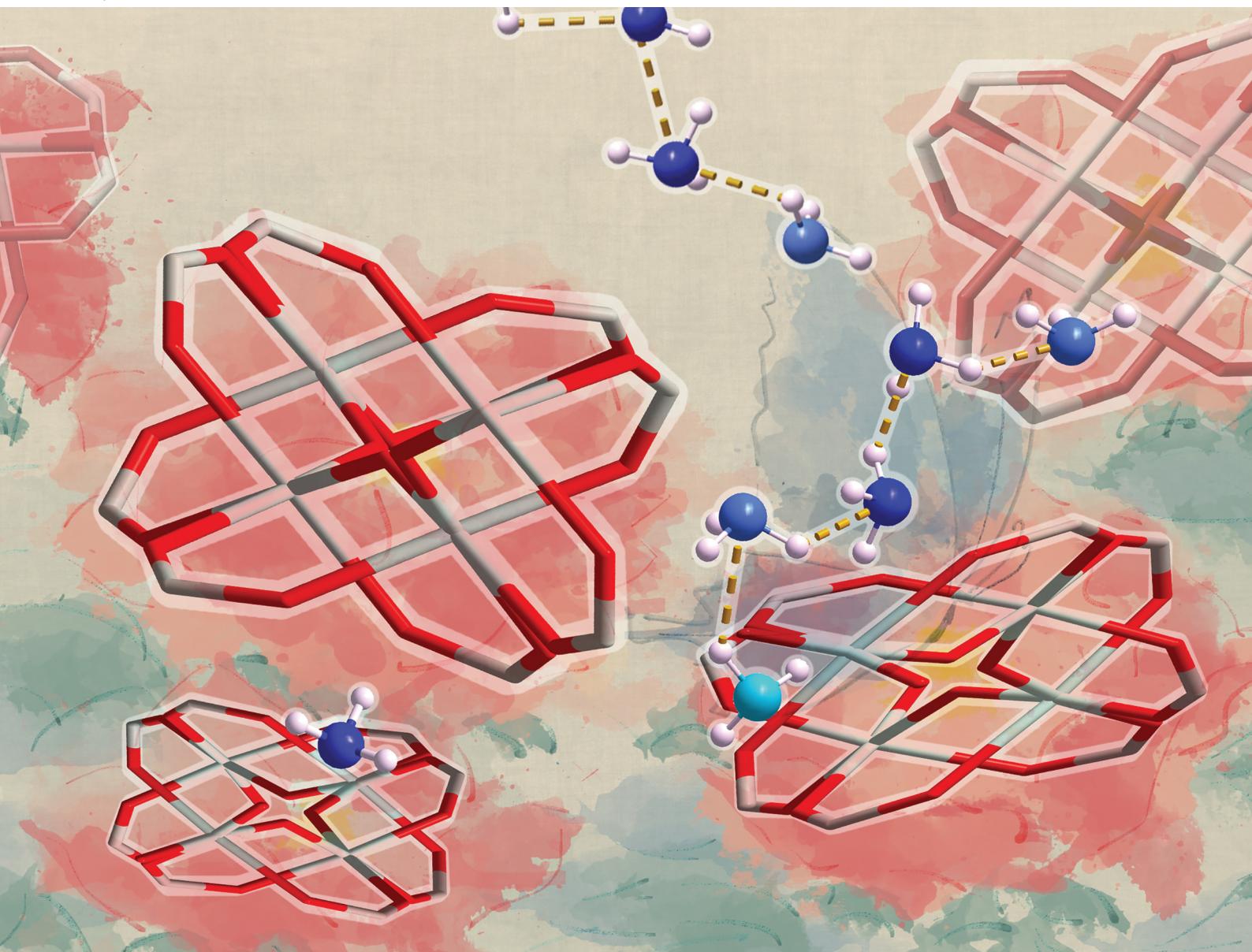


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## COMMUNICATION

Martin Schröder, Sihai Yang *et al.*  
High adsorption of ammonia in a titanium-based  
metal-organic framework



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We report the high adsorption of  $\text{NH}_3$  in a titanium-based metal–organic framework, MFM-300(Ti), comprising extended  $[\text{TiO}_6]_\infty$  chains linked by biphenyl-3,3',5,5'-tetracarboxylate ligands. At 273 K and 1 bar, MFM-300(Ti) shows an exceptional  $\text{NH}_3$  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  $\text{NH}_3$  at low concentration (1000 ppm). The combination of *in situ* neutron powder diffraction and spectroscopic studies reveal strong, yet reversible binding interactions of  $\text{NH}_3$  to the framework oxygen sites.

Ammonia ( $\text{NH}_3$ ) 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 ( $\sim 0.105 \text{ kg L}^{-1}$ ) and gravimetric (17.7 wt%) hydrogen densities of  $\text{NH}_3$  make it a promising renewable fuel and a potential hydrogen carrier for on-board storage. However, the highly toxic and corrosive nature of  $\text{NH}_3$  poses challenges in its safe storage and transportation. At present,  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_3$  adsorption<sup>8</sup> owing to their high accessible surface area, and their tailored porosity and pore environment. The MOFs displaying top performance for  $\text{NH}_3$  adsorption are primarily divalent/trivalent-based MOFs or MOF composites, such as  $\text{LiCl}@\text{MIL-53}-(\text{OH})_2$ <sup>9</sup> (33.9 mmol g<sup>-1</sup> at 298 K and 1 bar) and  $\text{Ni}_\text{acryl\_TMA}$ <sup>10</sup> (23.5 mmol g<sup>-1</sup> at 298 K and 1 bar). However, the stability of MOFs toward  $\text{NH}_3$  adsorption needs to be improved, and typically tetravalent metal-based MOFs (*e.g.*,  $\text{Zr}^{4+}$ ,  $\text{V}^{4+}$ ,  $\text{Hf}^{4+}$ ) exhibit enhanced thermal and chemical stability. However, the reported  $\text{Zr}$ -based MOFs show limited  $\text{NH}_3$  adsorption capacities (8.40 mmol g<sup>-1</sup> in  $\text{UiO-67}^{11}$ ). On the other hand, the study of  $\text{V}$ -based MFM-300(V) for  $\text{NH}_3$  adsorption has revealed that the incorporation of  $\text{V}^{4+}$  can effectively enhance the  $\text{NH}_3$  adsorption,<sup>12</sup> which is attributed to the charge transfer within the framework and the formation of  $\text{N}_2\text{H}_4$ .

Herein, we report a novel  $\text{Ti}^{4+}$ -based MOF, MFM-300(Ti) [ $[\text{Ti}_2(\text{O})_2(\text{C}_{16}\text{H}_6\text{O}_8)]$ ], which displays a reversible  $\text{NH}_3$  uptake of 23.4 mmol g<sup>-1</sup> at 273 K and 1 bar, among the best  $\text{NH}_3$  sorbent materials showing reversible adsorption to date. Significantly, the packing density of  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_3$  at low concentrations (1000 ppm). The binding sites of  $\text{NH}_3$  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), [ $[\text{Ti}_2(\text{O})_2(\text{C}_{16}\text{H}_6\text{O}_8)(\text{H}_2\text{O})_2(\text{C}_3\text{H}_6\text{O})_{0.7}]$ ], was prepared *via* a solvothermal reaction of  $\{\text{Ti}_8\text{AF}\}$  clusters,<sup>13</sup>  $\text{H}_4\text{L}$  (biphenyl-3,3',5,5'-tetracarboxylic acid,  $\text{H}_4\text{bptc}$ ), 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  $I4_{1}22$  and is isostructural to other MFM-300 materials.<sup>14</sup> The presence of *cis*- $\mu_2$ -O moieties rather than *cis*- $\mu_2$ -OH groups as

<sup>a</sup> Department of Chemistry, University of Manchester, Manchester, M13 9PL, UK.

E-mail: [M.Schroder@manchester.ac.uk](mailto:M.Schroder@manchester.ac.uk), [Sihai.Yang@manchester.ac.uk](mailto:Sihai.Yang@manchester.ac.uk)

<sup>b</sup> College of Chemistry and Molecular Engineering, Beijing National Laboratory for Molecular Sciences, Peking University, Beijing, 100871, China.

E-mail: [Sihai.Yang@pku.edu.cn](mailto:Sihai.Yang@pku.edu.cn)

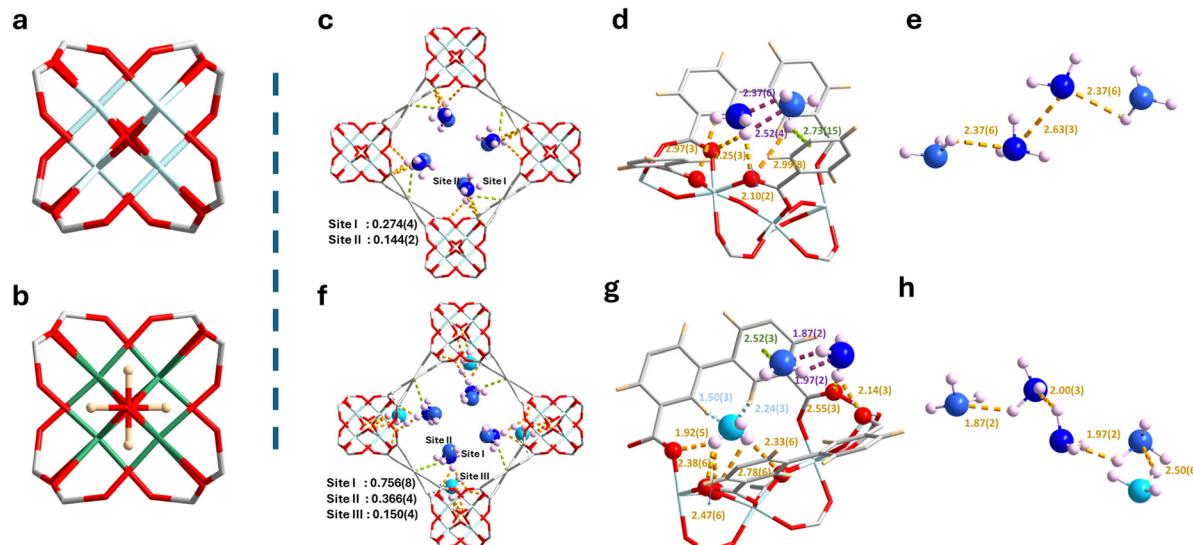
<sup>c</sup> Diamond Light Source, Harwell Science Campus, Oxfordshire, OX11 0DE, UK

<sup>d</sup> Neutron Scattering Division, Neutron Sciences Directorate, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

<sup>e</sup> ISIS Neutron and Muon Facility, Rutherford Appleton Laboratory, Didcot, OX11 0QX, UK

† 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( $\text{M}^{3+}$ ) 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†). 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†), 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†). 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†), variable temperature powder X-ray diffraction (VT-PXRD; Fig. S4, ESI†), PXRD analysis of samples soaked in various solutions (Fig. 1c and Fig. S5, ESI†), and the  $\text{CO}_2$  adsorption measurements for samples after various treatments to confirm the porosity (Fig. S6, ESI†).

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† 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†), comparable with other MOFs incorporating strong binding sites, such as  $\text{UiO-66Cu}(\text{II})^{15}$  (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 [ $\text{ND}_3 \cdots \text{O}_{\text{ligand}} = 2.10(2)$ – $2.97(3)$  Å]. Site II is adjacent to site I, stabilised by hydrogen bonding interactions [ $\text{ND}_3 \cdots \text{O}_{\text{ligand}} = 2.99(8)$  Å], electrostatic interactions [ $\text{ND}_3 \cdots \text{aromatic rings} = 2.52(3)$ – $2.73(15)$  Å], and guest–guest interactions [ $\text{ND}_3 \cdots \text{ND}_3 = 1.87(2)$ – $2.52(4)$  Å]. 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 [ $\text{C-H}_{\text{aromatic}} \cdots \text{N} = 1.50(3)$ – $2.24(3)$  Å,  $\text{ND}_3 \cdots \text{O}_{\text{ligand}} = 1.92(5)$ – $2.38(6)$  Å, and  $\text{ND}_3 \cdots \text{O}_{\text{bridge}} = 2.33(6)$ – $2.78(6)$  Å]. 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 [ $\text{N-D} \cdots \text{N} = 2.37(6)$ – $2.52(3)$  Å] between adsorbed  $\text{ND}_3$  molecules in MFM-300(Ti)-0.84  $\text{ND}_3$  decreases to [ $\text{N-D} \cdots \text{N} = 1.87(3)$ – $2.00(3)$  Å] 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

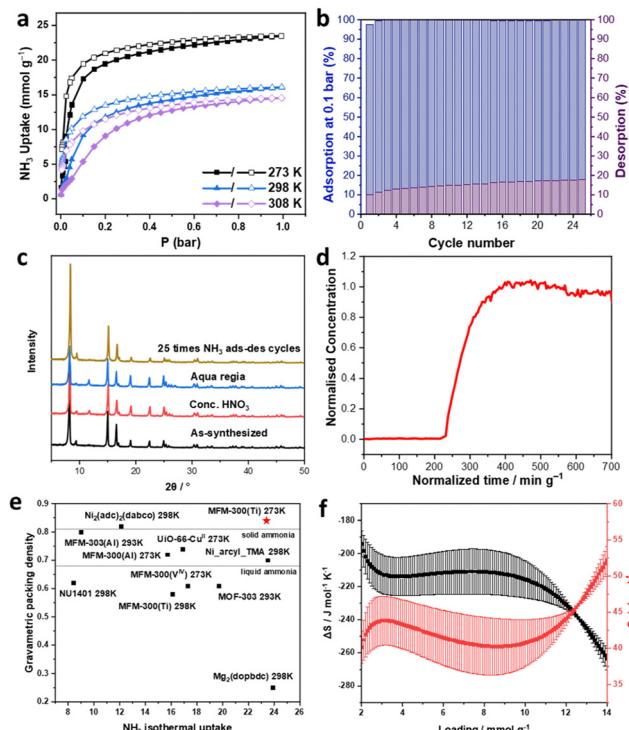


Fig. 2 (a) Adsorption isotherms of  $\text{NH}_3$  in MFM-300(Ti) at 273–308 K up to 1.0 bar (adsorption, solid symbols; desorption, open symbols). (b) Cyclic adsorption–desorption of  $\text{NH}_3$  in MFM-300(Ti) at 298 K between 0 and 0.1 bar; dark-coloured bars show the residual  $\text{NH}_3$  within 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) isosteric 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,

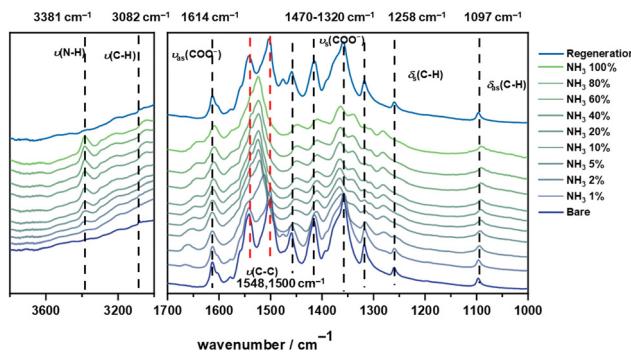
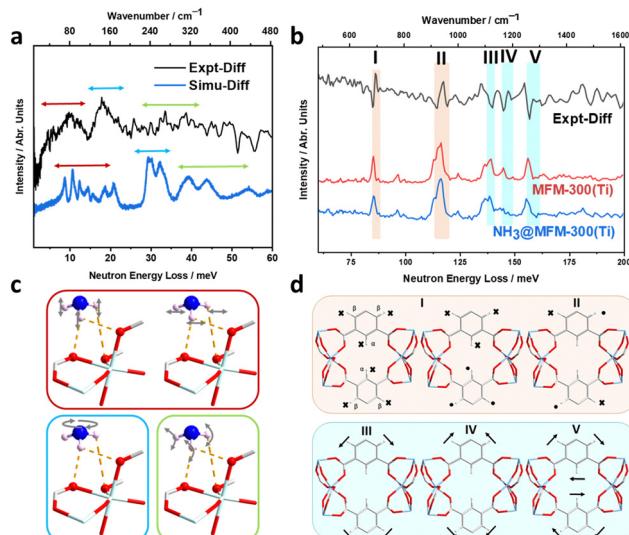


Fig. 3 *In situ* synchrotron FT-IR spectra of MFM-300(Ti) as a function of  $\text{NH}_3$  adsorption and of regenerated MFM-300(Ti) under a flow of dry  $\text{N}_2$  at  $100\text{ mL min}^{-1}$  at 298 K for 2 h.

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  $\nu_s(\text{COO}^-)$  of the carboxylate group in the framework, and all show redshifts 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  $1.458(2)$  Å in bare MFM-300(Ti) to  $\sim 1.497(4)$  Å in MFM-300(Ti)-0.84  $\text{ND}_3$  and further to  $\sim 1.500(7)$  Å 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.

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## Conflicts of interest

There are no conflicts to declare.

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