

Electronic Supplementary Information

Reversible, Solid State Capture of Carbon Dioxide by Hydroxylated Amidines

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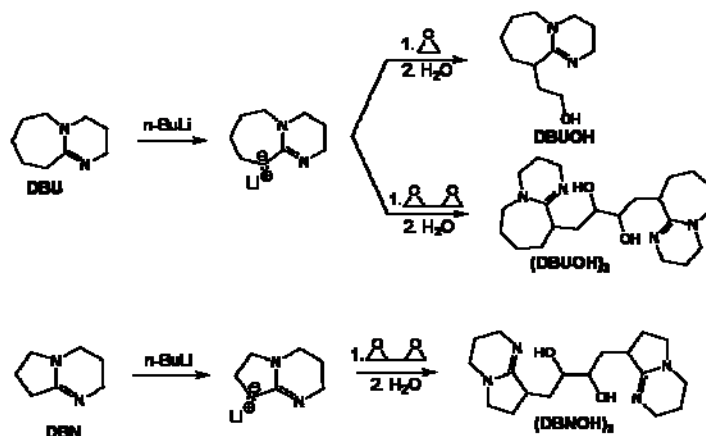
Materials and general methods. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, Aldrich, 98%) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN, TCI) were refluxed over CaH₂ and distilled under vacuum onto 4Å molecular sieves before use. n-BuLi (1.6M solution in hexane) was used as received. Ethylene oxide (Aldrich, 99.5%) and 1,3-butadiene diepoxide (TCI) were dissolved in dry THF before use. THF was distilled from sodium and benzophenone. Carbon dioxide (99.95%) was dried by passing through the CaSO₄ column before capture run. Amorphous silica (s60, Merck) with its specific surface area of 500m²/g, particle size of 0.040 mm~0.065 mm, and the pore size of 60 Å was baked at 150 °C under reduced pressure to remove adsorbed moisture.

¹H NMR spectra and ¹³C NMR spectra and HMQC were recorded on a Bruker DRX 600 spectrometer (600MHz) in CDCl₃ (reference 7.24 ppm for ¹H and 77.16 ppm for ¹³C NMR) or DMSO-d₆ (reference 2.50 ppm for ¹H and 39.52 ppm for ¹³C NMR). FTIR spectra were recorded on Perkin Elmer IR 2000 series using KBr pellet method. Thermogravimetry analysis was performed by TGA 2100 series of TA Instrument (sensitivity of 0.2 µg) with a heating rate of 10°C/min. GC/Mass spectra were recorded on a Shimadzu GCMS - QP 2010.

Syntheses of HAMs. These reaction were carried out on a scale of 10 g. Amidine (1.0 equiv.) was added to the dry THF (50 mL) and it was cooled to -78°C by dry ice-acetone bath. n-BuLi (1.6 M in hexane) (1.05 equiv.) was added into the solution at -78°C for 20 min. After stirring for 2 h at -78 °C and for 1 h at -20°C, a solution of epoxide (0.5 equiv.) in THF was added dropwise for 20 min at -10°C.

After stirring for 1 h at -10°C , the solution was warmed up to room temperature slowly. The mixture was stirred for 2 h and hydrolyzed by de-ionized water (1.05 equiv.) for 30 min. The mixture was filtered and evaporated. DBUOH was obtained by fractional distillation (60°C , 10^{-2} mmHg). $(\text{DBUOH})_2$ (mp 116°C) and $(\text{DBNOH})_2$ (mp 149°C) were purified by removal of unreacted amidines by heating at 120°C under reduced pressure (10^{-2} mmHg) and the product was used in the CO_2 capture experiment without further purification. The products were analyzed by ^1H NMR and ^{13}C NMR. For better assignment of peaks, HMQC was used. (see Fig. S1, S2 and S3)

GCMS Calcd for **DBUOH** ($\text{C}_{11}\text{H}_{20}\text{N}_2\text{O}$) MW196.29, found 196.15, 197.10, 195.15, for $(\text{DBUOH})_2$ ($\text{C}_{22}\text{H}_{38}\text{N}_4\text{O}_2$) MW 390.56, found 389.05, 390.20, 195, and for $(\text{DBNOH})_2$ ($\text{C}_{18}\text{H}_{30}\text{N}_4\text{O}_2$) MW 334.46, found 333.10



Scheme S1. Synthesis of HAMs

Preparation of HAM/silica hybrids. The HAM/silica with various HAM contents (10~50 wt%) was prepared. An adequate amount of dry HAM was charged into the one neck round flask and dissolved in 3 mL of dry THF under nitrogen atmosphere. Dry silica was added with stirring. The solvent was evaporated under reduced pressure. Each HAM/silica was thoroughly dried under vacuum for 1 day.

Carbon dioxide capture. CO₂ capture for Fig. S4a was conducted with 0.5g of dry DBUOH charged into 10 mL test tube under nitrogen atmosphere and sealed with rubber septum. Dry CO₂ was flowed into the tube through stainless steel needle and the excess of CO₂ was vented through vent needle.

For analytical purpose, HAM alkylcarbonates were prepared in THF solution. 0.1g of dry HAM was dissolved in 3 mL of dry THF and charged into the specially designed in-house 5 mL U tube under nitrogen atmosphere. And then the solution was bubbled with 100 mL/min of dry CO₂ gas through the needle. Within 5 min, the white amidinium alkylcarbonate salts were precipitated. The salts were filtered in the specially designed U tube under CO₂ flow without exposing to the air. The salts were analyzed by TGA, FTIR, and NMR.

For NMR analysis, HAM alkylcarbonates dissolved in DMSO-d₆ were charged into the NMR tube in N₂ charged glove box. And the NMR tubes charged with HAM alkylcarbonate were heated at 80 °C for 20 min to regenerate the HAMs. Each step, HAM, HAM-CO₂, and regenerated HAM, was analyzed by ¹H NMR and ¹³C NMR.

Prior to CO₂ capture or capture and release cycle on TGA, dry neat HAM or dry HAM/silica was loaded on the TGA pan and then baked at 110 °C for 10 min under nitrogen stream to remove adsorbed water. CO₂ capture was conducted under CO₂ flow of 100 mL/min at 25°C. CO₂ capture and release cycle was carried out by switching the experimental condition between CO₂ flow of 100 mL/min at 25°C for each experimental time (e. g. 120 min for DBUOH) and N₂ flow of 100 mL/min at 65°C for 30 min.

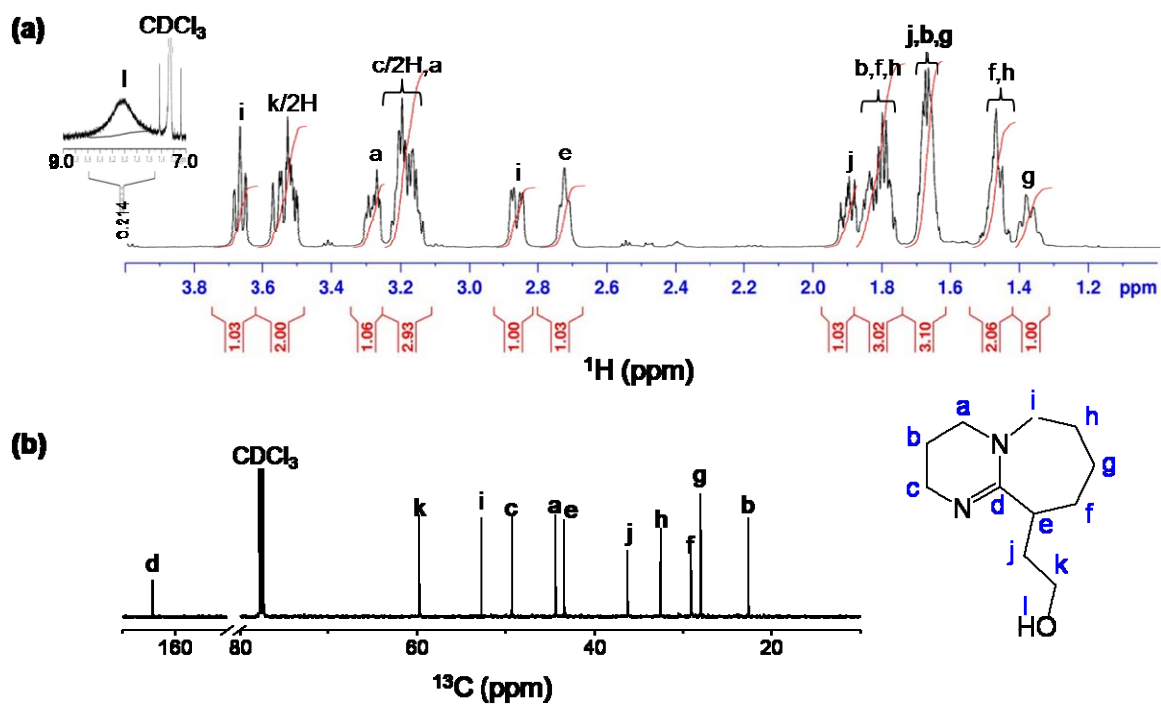


Fig. S1. (a) ^1H NMR and (b) ^{13}C NMR spectra of DBUOH in CDCl_3

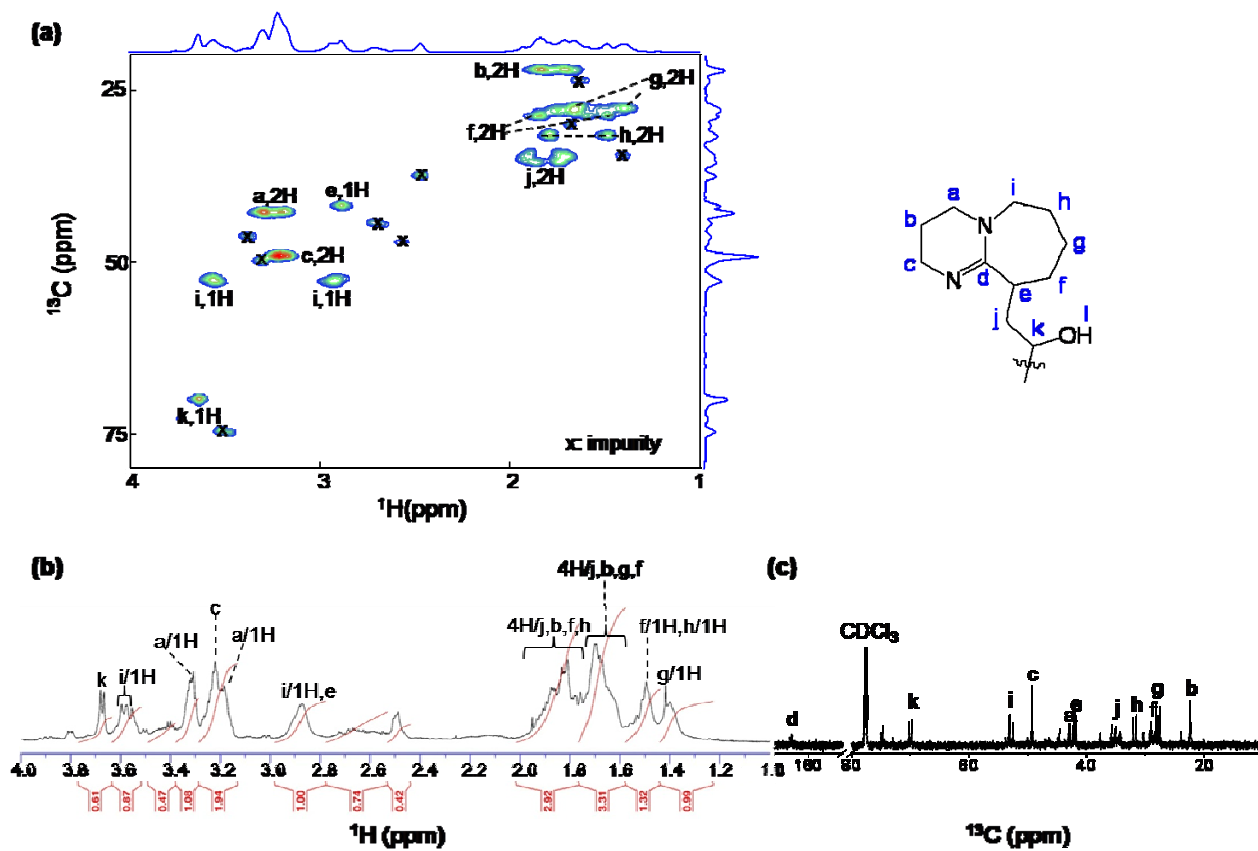


Fig. S2. (a) HMQC, (b) ^1H NMR and (c) ^{13}C NMR spectra of $(\text{DBUOH})_2$ in CDCl_3

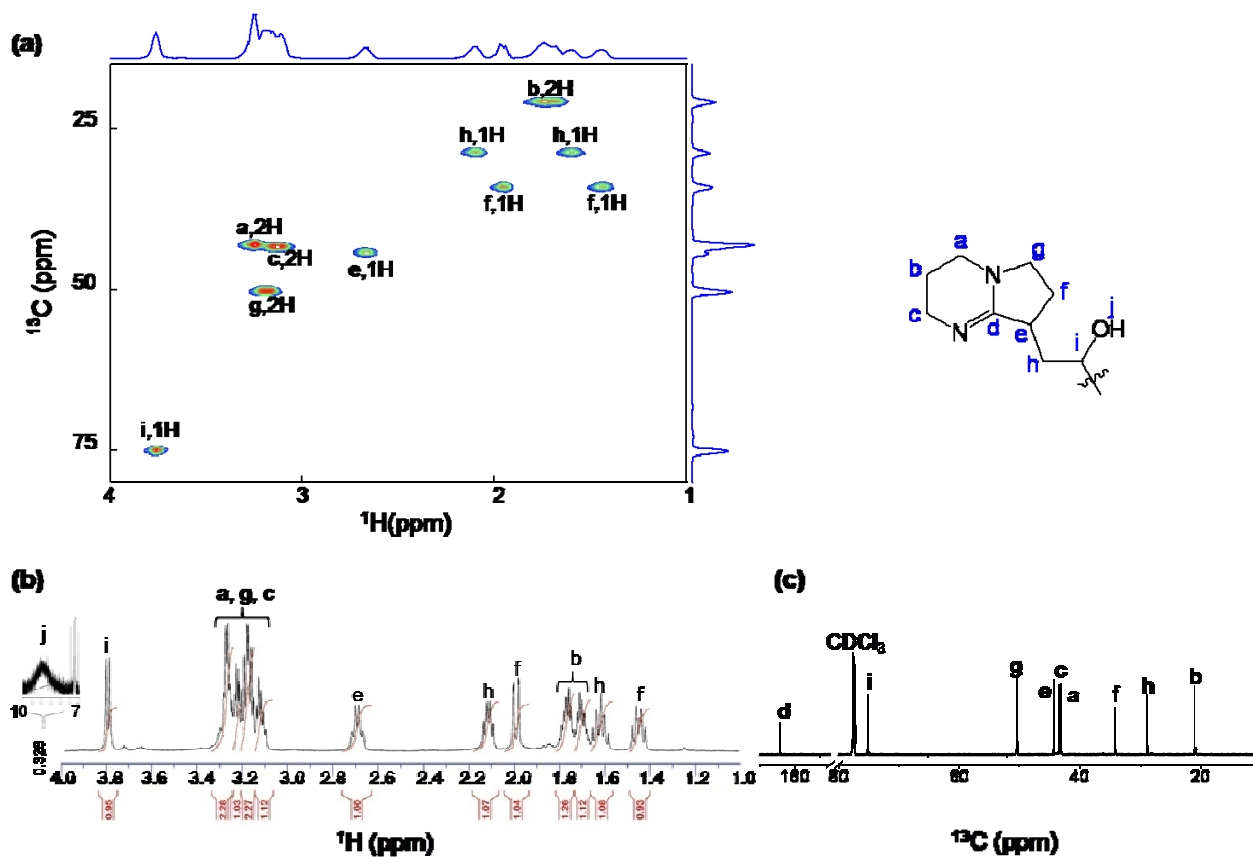


Fig. S3. (a) HMQC, (b) ^1H NMR and (c) ^{13}C NMR spectra of (DBNOH)₂ in CDCl_3

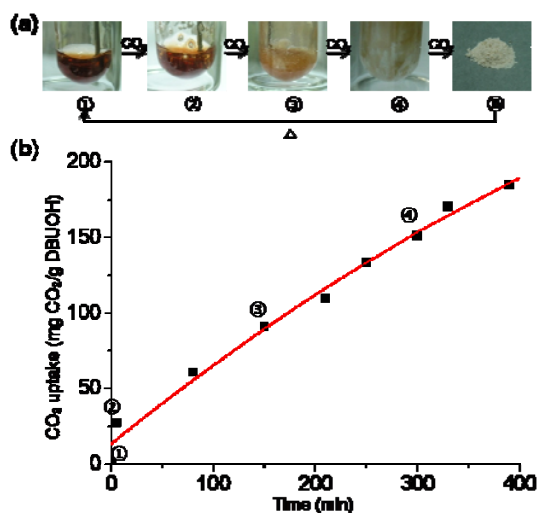


Fig. S4. The CO_2 capture and release by DBUOH. (a) The photographic images of the 0.5 g of DBUOH sample obtained while bubbling with anhydrous CO_2 gas. (b) The change in the weight of the bulk DBUOH sample used to get the images. The circled numbers designate the time when each of the photos in (a) was taken.

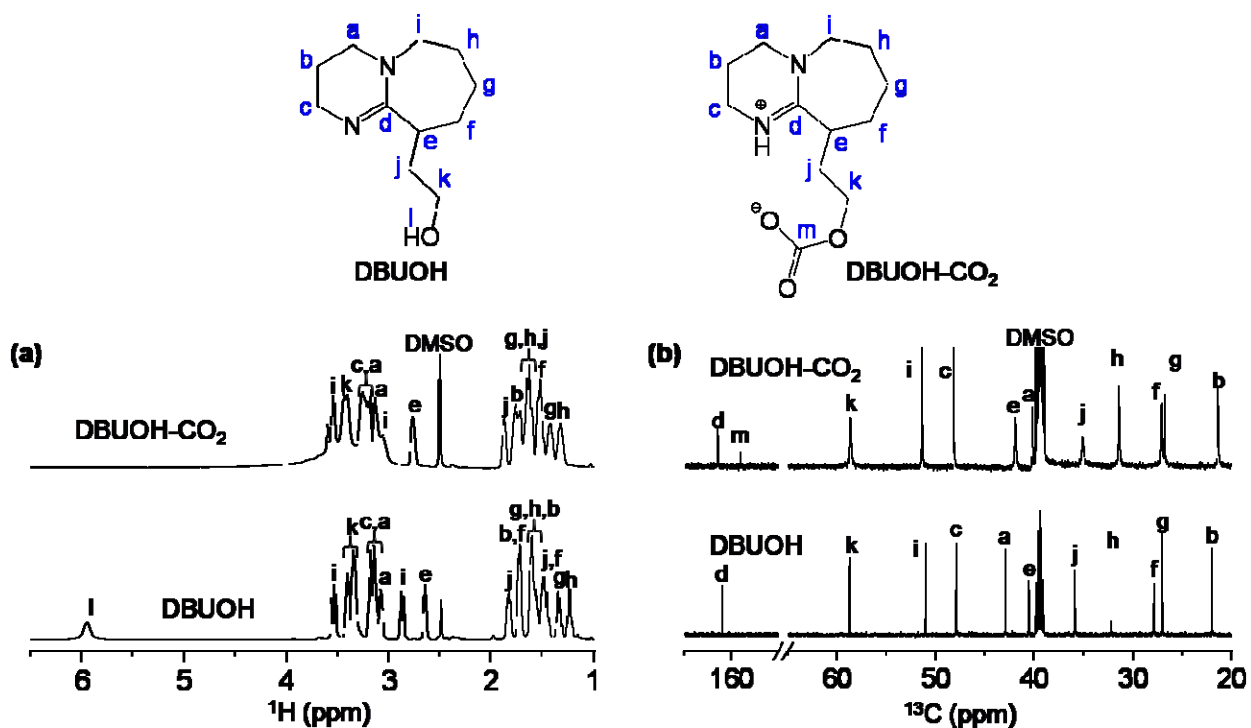


Fig. S5. ^1H NMR spectra of DBUOH and DBUOH- CO_2 in DMSO- d_6 .

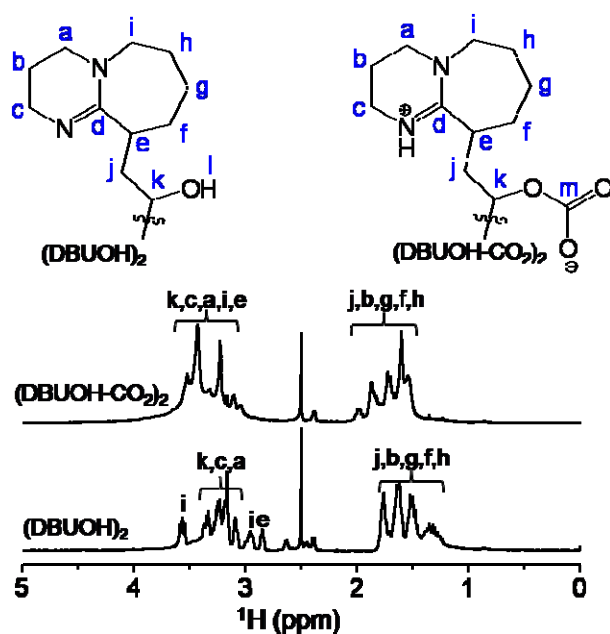


Fig. S6. ^1H NMR spectra of $(\text{DBUOH})_2$ and $(\text{DBUOH-}\text{CO}_2)_2$ in DMSO- d_6 .

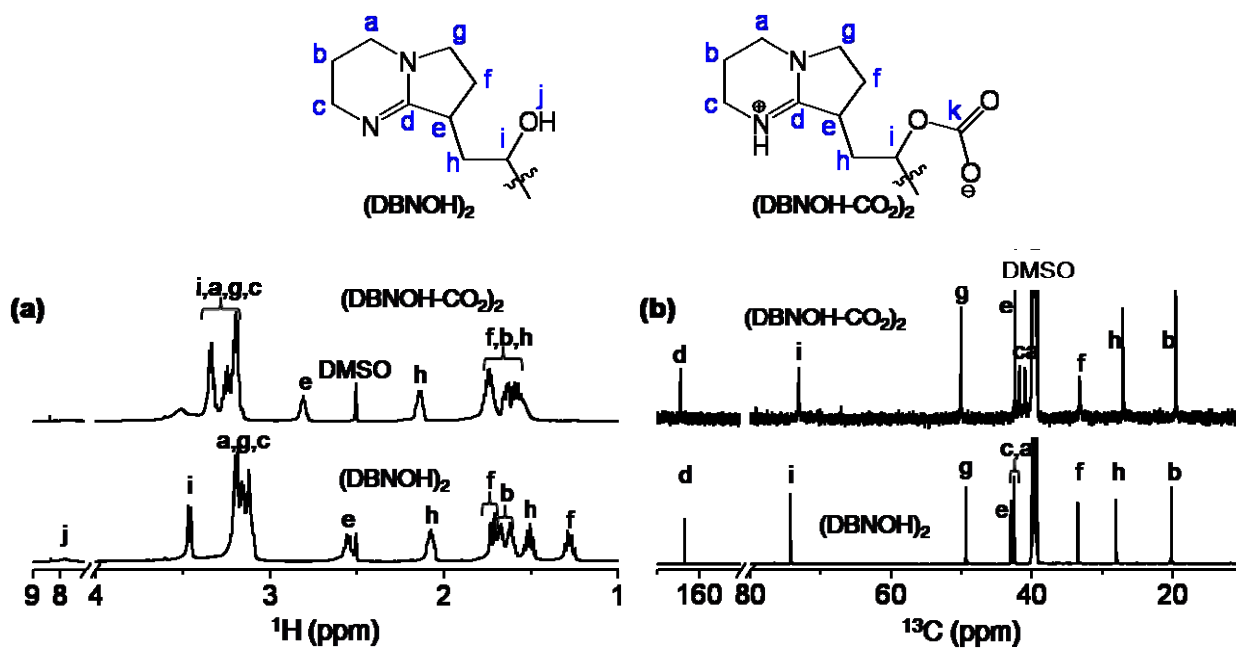


Fig. S7. ¹H NMR spectra of (DBNOH)₂ and (DBNOH-CO₂)₂ in DMSO-d₆.

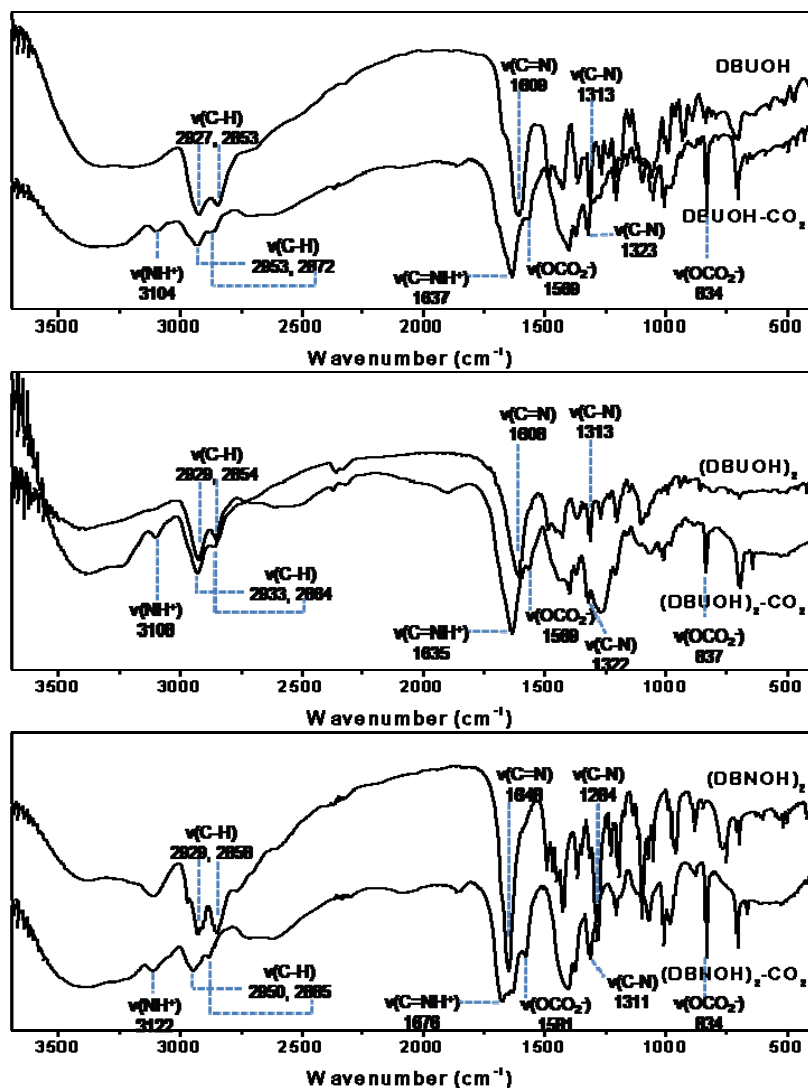


Fig. S8. FTIR spectra of the HAMs and HAM-CO₂ salts.

The DBU molecule has two main vibrational modes that are sensitive to the molecular interactions, the $\nu(\text{C}=\text{N})$ and $\nu(\text{CN})$ located at 1609 and 1313 cm^{-1} , respectively while DBN molecule has characteristic vibration at 1648 and 1284 cm^{-1} . After CO₂ bubbling, the N=C stretching frequencies of DBUOH and (DBUOH)₂ were replaced to bands for DBUOH-CO₂ and (DBUOH-CO₂)₂ at 1637 and 1569 cm^{-1} which is assigned to protonated amidine and carbonate stretches.^{1,2} Formation of a protonated amidine causes a similar frequency increase of 30 cm^{-1} of the $\nu(\text{C}=\text{N})$ in the case of (DBNOH)₂ as well from 1648 to

1676 cm^{-1} . There is also new band at 834 (DBUOH-CO_2 and $(\text{DBNOH-CO}_2)_2$), or 837 cm^{-1} (DBUOH-CO_2)₂ which is assigned to out-of-plane vibration of carbonate group.³

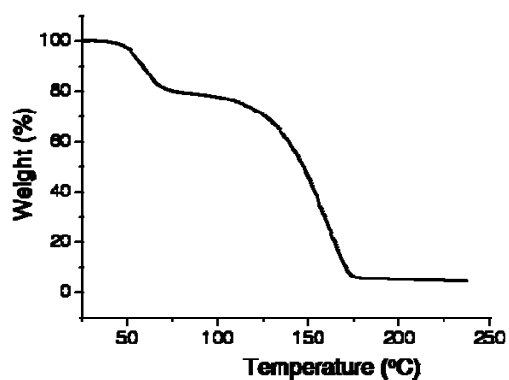


Fig. S9. The decarbonation TGA curve of in-situ-prepared HAM alkylcarbonate salt of neat DBUOH. DBUOH captures 220 mg CO_2/g DBUOH which is stoichiometric amount of CO_2 to the amidine moiety.

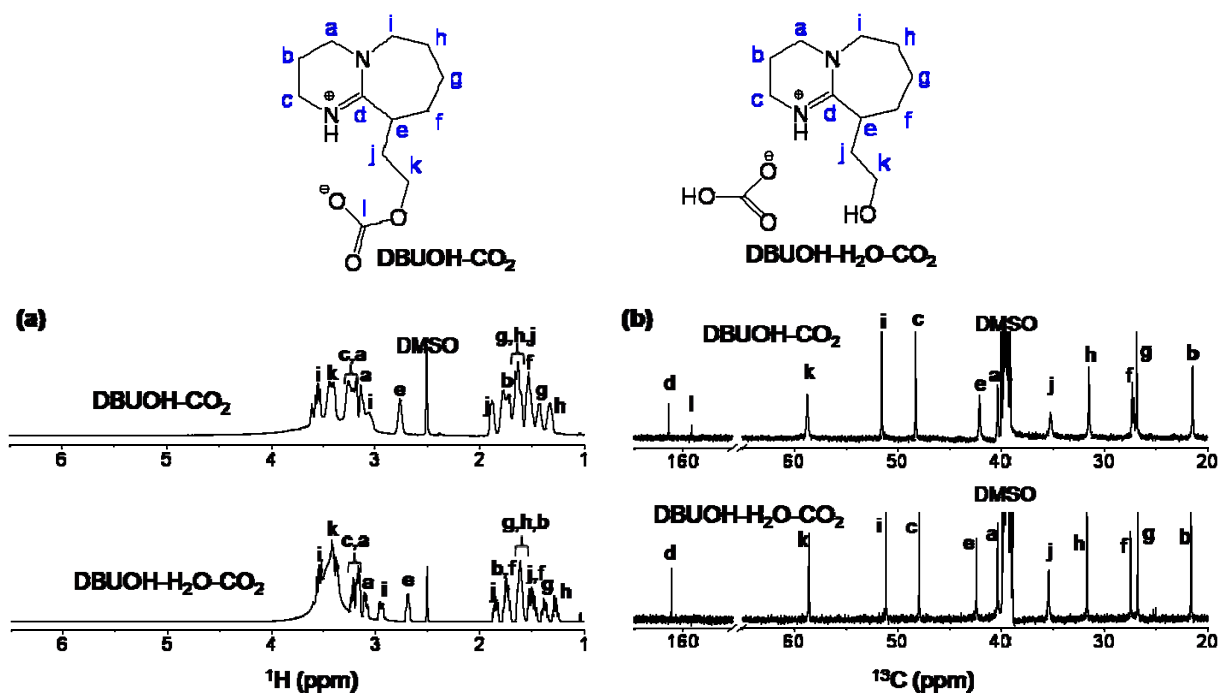


Fig. S10. Comparison of CO_2 capture property of DBUOH in the presence of moisture and in the dry condition. (a) ^1H NMR and (b) ^{13}C NMR spectra.

DBU- $\text{H}_2\text{O-CO}_2$ sample were prepared by bubbling 100 mL/min of dry CO_2 into dry DBUOH dissolved in THF (3 w/v%) with 1.0 equivalent of DI water. Alcohol(-OH) peak (δ 5.95 ppm in DMSO- d_6 , Fig.

S5) disappeared in both DBUOH-CO₂ and DBUOH-H₂O-CO₂ after capturing CO₂ (Fig. S10). There exist clear difference in position of the peaks e and i. Splitting patterns of the aliphatic proton peaks are also different. Broader spectra were obtained from viscous solution of zwitterionic DBUOH-CO₂.

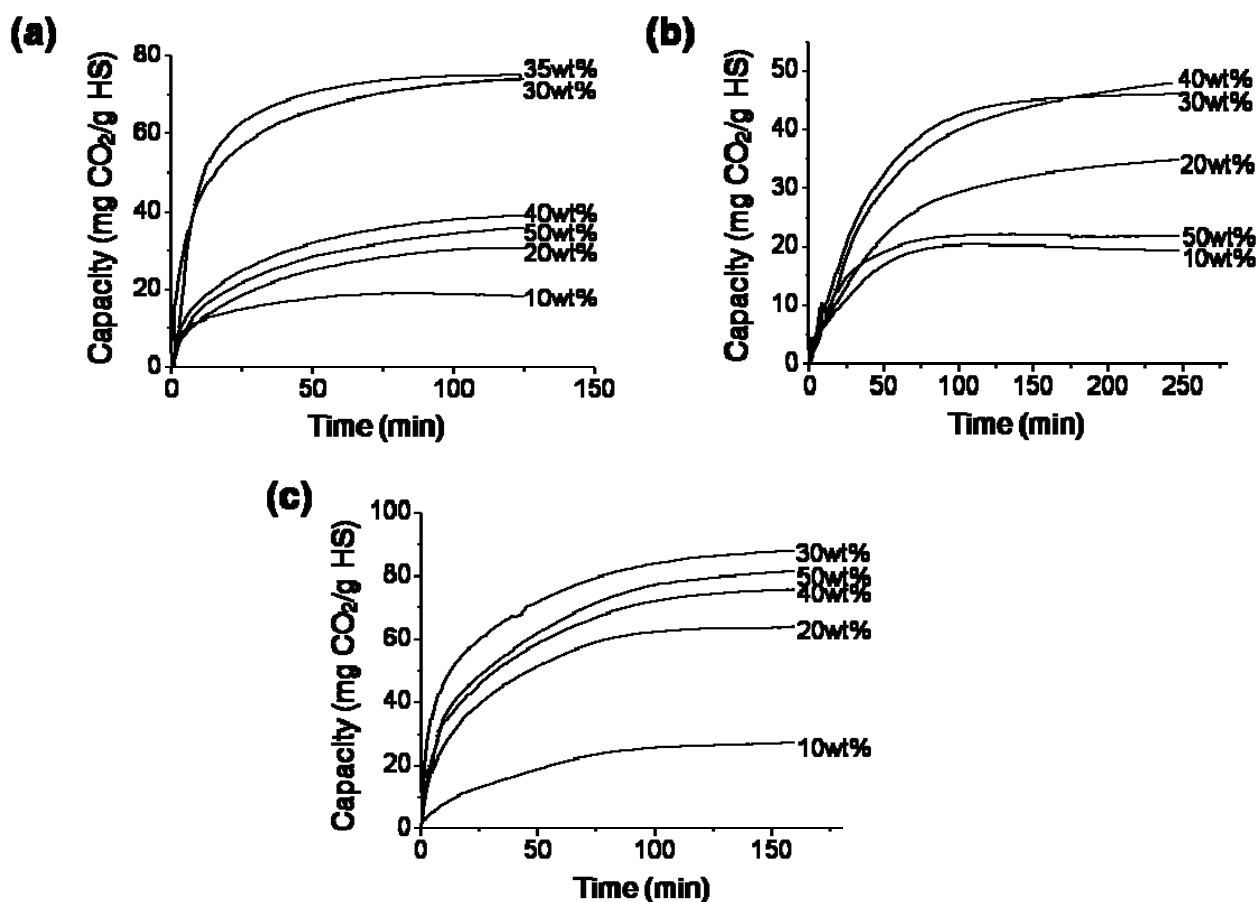


Fig. S11. CO₂ capture by silica-supported HAMS. Weight change of the HAM/silica at various HAM/silica compositions, recorded on the TGA with time by flowing CO₂ gas at 100 mL/min at 25 °C. (a) DBUOH/silica, (b) (DBUOH)₂/silica, and (c) (DBNOH)₂/silica

References

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