

# ChemComm

Chemical Communications

rsc.li/chemcomm



ISSN 1359-7345

**COMMUNICATION**

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 Cite this: *Chem. Commun.*, 2024, 60, 5912

 Received 29th March 2024,  
 Accepted 25th April 2024

DOI: 10.1039/d4cc01449a

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## High adsorption of ammonia in a titanium-based metal–organic framework†

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We report the high adsorption of NH<sub>3</sub> in a titanium-based metal–organic framework, MFM-300(Ti), comprising extended [TiO<sub>6</sub>]<sub>∞</sub> chains linked by biphenyl-3,3',5,5'-tetracarboxylate ligands. At 273 K and 1 bar, MFM-300(Ti) shows an exceptional NH<sub>3</sub> uptake of 23.4 mmol g<sup>-1</sup> with a record-high packing density of 0.84 g cm<sup>-3</sup>. Dynamic breakthrough experiments confirm the excellent uptake and separation of NH<sub>3</sub> at low concentration (1000 ppm). The combination of *in situ* neutron powder diffraction and spectroscopic studies reveal strong, yet reversible binding interactions of NH<sub>3</sub> to the framework oxygen sites.

Ammonia (NH<sub>3</sub>) is an important feedstock that is produced at a scale of ca. 150 million tonnes per year.<sup>1</sup> In addition, the high volumetric (~0.105 kg L<sup>-1</sup>) and gravimetric (17.7 wt%) hydrogen densities of NH<sub>3</sub> make it a promising renewable fuel and a potential hydrogen carrier for on-board storage. However, the highly toxic and corrosive nature of NH<sub>3</sub> poses challenges in its safe storage and transportation. At present, NH<sub>3</sub> is transported as a compressed liquid either at 10 bar at 25 °C or at ambient pressures at low temperature (liquefaction point of -33 °C).<sup>2</sup> Thus, the development of robust sorbents for reversible NH<sub>3</sub> adsorption under mild conditions is of great importance.

Porous materials, such as zeolites,<sup>3</sup> active carbons,<sup>4</sup> mesoporous silica,<sup>5</sup> and organic polymers<sup>6</sup> have been tested for NH<sub>3</sub> adsorption. However, these materials demonstrate limited capacities; for example, 9.3 mmol g<sup>-1</sup> in 13X zeolite,<sup>3</sup> 8.8 mmol g<sup>-1</sup> in MCM-41,<sup>5</sup> and 11.4 mmol g<sup>-1</sup> in Amberlyst 15.<sup>7</sup> Metal–organic frameworks (MOFs)

have demonstrated potential for NH<sub>3</sub> adsorption<sup>8</sup> owing to their high accessible surface area, and their tailored porosity and pore environment. The MOFs displaying top performance for NH<sub>3</sub> adsorption are primarily divalent/trivalent-based MOFs or MOF composites, such as LiCl@MIL-53-(OH)<sub>2</sub><sup>9</sup> (33.9 mmol g<sup>-1</sup> at 298 K and 1 bar) and Ni<sub>2</sub>acyl-TMA<sup>10</sup> (23.5 mmol g<sup>-1</sup> at 298 K and 1 bar). However, the stability of MOFs toward NH<sub>3</sub> adsorption needs to be improved, and typically tetravalent metal-based MOFs (*e.g.*, Zr<sup>4+</sup>, V<sup>4+</sup>, Hf<sup>4+</sup>) exhibit enhanced thermal and chemical stability. However, the reported Zr-based MOFs show limited NH<sub>3</sub> adsorption capacities (8.40 mmol g<sup>-1</sup> in UiO-67<sup>11</sup>). On the other hand, the study of V-based MFM-300(V) for NH<sub>3</sub> adsorption has revealed that the incorporation of V<sup>4+</sup> can effectively enhance the NH<sub>3</sub> adsorption,<sup>12</sup> which is attributed to the charge transfer within the framework and the formation of N<sub>2</sub>H<sub>4</sub>.

Herein, we report a novel Ti<sup>4+</sup>-based MOF, MFM-300(Ti) [Ti<sub>2</sub>(O)<sub>2</sub>(C<sub>16</sub>H<sub>6</sub>O<sub>8</sub>)], which displays a reversible NH<sub>3</sub> uptake of 23.4 mmol g<sup>-1</sup> at 273 K and 1 bar, among the best NH<sub>3</sub> sorbent materials showing reversible adsorption to date. Significantly, the packing density of NH<sub>3</sub> in MFM-300(Ti) (0.84 g cm<sup>-3</sup>, calculated using the pore volume derived from crystallographic data) is comparable to that of solid NH<sub>3</sub> at -80 °C (0.82 g cm<sup>-3</sup>), due to the strong guest–guest interaction within the pores. In addition, breakthrough experiments confirm that MFM-300(Ti) can effectively capture and separate NH<sub>3</sub> at low concentrations (1000 ppm). The binding sites of NH<sub>3</sub> in MFM-300(Ti) have been determined by *in situ* neutron powder diffraction (NPD), and its binding dynamics investigated by a combination of *in situ* inelastic neutron scattering (INS) and synchrotron IR microspectroscopy.

Solvated MFM-300(Ti), [Ti<sub>2</sub>(O)<sub>2</sub>(C<sub>16</sub>H<sub>6</sub>O<sub>8</sub>)(H<sub>2</sub>O)<sub>2</sub>(C<sub>3</sub>H<sub>6</sub>O)<sub>0.7</sub>], was prepared *via* a solvothermal reaction of {Ti<sub>8</sub>AF} clusters,<sup>13</sup> H<sub>4</sub>L (biphenyl-3,3',5,5'-tetracarboxylic acid, H<sub>4</sub>bptc), acetic acid, acetic anhydride and methanol at 180 °C for 12 h. Structure solution by NPD (Fig. 1a and b) confirms that MFM-300(Ti) crystallises in the tetragonal space group *I*<sub>4</sub>22 and is isostructural to other MFM-300 materials.<sup>14</sup> The presence of *cis*-μ<sub>2</sub>-O moieties rather than *cis*-μ<sub>2</sub>-OH groups as

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 † Electronic supplementary information (ESI) available. CCDC 2296493, 2296494 and 2296495. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d4cc01449a>




**Fig. 1** Views of crystal structures of bare and  $\text{ND}_3$ -loaded MFM-300(Ti) as determined by NPD at 10 K. The occupancy of each site has been converted to  $\text{ND}_3/\text{Ti}$  for clarity. (a) and (b) Views of MFM-300(Ti) and MFM-300( $\text{M}^{\text{III}}$ ) along the  $c$ -axis, respectively. (c) and (f) Views of packing of  $\text{ND}_3$  in MFM-300(Ti) along the  $c$ -axis in MFM-300(Ti)-0.84  $\text{ND}_3$  and MFM-300(Ti)-2.54  $\text{ND}_3$ , respectively. (d) and (g) Detailed views of host-guest interactions in MFM-300(Ti)-0.84  $\text{ND}_3$  and MFM-300(Ti)-2.54  $\text{ND}_3$ , respectively. (e) and (h) Guest-guest interaction along  $c$ -axis in MFM-300(Ti)-0.84  $\text{ND}_3$  and MFM-300(Ti)-2.54  $\text{ND}_3$ , respectively. Colour code for atoms: Ti, turquoise; O, red; C, grey; H, tan; N, blue (dark blue, blue, and light blue for site I, II, and III, respectively); D, purple.

observed in  $\text{M}^{3+}$ -based analogues is confirmed by NPD and FTIR spectra (Fig. 1a and b, Fig. S7, ESI<sup>†</sup>). MFM-300(Ti) exhibits an open framework structure comprising of chains of  $[\text{TiO}_4(\text{O})_2]$  moieties bridged by tetracarboxylate ligands  $\text{L}^{4-}$  to afford 1D channels along the  $c$  axis with a diameter of 7.4 Å. Desolvated MFM-300(Ti) displays a Brunauer-Emmett-Teller (BET) surface area of  $890 \text{ m}^2 \text{ g}^{-1}$  and pore volume of  $0.44 \text{ cm}^3 \text{ g}^{-1}$ , as determined from the  $\text{CO}_2$  isotherm at 195 K (Fig. S1, ESI<sup>†</sup>), consistent with the porosity derived from the crystal structure (pore volume of  $0.45 \text{ cm}^3 \text{ g}^{-1}$ ). Crystallites of MFM-300(Ti) show rod-like morphology (Fig. S2, ESI<sup>†</sup>). The excellent thermal stability up to 450 °C and the chemical stability of MFM-300(Ti) has been confirmed by thermogravimetric analysis (TGA; Fig. S3, ESI<sup>†</sup>), variable temperature powder X-ray diffraction (VT-PXRD; Fig. S4, ESI<sup>†</sup>), PXRD analysis of samples soaked in various solutions (Fig. 1c and Fig. S5, ESI<sup>†</sup>), and the  $\text{CO}_2$  adsorption measurements for samples after various treatments to confirm the porosity (Fig. S6, ESI<sup>†</sup>).

The adsorption isotherms for  $\text{NH}_3$  in MFM-300(Ti) were measured between 273 and 308 K at 1 bar (Fig. 2a). MFM-300(Ti) exhibits an exceptional and fully reversible  $\text{NH}_3$  uptake of  $23.4 \text{ mmol g}^{-1}$  at 273 K and 1.0 bar, comparable to state-of-the-art sorbents (Table S1, ESI<sup>†</sup> and Fig. 2e). Hysteresis in the  $\text{NH}_3$  isotherms was observed at all temperatures, indicating the presence of strong host-guest interactions. The pressure-swing experiment was conducted at 298 K from 0 to 0.1 bar. Little change in sorption capacity or structure was observed for MFM-300(Ti) after 25 cycles of adsorption and desorption of  $\text{NH}_3$  (Fig. 2b and c), confirming the excellent stability of MFM-300(Ti) towards  $\text{NH}_3$ . The residual  $\text{NH}_3$  observed on desorption during cyclic pressure-swing experiments suggests the presence of strong binding sites in the pore, consistent with

the observed hysteresis. The dynamic  $\text{NH}_3$  uptake of MFM-300(Ti) at low concentration (1000 ppm) was recorded as  $0.6 \text{ mmol g}^{-1}$  at 298 K, demonstrating an excellent capture capability (Fig. 2d). The heat of adsorption ( $Q_{\text{st}}$ ) of  $\text{NH}_3$  in MFM-300(Ti) was calculated to be 39–52  $\text{kJ mol}^{-1}$  (Fig. 2f and Table S2, ESI<sup>†</sup>), comparable with other MOFs incorporating strong binding sites, such as UiO-66Cu(II)<sup>15</sup> (25–55  $\text{kJ mol}^{-1}$ ).

*In situ* NPD data for  $\text{ND}_3$ -loaded MFM-300(Ti) were collected at 10 K ( $\text{ND}_3/\text{Ti} = 0.42, 1.27$ ), and Rietveld refinements afforded distinct binding sites for  $\text{ND}_3$ . At low-loading ( $\text{ND}_3/\text{Ti} = 0.42$ ; MFM-300(Ti)-0.84  $\text{ND}_3$ ) (Fig. 1c and d), two binding sites (I and II) are observed. Site I is anchored by hydrogen bonding between the  $\text{ND}_3$  molecules and the carboxylate oxygen atoms [ $\text{ND}_3 \cdots \text{O}_{\text{ligand}} = 2.10(2)\text{--}2.97(3) \text{ \AA}$ ]. Site II is adjacent to site I, stabilised by hydrogen bonding interactions [ $\text{ND}_3 \cdots \text{O}_{\text{ligand}} = 2.99(8) \text{ \AA}$ ], electrostatic interactions [ $\text{ND}_3 \cdots \text{aromatic rings} = 2.52(3)\text{--}2.73(15) \text{ \AA}$ ], and guest-guest interactions [ $\text{ND}_3 \cdots \text{ND}_3 = 1.87(2)\text{--}2.52(4) \text{ \AA}$ ]. Interestingly, when the loading was increased to 1.27  $\text{ND}_3/\text{Ti}$  (MFM-300(Ti)-2.54  $\text{ND}_3$ ) (Fig. 2e and f), an additional binding site was observed even closer to the  $[\text{TiO}_6]_{\infty}$  chain and stabilised by multiple supramolecular interactions [ $\text{C-H}_{\text{aromatic}} \cdots \text{N} = 1.50(3)\text{--}2.24(3) \text{ \AA}$ ,  $\text{ND}_3 \cdots \text{O}_{\text{ligand}} = 1.92(5)\text{--}2.38(6) \text{ \AA}$ , and  $\text{ND}_3 \cdots \text{O}_{\text{bridge}} = 2.33(6)\text{--}2.78(6) \text{ \AA}$ ]. In addition, the adsorbed  $\text{ND}_3$  molecules propagated to form a 1D network within the channel of MFM-300(Ti) (Fig. 1e and h). Moreover, the hydrogen bonding distance [ $\text{N-D} \cdots \text{N} = 2.37(6)\text{--}2.52(3) \text{ \AA}$ ] between adsorbed  $\text{ND}_3$  molecules in MFM-300(Ti)-0.84  $\text{ND}_3$  decreases to [ $\text{N-D} \cdots \text{N} = 1.87(3)\text{--}2.00(3) \text{ \AA}$ ] in MFM-300(Ti)-2.54  $\text{ND}_3$ . This tighter host-guest and guest-guest interaction with increasing  $\text{NH}_3$  loading is consistent with the trend of  $Q_{\text{st}}$  (Fig. 2f). Notably, the shortest distance between adsorbed  $\text{ND}_3$  molecules in MFM-300(Ti) is 1.87 Å, which is notably shorter than those previously observed [2.33 Å in MFM-300(Fe); 3.05 Å in





**Fig. 2** (a) Adsorption isotherms of  $\text{NH}_3$  in MFM-300(Ti) at 273–308 K up to 1.0 bar (adsorption, solid symbols; desorption, open symbols). (b) Cyclic adsorption–desorption of  $\text{NH}_3$  in MFM-300(Ti) at 298 K between 0 and 0.1 bar; dark-coloured bars show the residual  $\text{NH}_3$  within the MOF upon pressure-swing desorption at 298 K. (c) PXRD patterns of MFM-300(Ti), (black: as-synthesised, red: after soaking in concentrated  $\text{HNO}_3$  for one day, blue: after soaking in aqua regia for one day, dark yellow: after 25 adsorption–desorption cycles). (d) Breakthrough experiment for  $\text{NH}_3$  (1000 ppm diluted in He) through a fixed-bed packed with MFM-300(Ti). (e) Plot of  $\text{NH}_3$  isothermal adsorption capacities and  $\text{NH}_3$  packing density in stable MOF materials (f) isothermic enthalpy and entropy of adsorption for MFM-300(Ti) at different  $\text{NH}_3$  loadings.

MFM-300( $\text{V}^{\text{IV}}$ )<sup>15</sup> and reflects highly efficient packing of  $\text{NH}_3$  molecules in MFM-300(Ti), consistent with the high packing density derived from the adsorption isotherms. Compared with MFM-300( $\text{M}^{\text{III}}$ ),<sup>15</sup> the replacement of  $\mu_2\text{-OH}$  by  $\mu_2\text{-O}$  in MFM-300(Ti) reduces the steric hindrance between the bridging hydroxyl groups and guest molecules, providing additional binding sites and boosting the storage of  $\text{NH}_3$ . In MFM-300( $\text{V}^{\text{IV}}$ ), the presence of the vanadium centre promotes charge transfer between  $\text{NH}_3$  molecules, resulting in the observation of both  $\text{N}_2\text{D}_4$  and  $\text{ND}_4^+$  molecules in the pore,<sup>15</sup> which limits the reusability of the MOF. The utilisation of  $\text{Ti}^{4+}$  ions not only improves the structural stability of the material, but also hinders charge transfer to enhance the adsorption reversibility of  $\text{NH}_3$ .

The dynamics of host–guest binding has been analysed using *in situ* synchrotron IR microspectroscopy, INS, and density functional theory (DFT) calculations. The absence of the characteristic IR band of hydroxyl group at  $\sim 3600\text{ cm}^{-1}$  in activated MFM-300(Ti) (Fig. S7, ESI<sup>†</sup>) confirmed the presence of *cis*- $\mu_2\text{-O}$  as a result of the tetravalent  $\text{Ti}^{4+}$  sites, consistent with the NPD analysis. On loading  $\text{NH}_3$ , a new band at  $3381\text{ cm}^{-1}$  assigned to a  $\nu(\text{N-H})$  stretching vibration is observed,



**Fig. 3** *In situ* synchrotron FT-IR spectra of MFM-300(Ti) as a function of  $\text{NH}_3$  adsorption and of regenerated MFM-300(Ti) under a flow of dry  $\text{N}_2$  at  $100\text{ mL min}^{-1}$  at 298 K for 2 h.

confirming the adsorption in the framework (Fig. 3). The band at  $1614\text{ cm}^{-1}$  can be assigned to  $\nu_{\text{as}}(\text{COO}^-)$ , which broadens on loading of  $\text{NH}_3$ . The bands at  $1470\text{ cm}^{-1}$ ,  $1414\text{ cm}^{-1}$ ,  $1360\text{ cm}^{-1}$ , and  $1320\text{ cm}^{-1}$  can be assigned to different vibrations  $\nu_{\text{s}}(\text{COO}^-)$  of the carboxylate group in the framework, and all show red-shifts on increasing loading of  $\text{NH}_3$ . This suggests the presence of strong interactions between  $\text{NH}_3$  and the carboxylate groups of the bridging ligand. Simultaneously, as the concentration of  $\text{NH}_3$  increases from 2% to 5%, two bands at 1548 and  $1500\text{ cm}^{-1}$  corresponding to aromatic C–C stretching vibrations merge into one band ( $1525\text{ cm}^{-1}$ ), which is not observed in other MFM-300 materials. This indicates a notable change in the conjugated structure of the aromatic rings, which is further evidenced by the elongation of the C–C bonds in the biphenyl linker from  $1.458(2)\text{ \AA}$  in bare MFM-300(Ti) to  $\sim 1.497(4)\text{ \AA}$  in MFM-300(Ti)-0.84  $\text{ND}_3$  and further to  $\sim 1.500(7)\text{ \AA}$  in MFM-300(Ti)-2.54  $\text{ND}_3$ , as determined by the NPD analysis (Table S9, ESI<sup>†</sup>).

A combination of INS and DFT calculations has been employed to elucidate the dynamic behaviour of adsorbed  $\text{NH}_3$  within MFM-300(Ti). The congruence between experimental and simulated INS spectra for MFM-300(Ti) (Fig. S12, ESI<sup>†</sup>) and  $\text{NH}_3$ -loaded MFM-300(Ti) (Fig. S13, ESI<sup>†</sup>) is remarkable, allowing the assignments of INS peaks. Distinct peaks were observed in the INS difference spectra, which were obtained by subtracting the features of the bare MFM-300(Ti) and the sample cell from the spectra of  $\text{NH}_3$ -loaded MFM-300(Ti) (Fig. 4b). Translational and rotational modes of adsorbed  $\text{NH}_3$  molecules around its  $C_3$  axis are observed between 4.4–14.4 meV and 16.6–23.5 meV, respectively. The bands at 26.5–41.7 meV correspond to the rocking motions of  $\text{NH}_3$  around the N centre (Fig. 4c and d). In comparison to the spectrum of  $\text{NH}_3$  in the solid state, where each  $\text{NH}_3$  molecule forms a 3D hydrogen bonding network with six adjacent  $\text{NH}_3$  molecules, the bands in all regions for adsorbed  $\text{NH}_3$  exhibit shifts to lower energy and display broader features (for solid  $\text{NH}_3$ , 6.3–23.1 meV translational modes; 27.6–35.5 meV rotational modes; 36.7–56.9 meV rocking modes) (Fig. 4a). This phenomenon suggests a more dynamic environment for the adsorbed  $\text{NH}_3$  molecules within MFM-300(Ti). Specifically, the





**Fig. 4** Views of *in situ* INS spectra and the corresponding vibrational modes for MFM-300(Ti), before and after adsorption of NH<sub>3</sub>. Difference spectra were obtained by subtraction of the INS spectra of the bare MOF from that for the NH<sub>3</sub>-loaded MOF and are marked as Expt-Diff (experimental difference spectra). (a) Comparison of vibrational modes between solid NH<sub>3</sub> at 10 K (4.4–14.4 meV translational modes; 16.6–23.5 meV rotational modes; 26.5–41.7 meV rocking modes). (b) Experimental difference INS spectra for MFM-300(Ti) upon adsorption of NH<sub>3</sub> in the higher energy range. The scale factor for difference spectrum is 3. (c) and (d) Selected vibrational modes of confined NH<sub>3</sub> molecule and MFM-300(Ti).

rotational modes show more significant red shifts, attributed to the higher rotational flexibility of NH<sub>3</sub> in its adsorbed environment in MFM-300(Ti).

The vibrational features of the framework have been observed in the high energy region of the difference-INS spectra. Features at (I) 84.9, (II) 117.6, (III) 126.5, (IV) 145.1, and (V) 155.9 meV can be assigned to C–H out-of-C<sub>6</sub>-plane wagging (in-phase along the ring, meaning H atoms move in the same direction), C–H out-of-C<sub>6</sub>-plane twisting (anti-phase along the ring, meaning neighbouring H atoms move in opposite directions), C–H in-C<sub>6</sub>-plane scissoring mode, in phase, C–H in-C<sub>6</sub>-plane scissoring mode, anti-phase, and C–H in-C<sub>6</sub>-plane rocking mode, respectively (Fig. 4b and d). Compared with other MFM-300(M) materials, MFM-300(Ti) shows more versatile C–H bending modes, and the changes in the C–H bending peaks upon adsorption of NH<sub>3</sub> indicate the strong host–guest interactions between the benzyl ring of the framework and NH<sub>3</sub> molecules. These results are in excellent agreement with the NPD and FTIR study.

In summary, we report the high capacity and reversible adsorption of NH<sub>3</sub> within a novel titanium-based MOF, MFM-300(Ti). This framework features a unique structure composed of extended [TiO<sub>6</sub>]<sub>∞</sub> chains linked by tetra-topic ligands [(C<sub>16</sub>H<sub>6</sub>O<sub>8</sub>)<sup>4-</sup>]. Notably, at 273 K and 1 bar, MFM-300(Ti) shows an exceptional NH<sub>3</sub> uptake of 23.4 mmol g<sup>-1</sup> and a record-high packing density of 0.84 g cm<sup>-3</sup>. The volumetric and gravimetric adsorption capacity is 0.36 g cm<sup>-3</sup> and 0.28 g g<sup>-1</sup>, respectively. Dynamic breakthrough experiments confirm excellent adsorption of NH<sub>3</sub> at low concentration

(1000 ppm). The combination of *in situ* NPD, INS, FTIR and DFT studies reveal the molecular details on the host–guest binding interactions. This study has established MFM-300(Ti) as a highly efficient sorbent for NH<sub>3</sub>, demonstrating its potential for practical applications.

We thank EPSRC (EP/I011870, EP/V056409), University of Manchester, National Science Foundation of China and BNLS for funding. This project has received funding from the European Research Council (ERC) under the European Union Horizon 2020 research and innovation programme (grant agreement no. 742401, NANO-CHEM and PoC665632). We are grateful to the STFC/ISIS Facility and Diamond Light Source for access to beamlines WISH/TOSCA and B22 (SM30398), respectively. The computing resources were made available through the VirtuES and the ICE-MAN projects, funded by Laboratory Directed Research and Development program and Compute and Data Environment for Science (CADES) at ORNL.

## Conflicts of interest

There are no conflicts to declare.

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