### **RESEARCH ARTICLE**

### **GAS SEPARATIONS**

# Cooperative carbon capture and steam regeneration with tetraamine-appended metal-organic frameworks

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Natural gas has become the dominant source of electricity in the United States, and technologies capable of efficiently removing carbon dioxide ( $CO_2$ ) from the flue emissions of natural gas-fired power plants could reduce their carbon intensity. However, given the low partial pressure of  $CO_2$  in the flue stream, separation of  $CO_2$  is particularly challenging. Taking inspiration from the crystal structures of diamine-appended metal-organic frameworks exhibiting two-step cooperative  $CO_2$  adsorption, we report a family of robust tetraamine-functionalized frameworks that retain cooperativity, leading to the potential for exceptional efficiency in capturing  $CO_2$  under the extreme conditions relevant to natural gas flue emissions. The ordered, multimetal coordination of the tetraamines imparts the materials with extraordinary stability to adsorption-desorption cycling with simulated humid flue gas and enables regeneration using low-temperature steam in lieu of costly pressure or temperature swings.

arbon dioxide (CO2) emissions from fossil fuel combustion and industrial processes account for as much as 65% of anthropogenic greenhouse gas emissions (1-3). Carbon capture and sequestration (CCS), wherein  $CO_2$  is separated from the flue emissions of large point sources and permanently sequestered underground, is widely recognized as an essential component of strategies for meeting the ambitious climate targets established at the Paris Climate Conference (4). The development of capture technology has largely focused on coal flue emissions (5), but worldwide use of natural gas is projected to exceed that of coal by ~2032, necessitating the rapid development of CCS technology for natural gas emissions (6). The U.S. Department of Energy (DOE) has set an ambitious target of 90% capture of the CO<sub>2</sub> from natural gas flue streams (7), which is particularly challenging given that the CO<sub>2</sub> concentration in

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natural gas combined-cycle (NGCC) emissions is typically only ~4%, compared with ~12 to 15% for coal emissions (7, 8). Additionally, NGCC emissions contain high concentrations of O<sub>2</sub> (12.4%) and water (8.4%), and thus effective technologies must be stable and maintain CO<sub>2</sub> capture performance in the presence of these species (7, 9).

Aqueous amine solutions, the most mature carbon-capture technology as of now (10), are susceptible to oxidative and thermal degradation and have low CO<sub>2</sub> cycling capacities (11). Porous solid adsorbents such as zeolites, silicas, and metal-organic frameworks are emerging as promising CO<sub>2</sub>-capture materials because of their high surface areas, lower intrinsic regeneration energies, higher stabilities, and tunable surface chemistries (12, 13). Taking inspiration from amine-functionalized silicas (14), we and others have shown that aminefunctionalized metal-organic frameworks can capture  $CO_2$  in the presence of water (15, 16). A major consideration for adsorptive CO<sub>2</sub> capture from natural gas flue emissions is that the low partial pressure of CO<sub>2</sub> requires materials with high adsorption enthalpies. In turn, higher temperatures or lower pressures are needed to desorb captured CO<sub>2</sub>, and these regeneration conditions are costly and can substantially affect performance (12). The use of steam for  $CO_2$ recovery has been proposed as a cost-effective strategy for amine-functionalized adsorbents (17-22), particularly because low-grade steam is inexpensive and readily available in most industrial processes. Unfortunately, engineering adsorbents with stability in the presence of steam is an ongoing issue (19, 23-25).

We recently reported the promising  $CO_2$ capture properties of the diamine-appended framework N,N'-dimethylethylenediamineMg2[dobpdc (4,4'-dioxidobiphenyl-3,3'-dicarboxylate)] (Fig. 1A) (26). In this material,  $CO_2$  adsorption proceeds through a cooperative mechanism in which the gas inserts into the Mg-N bonds to form chains of oxygen-bound carbamate species charge-balanced by neighboring ammonium groups running along the pores (27). This mechanism gives rise to unusual stepshaped CO<sub>2</sub> adsorption profiles and improved material  $CO_2$  cycling capacities that can be achieved with smaller pressure or temperature swings than are required for traditional adsorbents (27). The  $CO_2$ -capture properties can further be tuned by varying the appended diamine, leading to adsorbents with potential for CO<sub>2</sub> capture from coal flue gas emissions (Fig. 1B) (28-31) and even NGCC emissions (32).

Nonetheless, these materials are susceptible to diamine volatilization upon regeneration, which has limited their applicability in practical capture processes (30). We now report that tetraamine-functionalized Mg<sub>2</sub>(dobpdc) materials (Fig. 1C) exhibited high thermal stability and cooperatively captured CO<sub>2</sub> at concentrations as low as parts per million (ppm), enabled by a two-step ammonium carbamate chain-formation mechanism. The ordered, multimetal coordination mode achieved with the tetraamines markedly increased the stability of these adsorbents and enables CO<sub>2</sub> desorption with inexpensive steam in tetraaminefunctionalized Mg<sub>2</sub>(dobpdc).

## Synthesis and structure of tetraamine-functionalized Mg<sub>2</sub>(dobpdc)

Our pursuit of tetraamine-functionalized Mg<sub>2</sub>(dobpdc) was motivated by structural analysis of diamine-appended analogs, which suggested that tetraamines with chain lengths on the order of two N-alkylethylenediamines could bridge nearest-neighbor metals across the pore (Fig. 1, B and C) (28). Such multiplemetal coordination could yield adsorbents exhibiting cooperative CO2 capture and greatly enhanced thermal and hydrolytic amine stability. Soaking Mg<sub>2</sub>(dobpdc) with various tetraamines (Fig. 1D) in toluene (materials and methods) produced loadings of ~1 tetraamine per Mg<sup>2+</sup> site, or twice the desired 1:2 tetraamine:metal ratio (Fig. 1C), as determined by <sup>1</sup>H nuclear magnetic resonance (NMR) of acid-digested samples. The desired loading could be achieved through subsequent thermal activation (materials and methods, figs. S3 and S4, and tables S1 and S2). Thermogravimetric analysis indicated that the tetraaminegrafted Mg<sub>2</sub>(dobpdc) materials were resistant to further diamine loss up to ~250° to 290°C (figs. S3 and S4). Here, we refer to the tetraamines using shorthand based on the number of carbon atoms in the alkyl groups bridging the amine moieties; for example, N.N'-bis(3aminopropyl)-1,3-diaminopropane and N.Nbis(3-aminopropyl)-1,4-diaminobutane are





referred to as 3-3-3 and 3-4-3, respectively (Fig. 1D).

Single-crystal x-ray diffraction (XRD) data obtained for 3-3-3- and 3-4-3-appended variants of the isostructural framework Zn<sub>2</sub>(dobpdc) revealed that the tetraamines coordinate in a highly ordered fashion (Fig. 1, E and F). Tetraamine 3-3-3 bound two metal centers separated by a distance of 10.4637(11) Å (Fig. 1E), whereas 3-4-3 bridged metal sites separated by 16.8312(19) Å (Fig. 1F). Longer tetraamines could ostensibly also be accommodated in the framework and bridge metal atoms at even greater distances. In 3-3-3-functionalized Zn<sub>2</sub>(dobpdc), extensive intramolecular hydrogen bonding was observed, whereas 3-4-3-Zn<sub>2</sub>(dobpdc) primarily exhibited intermolecular hydrogen bonding between adjacent tetraamines along the pore direction. These experimental structures confirmed the tetraamine coordination mode in M<sub>2</sub>(dobpdc) and accounted for the extremely high thermal stability of these materials.

### Adsorption properties and optimization for NGCC postcombustion capture

All of the Mg<sub>2</sub>(dobpdc)(tetraamine) variants exhibited sharp step-shaped CO<sub>2</sub> adsorption profiles consistent with cooperative adsorption and ammonium carbamate chain formation (Fig. 2 and figs. S14 to S16) (27, 28, 30, 32). In each case, the CO<sub>2</sub> adsorption capacity at

30°C approached the theoretical capacity of two CO<sub>2</sub> molecules per tetraamine. With the exception of Mg<sub>2</sub>(dobpdc)(3-3-3), the frameworks exhibited two-step adsorption profiles, with each step corresponding to half of the theoretical capacity. Analogous two-step adsorption profiles were previously observed in bulky diamine-appended variants of Mg<sub>2</sub>(dobpdc) and were attributed to steric conflict between neighboring ammonium carbamate chains across the pore (30). In the case of tetraamineappended Mg<sub>2</sub>(dobpdc), we hypothesize that initial chemisorption of CO2 occurred at one amine end, generating ammonium carbamates running along one vertex of the hexagonal pore. The formation of the second set of ammonium carbamate chains likely required reorientation of the unreacted, bound amines.

Consistent with this proposed mechanism, increasing tetraamine length coincides with a decrease in the material step separations up to 3-3-3, for which the functionalized framework displayed only a single adsorption step. Twostepped adsorption returned in the case of Mg<sub>2</sub>(dobpdc) appended with the slightly larger 3-4-3, which we attribute to this tetraamine likely bridging two metals at a longer distance than 3-3-3 and the other smaller tetraamines (Fig. 1, E and F). Furthermore, when appended with triamines 3-3 [bis(3-aminopropyl)amine] and 3-4 [*N*-(3-aminopropyl)-1,4-diaminobutane], which can only form one set of ammonium carbamate chains, the  $Mg_2(dobpdc)$  frameworks exhibited  $CO_2$  capacities that correspond to adsorption of one molecule of  $CO_2$  for every two  $Mg^{2+}$  sites (figs. S12 and S13). For practical applications, a single-step adsorption profile, or a two-step adsorption profile with closely spaced adsorption steps, is desirable to maximize the operating range over which the full material adsorption capacity can be accessed (32).

The temperatures of the first adsorption step for Mg<sub>2</sub>(dobpdc)(3-3-3) and Mg<sub>2</sub>(dobpdc)(3-4-3) are 163° and 150°C, respectively. These temperatures are among the highest reported for any amine-appended variant of Mg<sub>2</sub>(dobpdc) (26, 28-30, 32). Traditional adsorbents with Langmuir-type adsorption profiles typically show optimal performance at the lowest possible adsorption temperature, where the adsorption capacity is maximized. The high adsorption step temperatures for the tetraamineappended materials directly correlated with adsorption steps at low pressures sufficient to enable 90% CO<sub>2</sub> capture from an NGCC flue stream (Fig. 2B and figs. S14 to S16) (7). For example, the CO<sub>2</sub> adsorption isotherm for Mg<sub>2</sub>(dobpdc)(3-2-3) at 75°C indicated that the material should be able to reduce the  $CO_2$ content in an NGCC flue stream to 0.4% (fig. S16). Additionally, our preliminary results (figs. S28 and S39) indicate that these materials may also be suitable for direct capture of  $CO_2$  from air. Whereas most tetraamine-appended materials exhibit stable  $CO_2$  cycling capacities,  $Mg_2(dobpdc)(3-3-3)$  shows a gradual decrease in  $CO_2$  cycling capacity over time (fig. S10); thus, Mg(dobpdc)(3-4-3) was chosen for further study because of its practical step position and fundamentally interesting two-step adsorption behavior.

The adsorption data for  $Mg_2(dobpdc)(3-4-3)$  suggested that in a postcombustion-capture process from NGCC flue emissions, this frame-

### Fig. 2. CO<sub>2</sub> uptake in tetraamine-

**appended Mg<sub>2</sub>(dobpdc).** (**A**) Adsorption isobars obtained through thermogravimetric analysis of Mg<sub>2</sub>(dobpdc)(tetraamine) under pure CO<sub>2</sub> at atmospheric pressure. Dashed lines indicate the theoretical capacities for binding of one and two CO<sub>2</sub> molecules per tetraamine. (**B**) Adsorption (filled circles) and desorption (open circles) isotherms for CO<sub>2</sub> uptake in Mg<sub>2</sub>(dobpdc)(3-4-3) at 90°, 100°, 110°, and 120°C. The CO<sub>2</sub> pressures in an untreated NGCC flue emission stream (40 mbar) and after 90% capture (4 mbar) are indicated with light gray and dark gray lines, respectively.

### Fig. 3. Spectroscopic investigation of $CO_2$ adsorption in

Mg2(dobpdc)(3-4-3). (A) Raw in situ DRIFTS spectra of activated 3-4-3-Mg<sub>2</sub>(dobpdc) (gray curve), 3-4-3-Mg<sub>2</sub>(dobpdc) dosed with 400 mbar of <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> at 120°C (dark blue and yellow curves, respectively), and the isotopic difference spectrum (teal curve). The <sup>13</sup>CO<sub>2</sub> spectrum was used as a baseline to isolate vibrations caused by inserted CO2. Vibrations corresponding to diagnostic carbamate bands are labeled. (B) Room-temperature <sup>13</sup>C solidstate magic angle spinning NMR spectrum (16.4 T) of Mg<sub>2</sub>(dobpdc)(3-4-3) dosed with 1038 mbar of <sup>13</sup>CO<sub>2</sub>. The resonance at 162.6 ppm was assigned as carbamate. Asterisks mark spinning side bands. (C)  $^{1}H \rightarrow ^{13}C$  heteronuclear correlation (contact time 100 µs) spectrum and correlation assignments. (D) Predicted structures of Mg<sub>2</sub>(dobpdc)(3-4-3), Mg<sub>2</sub>(dobpdc)(3-4-3)(CO<sub>2</sub>), and Mg<sub>2</sub>(dobpdc)(3-4-3)(CO<sub>2</sub>)<sub>2</sub>

work could achieve a 90% CO<sub>2</sub> capture rate, referring to the removal of CO<sub>2</sub> to a residual concentration of 10% that of the feed (reduction from 40 to 4 mbar at atmospheric pressure). Single-component isotherms collected between 90° and 120°C reveal that step-shaped CO<sub>2</sub> capture at 4 mbar (corresponding to 90% capture) was retained up to 90°C under dry conditions (Fig. 2B). Using the Clausius–Clapeyron relationship, we calculated differential adsorption enthalpy ( $\Delta h_{ads}$ ) and entropy ( $\Delta s_{ads}$ ) values of 99 ± 3 kJ/mol and 223 ± 8 J/mol-K, respectively, at a loading of 1 mmol CO<sub>2</sub>/g (figs. S19 and S20). These values followed a correlation previously observed between  $\Delta h_{ads}$  and  $\Delta s_{ads}$  values determined for diamine-appended Mg<sub>2</sub>(dobpdc) (fig. S21) (28). The  $\Delta h_{ads}$  value for Mg<sub>2</sub>(dobpdc)(3-4-3) is among the highest reported for amine-functionalized materials. Such a high enthalpy of adsorption should enable CO<sub>2</sub> capture at high temperatures and result in lower energy consumption in a temperature-swing adsorption process by minimizing the required temperature swing



obtained from structural relaxations with vdW-corrected DFT. Green, gray, red, blue, and white spheres represent Mg, C, O, N, and H atoms, respectively.

(33-37). Additionally, Mg<sub>2</sub>(dobpdc)(3-4-3) exhibited minimal adsorption-desorption hysteresis at atmospheric pressure (fig. S11).

### Cooperative adsorption mechanism

We used in situ infrared (IR) and solid-state NMR spectroscopies to characterize Mg<sub>2</sub>(dobpdc)(3-4-3) before and after CO<sub>2</sub> adsorption to investigate the two-step cooperative adsorption mechanism. In situ diffuse reflectance IR spectroscopy (DRIFTS) characterization of the framework in the presence of CO2 revealed a characteristic carbamate C-N stretch at 1339 cm<sup>-1</sup> and a C-O stretch at 1689 cm<sup>-1</sup> (isotopic difference spectrum, Fig. 3A) (27-30). In addition, spectra collected simultaneously with a volumetric. equilibrium CO2 isotherm at 120°C indicated that the ammonium carbamate species was responsible for cooperative adsorption (fig. S25). Distinctive features corresponding to hydrogen bonding between neighboring ammonium carbamate chains were observed in the N-H regions of the difference spectrum (3300 to 3000 and 3500 to 3400 cm<sup>-1</sup>), and distinct hydrogen bonding environments were characterized for each of the two adsorption steps (fig. S26).

Corroborating evidence for ammonium carbamate formation was obtained from magic angle spinning solid-state NMR experiments. A single carbamate resonance was observed at 162.6 ppm in the <sup>13</sup>C NMR spectrum of  $Mg_2(dobpdc)(3-4-3)$  dosed with 1.04 bar of  ${}^{13}CO_2$ (Fig. 3B), which coincides with resonances reported previously for ammonium carbamate formed upon <sup>13</sup>CO<sub>2</sub> adsorption in diamineappended Mg<sub>2</sub>(dobpdc) (38). The presence of a single carbamate feature suggested that all of the chemisorbed CO<sub>2</sub> was in the same chemical environment after adsorption at 1 bar. We also observed five resonances for the tetraamine alkyl carbons, supporting a symmetric reaction between the tetraamine and CO2 at full capacity (Fig. 3B). Two-dimensional heteronuclear correlation data further revealed that  $CO_2$  reacted with the primary amine and that a secondary ammonium group formed nearby the carbamate (Fig. 3C) (38), and solidstate <sup>15</sup>N NMR data confirmed the symmetric formation of ammonium and carbamate species (fig. S27). The NMR and IR results confirmed that our tetraamine-functionalized Mg<sub>2</sub>(dobpdc) variants operated through the envisaged twostep cooperative adsorption mechanism.

The structures of  $Mg_2(dobpdc)(3-4-3)$  after adsorption of  $CO_2$  to half and full capacity were further investigated using van der Waals (vdW)-corrected density functional theory (DFT) calculations (Fig. 3D). Lattice parameters obtained from high-resolution powder XRD (PXRD) experiments under vacuum and after exposure to 1-bar  $CO_2$  were used as starting points for structural relaxations (fig. S29 and table S4). The computed binding

energies ( $\Delta E_{ads}$ ) for the structures are within ±10 kJ/mol of the corresponding experimental  $\Delta h_{ads}$  values (table S7) (38). At full CO<sub>2</sub> capacity (i.e., two molecules of CO<sub>2</sub> per tetraamine), our calculations support two-step cooperative insertion of CO<sub>2</sub>, and the calculated NMR chemical shifts for this structure are in good agreement with the experimental values (table S8) (38). The computed  $\Delta E_{ads}$  values indicate that the half-capacity structure was more stable than the full-capacity structure, which further supports our proposed twostep cooperative adsorption mechanism. In addition, the tetraamines in our optimized structure of activated Mg<sub>2</sub>(dobpdc)(3-4-3) bridged the set of metals spanning ~16.7 Å in the *ab*plane of the framework, consistent with the single-crystal structure of Zn<sub>2</sub>(dobpdc)(3-4-3). Comparing the activated and full CO<sub>2</sub> capacity structures with synchrotron PXRD patterns by Rietveld analysis shows reasonable fits (figs. S32 and S33 and table S9). Taken together, our results from XRD, NMR, IR, and DFT indicate that tetraamine-functionalized frameworks indeed enhance cooperative  $CO_2$  adsorption relative to diamine-appended materials.

## Carbon capture from flue gas with steam desorption

Because flue gas streams are saturated with water, any candidate carbon-capture material must be able to adsorb CO2 under humid conditions. When exposed to CO<sub>2</sub> streams with  $\sim 2.6\%$  H<sub>2</sub>O (materials and methods) (32), Mg<sub>2</sub>(dobpdc)(3-4-3) again exhibited step-shaped isobars, with steps shifted to higher temperatures relative to those under dry  $CO_2$  (fig. S40), as has been reported previously for diamineappended Mg<sub>2</sub>(dobpdc) (29, 30, 32). Notably, this temperature shift indicated that water enhanced CO<sub>2</sub> binding in the material and should promote CO<sub>2</sub> capture from a flue gas stream (29, 30, 32). Furthermore, essentially no changes in the CO<sub>2</sub> adsorption profile and capacity were observed after the material was held under flowing air at 100°C for 12 hours,



**Fig. 4. CO**<sub>2</sub> **adsorption in Mg**<sub>2</sub>(**dobpdc**)(3-4-3) in the presence of water. (A) CO<sub>2</sub> breakthrough profile for Mg<sub>2</sub>(dobpdc)(3-4-3) under simulated humid (~2.6% H<sub>2</sub>O) natural gas flue gas (4% CO<sub>2</sub> in N<sub>2</sub>) at 100°C and atmospheric pressure. (B) Extended temperature-swing cycling of Mg<sub>2</sub>(dobpdc)(3-4-3) carried out using a thermogravimetric analyzer at atmospheric pressure. Adsorption conditions: humid (~2.6% H<sub>2</sub>O) 4% CO<sub>2</sub> in N<sub>2</sub> for 5 min at 100°C; desorption conditions: humid (~2.6% H<sub>2</sub>O) CO<sub>2</sub> stream at 180°C for 1 min. (C) IR spectra showing 15 cycles of adsorption under humid CO<sub>2</sub> (bright green spectra) and desorption under simulated steam (light gray spectra, estimated 51 to 65% water content, balance N<sub>2</sub>). Increasingly darker colored curves indicate progressive cycles. Spectra of the activated framework under flowing steam and N<sub>2</sub> were used as a baseline. (D) Plot of the integrated area for the carbamate band in (C) (~1290 to 1360 cm<sup>-1</sup>) versus adsorption cycle number, illustrating stable formation of the carbamate species across 15 cycles.

indicating the stability of the framework to oxygen in the flue gas stream (fig. S43).

We also performed breakthrough experiments at 100°C under the same humid conditions to simulate a real fixed-bed adsorption process. Under these conditions, Mg<sub>2</sub>(dobpdc)(3-4-3) exhibited a high CO<sub>2</sub> capture rate of 90% with a breakthrough capacity of  $2.0 \pm 0.2 \text{ mmol/g}$ (Fig. 4A and figs. S45 to S48). It also exhibited minimal tetraamine volatilization during the course of 1000 CO2 adsorption-desorption cycles performed under humid conditions using a thermogravimetric analyzer, and the material remained crystalline with a stable cycling capacity of 13.6 g/100 g (Fig. 4B and fig. S50 and S51). Thus, Mg<sub>2</sub>(dobpdc)(3-4-3) could cycle a large quantity of  $CO_2$  while meeting the U.S. DOE target for capturing 90% of the CO<sub>2</sub> from natural gas flue emissions (7).

The high breakthrough capacity and exceptional stability of Mg<sub>2</sub>(dobpdc)(3-4-3) motivated us to explore the use of steam in place of heating at 180°C to desorb CO<sub>2</sub> from the material. Low-grade steam could offer advantages over both temperature-swing and pressureswing adsorption processes for postcombustion  $CO_2$  capture (17-22). The viability of using steam for CO<sub>2</sub> desorption was tested in a custom-built flow-through cell for in situ DRIFTS equipped to cycle between flowing humid  $CO_2$ and simulated steam (estimated 51 to 65% water content, balance N2; table S10) at 120°C and ~1 atm (Fig. 4, C and D). The IR spectra collected for  $Mg_2(dobpdc)(3-4-3)$  over the course of 15 cycles showed repeated growth and disappearance of both the ammonium  $(2800 \text{ to } 1800 \text{ cm}^{-1})$  and C-N  $(1339 \text{ cm}^{-1})$  bands associated with carbamate chain formation, indicating the stability of the cooperative insertion mechanism to steam-regeneration conditions. Postcycling isobaric analysis of the material revealed that step-shaped adsorption was retained to a high capacity ( $\sim 16.6$  g/100; figs. S52 to S55 and table S11), and <sup>1</sup>H NMR analysis revealed that the tetraamine loading remained unchanged (table S12). By contrast, the representative diamine-appended material Mg<sub>2</sub>(dobpdc)(N-ethylethylenediamine)<sub>2</sub> (28, 30) exhibited substantial amine volatilization after only a single steam desorption cycle (table S13 and fig. S56). The impressive performance of Mg<sub>2</sub>(dobpdc)(3-4-3) underscores the stabilization afforded by the multimetal coordination modes.

### Outlook

We have developed a class of tetraaminefunctionalized metal-organic frameworks that exhibit cooperative  $CO_2$  adsorption and greatly enhanced stability compared with previous diamine-functionalized materials as a result of multiple, ordered metal-amine interactions. The nature of amine coordination in these materials gives rise to two-step adsorption of

CO<sub>2</sub> and large adsorption enthalpies suitable for CO<sub>2</sub> capture from simulated natural gas flue streams. The top-performing material, Mg<sub>2</sub>(dobpdc)(3-4-3), achieved a large CO<sub>2</sub> adsorption capacity of  $2.0 \pm 0.2 \text{ mmol/g}$  in the presence of water while meeting the DOE target for 90% CO<sub>2</sub> capture from natural gas flue emissions. Most notably, however, the enhanced stability of these tetraamine-functionalized frameworks enables regeneration using direct steam contact, a pathway that could afford substantial energy savings compared with traditional processes. Overall, the molecular-level design strategy implemented in this work represents a step-change in the industrial viability of adsorption-based CO<sub>2</sub> capture from natural gas flue emissions, a separation of growing importance in the global energy landscape.

#### **REFERENCES AND NOTES**

- 1. Intergovernmental Panel on Climate Change (IPCC), "Climate change 2013: The physical science basis" (Cambridge Univ. Press, 2013).
- IPCC, "Climate change 2014: Mitigation of climate change" (Cambridge Univ. Press, 2014).
- International Energy Agency, "CO<sub>2</sub> emissions from fuel combustion highlights" (International Energy Agency, 2016).
- M. Bui *et al.*, *Energy Environ. Sci.* **11**, 1062–1176 (2018).
  R. L. Siegelman, P. J. Milner, E. Kim, S. C. Weston, J. R. Long,
- K. E. Stegenhan, F. S. Minler, E. Kin, S. O. Westen, S. K. Eong Energy Environ. Sci. 12, 2161–2173 (2019).
   U.S. Energy Information Administration, "International energy
- U.S. Energy Information Administration, International energy outlook 2019" (U.S. Energy Information Administration, 2019).
   U.S. Department of Energy, National Energy Technology
- C.S. Department of Energy, National Energy Technology Laboratory, "Cost and performance baseline for fossil energy plants. Volume 1a: Bituminous coal (PC) and natural gas to electricity. Revision 3" (U.S. Department of Energy, National Energy Technology Laboratory, 2015).
- E. S. Rubin, H. Zhai, *Environ. Sci. Technol.* 46, 3076–3084 (2012).
- U.S. Department of Energy, "Carbon capture opportunities for natural gas fired power systems" (U.S. Department of Energy, 2017).
- 10. G. T. Rochelle, Science 325, 1652-1654 (2009).
- S. A. Mazari, B. Si Ali, B. M. Jan, I. M. Saeed, S. Nizamuddin, Int. J. Greenh. Gas Control 34, 129–140 (2015).
- 12. T. C. Drage et al., J. Mater. Chem. 22, 2815-2823 (2012).
- H. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi, *Science* 341, 1230444 (2013).
   P. Pullini, S. A. Didas, C. W. Japas, J. Matar. Cham. 21.
- P. Bollini, S. A. Didas, C. W. Jones, J. Mater. Chem. 21, 15100–15120 (2011).
- 15. J. A. Mason et al., J. Am. Chem. Soc. 137, 4787-4803 (2015).
- Y. Lin, C. Kong, L. Chen, RSC Advances 6, 32598–32614 (2016).
- W. Chaikittisilp, H.-J. Kim, C. W. Jones, Energy Fuels 25, 5528–5537 (2011).
- R. Numaguchi et al., Energy Procedia 114, 2304–2312 (2017).
- N. Numagurin et al., *Energy Frocedia* **114**, 2304–2312
  W. Li et al., *ChemSusChem* **3**, 899–903 (2010).
- W. Li *et al.*, *Chemsuschem* 3, 899–903 (2010).
  E. S. Sanz-Pérez, C. R. Murdock, S. A. Didas, C. W. Jones,
- Chem. Rev. 116, 11840–11876 (2016).
- A. R. Kulkarni, D. S. Sholl, Ind. Eng. Chem. Res. 51, 8631–8645 (2012).
- C. Kim, H. S. Cho, S. Chang, S. J. Cho, M. Choi, *Energy Environ. Sci.* 9, 1803–1811 (2016).
- M. Jahandar Lashaki, S. Khiavi, A. Sayari, *Chem. Soc. Rev.* 48, 3320–3405 (2019).
- D. Andirova, Y. Lei, X. Zhao, S. Choi, *ChemSusChem* 8, 3405–3409 (2015).
- N. C. Burtch, H. Jasuja, K. S. Walton, Chem. Rev. 114, 10575–10612 (2014).
- T. M. McDonald et al., J. Am. Chem. Soc. 134, 7056–7065 (2012).
- 27. T. M. McDonald et al., Nature 519, 303-308 (2015).
- R. L. Siegelman et al., J. Am. Chem. Soc. 139, 10526–10538 (2017).
- 29. P. J. Milner et al., J. Am. Chem. Soc. 139, 13541–13553 (2017).
  - 30. P. J. Milner et al., Chem. Sci. 9, 160-174 (2017).
- 31. J. H. Choe et al., Mater. Chem. Front. 3, 2759-2767 (2019).

- R. L. Siegelman et al., J. Am. Chem. Soc. 141, 13171–13186 (2019).
- L. Joss, M. Gazzani, M. Hefti, D. Marx, M. Mazzotti, Ind. Eng. Chem. Res. 54, 3027–3038 (2015).
- L. Joos, K. Lejaeghere, J. M. Huck, V. Van Speybroeck, B. Smit, Energy Environ. Sci. 8, 2480–2491 (2015).
- 35. M.-W. Yang et al., Energy Procedia 63, 2351-2358 (2014).
- 36. A. Lee et al., Energy Procedia 4, 1199–1206 (2011).
- X. P. Wang, J. J. Yu, J. Cheng, Z. P. Hao, Z. P. Xu, Environ. Sci. Technol. 42, 614–618 (2008).
- A. C. Forse et al., J. Am. Chem. Soc. 140, 18016–18031 (2018).

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#### SUPPLEMENTARY MATERIALS

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### Cooperative carbon capture and steam regeneration with tetraamine-appended metal-organic frameworks

Eugene J. Kim, Rebecca L. Siegelman, Henry Z. H. Jiang, Alexander C. Forse, Jung-Hoon Lee, Jeffrey D. Martell, Phillip J. Milner, Joseph M. Falkowski, Jeffrey B. Neaton, Jeffrey A. Reimer, Simon C. Weston and Jeffrey R. Long

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Steaming out captured CO<sub>2</sub> Although natural gas is less carbon dioxide (CO<sub>2</sub>)-intensive than coal, capturing its emitted CO<sub>2</sub> can be more challenging because combined-cycle natural gas combustion has a CO<sub>2</sub> concentration that is only one-third of that of coal combustion and contains high concentrations of oxygen and water. Kime *et al.* report on a tetraamine-functionalized magnesium metal–organic framework that displays two-step cooperative CO<sub>2</sub> adsorption that leads to a high CO<sub>2</sub> capacity and adsorption enthalpy (see the Perspective by Peh and Zhao). This material could capture CO 2 from humid air and could be regenerated with steam, a method that is more economical than temperature or pressure swing methods.

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