,4-Phenylenebis(pyridine-4,2,6-triyl))tetra benzoic Acid (H₄L)



synthesis (Scheme S1). [Zn₆(μ₃-O)₄(μ₃-OH)₄(OH)₄(L)₂-(H₄L)_{0.7}] (MFM-600) was synthesized by heating a mixture of ZrCl₄, H₄L and benzoic acid as modulator in DMF at 120 °C for 24 h and was isolated as plate-shaped colorless single crystals. The single crystal X-ray structure shows that MFM-600 contains [Zr₆(μ₃-O)₄(μ₃-OH)₄(OH)₄]⁸⁺ clusters, first observed in UiO-66.¹² In this cluster the six Zr^{IV} ions form an octahedron with the 8 faces each capped by a μ₃-O or μ₃-OH. Eight of the edges of the octahedron are bridged by L^{4−} linkers via bidentate carboxylate groups with the remaining four equatorial edges each bridged by a H₄L linker (occ = 0.35) that is monodentate to each equatorial Zr(IV) center and bound through the C=O moiety of the carboxylate groups (Figure S4). The coordination sphere at the equatorial Zr(IV) centers is completed by a terminal OH[−] ligand.

MFM-600 was treated with an 8 M solution of HCl, which led to a structural phase transition to MFM-601, [Zn₆(μ₃-O)₄(μ₃-OH)₄(OH)₄(H₂O)₄(L)₂], the structure of which was determined by high resolution synchrotron powder X-ray diffraction with the {Zr₆} node assigned to the MIX-staggered

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proton topology.¹³ In MFM-601, the H₄L monodentate linkers from the equatorial positions of the {Zr₆} cluster have been removed (Figure 1) and replaced with terminal H₂O

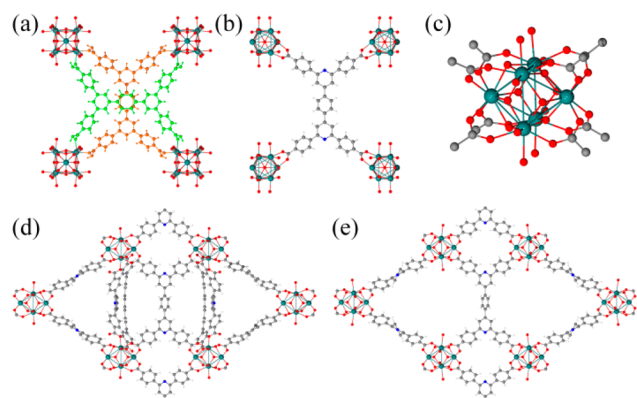


Figure 1. Views of (a) disordered H₄L linker present in MFM-600; (b) “fully bound” L^{4−} linker present in MFM-600 and MFM-601; (c) {Zr₆} node present in MFM-600 and MFM-601; (d) structure of MFM-600; (e) structure of MFM-601.

molecules. As a result, the alternating linkage between the [Zr₆(μ₃-O)₄(μ₃-OH)₄(OH)₄(H₂O)₄]⁸⁺ cluster and the L^{4−} linker yields two types of channels of ~9 Å (cylinder-shaped) and ~12 Å (waterdrop-shaped) diameter running through the structure of MFM-601 along the *c*-axis. This leads to an increase in the BET surface area from 2281 m²g^{−1} for MFM-600 to 3644 m²g^{−1} for MFM-601, a rise of ~60%. We note that MFM-601 has recently been reported (as BUT-15) as an adsorbent for Fe^{III} ions in water.¹⁴ Acid treatment has been previously reported as an efficient approach to remove free ligands such as surplus benzoic acid modulator in Zr-based MOFs¹⁵ and as a method of improving the N₂ uptake in UiO-66.¹⁶

Sorption isotherms of SO₂, CO₂ and N₂ were measured on desolvated samples. As expected, the higher BET surface area of MFM-601 allows a greater total uptake of all three gases. MFM-600 displays a two-step Type-IV isotherm for SO₂ with an excess uptake of 5.0 mmol g^{−1} at 298 K and 1.0 bar. Interestingly, in comparison, MFM-601 exhibits a type-I isotherm for SO₂ leading to an exceptionally high uptake of 12.3 mmol g^{−1} (146% enhancement) at 298 K and 1.0 bar, representing the highest value observed in porous solids and notably higher than a range of best-behaving SO₂ sorbents (Table S1). Importantly, no loss of adsorption capacity of SO₂ was observed in MFM-601 over five cycles of adsorption/desorption (Figure S17b). The SO₂ uptake in MFM-601 is further increased to 16.9 mmol g^{−1} at 273 K and 1.0 bar (Figure S17a). MFM-601 shows fully reversible adsorption of SO₂ at both 273 and 298 K, allowing the total evacuation of the framework upon desorption under pressure-swing conditions (Figure 2) with no structural phase change or framework collapse, as evidenced by the postsorption PXRD patterns (Figure S8). This is in contrast to the current leading SO₂ sorbent, MFM-202a, which undergoes irreversible phase change to MFM-202b upon SO₂ adsorption,¹⁷ and Ni(bdc)-(ted)_{0.5} and MOF-74(Mg), which release up to 40% of the captured SO₂ upon desorption.¹⁸ The desorption of SO₂ from SIFSIX-1-Cu has not been reported.^{20a} Interestingly, the high uptake of SO₂ in MFM-601 does not correlate with equivalent increases in uptake of CO₂ or N₂. The uptake of CO₂ in MFM-

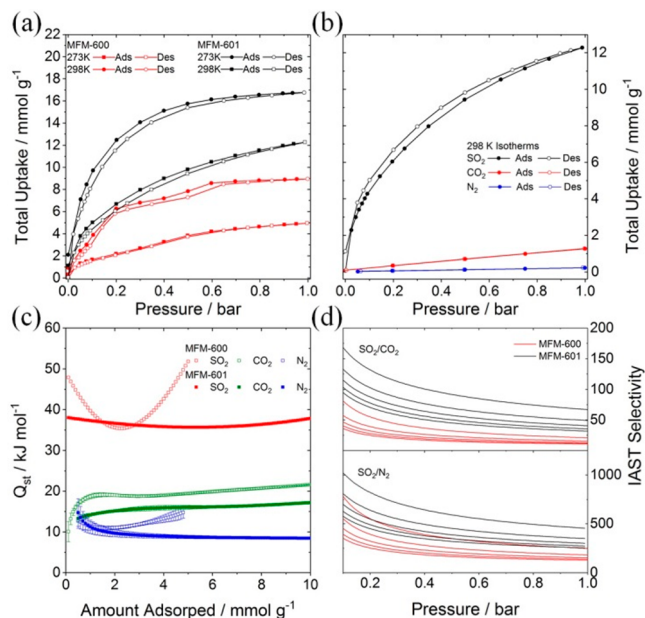


Figure 2. (a) SO₂ sorption isotherms in MFM-600 and MFM-601. (b) Comparison of SO₂, CO₂ and N₂ isotherms at 298 K in MFM-601. (c) *Q*_{st} values for SO₂, CO₂ and N₂ in MFM-600 and MFM-601. (d) IAST selectivities of SO₂/CO₂ and SO₂/N₂ at 298 K in MFM-600 and MFM-601 as a function of substrate ratios.

601 exhibits a type V isotherm with slow initial uptake at low pressures before the uptake increases more rapidly at intermediate pressures reaching a plateau at ~24 mmol g^{−1} at 30 bar and 298 K (Figure S15). Adsorption of N₂ in MFM-601 follows a type-I isotherm with a total uptake of ~12 mmol g^{−1} at 80 bar 298 K. Strikingly, despite the high uptake of SO₂ at 298 K and 1.0 bar, under the same conditions the CO₂ uptake in MFM-601 compares poorly to other MOFs in the literature,¹⁹ with a total CO₂ uptake of only 1.3 mmol g^{−1} and a negligible N₂ uptake. The isosteric heat of adsorption (*Q*_{st}) for SO₂, CO₂ and N₂ in MFM-600 and MFM-601 are compared in Figure 2c. The same trend is followed for both MOFs with N₂ having the lowest *Q*_{st}, followed by CO₂ and then SO₂ with the highest *Q*_{st}. Interestingly the *Q*_{st} values for SO₂ in MFM-600 are generally higher than in MFM-601, consistent with the smaller cages of MFM-600 affording greater overlap potentials between SO₂ molecules and the pore interior. In MFM-600 at low loadings SO₂ interacts with binding sites at the MOF surface. As these sites become less available *Q*_{st} reduces, but once SO₂ fills the pore, SO₂–SO₂ dipole interactions lead to an increase in *Q*_{st}.

Analysis of adsorption selectivities at 298 K using ideal adsorbed solution theory (IAST) shows that the transformation of MFM-600 to MFM-601 is accompanied by an increase in selectivity of SO₂ over both CO₂ and N₂ (Figure 2). The selectivity for equimolar mixtures of SO₂/CO₂ and SO₂/N₂ in MFM-601 at 298 K are 32 and 255, respectively, comparable with the leading MOFs in the literature.²⁰ The capability of selective separation of SO₂ from gas mixtures using fixed-bed packed with MFM-601 has been confirmed by dynamic breakthrough experiments (Figure 3 and SI).

In order to examine the origins of the preferential adsorption of SO₂ over CO₂ in MFM-601, *in situ* synchrotron X-ray powder diffraction studies were carried out (Figures 4 and 5). Rietveld refinement of PXRD data for CO₂-loaded MFM-601

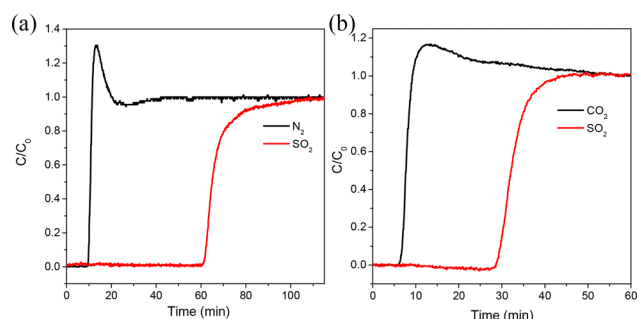


Figure 3. Breakthrough curves of 2500 ppm of SO₂ diluted in (a) 1:1 He:N₂ and (b) 1:1 He:CO₂ through a fixed-bed packed with MFM-601 at 298 K and 1 bar.

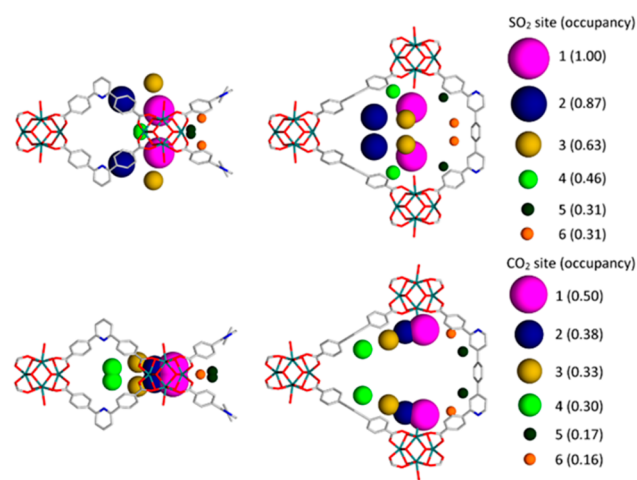


Figure 4. View of SO₂ (top) and CO₂ (bottom) in MFM-601; the size of the colored balls represent the occupancy at each site. Positions refined by *in situ* synchrotron PXRD.

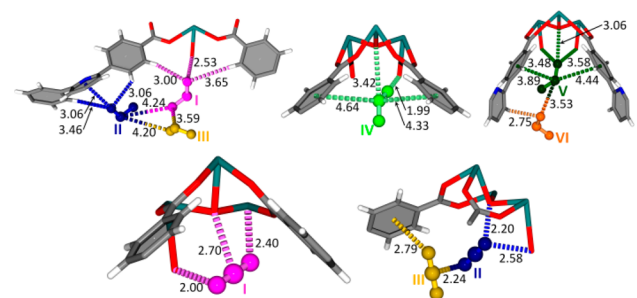


Figure 5. Binding sites of SO₂ (top) and CO₂ (bottom) in MFM-601.

at 200 K revealed six binding sites within the pores, giving a formula of $[\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{OH})_4(\text{L})_2][\text{CO}_2]_{5.52}$. The primary binding site of CO₂^I in MFM-601 (occupancy = 0.50) overlaps with the terminal oxygen of the zirconium cluster due to the removal of four H₂O molecules from each {Zr₆} cluster upon activation, leaving a terminal hydroxyl and an open zirconium site on each of the four equatorial edges of the $[\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{OH})_4]^{8+}$ cluster, thus accounting for the 0.5 occupancy of the terminal oxygen and CO₂^I. This positioning of CO₂^I puts it within close proximity to the open zirconium site [$\text{O}_{\text{CO}_2}\cdots\text{Zr} = 2.40(10)$ Å] as well as being within binding distance of the terminal hydroxyl [$\text{C}_{\text{CO}_2}\cdots\text{O} = 2.00(24)$ Å] and the $\mu_3\text{-O}$ of the Zr₆O₈ cluster [$\text{C}_{\text{CO}_2}\cdots\mu_3\text{-O} = 2.70(11)$ Å], similar to that observed in UiO-66.²¹ CO₂^{II} (occupancy =

0.38) and CO₂^{VI} (occupancy = 0.16) occupy similar environments either side of the zirconium cluster in that they are both in close proximity to the terminal hydroxyl [$\text{O}_{\text{CO}_2}\cdots\text{O} = 2.58(23)$ Å] and [$\text{O}_{\text{CO}_2}\cdots\text{O} = 3.31(44)$ Å], respectively, as well as the $\mu_3\text{-O}$ [$\text{O}_{\text{CO}_2}\cdots\mu_3\text{-O} = 2.20(10)$ Å] and [$\text{O}_{\text{CO}_2}\cdots\mu_3\text{-O} = 3.37(14)$ Å], respectively. The remaining sites, CO₂^{III} (occupancy = 0.33), CO₂^{IV} (occupancy = 0.30) and CO₂^V (occupancy = 0.17), are not within binding distance of the {Zr₆} cluster but are closer to the L⁴⁻ linker. CO₂^{III} is near the phenyl ring of the linker [$\text{O}_{\text{CO}_2}\cdots\text{Ph} = 2.79(8)$ Å] whereas CO₂^{IV} and CO₂^V are close to the pyridyl rings [$\text{O}_{\text{CO}_2}\cdots\text{N}_{\text{Pyr}} = 4.38(5)$ Å] and [$\text{O}_{\text{CO}_2}\cdots\text{H}_{\text{Pyr}} = 3.91(25)$ Å], respectively. All CO₂ sites are within intermolecular binding distance of one another with C \cdots O distances between 2.18(14) and 4.38(12) Å. However, no ordered CO₂ molecule was present at the center of the large pore of MFM-601, thus confirming that CO₂ positioning is dominated by host–guest interactions.

The crystal structure of SO₂-loaded MFM-601 at 298 K also shows six binding sites within the pore giving a formula of $[\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{OH})_4(\text{H}_2\text{O})_4(\text{L})_2][\text{SO}_2]_{10.71}$. The three SO₂ positions with the highest occupancies, SO₂^I (occupancy = 1.00), SO₂^{II} (occupancy = 0.87) and SO₂^{III} (occupancy = 0.63) form an intermolecular dipole bonding network with S \cdots O bond distances between 3.59(7) and 3.24(6) Å, thus exhibiting efficient packing as exhibited by the similarity to the intermolecular distances observed in solid SO₂.²² The highest occupied SO₂ position (SO₂^I) is located near the terminal hydroxyl of the {Zr₆} cluster [$\text{O}_{\text{SO}_2}\cdots\text{O} = 2.53(6)$ Å] with a similar SO₂-hydroxyl interaction to that observed in MFM-300(In).^{20b} SO₂^{II} sits away from the zirconium cluster, close to the pyridyl group of the L⁴⁻ linker [$\text{O}_{\text{SO}_2}\cdots\text{Pyr} = 3.06(6)$ Å].

Conversely, SO₂^{III} is not in close proximity to the pore wall and is only within interaction distance of other SO₂ molecules. SO₂^{IV} (occupancy = 0.46) occupies a position between two phenyl rings of two opposite linkers related by a mirror plane. It is in close proximity to both the terminal hydroxyl [$\text{O}_{\text{SO}_2}\cdots\text{O} = 1.99(10)$ Å] and the $\mu_3\text{-O}$ [$\text{S}_{\text{SO}_2}\cdots\mu_3\text{-O} = 3.42(5)$ Å] of the $[\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{OH})_4(\text{H}_2\text{O})_4]^{8+}$ cluster. As for SO₂^{IV}, SO₂^V (occupancy = 0.31) resides in between the phenyl rings of two opposite L⁴⁻ linkers and also is in close proximity to the terminal hydroxyl [$\text{O}_{\text{SO}_2}\cdots\text{O} = 3.48(15)$ Å] and the $\mu_3\text{-O}$ [$\text{O}_{\text{SO}_2}\cdots\mu_3\text{-O} = 3.06(15)$ Å] of the {Zr₆} cluster. The least occupied SO₂ site (SO₂^{VI}; occupancy = 0.31) lies near to a pyridyl ring of the organic linker [$\text{O}_{\text{SO}_2}\cdots\text{H}_{\text{Pyr}} = 2.75(19)$ Å] and also exhibits the potential for dipole–dipole interaction with SO₂^V [$\text{O}^{\text{VI}}\cdots\text{S}^{\text{V}} = 3.53(18)$ Å] (Figures 4 and 5).

In conclusion, exceptional adsorption of SO₂ and selective sorption of SO₂ over CO₂ and N₂ have been demonstrated in a robust Zr-based MOF, MFM-601. By locating the positions of CO₂ and SO₂ in MFM-601, key understanding of the observed uptake and selectivity has been gained. It has been shown that the dipole moment of SO₂ can be utilized by MFM-601 not only to provide stable binding within the pores but also to drive intermolecular interactions between SO₂ molecules.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b08433.

Data for (C_{47.5}H_{24.8}N_{21.6}O_{139.2}Zr₂₄) (CIF)

Data for C₄₄H₂₄N₂O₁₆Zr₃ (CIF)

Data for C₄₄H₂₄N₂O₁₄Zr₃, 7.36(CO₂) (CIF)

Data for $C_{44}H_{24}N_2O_{16}Zr_3$, 14.272(SO₂) (CIF)
 Synthesis, characterization, and analysis of crystal
 structures (PDF)

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Notes

The authors declare no competing financial interest.
 CCDC-1850112, 1854228, 1854229 and 1854234 contain the
 supplementary crystallographic data.

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