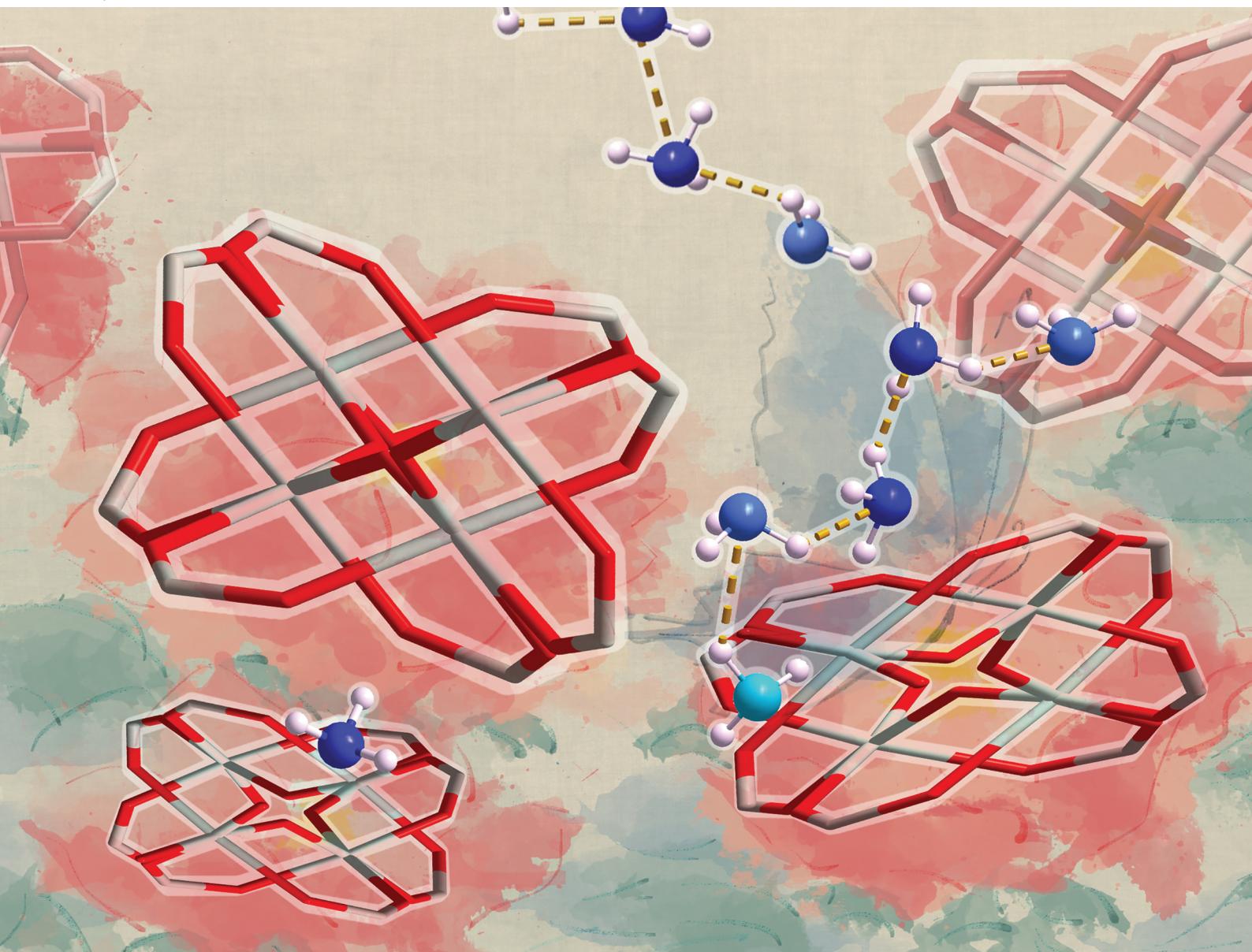


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High adsorption of ammonia in a titanium-based
metal-organic framework



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We report the high adsorption of NH_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 NH_3 uptake of 23.4 mmol g⁻¹ with a record-high packing density of 0.84 g cm⁻³. Dynamic breakthrough experiments confirm the excellent uptake and separation of 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 NH_3 to the framework oxygen sites.

Ammonia (NH_3) is an important feedstock that is produced at a scale of *ca.* 150 million tonnes per year.¹ In addition, the high volumetric ($\sim 0.105 \text{ kg L}^{-1}$) and gravimetric (17.7 wt%) hydrogen densities of 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 NH_3 poses challenges in its safe storage and transportation. At present, 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).² Thus, the development of robust sorbents for reversible NH_3 adsorption under mild conditions is of great importance.

Porous materials, such as zeolites,³ active carbons,⁴ mesoporous silica,⁵ and organic polymers⁶ have been tested for NH_3 adsorption. However, these materials demonstrate limited capacities; for example, 9.3 mmol g⁻¹ in 13X zeolite,³ 8.8 mmol g⁻¹ in MCM-41,⁵ and 11.4 mmol g⁻¹ in Amberlyst 15.⁷ Metal–organic frameworks (MOFs)

have demonstrated potential for NH_3 adsorption⁸ owing to their high accessible surface area, and their tailored porosity and pore environment. The MOFs displaying top performance for NH_3 adsorption are primarily divalent/trivalent-based MOFs or MOF composites, such as $\text{LiCl}@\text{MIL-53}-(\text{OH})_2$ ⁹ (33.9 mmol g⁻¹ at 298 K and 1 bar) and $\text{Ni}_\text{acryl_TMA}$ ¹⁰ (23.5 mmol g⁻¹ at 298 K and 1 bar). However, the stability of MOFs toward NH_3 adsorption needs to be improved, and typically tetravalent metal-based MOFs (*e.g.*, Zr^{4+} , V^{4+} , Hf^{4+}) exhibit enhanced thermal and chemical stability. However, the reported Zr -based MOFs show limited NH_3 adsorption capacities (8.40 mmol g⁻¹ in UiO-67^{11}). On the other hand, the study of V -based MFM-300(V) for NH_3 adsorption has revealed that the incorporation of V^{4+} can effectively enhance the NH_3 adsorption,¹² which is attributed to the charge transfer within the framework and the formation of N_2H_4 .

Herein, we report a novel 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 NH_3 uptake of 23.4 mmol g⁻¹ at 273 K and 1 bar, among the best NH_3 sorbent materials showing reversible adsorption to date. Significantly, the packing density of NH_3 in MFM-300(Ti) (0.84 g cm⁻³, calculated using the pore volume derived from crystallographic data) is comparable to that of solid NH_3 at -80 °C (0.82 g cm⁻³), 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_3 at low concentrations (1000 ppm). The binding sites of 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,¹³ H_4L (biphenyl-3,3',5,5'-tetracarboxylic acid, H_4bptc), 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.¹⁴ The presence of *cis*- μ_2 -O moieties rather than *cis*- μ_2 -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>



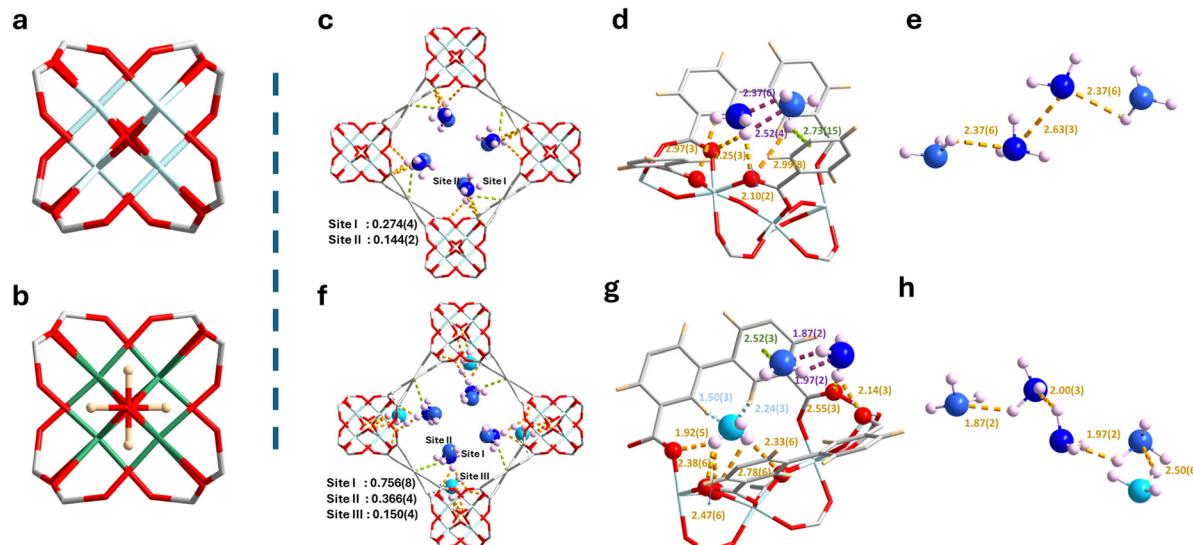


Fig. 1 Views of crystal structures of bare and ND_3 -loaded MFM-300(Ti) as determined by NPD at 10 K. The occupancy of each site has been converted to ND_3/Ti for clarity. (a) and (b) Views of MFM-300(Ti) and MFM-300(M^{3+}) along the c -axis, respectively. (c) and (f) Views of packing of ND_3 in MFM-300(Ti) along the c -axis in MFM-300(Ti)-0.84 ND_3 and MFM-300(Ti)-2.54 ND_3 , respectively. (d) and (g) Detailed views of host–guest interactions in MFM-300(Ti)-0.84 ND_3 and MFM-300(Ti)-2.54 ND_3 , respectively. (e) and (h) Guest–guest interaction along c -axis in MFM-300(Ti)-0.84 ND_3 and MFM-300(Ti)-2.54 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 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 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 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 CO_2 adsorption measurements for samples after various treatments to confirm the porosity (Fig. S6, ESI†).

The adsorption isotherms for 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 NH_3 uptake of 23.4 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 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 NH_3 (Fig. 2b and c), confirming the excellent stability of MFM-300(Ti) towards NH_3 . The residual 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 NH_3 uptake of MFM-300(Ti) at low concentration (1000 ppm) was recorded as 0.6 mmol g^{-1} at 298 K, demonstrating an excellent capture capability (Fig. 2d). The heat of adsorption (Q_{st}) of NH_3 in MFM-300(Ti) was calculated to be 39–52 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 kJ mol^{-1}).

In situ NPD data for 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 ND_3 . At low-loading ($\text{ND}_3/\text{Ti} = 0.42$; MFM-300(Ti)-0.84 ND_3) (Fig. 1c and d), two binding sites (I and II) are observed. Site I is anchored by hydrogen bonding between the 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 ND_3/Ti (MFM-300(Ti)-2.54 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 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 ND_3 molecules in MFM-300(Ti)-0.84 ND_3 decreases to [$\text{N-D} \cdots \text{N} = 1.87(3)$ – $2.00(3)$ Å] in MFM-300(Ti)-2.54 ND_3 . This tighter host–guest and guest–guest interaction with increasing NH_3 loading is consistent with the trend of Q_{st} (Fig. 2f). Notably, the shortest distance between adsorbed 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

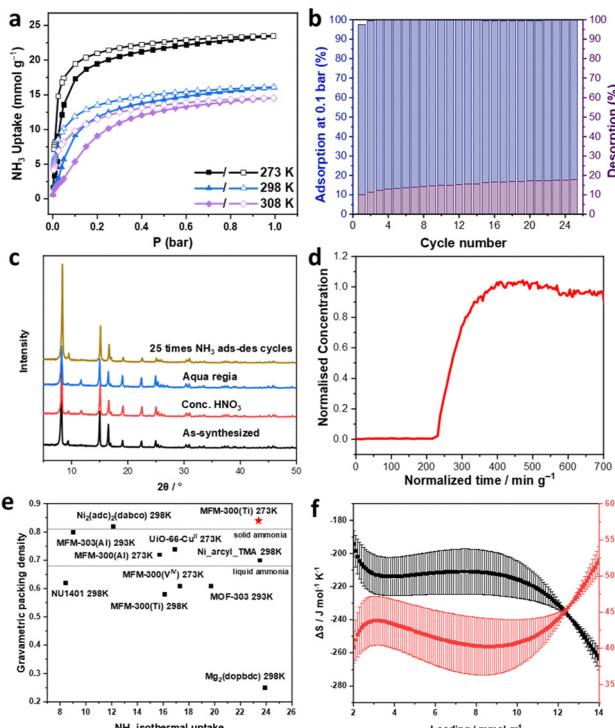


Fig. 2 (a) Adsorption isotherms of NH_3 in MFM-300(Ti) at 273–308 K up to 1.0 bar (adsorption, solid symbols; desorption, open symbols). (b) Cyclic adsorption–desorption of NH_3 in MFM-300(Ti) at 298 K between 0 and 0.1 bar; dark-coloured bars show the residual NH_3 within the MOF upon pressure-swing desorption at 298 K. (c) PXRD patterns of MFM-300(Ti), (black: as-synthesised, red: after soaking in concentrated 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 NH_3 (1000 ppm diluted in He) through a fixed-bed packed with MFM-300(Ti). (e) Plot of NH_3 isothermal adsorption capacities and NH_3 packing density in stable MOF materials (f) isosteric enthalpy and entropy of adsorption for MFM-300(Ti) at different NH_3 loadings.

MFM-300(V^{IV})¹⁵ and reflects highly efficient packing of NH_3 molecules in MFM-300(Ti), consistent with the high packing density derived from the adsorption isotherms. Compared with MFM-300(M^{III})¹⁵ 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 NH_3 . In MFM-300(V^{IV}), the presence of the vanadium centre promotes charge transfer between NH_3 molecules, resulting in the observation of both N_2D_4 and ND_4^+ molecules in the pore,¹⁵ which limits the reusability of the MOF. The utilisation of Ti^{4+} ions not only improves the structural stability of the material, but also hinders charge transfer to enhance the adsorption reversibility of 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 Ti^{4+} sites, consistent with the NPD analysis. On loading NH_3 , a new band at 3381 cm^{-1} assigned to a $\nu(\text{N-H})$ stretching vibration is observed,

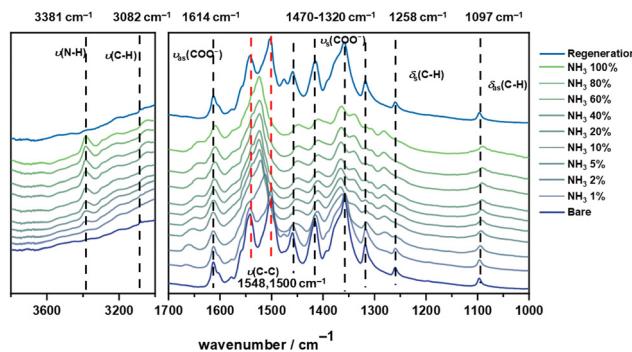


Fig. 3 *In situ* synchrotron FT-IR spectra of MFM-300(Ti) as a function of NH_3 adsorption and of regenerated MFM-300(Ti) under a flow of dry N_2 at 100 mL min^{-1} at 298 K for 2 h.

confirming the adsorption in the framework (Fig. 3). The band at 1614 cm^{-1} can be assigned to $\nu_{\text{as}}(\text{COO}^-)$, which broadens on loading of NH_3 . The bands at 1470 cm^{-1} , 1414 cm^{-1} , 1360 cm^{-1} , and 1320 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 NH_3 . This suggests the presence of strong interactions between NH_3 and the carboxylate groups of the bridging ligand. Simultaneously, as the concentration of NH_3 increases from 2% to 5%, two bands at 1548 and 1500 cm^{-1} corresponding to aromatic C–C stretching vibrations merge into one band (1525 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 ND_3 and further to $\sim 1.500(7)\text{ \AA}$ in MFM-300(Ti)- 2.54 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 NH_3 within MFM-300(Ti). The congruence between experimental and simulated INS spectra for MFM-300(Ti) (Fig. S12, ESI[†]) and 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 NH_3 -loaded MFM-300(Ti) (Fig. 4b). Translational and rotational modes of adsorbed 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 NH_3 around the N centre (Fig. 4c and d). In comparison to the spectrum of NH_3 in the solid state, where each NH_3 molecule forms a 3D hydrogen bonding network with six adjacent NH_3 molecules, the bands in all regions for adsorbed NH_3 exhibit shifts to lower energy and display broader features (for solid 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 NH_3 molecules within MFM-300(Ti). Specifically, the



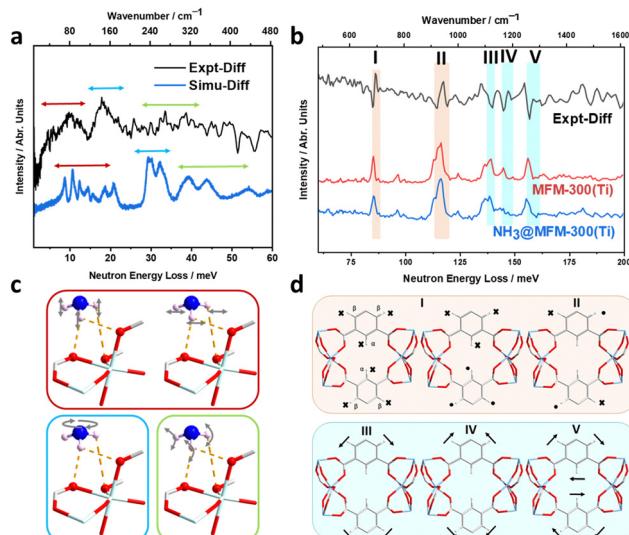


Fig. 4 Views of *in situ* INS spectra and the corresponding vibrational modes for MFM-300(Ti), before and after adsorption of NH₃. Difference spectra were obtained by subtraction of the INS spectra of the bare MOF from that for the NH₃-loaded MOF and are marked as Expt-Diff (experimental difference spectra). (a) Comparison of vibrational modes between solid NH₃ 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 NH₃ in the higher energy range. The scale factor for difference spectrum is 3. (c) and (d) Selected vibrational modes of confined NH₃ molecule and MFM-300(Ti).

rotational modes show more significant red shifts, attributed to the higher rotational flexibility of NH₃ 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-C₆-plane wagging (in-phase along the ring, meaning H atoms move in the same direction), C–H out-of-C₆-plane twisting (anti-phase along the ring, meaning neighbouring H atoms move in opposite directions), C–H in-C₆-plane scissoring mode, in phase, C–H in-C₆-plane scissoring mode, anti-phase, and C–H in-C₆-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 NH₃ indicate the strong host–guest interactions between the benzyl ring of the framework and NH₃ molecules. These results are in excellent agreement with the NPD and FTIR study.

In summary, we report the high capacity and reversible adsorption of NH₃ within a novel titanium-based MOF, MFM-300(Ti). This framework features a unique structure composed of extended [TiO₆]_∞ chains linked by tetra-topic ligands [(C₁₆H₆O₈)⁴⁻]. Notably, at 273 K and 1 bar, MFM-300(Ti) shows an exceptional NH₃ uptake of 23.4 mmol g⁻¹ and a record-high packing density of 0.84 g cm⁻³. The volumetric and gravimetric adsorption capacity is 0.36 g cm⁻³ and 0.28 g g⁻¹, respectively. Dynamic breakthrough experiments confirm excellent adsorption of NH₃ 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 NH₃, demonstrating its potential for practical applications.

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Conflicts of interest

There are no conflicts to declare.

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