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¹ Water Enables Efficient CO₂ Capture from Natural Gas Flue ² Emissions in an Oxidation-Resistant Diamine-Appended Metal-**Organic Framework**

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ABSTRACT: Supported by increasingly available reserves, 14 natural gas is achieving greater adoption as a cleaner-burning 15 alternative to coal in the power sector. As a result, carbon 16 capture and sequestration from natural gas-fired power plants is 17 an attractive strategy to mitigate global anthropogenic CO_2 18 emissions. However, the separation of CO₂ from other 19 20 components in the flue streams of gas-fired power plants is particularly challenging due to the low CO₂ partial pressure 21 2.2 $(\sim 40 \text{ mbar})$, which necessitates that candidate separation materials bind CO₂ strongly at low partial pressures (≤ 4 mbar) 23 to capture \geq 90% of the emitted CO₂. High partial pressures of 24 O_2 (120 mbar) and water (80 mbar) in these flue streams have 25 also presented significant barriers to the deployment of new 26



we demonstrate that functionalization of the metal-organic framework $Mg_2(dobpdc)$ (dobpdc⁴⁻ = 4,4'-dioxidobiphenyl-3,3'-28 dicarboxylate) with the cyclic diamine 2-(aminomethyl)piperidine (2-ampd) produces an adsorbent that is capable of \geq 90% 29 CO₂ capture from a humid natural gas flue emission stream, as confirmed by breakthrough measurements. This material 30 captures CO_2 by a cooperative mechanism that enables access to a large CO_2 cycling capacity with a small temperature swing 31 (2.4 mmol CO₂/g with $\Delta T \ge 100$ °C). Significantly, multicomponent adsorption experiments, infrared spectroscopy, magic 32 angle spinning solid-state NMR spectroscopy, and van der Waals-corrected density functional theory studies suggest that water 33 enhances CO_2 capture in 2-ampd-Mg₂(dobpdc) through hydrogen-bonding interactions with the carbamate groups of the 34 ammonium carbamate chains formed upon CO_2 adsorption, thereby increasing the thermodynamic driving force for CO_2 35 binding. In light of the exceptional thermal and oxidative stability of 2-ampd-Mg₂(dobpdc), its high CO₂ adsorption capacity, 36 and its high CO_2 capture rate from a simulated natural gas flue emission stream, this material is one of the most promising 37

adsorbents to date for this important separation. 38

INTRODUCTION 39

40 The combustion of fossil fuels in the energy sector is currently 41 responsible for the release of 32 Gt/year of CO₂ into the 42 atmosphere, or approximately 65% of annual anthropogenic 43 greenhouse gas emissions.^{1,2} To limit the contribution of these 44 emissions to global climate change, mitigation strategies are 45 needed during the transition to cleaner fuel sources.² One of 46 the most widely studied emission mitigation strategies is 47 postcombustion carbon capture and sequestration (CCS), in 48 which CO₂ is selectively removed from the flue gas streams of

fossil fuel- or biomass-fired power plants and sequestered 49 underground.¹⁻⁴ To date, the large majority of efforts toward 50 implementing CCS have focused on coal-fired power plants, 51 which are currently responsible for approximately 45% of 52 energy-related CO₂ emissions.^{4,5} However, global consump- 53 tion of natural gas has been increasing steadily, and its 54 contribution to global primary energy is anticipated to overtake 55

⁵⁶ that of coal by 2040 (New Policy Scenario, International ⁵⁷ Energy Agency).⁶ Furthermore, in economies where natural ⁵⁸ gas is prevalent, such as that of the United States, the rapid ⁵⁹ transition away from coal has resulted in CO_2 emissions from ⁶⁰ the combustion of natural gas already exceeding those from ⁶¹ coal, despite the fact that natural gas emits approximately half ⁶² as much CO_2 as coal per unit electricity produced.⁷ Therefore, ⁶³ new materials are urgently needed for the selective removal of ⁶⁴ CO_2 from the emissions of natural gas-fired power plants.^{8–10}

The flue gas stream produced at a natural gas combined 65 66 cycle (NGCC) power plant consists of approximately 74.4% 67 N₂, 12.4% O₂, 8.4% H₂O, 3.9% CO₂, and 0.9% Ar.¹¹ 68 Importantly, emissions from NGCC plants contain fewer 69 pollutants than emission streams from coal-fired plants, which 70 release SO_x, NO_x, heavy metals, and particulate matter.¹¹ 71 These contaminants pose environmental hazards and serve as 72 significant barriers to the deployment of CCS systems in coal-73 fired plants, particularly due to the known poisoning of a 74 number of CO_2 capture materials by SO_x and NO_x .^{12–19} The 75 CO2 partial pressure of NGCC flue gas (~40 mbar) is also 76 significantly lower than that of coal flue gas (\sim 150 mbar).¹¹ As 77 a result, gas-fired plants are cleaner-burning than coal-fired 78 plants, but CO_2 capture from the emissions of these power 79 stations is more technically challenging. Specifically, the U.S. 80 Department of Energy (DoE) has set a target of 90% capture ¹¹ s1 of CO_2 from the emission stream, ¹¹ requiring that candidate ¹² CO_2 capture materials bind CO_2 at concentrations as low as 83 0.4%. Materials that meet this requirement often possess high 20 adsorption enthalpies, 20 necessitating energy-intensive 85 cycling conditions and generating a potential trade-off between 86 heat management and CO₂ cycling capacity.²¹

⁸⁷ Owing to decades of development, aqueous amine solutions ⁸⁸ are the most technology-ready systems for large-scale CO₂ ⁸⁹ capture applications.^{22,23} However, amine solutions face ⁹⁰ technological barriers to deployment for CO₂ capture from ⁹¹ NGCC power plants due to their high regeneration energy ⁹² costs and susceptibility to oxidative and thermal degrada-⁹³ tion.^{24–27} As an alternative, solid adsorbents, such as zeolites, ⁹⁴ amine-functionalized silicas, porous organic networks, and ⁹⁵ metal–organic frameworks, may offer enhanced stability, ⁹⁶ greater CO₂ cycling capacities, and inherently lower regener-⁹⁷ ation energies.^{4,28–40} Despite the flourishing research areas of ⁹⁸ adsorptive CO₂ capture from coal flue gas and air, only a ⁹⁹ handful of reports have yet explored adsorbent design ¹⁰⁰ specifically for CCS from gas-fired power plants.^{36,41–48} ¹⁰¹ More research is also needed to design adsorbents with high ¹⁰² thermal and oxidative stabilities that can capture CO₂ ¹⁰³ selectively under humid conditions.

¹⁰³ selectively under humid conditions. ¹⁰⁴ Recently, we^{49–53} and others^{45,54–58} have demonstrated the ¹⁰⁵ potential of diamine-appended variants of the metal–organic ¹⁰⁶ framework Mg₂(dobpdc) (dobpdc^{4–} = 4,4'-dioxidobiphenyl-¹⁰⁷ 3,3'-dicarboxylate) as transformative materials for carbon ¹⁰⁸ capture applications.⁵⁹ The unique step-shaped adsorption ¹⁰⁹ profiles of these frameworks enable cycling of the full CO₂ ¹¹⁰ adsorption capacity with minimal temperature swings. We have ¹¹¹ further shown that the adsorption step of these materials can ¹¹² be tuned postsynthetically by changing the appended ¹¹³ diamine,⁵¹ a strategy that we employed to optimize an ¹¹⁴ adsorbent for CO₂ capture from coal flue gas.⁵² Our previous ¹¹⁵ work posited that *primary, secondary* (1°/2°) diamine-¹¹⁶ appended variants of Mg₂(dobpdc) are likely the most ¹¹⁷ promising for CO₂ capture from NGCC flue gas, on the ¹¹⁸ basis of their low CO₂ adsorption step pressures (<1 mbar at 40 °C) and minimal hysteresis upon CO₂ desorption.⁵¹ 119 However, these materials possess a trade-off between thermal 120 stability and CO₂ adsorption capacity. Specifically, the largest 121 $1^{\circ}/2^{\circ}$ diamines were the most resistant to amine volatilization 122 during temperature-swing cycling but also underwent a steric 123 rearrangement at half saturation $(0.5 \text{ CO}_2 \text{ per diamine})$, which 124 led to double-stepped CO₂ adsorption profiles.⁵³ As a result, at 125 the low partial pressures relevant for NGCC CCS systems, 126 only the capacity of the first CO₂ adsorption step (half of the 127 theoretical capacity) would be accessible with such materials. 128 While two similar base frameworks were shown to resolve the 129 issue of steric crowding to enable single-step adsorption 130 profiles with large diamines,⁵³ the initially studied 131 $Mg_2(dobpdc)(diamine)_2$ variants remain preferable due to 132 their inexpensive components and favorable gravimetric 133 $(\sim 3.5-4.0 \text{ mmol/g})$ and volumetric $(\sim 79-84 \text{ v/v})$ CO₂ 134 adsorption capacities.⁵¹ Additionally, Mg₂(dobpdc) has already 135 been prepared at the multikilogram scale,⁶⁰ facilitating rapid 136 technology development. 137

Herein, we demonstrate that appending the cyclic $1^{\circ}/2^{\circ}$ ¹³⁸ diamine 2-(aminomethyl)piperidine (2-ampd) to the metal ¹³⁹ sites in Mg₂(dobpdc) alters the steric interactions and ¹⁴⁰ thermodynamics of CO₂ adsorption, giving rise to a material ¹⁴¹ with two closely spaced adsorption steps. The adsorbent 2- ¹⁴² ampd-Mg₂(dobpdc) (Figure 1) is thermally stable and ¹⁴³ fill exhibits two CO₂ adsorption steps at pressures low enough ¹⁴⁴ to access the full chemisorptive capacity of the material (1 CO₂ ¹⁴⁵ per diamine) from NGCC flue gas. Importantly, we find that ¹⁴⁶



Figure 1. (a) Single-crystal X-ray diffraction structure of toluenesolvated 2-ampd– $Zn_2(dobpdc)$, which is isostructural to 2-ampd– Mg₂(dobpdc). The left-handed diamine is depicted in the righthanded framework (space group P3₁21). The structure was refined with a racemic mixture of 2-ampd in an inversion-twinned crystal. The enantiomeric diamine and toluene solvent molecules are omitted for clarity. (b) Chemical structures of the ligand dobpdc^{4–} and the diamine 2-ampd. (c) First coordination sphere of the Zn(II) site depicting coordination of the left-handed enantiomer of 2-ampd. The diamines were found to coordinate exclusively through the primary amine. Light blue, blue, red, gray, and white spheres represent Zn, N, O, C, and H atoms, respectively.

147 the presence of water greatly improves the CO₂ adsorption 148 characteristics of this material, enabling it to achieve \geq 90% 149 removal of CO₂ from simulated NGCC flue gas in break-150 through measurements. While other amine-functionalized 151 adsorbents have shown improvements in CO₂ capture 152 performance due to a humidity-induced mechanistic shift, 153 our van der Waals (vdW)-corrected density functional theory 154 (DFT) calculations and spectroscopy measurements show that 155 the improved performance of 2-ampd-Mg₂(dobpdc) under 156 humid conditions can instead be attributed to preferential 157 stabilization of the ammonium carbamate chains formed upon 158 CO₂ insertion. Our results demonstrate that 2-ampd-159 Mg₂(dobpdc) is among the most promising adsorbents 160 identified to date for this underexplored but extremely 161 important separation.

162 **EXPERIMENTAL SECTION**

General Procedures. ¹H NMR spectra were collected on a 163 164 Bruker AMX 300 MHz spectrometer and referenced to residual 165 dimethyl sulfoxide (δ = 2.50 ppm). Powder X-ray diffraction (PXRD) 166 patterns were collected with a laboratory Bruker AXS D8 Advance 167 diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å) or at the 168 Advanced Photon Source with synchrotron radiation ($\lambda = 0.45399$ Å), 169 as specified in the figure captions. Additional details for synchrotron 170 PXRD experiments under controlled atmospheres are given in 171 Supporting Information (SI) Section S15. All synthetic manipulations 172 were carried out under air unless noted otherwise. All solvents and 173 reagents, including diamines, were purchased from commercial sources and used without further purification unless otherwise 174 175 noted. The linker H₄ dobpdc was purchased from Hangzhou Trylead 176 Chemical Technology Co. The linker H₄ dotpdc was prepared 177 according to the literature procedure.⁵³ The metal-organic frame-178 works $Mg_2(dobpdc)$,⁵¹ $Mn_2(dobpdc)$,⁵² $Ni_2(dobpdc)$,⁵² 179 Co₂(dobpdc),⁵² Zn₂(dobpdc),⁶¹ and Mg₂(dotpdc)⁵³ were prepared 180 according to literature procedures (SI Section S1). Ultrahigh purity (>99.998%) gases were used for all adsorption experiments. 181

Infrared Spectra. Attenuated total reflectance (ATR) infrared 183 (IR) spectra were collected on a PerkinElmer Spectrum 400 Fourier 184 Transform (FT) IR spectrometer equipped with a Pike GladiATR and 185 a home-built glovebag accessory used to control the atmosphere. 186 Three vacuum–refill cycles were used to exchange the atmosphere of 187 the glovebag accessory when preparing the system for in situ 188 experiments. For humid FTIR spectra, samples were placed in 4 mL 189 vials and sealed in a 20 mL vapor-dosing chamber containing ~4 mL 190 of water. After at least 15 min of equilibration, the powder was 191 removed, and spectra were collected. Co-adsorption of water in the 192 sample was confirmed by observation of the H₂O IR vibrational bands 193 at 1638 and 3350 (broad) cm^{-1.62}

Diamine Grafting Procedure.⁵¹ A 20 mL scintillation vial was 194 195 charged with toluene (4 mL) and 2-ampd (1 mL). Methanol-solvated 196 Mg₂(dobpdc) (~15 mg) was filtered and washed with toluene (2 \times 197 10 mL). (Note: Mg₂(dobpdc) should not be allowed to dry 198 completely in air due to potential decomposition.⁴⁹) The filter-dried 199 Mg₂(dobpdc) was added to the diamine solution, and the vial was 200 swirled several times and allowed to stand at room temperature for at 201 least 12 h. After this time, the mixture was filtered, and the resulting powder was washed with toluene $(3 \times 20 \text{ mL})$ and allowed to dry for 2.02 203 ~3 min under reduced pressure, yielding ~25 mg of toluene-solvated 204 2-ampd-Mg₂(dobpdc). Other diamine-appended metal-organic 205 frameworks described in this work were prepared using a similar 206 procedure. Full characterization of all new diamine-appended 207 frameworks prepared as part of this work, including PXRD patterns, 208 IR spectra, dry N2 thermogravimetric decomposition profiles, and 209 CO₂ adsorption/desorption isobars, are included in the SI. Diamine 210 loadings were determined by suspending ~5 mg of the diamine-211 appended metal-organic framework in 0.5 mL of DMSO-d₆ and then 212 digesting the framework by adding several drops of DCl (35 wt % in $213 D_2O$) and heating until the mixture became homogeneous. The

resulting solutions were analyzed by ¹H NMR spectroscopy to 214 determine the ratio of diamine to organic linker. Representative 215 diamine loadings for all diamine-appended metal—organic frameworks 216 prepared as part of this work are included in the SI. 217

Thermogravimetric Analysis and Cycling Measurements. 218 Dry thermogravimetric analysis (TGA) experiments were conducted 219 using a TA Instruments TGA Q5000. Humid TGA experiments were 220 conducted using a TA Instruments TGA Q50. For humid experi- 221 ments, the incident gas stream was passed through two room- 222 temperature water bubblers in series, leading to an estimated water 223 content of 2.6%, as determined by comparison to the water isotherms 224 of 2-ampd $-Mg_2(dobpdc)$ (Figure S11). Premixed cylinders of CO₂ in 225 N2 were obtained from Praxair. Samples were activated under flowing 226 N_2 for 20-30 min until the mass stabilized; exact activation 227 conditions for each diamine-appended material were determined 228 through careful analysis of the dry N2 thermal decomposition profiles 229 and are included in the SI. Masses are uncorrected for buoyancy 230 effects. A flow rate of 25 mL/min was used for all TGA experiments. 231 Ramp rates for all isobaric measurements are included in figure 232 captions. A ramp rate of 1.5 °C/min was employed for all dry N2 233 decomposition experiments. 234

Gas Adsorption Measurements. Volumetric adsorption iso- 235 therms for N₂, O₂, and CO₂ were obtained using a Micromeritics 236 ASAP 2020 gas adsorption analyzer. Adsorption isotherms for water 237 were obtained using a Micromeritics 3Flex instrument. For water 238 isotherms, the stainless-steel vapor dosing apparatus was subjected to 239 three freeze-pump-thaw cycles to remove any dissolved gases, and 240 heat tape was used to keep the exposed portion of the glass sample 241 tube at elevated temperature to prevent condensation of water. The 242 maximum relative humidity accessible in measurements with water 243 was limited by the manifold temperature of 45 °C. Isotherms 244 collected at 40, 50, and 60 °C were measured using a circulating water 245 bath to control the sample temperature. Surface area measurements 246 with N₂ were carried out at 77 K using a liquid N₂ bath. Samples were 247 regenerated at 100 °C under reduced pressure (<10 μ bar) for 2–4 h 248 between isotherms. The isotherm data points were considered 249 equilibrated after <0.01% change in pressure occurred over an 250 average of 11 intervals of 15 s (for N2, O2, and CO2) or 30 s (for 251 H₂O). 252

Calculation of Differential Enthalpies and Entropies of 253 Adsorption. Using a linear spline interpolation method and the CO₂ 254 adsorption isotherms for 2-ampd-Mg₂(dobpdc) (Figure S7), the 255 exact pressures (p_q) corresponding to specific CO₂ loadings (q) were 256 determined at different temperatures (T). The Clausius-Clapeyron 257 relationship (eq 1) was used to calculate the differential enthalpies of 258 adsorption (Δh_{ads}) based on the slopes of the linear trendlines fit to 259 ln(p_q) vs 1/T (Figure S8). The y-intercepts of these linear trendlines 260 are equal to $-\Delta s_{ads}/R$ at each loading (assuming $p_0 = 1$ bar)⁶³ and 261 thus were used to determine the corresponding differential entropies 262 of adsorption (Figure S9).

$$\ln(p_q) = \left(\frac{\Delta h_{ads}}{R}\right) \left(\frac{1}{T}\right) + c \tag{1}_{264}$$

Breakthrough Measurements. See SI Section S11 for 265 experimental details and SI figures. 266

Solid-State Magic Angle Spinning (MAS) NMR Experiments. 267 Activation of 2-ampd–Mg₂(dobpdc) was carried out under flowing 268 N₂ at 150 °C for 30 min. The activated material was packed into a 3.2 269 mm rotor inside a N₂-filled glovebag and further activated under 270 vacuum inside a home-built gas manifold for 10 min at room 271 temperature. This manifold has the key feature of enabling gas dosing 272 of rotors at controlled pressures and subsequent sealing of dosed 273 rotors prior to removal from the manifold.⁶¹ Samples were dosed with 274 ¹³CO₂ gas (Sigma-Aldrich, 99 atom % ¹³C, < 3 atom % ¹⁸O) at room 275 temperature (~22 °C) and allowed to equilibrate for 30 min prior to 276 measurements, unless otherwise specified. For dosing with humid 277 CO₂, a sample that had already been dosed with dry ¹³CO₂ was 278 opened (the top and bottom rotor caps were removed), and the 279 sample was placed in a gas stream of humid CO₂ (relative humidity 280 281 ~70%, measured using a ThermoPro TP50 Hygrometer) that was 282 generated by flowing natural isotopic abundance CO_2 through a 283 bubbler containing deionized water for 1 h.

All solid-state NMR experiments were carried out at 16.4 T using a 284 285 Bruker 3.2 mm probe, and MAS rates were 15 kHz in all cases. All 286 solid-state ¹³C NMR spectra were acquired by cross-polarization from 287 ¹H (¹⁵N and ¹H contact RF field strengths of 20 kHz and 35 kHz, 288 respectively). All cross-polarization experiments were acquired with 289 continuous wave ¹H decoupling at 82 kHz RF field strength, and with 290 the contact times stated in the figure captions. All ¹H NMR spectra 291 were acquired using a 90° pulse-acquire sequence with a RF field 292 strength of ~38 kHz, and recycle delays were adjusted to obtain 293 quantitative spectra. The ¹H, ¹³C, and ¹⁵N chemical shifts were referenced to 1.8 ppm (adamantane), 38.5 ppm (adamantane tertiary 2.94 carbon, left-hand resonance), and 33.4 ppm (glycine), respectively. 295 Single-Crystal X-ray Diffraction. Synthetic and experimental 296 details for single-crystal X-ray diffraction experiments with 2-ampd-297 298 Zn₂(dobpdc) and molecular 2-ampd-CO₂ are included in SI Sections 299 S12-S14.

Density Functional Theory Calculations. Our first-principles 300 301 DFT calculations used a plane-wave basis and projector augmented-302 wave (PAW)^{65,66} pseudopotentials with the Vienna ab initio 303 Simulation Package $(VASP)^{67-70}$ code. To include the effect of the 304 vdW dispersive interactions on binding energies and NMR chemical 305 shifts, we performed structural relaxations with vdW dispersion-306 corrected functionals (vdW-DF2)⁷¹ as implemented in VASP. For all 307 calculations, we used (i) a Γ -point sampling of the Brillouin zone 308 (except for NMR calculations, as specified below), (ii) a 1000 eV 309 plane-wave cutoff energy, and (iii) a 10^{-7} eV self-consistency 310 criterion. We explicitly treat two valence electrons for Mg $(3s^2)$, six 311 for O $(2s^22p^4)$, five for N $(2s^22p^3)$, four for C $(2s^22p^2)$, and one for H 312 (1s¹). All structural relaxations were performed with a Gaussian 313 smearing of 0.05 eV.⁷² The ions were relaxed until the Hellmann-314 Feynman forces were less than 0.001 eVÅ⁻¹. To compute CO₂ and 315 H₂O binding energies, we optimized the structure of 2-ampd-316 Mg₂(dobpdc) prior to CO₂ and H₂O adsorption ($E_{ampd-MOF}$), 317 interacting with CO₂ and H₂O in the gas phase ($E_{CO2/H2O}$) within 318 a $15 \times 15 \times 15$ Å³ cubic supercell, and 2-ampd-Mg₂(dobpdc) with 319 adsorbed CO₂ and H₂O molecules ($E_{CO2-ampd-MOF}$) using vdW-320 corrected DFT. The binding energies (E_B) were obtained via the 321 difference:

$$E_{\rm B} = E_{\rm CO_2-ampd-MOF} - (E_{\rm ampd-MOF} + E_{\rm CO_2/H_2O})$$
(2)

323 For NMR simulations, we used a $1 \times 1 \times 3$ k-point. With this k-point, 324 the isotropic chemical shielding values (δ_{iso}) converged to 0.1 ppm. 325 Since the isotropic chemical shift (δ_{iso}) is obtained from $\delta_{iso} = -(\delta_{iso})$ 326 $-\delta_{ref}$) where δ_{ref} is a reference value, we needed to determine a δ_{ref} 327 value by comparing experimental δ_{iso} values to calculated δ_{iso} values. 328 The σ_{ref} values for ¹H (31.4 ppm) and ¹³C (160.1 ppm) were 329 obtained by first computing σ_{iso} values for cocaine (CSD refcode 330 COCAIN10 was used as the starting point, and the structure was 331 geometry optimized before NMR calculation; see SI for coordinates). 332 The computed values were then compared with experimental values 333 (Table S18, Figure S94).⁷³ The σ_{ref} value for ¹⁵N (215.9 ppm) was 334 determined by comparison of DFT-calculated σ_{iso} and the 335 experimental δ_{iso} value for glycine (Table S18).⁶¹ Additional DFT 336 figures and details are included in SI Section S21.

337 **RESULTS AND DISCUSSION**

Adsorbent Design for NGCC Post-Combustion Cap-339 ture. Our previous crystallographic and gas adsorption studies 340 of 1°,2° diamine-appended Mg₂(dobpdc) indicated that 341 unfavorable chain—chain interactions in the *ab* plane of the 342 framework give rise to the two-step adsorption profiles of these 343 materials.⁵³ We reasoned that tethering the alkyl chain to the 344 backbone of the diamine should alleviate these steric 345 interactions, thereby minimizing the gap between the two 346 CO₂ adsorption steps and enabling access to the full theoretical adsorption capacity. Accordingly, we grafted racemic 2- $_{347}$ (aminomethyl)piperidine (2-ampd, Figure 1b) to $_{348}$ Mg₂(dobpdc) using our previously reported procedure⁵¹ to $_{349}$ produce the adsorbent 2-ampd-Mg₂(dobpdc). Consistent $_{350}$ with our hypothesis, this material exhibits two closely spaced $_{351}$ steps in its CO₂ adsorption isotherms (occurring at 1.0 and 3.7 $_{352}$ mbar at 40 °C, respectively; see Figure 2). Importantly, both $_{353}$ f2



Figure 2. Pure CO₂ adsorption isotherms at 40, 50, and 60 °C (purple, blue, and red circles, respectively), and for O₂ (red triangles) and N₂ (blue squares) at 40 °C, for 2-ampd–Mg₂(dobpdc). The dashed black line indicates the approximate partial pressure of CO₂ in flue gas from a NGCC power plant (40 mbar).

steps occur at pressures low enough to facilitate \geq 90% removal 354 of CO₂ (residual pressure of \leq 4 mbar) from NGCC flue 355 emissions under idealized, equilibrium conditions at 40 °C. In 356 contrast, variants of Mg₂(dobpdc) functionalized with 357 diamines bearing long alkyl substituents, such as *N*-(*n*- 358 hexyl)ethylenediamine (*n*Hex-2),⁵³ have two widely spaced 359 CO₂ adsorption steps, restricting the quantity of CO₂ that can 360 be captured to the capacity of the lower-pressure step (~1.8 361 mmol/g at 40 mbar and 40 °C for *n*Hex-2, in contrast to 3.47 362 mmol/g for 2-ampd under the same conditions; Figure S16). 363

We hypothesize that step-shaped CO2 adsorption in 2- 364 ampd-Mg₂(dobpdc) arises as a result of cooperative insertion 365 of CO2 into the metal-amine bonds to form chains of 366 ammonium carbamate running along the pore axis, as reported 367 previously for related alkylethylenediamine-appended frame- 368 works.⁴⁹⁻⁵⁸ This conclusion is supported by spectroscopic 369 characterization (discussed below) and by the observed metal 370 dependence of the cooperative adsorption step position⁵⁰ for 371 2-ampd- M_2 (dobpdc) variants (M = Mg, Mn, Ni, Co, Zn; 372 Figure S85). In addition, appending 2-ampd within the 373 expanded terephenyl framework Mg₂(dotpdc) (dotpdc⁴⁻ = 374 4,4"-dioxido-[1,1':4',1''-terphenyl]-3,3''-dicarboxylate) produ- 375 ces an adsorbent with only one step in its CO₂ adsorption 376 isobar (Figure S21), confirming that the two adsorption steps 377 observed for 2-ampd-Mg₂(dobpdc) also arise from steric 378 interactions between adjacent diamines in the framework (SI 379 Section S4). Importantly, 2-ampd-Mg₂(dobpdc) possesses 380 comparable or superior thermal stability to all other $1^{\circ}/2^{\circ}$ 381 diamine-appended variants of Mg₂(dobpdc) evaluated to date 382 (Figure S6), withstanding 12 h of exposure to flowing, humid 383 CO₂ at a regeneration temperature of 140 °C (or even as high 384 as 180 °C) with minimal diamine volatilization (Table S15, see 385 also discussion below). Therefore, the cyclic diamine 2-ampd 386 uniquely affords the best attributes achieved with $1^{\circ}/2^{\circ}$ 387

388 diamine-appended $Mg_2(dobpdc)$ materials to date, namely, 389 high thermal stability coupled with a high CO_2 adsorption 390 capacity from a NGCC flue gas stream.

The single crystal X-ray diffraction structure of the sy2 isostructural framework 2-ampd– $Zn_2(dobpdc)$ (Figure 1) sy3 provides insight into the thermal stability and close CO₂ sy4 adsorption steps of 2-ampd– $Mg_2(dobpdc)$. The bulky sy5 piperidine ring of 2-ampd can maintain a stable chair sy6 conformation in the pores of the framework, with efficient sy7 packing in the *ab* plane and minimization of unfavorable sy8 interactions between adjacent diamines. Consistently, despite sy9 the high density of amine groups within the pores, 2-ampd– 400 $Mg_2(dobpdc)$ exhibits a high Brunauer–Emmett–Teller 401 surface area of $618 \pm 2 m^2/g$ (Figure S4), which should 402 enable rapid diffusion of CO₂ through the channels of the 403 framework, even after CO₂ adsorption.

Single-Component Adsorption Experiments. Follow-404 405 ing validation of these initial design criteria, we investigated 406 additional properties relevant to the application of 2-ampd-407 Mg₂(dobpdc) in CO₂ capture from NGCC flue emissions. 408 Isothermal adsorption profiles were collected at 40, 50, and 60 $^{\circ}$ C for CO₂ and at 40 $^{\circ}$ C for N₂ and O₂ (Figure 2). For CO₂, 409 410 two adsorption steps were observed at all temperatures. Both 411 adsorption steps occur below 40 mbar even at 60 °C and are 412 predicted to be operative in this target pressure range up to 413 approximately 69 °C (Figure S14). Importantly, because 2-414 ampd-Mg₂(dobpdc) adsorbs minimal CO₂ at partial pressures 415 beneath the first step pressure, processes with higher 416 adsorption temperatures can be considered without sacrificing 417 CO₂ adsorption capacity, as would be expected for a typical 418 Langmuir-type adsorbent. Eliminating the need to adsorb at 419 the lowest possible temperature can potentially reduce process 420 costs through relaxed requirements for flue gas cooling,⁷ 421 minimization of water coadsorption,47 and/or enhanced 422 tolerance to temperature rise in the adsorbent bed upon 423 exothermic CO₂ adsorption.²¹ In addition, despite demonstrat-424 ing strong adsorption of CO₂ at low partial pressures, 2-ampd-425 Mg₂(dobpdc) can be fully regenerated by heating to only 140 426 °C under a flow of dry or humid CO₂ at atmospheric pressure 427 (Figure S37). Furthermore, at the partial pressures relevant to 428 natural gas flue emissions, 2-ampd-Mg₂(dobpdc) demon-429 strates excellent noncompetitive CO_2/N_2 and CO_2/O_2 430 selectivities of 1320 and 694, respectively (Table S1), which 431 are among the highest reported for a nonsize-selective metal– 432 organic framework. $^{31,35,75-78}$ Because N_2 and O_2 cannot 433 participate in the CO₂-selective cooperative adsorption 434 mechanism, these values are anticipated to be reflective of 435 the multicomponent performance of the material.

436 The thermodynamics of CO₂ adsorption in 2-ampd-437 Mg₂(dobpdc) were analyzed using the data in Figure 2. A 438 spline interpolation method was used to calculate lines of 439 constant loading for the set of CO₂ isotherms from 40 to 60 440 °C. Employing the Clausius-Clapeyron relationship yielded a 441 differential enthalpy of adsorption (Δh_{ads}) of -73 ± 2 kJ/mol 442 at a loading of 1 mmol/g (Figure S8), similar to that observed 443 for other diamine-appended variants of $Mg_2(dobpdc)^{50-52}$ and 444 smaller in magnitude than the low-coverage enthalpies 445 reported for silicas functionalized with primary or secondary 446 amines.⁷⁹ From this adsorption enthalpy, we calculated a 447 projected regeneration energy of 2.8 MJ/kg CO2 for a 448 temperature swing adsorption (TSA) process consisting of 449 capture from a 40 mbar stream of CO_2 at 40 °C and 450 desorption under 1 bar of CO₂ at 140 °C (see SI Section S3;

note that only CO_2 was considered in this calculation). This 451 value is over 30% lower than the regeneration energy projected 452 for a polyamine-functionalized silica for a similar process (3.9 453 MJ/kg CO_2 , see SI Section S3),⁴⁸ reflecting the advantage of 454 cooperative adsorbents for CO_2 capture applications. Fur- 455 thermore, with a higher adsorption temperature of 60 °C, an 456 even lower projected regeneration energy of 2.7 MJ/kg CO_2 457 may be possible for 2-ampd $-Mg_2$ (dobpdc) (considering only 458 CO_2 ; see Table S2). Notably, the thermodynamics of 459 adsorption for 2-ampd $-Mg_2$ (dobpdc) were found to adhere 460 to the same enthalpy–entropy correlation as other diamine-461 appended variants of Mg_2 (dobpdc)⁵¹ (Figure S15), corrobo-462 rating the formation of ammonium carbamate chains upon 463 CO_2 adsorption in this material.

Mixed-Gas Adsorption Experiments. While single- 465 component equilibrium data are needed to guide adsorbent 466 design and characterize fundamental adsorption properties, 467 multicomponent experiments are critical to evaluate adsorbent 468 performance under more realistic process conditions. To that 469 end, we performed extensive dry and humid thermogravimetric 470 experiments with 2-ampd-Mg₂(dobpdc) using CO_2/N_2 471 mixtures and simulated NGCC flue emission streams. When 472 exposed to a flow of dry simulated NGCC flue gas (4% CO₂ in 473 N₂) at atmospheric pressure, 2-ampd-Mg₂(dobpdc) exhibits a 474 high CO₂ capacity of 16.0 g/100 g (3.63 mmol/g) at 40 °C 475 (Figure 3a, purple curve), consistent with the predicted 476 f3 capacity of 3.66 mmol/g for adsorption of 1 CO₂ per diamine. 477 This adsorption capacity is significantly higher than that of 478 other cyclic diamine-appended variants of Mg₂(dobpdc) 479 (2.02-2.33 mmol/g, Figure S30), as well as the representative 480 amine-functionalized silica MCM-41-PEI-50^{80,81} (1.48 mmol/ 481 g, Figure S79) under equivalent conditions. However, for a dry 482 0.4% CO2 in N2 stream, representing the lowest adsorption 483 pressure (4 mbar CO₂) required for 90% capture of CO₂ from 484 NGCC emissions, the adsorption capacity at 40 °C (2.81 g/ 485 100 g, or 0.639 mmol/g, Figure 3a) is significantly lower than $_{486}$ that observed in the 40 $^{\circ}C$ pure CO₂ isotherm at the same 487 CO_2 partial pressure (2.76 mmol/g). Even with extremely slow 488 isobaric cooling rates, similar discrepancies in the threshold 489 conditions for cooperative adsorption have been observed 490 between CO₂ adsorption isobars (collected under flowing 491 CO_2/N_2 mixtures) and volumetric isotherms (collected under 492 pure CO_2 starting from vacuum).^{82,83} In general, the isobaric 493 measurements show lower isobaric step temperatures (equiv- 494 alent to higher isothermal step pressures) than would be 495 expected given the measured equilibrium adsorption iso- 496 therms. These results suggest a smaller thermodynamic driving 497 force for CO₂ capture under the more realistic, mixed-gas flow 498 conditions. Additionally, we found that the adsorption capacity 499 decreased when a faster cooling ramp rate (0.2 versus 0.1 °C/ 500 min) was employed, suggesting that the adsorption kinetics are 501 limited in streams with low CO₂ partial pressures (SI Section 502 S9). This result is consistent with a previous report 503 investigating the adsorption kinetics of the related material 504 mmen-Mg₂(dobpdc) (mmen = N,N'-dimethylethylenedi- 505 amine).⁸⁴ Ultimately, thermodynamic and kinetic factors 506 under process-relevant flow conditions indicate that 2- 507 ampd-Mg₂(dobpdc) falls short of achieving the target of 508 \geq 90% CO₂ capture from NGCC flue gas under *dry* conditions. 509

We also analyzed the ability of 2-ampd-Mg₂(dobpdc) to 510 capture CO_2 in the presence of water, which can constitute up 511 to ~8% of NGCC flue gas by volume. Humid isobars were 512 collected by flowing CO_2/N_2 mixtures through two room- 513



Figure 3. Dry (a) and humid (b, ~2.6% H₂O) isobars at atmospheric pressure for pure CO₂ (green), 4% CO₂ in N₂ (purple), 0.4% CO₂ in N₂ (orange), and pure N₂ (blue) in 2-ampd–Mg₂(dobpdc). Solid lines depict adsorption (cooling), and dotted green lines depict desorption (heating) for the pure CO₂ isobars. The dashed black lines indicate the theoretical capacity for adsorption of 1 CO₂ per diamine. Temperature ramp rates: 0.5 °C/min for pure CO₂, 0.1 °C/min for 4% and 0.4% CO₂ in N₂, and 1 °C/min for pure N₂.

514 temperature water bubblers to generate an estimated water s15 content of ~2.6 vol % (Figure 3b; see Figures S37-S46 and 516 Tables S9 and S10 for direct comparisons of dry and humid 517 isobars). Importantly, the temperature of each CO₂ adsorption step increased by 6 °C under humid conditions, with the step 518 519 inflection points shifting from 111 to 117 °C and from 98 to 520 104 °C (solid green curves, Figure 3). These higher adsorption temperatures under humid conditions reflect thermodynami-521 cally more favorable cooperative adsorption of CO₂ in the 522 presence of water. Likewise, under a flow of humid 4% CO₂ 523 (40 mbar) in N_2 , the inflection point of the higher-temperature 524 s2s adsorption step increased by ~14 °C, from 68 to 82 °C (purple curves, Figure 3). Critically, while 2-ampd-526 527 Mg₂(dobpdc) captures limited CO₂ from a dry stream containing 0.4% (4 mbar) CO_2 in N_2 , the addition of humidity 528 529 under the same conditions results in a sharp CO₂ step in the 530 adsorption isobar, with an inflection point at 64 °C (orange 531 curves, Figure 3). While the composition of the adsorbed 532 phase cannot be determined directly from these experiments, a s33 comparison of the humid CO_2/N_2 mixture isobars with a 534 humid N₂ isobar indicates that the humid 0.4% CO₂ isobar 535 involves the adsorption of CO₂ (orange and blue curves,

Figure 3b). However, at lower temperatures, the saturation 536 capacities of the humid CO_2/N_2 mixture isobars exceed the 537 gravimetric uptake anticipated for adsorption of 1 CO_2 per 538 diamine, suggesting coadsorption of water. In summary, the 539 isobaric adsorption data indicate that while 2-ampd- 540 Mg₂(dobpdc) may fall below the target of \geq 90% CO₂ capture 541 from dry NGCC flue emissions, the presence of humidity in 542 the gas stream should enable the material to reach this target at 543 temperatures up to at least 60 °C.

To quantify the influence of water on the thermodynamics 545 of CO_2 capture, approximate CO_2 adsorption enthalpies were 546 calculated for the dry and humid CO₂/N₂ mixture isobars by 547 employing the Clausius-Clapeyron relationship at the 548 midpoint of each adsorption step. We note that while slow 549 temperature ramp rates were used to approximate equilibrium 550 conditions (SI Section S9), the enthalpies calculated from the 551 adsorption isobars were found to be systematically higher than 552 those calculated from the single-component, volumetric 553 isotherms. Nonetheless, the difference between the humid 554 and dry isobar enthalpies $(\Delta h_{ads,humid} - \Delta h_{ads,dry})$ should reflect 555 the enthalpic benefit of CO_2 adsorption in the presence of 556 water. Using this method, we attribute the increased 557 temperature of the first adsorption step to a 31 ± 2 kJ/mol 558 increase in the effective $-\Delta h_{ads}$ in the presence of water (dry: 559 81 ± 1 kJ/mol; humid: 112 ± 2 kJ/mol). Notably, within 560 error, the same increase in effective – $\Delta h_{
m ads}$ was found for the 561 lower-temperature adsorption step $(30 \pm 2 \text{ kJ/mol})$, indicating 562 that water uniformly increases the thermodynamic driving 563 force for both adsorption steps (Tables S7 and S8). 564 Interestingly, minimal change was observed in the isobaric 565 desorption step temperatures following saturation with CO₂/ 566 H₂O under the tested humidity, resulting in calculation of 567 equivalent enthalpies within error (dry: $101 \pm 1 \text{ kJ/mol}$; 568 humid: 99 \pm 1 kJ/mol; difference: -2 ± 2 kJ/mol). While 569 these results are complicated by the lower relative humidities at 570 the elevated desorption temperatures, the similar dry and 571 humid CO₂ desorption step temperatures suggest that water 572 desorbs before CO₂. 573

In order to quantify the influence of water on the 574 performance of 2-ampd-Mg₂(dobpdc), we collected single- 575 component water adsorption isotherms at 30, 40, 50, and 60 576 °C. For all temperatures, the isotherms show a plateau at a 577 loading of 1 H₂O per diamine, followed by condensation at 578 higher relative humidities (Figures S10 and S11). Using the 579 same spline interpolation method as for CO2, a differential 580 adsorption enthalpy of -65 ± 2 kJ/mol was calculated at a 581 loading of 1 mmol H_2O/g (Figure S12). Assuming 582 coadsorption and desorption cycling of 1 water molecule per 583 diamine-Mg²⁺ site alongside cycled CO₂, the regeneration 584 energy of 2-ampd-Mg₂(dobpdc) would increase by up to 1.5 585 MJ/kg CO₂ to a total of 4.3 MJ/kg CO₂ (SI Section S3). We 586 note that these values are only approximations, as they do not 587 account for potential differences in the adsorption enthalpy of 588 water on the CO2-inserted and diamine-bound phases (see 589 DFT calculations below), the potential effect of higher relative 590 humidity levels on adsorption or desorption, and the relative 591 adsorption/desorption kinetics of CO₂ vs H₂O in the ultimate 592 cycling configuration. Nonetheless, 2-ampd-Mg₂(dobpdc) is 593 still predicted to afford significant energy savings over 594 competing amine-based technologies such as a PEI-function- 595 alized silica, which requires a regeneration energy of 4.7 MJ/kg 596 CO₂ under similar conditions (SI Section S3)⁴⁸ and is 597 susceptible to degradative reaction pathways, such as urea 598

599 formation (Figures S74–S77, discussed in greater detail 600 below). Therefore, while these measurements indicate that 601 the presence of water in the incident gas stream improves the 602 thermodynamic driving force for CO_2 adsorption in 2-ampd– 603 Mg₂(dobpdc), this improvement comes at the potential cost of 604 an increase in the regeneration energy associated with the 605 desorption of coadsorbed water. The cocycled water would 606 then need to be condensed prior to compression and transport 607 of the captured CO_2 .

Fixed-Bed Adsorption Experiments. To evaluate the 608 609 performance of 2-ampd-Mg₂(dobpdc) in a fixed-bed 610 adsorption process, we conducted breakthrough experiments 611 under dry and humid simulated NGCC flue gas. These 612 experiments are particularly important for materials with step-613 shaped isotherms, which often give rise to complex, multi-614 modal breakthrough profiles. Such profiles were originally 615 anticipated for diamine-appended frameworks by Mazzotti and 616 co-workers in a comprehensive modeling study,⁴⁵ and a review 617 of the underlying theory is included in SI Section S10. In short, 618 the breakthrough profile can be predicted from an isotherm 619 with one or more inflection points by applying "Golden's 620 Rule," alternatively known as the rubber band rule or string 621 rule. 45,85-87 When applying this rule, an operating curve for 622 adsorption is constructed by stretching a hypothetical "rubber 623 band" beneath the adsorption isotherm from the initial state 624 (0% CO₂) to the feed state (4% CO₂). In concentration 625 regimes bounded by individual points of contact with the 626 rubber band, a compressive "shock" is anticipated in the 627 breakthrough profile. In concentration regimes where the rubber band runs along the isotherm, a dispersive "wave" is 628 629 expected. With a step-shaped isotherm, the result is often a 630 "shock-wave-shock" profile: an initial "shock" is generated as $_{631}$ CO₂ slips through the bed at concentrations beneath the step, 632 followed by a "wave" corresponding to a small increase in CO₂ 633 concentration during the onset of the cooperative adsorption 634 step, and finally a second "shock" at full breakthrough (see 635 Figure S52). Intuitively, the shock-wave-shock profile can be 636 understood as a manifestation of the general inability of a 637 cooperative adsorbent to capture CO₂once the CO₂ partial pressure 638 in the bed drops below the step pressure. Accordingly, this 639 behavior is the basis for our design criterion to achieve 90% 640 capture of CO₂ through the selection of adsorbents with step ⁶⁴¹ pressures at <10% of the feed concentration.⁵¹

Breakthrough experiments were conducted with 0.73 g of 642 643 semispherical pellets of 2-ampd-Mg₂(dobpdc) (350-700 μ m) 644 under 28 sccm of 4% CO₂ in N₂ at 1.1 bar (Figure 4; details of 645 pellet preparation and characterization are given in SI Section 646 S11). Considering the single-component CO_2 adsorption 647 isotherms, a CO₂ "slip" (initial shock) of ~0.02 mol % was 648 predicted under dry flue gas at 40 °C (obtained from Golden's 649 Rule, see Figure S54), corresponding to a capture rate of 99.5% 650 from a stream containing 4% CO₂ (calculated as $(1-0.02/4) \times$ 651 100%). However, with dry simulated flue gas, approximately 652 0.6 mol % CO₂ slip was detected at the outlet, corresponding $_{653}$ to a lower maximum capture rate of 86%. In addition, the CO₂ 654 capacity at exhaustion (full breakthrough) was found to be 2.4 $655 \pm 0.2 \text{ mmol/g}$, which fell short of the capacity of 3.5 mmol/g 656 predicted from the adsorption isotherm. The breakthrough 657 profile and capacity were highly reproducible following 658 activation of the material at 120 °C under flowing He (Figure 659 S55). Reducing the flow rate to 14 sccm at 40 °C improved the 660 capture rate (~0.4 mol % slip, or 90% capture rate) and 661 sharpness of the breakthrough profile, reflecting a potential

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Figure 4. Breakthrough experiments with 2-ampd-Mg₂(dobpdc) under 28 sccm of a simulated NGCC flue emission stream of 4% CO₂ in N₂ at 40 °C and ~1.1 bar. (a) Experiment with dry simulated flue gas. Capture rate: 86%; exhaustion capacity: $2.4 \pm 0.2 \text{ mmol/g.}$ (b) Second (filled symbols) and third (open symbols) breakthrough experiment cycles with humid flue gas following presaturation of the adsorbent bed with water. Capture rate: > 99%; usable capacity (average ≥90% capture): 2.2 and $2.3 \pm 0.1 \text{ mmol/g}$; exhaustion capacity: 2.4 and $2.5 \pm 0.1 \text{ mmol/g}$ for 2nd and 3rd cycles, respectively. (c) Overlay of dry and humid (3rd cycle) CO₂ breakthrough profiles. The *y*-axis is shown as normalized outlet flow rate (*F*/*F*₀) in (a) and (b) and as outlet composition in mol % in (c).

limitation in kinetics, but the breakthrough capacity at 662 exhaustion remained unchanged (Figure S56). As anticipated 663 from the isotherms and isobars, increasing the temperature to 664 60 °C increased the CO₂ slip, resulting in a measured capture 665 rate of only 62% (Figure S57; predicted capture rate, 88%). 666

667 The CO₂ breakthrough capacity at exhaustion was calculated 668 as $2.2 \pm 0.2 \text{ mmol/g}$, which again fell short of that predicted 669 from the isotherm (3.2 mmol/g) but was consistent with that 670 predicted from the CO₂ mixture isobars (2.2 mmol/g). 671 Therefore, these results suggest that isobars collected by 672 flowing dry CO₂ mixtures (Figure 3a) may reflect adsorbent 673 performance in dry breakthrough measurements more 674 accurately than single-component, volumetric isotherms 675 (Figure 2). We anticipate that the greater utility of mixed-gas 676 isobars versus single-component isotherms will apply generally 677 in the evaluation of other carbon capture materials, particularly 678 those with step-shaped adsorption isotherms.

To test the effect of CO₂ concentration on the elution 679 680 profile, a breakthrough experiment was conducted under 14 681 sccm of 15% CO2 in N2 at 40 °C and atmospheric pressure, 682 simulating coal flue gas (Figure S58). In this experiment, $_{683}$ negligible slip was observed (>99% CO₂ capture), and the CO₂ 684 capacity $(3.1 \pm 0.2 \text{ mmol/g})$ was consistent with that of the 685 equilibrium isotherm (3.6 mmol/g), considering the 92% 686 diamine loading of the pellets. Therefore, the deviations from 687 equilibrium behavior observed in breakthrough experiments 688 with lower CO₂ concentrations (Figure 4), particularly with 689 respect to high CO₂ slip and resulting low CO₂ capture rate, 690 can likely be attributed to limitations in kinetics. As a result, 691 nonequilibrium effects may limit the performance of diamine-692 appended frameworks with dry CO₂ mixtures at low partial 693 pressures, a hypothesis supported by a recent investigation of 694 another diamine-appended framework for CO₂ capture from 695 air.⁸⁴

We also evaluated the breakthrough behavior of the material 696 697 under humid flue gas mixtures containing ~ 2 vol % H₂O. 698 Gratifyingly, consistent with the humid isobar measurements 699 (Figure 3b), a dramatic enhancement in CO_2 capture 700 performance was observed in breakthrough experiments with 701 humid simulated NGCC flue gas following presaturation of the 702 adsorbent bed with water (Figure 4b). In particular, 703 humidification completely eliminated the initial CO2 slip at 704 40 °C, resulting in a CO_2 capture rate of >99% and a desirable 705 single, sharp CO₂ breakthrough front. The CO₂ exhaustion 706 capacity calculated at full breakthrough $(2.4 \pm 0.2 \text{ mmol/g})$ 707 was equivalent to that of the dry experiment, with a usable 708 CO₂ capacity of 2.2 \pm 0.1 mmol/g satisfying the DoE target of 709 an average of 90% CO₂ capture. This striking improvement in 710 performance is clearly visible in an overlay of the dry and 711 humid CO_2 breakthrough profiles at 40 °C (Figure 4c). 712 Breakthrough experiments at 60 °C revealed similarly dramatic 713 improvements in performance upon addition of humidity (Figures S59 and S60), with an increase in capture rate from 714 715 62% to >99% (see Table S11 for a summary of capture rate 716 results). The very high capture rate under humid conditions at 717 60 °C suggests that even higher adsorption temperatures could 718 be used to achieve smaller temperature swings. In ongoing 719 work, we are developing methods to predict the breakthrough 720 performance as a function of both relative humidity and 721 temperature. The promising performance of 2-ampd-722 Mg₂(dobpdc) in humid breakthrough experiments supports 723 its utility as a next-generation adsorbent for postcombustion 724 CO₂ capture from NGCC flue emissions.

⁷²⁵ **Influence of Water on CO₂ Adsorption.** Due to the ⁷²⁶ sensitivity of the adsorption threshold to the local environment ⁷²⁷ in cooperative adsorbents, it is of interest to determine whether ⁷²⁸ the presence of water changes the nature of the chemisorbed ⁷²⁹ phase or merely enhances the thermodynamic favorability of

the ammonium carbamate chain mechanism in diamine- 730 appended metal-organic frameworks. Considering related 731 materials, water is well-known to improve the CO₂ adsorption 732 capacity of amine-functionalized silicas.^{30,42,88–99} This effect is 733 generally ascribed to a mechanistic shift from ammonium 734 carbamate formation (0.5 CO2:amine) to bicarbonate or 735 stabilized carbamic acid formation (1 CO₂ per 736 amine),^{12,89-91,95,96,99-108} although some studies have debated 737 the formation of bicarbonates or carbonates.^{109–112} Further- 738 more, these reports largely focus on the influence of water on 739 the adsorption capacity, with minimal discussion of the 740 influence of water on the thermodynamics of adsorption and 741 the desorption temperature.^{89,92,113,114} Notably, our related 742 vdW-corrected DFT study of the framework mmen- 743 Mg₂(dobpdc) demonstrated a stabilization of up to 41 kJ/ 744 mol for the CO_2 -inserted phase in the presence of water. ¹¹⁵ 745 This result suggests that water enhances, rather than changes, 746 the ammonium carbamate chain adsorption mechanism, but to 747 date no study has yet combined experimental and computa- 748 tional methods to characterize the effect of water on the CO₂ 749 adsorption pathway, capacity, and breakthrough profile of a 750 diamine-appended metal-organic framework. Accordingly, we 751 employed IR and NMR spectroscopy and vdW-corrected DFT 752 calculations to probe the behavior of 2-ampd-Mg₂(dobpdc) 753 under dry and humid conditions. 754

We first collected IR spectra of 2-ampd $-Mg_2(dobpdc)$ in 755 the presence of dry N₂, dry CO₂, and humid CO₂ (Figure 5). 756 fs



Figure 5. Infrared spectra of 2-ampd–Mg₂(dobpdc) under dry N₂ (blue), dry CO₂ (green), and humid CO₂ (purple) at room temperature (~22 °C) and atmospheric pressure. The C(O)O⁻ vibration at 1648 cm⁻¹ and C–N//N–C(O)O⁻ vibrations at 1362 and 1342 cm⁻¹ are consistent with the proposed mechanism of ammonium carbamate chain formation under both dry and humid conditions.

Upon exposure to dry CO₂ at 22 °C and atmospheric pressure, 757 broad C(O)O⁻ (1648 cm⁻¹) and sharp C–N/N–C(O)O⁻ 758 (1362 and 1342 cm⁻¹) vibrations were observed, consistent 759 with the anticipated ammonium carbamate chain mecha- 760 nism.¹¹⁴ Similar new vibrations were observed at 1637 and 761 1340 cm⁻¹ in the IR spectrum of the molecular ammonium 762 carbamate 2-ampd–CO₂ compared to the spectrum of free 763 molecular 2-ampd (Figures S61–S63; crystallographic data 764 provided as SI). We note that the reported C(O)O⁻ stretches 765 are shifted to higher energies compared to those generally 766 assigned to carbamates in amine-functionalized silicas (1500– 767 1600 cm⁻¹),¹¹⁴ which we attribute to the strong hydrogen 768 bonding between the ammonium and carbamate units in these 769 770 materials. The presence of two C–N/N–C(O)O⁻ stretches in 771 the IR spectrum of CO₂-dosed 2-ampd–Mg₂(dobpdc) further 772 suggests the formation of two distinct ammonium carbamate 773 products upon CO₂ adsorption. The C–N/N–C(O)O⁻ 774 vibrations persist in the presence of humid CO₂, consistent 775 with preservation of a chemisorptive mechanism, while the 776 C(O)O⁻ band is obscured by the H–O–H bend at 1630 cm⁻¹ 777 arising from coadsorbed water.¹⁰²

⁷⁷⁸ Solid-state NMR spectra obtained under dry and humid ⁷⁷⁹ conditions provided greater experimental detail for the effect of ⁷⁸⁰ water on CO_2 adsorption in 2-ampd $-Mg_2(dobpdc)$ (Figure ⁷⁸¹ 6). The ¹³C NMR spectrum of 2-ampd $-Mg_2(dobpdc)$ dosed



Figure 6. (a) ¹³C NMR (16.4 T) MAS spectra of 2-ampd–Mg₂(dobpdc) dosed with 1025 mbar of dry ¹³CO₂ at 22 °C (bottom), and the same sample under a subsequent flow of humid, natural isotopic abundance CO₂ at atmospheric pressure (top). Spectra were obtained by cross-polarization from ¹H (contact time = 1 ms). Peaks corresponding to the framework linker are not observed due to the low natural abundance of ¹³C nuclei in the framework compared to the 99% ¹³C enrichment level for the chemisorbed CO₂. (b) ¹H NMR spectra obtained by single-pulse excitation for the same samples as in (a). The MAS rate was 15 kHz in all cases. Asterisks mark spinning sidebands.

782 with 1025 mbar of ${}^{13}\text{CO}_2$ at room temperature shows two 783 predominant overlapping resonances at 162 and 163 ppm, as 784 well as a weak shoulder at a higher chemical shift (Figure 6a), 785 all of which can be ascribed to chemisorbed CO₂ species. (See 786 Figure S87 for the ${}^{13}\text{C}$ spectrum of activated 2-ampd– 787 Mg₂(dobpdc) prior to exposure to CO₂.) We hypothesize that 788 the two main ${}^{13}\text{C}$ resonances (Figure 6a) correspond to two 789 conformations of ammonium carbamate chains, 61 consistent 790 with the IR spectrum collected under dry CO₂ (Figure 5). 791 Notably, our previous NMR characterization of diamines 792 exhibiting double-step CO₂ adsorption profiles also revealed multiple resonances for chemisorbed CO₂, which likely arise 793 due to spectroscopically distinct conformations of the sterically 794 hindered ammonium carbamate chains.⁶¹ The weak shoulder 795 at higher frequencies (Figure 6a) may be associated with 796 incomplete equilibration (see Figure S90). 797

To interpret these results, we carried out additional 2D and 798 ¹⁵N NMR experiments. A ¹H-¹³C HETCOR experiment with 799 a short contact time (100 μ s) was performed to probe 800 correlations with hydrogen atoms that are proximal to the 801 chemisorbed carbon species (i.e., within a few Å; Figure S89). 802 In the 2D experiment, the two ¹³C resonances each show a 803 major ¹H correlation at \sim 5 ppm. We assign this feature to the 804 N–H group of an ammonium carbamate species, while the ^{13}C 805 peaks are attributed to the carbamate carbon atoms of two 806 distinct conformations of ammonium carbamate chains.^{61,116} 807 The observed single N–H correlation supports CO₂ insertion 808 into metal-1° amine bonds to produce metal-bound 809 carbamate species, with proton transfer to neighboring 810 secondary amines to form charge-balancing ammonium 811 groups. This reactivity is consistent with the previous 812 crystallographic characterization of CO₂ insertion into 813 Zn₂(dobpdc) functionalized with 1°/2° diamines.⁵¹ Addition- 814 ally, the ¹⁵N NMR spectrum of 2-ampd–Mg₂(dobpdc) dosed 815 with 1025 mbar of ¹³CO₂ featured two peaks at 46 and 76 816 ppm, consistent with nitrogen atoms in ammonium and 817 carbamate groups, respectively (Figure S86).^{50,61} 818

After exposure of 2-ampd-Mg₂(dobpdc) to a flow of humid 819 CO_2 (natural isotopic abundance) for 1 h, the main two ${}^{13}C$ 820 resonances were retained, but smaller line widths were 821 observed (Figure 6a; see also Figure S90 for similar data 822 obtained with a longer CO₂ exposure time). Therefore, in 823 further agreement with the IR data, these NMR spectra 824 demonstrate retention of the ammonium carbamate product in 825 the presence of water and exclude a water-induced change in 826 the CO₂ chemisorption mechanism. Co-adsorption of water 827 was also confirmed by collection of ¹H NMR spectra before 828 and after exposure to wet CO₂. The difference ¹H spectrum 829 (Figure 6b) shows positive intensity that can be attributed to 830 coadsorbed water and reveals a narrow component at 4.6 ppm, 831 as well as broad components at ~ 9 and ~ 3 ppm. The highly $_{832}$ shifted (\sim 9 ppm) water peak supports the formation of strong 833 hydrogen bonds following exposure to water (Figure 6b). 834 Additionally, the ¹H NMR spectra of 2-ampd-Mg₂(dobpdc) 835 following exposure to dry or humid CO₂ (Figure 6b) show an 836 increase in line width of the amine resonances compared to the 837 NMR spectrum of activated 2-ampd-Mg₂(dobpdc) (Figure 838 S88), consistent with a reduction of amine mobility following 839 CO₂ insertion.

Due to the structural complexity of 2-ampd–Mg₂(dobpdc), 841 the CO₂-inserted structure could not be solved directly from 842 the X-ray diffraction pattern of the microcrystalline powder or 843 from single crystals of the isostructural Zn framework under 844 dry or humid conditions. We thus turned to vdW-corrected 845 DFT calculations to predict the structure and energetics upon 846 CO₂ adsorption, H₂O adsorption, and coadsorption of CO₂ 847 and H₂O in 2-ampd–Mg₂(dobpdc) (Figure 7). For simplicity, 848 f7 all calculations were carried out using the left-handed 849 enantiomer of the diamine in the right-handed enantiomer of 850 the framework. An adsorption energy of -70 kJ/mol was 851 calculated for insertion of CO₂ to form ammonium carbamate 852 chains in Mg₂(dobpdc)(2-ampd–CO₂)₂. This value is in good 853 agreement with the experimentally determined CO₂ adsorption 854 enthalpy of -72 ± 5 kJ/mol averaged over a loading of 0 to 1 855



Figure 7. Projections along the pore axis and first coordination spheres of Mg(II) sites for the vdW-corrected, DFT-calculated structures of evacuated *L*-2-ampd–*R*-Mg₂(dobpdc) (top left) and the framework following CO₂ insertion (bottom left), water adsorption (top right), and coadsorption of CO₂ and H₂O (bottom right). The vdW-corrected, DFT-calculated binding energies (ΔE) are provided for each adsorption process, and available experimental differential binding enthalpies (Δh_{ads}) are included in parentheses. Co-adsorption of water was found to enhance the CO₂ binding energy by -18 kJ/mol, and a combined binding energy of -139 kJ/mol 2-ampd was calculated for coadsorption of 1 CO₂ and 1 H₂O per diamine. Green, blue, gray, red, and white spheres represent Mg, N, C, O, and H atoms, respectively.

 856 CO_2 per diamine (Figure S8). In the calculated structure of 857 Mg₂(dobpdc)(2-ampd)₂(H₂O)₂, adsorbed water was found to 858 interact with 2-ampd by donating a hydrogen bond to the 859 secondary amine (O…N distance of 2.924 Å). Close H₂O… 860 H₂O contacts in the *ab* plane (O···O distance of 2.867 Å) 861 suggest that additional stabilization is provided by hydrogen 862 bonding between water molecules. In the absence of CO_{2} , an adsorption energy of -51 kJ/mol was calculated for H₂O. This 864 value is consistent with the experimental H₂O adsorption ses enthalpy of -50 ± 2 kJ/mol at low loadings (0.2 mmol/g, or 866 0.05 mmol H₂O per diamine) but is slightly lower than the 867 average experimental enthalpy of -65 ± 2 kJ/mol over a see loading range of 0 to 1 mmol H_2O per diamine (Figure S12). 869 In practice, while the structure shown here represents the 870 lowest-energy H₂O binding mode discovered in our 0 K 871 calculations, H₂O may sample other binding sites or 872 geometries within the pore at room temperature. Overall, the 873 adsorption energies corresponding to the calculated CO₂- and 874 H₂O-adsorbed structures of 2-ampd-Mg₂(dobpdc) are in 875 reasonable agreement with those determined from singlecomponent adsorption measurements. 876

The DFT-calculated structure of $Mg_2(dobpdc)(2-ampd 878 CO_2)_2(H_2O)_2$ shows a strong hydrogen bonding interaction 879 between H₂O and the metal-bound oxygen atom of the 880 carbamate (O···O distance of 2.786 Å). Additionally, each 881 H₂O molecule accepts a hydrogen bond from a carbamate 882 nitrogen atom of the neighboring ammonium carbamate chain 883 in the *ab* plane (N···O distance of 2.939 Å), resulting in a 884 channel of H₂O molecules between adjacent ammonium 885 carbamate chains (Figure S95). A CO₂ adsorption energy of 886 -88 kJ/mol was calculated for coadsorption of 1 CO₂ and 1 887 H₂O per diamine, indicating that water increases the 888 magnitude of the CO₂ binding energy by an estimated 18 889 kJ/mol compared to CO₂ insertion under dry conditions

(binding energy of -70 kJ/mol). This value is smaller than the 890 $31 \pm 2 \text{ kJ/mol}$ increase in $-\Delta h_{ads}$ calculated from the humid 891 vs dry pure CO₂ adsorption isobars, but a comparison of the 892 absolute values may be complicated by nonequilibrium effects 893 in the isobars and the inability to determine the precise 894 composition of the adsorbed phase. Notably, the DFT- 895 calculated binding energy of CO₂ is larger than that of water 896 in the coadsorbed structure, suggesting that the endothermic 897 penalty to desorb H₂O is smaller, and thus H₂O is likely to 898 desorb first. This result is consistent with the minimal 899 differences in the dry and humid CO₂ desorption temperatures 900 observed in mixed-gas isobars (Figure 3). We note that the 901 calculated and experimental NMR shifts for 2-ampd- 902 Mg₂(dobpdc) exposed to dry and humid CO₂ also agree 903 well with the experimental values (Table S20). 904

Taken together, the humid isobars, breakthrough measure- 905 ments, spectroscopic data, and vdW-corrected DFT calcu- 906 lations support an increase in the favorability of CO_2 insertion 907 under humid conditions, as a result of an enhancement of the 908 ammonium carbamate chain formation mechanism in the 909 presence of water. In humid breakthrough experiments, the 910 resulting effective decrease in the isothermal CO_2 adsorption 911 step pressure alters the propagation of the adsorption front 912 through the bed. In particular, the single "shock" in the humid 913 CO_2 breakthrough profile suggests that water reduces the 914 effective step pressure and/or alters the shape of the CO_2 915 adsorption profile at low partial pressures, leading to more 916 favorable performance under humid conditions (Figure S53). 917

Thermal, Oxidative, and Cycling Stability. Beyond the 918 thermodynamics and kinetics of adsorption, the long-term 919 stability of an adsorbent is a critical consideration for ultimate 920 industrial applications. In particular, the high oxygen content 921 of the NGCC flue gas stream (\sim 12%) is well-known to lead to 922 oxidative degradation of aqueous amine solutions.^{24–27} To 923

⁹²⁴ evaluate the oxidative stability of 2-ampd-Mg₂(dobpdc), the ⁹²⁵ material was exposed to a flow of dry air (~21% O₂ in N₂) at ⁹²⁶ 100 °C and atmospheric pressure for 5 h, and the dry, pure ⁹²⁷ CO₂ isobars were compared before and after exposure. ⁹²⁸ Minimal changes were observed in the CO₂ adsorption profile ⁹²⁹ or capacity after this extensive O₂ treatment (Figure 8). In



Figure 8. Dry, pure CO_2 adsorption isobars for 2-ampd-Mg₂(dobpdc) as synthesized (green curve), after exposure to a flow of dry air (~21% O_2 in N_2) at 100 °C for 5 h (orange curve), and after exposure to a flow of humid CO_2 at 140 °C for 12 h (blue curve). A ramp rate of 1 °C/min was used in all cases. The dashed black line indicates the theoretical capacity for adsorption of 1 CO_2 per diamine.

930 contrast, dry, oxygen-containing streams at 100 °C have been 931 found to cause significant degradation of silicas functionalized 932 with secondary amines.¹¹⁷ In addition, no diamine oxidation 933 products were detected by IR or by ¹H NMR spectroscopy 934 after digestion of the O₂-treated material (Figure S72). The 935 oxidative resistance of 2-ampd–Mg₂(dobpdc) is likely due in 936 part to the fixed, wide spacing of diamines at metal sites ~7 Å 937 apart along the channel direction, which serves to mitigate 938 bimolecular (2 amine molecules) oxidation pathways observed 939 in other materials.¹¹⁷

Adsorbents for carbon capture from NGCC flue gas must 940 941 also withstand repeated thermal cycling under humid 942 conditions. As part of this work, we found that the stability 943 of diamine-appended variants of Mg2(dobpdc) and related 944 materials can be rapidly assessed by exposing the adsorbent to 945 a flow of humid CO_2 for 12 h at the relevant desorption 946 temperature (here, 140 °C) in a thermogravimetric analyzer, 947 simulating hundreds of adsorption/desorption cycles (SI 948 Section S16). The humid CO₂ adsorption capacities before 949 and after such accelerated decomposition experiments can be 950 compared to evaluate any capacity loss, and the material can be 951 digested after the test to detect diamine volatilization or 952 degradation. Notably, after treatment with flowing humid CO₂ 953 at 140 °C for 12 h, 2-ampd-Mg₂(dobpdc) retains its step-954 shaped adsorption profile (Figure 8, blue curve) with only a 955 slight capacity loss at 40 °C (original: 4.20 mmol/g; after 956 humid CO₂ treatment: 4.11 mmol/g). In addition, almost no 957 diamine volatilization (\sim 2%) from the framework was 958 observed. We further tested the stability of 2-ampd-959 Mg₂(dobpdc) to accelerated decomposition experiments at 960 higher temperatures, representative of a potential process 961 failure. At temperatures as high as 180 °C, 2-ampdMg₂(dobpdc) retains more than 90% of its adsorption capacity 962 (Table S15), and the material remains highly crystalline even 963 after treatment with a humid CO₂ stream at 220 °C for 12 h 964 (Figure S70). Evaluation of a number of promising diamine- 965 appended variants of Mg₂(dobpdc) for CO₂ capture from 966 NGCC flue gas further revealed that the thermal stability of 2- 967 ampd-Mg₂(dobpdc) is nearly unparalleled among this family 968 of materials (Table S14). In addition, the stability of 2-ampd- 969 Mg₂(dobpdc) is far superior to that of the representative 970 amine-functionalized silica MCM-41-PEI-50, which undergoes 971 urea formation and significant capacity loss (~17%) at 40 °C 972 following exposure to humid CO₂ for 12 h at 140 °C (Figures 973 S75–S77). The exceptional stability of 2-ampd-Mg₂(dobpdc) 974 to humid gas streams at high temperatures makes it particularly 975 promising for long-term application in a CO₂ capture process.

The stability of 2-ampd $-Mg_2(dobpdc)$ in a TSA process 977 was further evaluated by performing 750 adsorption (humid 978 4% CO₂ in N₂, 40 °C) and desorption (humid CO₂, 140 °C) 979 cycles using a thermogravimetric analyzer (Figure 9, see SI 980 f9



Figure 9. Cycling data for the final 100 of 750 adsorption/desorption cycles for 2-ampd–Mg₂(dobpdc) in a simulated temperature swing adsorption process. Adsorption: humid 4% CO₂ in N₂, 40 °C, 5 min (black, cycle maxima). Desorption: Humid CO₂, 140 °C, 1 min (red, cycle minima). The cycled capacity (difference) is shown in blue. The baseline value of 0 g/100 g is defined as the mass after activation under 4% CO₂ in N₂ at 150 °C for 20 min prior to the first cycle. The diamine loading was reduced from 100% to 94% after this experiment. The same final loading was observed after 200 adsorption/desorption cycles, suggesting that the diamine loading stabilizes after initial loss. The weight loss due to diamine volatilization correlates with equilibration of the mass upon desorption to the observed negative baseline value.

Figure S80 for the full cycling data). Consistent with the 981 accelerated decomposition test results (Figure 8), 2-ampd– 982 Mg₂(dobpdc) exhibited a stable cycling capacity under humid 983 simulated NGCC flue gas (Figure 9). The same final diamine 984 loading (~94%) was observed after both 200 and 750 cycles, 985 suggesting that the loading stabilizes after a small amount of 986 initial diamine volatilization, likely from weakly bound defect 987 or surface sites. Notably, a high CO_2/H_2O cycling capacity of 988 16.0 g/100 g was observed for the 750th cycle, comparable to 989 the adsorption capacity from a dry 4% CO₂ in N₂ stream at 40 990 °C (15.8 g/100 g). Nearly the same cycled capacity (15.3 g/ 991 100 g) could also be achieved over 200 tested cycles with a 992 higher adsorption temperature of 60 °C (Figure S81). Short 993 adsorption (5 min) and desorption (1 min) times were used in 994

995 these experiments, indicating rapid kinetics despite the low 996 CO_2 content of the simulated flue gas stream. Overall, the 997 exceptional stability of 2-ampd-Mg₂(dobpdc) and excellent 998 performance in breakthrough and cycling experiments support 999 further development of this promising adsorbent for CO_2 1000 capture from the emissions of gas-fired power plants.

1002 Natural gas offers significant environmental advantages as an 1003 alternative to coal by enabling approximately 50% lower CO₂ 1004 emissions per unit of electricity produced. Capturing and 1005 sequestering the CO₂ emissions from gas-fired power plants 1006 provides an attractive option to achieve even greater emission 1007 reductions. We have shown that the metal-organic framework 1008 2-ampd-Mg₂(dobpdc) is a promising candidate for post-1009 combustion CO₂ capture from the emissions of NGCC power 1010 stations. In particular, as a result of the constituent cyclic 1011 diamine, this material overcomes the trade-off between stability 1012 and capacity encountered with related cooperative adsorbents 1013 featuring linear $1^{\circ}/2^{\circ}$ diamines. Importantly, in breakthrough 1014 experiments simulating a fixed-bed adsorption process, 2-1015 ampd-Mg₂(dobpdc) exhibits single-shock breakthrough pro-1016 files under humid conditions, in contrast to the multimodal 1017 elution profiles observed under dry conditions. This advanta-1018 geous result is attributed to stabilizing H₂O-carbamate 1019 interactions, a conclusion supported by mixed-gas adsorption 1020 experiments, spectroscopic characterization, and vdW-cor-1021 rected DFT calculations. Finally, 2-ampd-Mg₂(dobpdc) 1022 achieves the challenging practical criteria required of a material 1023 for CCS from NGCC emissions, namely a high CO₂ swing 1024 capacity as well as high thermal, oxidative, and cycling stability. 1025 Continued development of 2-ampd-Mg₂(dobpdc) at larger 1026 scales and in structured forms will enable modeling of heat and 1027 mass transfer and support bench-scale testing.

More broadly, this report achieves key advances toward the 1028 1029 deployment of cooperative adsorbents in industrial CO₂ 1030 separations. First, we have reiterated the importance of 1031 considering CO₂ "slip" in adsorbent and process design for 1032 CO2 capture applications with dry mixtures.^{45,84} Second, and 1033 most importantly, we have established that presaturating the 1034 adsorbent bed with water can significantly enhance the CO₂ 1035 capture performance of diamine-appended, cooperative 1036 adsorbents by mitigating or eliminating CO₂ slip. Third, we 1037 have shown that experiments under flow conditions (such as 1038 isobars collected with slow temperature ramp rates under 1039 varying CO₂ concentrations) may predict the performance of 1040 cooperative adsorbents more accurately than single-compo-1041 nent, volumetric adsorption isotherms. Finally, we have shown 1042 that TSA processes with cooperative adsorbents can utilize 1043 higher adsorption temperatures (here, 60 °C or higher instead 1044 of 40 °C) that could serve to mitigate water coadsorption and 1045 reduce operating costs related to cooling the flue gas stream. 1046 Moving forward, we expect that these discoveries will be of 1047 value in the design of cooperative adsorbents for other 1048 challenging CO₂ capture processes, such as the direct capture 1049 of CO₂ from air.

Full characterization of all adsorbents and additional 1054 experimental details (PDF) 1055 Crystallographic data for $Zn_2(dobpdc)(2-1056)$ $(CIF)_{1.76}(C_7H_8)_{0.79}$ 1057 Crystallographic data for 2-ampd $-CO_2$ (CIF) 1058 DFT-calculated structure of Mg₂(dobpdc)(2-ampd)₂ 1059 (CIF) 1060 DFT-calculated structure of Mg₂(dobpdc)(2-ampd-1061 CO_2 , (CIF)1062 DFT-calculated structure of Mg₂(dobpdc)(2-1063 $ampd)_2(H_2O)_2$ (CIF) 1064 DFT-calculated structure of Mg₂(dobpdc)(2-ampd- 1065 $CO_2)_2(H_2O)_2$ (CIF) 1066 DFT-calculated structure of cocaine (CIF) 1067 DFT-calculated structure of glycine (CIF) 1068 AUTHOR INFORMATION 1069 **Corresponding Author** 1070

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Notes

The authors declare the following competing financial 1084 interest(s): J.R.L. has a financial interest in Mosaic Materials, 1085 Inc., a start-up company working to commercialize metal- 1086 organic frameworks for gas separations. The University of 1087 California, Berkeley and ExxonMobil Research and Engineer- 1088 ing Company have applied for a patent on some of the 1089 materials discussed herein, on which P.J.M., R.L.S., S.C.W., and 1090 J.R.L. are included as inventors.

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