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# High capacity ammonia adsorption in a robust metal–organic framework mediated by reversible host–guest interactions†

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To understand the exceptional adsorption of ammonia (NH<sub>3</sub>) in MFM-300(Sc) (19.5 mmol g<sup>-1</sup> at 273 K and 1 bar without hysteresis), we report a systematic investigation of the mechanism of adsorption by a combination of *in situ* neutron powder diffraction, inelastic neutron scattering, synchrotron infrared microspectroscopy, and solid-state <sup>45</sup>Sc NMR spectroscopy. These complementary techniques reveal the formation of reversible host–guest supramolecular interactions, which explains directly the observed excellent reversibility of this material over 90 adsorption–desorption cycles.

Annual global production of ammonia (NH<sub>3</sub>) is around 170 million tonnes reflecting its role as a major feedstock for agriculture and industry.<sup>1</sup> The high hydrogen content (17.8 wt %) and hydrogen volume density (105 kg m<sup>-3</sup>) of NH<sub>3</sub> make it a desirable carbon-free hydrogen carrier, and NH<sub>3</sub> is therefore regarded as a surrogate for the H<sub>2</sub> economy. However, the corrosive and toxic nature of NH<sub>3</sub> makes the development of stable storage materials with high and reversible uptakes extremely challenging. Conventional sorbent materials such as zeolites,<sup>2</sup> activated carbons,<sup>3</sup> and organic polymers<sup>4</sup> have been investigated for the storage of NH<sub>3</sub>, but show low and often irreversible uptakes. Metal–organic framework (MOF) materials have been postulated as promising candidates for gas storage due to their high surface areas and versatile pore structures.<sup>5</sup> As opposed to conventional adsorbents, the affinities of MOF

materials to a target gas can be tailored by grafting the pore interior with functional groups to anchor the gas through coordination, hydrogen bonding, electrostatic interactions, acid–base interactions or π–π stacking.<sup>5–7</sup> A large number of MOFs with functional groups (*e.g.* –COOH,<sup>8</sup> –OH<sup>9</sup>) and open metal sites<sup>10</sup> have been reported to impart enhanced affinity to gas molecules. Several state-of-the-art MOFs, such as MOF-177,<sup>11</sup> M<sub>2</sub>Cl<sub>2</sub>Bbta [Bbta = 1*H*,5*H*-benzo(1,2-*d*:4,5-*d'*)bistriazole; M = Co, Mn],<sup>12</sup> M<sub>2</sub>Cl<sub>2</sub>(BTDD) {BTDD = bis(1*H*-1,2,3-triazolo[4,5-*b*],[4',5'-*i*])dibenzo[1,4]dioxin; M = Mn, Co, Ni and Cu}<sup>13</sup> as well as MFM-300(M) (M = Al, Fe, V, Cr, In),<sup>6,14</sup> have been investigated for NH<sub>3</sub> adsorption. However, due to the reactive and corrosive nature of NH<sub>3</sub>, many MOF systems showed structural degradation and/or significant loss of uptake after consecutive cycles owing to irreversible host–guest binding. So far, only a very limited number of MOFs exhibit reversible NH<sub>3</sub> sorption over multiple cycles.<sup>6,8,13–16</sup> Unravelling the molecular details of host–guest interactions is of critical importance if new efficient NH<sub>3</sub> storage systems are to be developed. This is however highly challenging, not least because hydrogen atoms are invisible in X-ray diffraction experiments and NH<sub>3</sub> molecules can act as a rapid rotor even in solid state.

The mechanism of adsorption of NH<sub>3</sub> in MFM-300(Sc) was examined systematically using gas isotherms, breakthrough experiments, *in situ* solid-state nuclear magnetic resonance (ssNMR) spectroscopy, synchrotron infrared microspectroscopy, neutron powder diffraction (NPD) and inelastic neutron scattering (INS) techniques, coupled with DFT modelling. Distinct new insights have been gained into the mechanism of adsorption compared with a recent report based on theoretical and infrared spectroscopic studies of this system.<sup>17</sup> Importantly, we found the exceptional NH<sub>3</sub> uptake (19.5 mmol g<sup>-1</sup> at 273 K and 1 bar) by MFM-300(Sc) was mediated by reversible host–guest and guest–guest hydrogen bond interactions. The moderate strength of the host–guest interaction in MFM-300(Sc) leads to excellent adsorption reversibility and stability with full retention of the capacity over 90 cycles.

MFM-300(Sc) shows a three-dimensional framework containing [ScO<sub>4</sub>(OH)<sub>2</sub>] octahedra which are connected *via* the

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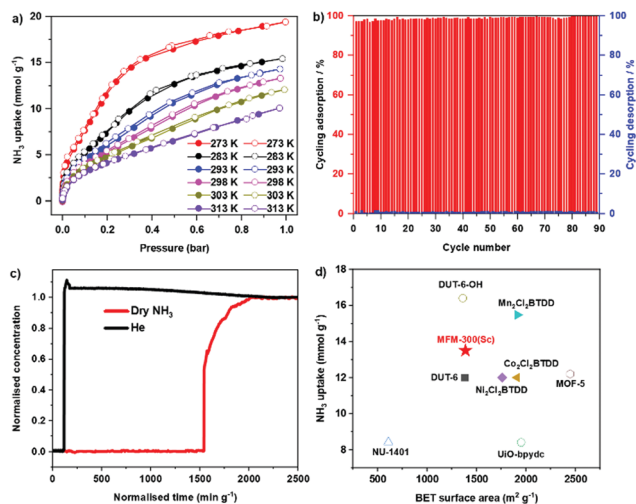
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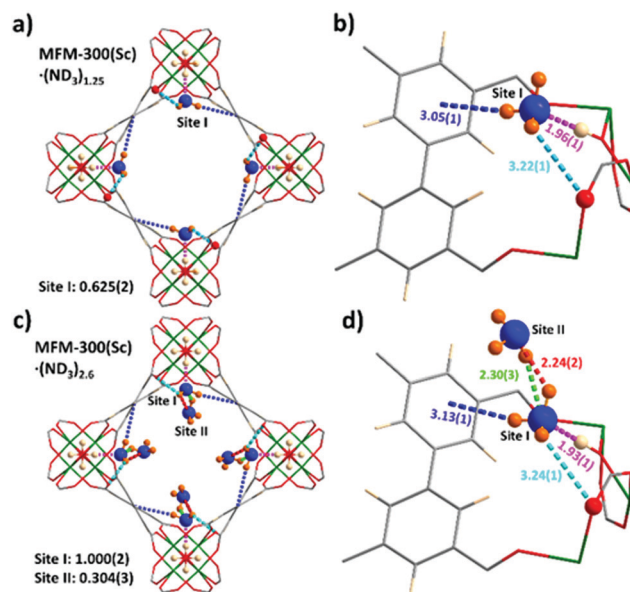
**Fig. 1** (a) Adsorption isotherms for  $\text{NH}_3$  in MFM-300(Sc) at 273–313 K (adsorption: solid symbols; desorption: open symbols). (b) 90 cycles of adsorption–desorption of  $\text{NH}_3$  in MFM-300(Sc) under pressure-swing conditions. (c) Breakthrough curve for  $\text{NH}_3$  (1000 ppm diluted in He) through a fixed-bed packed with MFM-300(Sc) at 298 K and 1.0 bar. (d) Comparison of  $\text{NH}_3$  uptake at 1 bar and 298 K for selected materials plotted against their surface areas (solid symbols: reversible sorption; hollow symbols: irreversible sorption; full details are given in the supplementary information).

*cis*- $\mu_2$ -OH groups into infinite chains, and further coordinated by the BPTC<sup>4-</sup> ligand ( $\text{H}_4\text{BPTC}$  = biphenyl-3,3',5,5'-tetracarboxylic acid) (Fig. S1, ESI<sup>†</sup>).<sup>18</sup> Desolvated MFM-300(Sc) shows a Brunauer–Emmett–Teller (BET) surface area of  $1390 \text{ m}^2 \text{ g}^{-1}$  and a pore volume of  $0.48 \text{ cm}^3 \text{ g}^{-1}$  (Fig. S2, ESI<sup>†</sup>). MFM-300(Sc) exhibits high thermal stability up to  $500 \text{ }^\circ\text{C}$  under  $\text{N}_2$  (Fig. S3, ESI<sup>†</sup>) and high chemical stability in aqueous solutions of pH of 7–12 as well as in various organic solvents (Fig. S4, ESI<sup>†</sup>).

Adsorption isotherms of  $\text{NH}_3$  for MFM-300(Sc) were measured at 273–313 K, where an exceptional uptake of  $19.5 \text{ mmol g}^{-1}$  was recorded at 273 K and 1.0 bar (Fig. 1a), reducing to  $13.5 \text{ mmol g}^{-1}$  at 298 K. MFM-300(Sc) shows the highest  $\text{NH}_3$  uptake among the MFM-300(M) family<sup>6,14</sup> primarily due to its large pore size and pore volume allowing the accommodation of additional  $\text{NH}_3$  molecules in the pore. MFM-300(Sc) shows an  $\text{NH}_3$  uptake of  $13.5 \text{ mmol g}^{-1}$  at 298 K and 1.0 bar, comparing favourably with state-of-the-art materials (Fig. 1d and Table S6, ESI<sup>†</sup>). The uptake of  $\text{NH}_3$  in MFM-300(Sc) between 273 and 313 K decreases gradually with increasing temperature, consistent with an exothermic adsorption mechanism.<sup>19</sup> The isosteric heat of adsorption ( $Q_{st}$ ) for  $\text{NH}_3$  in MFM-300(Sc) decreases from 60 to  $30 \text{ kJ mol}^{-1}$  with increasing loading of  $\text{NH}_3$  from 1 to  $10 \text{ mmol g}^{-1}$  (Fig. S7, ESI<sup>†</sup>), confirming the presence of moderate adsorbate–adsorbent binding interaction. The repeated isotherm of  $\text{NH}_3$  at 273 K using regenerated MFM-300(Sc) shows no loss in capacity with full retention of its porosity (Fig. S6, ESI<sup>†</sup>). 90 consecutive cycles of adsorption–desorption were conducted at 298 K and confirmed excellent reversibility and stability of adsorption (Fig. 1b), with retention of the crystal structure of MFM-300(Sc) as confirmed by powder X-ray diffraction (PXRD) (Fig. S5, ESI<sup>†</sup>). The ability of MFM-300(Sc) to capture  $\text{NH}_3$  at low concentrations (1000 ppm)

was confirmed by dynamic breakthrough experiments at 298 K with a dynamic uptake of  $1.65 \text{ mmol g}^{-1}$ , consistent with that measured by isotherms ( $1.74 \text{ mmol g}^{-1}$  at 10 mbar, equivalent to 1000 ppm; Fig. 1c). With an exceptional adsorption capacity and excellent regenerability, MFM-300(Sc) represents a promising candidate for applications in  $\text{NH}_3$  storage and transport.

*In situ* NPD data of MFM-300(Sc) as a function of  $\text{ND}_3$  loading were collected and Rietveld refinements revealed the preferential binding sites for  $\text{ND}_3$  (Fig. 2). Interestingly, the  $\text{NH}_3$ -induced rearrangement of metal–ligand (Sc–O) bonds *via* insertion of  $\text{NH}_3$  molecules into the MOF upon  $\text{ND}_3$  binding as predicted by a DFT study<sup>17</sup> was not observed here. For MFM-300(Sc)·( $\text{ND}_3$ )<sub>1.25</sub>,  $\{[\text{Sc}_2(\text{L})(\text{OD}_{0.6}\text{H}_{0.4})_2](\text{ND}_{2.05}\text{H}_{0.95})_{1.25}\}$ , only one binding site was found, interacting primarily with the bridging  $\mu_2$ -OH groups at the four corners of its square-shaped channel [ $\text{O}_{\text{bridge}}\text{-H}\cdots\text{ND}_3 = 1.96(1) \text{ \AA}$ ] (Fig. 2a and b). At the higher loading of MFM-300(Sc)·( $\text{ND}_3$ )<sub>2.6</sub>,  $\{[\text{Sc}_2(\text{L})(\text{OD}_{0.75}\text{H}_{0.25})_2](\text{ND}_{2.42}\text{H}_{0.58})_{2.6}\}$ , two distinct binding sites were identified (Fig. 2c and d). Site I is fully occupied by  $\text{ND}_3$  molecules ( $1 \text{ ND}_3/\text{Sc}$ ), with hydrogen bonding between the  $\mu_2$ -OH groups and the  $\text{ND}_3$  molecule [ $\text{O}_{\text{bridge}}\text{-H}\cdots\text{ND}_3 = 1.93(1) \text{ \AA}$ ]. This is complemented by additional electrostatic interactions [ $\text{ND}_3\cdots\text{aromatic rings} = 3.13(1) \text{ \AA}$ ], and hydrogen bonding [ $\text{ND}_3\cdots\text{O}_{\text{ligand}} = 3.24(1) \text{ \AA}$ ]. Site II ( $0.3 \text{ ND}_3/\text{Sc}$ ) exhibited hydrogen bonding with the  $\text{ND}_3$  at site I [ $2.30(3) \text{ \AA}$  and  $2.24(2) \text{ \AA}$ ], propagating along the 1D channel to form a cooperative  $\{\text{ND}_3\}_\infty$  network. Similar to other MFM-300 analogues,<sup>6,14</sup> hydrogen/deuterium site exchange was also observed between the adsorbed  $\text{ND}_3$  molecules and the  $\mu_2$ -OH group for MFM-300(Sc).



**Fig. 2** Views of binding sites for  $\text{ND}_3$  in MFM-300(Sc) determined by NPD at 10 K. The occupancy of each site has been converted into  $\text{ND}_3/\text{Sc}$  for clarity. (a and c) Views along the *c*-axis showing packing of the guest molecules of  $\text{ND}_3$  in MFM-300(Sc)·( $\text{ND}_3$ )<sub>1.25</sub> and MFM-300(Sc)·( $\text{ND}_3$ )<sub>2.6</sub>, respectively. (b and d) Detailed views of host–guest interactions between MFM-300(Sc) and adsorbed molecules of  $\text{ND}_3$ .



The analysis of the NPD data were entirely consistent with information from solid-state NMR spectroscopy. Upon loading MFM-300(Sc) with  $\text{NH}_3$ , only slight structural modifications were observed, and the crystalline nature of the framework was retained.  $^{45}\text{Sc}$  magic angle spinning (MAS) NMR spectroscopy confirmed that the geometry around the Sc(III) centre was not notably distorted by interaction with  $\text{NH}_3$ , with the  $\mu_2\text{-OH}$  groups (Fig. S11a, ESI $^\dagger$ ) and  $\{^1\text{H}\}\text{-}^{13}\text{C}$  CPMAS NMR spectra showing that the carboxyl resonance from the linker is unaffected upon  $\text{NH}_3$  loading (*i.e.* minimal metal site distortion). However, the resonances assigned to the aromatic carbons do shift, reflecting an interaction of the rings with the guest molecules (Fig. S11b, ESI $^\dagger$ ). The interaction of  $\text{NH}_3$  with the MOF was also investigated using 2D  $^1\text{H}\text{-}^{45}\text{Sc}$  dipolar correlation (HETCOR) NMR spectroscopy (Fig. 3). The spectrum of pristine MFM-300(Sc) (Fig. 3a) shows clear cross peaks between aromatic protons (from the linker), as well as from hydroxyl protons ( $\mu_2\text{-OH}$  groups), with the Sc(III) site, demonstrating a close proximity between these atomic environments. The corresponding spectrum of  $\text{NH}_3$ -loaded MFM-300(Sc) is substantially different. Whilst cross peaks with aromatic protons unchanged, cross peaks with  $\mu_2\text{-OH}$  groups have moved to higher chemical shifts, indicating the presence of hydrogen-bonding, and a new weak cross peak is observed and assigned to pore-confined  $\text{NH}_3$  protons. *In situ* synchrotron FTIR microspectra were recorded at 298 K (Fig. 3e and f). The characteristic

O–H stretching mode of the  $\mu_2\text{-OH}$  group is observed at  $3678\text{ cm}^{-1}$ , which reduces in intensity and broadens upon loading of  $\text{NH}_3$ . The band at  $3404\text{ cm}^{-1}$  is assigned to the N–H stretching of  $\text{NH}_3$ , and this exhibits a red shift to  $3390\text{ cm}^{-1}$ .<sup>6,14</sup> The bands at  $1614$  and  $1440\text{ cm}^{-1}$ , assigned to  $\nu_{\text{as}}(\text{COO}^-)$  and  $\nu_{\text{s}}(\text{COO}^-)$ , respectively,<sup>20</sup> show small red shifts upon adsorption of  $\text{NH}_3$  ( $\Delta = 4 - 7\text{ cm}^{-1}$ ), consistent with interaction between  $\text{NH}_3$  and carboxylate groups. The bands between  $3800$  and  $1400\text{ cm}^{-1}$  for the local framework remain unchanged upon re-activation, confirming the high structural stability of MFM-300(Sc). Thus, the ssNMR and FTIR studies verify that  $\text{NH}_3$  is hydrogen-bonded to the  $\mu_2\text{-OH}$  groups *via* the lone pair of electrons on nitrogen, fully consistent with the NPD analysis.

INS spectra of bare and  $\text{NH}_3$ -loaded MFM-300(Sc) were also collected (Fig. S12, ESI $^\dagger$ ) and simulated using DFT calculations based upon the structural models derived from NPD analyses (Fig. S13, ESI $^\dagger$ ). The difference spectra (Fig. 4a), which were obtained by subtracting the spectrum of the bare MOF from that of the  $\text{NH}_3$ -loaded MOF, show the vibrational features of both the adsorbed  $\text{NH}_3$  molecules and the changes for the MOF host. The peaks in the low energy region (Fig. 4b) are primarily due to the vibrational modes of adsorbed  $\text{NH}_3$  molecules, with a small contribution due to changes in the lattice modes of the framework. The agreement between experimental and simulated spectra in terms of the overall profile allows unambiguous assignment of all major peaks. Specifically, the bands between  $45$  and  $116\text{ cm}^{-1}$  are assigned to the translational motion of the  $\text{NH}_3$ , which includes the vibration of  $\text{NH}_3$  molecules perpendicular to and along the molecular  $C_3$  axis and the hybrid of these modes. Peaks at  $132$  and  $172\text{ cm}^{-1}$  are due to rotational motion of the  $\text{NH}_3$  around its  $C_3$  axis. Bands between  $207$  and  $334\text{ cm}^{-1}$  are assigned to the rocking modes of the  $\text{NH}_3$ . Compared to the spectrum of  $\text{NH}_3$  in the solid state, where each  $\text{NH}_3$  forms a 3D hydrogen bonding network with 6 adjacent  $\text{NH}_3$  molecules, bands in all regions for the adsorbed  $\text{NH}_3$  shift to lower energy and exhibit more broad features, indicating more dynamic environment for the adsorbed  $\text{NH}_3$ . The features in the higher energy region mainly reflect the modes of the framework (Fig. 4c). Features I and III are due to the broadening of the peaks at  $692$  and  $934\text{ cm}^{-1}$  for bare MFM-300(Sc), and are assigned to the C–H rocking out of the  $C_6$  plane, in-phase and anti-phase, respectively. Feature VI at higher frequency between  $1090$  and  $1163\text{ cm}^{-1}$  shows reduced intensity upon adsorption of  $\text{NH}_3$ , and is assigned to the  $\text{H}_{\text{ring}}$  rocking within the  $C_6$  plane. Features II and IV originate from a significant blue shift of the peak at  $754\text{ cm}^{-1}$  in the spectrum of bare MFM-300(Sc) to  $987\text{ cm}^{-1}$  in the spectrum of  $\text{NH}_3$ -loaded MFM-300(Sc). This is assigned to the rocking of  $\mu_2\text{-OH}$  within the Sc–O–Sc plane. Interestingly, the features involving the motions of  $\text{H}_{\text{ring}}$  show only broadening and a decrease in intensities, while the features involving the motion of the  $\mu_2\text{-OH}$  experience changes in energy. This indicates a stronger interaction between  $\text{NH}_3$  and the  $\mu_2\text{-OH}$  than with  $\text{H}_{\text{ring}}$  centres. Feature V in the difference spectrum is due to the umbrella motion of adsorbed  $\text{NH}_3$ . Thus, the combined INS and DFT study has visualised directly the host–guest binding dynamics,

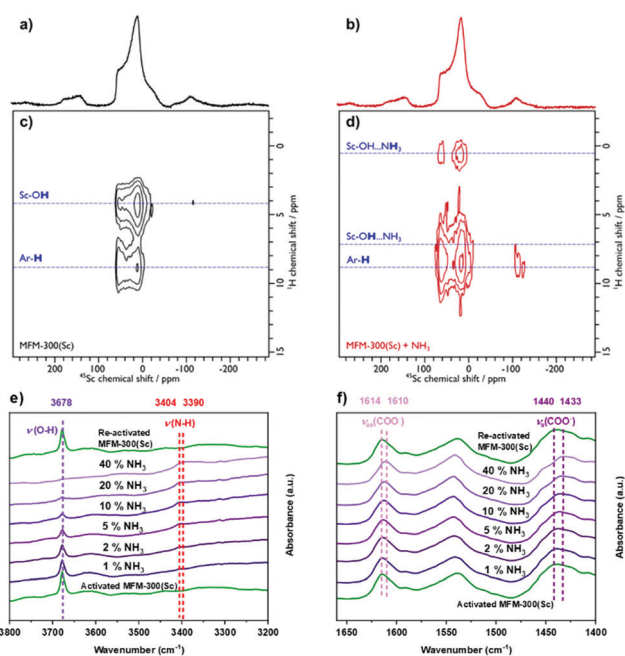


Fig. 3  $^1\text{H}\text{-}^{45}\text{Sc}$  Heteronuclear dipolar correlation spectroscopy (HETCOR) MAS NMR spectra of (a, c) pristine and (b, d)  $\text{NH}_3$ -loaded MFM-300(Sc), with corresponding  $^{45}\text{Sc}$  MAS NMR spectra (top). The spectra were recorded at 9.4 T using a MAS frequency of 12 kHz. The dashed blue lines highlight correlations between the Sc(III) site and various proton environments. *In situ* FTIR spectra of MFM-300(Sc) as a function of  $\text{NH}_3$  loading (diluted in dry  $\text{N}_2$ ) and re-activated under a flow of dry  $\text{N}_2$  at  $100\text{ mL min}^{-1}$  at 298 K for 2 h: (e)  $3800\text{--}3200\text{ cm}^{-1}$ , (f)  $1650\text{--}1400\text{ cm}^{-1}$ .



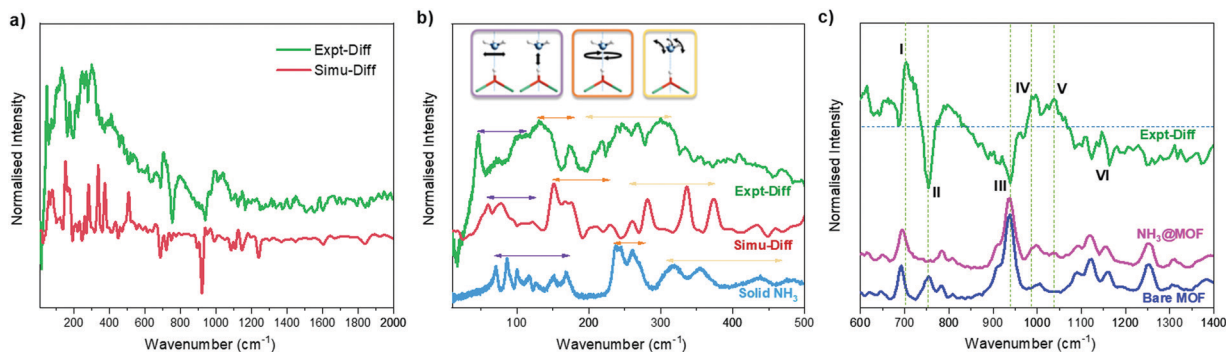


Fig. 4 Experimental and simulated INS difference spectra of the adsorbed  $\text{NH}_3$  within MFM-300(Sc), denoted as Expt-Diff and Simu-Diff, respectively. (b) Comparison of the INS spectra of adsorbed  $\text{NH}_3$  with solid  $\text{NH}_3$ . (c) Experimental INS spectra of bare MFM-300(Sc),  $\text{NH}_3$ -loaded MFM-300(Sc) and the difference spectrum at the higher energy region.

consistent with the reversible and high adsorption of  $\text{NH}_3$  in MFM-300(Sc).

In summary, MFM-300(Sc) comprised of metal-oxide chains with bridging  $-\text{OH}$  groups shows exceptional adsorption capacity ( $19.5 \text{ mmol g}^{-1}$  at 273 K and 1 bar) and regenerability for  $\text{NH}_3$ . *In situ* NPD analysis,  $^{45}\text{Sc}$  ssNMR spectroscopy, synchrotron FTIR and INS/DFT studies have unambiguously visualised the binding interactions and dynamics of  $\text{NH}_3$  within the pores of MFM-300(Sc). This in-depth understanding of the structure-function relationship with these host-guest systems will enable the rational design of potential materials with desired properties.

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## Conflicts of interest

The authors declare no competing interest.

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