Direct Observation of Ammonia Storage in UiO-66 Incorporating Cu(II) Binding Sites

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ABSTRACT: The presence of active sites in metal–organic framework (MOF) materials can control and affect their performance significantly in adsorption and catalysis. However, revealing the interactions between the substrate and active sites in MOFs at atomic precision remains a challenging task. Here, we report the direct observation of binding of NH3 in a series of UiO-66 materials containing atomically dispersed defects and open Cu(I) and Cu(II) sites. While all MOFs in this series exhibit similar surface areas (1111–1135 m² g⁻¹), decoration of the –OH site in UiO-66-defect with Cu(II) results in a 43% enhancement of the isothermal uptake of NH3 at 273 K and 1.0 bar from 11.8 in UiO-66-defect to 16.9 mmol g⁻¹ in UiO-66-CuI. A 100% enhancement of dynamic adsorption of NH3 at a concentration level of 630 ppm from 2.07 mmol g⁻¹ in UiO-66-defect to 4.15 mmol g⁻¹ in UiO-66-CuII at 298 K is observed. In situ neutron powder diffraction, inelastic neutron scattering, and electron paramagnetic resonance, solid-state nuclear magnetic resonance, and infrared spectroscopies, coupled with modeling reveal that the enhanced NH3 uptake in UiO-66-CuII originates from a {Cu(II)···NH3} interaction, with a reversible change in geometry at Cu(II) from near-linear to trigonal coordination. This work represents the first example of structural elucidation of NH3 binding in MOFs containing open metal sites and will inform the design of new efficient MOF sorbents by targeted control of active sites for NH3 capture and storage.

INTRODUCTION

Ammonia (NH3) is a major feedstock in the agricultural and chemical industries, but due to its toxic and corrosive nature, storage and transport of NH3 in large quantities is challenging. It is therefore of great interest to develop efficient sorbent materials that show significant chemical and physical stability and high adsorption capacity for NH3. Conventional sorbents, including zeolites, mesoporous carbons, and resins, have been studied for NH3 adsorption, but they show limited capacities and often undergo irreversible structural degradation upon desorption. In addition, fine-tuning and directed chemical manipulation of active sites in these materials at the atomic level can be problematic due to the lack of direct structural insights and limited structural diversity. Porous metal–organic framework (MOF) materials adopt well-defined structures, are designable, and can show exceptional structural diversity, enabling the control of active sites at atomic precision. Structural defects and open metal sites in MOFs are widely considered and used as active sites for binding of guest molecules. A variety of MOFs incorporating open metal sites or defects, such as [M₆(dobpdc)]⁶⁺ (dobpdc⁴⁻ = 4,4-dioxidobiphenyl-3,3-dicarboxylate), Cu₄Cl₄(BBTA) (BBTA = 1H,5H-benzo[1,2-d],(4,5-d′)bistriazole)⁴⁻, HKUST-1,⁵⁻ and UiO-67,⁷¹ have been reported for NH3 adsorption. However, it remains highly challenging to identify the precise role of these active sites in binding NH3 molecules, not least because of the relative invisibility of protons in NH3 by X-ray diffraction and the complex and rapid host–guest dynamics involved in NH3 binding. Revealing such insights will enable targeted control of active sites and thus deliver efficient NH3 stores by design. This will further inform the development of next-generation catalysts for the cracking of NH3 for portable applications relating to the hydrogen economy.

Here, we report the study of binding domains and dynamics of NH3 within UiO-66-defect (UiO-66 with a missing carboxylate ligand), UiO-66-CuI, and UiO-66-CuII based upon the direct observation of the location of atomically
dispersed active sites and their interactions with NH₃ molecules. The robustness of the framework in UiO-66 makes it an ideal platform for the study of NH₃ adsorption, and the incorporation of open Cu(II) sites can provide further strong binding and activation sites. Compared with UiO-66-defect, UiO-66-CuI shows significant enhancement of static (11.8 and 16.9 mmol g⁻¹, respectively, at 273 K and 1.0 bar) and dynamic (2.07 and 4.15 mmol g⁻¹, respectively, at 298 K and at 630 ppm concentrations) adsorption of NH₃ thus serving as a top-performing NH₃ sorbent. In situ neutron powder diffraction (NPD), inelastic neutron scattering (INS), coupled with density functional theory (DFT) modeling, electron paramagnetic resonance (EPR), solid-state nuclear magnetic resonance (ssNMR), infrared (IR), and ultraviolet–visible (UV–vis) absorption spectroscopies reveal the presence of reversible {Cu(II)···NH₃} interactions that underpin the observed high and reversible NH₃ uptake.

**EXPERIMENTAL SECTION**

NH₃ Adsorption Isotherms and Cycling Experiment. The synthesis and activation of MOF materials have been reported in our previous study and are described in detail in the Supporting Information. Static adsorption isotherms (0–1.0 bar) for NH₃ were measured on IGA (intelligent gravimetric analyzer, Hiden Isochema, Warrington, U.K.). Desolvated samples of UiO-66-defect, UiO-66-CuI, and UiO-66-CuII were generated in situ under dynamic vacuum (1 × 10⁻⁸ mbar) at 393 K for 24 h. NH₃ (research-grade) was purchased from BOC and used as received. For cycling experiments, UiO-66-defect, UiO-66-CuI, and UiO-66-CuII materials were loaded into cylindrical vanadium sample cells with an indium seal and degassed at 373 K under dynamic vacuum to remove the remaining trace guest water molecules. Dosing of ND₃ was carried out volumetrically at room temperature to ensure that ND₃ was present in the gas phase when not adsorbed and to ensure sufficient mobility of ND₃ inside the MOF framework. The temperature during data collection was controlled using a helium (He) cryostat (7 ± 0.2 K). The quality of the Rietveld refinements has been assured with low goodness-of-fit (Gof) factors, low weighted profile factors (Rwp), and well-fitted patterns with reasonable isotropic displacement factors.

Inelastic Neutron Scattering (INS). INS experiments were performed at TOSCA neutron spectrometer at the ISIS Facility at the Rutherford Appleton Laboratory (U.K.). Desolvated UiO-66-defect and UiO-66-CuII materials were loaded into cylindrical vanadium sample cells with an indium seal and degassed at 373 K under dynamic vacuum to remove the remaining trace guest water molecules. The temperature during data collection was controlled using a He cryostat (7 ± 0.2 K). The loading of NH₃ was performed volumetrically at room temperature, and background spectra of bare MOF samples were subtracted to obtain the difference spectra.

**Solid-State Nuclear Magnetic Resonance (ssNMR) Spectroscopy.** Magic angle spinning (MAS) NMR spectra were recorded using a Bruker 9.4 T (400 MHz ¹H Larmor frequency) AVANCE III spectrometer equipped with a 4 mm HFX MAS probe. Samples were desolvated and packed into 4 mm o.d. zirconia rotors under inert conditions and sealed with a Kel-F rotor cap. Experiments were carried out at ambient temperature using a MAS frequency of 12 kHz. ¹H-pulses of 100 kHz and ¹³C-pulses of 50 kHz were used, and ¹³C spin-locking at ~50 kHz was applied for 2 ms, with corresponding ramped (70–100%) ¹H spin-locking at ~73 kHz for CP experiments and with 100 kHz of SPINAL-64 heteronuclear ¹H decoupling throughout signal acquisition. Then, 640–8192 transients were collected for the CPMAS NMR spectra, depending on the sample. ¹H Hahn echo spectra used an inter-pulse delay of one rotor period, giving a total echo time of 0.167 ms. For the two-dimensional (2D) ¹H–¹³C FSLG-HETCOR dipolar correlation experiment, 2304...
on the porosity of resultant UiO-66 materials. X-ray absorption spectroscopic results, which confirmed the absence of aggregated (long-range magnetically coupled) or binuclear \((S = 1)\) Cu(II) species in UiO-66-Cu\(^{11}\). At 273 K and 1.0 bar, UiO-66-defect, UiO-66-Cu\(^{1}\), and UiO-66-Cu\(^{11}\) exhibit NH\(_3\) uptakes of 11.8, 12.6, and 16.9 mmol g\(^{-1}\) (Figure S2), respectively, comparable with state-of-the-art materials (Table S1). Thus, the variation of active sites in the pore interior has little impact on the porosity of resultant UiO-66 materials. X-ray absorption fine structure (XAFS) spectroscopy of UiO-66-Cu\(^{11}\) (Figure S2) shows a lower intensity for the features at a long distance (\(\sim 2.5\) Å) in the Fourier transform of the \(k^2\)-weighted data compared with that for CuO as a reference material. This strongly suggests that the Cu(II) sites in UiO-66-Cu\(^{11}\) are atomically dispersed\(^{22,27}\), in full agreement with the EPR spectroscopic results.

#### RESULTS AND DISCUSSION

NH\(_3\) Adsorption Analysis. Desolvated UiO-66-defect, UiO-66-Cu\(^{1}\), and UiO-66-Cu\(^{11}\) display BET surface areas of 1135, 1111, and 1124 m\(^2\) g\(^{-1}\), respectively (Table S1). Thus, the variation of active sites in the pore interior has little impact on the porosity of resultant UiO-66 materials. X-ray absorption fine structure (XAFS) spectroscopy of UiO-66-Cu\(^{11}\) (Figure S2) shows a lower intensity for the features at a long distance (\(\sim 2.5\) Å) in the Fourier transform of the \(k^2\)-weighted data compared with that for CuO as a reference material. This strongly suggests that the Cu(II) sites in UiO-66-Cu\(^{11}\) are atomically dispersed\(^{22,27}\), in full agreement with the EPR spectroscopic results, which confirmed the absence of aggregated (long-range magnetically coupled) or binuclear \((S = 1)\) Cu(II) species in UiO-66-Cu\(^{11}\). At 273 K and 1.0 bar, UiO-66-defect, UiO-66-Cu\(^{1}\), and UiO-66-Cu\(^{11}\) exhibit NH\(_3\) uptakes of 11.8, 12.6, and 16.9 mmol g\(^{-1}\) (Figure S2), respectively, comparable with state-of-the-art materials (Table S7). The isotherms display apparent hysteresis loops (Figure S3), indicating the presence of strong host–guest interactions at the binding sites within the two types of cages of the framework (tetrahedral and octahedral cages with diameters of 7 and 9 Å, respectively). UiO-66-defect, UiO-66-Cu\(^{1}\), and UiO-66-Cu\(^{11}\) show high packing density of NH\(_3\) of 65.2, 55.5, and 0.74 g cm\(^{-3}\), respectively, demonstrating efficient volumetric storage of NH\(_3\) (Table S3). It is worth noting that the packing density of UiO-66-Cu\(^{11}\) is comparable to that of liquid NH\(_3\) (0.68 g cm\(^{-3}\)) at 240 K. All three MOFs show high stability toward pressure-swing NH\(_3\) adsorption with retention of the structure, porosity, and NH\(_3\) uptakes over at least 15 cycles (Figures 1e, S1, S4, and S6). This is in direct contrast to reported MOFs incorporating four- or five-coordinated open Cu(II) sites that lead to irreversible sorption of NH\(_3\) and structural degradation upon desorption\(^{19,28–30}\). Upon desorption under pressure-swing conditions, higher residues of NH\(_3\) in UiO-66-Cu\(^{1}\) and UiO-66-Cu\(^{11}\) (49–67\%) were observed compared with UiO-66-defect (27–30\%), attributed to the interactions between NH\(_3\) molecules and Cu sites \(\text{vide infra}\). The residual NH\(_3\) in all three systems can be fully released \(\text{via}\) heating, reflecting a relatively strong binding of NH\(_3\) in these MOFs. The excellent ability of UiO-66-defect, UiO-66-Cu\(^{1}\), and UiO-66-Cu\(^{11}\) to capture NH\(_3\) at low concentrations (630 ppm) has been confirmed by dynamic breakthrough experiments at 298 K, where the dynamic NH\(_3\) uptakes were calculated to be 2.07, 3.07, and 4.15 mmol g\(^{-1}\), respectively (Figure 1d). The introduction of Cu(II) sites leads to 100% enhancement of the dynamic NH\(_3\) adsorption capacity at low concentrations, which is highly desirable for the capture of NH\(_3\) as a pollutant and/or at low concentrations.

Determination of the Binding Sites for Adsorbed ND\(_3\). Rietveld refinements of the \(\text{in situ}\) NPD data collected at

Figure 2. Structures of \((\text{Zr}_6)\) clusters in UiO-66 (a) without and (b) with a defect site in terms of a missing ligand and (c) in UiO-66-Cu\(^{11}\). Views of the binding sites of ND\(_3\) in (d) UiO-66-defect and UiO-66-Cu\(^{1}\) at (e) low and (f) high loadings, respectively. All structures were derived from Rietveld refinements of the NPD data collected at 7 K (C, gray; O, red; Zr, sky blue; Cu, orange; H, white; N, blue; D, pink).
The crystal structures for UiO-66-CuII and to the –OH defect site in UiO-66-defect-10.6ND3 and to the atomically dispersed Cu(II) sites in UiO-66-CuII-{3.34ND3} and UiO-66-CuII-{9.64ND3}. An additional low loading of ND3 was conducted for UiO-66-CuII to better elucidate the precise role of Cu(II) sites in binding ND3 at low concentrations. The structures of bare UiO-66 with and without a defect site are shown in Figures 2b and 2a, respectively. In UiO-66-defect-10.6ND3, three distinct binding sites (I, II, and III) are found (Figures 2d and S14). The primary binding site (Site I) of ND3 (occupancy of 6.02 ND3/ZN) is anchored by two –OH groups at the defect site, forming a series of strong host–guest hydrogen bonds to the μ3-OH and defect –OH groups [O μ3−H···ND3 = 1.63(8) Å; ND3···O defect−H = 2.81(7) Å; and ND3···O carboxylate = 2.59(1) Å]. Compared with the ND3@UiO-67,21 a stronger hydrogen bond between the defect –OH groups and ND3 molecules is observed in ND3@UiO-66-defect [O μ3−H···ND3 = 1.96(1) and 1.63(8) Å, respectively], resulting in higher NH3 uptake (8.4 and 11.8 mmol g−1, respectively). Site II (occupancy of 4.40 ND3/ZN) is bound to the framework mainly via electrostatic interactions [ND3···aromatic rings = 3.38(12)−3.59(29) Å], further supplemented by intermolecular hydrogen bonding between adsorbed ND3 molecules [ND3···ND3 II = 3.27(1)−3.43(32) Å]. Site III (occupancy of 0.18 ND3/ZN) exhibits no direct interaction with the framework and is stabilized by the interaction with adjacent ND3 molecules at Site II through hydrogen bonding [ND3···ND3 III = 4.29(13) Å].

The Cu(II) ion in UiO-66-CuII binds to two oxygen centers and shows a near-linear coordination geometry (Figure 2c). The crystal structures for UiO-66-CuII-{3.34ND3} and UiO-66-CuII-{9.64ND3} determined by NPD both show two binding sites (Figures 2f and S15). Site I is anchored simultaneously by the Cu(II) site [Cu μ3−···ND3 I = 2.90(8)−3.00(6) Å] and adjacent hydroxyl groups via hydrogen bonding [O μ3−H···ND3 I = 1.37(42)−1.58(1) Å; ND3···O defect = 2.90(3)−3.08(2) Å; ND3···O carboxylate = 2.66(3)−2.87(1) Å]. Site II is stabilized through electrostatic interactions [ND3···aromatic rings = 3.31(27)−3.54(39) Å], supplemented by intermolecular hydrogen bonding with surrounding ND3 molecules [ND3···ND3 II = 2.99(3)−3.49(59) Å]. At higher ND3 loading, the occupancy of ND3 molecules at Site I increases by 83% from 3.10 to 5.66 ND3/ZN. In contrast, the occupancy decreases by ca. 16 times at Site II from 0.24 to 0.98 ND3/ZN (Figure 3), unambiguously demonstrating the critical role of unique Cu(II) sites in binding ND3 at low concentrations, consistent with the ultrahigh dynamic uptake of NH3 at low concentrations. The overall binding distances decrease slightly upon increased loading, indicating stronger host–guest interactions between ND3 and the framework. Interestingly, hydrogen/deuterium (H/D) site-exchange1,32 is also observed between the μ3-OH group and adsorbed ND3 molecules in both UiO-66-defect and UiO-66-CuII, suggesting the direct interaction via proton exchange between ND3 and μ3-OH. Cooperative {ND3}∞ networks are observed in both systems with intermolecular hydrogen bonds [ND3···ND3 = 2.99(3)−4.29(13) Å; Figures 3, S14, and S15]. This is reminiscent of the structure of condensed ND3 in solid state, and is consistent also with the observed increase in Q8, with increasing loading of NH3 between 3.0 and 6.7 mmol g−1. Importantly, this study represents the first example of structural elucidation of NH3 binding in MOFs containing open metal sites.

Figure 3. Distribution of adsorbed ND3 molecules within the tetrahedral cage in (a) UiO-66-defect-10.6ND3, (b) UiO-66-CuII-{3.34ND3}, and (c) UiO-66-CuII-{9.64ND3} as determined from the refinement of NPD data. The radii of the colored balls of Site I (blue) and Site II (pink) are proportional to their crystallographic occupancies. (a) 6.02 ND3/ZN for Site I and 4.40 ND3/ZN for Site II; (b) 3.10 ND3/ZN for Site I and 0.24 ND3/ZN for Site II; (c) 5.66 ND3/ZN for Site I and 3.98 ND3/ZN for Site II.

Studies of Host–Guest Binding Dynamics. By combining in situ INS and DFT calculations, the vibrational modes of adsorbed NH3 molecules and that of the framework host can be deconvoluted and assigned to interpret the rapid dynamics of the system. The experimental and simulated INS spectra showed excellent agreement for bare and NH3-loaded UiO-66-defect and bare and NH3-loaded UiO-66-CuII. By subtracting the spectra of the MOF and sample cell from the NH3-loaded samples, difference INS spectra can be obtained. For the loading of 2NH3 per {Zn6} cluster, the NH3 molecules are primarily adsorbed at Site I (Figure 4a). In UiO-66-defect and UiO-66-CuII, librational modes of adsorbed NH3 molecules around its C3 axis are observed at 15.8 and 17.7 meV. The peaks at 29.3, 38.8, and 51.0 meV in NH3-loaded UiO-66-defect (29.4, 39.1, and 50.7 meV in UiO-66-CuII) correspond to the rocking motions of NH3 around the N center. The significant red shift of these peaks compared to solid NH3 (librational modes at 29.4−32.3 meV; rocking modes at 39.3−54.4 meV) are attributed to the rotational flexibility of NH3 in its adsorbed local environment, in contrast to the NH3 molecules in the solid state connected by the three-dimensional hydrogen-bonding network. The peaks (or dips) in the experimental difference INS spectra in the high energy region, mostly corresponding to variations of system dynamics upon NH3 binding, are also assigned (Figure 4b−d). Three changes are observed in both UiO-66-defect and UiO-66-CuII systems on loading with NH3 corresponding to the following vibrational modes: (I) at 92.3 meV, the μ3-OH in Zr−O−H plane bending and H−C out-C6−plane deformation; (II) at 105 meV, the H−C out-C6−plane deformation; (III) at 130 meV, NH3 umbrella motion. For UiO-66-CuII, two extra changes are observed in the difference spectrum and they correspond to (IV) at 110 meV, the μ3-OH out of Zr−O−H plane bending and H−C out-C6−plane deformation, and (V) at 137 meV, the
Figure 4. Views of in situ INS spectra, the DFT-calculated spectra, and the corresponding vibrational modes for UiO-66-defect and UiO-66-Cu\textsuperscript{II}, before and after NH\textsubscript{3} loading. Difference spectra were obtained by subtraction of the INS spectra of the bare MOF from that for the NH\textsubscript{3}-loaded MOF and are marked as ed (experimental difference spectra) and sd (simulated difference spectra). (a) Comparison of vibrational modes between solid NH\textsubscript{3} at 7 K (8.7–21.0 meV translational modes; 29.4–32.3 meV librational modes; 39.3–54.4 meV rocking modes), and adsorbed NH\textsubscript{3} in the MOF. (b, c) Experimental difference INS spectra for UiO-66-defect and UiO-66-Cu\textsuperscript{II} upon NH\textsubscript{3} adsorption in the higher energy range. (d) Selected vibrational modes of UiO-66-defect and UiO-66-Cu\textsuperscript{II}.
H–C in C₆-plane bending. The introduction of Cu(II) sites to the structural defects contributes to an increase of the acidity at the μ₃-OH moiety with stronger μ₃-OH out-of-plane (Zr–O–H) bending in UiO-66-CuI upon NH₃ adsorption, as evidenced by peak IV. This is in excellent agreement with the shorter distance of O–H···ND₃ hydrogen bonds observed in the NPD study [O₃₅(H···ND₃) of 1.58(1) and 1.63(8) Å in UiO-66-CuI and UiO-66-defect, respectively]. Compared with UiO-66-defect, a slight increase in the intensity of the H–C in C₆-plane bending peak is observed in UiO-66-CuI (peak V), which could be related to the shorter distance between NH₃ and the aromatic ring in this system [ND₃···O aromatic ring of 3.49(1) Å in UiO-66-CuI and 3.53(1) Å in UiO-66-defect]. Overall, the INS/DFT results afford excellent agreement with the structural models derived from NPD data and new insights into the binding dynamics of NH₃ in these decorated MOFs.

**Investigation of the Host–Guest Interactions.** *In situ* infrared and ssNMR experiments were carried out to further investigate the interactions of NH₃ in these porous materials. Upon introduction of NH₃, depletion of the O–H stretching bands at 3673 and 3646 cm⁻¹ was observed (Figure S16), consistent with the binding of NH₃ molecules to μ₃-OH and defect –OH sites. Interestingly, an additional band was observed at 1617 cm⁻¹ for NH₃-loaded UiO-66-CuII (Figure 5e) assigned to asymmetric vibration of adsorbed NH₃ molecules on Lewis acid sites [Cu(II) in this case]. The presence of possible charge transfer between Cu(II) sites and bound NH₃ molecules has been confirmed by in situ UV–vis spectra, which show an additional broad absorption band centered at around 680 nm in NH₃-loaded UiO-66-CuII (Figure S17). The presence of strong binding of NH₃ to Cu(I) and Cu(II) sites was also confirmed by temperature-programmed desorption of NH₃ (NH₃−TPD) (Figure S18) and ¹H ssNMR spectroscopy (Figure 5a). The additional TPD peaks at higher temperatures (150–300 °C, Figure S18b) for UiO-66-CuI and UiO-66-CuII, which are not observed in UiO-66-defect, indicate stronger binding of NH₃ at these Cu sites. In addition, the desorption peaks for UiO-66-CuII appear at higher temperatures compared with those of UiO-66-CuI, suggesting a stronger {Cu(II)···NH₃} interaction than {Cu(I)···NH₃}, consistent with the adsorption and breakthrough results. These conclusions are supported further by the corresponding ¹H magic angle spinning (MAS) NMR spectra of the NH₃-loaded materials (Figure 5a). For UiO-66-defect, a large narrow signal from NH₃ is observed (FWHM ≈ 650 Hz, centered at δ¹H = 2.8 ppm), suggesting rapid relative motion of NH₃ in the pores. For UiO-66-CuI and UiO-66-CuII, this large peak is absent but a broad signal (FWHM ~ 2 kHz, centered at δ¹H = 3.7 ppm) is present that stems from pore-confined NH₃ (Figure S19). Furthermore, for UiO-66-CuI and UiO-66-CuII, very broad signals are observed at negative chemical shifts (FWHM ~ 7 kHz, centered at δ¹H = −7.6 ppm for UiO-66-CuI and δ¹H = −15.0 ppm for UiO-66-CuII) corresponding to metal-bound NH₃ again consistent with the infrared and UV–vis spectroscopic studies. One-dimensional (1D) ¹³C and 2D ¹H–¹³C dipolar correlation MAS NMR spectra (Figure S19) also indicate a hydrogen-
bonding interaction between NH₃ molecules and the carboxylate moieties from the organic linkers of the MOFs.

The strong interaction between NH₃ and Cu(II) site was further elucidated by EPR spectroscopy. UiO-66-Cu\textsuperscript{II} in its hydrated form has an X-band continuous wave (CW) EPR spectrum (Figure 5b), with axial (within the resolution of the experiment) spin Hamiltonian parameters \( g_\parallel = 2.074, g_\perp = 2.320, A_{\text{Cu}}(\text{Cu}) = 480 \text{ MHz}, \) typical of isolated Cu(II) ions with a \( d_{x^2-y^2} \) or \( d_{xy} \) ground state and consistent with water coordinated in the \( xy \) plane; the latter is confirmed by HYSCORE measurements.\textsuperscript{23} Dehydration of the sample leads to loss of the coordinated water (Figures S20, S21, and S23) and significant intensity loss in the CW EPR spectrum.\textsuperscript{25} This phenomenon has been observed in several Cu(II)-doped zeolites [without reduction to Cu(I)], attributed to unusual low-coordinate geometries that can lead to near-degenerate ground states.\textsuperscript{23} This is also consistent with the NPD model that suggests a pseudo-linear geometry at the Cu(II) site (Figure 2c) and with the observation that the spectra (CW EPR, HYSCORE) of the solvated system are not restored by exposure to dry O\textsubscript{2} but are restored by exposure to air via the uptake of moisture.

Adsorption of NH₃ in an activated sample of UiO-66-Cu\textsuperscript{II} led to the recovery of the intensity of the signal within the CW EPR spectrum, indicating that the adsorbed NH₃ interacts with the Cu(II) sites. Two components are observed: (i) an isolated Cu(II) signal with modified parameters \( g_\parallel = 2.07, g_\perp = 2.27, A_{\text{Cu}}(\text{Cu}) = 530 \text{ MHz} \) and (ii) an unresolved, broad signal at \( g \approx 2.115 \) (Figures 5b and S20, and Table S5). Only the former is observed in echo-detected EPR spectroscopy (Figures 5c and S22), demonstrating their different origin and that the species giving rise to the broad signal relaxes quickly. The observed increase in \( g_\parallel \) and increase in \( A_{\text{Cu}}(\text{Cu}) \) (compared to the hydrated form) of the anisotropic component are consistent with a mixed O/N-donor set, and similar changes have been observed in NH₃ binding in Cu-doped zeolites.\textsuperscript{39} The origin of the broad signal is less clear: the lack of resolution and rapid relaxation may indicate exchange interactions between the Cu(II) ions. The nearest possible intra- and inter-node Cu···Cu distances are 4.4 and 5.8 Å, respectively, and an interaction would only need to be a few hundred MHz to affect the CW EPR response significantly. This could be mediated by the hydrogen-bonding network of adsorbed NH₃ molecules within the tetrahedral cages. Since the defects will be distributed statistically, both coupled and uncoupled spectra could be observed. An alternative explanation for the broad signal would be a fluxional process, which averages the EPR response. However, the spectra are unchanged on cooling to 4 K, which should freeze out any such process. Similar broad, near-isotropic CW EPR signals have been observed on NH₃ loading on the Cu(II)-MOF, HKUST-1, tentatively attributed to spin-exchange phenomena.\textsuperscript{29} In contrast to the HKUST-1 study, where the changes in NH₃ adsorption were irreversible,\textsuperscript{29} the CW EPR and HYSCORE spectra of UiO-66-Cu\textsuperscript{II} can be readily regenerated by degassing and exposure to air, confirming excellent stability and reversibility of this system (Figures 5b, S21, and S23). At 10⁻⁷ mbar at different temperatures, the broad signal is lost first (Figure S20), consistent with preferential loss of NH₃ molecules at Site II/III, which disrupts the hydrogen-bonding network that facilitates the Cu···Cu interaction.

Similar EPR spectra and behavior are found for UiO-66-Cu\textsuperscript{IV}, which indicates the presence of a minor amount of Cu(II) ions along with Cu(I) sites after the reduction. To compare the strength of Cu···NH₃ binding in UiO-66-Cu\textsuperscript{II} and UiO-66-Cu\textsuperscript{IV} materials, the desorption and regeneration processes after NH₃ adsorption were compared (Figures 5d and S21). The broad isotropic signal is lost more quickly for UiO-66-Cu\textsuperscript{II}, demonstrating stronger binding in the UiO-66-Cu\textsuperscript{II} system, consistent with the TPD and ssNMR analyses and the isothermal adsorption and breakthrough results.

**CONCLUSIONS**

In summary, robust UiO-66 materials incorporating atomically dispersed defects and open Cu(I) and Cu(II) sites show high and reversible NH₃ adsorption capacities. While the decoration of defects with open Cu(I) and Cu(II) sites exhibits little change to the BET surface area (1111–1135 m² g⁻¹), the latter Cu(II) system shows 43 and 100% enhancements in the static and dynamic adsorption of NH₃, respectively, compared with UiO-66-defect. This places UiO-66-Cu\textsuperscript{II} as one of the state-of-the-art NH₃ sorbents. The host–guest interactions between the frameworks and adsorbed NH₃ molecules have been investigated comprehensively at the molecular level. In situ NPD, ssNMR, EPR, IR, UV–vis, and INS/DFT studies have established the binding interactions between NH₃ and defect sites and the critical role of low-coordinate Cu(II) sites in stabilizing NH₃ molecules has been determined unambiguously. This is distinct from four and five-coordinated Cu(II) sites that lead to irreversible structural degradation upon desorption of NH₃. By combining NH₃−TPD, in situ ssNMR, IR, UV–vis, and EPR experiments, the host–guest interactions have been revealed, and this is accompanied by a reversible change of the unique, near-linear coordination geometry of Cu(II) sites as a function of NH₃ binding. This is the structural origin of the observed reversible NH₃ adsorption in this system involving open metal sites. These findings showcase the designed tuning of active sites in MOFs that can result in top-performing NH₃ adsorption without altering the porosity of a given material. We anticipate that this study will provide key insights into the design and preparation of new efficient sorbents for NH₃ via the full control of active sites with atomic precision.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c00952.

Additional experimental details, adsorption isotherms, breakthrough experiments, views of crystal structures, XAFS, powder X-ray diffraction (PXRD), NPD, IR, UV–vis, NH₃−TPD, EPR, and ssNMR data (Figures S1–S23 and Tables S1–S11) (PDF)

Accession Codes

CCDC 2124989−2124993 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.
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Notes

The authors declare no competing financial interest.

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