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COMMUNICATION

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

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A porphyrin-based metal-organic framework is shown to be structurally stable towards acid loading using either hydrochloric or formic acid. The capacity of this material as an ammonia sorbent was analysed using micro-breakthrough experiments in both dry and humid ammonia flows. The acid loaded material exhibited excellent uptake in comparison with the parent MOF.

Metal-organic frameworks (MOFs) are a class of porous crystalline materials consisting of organic linker units attached to inorganic nodes.^{1,2} With their high pore volume and tuneable functionality, the study of MOFs has been extensive in areas such as gas storage and separation,³⁻⁸ catalysis,⁹⁻¹² chemical sensing,¹³⁻¹⁵ drug delivery¹⁶ and light harvesting.^{17, 18} The use of MOFs as sorbents for toxic industrial chemicals (TICs) is receiving growing attention, with materials often outperforming activated carbon, the current mainstay employed in industrial and military filters.¹⁹⁻²¹ It has been shown that by tailoring the chemical environment within the pores of the MOF with regard to the chemical functionality of the TIC of interest, much higher uptake performance can be achieved. In the particular case of ammonia, the majority of examples either make use of coordinatively unsaturated metal sites within the framework to form coordinate covalent bonds with ammonia,²²⁻²⁵ or employ specific organic linkers that interact with ammonia via intermolecular forces such as hydrogen bonding.²⁵⁻²⁷ Examples of MOFs that exploit Brønsted acidic sites within the framework are far fewer.^{28,29} Herein we demonstrate the ability of a highly stable porphyrin based MOF to maintain its structure after loading with hydrochloric or formic acid, and its subsequent utility as an acid reservoir for the uptake of ammonia in both dry and humid conditions.

$\text{Al}_2(\text{OH})_2(\text{H}_2\text{TCCPP})$, referred to as Al-PMOF, is a permanently porous MOF with infinite $\text{Al}(\text{OH})\text{O}_4$ chains arranged in an almost square array by a free-base porphyrin linker, giving rise to three dimensional channels (Figure 1).³⁰ Al-PMOF was prepared according to the procedure developed by Fateeva,³⁰ yielding a highly crystalline material with a surface area of $1400 \text{ m}^2\text{g}^{-1}$. Following the removal of guest molecules (170 °C, 10^{-2} mbar), the material was loaded with HCl by setting the MOF in a sealed vessel containing conc. HCl for 16 h, exposing the MOF to the HCl vapour and atmospheric H_2O (Figure S2). It can be seen from powder X-ray diffraction (Figure

2a) and gas adsorption experiments (Figure 3a) that the Al-PMOF exhibits remarkable stability towards HCl. Upon HCl uptake, a colour change from purple to green is observed, attributed to protonation of the porphyrinic nitrogen atoms, and the powder X-ray diffraction acquires an amorphous hump in the $20\text{-}35^\circ$ 2θ region (Figure 2a). This is most likely a result of the short range order exhibited by HCl and H_2O within the pores of the framework. Indeed, it is observed from ion chromatography and thermogravimetric analysis (see Supporting Information) that Al-PMOF-HCl contains 6.5 HCl molecules and 15.3 H_2O molecules per porphyrin linker. Upon removal of these guest molecules (170 °C, 10^{-2} mbar), we see the crystallinity is largely restored, however a slight decrease in pore volume is observed (Figure 3a).

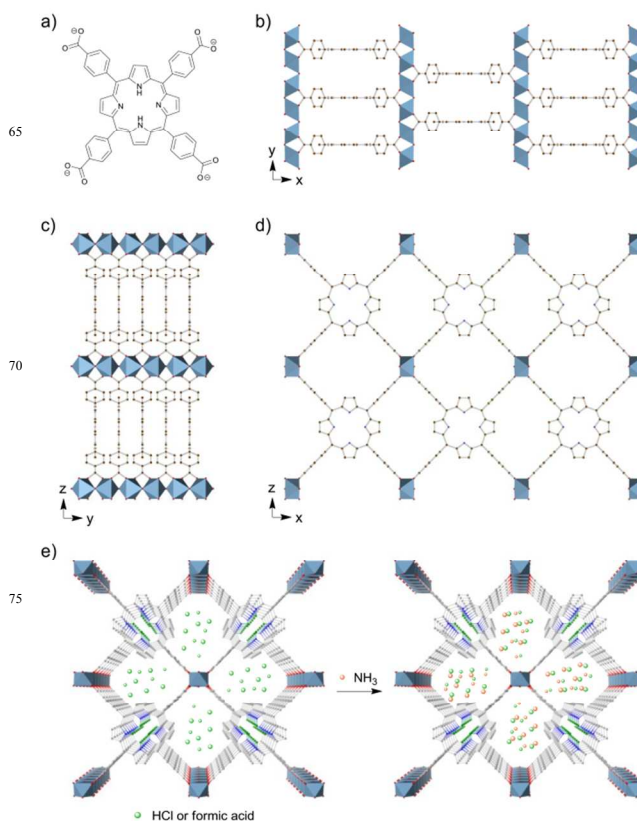


Fig 1. a) *meso*-tetra(4-carboxyl-phenyl) porphyrin (H_2TCCPP) linker. b-d) Crystal structure of Al-PMOF viewed along the [001], [100], and [010] directions, respectively. e) Schematic illustrating the effect of acid loading on NH_3 uptake.

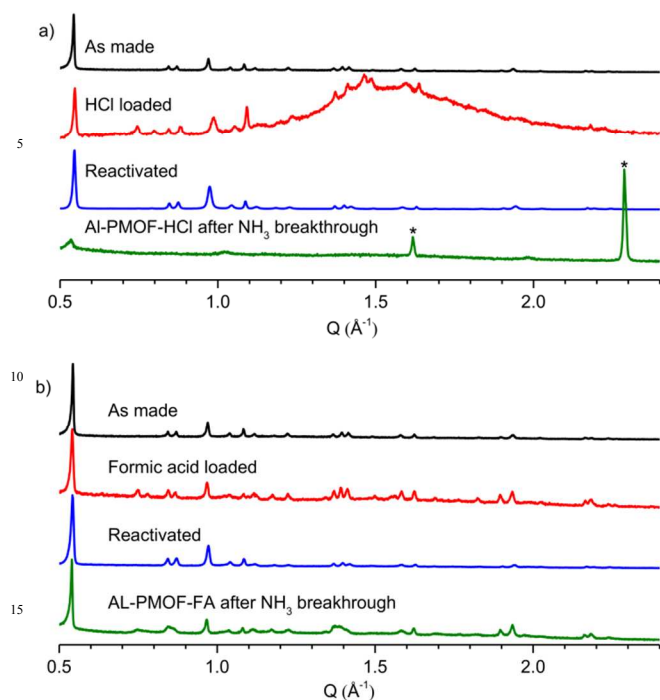


Fig 2. Powder X-ray diffraction patterns of the Al-PMOF as made (black) acid loaded (red) reactivated (blue) and following NH_3 breakthrough (green); a) HCl b) formic acid. Starred peaks correspond to ammonium chloride, ($Q=2\pi/d$).

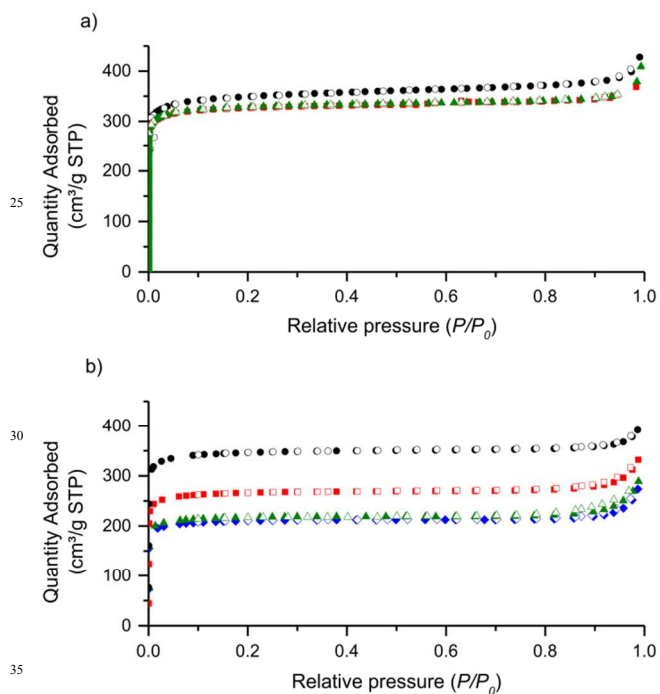


Fig 3. Nitrogen isotherms at 77K after cycling hydrochloric (a) and formic (b) acid uptake and removal at 170°C , 10^{-2} mbar. Fresh, activated Al-PMOF is shown in black circles; the first, second and third cycles are shown in red squares, blue diamonds and green triangles, respectively. Adsorption and desorption is denoted by filled and empty symbols.

40 unloading HCl afford no further decrease in pore volume. It is noted that desolvated Al-PMOF adsorbs only 1.8 H_2O molecules per porphyrin from the atmosphere in ambient conditions likely due to the hydrophobic nature of the porphyrin linker; the considerable increase observed in the acid loaded material is

45 likely due to the polar nature of the acids within the pores creating a more hydrophilic environment. The formic acid loaded material, Al-PMOF-FA, was prepared by sealing freshly activated Al-PMOF in a vessel with formic acid, exposing the MOF to formic acid vapour for 16 h. 50 Thermogravimetric analysis shows comparable loading could also be achieved by stirring Al-PMOF in neat formic acid for 1 h (Figure S4). Upon loading Al-PMOF with formic acid, we once again observed a colour change associated with porphyrin protonation. In contrast with Al-PMOF-HCl, it is observed that 55 crystallinity remains in Al-PMOF-FA (Figure 2b). We observed from ion chromatography and thermogravimetric analysis (Figure S3) that Al-PMOF-FA contains 6.4 HCOOH molecules and 4.0 H_2O molecules per porphyrin linker. From gas adsorption experiments however, the loading of formic acid is seen to be 60 more detrimental than HCl to the pore volume of the material, reducing it by 23 % on the first cycle, and a further 16% on the second cycle. A third cycle of loading and unloading formic acid afforded no further deterioration (Figure 3b).

In order to assess the capacity for ammonia uptake, 65 kinetic micro-breakthrough experiments were carried out under both dry and humid streams of ammonia (0 % and 80 % relative humidity (RH), respectively). (See ESI for micro-breakthrough apparatus and procedures). The results are summarised in Table 1. It is seen that free-base Al-PMOF outperforms BPL activated 70 carbon, with dry and humid breakthrough occurring after 13.5 min and 25 min respectively, compared to 7 and 13 min for carbon (Figure 4). We suggest that the bridging hydroxyl in the $\text{Al}(\text{OH})\text{O}_4$ chains and the porphyrin nitrogens can act as favourable hydrogen bonding sites for ammonia. The presence of 75 water is seen here to improve ammonia uptake, this is often the case in porous materials, a result of the high solubility of ammonia in the water film formed in the pores.³¹

Upon HCl loading, the performance of the framework is dramatically increased, with ammonia breakthrough occurring 80 after 133 and 226 minutes in dry and humid air respectively. It is seen from powder X-ray diffraction data that following exposure to ammonia, Al-PMOF-HCl loses much of its crystallinity, however the most intense peak of the parent material peak at 0.54 \AA^{-1} is still clearly present. Furthermore, an additional phase 85 appears which matches ammonium chloride (Figure 2a). The formation of NH_4Cl indicates that the interaction between the influent ammonia and the HCl within the pores is a simple Brønsted acid-base reaction.

Al-PMOF-FA also exhibits greatly improved 90 performance over the parent MOF, with ammonia breakthrough occurring after 110 and 159 minutes in dry and humid streams, respectively. Interestingly, powder X-ray diffraction of the sample after ammonia breakthrough shows no reflections associated with ammonium formate. Furthermore, though the 95 PXRD shows a slight loss of crystallinity in comparison with the parent phase, the ammonia treated Al-PMOF-FA is still highly crystalline, consistent with the reduced X-ray scattering power of

the constituent atoms of formate compared with chloride and thus their weaker impact on the diffraction pattern (Figure 2b).

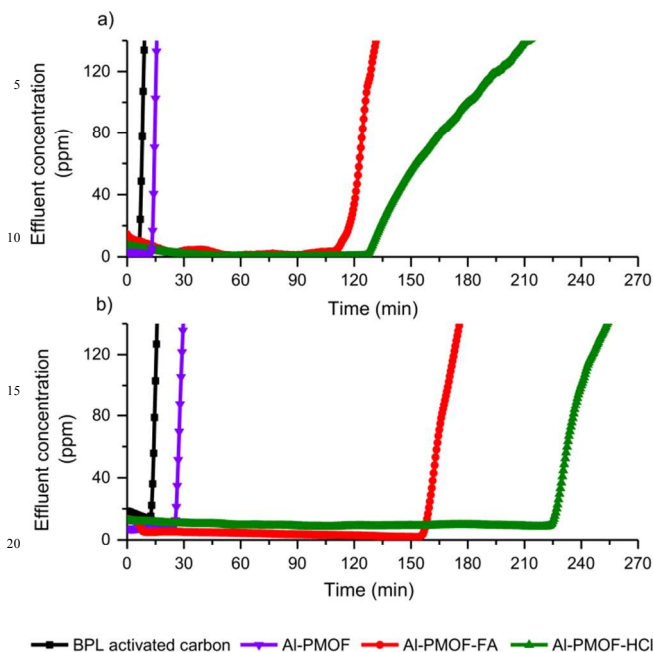


Fig 4. Dynamic ammonia breakthrough: a) 0% relative humidity; b) 80% relative humidity.

Table 1. Breakthrough times and uptake of ammonia

Material	RH (%)	Breakthrough time (min)	NH ₃ uptake at breakthrough	
			wt%	Per formula unit
Al-PMOF	0	13.5	0.5	0.3
	80	25	0.9	0.5
Al-PMOF-HCl	0	133	4.6	3.8
	80	226	7.9	6.4
Al-PMOF-FA	0	110	3.8	2.8
	80	159	5.5	4.0

These ammonia uptakes compare favourably with those recently reported for a wide range of other MOFs.³²

Conclusions

An aluminium porphyrin-based metal-organic framework has been shown to adsorb large quantities of both hydrochloric and formic acids. The material shows remarkable stability towards these reactive guests, even allowing cycling of acid loading despite vigorous removal conditions. By exploiting Brønsted acid-Brønsted base interactions, micro-breakthrough experiments have shown that we can utilize the high density of acid groups within the pores to afford greatly improved ammonia uptake in comparison to both the parent MOF and activated carbon, the current mainstay in single use protection. Furthermore, the materials exhibit an additional increase in performance against ammonia under humid conditions, with a capacity of up to 7.9 wt% ammonia at breakthrough.

Notes and references

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† Electronic Supplementary Information (ESI) available: Synthetic methods, details of micro-breakthrough procedure and equipment, TGA, UV-Vis and PXRD. See DOI: 10.1039/b000000x/

- H. Furukawa, K. E. Cordova, M. O'Keeffe and O. M. Yaghi, *Science*, 2013, **341**.
- M. L. Foo, R. Matsuda and S. Kitagawa, *Chem. Mater.*, 2014, **26**, 310-322.
- B. Van de Voorde, B. Bueken, J. Denayer and D. De Vos, *Chem. Soc. Rev.*, 2014, **43**, 5766-5788.
- H. Sato, W. Kosaka, R. Matsuda, A. Hori, Y. Hijikata, R. V. Belosludov, S. Sakaki, M. Takata and S. Kitagawa, *Science*, 2014, **343**, 167-170.
- Z. R. Herm, B. M. Wiers, J. A. Mason, J. M. van Baten, M. R. Hudson, P. Zajdel, C. M. Brown, N. Masciocchi, R. Krishna and J. R. Long, *Science*, 2013, **340**, 960-964.
- J.-R. Li, J. Sculley and H.-C. Zhou, *Chem. Rev.*, 2012, **112**, 869-932.
- E. D. Bloch, W. L. Queen, R. Krishna, J. M. Zadrozny, C. M. Brown and J. R. Long, *Science*, 2012, **335**, 1606-1610.
- J.-R. Li, R. J. Kuppler and H.-C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477-1504.
- J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang and C.-Y. Su, *Chem. Soc. Rev.*, 2014, **43**, 6011-6061.
- P. Garcia-Garcia, M. Mueller and A. Corma, *Chem. Sci.*, 2014, **5**, 2979-3007.
- M. Yoon, R. Srirambalaji and K. Kim, *Chem. Rev.*, 2012, **112**, 1196-1231.
- J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450-1459.
- V. Stavila, A. A. Talin and M. D. Allendorf, *Chem. Soc. Rev.*, 2014, **43**, 5994-6010.
- M. M. Wanderley, C. Wang, C.-D. Wu and W. Lin, *J. Am. Chem. Soc.*, 2012, **134**, 9050-9053.
- L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105-1125.
- P. Horcajada, R. Gref, T. Baati, P. K. Allan, G. Maurin, P. Couvreur, G. Ferey, R. E. Morris and C. Serre, *Chem. Rev.*, 2012, **112**, 1232-1268.
- M. C. So, G. P. Wiederrecht, J. E. Mondloch, J. T. Hupp and O. K. Farha, *Chem. Commun.*, 2015, **51**, 3501-3510.
- J.-L. Wang, C. Wang and W. Lin, *ACS Catal.*, 2012, **2**, 2630-2640.
- J. B. DeCoste and G. W. Peterson, *Chem. Rev.*, 2014, **114**, 5695-5727.
- E. Barea, C. Montoro and J. A. R. Navarro, *Chem. Soc. Rev.*, 2014, **43**, 5419-5430.
- N. A. Khan, Z. Hasan and S. H. Jung, *J. Hazard. Mater.*, 2013, **244-245**, 444-456.
- T. Grant Glover, G. W. Peterson, B. J. Schindler, D. Britt and O. Yaghi, *Chem. Eng. Sci.*, 2011, **66**, 163-170.
- T. Watanabe and D. S. Sholl, *J. Chem. Phys.*, 2010, **133**, 094509.
- G. W. Peterson, G. W. Wagner, A. Balboa, J. Mahle, T. Sewell and C. J. Karwacki, *J. Phys. Chem. C*, 2009, **113**, 13906-13917.
- D. Britt, D. Tranchemontagne and O. M. Yaghi, *Proc. Natl. Acad. Sci. U.S.A.*, 2008, **105**, 11623-11627.
- D. Saha and S. Deng, *J. Colloid Interface Sci.*, 2010, **348**, 615-620.
- C. Lieder, S. Opelt, M. Dyballa, H. Henning, E. Klemm and M. Hunger, *J. Phys. Chem. C*, 2010, **114**, 16596-16602.
- I. Spanopoulos, P. Xydias, C. D. Malliakas and P. N. Trikalitis, *Inorg. Chem.*, 2013, **52**, 855-862.
- W. Morris, C. J. Doonan and O. M. Yaghi, *Inorg. Chem.*, 2011, **50**, 6853-6855.
- A. Fateeva, P. A. Chater, C. P. Ireland, A. A. Tahir, Y. Z. Khimyak, P. V. Wiper, J. R. Darwent and M. J. Rosseinsky, *Angew. Chem. Int. Ed.*, 2012, **51**, 7440-7444.
- C. Petit, B. Mendoza and T. J. Bandosz, *Langmuir*, 2010, **26**, 15302-15309.
- H. Jasuja, G. W. Peterson, J. B. Decoste, M. A. Browe and K. S. Walton, *Chem. Eng. Sci.*, 2015, **124**, 118-124.