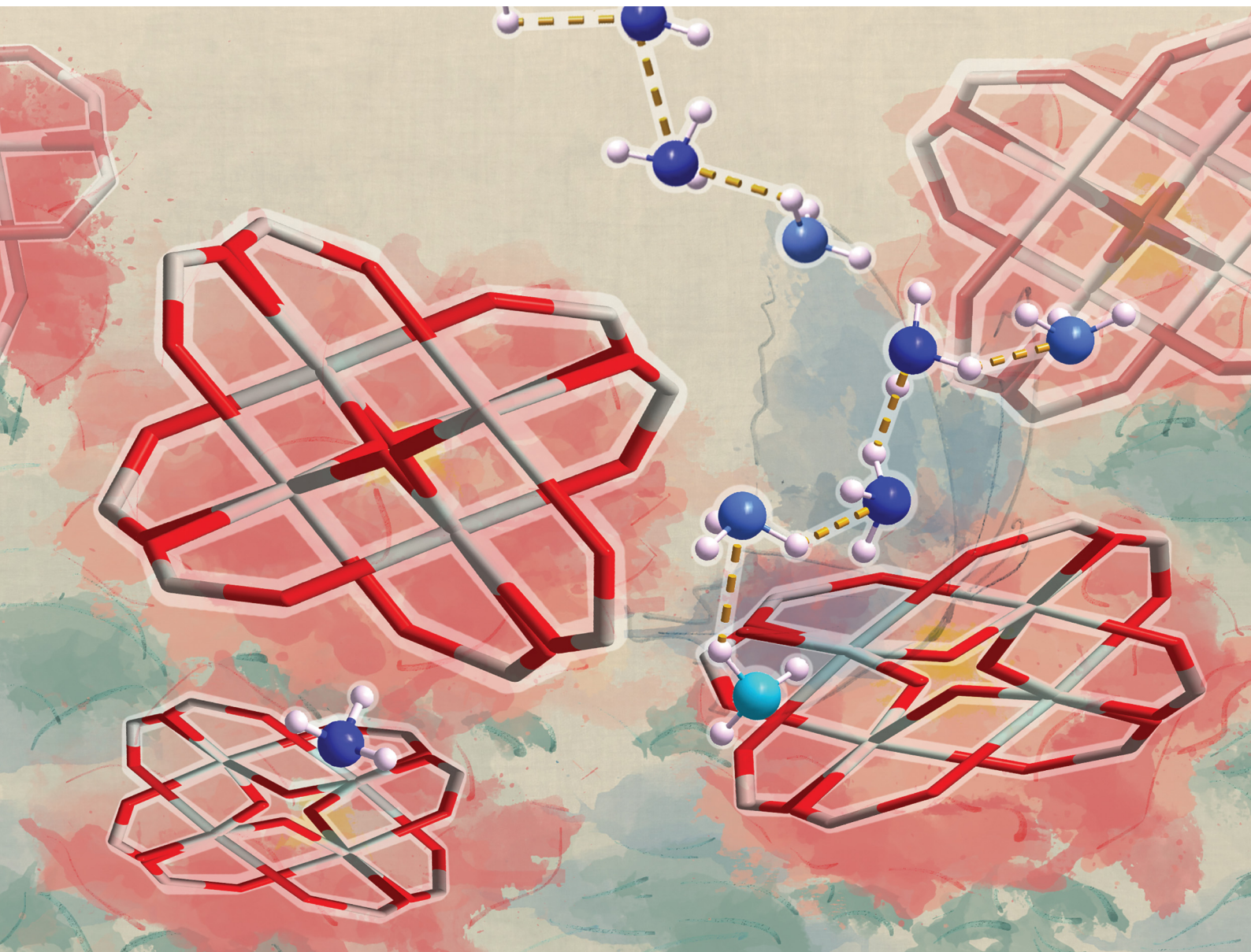


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# High adsorption of ammonia in a titanium-based metal–organic framework†

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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 ( $\sim 0.105$  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>acryl-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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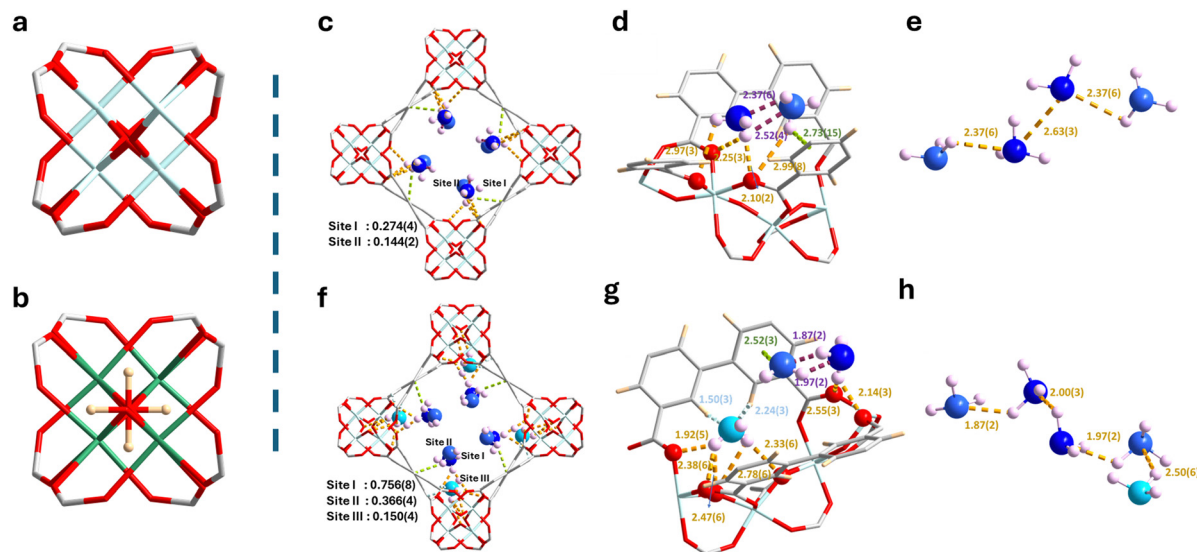
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**Fig. 1** Views of crystal structures of bare and  $\text{ND}_3$ -loaded MFM-300(Ti) as determined by NPD at 10 K. The occupancy of each site has been converted to  $\text{ND}_3/\text{Ti}$  for clarity. (a) and (b) Views of MFM-300(Ti) and MFM-300( $\text{M}^{\text{II}}$ ) 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.

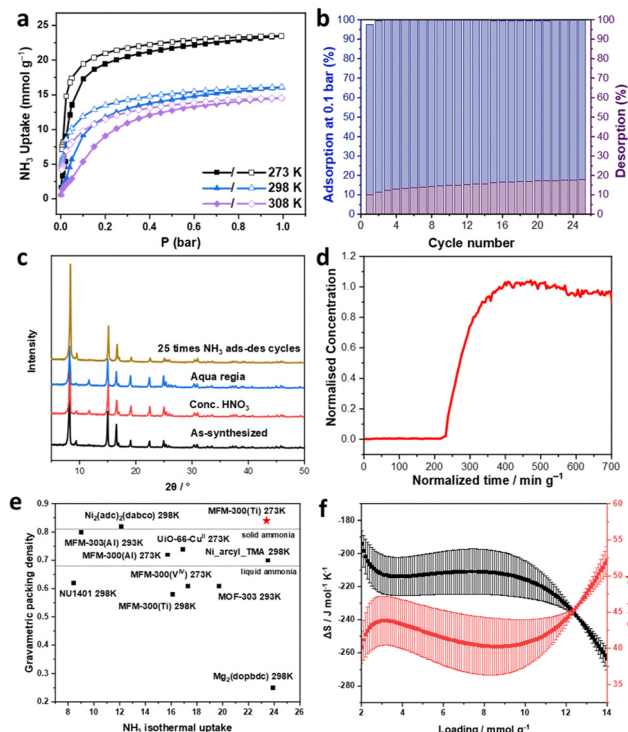
observed in  $\text{M}^{3+}$ -based analogues is confirmed by NPD and FTIR spectra (Fig. 1a and b, Fig. S7, ESI<sup>†</sup>). MFM-300(Ti) exhibits an open framework structure comprising of chains of  $[\text{TiO}_4(\text{O})_2]$  moieties bridged by tetracarboxylate ligands  $\text{L}^{4-}$  to afford 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  $39\text{--}52 \text{ kJ mol}^{-1}$  (Fig. 2f and Table S2, ESI<sup>†</sup>), comparable with other MOFs incorporating strong binding sites, such as UiO-66Cu(II)<sup>15</sup> ( $25\text{--}55 \text{ kJ mol}^{-1}$ ).

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

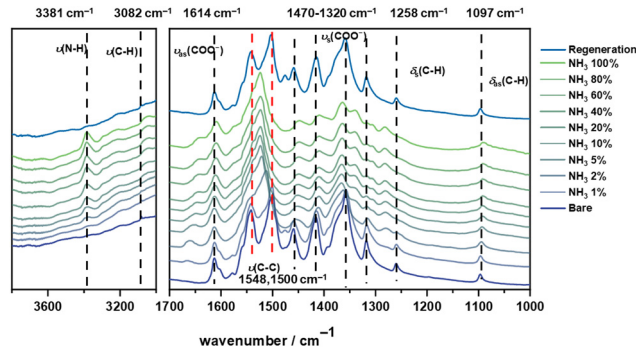




**Fig. 2** (a) Adsorption isotherms of  $\text{NH}_3$  in MFM-300(Ti) at 273–308 K up to 1.0 bar (adsorption, solid symbols; desorption, open symbols). (b) Cyclic adsorption-desorption of  $\text{NH}_3$  in MFM-300(Ti) at 298 K between 0 and 0.1 bar; dark-coloured bars show the residual  $\text{NH}_3$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

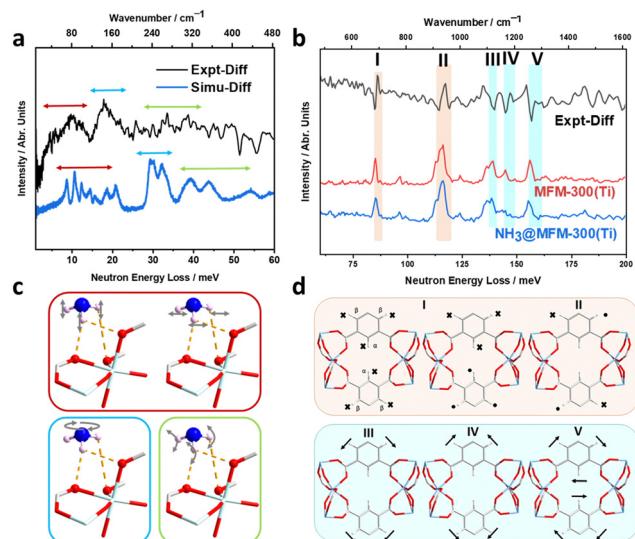
The dynamics of host-guest binding has been analysed using *in situ* synchrotron IR microspectroscopy, INS, and density functional theory (DFT) calculations. The absence of the characteristic IR band of hydroxyl group at  $\sim 3600\text{ cm}^{-1}$  in activated MFM-300(Ti) (Fig. S7, ESI†) confirmed 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†).

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†) and  $\text{NH}_3$ -loaded MFM-300(Ti) (Fig. S13, ESI†) 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  $4.4\text{--}14.4\text{ meV}$  and  $16.6\text{--}23.5\text{ meV}$ , respectively. The bands at  $26.5\text{--}41.7\text{ meV}$  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  $\text{NH}_3$ ,  $6.3\text{--}23.1\text{ meV}$  translational modes;  $27.6\text{--}35.5\text{ meV}$  rotational modes;  $36.7\text{--}56.9\text{ meV}$  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  $\text{NH}_3$ . Difference spectra were obtained by subtraction of the INS spectra of the bare MOF from that for the  $\text{NH}_3$ -loaded MOF and are marked as Expt-Diff (experimental difference spectra). (a) Comparison of vibrational modes between solid  $\text{NH}_3$  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  $\text{NH}_3$  in the higher energy range. The scale factor for difference spectrum is 3. (c) and (d) Selected vibrational modes of confined  $\text{NH}_3$  molecule and MFM-300(Ti).

rotational modes show more significant red shifts, attributed to the higher rotational flexibility of  $\text{NH}_3$  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- $\text{C}_6$ -plane wagging (in-phase along the ring, meaning H atoms move in the same direction), C–H out-of- $\text{C}_6$ -plane twisting (anti-phase along the ring, meaning neighbouring H atoms move in opposite directions), C–H in- $\text{C}_6$ -plane scissoring mode, in phase, C–H in- $\text{C}_6$ -plane scissoring mode, anti-phase, and C–H in- $\text{C}_6$ -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  $\text{NH}_3$  indicate the strong host–guest interactions between the benzyl ring of the framework and  $\text{NH}_3$  molecules. These results are in excellent agreement with the NPD and FTIR study.

In summary, we report the high capacity and reversible adsorption of  $\text{NH}_3$  within a novel titanium-based MOF, MFM-300(Ti). This framework features a unique structure composed of extended  $[\text{TiO}_6]_\infty$  chains linked by tetra-topic ligands  $[(\text{C}_{16}\text{H}_6\text{O}_8)^{4-}]$ . Notably, at 273 K and 1 bar, MFM-300(Ti) shows an exceptional  $\text{NH}_3$  uptake of 23.4 mmol  $\text{g}^{-1}$  and a record-high packing density of 0.84  $\text{g cm}^{-3}$ . The volumetric and gravimetric adsorption capacity is 0.36  $\text{g cm}^{-3}$  and 0.28  $\text{g g}^{-1}$ , respectively. Dynamic breakthrough experiments confirm excellent adsorption of  $\text{NH}_3$  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  $\text{NH}_3$ , demonstrating its potential for practical applications.

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## Conflicts of interest

There are no conflicts to declare.

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