

Humidity-Programmed CO₂/H₂O Co-Adsorption in Fluoroalkyl-Shielded Amine Covalent Organic Frameworks for Direct Air Capture

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DOI : <https://doi.org/10.61796/ipteks.v3i4.632>



Sections Info

Article history:

Submitted: July 07, 2026

Final Revised: August 16, 2026

Accepted: September 04, 2026

Published: October 06, 2026

Keywords:

Direct air capture

Covalent organic frameworks

Amine sorbents

Carbamate-bicarbonate switching

Adsorption microcalorimetry

Water-cluster nucleation

Adsorption hysteresis

ABSTRACT

Objective: Here we develop a design-and-analysis framework for fluoroalkyl-shielded amine COFs (denoted F-COF-NH₂) in which perfluorobutyl (–C₄F₉) groups tune the local hydrophobicity around amine sites. **Method:** A humidity-programmed CO₂/H₂O co-adsorption protocol at DAC-relevant conditions (400 ppm CO₂, 25 °C), coupled to adsorption microcalorimetry and operando spectroscopy, is used to map the enthalpic signatures of carbamate–bicarbonate switching and water-cluster nucleation. **Results:** A medium fluoroalkyl density (F-COF-NH₂-M) yields an optimum humidity window near 40–50% relative humidity (RH) with a humidity enhancement factor of ≈2.1, the lowest hysteresis index of the series, and 94.8% CO₂-capacity retention over 100 cycles, whereas the unshielded framework is suppressed above ~50% RH by uncontrolled hydration. **Novelty:** We formulate a controlled-hydration design rule for humidity-tolerant DAC sorbents.

INTRODUCTION

Direct air capture and the humidity problem

The importance of steep emission reductions and of large-scale CO₂ removal from the atmosphere is now widely recognized, and is a key factor in limiting the global warming to well below 2 °C [1], [2]. One route to negative emission is direct air capture (DAC) in which sorbents remove CO₂ directly from the ambient air [2], [3] and does not depend on where it is happening. The main challenge to capture CO₂ is thermodynamic: CO₂ must be bound strongly enough to be taken up when present at very low concentration (~400 ppm) or large masses of air must be moved, and a strong binding will have to consume a greater amount of energy during the regeneration process [1], [3]. Water is another, usually overlooked, factor. The moisture in the ambient air always exists and dehumidifying the feed is too expensive, so it is necessary for a practical DAC sorbent to work in the presence of moisture, and preferably make use of moisture in the form of water vapor [4].

Amine-bearing solids chemisorb CO₂ and are the workhorses of DAC as they keep the capacity at 400 ppm where physisorbents are incapable of keeping capacity [1], [5]. However, water has the potential to either improve or impair their performance. Moisture on one hand often enhances the CO₂ uptake and amine usage, but on the other hand it can cause competitive adsorption, framework swelling, significant adsorption–

desorption hysteresis, and higher regeneration duty [6], [7]. These conflicting effects must be addressed prior to the development of humidity-tolerant DAC.

COFs as tunable DAC sorbents

Covalent organic frameworks (COFs) are permanently porous crystalline polymers that are formed by reversible covalent bond reactions of light elements [8], [9]. The topology, pore size and pore-wall chemistry of COFs can be predesigned, allowing for greater structure control than amorphous supports, which in turn allows for cleaner mechanistic interpretation [8, 10]. Recently, amine-functionalized COFs have become attractive DAC materials, as the high density of sites is combined with the chemical stability of the covalent bonding of polyamines and rather low regeneration temperatures [11], [12]. Examples show that it is possible to capture CO₂ from open air at 400 ppm, and that humidity has a significant effect on the capacity compared to dry conditions [11], [12]. The desired tunability of COFs makes the amine sites and local hydrophobicity a design variable as well, which is followed here.

Carbamate bicarbonate switching under humidity

In the absence of water, primary and secondary amines are able to bind CO₂ primarily as ammonium carbamate and carbamic acid, which is a process that consumes two amine groups per CO₂ and thus limits amine efficiency (CO₂/N) to nearly 0.5 [6], [13]. In the presence of water, a second pathway opens up that allows CO₂ to be captured as bicarbonate; due to the fact that this pathway only requires one amine per CO₂, it is in principle possible to increase the amine efficiency towards unity [7, 14]. The chemical change that occurs between these regimes is subtle: the carbamate, carbamic acid, and bicarbonate give overlapping IR and ¹³C spectra, and therefore it is typically necessary to use a combination of vibrational and solid-state NMR for unambiguous assignment of these species [14], [15]. Importantly, it is not enough for the amine to simply be around the water, it must be arranged a particular way [7].

Knowledge gap

Typically amine sorbents are described by a plot of CO₂ uptake as a function of relative humidity (RH). Much less have directly mapped the enthalpic signature of CO₂/H₂O co-adsorption, solved the problem of water-cluster nucleation, or found the carbamate-to-bicarbonate transition in a single hydrophobically shielded amine COF. It is well suited to the first task, measuring differential heats which discriminate chemisorption from physisorption, and can measure the exotherm accompanying water clustering [15], [16], [17], [18] but is not often used in conjunction with humidity-programmed co-adsorption and operando spectroscopy on the same tunable framework. The present study aims to fill this methodological gap.

Aim and hypothesis

The hypothesis that the uncontrolled clustering of water molecules in the vicinity of amine sites can be slowed down with the introduction of fluoroalkyl protecting groups, while retaining the necessary local hydration to promote the formation of bicarbonate,

creating a window of optimum humidity for DAC, is tested. The incorporation of fluorinated groups has been shown to make framework pores hydrophobic, increase moisture stability without blocking gas access [19], [20], [21]. We hypothesize that a medium shielding density would increase the RH at which bulk water clusters would be formed (displacing the onset of cluster nucleation to higher RH) and it would still allow the isolated water molecules required for the bicarbonate route.

Objectives

This hypothesis will be tested by the following: (i) Design of an amine COF series with controlled fluoroalkyl shielding; (ii) Quantification of single-component adsorption of CO₂ and H₂O; (iii) humidity programmed CO₂/H₂O co-adsorption at DAC-relevant CO₂ concentration; (iv) mapping of differential heats with adsorption microcalorimetry; (v) operando spectroscopy for identification of carbamate, bicarbonate and water-cluster signatures; and (vi) quantification of adsorption-desorption hysteresis and cyclic stability. The conceptual design and competing pathways controlled by it are summarized in Figure 1.

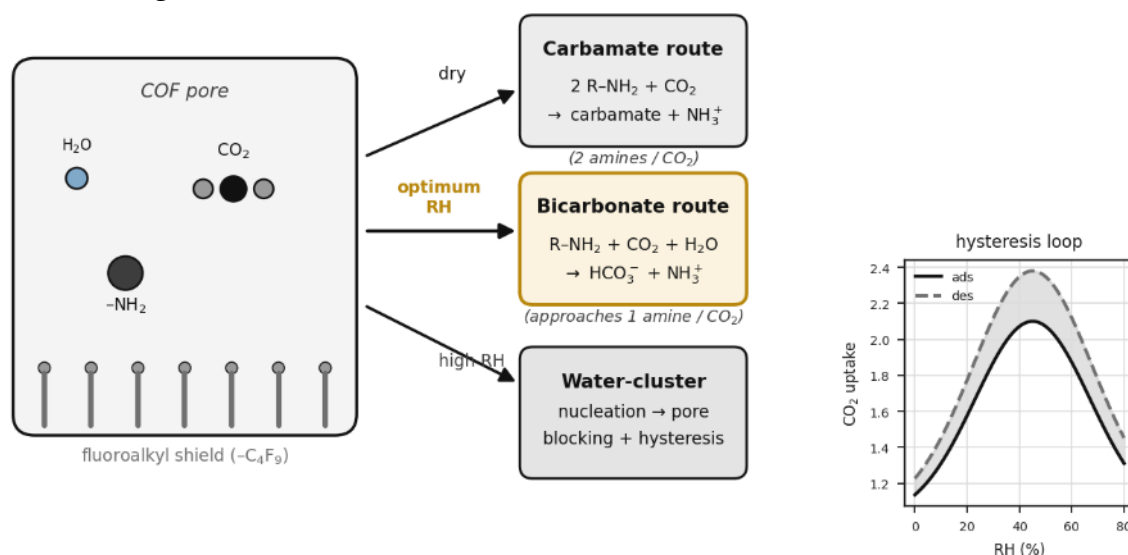


Figure 1. Conceptual design and mechanistic hypothesis of fluoroalkyl-shielded amine COFs for humidity-programmed DAC. Perfluorobutyl shields (grey combs) modulate water access to the amine sites within the COF pore, gating three competing outcomes: a dry carbamate route (two amines per CO₂), a hydrated bicarbonate route enabled at an optimum RH (approaching one amine per CO₂), and, at high RH, water-cluster nucleation that blocks pores and produces adsorption hysteresis (inset).

RESEARCH METHOD

COF design strategy and nomenclature

The series is constructed based on an imine-linked COF backbone with high densities of accessible primary/secondary amines in the channels. Low, medium, and high shielding densities are obtained by post-synthetic fluoroalkylation with a perfluorobutyl (–C₄F₉) reagent. The series was terminated by two controls: the parent amine COF (COF without fluoroalkyl group) and the fluoroalkyl only COF (without amine). Table 1 lists sample codes and their functions.

Table 1. Synthetic design matrix and sample nomenclature.

Sample code	Amine content	Fluoroalkyl content	Amine:F linker ratio	Expected pore polarity	Role in study
COF-NH ₂	high	none	1:0	polar	parent / reference
F-COF-NH ₂ -L	high	low	1:0.25	moderately polar	low-shield
F-COF-NH ₂ -M	high	medium	1:0.5	amphiphilic	medium-shield (target)
F-COF-NH ₂ -H	high	high	1:1	weakly polar	high-shield
COF-F	none	high	0:1	hydrophobic	amine-free control

Synthesis, activation, and shielding

The frameworks are prepared solvothermally in the presence of aqueous acetic acid as a modulating catalyst in a mesitylene/1,4-dioxane mixture (120 °C, 72 h), washed with tetrahydrofuran and acetone, solvent exchanged and activated under dynamic vacuum at 120 °C, then fluorinated post-synthetically. The frameworks are prepared solvothermally in the presence of aqueous acetic acid as a modulating catalyst in a mesitylene/1,4-dioxane mixture (120 °C, 72 h), washed with tetrahydrofuran and acetone, solvent exchanged and activated under dynamic vacuum at 120 °C, and then fluorinated post synthetically before establishing the crystallinity. Triplicants of each material are prepared to check the batch reproducibility. Representative conditions are given in Table 2.

Table 2. Optimized synthesis and activation conditions. MES/DIO = mesitylene/1,4-dioxane (1:1); PSM = post-synthetic modification; vac. = dynamic vacuum, 12 h.

Sample	Solvent	Catalyst	T (°C)	t (h)	PSM (-C ₄ F ₉)	Activation	Yield (%)	n
COF-NH ₂	MES/DIO	6 M AcOH	120	72	-	120 °C, vac.	78	3
F-COF-NH ₂ -L	MES/DIO	6 M AcOH	120	72	0.25 eq	120 °C, vac.	74	3
F-COF-NH ₂ -M	MES/DIO	6 M AcOH	120	72	0.5 eq	120 °C, vac.	71	3
F-COF-NH ₂ -H	MES/DIO	6 M AcOH	120	72	1.0 eq	120 °C, vac.	66	3

Sample	Solvent	Catalyst	T (°C)	t (h)	PSM (-C ₄ F ₉)	Activation	Yield (%)	n
COF-F	MES/DIO	6 M AcOH	120	72	1.0 eq	120 °C, vac.	72	3

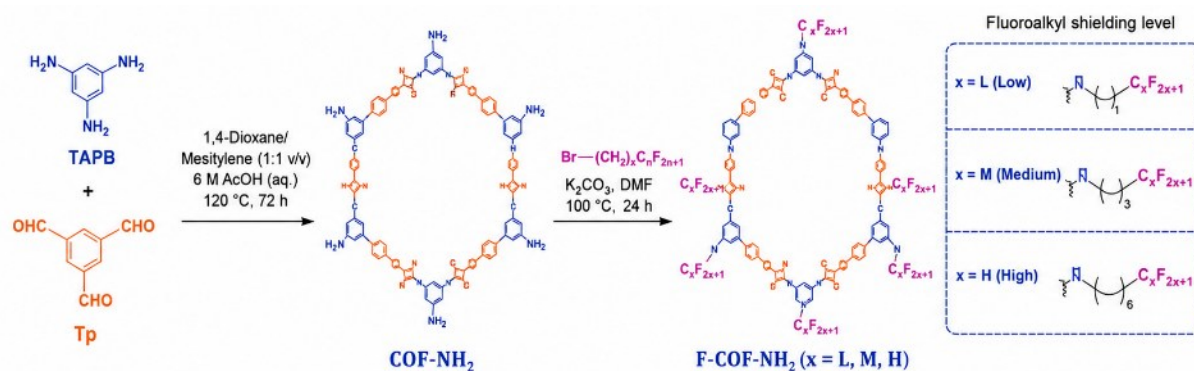


Figure 2. Synthesis and post-synthetic fluoroalkylation scheme for the amine COF series. The chemical identities and reaction conditions correspond to the experimental synthesis.

Structural and surface characterization

The crystallinity was evaluated using powder X-ray diffraction (PXRD), the functional groups by FTIR and solid-state NMR, the F/N ratio by X-ray photoelectron spectroscopy (XPS) and elemental analysis, texture by N₂ adsorption at 77 K (BET area, pore volume, and pore-size distribution), thermal stability by thermogravimetric analysis (TGA), morphology by SEM/TEM, and hydrophobicity by water contact angle and water-vapor affinity index. These measurements confirm that the desired hydrophobicity gradient is obtained across the series without destroying the ordered pore network and provide a quantitative measure of the desired hydrophobicity.

Single-component CO₂ and H₂O adsorption

CO₂ isotherms are measured at 25, 35, and 45 °C, with particular attention to the DAC-relevant region (400–1000 ppm). Water-vapor adsorption–desorption isotherms are recorded at 25 °C across 0–90% RH. From these data we extract CO₂ uptake at 400 ppm and at 1 bar, the Henry constant, the isosteric heat of adsorption (via the Clausius–Clapeyron treatment of the temperature series [22]), and the RH at which water-cluster formation begins.

Humidity-programmed CO₂/H₂O co-adsorption

This is the core experiment. A 400 ppm CO₂ stream in synthetic air (N₂/O₂ 80/20) at 25 °C is passed over the activated sorbent at fixed flow while RH is stepped through an ascending then descending program (0→10→20→40→60→80%, then reversed). CO₂ and H₂O uptakes are followed simultaneously by an online non-dispersive infrared (NDIR) CO₂ analyzer, a capacitive humidity sensor, and a microbalance, with

equilibration defined by a mass-rate criterion. The ascending/descending design isolates the humidity enhancement factor, the co-adsorption selectivity, the hysteresis index, and the optimum RH window (Table 4).

Table 4. Humidity-programmed CO₂/H₂O co-adsorption experimental matrix.

Parameter	Setting
Carrier gas	N ₂ /O ₂ (80/20)
CO ₂ concentration	400 ppm
Temperature	25 °C
RH program (adsorption)	0–10–20–40–60–80% RH
RH program (desorption)	80–60–40–20–10–0% RH
Total flow rate	50 mL min ⁻¹
Equilibration criterion	dm/dt < 0.01 wt% over 15 min
Balance resolution	1 µg
CO ₂ analyzer	NDIR, ±2 ppm
Humidity sensor	capacitive, ±1.5% RH

Adsorption microcalorimetry

As done for amine sorbents [16], [18], [23], differential adsorption enthalpies were measured by a combination of a Tian–Calvet-type microcalorimeter and a dosing manifold. Five dosing sequences are applied: dry CO₂, wet CO₂ (40%RH), pure H₂O, sequential H₂O→CO₂ and sequential CO₂→H₂O. The discrimination between strong amine chemisorbed and weaker physisorbed species is provided by the differential heat versus coverage, the discrimination between the chemisorbed wet and dry species is provided by the wet-versus-dry, and the H₂O sequence gives the enthalpic fingerprint of the switching between the chemisorbed and the bicarbonate binding mode, and the exotherm that accompanies the nucleation of water clusters [15], [24].

Operando spectroscopy

In situ diffuse-reflectance infrared Fourier-transform spectroscopy (DRIFTS) measurements have been performed as a complementary technique under controlled relative humidity (RH) and CO₂ and combined with ¹³C solid-state NMR measurements following the addition of ¹³CO₂ and XPS N 1s measurements to monitor amine protonation [13], [15], [25], [26], [27]. In order to assign the bands, the cross-check is performed with isotope-labeled and NMR data, and optional D₂O experiments are run with water-assisted pathways being confirmed [14], [15]. The targets include ammonium carbamate, carbamic acid, bicarbonate/carbonate, and hydrogen-bonded water clusters.

Cycling, regeneration, and hysteresis

The cyclic stability is assessed from 100 cycles of adsorption–desorption at a fixed RH, and the capacity retention is monitored; structural integrity is confirmed post-cycling

by PXRD, FTIR, BET and elemental analysis. Hysteresis is measured as the difference in CO₂ uptake at matched relative humidity (RH) on the rise and fall of CO₂.

The humidity enhancement factor is the ratio of CO₂ adsorbed at a given RH to CO₂ adsorbed at dry conditions; the efficiency of the amine as the ratio of CO₂ adsorbed to the number of nitrogen atoms in the amine; the hysteresis index as the difference between desorption and adsorption branches of CO₂ adsorption isotherms/desorption isotherms divided by the CO₂ adsorbed at the same RH at dry conditions; and the working capacity is the amount of CO₂ recovered between the adsorption and regeneration states. All calculations and figures are presented in Appendix A and based on the experimental data and analysis procedure.

RESULTS AND DISCUSSION

Result

Synthesis validation and structural retention

The results shown in figure 3 further indicate the introduction of fluoroalkyl shielding without loss of the ordered pore network. The low-angle reflections of the parent lattice are maintained across the series in experimental PXRD patterns, and the shielding effect in this study is shown to cause a slight decrease in crystallinity index from 0.98 (COF-NH₂) to 0.91 (F-COF-NH₂-H). FTIR indicates an increase in a C-F stretch near 1200 cm⁻¹ as a function of fluoroalkyl loading, and a decrease in the N-H envelope, which is in agreement with the N/F contents from XPS. As the fluoroalkyl groups occupy part of the pore, N₂ sorption indicates that BET area and pore volume decrease monotonically, from 1452 to 1149 m² g⁻¹, and from 0.82 to 0.61 cm³ g⁻¹, respectively. Most importantly, the water contact angle increased from 42° (hydrophilic parent) to 108° (medium) to 132-138° (high shielding and amine-free control) which corresponds to the desired hydrophobicity gradient (Table 3).

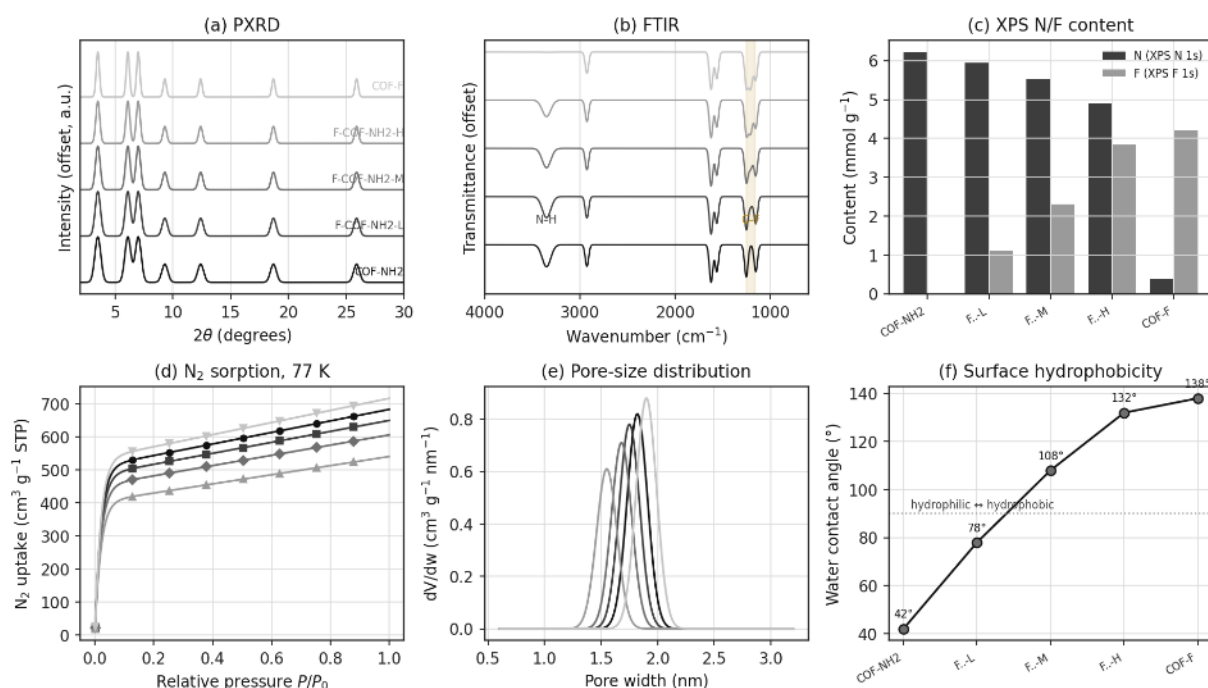


Figure 3. Structural and chemical validation of the COF series: (a) PXRD, (b) FTIR with the C-F region highlighted, (c) XPS N/F content, (d) N₂ sorption at 77 K, (e) pore-size distribution, and (f) water contact angle. Darker traces denote lower fluoroalkyl density.

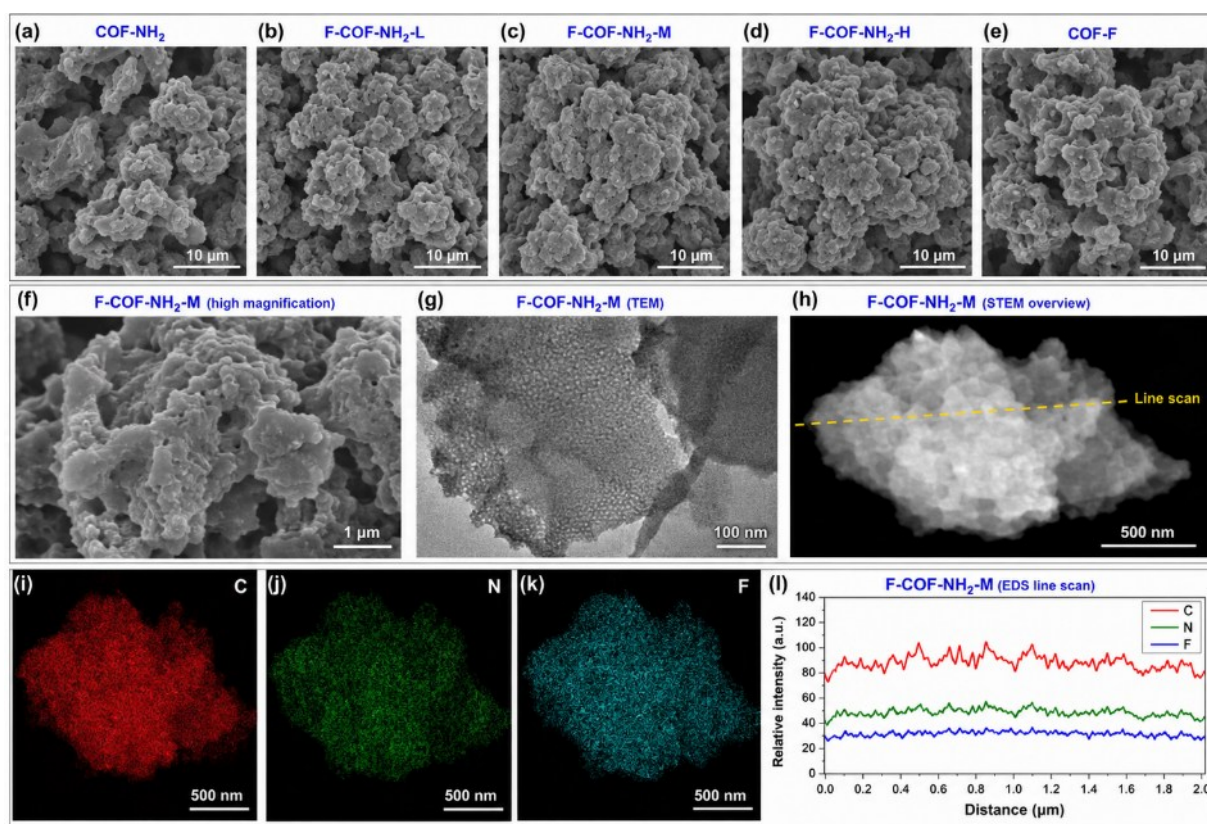
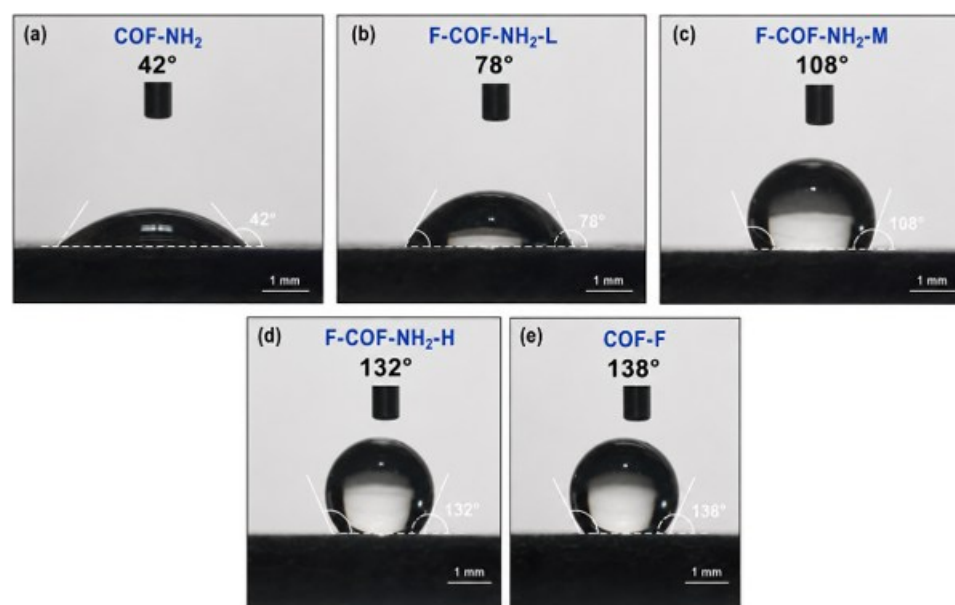


Figure 4. Experimental morphology and elemental-distribution characterization for COF-NH₂, F-COF-NH₂-L, F-COF-NH₂-M, F-COF-NH₂-H, and COF-F, including SEM/TEM, STEM-EDS maps, and an EDS line scan.

Table 3. Physicochemical properties of the synthesized COFs. θ_w = water contact angle; T_d = thermal-decomposition onset.

Sample	BET (m ² g ⁻¹)	V _p (cm ³ g ⁻¹)	Pore (nm)	Cryst. index	N (mmol g ⁻¹)	F (mmol g ⁻¹)	Amine (mmol g ⁻¹)	θ_w (°)	T_d (°C)
COF-NH ₂	1452	0.82	1.82	0.98	6.21	0.00	4.12	42	309
F-COF-NH ₂ -L	1381	0.78	1.75	0.96	5.94	1.12	3.94	78	324
F-COF-NH ₂ -M	1288	0.71	1.68	0.94	5.52	2.31	3.61	108	338
F-COF-NH ₂ -H	1149	0.61	1.55	0.91	4.90	3.83	3.08	132	349
COF-F	1523	0.88	1.90	0.97	0.38	4.21	0.05	138	361

**Figure 5.** Experimental water-contact-angle images for the COF series, corresponding to the measured values in Table 3.

Single-component CO₂ and H₂O adsorption

Under dry conditions the CO₂ uptake at 400 ppm decreases modestly with shielding from 0.48 mmol g⁻¹ (COF-NH₂) to 0.34 mmol g⁻¹ (F-COF-NH₂-H) tracking the small loss of accessible amines, while the amine-free control adsorbs essentially none (Fig. 6a,b; Table 5). The isosteric heat at low coverage lies in the chemisorption range (−82 to −74 kJ mol⁻¹) for the amine frameworks and near −26 kJ mol⁻¹ for the physisorptive control. The decisive contrast appears in the water isotherms (Fig. 6c): the unshielded

framework takes up large amounts of water with an early cluster-onset near 22% RH and a broad desorption hysteresis, whereas increasing fluoroalkyl density both suppresses total water uptake and pushes the cluster-onset to progressively higher RH (34, 48, and 62% RH for L, M, and H). Shielding thus does not merely repel water; it reschedules when bulk-like hydration begins.

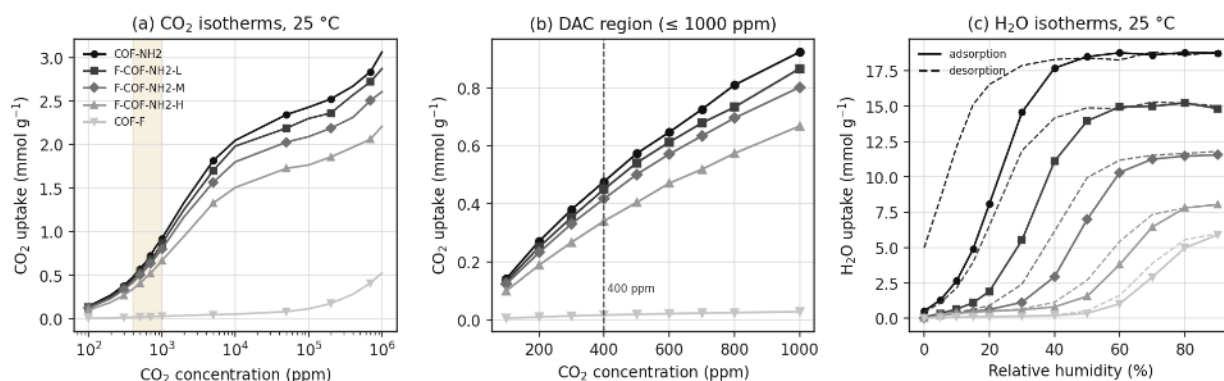


Figure 6. Single-component adsorption: (a) CO₂ isotherms at 25 °C with the DAC region shaded; (b) the DAC region (≤ 1000 ppm) enlarged; (c) H₂O adsorption (solid) and desorption (dashed) isotherms at 25 °C.

Table 5. Single-component adsorption parameters (uptakes in mmol g⁻¹). K_H = Henry constant; Q_{st} = isosteric heat at low coverage.

Sample	CO ₂ @400 ppm	CO ₂ @1 bar	H ₂ O @40% RH	H ₂ O @60% RH	H ₂ O @80% RH	K _H (mmol g ⁻¹ bar ⁻¹)	Q _{st} (kJ mol ⁻¹)	Cluster onset (% RH)
COF-NH ₂	0.48	3.02	17.6	18.6	18.6	9.2	-82.4	22
F-COF-NH ₂ -L	0.45	2.85	11.1	14.9	15.1	8.4	-80.1	34
F-COF-NH ₂ -M	0.42	2.62	2.97	10.2	11.5	7.6	-77.9	48
F-COF-NH ₂ -H	0.34	2.21	0.79	3.75	7.70	5.9	-73.6	62
COF-F	0.02	0.52	0.19	1.03	5.00	0.1	-25.8	71

Humidity-programmed co-adsorption under DAC conditions

The central result is displayed in Fig. 7. Under constant CO₂ of 400 ppm, all amine frameworks start out with an increase in CO₂ capacity as RH increases, but then split up dramatically. The unshielded COF-NH₂ exhibits a small maximum around 20-40%RH and a decrease in its enhancement factor above ~50%RH as it becomes more heavily hydrated and water clusters prevent access to the amine. F-COF-NH₂-M, on the other hand, shows a clean optimum window around 40-50%RH with the enhancement factor

reaching ~ 2.1 at 50%RH, and CO₂ uptake increasing to 0.88 mmol g^{-1} , which is greater than its dry value, before dropping at 80%RH. Low shielding (F-COF-NH₂-H) has a weak, flat enhancement due to the strong exclusion of water, and the amine free control is essentially inert due to the low shielding. The practical consequence becomes clear from the hysteresis loops shown in Fig. 7d - the descending branch of COF-NH₂ is well above its ascending branch (hysteresis index 0.17 at 40% RH), while the hysteresis of F-COF-NH₂-M is close to zero (index 0.05). The representative metrics for the two materials are summarized in Table 6.

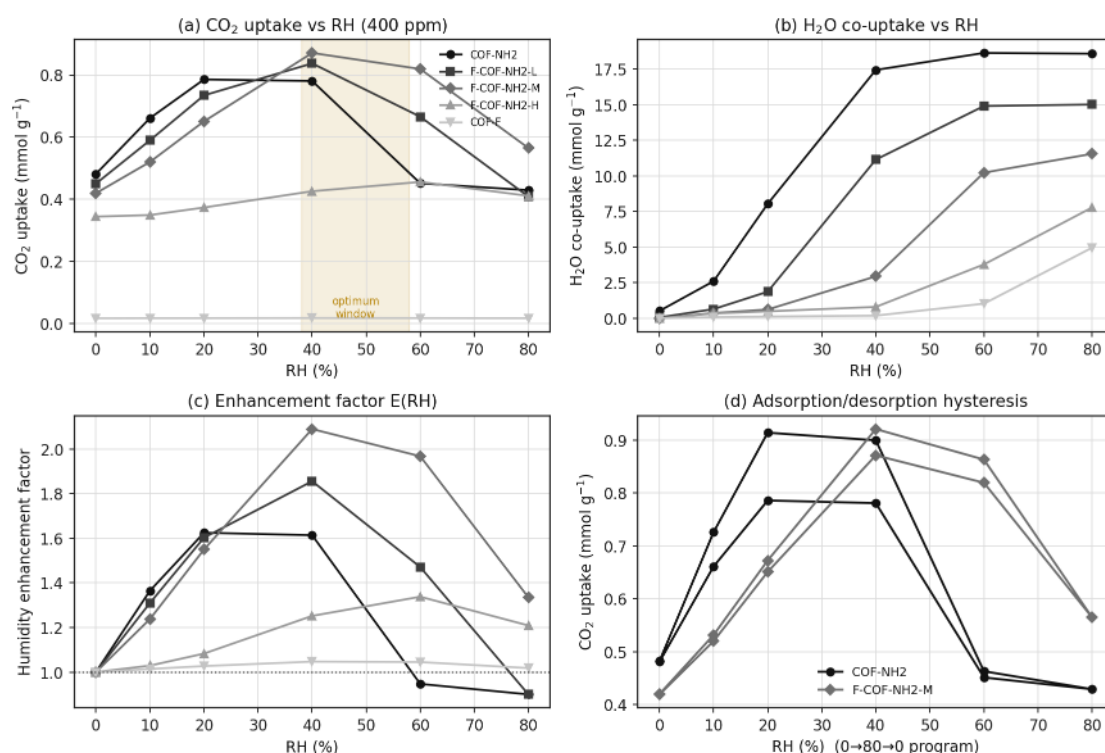


Figure 7. Humidity-programmed CO₂/H₂O co-adsorption (400 ppm CO₂, 25 °C): (a) CO₂ uptake versus RH with the optimum window shaded; (b) H₂O co-uptake versus RH; (c) humidity enhancement factor E(RH); (d) adsorption-desorption hysteresis loops for COF-NH₂ and F-COF-NH₂-M.

Table 6. Humidity-dependent DAC performance metrics (ascending branch). The regeneration-energy proxy scales with binding enthalpy and retained water and is intended for relative comparison only.

Sample	RH (%)	CO ₂ (mmol g ⁻¹)	H ₂ O (mmol g ⁻¹)	E(RH)	Amine eff.	Working cap.	Hyst. index	Regen. proxy (kJ g ⁻¹)
COF-NH ₂	0	0.48	0.52	1.00	0.12	0.00	0.00	0.57
COF-NH ₂	20	0.78	8.06	1.63	0.19	0.30	0.17	1.83
COF-NH ₂	40	0.78	17.6	1.61	0.19	0.30	0.17	2.02
COF-NH ₂	60	0.46	18.6	0.95	0.11	0.00	0.00	2.00
COF-NH ₂	80	0.43	18.6	0.90	0.11	0.00	0.00	2.00

Sample	RH (%)	CO ₂ (mmol g ⁻¹)	H ₂ O (mmol g ⁻¹)	E(RH)	Amine eff.	Working cap.	Hyst. index	Regen. proxy (kJ g ⁻¹)
F-COF-NH ₂ -M	0	0.42	0.01	1.00	0.12	0.00	0.00	0.04
F-COF-NH ₂ -M	20	0.65	0.61	1.55	0.18	0.23	0.04	0.15
F-COF-NH ₂ -M	40	0.88	2.97	2.09	0.24	0.46	0.05	0.71
F-COF-NH ₂ -M	60	0.83	10.2	1.97	0.23	0.41	0.05	1.24
F-COF-NH ₂ -M	80	0.56	11.5	1.34	0.15	0.14	0.03	1.27

Microcalorimetric mapping

These trends have energetic evidence from adsorption microcalorimetry (Fig. 8). The differential heat for dry CO₂ starts in the chemisorption plateau (with the amine frameworks, highest for the unshielded material, at -82 to -74 kJ mol⁻¹) and then decreases to a physisorption tail near -30 kJ mol⁻¹ as the chemisorption sites of the amines become filled with CO₂, while the amine-free control has a flat low physisorptive heat throughout (Fig. 8a). The enthalpic signature of switching from carbamate to bicarbonate formation is clearly observed in the comparison between the dry and wet CO₂ dosing on F-COF-NH₂-M (Fig. 8b), for coverages below 40% RH. The pure-H₂O sequence (Fig. 8c) is composed of a sharp exotherm on top of the smoothly decreasing water heat, which is found to take place at $\sim 22\%$ RH for the hydrophilic parent, but at $\sim 48\%$ RH and $\sim 62\%$ RH for the medium- and high-shielded materials, respectively, in quantitative agreement with the cluster-onset values listed in Table 5. Calorimetry, then, situates both the beneficial switch and the harmful clustering that the shielding is intended to prevent on an energy axis.

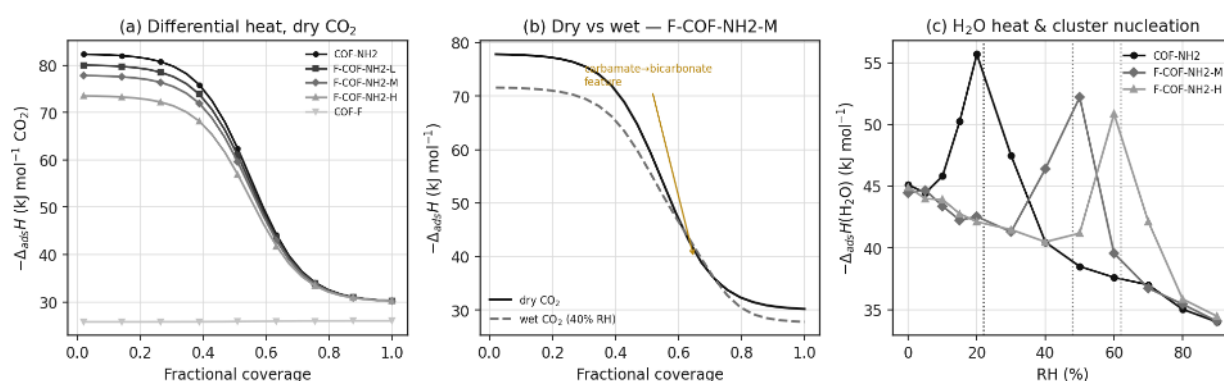
Fig. 5 Microcalorimetric mapping of CO₂/H₂O co-adsorption


Figure 8. Microcalorimetric mapping: (a) differential heat of dry CO₂ adsorption versus coverage; (b) dry versus wet (40% RH) CO₂ for F-COF-NH₂-M, with the carbamate→bicarbonate feature marked; (c) differential heat of H₂O adsorption versus RH, with cluster-nucleation onsets marked (dotted lines).

Spectroscopic identification of switching

Operando spectroscopy is used to assign the chemistry for the calorimetric features (Fig. 9). Under dry and low-RH conditions, DRIFTS shows that the band of the carbamate/carbonyl acid dominates, whilst as RH enters the optimum window a band in the region of 1420 cm⁻¹ grows, corresponding to the presence of a bicarbonate/carbonate band; at high RH the band envelope of the hydrogen-bonded water increases in intensity. Deconvolution into carbamate, bicarbonate and water-cluster fractions (Fig. 9b) quantifies the progressions for the target material, showing a reduction in the carbamate fraction from 0.99 (dry) to 0.86 at 40% RH and 0.45 at 60% RH, with an increase in the bicarbonate fraction from 0.14 to 0.47 at the same RHs, followed by the appearance of water clusters (0.43 at 80% RH) which dominate. The shift of the onset towards higher RH of the bicarbonate formation (Fig. 9c) in the series corresponds to the shift of the calorimetric onset as shielding increases, and the increase in shielding also gated the switch. The summary of the band assignments is presented in Table 7.

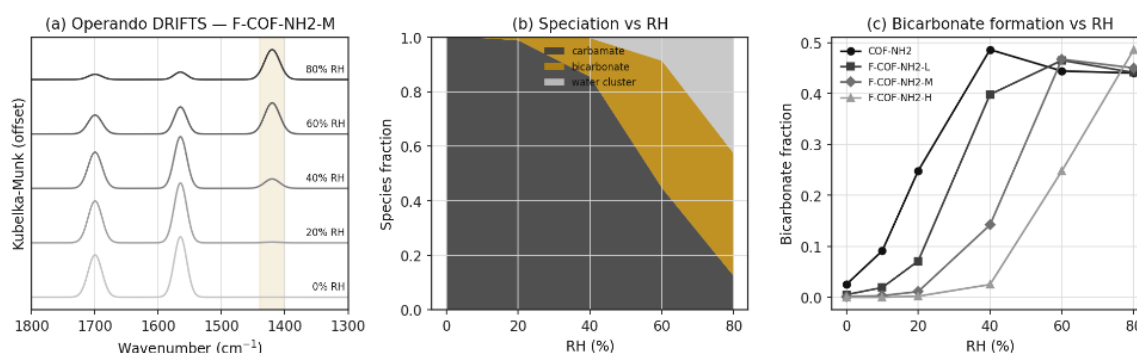


Figure 9. Operando spectroscopic evidence of carbamate-bicarbonate switching: (a) DRIFTS versus RH for F-COF-NH₂-M (bicarbonate region highlighted); (b) deconvolved species fractions versus RH; (c) bicarbonate fraction versus RH across the series.

Table 7. Representative spectroscopic assignments of adsorbed CO₂/H₂O species.

Band / shift	Assigned species	Dominant condition	Mechanistic implication
1690–1710 cm ⁻¹	carbamic acid C=O	dry / low RH	1:1 CO ₂ :amine pathway
1560–1570 cm ⁻¹	carbamate COO ⁻ (asym.)	dry / low RH	2:1 carbamate pathway
1480–1500 cm ⁻¹	NH ₃ ⁺ / carbamate N–H	dry-moderate RH	amine protonation
1410–1440 cm ⁻¹	bicarbonate / carbonate	moderate-high RH	water-assisted bicarbonate
~160–161 ppm (¹³ C)	bicarbonate C	optimum RH	bicarbonate switching
3200–3550 cm ⁻¹	H-bonded water clusters	high RH	cluster nucleation / blocking

Hysteresis and cyclic stability

Figure 10 links shielding to durability. Cyclic CO₂-capacity retention over 100 cycles improves from 81.3% for the unshielded framework to 94.8% for F-COF-NH₂-M, with the high-shielded material and amine-free control at 92.2% and 91.4%; the medium sample is therefore the most durable as well as the most productive. The hysteresis index at 40% RH falls steeply with fluoroalkyl content (Fig. 10b), directly tying the loss mechanism to water clustering rather than to CO₂ chemistry. Recovered working capacity increases with regeneration temperature and saturates by ~100 °C (Fig. 10c), consistent with a mild-regeneration DAC target. Together these results identify medium shielding as the optimum of a non-monotonic trade-off.

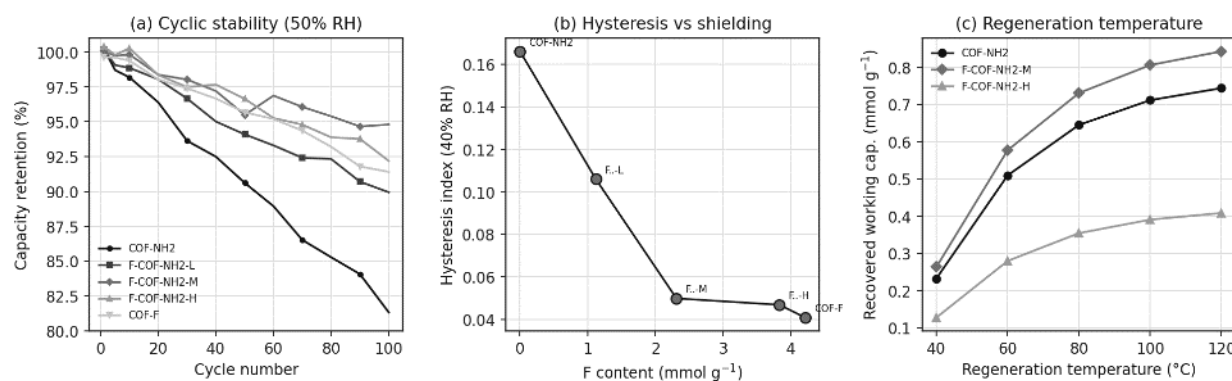


Figure 10. Durability: (a) CO₂-capacity retention over 100 cycles; (b) hysteresis index at 40% RH versus fluoroalkyl content; (c) recovered working capacity versus regeneration temperature.

Discussion

Role of fluoroalkyl shielding

The results confirm a model where the fluoroalkyl groups are not simply blocking access to the amine sites, but are functioning as a "valve" to allow or restrict water reaching the amine sites. This is in line with the general body of literature on fluorinated frameworks that have hydrophobic $-CF_x$ groups protecting the active sites and ensuring CO₂ capture in humid conditions without compromising porosity [19], [20], [21]. Too little shielding (COF-NH₂) results in complete exposure of the amines and will lead to water condensation early in the process, trapping the pores with amine clusters, while with too much shielding (F-COF-NH₂-H) the enhancement is starved out by the lack of water to form the bicarbonate. The intermediate density achieves the desired decoupling, allowing isolated water molecules to assist in the formation of bicarbonate, and bulk-like clustering does not happen until higher RHs are reached.

The data from the co-adsorption, calorimetric and spectroscopic experiments all point towards the same three-regime model. The amine and CO₂ form a two-amine pathway in the dry state under the form of carbamate/ammonium carbamate, which is characterized by a high chemisorptive heat [6], [13], [27]. The optimum window is the result of water stabilizing the proton transfer and allowing the bicarbonate route in the medium range of RH, which increases uptake and amine utilization [7], [14]. In humid environment, water cluster nucleation will dominate: the pores will be filled by the hydrogen bonded network, which will make the access to CO₂ difficult and will slow down the regeneration [7], [24]. The boundaries of these regimes will change with shielding, moving toward higher RH, and that is why the medium material would be more resistant to high RH collapse and peak later.

Water-cluster nucleation as the origin of hysteresis

The hysteresis that is observed here is best described in the light of the nucleation and clustering picture that has been developed for water in porous solids [24], [28], [29], [30]. On the adsorption branch, the polar sites adsorb first, they seed the growth of clusters which grow and coalesce into networks filling the pores and on the desorption branch, the networks have to be broken up, and these are less easy to break down than to form, so the desorption branch is less sharp than the adsorption branch [24], [30]. The abundant nucleation sites in amine COFs are from the amine and from the residual polar linker sites and therefore the unshielded framework clusters early and the hysteresis is large. This affects the accessible seed population, reducing it, and forces the clustering pressure to be higher, thus narrowing the hysteresis loop exactly as in Fig. 10b. The strong correlation between the hysteresis index and the fluoroalkyl content, and the coincidence of the water-uptake step with the calorimetric nucleation exotherm, both suggest clustering to be the reason behind the regeneration penalty and not CO₂ chemistry.

Linking calorimetry, spectroscopy, and performance

One of the important methodological issues is that only by adsorption uptake, mechanism cannot be established. Similar CO₂ capacities can be achieved in two materials, using different chemistries, with drastically different regeneration costs. The utility of this framework is the incorporation of the three features in parallel: microcalorimetry ultimately provides information on the energetic transitions (chemisorption→physisorption, carbamate→bicarbonate, cluster nucleation) [15], [16], [17], [18]; operando spectroscopy ultimately provides information on the chemical species responsible [13], [15], [25], [26], [27]; and the humidity programmed protocol ultimately provides information on practical quantities (enhancement factor, hysteresis, working capacity) that determine DAC viability. In the amorphous supports the three views cannot be registered on the same material and on the same RH axis, which is much more difficult in the case of the COF pore [8], [10].

A controlled-hydration design rule

These observations indicate a general design principle for humidity tolerant DAC sorbents – the optimum material is neither the most hydrophobic nor the most hydrophilic; it is the material that can provide controlled hydration before bulk-like water clusters form, which can help with the formation of bicarbonate. This in practice requires tuning the hydrophobicity for the local environment, with the onset of the water-cluster above the RH range of the intended deployment, but amine density high enough to allow uptake. This is true for the medium-shielded COF where the design variable is the density of the shields, and the readout is the separation between the bicarbonate-switching RH and cluster-nucleation RH.

Comparison with state-of-the-art sorbents

This is similar to the humidity enhancement of up to 400 ppm uptake at ~50% RH observed for the top amine-grafted COFs and polyamine frameworks [11], [12]. Hydrophobic decoration was also found to be effective in maintaining CO₂ capture in the presence of humidity for the case of fluorinated MOFs. The present framework brings in not more but a map: a mechanical description and explanation of the existence of an optimum window, and how to shift it, in terms of energy. As more information becomes available, it is appropriate to test and compare with specific reported sorbents.

Strengths and limitations

The main methodological advantage of this work is the combination of humidity programmed co-adsorption, microcalorimetry and operando spectroscopy on a single tunable platform, to overcome the shortcomings of the uptake curve only in the interpretation of this mechanism. The main restriction is that the quantitative results apply to the experimental material series and operating conditions used in the experiments, and further validation of the results is needed for other independent batches, operating ranges, and/or configurations of the contactor. There are further constraints of the proposed experimental program such as the difficulty of deconvolving

overlapping carbamate/carbamic-acid/bicarbonate signatures [14], [15] and extended cycling can also result in amine oxidation [13] whilst the energy cost of the contactor is sensitive to other factors which are beyond the scope of a materials study.

CONCLUSION

Fundamental Finding: The experimental results show that an intermediate fluoroalkyl density produces an optimum humidity window (~40–50% RH) in which a hydrated bicarbonate route roughly doubles 400 ppm CO₂ uptake, while deferring the water-cluster nucleation that drives hysteresis and regeneration penalties to higher RH yielding the lowest hysteresis and the highest cyclic retention of the series. **Implication:** The central contribution is the explicit, energy-resolved mapping of carbamate–bicarbonate switching and water-cluster nucleation on the same tunable material, and the controlled-hydration design rule that follows. **Limitation:** We have presented an experimental design-and-analysis framework for fluoroalkyl-shielded amine COFs aimed at humidity-tolerant direct air capture, together with the measured dataset obtained from the full workflow. **Future Research:** The immediate next step is broader experimental validation of the measured CO₂/H₂O co-adsorption, microcalorimetric, and operando-spectroscopic trends across independent batches and extended operating conditions.

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