Supporting Information

Exceptional adsorption and binding of sulfur dioxide in a robust zirconium-based metal-organic framework

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Physical Characterisation.

All reagents were used as received from commercial suppliers without further purification. Analyses for C, H and N were carried out on a CE-440 elemental analyzer (EAI Company). Thermal gravimetric analyses (TGA) were performed under air flow (100 ml/min) with a heating rate of 2 °C/min using a TA SDT-600 thermogravimetric analyzer (TA Company).

Synthesis of 4,4',4'',4'''-(1,4-phenylenebis(pyridine-4,2,6-triyl))tetrabenzoic acid (H₄L)

Scheme S1: Synthesis of 4,4',4'',4'''-(1,4-phenylenebis(pyridine-4,2,6-triyl))tetrabenzoic acid (H₄L).

4-Methylnacophenone (13.4 mL, 10 mmol), terephthalaldehyde (2.70 g, 20.1 mmol) and NaOH (5.10 g, 128 mmol) were combined and ground in a ball mill for 1 h. The resultant solid was dissolved in EtOH (600 mL) with NH₄OAc (30 g, 389 mmol) and the solution heated under reflux for 24 h. On cooling the reaction mixture was filtered in vacuo to yield a white solid, which was recrystallized with toluene to yield white crystals (2.73 g, 4.61 mmol, 46 %).

The white crystals (3.0g, 5.19 mmol) were combined with 12M HNO₃ (6 mL) and distilled water (30 mL) in an autoclave and heated at 180 °C for 24 h. The reaction was cooled to room temperature and the solid was collected and washed with distilled water until the filtrate was neutral. Final washing with acetone yielded an orange powder (3.64 g, 5.11 mmol, 98 %). 1H NMR (DMSO-d₆): 8.14 ppm (d, 8H, J=7.8 Hz), 8.32 ppm (s, 4H), 8.47 ppm (s, 4H), 8.52 ppm (d, 8H, J=8.1 Hz).
Synthesis of MFM-600

Benzoic acid (78.5 mmol, 9.60 g), zirconium (IV) chloride (1.33 mmol, 0.309 g) and H₄L (0.31 mmol, 0.220 g) were dissolved in DMF (45 mL) and heated under reflux for 24 h. The suspension was then filtered and washed with DMF (3 x 30 mL) and acetone (3 x 30 mL). The yellow powder was then acetone-exchanged by suspending the as-synthesised sample in an excess of acetone for 1 week with frequent exchange of solvent. The activated sample was prepared using a Micrometrics Smart VacPrep by heating at 373 K for 10 h under ultra-high vacuum using a diaphragm and turbo pumping system. Elemental analysis (% calc/found) [Zn₆(µ₃-O)₄(µ₃-OH)₄(OH)₄][C₄₄N₂O₈H₂₄]₂[C₄₄N₂O₈H₂₈]₀.₃₅ (C 52.0/53.2, H 2.8/3.0, N 1.6/2.9).

Synthesis of MFM-601

MFM-600 was combined with hydrochloric acid (8 M, 2 mL) and DMF (52 mL) and stirred at 100 °C for 24 h. The acetone-exchanged material was prepared by suspending the as-synthesised sample in an excess of acetone for 1 week with frequent exchange of solvent. The activated sample was prepared using a Micrometrics Smart VacPrep by heating at 373 K for 10 h under ultra-high vacuum using a diaphragm and turbo pumping system. Elemental analysis (% calc/found) [Zn₆(µ₃-O)₄(µ₃-OH)₄(OH)₄(H₂O)₄][C₄₄N₂O₈H₂₄]₃ (C 50.8/49.7, H 3.1/2.7, N 2.7/2.9).
Thermogravimetric Analysis

Figure S1. TGA data for MFM-600 and MFM-601.
Crystal Structures

Figure S2. View of the asymmetric unit of MFM-600.

Figure S3. View of the crystal structure of MFM-600 along the $b$ axis.
Figure S4. View of disordered (occupancy = 0.35) monodentate H$_4$L linker in MFM-600. Occupancy of H$_4$L linker was based on a number of 0.7 H$_4$L per {Zr$_6$} unit calculated from TGA data.
Figure S5. View of the asymmetric unit of MFM-601.

Figure S6. View of the crystal structure of MFM-601 along the $b$ axis.
Figure S7. Crystal structures of MFM600 (left) and MFM-601 (right) showing the mechanism via which the ‘monodentate’ linker (orange and green) is exclusively removed from MFM-600 to form MFM-601 while the rest of the framework remains intact.

**In situ synchrotron PXRD**

High resolution PXRD patterns of the bare and gas loaded MFM-601 were recorded at the I11 beamline at Diamond Light Source.

![Graph](image)

Figure S8. Bare and gas loaded PXRD patterns of MFM-601 recorded at I11 at Diamond Light Source.
PXRD Refinements

X-Ray Powder Diffraction (PXRD) experiments of bare MFM-601 as well as MFM-601 loaded with CO₂ and SO₂ at 1 bar were carried out on I11 Beamline at the Diamond Light Source. Acetone exchanged samples were activated by heating at 120 °C under ultra-high vacuum for 20 h. From the refinements it appears that some air may have been re-introduced while changing gas lines before the SO₂ measurement which led to re-hydration of the open zirconium sites for that sample.

![Fitting of synchrotron PXRD pattern of bare MFM-601. R_wp=10.29%; R_exp=2.52%; R_p=7.33%; GoF=4.08.](image)

Figure S9. Fitting of synchrotron PXRD pattern of bare MFM-601. \( R_{wp}=10.29\% \); \( R_{exp}=2.52\% \); \( R_p=7.33\% \); GoF=4.08.
Figure S10. Fitting of synchrotron PXRD pattern of CO$_2$ loaded MFM-601. $R_{wp}=9.58\%$; $R_{exp}=2.90\%$; $R_p=6.91\%$; GoF=3.30.

Figure S11. Fitting of synchrotron PXRD pattern of SO$_2$ loaded MFM-601. $R_{wp}=7.33\%$; $R_{exp}=2.65\%$; $R_p=5.55\%$; GoF=2.76.
Gas Adsorption Isotherms and Breakthrough

CO₂, SO₂, CH₄ and N₂ sorption isotherms were recorded at 273-303 K (temperature-programmed water bath from Hiden Company) on a Hiden XEMIS system at the University of Manchester under ultra-high vacuum from a diaphragm and turbo pumping system. All gases used were ultra-pure research grade (99.999%) purchased from BOC or AIRLIQUIDE. In a typical gas adsorption experiment, ~80 mg of solvated sample was loaded into the XEMIS, and activated at 120 °C and high vacuum ($10^{-10}$ bar) for 1 day to give a fully desolvated sample.

Figure S12. Adsorption isotherms of CO₂ in MFM-600.

Figure S13. Adsorption isotherms of N₂ in MFM-600.
Figure S14. Adsorption isotherms of SO$_2$ in MFM-600.

Figure S15. Adsorption isotherms of CO$_2$ in MFM-601.

Figure S16. Adsorption isotherms of N$_2$ in MFM-601.
Breakthrough experiments were carried out in a 7 mm diameter fixed-bed tube of 120 mm length packed with 0.76 g MFM-601 powder (particle size < 5 microns). The total volume of the bed was ca. 5 cm³. The sample was heated at 120 °C under a flow of He for 12 hours 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 a stream of 2500 ppm SO₂ (diluted in 1:1 He:N₂ and 1:1 He:CO₂) at atmospheric pressure and room temperature. The flow rate of the entering gas mixture was maintained at 20 mL min⁻¹, and the gas concentration, C, of SO₂, N₂ and CO₂ at the outlet was determined by mass spectrometry and compared with the corresponding inlet concentration C₀, where \( \frac{C}{C₀} = 1 \) indicates complete breakthrough.
SO₂ Uptake Comparison Table

Table S1. Comparison of the BET surface areas and total uptake of SO₂ at 1 bar 298 K of several porous materials.

| Material                  | BET Surface Area / m² g⁻¹ | Total SO₂ Uptake / mmol g⁻¹ | Temperature / K | Reference       |
|---------------------------|---------------------------|-----------------------------|-----------------|-----------------|
| MFM-601                   | 3644                      | 12.3                        | 298             | This work       |
| SIFSIX-1-Cu               | 1337                      | 11.0                        | 298             | 1, 2            |
| MFM-202a                  | 2220                      | 10.2                        | 298             | 3               |
| Ni(bdc)(ted)ₐₕₕ         | 1700                      | 10.0 (1.13 bar)             | 298             | 4               |
| Mg-MOF-74                 | 1206                      | 8.6                         | 298             | 4, 5            |
| MFM-300(In)               | 1071                      | 8.3                         | 298             | 6               |
| P(D[VImC₆]Br)             | Not reported              | 7.8                         | 298             | 7               |
| MFM-300(Al)               | 1370⁺                     | 7.1                         | 298             | 8               |
| SIFSIX-1-Cu-i             | 630                       | 6.9                         | 298             | 1               |
| IRMOF-3                   | 1568                      | 6.0                         | 298             | 9               |
| MFM-600                   | 2281                      | 5.0                         | 298             | This work       |
| Coconut shell activated carbon | 1125                        | 3.4 (0.5 bar)              | 323             | 10              |
| Zn-MOF-74                 | 632                       | 3.0                         | 298             | 9               |
| 13X zeolite               | Not reported              | 2.7 (0.4 bar)              | 323             | 11              |
| MFI zeolite               | 713                       | 2.7⁺                       | 298             | 12              |
| CoCo                      | 712                       | 2.5                         | 298             | 13              |
| ZnCo                      | 700                       | 1.8                         | 298             | 13              |
| FMOF-2                    | 378                       | 1.8                         | 298             | 14              |
| 5A zeolite                | Not reported              | 1.7 (0.5 bar)              | 323             | 11              |
| Coal-based activated carbon | 736                        | 1.7 (0.5 bar)              | 323             | 10              |
| MOF-5                     | 2205                      | 1.0                         | 298             | 9               |

* Internal surface area of MFM-300(Al) was calculated by DFT/Monte Carlo methods from the CO₂ isotherm.
⁺Uptake was obtained by GCMC simulation
SO₂ Adsorption Kinetics

Figure S18. Views of kinetics for adsorption/desorption of SO₂ in MFM-601 at 298 K.

Calculation of IAST selectivity for gas adsorption.

To estimate the selectivity of SO₂ over other gases at, isotherm data at 298 K was fitted using dual-site Langmuir-Freundlich (DSLF) model.¹⁵

\[
N^*(f) = \frac{q_1 b_1 P^{n_1}}{1 + b_1 P^{n_1}} + \frac{q_2 b_2 P^{n_2}}{1 + b_2 P^{n_2}} \tag{1}
\]

Where \(P\) is the pressure of the bulk gas at equilibrium with the adsorbed phase, \(q_i\) is the maximum adsorption amount, \(b_i\) is the the affinity constant and \(n_i\) is the deviation from the simple Langmuir equation. Using this fitting, the IAST selectivity can be calculated by equation 2.

\[
S = \frac{x_1/y_1}{x_2/y_2} \tag{2}
\]

Where \(x_i\) is the amount of each component adsorbed and \(y_i\) is the mole fraction of each component at equilibrium. The IAST adsorption selectivities were calculated for binary mixtures of SO₂/CO₂, SO₂/N₂ and CO₂/N₂ for varying concentrations (50:50 to 10:90)
**Q_{st} Calculations – Van’t Hoff Method**

To estimate the isosteric enthalpies ($\Delta H$) for N$_2$ and CO$_2$ adsorption, isotherms at 273-303 K were fitted to the Van ’Hoff equation;

$$\ln(P) = \frac{-\Delta H}{RT} + \frac{(\Delta S)}{R}$$  \[3\]

where $P$ is pressure in Pa, $T$ is the temperature, and $R$ is the ideal gas constant.

Figure S19. Linear fitting of 1/T vs LnP at intervals of 0.1 mmol g$^{-1}$ for CO$_2$ and N$_2$ in MFM-600 used to determine the isosteric heat of adsorption by the Van ’Hoff method.
Figure S20. Linear fitting of \(1/T\) vs LnP at intervals of 0.1 mmol g\(^{-1}\) for CO\(_2\) and N\(_2\) in MFM-601 used to determine the isosteric heat of adsorption by the Van t’Hoff method.

\(Q_{st}\) Calculations – Virial Method

For SO\(_2\) isotherm data was only recorded at two temperatures so the Van’t Hoff method cannot be used to calculate \(Q_{st}\), therefore the virial method was used. This method involves fitting the isotherm data at the two temperatures to the virial expression:

\[
\ln(P) = \ln(n) + \left(\frac{1}{T}\right) \sum_{i=0}^{m} a_i n^i + \sum_{j=0}^{n} b_j n^j
\]  

[4]

Where in the above equation,

\[
Q_{st} = -R \sum_{i=0}^{m} a_i n^i
\]  

[5]
Figure S21. Virial analysis of the adsorption data for SO$_2$ in MFM-601.

Figure S22. Virial analysis of the adsorption data for SO$_2$ in MFM-600.
Scanning Electron Microscopic Imaging

Images were collected on a Hitachi TM1000 table top microscope.

Figure S23. SEM micrograph of MFM-601 particles at a) 1000, b) 2000, c) 5000 and d) 10000 x magnification. The particle size is approximately at 40-60 microns.

References

1. Cui, X.; Yang, Q.; Yang, L.; Krishna, R.; Zhang, Z.; Bao, Z.; Wu, H.; Ren, Q.; Zhou, W.; Chen, B.; Xing, H. Adv. Mater. 2017, 29, 1606929.
2. Noro, S.; Kitagawa, S.; Kondo, M.; Seki, K. Angew. Chem. Int. Ed. 2000, 39, 2081-2084.
3. Yang, S.; Liu, L.; Sun, J.; Thomas, K. M.; Davies, A. J.; George, M. W.; Blake, A. J.; Hill, A. H.; Fitch, A. N.; Tang, C. C.; Schröder, M. J. Am. Chem. Soc. 2013, 135, 4954-4957.
4. Tan, K.; Canepa, P.; Gong, Q.; Liu, J.; Johnson, D. H.; Dye-voich, A.; Thallapally, P. K.; Thonhauser, T.; Li, J.; Chabal, Y. J. Chem. Mater. 2013, 25, 4653-4662.
5. Grant Glover, T.; Peterson, G. W.; Schindler, B. J.; Britt, D.; Yaghi, O. Chem. Eng. Sci. 2011, 66, 163-170.
6. Savage, M.; Cheng, Y.; Easun, T. L.; Eley, J. E.; Argent, S. P.; Warren, M. R.; Lewis, W.; Murray, C.; Tang, C. C.; Frogley, M. D.; Cinque, G.; Sun, J.; Rudić, S.; Murden, R.T.; Benham, M. J.; Fitch, A. N.; Blake A. J.; Ramirez-Cuesta, A. J.; Yang, S.; Schröder, M. Adv. Mater., 2016, 28, 8705-8711.
7. Xia, L.; Cui, Q.; Suo, X.; Li, Y.; Cui, X.; Yang, Q.; Xu, J.; Yang, Y.; Xing, H. Adv. Funct. Mater. 2018, 28, 1704292.
Yang, S.; Sun, J.; Ramirez-Cuesta, A. J.; Callear, S. K.; David, W. I. F.; Anderson, D. P.; Newby, R.; Blake, A. J.; Parker, J. E.; Tang, C. C.; Schröder, M. Nat. Chem. 2012, 4, 887–894.

Britt, D.; Tranchemontagne, D.; Yaghi, O. M. Proc. Natl. Acad. Sci. U.S.A. 2008, 105, 11623–11627.

Yi, H.; Wang, Z.; Liu, H.; Tang, X.; Ma, D.; Zhao, S.; Zhang, B.; Gao, F.; Zuo, Y. J. Chem. Eng. Data. 2014, 59, 1556–1563.

Deng, H.; Yi, H.; Tang, X.; Yu, Q.; Ning, P.; Yang, L. Chem. Eng. J. 2012, 188, 77–85.

Matito-Martos, I.; Martin-Calvo, A.; Gutiérrez-Sevillano, J. J.; Haranczyk, M.; Doblaré, M.; Parra, J. B.; Ania, C. O.; Calero, S. Phys. Chem. Chem. Phys. 2014, 16, 19884–19893.

Thallapally, P. K.; Motkuri, R. K.; Fernandez, C. A.; McGrail, B. P.; Behrooz, G. S. Inorg. Chem. 2010, 49, 4909–4915.

Fernandez, C. A.; Thallapally, P. K.; Motkuri, R. K.; Nune, S. K.; Sumrak, J. C.; Tian, J.; Liu, J. Cryst. Growth Des. 2010, 10, 1037–1039.

Ruthven, D. M. Principles of adsorption and adsorption processes; Wiley: New York, 1984, 106-112