Chemically reversible CO$_2$ uptake by dendrimer-impregnated metal-organic frameworks

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ABSTRACT

Industrialization over the past two centuries has resulted in a continuous rise of global CO$_2$ emissions. These emissions are changing ecosystems and livelihoods. Therefore, methods are needed to capture these emissions from point sources and possibly from our atmosphere. Though the amount of CO$_2$ is rising, it is challenging to capture directly from air because its concentration in air is extremely low, 0.04%. In this study, amines installed inside metal-organic frameworks (MOFs) are investigated for adsorption of CO$_2$, including at low concentrations. The amines used are polyamidoamine dendrimers that contain many primary amines. Chemically reversible adsorption of CO$_2$ via carbamate formation was observed, as was enhanced uptake of carbon dioxide via physisorption. Limiting factors in this initial study are comparatively low dendrimer loadings and slow kinetics for carbon dioxide uptake and release, even at 80 °C.
INTRODUCTION

Growing global awareness of climate change and its impact on humanity’s future has stimulated serious discussion of moving beyond lowering carbon dioxide emissions and implementing capture of CO₂ already present in our atmosphere – called direct air capture (DAC). CO₂ constitutes about 0.04% of air and has a partial pressure of ~40 Pa (0.0004 bar).¹ Therefore, any technology for direct air capture of CO₂ must function at low CO₂ partial pressures. Chemical bonding or strong chemical interactions have traditionally been used for CO₂ capture, especially with various amines.²⁻⁷ Capturing point-source-generated CO₂ with liquid amines (concentrated aqueous amine solutions), which is commonly known as amine scrubbing, is an established industrial process for CO₂ at high partial pressure (Scheme 1). However, regeneration of the amine and release of captured CO₂ require substantial amounts of energy; of additional concern is the substantial Bronsted basicity of these solutions and the potential for human injury or equipment corrosion by leaks or spills of the solutions.⁷

![Scheme 1. Chemically reversible carbamate formation via CO₂ adsorption on amines.](https://doi.org/10.26434/chemrxiv-2023-wl69w)

The use of liquid amines for CO₂ capture has inspired the use of other technologies, such as porous materials, that capture CO₂ using amines, but not in a liquid form. Notably, these technologies have the potential to ameliorate concerns about damage from spills of DAC media.
Among the porous materials explored are mesoporous silicas\(^2\)\(^-\)\(^4\)\(^-\)\(^6\)\(^-\)\(^8\) and metal-organic frameworks.\(^9\) The benefits of having amines in a porous scaffold include increased stability, reduced loss of amine, and slower degradation.\(^8\) An example of a stable porous scaffold is a metal-organic framework (MOF), which can be highly mesoporous, with wide channels that allow for facile transport of CO\(_2\).

![Figure 1](image-url)

Figure 1. (A) NU-1000. (B) NU-1000’s node with and without ligated formate. Images of nodes adapted with permission from *ACS Appl. Mater. Interfaces* 2021, 13, 17, 20081–20093. Copyright 2023 American Chemical Society.

In this work, we installed amines in the MOF NU-1000,\(^10\) which is a high stability MOF synthesized with zirconium oxide nodes; see linker, node, and framework structures in Figure 1. Instead of grafting amines directly onto the MOF, we impregnated the MOF with polyamidoamine (PAMAM) dendrimers, which are highly branched polymers with an ethylenediamine core and an amidoamine internal structure.\(^11\)\(^-\)\(^12\) PAMAM dendrimers have been explored as vectors in drug
delivery,\textsuperscript{11, 13} templates for nanoparticle synthesis,\textsuperscript{14} and confinement-enabled catalysts for chemical transformations.\textsuperscript{14} They have only seldomly been studied for CO\textsubscript{2} capture.\textsuperscript{15-17} Our own studies, specifically of PAMAM@MOF materials, have been limited to use of the dendrimers as stoichiometric Bronsted bases for MOF-node-catalyzed hydrolysis reactions and as sacrificial templates for creation of catalytic, zero-valent metal clusters for catalysis of gas-phase chemical transformations.\textsuperscript{14} PAMAM dendrimers are terminated with primary amines, which are anticipated to chemically bind CO\textsubscript{2} in much the same fashion as liquid amines, such as aqueous ethanolamine – in other words by reversible formation of carbamate species.\textsuperscript{18} Previous work has investigated PAMAM dendrimers for CO\textsubscript{2} capture on other supports and has employed other methods for gauging adsorption (e.g., thermogravimetric analysis).\textsuperscript{15-17} Here we have characterized NU-1000 containing Generation 2 and Generation 3 PAMAM dendrimers (Figure 2) by using a variety of techniques and have measured their CO\textsubscript{2} and water adsorption isotherms. We find that dendrimer-impregnated NU-1000 adsorbs more CO\textsubscript{2} than NU-1000 alone and that CO\textsubscript{2} forms carbamate species reversibility (albeit, slowly), allowing for full desorption of CO\textsubscript{2}.

Figure 2. Generation 2 and 3 PAMAM dendrimers. Images adapted with permission from \textit{Micro. Meso. Mat. 2009}, 123 (1), 140-149. Copyright 2023 Elsevier.
METHODS

NU-1000 was synthesized according to previously published procedures.\textsuperscript{19, 20} These procedures are now known to adventitiously incorporate ca. three formate ligands per hexazirconium(IV) node, where incorporation is at the expense of aqua/hydroxo ligand pairs.\textsuperscript{20, 21} (As indicated below, dendrimer incorporation is accompanied by nearly complete removal of formate.) Prior to the installation of PAMAM dendrimers, NU-1000 was activated by heating overnight under vacuum at 120 °C. The installation of the Generation 2 and Generation 3 PAMAM dendrimers was done following the procedure of Yang et al. where 0.6 mmol of dendrimer, in methanol solution, were used per mg of MOF.\textsuperscript{14}

Solid-state CP MAS NMR $^{13}$C spectra were collected on a Bruker Avance III HD 400 MHz system using a 4 mm probe and a 10 kHz spinning frequency. The samples were packed in a zirconia rotor. The chemical shifts were referenced to adamantane in KBr at 38.3 ppm. 256 scans were performed. Spectra were collected at IMSERC. $^1$H NMR spectra were collected using a Bruker S4 Avance III 500 MHz system with a DCH CryoProbe and automated BACS-60 autosampler.

Scanning electron microscopy (SEM) images were obtained on a JEOL 7900FLV SEM instrument, and samples were coated with 9 nm of OsO$_4$ to suppress charging. Energy Dispersive Spectroscopy (EDS) was performed with 5 kV accelerating voltage.

High resolution gas adsorption measurements for Ar, N$_2$, and CO$_2$ were performed on a commercial Autosorb-iQ$_2$ automatic volumetric adsorption analyzer (Anton-Paar, QuantaTec, formerly Quantachrome, Boynton Beach, FL, USA) equipped with 1, 10, and 1000 Torr
transducers. For the Ar and N\textsubscript{2} experiments, the temperature was controlled using liquid Ar (87 K) or liquid N\textsubscript{2} (77 K), respectively. A circulating water bath was used to control the temperature for the CO\textsubscript{2} experiments. Pristine NU-1000 was degassed under dynamic vacuum at 120 °C for 12 hours, and NU-1000 samples with installed PAMAM dendrimer were degassed at 80 °C for 12 hours.\textsuperscript{14} When calculating the multi-point Brunauer-Emmett-Teller (BET) area, the p/p\textsubscript{0} points selected gave a correlation coefficient of 0.999 for the fit to the BET equation. Pore size distributions were calculated as follows. For the N\textsubscript{2} data, the DFT model used was N\textsubscript{2} at 77 K on silica (cylindrical pore, non-local density functional theory (NLDFT) equilibrium model). For the Ar data, the DFT model used was Ar at 87 K zeolite/silica (cylindrical pore, NLDFT equilibrium model).

Water isotherms were measured at 25 °C with a volumetric (manometric) sorption analyzer (Vstar2, QuantaTec-Anton Paar). The manifold was held at temperatures above 100 °C to obtain highly accurate water adsorption measurements. A second cycle was measured without subjecting the MOF again to thermal-vacuum activation.

X-ray photoelectron spectroscopy (XPS) spectra were collected on the Thermo Scientific ESCALAB 250X (Al K\textalpha{} radiation, 1486.6 eV) at the Keck-II facility of Northwestern University’s NUANCE Center. XPS was used to determine the loading of PAMAM dendrimers in NU-1000 based on the spectra for Zr and N. Etching was also performed to determine the loading of PAMAM dendrimers slightly below the surface. Etching on the instrument is done at an average of 0.07 to 0.17 nm per second, though the exact depth etched cannot be measured with the instrument. Etching was done for 345 seconds, which resulted in an estimated depth of a few tens of nm.
PXRD data were collected at room temperature using a Debye-Scherrer geometry on a STOE-STADI-P powder diffractometer equipped with an asymmetric curved Germanium monochromator (CuKα1 radiation, λ = 1.54056 Å) and one-dimensional silicon strip detector (MYTHEN2 1K from DECTRIS). The line focused Cu X-ray tube was operated at 40 kV and 40 mA. Powder was packed in a 0.7 mm borosilicate capillary, which was spun during collection. Intensity data from 1 to 32 degrees two theta were collected over a period of 15 mins. The instrument was calibrated against a NIST silicon standard (640d) prior to the measurement. Data were collected at IMSERC.

Rietveld refinements were performed with GSAS-II. Background was modeled with 5 parameters using a Chebyshev function. Unit cell parameters and microstrain were refined and all atomic coordinates and thermal factors were fixed to the values obtained by single crystal refinement. Instrument parameters were determined by measuring a LaB₆ standard, and parameters were fixed during the refinement of the samples. The solvent containing model of NU-1000 was used to see the difference in electron density of the model versus experiment.

Thermogravimetric analysis (TGA) measurements were done on a TA Instruments TGA2950 using synthetic air (80/20) and Pt sample holders with a set heating rate of 5 K/min.

A diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) system (Jasco FT/IR-410) was used in situ to monitor the adsorption of CO₂ in NU-1000, NU-1000+G2, and NU-1000+G3. The resolution was 4.0 cm⁻¹, and 64 scans were collected for each spectrum from 4500 to 900 cm⁻¹. The Praying Mantis diffuse reflectance accessory was used, and the dome had ZnSe windows. The samples were diluted with CaF₂ in approximately a 50:50 mixture. Each sample was prepared for the experiment using the following steps: (1) in a 50:50 mixture, CaF₂ was mixed with the sample using a mortar and pestle; (2) the mixture was activated at 80 °C for 2
hours under Ar (note that the samples were activated after their synthesis, NU-1000 at 120 °C and NU-1000+G2 and NU-1000+G3 at 80 °C, for 12 hours each); (3) after activation, the sample was cooled to 30 °C, which was the starting temperature of the in situ experiment with CO₂. CO₂ adsorption was analyzed at 30, 40, 60, 75, 90, 100, and 120 °C. Spectra were collected using the following steps: (1) for each temperature, a spectrum under Ar was collected prior to switching to pure CO₂; (2) CO₂ flowed over the sample for 10 minutes and spectra was collected right after the switch and after 10 minutes; (3) the gas was switched back to Ar for a total of 10 minutes; (4) within those 10 minutes of Ar flow, a spectrum was collected after 5 minutes; (5) after 5 minutes, the temperature was raised to the next temperature and the cycle started again at collecting a spectrum prior to switching to CO₂. The samples with dendrimer were left to cool and a spectrum was collected. The spectra were normalized to an internal standard, a signal around 1181 cm⁻¹.
RESULTS

The installation of the PAMAM dendrimers in NU-1000 was qualitatively confirmed using $^{13}$C CP MAS NMR. The peaks in the alkane region of the spectrum indicate that the dendrimer was installed (Figure S1). EDS elemental mapping showed that the molar ratio of N to Zr doubled after the dendrimer was installed (Figure S2). The N present in the sample before installing the dendrimer is likely from residual solvent, such as dimethylformamide, that was used in the synthesis. EDS provides a weighted average of elements within ~1 micron from the MOF external surface.

XPS spectra were collected of NU-1000 with and without PAMAM dendrimers to quantify their loadings using Zr and N scans (Figures S4, S5, and S6). The N scan of NU-1000 indicates there is little to no N present (Figure S4). Table 1 presents the dendrimer loadings with and without etching of the surface. The XPS spectra etched into the hexagonal cross-sectional area samples the MOF below the surface of the crystallite. The loading of dendrimer for each type of dendrimer was consistent—samples prepared with Generation 2 all had similar loadings of Generation 2. The loadings significantly decrease past the external surface; however, the internal surface area greatly exceeds the external area, suggesting that the overwhelming majority of the installed dendrimers reside within the interior of the MOF crystals.
Table 1. Loading of PAMAM dendrimers in NU-1000 from XPS. Recall that XPS measurements probe only the outermost few nanometers of a solid material.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Not etched</th>
<th>Etched</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GX per Zr&lt;sub&gt;6&lt;/sub&gt;</td>
<td>1° amine per Zr&lt;sub&gt;6&lt;/sub&gt;</td>
</tr>
<tr>
<td>NU-1000+G2</td>
<td>0.25</td>
<td>3.92</td>
</tr>
<tr>
<td>NU-1000+G3</td>
<td>0.11</td>
<td>3.52</td>
</tr>
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Figure 3. Difference Fourier electron density map of NU-1000+G2. The yellow electron density isosurface is set at 0.2 e/Å<sup>3</sup>. (A) View along the c-axis and (B) a-axis. (C) PXRD data of NU-1000 and NU-1000+G2.

The difference Fourier electron density mapping of NU-1000 and NU-1000+G2 was determined from Rietveld refinement (Figure 3A, B). Most of the electron density introduced by the dendrimer is in the c-pore, and there is some electron density in the micropore. Yang et al. also observed via difference envelope density analysis that a related dendrimer resided, in part, in the
c-pore between the Zr₆ nodes, and they suggest that its siting in the c-pore is likely enabled by the deformation of the dendrimer when it interacts with a curved surface. PXRD data (Figure 3C) show that the structural integrity and crystallinity of NU-1000 are maintained after the dendrimer is installed. The installation of the Generation 3 PAMAM dendrimer showed qualitatively similar results for the electron density mapping and PXRD of NU-1000+G3 (Figure S8).

Argon and nitrogen isotherms of NU-1000, NU-1000+G2, and NU-1000+G3 (Figures 4A and S9A) show that the installation of the dendrimer causes the uptake of Ar and N₂ and the BET area to decrease – albeit only slightly. (Isotherms on a log pressure scale are shown in Figure S10.) Figure S11 shows the N₂ uptake of NU-1000 shortly after its synthesis and several months later. After eight months, its N₂ uptake decreased slightly, as did its BET area, from 2290 to 2090 m²/g. For consistency, the N₂ isotherms in Figure S9 were collected around the same time on the same instrument. Decreases in N₂ uptake have been reported for NU-1000 with PAMAM dendrimers installed. There are no previously reported BET areas for PAMAM dendrimers in NU-1000. Decreases in BET areas following PAMAM dendrimer installation in other support materials (organoclays) have been reported.

![Figure 4. (A) Ar isotherms at 87 K and (B) the corresponding pore size distributions for NU-1000, NU-1000+G2, and NU-1000+G3. BET areas are indicated in panel A.](https://doi.org/10.26434/chemrxiv-2023-wl69w)
The pore size distributions (PSD) calculated from Ar isotherms (Figures 4B) show that the installation of the PAMAM dendrimers decreases the mesopore diameter by ~0.1 nm and the micropore diameter does not detectably change. (Ar is preferred for micropore analysis.\textsuperscript{23}) The cumulative pore volumes of the three samples show that the mesopore volume decreases by a small amount after the dendrimer is installed (Figure S12). The micropore volume is not detectably changed (Figure S12A). The total decreases in pore volume are 0.12 cm$^3$/g for NU-1000+G2 and 0.09 cm$^3$/g for NU-1000+G3, which are approximately 9% and 7%, respectively, of NU-1000’s total pore volume. NU-1000’s pore volume is 29% microporous and 71% mesoporous. The volumes of single G2 and G3 dendrimers are $1.28 \times 10^{-20}$ and $2.44 \times 10^{-20}$ cm$^3$, respectively, when assuming that they are spheres. Using the loadings from the etched XPS spectra, the volume of dendrimer in NU-1000 is 0.13 cm$^3$/g for NU-1000+G2 and 0.07 cm$^3$/g for NU-1000+G3, which are close to the volume changes obtained from Ar and N$_2$ measures of cumulative pore volumes.

The electron density map (Figure 3), which is a qualitative method of analysis (at least as employed here), suggests that the dendrimer is sited mostly in the micropore and c-pore. The PSD suggests a reduction in the mesopore diameter. This seems contradictory. Note, however, that the PSD does not provide insight on the c-pore volume. In addition, it is possible that the distorted dendrimer in the c-pore protrudes into the mesopore, occupying some of its volume and decreasing its diameter. For example, the diameter of the Generation 2 PAMAM dendrimer is 2.9 nm, and the c-pore diameter is ~1 nm.

Changes to the amount of formate on the Zr$_6$ node could be another contributor to the changes to the mesopore’s diameter and volume. The NU-1000 used in this study initially contains chelated formate in place of roughly three-quarters of the node’s aqua & terminal-hydroxo groups.
(Figure S13). \(^1\)H NMR spectra of samples digested with NaOD show that the amount of formate on the Zr\(_6\) goes from 3.8 to 0.5 upon installation of the dendrimer (Figure S13). The changes in pore diameter are not as substantial as reported by Lu et al. Reversible pore contraction (albeit, to a greater extent than detected here) can occur when formate removal is followed by thermal removal of node aqua ligands – provided that new ligands are not introduced.\(^{20}\) We speculatively posit that a similar scenario may be playing out here. This scenario would not be inconsistent with partial sitting of the dendrimer in the MOF c-pore.

Figure 5 shows a comprehensive report of CO\(_2\) isotherms for NU-1000, including both adsorption and desorption branches at various temperatures. (The NU-1000 used for the isotherms in Figure 5 is formate-containing NU-1000.) All isotherms are linear and exhibit no hysteresis. An N\(_2\) isotherm collected on NU-1000 after a CO\(_2\) isotherm at 353 K (Figure S15A) shows that the sample remains essentially unchanged. The uptake values at 1 bar at 273, 293, and 298 K (Figure 5) are in good agreement with what has been reported in the literature.\(^9,24,25\) As expected for rapid, reversible physisorption, we find that the uptake of CO\(_2\) decreases as the temperature increases.
Figure 5. CO\textsubscript{2} adsorption isotherms at 273, 293, 298, 313, and 353 K for NU-1000 on a (A) linear pressure, and (B) log pressure scale.

The isosteric enthalpy of adsorption (\(\Delta H_{\text{ads}}\)), which is commonly called the isosteric heat of adsorption, was calculated at several CO\textsubscript{2} pressures\textsuperscript{26}. The pairs of temperatures used were 273 and 293 K, and 293 and 313 K, because a \(\Delta T\) of 10 to 20 K is recommended\textsuperscript{26}. The \(\Delta H_{\text{ads}}\) values are roughly constant with changing loading at around 20 kJ/mol (Figure 6) for 273 and 293 K. For 293 and 313 K, the \(\Delta H_{\text{ads}}\) values are mostly between 20 and 25 kJ/mol. Previously reported isosteric heats of adsorption values have been ~18 kJ/mol\textsuperscript{9} and 17 kJ/mol\textsuperscript{25} (Recall that, by convention, exothermic isosteric heats of adsorption, are reported as positive values.)
Figure 6. $\Delta H_{\text{ads}}$ versus CO$_2$ loading for NU-1000 calculated from the CO$_2$ isotherms at 273 and 293 K and at 293 and 313 K.

Although several attempts were made to collect CO$_2$ isotherms at 273 K for NU-1000+G2 and NU-1000+G3, we found that, particularly at low pressures, equilibrium could not be reached, even over extremely long times. There are no literature reports of CO$_2$ isotherms for NU-1000 with PAMAM dendrimers installed, but there are many studies of amines on silicas and other supports.$^{2-6, 27}$ There is also a study by Fadhel et al. of PAMAM dendrimers in SBA-15.$^{15}$ The majority of these studies report CO$_2$ uptake measurements using TGA.$^{2, 4, 15, 28, 29}$ TGA typically reports only the uptake at one point (partial pressure) of an isotherm. In principle, however, many TGA measurements could be done separately at different pressures to generate a full isotherm.

Many studies involving silicas discuss issues with the equilibration of CO$_2$ uptake and its dependence on the quantity of amines and the temperature of the experiment.$^{2, 3, 30, 31}$ Heydari-Gorji et al. reported that samples with low loading of amines took up less CO$_2$ when the temperature of the experiments was raised, suggesting that thermodynamic equilibrium was achieved.$^{2}$ In contrast, for samples with higher loading of amines, CO$_2$ uptake increased with
increasing temperature – behavior that was attributed to greater mobility of the amines and thus more amines being exposed.\textsuperscript{2, 30, 32} These findings suggest that a greater loading of amines leads to an increased diffusion resistance and slower reaction kinetics, which can be overcome with higher temperatures, e.g., 75 or 105 °C.\textsuperscript{2, 30, 32} Fadhel et al. found that CO\textsubscript{2} adsorption increased with an increase in temperature for SBA-15+G0.\textsuperscript{15} They also found that neat dendrimer adsorbed less than a quarter of the CO\textsubscript{2} adsorbed by SBA-15+G0 at high temperatures.\textsuperscript{15} This difference was well explicated by molecular dynamics simulations that showed when the dendrimer is in a mesoporous support, at high loading, its hydrogen bonds can be disrupted, making amines accessible to CO\textsubscript{2}.\textsuperscript{15} These reports illustrate that it can be difficult to equilibrate amine-containing samples during CO\textsubscript{2} gas adsorption measurements.

Taking previous studies into consideration, CO\textsubscript{2} isotherm measurements were attempted at 353 K (80 °C) in NU-1000, NU-1000+G2, and NU-1000+G3; see Figure 7. (The corresponding log-scale graphs can be found in Figure S18.) Both NU-1000+G2 and NU-1000+G3 take up more CO\textsubscript{2} than does NU-1000, while NU-1000+G2 takes up more than NU-1000+G3. The loadings for the etched samples in Table 1 show that NU-1000+G2 has twice as many primary amines as NU-1000+G3, so differences in CO\textsubscript{2} uptake are not unexpected. N\textsubscript{2} isotherms collected for the samples after a CO\textsubscript{2} isotherm show only small changes to their uptake, BET area, and PSD (Figure S19).
Figure 7. (A) CO$_2$ adsorption isotherms at 353 K for NU-1000, NU-1000+G2, and NU-1000+G3. (B) The number of CO$_2$ molecules adsorbed per primary amine for NU-1000+G2 and NU-1000+G3 at 353 K after subtracting the uptake of NU-1000.

The isotherms for NU-1000+G2 and NU-1000+G3 can be divided into 3 regions: below 0.1 bar, between 0.1 and 0.5 bar, and from 0.5 to 1 bar. In the early part of the isotherm, the uptake of CO$_2$ rises sharply until 0.1 bar (Figure 7A). This rise is more significant for NU-1000+G2, which has double the uptake of NU-1000+G3 at 0.1 bar. For NU-1000+G2 and NU-1000+G3, the uptake of CO$_2$ within this first region was the slowest compared to the rest of the isotherm. It is likely that the chemisorption of CO$_2$ on the dendrimer is the primary type of adsorption in this region. For DAC, the relevant CO$_2$ partial pressure is 0.0004 bar. We were unable to assess CO$_2$ uptake in NU-1000+G2 and NU-1000+G3 at 0.0004 bar, presumably due to slow kinetics. Below 0.1 bar of CO$_2$, dendrimer-free NU-1000 shows very little adsorption, consistent with the notion that strong CO$_2$ binding sites, such as those in the dendrimers, are necessary for CO$_2$ uptake in this regime. The large slope below 0.1 bar, specifically for NU-1000+G2, suggests that it has a high affinity for CO$_2$ and could be promising for DAC, especially if the dendrimer loading could be increased. Between 0.1 and 0.5 bar, the isotherms continue to rise, and NU-1000 itself starts to take up CO$_2$ (Figure 7). Assuming physisorption of CO$_2$ by the framework occurs in parallel with
adsorption by the dendrimer, the magnitude of the latter can be estimated by subtracting from NU-1000+G2 and NU-1000+G3 the observed uptake by dendrimer-free NU-1000.

At 1 bar, NU-1000+G2 and NU-1000+G3 adsorb 3.2 and 1.4 wt.% of CO₂, respectively. The dendrimer loadings are approximately 6 wt.% (G2) and 3 wt.% (G3). These loadings correspond to occupation of only a small fraction of the available pore volume. Fadhel et al. reported a 50 wt.% loading of G0 to G3 dendrimers in SBA-15. These loadings correspond to essentially complete filling of the ~5 nm diameter channels of SBA-15. Thus, dendrimers are unavoidably in van der Waals contact with other dendrimers. Fadhel et al. reported CO₂ adsorption capacities under 3 wt.% at 75 °C with 0.9 bar of CO₂ (+0.1 bar Ar).¹⁵ SBA-15 with the G0 dendrimer displayed the greatest uptake of CO₂ at 75 °C in their experiment, ~2.8 wt.%.¹⁵ Samples with G2 and G3 took up less than half that with G0.¹⁵ Greater and faster uptake was observed at 105 °C, with uptake reaching about 50% of the maximum anticipated based on carbamate formation.

Returning to Figure 7B, sorption results for NU-1000+G2 and NU-1000+G3 are framed in terms of the number of CO₂ taken up per primary amine after correcting for framework adsorption by subtracting uptake by dendrimer-free NU-1000. (Other nitrogen-presenting moieties, i.e., amides and tertiary amines, are not anticipated to chemisorb CO₂.) Notably, framework-corrected CO₂ uptake at 1 bar by both NU-1000+G2 and NU-1000+G3 greatly exceeds the theoretical maximum uptake achievable by carbamate formation, i.e., 0.5 per amine. We speculatively attribute excess uptake to CO₂ physisorption within the void spaces of the dendrimer interiors. We further speculate that physisorption is slow due to channel blocking by installed dendrimers or due to slow permeation of the periphery of the dendrimer itself. It will be interesting to see whether enhanced uptake persists when dendrimer loading is much higher.
The isotherms in Figure 8A include the desorption branches for the data in Figure 7. Wide hysteresis loops are observed. Notably, the uptake continued to increase during the initial stages of the desorption branch, even as the pressure decreased. Thus, we attribute the hysteresis loops to intrinsically slow adsorption/desorption equilibration. As the low-pressure region is approached on the desorption branch, CO\(_2\) can be completely desorbed (Figure S18), which indeed would be expected by physisorption hysteresis solely caused by non-equilibrated physisorption adsorption/desorption branches.\(^{15}\)

Figure 8. (A) CO\(_2\) adsorption and desorption isotherms at 353 K for NU-1000, NU-1000+G2, and NU-1000+G3. (B) Normalized DRIFTS spectra of (top) NU-1000+G2 and (bottom) NU-1000+G3.

However, in vibrational spectroscopy data, bands between 1200 and 1650 cm\(^{-1}\) have been reported when flowing CO\(_2\) over amines.\(^{18,27}\) The DRIFTS spectra in Figure 8B show that in the presence of CO\(_2\) a peak appears at 1645 cm\(^{-1}\), providing evidence for chemisorption via carbamate formation, in addition to the observed CO\(_2\) physisorption. Following removal of the CO\(_2\) source, this peak gradually disappears. The assignment at 1645 cm\(^{-1}\) to a carbamate comes from similar literature reports on CO\(_2\) adsorption by amines.\(^{5,18,27,28,33}\) The peak is absent in spectra for NU-
1000 (Figure 8B and S21). There is a band at 1220 cm$^{-1}$ in the spectra of NU-1000+G2 and NU-1000+G3 under CO$_2$ that is characteristic of aliphatic C-N stretching.$^{34}$ A similar band at 1313 cm$^{-1}$ has been reported to be from C-N bonds.$^{18}$ In Figure 8B we see that the band disappears when CO$_2$ desorbs. This signature is likely from the bond that carbon from CO$_2$ forms with the nitrogen from the amine. There are bands related to the dendrimer’s structure that we observe in Figure S20. NU-1000+G2 and NU-1000+G3 have slightly broader features than NU-1000 around 3300 cm$^{-1}$ that correspond to the N-H stretches of primary amines.$^{34}$ Similar features were reported by Yang et al. when they installed dendrimers inside NU-1000.$^{14}$ There are also some broad features between 2750 and 3000 cm$^{-1}$ that correspond to N-CH$_2$ stretches of the dendrimer backbone.$^{34}$

Because water vapor is often present in CO$_2$-containing atmospheres, we collected water isotherms for NU-1000, NU-1000+G2, and NU-1000+G3 at 25 °C (Figure 9). The results for dendrimer-free NU-1000 are in good agreement with previous work.$^{35}$ For all three samples, modest uptake at low and intermediate relative humidities ($p/p_0$ values) is followed by sharp uptake, characteristic of condensation-based filling of mesopores, starting at $p/p_0$~0.65, and finally modest additional uptake beyond $p/p_0$~0.8. The vapor pressure marking the onset of mesopore filling can be shifted lower by enhancing mesopore hydrophilicity and shifted higher by diminishing it. The introduction of G2 or G3 dendrimers engenders little change, implying that the mesopore hydrophilicity is little affected – a result that might simply reflect the comparatively low loadings for the dendrimers. Desorption is marked by hysteresis, starting in the region characterized by mesopore evacuation. The effect is most prominent for dendrimer-free NU-1000 but is evident for all three materials. Hysteresis is expected when mesopore filling is dominated by condensation. For the second water adsorption-desorption cycle, for all three materials (see Figure S24), the mesopore step is missing and the water capacities for all three are greatly
diminished. These observations are indicative of catastrophic collapse of mesopores – behavior that is generally traceable to destructive capillary forces associated with water or other high-surface-tension fluids.\textsuperscript{36} Consistent with these notions, N\textsubscript{2} based measurements of BET areas, before and after two water adsorption-desorption cycles, reveal decreases from 2090 to 230 m\textsuperscript{2}/g for NU-1000, from 1990 to 200 m\textsuperscript{2}/g for NU-1000+G2, and from 2070 to 340 m\textsuperscript{2}/g for NU-1000+G3. (Water isotherms collected for NU-1000+G2 after a CO\textsubscript{2} isotherm at 80 °C (Figure S25) are closely similar to those collected without prior CO\textsubscript{2}, underscoring the \textit{absence} of capacity degradation by CO\textsubscript{2} uptake and release.)

![Water isotherms at 25 °C of NU-1000, NU-1000+G2, and NU-1000+G3. Inset image highlights the adsorption points in the low- to medium-pressure region.](https://doi.org/10.26434/chemrxiv-2023-wl69w)

Figure 9. Water isotherms at 25 °C of NU-1000, NU-1000+G2, and NU-1000+G3. Inset image highlights the adsorption points in the low- to medium-pressure region.

Returning to Figure 9, the most striking difference between dendrimer-free and dendrimer-containing samples is the loss of mesopore capacity for the latter, as evidenced by a much smaller size for the step that starts at p/p\textsubscript{o}~0.65. The losses are disproportionately large compared with the
small losses in overall pore capacity uncovered by Ar sorption measurements (Figure 4) and anticipated based on the comparatively low loadings of G2 and G3. We speculatively suggest either of two explanations. First, the dendrimers might, for unknown reasons, engender capillary-force-facilitated (water-facilitated), partial collapse of mesopores during water sorption. Generally, however, collapse occurs during pore evacuation rather than pore filling. Second, a fraction of the dendrimers might behave as water-impermeable stoppers in mesopores. DED measurements point to very little dendrimer sitting in mesopores, relative to triangular micropores and c-pores. Presumably, however, very little dendrimer would be needed to effectively block mesopores. Confirmation or refutation, however, will need to await experimental and/or computational studies that are beyond the scope of this investigation.

Finally, the inset for Figure 9 indicates at low and intermediate relative humidity, substantially greater water uptake by dendrimer-containing versus dendrimer-free NU-1000. It is tempting to ascribe the differences to greater inherent hydrophilicity for the dendrimer, relative to the empty framework, despite the low absolute loadings of G2 and G3. Recall, however, that dendrimer-free NU-1000, as used here, contains node-ligated, hydrophobic formate ligands (see Figure 1B) whereas dendrimer-containing NU-1000 does not. Separate studies of water sorption by dendrimer-free, formate-free NU-1000 have yielded water isotherms\(^{37}\) that reasonably match, in the low- to medium-p/p\(_0\) range, those presented here for NU-1000+G2 and NU-1000+G3.

CONCLUSIONS

PAMAM dendrimers were successfully installed inside NU-1000, and they provided greater CO\(_2\) adsorption compared to dendrimer-free NU-1000. The loadings of dendrimer indicate a surfeit at the external surface of the crystalline, but much lower loading in the MOF interior.
Nevertheless, for the crystallites of the size used here (hexagonal rods, several microns long and a few microns wide) the high dendrimer loading at the external surface contributes little to the overall loading. At elevated temperature (80 °C), NU-1000+G2 and NU-1000+G3 exhibit chemically reversible, but kinetically slow, uptake of CO₂. DRIFTS measurements show that at least a portion of the uptake involves chemically reversible carbon-nitrogen bond formation and conversion of the full complement of dendrimer primary amines to carbamates. Curiously, however, the dendrimer-enhanced uptake of carbon dioxide exceeds by two- to four-fold the amounts expected based on conversion of pairs of primary amines to carbamates and ammonium ions, at least at and near 1 bar. We speculatively ascribe the unanticipated additional uptake to enhanced physisorption within the confined voids of the dendrimer. Our foci going forward, are to: boost dendrimer loadings by at least an order of magnitude, with the aim of similarly boosting CO₂ uptake; better control the siting of dendrimers, in part by blocking framework c-pores; understand and enhance the kinetics of uptake and release; and examine the consequences of water co-adsorption for uptake and release of carbon dioxide. Advances in these areas conceivably could lead to usefully large capacities for sorption-based capture and/or separation of CO₂ from gas and vapor mixtures. To the extent that uptake entails carbamate formation, dendrimer@MOF assemblies might also serve to pre-activate CO₂ for chemical, electrochemical, or photochemical reduction.
ASSOCIATED CONTENT

Supporting Information. Solid-state $^{13}$C CP MAS NMR, SEM images, EDS elemental mapping, EDS line scans, XPS spectra, Difference Fourier electron density map, nitrogen isotherms, pore size distributions, Cumulative pore volumes, $^1$H NMR spectra, TGA, CO$_2$ isotherms, DRIFTS spectra, and water isotherms.

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Notes

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