

Tailoring Hydrophobicity and Pore Environment in Physisorbents for Improved Carbon Dioxide Capture under High Humidity

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ABSTRACT: CALF-20, a Zn-triazolate-based metal-organic framework (MOF), is one of the most promising adsorbent materials for CO₂ capture. However, competitive adsorption of water severely limits its performance when the relative humidity (RH) exceeds 40%, limiting the potential implementation of CALF-20 in practical settings where CO₂ is saturated with moisture, such as post-combustion flue gas. In this work, three newly designed MOFs related to CALF-20, denoted as **NU-220**, **CALF-20M-w**, and **CALF-20M-e** that feature hydrophobic methyl-triazolate linkers are presented. Inclusion of methyl groups in the linker is proposed as a strategy to improve CO₂ uptake in the presence of water. Notably, both **CALF-20M-w** and **CALF-20M-e** retain over 20% of their initial CO₂ capture efficiency at 70% RH – a threshold at which CALF-20 shows negligible CO₂ uptake. Grand canonical Monte Carlo (GCMC) simulations reveal that the methyl group hinders water network formation in the pores of **CALF-20M-w** and **CALF-20M-e** and enhances their CO₂ selectivity over N₂ in the presence of high moisture content. Moreover, calculated radial distribution functions indicate that introducing the methyl group into the triazolate linker increases the distance between water molecules and Zn coordination bonds, offering insights into the origin of the enhanced moisture stability observed for **CALF-20M-w** and **CALF-20M-e** relative to CALF-20. Overall, this straightforward design strategy has afforded more robust sorbents that can potentially meet the challenge of effectively capturing CO₂ in practical industrial applications.

Introduction:

Due to the ability of carbon dioxide (CO₂) to trap heat as a greenhouse gas, the accumulation of anthropogenic CO₂ in the Earth's atmosphere from fossil fuel combustion is influencing the climate and contributing to the increasing frequency of natural disasters.¹ As a result, the global community is seeking to reduce atmospheric carbon and achieve carbon neutrality in the next few decades.² While renewable

energy sources have shown promise to limit CO₂ emissions, carbon capture has emerged as a critical and complementary strategy for mitigating carbon emissions and more rapidly addressing the wide-ranging impacts of climate change.^{3,4} Currently, multiple carbon capture technologies are available for capturing CO₂ from industrial processes, including pre-combustion capture, oxy-fuel combustion

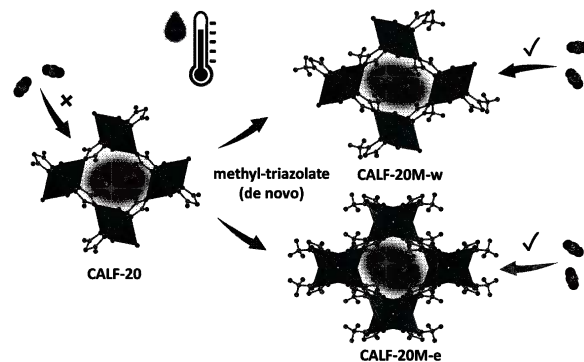
capture, and post-combustion capture, and each option exhibits distinct advantages and limitations.^{5, 6} Among these approaches, post-combustion CO₂ capture methods have garnered the most attention,⁷ primarily due to their adaptability, as these capture devices can be retrofitted into existing facilities.⁵

Solid adsorbents, such as porous carbons, zeolites, silicas, and resins, have shown promise as carbon capture materials⁸ and demonstrated the ability to bind CO₂ through both physisorption and chemisorption.⁷ Although chemisorption, for example with amines, often has high selectivity, in most instances, CO₂ chemisorbents bind CO₂ quite strongly, creating a high energy penalty for the regeneration of the material.^{9, 10, 11} In contrast, physisorbents require less energy for regeneration, and the challenge is to find materials with good selectivity and capacity. There are suggestions in the literature that physisorbents with moderate CO₂ selectivity and uptake are promising for industrial-scale CO₂ capture.¹²⁻¹⁴ However, in addition to capacity and selectivity, the material must also exhibit high stability in the presence of water, as many CO₂ point sources contain high moisture content. Among the many adsorbents considered to date for CO₂ capture, metal-organic frameworks (MOFs) have shown great promise, since these porous crystalline structures are highly tunable, offering control over properties such as pore volume, surface area, and surface chemistry for CO₂ capture applications.^{7, 9, 15-21}

Recently, a Zn-triazolate-based MOF known as CALF-20, has shown great promise as a CO₂ physisorbent, as it demonstrates selective CO₂ capture, high CO₂ capacity, rapid kinetics, and requires modest energy for regeneration.^{22, 23} In fact, the Canadian company Svante is now employing CALF-20 in their carbon capture process.²⁴ However, the CO₂ adsorption capacity of CALF-20 is significantly compromised at high relative humidity (RH) values, and water uptake begins to surpass CO₂ uptake at 40% RH.^{22, 25} As a result, CALF-20 is unsuitable for direct use in carbon capture settings where water saturation is prevalent, such as wet flue gas conditions, and requires an initial dehydration step (e.g. compressor inter-stage cooling, guard-beds of solid desiccants, liquid desiccants) that adds complexity and reduces the overall process efficiency.²⁶⁻²⁸ We hypothesized that incorporating hydrophobic groups, such as a methyl (-CH₃) group, into the triazolate linker of CALF-20 would enhance its CO₂ capture performance at high RH values. In addition, we envisioned that replacing the hydrogen atom on the 3-position of the 1,2,4-triazole (ta) ring with a methyl group would increase the water stability of this material, resulting in a material with better CO₂ adsorption properties and better stability (**Scheme 1**).

Using this strategy, we synthesized three distinct MOFs using the 3-methyl-1H-1,2,4-triazole (mta) linker and zinc oxalate (ZnOx) and found that the solvent and reaction conditions determine the structure of the MOF product. While methanol-assisted synthesis results in a novel MOF, denoted as **NU-220**, reactions performed in water or ethanol afford **CALF-20M-w** and **CALF-20M-e**, respectively, which are both isostructural to CALF-20. Notably, these materials exhibit between 1.81 and 2.13 mmol g⁻¹ CO₂ uptake at 0.15 bar (i.e., the typical CO₂ partial pressure in flue gas), which corresponds to 69-78% of the capacity of CALF-20 at this pressure, confirming that introducing the methyl group does not significantly decrease the CO₂ uptake capacity.

Importantly, at the high RH value of 70%, **CALF-20M-w** and **CALF-20M-e** maintain approximately 0.5 and 0.6 mmol g⁻¹ of CO₂ capture capacity, respectively, whereas CALF-20 demonstrates no CO₂ uptake under these conditions, entirely compromising its carbon capture capability. In this work, experimental and computational studies show how differences in the MOF structures result in distinct differences in performance for CO₂ capture in both dry and humid environments. More broadly, this work indicates that these new methyl-triazolate-based sorbents are more suitable for post-combustion carbon capture applications that contain high humidity than their non-methylated counterpart.



Scheme 1. Enhancement of CO₂ capture under high relative humidity with **CALF-20M-w** and **CALF-20M-e** via modification of CALF-20 with a hydrophobic methyl group.

Results and discussion

Synthesis and Structural Characterization

To begin our investigation, we screened the reactions of mta with ZnOx in different solvents. The individual components were pre-mixed in methanol, ethanol, or water separately and heated at 180 °C for 3 days in a Parr vessel (**see supporting information for details**). Similar to the synthesis of CALF-20, all three reactions generate a white material that precipitates out. Interestingly, powder X-ray diffraction (PXRD) analysis of the products indicates each of the three solvents produces a different crystalline material, which contrasts the behavior of CALF-20, as the same phase-pure sample can be synthesized from either methanol or ethanol.²² The new polymorphic phases isolated from methanol and water, which we denoted as **NU-220** and **CALF-20M-w**, were further characterized by single crystal X-ray diffraction (SCXRD) analysis (*vide infra*). Despite repeated attempts to produce a single crystal of the polymorphic phase isolated from ethanol, **CALF-20M-e**, we were unable to synthesize a crystal that was suitable for SCXRD analysis. However, we successfully employed microcrystal electron diffraction (MicroED) to obtain and refine the structural parameters of **CALF-20M-e** (**crystal data in Table S1**). **Figure 1** illustrates the structures of these three new MOFs, as well as the structure of CALF-20.

CALF-20, which has a structural formula of [Zn(ta)(ox)_{0.5}], is composed of layers of zinc (II) ions that are connected by oxalate ions and triazolate units (**Figure 1b**). The Zn(II) center is five-coordinate and has a distorted trigonal bipyramidal geometry with Zn-O distances of 2.022(2) and 2.189(3) Å and Zn-N distances of 2.007(2), 2.016(3), and 2.091(3) Å (**Table S2**).²² The N atoms in the 1,2 positions of the triazolate linker bridge Zn dimers, which are linked to

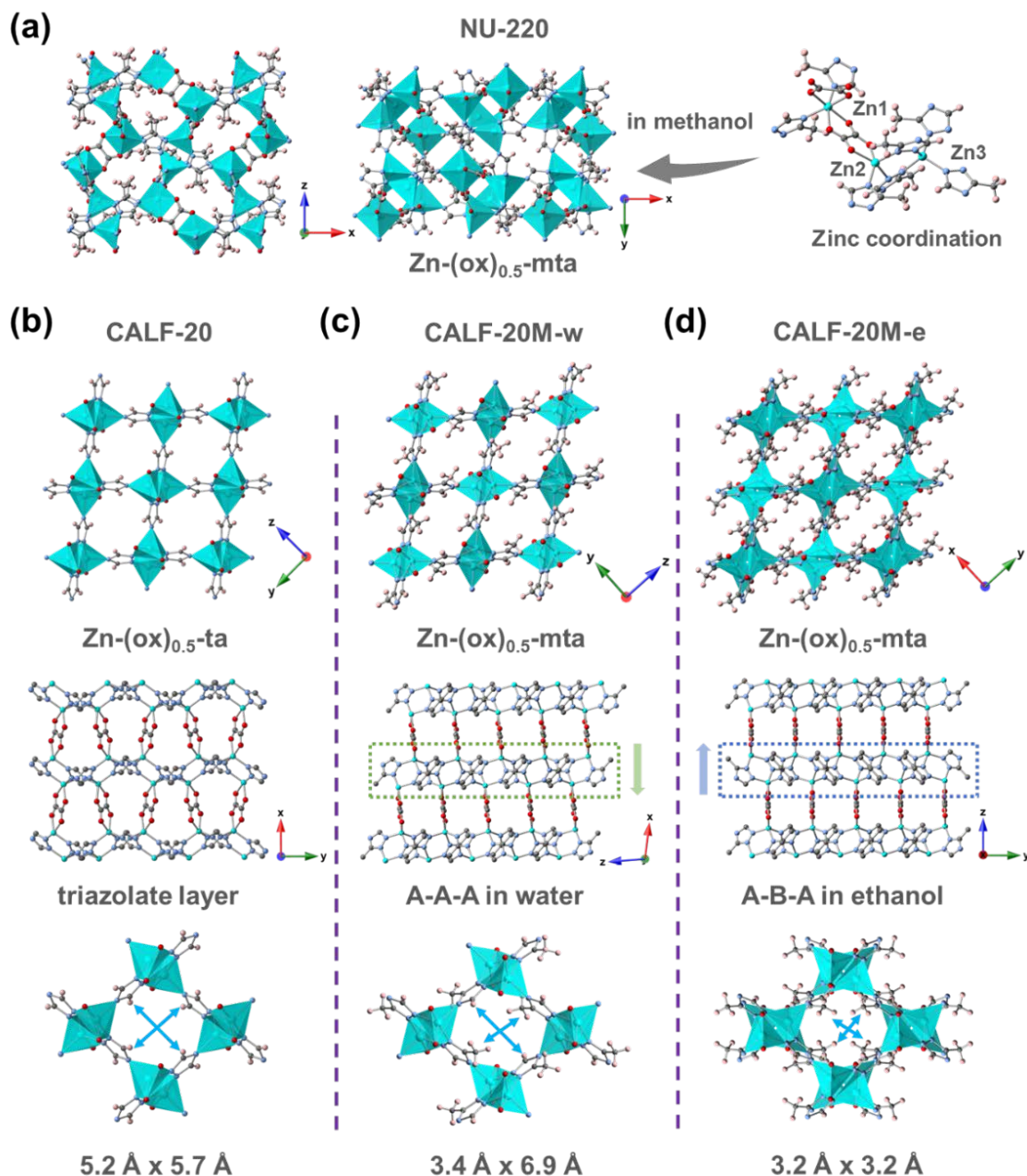


Figure 1. (a) Structure of **NU-220** and view of the zinc coordination. Crystal structures of (b) **CALF-20** (c) **CALF-20M-w** and (d) **CALF-20M-e**, including the structure of zinc-triazolate layer, orientation of each layer pillared by oxalate and corresponding single pore channel. Color scheme (C: grey; N: blue; O: red; Zn: cyan; H: pink)

the next dimer by the N atom in the 4-position. The Zn coordination is completed by two oxygen atoms of a chelating oxalate group, and there are no open coordination sites. Following the reaction in methanol, **NU-220** crystallizes in the tetragonal space group $P4_32_12$ (Figure 1a) with a formula of $[\text{Zn}(\text{mta})(\text{ox})_{0.5}]$ and novel topology (Figure S1) that differs from the monoclinic $P2_1/c$ system known for **CALF-20**. **NU-220** has three types of zinc moieties (Figure S2 and Table S2): 1) hexa-coordinated zinc where the metal center is connected with two triazolate linkers and two cis-oxalate linkers ($\text{Zn-O} = 2.093(4)$ and $2.189(4) \text{ \AA}$; $\text{Zn-N} = 2.090(5) \text{ \AA}$); 2) penta-coordinated zinc (similar to that found in **CALF-20**) where it is connected with three triazolate linkers ($\text{Zn-N} = 2.034(5)$, $2.036(4)$ and $2.122(4)$), and one bridged

oxalate linker ($\text{Zn-O} = 2.038(4)$ and $2.085(4) \text{ \AA}$); 3) tetra-coordinated zinc that is connected to four triazolate linkers ($\text{Zn-N} = 1.983(5)$ and $2.022(4) \text{ \AA}$).

In contrast, reactions in water and ethanol lead to the formation of **CALF-20M-w** and **CALF-20M-e**, respectively, which crystallize in the monoclinic $P2_1/c$ and orthorhombic $Pbcn$ space groups with a formula of $[\text{Zn}(\text{mta})(\text{ox})_{0.5}]$ (Figure 1c-d). Both MOFs exhibit penta-coordinated zinc ions in a distorted trigonal bipyramidal geometry (Figure S3), similar to the zinc ions in **CALF-20**. The Zn-O distances in **CALF-20M-w** are $2.026(3) \text{ \AA}$ and $2.176(3) \text{ \AA}$, while the Zn-N distances span $2.108(3) \text{ \AA}$, $2.016(3) \text{ \AA}$, and $2.037(3) \text{ \AA}$. Similarly, **CALF-20M-e** features Zn-O distances of $2.00(5) \text{ \AA}$

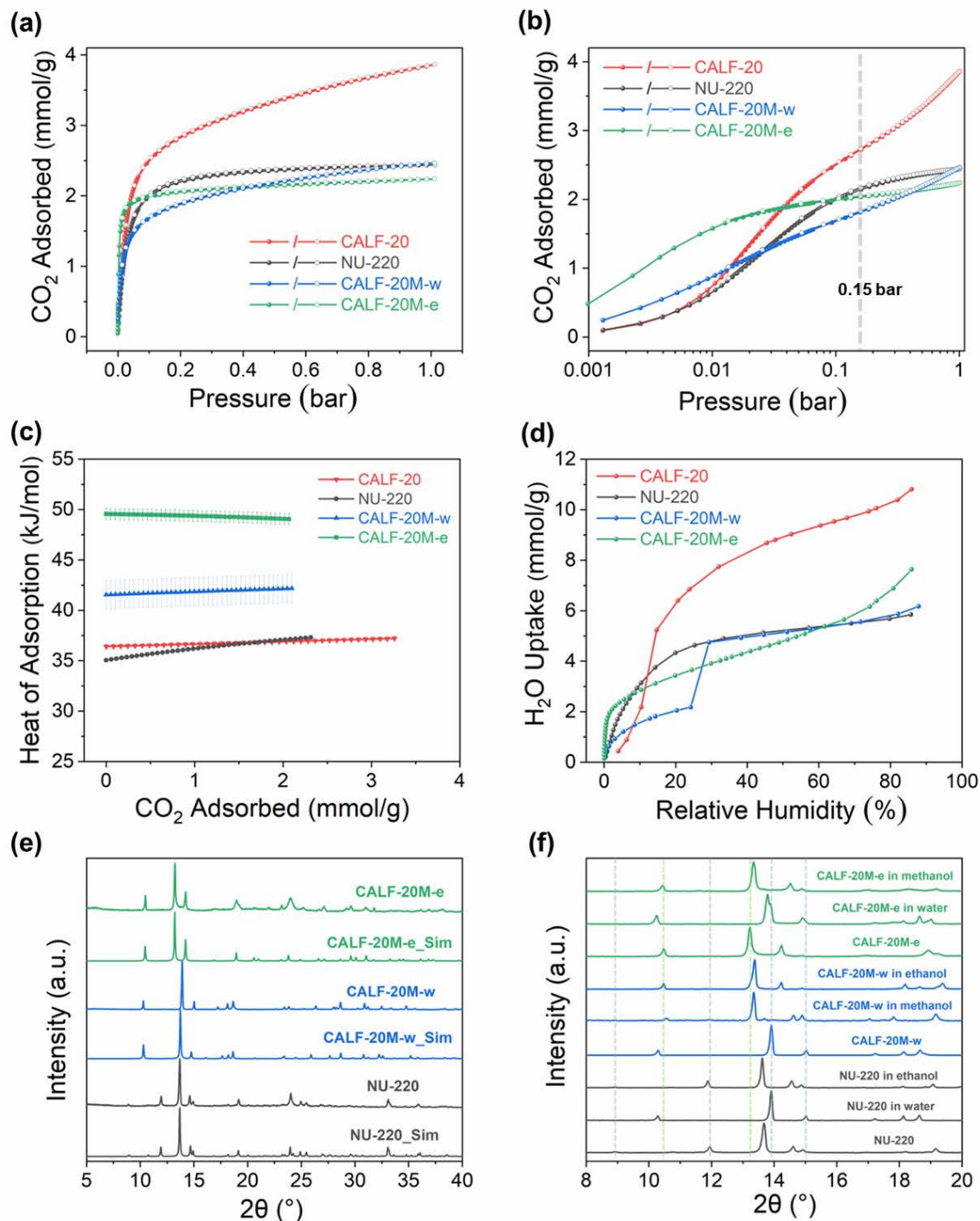


Figure 2. Sorption isotherms and PXRD for CALF-20, NU-220, CALF-20M-w and CALF-20M-e: (a-b) CO₂ isotherms at 298 K and (d) water isotherms at 298 K. (c) Heat of adsorption of CO₂ of all sorbents obtained from CO₂ isotherms at 273 K, 298 K and 313 K. (e) PXRD of simulated and as-synthesized sorbents. (f) PXRD profiles relevant to phase transition after boiling in different solvents (water, methanol and ethanol) at 453 K for 24 hours.

and 2.12(3) Å and Zn-N distances of 1.99(5) Å, 2.05(5) Å, and 2.12(4) Å (**Table S2**). Although the space group and unit formula of CALF-20M-w resemble those of CALF-20, the structure of CALF-20M-w differs slightly. For instance, due to the steric hindrance of the methyl group in CALF-20M-w, the interplanar angle between the oxalate group and the Zn₂(ta)₂ moiety is higher (63.65°) compared to the analogous angle in CALF-20 (50.85°) (**Figure S4**), making CALF-20M-w a unique isomer of CALF-20. Such a distortion is common for molecular trigonal bipyramidal complexes.²⁹

Structural analysis of CALF-20M-w and CALF-20M-e unveiled noteworthy alterations in the pore properties relative to those of CALF-20 that arise from the presence of the methyl groups that line the pores. Specifically, the pore apertures for CALF-20M-w and CALF-20M-e are 3.4 Å × 6.9 Å and 3.2 Å × 3.2 Å, respectively, which are significantly reduced from the pore aperture of 5.2 Å × 5.7 Å found in CALF-20. Notably, the structures of CALF-20M-w and CALF-20M-e differ from one another in the orientation of the layers within each material. The triazolate layers in CALF-20M-w exhibit a unidirectional arrangement, denoted as A-A-A,

while those in **CALF-20M-e** display an alternating orientation pattern of A-B-A. This difference in layer orientation further impacts the dimensions of the pore channels, resulting in a smaller effective 1D channel and 18% reduction of unit cell volume for **CALF-20M-e**. In contrast, the triazolate layer in **CALF-20** and its hydrated form do not adopt a similar configuration.³⁰⁻³² As three different structures with the same linker were obtained by only varying the solvents used in the synthesis, it can be assumed that different solvents interact with MOF precursors and significantly influence the nucleation, crystal growth, and self-assembly processes involved in the synthesis.

Irreversible Solvent-dependent Phase Transitions of Polymorphs

To investigate phase transitions among the three polymorphs, we incubated the corresponding MOFs (~50 mg) at 453 K for 24 hours in two alternative solvents (10 mL) separately and observed the dynamic response of the framework to solvent stimuli (*e.g.*, methanol-synthesized **NU-220** incubated in water and ethanol separately), highlighting the pivotal role of solvents in directing the structure from thermal kinetics aspects. We monitored the phase transitions using PXRD (**Figure 2f**). Notably, incubating **NU-220** in water at 453 K afforded a phase transition into **CALF-20M-w**, but this transition was not observed upon incubation of **NU-220** in ethanol under otherwise analogous conditions (**Figure S5-7**). This phase transition is found to be irreversible, as incubating **CALF-20M-w** in methanol at 453 K for 24 hours fails to induce the transformation back to the **NU-220** phase (**Figure S5**). However, incubating **CALF-20M-w** in ethanol results in an unexpected transition to a new phase that exhibits slight differences from **CALF-20M-e**, as evidenced by variations in peak positions in the PXRD patterns (**Figure S7**). Specifically, the 2θ values of peaks originally located at 10.3° , 13.9° , and 15.0° in **CALF-20M-w** shift to 10.5° , 13.4° , and 14.2° , respectively, and the peak at 13.2° in **CALF-20M-e** is absent from the pattern for the new material. Nevertheless, upon analyzing the CO_2 isotherms, it is evident that the similarity in shape and trend closely aligns with that observed in **CALF-20M-w** (**Figure S8**), suggesting that ethanol initiates structural transformations, but these ethanol-induced changes are insufficient to fully reorient the triazolate-layer to match the orientation observed in **CALF-20M-w**. A similar phenomenon was observed after incubating **CALF-20M-e** in water, supporting an irreversible transition to **CALF-20M-w** (**Figures S6 and S8**).

The effects could encompass diverse mechanisms, including lattice swelling or contraction, solvent coordination, and hydrogen bonding. We hypothesize that during the synthesis of **CALF-20M-e**, the solvent ethanol serves as a template and fills the voids within the structure. However, the ultramicroporous space of **CALF-20M-w** limits the diffusion of ethanol, thereby hindering its phase transition to **CALF-20M-e**. The results suggest that a potential energy barrier inhibits the reversal of the triazolate layers from the A-B-A pattern in **CALF-20M-e** to the A-A-A pattern in **CALF-20M-w**. Variations between solvents, including differences in polarity, coordinating abilities, and hydrogen bonding capabilities, afford varying effects on the coordination environment, intermolecular interactions, and packing arrangements within the MOF structure.³³ In these materials, solvents interact with the structural components to induce

alterations in the packing arrangement and bonding interactions, resulting in a dynamic response at elevated temperatures. For instance, methanol displays intermediate polarity and molecular size in comparison to water and ethanol. The presence of a larger dipole moment and fewer carbon atoms in methanol results in stronger hydrogen bonding and dipole-dipole interactions compared to ethanol. The same phase products were observed in propanol (1-propanol and isopropanol) and butanol (**Figure S9**), and a binary mixture of water and ethanol resulted in an A-A-A pattern like **CALF-20M-w**.³⁴ Methanol potentially serves as a template with proper molecular dimension for the growth of the framework around methanol molecules in **NU-220**. Overall, these experimental findings suggest that the solvent not only has effects during the nucleation, crystal growth, and self-assembly processes, but also contributes to the phase transition behavior of these MOFs under different media.

Analysis of Pure Gas and Vapor Adsorption.

We then collected CO_2 sorption isotherms for **NU-220**, **CALF-20M-w**, **CALF-20M-e**, and **CALF-20** at 298 K and observed that the shape of the **CALF-20M-w** isotherm closely resembles that of **CALF-20**, while the isotherms of **NU-220** and **CALF-20M-e** feature slightly different shapes based on the slope of the plateau region (**Figure 2a**). Notably, the CO_2 isotherm for **CALF-20M-w** exhibits an uptake of 1.0 mmol g^{-1} at 13 mbar, which is comparable to that of **CALF-20** at this pressure, but the **CALF-20M-w** isotherm is shifted downward at higher pressures compared to the **CALF-20** isotherm due to the reduced total pore volume (**Figure 2b**). Interestingly, **CALF-20M-e** demonstrates the highest CO_2 adsorption of $\sim 1.87 \text{ mmol g}^{-1}$ among the four sorbents at low CO_2 concentrations of $\sim 0.03 \text{ bar}$, and it reaches a plateau of 2.05 mmol g^{-1} at 0.15 bar. The calculated heats of adsorption (Q_{st}) of approximately $35\text{--}50 \text{ kJ mol}^{-1}$ for **CALF-20**, **NU-220**, **CALF-20M-w** and **CALF-20M-e** indicate that physisorption plays a dominant role in the CO_2 capture mechanism (**Figure 2c**). The Q_{st} values were calculated based on three isotherms at 273, 298 and 313 K and fitted with the virial method (**Figure S10-17**). Among these four adsorbents, **CALF-20M-e** exhibits the highest calculated Q_{st} value of 50 kJ mol^{-1} , indicating this MOF features the strongest interactions for CO_2 capture among this series. The experimentally observed trend for Q_{st} values (**CALF-20M-e** > **CALF-20M-w** > **NU-220** $\approx$ **CALF-20**) matches well with the sequence of adsorption energies calculated by finding the minimum energy for a single adsorbate molecule in the MOFs using a classical force field (**Table 1**). Notably, we observed that the CO_2 isotherms in **NU-220** and **CALF-20M-e** reach saturation before 0.2 bar, while the **CALF-20** and **CALF-20M-w** isotherms continue to rise over the pressure range we studied. Furthermore, we observed that for **CALF-20M-e** the isotherms at 313 K and 298 K exhibit a plateau (**Figure S16**), but when the temperature is decreased to 273 K, the CO_2 isotherm does not plateau and exhibits a gradual increase in CO_2 uptake up to 1 bar, suggesting structural flexibility and a variation in the adsorption mechanism (**Figure S16**), which is not observed in **NU-220** (**Figure S12**).

Next, we obtained H_2O sorption isotherms at 298 K for **CALF-20**, **NU-220**, **CALF-20M-w**, **CALF-20M-e**, with the results presented in **Figure 2d**. The water isotherm in **CALF-**

20 exhibits an inflection point around 10% RH and has the highest uptake at higher RH, approaching ~ 8 mmol/g at 35% RH. **NU-220** reaches ~ 5 mmol/g of water sorption at approximately 20% RH, with a more gradual increase at higher RH. **CALF-20M-w** and **CALF-20M-e** generally exhibit lower water uptake than **CALF-20** at RH, suggesting a diminished affinity between water and the sorbent pores at high loading. At very low RH (below 10% RH), however, the three new polymorphs actually show higher water uptake than **CALF-20**. From the viewpoint of surface chemistry, the methyl group in the mta linker of **NU-220**, **CALF-20M-w** and **CALF-20M-e** should increase the hydrophobicity of the pores relative to that of the non-methylated linker in **CALF-20**, and indeed this was our initial motivation for including methyl groups. It is, thus, somewhat surprising that the isotherms in **Figure 2d** show that the new MOFs containing methyl groups exhibit higher water adsorption than **CALF-20** at low RH. The surprising increase in hydrophilicity (higher water uptake at low RH) of the methyl-containing MOFs seen in **Figure 2d** is consistent with the water adsorption energies calculated from atomistic modeling in **Table 1**.

Table 1. Adsorption energy of a single adsorbate molecule (kJ/mol) after energy minimization utilizing classical force field and experimental heat of adsorption (Q_{st}) for all four sorbents.

Structure	Q_{st} (CO ₂)	CO ₂	H ₂ O	N ₂
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CALF-20	36.8 (± 0.2)	-39.9	-42.1	-22.4
NU-220	36.3 (± 0.1)	-44.1	-49.1	-24.5
CALF-20M-w	41.9 (± 1.4)	-48.6	-50.9	-24.8
CALF-20M-e	49.3 (± 0.5)	-53.0	-50.9	-25.3

From the single-component CO₂ and water isotherms, we see that the reduced pore sizes of **CALF-20M-w** and **CALF-20M-e** enhance both the CO₂ and H₂O uptake at low pressures. The minimal N₂ adsorption at 77 K in **CALF-20M-w** and **CALF-20M-e** (**Figure S18**) is consistent with smaller pores. However, as we show below, for multicomponent adsorption, **CALF-20M-w** and **CALF-20M-e** suppress adsorption of water in mixtures with CO₂ and N₂.

Accelerated Aging and Thermal Stability Characterization.

The stability and regenerability of CO₂ sorbents are critical factors in their suitability for operational conditions and efficient CO₂ capture in flue gas systems. Long-term stability is paramount to ensure the extended lifespan of sorbents, including in the presence of competing gases and vapors. To evaluate the stability of the activated samples under harsh conditions of elevated temperatures and high RH, we conducted standardized accelerated aging (SAA) experiments.

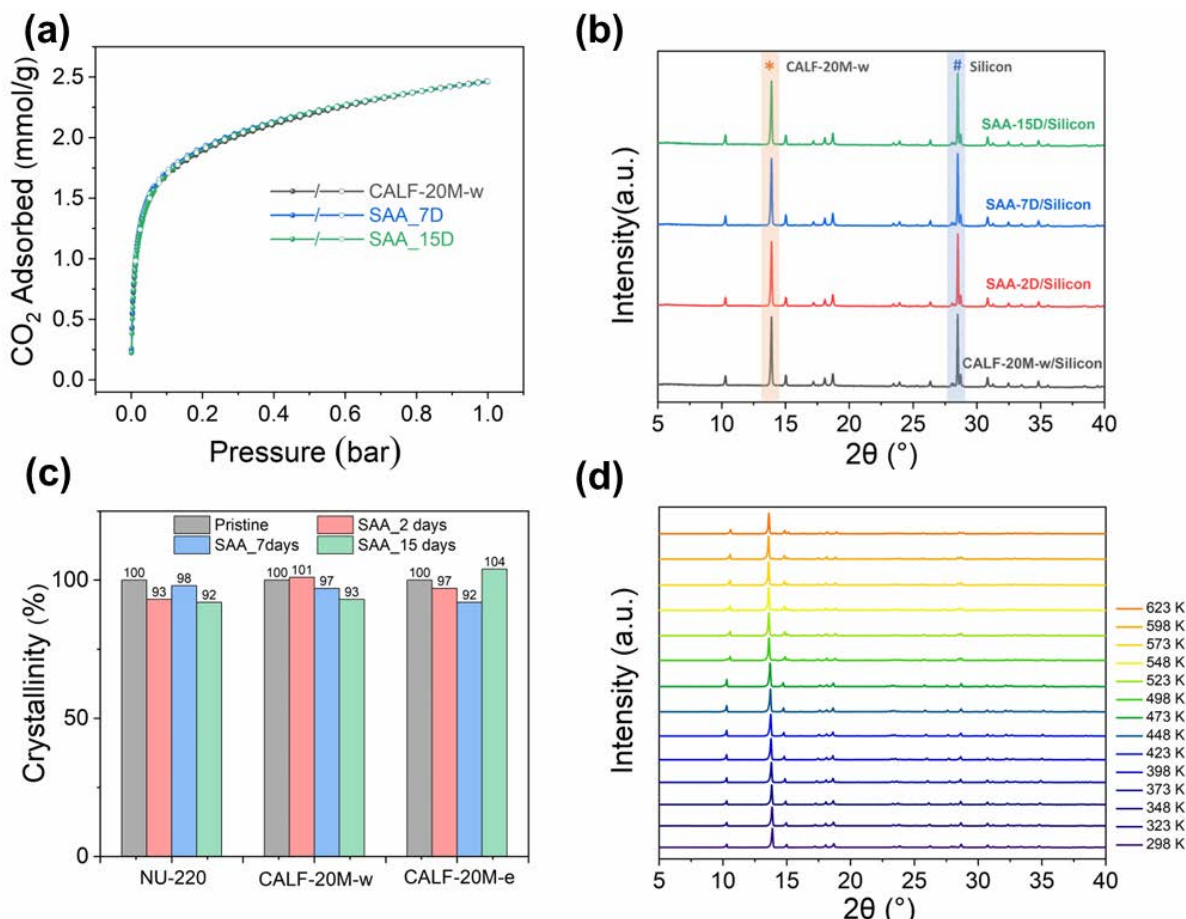


Figure 3. (a) CO₂ isotherms at 298 K and (b) PXRD of **CALF-20M-w** before and after aging at 343 K, 80% RH for 7 and 15 days. Silicon was mixed with the sorbent to quantitatively analyze variations in intensity from characteristic peaks. (c) Crystallinity changes after SAA experiments at 343 K, 80% RH for 2, 7, 15 days compared to the pristine samples. (d) VT-PXRD for **CALF-20M-w** from 298 to 623 K. The temperature ramp was set to 5 K min⁻¹, holding for 5 min at each set point.

Specifically, we incubated the activated sorbents in a humidity oven at 343 K and 80% RH for 15 days to accelerate the aging process. To evaluate the degradation rate of sorbents, we re-activated the aged samples and measured their CO₂ sorption isotherms after 7 and 15 days. It was found that all three sorbents exhibit consistent CO₂ isotherms throughout the aging process, confirming their stability (**Figure 3a and S20-22**).

Additionally, we performed a quantitative analysis of PXRD patterns to directly assess the changes in crystallinity utilizing silicon as an internal standard (**Figure S23 and Table S3**). Specifically, we evaluated the ratio of peak intensities ($R = p1/p2$), where p1 represents the intensity of the selected characteristic peak of the sorbent and p2 corresponds to the intensity of silicon. (In pure silicon, both p1 and p2 represent two different peaks from silicon.) To account for potential fluctuating mass effects on diffraction intensity, a small portion of the sample was taken from the pre-mixed samples for PXRD during SAA experiments. To quantify the crystallinity changes, we selected the characteristic peaks of **NU-220** at 13.66° {201} (**Figure S24**), **CALF-20M-w** at 13.91° {001} (**Figure 3b**), **CALF-20M-e** at 13.79° {110} (**Figure S25**) for the sorbents (p1), and 28.52° {111} (p2) for silicon, respectively. The results provided comparable R values for the characteristic diffraction peaks in all three aged sorbents, indicating unchanged crystallinity. R values for **NU-220**, **CALF-**

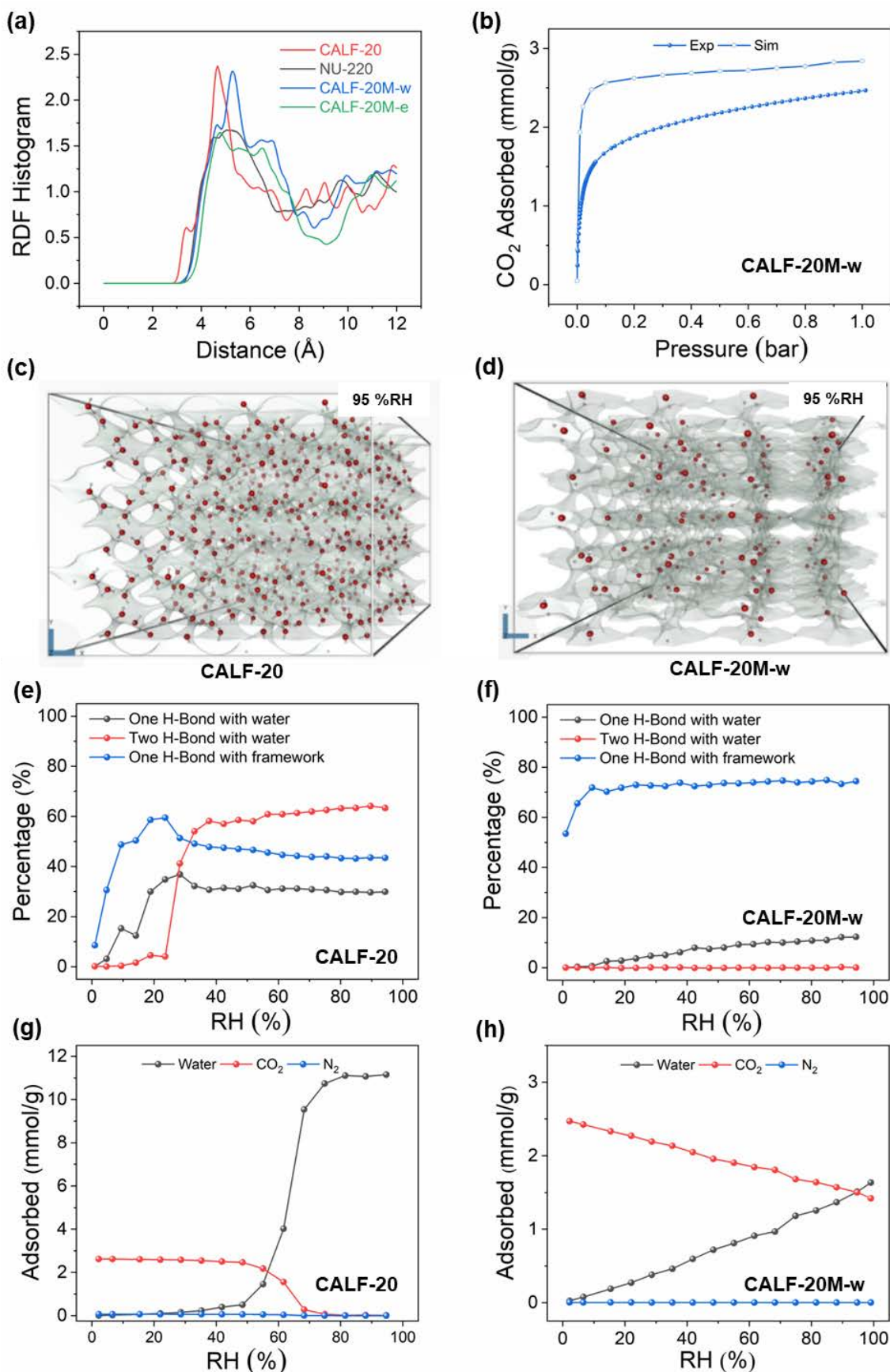


Figure 4. Results from GCMC simulations. (a) Radial distribution functions (RDF) between the Zn-N bond and the water molecules in four sorbents. (b) Comparison of experimental and simulated CO₂ isotherms at 298 K in **CALF-20M-w**. (c-d) Configurations of water molecules at 95% RH from single-component simulations (Color code: O: red, c: grey, frameworks shown in transparent gray) and (e-f) percentage of water molecules with one or two H-bonds with other water molecules and one H-bond with the framework in CALF-20 and **CALF-20M-w**. (g-h) Simulated competitive isotherms for CO₂, water and N₂ at 298 K for CALF-20 and **CALF-20M-w**.

20M-w and **CALF-20M-e** fluctuate in the range of 0.84–1.00, 0.89–0.97 and 0.33–0.37, respectively (**Table S3**). We evaluated the crystallinity (R/R_0 , where R_0 represents the R value before aging) of each material based on the relative R values and found that for all cases, the quality of each crystalline structure shows only negligible degradation (**Figure 3c**). We then employed scanning electron microscopy (SEM) to corroborate these observations, and we verified that minimal changes in particle size and morphology occur following the aging measurements (**Figure S26**), further supporting the remarkable stability of three sorbents under the specified conditions.

Following SAA stability assessments, we shifted our attention to probing the thermal stability of **NU-220**, **CALF-20M-w**, and **CALF-20M-e** and conducted variable-temperature PXRD (VT-PXRD) measurements from 298 to 673 K. Remarkably, **NU-220** and **CALF-20M-w** preserved their structural integrity up to 648 K (**Figures S27 and 3d**), while **CALF-20M-e** undergoes a loss of crystallinity at 623 K (**Figure S28**). The results align well with the findings from the thermal gravimetric analysis (TGA) (**Figures S29–31**), where sorbents start losing weight around 623 K under both N_2 and air. Moreover, the VT-PXRD analysis of **CALF-20M-w** reveals distinctive evidence of structural flexibility, as some of the peaks shift positions—a phenomenon absent in **NU-220** (**Figures S32–34**). For instance, the characteristic peaks at 10.31° {110} and 13.69° {011} shift to 10.58° and 13.63° at 448 K, indicating a variable unit cell at elevated temperature (**Figure S33**). This is also observed in **CALF-20M-e** where the peaks shifted from 23.87° to 23.53° (**Figure S34**). To better assess the chemical stability under practical conditions, such as exposure to acidic gases (typically <500 ppm), the sorbents were subjected to high concentrations of NO_x and SO_2 (1 bar) for three hours. PXRD profiles affirmed that their crystallinity remained unchanged. (**Figures S35–37**) Both **NU-220** and **CALF-20M-e** displayed identical CO_2 adsorption isotherms at 298 K (**Figures S38 and S40**), while **CALF-20M-w** exhibited a slightly reduced capacity ($\sim 2\%$, **Figure S39**). Overall, these experiments demonstrate the high thermal and chemical stability of these materials.

Modeling analysis

To better understand the behavior of these MOF sorbents, we performed grand canonical Monte Carlo (GCMC) simulations (see **Supporting Information** for details). First, to elucidate the demonstrated robustness under SAA conditions, we simulated pure water adsorption and examined the distribution of water molecules within the framework. The distance between the Zn–N bonds and adsorbed water molecules was quantified by the radial distribution function (RDF) at 95% RH. As illustrated in **Figure 4a**, **CALF-20** shows the minimal distance (<4.0 Å) between water and the Zn–N bond, suggesting a heightened likelihood of water disrupting the Zn–N bond through substitution. Conversely, we observed shortest distances greater than 4 Å in **NU-220**, **CALF-20M-w**, and **CALF-20M-e**. Although a distance of ~ 3 Å is insufficient to form a Zn–water coordination bond in **CALF-20**, the incorporation of bulky methyl groups into the triazolate linkers further impedes water proximity to Zn–N bonds, thereby bolstering the framework's robustness to a higher level.

The minimum interaction energy between a single molecule (CO_2 , H_2O , or N_2) and each sorbent was calculated using the same force field as used for the GCMC simulations (**modeling details in Supporting Information**). As shown in **Table 1**, N_2 has a very similar interaction energy with all four sorbents, whereas water has similar interaction energies (around -50 kJ/mol) with **NU-220**, **CALF-20M-w**, and **CALF-20M-e** but a less favorable interaction (-42.1 kJ/mol) with **CALF-20**. Given that the newer adsorbents contain methyl groups – which were added due to their supposed hydrophobicity – this is surprising. However, as noted above, the results are consistent with the low-pressure trends in the experimental water isotherms (**Figure 2d**). For CO_2 , the interaction energies increase in magnitude in the order **CALF-20** < **NU-220** < **CALF-20M-w** < **CALF-20M-e** (**Table 1**). To discern the primary factors contributing to the higher CO_2 adsorption energies for the latter three MOFs, we examined the van der Waals (vdW) and Coulombic contributions of each atom in the CO_2 molecule with the MOF frameworks. The results are provided in **Table S4**. It can be seen that the total vdW energy consistently surpasses the total Coulombic energy. Although the vdW contribution of each CO_2 oxygen ([O]–C–O and O–C–[O]) exceeds that of carbon (O–[C]–O), both contributions are found to be favorable (< 0). On the other hand, the Coulombic interactions of the CO_2 carbon atoms with the MOF are favorable, while those of the CO_2 oxygen atoms are unfavorable. This suggests that the CO_2 carbon atoms preferentially form favorable interactions with negatively charged framework atoms like oxygen and nitrogen, and it is the increased Coulombic interaction that makes CO_2 adsorption more favorable in **CALF-20M-e** than **CALF-20** (-17.4 versus -8.7 kJ/mol).

Next, the single-component CO_2 and water isotherms for all four sorbents were determined by GCMC simulations. The simulated results for CO_2 at 298 K closely match the experimental isotherms for **CALF-20** and **NU-220** (**Figures S41–S42**), and for **CALF-20M-w** and **CALF-20M-e**, the simulated isotherms have the same shape as those from experiment, but with higher loadings predicted at higher pressures (**Figures 4b and S43**). Water isotherms tend to be more difficult to predict, and the agreement between simulation and experiment (**Figures S45–S48**) is reasonably good, with similar trends as seen in experiment (compare **Figure 2d** and **Figure S49**). To elucidate the water-sorbent interactions, we calculated the adsorbate-adsorbate energy, host-adsorbate energy, and total potential energy of all sorbents as a function of RH (**Figures S50–S53**).

In the case of **CALF-20**, the water-water interactions increase dramatically around 25% RH, which is also the range where the isotherm rises sharply, suggesting the emergence of a hydrogen bonding network among water molecules (**Figure S50**). This is also observed in **NU-220** (**Figure S51**) but at even lower RH values ($< 20\%$ RH). In contrast, **CALF-20M-w** and **CALF-20M-e** demonstrate minimal water-water interactions (as shown in **Figures S52–S53**), demonstrating that the modifications in pore dimension and shape dramatically impact the ability of water to form hydrogen bonding networks. This observation suggests that methyl functionalization presents a promising opportunity for **CALF-20M-w** and **CALF-20M-e** to effectively capture CO_2 under high humidity conditions.

To compare the water network in all frameworks, we visualized the distribution of water molecules in the pores at

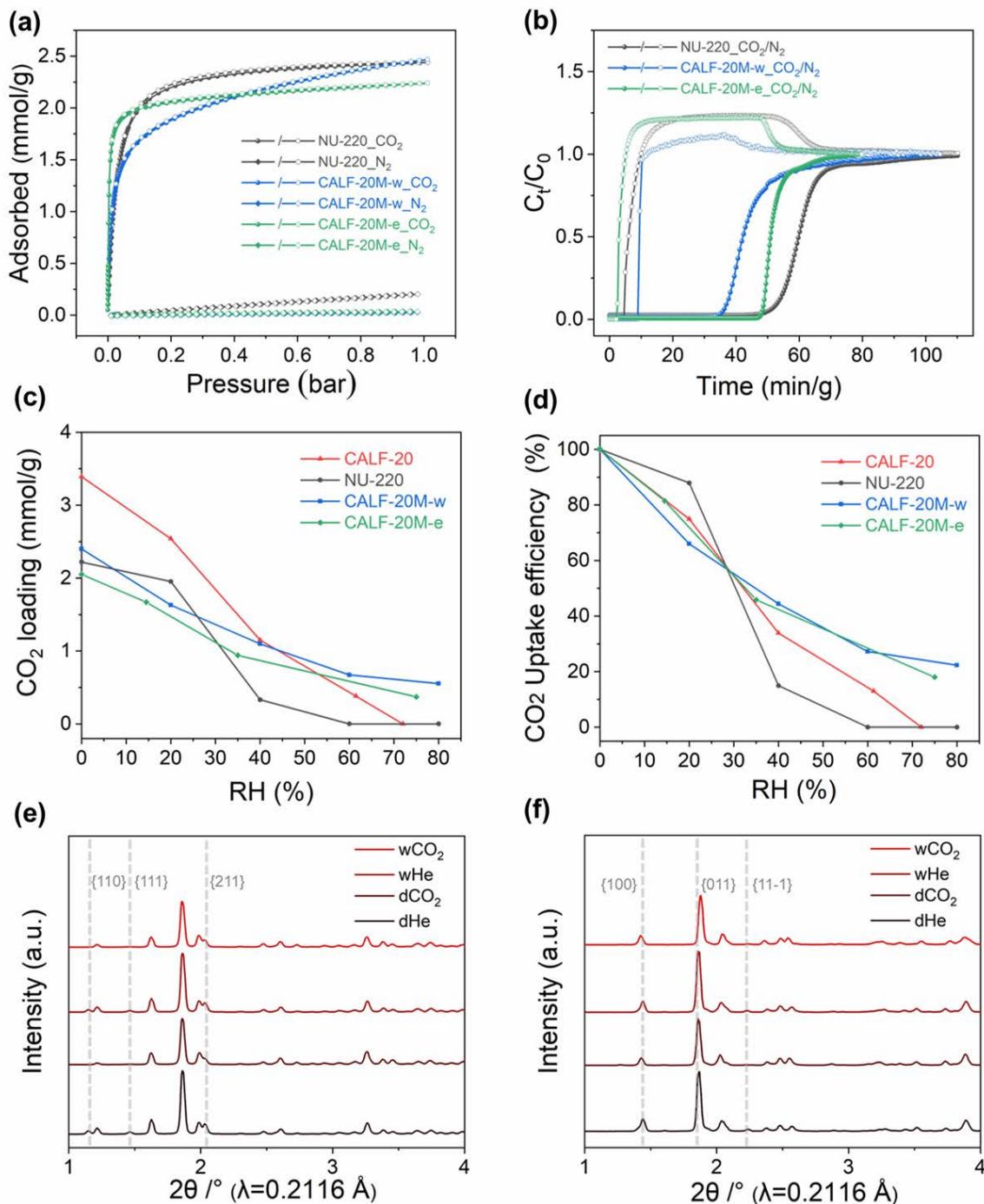


Figure 5. (a) CO₂ and N₂ isotherms in NU-220, CALF-20M-w, and CALF-20M-e at 298 K. (b) Experimental breakthrough curves of NU-220, CALF-20M-w and CALF-20M-e with the binary mixture of CO₂/N₂ (15/85, v/v). The flow rate was set at 5 cc/min, and the experiments were conducted at 1 bar and 298 K. Solid circles represent CO₂ and hollow circles represent N₂. (c-d) CO₂ captured amount and efficiency under different humidities for CALF-20, NU-220, CALF-20M-w and CALF-20M-e. Data from an *in-situ* gas loading PXRD experiment ($\lambda = 0.2116$ Å) on (e) NU-220 and (f) CALF-20M-w. The sample was loaded under dry conditions with dry helium (dHe), dry CO₂ (dCO₂), and humid conditions (100% RH) with helium (wHe) and humid CO₂ (wCO₂).

95% RH (Figures 4c, 4d, and S54) and quantified the proportion of water molecules that form hydrogen bonds with other water molecules and with the framework (Figures 4e, 4f, and S55-S56). The criteria to define a hydrogen bond were an O-H-O angle greater than 150° and an O-H distance less than 2.5 Å.³⁵ The results show that both CALF-20 and NU-220 contain a significant proportion of molecules that form two hydrogen bonds with other water molecules, consistent with the conclusion from the water-water potential energy analysis (Figures S50-S51). On the other hand,

CALF-20M-w and CALF-20M-e show very few water molecules forming two hydrogen bonds with other water molecules. Analysis of the hydrogen bonds between water molecules and the framework showed that hydrogen bonding with the oxalate groups was particularly favored, and all four materials have a high fraction of water molecules that form one hydrogen bond with the framework.

Finally, we simulated competitive isotherms with the total pressure fixed at 1 bar, the gas-phase mole fraction of CO₂ fixed at 14%, variable RH, and the balance of the gas phase

as nitrogen. The results in **Figures 4g, 4h and S57-S58** show that the loading of CO₂ in CALF-20 drops dramatically when the humidity exceeds 50% RH, and nearly no adsorption was observed at 75% RH (**Figure 4g**). However, the presence of methyl groups enabled **CALF-20M-w** to retain a CO₂ capacity of ~0.8 mmol/g even when the RH reached 90 % (**Figure 4h**).

Dynamic Breakthrough and Competitive CO₂ Capture Under Humidity

Inspired by the multicomponent GCMC results, we assessed the CO₂/N₂ separation performance of **NU-220**, **CALF-20M-w**, **CALF-20M-e** through pure gas isotherms and kinetic experimental breakthrough tests. The pure CO₂ and N₂ sorption isotherms for the four sorbents were measured at 298 K (**Figures 5a and S59**) and employed with ideal adsorbed solution theory (IAST) to assess the separation performance. **NU-220** shows a somewhat higher selectivity (440 versus 350 at 1 bar) for CO₂ over N₂ (15/85, v/v) compared to CALF-20 (**Figure S60**). However, **CALF-20M-w** and **CALF-20M-e** displayed negligible single-component N₂ uptake at 298 K, suggesting even higher selectivity. Next, we performed dynamic column breakthrough experiments (DCB) to more directly examine the CO₂/N₂ separation performance for these MOFs. A binary mixture of CO₂/N₂ with a composition of 15/85 (v/v), representing a typical flue gas composition, was passed through a packed column containing glass beads and the sorbents. All three polymorphs exhibit sharp breakthrough curves in the N₂ profile, indicating rapid breakthrough of N₂ (**Figure 5b**), without noticeable changes after three cycles (**Figures S61-S63**). In addition, we observed distinct breakthrough retention times for the CO₂ concentration profiles for each MOF. Specifically, the retention times as shown in **Figure 5b** followed the sequence: **NU-220** (55 min g⁻¹) > **CALF-20M-e** (48 min g⁻¹) > **CALF-20M-w** (33 min g⁻¹). The elution times align closely with the CO₂ adsorbed amount at 0.15 bar, suggesting that the uptake capacity was the primary factor in the retention.

Considering the adsorption energies in **Table 1**, the relevance of N₂ uptake within this study is minor, and preferential adsorption of either CO₂ or H₂O was indicated in both simulations and experiments, signifying a pronounced CO₂ to N₂ selectivity especially for **CALF-20M-w** and **CALF-20M-e**. To probe the CO₂ uptake performance for these MOFs in the presence of humidity, we employed an experimental setup involving humid CO₂ capture experiments using a flow gas system in which we subjected each sorbent to streams of CO₂ with varying RH values (**Scheme S1 and setup details in Supporting Information**). Specifically, we placed the sorbent samples in a ceramic container and positioned them within a tube furnace. To ensure proper activation, the sorbents were treated with dry nitrogen followed by heating to 413 K before cooling to room temperature for humid CO₂ capture experiments. Next, we performed the subsequent analysis using a thermogravimetric analysis instrument equipped with gas chromatography mass spectrometry (TGA-GCMS) to accurately measure the quantity of loaded CO₂. For desorption experiments, the sorbent samples were heated to 413 K under a continuous flow of Ar as the carrier gas. GC-MS analysis enabled the identification and quantification of the amount of the resulting exhaust gases, which contained CO₂ and H₂O. Notably, the experimentally quantified amount of CO₂ adsorbed is

possibly underestimated compared to the actual amount adsorbed due to the slight loss of CO₂ that occurs during the transfer/mounting of saturated sorbents from the furnace to the TGA-GCMS instrument, which necessitated exposure of the samples to ambient conditions after uncapping. Thus, a large amount of sorbent (>100 mg) was utilized to minimize the effect.

The results in **Figure 5c** illustrate a gradual reduction in the CO₂ adsorption capacity of CALF-20 as the RH increases. Eventually, at an RH level of ~70%, the CO₂ adsorption capacity approaches zero, and water emerges as the dominant adsorbed species at high RH. A comparable trend was seen in **NU-220**, where there was a marked reduction in CO₂ adsorption at around 60% RH, but it maintained higher capture efficiency below 30% RH (**Figure 5d**). Consequently, **NU-220** proves unsuitable for capturing CO₂ from humid flue gas, as the CO₂ uptake becomes negligible around 60% RH.

On the other hand, the results for **CALF-20M-w** and **CALF-20M-e** in **Figure 5c and 5d** reveal that some CO₂ capacity remained even at high humidity levels. Unlike in the case of **NU-220**, the methyl functional groups in **CALF-20M-w** and **CALF-20M-e** efficiently limit the formation of hydrogen bonding networks, as discussed above. These two sorbents exhibit superior CO₂ uptake capacity above 45% and 55% RH, approximately 1.0 and 0.7 mmol/g CO₂, respectively, despite lower inherent pore volumes compared to that of CALF-20. The large amount of water uptake observed in single-component water isotherms in CALF-20 (**Figure 2d**) results in a loss of approximately 30% in CO₂ uptake efficiency at 20% RH in the multicomponent measurements. In contrast, **CALF-20M-w** and **CALF-20M-e** demonstrate a more gradual decrease in CO₂ capture performance with increasing RH, showing 20% CO₂ uptake capacity at 80% RH. These results are qualitatively consistent with the modeling results (**Figures 4h and S58**) and suggest that **CALF-20M-w** and **CALF-20M-e** provide considerable promise for CO₂ capture from moist flue gas compared to CALF-20 under the same humid conditions.

A potential reason for the difference between the simulated and experimental pure and multicomponent isotherms for **CALF-20M-w** and **CALF-20M-e** is structural flexibility of the MOFs (**Figures 4b, 4h and S43, S58**). Thus, *in situ* PXRD measurements were carried out with CO₂ sorption to investigate the structural changes during CO₂ capture. The activated sample was loaded under dry conditions with dry helium (dHe), dry CO₂ (dCO₂), and under humid conditions with humid helium (wHe) and humid CO₂ (wCO₂) (**details in Supporting Information**). The PXRD data (**Figures 5e-f and S65**) is presented for the sample subjected to gas adsorption and desorption cycles, transitioning between dry and humid conditions. We performed a Pawley refinement for the model for **NU-220** to determine the purity (**Figure S64**). Notably, the annotated reflections {110}, {111}, and {211} in **NU-220** (**Figure 5e**) demonstrate diminished intensity, potentially attributable to the CO₂ uptake, signifying an almost instantaneous structural transition that remains reversible. Crucially, the intrinsic order of the MOF remains predominantly unaltered under these conditions, even at elevated RH levels, indicating the rigid structure of **NU-220**. Subsequently, we performed an analogous *in situ* PXRD analysis for **CALF-20M-w** and **CALF-20M-e**, against the data for helium-loaded samples under dry and humid

conditions. **Figure 5f** shows the PXRD patterns of **CALF-20M-w** throughout the whole dHe, dCO₂, wHe, wCO₂ adsorption cycle. During dry and humid CO₂ capture, characteristic peaks at 1.86° (annotated reflection {011}) shifted to 1.88°, demonstrating the structural alternation in **CALF-20M-w** during CO₂ capture (**Figure 5f**). The observed decrease in intensity of the annotated reflection {11-1} in **CALF-20M-w** can be attributed to the adsorption of CO₂. A similar observation was made with the annotated reflection {110} of **CALF-20M-e**, where the peak shifted from 1.85° to 1.87°. (**Figure S65**). The *in situ* gas loading experiments successfully demonstrated the structural transition during wCO₂ capture and helped explain the difference between experimental results and simulation for mixture adsorption. For instance, the simulated multicomponent isotherms for **CALF-20M-e** do not indicate any large changes in CO₂ uptake at elevated RH values, which remains at >90% of the initial CO₂ uptake, even under 100% RH (**Figure S58**). In contrast, experimental results indicate **CALF-20M-e** preserves only ~20% of its initial CO₂ uptake capacity at 80% RH, which is significantly lower than the value predicted by simulation. As for **CALF-20M-w**, even when accounting for the inherent loss of sequestered CO₂, it retains 23% of its efficiency experimentally, in contrast to the 57% projected by the modeling. Despite the structural flexibility demonstrated by **CALF-20M-w** and **CALF-20M-e**, these experimental results still highlight their great potential for capturing CO₂ from highly humid flue gas.

Conclusion

In this work, we demonstrated that incorporating methyl groups into the triazolate linkers affords robust materials better tailored than the related material without methyl groups to capture CO₂ from post-combustion flue gas in the presence of water. Specifically, we synthesized three new MOFs, denoted as **NU-220**, **CALF-20M-w**, and **CALF-20M-e**, from the same metal salt and organic linker precursors but from different solvents. **NU-220** features a different topology than that of **CALF-20**, whereas **CALF-20M-w** and **CALF-20M-e** are isostructural to **CALF-20**. In all three cases, the presence of methyl groups resulted in significant modifications to the pore size and pore environment. Molecular simulations suggest that the methyl groups sterically hinder the formation of hydrogen bonding networks by water molecules and further repel water molecules from approaching framework Zn-N bonds relative to the non-methylated analogues, supporting the experimentally observed increase in stability in the presence of water for these new MOFs. Humid CO₂ capture experiments confirm that incorporating the methyl group results in a significant improvement in CO₂ uptake at high RH values, as **CALF-20M-w** and **CALF-20M-e** maintain about 20% of their initial CO₂ uptake at 80% RH, whereas **CALF-20** loses all of its initial CO₂ uptake at this same RH. As a result, **CALF-20M-w** and **CALF-20M-e** show promise for CO₂ capture in post-combustion flue gas environments, while **NU-220** excels among this series for CO₂ capture in dry or low RH conditions. Overall, this simple design strategy has afforded new adsorbent materials that are better suited for practical CO₂ capture conditions from humid post combustion flue gas streams than **CALF-20**, overcoming a significant drawback for this CO₂ adsorbent and increasing the potential success of this class of physisorbents in carbon capture technologies.

ASSOCIATED CONTENT

Supporting Information. Detailed material synthesis and characterization, modeling details, and additional results are available free of charge via the Internet at <http://pubs.acs.org>.

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Conflicts of Interest

O.K.F. and R.Q.S. have a financial interest in NuMat Technologies, a startup company that is seeking to commercialize MOFs.

Author Contributions

The manuscript was written through contributions of all authors.

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