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Article

Cooperative Carbon Dioxide Capture in Diamine-Appended Magnesium–Olsalazine Frameworks

Ziting Zhu, Surya T. Parker, Alexander C. Forse, Jung-Hoon Lee, Rebecca L. Siegelman, Phillip J. Milner, Hsinhan Tsai, Mengshan Ye, Shuoyan Xiong, Maria V. Paley, Adam A. Uliana, Julia Oktawiec, Bhavish Dinakar, Stephanie A. Didas, Katie R. Meihaus, Jeffrey A. Reimer, Jeffrey B. Neaton, and Jeffrey R. Long*

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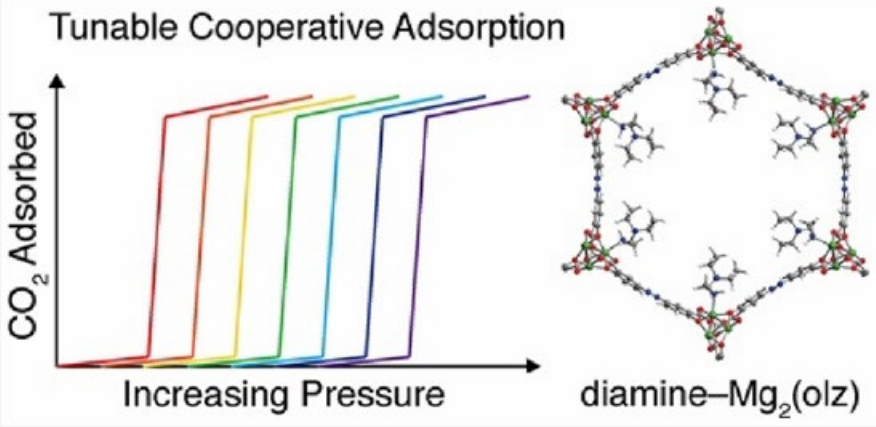

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Sonali Seth
04.05.2024

Background

PERSPECTIVE

Amine Scrubbing for CO_2 Capture

Gary T. Rochelle

Amine scrubbing has been used to separate carbon dioxide (CO_2) from natural gas and hydrogen since 1930. It is a robust technology and is ready to be tested and used on a larger scale for CO_2 capture from coal-fired power plants. The minimum work requirement to separate CO_2 from coal-fired flue gas and compress CO_2 to 150 bar is 0.11 megawatt-hours per metric ton of CO_2. Process and solvent improvements should reduce the energy consumption to 0.2 megawatt-hour per ton of CO_2. Other advanced technologies will not provide energy-efficient or timely solutions to CO_2 emission from conventional coal-fired power plants.

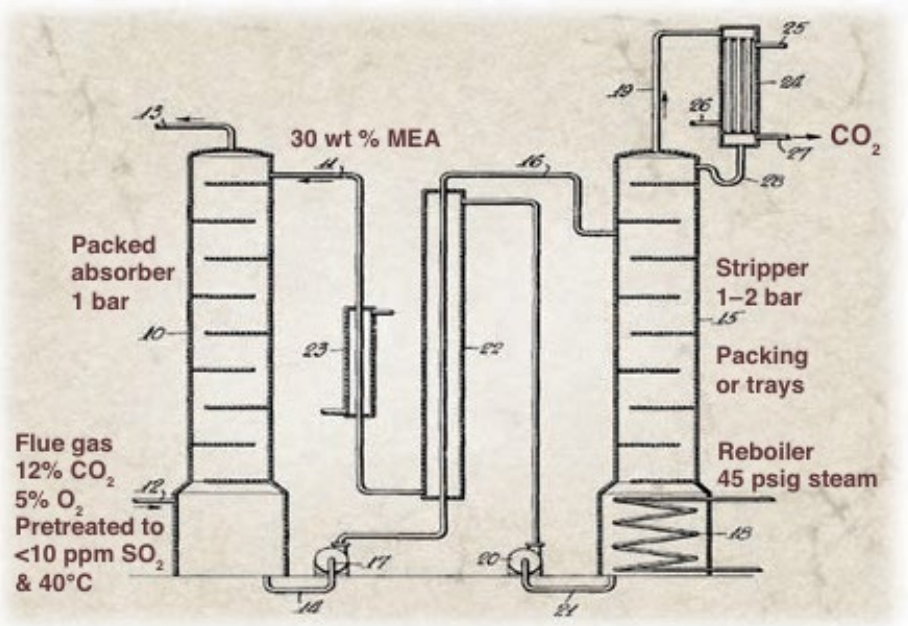

Fig. 1. The amine scrubbing process invented by Bottoms in 1930 (7).

RESEARCH ARTICLE | CARBON CAPTURE

A scalable metal-organic framework as a durable physisorbent for carbon dioxide capture

JIAN-BIN LIN, TAI T. T. NGUYEN, RAMANATHAN VAIDHYANATHAN, JAKE BURNER, JARED M. TAYLOR, HANA DUREKOVA, FARID AKHTAR, ROGER K. MAH, OMID GHAFFARI-NIK, [...], AND GEORGE K. H. SHIMIZU +8 authors Authors Info & Affiliations

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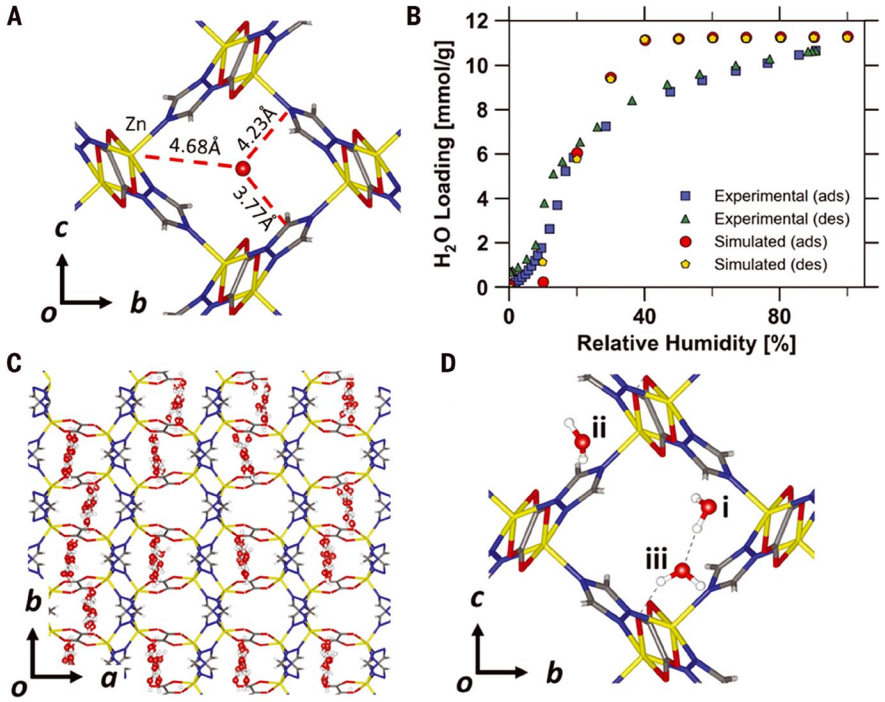
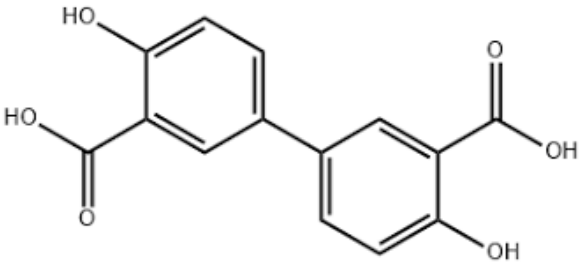


RESEARCH ARTICLE

GAS SEPARATIONS

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

Eugene J. Kim[1], Rebecca L. Siegelman[1,2]*, Henry Z. H. Jiang[1], Alexander C. Forse[1,3,4]†, Jung-Hoon Lee[5,6,7], Jeffrey D. Martell[1]‡, Phillip J. Milner[1]§, Joseph M. Falkowski[8], Jeffrey B. Neaton[5,6,9], Jeffrey A. Reimer[2,3], Simon C. Weston[8], Jeffrey R. Long[1,2,3]¶



Cross-linker

(dobpdc4−=4,4′ dioxidobiphenyl-3,3′-dicarboxylate)

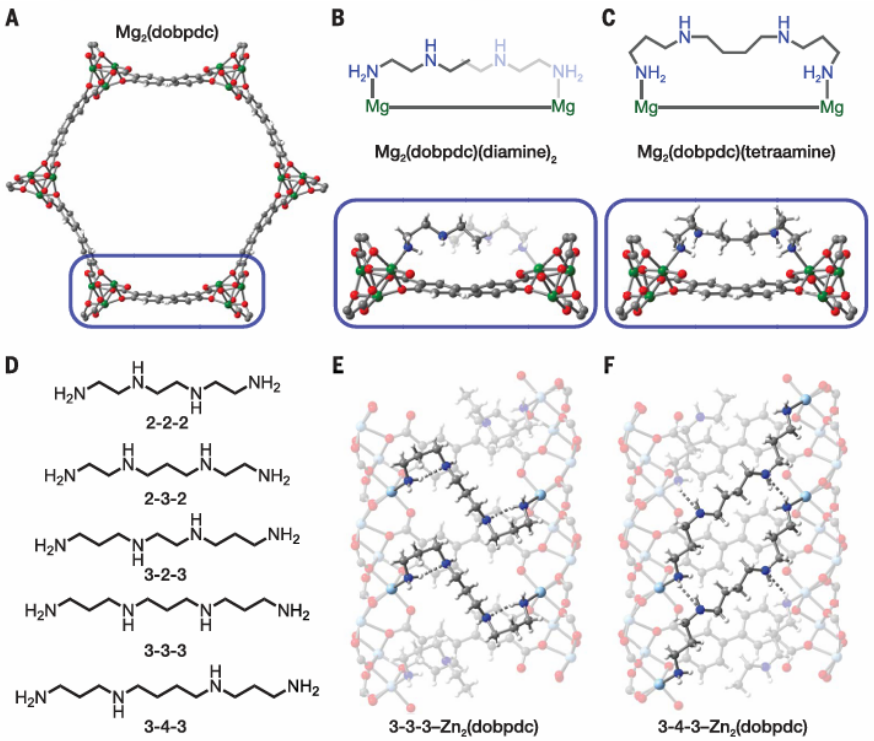


Fig. 1. Diamine versus tetraamine coordination in M_2(dobpdc). (**A**) Illustration of a hexagonal channel of Mg_2(dobpdc) viewed in the *ab*-plane, using single-crystal XRD data for the isostructural framework Zn_2(dobpdc). (**B** and **C**) Diamine-functionalized material features coordination of one diamine to each Mg^{2+} site (*28*) (B), whereas tetraamines can coordinate to two Mg^{2+} sites (C). (**D**) Tetraamines explored in this work and their abbreviations. (**E** and **F**) Single-crystal XRD structures (100 K) of Zn_2(dobpdc) functionalized with 3-3-3 and 3-4-3 tetraamines, respectively. The tetraamines span metal centers across the pore that are 10.4637(11) Å apart (3-3-3) and 16.8312(19) Å apart (3-4-3). Green, light blue, gray, red, blue, and white spheres represent Mg, Zn, C, O, N, and H, respectively.

Bulky amines in the pores enhance the stability of adsorption/desorption cycles

Double-step adsorption limits the capacity of MOF in CO_2 capture and leads to higher regeneration temperature.

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Cooperative insertion of CO_2 in diamine-appended metal-organic frameworks

Thomas M. McDonald, Jarad A. Mason, Xueqian Kong, Eric D. Bloch, David Gygi, Alessandro Dani, Valentina Crocellà, Filippo Giordanino, Samuel O. Odoh, Walter S. Drisdell, Bess Vlaisavljevich, Allison L. Dzubak, Roberta Poloni, Sondre K. Schnell, Nora Planas, Kyuho Lee, Tod Pascal, Liwen F. Wan, David Prendergast, Jeffrey B. Neaton, Berend Smit, Jeffrey B. Kortright, Laura Gagliardi, Silvia Bordiga, ... Jeffrey R. Long

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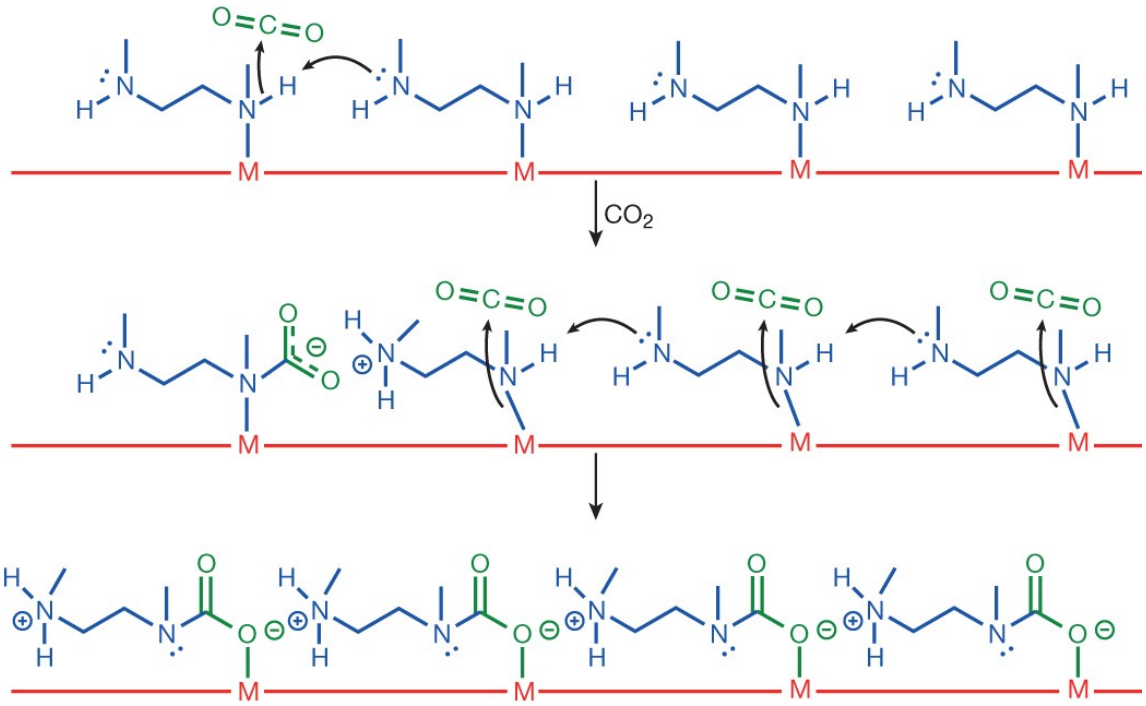


Why this paper?

- Single-step CO_2 adsorption.
- Selective for CO_2 capture.
- This paper tells that by tuning the stearic bulk and basicity of pore-dwelling amine, CO_2 capture capacities can be tuned.
- ee-2-Mg(olz) captures CO_2 from coal flue gas.
- Basicity plays a major role in CO_2 capture at high temperature and low pressure.

Introduction

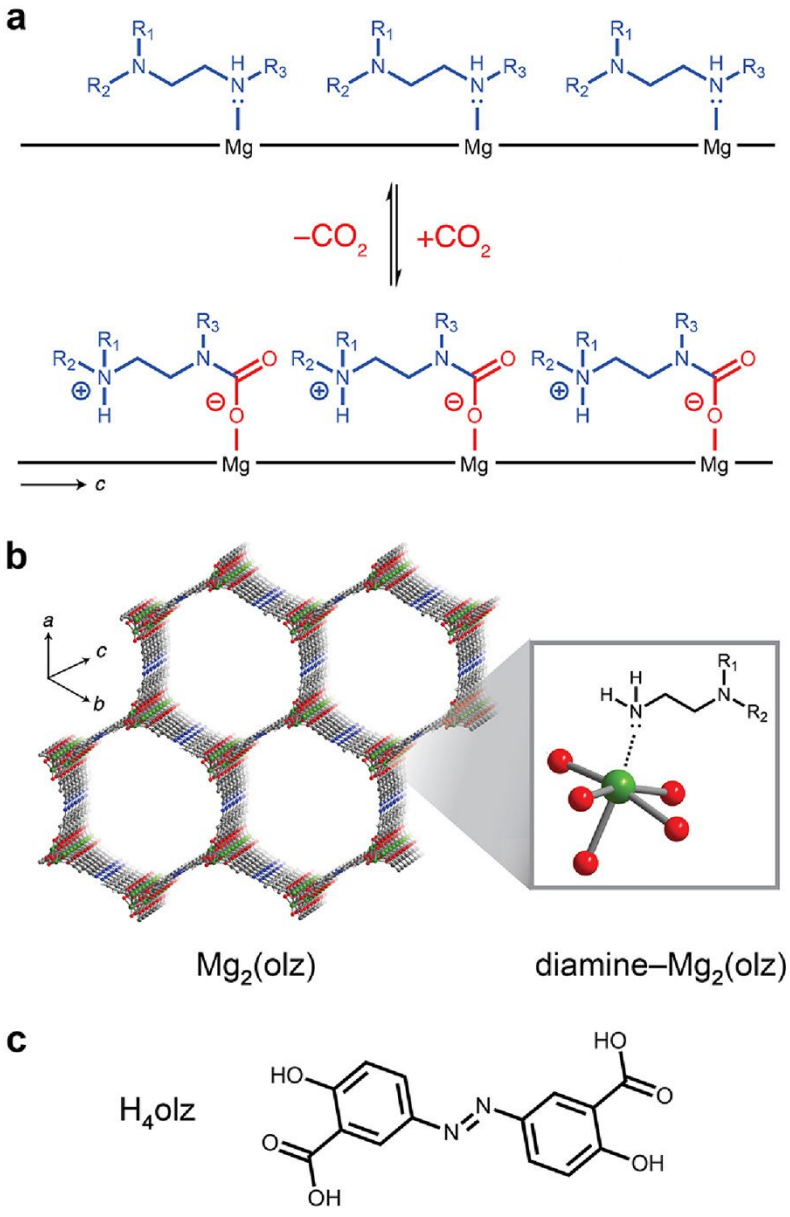
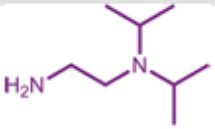
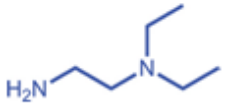
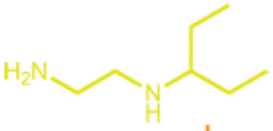
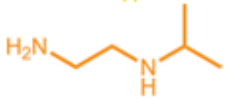
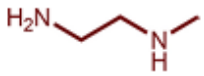


Figure 1. (a) Depiction of cooperative CO_2 insertion into diamine–Mg_2(dobpdc) to form chains of ammonium carbamate. (b) Structure of activated Mg_2(olz), which was postsynthetically functionalized with diamines to generate diamine–Mg_2(olz). Green, red, blue, gray, and white depict the Mg, N, C, and H atoms, respectively. (c) Structure of the H_4olz linker.

Table 1. Structures and Shorthand for Diamines Used in This Work

Diamine	Structure	Abbreviation
N,N-diisopropyl ethylenediamine		ii-2
N,N–dimethyl ethylenediamine		mm-2
N,N–diethyl ethylenediamine		ee-2
1,2-diamino-2-methylpropane		dmen
N–(3-pentyl) ethylenediamine		3-pent-2
N–isopropyl ethylenediamine		i-2
N–propyl ethylenediamine		p-2
N–ethyl ethylenediamine		e-2
N–methyl ethylenediamine		m-2

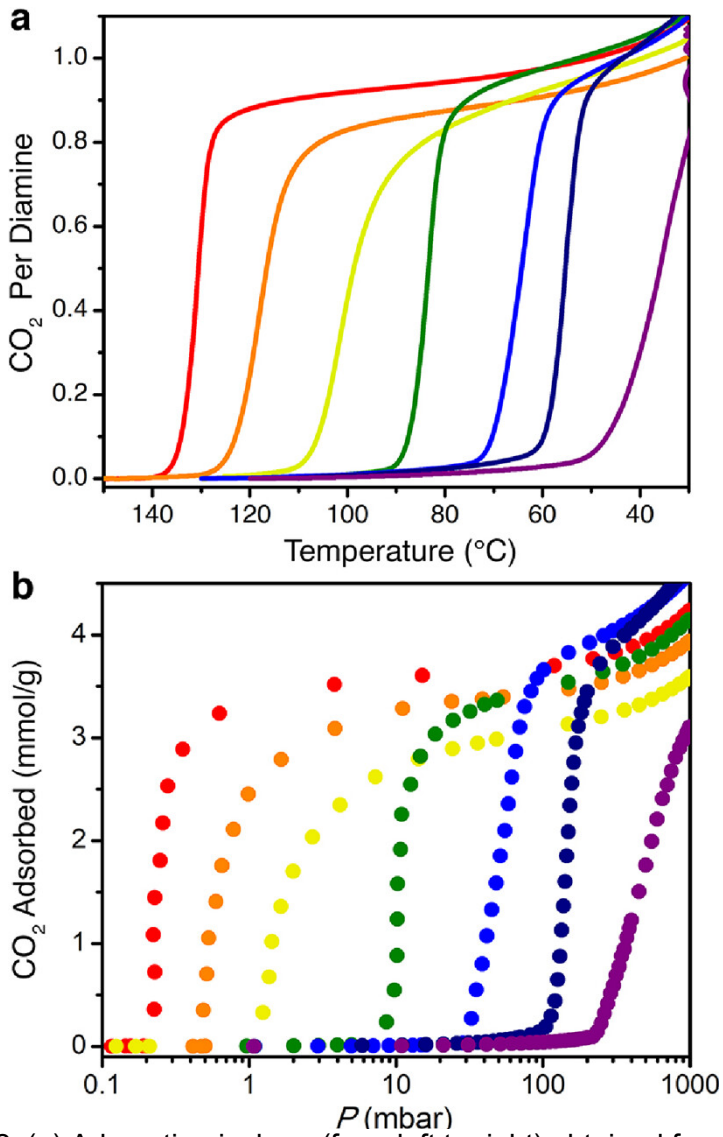


Figure 2. (a) Adsorption isobars (from left to right) obtained for e-2–, i-2–, 3-pent-2–, dmen–, ee-2–, mm-2–, and ii-2–Mg_2(olz) under pure CO_2, as measured by thermogravimetric analysis. (b) Pure CO_2 adsorption isotherms (from left to right) obtained at 40 °C for e-2–, i-2–, 3-pent-2–, dmen–, ee-2–, mm-2–, and ii-2–Mg_2(olz). The data for m-2–Mg_2(olz) and p-2–Mg_2(olz) nearly overlay those collected for e-2–Mg_2(olz) and are omitted here for simplicity. See Figure 3a for the corresponding isotherms at 85 °C for all three 1°,2°-diamines bearing linear alkyl substituents.

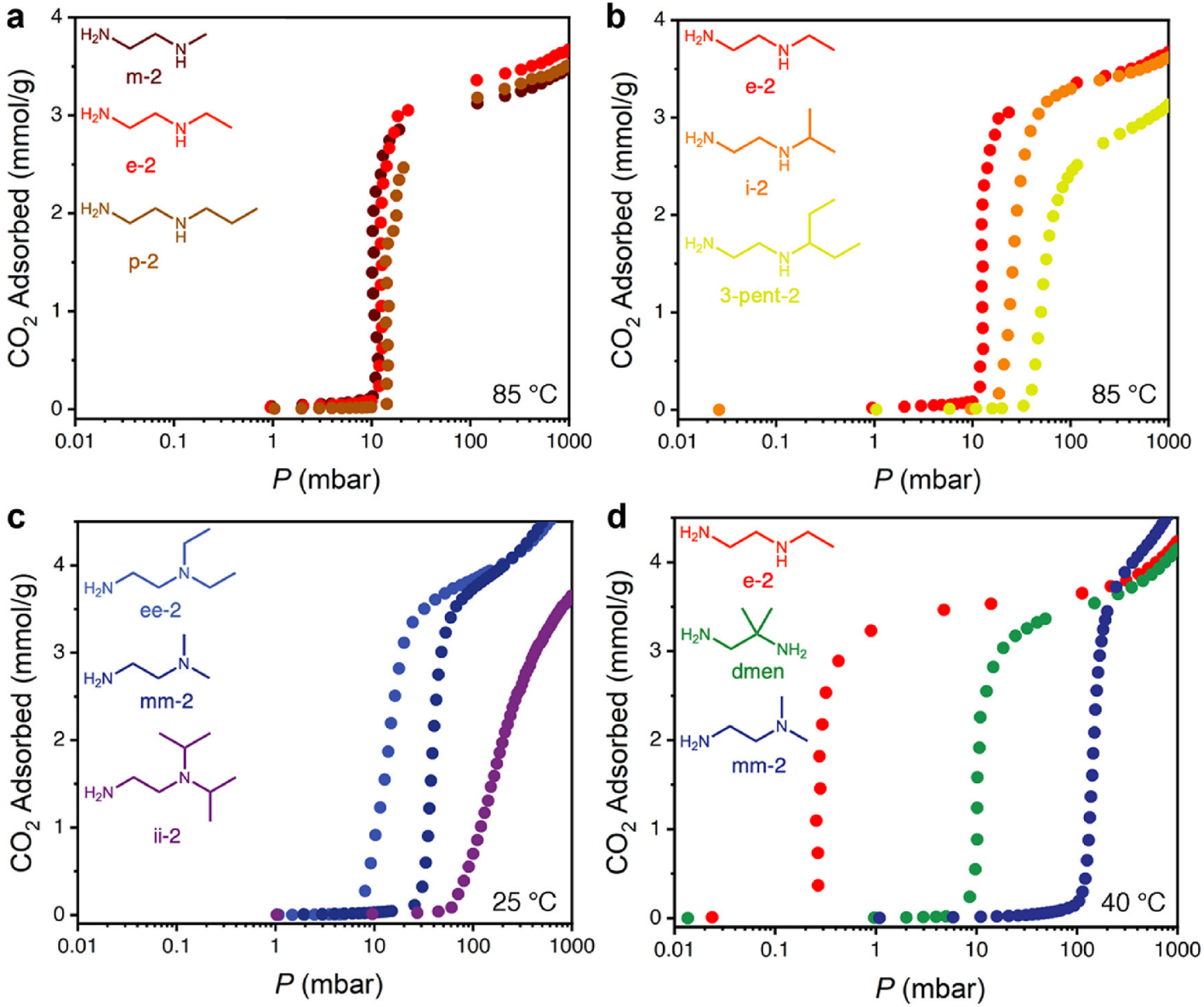


Figure 3. Comparisons of adsorption isotherms under pure CO_2 for different series of diamine–Mg_2(olz) variants illustrating the effect of the diamine structure on the adsorption step pressure. (a) 1°,2°-Diamines bearing linear alkyl substituents, (b) 1°,2°-diamines with increasingly branched substituents, (c) 1°,3°-diamines with different degrees of substituent branching, and (d) diamines with two-carbon alkyl substitutions. Note the distinct isotherm temperatures for each series: data were collected at 85 °C for panels (a) and (b), 25 °C for panel (c), and 40 °C for panel (d).

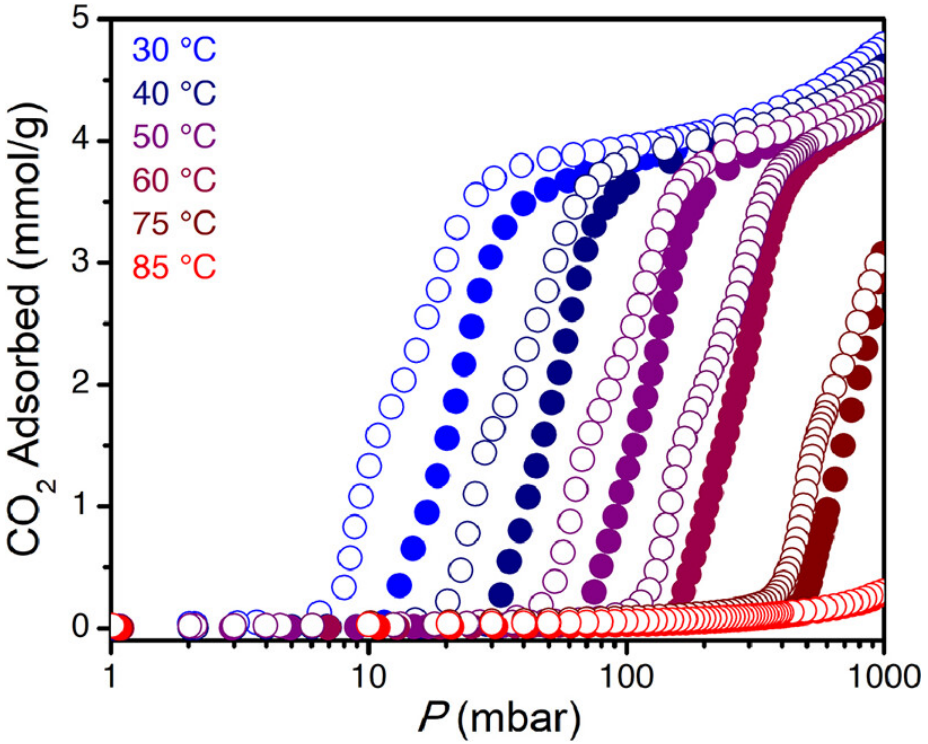


Figure 4. Carbon dioxide adsorption isotherms for ee-2–Mg_2(olz) collected at the indicated temperatures with pressure plotted on a logarithmic scale. The filled and empty circles represent the adsorption and desorption data, respectively.

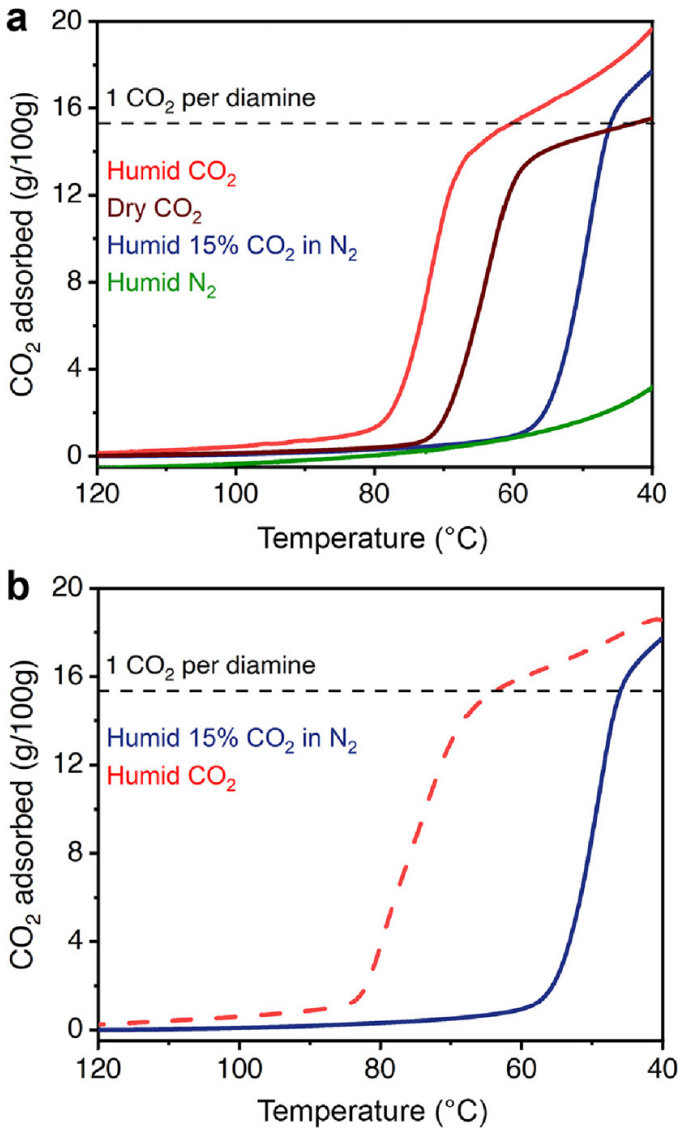


Figure 5. (a) Comparison of humid CO_2 (~1.5% H_2O), dry CO_2, humid 15% CO_2 in N_2 (~1.5% H_2O), and humid N_2 (~1.5% H_2O) adsorption isobars for ee-2–Mg_2(olz) at atmospheric pressure. (b) Humid 15% CO_2 in N_2 (~1.5% H_2O) adsorption isobar (cooling, solid blue line) and humid CO_2 (~1.5% H_2O) desorption isobar (heating, dashed red line) for ee-2–Mg_2(olz) under atmospheric pressure. A ramp rate of 1 °C/min was used for all of the isobaric experiments.

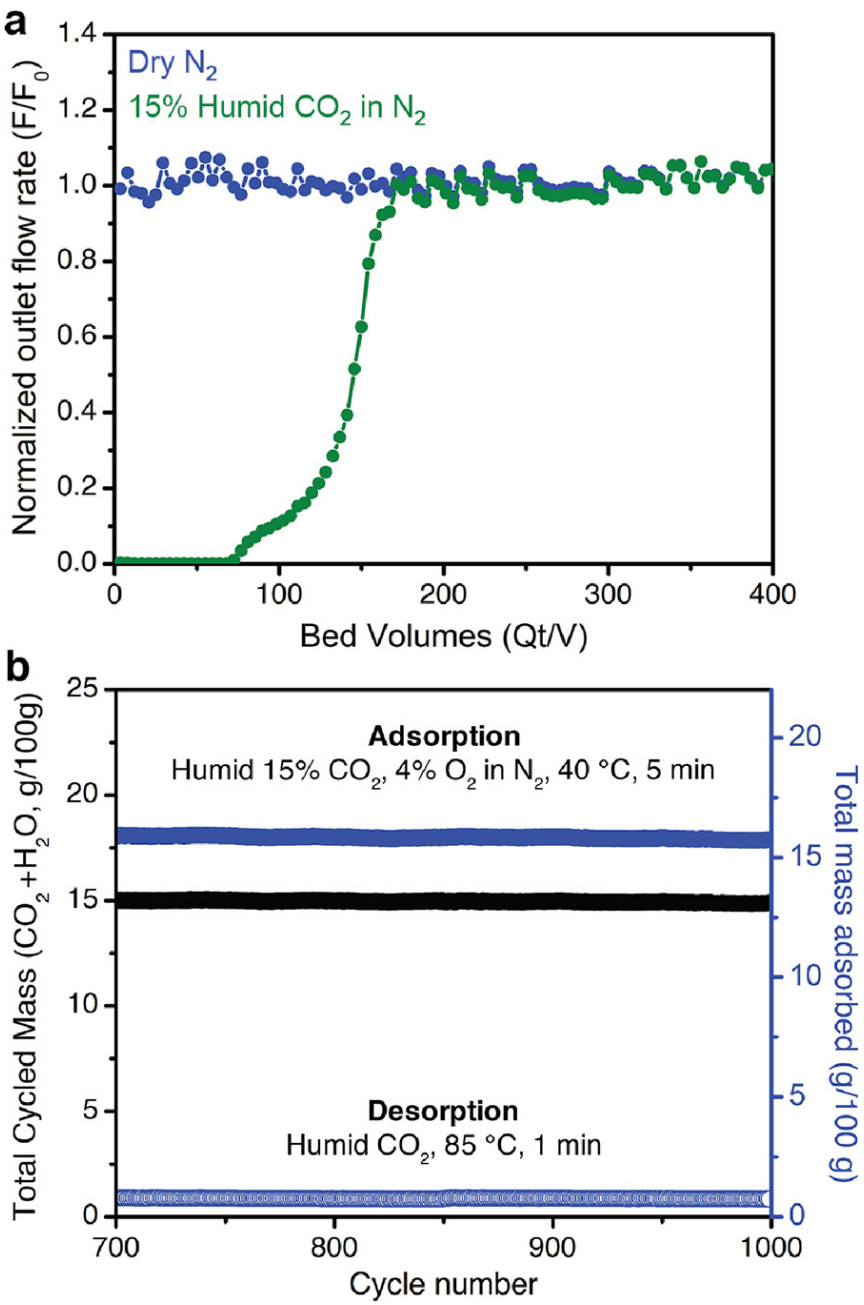


Figure 6. (a) Breakthrough data for ee-2–Mg_2(olz) collected under humid (~2.3% H_2O) 15% CO_2 in N_2 at 40 °C with a flow rate of 10 sccm and ~1 bar feed pressure. Breakthrough of N_2 occurred nearly immediately, indicating negligible N_2 uptake. The CO_2 breakthrough profile exhibits a favorable sharp shape and corresponds to a total capacity of 3.9 ± 0.3 mmol/g. (b) Last 300 of 1000 thermogravimetric temperature-swing cycles conducted on ee-2–Mg_2(olz) under simulated humid coal flue gas at atmospheric pressure. Adsorption, 40 °C, humid (~2.3% H_2O) 15% CO_2, 4% O_2 in N_2, 5 min; desorption, 85 °C, humid (~2.3% H_2O) CO_2, 1 min

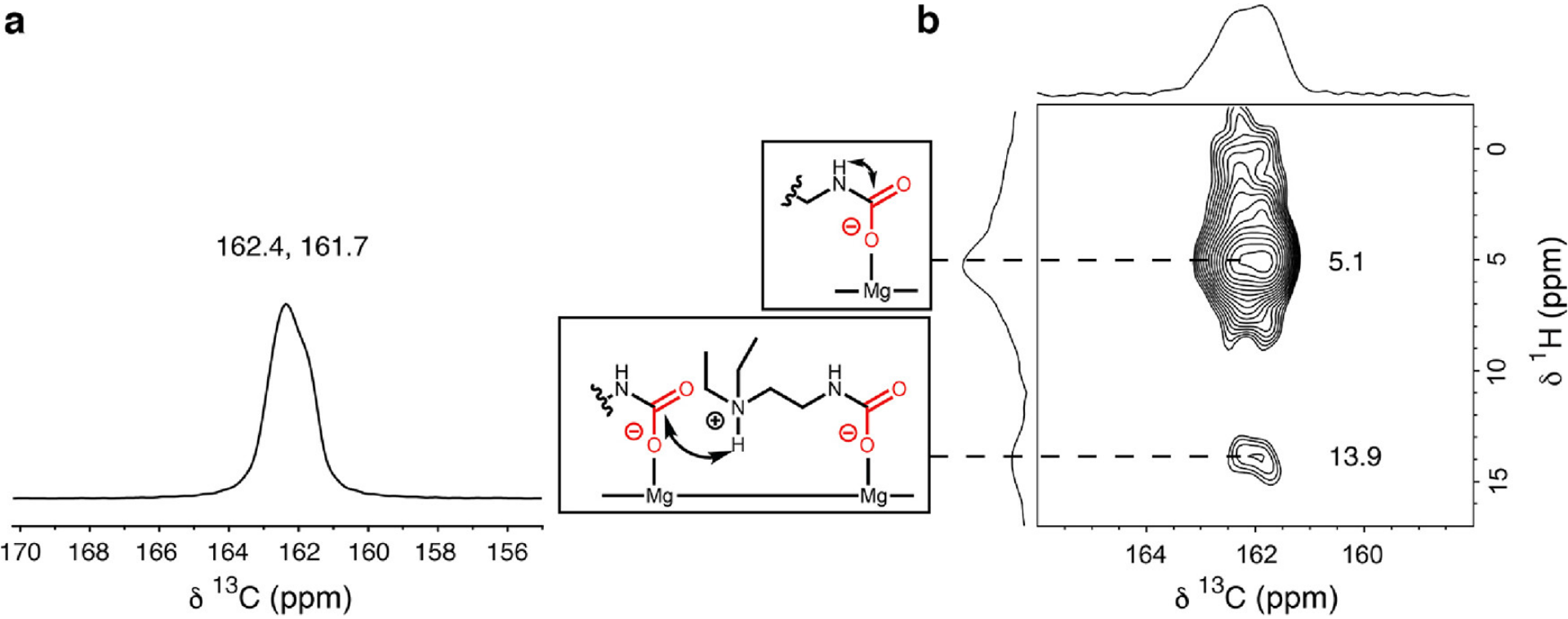


Figure 7. Room-temperature solid-state magic angle spinning NMR (16.4 T) spectra of ee-2–Mg_2(olz) dosed with 1 bar $^{13}CO_2$. (a) ^{13}C NMR spectrum obtained by cross-polarization (with continuous-wave decoupling of ^{1}H). (b) $^{1}H \rightarrow {}^{13}C$ HETCOR (contact time 100 μs) spectrum and correlation assignments.

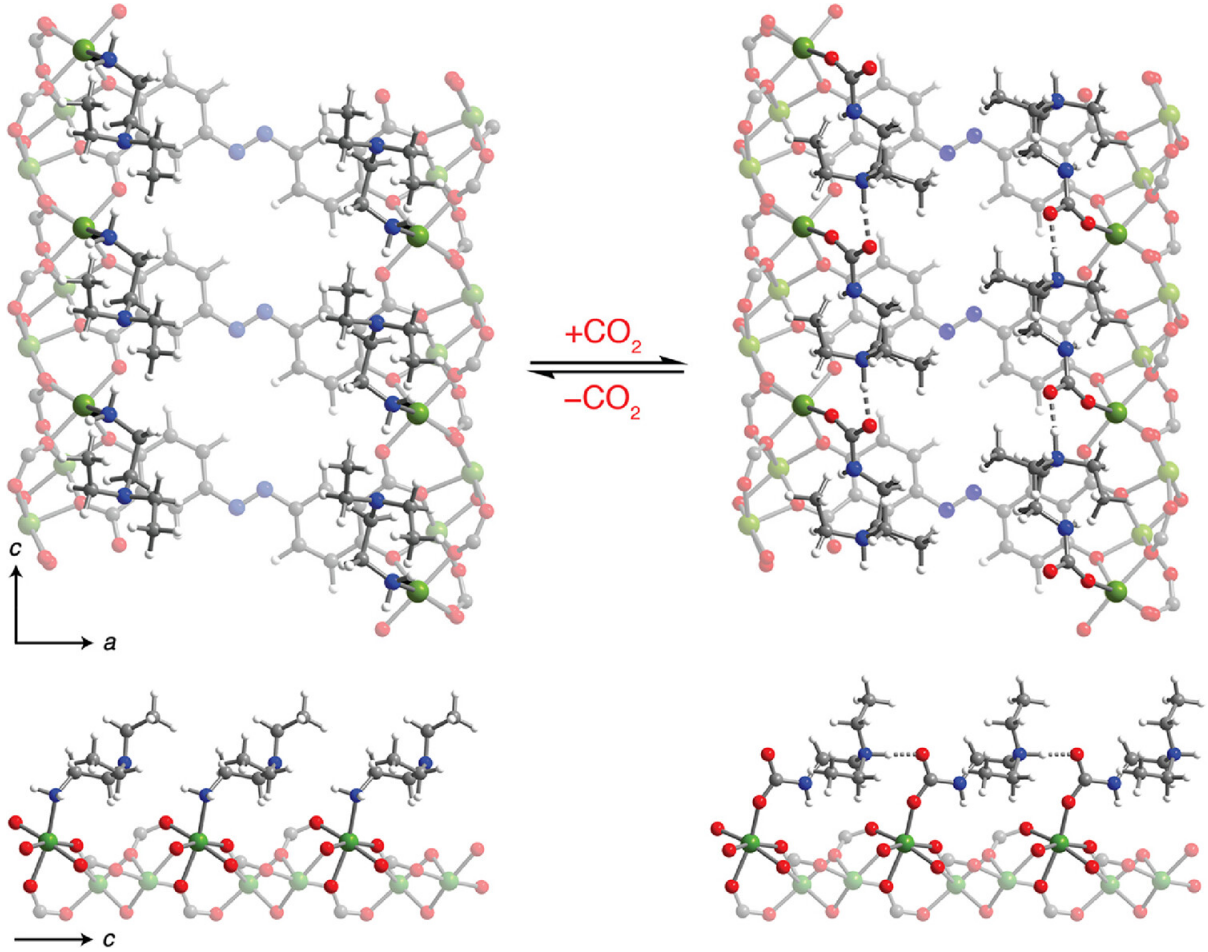


Figure 8. Proposed structures of (left) evacuated ee-2–Mg_2(olz) and (right) ammonium carbamate chains formed upon the adsorption of CO_2 in ee-2–Mg_2(olz). Green, red, blue, gray, and white spheres represent Mg, O, N, C, and H, respectively.

Theoretical BE- -66.4 Kj/mol
Experimental BE- -69.9 Kj/mol

Conclusion

A class of MOFs has been developed where small temperature swings can be used to capture CO_2.

Both the steric factor and the basicity of the pore-dwelling amine are important factors to consider in tuning the CO_2 adsorption step pressure or temperature.

Amine steric bulk is inversely proportional to the degree of CO_2 cooperativity.

MOF was thermally and oxidatively stable