Supporting Information

A diamine-grafted metal-organic framework with top-performing CO$_2$ capture properties and a facile coating approach for imparting exceptional moisture stability

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Preparation.

All chemicals and solvents in the synthesis were reagent grade and used as received. H4dobpdc was prepared according to the literature.  

\[ [M_2(dobpdc)(een)(H_2O)_3] \text{[een-M}_2\text{dobpdc}] \]. We used the same procedure with the synthesis of 1-een. Elemental analysis (%) calcd for [Mg2(dobpdc)(een)1.7(H2O)0.3] (H2O)1.5 (een-Mg2(dobpdc)-1.1H2O): C 49.86, H 6.03, N 9.50; found: C 49.62, H 5.74, N 9.24; [Co2(dobpdc)(een)1.85(H2O)0.15](H2O)1.55 (een-Co2(dobpdc)-1.55H2O): C 44.18, H 5.47, N 8.91; found: C 44.62, H 5.52, N 9.24; [Ni2(dobpdc)(een)1.9(H2O)0.1](H2O)1.1 (een-Ni2(dobpdc)-1.1H2O): C 44.99, H 5.45, N 9.23; found: C 44.69, H 5.4, N 9.56; [Zn2(dobpdc)(een)1.6(H2O)0.1](H2O)1.5 (een-Zn2(dobpdc)-1.5H2O): C 43.60, H 5.52, N 9.24; found: C 43.92, H 5.62, N 9.15. To check the structural change upon CO2 adsorption, we exposed een-M2(dobpdc) to 100% CO2 at 40 °C for 30 min, affording een-M2(dobpdc)-CO2. een-M2(dobpdc)-regenerated was obtained by heating een-M2(dobpdc)-CO2 at 140 °C (Mg) and 120 °C (Co, Ni, Zn) for 30 min. Synchrotron PXRD data were collected to analyse the cell volume variation during CO2 adsorption and regeneration (Fig. S1).

Powder X-ray Diffraction and Structure Modeling. PXRD data were recorded using Cu Kα (\(λ = 1.5406 \text{ Å} \)) on a Rigaku Ultima III diffractometer with a scan speed of 2°/min and a step size of 0.01°. The synchrotron powder X-ray diffraction data were collected at 298 K with the 240 mm of detector distance in 2400 s exposure with synchrotron radiation (\(λ = 1.09998 \text{ Å} \)) using a 2D SMC ADSC Quantum-210 detector with a silicon (111) double crystal monochromator at the Pohang Accelerator Laboratory. The ADX program\(^2\) was used for data collection, and Fit2D program\(^3\) was used for converting a two-dimensional diffraction image to a one-dimensional diffraction pattern. The unit cell dimensions of 1-een, 1-een-CO2, and 1-een-regenerated were determined by conducting a full-pattern decomposition with the Le Bail method (Pawley refinement) implemented in TOPAS-Academic. The trigonal space group \(P3_21\) was utilized for the refinements, due to the isomorphism with Zn2(dobpdc).\(^3\) Based on the unit cell dimensions obtained, the geometry of the backbones was optimized via an energy minimization algorithm using the universal force field implemented in the Forcite module of Materials Studio.\(^4\)

Gas Sorption Measurements. Gas sorption isotherms were measured using a Micromeritics 3FLEX instrument up to 1 atm of gas pressure unless otherwise stated. The highly pure N2 (99.999%) and CO2 (99.999%) were used in the sorption experiments. N2 gas isotherms were measured at 77 K and CO2 uptake was measured at 298 K, 313 K, 333 K, 353 K, 373K, 393 K, 403 K, 413 K, and 423 K.

Thermogravimetric Analyses and Gas Cycling Measurements. Thermogravimetric analyses (TGA) were carried out at a ramp rate of 2 °C/min in an Ar (99.999 %) flow using a Scinco TGA N-1000 instrument and TA instrument Discovery TGA. CO2 cycling experiments of the activated 1-een were carried out on the instrument with 15% CO2 in N2. A flow rate of 70 mL/min was applied for all gases.

Infrared Spectroscopy Measurements. In situ IR spectra were obtained with an air-tight homemade IR cell composed of KBr windows by using a Nicolet iS10 FTIR spectrometer. Before the IR measurements, high-purity N2 (99.999%) was purged into the sample chamber, detector, and IR source to remove atmospheric CO2 from the IR spectrometer. We also recorded IR spectra with an attenuated total reflectance (ATR) module by using Nicolet iS10 FTIR spectrometer.
**Other Physical Measurement.** Adsorption properties in the wet streams were measured by an automated chemisorption analyzer (Micromeritics Autochem II 2920). Elemental analyses for C, H, and N were performed at the Elemental Analysis Service Center of Sogang University. XPS was measured at Semiconductor & Display Green Manufacturing Research Center (GMRC) at Korea University. Contact angle was measured by Phoenix-MT(T). SEM images were measured by S-4600 at Korea Basic Science Institute (KBSI). TEM analyses were measured by XFEG-Titan 300 kV FE-TEM by S-4600 at Korea Basic Science Institute (KBSI).

[Reference]
3. Fit2D Program: Hammersley, A. (E-mail: hammersley@esrf.fr), ESRF, 6 RUE JULES HOROWITZ BP 220 38043 GRENOBLE CEDEX 9 FRANCE.
Fig. S1. Synchrotron powder X-ray diffraction pattern of (a) 1-een, (b) 1-een-CO$_2$, and (c) 1-een-regenerated (red) with calculated diffraction patterns (blue) from Pawley refinement. The difference is shown in black.
Fig. S2. FT-IR data of 1-DMF and 1-MeOH.

Fig. S3. Powder X-ray diffraction pattern of 1-DMF, 1-MeOH, and 1-een.
Fig. S4. $\text{N}_2$ adsorption isotherms of (a) 1 and (c) 1-ehen at 77 K. DFT pore size distribution for (b) 1 and (d) 1-ehen calculated from $\text{N}_2$ adsorption at 77 K using a Tarazona NLDFT with a cylinder pore geometry.
Fig. S5. Synchrotron powder X-ray diffraction pattern of (a) een-Mg₂(dobpdc), (b) een-Mg₂(dobpdc)-CO₂, and (c) een-Mg₂(dobpdc)-regenerated (red) with calculated diffraction patterns (blue) from Pawley refinement. The difference is shown in black.
Fig. S6. Synchrotron powder X-ray diffraction pattern of (a) een-Co$_2$(dobpdc), (b) een-Co$_2$(dobpdc)-CO$_2$, and (c) een-Co$_2$(dobpdc)-regenerated (red) with calculated diffraction patterns (blue) from Pawley refinement. The difference is shown in black.
Fig. S7. Synchrotron powder X-ray diffraction pattern of (a) een-Ni$_2$(dobpdc), (b) een-Ni$_2$(dobpdc)-CO$_2$, and (c) een-Ni$_2$(dobpdc)-regenerated (red) with calculated diffraction patterns (blue) from Pawley refinement. The difference is shown in black.
Fig. S8. Synchrotron powder X-ray diffraction pattern of (a) een-Zn$_2$(dobpdc), (b) een-Zn$_2$(dobpdc)$_2$CO$_2$, and (c) een-Zn$_2$(dobpdc)-regenerated (red) with calculated diffraction patterns (blue) from Pawley refinement. The difference is shown in black.
Fig. S9. Adsorption isotherms of CO$_2$ for een-M$_2$(dobpdc) with M = (a) Mg, (b) Co, (c) Ni, and (d) Zn at the indicated temperatures. The CO$_2$ partial pressure of flue gas (150 mbar CO$_2$) is highlighted by dashed lines. The solid lines are eye-guides.
Fig. S10. Isosteric heat of CO$_2$ adsorption onto 1-een.
Fig. S11. (a) In situ IR spectra of 1-een in the high- and low-frequency regions showing N-H stretching and C-N vibration, respectively. The IR data represent the peak variations over time under a flow of 100% CO$_2$. (b) In situ IR spectra of 1-een under a 100% CO$_2$ stream with increasing temperature. (c) One of possible CO$_2$ adsorption mechanism with AA mode showing CO$_2$ insertion between Mn-N(primary) in carbamate unit. If CO$_2$ inserted into between Mn-N(secondary), it is assigned as B mode. Therefore, there are four possible modes of AA, AB, BA, and BB. The color indicates the vibrations of functional groups corresponding to the IR peaks in (a) and (b). The free amines could be subject to hydrogen binding between neighboring amine groups.
Fig. S12. Working capacities (WC) for (a) 1-een and (b) een-Mg₂(dobpdc) calculated by the difference between adsorbed amount at 60 °C and 15% CO₂, and that at 120 °C and 100% CO₂.
Fig. S13. TGA curves (blue lines) for 1-een, at desorption temperature (T\textsubscript{des}) of (a) 80 °C, (b) 90 °C, (c) 100 °C, and (d) 110 °C. The temperature profiles are represented by red lines. Adsorption occurred at increased temperatures and 15% CO\textsubscript{2} for 60 min and desorption occurred at different temperatures (T\textsubscript{des}) and under pure CO\textsubscript{2} flowing for 60 min.
Fig. S14. Adsorption capacity of 1-eeen under dry (15% CO\textsubscript{2} and 85% He) and wet (15% CO\textsubscript{2}, 3.75% H\textsubscript{2}O, and 81.25% He) conditions. The flow rate of the mixed gas was 80 mL/min.
Fig. S15. IR spectra of PDMS, 1-een, and PDMS-coated samples.

Fig. S16. PXRD profiles of 1-een coated by PDMS with different loading concentrations.
Fig. S17. SEM images of (a) 1-een, (b) 1-een@PDMS5, (c) 1-een@PDMS10, (c) 1-een@PDMS20, and (d) 1-een@PDMS50.
Fig. S18. High resolution TEM images of (a) 1-een, (b) 1-deen@PDMS5, (c) 1-deen@PDMS10, and (d) 1-deen@PDMS50.
Fig. S19. STEM images of (a) 1-een, (c) 1-een@PDMS5, (f) 1-een@PDMS10, and (i) 1-een@PDMS50. Elemental mapping analysis of (b) 1-een, (d) 1-een@PDMS5, (g) 1-een@PDMS10, and (j) 1-een@PDMS50. Cross-sectional line profiles of data of (e) 1-een@PDMS5, (h) 1-een@PDMS10, and (k) 1-een@PDMS50.
Table S1. Compositional analysis (atomic%) of Mn and Si determined by the line-scan profiles.

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<th>1-teen@PDMS5</th>
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Fig. S20. XPS of (a) 1-een@PDMS5, (b) 1-een@PDMS10, (c) 1-een@PDMS20, and (d) 1-een@PDMS50 with the reference of 1-een.
Fig. S21. $N_2$ isotherms of the coated samples at 77 K.

Fig. S22. $CO_2$ isotherms of 1-een and the coated samples at 313 K.
Fig. S23. PXRD profiles of 1-een and 1-een@PDMS20 before and after exposure to 100% relative humidity at room temperature.
Fig. S24. Relative CO₂ uptake of 1-een and 1-een@PDMS20 before and after exposure to water vapor up to 6 h.
Fig. S25. PXRD profiles of 1-een and 1-een@PDMS20 before and after exposure to 100% relative humidity at room temperature.
**Fig. S26.** Cyclic CO$_2$ adsorption capacity for (a) 1-teen and (b) 1-teen@PDMS20 under wet streams (15% CO$_2$, 3.75% H$_2$O, and 81.25% He), measured by Autochem II 2920. Adsorption occurred at 70 °C for 30 min and desorption occurred at 100 °C for 30 min.