Supporting Information

Exceptional packing density of ammonia in a dual-functionalised metal-organic framework

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1. Experimental methods and procedures

**NH$_3$-ABR-TPD experiments.** The sample was placed into a packed bed reactor of the lab-developed TPD equipment equipped with a Bruker Matrix MG5 FTIR spectrometer (resolution = 0.5 cm$^{-1}$) for gas analysis and was first activated at 120 °C under He at 100 mL min$^{-1}$ (99.999%, BOC gas Ltd.) for 20 h in order to remove adsorbed guest molecules. After the activation, the temperature of the sample was decreased to 25 °C and the temperature maintained until a stable IR baseline signal was achieved. Then a gas mixture of 5000 ppm NH$_3$ diluted in He was introduced to establish the saturated NH$_3$ signal (i.e. the breakthrough of NH$_3$ adsorption). After that, the gas was switched to pure He (at 100 mL min$^{-1}$) to purge the physically adsorbed NH$_3$ from the sample until obtaining a stable NH$_3$ signal. The temperature of the reactor was then increased at a rate of 5 °C min$^{-1}$ whilst maintaining a flow of pure He to measure the NH$_3$ desorption.
2. Crystallographic data for MFM-303(Al)

**Supplementary Table S1.** Summary of crystallographic data for as-synthesised MFM-303(Al)

| Crystal data |  |
|--------------|---|
| **Chemical formula** | C₁₆H₈AlO₉·2.75(H₂O) |
| **Mᵣ** | 421.76 |
| **Crystal system, space group** | Monoclinic, C₂/c |
| **Temperature (K)** | 120 |
| **a, b, c (Å)** | 13.705(3), 20.837(2), 13.287(12) |
| **β (°)** | 92.544(13) |
| **V (Å³)** | 3790.7(11) |
| **Z** | 8 |
| **Radiation type** | Synchrotron, λ = 0.6889(2) Å |
| **μ (mm⁻¹)** | 0.16 |
| **Crystal size (mm)** | 0.05 × 0.05 × 0.02 |
| **Absorption correction** | Multi-scan. CrysAlis PRO, Agilent Technologies, Version 1.171.37.35 (release 13-08-2014 CrysAlis171.NET) (compiled Aug 13 2014, 18:06:01) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. |
| **Tₘᵡₜ, Tₘₜ₝** | 0.741, 1.000 |
| **No. of measured, independent and observed [I > 2σ(I)] reflections** | 16953, 2310, 1655 |
| **Rₑₐₑ** | 0.143 |
| **θₘᵡₜ (°)** | 21.3 |
| **(sin θ)/λₘᵡₜ (Å⁻¹)** | 0.526 |

| Refinement |
|---|
| **R[F² > 2σ(F²)], wR(F²), S** | 0.148, 0.410, 1.64 |
| **No. of reflections, no. of parameters, no. of restraints** | 2310, 281, 355 |
| **H-atom treatment** | H atoms treated by a mixture of independent and constrained refinement |
| **Qₑₘᵡ, Qₑₘᵢₙ (e Å⁻³)** | 1.26, -0.67 |

Computer programs: *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.35 (release 13-08-2014 CrysAlis171.NET) (compiled Aug 13 2014, 18:06:01), *SHELXS¹*, *SHELXL²*, Olex2³

**Details of refinement of the single crystal structure of MFM-303(Al).**

The X-ray diffraction of the crystal had a resolution limit of around 0.95 Å, and data beyond this resolution were omitted from the refinement using a SHEL command. As a consequence the structure has a low data to parameter ratio, and so where possible restraints were applied to the geometries and atomic displacement parameters of the atoms to aid refinement. The possibility of further unmodelled disorder in the ligand position is suggested by the shape of the displacement ellipsoids and large U₃/U₁ ratio for the average U(i,j) tensor (4.8). However, more complex disorder models did not yield a plausible structure or better fit with the data. Rigid bond restraints have been applied to the anisotropic displacement parameters of all atoms in the structure (RIGU).

The carboxylic acid group C61-O63 is disordered over two orientations whose occupancies have been refined and constrained to sum to unity, resulting in values of 0.61(5) and 0.39(5). The position and anisotropic displacement parameters of the carbon atom of each disorder component have been constrained to be identical.
(EAXY, EADP). The 1,2 and 1,3 bond distances of the two components have been restrained to be similar (SAME) and each component has been constrained to have planar geometry coincident with phenyl carbon atom C25 (FLAT). The anisotropic displacement parameters of the disordered oxygen atoms have been restrained to be similar and isotropic (SIMU, ISOR).

The isotropic displacement parameters of water residues O1W, O2W and O3W were fixed to have values of 0.08 whilst their occupancies were allowed to refine resulting in values of 0.94(1), 0.48(1) and 0.39(1) respectively. The water residues have been included in the unit cell contents at full occupancy. Hydrogen atoms on the phenyl rings were geometrically placed and refined with a riding model. Electron density peaks in suitable positions for hydrogen atoms were observed close to the hydroxyl-oxygen atom O1H, carboxylic acid hydroxyl-oxygen atom O42 and the water residue O2W. The positions of these hydrogen atoms were allowed to refine under the influence of geometric restraints. Further electron density peaks were observed close to water residues O1W and O3W; however, they could not be developed into sensible models for hydrogen atoms. These potential hydrogen atoms were not included in the model, but were included in the unit cell contents at full occupancy.

The hydroxyl hydrogen position at O1H is disordered over two positions with each refined to have half occupancy. The O-H bond lengths were restrained to suitable target values (DFIX) whilst all the H...Al 1,3 distances were restrained to be the same (SADI). Their isotropic displacement parameters were fixed at a value of 0.1. The positions of both atoms were weakly restrained to donate hydrogen bonds to water residue O2W. The 1,2 and 1,3 distances of the hydrogen atoms of water residue O2W were restrained to have suitable values (DFIX). Further weaker restraints were applied to their positions to make them donate hydrogen bonds to adjacent water residue O3W and carboxylic acid oxygen O63A. Their isotropic displacement parameters were fixed at a value of 0.12. An electron density peak was observed almost equidistant from, and directly between carboxylic acid oxygen atoms O42 and O62A. The electron density was modelled as a full occupancy hydrogen atom and its position allowed to refine freely. The isotropic displacement parameter of the hydrogen atom was fixed at 1.5 x Ueq of oxygen atom O42. Further disordered solvent molecules could not be sensibly modelled, so the structure was treated with PLATON SQUEEZE. A total of 32 electrons were accounted from the P1 cell in this, equating to a quarter of a water molecule per asymmetric unit, which have been included in the unit cell contents and calculation of derived parameters.
**Supplementary Table S2.** Summary of crystallographic data of MFM-303(Al)·4.36NH₃.

| Parameter                  | Value                                      |
|----------------------------|--------------------------------------------|
| Chemical formula           | C₁₆H₈AlO₉·4.36NH₃                         |
| Mr                         | 423.33                                    |
| Crystal system, space group| Monoclinic, C2/c                          |
| Temperature (K)            | 273                                       |
| a, b, c (Å)                | 15.52974(17), 19.62387(17), 13.14259(12)  |
| β (°)                      | 92.3435(8)                                |
| V (Å³)                     | 4001.90(7)                                |
| Z                          | 8                                         |
| Radiation type             | synchrotron, λ = 0.825774(2) Å            |
| Rwp                        | 7.54%                                     |
| Rexp                       | 1.63%                                     |
| Rp                         | 5.54%                                     |
| GoF                        | 4.62                                      |

**Supplementary Figure S1.** Rietveld refinement graph for NH₃@MFM-303(Al) (λ = 0.825774 Å).
Supplementary Figure S2. Pawley fitting of bulk sample of MFM-303(Al) confirming the phase purity of the material ($\lambda = 1.5406 \, \text{Å}$, $R_p=4.13\%$, $R_w=5.31\%$, goodness-of-fit = 1.37)
3. Solvent and pH stability tests

**Supplementary Figure S3.** Stability of MFM-303(Al) under different organic and aqueous solvents measured by PXRD. **a,** PXRD patterns of MFM-303(Al) after immersion in aqueous solutions of different pH for 16 h. **b,** PXRD patterns of MFM-303(Al) after immersion in different solvents for 16 h.
4. N₂ adsorption isotherm

**Supplementary Figure S4.** Adsorption isotherm of N₂ in MFM-303(Al) at 77 K demonstrating poor uptake most likely due to activation diffusion effects of N₂ molecules through the narrow pores of MFM-303(Al).
5. CO$_2$ isotherms and DFT/Monte-Carlo fitting for surface area and pore volume determination

**Supplementary Figure S5.** DFT/Monte-Carlo fitting for the adsorption isotherm for CO$_2$ in MFM-303(Al) at 273 K; this gave a surface area of 723 m$^2$ g$^{-1}$ and pore volume of 0.150 cm$^3$ g$^{-1}$ based upon the CO$_2$ isotherm.$^4$

**Supplementary Figure S6.** DFT/Monte-Carlo pore volume distribution plot for MFM-303(Al) to give a pore diameter centred at ~5.0 Å.
6. Additional NH₃ isotherms

**Supplementary Figure S7.** Adsorption isotherms for NH₃ in MFM-303(Al).

7. Water sorption isotherm

**Supplementary Figure S8.** Adsorption isotherm for water in MFM-303(Al) at 283 K.
8. Thermogravimetric analysis

**Supplementary Figure S9.** Thermogravimetric analysis of as-synthesised MFM-303(Al) under a flow of N\textsubscript{2} at a heating rate of 10 °C min\textsuperscript{-1} with mass spectrometric data for the peak at m/z = 18 (corresponding to water).
Supplementary Figure S10. TGA-MS data for MFM-303(Al) pre-loaded with NH$_3$. The sample was activated at 150 °C under vacuum and then exposed to NH$_3$ at 1 bar and excess gas removed. The sample was then transferred to the TGA-MS. A peak at 113 °C and ending at 190 °C corresponds to a weight loss of 94.55-90.80 = 3.75, equating to 2.42 mmol g$^{-1}$. 
9. Differential scanning calorimetry

Differential scanning calorimetry was performed on a Thermal Analysis SDT650 analyser, and was used to determine the enthalpy of adsorption. The sample was heated under a flow of N$_2$ (50 mL min$^{-1}$) at 200 °C for 2 h to remove adsorbed solvent molecules. After cooling to 30 °C, NH$_3$ (0.5% diluted in He) was introduced at a flow rate of 10 mL min$^{-1}$ and the sample allowed to equilibrate. The heat of adsorption was calculated by integrating the area under the normalised heat flow curve.

Supplementary Figure S11. DSC curve for activated MFM-303(Al) under NH$_3$ (0.5% diluted in He) at a flow rate of 10 mL min$^{-1}$. The enthalpy of adsorption is calculated to be 61.5 kJ mol$^{-1}$. 

10. FTIR-breakthrough experiments

Supplementary Figure S12. Temperature-programmed desorption (TPD) experiments performed on NH$_3$ in MFM-303(AI) using FTIR to detect the gases eluting from the column.
11. Density function theoretical (DFT) calculations

Modelling by Density Functional Theory (DFT) of the bare and NH$_3$/CO$_2$-loaded MOFs was performed using the Vienna Ab initio Simulation Package (VASP). The calculation used the Projector Augmented Wave (PAW) method to describe the effects of core electrons, and Perdew-Burke-Ernzerhof (PBE) implementation of the Generalized Gradient Approximation (GGA) for the exchange-correlation functional. Energy cutoff was 800 eV for the plane-wave basis of the valence electrons. The lattice parameters and atomic coordinates determined by X-ray single crystal diffraction in this work were used as the initial structure. Due to the large unit cell (~300 atoms), all electronic structure and phonon calculations were performed on the Γ point only. The total energy tolerance for electronic energy minimization was $10^{-8}$ eV, and for structure optimization it was $10^{-7}$ eV. The maximum interatomic force after relaxation was below 0.001 eV/Å. The optB86b-vdW functional for dispersion corrections was applied. The vibrational eigen-frequencies and modes were then calculated by solving the force constants and dynamical matrix using Phonopy. The OClimax software was used to convert the DFT-calculated phonon results to the simulated INS spectra. Simulation of the INS spectra for NH$_3$-loaded MFM-303(Al) was conducted with NH$_3$ presenting at site II due to its strong interaction with the –OH group of the framework. The simulation of NH$_3$ at site I breaks the symmetry of the model and unfortunately makes the calculation impractical.

Supplementary Figure S13. View of NH$_3$ site II derived from the model used to simulate INS spectra and its proximity to carbon atoms on the aromatic ring and to the µ-OH moiety.
12. Additional views of the structure of MFM-303(Al)

**Supplementary Figure S14.** View of the structure of MFM-303(Al) showing the C-O and C=O bond lengths in adjacent ligand units and disordered atoms O62, O63 and C61.

**Supplementary Figure S15.** View of NH₃ sites in NH₃@MFM-303(Al) showing intermolecular distances (N atom size and colour corresponds to site number). Colour of bonds denote the intermolecular distance.
Supplementary Figure S16. View of the as-synthesised MFM-303(Al) containing water (O atoms shown only for clarity), highlighting O···O intermolecular distances.

13. Stability of MFM-303(Al) after breakthrough experiments

Supplementary Figure S17. PXRD patterns for as-synthesised MFM-303(Al) and after breakthrough with dry and then wet NH₃, demonstrating the stability of this material.
14. Formation of defects in MFM-303(Al)

One possible explanation for the high density of NH$_3$ in MFM-303(Al) is the presence of defects within the material. The determination of defects typically relies on a combination of methods to characterise. For MFM-303(Al), PXRD data provided little evidence; the bulk material was refined using a Pawley fit and no unexpected peaks or features in the baseline were observed (Figure S2). To investigate the possible presence of defects, 100 mg MFM-303(Al) was boiled at 120 °C in DMF overnight then boiled in MeOH at 70 °C for 1 day. A small sample (~5 mg) was completely dissolved using a digestion solution (20 µL trifluoroacetic acid in 600 µL DMSO-d6) and $^1$H NMR spectrum obtained with a Bruker Avance 400 MHz spectrometer. As shown in Figure S18, the ligand peaks are present as is some MeOH. No other peaks are observed suggesting there is little evidence for other species, such as formate from DMF, binding to potential defect sites such as those missing cluster units.

Supplementary Figure S18. $^1$H NMR spectrum of digested MFM-303(Al) sample after methanol exchange.

Thermogravimetric analysis in air was also used to probe the possibility of defects (Figure S19). Assuming complete thermal decomposition to Al$_2$O$_3$, a 1:0.50 ratio of MOF:Al$_2$O$_3$ would be expected. The actual ratio was found to be 1:0.52, which could suggest the presence of trace amount of missing linker.
Supplementary Figure S19. TGA of MFM-303(Al) under a flow of air, suggesting that defects may be present but only at low concentration.
15. Comparison of MFM-303(Al) to other materials

**Supplementary Table S3.** Dynamic breakthrough capacity of porous materials compared with MFM-303(Al)

| Material                  | NH$_3$ concentration (ppm) | Dynamic NH$_3$ capacity (mmol g$^{-1}$) | Reduction in adsorption capacity | Stability after NH$_3$ sorption | Ref |
|---------------------------|-----------------------------|----------------------------------------|----------------------------------|--------------------------------|-----|
| MFM-303(Al)               | 833                         | 2.9                                    | 2.4                              | 17%                           | Stable This work |
| MFM-300(VIII)             | 1,000                       | 1.9                                    | (not measured)                   | -                             | Stable 13 |
| Mg$_2$(dobpdc)            | 1,000                       | 8.37                                   | 6.14                             | 27%                           | Stable 14 |
| Co$_2$Cl$_2$BTDD          | 1,000                       | 4.78                                   | 3.38                             | 29%                           | Unstable 15 |
| Co$_2$Cl$_2$BBTA          | 1,000                       | 8.56                                   | 4.36                             | 49%                           | Unstable at 1 bar, partially stable at 1 mbar 15 |
| Mg-MOF-74                 | 1,440                       | 7.60                                   | 1.70                             | 78%                           | Not reported 16 |
| UiO-66-OH                 | 2,880                       | 5.69                                   | 2.77                             | 51%                           | Not reported 17 |
| UiO-66-(COOH)$_2$         | 1,431                       | 2.83                                   | 1.83                             | 35%                           | Not reported 17 |
| Zeolite 13X               | 1,440                       | 2.86                                   | 0.62                             | 78%                           | Not reported 16 |

*As determined by PXRD

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