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Supporting Information

Acid loaded porphyrin-based metal-organic framework for ammonia uptake

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Synthesis

Reagents and solvents were purchased from Sigma-Aldrich. The porphyrin linker TCPP (5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin) was purchased from TCI UK. All were used without further purification.

BPL is a coal-based carbon manufactured by Chemviron Carbon Ltd, with a surface area of around 1100 m^2/g.

Al-PMOF

An aqueous stock solution of $AlCl_3$ was made by dissolving $AlCl_3 \bullet 6H_2O$ (875mg, 3.63 mmol) in 25 mL deionised water. 5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin (300 mg 0.379 mmol) was added to a 125 mL Teflon liner, followed by 24 mL deionised water. $AlCl_3$ stock solution (5.14 mL, 0.75 mmol) was then introduced to the Teflon liner. The suspension was stirred for 5 minutes at room temperature before being sealed in a stainless steel autoclave and heated up to 180°C at a rate of 10°C per minute, for 16 h. The solution was allowed to cool with a cooling rate 2°C per minute. The solid was recovered by centrifugation, washing 10 times with DMF (10 × 30 mL) and once with THF (1 × 30 mL) in order to remove any unreacted porphyrin. After drying at room temperature, 70 mg of material was obtained as a purple solid. The material was then activated at 170^oC under vacuum (3×10^{-2} mbar) to remove any guest molecules. Following reintroduction to air, atmospheric moisture is adsorbed affording the final product (50mg) with formula $Al_2(OH)_2(H_2TCPP)(H_2O)_{1.8}$. Elemental microanalysis; calculated: C 63.55, H 3.51, N 6.18; experimental: C 63.72, H 3.05, N 6.05

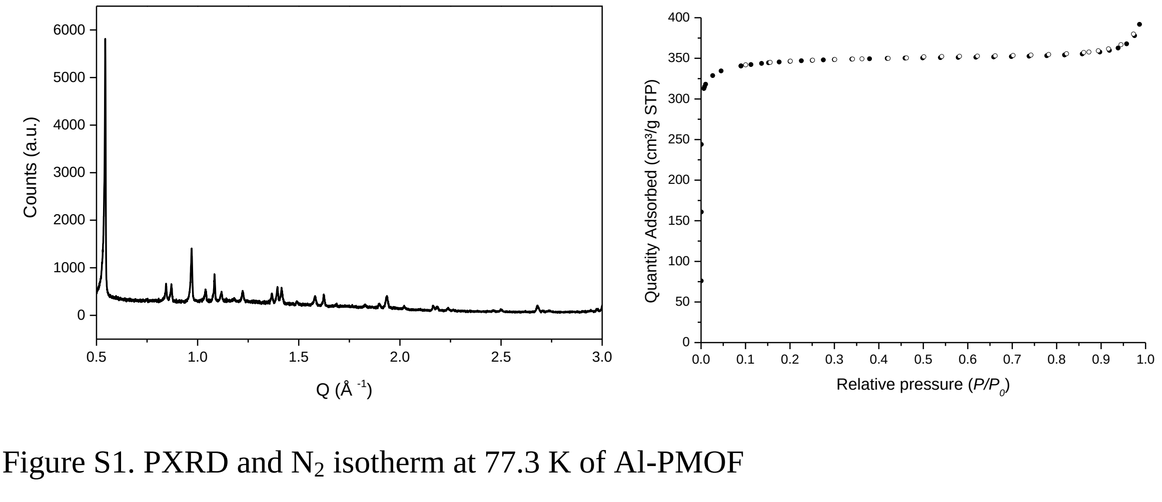


Figure S1. PXRD and N_2 isotherm at 77.3 K of Al-PMOF

Acid loading

Al-PMOF-HCl

Activated Al-PMOF (50mg) was inserted into a lidless 20mL glass vial, which was then inserted into a jar containing conc. hydrochloric acid (12 M, 5 mL). The jar was sealed and left standing for 16 h. The bright green solid was then removed and exposed to flowing N_2 for 2 h to remove any excess surface HCl.

Al-PMOF-Formic

Activated Al-PMOF (50mg) was inserted into a lidless 20mL glass vial, which was then inserted into a jar containing reagent grade formic acid. The jar was sealed and left standing for 16 h. The dark green solid was then removed and exposed to flowing N_2 for 2 h to remove any excess formic acid.

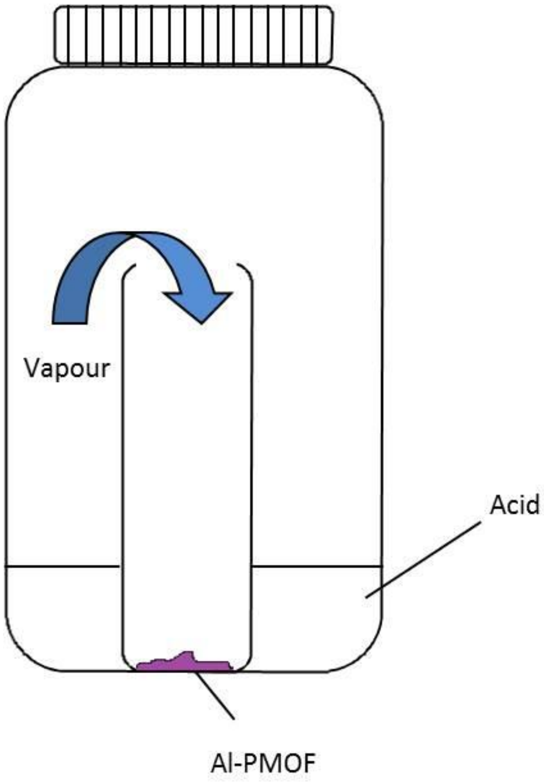
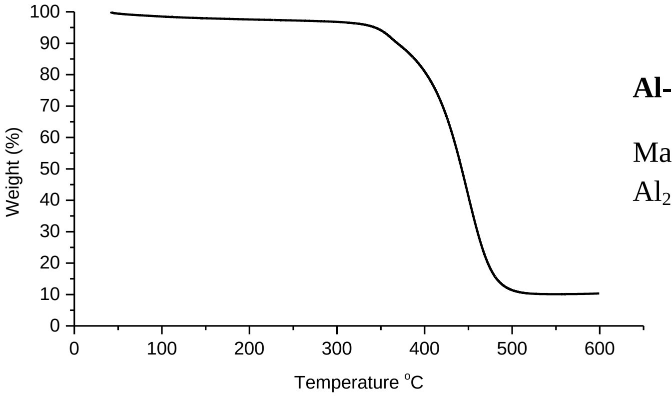


Figure S2. Method for acid insertion. Open vial containing Al-PMOF is sealed in a glass jar containing either conc. hydrochloric or formic acid, allowing the MOF to adsorb the acid vapour.

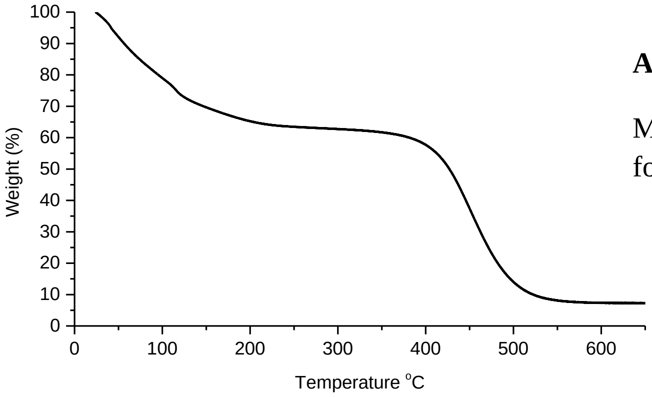
TGA

TGA was performed using a TA Instruments Q-500 thermogravimetric analyser. A heating rate of 10°C/min under a 10 ml/min flow of air was used.



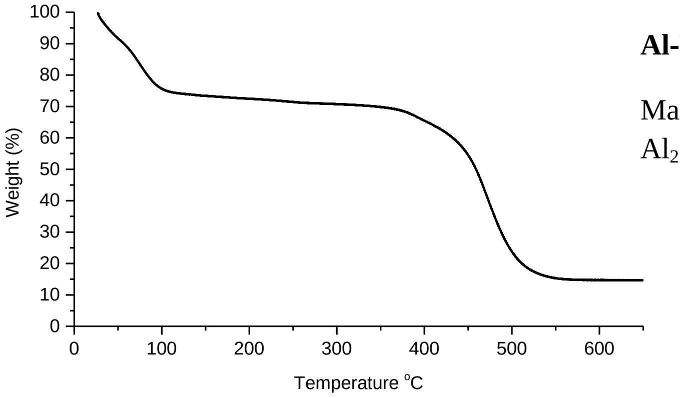
Al-PMOF

Mass loss of 4%, consistent with the formula $Al_2(OH)_2(H_2TCPP)\cdot(H_2O)_{1.8}$



Al-PMOF-HCl

Mass loss of 37.0%, consistent with the formula $Al_2(OH)_2(H_2TCPP)(HCl)_{6.5}(H_2O)_{15.3}$



Al-PMOF-FA

Mass loss of 29.6%, consistent with the formula, $Al_2(OH)_2(H_2TCPP)(HCOOH)_{6.4}(H_2O)_{4.0}$

Figure S3. Thermogravimetric analysis of the Al-PMOF, Al-PMOF-HCl and Al-PMOF-FA

Ion chromatography

Formate and chloride concentrations were measured using a Dionex ICS5000 Dual Channel I.C. at the Manchester Analytical Geochemistry Unit, University of Manchester.

59.6mg of Al-PMOF-HCl was dissolved in 10mL 1.0M potassium hydroxide solution; sonication was used for 15 seconds to ensure full dissolution. The sample was diluted with water by a factor of 10. This sample was then run through a Dionex ICS5000 Dual Channel I.C. to determine chloride content.

Chloride run 1 (mg/L)	**Chloride run 2 (mg/L)**	**Mean Chloride (mg/L)**
99.4	99.4	**99.4**

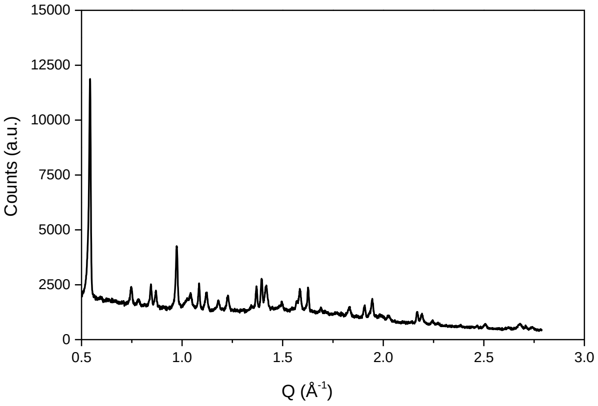
53.7mg of Al-PMOF-FA was dissolved in 10mL 1.0M potassium hydroxide solution; sonication was used for 15 seconds to ensure full dissolution. The sample was diluted with water by a factor of 10. This sample was then run through a Dionex ICS5000 Dual Channel I.C. to determine formate content.

Formate run 1 (mg/L)	**Formate run 2 (mg/L)**	**Mean Formate (mg/L)**
126.5	123.3	**124.9**

Loading using neat formic acid

Activated Al-PMOF (50mg) was inserted into a 40 mL glass vial containing reagent grade formic acid (5 mL) and was magnetically stirred for 1h. The dark green solid was then recovered by centrifugation and exposed to flowing N_2 for 2 h to remove any excess formic acid.

a)



b)

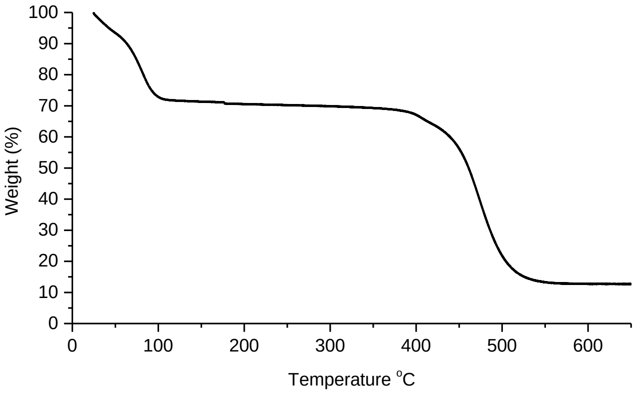
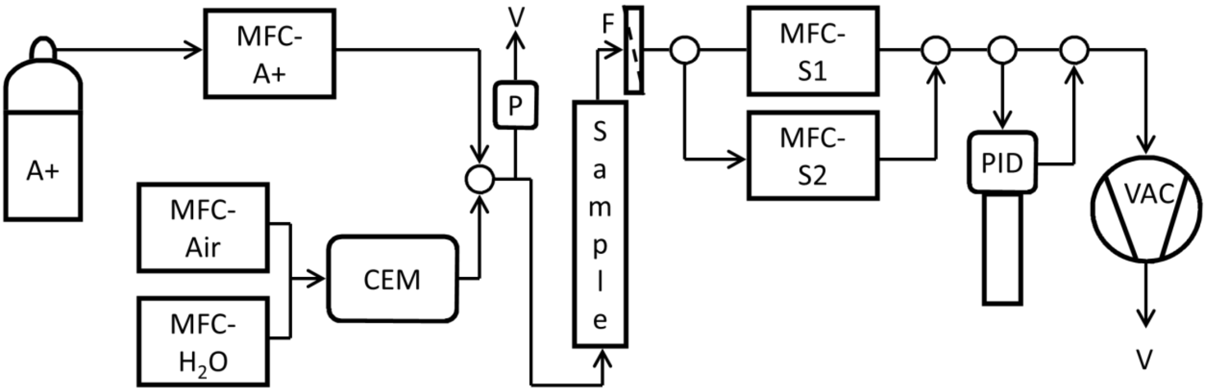


Figure S4. a) PXRD following neat formic acid loading b) TGA PXRD following neat formic acid loading, showing a weight loss of 30.0%, comparable to vapour loading (Figure S3).

Breakthrough apparatus

All breakthrough measurements were conducted at the Defence Science and Technology Laboratory, Porton Down using a custom micro-breakthrough rig detailed below.

Breakthrough experiments were carried out by loosely packing a 4 mm internal diameter glass tube with 30 mg of adsorbent and plugging both ends with glass wool. Assisted by a vacuum pump at the end of the flow line, mass-flow controllers regulated a flow of ammonia and air through a Bronkhorst Controlled Evaporation and Mixing system to produce a gas flow with a concentration of 500 ppm and a flow rate of 30 mL/min. Two photo-ionisation detectors (PIDs) were attached to the line directly before and after the sample tube in order to monitor the concentration of ammonia. Before each run, a flow of dry air was passed through the sample until the concentrations measured by each of the PIDs were equal to each other and in accordance with background levels of under 10 ppm.



A+ = Agent
MFC = Mass flow controller
MFC S1 = Low sample flow mass flow controller
MFC S2 = High sample flow mass flow controller
CEM = Controlled evaporator mixer
P = Relative humidity and temperature probe
F = PTFE dust filter
VAC = Diaphragm vacuum pump
PID = Photo-ionisation detector
V = Vent to fume cupboard
O = Tube junction

Figure S5. Breakthrough apparatus schematic

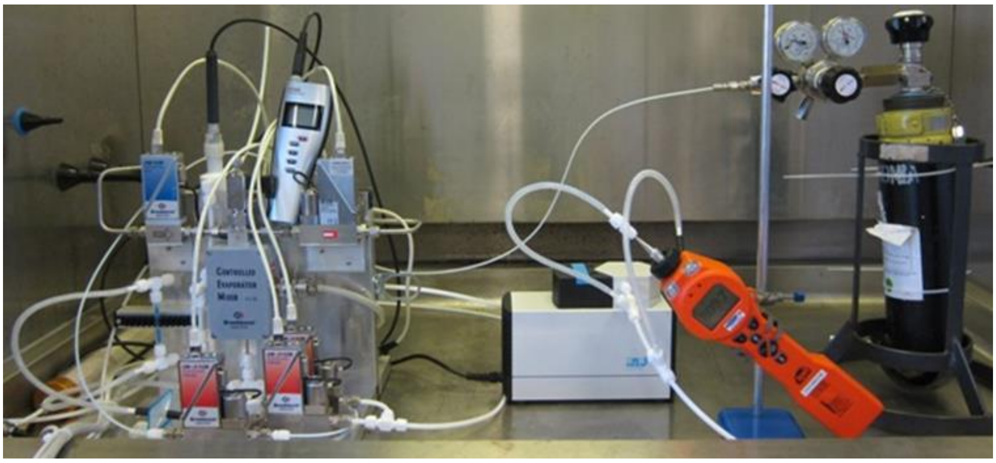


Figure S6. Photograph of breakthrough apparatus

UV-Visible Spectroscopy

UV/vis spectra was collected in a solid state holder at room temperature on a Perkin–Elmer Lambda 650S UV/vis spectrometer equipped with Labsphere , using BaSO4 reflectance standards.

Upon HCl loading, the Soret band is red shifted, and the four Q-bands collapse, consistent with porphyrin protonation due to increased symmetry.[1]

Upon formic acid loading there is a lesser red shift of the Soret band, and the Q-bands are still visible, suggesting partial protonation of the porphyrin.

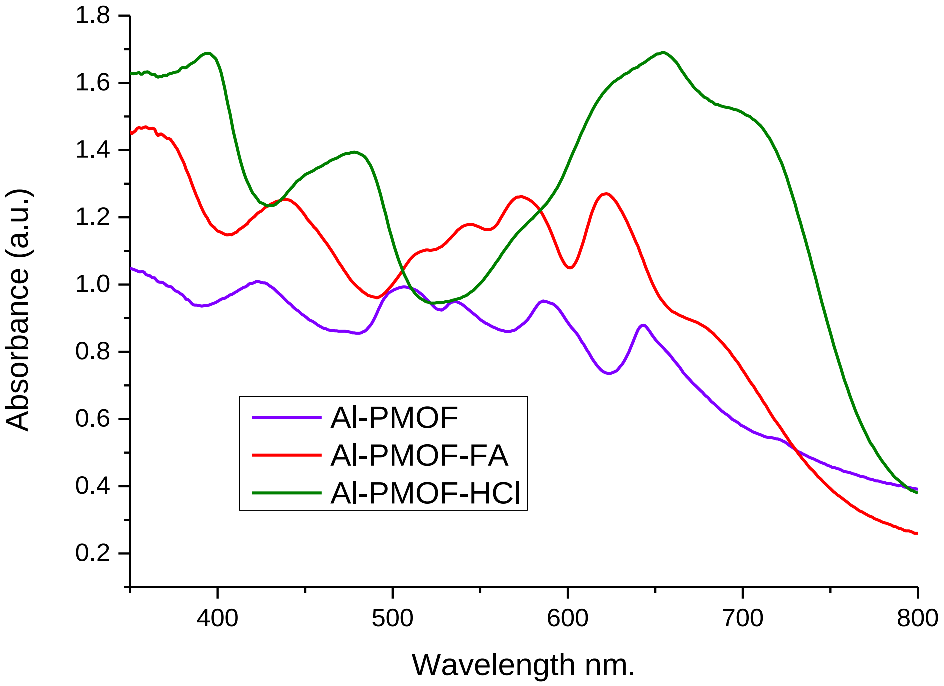


Figure S7. UV/vis spectra of the Al-PMOF (purple), Al-PMOF-HCl (green) and Al-PMOF-FA (red)

Figure S8. From left to right, Al-PMOF, Al-PMOF-HCl, Al-PMOF-FA

Accessible pore volume

Calculations using OLEX^2 [2] were performed to calculate the maximum accessible volume of Al-PMOF to guests. Kinetic diameters of 3.2Å[3], 5.40 Å[4] and 2.65 Å[3] were used for HCl, HCOOH and H_2O. Maximum loading was calculated by using the liquid density of the adsorbate.

Adsorbate	Calculated accessible volume (Å^3 per unit cell)	Maximum loading (guests per porphyrin)	Experimental loading (guests per porphyrin)
HCl	1954.7	19.23	6.5
HCOOH	1299.6	10.37	6.4
H_2O	2011.0	33.61	15.3(Al-PMOF-HCl), 4.0(Al-PMOF-FA)

Table S1. Calculated maximum guest loading in comparison with experimental loading

It is calculated that Al-PMOF-HCl guests occupy 78% of the accessible pore volume, whereas Al-PMOF-FA guests occupy 52% of the accessible pore volume.

Gas Sorption Measurements

Isotherms were measured using N_2 (Research grade 5.5, purity 99.9995% from BOC®) at 77K using a Micromeritics ASAP 2020 and a Micromeritics TriStar II. Samples were degassed at 170°C under vacuum (10^{-2} mbar) overnight before analysis.

Elemental analysis

C, H, and N contents were measured using a Thermo EA1112 Flash CHNS-O Analyzer in the University of Liverpool.

XRD

X-ray powder diffraction data was collected at room temperature on a Panalytical X'Pert Pro diffractometer using Cu $K\alpha$ radiation operating in transmission mode.

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