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High ammonia adsorption in copper-carboxylate materials: host–guest interactions and crystalline–amorphous–crystalline phase transitions†

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We report the high NH₃ uptake in a series of copper-carboxylate materials, namely MFM-100, MFM-101, MFM-102, MFM-126, MFM-127, MFM-190(F), MFM-170, and Cu-MOP-1a. At 273 K and 1 bar, MFM-101 shows an exceptional uptake of 21.9 mmol g⁻¹. The presence of Cu(II) ··· NH₃ interactions and changes in coordination at the [Cu₂(O₂CR)₄] paddlewheel are analysed and discussed.

Ammonia (NH₃) is an essential feedstock for the manufacture of fertilizers and pharmaceuticals, and for proton transport in fuel cells.¹ NH₃ can be compressed for transport to a liquid at ~10 bar and room temperature or by cooling to -33 °C at atmospheric pressure. Due to its high gravimetric and volumetric hydrogen densities and potential clean combustion products (ideally N₂ and H₂O only), NH₃ is also considered as a potential hydrogen storage medium and renewable liquid fuel.² However, the toxicity and caustic nature of NH₃ means that it is necessary to develop safe and efficient materials for NH₃ storage.^{3,4} Porous materials for the physical or chemical adsorption of NH₃ are regarded as promising hosts that are capable of high energy efficiency and low operational cost.⁵ Conventional porous materials generally show low NH₃ adsorption capacities, for example, up to 11.4 mmol g⁻¹ in Amberlyst15.⁶ Metal-organic framework (MOF) materials have attracted much interest for NH₃ adsorption.⁷ Their superior surface area, controllable pore geometry, and flexibility to incorporate acidic and basic

functional groups and open metal sites enable further enhancement of their adsorption performance.⁸ Recently, MOFs have shown high NH₃ uptakes: 23.5 mmol g⁻¹ in Ni_{acryl}TMA incorporating BTDD (bis(1*H*-1,2,3-triazolo[4,5-*b*],-[4',5'-*i*])dibenzo-[1,4]dioxin) bridging ligands, and 19.8 mmol g⁻¹ in [Cu₂Cl₂(BBTA)] [H₂BBTA = 1*H*,5*H*-benzo(1,2-*d*:4,5-*d'*)bistriazole] at 298 K and 1 bar.⁹ Reversible adsorption of NH₃ has also been observed in a series of ultra-stable MOFs, MFM-300(M) (M = Cr, Fe, V^{III}, V^{IV}), showing uptakes of up to 17.3 mmol g⁻¹ at 273 K and 1 bar.¹⁰

MOFs incorporating open metal sites can demonstrate preferential binding of gases, but they often exhibit poor stability upon adsorption of reactive gases, such as NH₃, leading to irreversible desorption and/or structural collapse.¹¹ NH₃-induced structural transformation has been observed recently in [Cu(CYHDC)] (CYHDC²⁻ = *trans*-1,4-cyclohexanedicarboxylate) with a reported crystalline phase transition from 3D porous framework to 1D coordination polymer.¹² Here, we report the high adsorption of NH₃ in a series of Cu(II)-based MOFs and metal-organic polyhedra (MOP) and the comprehensive investigation of the mechanisms of adsorption by *in situ* synchrotron X-ray powder diffraction (SPXRD), single crystal synchrotron Fourier transform infrared (FTIR) micro-spectroscopy, X-ray pair distribution function (XPDF) and electron paramagnetic resonance (EPR) spectroscopy.

MFM-100, MFM-101, MFM-102, MFM-126, MFM-127, MFM-190(F), MFM-170, and Cu-MOP-1a were synthesised based upon our previously reported methods (Fig. S1, ESI†).¹³ All of these materials are based upon [Cu₂(O₂CR)₄] paddlewheel nodes. The isotopological MFM-100, MFM-101 and MFM-102 are composed of di-, tri-, and tetra-phenyl tetracarboxylate linkers, respectively, and exhibit interconnected cages with pore size dimensions of 12 × 12 × 12 Å, 12 × 12 × 22 Å and 12 × 12 × 28 Å, respectively. Another group of isostructural MOFs, MFM-126 and MFM-127, feature pyrimidine-dicarboxylate ligands and each afford two different types of cages (12 × 12 × 12 Å and 10 × 10 × 15 Å; 12 × 12 × 13 Å and 12 × 12 × 16 Å,

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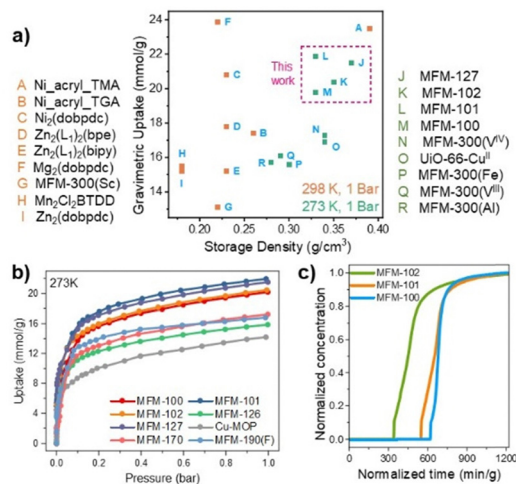


Fig. 1 (a) Plot of gravimetric uptake and storage densities for NH_3 in selected MOFs at 1 bar: orange 298 K, green 273 K (Tables S4–S6, ESI[†]). (b) Adsorption isotherms for NH_3 in MFM-100, MFM-101, MFM-102, MFM-126, MFM-127, MFM-190(F), MFM-170 and Cu-MOP-1a at 273 K. (c) Breakthrough curves for NH_3 (1000 ppm diluted in He) through fixed beds of MFM-100, MFM-101 and MFM-102 at 298 K at 1.0 bar.

respectively). MFM-190(F) incorporates a fluoro-functionalised pyridyl ring and shows two cages with dimensions of $18 \times 18 \times 14 \text{ \AA}$ and $18 \times 18 \times 24 \text{ \AA}$. MFM-170 is constructed with a pyridyl-tetracarboxylate linker and has three interconnected cages ($12 \times 12 \times 12 \text{ \AA}$, $12 \times 12 \times 16 \text{ \AA}$ and $16 \times 16 \times 22 \text{ \AA}$). Cu-MOP-1a incorporates a tripodal tricarboxylate ligand and has three different types of spherical cages with diameters of 5, 6 and 15 \AA . The gravimetric NH_3 adsorption isotherms for these materials were recorded at 273–298 K up to 1 bar, and the corresponding volumetric uptakes measured (Table S1, ESI[†]). At 273 K and 1 bar, the isotherms show NH_3 uptakes ranging from 14.2 to 21.9 mmol g^{-1} (Fig. 1a and b). Broad hysteresis loops and high residues of NH_3 (up to 14.6 mmol g^{-1} for MFM-127) are observed for all materials upon pressure-swing desorption (Fig. S2 and S3, ESI[†]), indicating the presence of strong host–guest interactions in these systems. Heating up to 150 $^\circ\text{C}$ under vacuum leads to removal of all NH_3 . For all the studied MOFs, loss of crystallinity is observed upon adsorption of NH_3 at 1 bar characterized by loss of peaks by PXRD (Fig. S4, ESI[†]). However, MFM-100, MFM-101 and MFM-102 show a degree of structural stability towards adsorption of NH_3 up to 50 mbar (Fig. S5, ESI[†]) and were of special interest due to their high uptakes of NH_3 at 1 bar, 19.8, 21.9 and 20.4 mmol g^{-1} at 273 K and 15.7, 14.9 and 13.7 mmol g^{-1} at 298 K. It should be noted that MFM-100 demonstrates much the best structural stability up to 50 mbar in comparison to MFM-101 and MFM-102, probably due to greater rigidity of the framework incorporating a shorter linker.

Despite the loss of crystallinity upon exposure to NH_3 at 1 bar, MFM-100, MFM-101 and MFM-102 maintained their NH_3 uptake over five cycles of pressure-swing adsorption–desorption up to 0.15 bar NH_3 at 298 K (Fig. S6, ESI[†]). The loss of crystallinity up to 1 bar NH_3 (Fig. S4, ESI[†]) suggests loss

of long-range structural periodicity in these materials rather than full framework collapse (see below). Relatively strong host–guest interactions are suggested by the measured high heats of adsorption (30 to 90 kJ mol^{-1} , Fig. S7, ESI[†]). Temperature-programmed desorption of NH_3 (NH_3 -TPD) showed a main desorption peak for MFM-100 at 100 $^\circ\text{C}$, while for MFM-101 and MFM-102 this peak is broadened and shifted towards higher temperatures (100–250 $^\circ\text{C}$) (Fig. S8, ESI[†]). To study further the performance of these materials for capture of NH_3 at low concentrations (1000 ppm), conditions under which these materials are stable and remain crystalline, breakthrough experiments were performed at 298 K. These show dynamic uptakes of 3.3, 4.1 and 4.5 mmol g^{-1} , respectively, for MFM-100, MFM-101 and MFM-102 (Fig. 1c), consistent with the observed isothermal uptakes at 1 mbar (3.6, 4.4 and 4.9 mmol g^{-1} , respectively, Table S5, ESI[†]). The highest dynamic uptake was observed for MFM-102, the material with the largest pore size which allows rapid adsorption equilibrium under flow conditions.

The preferred binding domains of NH_3 in MFM-100 were determined by the Rietveld refinement of *in situ* SPXRD data of gas-loaded MFM-100 (Fig. S9 and S10, ESI[†]). At 50 mbar of NH_3 , conditions under which the material is stable, three binding sites are observed in MFM-100-4.4 NH_3 [$\text{Cu}_2(\text{C}_{16}\text{O}_8\text{H}_6)\cdot 4.4\text{NH}_3$] (Fig. 2a–c), corresponding to a crystallographic uptake of 9.69 mmol g^{-1} . This is consistent with the isothermal uptake of 10.8 mmol g^{-1} at 50 mbar. All three binding sites are found within the rhombic cage, where the predominant position, Site I [occupancy = 0.80(3)] is bound to Cu(II) [$\text{Cu}\cdots\text{NH}_3 = 2.78(29) \text{ \AA}$], consistent with the notable shift of ligand-field (d–d) transitions

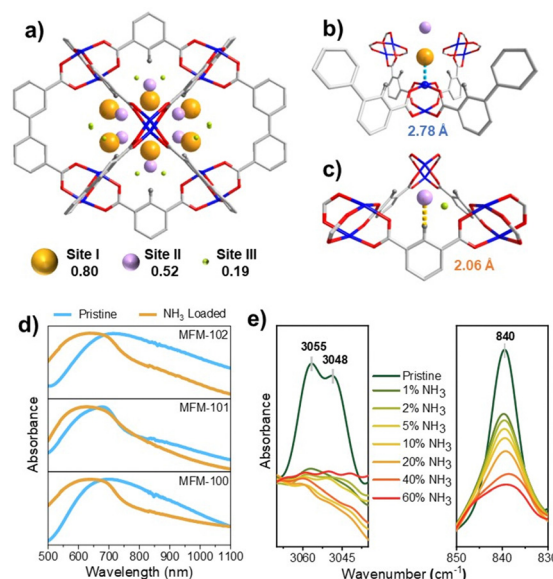


Fig. 2 (a) Location of NH_3 in MFM-100-4.4 NH_3 determined by SPXRD with the radius of the sphere proportional to occupancy. (b) Binding site I shows interaction of NH_3 with open Cu(II) site. (c) Binding site II shows aromatic C–H \cdots NH_3 hydrogen bonding. (d) UV-vis spectra of MFM-100, MFM-101 and MFM-102 upon adsorption of NH_3 . (e) *In situ* synchrotron FTIR spectra for single crystals of MFM-101 at various partial pressures of NH_3 (diluted in dry N_2) at 298 K.



from 700 to 620 nm in the UV-vis spectrum typically observed for the formation of Cu-NH₃ complexes (Fig. 2d).¹⁴ Site II [occupancy= 0.52(3)] is located towards the centre of the cage and binds to the ligand *via* hydrogen bonding [C-H_{aromatic}···NH₃ = 2.06(10) Å]. The *in situ* synchrotron FTIR spectra show that the aromatic C-H stretching modes (3055 and 3048 cm⁻¹) and bending mode (840 cm⁻¹) decrease in intensity with increasing NH₃ partial pressure (Fig. 2e and Fig. S11–S13, ESI†).¹⁵ Only guest-guest interaction is observed for NH₃ at site III [occupancy= 0.19(3)], with adjacent molecules in the pore exhibiting intermolecular hydrogen bonding [N¹···N² = 2.57(31) Å, N²···N³ = 2.58(48) Å] to afford efficient packing of adsorbed NH₃ molecules in the pore.

Significantly, MFM-100, MFM-101 and MFM-102 retain a degree of structural integrity under low pressures of NH₃ up to 50 mbar (Fig. S5, ESI†), and it is within this regime that structural determination can be undertaken for NH₃-loaded MFM-100 (as described above). However, at higher pressures of NH₃ up to 1 bar loss of crystallinity (lattice periodicity) was observed. This is also evident in the loss or reduction of many of the infrared bands for the framework above 50 mbar (Fig. S11–S13, ESI†). The materials remain amorphous on removal of NH₃ under vacuum. However, new crystalline MOF materials can be generated from these amorphous materials on desorption of NH₃ under vacuum for 12 h followed by addition of H₂O at 298 K for 24 h (Fig. S14, ESI†). This does not re-generate the starting material but another porous crystalline material (denoted R1) with both uptake capacity and crystallinity partially recovered (Fig. 3a and Fig. S15–S17, ESI†).

X-ray pair distribution function (XPDF) is an extremely powerful method to determine the local coordination environment and interatomic distances in poorly or non-crystalline materials.¹⁶ In the short-range region (< 5 Å), XPDF patterns afford information on bond formation and cleavage within the first and second coordination sphere, reflected by peak widths and intensities. The long-range region (5–15 Å) carries information of order of periodicity defined by the position of the last significant peak. For bare MFM-100, MFM-101 and MFM-102 long-range peaks are observed, confirming the rigidity and order of the structure. Upon adsorption and desorption of NH₃ at 298 K and 1 bar, a significant decrease in intensity in these peaks (5–15 Å) was observed for MFM-102 compared to the more structurally rigid MFM-100 (Fig. S18, ESI†). This suggests the loss of long-range periodicity, paralleling the decrease in intensity of Bragg peaks in the PXRD patterns. In contrast, distinctive peaks are observed in the short-range regions (< 5 Å) after NH₃ loading and on regeneration of a new phase on addition of H₂O. The assignment of peaks below 3.2 Å is illustrated in Fig. 3b. Peaks at 1.8–2.1, 2.4–2.7, and 2.8–3.2 Å are assigned to the Cu–O, Cu–Cu or O–O contacts within the [Cu₂(O₂CR)₄] paddlewheels, respectively. For MFM-100, only small changes in intensity are observed for these peaks on NH₃ uptake and release, while notable changes of intensity and shift of peak positions were observed for MFM-102 (Fig. 3c and d). A Cu(II)···NH₃ interaction is observed in MFM-100 and MFM-102 with distances ranging from 2.4 to 2.8 Å, consistent with the SXPD result. The XPDF result suggests that these MOFs

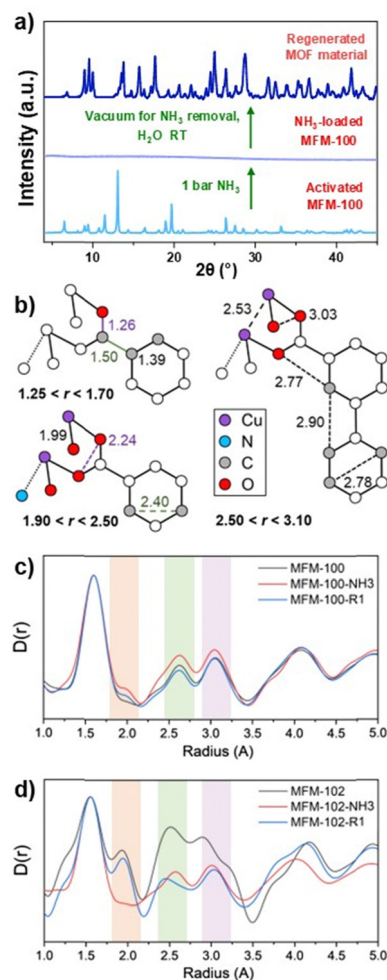


Fig. 3 (a) PXRD patterns for as-synthesised and for NH₃-loaded MFM-100, and for the regenerated crystalline MOF material (R1) formed by placing NH₃-loaded MFM-100 under vacuum followed by treatment with H₂O. (b) Structural details of coordination sphere at Cu(II) in the water-regenerated MOF material: Cu, purple; N, blue; C, grey; O, red. (c) and (d) XPDF pattern of MFM-100 and MFM-102 (bare material), NH₃-loaded and water regenerated material (R1) in the short-range region with each data set normalized to the most intense peak.

undergo relatively small changes in local O-coordination upon adsorption and desorption of NH₃, but on NH₃-loading at 1 bar the resultant amorphous MOFs show a lack of long-range order but still retain structural connectivity within the material.

In situ EPR spectroscopy was employed to probe the changes to Cu(II) sites in MFM-100, MFM-101 and MFM-102 during activation, adsorption and regeneration processes. In [Cu₂(O₂CR)₄] paddlewheel structures the two neighbouring Cu(II), *S* = 1/2 ions couple antiferromagnetically to give an *S* = 0 ground state (EPR silent) and an excited *S* = 1 state (singlet-triplet gap *ca.* 300 cm⁻¹), and this is maintained when the paddlewheels are incorporated into MOFs.¹⁵ The EPR spectra for pristine materials obtained at 150 K at Q- and X-bands (Fig. 4a–d) show characteristic features of the thermally populated *S* = 1 state, spread over a wide field range due to a zero-field splitting ($|D|$ *ca.* 0.3 cm⁻¹; Tables S2 and S3 and Fig. S19, ESI†). Two further features are observed around the *g* = 2



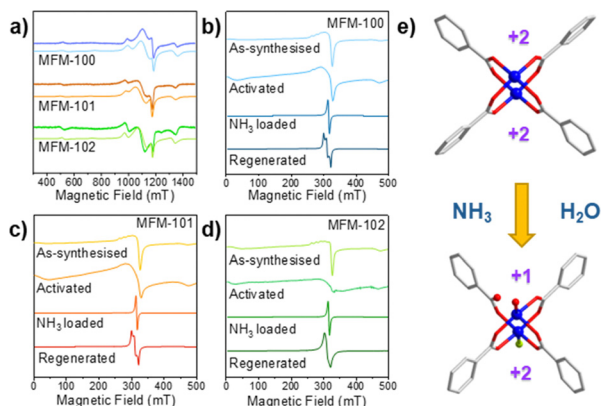


Fig. 4 (a) Q-band EPR spectra for MFM-100, MFM-101 and MFM-102 at 150 K (experimental: dark colour; simulated: light colour). (b) to (d) X-band EPR spectra of MFM-100, MFM-101 and MFM-102 at 150 K as-synthesised, activated, NH_3 -loaded and the MOF material regenerated by placing NH_3 -loaded material under vacuum followed by treatment with H_2O . (e) Schematic representation of coordination at $\text{Cu}(\text{II})$ in activated and regenerated (R1) MOF materials (C, white; O, red; Cu, blue; N, green).

region (Fig. S19, ESI[†]): (i) a broad isotropic feature at $g \approx 2.1$ arising from inter-dinuclear exchange ($J' \approx 1 \text{ cm}^{-1}$; Tables S2 and S3, ESI[†]) between neighbouring $S = 1$ populated $[\text{Cu}_2(\text{O}_2\text{CR})_4]$ paddlewheels *via* the aryl linker,¹⁷ and (ii) a sharper, near-axial signal due to monomeric, $S = \frac{1}{2}$ $\text{Cu}(\text{II})$ sites. In $[\text{Cu}_2(\text{O}_2\text{CR})_4]$ paddlewheel MOFs such spectra for monomers have been attributed to extra-framework complexes formed during synthesis. On cooling to 10 K only the isolated $\text{Cu}(\text{II})$ site signals remain as the $S = 1$ state of the paddlewheels is depopulated (Fig. S20, ESI[†]).¹⁸ Similar powder patterns have been reported for many materials based on $[\text{Cu}_2(\text{O}_2\text{CR})_4]$ paddlewheel units.

By EPR spectroscopy, the $[\text{Cu}_2(\text{O}_2\text{CR})_4]$ paddlewheel structures of all the three materials remain intact upon activation (Fig. S21 and S22, ESI[†]). Adsorption of NH_3 at 298 K and 1 bar leads to an intense, relatively sharp isotropic signal at $g = 2.14$, observed at both 10 K and 150 K (Fig. 4b–d and Fig. S21 and S22, ESI[†]). We have been unable to detect a spin echo in pulsed EPR experiments, which suggests rapid electron spin relaxation. This may indicate exchange interactions between $\text{Cu}(\text{II})$ ions, which could be mediated by the hydrogen-bonding network of adsorbed NH_3 molecules.¹⁹ No changes in spectra were observed upon desorption of NH_3 under heating at 100 °C for 2 h, consistent with strongly bound NH_3 molecules. The spectra of the regenerated R1 materials show a relatively sharp rhombic signal (Fig. 4b–d and Fig. S20–S22, ESI[†]). The g -values (all $> g_e$; Tables S2 and S3, ESI[†]) indicate these are associated with $\text{Cu}(\text{II})$, and the lack of Cu hyperfine splitting suggests interaction between sites. We were again unable to detect a spin echo from these signals suggesting that these are due to the framework and not extraneous $\text{Cu}(\text{II})$ sites. The rhombicity suggests a distorted environment, which could indicate induced $\text{Cu}(\text{II})$ defects or ligand displacement after contact with water.²⁰ Thus, the rhombicity of the $\text{Cu}(\text{II})$ coordination environment observed here is tentatively assigned to the partial hydrolysis of a Cu–O

bond, linked to binding of H_2O at site I (Fig. 4e). This is also consistent with XPDF results.

In summary, we confirm the adsorption of NH_3 in a series of $\text{Cu}(\text{II})$ -carboxylate MOFs. MFM-101 shows an NH_3 uptake of 21.9 mmol g^{-1} at 273 K and 1 bar. Strong $\text{Cu}(\text{II}) \cdots \text{NH}_3$ interactions and subtle changes in the coordination geometry of $[\text{Cu}_2(\text{O}_2\text{CR})_4]$ paddlewheels are observed within a crystalline–amorphous–crystalline phase transition. This work affords insights into NH_3 adsorption in copper-based porous materials and will inform future development of efficient sorbents for NH_3 .

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Data availability

Data and analyses supporting this article are included in ESI[†]

Conflicts of interest

There are no conflicts to declare.

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